

Vysoká škola chemicko-technologická v Praze
Fakulta chemicko-inženýrská
Ústav fyziky a měřicí techniky

HABILITAČNÍ PRÁCE

Vodivé polymery pro organickou elektroniku

Ing. Dušan Kopecký, Ph.D.

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Ing. Dušan Kopecký, Ph.D.

Abstrakt

Vodivé polymery patří mezi perspektivní materiály s polovodičovým chováním typickým pro anorganické látky a mechanickými vlastnostmi látek organických. Z tohoto důvodu našla řada vodivých polymerů své uplatnění v moderním oboru organické elektroniky při výzkumu a vývoji nových zařízení typu organických fotovoltaiických článků, tranzistorů, světlo vyzařujících diod, senzorů, biosenzorů, pasivních elektronických součástek, superkapacitorů i baterií.

Předkládaná habilitační práce shrnuje, formou komentářů, výsledky experimentů s vodivými polymery – polyanilinem a polypyrrolem – zejména v oblasti senzorů a biosenzorů. Tato specifická oblast organické elektroniky, zaměřená na získávání fyzikálních a chemických informací o vlastnostech okolního prostředí, klade vysoké požadavky na kvalitu použitých materiálů. Popsané experimenty jsou proto zaměřeny na velikost a stabilitu parametrů citlivého materiálu (např. elektrické vodivosti či specifického povrchu), jeho chemickou strukturu (na molekulární i supramolekulární úrovni), zpracovatelnost (určenou např. mírou rozpustnosti v rozpouštědlech nebo schopností vytvářet nanokompozity) či odolnost vůči environmentálním podmínkám (např. teplotě, vzdušnému kyslíku, UV záření). Aplikace organických látek v senzorech jsou zpravidla spojeny s méně konvenčními technologiemi výroby jemných motivů a tenkých vrstev. Práce se proto odvolává zejména na výsledky experimentů s laserovými depozičními technologiemi a technologií inkoustového tisku. Vzhledem k charakteru připravených senzorů jsou zde také diskutovány méně konvenční strategie pro zpracování jejich výstupů (např. měření fázové citlivosti či spektrální analýza šumů). Výsledky vývoje a výzkumu senzorů a biosenzorů uvedené v této práci jsou multidisciplinární a pokrývají širokou oblast chemie, fyziky i kybernetiky.

Práce sleduje celý proces výroby senzoru. Od syntézy, optimalizace a charakterizace citlivého materiálu, přes přípravu motivů senzorové platformy a depozici citlivého materiálu, po zpracování výstupního signálu senzoru a testování jeho citlivosti či selektivity. V textu je citováno 22 prací autora a odkazuje na 121 stěžejních vědeckých prací z oblasti vodivých polymerů a organické elektroniky. Odkazy na původní práce autora jsou v textu pro přehlednost zvýrazněny modrou barvou.

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1 Aktuální trendy v organické elektronice

Moderní éra oboru *Organické elektroniky* se začala odvíjet v 60. letech 20. století s objevem volných nosičů elektrického náboje v konjugovaných systémech organických molekul [1]. Zpočátku byl význam těchto výsledků podceňován, ale v 70. letech byla provedena řada experimentů s dopováním nejjednoduššího konjugovaného systému – polyacetyleny, což vedlo k nárůstu jeho elektrické vodivosti až o sedm řádů [2]. Tento zlomový okamžik natrvalo změnil paradigma ve vnímání organických látek, zejména polymerů, jakožto materiálů vhodných pouze pro výrobu plastových výrobků a levného spotřebního zboží. Prvotní nadšení z nové třídy látek schopných vést elektrický proud vystřídala fáze ochlazení, která pramenila ze skutečnosti, že strukturální nedokonalost tehdy připravených organických polovodičů velmi omezovala pohyblivost nosičů elektrického náboje uvnitř materiálu. Byl to problém, jenž například způsobil dlouhou stagnaci ve vývoji organických tranzistorů OTFT (z angl. *Organic Thin-film Transistor*), a který se podařilo překonat až o mnoho let později. OTFT připravené na bázi dvojvrstvy pentacenu dosáhly pohyblivosti nosičů náboje srovnatelné s křemíkovými tranzistory až v roce 1997 [3].

Mezitím se však dařilo posouvat kupředu parametry dalších elektronických součástek, které znamenaly revoluci v oblasti využití organických materiálů. Nejvýznamnější z nich jsou organické světlo vyzařující diody OLED (z angl. *Organic Light Emitting Diode*), které využívají schopnosti elektroluminiscence některých typů organických látek (tj. luminoforů, mezi které patří např. vodivý polymer poly(*p*-fenylen) vinylen). Tyto elektronické součástky vydávají po přiložení relativně nízkého napětí velmi intenzivní záření zejména v oblasti viditelného spektra. Objev OLED přinesl zatím zřejmě nejviditelnější výdobytek organické elektroniky do běžného lidského života [4]. V současné době, o pouhých 30 let později od objevu těchto zařízení, je spotřebitelský trh celého světa doslova zaplaven různými typy displejů na bázi OLED. Nalezneme je zejména v mobilních telefonech a drobných elektronických zařízeních. Kvalita technologie výroby se však posouvá kupředu mílovými kroky a dnes jsou již na trhu nabízeny i rozměrné obrazovky založené na OLED technologiích s extrémním rozlišením 4K (byť stále ještě za velmi vysokou cenu v porovnání např. s technologiemi LCD).

Organické látky jsou také zajímavou alternativou pro fotovoltaické články. Organické fotovoltaické články OPV (z angl. *Organic Photovoltaic*) sice zdaleka nedosahují účinnosti anorganických protějšků (účinnost mají stále pouze řádu jednotek %), ale překonávají je svoji příznivější cenou či lepšími mechanickými vlastnostmi [5]. Další velkou oblastí, kde organické látky našly své uplatnění, a to zejména ve spojení s tiskovými technologiemi, jsou čipy identifikace na rádiové frekvenci RFID (z angl. *Radio-frequency Identification*), které mají za úkol postupně nahradit optické čárové kódy a sloužit při identifikaci a ochraně zboží. Nadějnou oblastí využití organických látek jsou také zařízení pro ukládání energie, například elektrochemické polymerní baterie vyznačující se nízkou hmotností a vysokou hustotou uloženého náboje, a v neposlední řadě také paměťové čipy či tištěné pasivní elektronické součástky (např. elektrické odpory, cívky, kondenzátory) [6].

Během 40 let vývoje se organická elektronika přesunula z univerzitních laboratoří a výzkumných center do průmyslového vývoje a řada z výrobků se úspěšně komercializovala. Mnohem více zařízení na bázi organické elektroniky však stále ještě čeká na dobu, kdy bude odstraněna většina jejich stávajících nedostatků, které jim brání v průniku do sofistikovaných aplikací a dále na světové trhy.

Předkládaná habilitační práce „*Vodivé polymery pro organickou elektroniku*“ shrnuje formou komentářů a poznámek 10 let mé činnosti v další, dosud nezmíněné, oblasti organické elektroniky,

a sice v oblasti senzorů na bázi organických materiálů určených pro detekci toxických a výbušných plynů a par. Tato oblast je natolik mladá, že dosud jen velmi málo senzorů tohoto typu spatřilo světlo světa jako komerční výrobek. Na druhou stranu je natolik zajímavá a dynamická, že výzkum senzorů na bázi organických látek pravidelně plní stránky předních světových časopisů, jako jsou například prestižní časopisy *Sensors and Actuators*, *Thin Solid Films*, *Electroanalysis*, *Electrochimica Acta*, *Biosensors and Bioelectronics* a mnohé další.

Během své práce v oblasti výzkumu a vývoje chemických senzorů jsem měl možnost nahlédnout do mnoha zákoutí této disciplíny i pracovat s předními odborníky, kteří měli na moji práci zcela zásadní vliv. Předkládaná práce zahrnuje několik oblastí – počínaje syntézou materiálu, přes depozici tenkých vrstev, měření odezvy senzorů až po zpracování signálů a šumů senzorů a vede skrze ni jednotlicí linii reprezentovaná heslem **vodivý polymer pro chemický senzor**. V několika případech jsem se podílel i na výzkumu dalších zařízení organické elektroniky, např. biosenzorů či OPV, což mi umožnilo získat nové nápady a myšlenky. Díky této rozmanité činnosti jsem se mohl podívat na výzkum a vývoj chemických senzorů na bázi organických materiálů z mnoha úhlů a získat určitý nadhled a zpětnou vazbu, např. snažit se optimalizovat syntézu vodivého polymeru tak, aby se minimalizovaly „slabiny“ připravených senzorů.

10 let intenzivní práce v oblasti organické elektroniky mi umožnilo vidět a zažít mnoho významných změn, které se v oboru udály. Několik těchto evolučních skoků se promítlo i do mé další práce. Velký vliv na její směřování mělo například zavedení výzkumu supramolekulárních struktur vodivých polymerů, či moderních depozičních technologií jako jsou technologie inkoustového tisku či laserové depoziční technologie. Měl jsem také příležitost se podílet na několika důležitých studiích, jako je například první laserová depozice vodivého polymeru polypyrrolu (PPy) [7] či popis mechanismu tvorby nanotrubek PPy [8]. Během své práce jsem byl nucen nahlédnout do oblastí chemie, fyziky, kybernetiky, materiálového a chemického inženýrství, fyzikální chemie, měřicí a řídicí techniky i programování a výpočetní techniky. V mnoha těchto oblastech jsem měl možnost se setkat i využít pomoci skvělých odborníků a mnoho z nich dnes mohu s hrdostí považovat za své kolegy a přátele.

1.1 Role organických polovodičů ve světě ovládaném křemíkem

Nezúčastněně pozorovatele výzkumu organické elektroniky jistě napadne otázka, jaké výhody skýtá organická elektronika oproti elektronice na bázi křemíku či obecně elektronice založené na anorganických materiálech. Zda jsou organické polovodiče schopné konkurovat těmto léty prověřeným materiálům, a tudíž jestli jsou obrovské investice, které dnes plynou do oblasti výzkumu a vývoje organické elektroniky, vůbec oprávněné.

V první řadě je nutné hned na začátku konstatovat, že cílem organické elektroniky není nahradit křemíkové technologie a zařízení. Chemie a technologie křemíku a některých jeho sloučenin je, díky polovodičové technice, velice dobře prozkoumaná, což mu dává mnohaletý náskok ve výzkumu a vývoji před ostatními prvky, které by jeho postavení mohly ohrozit. Jeden z mála takových prvků je uhlík, ležící v periodické tabulce prvků ve skupině přímo nad křemíkem. Uhlík je schopen vytvářet uspořádané struktury, které jsou díky kratším vazbám, zejména diamantové mřížky, jemnější (délka vazby v křemíku je 5,43 Å, délka vazby v diamantu je 3,56 Å), a navíc některé allotropy uhlíku (diamant, fulleren, grafen) jsou termodynamicky stabilnější. Na druhou stranu šířka zakázaného pásu diamantu je 5,4 eV oproti 1,17 eV v křemíku. Někteří vědci jsou přesto přesvědčeni, že po překonání problémů s výrobou diamantu ve velkém měřítku, bude diamantová elektronika směle konkurovat té křemíkové [9].

Organická elektronika naproti tomu využívá převážně látky polymerního nebo oligomerního charakteru. Tyto látky jsou sice charakteristické větší koncentrací nosičů náboje v porovnání s křemíkem (míra jejich dopování je řádově větší), ale zároveň obsahují tolik defektů a nedokonalostí, že mobilita jejich nosičů elektrického náboje je velice omezená, což je pro mnohé aplikace vyžadující rychlou odezvu velmi limitující. Organická elektronika těží především ze tří svých předností – i) flexibility složení organických látek, ii) jejich snadné zpracovatelnosti pomocí moderních technologií (např. pokročilého tisku a sítotisku) s relativně malým počtem kroků a ve velkých objemech a v neposlední řadě z iii) velmi nízké ceny, která je důsledkem velkosériové výroby a nízkých cen zdrojových látek, jež jsou většinou získávány z ropy. Organická elektronika proto spíše hledá své místo tam, kde rigidní krystalické či amorfnní křemíkové či jiné anorganické materiály nelze uplatnit.

Obrovský impuls ve výzkumu organické elektroniky byl dodán v souvislosti s moderními tiskovými technologiemi. Řada organických látek je snadno zpracovatelná za nízkých teplot do cca 200 °C ve formě kapalných inkoustů, což je spolu s technologiemi typu Ink-Jet, sítotisku či rotačního tisku ideální pro tisk interaktivních elektronických prvků (her, indikátorů, interaktivní reklamy, paměťových buněk) na flexibilní substráty (papír, plastové fólie). Samostatnou kapitolu potom tvoří tisk RFID čipů, OLED displejů, či fotovoltaických panelů. Lepší představu o výhodách výroby organické elektroniky tiskovými technologiemi si lze udělat z následujícího zjednodušeného příkladu: moderní tiskárny jsou schopny potisknout substráty rychlostí více než 500 m² za minutu, což za hodinu vytvoří větší objem vytištěné elektroniky než ekvivalent roční produkce elektroniky v továrně na výrobu křemíkových čipů [6].

1.2 Návrh a konstrukce mikrostruktur na bázi organických materiálů

Při zvažování organických látek jakožto materiálů prvního výběru pro nové elektronické zařízení je nutné vždy promyslet řadu otázek, např. jaký typ látky vyhovuje dané části elektronického prvku, jaká je vzájemná kompatibilita použitých materiálů, jak tyto látky interagují na svém rozhraní apod. Výběr materiálu je navíc téměř vždy podmíněn některou specifickou vlastností (např. hodnotou měrné elektrické vodivosti, mechanickou pevností, ohebností, velikostí specifického povrchu apod.), která ovlivňuje finální rozhodnutí. Ačkoliv je tato práce úzce zaměřena pouze na organické polovodiče a jejich vlastnosti, zejména pak elektrickou vodivost, v organických materiálech lze nalézt látky s diametrálně odlišnými vlastnostmi. V případě již zmíněné elektrické vodivosti je tedy možné použít organické látky s vlastnostmi izolantů, polovodičů a v extrémních případech i látky s metalickým chováním [10]. Moderní zařízení je proto možné kompletně navrhout a postavit pouze na bázi organických látek.

Organické látky se také často kombinují se stávajícími anorganickými materiály (např. Si, Au, Al₂O₃ apod.) již hotových substrátů, které vykazují známé charakteristiky a jsou zpravidla vytvořeny osvědčenými technikami (fotolitografií, leptáním, řezáním, leštěním apod.). Objevují se zde však jiná úskalí – spojená s chováním např. kontaktů mezi kovem a organickými látkami či rozhraní anorganická/organická látka. Výše uvedené problémy nelze předem beze zbytku předpovědět a např. v oblasti FET transistorů se jedná o časté překážky, které je nutné řešit změnou technologie výroby či materiálu [11].

Při návrhu nového zařízení na bázi organické elektroniky lze narazit na limit velikosti rozlišení (v horizontálním i vertikálním směru) jednotlivých prvků, který je dán zpravidla použitou depoziční technologií. Stávající technologie inkoustového tisku (což je v současnosti pravděpodobně nejdůležitější technologie výroby organických motivů) dosahují horizontálního rozlišení v řádu

jednotek až desítek μm , tedy o několik řádů horšího než v případě nejnovějších fotolitografických postupů (aktuální tranzistory v mikroprocesorech vytvořené touto cestou dosahují rozměrů 7-10 nm). Velký důraz v organické elektronice se proto klade i na vývoj nových technologií, které by tuto překážku odstranily. Potenciál pro zlepšení této oblasti mají proto i stále ještě experimentální depoziční technologie elektrohydrodynamického tisku či laserového psaní.

Řada organických látek podléhá degradaci okolními podmínkami (např. UV-zářením, vyšší teplotou, vzdušným kyslíkem či vlhkostí apod.) snadněji než ty organické. Výsledkem je rychlé stárnutí zařízení, které se projevuje např. postupným snižováním intenzity záření u OLED, poklesem účinnosti OPV či změnou citlivosti chemických senzorů. V době rychlé spotřeby a morálního zastarávání elektronických zařízení se však paradoxně nemusí jednat o velkou překážku, neboť mnoho zařízení je obměněno za nové v průběhu jednoho či dvou let. Návrh zařízení může také v některých případech (s ohledem na nízké ceny plynoucí z masové výroby) počítat pouze s jeho jednorázovým použitím [12].

1.3 Senzory na bázi organických polovodičů a jejich vlastnosti [13-17]

Senzory na bázi organických látek tvoří poměrně specifickou podskupinu organické elektroniky. Cílem senzorů je získávat informace o fyzikálních a chemických vlastnostech svého okolí. Při konstrukci senzorů na bázi organické elektroniky lze vycházet z konceptu a struktury již existujících zařízení organické elektroniky. Např. OTFT může být snadno upraven tak, aby byl schopen sloužit jako převodník měřené veličiny na elektrický signál. Senzory na bázi OTFT slouží jako chemické senzory při detekci řady plynů (např. O_2 , NO_2 apod.), případně jako fyzikální senzory zatížení (tenzometry), tlaku a teploty (pyroelektrické senzory). OLED lze s výhodou použít jako zdroje záření v mikrofluidních systémech pro detekci rozpuštěného kyslíku či glukózy a OPV je možné adaptovat na fotodetektor elektromagnetického záření [18]. Samozřejmě lze vyvinut i struktury zcela nové.

Častější je však využití existujících platform fyzikálních a chemických senzorů (např. SAW, QCM, chemoresistor, FET, kapacitní senzor), které vede ke konstrukci hybridních zařízení založených na anorganickém rigidním substrátu a organické citlivé vrstvě. Tyto v podstatě inovované typy senzorů se vyznačují zajímavými parametry plynoucími z využití organických látek (např. schopností detekce za laboratorní teploty citlivé vrstvy) a propracovaným způsobem vyhodnocování odezvy díky známé platformě. Použití známé platformy při vývoji nových senzorů na bázi organických látek umožňuje soustředit se pouze na vlastnosti organické citlivé vrstvy senzoru.

Vhodným příkladem tohoto přístupu jsou senzory na bázi krystalových mikrovážek QCM (z angl. *Quartz Crystal Microbalance*) s tenkou vrstvou vodivého polymeru PPy¹ [13]. QCM krystal ve formě křemenného AT-výbrusu patří mezi léty prověřenou senzorovou platformu, která se dnes úspěšně používá např. v průmyslových analyzátoch vlhkosti plynů [14]. Důležitou částí těchto senzorů vlhkosti je sorpční vrstva, která interaguje s detekovaným plynem a absorbuje z něj molekuly vodní páry. Absorpcí molekul vodní páry citlivou sorpční vrstvou dochází ke změně celkové hmotnosti QCM krystalu, což se projeví ve změně rezonanční frekvence kmitání senzoru. Problémem mnoha průmyslových analyzátorů vlhkosti založených na QCM krystalech je však

¹ PPy je organický polymer s teplotní závislostí měrné vodivosti charakteristickou pro polovodiče, jehož hlavní předností je vysoká elektrická vodivost (až $200 \text{ S}\cdot\text{cm}^{-1}$). PPy je proto s oblibou používán v chemorezistorech (detailněji o PPy viz následující kapitoly), ale, vzhledem k jeho schopnosti sorbovat polární páry do svého objemu, může být použit i jako sorpční materiál na povrchu QCM senzoru.

existence interferentů, které se v měřeném plynu vyskytují spolu s vodní párou (např. methanol, amoniak) a vytvářejí falešnou odezvu. Řešení tohoto problému spočívá buď ve využití sorpční vrstvy necitlivé k danému interferentu (nalezení takového materiálu však může být velice obtížné) anebo ve zvýšení selektivity pomocí vhodné metody zpracování signálu, např. spektrální analýzou šumů QCM krystalu.

Sedlák a kol. [13] použil spektrální analýzu šumových složek QCM krystalu (šum QCM senzoru se skládá se z tepelného šumu, $1/f$ šumu pocházejícího z vnitřního tření krystalu, šumu vznikajícího adsorpcí a desorpcí měřeného plynu či páry, termo-mechanického šumu, šumu pocházejícího z teplotních fluktuací senzoru a šumu elektronického oscilátoru) pro popis procesu absorpce a desorpce vodní páry na povrch/ z povrchu tenké citlivé vrstvy PPy. Touto metodou se mu podařilo získat model šumu vznikajícího při procesu absorpce-desorpce vodní páry tenkou vrstvou a matematicky jej popsat pomocí Kolmogorovovy rovnice vycházející z modelu dvou zásobníků vodní páry – analyzovaného plynu při dané koncentraci, teplotě a parciálním tlaku, a povrchu senzoru s určitým počtem míst obsazených analyzovaným plynem. Detailní znalost jednotlivých komponent šumových charakteristik QCM senzoru a zejména šumu vznikajícího adsorpcí a desorpcí měřeného analytu otevírá možnosti, jak zvyšovat citlivost a selektivitu senzoru k molekulám vodní páry.

Možností, jak získat informace o citlivosti či selektivitě senzorů, jejichž citlivé vrstvy tvoří složité systémy organických molekul je však více. Seidl a kol. [15] použil analýzu odezvy chemorezistorů na bázi směsi acetyl-acetonátu cínu (SnAcAc) a oxidu cíničitého (SnO_2) při měření DC- a AC-signálem a porovnal výsledky standardní stejnosměrné citlivosti (S_{DC} ; rovnice 1) a tzv. fázové citlivosti (S_{AC} ; rovnice 2), která je v oblasti vyhodnocování citlivosti chemorezistorů relativně novým nástrojem:

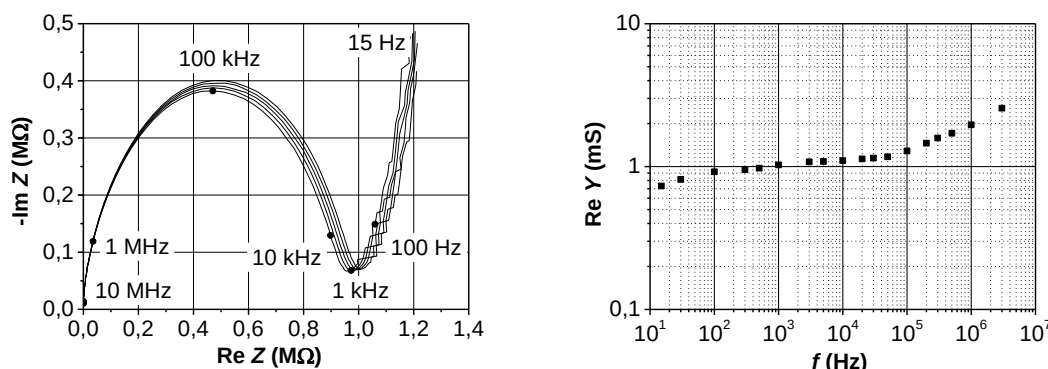
$$S_{DC}(T, c) = \frac{R_{air}(T)}{R_{gas}(T, c)} \quad (1)$$

$$S_{AC}(T, f, c) = \theta_{air}(T, f) - \theta_{gas}(T, f, c) \quad (2)$$

kde T je provozní teplota senzoru, c je koncentrace analytu a f je frekvence střídavého měřicího signálu. Měření S_{AC} se ukázalo nejenom robustnější vůči teplotním fluktuacím senzoru, ale je také vhodné pro srovnávání citlivosti senzorů anorganických (SnO_2), anorganicko-organických (směs SnAcAc a SnO_2) i čistě organických (PPy). Fázová citlivost S_{AC} se ukazuje jako zásadní také pro zlepšení selektivity senzoru. Měření senzorů AC signálem nabízí oproti DC měřením ještě jeden nezanedbatelný, i když z hlediska interpretace relativně obtížný nástroj, a sice tzv. impedanční spektroskopii. Impedanční spektroskopie umožňuje spojit konkrétní elektrické chování měřeného senzoru (pozorovatelné např. na průběhu tzv. Nyquistových diagramů) s jeho materiálovými vlastnostmi (velikostí zrn, typem nosičů elektrického náboje apod.), pomocí matematického modelování náhradních elektrických obvodů senzoru. Toto modelování bylo použito i v případě $\text{SnAcAc}/\text{SnO}_2$ chemorezistorů v práci Seidl a kol. [15].

Z výsledků impedanční spektroskopie senzorů na bázi organických materiálů lze vysvětlit i některé jevy, které DC měření nedovede snadno odhalit. Vršata a kol. [16] pomocí impedanční spektroskopie chemorezistorů s tenkými citlivými vrstvami PPy zjistil, že tento vodivý polymer s charakterem polykationtového řetězce a aniontových dopantů vykazuje poměrně vysokou iontovou vodivost (viz průběh Nyquistova diagramu v rozsahu 15 Hz až 1 kHz na obrázku 1 (vlevo)), kterou lze přisoudit pohybu jeho protiontů (dopantů PPy) v elektrickém poli. PPy se tak chová do jisté míry jako pevný elektrolyt, což se při měření signálem s nenulovou stejnosměrnou složkou

projevuje postupným driftem elektrického odporu směrem k vyšším hodnotám tím, jak se vyčerpávají volné ionty elektrolytu a dochází k polarizaci elektrod.



Obrázek 1 - Nyquistův diagram získaný impedanční spektroskopií chemorezistoru na bázi PPy v rozsahu frekvencí 15 Hz - 10 MHz (vlevo) a závislost jeho reálné složky komplexní admittance na frekvenci (vpravo) [16]

Impedanční spektroskopie nabízí několik způsobů zobrazení naměřených dat, které umožňují získat řadu materiálových parametrů. Mezi ně patří i závislost reálné složky komplexní admittance na frekvenci (obrázek 1 (vpravo)), z jejíhož průběhu lze získat informace o charakteru transportu náboje uvnitř materiálu (řetězcová děrová vodivost vs. přeskokové mechanismy např. VRH (z angl. *Variable Range Hopping*)), z čehož lze usuzovat i míru stárnutí použitého polymeru. S rostoucím stářím polymeru totiž dochází vlivem degradace materiálu k rozpadu na uspořádané (metalické) a neuspořádané (amorfní) ostrůvky polymeru a k postupnému potlačování řetězcové děrové vodivosti materiálu na úkor přeskového mechanismu přenosu děr.

Impedanční spektroskopie se ukázala užitečná i při analýze řady dalších chemorezistorů na bázi organických materiálů, např. chemorezistorů na bázi tetrasulfonovaných ftalocyaninů mědi a niklu [17]. Nicméně, vzhledem k velkému množství stupňů volnosti, které se nabízí při vyhodnocování a interpretaci získaných grafů, je vždy nutná jistá obezřetnost k získaným výsledkům a z tohoto pohledu se proto jedná o velmi obtížnou metodu. Více informací k impedanční spektroskopii lze získat např. z rozsáhlé publikace Barsoukov a MacDonald [19].

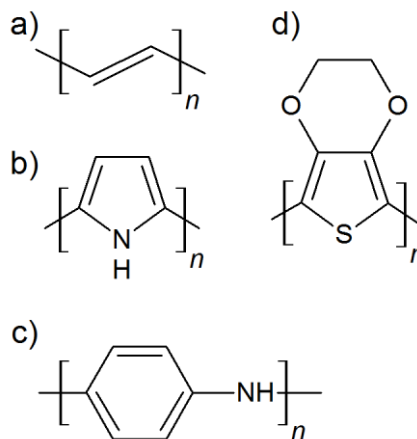
1.4 Inteligentní materiály pro 21. století – vodivé polymery [20-22]

Vodivé polymery² (VP) tvoří pestrou skupinu polymerů, které se svými elektrickými vlastnostmi podobají anorganickým polovodičům či kovům, přesto si však zachovávají mechanické vlastnosti organických látek (např. flexibilitu, nízkou hustotu, snadnou modifikovatelnost chemické struktury apod.). VP jsou v základním stavu elektrickými izolanty s elektrickou vodivostí v řádech $10^{-10} - 10^{-5} \text{ S}\cdot\text{cm}^{-1}$. Procesem zvaným dopování (více o dopování VP viz oddíl 3.2), však mohou o několik řádů zvýšit svou elektrickou vodivost a to až na úroveň klasických anorganických polovodičů, případně i kovů. Typická hodnota elektrické vodivosti dopovaných VP se pohybuje v rozsahu $1 - 10^4 \text{ S}\cdot\text{cm}^{-1}$. Hlavní příčinou řetězcové děrové vodivosti VP je konjugovaný systém vazeb s π -elektrony delokalizovanými podél celého skeletu molekuly a volnými nosiči náboje,

² Vodivé polymery jsou někdy také nazývány jako konjugované polymery; v angl. se lze také setkat s pojmy *synthetic metals* nebo, méně často, s *electronic polymers*, u nichž se však český ekvivalent nepoužívá.

které vytváří médium schopné transportovat díry (fakticky elektrony) podél lineárního řetězce molekuly [23].

Od svého znovuobjevení v 70. letech 20. století při experimentech s polyacetylenem exponovaným halogeny [2] prodělaly VP závratnou genezi, která byla navíc akcelerovala udělením Nobelovy ceny za chemii v roce 2000 Alanu J. Heegerovi, Alanu G. MacDiarmidovi a Hideki Shirakawovi za objev nové skupiny látek, která vedla k rozvoji nových vědních oborů [24]. Postupně také došlo k dělení výzkumu VP do různých odvětví podle oborů výzkumu i podle aplikací, které v daném polymeru, technologii syntézy či jeho způsobu funkcionizace a zpracování spatřovaly největší potenciál. V současné době lze pozorovat diferenciaci oblastí chemické a elektrochemické syntézy VP s ohledem na jejich aplikace; VP připravené chemickou syntézou jsou zpravidla vhodné pro zařízení využívající povrchové reakce na rozhraní plyn-pevná látka (senzory), a také pro uchovávání energie (baterie a superkapacity), elektrochemicky připravené VP jsou preferovány při konstrukci zařízení pracujících s rozhraním kapalina-pevná látka (biosenzory). Oba způsoby přípravy VP však neurčují budoucí aplikaci VP zcela striktně a lze najít též určitý průnik společných aplikací, mimo jiné i v oblasti elektronických součástek, ochranných povrchů a katalýzy.



Obrázek 2 - Vodivé polymery: a) polyacetylen (trans - mezomer); b) polypyrrol; c) polyanilin (leukoemeraldin); d) poly-3,4-ethylenedioxythiopen

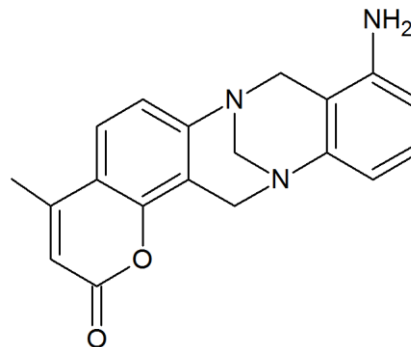
Základním VP je polyacetylen (PAC), zobrazený na obrázku 2a, s lineárním řetězcem, ve kterém se střídají jednoduché a dvojné vazby. PAC se využívá jako modelový příklad konjugovaného systému. Z hlediska možných aplikací je však zajímavější polyanilin (PANI) a dvojice heterocyklických polymerů polypyrrol a poly-3,4-ethylenedioxythiopen (PEDOT) (viz obrázek 2b-c), které jsou v porovnání s PAC stabilnější na vzduchu. Kromě této čtveřice existuje ještě pestrá paleta dalších VP, jejichž příprava, struktura a vlastnosti jsou detailně popsány v řadě přehledových článků a knih [25,26].

PANI, PPy a PEDOT patří mezi VP, jejichž vlastnosti jsou v současné době prozkoumány na takové úrovni, že je možné uvažovat o jejich pokročilých biotechnologických aplikacích, jako jsou například biosenzory, umělé tkáně a neurální sondy [27,28]. Jednu z těchto úspěšných aplikací lze demonstrovat na PANI, který byl použit jako receptor pro detekci salicylátů a jejich analogů [20].

Salicyláty jsou látky používané k tlumení bolesti, horečky, či zánětu. Nejznámější z nich je bezesporu kyselina acetylsalicylová, která se používá pod obchodním názvem Aspirin, Acylpyrin či Anopyrin. Selektivní detekce těchto látek ve vodných roztocích je proto klíčová zejména v oblasti medicíny a farmacie. Jednou z cest, jak dosáhnout selektivní detekce salicylátů, je použít iontově selektivní elektrody (ISE) s vhodnými salicylátovými receptory. Některé z úspěšných aplikací ISE pro detekci salicylátů jsou založeny na organokovových materiálech. **Vodivé polymery však v biosenzorech obvykle nevystupují v roli přímého receptoru, ale spíše jako platforma pro imobilizaci receptorů.** Konkrétně PANI se v minulosti osvědčil zejména jako platforma pro imobilizaci vhodných enzymatických či bioafinitních receptorů [29]. V případě salicylátů však lze uvažovat o využití PANI jako přímého receptoru bez nutnosti navázání dalších funkčních látek, a to zejména díky molekulovým vazebným interakcím (π - π interakce, vodíkové můstky a dipólové interakce), které vznikají mezi molekulou salicylátu a PANI.

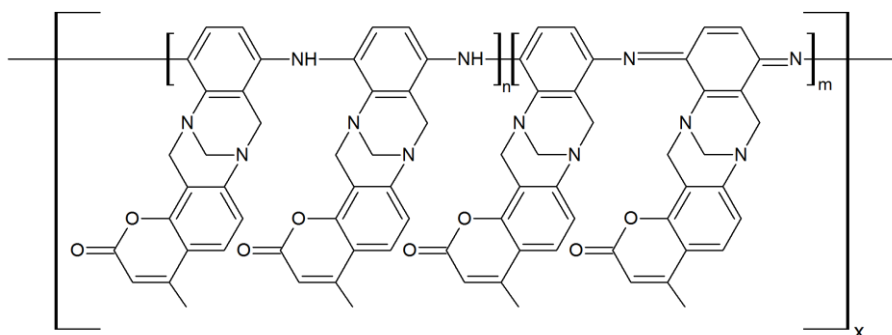
Nespornou výhodou PANI je jeho relativně snadná chemická příprava. Anilin lze polymerizovat ve vodném prostředí pomocí oxidačního činidla $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (APS)³ a pokud je v reakčním médiu přítomen vhodný hydrofilní povrch, dochází ke vzniku tenké vrstvy *in-situ* na povrchu, čím se značně zjednoduší technologický proces výroby tenké vrstvy [30]. Vhodnou hydrofilní membránou, na které lze PANI polymerizovat a zároveň může sloužit jako základ pro ISE je směs poly(vinyl chloridu) (PVC) a 2-nitrofenyl oktyl etheru (NPOE) v poměru 2 : 1.

Výsledek potenciometrického měření s touto iontově selektivní membránou ukázal, že velmi závisí i na struktuře povrchu a krystalinitě PANI, která může být do značné míry ovlivněna přidávkou pomocné látky v průběhu polymerizace; např. přidávek NaCl zvyšuje krystalinitu PANI a tím i uspořádanost jeho řetězců [31], která se projeví zvýšenou elektrickou vodivostí iontově selektivní membrány. Důsledkem tohoto jevu je i vyšší citlivost takovéto membrány k salicylátům, která je spolu se selektivitou srovnatelná (či dokonce lepší), než u dosud použitých receptorů.



Obrázek 3 - Amino-substituovaný kumarinový derivát Trögerovy báze

Výše uvedená práce je ukázkou snadného využití VP ve velmi pokročilých aplikacích. Polymerizační reakce anilinu lze však s výhodou využít i při přípravě tenkých filmů složitějších látek jako jsou amino-substituované kumarinové deriváty Trögerových bází (CTB)⁴ [21]. Chemická struktura této látky je na obrázku 3.



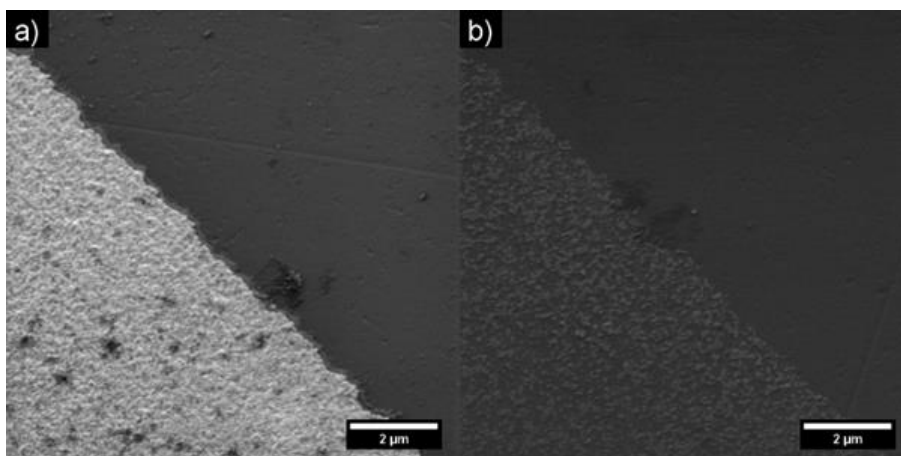
Obrázek 4 - Polymer amino-substituovaného kumarinového derivátu Trögerovy báze [21]

Tenké filmy PANI vznikají snadno nejenom chemickou cestou, ale i elektrochemickou polymerizací, která vede k tvorbě tenkých filmů na povrchu elektrodových systémů [32]. Pokud má takto vyrobený polymer sloužit například jako biosenzor, znamená to ukotvit do vrstvy specifické receptory, protože, jak již bylo řečeno výše, PANI je většinou využíván pouze jako platforma pro imobilizaci receptorů. To zpravidla obnáší nutnost dalšího technologického kroku, který výrobu biosenzoru značně prodlužuje a ve svém důsledku i prodražuje. Řešením může být využití makromolekul, které kombinují receptorovou část s částí schopnou polymerizace podle mechanismu polymerizace VP. CTB ukázalo, že je schopné spojit kumarinovou funkční skupinu s aminoskupinou, jejíž mechanismus polymerizace je stejný jako u nefunkcionalizovaného PANI. Jedním polymerizačním krokem zde dochází ke vzniku polymeru (obrázek 4), tenké vrstvy, do které

³ Zkratka APS pochází z anglického názvu ammonium peroxydisulfate.

⁴ Zkratka CTB vychází z angl. *amino-substituted coumarin derivative of Tröger base*.

jsou navíc vnesena receptorová místa (obrázek 5). Konkrétně toto uspořádání by v budoucnu mohlo sloužit v biosenzorech markerů signalizujících neuroblastomy.



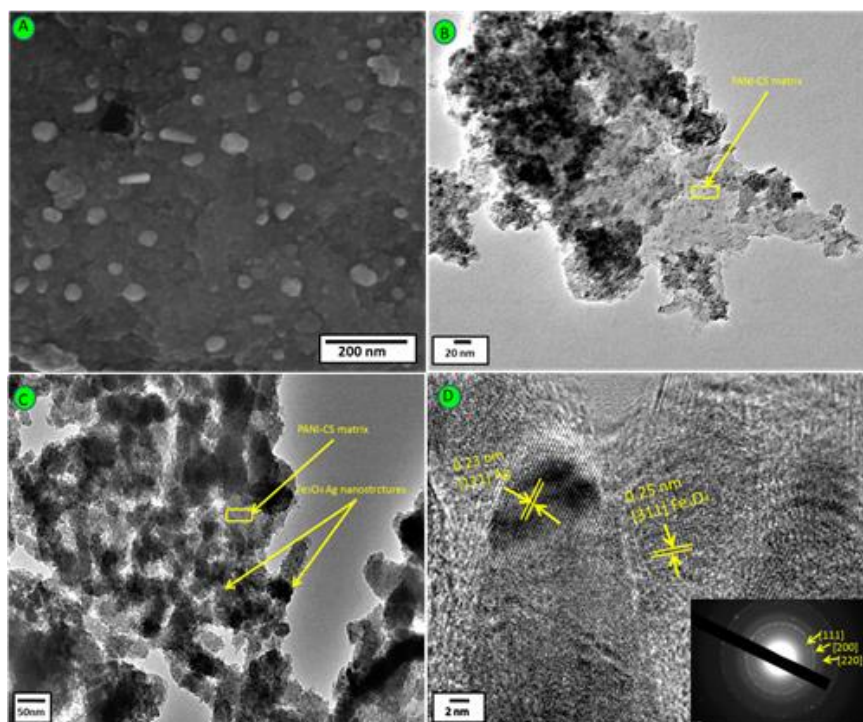
Obrázek 5 - Rozhraní zlatá elektroda/substrát biosenzoru a) nepokrytého a b) elektrochemicky pokrytého polymerním filmem CTB [21]

Chemická i elektrochemická příprava různých typů kompozitů VP je v současné době populární cestou, jak získat funkcionalizované materiály, které využívají přednosti VP a zároveň potlačují jejich nedostatky nebo přidávají vlastnosti zcela nové. Konkrétní ukázkou tohoto přístupu je současná práce od Ayad a kol. [22] věnovaná syntéze multifunkčního kompozitu PANI s biopolymerem chitosanem (CS), magnetickými částicemi Fe_3O_4 a nanočásticemi Ag. Na první pohled složitý kompozit důmyslně využívá jednoduché polymerizační reakce PANI, kdy v jednom reakčním kroku vzniká pomocí oxidačního činidla $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ za přítomnosti CS z anilinu kompozit PANI-CS. Přidáním NaOH dochází k reakci s FeCl_2 , který je zbytkovým produktem předchozí polymerizační reakce, za vzniku částic Fe_3O_4 majících magnetické vlastnosti. Na závěr jsou elegantně využity redukční vlastnosti PANI, které jsou charakteristické pro některé VP [33] (detailněji budou diskutovány dále v oddíle 4.4). Přidáním AgNO_3 do kompozitu PANI-CS- Fe_3O_4 , dojde k redukci stříbrného kationtu na kovové stříbro, a vzniká tedy finální multifunkční kompozit $\text{Ag@PANI-CS-Fe}_3\text{O}_4$ (obrázek 6 a obrázek 7) s nanočásticemi stříbra, které dekorují nosič z vodivého polymeru.

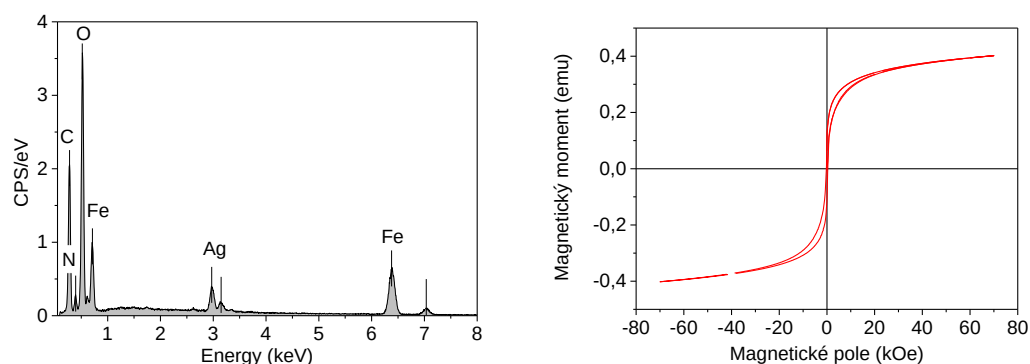
Využití podobného kompozitu je nasnadě. Chitosan spolu s PANI umožňuje dobrou dispergovatelnost kompozitu ve vodných roztocích, zároveň je známo, že VP jsou dobrými absorbéry aromatických znečišťujících látek (například azobarviv, které se používají v textilním průmyslu [34]), které vážou slabými vazebnými interakcemi [35]. Magnetický charakter kompozitu umožňuje snadnou zpětnou separaci VP z vodného roztoku, například permanentním magnetem. Přidané nanočástice Ag pak vykazují katalytické vlastnosti, které jsou schopny převádět znečišťující látku na látku méně nebezpečnou. V tomto konkrétním případě byly katalytické vlastnosti kompozitu $\text{Ag@PANI-CS-Fe}_3\text{O}_4$ úspěšně otestovány při redukci nitroaromatického 4-nitrofenolu.

Z výše uvedených prací je zřejmé, že VP vynikají relativně jednoduchou (často „one pot“) syntézou, kterou lze vhodným způsobem modifikovat tak, že je možné připravit pomocí malého počtu technologických kroků funkcionalizované tenké vrstvy nebo multifunkční kompozity. Příprava těchto látek navíc není finančně nákladná, protože lze pracovat v malých množstvích, se snadno dostupnými reaktanty a bez toxického odpadu. VP jsou schopny v mnoha případech nahradit daleko složitější látky a v mnoha praktických aplikacích dosáhnout srovnatelného výsledku s mnohonásobně dražšími materiály. Spolu se svými schopnostmi měnit velikost své měrné

elektrické vodivosti jako odezvu na změnu okolních podmínek či vytvářet supramolekulární struktury s velkým specifickým povrchem patří VP mezi inteligentní materiály s nadějnou budoucností.



Obrázek 6 - SEM kompozitu Ag@ PANI-CS-Fe₃O₄ (A), TEM kompozitu PANI-CS-Fe₃O₄ (B) a Ag@PANI-CS-Fe₃O₄ kompozitu (C), a HRTEM kompozitu Ag@PANI-CS-Fe₃O₄ (D). Výřez zobrazuje SAED kompozitu Ag@PANI-CS-Fe₃O₄ [22]



Obrázek 7 - Kompozit Ag@PANI-CS-Fe₃O₄ – prvkové složení měřené pomocí EDS (vlevo) a magnetické vlastnosti měřené vibračním magnetometrem (vpravo)

2 Moderní technologie pro výrobu organické elektroniky

Výroba miniaturních, horizontálních i vertikálních motivů, z organických polovodičů (např. 2D planárních tenkých vrstev, vodivých spojů, elektrodových systémů, 3D vertikálně vrstvených sendvičových struktur či přímo funkčních zařízení typu OTFT, OPV, OLED, RFID, fyzikálních a chemických senzorů atd.) s rozlišením obvykle jednotek či desítek mikrometrů, případně až stovek nanometrů, klade nemalé nároky na použité technologie zpracování a depozice materiálu. Základní podmínkou je, že použitá technologie nesmí ovlivnit vlastnosti a tím i funkci materiálu,

z něhož požadovaný motiv vzniká. Organické polovodiče jsou však ze své podstaty náchylné k poškození a dochází u nich snadno ke změně chemické struktury vlivem elektromagnetického záření (zejména z oblasti UV spektra), tepelného a mechanického namáhání, či chemické reakce (nežádoucí reakce s rozpouštědly, okolními plyny apod.). Navíc řada organických polovodičů je charakterizována velkou molekulovou hmotností (zejména v případě látek polymerního charakteru), což omezuje nebo zcela vylučuje jejich převedení do plynné fáze, či malou rozpustností v polárních či nepolárních rozpouštědlech, což ztěžuje možnost vytvoření jejich roztoků.

Výše jmenované rysy organických polovodičů neumožňují využít některé z osvědčených technologií pro opracování či tvorbu motivů z anorganických polovodičů. Fotolitografie, leptání, magnetronové napařování či napařování totiž značně chemicky a tepelně namáhají zpracovávaný materiál.

Speciální místo v oblasti přípravy motivů organických materiálů mají proto nedestruktivní tiskové technologie. Své uplatnění v organické elektronice našla technologie sítotisku, dále hlubotisku, ofsetu či flexotisku spojených se zpracováním převíjením substrátu (angl. *Roll-to-roll processing*), tampónový tisk a také technologie inkoustového tisku (zkracované jako Ink-Jet).

Kromě tiskových technologií se používají technologie typu spin-coating, dip-coating, spray-coating či příprava vrstev metodou Langmuir-Blodgett, alternativně lze použít speciálně uzpůsobené napařování organických materiálů OME (z angl. *Organic Molecular Evaporation*) či některou z laserových depozičních technik, např. MAPLE (z angl. *Matrix Assisted Pulsed Laser Evaporation*).

V této části práce budou diskutovány zejména dvě technologie i) Ink-Jet (oddíl 2.1) a ii) MAPLE (oddíl 2.2). Obě jmenované technologie se naší výzkumné skupině osvědčily při přípravě chemorezistorů [7,16,36,37] či adsorpčních vrstev QCM senzorů [13] na bázi VP. Laserové depoziční technologie byly navíc úspěšně testovány i při přípravě tenkých vrstev chemorezistorů na bázi acetyl-acetonátů, ftalocyaninů či porfyrinů [15,17,38,39].

2.1 Příprava substrátů chemorezistorů pomocí technologie Ink-Jet [36]

Principem technologie Ink-Jet je kontinuální dodávání tisknutého kapalného roztoku funkční látky (inkoustu) do tiskové hlavy, odkud je vystřelován ve formě kapiček na potiskované médium, kde vytváří požadovaný motiv.

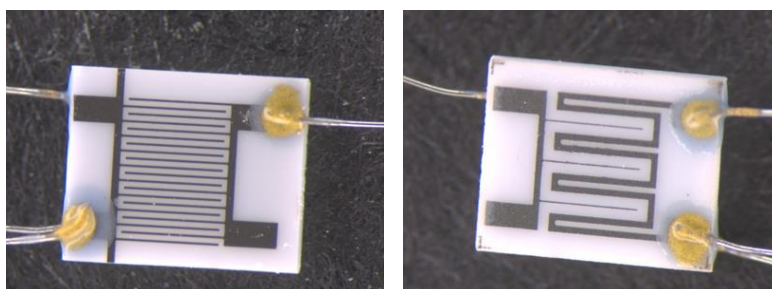
Technologie Ink-Jet je z mnoha důvodů považována za jednu z progresivních technologií pro masovou výrobu organické elektroniky. Je totiž nedestruktivní pro zpracovávaný materiál, relativně rychlá a bezkontaktní. Navíc se jedná o technologii aditivní, která nanáší materiál cíleně pouze do míst, kde je to vyžadováno, čímž šetří množství spotřebovaného materiálu. Vytvářet lze jemné planární motivy i vícevrstvé struktury. Běžně se používá pro tisk OPV, RFID čipů, OLED, pasivních elektronických prvků apod., uzpůsobit ji lze však pro širokou škálu dalších aplikací, např. pro tisk optických čoček a multiplexerů, fyzikálních a chemických senzorů a biosenzorů, mikroelektromechanických zařízení, polovodičových laserů, cínových spojů pro pájení, dále pro pokrývání umělých cév či implantovatelných elektrod biokompatibilním materiálem, enkapsulaci léčivých látek, přesné odměřování malých objemů, generování kalibračních směsí par o stopových koncentracích, jako dávkovač při chromatografii malých objemů apod.

Dnešní technologie Ink-Jet je uzpůsobena pro tisk kovů v podobě suspenzí nanočástic (např. stříbrný, či měďný inkoust) či pájecích hmot (např. cín, olovo), dále anorganických polovodičů (např. ITO, TiO₂), a samozřejmě organických látek ve formě kapalných krystalů, kvantových teček,

latexových suspenzí, olejů, lubrikantů, vosků, polymerů a v neposlední řadě organických polovodičů typu VP či ftalocyaninů. Potiskovat lze širokou škálu substrátů, např. sklo, ITO, polyester, polykarbonáty a polyimidy, optická vlákna, epoxid, teflon, křemík, oxid hlinitý, hliník a další kovy, obvyčejný i specializovaný papír apod. [40].

Široký výběr inkoustů i substrátů pro tisk dělá z technologie Ink-Jet zajímavou alternativu pro výrobu chemorezistorů. Následující původní výsledky nebyly (na rozdíl od zbytku mých zde citovaných prací) doposud publikovány v žádném recenzovaném vědeckém časopise či monografii, nicméně dokreslují komplexnost a záběr výzkumu v oblasti organické elektroniky a zejména senzorů na Ústavu fyziky a měřicí techniky VŠCHT Praha (ÚFMT).

Chemické senzory prezentované v oddíle 1.3 jsou hybridními zařízeními, která využívají odsvědčené senzorové platformy (destičky z Al_2O_3 s Pt topením a interdigitálním elektrodovým systémem, obrázek 8) a organické tenké vrstvy tvořené vodivým polymerem (PPy, PANI, PEDOT atd.). Tyto substráty však mají několik nevýhod, které jsou dostatečně motivační pro vývoj substrátů nových, pomocí technologie Ink-Jet. Největší nevýhodou je jejich vysoká cena, která pramení z množství technologických kroků, jež je při výrobě substrátu třeba učinit (fotolitografie, řezání, kontaktování apod.). V oblasti výzkumu a vývoje chemických senzorů na bázi VP se tak často jedná o nejdražší položku nového senzoru. Na spodní straně tohoto substrátu je navíc Pt topný meandr, který není nutné používat u řady senzorů na bázi organických látek, protože s výhodou pracují za laboratorní teploty.

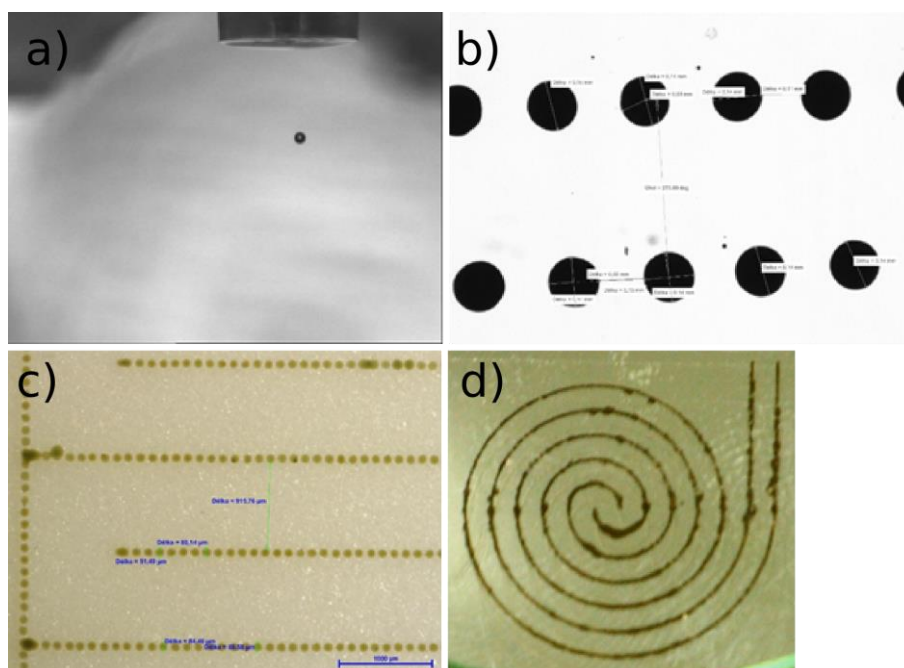


Obrázek 8 - Senzorový substrát z Al_2O_3 s interdigitálními elektrodami na svrchní straně (vlevo) a Pt topným meandrem (vpravo); rozměry $2,5 \times 2,5$ mm

Při návrhu nového substrátu pro chemorezistory na bázi vodivých polymerů, jenž by bylo možné kompletně vytisknout metodou Ink-Jet, se vycházelo z předpokladu, že substrát musí být ohebný, aby mohla být využita jedna z hlavních výhod organické elektroniky – flexibilita zařízení. Z pohledu izolačních vlastností, odolnosti proti tepelné námaze a agresivním chemickým rozpouštědlům byl po úvodních neúspěšných pokusech s klasickými polymerními podklady (PET, PE, PMMA) vybrán tepelně i chemicky odolný polyimid prodáváný pod značkou *Kapton*. Kromě podložky substrátu bylo nutné vybrat vhodný materiál na elektrodový systém, který by vykazoval dobrou adhezi k povrchu flexibilního substrátu, byl elektricky vodivý a vytvářel nejlépe Ohmický kontakt s organickou citlivou vrstvou. Výběr padl zejména na komerčně dodávané inkousty stříbrných a měděných nanočástic. Dráhy vytvořené z těchto inkoustů se musí po nanesení zformovat vysokou teplotou, aby došlo ke slnutí kovových částic a odpaření (pyrolýze) organického nosiče [40].

Na obrázku 9 je snímek kapky stříbrného inkoustu vylétající z piezoelektrické trysky, který byl pořízen stroboskopickou kamerou umístěnou na aparatuře určené pro depozici látek metodou Ink-Jet, a dále snímky pořízené v průběhu přípravy nových substrátů chemorezistorů. Tyto výsledky, jichž bylo dosaženo v bakalářské práci studenta J. Mikeše [36] pod vedením autora předkládané práce jsou spíše technologickou demonstrací možností a limitů nové aparatury pro

tvorbu jemných motivů metodou Ink-Jet, která byla vybudována na ÚFMT. Intenzivnější nasazení této metody pro tisk senzorů na bázi VP se předpokládá po překonání některých dílčích problémů, které jsou spojeny s vlastnostmi VP (např. horší adheze k substrátu, či obecná tendence k agregaci částic v inkoustu).



Obrázek 9 - Příprava substrátů chemických senzorů technologií Ink-Jet: a) kapka vylétající z trysky aparatury Ink-Jet, b) obrazová analýza řady nespojených kapek; c) tištěný základ pro tvorbu interdigitálních elektrod chemorezistoru; d) prototyp sensorové platformy se svinutými elektrodami [36]

2.2 Příprava citlivých vrstev senzorů pomocí laserových depozičních technologií [7, 13,15-17,37-39,41]

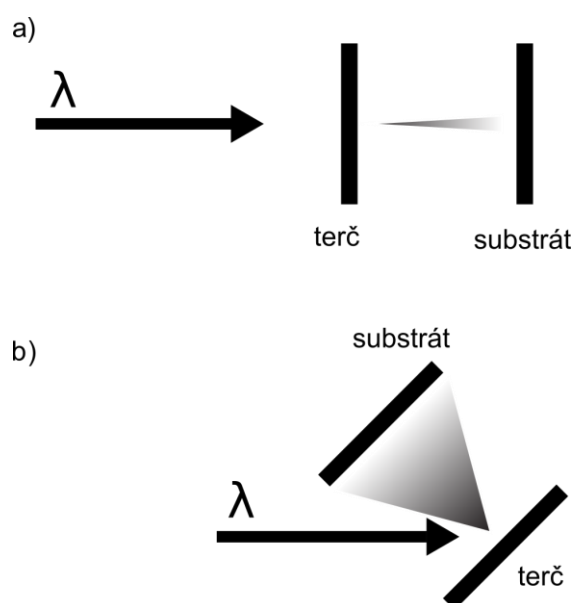
Historie vzniku laserových depozičních technologií je úzce spjata s léty bezprostředně následujícími po sestrojení prvního funkčního laseru. K tomu došlo v 60 letech 20. století a hned poté byl laser využit v mnoha experimentech. Pro materiálové inženýrství byla zajímavá zejména interakce vysoce energetického, monochromatického, koherentního záření s hmotou, neboť laser (zejména v pulsním režimu) je schopen soustředit energii do extrémně krátkého časového pulsu a/nebo extrémně prostorově lokalizovaného působení, čímž lze dosáhnout velice rychlých fázových změn opracovávaného materiálu a zformování termodynamicky metastabilních fází. Na počátku výzkumu laserových depozičních metod byl proto sledován pouze vliv laserového záření na původní, definované vlastnosti ozařovaného terče materiálu. Teprve později se staly předmětem zájmu i molekuly materiálu uvolněné z terče při ozařování laserovým paprskem (tzv. ablace), které kondenzují a vytvářejí tenké vrstvy (tzv. depozity) na površích okolo terče.

Původní technologie, nazývaná pulsní laserová depozice PLD (z angl. *Pulsed Laser Deposition*), jež je vhodná pro depozice spíše anorganických látek, se v průběhu let rozrostla o řadu modifikací, které jsou schopny nanášet anorganické materiály do tenkých vrstev i tvořit jemné motivy z látek organických. Patří mezi ně matricová pulsní laserová depozice MAPLE (z angl. *Matrix Assisted Pulsed Laser Evaporation*) a technologie laserového psaní LIFT (z angl. *Laser Induced Forward Transfer*) a MAPLE-DW (z angl. *Matrix Assisted Pulsed Laser Evaporation – Direct Write*). Detailní informace o historii, mechanismu přenosu molekul, rozdílech mezi technologiemi, využití

ve výzkumu, vývoji i při průmyslové výrobě jsou popsány ve specializované kapitole Kopecký a Škodová [41] v monografii věnované laserům a laserovým technologiím.

Technologie LIFT a MAPLE-DW patří mezi sériové depoziční technologie, PLD a MAPLE mezi paralelní depoziční technologie [42]. Při sériové laserové depozici dochází k přenosu materiálu sekvenčně, tedy v danou chvíli se nanáší pouze určitá část substrátu (obrázek 10a), což je výhodné pro tvorbu jemných motivů. Paralelní laserové depozice naproti tomu nanášejí materiál na všechna místa substrátu zároveň (obrázek 10b) za vzniku tenké vrstvy. Pokud je důležité nanášet materiál pouze na určité místo, je nutné použít speciální masku či stínítko, které je v případě tvorby složitějšího motivu nepraktické.

Základem PLD je vysokoenergetický laser pracující v pulsním režimu. Laserové pulsy dopadají na povrch ozařovaného materiálu – nazývaného zpravidla jako terč – odkud vyrážejí plazmový oblak, který ulpívá na protilehlém substrátu (obrázek 11). Laserový svazek dopadá na terč většinou pod úhlem 45° a vyráží materiál opačným směrem.



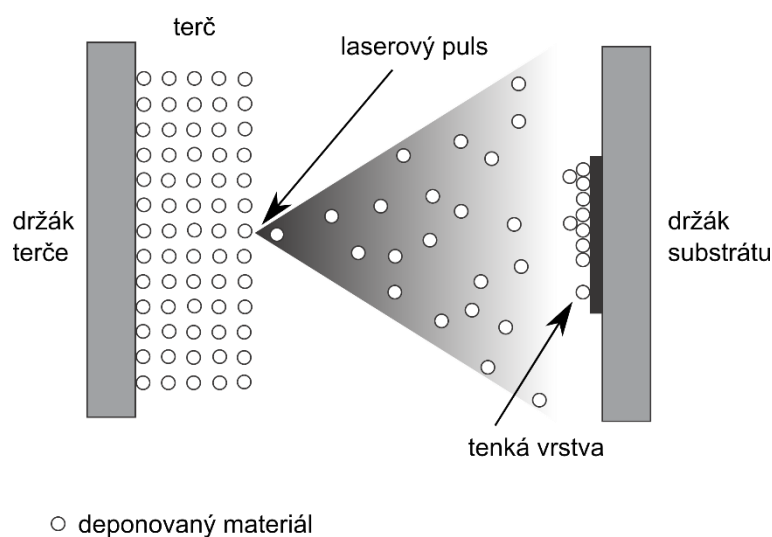
Obrázek 10 - Sériové (a) a paralelní (b) laserové depoziční technologie [41]

Mechanismus přenosu materiálu je založen na předávání termální energie laserového svazku ablovanému materiálu a následnému explozivnímu uvolnění materiálu z terče v důsledku lokálního přehřátí. V místech lokálního přehřátí dochází k pyrolytickému a fotolytickému rozkladu materiálu a vzniku plazmatického oblaku tvořeného nejenom molekulami deponovaného materiálu, ale i jejich shluky, fragmenty, elektrony, radikály apod. Tato vlastnost je jednou z prvních a hlavních limitací pro široké nasazení PLD při depozicích "křehkých" organických materiálů, existují však výjimky [41].

Obecně lze hovořit o třech kategoriích organických látek [41], u kterých je možné používat metodu PLD: (i) první kategorií látek jsou látky se schopností samoskladby po dekompozici laserovým zářením, klasickým materiálem této skupiny je polytetrafluoroethylen (PTFE) [43], (ii) do druhé kategorie spadají všechny látky – polymery, makromolekuly a biologicky aktivní látky – u nichž sice dochází vlivem laserového přenosu k částečné dekompozici, množství a rozsah poškození materiálu však neovlivní jeho funkci [44], (iii) v posledním případě je degradace materiálu při

depozici zjevná a postihuje většinu přenášených molekul, není však překážkou, pokud je cílem příprava metastabilních materiálů, segmentů molekul s novými vlastnostmi nebo dokonce vlastní studium pyrolytického rozkladu látek [45].

Příkladem práce, jež využívá PLD pro depozici tenkých vrstev organických polovodičů, je práce Fryček a kol. [46] a na práce na ni tematicky navazující Fitl a kol. [38], které se zabývaly přípravou chemorezistorů na bázi acetyl-acetonátů india a cínu. Při dopadu záření KrF resp. Nd:YAG laseru na tyto organické polovodiče dochází vždy k jejich nevratné chemické přeměně. Určení finálního chemického složení takové vrstvy však není jednoduché, protože při depozici metodou PLD vzniká řada fragmentů a nestabilních produktů pyrolýzy a fotolýzy. Mnohem důležitějším výsledkem je však skutečnost, že materiál po této přeměně neztrácí své detekční vlastnosti a naopak získává např. vyšší citlivost k vybraným plynům a parám, např. ozónu, vodíku, *n*-butanolu apod.



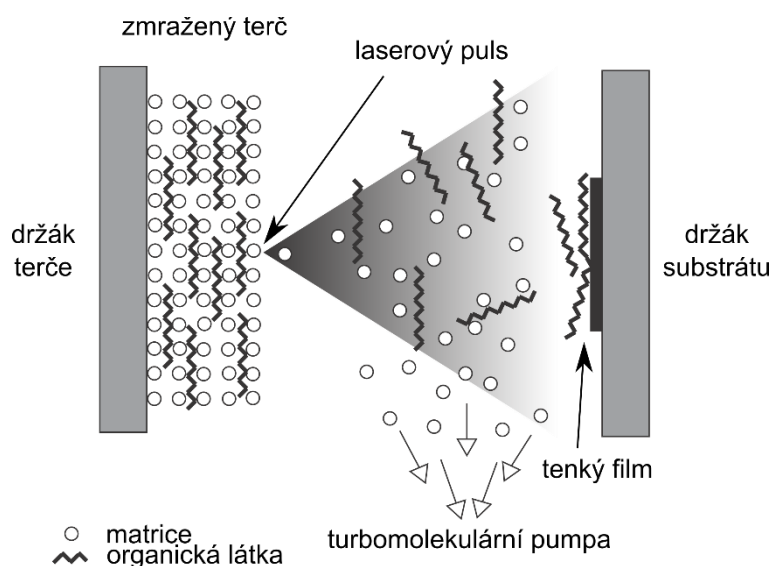
Obrázek 11 - Princip funkce PLD [41]

Mnohem větší spektrum organických polovodičů však při depozici PLD zcela degraduje a ztrácí své fundamentální vlastnosti, jež by byly využitelné v organické elektronice. Pro tento typ látek je metoda PLD nevhodná a byla proto vyvinuta metoda MAPLE [47], která je schopna přenášet nejenom organické polovodiče, ale obecně i "křehké" organické a biologické materiály s charakterem polymerů, makromolekul, biologicky funkčních celků, a dokonce i živých buněk.

MAPLE disponuje výrazně jemnějším mechanismem ablace terče v porovnání s PLD. Jemnější mechanismus je dán odlišným složením ozařovaného terče, který je tvořen nejenom deponovaným materiálem, ale i tzv. maticí. Matrice je látka o nízké molekulové hmotnosti, jejíž absorpční pás má v ideálním případě na vlnové délce použitého laserového záření své maximum [42]. Laserové záření dopadající na terč je poté absorbováno převážně maticí, která funguje jako účinný štít chránící deponovaný materiál před pyrolytickým a fotolytickým poškozením. Jako matrice se nejčastěji využívají těkavá organická rozpouštědla (např. methanol, dimethylsulfoxid, toluen atd.), ale třeba i voda. Většina organických látek vykazuje v UV oblasti rovněž výrazné absorpční pásy. Z tohoto důvodu bývá typická koncentrace deponovaného materiálu v matici přibližně jednotky hm. %, čímž se minimalizuje pravděpodobnost interakce deponovaného materiálu s UV zářením [41].

Terč pro depozici je vytvořen zchlazením roztoku či disperze deponované látky v matici do pevného stavu na teplotu kapalného dusíku. Vlastní depozice probíhá v evakuované komoře

obdobné jako v případě PLD. Laserový paprsek dopadá na terč pod úhlem 45°; uspořádání odpovídá paralelní depoziční metodě (obrázek 12). Po dopadu laserového pulsu na terč dochází k absorpci energie laserového pulsu matricí. Tento jev lze popsat jako fototermální proces. Energie fotonů absorbovaná matricí se přemění na tepelnou energii, která způsobí prudké lokální přehřátí matrice a její odpaření do plynné fáze. Deponovaný materiál chráněný před laserovým zářením vysokou absorpční schopností matrice, získává kolektivními kolizemi s jejími molekulami dostatečnou kinetickou energii, což umožňuje vznik oblaku ablovaného materiálu a jeho transfer na substrát. Na povrchu substrátu se vytváří rovnoměrný homogenní tenký film deponovaného materiálu. Matrice se díky nízkému tlaku par rychle odpařuje a je průběžně odčerpávána turbomolekulární vývěvou tak, aby nedocházelo k nárůstu tlaku v komoře [41].



Obrázek 12 - Princip funkce MAPLE [41]

Terč pro MAPLE je v ideálním případě tvořen pravým roztokem. Problém rozpustnosti některých látek je ovšem komplikovaný. Např. v případě vodivých polymerů je jejich rozpustnost neřešitelná bez použití pomocných látek, neboť vodivé polymery nejsou rozpustné ani v polárních ani v nepolárních rozpouštědlech, případně je jejich rozpustnost velice omezená a dochází k rychlé agregaci částic. Nejefektivnějším způsobem, jak zvýšit rozpustnost vodivých polymerů, je použít jako pomocných látek některého ze zástupců široké plejády surfaktantů a sulfonových kyselin [48].

Práce Kopecký a kol. [49] se zabývá syntézou PPy ve formě roztoku vhodného přímo pro depozice metodou MAPLE. Jako pomocné látky byly použity čtyři různé sulfonové kyseliny a surfaktanty: kys. *p*-toluensulfonová, kys. dodecylbenzensulfonová, dioktysulfosukcinát a kys. kafrsulfonová. Bližší informace o těchto syntézách lze nalézt v odstavci 3.3 věnovaném syntéze PPy. Výše jmenované látky výrazně zvyšují rozpustnost PPy v dimethylsulfoxidu (DMSO), případně ve vodě, a umožňují depozice metodou MAPLE pomocí KrF (248 nm) i Nd:YAG (266 nm) laseru.

V práci Kopecký a kol. [7] a Sedlák a kol. [13] byl deponován rozpustný PPy z vodného roztoku či roztoku DMSO metodou MAPLE. Takto přenesený materiál, nepoškozen laserovým zářením, posloužil jako tenká citlivá vrstva chemorezistorů, resp. QCM senzorů (viz oddíl 1.3).

Problematika depozic vodivých polymerů pomocí metody MAPLE je však komplexnější, protože vyžaduje znalost i řady dalších dílčích podmínek a parametrů depozice (např. počtu použitých

pulsů laserového záření, teploty terče či energie laserového záření) a navíc je pro depozice nezbytná poměrně složitá a nákladná aparatura. Část problematiky laserových depozic a s tím souvisejících vlastností deponovaných materiálů je rozebrána v referencích [7,49], přehled historie, principů a využití všech zmíněných laserových depozičních metod v oblasti depozic organických látek je proveden v kapitole Kopecký a Škodová [41] monografie věnované laserovým technologiím, a detailní shrnutí depozic vodivých polymerů lze nalézt v monografii Kopecký a kol. [37].

Závěrem lze shrnout, že laserové depoziční technologie mají dobrou perspektivu pro depozice tenkých vrstev a jemných motivů na bázi organických látek, i když je nutné zvážit zejména náročnost těchto technologií na zkušenosti a znalosti obsluhy i celkově vysoké náklady na výrobu jednoho zařízení. V oblasti masové výroby organické elektroniky tak bude mít tisk i nadále velký náskok. Některé z laserových depozičních metod však již byly použity jako průmyslové technologie výroby produktů, a tak je možné, že se s nimi budeme v budoucnu v oblasti organické elektroniky setkávat častěji [50]. Naproti tomu pro laboratorní experimenty a základní výzkum je role laserových depozičních technik nezastupitelná.

3 Polypyrrol: chemická struktura a syntéza

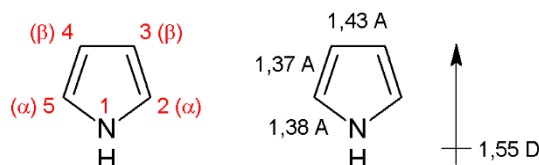
Následující část je věnována zejména syntéze a charakterizaci vodivého polymeru PPy. V předchozích odstavcích byl PPy několikrát zmíněn v souvislosti s chemorezistory, QCM senzory a depozičními technologiemi, které umožňují přípravu jeho tenkých citlivých vrstev. PPy, který byl používán úplně na počátku experimentů prováděných na ÚFMT, byl komerčně dodávaným produktem, jehož přesné složení podléhalo průmyslovému utajení. Pro výzkumné účely zahrnující objasňování mechanismů (např. depozice, detekce, elektrické vodivosti apod.) to tedy byl materiál nepříliš vhodný a bylo velkou snahou kupovaný materiál nahradit jiným, se známými parametry. Postupně se z jednoduchých syntéz přecházelo na stále sofistikovanější a díky tomu se podařilo získávat materiál s velmi zajímavými vlastnostmi (např. lepší rozpustností, elektrickou vodivostí, supramolekulární strukturou apod.). Následující odstavce jsou věnovány výsledkům syntézy a charakterizace PPy, které pomáhají objasňovat některé doposud neznámé příčiny nestandardního chování senzorů na bázi VP (např. driftu citlivosti).

3.1 Monomer – pyrrol

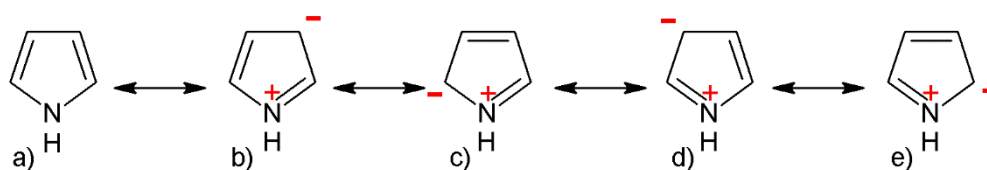
Základním stavebním kamenem PPy je monomerní pyrrol (obrázek 13 (vlevo)), patřící do kategorie pětičetných aromatických heterocyklů. Struktura pyrrolu se sestává ze čtyř sp^2 -hybridizovaných atomů uhlíku a jednoho sp^2 -hybridizovaného atomu dusíku. Pyrrol tedy obsahuje 6 elektronů π (4 z p orbitalů uhlíku a 2 z volného elektronového páru p orbitalu dusíku) a vytváří konjugovaný aromatický systém dvojných vazeb. Jednotlivé atomy pětičetného aromatického kruhu jsou zpravidla číslovány počínaje heteroatomem (dusíkem) a řeckým písmenem jsou zvýrazněny uhlíky se stejnou reaktivitou (uhlíky 2,5 jsou označovány jako α , uhlíky 3,4 jsou označovány jako β). Tento systém je následně používán i u PPy.

Molekula pyrrolu se vyskytuje v pěti rezonančních formách. U první z nich nedochází k separaci náboje (obrázek 14a), u dalších dvou párů ekvivalentních rezonančních struktur dochází k separaci náboje a tedy driftu elektronů směrem od dusíku. Těchto pět rezonančních struktur nepřispívá do struktury pyrrolu stejnou měrou a jejich důležitost klesá směrem a) > c), e) > b), d). Vyšší pravděpodobnost existence struktury c) a e) způsobuje, že při polymerizaci pyrrolu dochází

pravděpodobněji ke vzniku vazeb v polohách α - α a výsledný polymer je lineární s jednotkami natočenými o 180° (viz oddíl 3.2).



Obrázek 13 - Monomerní pyrrol s vyznačením jednotlivých pozic (vlevo); délky vazeb a dipólový moment pyrrolového kruhu (vpravo)



Obrázek 14 - Rezonanční struktury pyrrolu

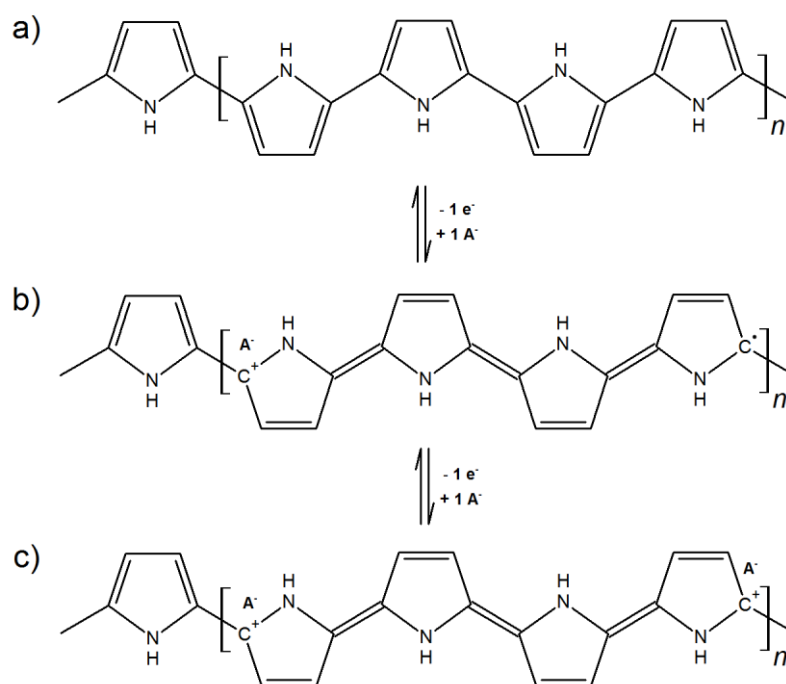
Elektronegovnější dusík (elektronegativita 3) přitahuje elektrony ze sousedních uhlíků (elektronegativita 2,5). Silnější rezonance však způsobuje, že vzniklý dipólový efekt směřuje směrem od dusíku a dochází k deformaci délky všech vazeb v pyrrolovém kruhu. Nejdelší vazbou pyrrolového kruhu je vazba 3,4 (obrázek 13).

Pyrrol díky svému elektronově bohatému aromatickému kruhu podléhá elektrofilní substituci. Elektrofilní substituce probíhá z důvodu vyšší elektronové hustoty primárně na α uhlíku pyrrolového kruhu. Elektronově bohatý pětičlenný heterocyklus také umožňuje elektrofilní radikálovou substituci v poloze α . Pyrrol je také náchylný k deprotonaci *N*-vodíku pomocí silných alkálií, protože hodnoty disociační konstanty pyrrolu pro ztrátu *N*-vodíku jako protonu jsou $pK_a = 14 - 18$. Vzniklý *N*-anion je nukleofilní a reaguje substituční reakcí s elektrofilny. Standardně (bez deprotonačního kroku) však elektrofilní substituce na heteroatomu pyrrolu neprobíhá, protože by vzniklý produkt nebyl rezonančně stabilizován [51].

3.2 Chemická struktura polypyrrolu a její vliv na elektrickou vodivost

PPy patří mezi heterocyklické aromatické VP s relativně vyšší chemickou stabilitou a elektrickou vodivostí. Dosud nejvyšší publikovaná hodnota měrné elektrické vodivosti práškového PPy syntetizovaného chemickou cestou dosáhla hodnoty $220 \text{ S} \cdot \text{cm}^{-1}$ [52], a to je jedním z důvodů, proč je PPy považován za klíčovou látku při vývoji nových typů elektronických zařízení, elektrod pro dobíjecí baterie a superkapacitory, pevných elektrolytů kondenzátorů, materiálů pro elektromagnetické stínění, senzorů, korozivzdorných povrchů, spínačů a jiných akčních členů, elektrochromních zařízení či membrán [26].

Idealizovaná představa PPy předpokládá lineární řetězec s pyrrolovými jednotkami vzájemně natočenými o 180° (obrázek 15a). Dvojně vazby a volný elektronový pár dusíku vytváří π -delokalizovaný systém se zakázaným pásem o šířce 3,16 eV, který za laboratorní teploty znemožňuje snadnou excitaci valenčních elektronů do vodivostního pásu. Řetězec idealizovaného PPy proto neobsahuje volné nosiče náboje a chová se jako izolant.



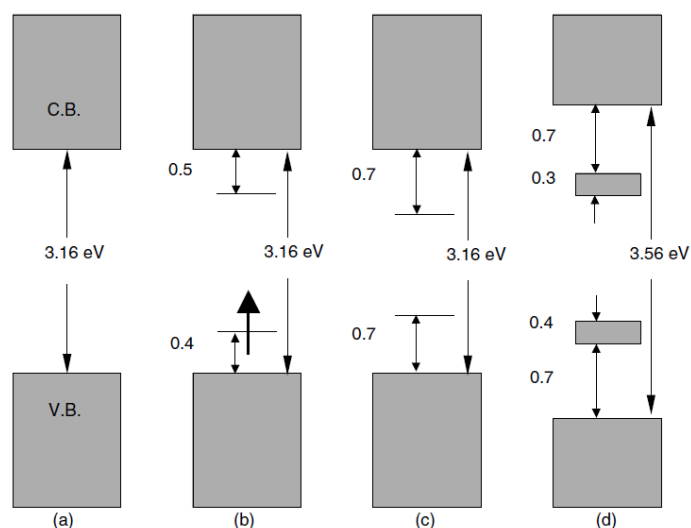
Obrázek 1 - Formy PPy: a) elektricky nevodivý idealizovaný řetězec a jeho b) polaron a c) bipolaron

Elektrická vodivost je však spojena s existencí nosičů náboje a ty jsou ve VP vytvářeny procesem nazývaným dopování. Dopování vede (velmi zjednodušeně řečeno) k přidávání či ubírání elektronů z řetězce VP, což má za následek vznik volných nosičů náboje. Většina VP je dopována oxidačně-redukčním procesem, u PANI je však znám i proces dopování protonací silnou kyselinou (např. HCl) [53]. Obvyklou cestou dopování PPy je tedy chemická nebo elektrochemická (anodická) oxidace, která vede postupně ke vzniku kation-radikálu (polaronu) a následně dikation (bipolaronu); obě elektricky vodivé formy jsou zobrazeny na obrázku 15b,c. Existence bipolaronů je charakteristická zejména pro vysoce dopované VP.

Z hlediska náboje volných nosičů je výsledný polykation PPy polovodičem typu *p*. Ve VP jsou však známy i polovodiče typu *n*; například PAC může být redukován na polyanion. Problémem *n*-dopovaných VP je jejich vysoká reaktivita, která způsobuje prudký pokles elektrické vodivosti při expozici vzdušným kyslíkem [25].

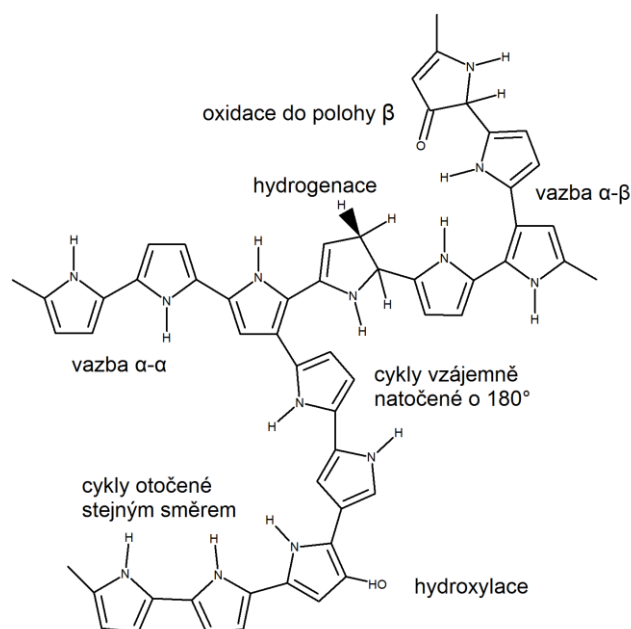
Dopanty ve formě protiontů jsou tedy neoddelitelným doprovodem polykationtového polymerního řetězce PPy, protože zachovávají elektroneutralitu materiálu. Navíc, i s ohledem na jejich velké množství (až jednotky procent molárních), ovlivňují šířku zakázaného pásu PPy a řadu dalších materiálových vlastností, jako je například rozpustnost (o vlivu dopantů na rozpustnost VP pojednává detailněji oddíl 3.3).

Relativně široký zakázaný pás PPy se v závislosti na množství a typu dopantu zužuje a vzniká postupně již zmíněný polaron a bipolaron, až při plně dopovaném PPy dojde ke vzniku struktury s podstatně užšími zakázanými pásy (obrázek 16).



Obrázek 16 - Struktura pásového diagramu a) neutrálního PPy, b) polaronu, c) bipolaronu a d) plně dopovaného PPy; upraveno podle [26]

Dopování VP evokuje obdobný proces, kterým je dosahováno děrové či elektronové vodivosti u křemíku. Rozdíl je zde však zejména v množství dopantu, který musí být do organického polovodiče přidán, aby vznikl dostatečný počet nosičů náboje. Běžný VP je dopován v řádech až jednotek mol. %, zatímco u křemíku se jedná pouze o stopová množství dopantů (10^{-4} až 10^{-2} mol. %). Plně dopované vodivé polymery obsahují 10^{21} až 10^{23} nosičů náboje na cm^3 , což je o čtyři až pět řádů více, než obsahují anorganické polovodiče [26]. Nižší vodivost VP oproti anorganickým polovodičům je dána zejména nižší pohyblivostí nosičů náboje v polymeru v důsledku jeho nízké krystalinity a existence řady defektů. Někdy se v této situaci výstižně popisuje jako "mobility gap".

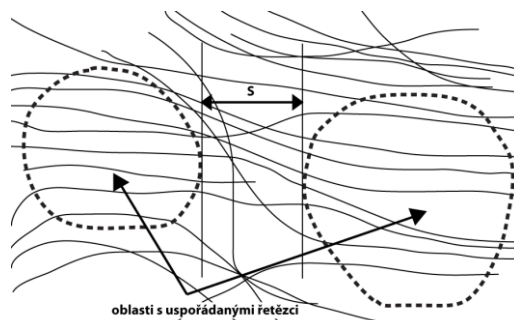


Obrázek 17 - Vazby a poruchy vyskytující se v reálném PPy; upraveno podle [54]

Reálnější pohled na strukturu PPy je proto na obrázku 17. Během syntézy a následného zpracování materiálu se v řetězci PPy objeví řada poruch a defektů, které jsou způsobeny nejčastěji přítomností vody či vzdušného kyslíku. Nezanedbatelné množství poruch také vzniká

dlouhodobým stárnutím v důsledku působení tepla, světla, mechanického namáhání či chemicky reaktivních látek. Bližší pohled na tento proces přináší oddíl 4.3. Všechny tyto poruchy porušují planaritu a linearitu idealizovaného řetězce PPy a snižují míru překryvu π -orbitalů.

Pohyblivost nosičů náboje je tedy určujícím parametrem pro velikost elektrické vodivosti ve VP. Z hlediska členění rozlišujeme pohyblivost řetězcovou, kdy se nosiče náboje pohybují po řetězci VP, a meziřetězcovou, kdy dochází k přeskokům a tunelování mezi dvěma řetězci VP. Při řetězcové vodivosti dochází po vložení externího napětí k postupnému přeuspořádání jednoduchých a dvojných vazeb konjugovaného řetězce a tím k pohybu polaronu či bipolaronu podél řetězce VP. Tento pohyb vyžaduje daleko méně energie než přeskoky či tunelování, k nimž dochází, pokud polaron či bipolaron dorazí na okraj poruchy či konec řetězce. Z tohoto důvodu je meziřetězcová pohyblivost nejvíce limitujícím faktorem pro celkovou pohyblivost [26]. Míra meziřetězcové pohyblivosti je dána uspořádáním jednotlivých řetězců do domén s vyšší či nižší krystalinitou. Představu o tomto problému si lze vytvořit ze schématu na obrázku 18. Domény s vyšší krystalinitou vykazují vyšší pohyblivost nosičů náboje, kdežto domény s menší krystalinitou tvoří potenciálové bariéry, které mohou být nosičem náboje přeskoceny nebo tunelovány pouze tehdy, pokud do systému vložíme dostatek energie (např. teplem, světlem, vysokým napětím apod.).



Obrázek 18 - Krystalické domény ve VP; kóta S vytyčuje potenciálovou bariéru

Tvorbu domén s vyšší krystalinitou lze ovlivnit mj. volbou vhodného dopantu. Mitchell a kol. [55] provedl experiment s dopováním PPy pomocí malých sférických (SO_4^- , Cl^-) a velkých planárních aromatických (toluensulfonátové či naftalensulfonátové anionty) dopantů, který vedl k zjištění, že typ a struktura dopantu významně ovlivňují izotropii uspořádání molekul PPy. Zatímco dopování pomocí malých sférických dopantů vede k tvorbě materiálu s výrazně izotropním uspořádáním molekul, velké planární molekuly interagují pomocí slabých vazebných interakcí (zejména pomocí π - π interakce) s aromatickými kruhy PPy, a tím snižují vzdálenosti mezi jednotlivými řetězci, zkompatňují materiál a zvyšují anizotropii uspořádání molekul. Při dopování PPy pomocí planárních aromatických molekul tedy vznikají větší krystalické domény. Podobný jev, avšak u supramolekulárních struktur PPy, sledoval i Kopecký a kol. [56]; detailněji je tento problém diskutován v oddíle 4.2.

3.3 Syntéza polypyrrolu [49]

PPy je získáván polymerizací pyrrolu chemickou nebo elektrochemickou cestou. Elektrochemická cesta (tedy anodická oxidace monomeru v přítomnosti dopantů) vede zpravidla k syntéze PPy s vyšší mírou uspořádanosti řetězců, a tedy i s vyšší elektrickou vodivostí. Elektrochemická syntéza také nabízí možnost připravovat tenké vrstvy PPy *in-situ* přímo v reakčním roztoku. Jedná se však o tematiku, jejíž rozsah výrazně překračuje možnosti této práce, a proto bude v textu diskutována pouze okrajově. Detailní informace o elektrochemické syntéze PPy lze nalézt například v přehledových článcích [57] či specializovaných knihách [26,54].

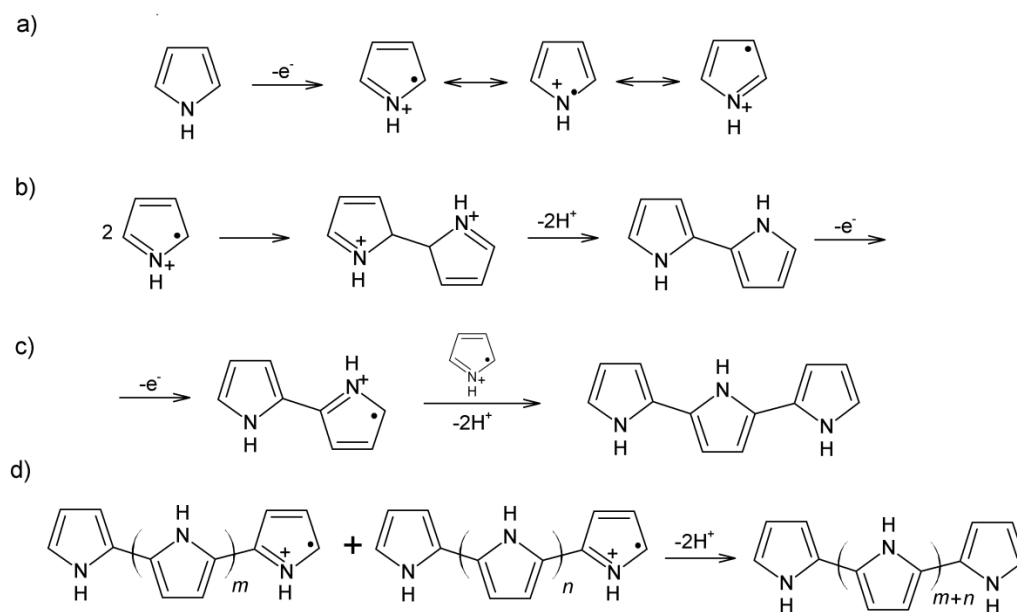
V případě chemické syntézy je PPy syntetizován oxidací (chemickým činidlem, nikoli anodicky) pyrrolu, zpravidla ve vodných roztocích, méně časté jsou syntézy v jiných rozpouštědlech, např.

v reverzní mikroemulzi [58], v alkoholech [52], v pevné fázi (ledu) [59], či v plynné fázi (polymerizace v parní fázi) [60].

Pyrrol snadno spontánně polymerizuje vlivem světla, tepla i atmosférického kyslíku. Jedná se však o velmi pomalé děje. Při standardní chemické polymerizaci se používá vhodné oxidační činidlo, nejčastěji kationtové oxidační činidlo solí přechodných kovů. Mezi běžná oxidační činidla patří např. železité ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, $\text{K}_3\text{Fe}(\text{CN})_6$, FeBr_3), měďnaté ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, CuBr_2) nebo stříbrné soli (AgNO_3) [61], nebo exotičtější oxidační činidla např. $\text{Ce}(\text{SO}_4)_2$, PdCl_2 [62], či aniontová oxidační činidla jako například APS [63].

Syntézu PPy je možné provádět za běžné laboratorní teploty. Jedná se o reakci exotermickou, a reakční směs je tedy nutné ve velkých objemech kontinuálně ochlazovat. Výsledný PPy však vykazuje vyšší stabilitu i hodnoty elektrické vodivosti, pokud je reakce prováděna za nízkých teplot [52][59]. Kromě teploty jsou finální vlastnosti PPy ovlivněny i koncentrací a stechiometrií reaktantů, dobou syntézy, mechanickým mícháním či prací v ochranné atmosféře.

Mechanismů popisujících průběh polymerizační reakce pyrrolu bylo popsáno několik. Na obrázku 19 je zobrazen obecně přijímaný mechanismus, popisující iniciační fázi polymerizační reakce, ve které při oxidaci pyrrolu dochází k vzniku kation-rádikalů (obrázek 19a) a následně jejich spojením vzniká bipyrrol (obrázek 19b). Ve fázi propagace řetězce, vznikají oxidací radikály bipyrrolu, a následně oligopyrrolů, které se dále řetěží. Se zvyšující se délkou řetězce dochází k překročení meze rozpustnosti polymeru v reakčním roztoku a vzniká černý precipitát [26].



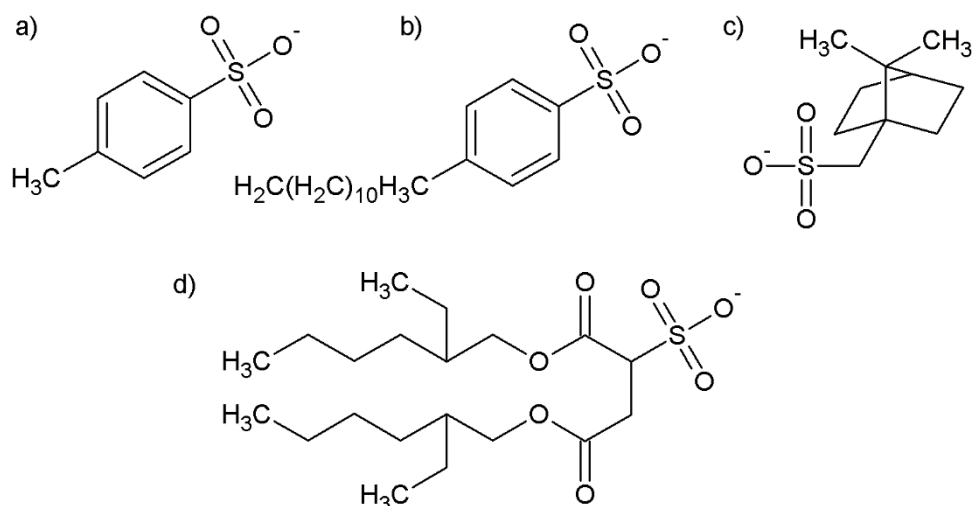
Obrázek 19 - Mechanismus polymerizační reakce pyrrolu

PPy připravený chemickou polymerizací je zpravidla nerozpustný ve vodě i organických rozpouštědlech, což limituje jeho použití v řadě moderních depozičních technologií (např. Ink-Jet, Spin-Coating atd.), kde jsou funkční materiály deponovány z kapalné fáze. Nerozpustnost PPy je způsobena zejména meziřetězcovými interakcemi (např. π - π interakce heteroaromatických kruhů) a jejich vliv lze potlačit výběrem vhodných dopantů. Nejběžnějším typem dopantu, který se vyskytuje v dopovaném PPy, jsou malé anorganické anionty (Cl^- , FeCl_4^- , SO_4^{2-} , HSO_4^- , NO_3^- apod.), které jsou do materiálu zaneseny v průběhu polymerizace z použitého oxidačního činidla. Jejich přítomnost v PPy však nemá téměř žádný vliv na jeho rozpustnost.

Experimentování s dopanty však ukázalo, že pokud jsou použity velké organické molekuly typu surfaktantů či sulfonových kyselin, je možné významně rozpustnost VP zvýšit a získat koloidní roztok VP [48,64-68]. Příkladem tohoto přístupu je syntéza PPy v přítomnosti čtyř různých organických dopantů: i) aniontu *p*-toluensulfonátu (*p*-TSA); ii) aniontu dodecylbenzensulfonátu (DBSA); iii) aniontu dioktylsulfosukcinátu (DEHS) a iv) aniontu kafrsulfonátu (CAMP), která byla prováděna s cílem získat PPy s vysokou rozpustností v organickém rozpouštědle dimethylsulfoxid (DMSO) pro depozice metodou MAPLE (viz oddíl 2.2) [49].

Referenční vzorky PPy byly syntetizovány pomocí dvou různých oxidačních činidel – FeCl_3 a APS a připravený polymer tedy obsahoval pouze malé ionty Cl^- , resp. SO_4^{2-} . Další vzorky byly syntetizovány v přítomnosti vždy jedné z výše jmenovaných pomocných látek (*p*-TSA, DBSA, DEHS, CAMP, viz obrázek 20). Molární poměr reaktantů pyrrol : pomocná látka byl vždy 5 : 1. Vzorky byly syntetizovány za snížené teploty, 0 °C. Syntetizovaný PPy obsahoval vždy dopanty, které byly do materiálu zaneseny z oxidačního činidla (tedy buď ionty Cl^- , nebo SO_4^{2-}) a v případě použití pomocné látky ještě navíc aniont příslušné sulfonové kyseliny či surfaktantu.

Měření rozpustnosti připravených vzorků ukázalo, že PPy dopovaný pouze malými anorganickými ionty v roztoku sedimentoval v řádu jednotek minut. Ani relativně malé molekuly sulfonových kyselin *p*-TSA a CAMP výrazně nepřispěly k vyšší rozpustnosti PPy v DMSO i destilované vodě, pouze PPy syntetizovaný pomocí APS v přítomnosti CAMP bylo možné považovat za rozpustný s výrazným rozdílem rozpustnosti v DMSO (6,5 hm. %) a ve vodě (1,8 hm. %). V případě použití surfaktantů DBSA a DEHS se situace výrazně zlepšila. PPy syntetizovaný v přítomnosti DEHS, DBSA vykazoval dobrou rozpustnost v DMSO (4 resp. 5 hm. %). Rozpustnost DBSA byla shodná jak pro DMSO, tak pro destilovanou vodu. V případě DEHS bylo v destilované vodě dosaženo pouze relativně nízké rozpustnosti (cca. 2,5 hm. %), celkově však PPy připravený v DEHS vykazoval nejmenší velikost rozpuštěných částic a měl nejbližší k pravému roztoku.



Obrázek 20 - Organické dopanty a) anion kys. *p*-toluensulfonové (*p*-TSA); b) anion kys. dodecylbenzensulfonové (DBSA); d) anion kafrsulfonátu; c) anion dioktyl-sulfosukcinátu (DEHS).

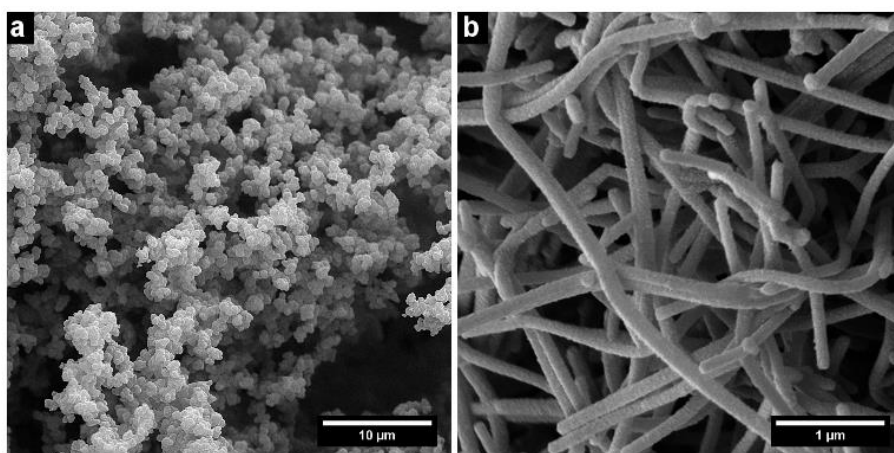
Zajímavou korelaci mezi velikostí dopantů a elektrickými vlastnostmi ukázalo měření elektrické vodivosti připravených vzorků PPy. Z dřívějších prací je známo, že velké planární molekuly aromatických dopantů zvyšují elektrickou vodivost PPy, protože vzniká kompaktní materiál s vyšší mírou krystalinity [55]. Vyšší hodnoty elektrické vodivosti bylo možné pozorovat i v případě PPy

filmů, ve kterých bylo použito DEHS a *N*-metyl-2-pyrrolidon jako rozpouštědlo [66]. V případě výše popsaných experimentů [49] byla elektrická vodivost PPy syntetizovaného v přítomnosti *p*-TSA, DBSA, DEHS, CAMP skutečně vyšší (obecně v řádech $10^{-1} \text{ S}\cdot\text{cm}^{-1}$), než u referenčních vzorků (v řádech $10^{-2} \text{ S}\cdot\text{cm}^{-1}$), avšak obecně se stále jedná o nízké hodnoty. Elektrická vodivost nejrozpuštěnějšího vzorku PPy syntetizovaného v přítomnosti DEHS dosáhla dokonce hodnot v řádu $10^{-1} \text{ S}\cdot\text{cm}^{-1}$. Až v pozdějším výzkumu PPy syntetizovaného v přítomnosti methyl oranže (MO) bylo ukázáno, že pro organické dopanty tohoto typu existuje maximum koncentrace pomocné látky, kterou je možné při syntéze použít a po jejím překročení dochází k prudkému poklesu vodivosti (a to vlivem tvorby nežádoucího kompozitu) [56].

Závěrem lze tedy shrnout, že dopanty hrají podstatnou roli nejenom při modifikaci elektrické vodivosti VP, ale jejich struktura a vlastnosti vzhledem k jejich relativně velkému množství ovlivňují řadu dalších důležitých parametrů VP, a jejich variací lze připravovat VP na míru dané aplikace.

4 Supramolekulární struktura polypyrrolu

Výsledkem syntézy PPy standardní chemickou cestou, tedy bez přídavku jakékoliv látky vyjma monomeru pyrrolu a oxidačního činidla, je vždy materiál s izotropními vlastnostmi a morfologií, která z makroskopického pohledu připomíná hlávku kvěťáku (obrázek 21). PPy s touto morfologií se v odborné literatuře nazývá globulárním PPy (PPy-G) a v dnešní době je zpravidla používán pouze jako referenční materiál pro moderní syntézy nano- a mikro-strukturovaného PPy. Význam PPy-G pro reálné aplikace postupně upadá, protože byl v mnoha ohledech strukturovanými protějšky překonán (např. velikostí měrné elektrické vodivosti či specifického povrchu).



Obrázek 21 - Standardní globulární PPy (a) a nanotubulární PPy připravený pomocí azobarviva methyl oranž (b) pro porovnání

Na počátku 90. let 20. stol. provedl Martin a kol. [69-72] sérii experimentů, které lze považovat za průkopnické v oblasti supramolekulárních struktur VP, protože jejich cílem bylo usměrnit polymerizaci VP a získat tak materiál s nano-tubulární či vláknitou morfologií, jejíž jednotlivé částice budou mít definované rozměry (zejména průměr ale i délku). Pro tento typ syntézy použil tzv. "tvrdou šablonu" - tedy šablonu tvořenou mikroporézní membránou polykarbonátového filtru s válcovými otvory o průměru 0.5 μm. Membrána oddělovala oxidační činidlo a monomer tak, aby polymerizační reakce probíhala uvnitř válcových otvorů, což v závislosti na délce reakce vedlo

k tvorbě nanotrubelek či nanodráťů⁵. Poprvé se zde také ukázalo, že výsledné struktury vykazují vyšší elektrickou vodivost než globulární morfologie v důsledku pravidelnějšího uspořádání polymerních řetězců, což vedlo k rozvoji této metody i ke vzniku řady dalších metod pro přípravu uspořádaných supramolekulárních VP jež se používají dnes.

4.1 Metody přípravy supramolekulárního polypyrrolu

Syntézy strukturovaných VP Martina a kol. [69-71] znamenaly významný skok v základním výzkumu supramolekulárních struktur VP. Postup, který byl zde navržen, tj. "**tvrdá šablona**", je univerzální a není omezen pouze na konkrétní VP či šablonu. Dnes se kromě polykarbonátových membrán běžně používají např. disky anodizovaného Al_2O_3 [73]. Metoda má řadu předností – vzniklé struktury polymerů mají uniformní průměr i délku, ve spojení s elektrochemickou syntézou je lze použít pro přípravu tenkých vrstev s orientovanými nanostrukturami (hřebenovité vrstvy) [74]. Nevýhodou, která je však pro mnohé aplikace velmi omezující, je fakt, že tímto procesem nelze připravit velké objemy materiálu, a také je nutné použít značně agresivních metod (např. leptání) pro odstranění šablony po skončení polymerizace, což může být ve výsledku destruktivní pro syntetizovaný materiál.

V průběhu několika následujících let byla proto vyvinuta řada dalších metod, které měly za cíl tyto překážky překonat. Jednou z nich byla **adaptace elektrospiningu** pro přípravu nanovláken VP [75]. Ačkoliv se ukázalo, že tímto způsobem lze připravovat relativně snadno velké množství materiálu, metoda se neujala, a to zejména kvůli striktnímu omezení na VP dopované surfaktanty, které jsou jako jedny z mála dostatečně rozpustné a tvoří roztok vhodný pro depozici.

Velmi specifickou metodou přípravy supramolekulárního VP je **syntéza PANI v prostředí nízkého pH**, kterého se dosahuje pomocí různých typů běžných anorganických kyselin (HCl , HNO_3 , H_2SO_4 apod.). Tímto postupem byly připraveny nejenom nanotrubky [76], ale i struktury daleko komplikovanější s mnohdy překrásnými tvary [77][78]. Bohužel tato metoda funguje jenom pro syntézu supramolekulárního PANI a žádný jiný VP tímto způsobem nevytváří uspořádané supramolekulární struktury.

Samostatnou a rozsáhlou oblastí je syntéza nanostruktur VP na povrchu porézních elektrod při elektrochemické polymerizaci [79]. Jedná se o jednoduchou metodu, se všemi výhodami a nevýhodami zmíněnými pro elektrochemické syntézy.

Zásadní metodou, jež znamenala průlom v přípravě supramolekulárních struktur VP, je **polymerizace v přítomnosti tzv. „structure guiding agents“**⁶ tedy pomocných látek, které jsou schopné se ve vodných roztocích samouspořádat do vyšších supramolekulárních struktur, a poté slouží jako šablona ("měkká předloha"), na jejíž povrchu dochází k polymerizaci VP. Mezi látky, které podporují supramolekulární růst VP, patří rozměrné planární sulfonové kyseliny, které jsou schopny se skládat pomocí π - π interakcí, např. kys. β -naftalen sulfonová (NSA) [80-83], DBSA [84], kys. kafrsulfonová [85-87], micelární systémy surfaktantů, např. DEHS [88,89], hexadecyltrimethylammonium bromid (CTAB) [90,91], sodium dodecylsulfátu (SDS) [92], pevné a kapalně krystalizující azosloučeniny a azobarviva, např. kys. *p*-hydroxyl-azobenzen sulfonová [93] a

⁵ V této souvislosti je nutné poznamenat, že předložka nano zde není používána ve stejném významu, jako např. u uhlíkových nanotrubelek. Obecný úzus označující uhlíkové trubičky jako nanotrubky předpokládá, že tyto trubky nebudou dosahovat průměrů větších než 100 nm. V oblasti vodivých polymerů není tato hranice striktně vymezena a zcela běžně se označují nanotrubkami i trubky o průměru do 1 μm .

⁶ V českém jazyce neexistuje pro tento výraz ustálený překlad.

zejména MO [94-96] či Acid Red 1 [97], a řada dalších méně obvyklých látek, např. kys. salicylová [98].

Výhoda těchto syntéz spočívá zejména ve skutečnosti, že na rozdíl od polymerních membrán či leptaného Al_2O_3 , šablony pomocných látek vznikají a často i zanikají přímo v průběhu polymerizační reakce VP a po skončení reakce je lze z produktu snadno odstranit (např. promýváním destilovanou vodou či acetonem), bez vlivu na výsledný produkt. Vznik šablony, tedy samouspořádání těchto látek, je však podmíněn použitím vhodné koncentrace pomocné látky či teploty syntézy [80]. Řada z těchto látek také zůstává v malém množství ve VP jako dopant (aniont), který nahradil či doplnil dopanty vzniklé z oxidačního činidla. To s sebou přináší řadu dalších vedlejších důsledků, např. snížení elektrické vodivosti při velmi vysokých koncentracích pomocných látek v důsledku tvorby kompozitu [56].

Předchozí výčet syntéz supramolekulárních struktur VP lze rozdělit do jednotlivých skupin, jejichž označení je běžně užíváno při syntézách supramolekulárních struktur VP a bude používáno i dále v tomto textu [99]. Již zmíněné syntézy s polymerními membránami či leptaným Al_2O_3 patří mezi tzv. syntézy s **tvrdou šablonou**; charakteristickou vlastností těchto syntéz je, že šablona je vytvářena samostatně mimo reakční roztok, často pomocí odlišných chemických a fyzikálních metod, než jaké se uplatňují při vlastní polymerizaci. Po skončení polymerizační reakce zůstává šablona trvalou součástí polymeru, nebo je odstraněna chemicky, nejčastěji leptáním či rozpouštěním v rozpouštědlech. Mezi syntézy s tvrdou šablonou se proto zpravidla řadí i polymerizace VP na povrchu struktur tvořených anorganickými oxidy (např. nanotrubelek V_2O_5 , TiO_2) [100-102], kovy, či polymery [103,104] neboť tyto reakce splňují výše uvedené charakteristiky.

Syntézy, které používají pomocné látky, jež se samouspořádávají ve vodných roztocích při vhodné koncentraci i teplotě reakčního roztoku, se nazývají syntézy s **měkkou předlohou**. Charakteristickou vlastností těchto syntéz je, že šablona je vytvořena přímo v reakčním roztoku a po skončení reakce ji lze relativně snadno odstranit z produktu. Pomocné látky často zůstávají v polymeru v malém množství ve formě dopantů. Pro syntézy s měkkou předlohou využívají obecně pomocné látky, které samy vytvářejí supramolekulární struktury, např. micely, nematické kapalně krystaly i krystaly pevné. Při jejich tvorbě se zpravidla uplatňují zejména slabé vazebné interakce, např. π - π interakce, dipól-dipólové interakce, vodíkové můstky, ale předpokládá se, že v některých případech dochází i ke vzniku koordinačně kovalentní vazby [97]. Je nutné zdůraznit, že rozdíl mezi tvrdou a měkkou šablonou není ostře ohraničen, zejména tam, kde samouspořádáním pomocných látek vznikají pevné krystaly, je občas toto rozdělení zpochybňováno. V této práci bude dále diskutována zejména syntéza s měkkou šablonou, a to tak, jak je definována výše.

Pro úplnost je nutné dodat, že existuje ještě skupina **bezšablonových syntéz**. Základní princip je zřejmý již z názvu této skupiny, reakce nevyžadují žádnou šablonu, a přesto je výsledkem VP se supramolekulární strukturou. Patří mezi ně již zmíněná elektrochemická syntéza a elektrospinning, ale také plazmová polymerizace [105], zvlákňování z kapaliny [106,107], sonochemické [108,109] či radiolytické metody [110]. Kromě elektrochemické syntézy však žádná z těchto metod nedosáhla obliby, jaké se těší syntézy s měkkou šablonou.

4.2 Syntéza s měkkou předlohou využívající azobarviv [8,56]

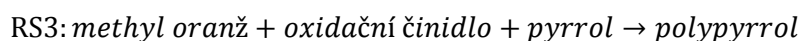
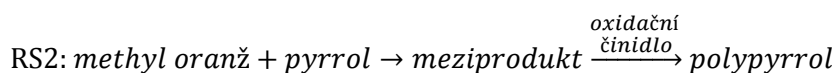
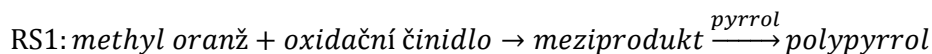
V současné době se těší velikému zájmu vědecké komunity příprava supramolekulárních struktur VP pomocí azobarviv. Tato syntéza s měkkou předlohou se osvědčila při přípravě nanostruktur

PANI i PEDOT [95,111], zcela zásadní je však zejména pro přípravu supramolekulárních struktur PPy.

Stěžejní prací, která iniciovala rozsáhlý výzkum v této oblasti, je syntéza nanotrubek PPy v přítomnosti azobarviva MO, které se běžně používá jako acidobazický indikátor. První syntézu provedl Hu et al. [112], ale větší pozornosti vědecké komunity se dostalo až práci stejného výzkumného týmu Yang et al. [94]. Yang syntetizoval jednoduchou procedurou (postupného přidávání monomeru a oxidačního činidla do vodného roztoku MO) uniformní nanotrubky o průměru 50 nm. Tato reakce je v mnoha ohledech výhodnější než doposud používané syntézy se sulfonovými kyselinami či v prostředí reverzních micelárních systémů, zejména co se týče kvality získaných nanotrubek (např. vyšší elektrická vodivost), relativní jednoduchosti provedení syntézy či separace nanostruktur z reakčního prostředí. Nanotrubky PPy se díky této reakci staly snadněji dostupnými ve velkém množství a bylo je možné otestovat v řadě aplikací, např. v senzorech [113,114], v superkapacitorech a bateriích [115-119], v aerogelech [120], v syntetických absorbentech [121], jako antioxidant [122,123], redukční činidlo [33], katalyzátor [124], fotokatalyzátor [125], nebo v elektricky vodivých textiliích [126].

Yang et al. [94] navrhl ve své práci jednoduchý mechanismus vzniku nanotrubek PPy, který předpokládá, že v první fázi syntézy dochází přimícháním oxidačního činidla FeCl_3 do vodného roztoku MO k vytvoření jehlicových krystalů komplexu MO- FeCl_3 . Po přidání pyrrolu ve druhé fázi, polymerizace probíhá na povrchu předtím vzniklých šablon a FeCl_3 je redukován na FeCl_2 díky čemuž se komplex rozpadá a produktem je nanotrubka PPy s podélnou vnitřní kavitou o rozměrech původní šablony. Svoji koncepci Yang nazval reaktivní samorozkladnou šablonou. Pro tento koncept hovoří např. schopnost azobarviv fungovat jako ligand v donor-akceptorové vazbě s Al^{3+} či Fe^{3+} [127], proti němu pak ne zcela shodné rozměry nanotrubek (vnitřní průměr a délka) s použitými šablonami a zejména neschopnost šablon samostatně oxidovat pyrrol po výměně okolního roztoku za destilovanou vodu [8].

Detailnějšímu výzkumu funkce MO při syntéze nanotrubek PPy a mechanismům jejich růstu se věnuje současná práce Kopecká a kol. [8]. V rámci této práce byla provedena sada experimentů, které využívaly tří různých reakčních schémat způsobu směšování reaktantů (RS1-RS3, viz níže), mezi něž patřila i taková, která na počátku nevedla ke vzniku pevných krystalů podpůrných šablon (RS2 a RS3). Společně s variací koncentrace MO ve vodném roztoku byl tak získán robustní soubor vzorků. Rozbor výsledků pak vnesl světlo na některé dosud málo známé aspekty mechanismu této reakce.



Produktem všech reakcí (provedených podle navržených reakčních schémat) byla překvapivě vždy nanotubulární morfologie. Zajímavým výsledkem tohoto experimentu bylo též zjištění, že variace pořadí přidávání jednotlivých reaktantů vede ke vzniku nanotrubek odlišného tvaru průřezu a různé velikosti. Zatímco v reakci, která měla na počátku zřetelně vyvinuté šablony (RS1), vznikaly rozměrné nanotrubky (řádově stovky nm) čtvercového průřezu, v případě, kdy šablony nebyly na počátku v reakčním roztoku přítomny (RS2 a RS3), byly získány tenké (řádově desítky nm) nanotrubky kruhového průřezu s lepšími mechanickými vlastnostmi. Použitý pracovní postup se

odrážel i v naměřené elektrické vodivosti, která byla nejvyšší u tenkých nanotrubech s kruhovým průřezem.

Výše popsané experimenty umožnily zpřesnit poznání mechanismů tvorby supramolekulárních struktur PPy pomocí MO. Výchozím bodem pro jejich popis je mechanismus vzniku morfologie globulární struktury VP, který předpokládá nejprve reakci několika monomerních jednotek; ty jsou po překročení meze rozpustnosti vyloučeny z roztoku a vytvoří nukleáty. Nukleáty fungují jako iniciační centra, na jejichž povrchu dochází k náhodnému růstu polymerního řetězce. Tím vznikají charakteristické kulové útvary globulárního polymeru [128]. Pokud je do tohoto roztoku vložen vhodný objekt, vzniká na rozhraní jeho povrchu a kapaliny tenký film VP [129].

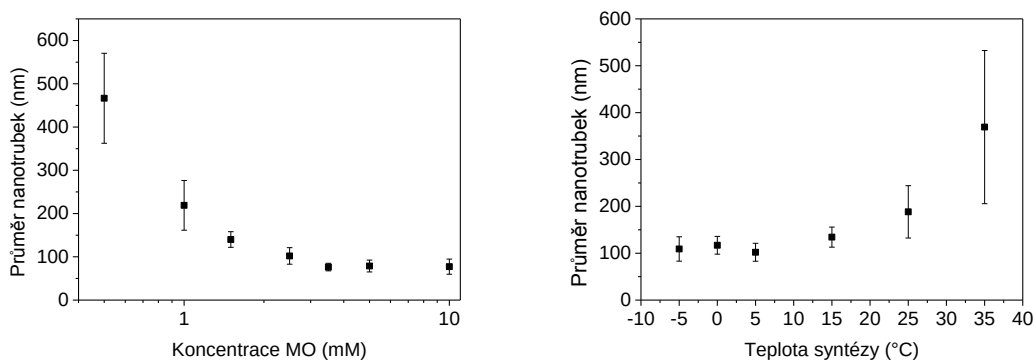
V případě, že v roztoku existují na počátku reakce šablony ve formě pevných jehlicových krystalů, lze tedy uvažovat o pokrývání krystalů tenkým filmem. Řada pozorovaných nanotrubech však byla značně delší než původní šablony, navíc jejich konce nebyly uzavřené, růst tedy nebyl izotropní, jak by se dalo očekávat od struktur kompletně pokrytých tenkou vrstvou. Lze tedy spekulovat, že šablony MO-FeCl₃ pouze iniciují počáteční anizotropní růst polymeru, který se dále propaguje bez další podpory. Ještě více tuto teorii podporují reakce, ve kterých byl nejprve mísen pyrrol s roztokem MO, a teprve poté bylo přidáno oxidační činidlo FeCl₃ (tedy postup RS2). V tomto typu reakce na počátku neexistuje šablona, která by mohla být tvořena komplexem MO-FeCl₃, jsou zde však přítomny planární molekuly MO, které se v závislosti na koncentraci skládají pomocí π - π interakcí do di- či trimerů, popřípadě oligomerů obsahující jednotky molekul MO [130]. Zdá se, že tyto malé samouspořádané struktury MO jsou zcela postačující k tomu, aby umožnily propagaci růstu nanotrubky, která je schopná dosáhnout délky až několika μ m beze změny průměru. Tento v zásadě prostý závěr vysvětluje např. růst nanotrubech pomocí oxidačních činidel, která netvoří komplexy s MO [131], a také otevírá prostor pro řadu azobarviv, která netvoří ve vodných roztocích pevné krystaly [132].

Experimenty provedené v práci Kopecká et al. [8] naznačily ještě jeden velmi zajímavý trend, který dále komplikuje obecné představy o růstu nanotrubech VP jako o pokrývání šablon tenkou vrstvou polymeru. Průměr syntetizovaných nanotrubech se totiž zmenšuje se zvyšující se koncentrací MO. Paradoxně tak (oproti očekávání) v roztocích o nízkých koncentracích MO vznikají nanotrubky s největším průměrem.

Práce Kopecký a kol. [56] se mimo jiné věnovala i tomuto problému. Syntéza nanotrubech PPy probíhala v prostředí, na jehož počátku se vyskytují pouze samouspořádané oligomery MO tedy postupem RS2. V prvním kroku je přidáván pyrrol do vodného roztoku MO a ve druhém kroku je přikapáváno oxidační činidlo FeCl₃. Tím je zaručeno, že nedojde k tvorbě jehlicovitých krystalů komplexů MO-FeCl₃. Koncentrace MO byla pro každou syntézu odlišná a měnila se v řadě 0,5; 1; 1,5; 2,5; 3,5; 5; 10; 25 mM. Důležitým stupněm volnosti byla i variace teploty syntézy, a to v řadě (-5, 5, 15, 25, 35 °C). Sledována byla zejména morfologie vznikajících nanočástic, a dva parametry důležité pro aplikace v organické elektronice – hodnota měrné elektrické vodivosti a specifického povrchu.

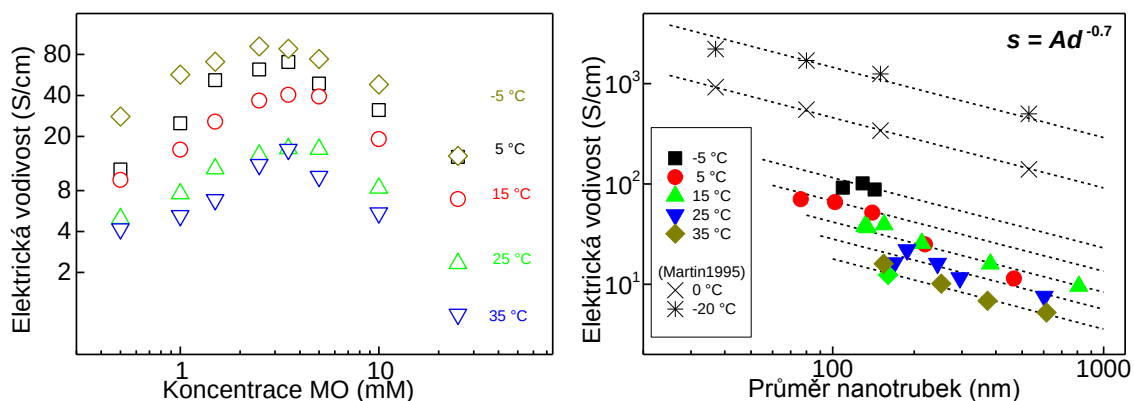
Z grafů na obrázku 22 je patrné, že průměr nanotrubech se vzrůstající koncentrací MO klesá a se vzrůstající teplotou naopak roste. Oba dva trendy doplnily představy o mechanismu růstu nanotrubech. Dle výsledků je tedy velmi pravděpodobné, že na tvorbě nanotrubech se podílejí pouze relativně malá iniciační centra tvořená několika samouspořádanými molekulami MO. Iniciační centra nastartují růst nanotrubech, a ty poté pokračují v růstu samy bez další podpory. Při malé koncentraci MO je těchto iniciačních center pouze velmi málo a supramolekulární struktury proto v přebytku pyrrolu vyrostou do větších rozměrů, celkově však menšího počtu částic. Se zvyšující

se koncentrací MO vzniká větší množství iniciačních center, a tak polymerizace probíhá ve více místech simultánně, díky čemuž vzniká velké množství velmi tenkých nanotrubeček. Teplota syntézy určuje zejména počet iniciačních míst v reakčním roztoku a rychlost reakce. Se zvyšující se teplotou syntézy počet iniciačních míst klesá a dochází k rychlému růstu velkých, méně kvalitních nanotrubeček PPy.



Obrázek 22 - Průměr nanotrubeček PPy syntetizovaného v přítomnosti MO v závislosti na koncentraci MO (vlevo) a teplotě syntézy (vpravo) [56].

Měření elektrické vodivosti (obrázek 23), specifického povrchu a následně také prvkového a strukturního složení nanotrubeček PPy ukázalo ještě jeden důležitý trend. MO zůstává v materiálu částečně jako dopant a do určité koncentrace v matečném roztoku (zde 3,5 mM) zvyšuje elektrickou vodivost vznikajících nanotrubeček, protože snižuje meziřetězcovou vzdálenost PPy [55]. Avšak v případě vysokých koncentrací MO jsou tyto dopanty složené nikoliv z jednotek samospořádaných molekul, ale v polymerním řetězci jich zůstává tolik, že se stávají složkou nového kompozitu PPy-MO a kvůli své nižší elektrické vodivosti potlačují celkovou elektrickou vodivost nanotrubeček.



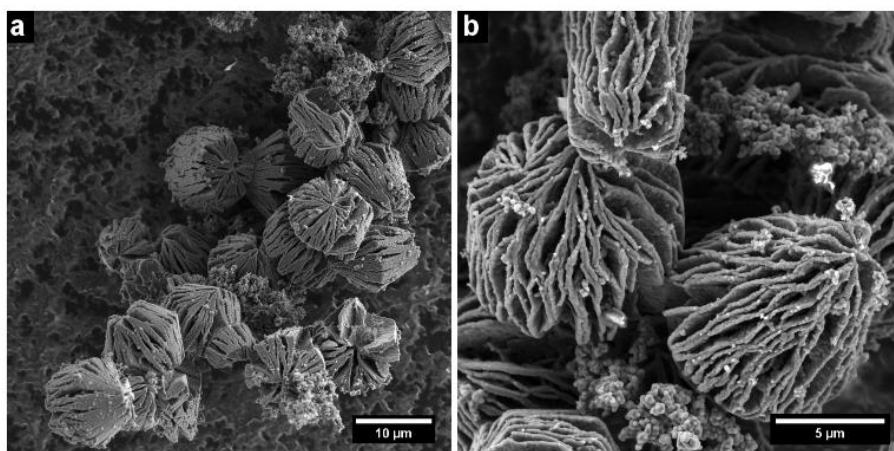
Obrázek 23 - Závislost elektrické vodivosti nanotrubeček PPy na koncentraci MO a teplotě syntézy (vlevo) a závislost elektrické vodivosti na průměru nanotrubeček (vpravo) [56].

Při výzkumu vztahů mezi rozměry nanotrubeček PPy syntetizovaných v přítomnosti MO a jejich elektrickými parametry (obrázek 23) se také podařilo experimentálně odvodit matematický vztah popisující závislost mezi elektrickou vodivostí nanotrubeček s a jejich průměrem d ; A označuje prefaktor Arrheniovy rovnice (obrázek 23, vpravo nahoře) [56]. **Tento matematický vztah má podle stávajících indicií obecnou platnost a byl úspěšně testován na dostupných datech z prací jiných autorů, např. Martin a kol. [71].**

Dvě výše popsané práce [8,56] přinášejí velice detailní fyzikálně-chemický pohled na supramolekulární struktury PPy. Zdaleka se nejedná o vyčerpávající studie, pro aplikace v organické elektronice se však jejich záběr může zdát příliš hluboký. Z praktického hlediska se však ukazuje, že bez detailní znalosti mechanismu vzniku materiálu je zhora nemožné pochopit jeho výsledné vlastnosti a efektivně řídit postup syntézy.

Výsledky, které přinesly práce Kopecká a kol. [8] a Kopecký a kol. [56] ukázaly, že tvar připravených nanostruktur PPy nekopíruje vložené šablony přesně, ale že šablony pouze iniciují počáteční polymerizaci. Konečný tvar, který na počátku udá iniciační centrum, je tak výsledkem uspořádaného růstu bez potřeby šablony. Toto důležité zjištění vedlo k otázce, zda jiná azobarviva, která mají výrazně odlišenou hydrofilní a hydrofobní část molekuly, jsou také schopna iniciovat vznik uspořádaných struktur PPy.

Velmi zajímavých výsledků bylo v této otázce dosaženo v práci Valtera a kol. [132], která se zabývala syntézou supramolekulárního PPy v přítomnosti tří azobarviv (Acid Red 1, Orange G a Sunset Yellow FCF), která mají v molekule obsažený společný naftylfenyldiazenový skelet. První dvě jmenovaná barviva vytvářejí, v závislosti na koncentraci, ve vodném roztoku pevné tyčovité krystaly, které by podle obecných předpokladů mohly vést k nanotubulární morfologii PPy, třetí barvivo, Sunset Yellow FCF, nevytváří pevné krystaly vůbec, chová se však jako typický nematický kapalný krystal [133]. Syntéza PPy v přítomnosti struktur těchto látek překvapivě ukázala, že nanotubulární morfologie vzniká pouze v případě Acid Red 1, druhé barvivo, Orange G, vedlo ke vzniku rozměrných plátů o velikostech v řádech mikrometrů. Daleko zajímavějším výsledkem však byly uniformní soudkovité mikrostruktury PPy, které vznikly při polymerizaci PPy v roztoku Sunset Yellow FCF, viz obrázek 24.



Obrázek 24 - Mikrostruktury PPy připravené polymerizací pyrrolu v roztoku Sunset Yellow FCF [132]

Podobné soudkovité supramolekulární struktury PPy nebyly doposud výzkumníkům z oblasti VP známy, a proto byl proveden důkladný rozbor jejich vlastností a ty byly následně srovnány se známými vlastnostmi nanotrubek PPy připravených v přítomnosti MO. Z měření prvkového (EDX) a chemického složení (FTIR a Raman) se ukázalo, že tyto struktury zadržují daleko méně zbytků azobarviva ve formě dopantů či kompozitní příměsi. Toto zjištění je pozitivní z hlediska možných budoucích aplikací, protože zbytkové azobarvivo může být toxické, navíc má malou elektrickou vodivost, a proto ve vyšších koncentracích snižuje celkovou vodivost materiálu.

Elektrická vodivost těchto soudkovitých útvarů je srovnatelná s elektrickou vodivostí nestrukturovaného PPy (cca jednotky $\text{S}\cdot\text{cm}^{-1}$) a v porovnání s nanotrubkami připravenými pomocí

barviva MO (cca desítky $\text{S}\cdot\text{cm}^{-1}$) je nižší. Důvodem může být skutečnost, že kontaktní odpor těchto mikrostruktur je příliš velký a jeho vliv zastiňuje vlastní elektrickou vodivost soudkových struktur. K tomuto závěru vedou výsledky měření kontaktního odporu nanotrubek VP, které provedl Long a kol. [99].

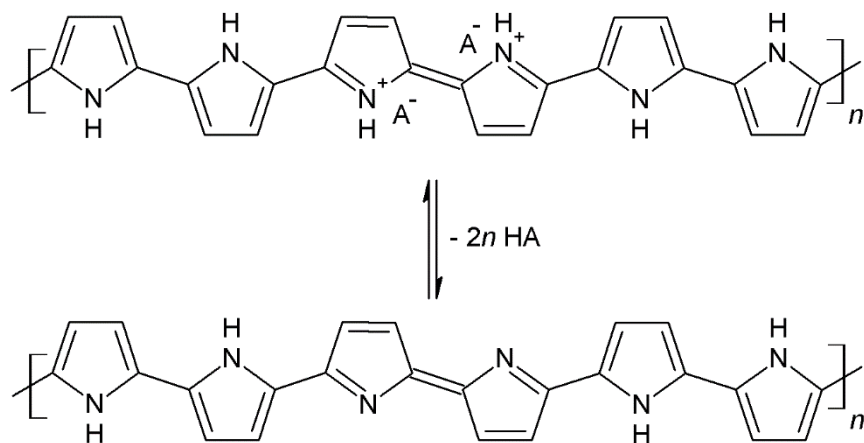
Dosažené výsledky jsou důležitou demonstrací budoucích možností přípravy různých typů supramolekulárních struktur, která ukazuje dosud nevyužitý potenciál pomocných látek používaných pro stimulaci růstu supramolekulárních VP.

4.3 Stabilita polypyrrolu v enviromentálních podmínkách [134-136]

Problémem, který dosud limituje využití VP, je velké množství defektů, které jsou do struktury materiálu vnášeny již při samotné syntéze či se objevují v důsledku stárnutí materiálu, a také relativně menší odolnost vůči enviromentálním podmínkám jako je vzdušný kyslík, vlhkost či světelné záření. Všechny zmíněné jevy se v řetězci VP projevují zejména ztrátou konjugací délky a výskytem atomů kyslíku v různých funkčních skupinách ($-\text{OH}$; $=\text{O}$; $-\text{COOH}$ a dalších). Některé z těchto problémů lze opakovaně odstraňovat a VP „revitalizovat“, jiné jsou však permanentní a vedou k trvalé ztrátě, zejména elektrických vlastností.

Jedním z důležitých a velice sledovaných parametrů je míra deprotonace a reprotonace řetězce v neutrálním a mírně alkalickém prostředí, která ovlivňuje množství nosičů náboje v řetězci VP. Tato informace je důležitá zejména pro konstrukce nových typů zařízení pro uchovávání energie a biomedicínské aplikace. Při deprotonaci pomocí alkálií VP přechází do svého základního stavu (viz odstavec 3.2), pohyblivé díry (polarony a bipolarony) v řetězci náboje zanikají, s nimi odcházejí i vázané proti-ionty; v důsledku toho elektrická vodivost klesá. Reprotonaci s následným opětovným vznikem děr lze vyvolat například ponořením polymeru do roztoku anorganické kyseliny. Rozdíl elektrické vodivosti mezi deprotonovaným a reprotonovaným stavem polymeru může být značný, často se jedná o řádové změny, například PPy-G s počáteční vodivostí $0,24 \text{ S}\cdot\text{cm}^{-1}$ byl deprotonován na hodnotu vodivosti $3,8 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ poté, co byl ponořen do roztoku $1 \text{ M NH}_4\text{OH}$, a na hodnotu $6,4 \times 10^{-10} \text{ S}\cdot\text{cm}^{-1}$ v roztoku 1 M NaOH [48].

Studie Stejskal a kol. [134] je ojedinělou prací, která se zaměřuje čistě na problematiku deprotonací/reprotonací nanotrubek PPy. Mezi teoretickým mechanismem deprotonace PPy-G a nanotubulárního PPy není rozdíl. Podle mechanismu na obrázku 25 při deprotonaci řetězec ztrácí volné polarony a současně z materiálu odcházejí proti-ionty.



Obrázek 25 - Mechanismus deprotonace a reprotonace PPy

V případě deprotonace PPy-G je tedy odejmuta kyselina HCl, u nanotubulárního PPy dochází ještě navíc ke ztrátě kyselé formy MO. MO je za normálních okolností v řetězci částečně zabudována jako dopant a pomocí π - π interakcí snižuje meziřetězcovou vzdálenost, což vede k vyšší elektrické vodivosti. Výsledkem deprotonace pomocí 1 M NH_4OH je pokles elektrické vodivosti z $1,55 \text{ S}\cdot\text{cm}^{-1}$ u PPy-G na $0,012 \text{ S}\cdot\text{cm}^{-1}$ a z $49,8 \text{ S}\cdot\text{cm}^{-1}$ na $1,42 \text{ S}\cdot\text{cm}^{-1}$ u nanotubulárního PPy. Při opětovné reprotonaci pomocí 1 M HCl však nedochází k návratu na původní hodnotu elektrické vodivosti. PPy-G dosáhl hodnoty $0,026 \text{ S}\cdot\text{cm}^{-1}$ a nanotubulární PPy hodnoty $3,64 \text{ S}\cdot\text{cm}^{-1}$. Děj tedy není zcela vratný a problém nekompletní reprotonace u PPy-G je dlouhodobě známý [137]. Předpokládá se, že dochází k nevratnému narušení řetězce silným alkalickým činidlem. U nanotubulárního PPy může navíc hrát svoji roli i skutečnost, že při odejmutí dopantů tvořených planárními molekulami MO dochází k nevratné změně vzájemného uspořádání řetězců. Předpokládá se také, že během deprotonace je část dopantů (proti-iontů) nahrazena hydroxidovým aniontem (OH^-) [138]. V porovnání s ostatními VP včetně svého globulárního protějšku je však odolnost nanotubulárního PPy vůči deprotonaci velmi dobrá a elektrická vodivost zůstává ve značné míře zachována.

Aplikace VP v organické elektronice jsou ovlivňovány stárnutím materiálu⁷, spojeným s postupným zhoršováním řady parametrů (např. poklesem elektrické vodivosti, pružnosti, mechanické pevnosti, čistoty materiálu apod.). V případě VP jsou hlavními činiteli způsobujícími stárnutí materiálu vzdušný kyslík, UV záření, teplota a vzdušná vlhkost.

V práci Varga a kol. [135] byl po 3 roky sledován postupný pokles elektrické vodivosti PPy-G i nanotubulárního PPy (připraveného v přítomnosti MO podle článku Kopecká a kol. [8]) v důsledku stárnutí. Paralelně s tímto experimentem byly provedeny pokusy s umělým stárnutím, které využívají zvýšené teploty (zde 120°C), jež celý proces akcelerovaly (je nutné zdůraznit, že tento typ stárnutí není zcela totožný s přirozeným stárnutím, neboť nezohledňuje například vliv UV záření).

Ukázalo se, že elektrická vodivost nanotubulárního PPy je časově o řád stabilnější než u PPy-G a její hodnota klesne během 3 let na 0,2násobek původní hodnoty. Umělé stárnutí naproti tomu vedlo k velmi rychlému poklesu elektrické vodivosti u obou typů PPy až o 7 řádů během 1000 h (41 dnů). Zároveň bylo zjištěno, že zbytková MO používaná jako pomocná látka v polymerizační reakci, stabilizuje materiál a zpomaluje proces stárnutí.

Důležitým výsledkem je, že u nanotubulárního materiálu nedochází v důsledku stárnutí k rozkladu supramolekulární struktury, ale pouze k určité změně chemického složení. Měření prvkového složení pomocí EDX a chemické struktury PPy pomocí FTIR odhalilo, že pokles elektrické vodivosti v důsledku přirozeného stárnutí je spojen především s deprotonací PPy řetězce a postupnou karbonylací uhlíků pyrrolového kruhu vzdušným kyslíkem. Z makroskopického hlediska se podle elektrické tomografie PPy rozpadá homogenně a z původního uspořádaného materiálu, jehož elektrické parametry nebyly daleko od přechodu z vlastností polovodiče na vlastnosti kovů, se stal velice neuspořádaný materiál v důsledku množství poruch.

Porozumění principu přirozeného stárnutí VP je velmi důležité pro pochopení chování materiálu v podmínkách, za kterých funguje běžná organická elektronika. Zrychlené (umělé) stárnutí pomocí zvýšené teploty pak vypovídá o dopadu jednoho konkrétního činitele (teploty) na elektrickou vodivost. Pro pochopení vlivu dalších činitelů (např. vzdušného kyslíku, UV záření

⁷ V úvodu práce bylo zmíněno, že organická elektronika je v mnoha případech koncipována jako jednorázová či pro pouze krátkodobé použití (1-2 roky). Z tohoto pohledu nemusí být proto proces dlouhodobého stárnutí velkou překážkou.

apod.) na morfologii i elektrickou vodivost PPy je však nezbytné použít jiné metody zrychleného stárnutí materiálu.

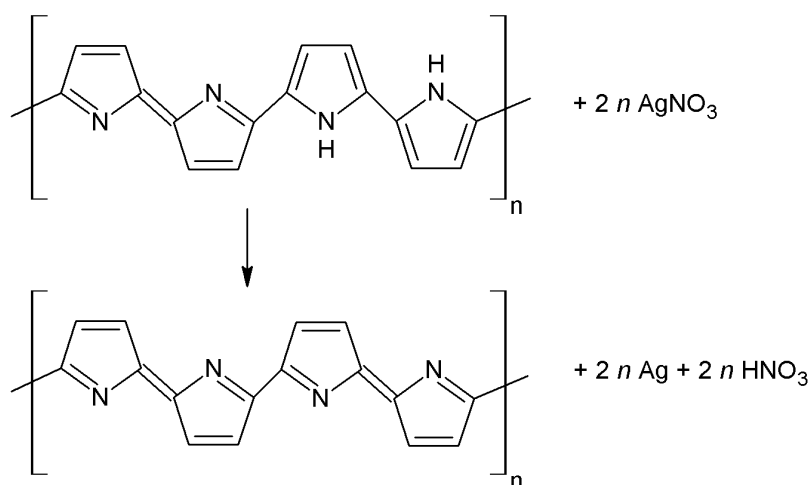
Jiný pohled na proces stárnutí přináší práce Galář a kol. [136] v níž bylo použito nízkoteplotního plazmatu (NTP) pro generování reaktivních částic ve vodném roztoku. Mezi tyto částice patří zejména stabilní molekuly O_3 , H_2O_2 , HNO_2 , HNO_3 , N_2O , N_2O_5 a nestabilní částice typu radikálů a iontů [139]. Takto obohacený vodný roztok silně interaguje s globulárním i nanotubulárním PPy. Výhoda této metody je, že při ní nedochází k zahřívání materiálu, a tak s jistým zjednodušením představuje komplementární metodu umělého stárnutí k výše uvedenému stárnutí zvýšenou teplotou.

Podobně jako v předchozím případě se PPy-G ukázal jako méně stabilní než PPy nanotubulární; elektrická vodivost poklesla 14krát pro PPy-G respektive 2krát pro nanotubulární PPy během 60 minut. Příčinou tohoto chování je zřejmě vyšší kompaktnost nanotubulárního PPy, který proto snadněji odolává reaktivním částicím ve vodě aktivované NTP. Stejně jako v případě přirozeného či umělého stárnutí nedošlo k poškození morfologie testovaného materiálu a za hlavní příčinu poklesu elektrické vodivosti lze opět označit rychlý pokles chloridových dopantů (deprotonace) spojený s nárůstem obsahu kyslíku, který se v řetězci objevil v důsledku oxidace PPy řetězce a vzniku funkčních ($-OH$, $-C=O$, $-COOH$) skupin.

4.4 Kompozity nanostrukturovaného polypyrrolu a jejich vlastnosti [33]

V oddíle 1.4 bylo zmíněno, že VP fungují jako efektivní redukční činidla, která lze použít pro přípravu kompozitů VP a kovových nanočástic. Např. Ayad a kol. [22] použil této vlastnosti pro přípravu nanokompozitu PANI s biopolymerem chitosanem (CS), magnetickými částicemi Fe_3O_4 a nanočásticemi Ag. Redukční schopnosti supramolekulárního PPy však dosud nebyly dostatečně prozkoumány. Škodová a kol. [33] proto zkoumali redukční schopnosti nanotubulárního PPy při redukci $AgNO_3$ za vzniku Ag a porovnávali je s redukčními schopnostmi globulárního PPy (tedy PPy soli) a jejich deprotonovaných forem (tzv. PPy báží).

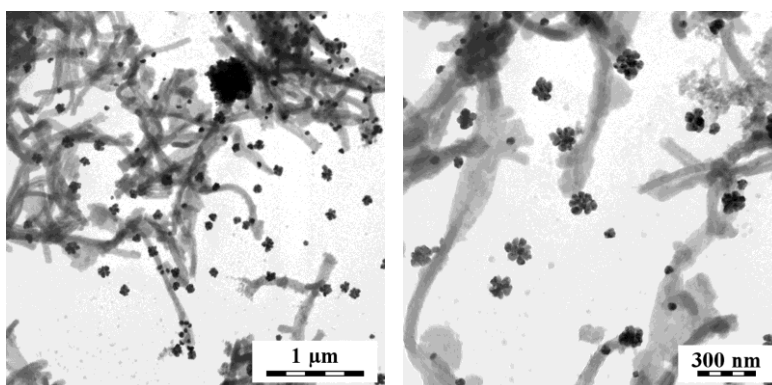
Výsledky ukázaly, že redukční schopnosti všech čtyř forem PPy (nanotubulární soli, nanotubulární báze, globulární soli a globulární báze) jsou dostatečné na to, aby byly schopny vyredukovat ionty Ag za vzniku metalických nanočástic Ag podle níže uvedené rovnice (obrázek 26).



Obrázek 26 - Mechanismus redukce $AgNO_3$ na Ag pomocí PPy

Nanotubulární PPy se však ukázal jako efektivnější redukční činidlo než jeho báze (odpovídající kompozity obsahují 21,1 hm.% resp. 15,3 hm.% vyredukovaného Ag). Použití různých forem PPy navíc vedlo ke vzniku odlišné morfologie Ag nanočástic (nepravidelné i pravidlené shluky, nanodráty apod.). Snímek vyredukovaných Ag nanočástic a jejich pravidelného uspořádání je na obrázku 27.

Zároveň se ukázalo, že vzniklý nanokompozit PPy a Ag vykazuje nižší elektrickou vodivost v případě, že byla použita sůl nanotubulárního PPy (pokles z $35,7 \text{ S}\cdot\text{cm}^{-1}$ na $20,9 \text{ S}\cdot\text{cm}^{-1}$) a vyšší elektrickou vodivost v případě použití PPy báze (nárůst z $0,056 \text{ S}\cdot\text{cm}^{-1}$ na $1,38 \text{ S}\cdot\text{cm}^{-1}$). Důvodem pro pokles elektrické vodivosti PPy/Ag nanokompozitu je pravděpodobně vyšší nárůst kyslíku v řetězci polymeru v důsledku jeho oxidace kyslíkem v průběhu reakce.

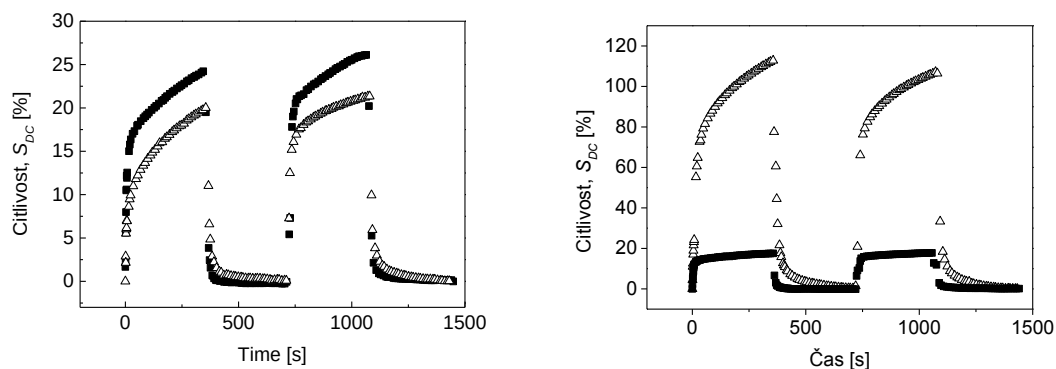


Obrázek 27 - Kompozit PPy vzniklý redukcí AgNO_3 pomocí nanotubulárního deprotonovaného PPy

4.5 Senzory na bázi nanotubulárního PPy [140]

Výsledky, kterých bylo dosaženo v pracích Kopecká a kol. [8] a Kopecký a kol. [56] byly použity při konstrukci senzoru pro detekci organických těkavých látek VOC (z angl. *Volatile Organic Compound*) – nepolárního *n*-heptanu a polárního ethanolu; oba VOC mají podobný tlak nasycených par. Jako citlivý materiál byl testován PPy-G a nanotubulární PPy ve standardním a karbonizovaném stavu. Karbonizace materiálu proběhla při 650°C v inertní atmosféře podle dříve otestovaných postupů [141]. Při karbonizaci PPy nanotrubek vzniká na vzduchu stabilní materiál s vyšším specifickým povrchem a zachovalou supramolekulární strukturou [142]. Konkrétně PPy-G (specifický povrch $26 \text{ m}^2\cdot\text{g}^{-1}$) zvýšil po karbonizaci svůj specifický povrch na $150 \text{ m}^2\cdot\text{g}^{-1}$ a nanotubulární PPy (specifický povrch $75 \text{ m}^2\cdot\text{g}^{-1}$) na $211 \text{ m}^2\cdot\text{g}^{-1}$.

Všechny výše zmíněné citlivé materiály byly otestovány na sensorové platformě tvořené polyuretanovou membránou [140]. Výsledky měření stejnosměrné citlivosti S_{DC} ukázaly, že nejlepší odezvu vykazovaly PPy nanotrubky na nepolární *n*-heptan (cca 110 %). Vzhledem k obecně velmi nízké odezvě VP na nepolární VOC, jež se pohybuje zpravidla v řádech jednotek % [143] se jedná o unikátní výsledek. Ukázka z měření obou VOC je na obrázku 28. Odezva karbonizovaného nanotubulárního PPy byla ve všech případech rychlejší.



Obrázek 28 - Profil S_{DC} v závislosti na čase pro absorpční a desorpční cykly 7,7 obj. % ethanolu (vlevo) a 6,0 % *n*-heptanu (vpravo); trojúhelník značí nanotubulární PPy a plný čtverec karbonizovaný nanotubulární PPy [140]

5 Závěr

Organická elektronika je moderní a rychle se rozvíjející obor, jenž absorbuje výsledky z širokého spektra odvětví výzkumu a vývoje. Vodivé polymery, jako např. polyanilin či polypyrrol, se svojí vysokou elektrickou vodivostí a relativně dobrou stabilitou v něm proto zcela jistě najdou své uplatnění, například jako citlivé materiály chemických senzorů.

Experimenty shrnuté na těchto stránkách ukazují některé perspektivní směry ve vývoji a výzkumu chemických senzorů na bázi vodivých polymerů:

i) Do budoucna lze očekávat, že supramolekulární vodivé polymery jako citlivé materiály chemických senzorů zcela převáží nad svými nestrukturovanými protějšky, což lze dobře demonstrovat při srovnání vlastností supramolekulárního a standardního globulárního polypyrrolu. Hlavním důvodem je zejména vyšší stabilita parametrů (měsíce až roky u nanotubulárního polypyrrolu vs. dny u globulárního polypyrrolu), vyšší elektrická vodivost (až desítky $S \cdot cm^{-1}$ vs. jednotky u globulárního polypyrrolu) a specifický povrch (cca desítky $m^2 \cdot g^{-1}$ vs. jednotky $m^2 \cdot g^{-1}$ u globulárního polypyrrolu). Řádově vyššího specifického povrchu lze navíc dosáhnout karbonizací supramolekulárních struktur polypyrrolu (cca stovky $m^2 \cdot g^{-1}$), karbonizací také zároveň dochází k stabilizaci parametrů, což se projevuje i na menších časových driftech vlastností senzorů.

ii) Supramolekulární struktury vodivých polymerů mohou mít různé tvary v závislosti na způsobu syntézy, které dále modifikují specifické vlastnosti materiálu. V práci byly srovnány vlastnosti zejména nanotubulárního polypyrrolu připraveného v přítomnosti azobarviva methyl oranže a soudkovitých útvarů polypyrrolu připravených v přítomnosti azobarviva Sunset Yellow FCF. Druhý z nich sice dosáhl jen průměrné elektrické vodivosti (jednotky až desítky $S \cdot cm^{-1}$) oproti nanotubulárnímu polypyrrolu obsahoval v průměru menší množství zbytkového azobarviva, které je v mnoha aplikacích nežádoucí. Vzhledem k tomu, že azobarviva jsou pestrou a rozsáhlou skupinou látek, lze očekávat, že řada nových tvarů a s tím související vlastností polypyrrolu bude teprve objevena.

iii) V průběhu experimentů zejména s polypyrrolu se podařilo zpřesnit mechanismus tvorby nanostruktur. Tyto znalosti jsou důležité při hledání cesty, jak jednotlivé struktury orientovat, tak aby vytvořily uspořádané tenké vrstvy s anizotropními vlastnostmi. Tyto vrstvy pak bude možné následovně funkcionalizovat, např. chemickým či fyzikálním kotvením receptorů pro biosenzory či

přidáním funkčních skupin do řetězce vodivého polymeru (např. skupinou -COOH) a vytvářet senzory či biosenzory se specifickou detekcí analytů.

iv) Velkou roli při zpracování vodivých polymerů metodami tisku či laserovými depozičními metodami hraje jejich rozpustnost. Velmi dobrých výsledků bylo dosaženo při syntéze polypyrrolu v přítomnosti sulfonových kyselin či surfaktantů. Rozpustnost takto připraveného polypyrrolu v polárních rozpouštědlech výrazně vzrostla, a to až na jednotky hm.%, které jsou dostatečné pro výše zmíněné depoziční technologie. Do budoucna je však nutné zvýšit i rozpustnost supramolekulárních vodivých polymerů, čemuž by mohly napomoci i možnost ovlivňovat tvar připravených struktur volbou vhodného azobarviva.

v) Příprava tenkých citlivých vrstev vodivých polymerů může být realizována pomocí technologie inkoustového tisku i laserových depozičních technologií. Technologie inkoustového tisku umožňuje připravovat i jemné motivy elektrodových systémů, v případě laserových depozičních technologií se pro tento úkol hodí lépe některá ze sériových technologií. Technologie inkoustového tisku je perspektivnější z hlediska nasazení při masové výrobě organické elektroniky. Laserové depoziční technologie jsou pro tento úkol méně vhodné. Velkým úkolem do budoucna je příprava tenkých vrstev či jemných motivů ze supramolekulárních struktur vodivých polymerů.

vi) Senzory na bázi vodivých polymerů mohou sloužit pro detekci analytů v kapalném i plynném prostředí, zároveň mohou sloužit jako nosiče receptorů či přímo jako receptory. Vodivé polymery také vykazují značné redukční schopnosti, což jim umožňuje vyredukovat kovové ionty ve formě nanočástic, které poté dekorují vodivý polymer. Tímto způsobem je možné v budoucnu připravovat i nanočástice s katalytickými účinky, které budou přímo součástí polymeru.

vii) Vodivé polymery ve standardním globulárním stavu vykazují pouze malou selektivitu k analytům. Vyšší selektivity lze dosáhnout přípravou supramolekulárních struktur vodivých polymerů, vhodnou kombinací vodivého polymeru, receptoru či katalyzátoru, anebo vhodným zpracováním signálu, např. analýzou šumového spektra, či použitím střídavého měření fázové citlivost. Řada těchto metod však vyžaduje ještě mnoho práce a optimalizace.

Experimenty, které byly provedeny v rámci této práce, připravily materiálový základ pro nové typy chemických senzorů na bázi supramolekulárních vodivých polymerů, a zejména vodivého polymeru polypyrrolu. Zároveň byla provedena řada pilotních experimentů s depozicemi a tvorbou jemných motivů i zpracováním a analýzou signálů ze senzorů. Podařilo se také doplnit některé základní otázky týkající se mechanismů růstu supramolekulárních struktur, depozice vodivých polymerů i dlouhodobé stability senzorů. Do budoucna se však zároveň otevřela řada nových výzev, které bude nutné teprve vyřešit a zodpovědět.

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7 Seznam veličin a zkratk

A	prefaktor Arrheniovy rovnice
APS	peroxodisulfát amonný (z angl. <i>ammonium peroxydisulfate</i>)
c	koncentrace
CAMP	anion kafrsulfonátu
CS	chitosan
CTB	amino-substituované kumarinové deriváty Trögerových bází
d	průměr nanotrubek polypyrrolu
DBSA	anion dodecylbenzensulfonátu
DEHS	anion dioctylsulfosukcinátu
DMSO	dimethylsulfoxid
EDX	energieově-disperzní spektroskopie
f	frekvence
FET	tranzistor řízený elektrickým polem (z angl. <i>Field-Effect Transistors</i>)
LIFT	technologie laserového psaní (z angl. <i>Laser Induced Forward Transfer</i>)
MAPLE	matricová pulsní laserová depozice (z angl. <i>Matrix Assisted Pulsed Laser Evaporation</i>)
MAPLE-DW	matricová pulsní laserová depozice – přímé psaní (z angl. <i>Matrix Assisted Pulsed Laser Evaporation – Direct Write</i>)
MO	methyl oranž
NPOE	2-nitrofenyl oktyl ether
NSA	β -naftalen sulfonová kyselina
NTP	nízkoteplotní plazma
OLED	organická světlo vyzařující dioda (z angl. <i>Organic Light Emitting Diode</i>)
OME	napařování organických látek (z angl. <i>Organic Molecular Evaporation</i>)
OPV	organická fotovoltaika (z angl. <i>Organic Photovoltaic</i>)
OTFT	organický tenkovrstvý tranzistor (z angl. <i>Organic Thin-film Transistor</i>)
PAC	polyacetylen
PANI	polyanilin
PEDOT	poly-3,4-ethylendioxythiofen
PLD	pulsní laserová depozice (z angl. <i>Pulsed Laser Deposition</i>)

PPy	polypyrrol
PPy-G	polypyrrol s globulární morfologií
PTFE	polytetrafluoroethylen
PVC	poly(vinyl chlorid)
QCM	krystalové mikrováčky (z angl. <i>Quartz Crystal Microbalance</i>)
RFID	identifikace na rádiové frekvenci (z angl. <i>Radio-frequency Identification</i>)
RS1, RS2, RS3	reakční schémata 1-3
s	měrná elektrická vodivost
SAW	povrchová akustická vlna (z angl. <i>Surface Acoustic Wave</i>)
S_{AC}	fázová citlivost
S_{DC}	stejnoseměrná citlivost
SnAcAc	acetyl-acetonát cínu
T	teplota
p -TSA	anion p -toluensulfonátu
ÚFMT	Ústav fyziky a měřicí techniky, Vysoká škola chemicko-technologická v Praze
VOC	organické těkavé látky (z angl. <i>Volatile Organic Compound</i>)
VP	vodivé polymery
VRH	přeskokový mechanismus přenosu náboje (z angl. <i>Variable Range Hopping</i>)

8 Seznam příloh

Následující seznam příkládaných článků publikovaných ve vědeckých časopisech je řazen vzestupně chronologicky. Monografie, kapitoly v monografiích ani citované studentské práce nejsou z důvodu svého rozsahu součástí příloh.

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Deposition of organic metalocomplexes for sensor applications by MAPLE

R. Fryček^a, F. Vysloužil^b, V. Myslík^{a,*}, M. Vršata^b, D. Kopecký^b,
O. Ekrť^b, P. Fitl^a, M. Jelínek^c, T. Kocourek^c, R. Šípula^a

^a Department of Solid State Engineering, Institute of Chemical Technology, Prague 6 166 28, Czech Republic

^b Department of Physics, Institute of Chemical Technology,
Prague 6 166 28, Czech Republic

^c Czech Academy of Sciences, Prague 8 182 21, Czech Republic

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Abstract

Complexes of metals with organic ligands are known to be widely used materials for active layers of chemical gas sensors. Among these materials especially those containing a system of conjugated double bonds in ligands have suitable properties for gas sensing. This article deals with deposition and characterization of three materials commonly used in detection of oxidizing gases: indium acetylacetonate (InAcAc), nickel phthalocyanine (NiPc) and copper(II) *para*-tetratolylmethylporphyrine (CuTTMP). The layers are deposited by a non-conventional matrix-assisted pulsed laser evaporation (MAPLE) method. The choice of a proper matrix and investigation of the deposition rate versus energy density dependence are made. Prepared layers are characterized by Raman spectra and also by measuring their responses to oxidizing gases. The best dc-gas-response was exhibited with an InAcAc layer ($S \sim 10$ – 100 ppb of ozone at 100 – 160 °C and $S \sim 8$ – 1 ppm of NO_2 at 230 °C).

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1. Introduction

For the next generation of microelectronics and optoelectronics, surface coatings, intelligent multifunctional materials and technologies of thin organic film preparation are needed. Organic materials provide high variability of chemical composition and thus flexibility of their electrophysical properties. In the past few years also the research oriented to gas sensor applications is focused on organic, polymeric and biological materials. Basic advantages of organic materials in sensor applications are low working temperature, reaching higher selectivity and a wide range of detectable gases.

Thin organic or polymeric films can be deposited by a variety of “wet” techniques using solvents (aerosol, dip coating, spin coating, electrochemical) or non-solvent techniques (vacuum

evaporation, plasma polymerization). Recent works confirmed the suitability of laser technologies (pulse laser deposition, PLD and matrix assisted pulsed laser evaporation, MAPLE for depositing thin active layers for gas sensor applications [1–5]. Laser deposition technologies utilize highly non-equilibrium conditions of mass transfer and they also enable precise control of deposition rate and layer thickness.

The MAPLE technology includes the following steps. The material which is to be deposited (basic material) is embedded in a frozen volatile matrix (solvent). The necessary condition is that the solvent dissolves the basic material without chemical reaction. The solvent has a higher absorption coefficient than the basic material and thus preferentially absorbs the incident laser pulse. Molecules of basic material obtain sufficient kinetic energy through collective collisions with the vaporized matrix molecules to be transferred to the gas phase. Small molecules of matrix are pumped away from the working chamber, while the molecules of basic material are incident on the sensor substrate.

* Corresponding author.

E-mail address: vladimir.myslik@vscht.cz (V. Myslík).

Table 1
Deposition conditions and parameters of resulting layers for InAcAc

Deposition	Number of pulses	Repetition rate, f_{rep} (Hz)	Laser fluence, F (mJ cm^{-2})	Laser spot (mm^2)	Layer thickness (nm)	Deposition rate (nm pulse^{-1})
Ac-1	20,000	10	70	20	120	0.006
Ac-2	20,000	10	100	20	800	0.04
Ac-3	10,000	10	150	20	6100	0.61

Composition of source targets was InAcAc 5 wt.% + acetone.

Hence the dominating principle of MAPLE technique is in the fact that large molecules of basic material are “mechanically” transported from the target to the substrate by “explosion” of small matrix molecules, which absorb major part of laser energy. Thus the molecules of basic material should be damaged by neither photothermal nor photolytic process.

Under these circumstances a wide spectrum of organic and even biological materials are grown. The main advantage of MAPLE technology is in good similarity of chemical composition between source and deposited materials. It is also known that MAPLE-prepared layers are porous and have large surface, which is suitable for sensor applications.

2. Experimental

In our experiments MAPLE depositions were carried out from three systems (basic material, matrix): (i) InAcAc, acetone; (ii) NiPc, dimethylsulfoxide; (iii) CuTTMP, chloroform. The basic materials were chosen with respect to their applicability for gas sensors and also in order to test possibility of deposition of molecules with increasing complexity. Powder of a basic material (Sigma–Aldrich) was diluted in a corresponding liquid matrix and the resulting solution (concentration varied from 0.1 to 5 wt.%) was then filtered. After filtration source targets were fabricated by freezing this solution at liquid nitrogen temperature.

The deposition conditions were as follows: KrF excimer laser 248 nm, laser fluence $F = 50\text{--}600 \text{ mJ cm}^{-2}$, repetition rate of laser pulses $f_{\text{rep}} = 10 \text{ Hz}$, pulse duration 15 ns, residual pressure of the deposition chamber 10^{-4} Pa , working atmosphere 3 Pa of N_2 , target-substrate distance 35 mm.

The layers were deposited onto two types of substrates: (a) polished silicon chips for measurement of Raman spectra and layer thickness; (b) sensor chips made of alumina for layer resistance and dc-gas-response measurements.

The layer thickness was measured by Talystep and layer surface was also observed by SEM for completeness. Alumina sensor chips were equipped with sputtered platinum electrodes in interdigital configuration. The distance between electrode “combs” was $45 \mu\text{m}$ and the area between them was 0.8 mm^2 . The gas-response measurements were carried out in a flow system. Ozone (100 ppb) was generated by a Hg-low pressure lamp. Nitrogen dioxide (1 ppm), Linde Technogas, was mixed with a calibrated mass flow controller. Reference gas was “pure” synthetic air in both cases.

3. Results

3.1. Deposition of InAcAc

The deposition of InAcAc was carried out from an acetone matrix because of its chemical similarity and hence good solubility of InAcAc in acetone. Table 1 presents the dependence of InAcAc deposition rate versus laser fluence. It is obvious that in the studied range of laser fluence ($F = 70\text{--}150 \text{ mJ cm}^{-2}$) the deposition rate strongly increases (increasing F by about 40% corresponds to an increase in deposition rate by one order of magnitude). The ablation threshold F_{th} was determined from the derivative of the deposition rate versus laser fluence dependence. The F_{th} is the laser fluence for which the derivative is 10 times higher than that in the coordinate origin. For the InAcAc-acetone system the ablation threshold was estimated to be $F_{\text{th}} \sim 80 \text{ mJ cm}^{-2}$.

Raman spectra of InAcAc layers exhibit very good similarity of chemical composition between source (Fig. 1a) and deposited InAcAc (Fig. 1b and c). There are two significant bands typical for acetylacetonetic chelates $\nu(\text{C}=\text{O})$ in the vicinity of 1370 cm^{-1} and $\nu(\text{C}=\text{C})$ near 1270 cm^{-1} and one band corresponding to In–O stretching at 450 cm^{-1} . All these dominating bands retain their positions. There is only a slight change to lower frequency in the position of In–O stretching for laser fluence $E_L = 150 \text{ mJ cm}^{-2}$. Also the ratio of $\nu(\text{C}=\text{C})/\nu(\text{C}=\text{O})$ intensities increases with increasing the laser fluence ($E_L = 150 \text{ mJ cm}^{-2}$ produces an increase in $\nu(\text{C}=\text{C})/\nu(\text{C}=\text{O})$ ratio of about 10% relatively). These two last-mentioned facts indicate that a higher E_L produces stronger In–O bonds and weaker C=O bonds.

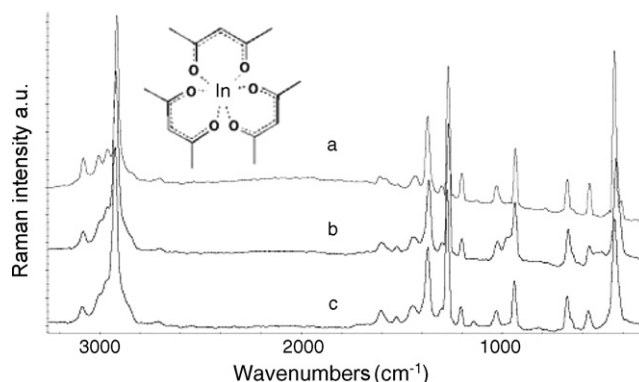


Fig. 1. Raman spectra of (a) source InAcAc, (b) layers prepared by MAPLE-laser fluence $E_L = 150 \text{ mJ cm}^{-2}$, and (c) $E_L = 70 \text{ mJ cm}^{-2}$.

Table 2
Deposition conditions and parameters of resulting layers for NiPc

Deposition	Number of pulses	Repetition rate, f_{rep} (Hz)	Laser fluence, F (mJ cm^{-2})	Laser spot (mm^2)	Layer thickness (nm)	Deposition rate (nm pulse^{-1})
Pc-1	10,000	10	150	20	50	0.005
Pc-2	8,000	10	315	20	40	0.005
Pc-3	4,000	10	430	20	80	0.02
Pc-4	2,000	10	500	20	120	0.06
Pc-5	1,100	10	600	20	NA	NA

Composition of source targets was NiPc 0.1 wt.% + DMSO.

We can also observe strong bands in the $2920\text{--}2930\text{ cm}^{-1}$ region corresponding to the fundamental $\nu(\text{C--H})$ asymmetric and symmetric stretching vibrations. However these bands are not specific for acetylacetonates.

3.2. Deposition of NiPc

MAPLE deposition of NiPc is limited by low solubility of phthalocyanines in a majority of organic solvents (acetone, chloroform). For this purpose dimethylsulfoxide (DMSO) was more acceptable, but nevertheless the concentration of resulting solution was only 0.1 wt.%. Because of the low content of basic material in the given volume of target only relatively thin layers can be prepared (Table 2). The ablation threshold F_{th} was estimated to be 380 mJ cm^{-2} . The highest laser fluence $E_L = 600\text{ mJ cm}^{-2}$ produced very rough surface (non-measurable thickness).

Phthalocyanines are relatively large molecules with complicated Raman spectra; the situation is further complicated by interaction of their molecules with the matrix. That is why measured characteristic Raman shifts are compared with those obtained by computer modeling [6]. Raman spectra of source and deposited NiPc are presented in Fig. 2. The fundamental Raman shift in the spectrum of pure NiPc (Fig. 2a) is at 1548.6 cm^{-1} , corresponding to breathing vibration of the molecular cavity whose dimension is approximately 0.37 nm . Other significant shifts are present at 1336.9 , 1140.3 and 684.4 cm^{-1} .

The MAPLE deposited NiPc layers (Fig. 2b–d) exhibit the presence of weak band of molecular cavity vibration but there is a strong band in the neighborhood of 1340 cm^{-1} corresponding

to molecular fragments. The fragmentation is probably due to photochemical decomposition of phthalocyanine molecules.

3.3. Deposition of CuTTMP

Porphyrines are heterocyclic molecules with promising properties applicable for both chemical and optical sensors. Copper(II) *para*-tetratolylmethylporphyrine dissolves readily in a chloroform matrix. The deposition was carried out from 5 wt.% solution (Table 3). The ablation threshold is $F_{\text{th}} = 220\text{ mJ cm}^{-2}$.

The Raman spectrum of source CuTTMP (Fig. 3a) is even more complicated because of the complexity of its molecule and existence of many possible vibrations. The spectrum contains significant bands at 1575.4 , 1558.5 and 1527.4 cm^{-1} , resulting from various C–C vibrations in the molecular cavity and also in substituent phenyles. The C–N bond in macro cycle is represented by a strong band at 1363 cm^{-1} and C–C bonds to terminal methyles by a band at 1237.8 cm^{-1} [7].

The layers prepared by MAPLE (Fig. 3b–d) exhibit the presence of all the above-mentioned Raman shifts and also the ratio of their intensities is retained constant. The differences in band positions are minimal (up to 1 cm^{-1}), so that it can be concluded that the chemical composition of the deposited layers is practically identical with the source material.

3.4. SEM portrait of deposited layers

The morphology of MAPLE deposited layers was characterized by SEM. The quality of surface is in general affected

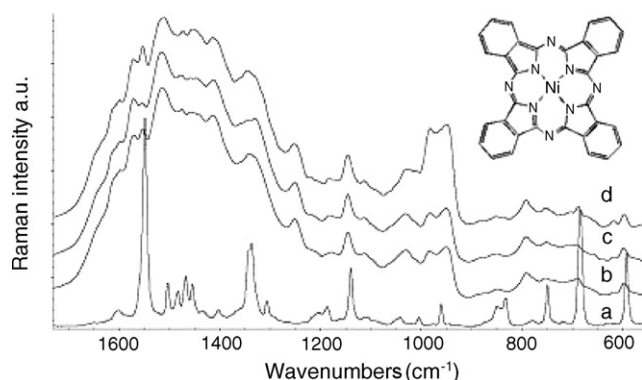


Fig. 2. Raman spectra of (a) source NiPc, (b) layers prepared by MAPLE-laser fluence $E_L = 300\text{ mJ cm}^{-2}$, (c) $E_L = 400\text{ mJ cm}^{-2}$, and (d) $E_L = 500\text{ mJ cm}^{-2}$.

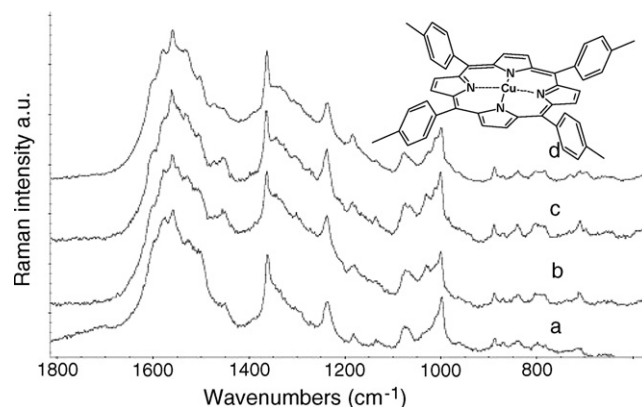


Fig. 3. Raman spectra of (a) source CuTTMP, (b) layers prepared by MAPLE-laser fluence $E_L = 50\text{ mJ cm}^{-2}$, (c) $E_L = 100\text{ mJ cm}^{-2}$, and (d) $E_L = 200\text{ mJ cm}^{-2}$.

Table 3

Deposition conditions and parameters of resulting layers for CuTTMP

Deposition	Number of pulses	Repetition rate, f_{rep} (Hz)	Laser fluence, F (mJ cm^{-2})	Laser spot (mm^2)	Layer thickness (nm)	Deposition rate (nm pulse^{-1})
Po-1	20,000	10	50	20	400	0.02
Po-2	10,000	10	100	20	600	0.06
Po-3	10,000	10	200	20	4900	0.49
Po-4	1,000	10	300	20	700	0.70

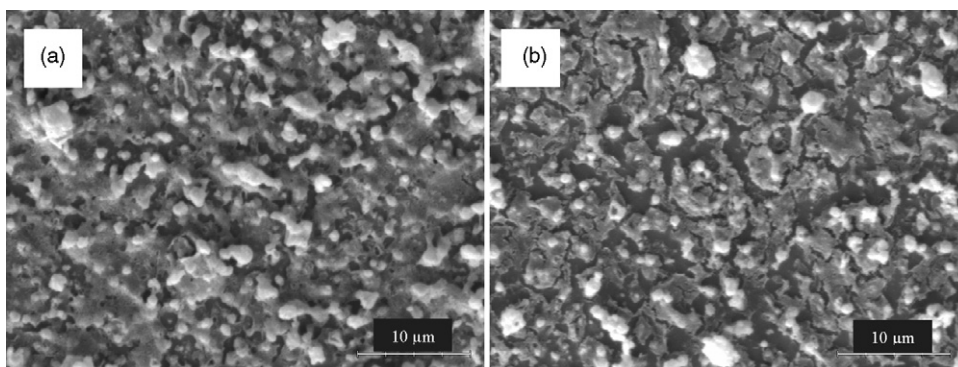
Composition of source targets was CuTTMP 5 wt.% + CHCl_3 .

Fig. 4. SEM images of an InAcAc layer (sample Ac-2 in Table 1). Part (a) represents the as-deposited layer and part (b) the same layer after measurement of responses to ozone and nitrogen dioxide in temperature range 100–350 °C.

by laser fluence. Fig. 4 gives an example of SEM image of an InAcAc layer. It is apparent that $E_L = 100 \text{ mJ cm}^{-2}$ is sufficient to ensure rough surface advantageous for sensor applications. The sensors based on this layer (sample Ac-2 in Table 1) exhibit the highest dc-response to both gases.

3.5. Deposition rate and roughness of prepared layers

From the technological point of view, there are two important outputs of our experiments: deposition rate and roughness of produced layers. The roughness (r_a) was measured by Talystep on the distance (L)—approx. 100 μm . It was calculated from (Eq. (1)) as the mean value of deviations of layer thickness $r(x)$ from its mean value r_0 related to distance (L):

$$r_a = \frac{1}{L} \int_0^L |r(x) - r_0| dx \quad (1)$$

Fig. 5 presents the deposition rate and roughness of a prepared CuTTMP layer for laser fluences ranging from 0.05 to 0.30 J cm^{-2} . A significant increase of layer roughness in the vicinity of ablation threshold is potentially advantageous for sensor applications.

3.6. Sensing properties of deposited layers

In the next step the MAPLE deposited layers were tested as active layers of gas sensors. The dc-gas-response $S_{\text{dc}} = R_{\text{gas}}/R_{\text{air}}$ was evaluated as the ratio of the layer resistance in air R_{air} and in the atmosphere containing detected gas R_{gas} at a given temperature. Fig. 6 depicts the dependence of the layer resistance on temperature (Table 1, sample Ac-2) when atmosphere changes

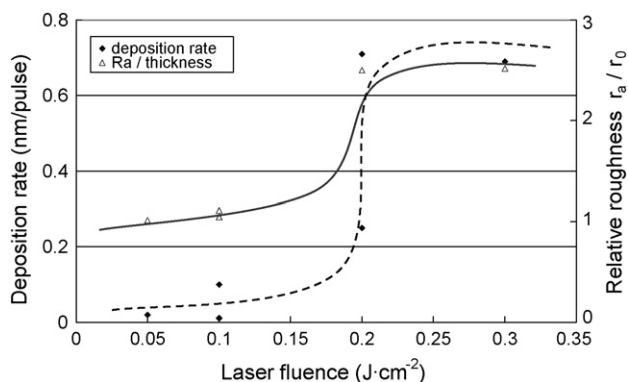
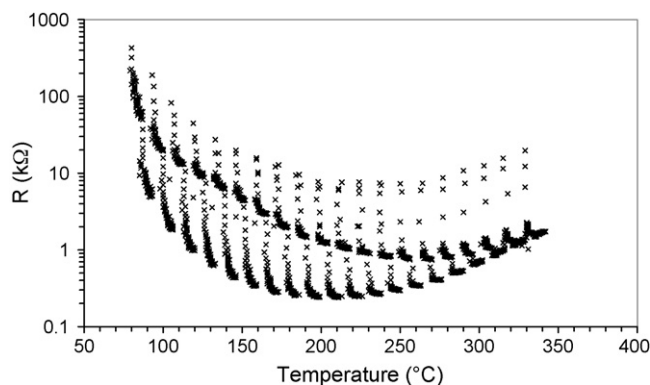
Fig. 5. Deposition rate (left) and relative roughness r_a/r_0 (right) vs. laser fluence for layers prepared from the CuTTMP–chloroform system.

Fig. 6. Dependence of layer resistance (InAcAc, sample Ac-2) on temperature when atmosphere changes every 3 min from “pure” synthetic air to synthetic air containing 100 ppb of ozone and vice-versa.

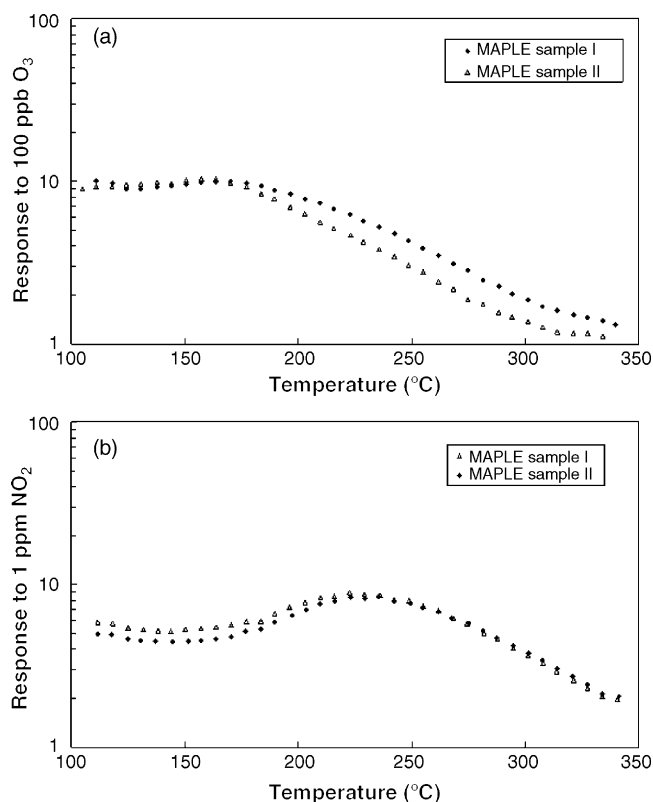


Fig. 7. The gas-response (S_{dc}) of the sensor based on a MAPLE-deposited InAcAc layer to (a) 100 ppb of ozone and (b) 1 ppm of NO_2 .

every 3 min from “pure” synthetic air to synthetic air containing 100 ppb of ozone and vice-versa. In this figure the upper envelope represents R_{gas} and down envelope R_{air} .

Fig. 7 presents responses to ozone (1 ppm) and nitrogen dioxide (100 ppb) of InAcAc-based sensors originated from the deposition marked as Ac-2 (see Table 1). The measurement was carried out on two samples with relatively low variance of obtained data. Maximal values $S_{dc} \sim 10$ for ozone were achieved in the range 100–160 °C and maximal values $S_{dc} \sim 8$ for nitrogen dioxide in the range 200–260 °C.

4. Conclusions

We have deposited three organic substances by MAPLE technology. The complexity of their molecules increases in the sequence of InAcAc ($M_w = 412$) < NiPc ($M_w = 571$) < CuTTMP ($M_w = 743$).

The Raman spectra showed that the chemical composition of basic material was retained in the cases of InAcAc and CuTTMP. On the contrary, deposition of NiPc did not bring acceptable results. It means that the result of MAPLE deposition is strongly dependent on the properties of both basic material and matrix components. In our case the choice of a proper matrix was primarily made on the basis of three criteria: (1) high absorption coefficient at laser wavelength; (2) solubility of basic material in matrix; (3) absence of chemical degradation of basic material in matrix. It is apparent, however, that these conditions are not complete (also melting and boiling points of

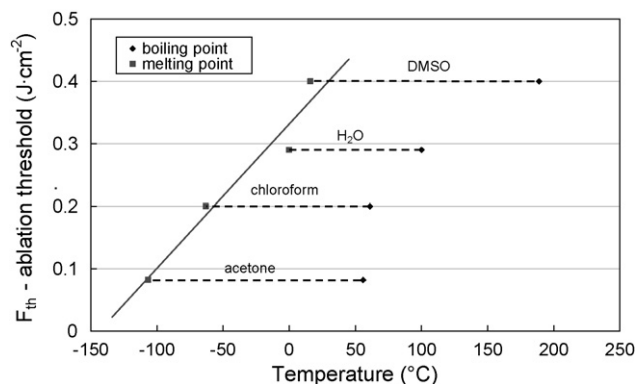


Fig. 8. The relation between ablation threshold and melting or boiling point of matrix.

matrix, heat of evaporation or sublimation, etc. play an important role).

An interesting result is the relation between the ablation threshold and the melting or boiling point of matrix. This relation is presented in Fig. 8. Besides three matrixes used in this work (acetone, chloroform and DMSO), water was also included. Water matrix was employed in our experiments concerning deposition of polypyrrole [8]. We can observe a nearly proportional increase of ablation threshold in relation to the melting point of matrix. Based on this fact we can estimate ablation threshold of a given matrix from its melting point and thus reduce the number of optimizing experiments. On the other hand, the ablation threshold is not clearly related to the boiling point (eventually sublimation point) of matrix. It is well known that boiling or sublimation points are strongly dependent on the ambient pressure. The working pressure is approx. 3 Pa, but the local pressure near target surface dramatically increases during interaction with laser pulse.

In this context, absorbance of all these source systems (i.e. basic material + matrix) on KrF laser wavelength was measured. It was shown that the differences in absorbance are in the range of $\sim 5\%$ rel. and hence cannot play any significant role.

From the point of sensing properties of MAPLE deposited layers the best results were achieved with InAcAc samples. They represented maximal values $S_{dc} \sim 10$ to ozone in the range 100–160 °C and maximal values $S_{dc} \sim 8$ to nitrogen dioxide in the range 200–260 °C. Such layers are perspective for low-temperature detection of ozone. As for dynamic properties of ozone detection it is apparent from Fig. 6 that at temperatures above 150 °C the time necessary for stabilization of layer resistance is shorter than 3 min.

The sensors containing deposited NiPc-based and CuTTMP-based active layers were also prepared, but their R_{air} values were higher than 100 M Ω at temperatures ranging from 100 to 350 °C. These results have no practical utilization.

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Biographies

Rudolf Fryček was born in Karlovy Vary on 28 April 1978. He graduated from the Institute of Chemical Technology in Prague in 2001, specializing in materials engineering. Since 2001 until 2004 he had been studying as a postgraduate student at the Institute of Chemical Technology in Prague at the Department of Solid State Engineering. He worked on the subjects of technology and measurement of sensor structures and their applications.

Filip Vysloužil was born in Praha on 18 March 1971. He has graduated from the Institute of Chemical Technology in Prague in 1996, specializing in materials engineering. Since 1996 until 1999 he had been studying the same specialization as a postgraduate student. In 2003 he was working in electro technical factory ELEKTROISOLA, a.s. as a developer engineer, then in 2004–2005 he had worked as a metrologist at the Czech Metrology Institute, working on metrology in chemistry. Since 1999 until present he has been working at the Institute of Chemical Technology in Prague on the subject of chemical conducting sensors with active layers deposited using the technologies PLD and MAPLD.

Vladimír Myslík was born in Dražice nad Jizerou on 1 May 1944. He graduated from the Czech Technical University, Faculty of Electrical Engineering with specialization in Electronic Engineering and has received his PhD degree at the same department in 1974. He has become associate professor of microelectronics at the Czech Technical University, Faculty of Electrical Engineering in 1983 and a year later started working at the Institute of Chemical Technology in Prague where he has been working until today. At present, he works on the subjects of

technology and measurement of optoelectronic structures, application of laser technology in electronics and chemical conducting sensors.

Martin Vřňata was born in Praha on 6 May 1970. He graduated from the Institute of Chemical Technology in Prague in 1993, specializing in materials engineering. Since 1993 until 1996 he had been studying the same specialization as a postgraduate student and has completed studies in 1999 by defending dissertation: “Laser Annealed Ohmic Contacts on Semiconductors A^{III}B^V”. At present, he works as an associated professor at the Department of Physics and Measurements at the Institute of Chemical Technology in Prague.

Dušan Kopecký was born in Vrchlabí on 14 April 1983. He is currently PhD student from the Department of Physics and Measurements, Institute of Chemical Technology in Prague. He graduated in 2006, theme of his work was chemical gas sensors with active layers deposited by matrix assisted pulsed laser evaporation. His work deals with chemical gas sensors based on organic semiconductors with specialization on laser deposition methods. He deals with computer controlled measurements.

Ondřej Ekrt was born in Beroun on 29 May 1976. He graduated from the Institute of Chemical Technology in Prague in 1999 specializing in materials engineering. He has completed stay a in the USA at the Purdue University where he worked on heterogeneous catalysis. Since 2001 until 2004 he had been studying as a postgraduate student at the Institute of Chemical Technology in Prague at the Department of Metals and Corrosion Engineering.

Přemysl Fitl was born in Vrchlabí on 10 August 1980. He graduated from the Institute of Chemical Technology in Prague with specialization in material engineering in 2004. At present he is a postgraduate student at the Institute of Chemical Technology in Prague. The aim of his work is research in the field of chemical conductive sensors. He is employed in the Department of Natural Sciences, Czech Technical University as well.

Miroslav Jelínek was born in Desná on 13 June 1946. He has graduated from the Czech Technical University in Prague specializing in technical cybernetics. He has received his PhD in 1978 by defending dissertation: “Laser Measurement of the Raman Spectra of Air Polluting Materials” at the Faculty of Nuclear Science and Physical Engineering. He has been working at the Institute of Physics CAS since 1984. He has become the head of the Department of Natural Sciences, Czech Technical University in 2005 as well as associate professor in the same year. At present, he works on the subject of laser deposition of thin films.

Tomáš Kocourek was born on 29 May 1971. In the year 1995 he finished his bachelor study at the Czech Technical University, Faculty of Nuclear Science and Physical Engineering. Since 1996 he has worked at Institute of Physics. He has graduated from the Czech Technical University in 2003. In the year 2004 he started his postgraduate study. At present, he works on the subject of laser deposition of thin films.

Radomír Šípula was born in Havířov on 7 July 1982. He graduated from the Institute of Chemical Technology in Prague with specialization in material engineering in 2006. At present he is a postgraduate student at the Institute of Chemical Technology in Prague. The aim of his work is research in the field of chemical conductive sensors and signal processing.



Impedance properties of polypyrrolic sensors prepared by MAPLE technology

Martin Vršná^{a,*}, Dušan Kopecký^a, Filip Vysloužil^a, Vladimír Myslík^b, Přemysl Fitl^b, Ondřej Ekrt^a, Jaroslav Hofmann^a, Lukáš Kučera^a

^a Institute of Chemical Technology Prague, Department of Physics and Measurements, Technická 5, Praha 6, 166 28 Czech Republic

^b Institute of Chemical Technology Prague, Department of Solid State Engineering, Technická 5, Praha 6, 166 28 Czech Republic

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ABSTRACT

Thin sensitive layers of polypyrrole (PPY) are deposited onto alumina sensor substrates by matrix-assisted pulsed laser evaporation (MAPLE) technology. The depositions are carried out with the KrF excimer laser from dimethylsulfoxide (DMSO) matrix. After 1-month “ageing” period the complex impedance of prepared sensors is measured in the frequency range from 15 Hz to 10 MHz in following atmospheres: “pure” synthetic air and synthetic air with variable (23% or 90%) relative humidity. The general character of Nyquist diagrams, plots of complex admittance versus frequency, parameters of sensor equivalent circuit and phase-angle sensitivities are then evaluated from the obtained impedance data. While equivalent circuit capacity (C) of PPY-based sensors remains from 1.7 to 2.0 pF in all the above-mentioned atmospheres, equivalent circuit resistance (R) varies widely from 6 to 140 MΩ, mostly in dependence on surrounding atmosphere humidity. The differences in charge-transport mechanisms between PPY and tin dioxide sensitive layers and also influence of surrounding atmosphere to electric properties of PPY are discussed.

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1. Introduction

Polypyrrole and its composites are promising materials for active layers of chemical sensors detecting both reducing and oxidizing gases. The doped polypyrrole (PPY) joins flexibility in chemical composition of organic substances with possibility to affect physical properties of thin layer of material, typical for inorganic semiconductors. In general, there are two necessary conditions for applicability of PPY in sensors: (a) increasing of “basic” conductivity of this material by oxidation of the neutral polymer backbone (connected with formation of positively charged centres—polarons or bipolarons) together with introduction a proper counter-anion called as dopant; (b) the ability of PPY to change electric conductivity during sorption and/or desorption of gas molecules on its surface.

There are three contributions to resulting conductivity of the doped polypyrrole: (i) transfer of polarons (in reality electrons) along the polymer backbone; (ii) hopping of electrons across the interchains; (iii) mobility of the dopant counter-anions. Hence, PPY is a mixed conductor with both electronic (i)–(ii) and ionic (iii) conductivity mechanisms [1].

It is well known that ionic conductivity in doped PPY can be stimulated by presence of humidity in the material (in connection with

humidity of surrounding atmosphere) [2,3], similar behaviour was observed for other conductive polymers such as polyaniline [4,5]. Increasing content of water leads to higher mobility of the dopant counter-anions. In “wet” material the conductivity mechanism (iii) can be dominating, especially when small inorganic dopants are used. Paradoxically, water molecules, even at low concentrations, disturb the conjugation of double bonds in polymer backbone (due to hydroxylation and formation of hydrogen bonds) and hence they reduce the mobility of polarons (i) [6].

This contribution deals with impedance measurement of PPY-based sensors. It presents some consequences between the appearance of Nyquist plots and their drift on one side and conductivity mechanisms in PPY on the other side.

2. Experimental

2.1. Preparation of PPY layers by the MAPLE method

The source target for MAPLE was prepared from 5 wt% water solution of polypyrrole ($M_w = 10,000$ a.u.) doped with dodecylbenzene sulfonic acid-specific electrical conductivity of the solution: $\sigma = 10\text{--}40 \text{ S cm}^{-1}$ (Sigma–Aldrich). The water solvent was substituted by dimethylsulphoxide (Sigma–Aldrich, purity >99.5%, DMSO) in order to obtain the DMSO matrix for the polypyrrole layers growth. The substitution of the solvents was carried out by water evaporation from the original water solution at 70 °C and subsequent transfer of the obtained solid phase into DMSO. The

* Corresponding author.

E-mail address: kopeckyd@vscht.cz (M. Vršná).

resulting solution was stirred and homogenized by an ultrasonic device. Subsequently the solution was frozen in the tubular mould by liquid nitrogen.

The prepared target was inserted into the deposition chamber and placed on the shaft of the target holder. During the deposition the uniform ablation of the material from the target surface was achieved by constant shaft rotation and the holder was simultaneously cooled by liquid nitrogen. The deposition chamber was evacuated by a turbomolecular pump to a residual pressure of 5×10^{-3} Pa. The background gas was not used and the pressure in the chamber did not exceed 3 Pa during the deposition process.

The depositions were carried out with a KrF excimer laser (LUMONICS) emitting at 248 nm. The laser was used in a pulse mode with 10 Hz repetition rate. The fluence F of the laser radiation was set by an attenuator to a constant value of 0.3 J cm^{-2} . The laser spot was adjusted to the size of $8 \times 25 \text{ mm}$.

The alumina sensor substrates were placed parallel with the target surface at a distance of 30 mm. The substrates are equipped with Pt-sensing electrodes in the interdigital arrangement on one side and Pt-heating meander on the other side. The distance between “combs” of sensing electrodes was $45 \mu\text{m}$ and the area between them was 0.8 mm^2 . The substrate holder was rotated during the deposition so that a uniform layer thickness was achieved. The PPY active layers were deposited by 10,000 pulses and have an average thickness of $\sim 670 \text{ nm}$.

The as-deposited PPY-based sensors were stored in a desiccator for 1 month before impedance measurement.

2.2. Preparation of tin dioxide layers by PLD method

In order to investigate Nyquist diagram of an inorganic material, tin dioxide active layers were deposited by pulsed laser deposition (PLD) method. The single-component targets for PLD were pressed from SnO_2 powder (Sigma–Aldrich, purity > 99.5%) at pressure of 85 MPa without sintering and using adhesives. The volume contraction was estimated to be at about 1/4. For both PLD and MAPLE depositions the same KrF excimer laser was used. The PLD deposition was carried out in oxygen working atmosphere at a pressure of 5 Pa, laser fluence $F = 0.6 \text{ J cm}^{-2}$, repetition rate of laser pulses $f_{\text{rep}} = 5 \text{ Hz}$, pulse duration 15 ns. The growth rate of SnO_2 layer under these conditions achieved 50 nm min^{-1} . Further technological details have been reported in recent works [7,8].

2.3. Measurement of sensor impedance

The Nyquist diagrams (i.e. real part versus imaginary part of complex impedance) were measured with a HP4194A impedance analyser. The frequency of testing signal ranged from 15 Hz to 10 MHz and its amplitude has a constant level of 100 mV. No bias dc-voltage was applied. The measured sensor was placed in a shielded Teflon chamber and its interdigital electrodes were connected with impedance analyser by a 4-TP professional adapter (four-wire arrangement). The measurement of the Nyquist diagram in a given atmosphere was carried out in a flow system (dead volume approx. 20 ml, gas flow rate 40 ml min^{-1}).

3. Results

3.1. The general character of Nyquist diagrams of PPY- and SnO_2 -based sensors

The Nyquist diagrams of PPY- and SnO_2 -based sensors are depicted in Figs. 1 and 2, respectively. It was necessary to measure PPY sensors in 90% r.h. in order to investigate Nyquist diagram in the whole frequency range (in dry synthetic air the absolute value of

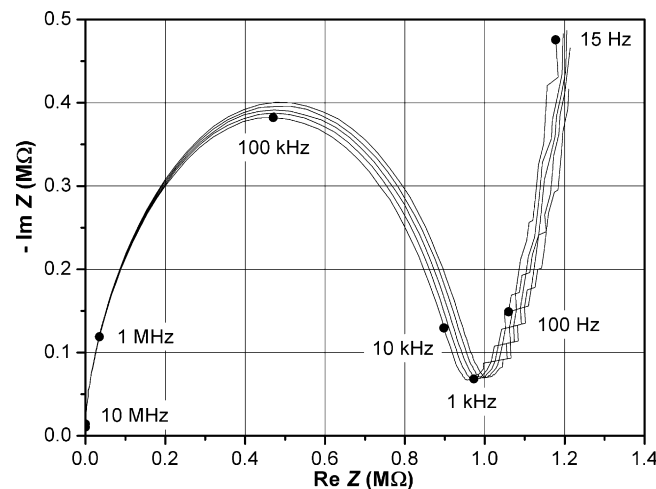


Fig. 1. Nyquist diagram of PPY-based sensor in synthetic air containing 90% r.h. at isothermal conditions ($t = 22^\circ\text{C}$)—measured repeatedly during 5 min.

complex impedance was in the order of $10^8 \Omega$ for frequency under 1 kHz).

The character of both diagrams differs significantly: while for PPY-based sensors (Fig. 1) the absolute value of the imaginary part of complex impedance ($|\text{Im}Z|$) achieves an absolute maximum at low frequency, the same quantity ($|\text{Im}Z|$) for SnO_2 -based sensors (Fig. 2) limits to zero at comparable low frequency. Simultaneously, Nyquist diagrams of tin acetylacetonate-based sensors, reported in previous work [8], have the same character as those of SnO_2 -based sensors. Thus only the fact, that the sensitive layer material belongs to either inorganic or organic substances, does not determine the character of its impedance behaviour at low frequencies.

The appearance of Nyquist diagrams similar to that in Fig. 1 is well known from impedance measurement of solutions containing ionic charge carriers [9]. In such solutions the impedance value at lower frequency is controlled by diffusion of ions (the “tail” in the right part of Nyquist diagram) while at higher frequency the impedance is controlled by charge transfer through the energy barriers existing in the system (the semicircle in the left part of Nyquist diagram). The occurrence of the “tail” in Fig. 1 is hence caused by diffusion of counter-anions that are present in PPY. On the contrary, there are no anions in tin dioxide, so the character of Nyquist

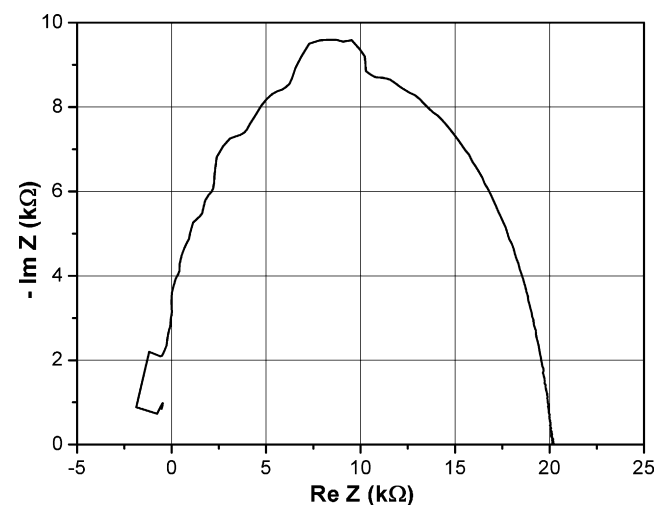


Fig. 2. Nyquist diagram of SnO_2 -based sensor in synthetic air containing 90% r.h. at isothermal conditions ($t = 22^\circ\text{C}$).

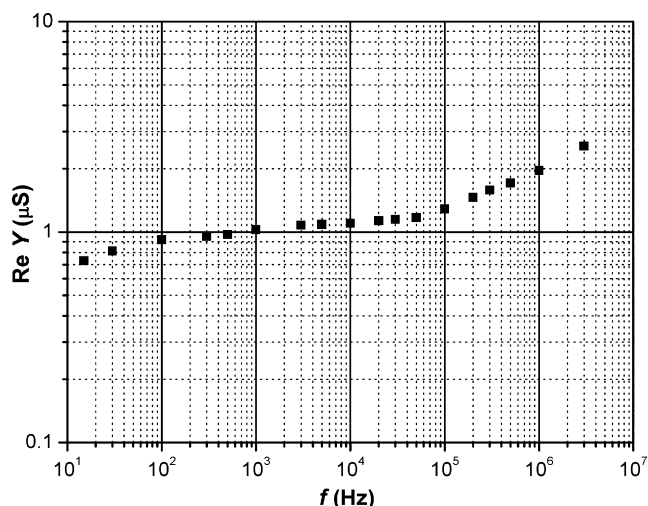


Fig. 3. The log–log plot of real part of complex admittance vs. frequency of signal for PPY-based sensor in synthetic air containing 90% r.h. at isothermal conditions ($t = 22^\circ\text{C}$).

diagram at low frequencies (Fig. 2) is profoundly different in this case.

In order to ensure unambiguous determination of equivalent circuit parameters and to calculate phase-angle sensitivity [8] of PPY-based sensors, all the subsequent Nyquist diagrams were measured only for frequency higher than 1 kHz (i.e. only “left part” of diagram in Fig. 1).

There is also another possibility to characterize electrical properties of disordered materials and namely conducting polymers. This alternative method is based on investigation of log–log plot of *real part of complex admittance versus frequency* (i.e. $\text{Re } Y$ versus f) [10]. While at small f the $\text{Re } Y$ values are frequency-independent, after reaching certain critical value, the so called cross-over frequency f_c , sublinear increase of $\text{Re } Y$ with increasing f takes place. It was found that $\text{Re } Y$ grows proportional to f^n for frequencies exceeding f_c . The exponent of this growth (n) is called fractional exponent. It holds $n \leq 1$ for conducting polymers. The values of f_c and n are important material parameters.

Fig. 3 is the log–log plot of *real part of complex admittance versus frequency* for PPY-based sensor. It can be estimated that in our case $f_c \approx 5 \times 10^4 \text{ Hz}$ and $n \approx 0.18$. According to [10] the f_c values decrease from $3 \times 10^5 \text{ Hz}$ for “fresh” polypyrrole to $1 \times 10^5 \text{ Hz}$ for “aged” material. The smaller f_c values indicate that there is partial fragmentation of PPY backbone as a result of material “ageing”. The value of fractional exponent n of our samples is significantly smaller than unity, it means that the charge transfer properties are not predominantly determined by mobility of polarons in the polymer backbone, but they are strongly affected by presence of dopants (counter-anions) and impurities in PPY.

3.2. Nyquist diagrams of PPY-based sensors in dependence on working temperature and humidity of synthetic air

Fig. 4 represents Nyquist diagram of PPY-based sensor in dry synthetic air (0% r.h.), Figs. 5 and 6 the same diagrams in synthetic air containing 23% and 90% r.h., respectively. All of these diagrams were measured under following conditions: (i) the frequency ranged from 1 kHz to 10 MHz; (ii) the initial working temperature of the sensor ($t_1 = 21^\circ\text{C}$) was elevated to $t_2 = 27^\circ\text{C}$; (iii) the relative humidity of synthetic air was kept constant during this experiment. So Figs. 4–6 represent the response of sensor to a defined working temperature step. This methodics was selected in order to simulate typical sensor operation conditions in practice (variable, but in gen-

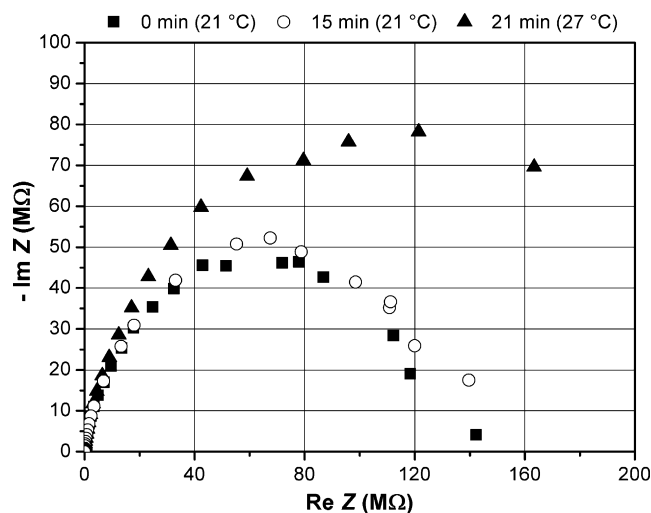


Fig. 4. Nyquist diagram of PPY-based sensor in dry synthetic air (frequency 1 kHz–10 MHz). The temperature of sensor was: $t_1 = 21^\circ\text{C}$ in the period $\tau\text{C} < 0 \text{ min} < \text{time} < 15 \text{ min}$; $t_2 = 27^\circ\text{C}$ in the period $\tau\text{C} < 15 \text{ min} < \text{time} < 21 \text{ min}$.

eral low working temperature of PPY sensor, constant temperature and composition of analyzed gas).

It is apparent that the absolute value of complex impedance decreases monotonously with increasing relative humidity of synthetic air. When the relative humidity changes from 0% to 90%, the corresponding decrease of complex impedance represents more than one order of magnitude. A significant variance of the obtained data in the right part of Fig. 4 is caused by higher noise when measuring impedance values exceeding $10^8 \Omega$.

There is a certain drift of impedance (Figs. 5 and 6) at the temperatures t_1 and t_2 . The long-term measurement of this drift showed that even after 3 h at the increase of absolute value of impedance stayed linear without any steady state features. According our opinion it is caused by changes in structure of PPY backbone. After exposition of the layer by humidity the absolute value of impedance rapidly decrease, because relative humidity increases ion conductivity, but simultaneously the water molecules cause hydroxylation of polymer backbone, which is a very slow process at laboratory temperature and cause long-term decrease of absolute value of impedance (long-term degradation of PPY backbone).

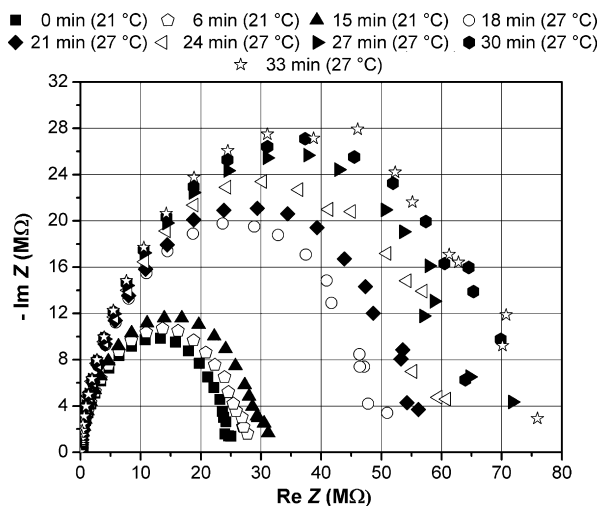


Fig. 5. Nyquist diagram of PPY-based sensor in synthetic air containing 23% r.h. (frequency 1 kHz to 10 MHz). The temperature of sensor was: $t_1 = 21^\circ\text{C}$ in the period $\tau\text{C} < 0 \text{ min} < \text{time} < 15 \text{ min}$; $t_2 = 27^\circ\text{C}$ in the period $\tau\text{C} < 15 \text{ min} < \text{time} < 33 \text{ min}$.

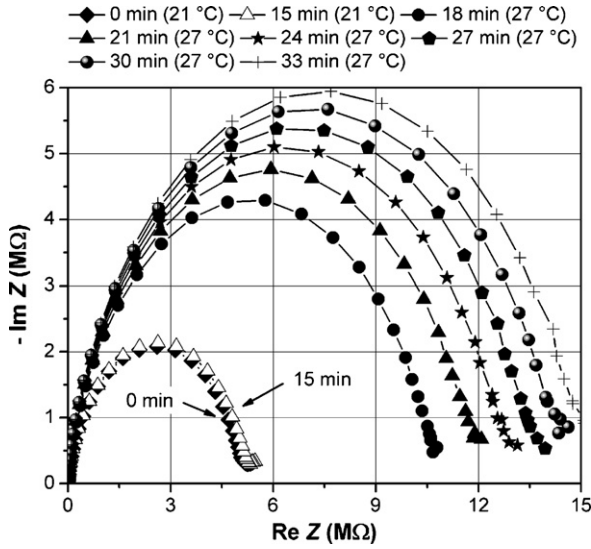


Fig. 6. Nyquist diagram of PPY-based sensor in synthetic air containing 90% r.h. (frequency 1 kHz to 10 MHz). The temperature of sensor was: $t_1 = 21^\circ\text{C}$ in the period $\tau C < 0 \text{ min} < \text{time} < 15 \text{ min}$; $t_2 = 27^\circ\text{C}$ in the period $\tau C < 15 \text{ min} < \text{time} < 33 \text{ min}$.

After switching of temperature to higher t_2 the drift proceeds faster. It can be caused by two factors: (a) by slow hydroxylation of the polymer backbone mentioned before, (b) by slow evaporation of water molecules from the active layer of sensor to reach new thermodynamic equilibrium with water molecules in the surrounding atmosphere. Nevertheless, the further investigation of these phenomena is still needed.

3.3. Parameters of equivalent circuit of PPY-based sensors

As mentioned in Section 3.1, the Nyquist diagram of PPY-based sensors exhibits in general one semicircle corresponding to a parallel R – C element (Fig. 7). The values of equivalent circuit resistance (R) and capacity (C) are calculated as follows: (i) the resistance value (R) is determined by the semicircle diameter, which can be read directly on real axis; (ii) the imaginary part of complex impedance achieves its extreme at certain frequency f_{ext} :

$$f_{\text{ext}} = \frac{1}{2\pi CR} \quad (1)$$

(iii) when knowing the f_{ext} and R , the equivalent circuit capacity C is obtained from Eq. (1).

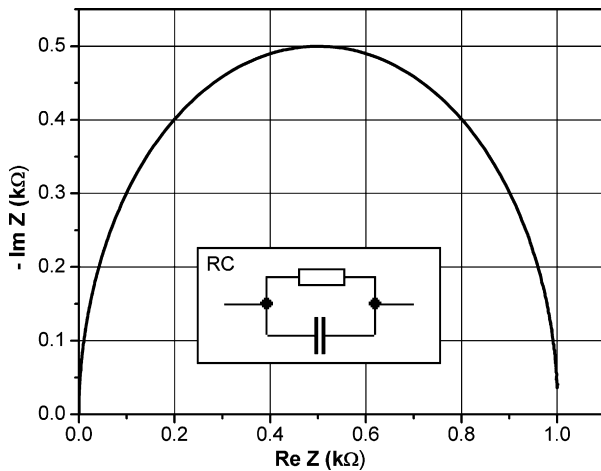


Fig. 7. Nyquist diagram and equivalent circuit of resistor–capacitor parallel element.

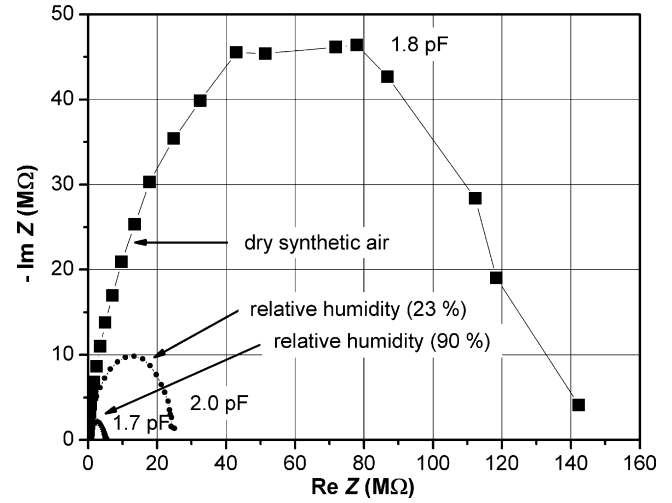


Fig. 8. Nyquist diagram and equivalent circuit parameters of PPY-based sensor at isothermal conditions ($t = 22^\circ\text{C}$) at different relative humidity (dry synthetic air, synthetic air containing 23% r.h., synthetic air containing 90% r.h.).

Fig. 8 shows Nyquist diagrams measured at isothermal conditions for following sequence of atmospheres: dry synthetic air $\rightarrow$ synthetic air containing 23% r.h. (i.e. 5 700 ppm of water) $\rightarrow$ synthetic air containing 90% r.h. (i.e. 22,300 ppm of water). The following relation holds for absolute value of complex impedance $|Z|$ of the PPY sensors: $|Z_{\text{dry air}}| > |Z_{23\% \text{ r.h.}}| > |Z_{90\% \text{ r.h.}}|$.

From Nyquist diagrams presented in Fig. 8 the parameters of sensor's equivalent circuit were calculated (Table 1). An interesting fact follows from these data: while the value of R changes dramatically in dependence on the composition of surrounding atmosphere, the value of C remains almost constant (it has relative variance approx. 10% only).

3.4. Phase-angle sensitivity of PPY sensors

The phase-angle sensitivity S_{pa} of gas sensor is evaluated for given temperature of measurement and concentration of detected gas component as a difference of phase angles θ of complex impedance of the sensor in a “pure” synthetic air (=reference) and complex impedance of the sensor in a given concentration of detected gas:

$$S_{\text{pa}} = \theta_{\text{air}} - \theta_{\text{gas}} \quad (2)$$

This quantity is dependent on concentration of detected gas, temperature and frequency of measuring signal. The details concerning phase-angle sensitivity are discussed in [8].

Fig. 9 depicts phase-angle sensitivities of PPY sensor in synthetic air containing 23% r.h. and synthetic air containing 90% r.h. The phase-angle sensitivity achieves its maxima in the range of frequencies from 10^3 to 10^4 Hz. When analogous measurements were made on tin dioxide sensors [8], the maximum of phase-angle sensitivity was observed at frequency approx. 7×10^5 Hz.

Table 1

Parameters of sensor's equivalent circuit in dependence on relative humidity.

Relative humidity (%r.h.)	Equiv. circ. resistance, R (MΩ)	Equiv. circ. capacity, C (pF)
0	~140	1.8
23	~25	2.0
90	~6	1.7

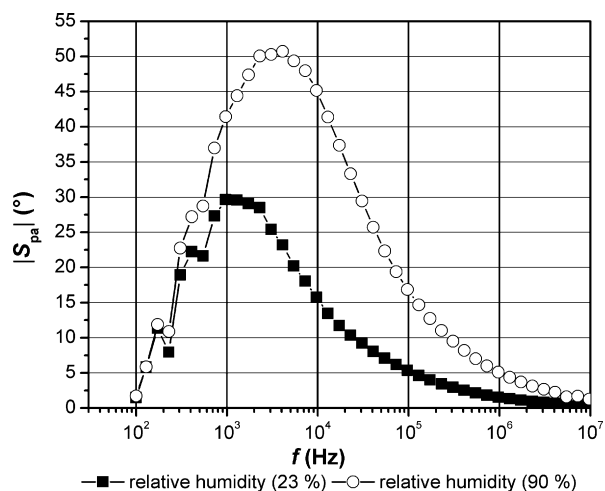


Fig. 9. Phase-angle sensitivity of PPY sensor in various atmospheres (synthetic air containing 23% r.h.; synthetic air containing 90% r.h.) at isothermal conditions ($t = 21^\circ\text{C}$). Reference gas in all cases—dry synthetic air.

4. Conclusions

Impedance spectroscopy is a powerful tool for studying electrophysical properties of conducting polymers. The data obtained by this method help us to better understand charge-transport mechanisms and interaction of sensitive layers based on polymers with surrounding atmosphere. Finally the phase-angle sensitivity is defined on the basis of impedance measurement.

In the presented contribution the impedance properties of PPY-based sensors were investigated. Some general comments to our results can be made:

- There is a principal difference in the character of Nyquist diagram at low frequency between the materials with ionic conductivity (PPY containing dodecylbenzene sulfonic acid as a dopant) or without it (tin dioxide, tin acetylacetonate). While in the former case $\text{Im}Z$ achieves absolute maximum at 15 Hz, in the latter one $\text{Im}Z$ limits to zero at comparable low frequencies.
- The meaningful contribution of ionic conductivity to electrical properties of PPY is documented by small value of fractional exponent ($n=0.18$) and also by the fact that sensor impedance is determined by content of water in sensitive layer. The varying impedance during the changes of sensor temperature is mostly a result of varying water content in the layer. This hypothesis is supported by long time constants (tens of minutes) of impedance transient after sudden change of temperature. The long time constants are connected with diffusion of water into- or out of the active layer.
- The equivalent circuit capacity (C) of the sensor ranges from 1.7 to 2.0 pF and is primarily determined by sensor “internal” factors (composition of sensitive layer, arrangement of sensor substrate)—it is almost independent on “external” composition of the surrounding atmosphere.
- The equivalent circuit resistance (R) is strongly affected by atmosphere composition, primarily by atmosphere humidity ($R = 140\text{ M}\Omega$ in 0% r.h., $R = 25\text{ M}\Omega$ in 23% r.h. and $R = 6\text{ M}\Omega$ in 90% r.h.).
- The PPY-based sensors are applicable as humidity sensors in the whole range of concentrations (0–100% r.h.). They operate at laboratory temperature without necessity to use heating. Both dc- and ac-operating mode is possible. The previous results of dc-measurements of PPY-based sensors are summarized in [11]. In dc-mode the response time (τ_r) of the sensor depends on relative humidity and varies from $\tau_r \sim 1$ min when detecting changes

in lower range (up to 60% r.h.) to $\tau_r = 3\text{--}4$ min for higher range (80–100% r.h.).

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Biographies

Martin Vršata was born in Praha on 6 May 1970. He graduated from the Institute of Chemical Technology in Prague in 1993, specializing in materials engineering. Since 1993 until 1996 he had been studying the same specialization as a postgraduate student and has completed studies in 1999 by defending dissertation: “Laser Annealed Ohmic Contacts on Semiconductors $\text{Al}^{\text{III}}\text{B}^{\text{V}}\text{V}''$ ”. At present, he works as an associated professor at the Department of Physics and Measurements at the Institute of Chemical Technology in Prague.

Dušan Kopecký was born in Vrchlabí on 14 April 1983. He is currently PhD student from the Department of Physics and Measurements, Institute of Chemical Technology in Prague. He graduated in 2006, theme of his work was chemical gas sensors with active layers deposited by matrix-assisted pulsed laser evaporation. His work deals with chemical gas sensors based on organic semiconductors with specialization on laser deposition methods. He deals with computer controlled measurements.

Filip Vysloužil was born in Praha on 18 March 1971. He has graduated from the Institute of Chemical Technology in Prague in 1996, specializing in materials engineering. Since 1996 until 1999 he had been studying the same specialization as a postgraduate student. In 2003 he was working in electro technical factory ELEKTROISOLA, a.s. as a developer engineer, then in 2004–2005 he had worked as a metrologist at the Czech Metrology Institute, working on metrology in chemistry. Since 1999 until present he has been working at the Institute of Chemical Technology in Prague on the subject of chemical conducting sensors with active layers deposited using the technologies PLD and MAPLD.

Vladimír Myslík was born in Dražice nad Jizerou on 1 May 1944. He graduated from the Czech Technical University, Faculty of Electrical Engineering with specialization in Electronic Engineering and has received his PhD degree at the same department in 1974. He has become associate professor of microelectronics at the Czech Technical University, Faculty of Electrical Engineering in 1983 and a year later started working at the Institute of Chemical Technology in Prague where he has been working until today. At present, he works on the subjects of technology and measurement of optoelectronic structures, application of laser technology in electronics and chemical conducting sensors.

Přemysl Fítl was born in Vrchlabí on 10 August 1980. He graduated from the Institute of Chemical Technology in Prague with specialization in material engineering in 2004. At present he is a postgraduate student at the Institute of Chemical Technology in Prague. The aim of his work is research in the field of chemical conductive sensors. He is employed in the Department of Natural Sciences, Czech Technical University as well.

Ondřej Ekrt was born in Beroun on 29 May 1976. He graduated from the Institute of Chemical Technology in Prague in 1999 specializing in materials engineering. He has completed stay in the USA at the Purdue University where he worked on heterogeneous catalysis. Since 2001 until 2004 he had been studying as a postgraduate student at the Institute of Chemical Technology in Prague at the Department of Metals and Corrosion Engineering.

Jaroslav Hofmann was born in Jeseník on 2 September in 1953. He graduated from the Czech Technical University in Prague, specializing in Electrical Engineering (1976). He continued there as postgraduate student; PhD topic: Electrical field with space charge (1981). At present, he works as an associated professor and head of department at the Department of Physics and Measurements at the Institute of Chemical Technology in Prague.

Lukáš Kučera was born in Chomutov on 27 February 1983. He is currently PhD student from the Department of Physics and Measurements, Institute of Chemical Technology in Prague. He graduated in 2007, theme of his work was multi-sensor apparatus for experiments with chemical gas sensors. Current activities are: laboratory automation for gas sensors research based on self-made solutions using AVR microcontrollers, firmware development in AVR assembler and automated gas samples preparation.



Polypyrrole thin films for gas sensors prepared by Matrix-Assisted Pulsed Laser Evaporation technology: Effect of deposition parameters on material properties

Dušan Kopecký^{a,*}, Martin Vršata^a, Filip Vysloužil^a, Vladimír Myslík^b, Přemysl Fitl^b, Ondřej Ekrt^a, Pavel Matějka^c, Miroslav Jelínek^d, Tomáš Kocourek^d

^a Institute of Chemical Technology Prague, Department of Physics and Measurements, Technická 5, Praha 6, 166 28-CZ, Czech Republic

^b Institute of Chemical Technology Prague, Department of Solid State Engineering, Technická 5, Praha 6, 166 28-CZ, Czech Republic

^c Institute of Chemical Technology Prague, Department of Analytical Chemistry, Technická 5, Praha 6, 166 28-CZ, Czech Republic

^d Czech Academy of Sciences, Institute of Physics, Na Slovance 2, Prague 8, 182 21-CZ, Czech Republic

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ABSTRACT

Thin films of polypyrrole (PPY) were prepared by Matrix-Assisted Pulsed Laser Evaporation (MAPLE) technology from two matrices: water and dimethylsulfoxide (DMSO). The deposition was carried out using a KrF excimer laser (laser fluence F ranged from 0.1 to 0.6 J cm⁻²). This work deals with optimization of two deposition parameters – laser fluence and number of pulses – for both matrices. From the deposition curves, the fluence thresholds, F_{th} , and maximum growth rates were subsequently determined (water matrix: F_{th} ~0.40–0.45 J cm⁻², maximum growth rate 0.16 nm pulse⁻¹; DMSO matrix: F_{th} ~0.25–0.30 J cm⁻²; maximum growth rate 0.20 nm pulse⁻¹). The changes in chemical composition of deposited layers were studied by Attenuated Total Reflection Fourier Transform Infrared spectroscopy. Surface morphology was characterized by Atomic Force Microscopy. A discussion is also presented concerning relationships between laser fluence and chemical composition of deposited layers with respect to their potential application in gas sensors. Finally, the response of a sensor with a MAPLE deposited PPY active layer to air humidity is presented.

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1. Introduction

The doped polypyrrole (PPY) combines the flexibility of the chemical composition of organic substances with the possibility to influence the physical properties of a thin layer of material, typical for inorganic semiconductors. In general, there are two conditions that are necessary for the application of PPY in sensors: a) the increase of the “basic” conductivity of this material by the oxidation of the neutral polymer backbone (associated with the formation of positively charged centers – polarons), together with the introduction of a proper counter-anion called a dopant; and b) the ability of PPY to change electric conductivity during the sorption and/or desorption of the gas molecules on its surface.

The latter property of PPY is attributed to the following mechanisms [1]: (i) interaction of gas molecules with charge carriers (polarons) in the polymer backbone affecting the charge carriers' mobility in the system of conjugated double bonds; (ii) changing barrier height for hopping of charge carriers between distinct backbones (especially in the presence of gases with high dipole moments); (iii) interaction of detected gas with dopant counter-anions.

The physical properties of polypyrrolic materials (density, viscosity) that are important from the standpoint of deposition technology, together with the structural properties (layer porosity) desirable for the given application, can be tailored by the formation of composite of PPY with a dielectric polymer (e.g. polymethyl methacrylate).

Preparation and characterization of doped PPY and its composites are described in many works, e.g. [2–9]. They probe optimal properties of PPY material suitable for application in chemical gas sensors [2–7] and biosensors [8,9]. Chemical gas sensors are simple devices for detection of various gases and vapors in the atmosphere (work-place safety and automation in industry, monitoring of air pollutants in environment). Chemical gas sensors have advantages over other gas analyzers (e.g. gas chromatographs, spectrophotometers) – small size, portability, low cost, and low power consumption. Their active layers can be relatively easily prepared using suitable deposition method.

The depositions of PPY layers are carried out using several methods. The selection of the deposition method has a fundamental influence on both the physical and structural properties of the prepared layer (resistivity, thickness, morphology and porosity, and adhesion to substrate). The widely used conventional deposition methods are spin coating and dip coating [10]. They are both “non-destructive” (chemical decomposition of deposited PPY does not take place), cheap and fast. However, spin coating and dip coating are not suitable for “sandwich” layer fabrication, and simple control of layer

* Corresponding author.

E-mail address: kopeckyd@vscht.cz (D. Kopecký).

thickness is complicated. In addition, the source solution has to have suitable viscosity and wettability, necessitating the use of plasticizers [11], which are mostly toxic.

This study focuses on the investigation of both the chemical changes and the structure of PPY layers using an improved deposition method, Matrix-Assisted Pulsed Laser Evaporation (MAPLE).

The MAPLE technology [12–15] is a laser deposition method providing gentle mechanism for organic layer deposition. In MAPLE, a frozen phase consisting of a dilute solution of a high-molecular-weight compound (basic material) in a low-molecular-weight solvent (matrix) is used as the laser target. The matrix should fulfill certain criteria: a) it should dissolve basic material; b) it should not react with the basic material; c) it should strongly absorb the radiation of the laser employed, and d) it should have sufficient volatility. Deposition takes place after the impact of a laser pulse with the surface of the frozen target. In an optimal case, the energy of the laser pulse is completely absorbed by the matrix, resulting in a strong local increase of temperature. The matrix molecules transfer their kinetic energy of thermal motion to the molecules of basic material. Hence the molecules of basic material are transferred to the substrate “mechanically”, with neither photolytic nor pyrolytic damage.

The advantages of MAPLE in comparison with conventional methods can be summarized as follows: (a) The thickness of the prepared layers can be simply controlled by setting laser fluence and number of pulses. Thus, reproducible preparation of thin layers having thicknesses of the order of tens of nanometers is possible. (b) The prepared layers are porous (i.e. they have a high surface/volume ratio), so they are suitable for sensor applications. (c) “Sandwich” structures can be fabricated in situ in one step by changing targets during the deposition. (d) The effect of the laser pulse is strongly limited in time and localized in space, hence there is a possibility to create various patterns by Matrix-Assisted Pulsed Laser Evaporation – Direct Write method [16].

2. Experimental details

2.1. Preparation of thin layers by the MAPLE method

The source target for MAPLE was prepared from 5 wt.% water solution of polypyrrole ($M_w = 10\,000$) doped with dodecyl sulfonic acid – specific electrical conductivity of the solution: $\sigma = 10\text{--}40\text{ S cm}^{-1}$ (Sigma Aldrich). In the second case, the water matrix was substituted by dimethylsulfoxide (DMSO) (Sigma Aldrich, purity >99.5%) in order to study the effect of the matrix on the polypyrrole layers' growth. The substitution of the solvents was carried out by water evaporation from the original water solution at 70 °C and subsequent transfer of the obtained solid phase into DMSO. The Fourier Transform Infrared (FTIR) spectra did not show any change for the chemical composition of the PPY in the DMSO solution that was prepared. Both PPY solutions were stirred and homogenized by an ultrasonic device. Subsequently, these solutions were frozen to -196 °C in the tubular mould using liquid nitrogen.

The prepared target was inserted into the deposition chamber and placed on the rotating shaft of the target holder. Uniform ablation of the material from the target surface was achieved by constant rotation during the deposition. The holder was simultaneously cooled by liquid nitrogen throughout the deposition. The deposition chamber was evacuated by a turbomolecular pump to a residual pressure of $5 \cdot 10^{-3}\text{ Pa}$. The pressure in the chamber did not exceed 3 Pa during the deposition process (a background gas was not used).

The depositions were carried out using a KrF excimer laser (LUMONICS) emitting at 248 nm. The laser was used in a pulse mode with a 10-Hz repetition rate. The fluence F of the laser radiation was set by an attenuator in the range of 0.1 J cm^{-2} to 0.6 J cm^{-2} . The laser spot was adjusted to the size of $8 \times 25\text{ mm}$. Variable deposition parameters were the number of laser pulses and laser fluence.

Two alumina sensor substrates were placed parallel to the target surface at a distance of 30 mm. The substrates are equipped with Pt sensing electrodes in the interdigital arrangement on one side and Pt-heating meander on the other side. The distance between “combs” of sensing electrodes was $45\text{ }\mu\text{m}$ and the area between them was 0.8 mm^2 . A polished silicon wafer was placed next to the sensor substrates for thickness measurements. Both FTIR spectra and surface morphology were measured on this wafer. The substrate holder was rotated throughout the deposition so that a uniform layer thickness was achieved.

2.2. Measurement of layer thicknesses, FTIR spectra, and study of the surface morphology

Chemical composition of the layers was analyzed from the IR spectra scanned by the Attenuated Total Reflection Fourier Transform Infrared spectroscopy. Spectra of all samples were scanned using a BRUKER IFS 66 V device (germanium crystal) in the intervals of wavenumbers ranging from 400 cm^{-1} to 4000 cm^{-1} , with a 4 cm^{-1} step.

The following samples were measured: a) The powder obtained by evaporating the solvent from the original water- or DMSO-solution of PPY. b) The samples of PPY subjected to repeated freezing by liquid nitrogen and subsequent melting. This process takes place during preparation of targets. c) The material of the thin deposited layers. In all these samples, a)–c), the amount of residual water or DMSO were checked by comparison of the measured spectra with those of the solvents.

Thickness of the layers prepared on the silicon wafer was measured using an Alfa-step profilometer. The zero level for the thickness measurement was the polished silicon surface.

The surface morphology of the layers on the silicon wafer was acquired using Atomic Force Microscopy (AFM). The AFM images were taken under ambient conditions on a Digital Instruments CP II apparatus. For sample characterization, ‘Tapping mode’ rather than ‘Contact mode’ was chosen to minimize damage to the sample surfaces. A Veeco oxide-sharpened silicon probe RTESPA-CP attached to a flexible microcantilever was used at its resonant frequency of 300 kHz. The scans were acquired in air at a rate of 1 Hz. The image resolution was 256×256 pixels. The dimensions of the AFM scanned area ($5 \times 5\text{ }\mu\text{m}$) were selected so as to be representative enough, as they are greater than the dimensions of a typical surface roughness by one order of magnitude.

3. Results and discussion

3.1. Parameters of deposited layers

Deposition by MAPLE technology is a rather complicated process with many adjustable parameters. The most significant of them are: laser fluence, number of laser pulses, working pressure in the deposition chamber, target–substrate distance, temperature of frozen target, and laser spot area. Another important parameter is the target composition; the absorbance of the matrix at the excimer laser wavelength used. Therefore, the deposition process has many degrees of freedom.

Table 1 shows an overview of the deposited samples and their variable parameters – the matrix used for target preparation, laser fluence, and number of laser pulses. The other deposition parameters mentioned in the previous paragraph were kept constant. Table 1 also includes deposition results – thickness and growth rates of layers.

In order to obtain layers with approximately uniform thicknesses, we took into account results of our previous experiments with similar materials [17,18]. Hence laser fluence and number of laser pulses were set in order to reach layer thicknesses close to $1\text{ }\mu\text{m}$. This is necessary to compare layer morphology with detection properties.

Growth rate was calculated as the ratio of layer thickness to number of pulses. All the depositions mentioned in Table 1 were

Table 1
Overview of deposited samples and their parameters

Sample no.	Solvent	Laser fluence (J·cm ⁻²)	No. of pulses (× 10 ³)	Thickness (nm)	Growth rate (nm·pulse ⁻¹)
W-1	H ₂ O	0.1	50	580	0.012
W-2	H ₂ O	0.2	40	560	0.014
W-3	H ₂ O	0.3	30	760	0.025
W-4	H ₂ O	0.4	15	630	0.042
W-5	H ₂ O	0.5	10	1580	0.158
W-6	H ₂ O	0.6	5	780	0.156
D-1	DMSO	0.1	30	1170	0.039
D-2	DMSO	0.2	20	1260	0.063
D-3	DMSO	0.3	13	1800	0.138
D-4	DMSO	0.4	5	960	0.192
D-5	DMSO	0.5	3	610	0.203

carried out using thousands of pulses, so the growth rate represents a mean value, which is important from the technological point of view when depositing active layers of gas sensors.

3.2. Growth rate and determination of fluence threshold

The results presented in Fig. 1 confirm that the so-called “deposition curve”, i.e. dependence of growth rate on laser fluence has the typical “lazy S”-shaped form. This behavior is similar to effects observed during ablation of polymers by UV laser [19] and includes information concerning the fluence threshold F_{th} . The methodology of fluence threshold evaluation was described in previous work [18]. Determination of fluence threshold is important for subsequent preparation of chemical gas sensors. This threshold represents the optimal value of laser fluence where layer growth is sufficiently fast while the deposited material is not subjected to excessive thermal stress.

Evaluation of the deposition curves in Fig. 1 shows the existence of the fluence threshold F_{th} in the range 0.40–0.45 J cm⁻² for the H₂O matrix and in the range 0.25–0.30 J cm⁻² for the DMSO matrix.

It is apparent that the growth rates of layers prepared from the DMSO matrix are 1.4–5 times higher than the growth rates of layers prepared from the H₂O matrix. These results are in accordance with the actual different absorption coefficients α of both matrices ($\alpha_{H_2O}=0.030$ cm⁻¹ and $\alpha_{DMSO}=3.912$ cm⁻¹ at 248 nm). The spectra of water and DMSO in UV region are also discussed in [20]. Higher growth rate of PPY prepared from the DMSO matrix correspond to higher absorption coefficient of DMSO at 248 nm.

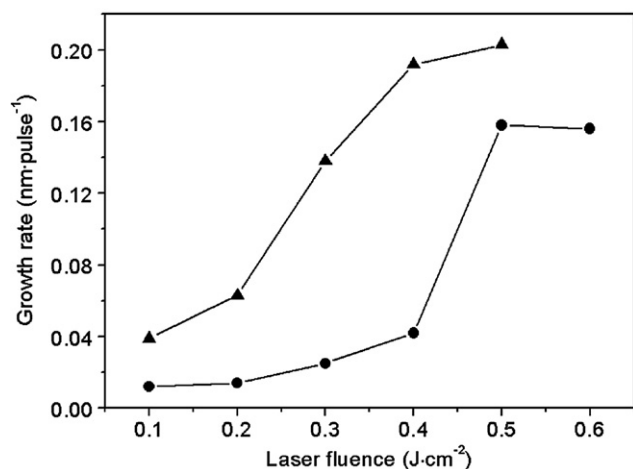


Fig. 1. Deposition rate as a function of laser fluence for sample prepared from H₂O (●) and DMSO (▲).

3.3. FTIR spectroscopy of basic material and deposited layers

Pure PPY has characteristic absorption bands [21,22] at wavenumbers 1549 cm⁻¹ and 1472 cm⁻¹ (stretching vibration of pyrrolic ring), 1302 cm⁻¹ (stretching vibration of C–N bond), 1225 cm⁻¹ (nonplanar deformation vibration of pyrrolic ring), 1094 cm⁻¹ (planar vibration N⁺–H), 965 cm⁻¹ (out-of-plane vibration C–C), 899 cm⁻¹ (out-of-plane vibration C_β–H), 784 cm⁻¹ (deformation vibration of pyrrolic ring), and 678 cm⁻¹ (out-of-plane deformational vibration C–C).

The presence of dopants causes a shift of characteristic PPY bands to higher or lower values. Simultaneously, the characteristic bands of dopants appear in such case.

The spectra of PPY obtained from original (Sigma Aldrich) – Fig. 2a – and frozen solution – Fig. 2b – show bands at wavenumbers 1560 cm⁻¹, 1490 cm⁻¹, 1225 cm⁻¹, 1128 cm⁻¹, 1036 cm⁻¹, 969 cm⁻¹, and 676 cm⁻¹. As both these spectra are similar, it can be assumed that the structure of PPY was not damaged due to solvent exchange, chemical reaction with solvent, or freezing to –196 °C.

There is a separate band in both these spectra (Fig. 2a,b) occurring at wavenumber 1710 cm⁻¹. This indicates the presence of carbonyl group C=O on β -carbons of pyrrolic ring. This group arises from the oxidation of PPY chains by atmospheric oxygen and/or oxygen incorporated in PPY chains as the dopant. This PPY chain oxidation and its mechanism were previously described [21,22] and cannot be avoided under normal conditions. It was found, however, that in the spectra of all our samples, the intensity of the 1710 cm⁻¹ band in relation to the intensities of the other PPY characteristic bands does not change significantly. Hence, it can be concluded that the degree of PPY oxidation in normal atmosphere remains constant.

Fig. 2c presents spectra of PPY deposited from H₂O and Fig. 2d PPY deposited from DMSO matrix. The depositions were carried out at an energy density of 0.4 J cm⁻² in cases c–d. There are significant differences among these spectra, especially in the range of

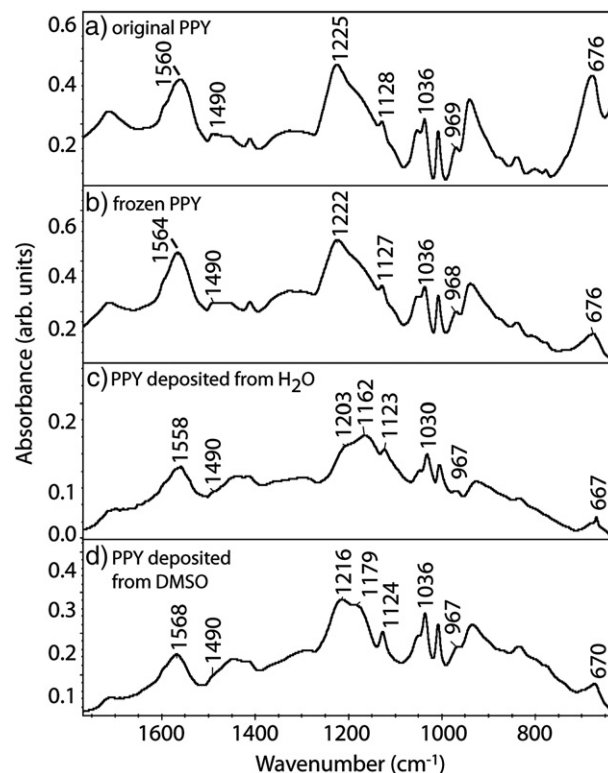


Fig. 2. FTIR spectra of (a) original PPY; (b) frozen PPY; (c) PPY deposited from H₂O at 0.4 J cm⁻²; (d) PPY deposited from DMSO at 0.4 J cm⁻².

wavenumbers from 1230 to 1160 cm^{-1} . A broad spectral feature containing series of overlapping bands is observed in this region. The above-mentioned band at 1225 cm^{-1} is attributed to a nonplanar deformation mode of pyrrolic cycle [21,22]. According to [23], there are characteristic bands in this region which can be assigned to population of two types of charge carriers in the polymer backbone: polarons (1227 cm^{-1} and 1196 cm^{-1}) and bipolarons (1165 cm^{-1}). Furthermore, the band positions of the vibrational modes of both polarons and bipolarons depend on PPY conductivity; particularly, the band corresponding to bipolarons shifts strongly in dependence on PPY conductivity from 1186 cm^{-1} (less conductive) to 1165 cm^{-1} (more conductive material) [24]. Hence, the resulting appearance of the region from 1230 to 1160 cm^{-1} is strongly affected both by changes of intensity ratios of all the above-mentioned bands and by shifts of bands, namely those corresponding to bipolarons.

The shift of bands corresponding to vibration of C=C double bonds in pyrrolic cycle of PPY deposited from H_2O and from DMSO is depicted in Fig. 3a and b, respectively. The isolated C=C bond creates a band in the vicinity of 1600 cm^{-1} . It is known that this band shifts to 1560 cm^{-1} with an increasing degree of conjugation. This is apparent in original PPY (Fig. 2a), where the strong band is present directly at 1560 cm^{-1} . The presence of non-reduced form with high degree of conjugation is crucial for high electrical conductivity of PPY and hence its “detection capability”. Fig. 3a proves that when deposition is made from a H_2O matrix, increasing laser fluence leads to a shift of C=C vibration toward lower wavenumbers. On the contrary, during deposition from DMSO matrix (Fig. 3b), this band stays almost unchanged at 1560 cm^{-1} .

It can be concluded from Figs. 2 and 3 that PPY is damaged when deposited from a H_2O matrix, as increasing isolation of C=C bonds signifies decomposition of the pyrrolic ring. On the other hand, in the case of DMSO matrix, the pyrrolic ring is not damaged by laser radiation.

The trend of stronger decomposition of the pyrrolic ring with decreasing values of laser fluence in samples deposited from H_2O was

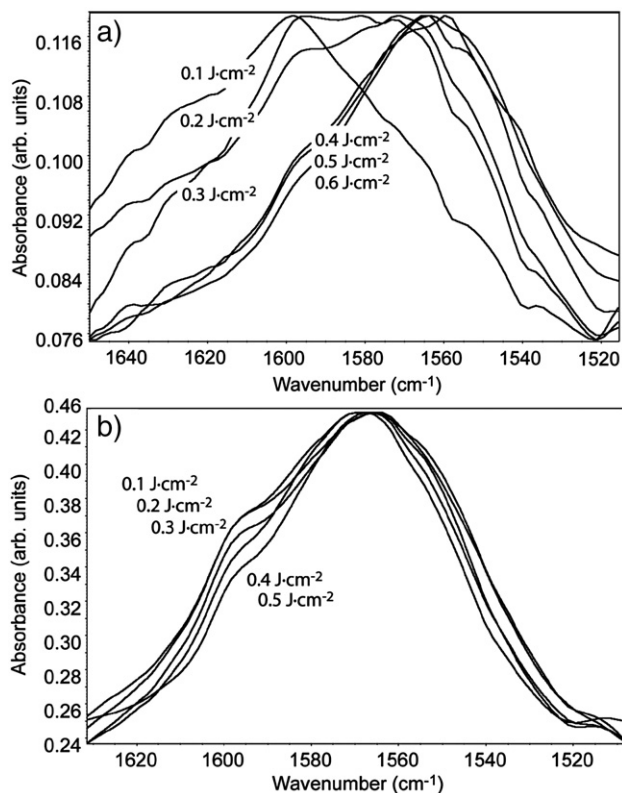


Fig. 3. FTIR spectra in the 1500–1670 cm^{-1} of PPY deposited from (a) H_2O and (b) DMSO as a function of laser fluence.

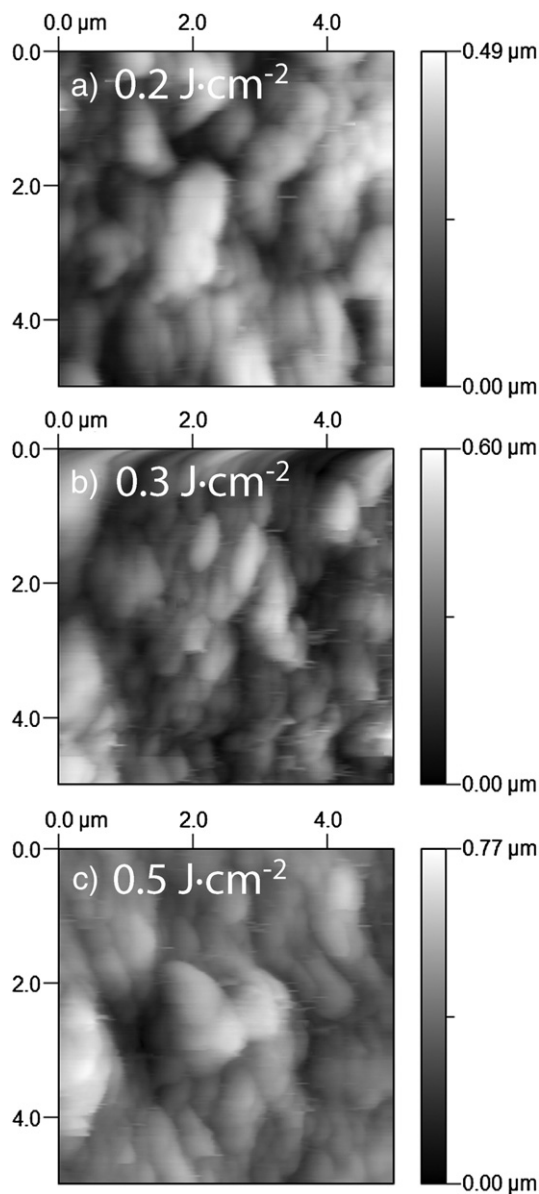


Fig. 4. AFM images of PPY samples deposited from H_2O at laser fluence of (a) 0.2, (b) 0.3 and (c) 0.5 $\text{J}\cdot\text{cm}^{-2}$.

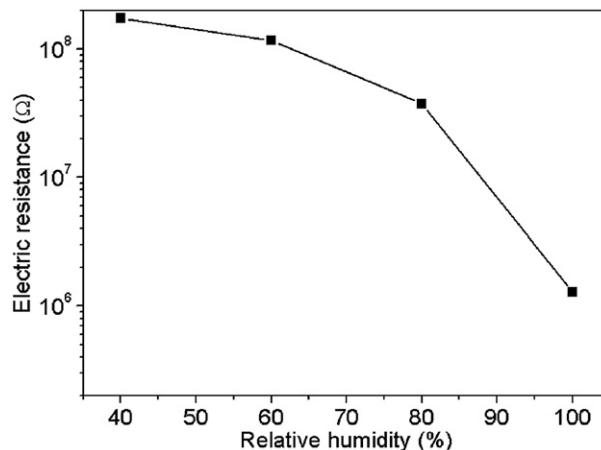


Fig. 5. Electrical resistance of MAPLE deposited PPY sensor (deposition from water matrix; $F=0.5 \text{ J}\cdot\text{cm}^{-2}$). The measurement was carried out in “pure” synthetic air with variable relative humidity at constant sensor temperature $t=25^\circ\text{C}$.

not expected. Explanation for this effect can be attributed to the combination of slow material ablation during the deposition and the relatively low absorption coefficient of the matrix (resulting in a higher penetration depth of radiation). Under these circumstances, the target material remains under the influence of laser radiation for a longer time than in the case of the layers deposited from DMSO.

3.4. Morphology of the deposited layers

The morphology of the deposited layers was studied by AFM. Fig. 4 shows examples of layers deposited from the water matrix with laser fluences of 0.2–0.5 J cm⁻². The z-axis values represent the roughness of the layer surface expressed as the difference between minimum and maximum thickness of the deposited layer (area 5×5 μm). It is apparent from Fig. 4 that the layers deposited at lower values of laser fluence have in general smaller surface roughness. At the same time, these layers are built from smaller particles and therefore they are more segmented.

A similar trend was observed for layers deposited from DMSO matrix, i.e. the lower laser fluence, the smaller surface roughness.

This trend can be explained as follows: a laser beam with high fluence causes local overheating of the matrix on the laser spot. Hence, the subsequent release of material has the character of an explosion, which is associated with the rough craters on the target surface produced during this process. The ablated material is expelled in larger particles and creates a layer with a greater dispersion of minimum and maximum values of layer thickness. Material, which is ablated by smaller laser fluence, is carried away gently (in smaller particles), which manifests itself as a smooth abrasion of the target. Consequently, the layer that is produced is composed of smaller particles, and it is also less rough.

Gas sensors require porous (in order to achieve compromise between two contradictory requirements: high sensor sensitivity and short response time) material with high segmentation. This requirement can be fulfilled by depositing at lower laser fluences. Simultaneously, as it was stated in Section 3.3, low fluence leads to degradation of the deposited PPY when deposition of the layer is from a water matrix. This is the reason why the deposition of active layers of sensors at a laser fluence in the vicinity of the fluence threshold, F_{th} , is optimal.

3.5. Sensing properties of deposited PPY

A thin layer of PPY was deposited (water matrix; laser fluence $F = 0.5$ J cm⁻²; thickness of resulting layer ~300 nm) onto the sensor substrate described in Section 2.1 in order to measure the change in electrical resistance at various humidities in the surrounding atmosphere. The results of these measurements are presented in Fig. 5. The sensor resistance in dry synthetic air is immeasurably high. It strongly decreases with increasing content of water vapor in the atmosphere. Such character of *sensor resistance vs. humidity* dependence was found to be typical for PPY sensors [1].

4. Conclusions

The depositions of PPY by MAPLE presented in this work are early attempts of this kind. Polypyrrole layers have been deposited by various technologies, but the influence of laser radiation and laser deposition conditions on chemical composition of PPY has not been investigated systematically till now.

One of the important deposition parameters is the selection of the matrix. The results of the presented work show that in general both DMSO and water matrices are applicable for deposition of thin layers of polypyrrole. The samples deposited from the water matrix have characteristic changes in FTIR spectra, especially at wavenumbers 1560 cm⁻¹ (degree of conjugation of double bonds) and in the region

from 1230 to 1160 cm⁻¹ (non-planar deformation mode of pyrrolic ring; type and population of charge carriers in PPY backbone). These changes correspond to partial breaking of the pyrrolic cycle and hence degradation of PPY. When the layer is deposited from the water matrix, the intensity of interaction between laser radiation and deposited PPY is higher. Thus DMSO is a better matrix than water — based on FTIR spectra of deposited layers and also higher growth rates of layers deposited from DMSO.

The fluence threshold, F_{th} , ranged from 0.40 to 0.45 J cm⁻² for layers deposited from a water matrix, and 0.25–0.30 J cm⁻² for layers deposited from DMSO. The higher growth rates and lower fluence thresholds achieved for DMSO matrices are explained by the higher absorption coefficient of DMSO at a laser wavelength of 248 nm. In general, it is desirable to carry out depositions at laser fluences close to F_{th} . This range is a compromise between the necessity for sufficiently high growth rate on one side and the risk of material damage by excessive irradiation on the other side.

The results of AFM analysis of thin layers prepared confirm that surface roughness and granularity of the layer are correlated with applied laser fluence. These relations can be explained by the existence of different mechanisms of material transfer at different laser fluences. From the point of sensor applications (i.e. requirement of sufficiently high porosity and segmentation of produced layers), it can be concluded that optimal laser fluences are close to F_{th} .

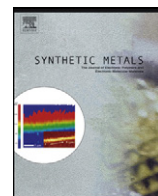
Finally, we can conclude that PPY is a promising material for depositions of active layers of sensors by MAPLE. Investigation of parameters of these sensors and their response to various gases and vapors will be the theme of further work.

Acknowledgement

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Doped polypyrrole for MAPLE deposition: Synthesis and characterization

Dušan Kopecký^a, Martin Vršata^{a,*}, Filip Vysloužil^a, Přemysl Fitl^a, Ondřej Ekrt^a, Jaromír Seidl^a, Vladimír Myslík^b, Jaroslav Hofmann^a, Josef Náhlík^b, Jan Vlček^a, Lukáš Kučera^a

^a Institute of Chemical Technology Prague, Department of Physics and Measurements, Technická 5, Praha 6, 166 28 Czech Republic

^b Institute of Chemical Technology Prague, Department of Solid State Engineering, Technická 5, Praha 6, 166 28 Czech Republic

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ABSTRACT

The contribution deals with synthesis and characterization of conductive polypyrrole (PPY), which should be suitable for depositions of thin layers by Matrix Assisted Pulsed Laser Evaporation (MAPLE) method. The samples of doped PPY containing various organic dopants – (i) p-toluenesulfonic acid, (ii) dodecylbenzenesulfonic acid, (iii) dioctyl-sulfosuccinic acid and (iv) camphorsulfonic acid – were synthesized by polymerization of pyrrole in acidic or neutral solution. Solubility of synthesized PPY and settlement time of PPY particles in water and dimethylsulfoxide – parameters critical for MAPLE method – were investigated. The composition of prepared PPY was verified by FTIR spectroscopy. Conductivity of the polymer in solid state was determined to be in range from $\sigma = 2.6 \times 10^{-6} \text{ S cm}^{-1}$ to $\sigma = 6.0 \times 10^{-2} \text{ S cm}^{-1}$. The optimal material for MAPLE deposition is PPY containing organic dopants (ii)–(iv), dissolved in DMSO matrix (solubility from 4.1% to 6.5% by weight and settlement time 140–240 h).

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1. Introduction

The MAPLE technology [1–4] is a laser deposition method providing gentle mechanism for organic layers deposition. By MAPLE, a frozen phase consisting of a dilute solution of a high-molecular-weight compound (basic material) in a low-molecular-weight solvent (matrix) is used as the laser target. Deposition takes place in a vacuum after impact of a laser pulse with the surface of the frozen target. In an optimal case, the energy of the laser pulse is completely absorbed by the matrix, resulting in a strong local increase of temperature. The matrix molecules transfer their kinetic energy of thermal motion to the molecules of basic material. Hence the molecules of basic material are “mechanically” ejected to vapour phase and subsequently collected on the substrate with neither photolytic nor pyrolytic damage, while small molecules of the matrix are evacuated with a pump.

The advantages of MAPLE in comparison with conventional deposition methods (deposition from aerosol, spin-coating and dip-coating) can be summarized as follows:

- The thickness of prepared layers can be simply controlled by setting laser fluence and number of pulses. Thus, reproducible preparation of thin layers having thicknesses on the order of tens of nanometers is possible.

- The prepared layers are porous (i.e. they have a high surface/volume ratio), which can be advantageous for sensor applications.
- “Sandwich” structures can be fabricated in situ in one step by changing targets during the deposition.
- The effect of the laser pulse is strongly limited in time and localized in space.

Since its development at the end of nineties, the MAPLE technology was applied for depositions of variety of organic compounds, starting from small molecules (acetyl-acetonates, phthalocyanines [5] or glucose) and continuing to polymers (polyethylene glycol [6] or fluoroalcoholpolysiloxane) or even enzymes (lysozyme [7]).

The only reference concerning MAPLE deposition of PPY is [8]. This study gives an overview of possibilities of deposition various organic materials by MAPLE technology. Polypyrrole was deposited from the target containing a 0.96 wt.% deionized water solution of doped PPY (Aldrich). The deposition was performed with ArF excimer laser operating at 193 nm using a laser fluence of 0.19 J cm^{-2} . The MAPLE deposited films exhibited conductivity $\sigma = 0.6 \text{ S cm}^{-1}$. However, the composition of dopants is not declared for the commercially distributed polypyrrole, so these results can provide only rough orientation.

Based on the mechanism of MAPLE deposition, it is possible to determine basic property of the synthesized PPY that is necessary for its applicability in MAPLE technology.

PPY for depositions should be soluble in (or at least miscible [9] with) matrix, i.e. liquid possessing high absorption coefficients on wavelengths of laser radiation used in MAPLE. These wavelengths

* Corresponding author. Tel.: +420 605290285.

E-mail address: martin.vrsata@vscht.cz (M. Vršata).

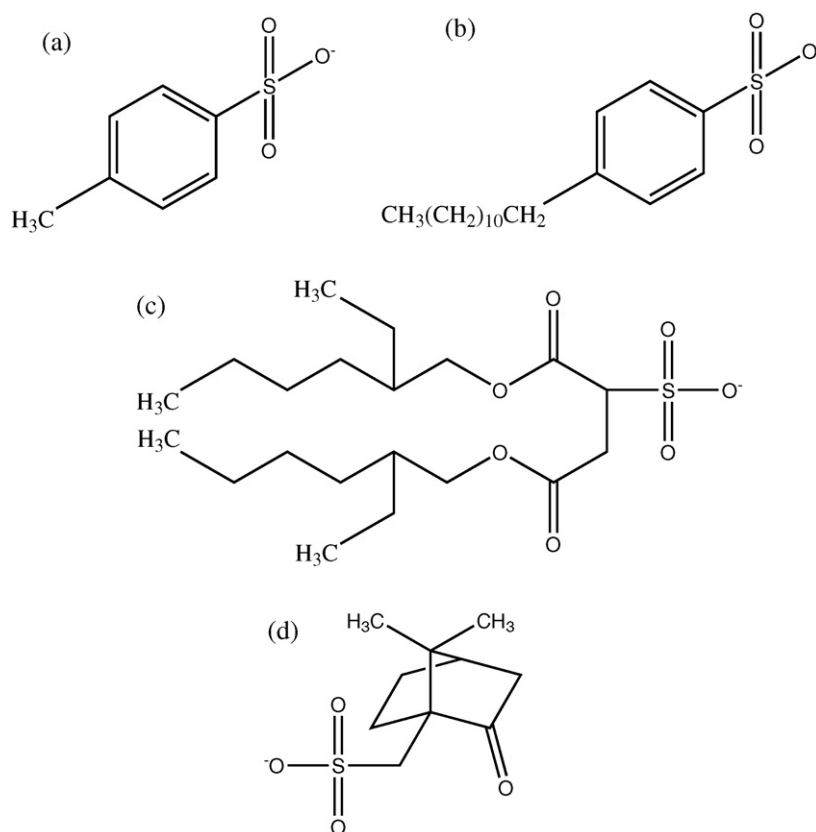


Fig. 1. Organic dopants in synthesized PPY: (a) p-toluenesulfonic acid (p-TSA); (b) dodecyl-benzenesulfonic acid (DBSA); (c) dioctyl-sulfosuccinic acid (DEHS) and (d) camphorsulfonic acid (CAMP).

are, for example, 248 nm (KrF excimer laser) or 266 nm (the fourth harmonic of Nd:YAG laser). Dimethylsulfoxide (DMSO) is a representative of such matrices previously investigated by our group [10]. The condition of solubility of prepared PPY is crucial and simultaneously difficult to fulfil, as the solubility of PPY in various liquids is low in general. Poor solubility of PPY in common organic solvents is explained by the presence of strong interchain interactions [11]. A promising approach, how to overcome this problem, was suggested in [12]. Solubility of PPY in various solvents (from weakly polar chloroform to polar DMSO or water) can be increased by using “detergent-type” dopant, whose molecules contain both relatively long, non-polar alkyl chains and strongly polar (e.g. sulfonic) group.

The occurrence of dopants in PPY (even at higher concentrations) does not affect the suitability of this material for MAPLE technology provided that the absorption coefficients of both PPY and dopants are lower than that of the matrix.

Thin layers of PPY are commonly used as anti-static coatings, electromagnetic shielding [13] and above all as active layers of chemical sensors [14]. So electric properties and namely conductivity of prepared polymer are of cardinal importance.

FTIR spectroscopy is a powerful tool for characterizing chemical composition of both synthesized- and MAPLE deposited-PPY. Amongst much information obtainable from FTIR spectra of the polymer we will focus attention to: degradation of PPY by oxidation (resulting to presence of carbonyl group on β -carbon of pyrrolic ring); observation the degree of conjugation of double bonds in PPY chain; monitoring the incorporation of dopants in the polymer. These parameters are certain measure of “quality” of both synthesized and deposited polymer. They can also be related to previously measured conductivity.

Hence the presented study is aimed to synthesis of PPY containing various inorganic and organic dopants, investigation of miscibility or solubility of this PPY in DMSO (proper matrix for MAPLE) and water (native solution), measurement of conductivity and analysis of FTIR spectra of the prepared polymer.

2. Experimental

2.1. Synthesis

For the synthesis of doped PPY following chemicals were used: (a) pyrrole as a monomer; (b) iron(III) chloride anhydrous or ammonium persulfate (APS) as oxidizing agents and (c) p-toluenesulfonic acid (p-TSA), sodium salt of p-toluenesulfonic acid $\text{Na}^+(\text{p-TSA})^-$ – Fig. 1a, dodecyl-benzenesulfonic acid (DBSA) – Fig. 1b, sodium salt of dioctyl-sulfosuccinate $\text{Na}^+(\text{DEHS})^-$ – Fig. 1c or camphorsulfonic acid (CAMP) – Fig. 1d as doping agents. All of these chemicals were reagent grade (Sigma–Aldrich).

The polymerization was carried out either in acidic (p-TSA, DBSA and CAMP) or neutral solution ($\text{Na}^+(\text{p-TSA})^-$ and $\text{Na}^+(\text{DEHS})^-$). An overview of synthesized materials is summarized in Table 1. Typical molar ratio of *pyrrole:oxidizing agent:doping agent* (when present) was 5:10:1, which means the polymerization proceeds in excess of oxidizing agent.

For example, synthesis S3 in Table 1 proceeds as follows: firstly 0.05 mol of pyrrole and 0.01 mol of (p-TSA) were added to 100 ml of distilled water at 0 °C. This mixture continuously cooled was stirred for 20 min until pyrrole and p-TSA completely dissolved. The solution of 0.1 mol of iron(III) chloride in 200 ml of distilled water (0 °C) was prepared separately. Then both the above mentioned solutions were mixed together. The polymerization started immediately (for-

Table 1

Overview of synthesized PPY materials. The SO_4^{2-} and Cl^- dopants are residuals of APS and FeCl_3 respectively.

Synthesis no.	Oxidizing agent	Doping agent	Dopants awaited in product
S1	APS	–	SO_4^{2-}
S2	FeCl_3	–	Cl^-
S3	FeCl_3	p-TSA	Anion p-TSA, Cl^-
S4	FeCl_3	$\text{Na}^+(\text{p-TSA})^-$	Anion p-TSA, Cl^-
S5	FeCl_3	DBSA	Anion DBSA, Cl^-
S6	FeCl_3	$\text{Na}^+(\text{DEHS})^-$	Anion DEHS, Cl^-
S7	FeCl_3	CAMP	Anion CAMP, Cl^-
S8	APS	p-TSA	Anion p-TSA, SO_4^{2-}
S9	APS	$\text{Na}^+(\text{p-TSA})^-$	Anion p-TSA, SO_4^{2-}
S10	APS	DBSA	Anion DBSA, SO_4^{2-}
S11	APS	$\text{Na}^+(\text{DEHS})^-$	Anion DEHS, SO_4^{2-}
S12	APS	CAMP	Anion CAMP, SO_4^{2-}

mation of a characteristic precipitate). After 2 h the precipitate of doped PPY was filtered in Buchner funnel, washed with distilled water and finally dried in a vacuum drier at 75 °C for 2 h.

2.2. Measurement of conductivity, solubility and chemical composition of doped PPY

The dried PPY was comminuted in mortar to a homogeneous powder and then formed in hydraulic press to tablets (12 mm in diameter, 3 mm thick). As the conductivity of the material is partially dependent on applied pressure, it was necessary to prepare all tablets at the constant pressure of 66 MPa. Gold electrodes were vaporized onto opposite faces of the tablet. Resistance of prepared samples was measured with Agilent 34401A multimeter by two-electrode method (constant applied potential of 500 mV). The measurement of resistance was carried out at temperature of 22 °C in dry synthetic air. Conductivity (σ) of doped PPY was calculated from the value of resistance and dimensions of a given tablet.

The solubility of synthesized PPY in water and DMSO was investigated as follows: 30 ml of a given solvent was transferred to a beaker, and then powder of synthesized PPY was added in small portions until gel was formed on the bottom of a beaker. The occurrence of gel is attributed to cross-linking of dispersed polymer particles. After formation of gel the solution was homogenized by sonification for 30 min and allowed to stay. Five millilitres of the solution from the upper part was then placed to crystallizing dish and dried in a vacuum drier at 75 °C. Then the weight of evaporation residue was determined.

Chemical composition of doped PPY was analyzed from the IR spectra scanned by the Attenuated Total Reflection Fourier Transform Infrared spectroscopy. Spectra of all samples were scanned using a BRUKER IFS 66 V device (diamond crystal) in the intervals of wave numbers from 600 to 1800 cm^{-1} (it covers finger-print of PPY molecule).

3. Results and discussion

3.1. Solubility of prepared PPY in water and DMSO

As discussed earlier, the necessary condition for applicability of MAPLE technology is miscibility of synthesized polymer with low-molecular-weight “solvent” (matrix) absorbing at the employed laser wavelength. In this contribution, solubility in binary systems PPY-DMSO and PPY-water was tested (Table 2). Dimethylsulfoxide is a common matrix for MAPLE depositions at laser wavelengths from 220 to 270 nm. Water is not a proper matrix [10], but all the syntheses of PPY (S1–S12) were carried out in water solution, so from the practical point of view it is important to have information concerning solubility in PPY-water system.

Table 2

Solubility of doped PPY in water and dimethylsulfoxide (in % by weight). The table includes only the samples classified as “miscible” or “soluble” (see the text). Solubility of all other samples was zero.

Synthesis no.	Dopants	Dimethylsulfoxide	Water
S5	Anion DBSA, Cl^-	5.2	5.5
S6	Anion DEHS, Cl^-	4.0	2.6
S10	Anion DBSA, SO_4^{2-}	5.1	5.4
S11	Anion DEHS, SO_4^{2-}	4.4	2.3
S12	Anion CAMP, SO_4^{2-}	6.5	1.8

There are three different situations observed when investigating solubility of synthesized PPY. (i) All the samples of PPY containing only inorganic dopants (Cl^- and SO_4^{2-}) and/or p-TSA anion were *non-miscible* with neither DMSO nor water at all. In these cases (samples S1–S4, S8 and S9) the precipitate particles of doped PPY settled spontaneously in a few seconds to the bottom of beaker. It seems that incorporation of inorganic or small organic (even polar, such as p-TSA) dopants cannot decrease interchain interactions in PPY and hence the synthesized polymer remains insoluble. Surprisingly, sample S7 (PPY oxidized by FeCl_3 with CAMP dopant) also falls to this category, unlike S12 (PPY oxidized by APS with CAMP dopant). (ii) In the cases S5, S6, S10 and S12, the prepared polymer was *miscible* with both DMSO and water; however it forms small micelles that can be filtered out by common filter paper. These systems have a character of dispersion. (iii) The sample marked as S11 – PPY containing DEHS and SO_4^{2-} anions – was *soluble* in both solvents and no precipitate remained on the filter paper. The behaviour of S11 is the closest to model of ideal solution. This is probably caused by the above mentioned “detergent effect”.

In general, when applying DBSA dopant, the solubility of synthesized PPY in water and DMSO is almost the same (samples S5 and S10), but on the contrary for DEHS and CAMP dopants we can observe significantly higher solubility in DMSO.

Another important parameter characterizing behaviour of PPY-DMSO and PPY-water binary systems is settlement time of PPY particles, summarized in Table 3. When leaving to stay, all the samples settle in the time range of 0.1–240 h and the liquid above the fine black sediment is almost clear. One can notice high values of settlement time for samples S10–S12 in DMSO, indicated smaller particles of PPY and hence better homogeneity of these systems. According to our opinion this is not only a consequence of organic dopant properties (i.e. polar, detergent-like), but is also caused by “synergetic” effect of combination of both used organic dopant and APS oxidizing agent (see Table 3, the third column).

3.2. Conductivity

Conductivity (σ) of doped PPY synthesized by reactions S1–S12 is summarized in Fig. 2. It ranges in about four orders from $\sigma = 2.6 \times 10^{-6} \text{ S cm}^{-1}$ (S11) to $\sigma = 6.0 \times 10^{-2} \text{ S cm}^{-1}$ (S5).

We can also observe that (to some extent) shorter time of polymerization leads to higher values of conductivity, but the stability of short-synthesis-time materials is poor. According to Fig. 2, several relationships between conductivity and parameters of synthesis can be found:

Table 3

Settlement time (hours) of PPY particles in dimethylsulfoxide and water.

Synthesis no.	Dopants	Dimethylsulfoxide	Water
S5	Anion DBSA, Cl^-	1	1
S6	Anion DEHS, Cl^-	12	0.1
S10	Anion DBSA, SO_4^{2-}	240	12
S11	Anion DEHS, SO_4^{2-}	140	1
S12	Anion CAMP, SO_4^{2-}	120	1

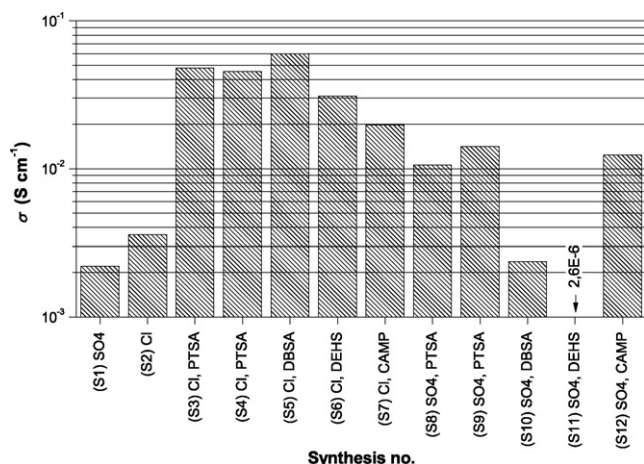


Fig. 2. Conductivity of doped PPY synthesized by reactions S1–S12.

- The values of σ (S1) and σ (S2) are significantly lower than σ values of most other samples (the exception is σ (S11), which will be explained later). The samples S1 and S2 contain only “small” inorganic dopants. On the contrary, the presence of “large” organic dopants (S3–S9) and S12 causes the conductivity to be in average of about one order of magnitude higher.
- As σ (S3) $\sim$ σ (S4) and simultaneously σ (S8) $\sim$ σ (S9), there is no significant difference between polymerization in the presence of p-TSA (acidic solution) or Na⁺(p-TSA)⁻ (neutral solution).
- It is also apparent that the samples prepared using FeCl₃ as an oxidizing agent have in general higher conductivity than those oxidized by APS.
- There is no simple relation between conductivity of samples containing organic dopants and complexity of organic dopant molecule.
- The synthesis S11 (oxidizing agent APS and doping agent DEHS) constitutes a special situation. Low value of σ (S11) is probably given not only by parameters of synthesis, but also by the method of obtaining PPY powder from the native aqueous solution. This doping agent acts as a highly effective detergent, so this is the only case when the as-prepared PPY cannot be filtered out. Elevation of temperature to above 40 °C leads to formation of foam, hence it was necessary to evaporate water at low temperature for a long period. Degradation of polymer connected with decrease of conductivity probably takes place during this process. On the other hand, PPY containing DEHS in water represents the system closest to ideal solution advantageous for deposition by MAPLE technology.

Generally, the conductivity results of our samples (except S11) correspond to values published in [12], where conductivity of the

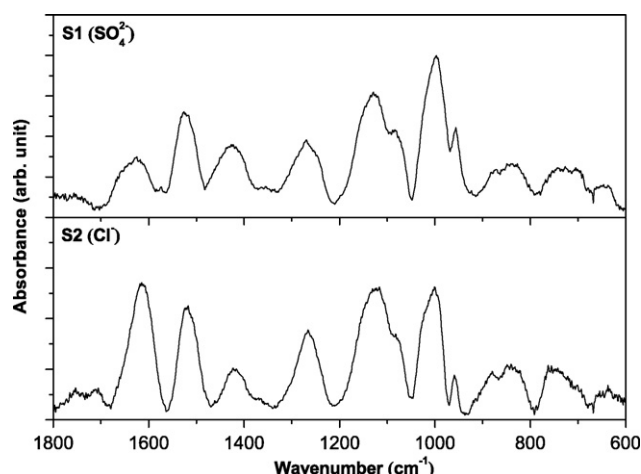


Fig. 3. FTIR spectra of samples S1 and S2 respectively (detailed view).

synthesized PPY in the solid state was reported to be in the range from 1×10^{-3} to 3×10^0 S cm⁻¹. Similar results were obtained also in [15]. In this case polypyrrole bearing sulfonic group doped with DEHS, i.e. PPY(SO₃H)⁻ DEHS has conductivity $\sigma = 5 \times 10^{-1}$ S cm⁻¹.

3.3. Chemical composition

The FTIR spectra of all samples were measured in order to verify chemical composition of the synthesized material and to consider incorporation of dopants into the polymer. The spectra were observed in an important region from 1800 to 600 cm⁻¹ (it covers finger-print of PPY molecule).

Fig. 3 displays the detailed spectra of PPY containing only small inorganic dopants (samples S1 and S2). It also depicts influence of type of oxidizing agent on the composition of resulting PPY. Both spectra are very similar. There is only one significant shift: the band, which appears at 1628 cm⁻¹ in the spectrum of S1 shifts to 1615 cm⁻¹ in the spectrum of S2. This shift is related to degree of conjugation of double bonds in polymer backbone and hence to its conductivity. Lower wave number corresponds to higher degree of conjugation and hence higher conductivity of S2 sample compared with that of S1 (Fig. 2).

Table 4 shows the characteristic bands of PPY and also includes the assignment of corresponding vibrations. There are also wave numbers of PPY characteristic bands measured by other research teams [16–18]. Our values are in good accordance with these values. The only shift is noticeable in wide bands of out of plane vibrations of PY circle, but these bands are flat and their maxima are fuzzy.

Fig. 4 presents an overview of FTIR spectra of the synthesized PPY samples (S1–S12). All these spectra contain the above men-

Table 4
The assignment of vibrations to bands in PPY spectra.

Identified bands		Bands identified by other groups			Vibrations according to Refs. [16–18]
S1 (SO ₄ ²⁻)	S2 (Cl ⁻)	[17] PPY(SO ₄ ²⁻)	[17] PPY(Cl ⁻)	[18] PPY	
1628	1615	1638	–	–	C–C, C=C stretching
1517	1518	1552	1540	1529	C–C, C=C stretching
1430	1428	1476	1459	1445	C=C, C–N stretching
1270	1266	1289	1308	1295	C–H, C–N in plane deformation
1124	1124	1197	1166	1210	Breathing vibration of the PY ring
1085	1085	1123	1094	1080	C–H, N–H in plane deformation
997	1001	1050	1050	1020	C–H in plane deformation
957	959	967	967	960	C–C out of plane deformation
838	840	920	915	930	C–H, N–H out of plane deformation
732	733	796	796	760	C–H, N–H out of plane deformation
646	648	678	678	660	C–C out of plane deformation

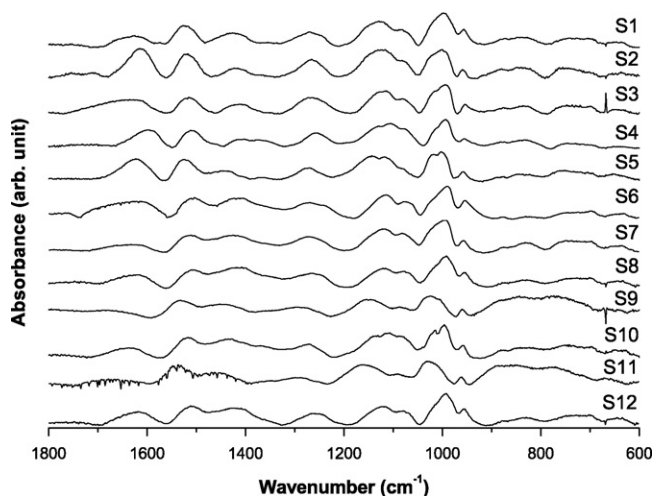


Fig. 4. Comparison of FTIR spectra of all synthesized samples.

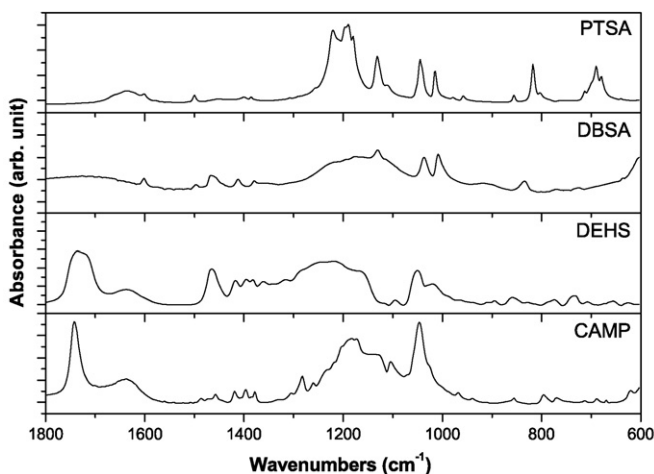


Fig. 5. FTIR spectra of organic dopants.

tioned (Fig. 3) characteristic bands of PPY. The “wide” shape of some absorption bands is caused by certain dispersion of molecular weight together with variable oxidation degree of the polymer backbone.

Fig. 5 summarizes spectra of the organic dopants. When comparing Figs. 4 and 5, one can observe that the characteristic bands of organic dopants are not significant in the spectra of PPY samples. It must be taken into account, that the molar quantity of dopants is five times lower than the quantity of pyrrole units (Section 2.1) and hence most of dopants-bands are overlapped by PPY-bands in the spectrum. There is only one exception: the presence of DBSA can be demonstrated in both S5 (1118, 1017 and 1002 cm^{-1}) and S10 (1110, 1014 and 1002 cm^{-1}) sample.

4. Conclusions

There has not been published as yet a relevant study concerning the relation between particle size on one side and quality of MAPLE deposited layers, ablation thresholds and growth rates on the other

side. However, based on our previous experience [10] with MAPLE depositions of commercially distributed PPY (Aldrich) we can conclude that the samples should be in group (ii) – miscible – i.e. S5, S6, S10 and S12 or in group (iii) – soluble – i.e. S11 in order to be suitable for MAPLE depositions from DMSO matrix.

The weight fraction of doped PPY dispersed/diluted in DMSO varies from 4.0% to 6.5%, which is significantly higher value, than the concentration used for successful MAPLE depositions of PPY (0.96%) reported in [8].

The synthesized PPY dispersed/diluted in DMSO has significantly higher settlement time than PPY dispersed/diluted in water (especially samples S10–S12). It means that PPY–DMSO binary system possesses better homogeneity than PPY–water system, which is advantageous for MAPLE depositions from DMSO matrix. With respect to the requirements of miscibility or at least solubility and simultaneously homogeneity and stability of PPY–matrix system we can conclude that optimal for MAPLE depositions are PPY samples S10–S12 in DMSO matrix.

As for FTIR spectra of the synthesized samples, the characteristic bands of organic dopants are in most cases overlapped by PPY-bands. Hence FTIR spectroscopy is a valuable tool for verification of structure of primarily synthesized PPY and for checking secondary structural changes in polymer during its subsequent MAPLE deposition [10]. On the contrary, using FTIR spectroscopy in order to prove the presence of dopants in PPY can be disputative.

Acknowledgement

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AC Analysis of Organocomplex Sensing Layer with Pd Catalyst

Jaromír Seidl^{1,*}, Filip Vysloužil¹, Martin Vrnáta¹, Ondřej Ekrť¹, Vladimír Myslík²,
Dušan Kopecký¹, Přemysl Fitl¹, Jaroslav Hofmann¹, and Jakub Nápravník²

¹*Institute of Chemical Technology Prague, Department of Physics and Measurements, Technická 5, Praha 6, 166 28, Czech Republic*

²*Institute of Chemical Technology Prague, Department of Solid State Engineering, Technická 5, Praha 6, 166 28, Czech Republic*

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Gas sensing structure was deposited from the tin dioxide/tin acetylacetonate (SnO₂ 90 wt%/SnAcAc 10 wt%) target by Pulsed Laser Deposition method. The prepared layer was improved by Pd catalyst via subsequent diode sputtering technique. The Nyquist diagrams were measured. DC sensitivity and Phase response to hydrogen in synthetic air and dynamic properties were investigated. The optimised parameters were following: sensor temperature and frequency of AC measuring signal. The sensor response was measured at different concentration of hydrogen. Measured data were fitted to an equivalent circuit. The obtained results were compared with those of SnO₂ and polypyrrole sensing layers.

Keywords: Gas Sensors, Organocomplex Layer, Sensing Layer, Impedance Measurement, Phase Response.

1. INTRODUCTION

Tin dioxide is known as the most widely used inorganic basic material for gas sensors utilising change of surface conductivity. The surface of some organic substances also exhibits an ability to enter into reversible chemical reaction with gases. The principle of conductivity changes of organic systems is in high polarizability of delocalized π -electrons in the system of conjugated double bonds. Metal complexes of acetyl-acetone (MeAcAc) are rich in delocalized electrons and in combination with semi-conductive tin dioxide are apparently active. In our previous works^{1,2} we recognized that high DC-sensitivity ($S_{dc} \approx$ tens to hundreds) at elevated working temperature (300–400 °C) is typical for SnO₂-based sensor layers. On the contrary metallic acetylacetonate (MeAcAc)-based layers achieved relatively good sensitivity at low working temperature (up to 200 °C). We can suppose that addition of SnAcAc to SnO₂ results to increasing specific surface of layer corresponding to higher “porosity,” i.e., ratio (area of material surface/layer volume). It also leads to changes in mechanism of sorption–desorption process (shorter recovery time of sensor) and to decrease of activation energy. In all cases presence of Pd plays an important role.^{3–5}

Metallic Pd acts as catalyst (increase of sensor response and decrease of temperature necessary for detection). Palladium in oxidized state (Pd²⁺) acts as an acceptor in basic material and also as inhibitor of grain growth.⁶

Pulsed laser deposition (PLD) method can be used for deposition of both organic and inorganic substances. The main advantages of PLD method are in its relative simplicity and high flexibility in connection with a good reproducibility of chemical composition and convenient surface morphology of prepared layer.

The most significant group of chemical sensors operates on the basis of surface DC conductivity changes. A different approach considering possibilities of chemical sensors may be derived from AC measurements.^{7–9} These measurements are a valuable tool for material characterization (grain size, conduction mechanisms, character of junctions between the active layer and the metallic contacts). In this contribution, an alternative Phase response (S_{pa}) resulting from AC measurements is calculated. The values of S_{pa} for different materials of sensing layer are also compared.

2. EXPERIMENTAL DETAILS

The PLD of sensing layers was carried out from source targets containing SnO₂ (90 wt%) + SnAcAc (10 wt%).

*Corresponding author; E-mail: seidlj@vscht.cz

The targets were prepared by mixing powder materials (Fluka Chemicals) and subsequent pressing operation at a pressure of about 85 MPa. The estimated volume contraction of the mixture during pressing process is one third. $\text{SnO}_2/\text{SnAcAc}$ layers were then prepared by PLD (KrF excimer laser, $\lambda = 248$ nm, energy density $0.6 \text{ J} \cdot \text{cm}^{-2}$, pulse duration 3 ns, repetition rate of laser pulses $f = 5$ Hz, nitrogen working atmosphere $p = 5$ Pa). The technological set-up for PLD is depicted in Figure 1. The as-deposited layers were ~ 100 nm thick. These layers were deposited to sensor substrates—i.e., small alumina plates equipped with interdigital Pt electrodes for reading sensor response (Figs. 2–3). The substrates had Pt heating element on reverse side. This element served also as Pt thermometer. The interdigital electrodes were on the area of $1300 \mu\text{m} \times 1400 \mu\text{m}$, the distance between “combs” of interdigital electrodes was $40 \mu\text{m}$. In order to improve sensor properties, a Pd catalyst was diode sputtered on surface of compound layers. Optimal equivalent thickness of sputtered catalyst was 0.75 nm.

The as-deposited sensors were thermally activated at 350°C in a special atmosphere. These conditions of activation were applied in order to simulate subsequent real operation of the sensor.

The experimental details of sensor DC resistance measurement and DC sensitivity (S_{dc}) evaluation were described in previous work.¹ The DC sensitivity was evaluated for sensor temperature (T) and hydrogen concentration as a ratio of layer resistance in the pure air (R_{air}) and the resistance in the atmosphere containing hydrogen (R_{gas}):

$$S_{\text{dc}}(T, c) = \frac{R_{\text{air}}(T)}{R_{\text{gas}}(T, c)} \quad (1)$$

Optimal sensor temperature is assumed for the value when the S_{dc} reaches maximum with respect to tolerable thermal stress of the sensor.

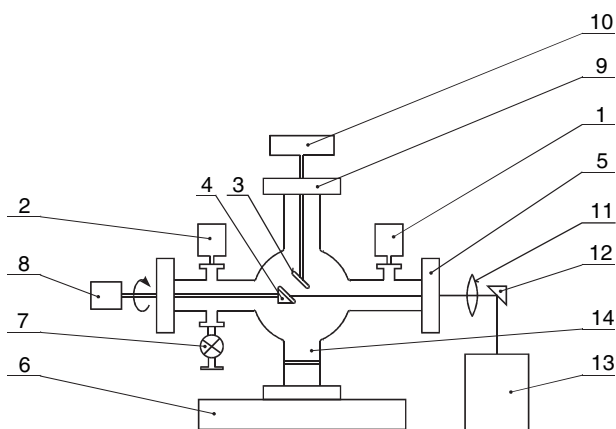


Fig. 1. Technological setup of PLD 1-penning gauge, 2-pirani gauge, 3-substrate holder, 4-rotating target, 5-silica window, 6-vacuum system, 7-needle valve, 8-target rotation mechanism, target changer 9-temperature measurement, 10-heating, 11-lens, 12-prism, 13-KrF excimer laser, 14-filter system.

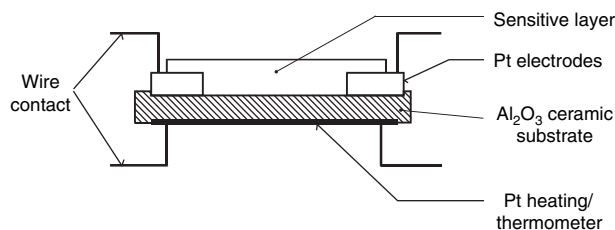


Fig. 2. Schema of the sensor chip.

Nyquist diagrams (i.e., real part vs. imaginary part of complex impedance, Fig. 4) were measured using a HP4194A impedance analyser. The frequency of testing signal ranged from 40 Hz to 110 MHz and its amplitude had a constant level of 500 mV. No bias DC-voltage was applied. The measured sensor was placed in a shielded Teflon chamber and its interdigital electrodes were connected with impedance analyser by a 4-TP professional adapter (four-wire arrangement). The measurement of the Nyquist diagram in a given atmosphere was carried out in a flow system (dead volume approx. 10 ml, gas flow rate $40 \text{ ml} \cdot \text{min}^{-1}$).

The Nyquist diagram of $\text{SnO}_2/\text{SnAcAc}$ sensors exhibits in general one semicircle corresponding to a parallel RC element (Fig. 4). The values of equivalent circuit resistance (R) and capacity (C) are calculated as follows: (i) the resistance value (R) is determined by the semicircle diameter, which can be read directly on real axis; (ii) the imaginary part of complex impedance achieves its extreme at certain frequency f_{ext} :

$$f_{\text{ext}} = \frac{1}{2\pi RC} \quad (2)$$

(iii) when knowing the f_{ext} and R , the equivalent circuit capacity C is obtained from Eq. (2). Fitted course of Nyquist diagram is showed in the Figure 4 as well. For comparison, there was calculated a CPE model using the Z-View software.^{13, 14} The CPE model fits measured data better, but resistance parts are similar, $R(\text{fit to circuit}) = 10360 \Omega$, $R(\text{CPE method}) = 10580 \Omega$. Parameter $\text{CPE-P} = 0.84$ (ideal capacitor $\text{CPE-P} = 1$).

Definition of the Phase response (S_{pa}) is conspicuous from the Figure 5. S_{pa} is evaluated as a difference:

$$S_{\text{pa}}(T, f, c) = \theta_{\text{air}}(T, f) - \theta_{\text{gas}}(T, f, c) \quad (3)$$

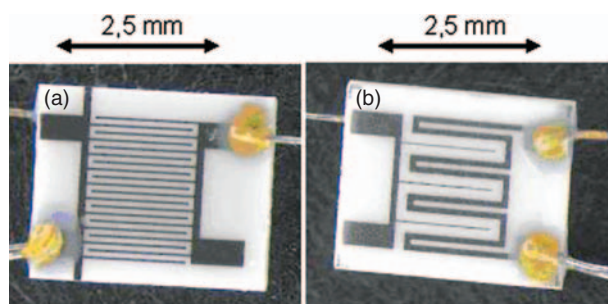


Fig. 3. Sensor substrates: (a) electrodes, (b) heating.

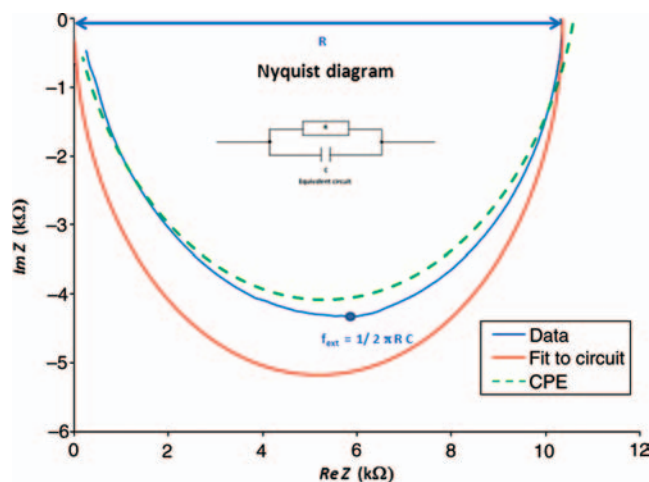


Fig. 4. Nyquist diagram, measured in atmosphere of hydrogen concentration 10 ppm, $T = 300\text{ °C}$, fit to circuit: $R = 10360\ \Omega$, $C = 5.13\text{ pF}$, CPE method: $R = 10580\ \Omega$, $\text{CPE-T} = 7.14 \cdot 10^{-11}\text{ s}^n\ \Omega^{-1}$, $\text{CPE-P} = 0.84$ (calculated by Z-View software).

where θ_{air} is an argument of sensor complex impedance in pure air and θ_{gas} is an argument of sensor complex impedance in the air atmosphere containing hydrogen. The defined response depends on sensor temperature T , frequency of testing signal f and hydrogen concentration c . The typical shape of Phase response versus frequency dependence is demonstrated by Figure 6. There are explained definition of $S_{\text{pa max}}$ (maximum value in frequency dependence) and f_{max} (frequency value for $S_{\text{pa max}}$). The plot contains also the fitted course according to RC network model of sensing layer.

3. RESULTS AND DISCUSSION

Sensor temperature is an important parameter for optimal sensor function. Figure 7 exhibits the DC sensitivity and Phase response on the temperature dependence in range

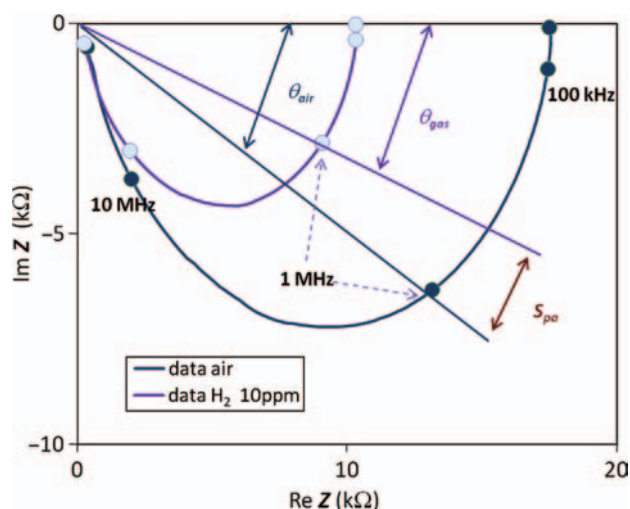


Fig. 5. Phase response (S_{pa}) evaluation, measured in atmosphere of hydrogen concentration 10 ppm, $T = 300\text{ °C}$.

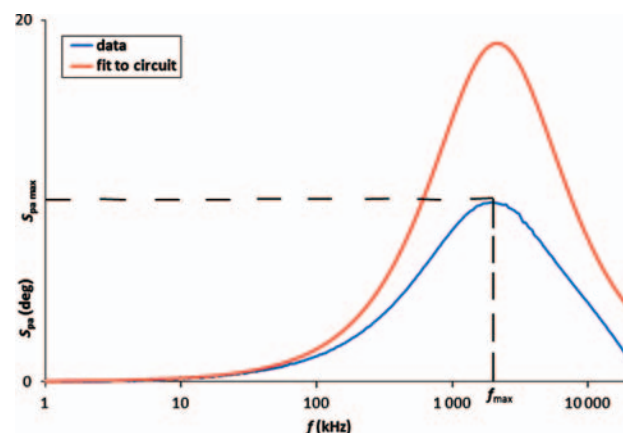


Fig. 6. Phase response to 10 ppm of H_2 , $T = 300\text{ °C}$.

from 100 °C to 300 °C . The phase response (S_{pa}) is “flat” in the sensor temperature range from 200 °C to 300 °C . It is advantageous for operating point maintenance of the sensor. On the contrary, the DC response can be very strongly affected by temperature fluctuation. The value of 300 °C was chosen as the optimal working temperature.

Dependence of the sensor response to different hydrogen concentration was investigated. The sensor temperature was set to 300 °C (optimized value). It was chosen the logarithmic scale for the concentration: 10, 40, 200, 400 and 1000 ppm vol. The results (also in logarithmic scale) are summarized in Figure 8. The plot contains the data for DC sensitivity (green), for maximum Phase response (blue) and the data of maximum Phase response fitted to RC network model (red). It can be observed the S_{dc} exhibits power course (“linear” in logarithmic scale). On the other hand S_{pa} increases by concentration logarithmically. The regression equations are presented. Fitted S_{pa} course has similar shape to measured data, but the values are shifted. The model is not valid for concentration higher than 400 ppm. Further improving of the S_{pa} model will

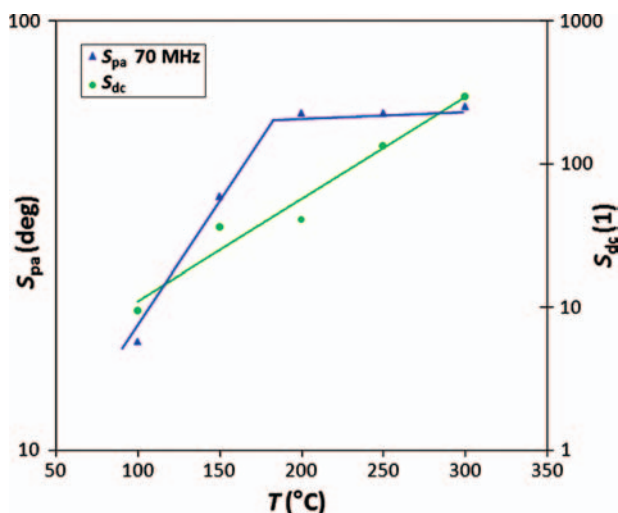


Fig. 7. Phase response and DC sensitivity versus sensor temperature (1000 ppm H_2).

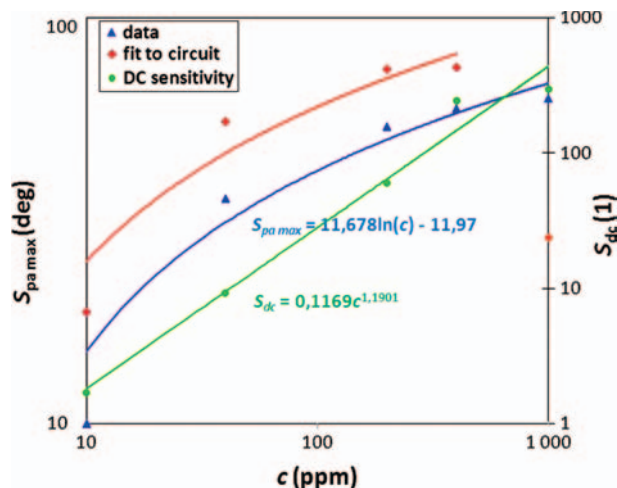


Fig. 8. Max. Phase response and DC sensitivity versus H_2 concentration, $T = 300\text{ }^{\circ}\text{C}$.

be investigated. Qualitative agreement of the model with measured data is evident from the Figures 4 and 6 as well. In case of $f_{\max}$ (Fig. 9), it can be enunciate good consent of model values to measured data for range from 10 to 200 ppm.

Both DC and Phase sensor responses are not only given by the sensor temperature, frequency of testing material and hydrogen concentration. These are also significantly affected by the material of the sensing layer. Table I compares previously investigated materials—polypyrrole and mixture of SnO_2 and Fe_2O_3 (composition 99:1 perceptually) with actual sensing material ($\text{SnO}_2/\text{SnAcAc}/\text{Pd}$). $S_{\text{dc max}}$, T (optimal sensor temperature for S_{dc}), $S_{\text{pa max}}$ and $f_{\max}$ depend significantly on the sensitive layer material, $f_{\max}$ changes even in three orders. Polypyrrole sensor can operate at low (room) temperature, but the DC and Phase sensitivities are very low. Detection properties are the best for $\text{SnO}_2/\text{SnAcAc}/\text{Pd}$ sensor in this collection, but $S_{\text{pa max}}$ is achieved at high frequency. An interference effect is

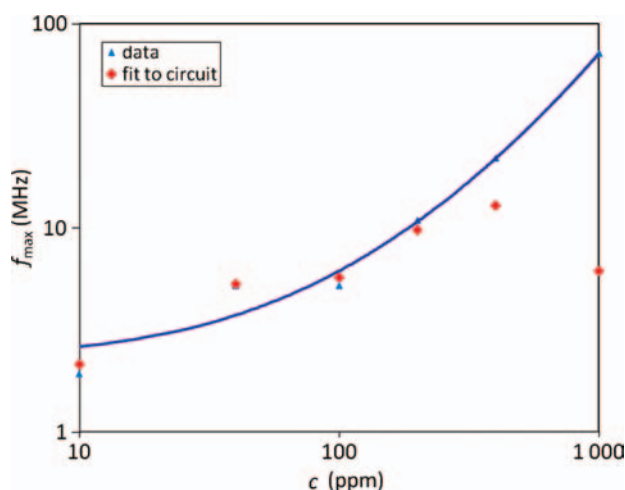


Fig. 9. Frequency of maximal Phase response $f_{\max}$ versus H_2 concentration, $T = 300\text{ }^{\circ}\text{C}$.

Table I. S_{dc} , $S_{\text{pa max}}$ and $f_{\max}$ versus material of sensitive layer dependence, 1000 ppm of H_2 .

Material	$T(^{\circ}\text{C})$	$S_{\text{dc max}}(1)$	$S_{\text{pa max}}(\text{deg})$	$f_{\max}$
Polypyrrole	23	1.7	6	26 kHz
SnO_2	330	6	40	1 MHz
$\text{SnO}_2/\text{SnAcAc}/\text{Pd}$	300	300	63	70 MHz

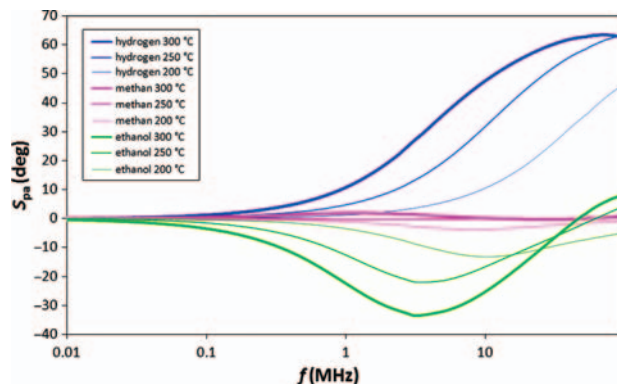


Fig. 10. Phase response for different gases and temperatures (H_2 , CH_4 , ethanol).

a general problem of the gas sensors. Layers of sensors are differently sensitive for various temperatures and gases. It can be used for gas recognition in multicomponent gas mixtures. There are phase responses for different gases (H_2 , CH_4 , ethanol) and different temperatures in the Figure 10. Apparently, there are various responses of gases, f.e. for frequency about 3 MHz. Methan is little sensitive. The phase response of ethanol is negative and response of hydrogen is positive.

4. CONCLUSIONS

The conductive gas sensor with $\text{SnO}_2/\text{SnAcAc}/\text{Pd}$ sensitive layer was investigated. Nyquist diagrams of gas sensor on various conditions were measured and phase response (S_{pa}) was evaluated from these diagrams and DC sensitivities as well. The phase response (S_{pa}) is “flat” in the sensor temperature range from $200\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$. It is advantageous for operating point maintenance of the sensor. On the contrary, the DC one is very strongly affected by temperature fluctuation. The value of $300\text{ }^{\circ}\text{C}$ was chosen as the optimal working temperature. Measured data were fitted using model of simple parallel RC network and a CPE method was also introduced. The validity of this model was confirmed in both Nyquist and Phase response diagrams. The behaviour of “classical” DC sensitivity (S_{dc}) and Phase response (S_{pa}) was compared. DC sensitivity versus H_2 concentration dependence exhibits power course (“linear” in logarithmic scale). Phase response has logarithmic behaviour in the same dependence. Maximum response values were reached ($300\text{ }^{\circ}\text{C}$, 1000 ppm H_2): phase response $\sim 63^{\circ}$ (frequency 70 MHz), DC sensitivity ~ 300 .

Both methods allow quantifying H_2 from concentration levels under 10 ppm. It was found that DC sensitivity, optimal sensor temperature, Phase response and frequency of maximum response depend significantly on the sensitive layer material. DC sensitivity and Phase response of presented $SnO_2/SnAcAc/Pd$ sensor is better than those of the polypyrrole and SnO_2/Fe_2O_3 sensors.

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Sensing Properties of Tin Acetylacetonate-Based Thin Films Doped with Platinum

Přemysl Fitl^{*,1,3}, Vladimír Myslík², Martin Vřnata¹, Josef Náhlík²,
Dušan Kopecký¹, Jan Vlček¹, Jaroslav Hofmann¹ and Ján Lančok³

¹Department of Physics and Measurements, Institute of Chemical Technology,
Technická 5, 166 28, Prague 6, Czech Republic

²Department of Solid-State Engineering, Institute of Chemical Technology,
Technická 5, 166 28, Prague 6, Czech Republic

³Institute of Physics, Academy of Sciences of the Czech Republic,
Na Slovance 2, 182 21 Prague 8, Czech Republic

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Thin sensing films based on tin acetylacetonate (SnAcAc) with a platinum catalyst were prepared *in situ* by pulsed laser deposition (PLD) with a Nd:YAG laser. The morphology and roughness of both as-deposited and annealed layers were characterized. These layers were also deposited on alumina sensor substrates with interdigital Pt electrodes and then used for the detection of hydrogen, *n*-butanol, toluene, and water vapors in synthetic air. The temperature dependence of the response of the prepared sensors was measured in the range of 40–350°C. It was proved that the selectivity to the above mentioned gases is easily tunable by adjusting the operating temperature of the sensor. The maximum response was achieved at 110°C for hydrogen, 220°C for *n*-butanol, 300°C for toluene, and 340°C for water vapor. The activation energy of surface reactions taking place during the detection process was also calculated.

1. Introduction

Pulsed laser deposition (PLD) is commonly used for the deposition of both inorganic and organic substances. The high flexibility of this method allows us to carry out the deposition of multilayer or mixed structures *in situ* in one technological step. Prepared layers exhibit high porosity resulting in a large specific surface, which is advantageous

*Corresponding author: e-mail: fitlp@vscht.cz

for gas sensing applications. When depositing catalytic metal by PLD, it is possible to create metallic nanoparticles or islands with dimensions even in the order of nanometers.^(1–3) Such a dispersion of the catalyst ensures a high concentration of active sites on which elementary steps of detection take place.

It is well known that plasma depositions of metal acetylacetonates lead to the polymerization of molecules of acetylacetic ligands, which is connected with a significant increase in thermal stability and with a very good response to reducing gases.^(4–6) According to our previous experience,^(7,8) the layers also prepared from acetylacetonates by the PLD method (where the deposited material is transferred through a plasma plume) are thermally stable and simultaneously sensitive to hydrogen, alcohol vapors, and ozone, for example.

Considering the detection of different gases or gas mixtures, the selectivity of sensors is a complex problem. There is a possibility of improving the sensor selectivity by setting its operating temperature. The higher the reactivity of detected gas (represented by the low activation energy for the surface chemical reaction), the lower the sensor operating temperature suitable to achieve maximum response and vice versa.

In this work, we investigated laser-deposited SnAcAc-based layers containing embedded Pt catalyst from the following viewpoints: (a) content of platinum in the layers; (b) layer morphology studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM); determination of layer roughness; (c) values of sensor parameters (layer resistance, dc response, sensing dynamics, activation energy of surface reactions) and their dependence on operating temperature as well as on the nature of the tested gas.

2. Materials and Methods

The sensing films were deposited from pure SnAcAc (pressed powder, Sigma-Aldrich, reagent grade) and platinum (bulk metal, purity 99.99%) targets by the PLD method. The 4th harmonic frequency of the Nd:YAG laser (Quantel Brilliant) at a wavelength of 266 nm, pulse duration of 4 ns, and repetition rate of 10 Hz was used. The sensitive layers were prepared in two steps: (i) deposition from the SnAcAc target with 1,500 pulses (resulting equivalent thickness is approximately 350 nm) followed by (ii) deposition from the Pt target with 500 pulses (representing an equivalent thickness of approximately 4 nm). The energy density of the laser beam was 0.6 J cm^{-2} in the case of the SnAcAc target and 4.0 J cm^{-2} for the Pt target. The deposition took place under nitrogen (5 Pa) atmosphere. It is well known that the as-deposited layers of acetylacetonates exhibit very high electric resistance, so the next necessary technological step includes their activation in order to acquire gas sensing properties.^(4,5,7,8) The thermal activation process developed in our laboratory, i.e., treatment by controlled heating in a furnace (up to 400°C, 9 h, synthetic air atmosphere containing 5,000 ppm hydrogen), is discussed in detail in a previous work.⁽⁹⁾

The depositions were carried out on three types of substrate: (a) glass slides (samples for SEM and energy-dispersive X-ray analysis), (b) polished silicon wafers (samples for AFM analyses), (c) alumina sensor substrates equipped with interdigital Pt contacts on one side and resistance heating on the opposite side (measurement of response to various gases).

The presence and content of platinum in the layers were analyzed by energy-dispersive X-ray (EDX) analysis. The microstructure of the prepared layers was studied by scanning electron microscopy (SEM). Both these analyses were carried out on a Philips XL30 CP instrument equipped with a detector of secondary electrons and the EDX detector PV 9760. The accelerating voltage ranged from 5 to 25 kV, depending on the thickness of the deposited layer.

The surface morphology and average roughness (R_a) of the samples were examined using an atomic force microscope (Digital Instruments CP II Veeco) working in the contact mode with silicon P-doped probes CONT20A-CP and a spring constant of 0.9 N/m.

Surface roughness was also measured using a confocal microscope (Olympus Lext OLS 3100) in order to obtain the values of R_a by a noncontact optical method.

The prepared sensitive layers with Pt catalyst were tested for hydrogen, toluene, *n*-butanol, and water vapor detection. The testing proceeded in special measuring equipment developed in our laboratory.^(7,8) This system measures the resistance values automatically and calculates the dc response in relation to the sensor temperature or concentration of detected gas. It also enables us to process and analyze the measured data, and to fit them with a suitable function. During measurements, the atmosphere was switched every 2 min from “pure” synthetic air to synthetic air containing the detected gas and vice versa. The values of sensor resistance were logged each second. Dc response to the tested gas (at the defined concentration and operating temperature) was calculated as the ratio of the sensor electrical resistance in a reference atmosphere of “pure” synthetic air (R_0) to its electrical resistance (R) in synthetic air containing the detected gas:^(7,8)

$$S_{dc} = R_0/R. \quad (1)$$

In order to better describe the chemical processes during detection, the activation energy (E_a) of surface reactions was determined. Activation energy is a certain measure of the reactivity of detected gases; there is also a correlation between E_a values and the temperature of the response maximum. Several references deal with the calculation of activation energy on oxidic materials of the active layer (tin oxide, titanium dioxide, indium sesquioxide with catalysts).^(10–12) To the best of our knowledge, no estimation of activation energy for layers based on acetylacetonates has been published to date. In this manuscript, the activation energy was computed by solving the model of the first-order reaction according to ref. 12.

When the concentration of the detected gas is kept constant, the reaction rate depends (at a given thermodynamic temperature T of the sensor) only on the concentration of free active sites:

$$-\frac{dc_x}{d\tau} = kc_x [T = \text{const.}], \quad (2)$$

where c_x is the concentration of free active sites, τ is time, and k is a temperature-dependent rate constant of the surface reaction. The quantity c_x is nominally measurable;

however, one can assume that the change in this quantity corresponds to the change in the sensor resistance (R).⁽¹²⁾ After integration with boundary and starting conditions, where when $\tau = 0$, then c_x is proportional to R_0 (starting resistance of the sensor), and when $\tau = \tau'$, then c_x' is proportional to R (resistance of a sensor after a sudden change in atmosphere), we obtain the following expression for the rate constant k as a function of sensor resistance:

$$k\tau = \ln\left(\frac{R_0}{R}\right). \quad (3)$$

Activation energy E_a was then assumed to enter the Arrhenius equation for the temperature dependence of the rate constant:

$$k = Z \exp\left(-\frac{E_a}{BT}\right), \quad (4)$$

where Z is a pre-exponential factor, B is the Boltzmann constant, and T is the thermodynamic temperature of the sensor. Hence, activation energy E_a can be obtained if the rate constant is known at least for two different temperatures.

The dynamic properties of the prepared sensors were characterized from the following model. The time dependence of the sensor resistance, i.e., quantity $R(\tau)$, can be expressed from eq. (3) as

$$R(\tau) = R_\infty - (R_\infty - R_0)\exp(-k\tau), \quad (5)$$

where R_∞ is a steady-state resistance of the sensor (after atmosphere switching). This model is derived under the assumption of a first-order reaction. On the basis of extensive experimental data $R(\tau)$ obtained for each sensor, three characteristic parameters, R_0 , R_∞ , and k , were fitted. In the next step, the parameters “computed response (2 min)” and “computed response (10 min)” were extrapolated from model eq. (5) to subsequent 2 or 10 min following each atmosphere switching. The difference between these calculated parameters and “real time response” obtained from eq. (1) can provide useful information, i.e., whether the sensing layer achieves a steady state for a given testing gas and switching interval.

3. Results

3.1 Chemical composition of prepared layers

Compositions (in atomic percent) of the SnAcAc source, as-deposited layer, and the layer after annealing are summarized in Table 1. Microprobe analysis proved the presence of Pt in the deposited layers. The quantity of Pt in the as-deposited layer is rather small considering the fact that there were 1,500 pulses from the SnAcAc target and 500 pulses with a significantly higher energy density from the Pt target during the

deposition. The as-deposited layer is relatively rich in carbon, but during the activation process, the relative content of carbon rapidly decreases, as carbon escapes in the form of volatile compounds.

The detailed investigation of FTIR spectra of the PLD-deposited layers from the SnAcAc source (both as-deposited and after thermal activation) was reported in ref. 9. The above-mentioned “escape” of carbon during the activation process, accompanied by the partial transformation of SnAcAc to tin carboxylate, was also reported in ref. 9.

3.2 Morphology and roughness

SEM images of as-deposited layers and the layers after activation (annealing) are presented in Figs. 1 and 2, respectively. Layer morphology in the as-deposited state could be described as homogeneously deployed wrinkled hills originating from the laser-induced plasma polymerization of SnAcAc. It is apparent that after activation,

Table 1
Elemental composition of the layers (in atomic %).

Element	Material		
	Pure SnAcAc	As-deposited layer	After annealing
Sn	3.23	2.13	7.51
C	32.26	30.45	28.11
Pt	0	0.08	0.63
Ratio C/Sn	10.0	14.3	3.74

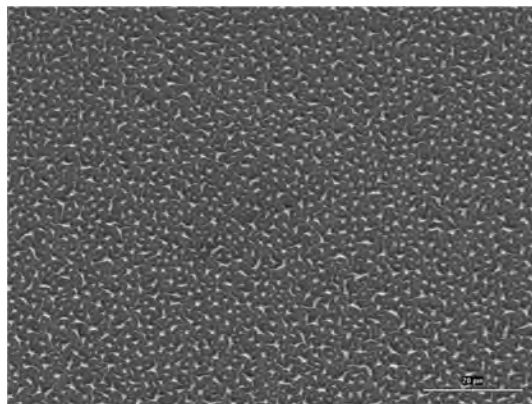
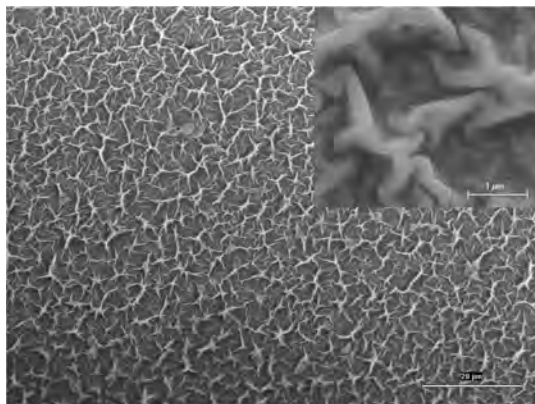


Fig. 1 (left). Surface morphology of as-deposited tin acetylacetonate/Pt layer.

Fig. 2 (right). Surface morphology of laser-deposited tin acetylacetonate/Pt layer after activation process (annealing at 400°C for 4 h in synthetic air).

the layer surface becomes less wrinkled (less structured) and smoother, but the layer remains compact. This is probably a result of polymeric material creeping taking place at elevated temperature.

AFM portraits of the same layers are shown in Figs. 3 and 4. Because the analyzed area is significantly smaller than in the SEM images, the AFM portraits show details of the above-mentioned wrinkled hills. Although the SEM images before and after the activation process look different, repeated AFM scan of the surface shows the same character of layer morphology at small scales. Table 2 shows the average roughness of the samples before and after the activation process. R_a was measured using a confocal microscope and AFM in an area of $50 \times 50 \mu\text{m}^2$. It is also important that the R_a values obtained by contact and noncontact methods are comparable (i.e., the deposited organic

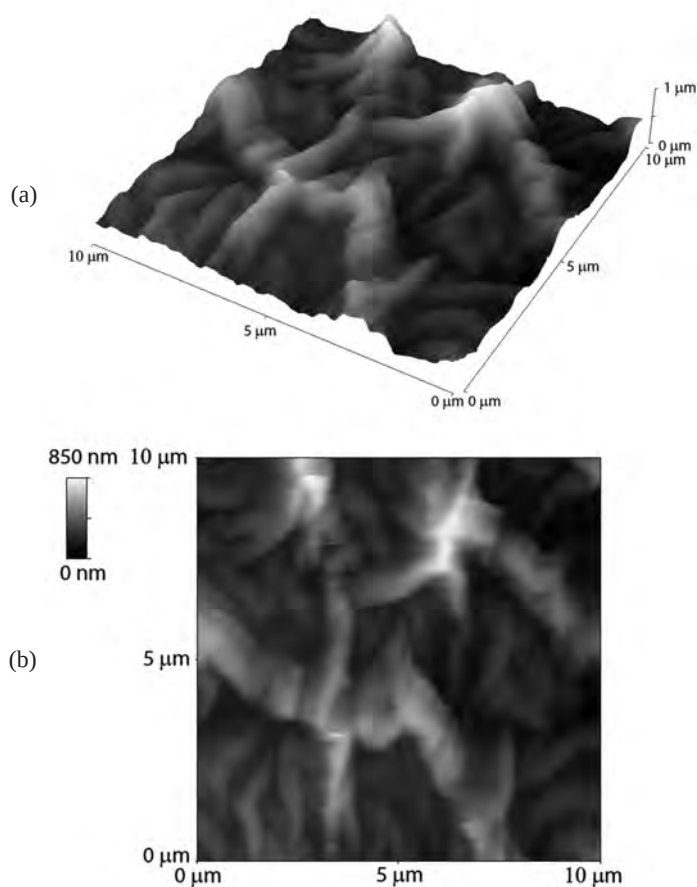


Fig. 3. AFM portrait of as-deposited tin acetylacetonate/Pt layer.

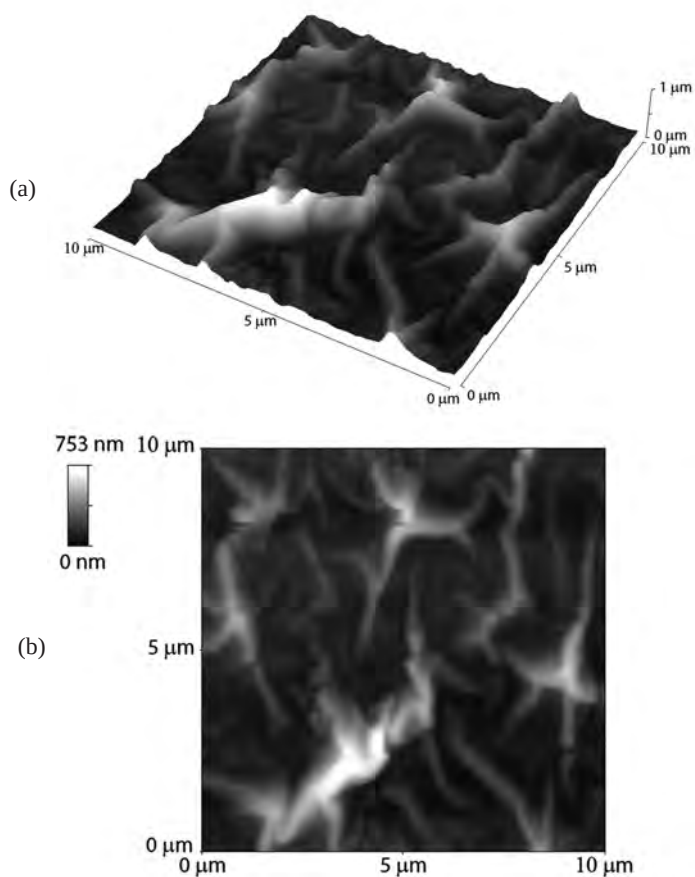


Fig. 4. AFM portrait of laser deposited tin acetylacetonate/Pt layer after activation process (annealing at 400°C for 4 h in synthetic air).

Table 2
Roughness of the layers (in nm).

	As-deposited layer	After annealing
Confocal microscope	107	80
AFM	102	84

material is sufficiently “hard” and fixed to the substrate). The decrease in roughness after activation, apparent in Table 2, also indicates the above-mentioned creeping.

3.3 Sensing properties of prepared sensors

Figures 5–9 show the sensing response of SnAcAc/Pt layers to various gases and vapors. The labels have the following meanings. “Resistance” represents changes in measured resistance values during the whole measurement process. “Response” is evaluated according to eq. (1) from the last ten resistance values logged immediately before atmosphere change. This parameter is a “real-time” response of the sensor. The “computed response (2 min)” and “computed response (10 min)” were extrapolated according to model eq. (5) to the next 2 or 10 min following atmosphere switching.

The temperature of response maxima ($T_{\max}$) was observed to be 110°C for hydrogen (Figs. 5–6), 220°C for *n*-butanol (Fig. 7), 300°C for toluene (Fig. 8), and 340°C for water vapor (Fig. 9). In the detection of hydrogen at operating temperatures higher than approx. 150°C, 2 min is sufficient for the sensor response to achieve a steady state. In contrast, in the case of *n*-butanol, the model shows that the sensor response does not reach the steady state in 2 min for any temperature. In such a situation, the response can be improved by prolonging the gas switching time. In the case of the detection of toluene and water vapor, there is some discrepancy as the “computed response (10 min)” is slightly lower than the real-time response. This is probably due to the higher complexity of the mechanism underlying the detection process mechanism than that corresponding to a first-order reaction.

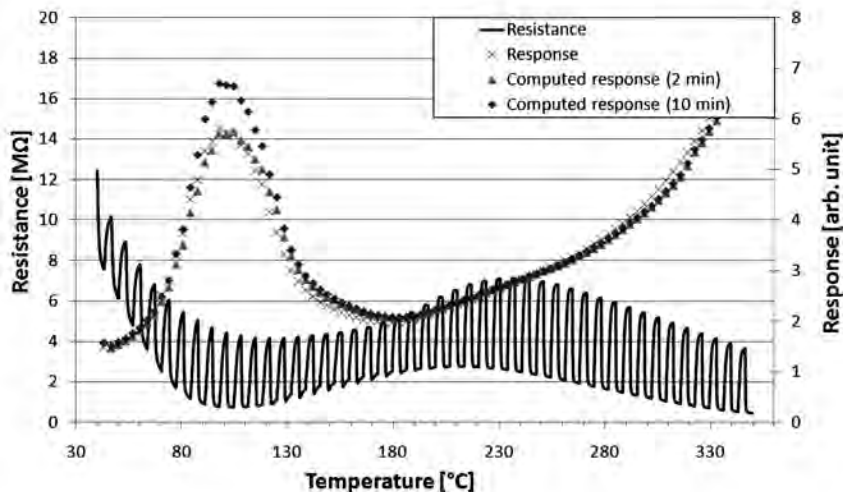


Fig. 5. Temperature dependence of resistance and response to 1,000 ppm of hydrogen (reference gas synthetic air).

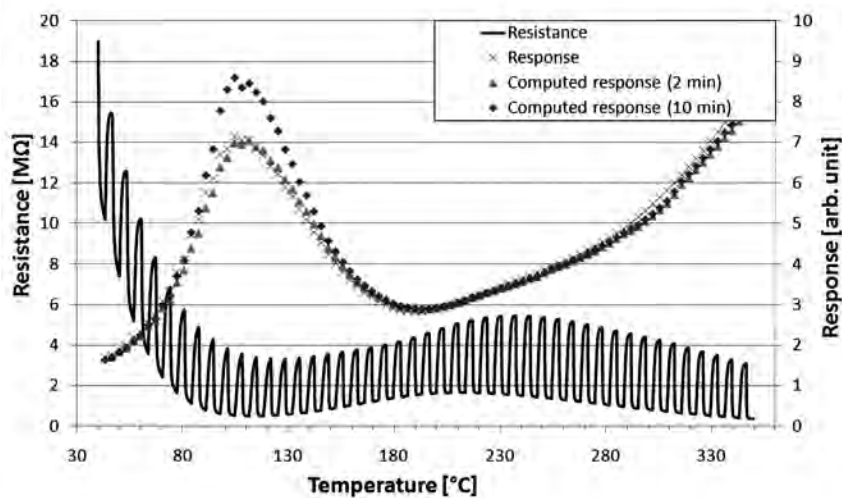


Fig. 6. Repeated measurement of resistance and response to 1,000 ppm of hydrogen (the same conditions as in Fig. 3; delay between measurements, 5 h).

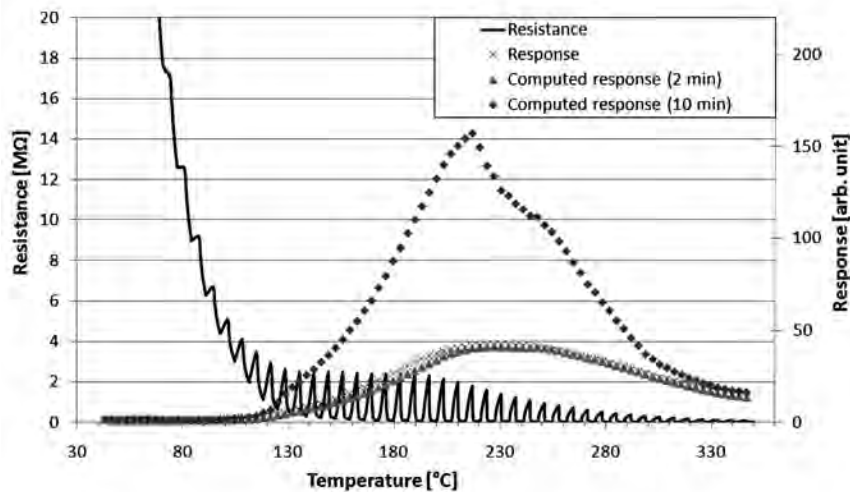


Fig. 7. Temperature dependence of resistance and response to 10,000 ppm *n*-butanol vapor (reference gas: synthetic air).

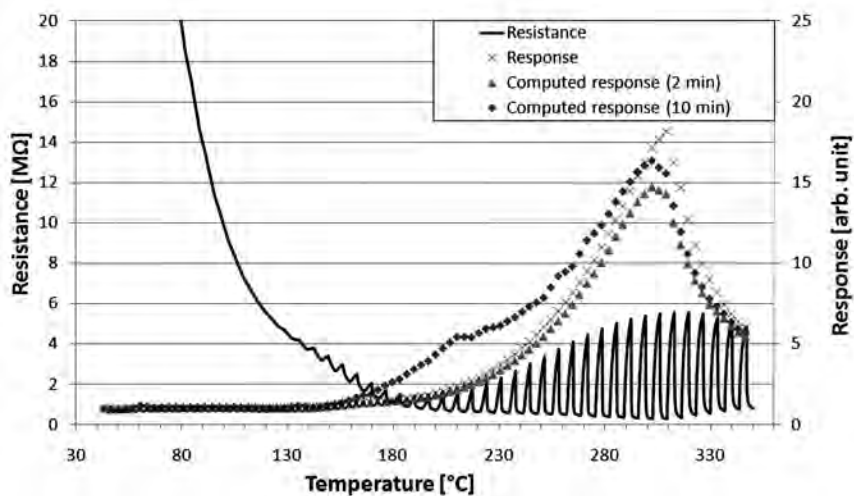


Fig. 8. Temperature dependence of resistance and response to 10,000 ppm toluene vapor (reference gas: synthetic air).

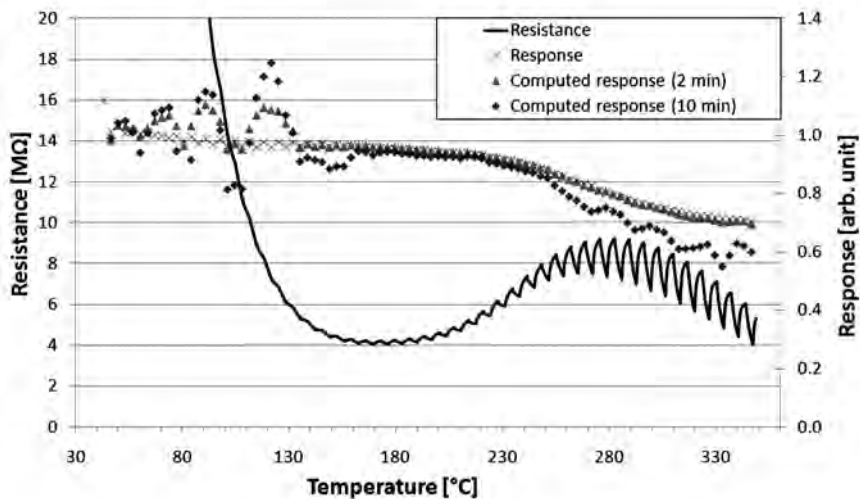


Fig. 9. Temperature dependence of resistance and response to 10,000 ppm water vapor (reference gas: synthetic air).

According to eq. (4) we also obtained the following activation energies of the detection process (detection proceeds on a sensitive SnAcAc layer containing platinum): 0.428 eV for hydrogen, 0.891 eV for *n*-butanol, 2.322 eV for toluene, and 2.558 eV for water vapor. According to ref. 12, the computed activation energy for the detection of hydrogen on a sensitive SnO₂ layer containing platinum is 0.053 eV.

The repeatability of the sensor response is another important parameter. It was tested by a second temperature scan measurement delayed for 5 h after the first one. The relative difference between the measured values of the response was less than 15% for all the tested gases. Figures 5 and 6 illustrate the reproducibility in the case of hydrogen sensing.

4. Discussion and Conclusions

The layers described in this article were prepared by an original technological procedure comprising the pulsed laser deposition of an active layer from acetylacetonate targets (i.e., laser-induced plasma polymerization) with the subsequent deposition of a catalyst in one technological step. Annealing (activation) of the as-deposited layers led to their thermodynamical and structural stabilization and also ensured a good stability under the operating conditions of the sensor.

From the practical point of view it is important that the layers have clearly differentiated temperatures of response maxima to distinct gases: $T_{\max} = 110^{\circ}\text{C}$ for hydrogen, $T_{\max} = 220^{\circ}\text{C}$ for *n*-butanol, $T_{\max} = 300^{\circ}\text{C}$ for toluene, and $T_{\max} = 340^{\circ}\text{C}$ for water vapour. Such properties are highly beneficial for use in multisensor arrays, so only one kind of active layer is sufficient for this purpose. The selectivity can then be ensured by setting only the operating temperature.

The sensor also enables us to distinguish between the response to hydrogen, *n*-butanol, and toluene on one side and water vapor on the other side. Hydrogen, *n*-butanol, and toluene behave like reducing agents during detection; an inverse response was observed in the case of water vapor. The prepared sensors were also tested for long-term stability (their response was periodically observed for one year). During this period, the sensors exhibit the same operating-temperature-related selectivity. On the basis of these findings, we judge our sensors to be suitable for application in practice.

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Adsorption–desorption noise in QCM gas sensors

Petr Sedlak^{a,*}, Josef Sikula^a, Jiri Majzner^a, Martin Vrnata^b, Premysl Fitl^b, Dusan Kopecky^b, Filip Vysloulzil^b, Peter H. Handel^c^a Dept. of Physics, FEEC, Brno University of Technology, Brno, Czech Republic^b Dept. of Physics and Measurement, Institute of Chemical Technology, Prague, Czech Republic^c Dept. of Physics and Astronomy, University of Missouri, St. Louis, USA

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ABSTRACT

There are several mechanisms that are related to the fluctuation phenomena in QCM. The aim of our research is to study the sensitivity and the influence of different kinds of noise on sensor resolution. Our experiments are performed on sensors with a sorption layer of polypyrrole which is suitable for detection of water vapor. Based on these experiments, we conclude that $1/f$ noise caused by quartz internal friction and adoption–desorption (generation–recombination) noise from analyzed gas cause the main components of the measured noise spectral density. The adoption–desorption noise power depends on the physical and chemical parameters of the analyzed gas and it is proportional to the gas density. The adsorption–desorption kinetics is described by Kolmogorov's equation and is compared with the Wolkenstein and Langmuir equations.

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1. Introduction

Quartz crystal microbalance (QCM) represents a high-sensitivity sensor for detection of chemical substances, and is widely utilized as a result of its robust nature, availability and affordable interface electronics [1]. The heart of the sensor is AT-cut quartz crystal whose electrodes are covered by sorption layers with affinity to the molecules of the detected matter. Since the resonance frequency of quartz crystal depends on the total oscillating mass, the principle of QCM is a frequency shift caused by the addition of sorbed matter (molecules of the detected mass) to the electrodes or its removal from them. Thus, the sensitivity depends on the stability of the oscillator and the accuracy and stability of the devices measuring the parameters of the quartz resonator. The selectivity is given by the choice of the material of the sorption layer.

Analyses of noise measurements represent the approach of extracting more selective response from chemical sensors, such as resistive [2–6] and surface acoustic wave [7] sensors. Experimental results showed that the noise spectral density of the sensor's resistance fluctuations is modified by exposure to different gases as well as by exposure to different concentration of gases [5]. Thus, noise spectroscopy might be highly useful for improving gas sensors selectivity if both theoretical models and adequate

sensing devices can be developed [3]. Gomri et al. [4] proposed a model of adsorption–desorption noise in metal oxide gas sensors, based on the free electron density fluctuation produced by the gas adsorption. Using this model for simulating the oxygen chemisorption–induced noise, they found that the contribution of oxygen adsorption–desorption noise to the noise spectra is a Lorentzian component having a corner frequency and low frequency magnitude which are specifics of the adsorbed gas.

The paper deals with an experimental study how absorption of detected gas molecules affects frequency fluctuations of QCM, and presents the model of adsorption–desorption noise which is devoted on the basis of Kolmogorov equation for interaction between two reservoirs.

2. Experimental setup

Two standard approaches of QCM measurement exist, namely the active method and the passive method. In the first one, the quartz crystal is a part of a wideband oscillator circuit whose frequency is controlled by the crystal properties [1] and is measured by a frequency counter with a resolution of 1 Hz, 0.1 Hz or 0.01 Hz. Some researchers [6] use a reference oscillator to avoid ambient effects. In that case, a counter measures the frequency difference between the output signal of the sensor based oscillator, and the output signal of the reference quartz based oscillator. In the passive approach, a QCM receives a frequency which is determined by an external source [2]. Thus, the frequency shift and the shift in bandwidth (proportional to dissipation) can be obtained by recording

* Corresponding author at: Department of Physics, Faculty of Electrical Engineering and Communication, Brno University of Technology, Technická 8, Brno 616 00, Czech Republic. Tel.: +420 541143208; fax: +420 541143133.

E-mail address: sedlakp@feec.vutbr.cz (P. Sedlak).

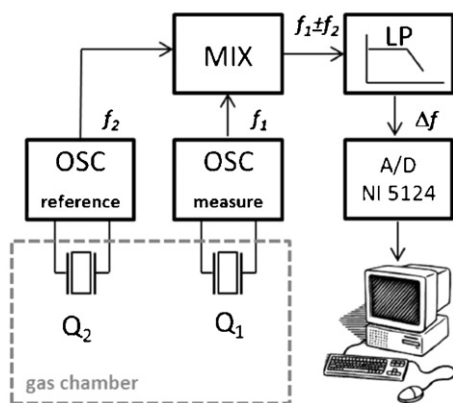


Fig. 1. Noise measurement setup for quartz crystal microbalance.

the complex admittance around a resonance frequency and fitting resonance curves to the admittance spectra.

In order to study a small frequency fluctuation of QCM, the active method was modified to measure instantaneous frequency of QCM. The scheme of our measurement setup is shown in Fig. 1. The measurement setup consists of a quartz crystal with deposited sorption layers (measuring oscillator) and a quartz crystal without sorption layers (reference oscillator). These crystals are driven by two independent oscillator circuits that regulate frequency of each quartz crystal at the minimum impedance which corresponds to serial resonance. The frequency difference Δf between these two oscillators is a result of mixer procedure and low-pass filtering. This signal is led to an input of a data-acquisition card (NI 5124) which triggers on the rise-edges of the output signal and stores the corresponding times at which the instantaneous frequency is estimated by own-written software.

3. Samples preparation

The experiments were performed on sensors with a thin sorption layer of polypyrrole (PPY) which is a material suitable for construction of QCM humidity sensors. The change of relative humidity from 0% RH to 25% RH causes a change of resonant frequency (Δf) in the range 50–150 Hz. Sensor parameters (e.g. sensitivity, dynamic properties, time stability of response) depend not only on the composition but even on the way of deposition of the sorption layer. Thus, PPY was deposited using Matrix Assisted Pulsed Laser Evaporation (MAPLE). This technology [12–16] is a laser deposition method providing a gentle mechanism for organic layer deposition. In MAPLE, a frozen phase consisting of a dilute solution of a high-molecular weight compound (basic material) in a low-molecular-weight solvent (matrix) is used as the laser target. Deposition takes place after the impact of a laser pulse with the surface of the frozen target. In an optimal case, the energy of the laser pulse is completely absorbed by the matrix, resulting in a strong local increase of temperature. The matrix molecules transfer their kinetic energy of thermal motion to the molecules of basic material. Hence the molecules of basic material are transferred to the substrate “mechanically”, with neither photolytic nor pyrolytic damage.

The advantages of MAPLE in comparison with conventional methods can be summarized as follows: (a) the thickness of the prepared layers can be simply controlled by setting laser fluence and the number of pulses. Thus, reproducible preparation of thin layers having thicknesses of the order of tens of nanometers is possible. (b) The prepared layers are porous (i.e. they have a high surface/volume ratio), so they are suitable for sensor applications. (c) “Sandwich” structures can be fabricated in situ in one step by

changing targets during the deposition. (d) The effect of the laser pulse is strongly limited in time and localized in space, hence there is a possibility to create various patterns by Matrix-Assisted Pulsed Laser Evaporation – Direct Write method.

The source target for MAPLE was prepared from 5 wt.% water solution of polypyrrole (Mw = 10,000) doped with dodecyl sulfonic acid-specific electrical conductivity of the solution: $\sigma = 10\text{--}40 \text{ S cm}^{-1}$ (Sigma Aldrich). This solution was stirred and homogenized by an ultrasonic device. Subsequently, it was frozen to -196°C in the tubular mould using liquid nitrogen. The prepared target was inserted into the deposition chamber and placed on the rotating shaft of the target holder. The holder was simultaneously cooled by liquid nitrogen. Uniform ablation of the material from the target surface was achieved by constant rotation during the deposition process. The deposition chamber was evacuated by a turbomolecular pump to a residual pressure of $5 \times 10^{-3} \text{ Pa}$. The pressure in the chamber did not exceed 3 Pa during the deposition process (a background gas was not used).

The depositions were carried out using Nd:YAG laser (Quantel), operating at the fourth harmonic frequency (wavelength 266 nm). The Nd:YAG laser was used in a pulse mode with a 10 Hz repetition rate. The fluence F of the laser radiation was set by an attenuator to be $F = 0.4 \text{ J cm}^{-2}$. The substrate-quartz crystal (without any surface masking) was placed at a distance of 60 mm. The deposited PPY layers have a thicknesses ranging from 80 to 400 nm.

Fig. 2 shows good agreement between relative humidity measurements, where a commercial available humidity sensor (FH A646-1, ALBHORN) and a QCM with deposited polypyrrole were used. RH increase from 25% to 85% causes a rise of frequency difference Δf between measuring oscillator and reference oscillator for about 400 Hz.

4. Results and fluctuation mechanisms in QCM

Several mechanisms related to fluctuation phenomena exist in QCM. The fundamental noise includes thermal noise, $1/f$ noise due to the quantum fluctuation and phonon scattering by defects, adsorption–desorption noise from the analyzed gas, thermo-mechanical noise, temperature fluctuation noise, and electronic oscillator noise. The mechanisms can be separated into two groups; the first one is related to the quartz crystal and its electrical circuit, while the second one is related to the adsorption–desorption processes on a sorbent layer. Experimental

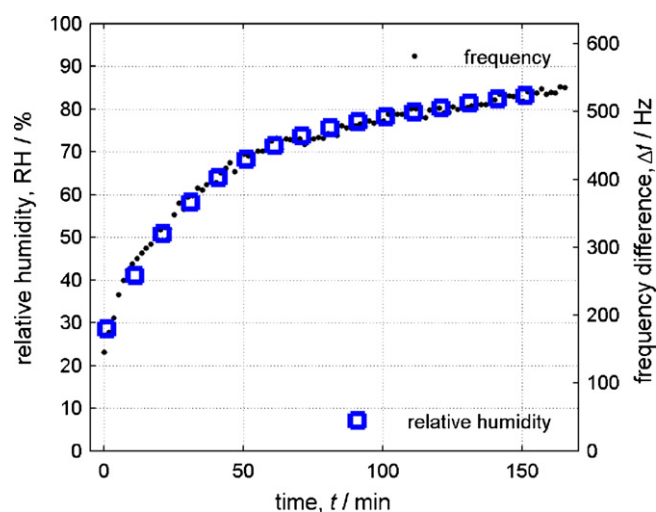


Fig. 2. The frequency difference Δf between measuring and reference oscillators, and relative humidity as a function of time after certain amount of water being put into gas chamber and sensors being exposed.

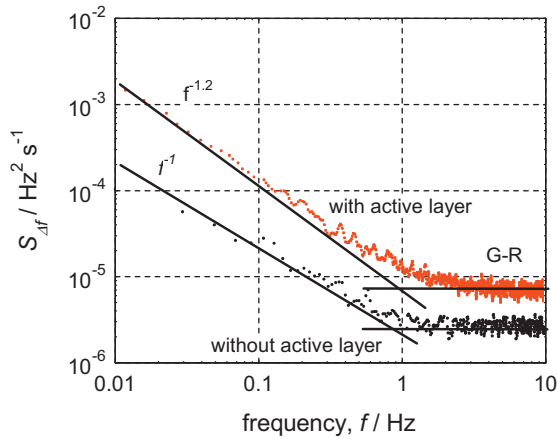


Fig. 3. The spectral density $S(\Delta f)$ of frequency difference fluctuation of the polypyrrole QCM at relative humidity 30% and spectral density of frequency difference fluctuation of the two identical quartz crystals without active layer.

results shown in Fig. 3 reveal that the $1/f$ noise, thermal noise and generation–recombination (adsorption–desorption) noise seem to be the main noise components. Fig. 3 also shows the spectral density of QCM has a higher slope of $1/f$ noise part and a higher value of GR component in comparison to the noise spectrum of the measurement system, which was determined on the basis of the measurement of frequency difference fluctuation using two identical quartz crystals without active layer.

There are various models and mechanisms that could be responsible for the observed noise, especially for $1/f$ noise (e.g. [8–11]); however, this paper focuses only on fluctuation mechanisms connected with chemical processes on the active layer of QCM.

Fig. 4 illustrates how the spectral density $S_{\Delta f}(f)$ of the frequency difference fluctuations is affected by the absorption/desorption of water molecules by the QCM sensor. When the RH increases, the $1/f$ noise component changes insignificantly while the G–R component noticeably increases with a rise of RH value. The authors of this paper suppose that thermal noise component and $1/f$ noise component are mainly associated with quartz crystal properties represented by its equivalent circuit, while generation–recombination noise results from adsorption–desorption processes which are present on the active layer of the QCM sensor. Further, it can be assumed that a shift of G–R noise is caused by increased flux density between the sorbent layer of QCM and the ambient environment. Considering these interactions between the two reservoirs, a model of

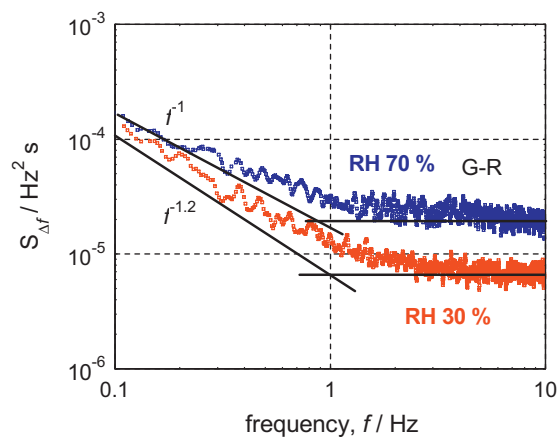


Fig. 4. Spectral density $S(\Delta f)$ of frequency difference fluctuations of the polypyrrole QCM at relative humidity 30% and 70%.

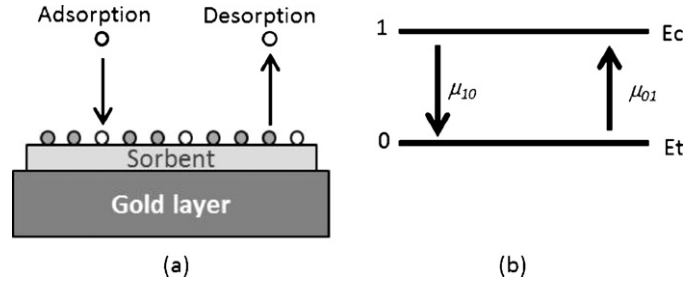


Fig. 5. (a) a model of adsorption–desorption processes on the quartz crystal layer and (b) the transition probability intensity for emission and capture.

adsorption–desorption noise could be formulated on the basis of Kolmogorov equation.

5. Adsorption–desorption noise

This section presents a model of adsorption desorption noise related to RH concentration. The value of the adoption–desorption noise depends on the physical and chemical parameters of the analyzed gas. Adsorption–desorption kinetics is described by the Kolmogorov equation and compared with the Langmuir and Wolkenstein equations.

5.1. Kolmogorov equation

A proposed model of adsorption–desorption noise is based on interaction between two reservoirs:

- analyzed gas with concentration n , temperature T and partial pressure p ,
- sensor sorbent surface with total surface density of sites for the adsorption of analyzed gas N_0 , with surface density of sites occupied by analyzed gas molecules N_t

5.1.1. Transition probability intensities

The model supposes that the system is: (i) Markowian, (ii) near equilibrium, and (iii) generation–recombination processes may take place between these two reservoirs. The random process of the surface site is assumed to have two states and to be stationary with a constant transition probability density μ_{ij} defined by

$$\mu_{ij} = \lim_{t \rightarrow s} \frac{p_{ij}(s, t)}{t - s} \quad (1)$$

where p_{ij} devotes the transition probability at time s from the i -state to the j -state at time t . Fig. 5a shows the model of adsorption–desorption process on the quartz crystal sorbent layer. Desorption corresponds to molecule emission from sorbent, i.e. generation of free particle, and the process of adsorption corresponds to recombination. Thus, the process is similar to generation–recombination in semiconductors. The transition probability density for emission and capture is schematically shown in Fig. 5b, where μ_{01} is the transition probability density for the molecule emission and μ_{10} for capture. There are two physical quantities: the characteristic time τ_c for a molecule to be captured on the surface site which is inversely proportional to the transition probability density μ_{10}

$$\mu_{10} = \frac{1}{\tau_c} \quad (2)$$

and the characteristic time τ_e for molecule emission from the surface site which is inversely proportional to the transition probability density μ_{01}

$$\mu_{01} = \frac{1}{\tau_e} \quad (3)$$

The probabilities $p_{ij}(t)$ of the transition from the state i into the state j are found by solving the Kolmogorov differential equations

$$\frac{dp_{ij}(t)}{dt} = \sum_{k \in I} \mu_{ik} p_{kj}(t) \quad (4)$$

for $i, j = 0, 1$, with the conditions $p_{ii}(0) = 1, p_{ij}(0) = 0$, for $i \neq j$. In thermodynamic equilibrium, the statistics, that the surface site is free or occupied by a molecule, is described by the absolute probability distributions Π_0 and Π_1 . These ones are given by solving the Kolmogorov equation [17] for stationary state in the form

$$\sum_{k \in I} \Pi_i \mu_{ik} = 0, \quad (5)$$

where

$$\Pi_0 = \left[1 + \frac{\mu_{01}}{\mu_{10}} \right]^{-1} \quad (6)$$

$$\Pi_1 = \left[1 + \frac{\mu_{10}}{\mu_{01}} \right]^{-1} \quad (7)$$

The absolute probability distributions Π_0 and Π_1 are similar to the Fermi–Dirac statistics.

5.1.2. Kinetic equation

Kinetic equation describing surface density of adsorbed molecules follows from (5) in the form

$$\frac{dp_{10}}{dt} = \mu_{10} \Pi_0 + \mu_{11} \Pi_1 \quad (8)$$

$$\frac{dp_{01}}{dt} = \mu_{00} \Pi_0 + \mu_{01} \Pi_1 \quad (9)$$

where μ_{00}, μ_{11} are densities that the system is persisting in the state 0 or 1, respectively. With $\mu_{01} = C_N n_1$ for generation, $\mu_{10} = C_N n$ for recombination and C_N as coefficient of capture,

$$\frac{dN}{dt} = \text{adsorption}(N) - \text{desorption}(N) = C_N n (N_0 - N) - C_N n_1 N. \quad (10)$$

The surface density of adsorbed molecules is proportional to the coefficient of capture C_N , concentration of adsorbed molecules n , sensor surface density of sites N_0 and the effective concentration of occupied sites n_1 .

5.2. Langmuir adsorption kinetics

The rate of formation of the monolayers can be written as [18]

$$\frac{d\Theta}{dt} = \text{adsorption}(\Theta) - \text{desorption}(\Theta) = k_a(1 - \Theta)C - k_d\Theta \quad (11)$$

where $\Theta = N/N_0$, C denotes concentration of analyzed gas molecules, k_a and k_d are the rate constants for adsorption and desorption processes, respectively. Integration of (11) and substitutions $k_{obs} = k_a + k_b$ and $k' = C/(C + k_d/k_a)$ lead to

$$\Theta(t) = k'(1 - e^{-k_{obs}t}) \quad (12)$$

If the fractional coverage Θ is measured as a function of time t , coefficients k_{obs} and k' can be determined by fitting of (11) on the experimental data.

5.3. Wolkenstein adsorption kinetics

The rate of formation of monolayers is [3,4]

$$\begin{aligned} \frac{dN}{dt} &= \text{adsorption}(N) - \text{desorption}(N) \\ &= \alpha p (N_0 - N) - N \nu \exp\left(\frac{-E_b}{kT}\right) \end{aligned} \quad (13)$$

$$\alpha = \frac{\Pi \sigma}{\sqrt{2\pi m k T}} \quad (14)$$

$$p = nkT \quad (15)$$

where Π is the probability that a molecule approaching an adsorption center will be fixed on the sensor surface, p is the pressure of adsorbed gas, m is the adsorbed molecule mass, σ is the sensor site adsorption cross section, E_b is the binding energy of the adsorbed molecule and ν is the oscillation frequency of the corresponding particle (typically $\nu = 10^{12}$ Hz).

5.4. Modeling of the adsorption–desorption noise

In order to find the dependence of the fluctuation $\delta N(t)$ around the value N_0 at the adsorption–desorption equilibrium on the thickness of the sensing layer, small fluctuations of N around the value N_0 are considered as done in [3,4]. After some calculation procedures, the following differential equation is obtained [4]:

$$\frac{d\delta N}{dt} = -\frac{\delta N}{\tau} \quad (16)$$

where

$$\tau = \left[\left(\frac{d(\text{desorption}(N))}{dN} - \frac{d(\text{adsorption}(N))}{dN} \right)_{N_0} \right]^{-1} \quad (17)$$

In order to determine the power spectral density of the adsorbed molecules density fluctuation, Wiener–Khinchin theorem [19] can be applied. The theorem states that spectral density of a wide-sense stationary random process (domain $\omega \in (-\infty, \infty)$ is considered) is the Fourier transform of the corresponding autocorrelation function. Since frequencies can be only positive in physical processes, the above mentioned spectral density equals two times Fourier transform. Autocorrelation function is an even function, thus, factor two is included again, the power density spectrum of the adsorbed molecules density fluctuation writes [20]:

$$S_{\delta N} = 4 \int_0^{+\infty} \sigma^2 e^{-|t|/\tau} \cos \omega t dt = \frac{4\sigma^2 \tau}{1 + \omega^2 \tau^2}, \quad (18)$$

where σ^2 denotes the mean square value of δN .

As mentioned above, the experimental results of humidity measurements show that the concentration of detected matter affects the spectral density of frequency difference fluctuations. The low-frequency component ($1/f$ noise) changes insignificantly, while G–R component increases with a rise of concentration. Thus, it can be assumed that a shift of G–R noise is caused by increased flux density between the sorbent layer of QCM and the ambient environment. The increased flux of molecules corresponds to the increased variation of frequency difference fluctuations. Relation (18) can be rewritten

$$S_{\Delta f} = \frac{4\sigma_{\Delta f}^2 \tau}{1 + \omega^2 \tau^2}, \quad (19)$$

where $\sigma_{\Delta f}^2$ denotes the variance of frequency difference fluctuations. On the basis of the model and experimental results (frequency change and its second statistical moment), the time τ for molecule capture can be estimated. Concerning Fig. 4 and the

relative humidity 30% at frequency 2 Hz, the time constant equals to 1.26 μ s and is calculated on the basis of parameters estimated from the measurement, spectral density $S_{\Delta f} = 7.26 \times 10^{-6}$ Hz²/s and standard deviation $\sigma_{\Delta f} = 1.21$ Hz. For the relative humidity 70% at frequency 2 Hz, the time constant $\tau = 1.23$ μ s is calculated from values $S_{\Delta f} = 2.15 \times 10^{-5}$ Hz²/s and standard deviation $\sigma_{\Delta f} = 2.11$ Hz.

6. Conclusions

Experimental results showed that absorption of detected matter affects the frequency fluctuations. The paper focuses on adsorption–desorption noise without consideration of the diffusion process in an active layer, and presents its model, which is developed on the basis of the Kolmogorov equation for interaction between two reservoirs. The probability, that molecules will be captured on an active layer of the sensor, is proportional to the adsorbed molecule thermal velocity and the surface site cross section. The probabilities, that surface sites are free or occupied by molecules, are implied by the Kolmogorov equation in the case of thermodynamic equilibrium, when the flux of emitted particles is the same as the flux of captured particles on the active layer of the sensor. The derived probability distributions are similar to the Fermi–Dirac statistics for semiconductors. The surface density of adsorbed molecules is proportional to the surface site cross section, adsorbed molecule thermal velocity, concentration of adsorbed molecules and sensor surface density of the sites. The adsorption–desorption kinetics described by the Kolmogorov equation is compared with the Wolkenstein and Langmuir equations.

The observed relative changes of noise spectral density at different RH values correspond to the frequency shift. Further, these changes represent information, which can enhance selectivity and sensitivity of the QCM sensor. On the basis of the model and experimental results (frequency change and its second statistical moment), the time τ for molecule capture can be estimated which can give additional information about processes on the sorption layers. Thus, we can conclude that fluctuation enhanced noise sensing can be utilized for gas measurements by QCM sensors.

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Biographies

Petr Sedlak was born in 1980. He received his M.Sc. in 2003 and his Ph.D. in 2007 from Brno University of Technology. From 2007 to 2009, he was a postdoctoral researcher at the Department of Materials Engineering at the University of Tokyo, Japan. Currently, he is an assistant professor at the Department of physics at the Brno University of Technology. His research interests include fluctuation phenomena in solids, sensorics and non-destructive testing.

Josef Sikula was born in 1933. He received his M.Sc. degree in Electronics from the Technical University of Prague in 1957, and his M.Sc. degree in Physics from Komenský University, Bratislava in 1960. He received his Ph.D. degree in Semiconductor Physics in 1965. From 1980 he is Professor of Applied Physics at Brno University of Technology. In 1970 he founded a group dealing with studies of noise and fluctuation phenomena in solids. His main interests are the noise spectroscopy, non-destructive testing, and defect engineering. He received in 2006 Dr. Felix Zandman Passive Electronic Industry Technology Award in recognition of Acknowledged Industry Leadership and Perseverance of Vision.

Jiri Majzner was born in 1976. He received his M.Sc. in 2001 and his Ph.D. in 2008 from Brno University of Technology. His main interests are noise measurements, and non-destructive testing.

Martin Vršata was born in 1970. He received his M.Sc. in 1993 and Ph.D. in 1996 from Institute of Chemical Technology in Prague. Currently, he is an associated professor at the Department of Physics and Measurements, Institute of Chemical Technology in Prague. His research interest is focused on theory of gas sensing and application of organic semiconductors in sensors.

Premysl Fitl was born in 1980. He received his M.Sc. degree (Material Engineering) in 2004 and his Ph.D. degree (Materials for Electronics) in 2011 from Institute of Chemical Technology in Prague. Currently, he works as an assistant professor at the Department of Physics and Measurements at the Institute of Chemical Technology in Prague. His research interests include laser and vacuum deposition techniques, gas sensors and measurement of electro-physical properties.

Dusan Kopecký was born in 1983. He received his Ph.D. in 2009 from Institute of Chemical Technology in Prague. Currently, he is an assistant professor at the Department of Physics and Measurements, Institute of Chemical Technology, Prague. His work deals with chemical gas sensors based on organic semiconductors with specialization on laser deposition methods.

Filip Vysloulzil was born in Prague in 1971. He received his M.Sc. in 1996 and Ph.D. in 1999 from Institute of Chemical Technology in Prague. He is interested in chemical gas sensors. Currently he works at Institute of Chemical Technology in Prague.

Peter H. Handel is a professor at Department of Physics and Astronomy at University of Missouri. He received his MS in physics from University of Bucharest, Romania, 1959; and Doctoral degree in Solid State Physics, at the same university in 1965. His main scientific contributions include the quantum $1/f$ noise effects, contributions to the theory of instabilities and turbulence, inclusion of spin–orbit effects into the index of refraction formalism for slow neutrons and others.

PAPER

Polypyrrole–silver composites prepared by the reduction of silver ions with polypyrrole nanotubes

Cite this: *Polym. Chem.*, 2013, **4**, 3610Jitka Škodová,^a Dušan Kopecký,^a Martin Vrnáta,^{*a} Martin Varga,^b Jan Prokeš,^b Miroslav Cieslar,^b Patrycja Bober^c and Jaroslav Stejskal^c

Polypyrrole nanotubes were prepared by the oxidation of pyrrole with iron(III) chloride in the presence of methyl orange. They were subsequently used for the reduction of silver ions to silver nanoparticles. The nanotubular form of polypyrrole is compared with the classical globular morphology in its ability to reduce silver ions. Both polypyrrole salts and bases were used in the experiments. The content of metallic silver in the resulting composite, determined by thermogravimetric analysis, was 21–31 wt%. Elemental composition is also discussed on the basis of energy-dispersive X-ray spectroscopy. Contrary to the expectation, the conductivity of polypyrrole nanotubes in salt form, 35.7 S cm^{-1} , was reduced to 20.9 S cm^{-1} after the incorporation of silver. The presence of silver had generally little effect on the conductivity. The temperature dependence of conductivity reveals that the composites maintain the semiconducting character of polypyrrole and their conductivity increased with increasing temperature. The conductivity of the composites surprisingly increased when the samples were placed *in vacuo*.

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Introduction

The combination of conducting polymers and noble metal nanoparticles has recently become a tool in the preparation of new materials. The composites combining two conducting components, a metal and an organic semiconductor, are expected to exhibit a good level of electrical conductivity, as well as tunable physical, chemical, and responsive properties. Among them, polypyrrole (PPy) and polyaniline (PANI) composites with silver have become frequently studied.¹

The ability of PPy to reduce silver ions to metallic silver has been reported many times. The paper by Pickup *et al.*² is important from a historical point of view. In this early study, the authors illustrated the ability of electrochemically prepared PPy film to reduce silver ions to silver, and this was confirmed in follow-up experiments.^{3,4} The progress of reaction, the reduction of silver cations on PPy film, was followed by a quartz microbalance.⁵ This reaction was used especially for silver recovery from solutions of its salt.² Counter-ions in PPy were demonstrated to have a significant effect on the silver yield,⁶ because some of them, such as chlorides or, to a certain extent, sulfates, may form insoluble salts with silver cations. Polypyrrole was also deposited on supports, such as sawdust⁷ or

porous carbon⁸ for recovery purposes. In addition, some studies assumed the complexation of silver ions with nitrogen atoms in PPy,⁸ rather than the chemical reaction between both species. Polypyrrole was used as-prepared, *i.e.* in the form of salt. Only exceptionally it was reduced with sodium borohydride at first,⁹ or converted to PPy base in alkalis. Recent applications concern, *e.g.*, supports for surface-enhanced Raman scattering,¹⁰ catalytic reduction of hydrogen peroxide¹⁰ or efficient antimicrobial agents.¹¹

Depending on the conditions, the reduction of silver ions with PPy yielded silver particles with sizes below 10 nm,^{12,13} tens of nanometres or micrometres.^{10,11,14} Larger objects, such as silver triangles,⁵ nanosheets^{15,16} and nanocables,^{17,18} have also been observed.

The morphology of PPy entering the reaction was also considered, and attention has been paid especially to nanotubes. PPy nanotubes were prepared by the coating of vanadium(v) oxide nanowires with PPy and subsequent dissolution of the template. When exposed to silver nitrate solutions, 4–8 nm silver nanoparticles were produced on their surface and also agglomerated inside the nanotube cavity.¹⁹ Aluminium oxide membranes have been used as a hard template for the reduction of silver ions.¹¹ Similar experiments have also been made with PANI nanotubes and silver was occasionally located inside the nanotubes.^{20,21} In another approach, PPy nanotubes, prepared in the presence of methyl orange as a structure-guiding agent, were immersed in silver nitrate solution and thus decorated on the surface with silver nanoparticles.^{22–24} In these experiments, however, poly(*N*-vinylpyrrolidone) has been

^aFaculty of Chemical Engineering, Institute of Chemical Technology Prague, 166 28 Prague 6, Czech Republic. E-mail: vrnatam@vscht.cz

^bCharles University in Prague, Faculty of Mathematics and Physics, 180 00 Prague 8, Czech Republic

^cInstitute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

used as an additive to prevent the aggregation of silver nanoparticles. Another report used similar PPy nanotubes functionalized with carboxyl groups.¹⁰

In the present study, PPy nanotubes were prepared also in the presence of methyl orange, but in the absence of any additives and without any modification. Their ability to reduce silver ions is compared with that of the classical globular form of PPy. In addition, both PPy salts and PPy bases have been used in the experiments. Attention has been paid especially to the electrical conductivity of the composites.

Experimental

Preparation of granular PPy and PPy nanotubes

Granular PPy was prepared by the chemical polymerization of pyrrole monomer with iron(III) chloride hexahydrate at an equimolar ratio in water. Iron(III) chloride hexahydrate (3.9 g; 14 mmol) was dissolved in 287 mL of distilled water, then pyrrole (1 mL; 14 mmol) was added. Molar concentrations of both reactants were 50 mM, the total volume of reaction mixture was 288 mL. The stirred reaction mixture was kept at 5 °C for 24 h. The precipitated PPy was separated by filtration, rinsed with acetone and ethanol, and dried at 40 °C *in vacuo*.

Polypyrrole nanotubes were synthesized in a similar manner in the presence of structure-guiding agent, methyl orange, (4-[4-(dimethylamino)phenylazo]benzenesulfonic acid sodium salt).^{10,22–24} Methyl orange solution in distilled water (287 mL; 2.5 mM) and pyrrole (1 mL) were mixed. Then iron(III) chloride hexahydrate (3.9 g) was dissolved in distilled water (33 mL) and added dropwise over two hours into the reaction solution. Both solutions were cooled to 5 °C before mixing. Thus the molar concentrations of reactants were 45 mM pyrrole, 45 mM iron(III) chloride hexahydrate, and 2.2 mM methyl orange. After 24 h, precipitated PPy nanotubes were separated by filtration, rinsed with water and subsequently purified by Soxhlet extraction to remove residual methyl orange using acetone until the extract was colourless. Finally, extracted PPy was rinsed with ethanol. Polypyrrole nanotubes were dried as above. Parts of PPy salts were converted to the corresponding bases²⁵ by immersion in an excess of 1 M ammonium hydroxide, rinsed with acetone, and dried. Thus obtained PPy powders of salts or bases were immersed in an excess of 0.1 M aqueous solution of silver nitrate and left for 24 h to interact. The solids were collected on a filter, rinsed with water, and dried. Nitric acid is the by-product of these reactions⁴ and its presence could cause a partial reprotonation of the original PPy bases.

Characterization

A transmission electron microscope (TEM) JEOL JEM 2000 FX was used to assess the morphology. Thermogravimetric analysis (TGA) was performed in a 50 cm³ min^{−1} air flow at a heating rate of 10 °C min^{−1} with a Perkin Elmer TGA 7 Thermogravimetric Analyzer. Elemental analysis was done with an elemental analyzer Elementar Vario EL III (Elementar Analysensysteme GmbH) with accuracy <0.1 wt%. Surface composition was characterized by energy-dispersive X-ray

spectroscopy (EDS) using a JEOL JXA 50A electron microprobe equipped with a Bruker AXS 4010 XFlash SD detector. The conductivity of the granular PPy was estimated from powder placed between two conducting pistons by a two-probe method with an applied pressure of *ca* 23 kPa and using a Keithley 6517 electrometer. In contrast to the nanotubes, granular PPy could not be compressed to pellets. The room temperature conductivity of PPy nanotubes was determined on pellets compressed at 700 MPa by a four-point method in the van der Pauw arrangement using a Keithley 220 Programmable Current Source, a Keithley 2010 Multimeter as a voltmeter and a Keithley 705 Scanner equipped with a Keithley 7052 Matrix Card.

The temperature dependence of conductivity in the range of 2–318 K, and conductivity under dynamic vacuum ($\sim$ units of Pa), were measured on a commercial device Quantum Design PPMS by the conventional four-point method on bar-shaped samples where current probes were placed on the edges of the bar and voltage probes were situated in the middle of the bar.

Results and discussion

Polypyrrole prepared by the oxidation of pyrrole in acidic aqueous media is obtained as a salt. In an idealized case, proposed in analogy with PANI,²⁵ the PPy salts convert to PPy bases when exposed to alkalis, such as ammonium hydroxide (Fig. 1). While in the case of PANI the salt–base transition has been well established, in the case of PPy it is mentioned only rarely and in the course of other studies.^{26–28}

Both the PPy salt and PPy base are able to reduce silver cations to silver. A formal reaction scheme of the reduction of silver ions with PPy can be proposed (Fig. 2), again in analogy with a similar reaction involving a closely related polymer, PANI. In the latter case, the emeraldine form of PANI converts to pernigraniline^{29,30} and silver ions are reduced to silver metal. As the reaction between silver ions and PPy has been proven to take place, an oxidized form of PPy, and an analogous form of pernigraniline in PANI, is likely to exist (Fig. 2).

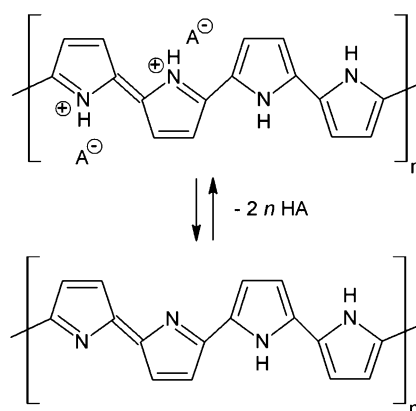


Fig. 1 PPy salts convert in alkaline media to the corresponding base. HA is an arbitrary acid, here hydrochloric acid.

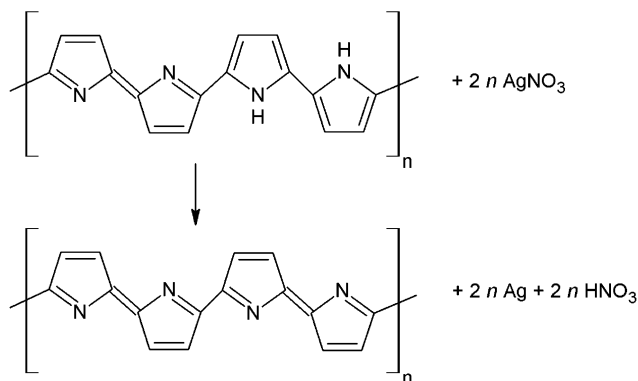


Fig. 2 PPy base reduces silver salts, such as silver nitrate, to metallic silver. Nitric acid is a by-product.

Polypyrrole morphology

The classical oxidation of pyrrole with iron(III) chloride in water yields PPy with a globular morphology (Fig. 3a). The introduction of a small amount of some additives, such as *p*-phenylenediamine, was demonstrated to considerably affect the morphology of PANI.³¹ The presence of methyl orange in the oxidation of pyrrole results in the formation of nanotubes (Fig. 3b). The nanotubular morphology, *i.e.* the existence of the cavity, is demonstrated by transmission electron microscopy (Fig. 4). Both PPy morphologies, globules and nanotubes, in their salt and base forms, have been tested for their ability to reduce silver ions.

Reduction of silver ions with PPy

Transmission electron microscopy is a convenient tool in the assessment of PPy–silver composites as it provides a good contrast between both phases (Fig. 5–8). The reaction of globular PPy salt with silver ions generates aggregates of silver nanofibers (Fig. 5). On the contrary, the nanotubular PPy salt produces aggregates of globular nanoparticles (Fig. 6).

The PPy bases act in a different manner. The globular PPy base enforced the globular morphology to silver (Fig. 7), while PPy nanotubes provide flower-like silver aggregates (Fig. 8). It has to be stressed, that PPy and silver are separated in all cases. The micrographs, however, show just a small part of the sample and need not represent the sample as a whole.

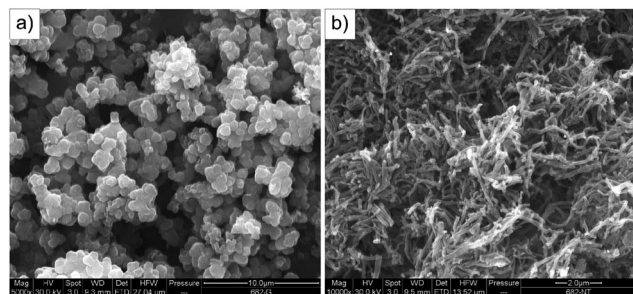


Fig. 3 Scanning electron microscopy of (a) granular and (b) nanotubular PPy.

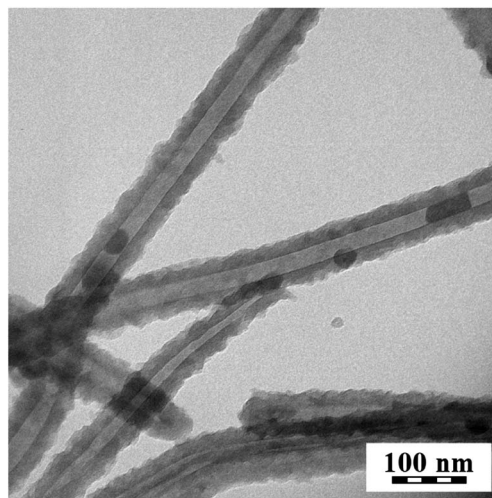


Fig. 4 Transmission electron microscopy illustration of nanotubular structure.

Silver content and elemental analysis

The silver content in the composites is an important factor. Stoichiometry according to Fig. 2 expects 45.7 wt% Ag. The silver content (Table 1) can be determined by thermogravimetric analysis of a residue (Fig. 9). The analysis has to be made in air; in nitrogen PPy is carbonized,^{32,33} but not decomposed, similarly to PANI^{34,35} and the residue after analysis would be much higher. Even in air, PPy alone leaves a residue of 3.1 or 3.8 wt% for globular and nanotubular forms, respectively, which was subtracted when calculating the silver content, and is associated most likely with iron oxides.

The results of the elemental analysis of C, H, and N (Table 1) refer only to the PPy part of the composite, but not to the composite as a whole. After the conversion of the PPy salts to bases, the relative contents of carbon and nitrogen increase, due to the removal of inorganic acid (Fig. 1). The content of sulfur (associated with the potential presence of methyl orange) was below the detection limit.

Elemental composition by EDS

The subsequent analysis has been limited to PPy nanotubes only, as they are a more interesting object from the

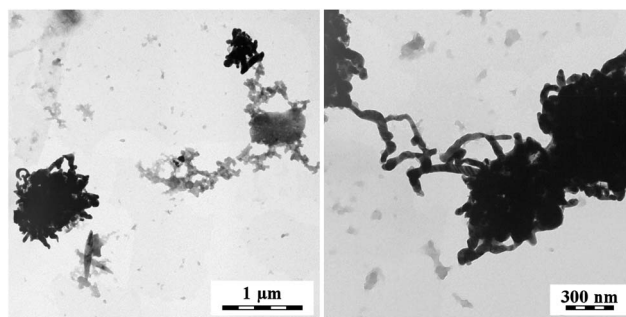


Fig. 5 PPy composites obtained by the reduction of silver nitrate with *globular* PPy salt. Two magnifications.

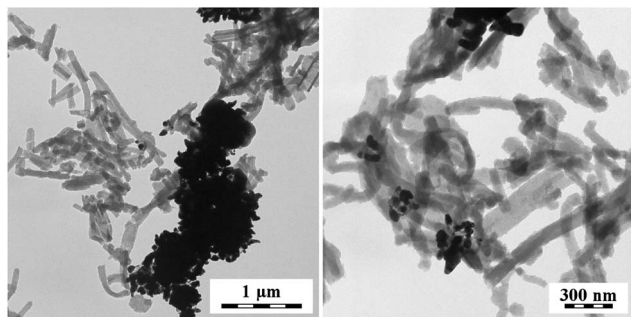


Fig. 6 PPY composites obtained by the reduction of silver nitrate with *nanotubular* PPY salt. Two magnifications.

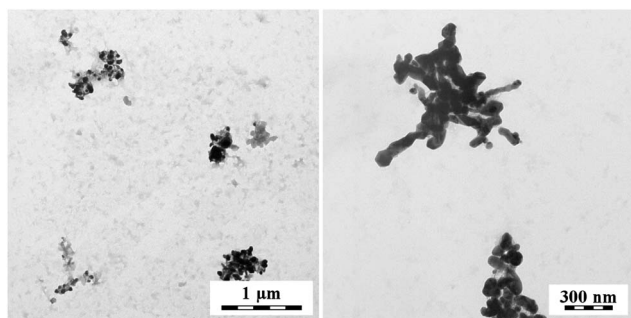


Fig. 7 PPY composites obtained by the reduction of silver nitrate with *globular* PPY base. Two magnifications.

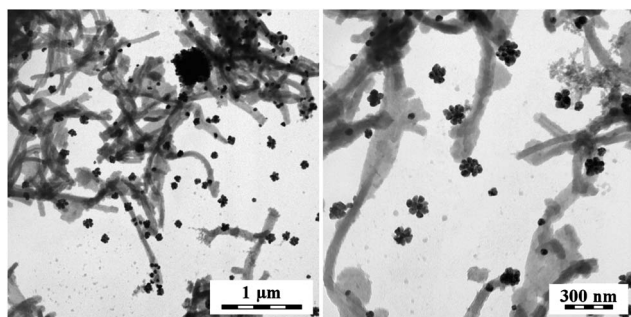


Fig. 8 PPY composites obtained by the reduction of silver nitrate with *nanotubular* PPY base. Two magnifications.

Table 1 Composition and conductivity of PPY salts and bases before and after deposition of silver

Polypyrrole	Composition [wt%]				Conductivity [S cm^{-1}]	
	Ag	C	H	N	As prepared	With silver
Nanotubes, salt	21.1	57.7	4.6	16.2	35.7	20.9
Nanotubes, base	15.3	61.3	4.6	17.2	0.056	1.38
Globular, salt	21.0	56.0	4.4	16.5	0.012	0.028
Globular, base	30.6	61.5	4.3	17.4	3.7×10^{-5}	1.1×10^{-4}

morphological point of view. EDS is a straightforward way to prove the presence of silver in the composites and to

determine its content (Table 2). From this point of view, nanotubular PPY salt seems to be a more efficient reducing agent (compared with PPY base) of silver ions. A more critical observer, however, may object that a part of silver in the composite with PPY salt may be present as silver chloride, due to chloride ions originating from iron(III) chloride oxidant. Indeed, after the deprotonation of the composite with ammonium hydroxide, which would dissolve silver chloride, the content of silver would be reduced, as observed. Furthermore, the previous study³⁶ devoted to a similar study on PANI protonated with various acids (H^+A^-) revealed that the decreasing solubility product of the corresponding silver salt (Ag^+A^-) correlates with the increasing content of silver in the resulting composite, either in the form of insoluble salt or in metallic form. On the other hand, there was no connection between the presence of silver salt and conductivity of the composite.

The content of silver determined by EDS (Table 2) is considerably lower than by TGA (Table 1). This is due to the fact that EDS characterizes especially the composite surface, which may differ in silver content from the bulk materials characterized by TGA. It has often been observed that silver particles are coated with PPY^{1,37} and this may reduce the silver participation observed by EDS.

Polypyrrole formulae shown in Fig. 1 and 2 are idealized but serve well for the discussion of many PPY properties. A more realistic view has to account for the presence of oxygen atoms in the PPY structure. While the C/N atomic ratio is lower than the theoretical value of 4, as much as one oxygen atom per nitrogen atom seem to be present in reality (Table 2). This is probably a similar situation as with polyaniline, in which the quinonoid and semiquinonoid constitutional units have to be considered³⁸ in addition to the classical concept based entirely on nitrogen-based structures.

The presence of sulfur atoms in the composites (Table 2) suggests the presence of methyl orange, which could not be removed completely, even after exhaustive extraction with acetone. The content of this dye is reduced after deprotonation with ammonium hydroxide but can still be identified in PPY bases. The sulfonate group in methyl orange may also contribute to the oxygen content.

The fact that PPY constitutes a salt with hydrochloric acid (Fig. 1) produced by the hydrolysis of oxidant, iron(III) chloride, is well illustrated by the presence of chlorine atoms (Table 2). The stoichiometry shown in Fig. 1 assumes the Cl/N ratio of 0.5. A considerably lower value is observed in the EDS experiment (Table 2). This can be explained by various means, the washing of samples with water and subsequent partial deprotonation seems to be the most plausible reason.

The deprotonation of PPY salt to PPY base after the treatment with ammonium hydroxide solution is well documented by the reduction of the content of chloride counter-ions (Table 2, Fig. 1). The fact that the oxidized form of PPY in PPY-silver composites has a lower degree of protonation is also supported by EDS (Table 2). The observation of a small amount of iron atoms suggests the presence of complex FeCl_4^- counter-ions in addition to simple chlorides.

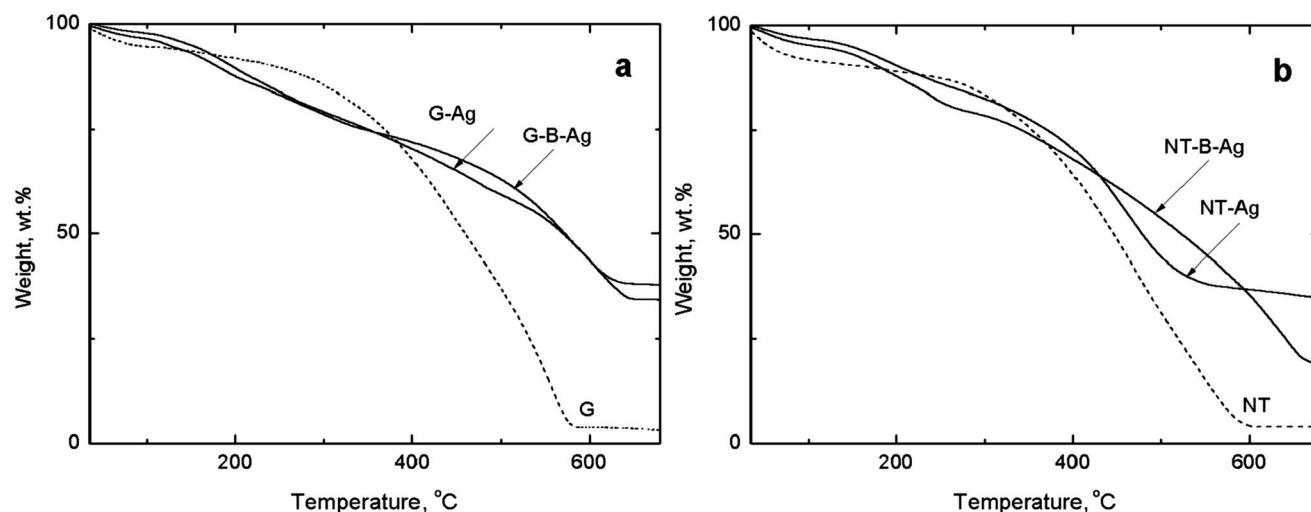


Fig. 9 Thermogravimetric analysis of (a) globular and (b) nanotubular PPy and the composites of its salt and base forms with silver.

Table 2 Elemental composition of the PPy nanotubes and its composites with silver determined by EDS (wt%) and selected atomic ratios

Sample	Ag	C	N	O	S	Cl	Fe	C/N	O/N	Cl/N
PPy	—	58.1	19.3	11.3	2.5	8.0	0.8	3.54	0.51	0.16
PPy/Ag	13.7	45.6	14.9	17.9	2.5	4.8	0.6	3.57	1.05	0.13
PPy base	—	60.5	20.4	16.3	1.5	0.9	0.3	3.45	0.70	0.02
PPy base/Ag	8.5	48.5	18.4	21.2	1.7	1.6	0.1	3.07	1.01	0.03

Conductivity

The conductivity of the PPy nanotubes, 35.7 S cm^{-1} , is considerably higher than that of the globular form (Table 1) and also of other conducting polymers, such as polyaniline.³⁰ This value was confirmed in repeated experiments. The deposition of silver reduced the conductivity PPy nanotubes (Table 1) due to the expected oxidation of PPy (Fig. 2).

It has been reported that the conductivity of PPy increased when its preparation was carried out in the presence of anionic surfactants bearing a sulfonic group.^{39,40} Molecules of water-soluble organic dyes are generally composed of a large light-absorbing system of conjugated double bonds and ionic groups, such as a sulfonic group, that ensure the solubility. They therefore resemble surfactants from a colloidal point of view. Methyl orange, a molecule having also a large organic part and a terminal sulfonic group, may thus play a similar role as surfactants and be responsible for good conduction.

In addition to an exceptionally high level of conductivity, PPy nanotubes maintain a good level of conductivity, 0.056 S cm^{-1} (Table 1), after treatment with ammonia solutions and consequent conversion to PPy base (Fig. 1). This is an even higher value than the conductivity of PPy salt in globular form, as confirmed in repeated experiments. This is an important observation, especially for potential applications in biomedicine, such as hyperthermal cancer therapy,⁴¹ where a good level of conductivity has to be maintained as physiological $\text{pH} \geq 7$. In this case, the incorporation of silver resulted in a moderate

increase in the conductivity to 1.38 S cm^{-1} (Table 1), which would be an additional benefit of PPy–silver composites in these types of applications.

Temperature and time dependence of conductivity

Polypyrrole nanotubes exhibit semiconducting behaviour, as obvious from the temperature dependence of conductivity (Fig. 10) where conductivity increases with increasing temperature, with a large conductivity ratio $\sigma(300 \text{ K})/\sigma(2 \text{ K}) \approx 128$ for PPy salt nanotubes alone and 16 700 for the composite with silver, respectively, where measurements could be performed down to 2 K. This ratio was $\sigma(300 \text{ K})/\sigma(77 \text{ K}) \sim 41\,000$ for PPy base and 54 for the composite with silver, respectively, where resistance was too high to be determined at 2 K. Such a high value of ratio is typical for highly disordered materials at the insulator side far away from the metal–insulator transition.⁴²

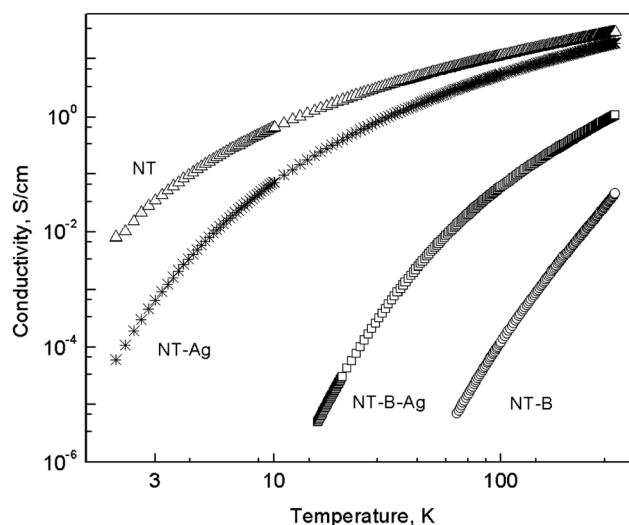


Fig. 10 Temperature dependence of the conductivity of the PPy nanotubes in salt and base (B) forms and of their composites with silver.

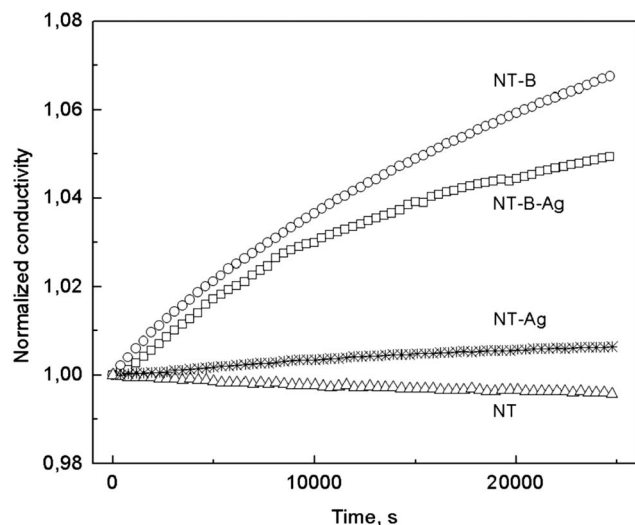


Fig. 11 Time evolution of conductivity normalized to the initial value for PPy nanotubes in dynamic vacuum (units of Pa).

The amount of silver in the composites, *i.e.* 15–30 wt% (Table 1), is then not sufficient for the formation of metallic conducting pathways and, from this point of view, the composites lie in the region below any percolation threshold. Silver nanoparticles thus have probably only a secondary influence on the charge transport properties of composites leaving the key role to the conducting polymer matrix in a similar way as it was observed in PANI–silver composites.⁴³ However, its effect is not easy to understand since, in the case of nanotubular PPy base, silver enhances electrical conductivity and decreases its temperature dependence while for nanotubular PPy salt the effect is exactly opposite, but much smaller. From the TEM study we know that there are differences in morphology that can give at least intuitive insight. Silver nanoparticles form relatively uniformly dispersed small clusters outside the nanotubes (Fig. 8). Then, silver possibly can participate in transport *via* tunnelling between these metallic islands as it was proposed for granular metals.⁴⁴ On the other hand, large clusters formed close to nanotubes were found for salts (Fig. 6), but their contribution to transport may be negligible and overall conductivity is probably decreased by the oxidation of PPy salt. Further and deeper analysis and measurements, *e.g.*, magnetoconductance, are essential for the understanding of the charge transport in such a complex system and will be reported in a separate paper.

The effect of dynamic vacuum, in particular moisture removal, on conductivity was also studied (Fig. 11). It turned out to be surprisingly positive, but at the same time it is almost negligible in contrast to other conducting polymer systems, for instance, to recently published results for PANI hydrochloride pellets where moisture is believed to influence conductivity more.⁴⁵

Conclusions

(1) Polypyrrole is able to reduce silver ions to metallic silver. This applies both to granular and nanotubular forms of PPy, and both to PPy salts and PPy bases.

(2) Polypyrrole salt produces other silver morphologies than the PPy base does. The content of silver is higher in the composites prepared from PPy salts than from PPy bases. Clusters of silver nanoparticles are generated outside PPy. Silver is not produced inside nanotubes.

(3) When PPy salt containing chloride counter-ions reacts with silver nitrate solution, one has to admit that a certain part of silver ions is rather precipitated in the form of water-insoluble silver chloride than reduced into metallic silver.⁶

(4) The conductivity of PPy nanotubes is high, 35.7 S cm^{-1} , and is moderately reduced by the incorporation of silver. PPy nanotubes maintain a good level of conductivity, 0.056 S cm^{-1} , even after deprotonation with ammonia solution. In the latter case, the presence of silver increased the conductivity to 1.38 S cm^{-1} . This is a high level when considering the potential operation under alkaline conditions.

(5) All PPy samples exhibit semiconducting behaviour and very high temperature resistivity ratio. Silver is believed to have only a secondary role in charge transport in PPy salts. In less conducting PPy bases, it enhances the charge transport. Further, the electrical properties of PPy salts are very stable against applied dynamic vacuum, especially against potential moisture removal.

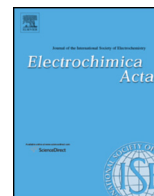
Acknowledgements

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Application of polyaniline for potentiometric recognition of salicylate and its analogues



Tatiana V. Shishkanova^{a,*}, Kateřina Videnská^a, Svetlana G. Antonova^b, Martin Krondřák^a, Přemysl Fitl^c, Dušan Kopecký^c, Martin Vršnáta^c, Vladimír Král^a

^a Department of Analytical Chemistry, Institute of Chemical Technology in Prague, Technická 5, 166 28 Prague 6, Czech Republic

^b Department of Physical and Analytical Chemistry, Tomsk Polytechnic University, Lenin Avenue 30, 634050 Tomsk, Russia

^c Department of Physics and Measurements, Institute of Chemical Technology in Prague, Technická 5, 166 28 Prague 6, Czech Republic

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ABSTRACT

Presented work proves usability of polyaniline (PANI) as a receptor for potentiometric detection of salicylates. The potentiometric selectivity of PANI-coated membranes based on tridodecylmethylammonium chloride (TDDMACl) towards salicylate is at least as good as the selectivity of membranes based on “conventional” specific supramolecular receptor systems such as Sn(IV) and Al(III) phthalocyanates. X-ray diffraction (XRD) and electric impedance spectroscopy (EIS) techniques are used to insight into the phenomena leading to improvement of salicylate-selectivity of PANI. These studies reveal the relative role of sodium chloride during the PANI polymerization that leads to preparing of partially crystalline polymer and decreasing of the “bulk” resistance of membrane. The “bulk” resistance change is attributed to introduction of the electronic conductivity into the system PANI/Salicylate. Determination of acetylsalicylate in pharmaceutical preparations with recovery at about 98–100% is reported. Additionally, the ability to detect $(0.11 \pm 0.01) \times 10^{-3}$ M of salicylate present in a synthetic serum sample is demonstrated.

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1. Introduction

Potentiometric detection based on ion-selective electrodes (ISEs) is a simple method that offers great advantages such as high speed of measuring process, reasonable selectivity, wide linear dynamic range and low cost. Because of their selectivity, small size, portability and low cost, the potentiometric sensors are instruments being successfully applied in both chemical and clinical analyses. In contrast to the first impression, the development of potentiometric sensor is not easy due to the necessity to design a receptor capable of providing selective complex analyte of interest. An illustrative example can be the development of sensors for potentiometric detection of salicylate and its analogues, including acetylsalicylate (aspirin). The reliable salicylate-selective potentiometric sensor attracts lasting interest in the field of both medical and pharmaceutical applications [1]. A number of synthetic receptors based on guanidinium [2], metalloporphyrins [1], metallophthalocyanates [3], metallosalophenes [4], and metallocenes [5] have been proposed. Their selectivity is based on a biomimetic approach [2], a specific coordination of salicylate to metal center [1,3,4] or a specific interaction of salicylate with π -electron accepting system of receptor [5].

Conducting polymers (CPs) have found widespread use in the development of sensor technology [6] and in biomedical engineering [7,8]. Polyaniline (PANI) has proven useful for electrochemical detection of biologically active molecules, such as anticancer drugs [9], immunosuppressives [10], antibiotics [11]. The corresponding electrodes were often covered with a PANI composite [12], nanostructured PANI [13] or PANI immobilized onto silver nanoparticles/carbon multiwalled nanotubes [14]. Special attention was also paid to the dimensional CPs that exhibit unique properties such as greater conductivity and more catalytic activity [13,15]. These materials can be combined with metallic and semiconducting supports and open new perspectives for a development of sensor surface and properties [14,16,17]. Example of such biosensor can be polyphenol biosensor based on silver nanoparticles/carbon multiwalled nanotubes/PANI [14]. In contrary to earlier enzyme sensors, it has no leakage of enzyme during reuse and is unaffected by the external environment due to the protective PANI microenvironment.

Based on the above-mentioned trends, the purpose of this contribution is to introduce a new kind of receptor system for the potentiometric detection of salicylate and its analogues. The key innovation lies in replacing specific supramolecular receptor with a conducting polymer, specifically PANI. The salicylate-selectivity of PANI as a receptor of potentiometric sensor is discussed. The relations between PANI structure and its sensing properties are analyzed. Finally, applicability of proposed potentiometric sensor

* Corresponding author. Tel.: +420 220 444 227, fax: +420 220 444 352.

E-mail address: Tatiana.Shishkanova@vscht.cz (T.V. Shishkanova).

Table 1
Potentiometric characteristics for uncoated (A) and PANI-coated (B, C) membranes.

Membrane (composition)	Chloride	Acetate	Benzoate	Salicylate
	Slope, mV/decade* Linear range, M	Slope, mV/decade* Linear range, M	Slope, mV/decade* Linear range, M	Slope, mV/decade* Linear range, M
A (TDDMACI)	–39 (6.4) 2×10^{-3} – 2×10^{-2}	–53 (9.8) 2×10^{-4} – 2×10^{-2}	–45 (3.5) 2×10^{-4} – 2×10^{-2}	–59 (2.3) 2×10^{-4} – 2×10^{-2}
B (TDDMACI/PANI)	–64 (3.1) 4×10^{-6} – 2×10^{-2}	–68 (6.8) 2×10^{-4} – 2×10^{-2}	–67 (3.8) 4×10^{-6} – 2×10^{-2}	–76 (4.0) 4×10^{-6} – 2×10^{-2}
C (TDDMACI/PANI + NaCl)	–52 (0.7) 4×10^{-6} – 2×10^{-2}	–58 (6.1) 2×10^{-4} – 2×10^{-2}	–60 (1.0) 4×10^{-6} – 2×10^{-2}	–62 (1.6) 4×10^{-6} – 2×10^{-2}

* The values of relative standard deviation for slope of set of sensors ($n = 3$) based on tested membranes are given in parentheses

in two areas of practical interest is demonstrated: measuring of salicylate in a synthetic serum and monitoring of acetylsalicylate in drugs.

2. Experimental

2.1. Reagents

Poly(vinyl chloride) (PVC) of high molecular weight, 2-nitrophenyl octyl ether (NPOE), tridodecylmethylammonium chloride (TDDMACI), tetrahydrofuran (THF, stored over a molecular sieve) were purchased from Fluka (Selectophore grade, Switzerland). Aniline (>99%) and 2-[4-(2-hydroxyethyl)-1-piperazino]-ethanesulfonic acid (HEPES) were obtained from Sigma-Aldrich (Germany). Acids and various inorganic/organic salts of analytical grade used in the potentiometric measurements were bought from Lachema (Czech Republic). The commercial tablets of aspirin C (Bayer Bitterfeld GmbH, Greppin, Germany Herbacos-Bofarma, s.r.o.), acylpyrin (Zentiva, a.s., Czech republic), acylcoffin (Hlohovec, Slovak republic) used in this study were purchased at a local drugstore in Prague. All standard solutions and buffers were prepared using distilled water.

2.2. Preparation of membranes and deposition of polyaniline

The membranes were prepared by dissolving 3 mg of TDDMACI, 32.3 mg of NPOE and 64.7 mg of PVC in 1.0 mL THF at ambient temperature. The prepared membrane mixture was deposited onto a metallic ring of 16 mm internal diameter resting on a glass plate, and dried in air.

The oxidation polymerization of aniline was carried out with 10 ml of aqueous solution of aniline (0.08 M) and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.08 M) in 1.5 M HCl at 0 °C in the presence of TDDMACI-based membrane immersed in the reaction medium. When specified, 3.3 M NaCl was added in the polymerization mixture [16,17]. Uncoated membrane is referred to as membrane A. The membranes coated with PANI in the absence or in the presence of NaCl are referred to as membranes B and C, respectively. After polymerization, the PANI-coated membrane was removed, rinsed with 1.5 M HCl aqueous solution [18], treated ultrasonically for 10 min in 1.5 M HCl aqueous solution and dried at ambient temperature.

2.3. Potentiometric measurements

A disk of 10-mm diameter was punched from ion-selective membranes prepared as described above, glued onto a polymeric ring of 8 mm internal diameter with a PVC/THF paste, and mounted in the electrode body for potentiometric measurements. All measurements were carried out at ambient temperature with cell of the following type:

Ag; AgCl; 3 M KCl || sample solution | membrane | inner filling solution; AgCl; Ag.

An aqueous solution of 10^{-3} M corresponding sodium salt was used as the inner filling of the electrode. Prior to the potentiometric experiment, the electrodes were soaked in a solution of 10^{-3} M corresponding sodium salt. The potentiometric response (ΔE) was measured with digital ion-meter PHI 04 MG (Labio, Czech Republic). The potentiometric response of the prepared membranes toward chosen analytes (Table 1) was observed by adding 2 μL , 10 μL , 100 μL , 1 mL and 10 mL of the corresponding sodium salt solution (0.1 M) into 50 mL of stirred water solution ($\text{pH } 5.5 \pm 0.3$). After the potentiometric measurements the PANI-coated membranes were regenerated in 0.02 M NaOH for 10 min and then washed with distilled water for 1 min.

The values of potentiometric selectivity coefficients ($\log K^{\text{Pot}}_{\text{I,J}}$) were determined by the separate solution method (SSM) [19] with the primary ($\text{I} = \text{salicylate}$) and interfering ($\text{J} = \text{chloride, acetate, benzoate}$) ions at concentration being 0.01 M in aqueous solution at $\text{pH } 5.5 \pm 0.3$ (Table 2).

A program ACD/LogP DB was used to calculate the logarithm of partition coefficient ($\log P$) values for a series of studied carboxylates.

2.4. Electric impedance spectroscopy measurements

All electric impedance spectroscopy (EIS) measurements were carried out using Potentiostat/Galvanostat M263 (PAR, Princeton, USA) connected with Lock-in amplifier 5110 (EG&A, Wellesley, USA). Measurements were realized in the frequency range of 0.1 MHz–0.01 Hz in 0.01 M testing aqueous solution in a shielded cell. The cell consisted of two acryl cuvettes ($10 \times 10 \times 45$ mm) separated by membrane of 0.785 cm^2 area. The experimental membrane was glued between the two compartments of the measuring cell using mixture of PVC and THF. Before EIS measurements both sides of the fixed membrane were soaked overnight in 0.01 M aqueous solution of the tested analyte. Both cell compartments were filled with sodium salt of the studied analyte. The electrodes were placed into both compartments.

Table 2
Comparison of potentiometric selectivity coefficients ($\log K^{\text{Pot}}_{\text{Salicylate,J}}$) for the membranes obtained in this work with the ones described in the literature.

Membrane	Chloride	Acetate	Benzoate
Membrane A (TDDMACI)	–	–1.9	–1.6
Membrane C (TDDMACI/PANI + NaCl)	–3.0	–3.4	–2.1
Aliquat 336S [26]	–1.96	<–2.7	–1.15
Sn[TPP]Cl ₂ [1]	–3.8	–3.9	–1.4
Sn (IV) phthalocyanate [3]	–1.53	–1.84	–1.12
Al(III) phthalocyanate [3]	–1.85	–1.7	–1.12

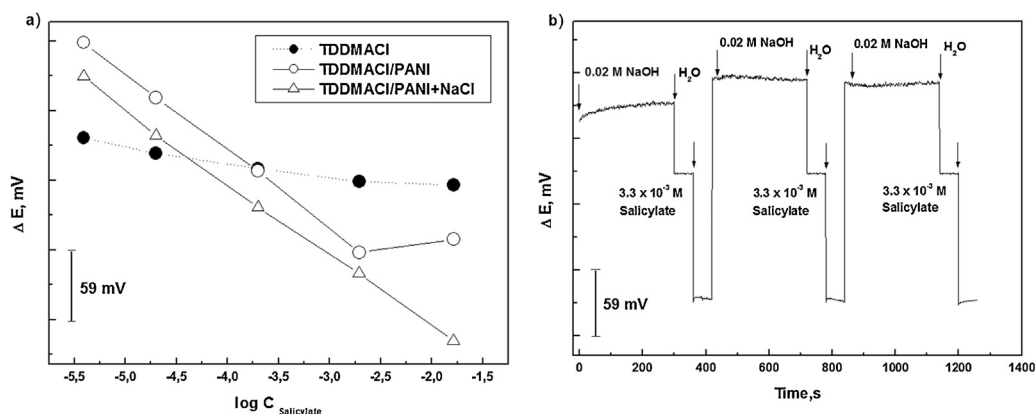


Fig. 1. (a) Potentiometric responses for uncoated membrane (●) and membranes coated by PANI in absence (○) and in presence of NaCl (Δ) recorded after 15 days. (b) Repeatability of the potentiometric response of the membrane (TDDMACI/PANI + NaCl) toward 3.3×10^{-3} M salicylate after regeneration in 0.02 M NaOH and water within day.

2.5. Structural characterization of polyaniline

X-ray diffraction (XRD) experiments of the PANI samples obtained by polymerization in absence and in the presence of NaCl were carried out at ambient temperature using Philips X'Pert diffractometer in reflection mode ($\text{CuK}\alpha$, radiation, $\lambda = 1.542 \text{ \AA}$).

2.6. Analytical application

The determination of both acetylsalicylic acid in pharmaceutical preparations and salicylic acid in synthetic serum sample was performed using the method of standard addition [20]. The potentiometric analysis of analgesics was carried out (without subjecting acetylsalicylic acid to hydrolysis) at 0.1 M HEPES with pH = 7.1. The procedure of preparation and analysis of acetylsalicylic acid was taken from [21]. The composition of synthetic serum was prepared accordingly to Ref. [4,22] in aqueous solution.

3. Results and Discussion

Our previous findings led us to conclusion that the ordering PANI film should be potentially useful for potentiometric applications [23]. This key problem was solved on the basis of the results published by prof. N. Gospodinova [16,17] and studies conducted within project "COST-STSM-P12-01673" [24]. Prof. N. Gospodinova et al. have demonstrated that the high concentration of NaCl in the polymerization mixture prevents aggregation of the polymeric particles and influences the particle size. For this reason, PANI obtained in the presence of NaCl was constituted from much smaller particles formed by more ordered polymer. On the other hand, the driving force of the PANI adsorption onto the membrane surface is the degree of hydrophilicity of the plasticized PVC. The hydrophilicity of plasticized PVC was dependent on the ratio between plasticizer and PVC in membrane matrix [24]. It was found that the ratio for PVC/NPOE should correspond to 2:1 (m/m).

Therefore, the main attention of the present work is directed onto PANI as a receptor system that was deposited in the presence of the high concentration of NaCl onto the surface of PVC/NPOE, 2:1 (m/m), membranes based on TDDMACI (membrane C). For comparison, membranes coated with PANI in the absence of NaCl (membrane B) were introduced.

3.1. Potentiometric measurements

Potentiometric results were evaluated and compared for uncoated (A) and PANI-coated in absence (B) and in presence of

NaCl (C) membranes (Table 1). For uncoated membrane A, the potentiometric responses were mostly obtained in a narrow concentration range.

Regarding the PANI-coated membranes, better potentiometric characteristics were obtained for membrane C, where PANI was deposited in the presence of NaCl. For all tested anionic species, the sensitivity of the membrane C was near to the theoretical value at the concentration range from 4×10^{-6} M to 2×10^{-2} M (with the only exception for acetate). Coating of the membranes with PANI in the absence of NaCl (membrane B) affected their sensitivity; the sensitivity attained the super-Nernstian values independently on the kind of the measured anionic species. The reason of observed super-Nernstian response is probably in the differences of anion-exchange process that likely originates from structural features of polymer deposited onto the membrane surface [17]. In contrary to the membrane B, the linear concentration range of the membrane C was unchangeable during long-term testing (Fig. 1a). In addition, the potentiometric signal for the membrane C was well reproducible after a regeneration procedure (Fig. 1b). Therefore the further potentiometric studies were carried out with the membranes C (TDDMACI/PANI + NaCl).

Potential analytical application of the potentiometric sensor is always preceded by the determination of its selectivity. The key factor that determines selectivity of a specific potentiometric sensor is the difference in free energies of the ion transfer of the analyte versus the interferent from the sample matrix into the membrane phase [25]. The potentiometric selectivity of the membranes coated with PANI was estimated using salicylate as the primary analyte (I) and chloride, acetate, benzoate as interfering analytes (J). The comparison of the potentiometric selectivity coefficients ($\log K^{\text{Pot. Salicylate}_J}$) obtained experimentally with those found in the literature [1,3,26] is summarized in Table 2.

As can be seen from Table 2, the deposition of PANI in the presence of NaCl improved the selectivity of TDDMACI-based membrane towards salicylate in comparison with membranes based on charged carriers (phthalocyanates) [3] and on conventional anion exchangers (membrane A from the present study, Aliquate 336S [26]). The selectivity of the ion-selective membrane is based on a specific receptor stems from highly specific interaction between the receptor and salicylate. As far as the interaction between anion and anion exchanger is not specific, the main factor affecting the selectivity is the lipophilicity of corresponding anions. In the very first approximation the relative lipophilicity of two ions can be characterized by the ion exchange constant, and this parameter is in quite a good correlation with the selectivity coefficient [27]. One should note, that acetate and shape with

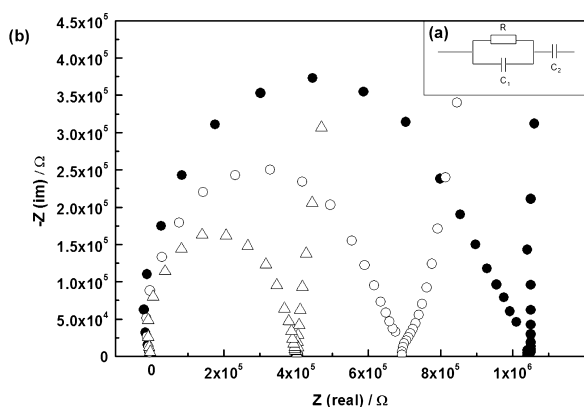


Fig. 2. (a) Equivalent circuit used to fit the data shown in part (b). (b) The EIS spectra recorded in 0.01 M sodium salicylate for uncoated membrane (○) and membranes coated by PANI in absence (●) and in presence of NaCl (△).

salicylate (e.g. “Y-shaped” anions), but they differ by lipophilicity: acetate ($\log P = -0.29$) < benzoate ($\log P = 1.89$) < salicylate ($\log P = 2.06$). Whereas the uncoated TDDMACI-based membrane (A) slightly discriminated oxoanions, the membrane C gave the gain in selectivity of 0.5 and 1.5 logarithmic units for benzoate and acetate, respectively. The effect of polymer on selectivity of TDDMACI-based membranes might be related with the variations of exchange constants for acetate and benzoate. Obviously, the membrane C demonstrated appreciable higher selectivity than membranes based either on Sn (IV) or Al(III) phthalocyanates [3]. In the determination of salicylate in biological samples, possible interference of chloride ions always has to be accounted to. Therefore, the selectivity of salicylate *versus* chloride should be maximized [2]. In comparison with metalphthalocyanate-based membranes [3], the PANI-coated membrane C showed increased selectivity toward salicylate *versus* chloride. Therefore incorporating of specific receptor into the membrane containing PANI is not necessary.

The studies of Egorov's group shown that anion selectivity of liquid anion exchanger is affected by the nature of anion exchanger [27]. In particular, (i) ion exchangers containing hydroxyl groups near the exchange center are prospective for anions bearing a hydrocarbonic radical and a hydrophilic carboxyl, (ii) ion exchangers with the maximally sterically hindered exchange center are suitable for large hydrophobic anions. However, the synthesis of similar ion exchangers is connected with considerable experimental difficulties. Taking into account the results of Egorov's group, PANI might be regarded as a special kind of anion-exchanger deposited onto membrane surface and contributing to its potentiometric selectivity. The structure of polymer including phenyl rings, protonated imino and neutral amino groups might allow to form three kinds of interactions: $\pi - \pi$ stacking, coulombic interactions and hydrogen bondings with aromatic, carboxy and hydroxy groups of tested carboxylates. The features of polymer structure lead us to propose that PANI might be regarded as the specific receptor system deposited onto membrane surface.

3.2. Electric impedance spectroscopy measurements

Results of the EIS measurements of the membranes are presented in Fig. 2 in the form of Nyquist plots, i.e. imaginary part of complex impedance *versus* real part of complex impedance where measuring signal frequency is a parameter. As a general comment it should be noted that all Nyquist plots show in the left part the high frequency semicircle corresponding to the “bulk” membrane resistance (R) and its parallel capacity (C1) [28]. Absence of the second semicircle seems to be related to the negligible contribution of

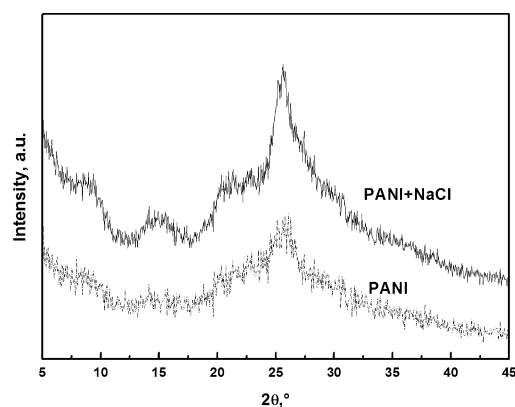


Fig. 3. X-ray diffractions patterns of polyaniline prepared in absence (PANI) and in presence of NaCl (PANI + NaCl).

the surface defects as well as to high mobility of the charge carriers from electrolyte. The lower-frequency “tail” in the right part is typical for the presence of ionic conductivity [29]. The “bulk” resistance of the membranes is increased in the following sequence: membrane C (400 kΩ) < membrane B (690 kΩ) < membrane A (1040 kΩ). While the uncoated membrane has only ionic conductivity, deposition of conducting polymer introduces electronic conductivity, which is always present in polymer backbone. This fact explains the observed higher resistance of uncoated membrane.

Based on theoretical investigations, Foreman et al. [30] concluded that, the creation of a hydrogen bond between amine group of PANI and the sulfonic acid group of model molecules acts to increase the ability of phenyl-nitrogen-phenyl backbone to transfer electron density. Hence electronic conductivity of polyaniline backbone can only be enhanced by the act of hydrogen bonding a sulfonic acid group to it. Further, locally obtained partial structure of oligomeric PANI doped with camphorsulfonic acid (CSA) indicates that the sulfonic acid repeatedly bridges two adjacent PANI chains, locking them together with hydrogen bonding. In analogy with the systems described in Ref. [30], we suggest that the similar interactions can occur between carboxylate anions (which are present in our analytes) and PANI onto membrane surface. Thus, a form of “molecular recognition” exists in the system (TDDMACI/PANI... Carboxylate) and is analogous to that observed in specific supramolecular receptor systems [31].

3.3. Structural characterization of PANI

Fig. 3 shows X-ray diffraction patterns obtained for PANI samples prepared in absence and in presence of NaCl, respectively. The general note is that both polymer samples include both amorphous and crystalline phases. However, an addition of NaCl to polymerization mixture leads to appearance of a sharp peak at ca 26° and two broad peaks at ca 15° and 20°. Moon et al. have demonstrated that the two peaks near $2\theta = 20^\circ$ and 26° arise from momentum transfer perpendicular to the chain direction [32]. These changes can be

Table 3

Direct potentiometric determination of acetylsalicylate added to 0.1 M HEPES at pH = 7 (n = 4).

Amount added (C × 10 ³ M)	TDDMACI/PANI + NaCl)-based membrane	
	Amount found (C × 10 ³ M)*	Recovery (%)
6.98	7.05 ± 0.17	101.0 ± 2.4
9.09	9.27 ± 0.22	101.9 ± 2.5
11.11	11.47 ± 0.28	103.3 ± 2.5

* The values of relative standard deviations for single electrode is equalled 1.51 – 1.53%

Table 4
Results of the analysis of acetylsalicylic acid in pharmaceutical preparations ($n \leq 4$).

Commercial tablet	Acetylsalicylic acid nominal content (mg/tablet)	Acetylsalicylic acid (% of the nominal value)		
		Volumetry [21]	Potentiometry with ion-selective membranes Calix[2]pyridino[2]pyrrole-based membrane ^a [21]	(TDDMACI/PANI + NaCl)-based membrane
Acylpyrin	500	95.0 ± 4.4	99.6 ± 4.4	98.1 ± 1.1
Acylcoffin	450	102.0 ± 5.8	102.0 ± 4.2	100.0 ± 0.3
Aspirin-C	400	–	99.5 ± 4.8	100.0 ± 0.9

^a meso-octamethyldichlorocalix[2]pyridino[2]pyrrole (CPP)-based membranes were prepared with 63.6 wt.% NPOE, 31.8 wt.% PVC and 3 wt.% carrier (49 mol.% TDDMACI relative to carrier CPP) [21]

interpreted as the transfer from amorphous to partially crystalline phase, namely as increasing of crystallinity of polymer coating [33].

3.4. Analytical applications

The membrane C (TDDMACI/PANI + NaCl) showed stable sensitivity (-60 ± 2 mV/decade) and detection limit (ca 2.5×10^{-6} M) toward salicylate during intensive utilization for over 6 months period. From this point of view, such membrane is beneficial for potentiometric detection of salicylates.

Next, the membrane C was used to determine salicylic acid in the sample of synthetic serum. The composition of synthetic serum approximates composition of authentic human serum [4,22]. The normal level of salicylate in serum is $\geq 0.15 \times 10^{-3}$ M; the therapeutic level of salicylate in this fluid ranges from approximately 5×10^{-4} M to 1.5×10^{-3} M [2]. Therefore, the synthetic serum was spiked to 0.12×10^{-3} M with salicylic acid and the found concentration corresponded to $(0.11 \pm 0.01) \times 10^{-3}$ M. This result proves the feasibility of our electrode to be an alternative device to direct determination of salicylate in biological samples. Recently, Tomassetti's group has proposed an enzymatic biosensor for determination of salicylic acid in urine and drugs [34]. Relatively good recoveries (about 83–109%) and acceptable precision (R.S.D about 8%) for their biosensor have been noted. Taking the data of the Tomassetti's group and the data obtained by us into account, our potentiometric sensor with PANI as receptor is well competitive.

Finally, the membrane C (TDDMACI/PANI + NaCl) was tested for the potentiometric determination of acetylsalicylic acid content in commercial tablets. As shown in Fig. 4 and Table 3, the membrane C provides an alternative device for determination of acetylsalicylate.

The obtained results are in a good agreement with the nominal value declared by the producer (Table 4). Precision of the potentiometric analysis with membranes coated with PANI is even higher

than precision of the validated volumetric analysis and potentiometric analysis using membranes based on specific receptor, i.e. calix[2]pyrrole[2]pyridine [21]. Recoveries of 98.1–100% and relative standard deviation ranging between 0.2 and 0.4 % demonstrate suitability of the membranes C for acetylsalicylic analysis in pharmaceutical preparations.

4. Conclusions

In this study, a salicylate sensor was fabricated by deposition of PANI containing partially crystalline phase onto anion-exchange membrane (TDDMACI/PANI + NaCl). This kind of coating can be considered as a new kind of receptor system for potentiometric detection of salicylate. Compared to Sn(IV) and Al(III) phthalocyanates, the PANI-coated membranes achieved higher selectivity. High selectivity of PANI to salicylate was explained on the basis of triple interaction between the polymer and the analyte: $\pi - \pi$ stacking, coulombic interactions and hydrogen bonding. Moreover, the membrane (TDDMACI/PANI + NaCl) showed stable sensitivity (-60 ± 2 mV/decade) and detection limit (ca 2.5×10^{-6} M) toward salicylate during intensive utilization for over 6 months period. The obtained results indicated that present sensor can be used for detecting of salicylate content in concentrations as low as $(0.11 \pm 0.01) \times 10^{-3}$ M in a synthetic serum and for monitoring of acetylsalicylate in drugs.

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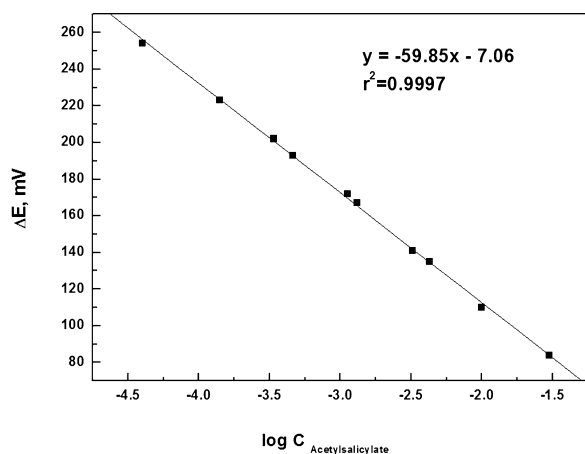
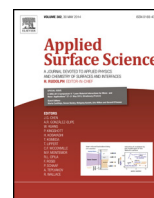


Fig. 4. Calibration plots for acetylsalicylate in standard solutions for the membrane C coated by PANI in the presence of NaCl (TDDMACI/PANI + NaCl).

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Laser deposition of sulfonated phthalocyanines for gas sensors



Premysl Fitl^{a,b,*}, Martin Vrnata^a, Dusan Kopecky^a, Jan Vlcek^a, Jitka Skodova^a, Jiri Bulir^b, Michal Novotny^b, Petr Pokorny^b

^a Department of Physics and Measurements, Institute of Chemical Technology Prague, Technická 5, Prague 6 CZ-166 28, Czech Republic

^b Department of Analysis of Functional Materials, Institute of Physics AS CR v.v.i, Na Slovance 1999/2, Prague 8 CZ-182 21, Czech Republic

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ABSTRACT

Thin layers of nickel and copper tetrasulfonated phthalocyanines (NiPcTS and CuPcTS) were prepared by Matrix Assisted Pulsed Laser Evaporation method. The depositions were carried out with KrF excimer laser (energy density of laser radiation $E_L = 0.1\text{--}0.5\text{ J cm}^{-2}$) from dimethylsulfoxide matrix. For both materials the ablation threshold E_{L-th} was determined. The following properties of deposited layers were characterized: (a) chemical composition (FTIR spectra); (b) morphology (SEM and AFM portraits); and (c) impedance of gas sensors based on NiPcTS and CuPcTS layers in the presence of two analytes – hydrogen and ozone. The prepared sensors exhibit response to 1000 ppm of hydrogen and 100 ppb of ozone even at laboratory temperature.

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1. Introduction

Matrix Assisted Pulsed Laser Evaporation (MAPLE), introduced by Piqué et al. in 1999, is one of the experimental laser deposition methods used for deposition of thin uniform films of organic [1] and even biological materials [2].

MAPLE is characterized by indirect contact of the laser radiation with deposited material. The target used for MAPLE consists of two substances; each has a different function during the deposition process. The first one is the deposited material itself, the second is a matrix, which has majority representation (approximately 95% of target). Matrix has usually a character of low molecular weight volatile solvent of the material, which is to be deposited. Both substances are mixed together and frozen to liquid nitrogen temperature to suppress sublimation of the matrix. In case of correct setting of the deposition conditions, majority of the energy of laser pulse is absorbed by matrix. The matrix has two functions: (i) it protects the environment of a “fragile” deposited material from high-energy laser radiation and (ii) serves as an energy transmitter from electromagnetic radiation to kinetic energy of the molecules, which causes ablation of a deposited material to a plasma state and its subsequent deposition. Selection of a suitable matrix is therefore essential for successful and non-destructive deposition of large organic molecules.

The mechanism of MAPLE deposition is shown in Fig. 1. Frozen target is placed in a vacuum and is struck by laser pulses, whose energy is absorbed preferentially by the matrix, which leads to local overheating of the frozen target, followed by abrupt release of the matrix – so-called surface ablation of target. Through collective collisions, matrix molecules pull the molecules of the deposited material and impart them sufficient kinetic energy required to overcome the target-substrate distance. Large molecules of the deposited material have lower vapor pressure than volatile small molecules of matrix and therefore they are less often pumped away by vacuum system; so the substrate is gradually covered with a thin layer of deposited material with minimum content of matrix molecules.

Chemical gas sensor is a passive sensing element which converts chemical input quantity (concentration of detected gas) to electrical output signal (change of sensor resistance). The most significant group of chemical gas sensors operates on the basis of ability of thin semiconductive layers (=sensitive layers) to chemisorb various gaseous analytes on their surfaces with subsequent exchange of electrons between analyte and sensitive layer [3]. While reducing gases possess ability to act as electron donors, the oxidizing ones are electron acceptors, i.e. they extract electrons from the sensitive layer. At present, some classes of organic substances (conducting polymers [4], complexes of organic ligands with metallic cation [5], etc.) are intensively investigated as prospective materials for sensitive layers. In general, the suitable materials can be characterized as organic molecules containing conjugated system of double bonds, where π -electrons form delocalized and highly polarizable system in which charge can be easily transported. In the case of organic sensitive layers the detection mechanism is not limited to exchange of

* Corresponding author at: Department of Physics and Measurements, Institute of Chemical Technology Prague, Technická 5, Prague 6 CZ-166 28, Czech Republic. Tel.: +420 220443351.

E-mail address: fitlp@vscht.cz (P. Fitl).

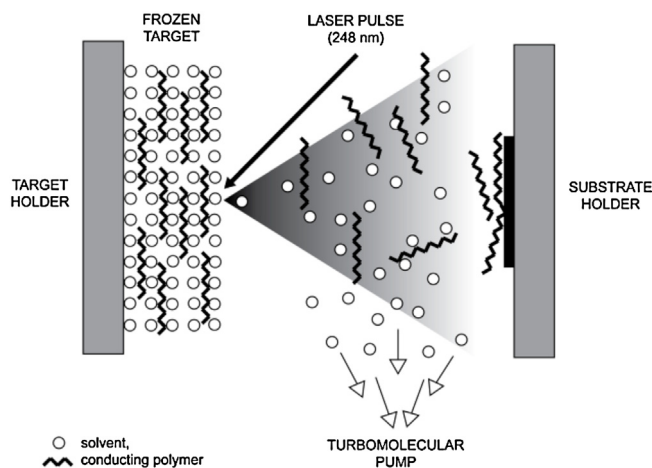


Fig. 1. Principle of MAPLE method.

electrons, but there are also several simultaneous detection mechanisms following from the interaction between organic layer and the analyte (e.g. creation of hydrogen bonds, π – π stacking, influencing of polaron-conductivity, influencing of mobility of ionic species contained in the material etc. [6]). As a result of all the above mentioned mechanisms the sensor resistance is modulated.

Among organocomplexes, both phthalocyanines and substituted phthalocyanines are known to be excellent materials for gas sensing [7,8]. However, when one selects proper method for depositing sensitive layer, there is a significant difference between them: while phthalocyanines are almost insoluble in all solvents, some of their substituted derivatives exhibit a good solubility in low molecular solvents. Due to this fact substituted phthalocyanines (unlike non-substituted ones) can be deposited by MAPLE method.

The presented paper deals with preparation of gas sensor sensitive layers based on tetrasulfonated phthalocyanines (NiPcTS and CuPcTS). The depositions were carried out from dimethylsulfoxide matrix by MAPLE method, providing tool for gentle, non-destructive and easily adjustable grown of organic materials. Responses of prepared sensors to hydrogen and ozone are also presented.

2. Experimental

2.1. Deposition of NiPcTS and CuPcTS thin layers by MAPLE method

In our experiments MAPLE instrumentation was carried out as follows: Powder of NiPcTS or CuPcTS (Sigma–Aldrich) was diluted in dimethylsulfoxide matrix to obtain solution containing 0.2 wt%. Dimethylsulfoxide matrix was recently proved to be

suitable for depositions with KrF excimer laser [9]. After sonification the resulting solution was filtered and then frozen by liquid nitrogen. The freezing process proceeded in a tubular mold so as to produce targets for MAPLE in the form of tablets (approx. 40 mm in diameter and 10 mm thick). Then the deposition conditions were set (KrF excimer laser operating at 248 nm; energy density of laser radiation E_L ranging from 0.1 to 0.5 J cm^{−2}; repetition rate of laser pulses $f_{rep} = 10$ Hz, pulse duration 15 ns; residual pressure in the deposition chamber 10^{−4} Pa; working atmosphere during depositions was 3 Pa of nitrogen; target–substrate distance 35 mm).

2.2. Characterization of chemical composition and morphology of the layers

Chemical composition of the deposited layers was analyzed from the IR spectra scanned by the Attenuated Total Reflection Fourier Transform Infrared spectroscopy (ATR FTIR). The spectra were scanned using a BRUKER IFS 66V device (diamond crystal) in the interval of wavenumbers from 600 to 1800 cm^{−1} covering finger-print of MePcTS molecules.

The surface morphology of the samples deposited on polished silicon wafer was acquired using Atomic Force Microscopy (AFM). The AFM images were taken on Veeco Digital Instruments CP II apparatus. For sample characterization, 'Tapping mode' rather than 'Contact mode' was chosen to minimize damage of the sample surfaces. A Veeco oxide-sharpened silicon probe RTESPA-CP attached to a flexible microcantilever was used at its resonant frequency of 300 kHz. The image resolution was 256 × 256 pixels. Layers morphology was further characterized by Scanning Electron Microscopy (SEM) with JEOL JSM-7500F instrument.

2.3. Measuring of gas sensor response

In order to test gas sensing properties the layers were deposited onto alumina sensors substrates (2.0 × 2.5 mm²) equipped with interdigital electrodes (Fig. 2). The sensor impedance was measured in "pure" synthetic air (as a reference atmosphere) and in synthetic air containing 1000 ppm of hydrogen or 100 ppb of ozone respectively. The impedance measurements were performed with a HP4192LF impedance analyzer with frequency of testing signal from 15 Hz to 10 MHz and amplitude remained constant at 100 mV. The obtained data were represented as Nyquist Diagrams – i.e. they are plotted as imaginary part of complex impedance vs. real part of complex impedance with frequency of testing signal as a parameter. From Nyquist diagrams the so-called phase-angle sensitivity S_{pa} [°] of sensors was evaluated. The detailed definition of S_{pa} is in [10,11] and see also Fig. 3.

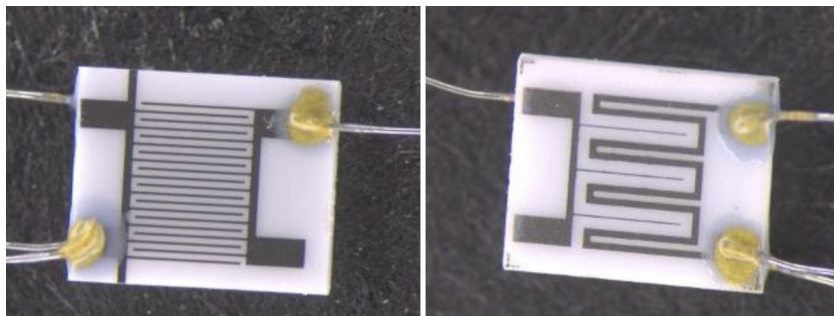


Fig. 2. Sensor substrate – front side with interdigital electrodes (left); back side with resistance heating (right).

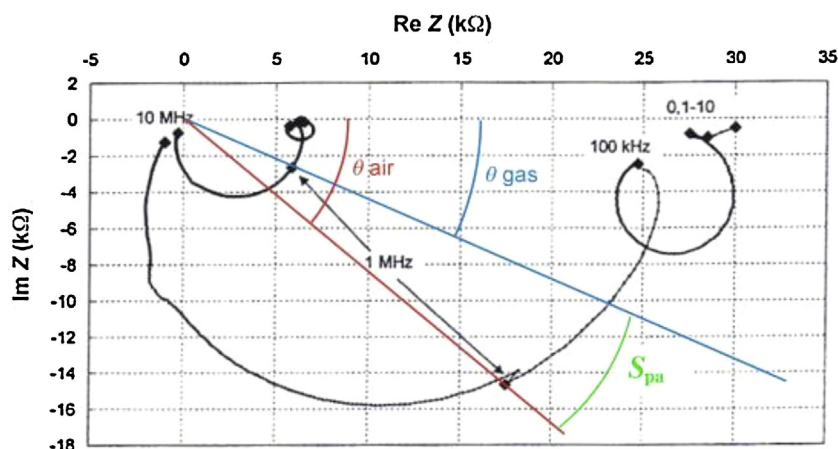


Fig. 3. A typical Nyquist diagram of gas sensor with MePcTS sensitive layer in synthetic air (reference).

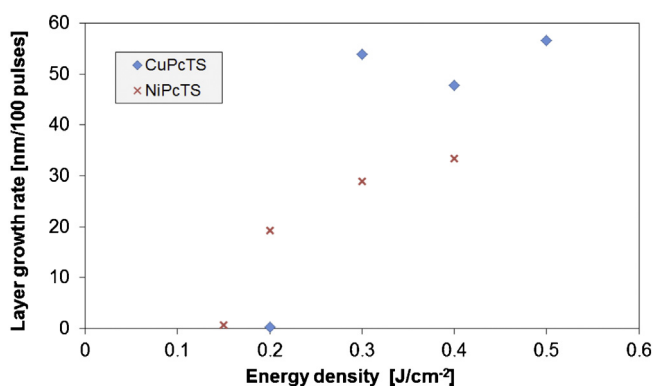


Fig. 4. Ablation curves for NiPcTS and CuPcTS.

3. Results and Discussion

3.1. Determination of ablation threshold

The depositions made by KrF laser in the range of energy density of laser radiation from 0.1 to 0.6 J cm⁻² can be assembled into a dependence of growth rate on laser fluence, known as the

ablation curve (Fig. 4). On basis of these curves, the ablation thresholds E_{L-th} were determined to be $E_{L-th} \sim 0.2$ J cm⁻² for NiPcTS and $E_{L-th} \sim 0.3$ J cm⁻² for CuPcTS and measured gas (1000 ppm of hydrogen). In this example phase-angle sensitivity S_{pa} is evaluated as a difference of sensor impedance arguments (θ angle) for 1 MHz frequency of testing signal.

Ablation threshold is a parameter important from the practical point of view, as it corresponds to energy density sufficient for effective layer grown on one side, while there is no excessive photo- and heat-stress of deposited material on the other side.

3.2. FTIR spectra of source substances and deposited layers

Infrared spectra of source substances were compared to those of deposited materials (Figs. 5a and b and 6a and b) in order to evaluate the degree of material decomposition during MAPLE process. Both materials were deposited at energy densities corresponding to their ablation threshold. Analyzing spectra of source materials (Figs. 5a and 6a) one may notice that absorption bands are rather wide. This phenomenon can be attributed to occurrence of traces of mono-, di- and tri-sulfonated phthalocyanines in commercially distributed metal tetrasulfonated phthalocyanines (MePcTS). Nevertheless, it is apparent, that in both cases the transfer of material by MAPLE method was successful, as the positions and in most

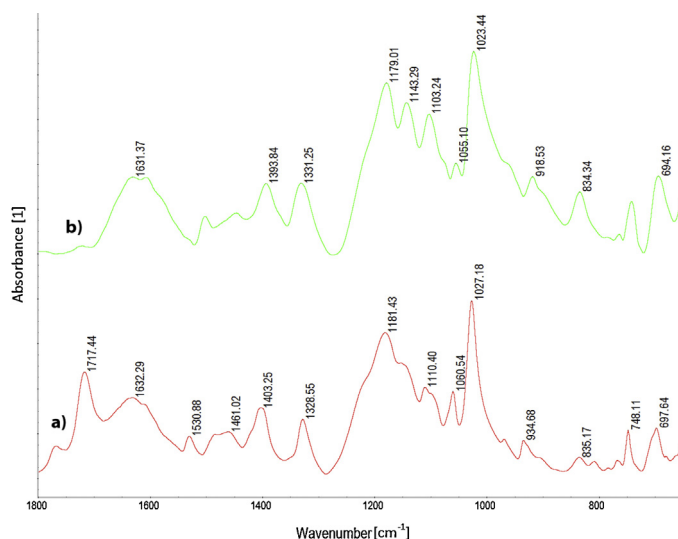


Fig. 5. FTIR spectrum of NiPcTS: source material (a) and layer deposited at $E_{L-th} = 0.2$ J cm⁻² (b).

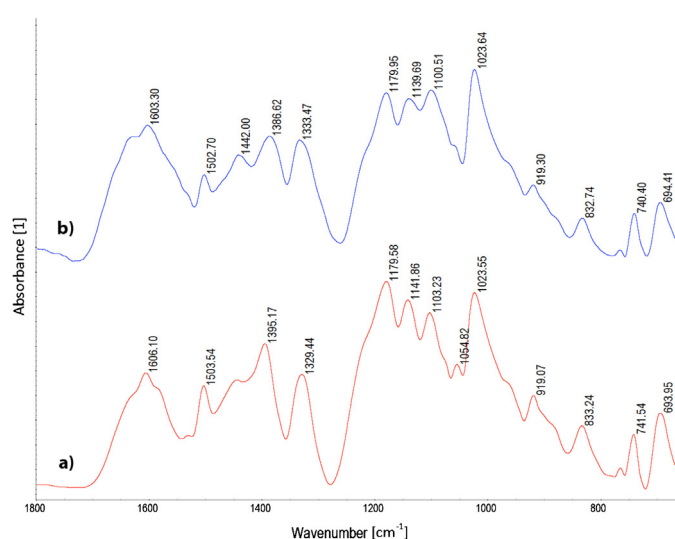


Fig. 6. FTIR spectrum of CuPcTS: source material (a) and layer deposited at $E_{L-th} = 0.3$ J cm⁻² (b).

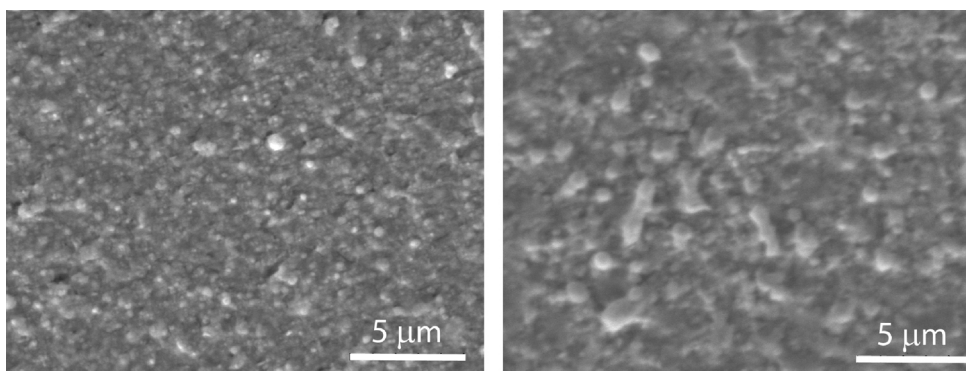


Fig. 7. SEM portraits of NiPcTS (left) and CuPcTS (right).

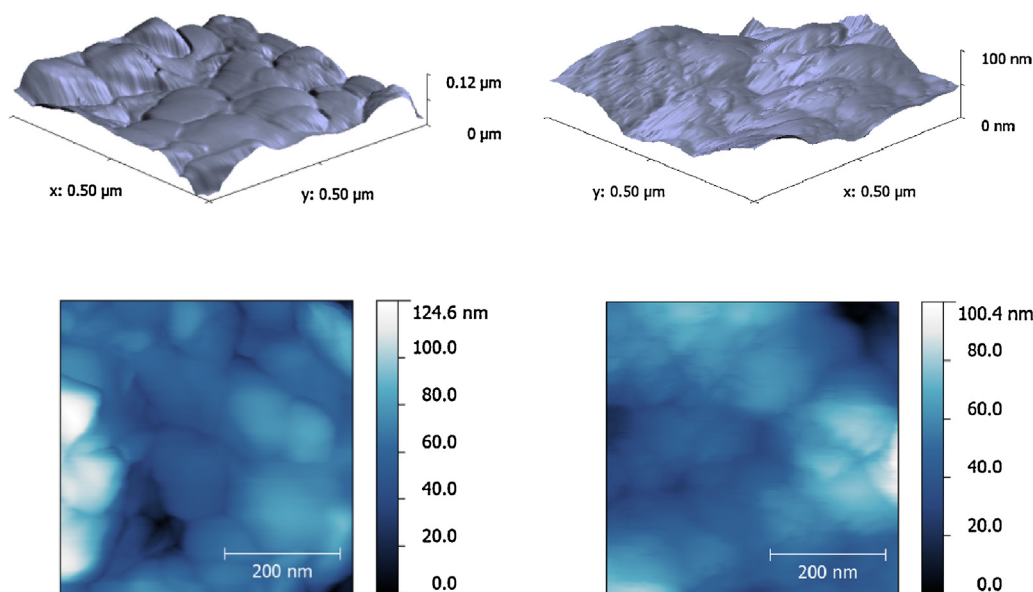


Fig. 8. AFM portrait of NiPcTS (left) and CuPcTS (right).

cases also amplitudes of absorption maxima are retained when comparing Fig. 5a with Fig. 5b or Fig. 6a with Fig. 6b. An overview of absorption bands of phthalocyanines is summarized in [12].

3.3. Layers morphology

The layers deposited at ablation thresholds were also studied by SEM (Fig. 7) and AFM (Fig. 8) methods. The portraits resulting from these methods reveal that the structure of MAPLE deposited layer is rather segmented with high surface/volume

ratio; these properties are favorable for applications in gas sensing (the detection process is localized on the surface of sensitive layer).

3.4. Impedance measurements and phase-angle sensitivity

The NiPcTS and CuPcTS layers were deposited to sensor substrates, the impedance of obtained structures was measured and phase-angle (S_{pa}) sensitivity to 1000 ppm of hydrogen and 100 ppb

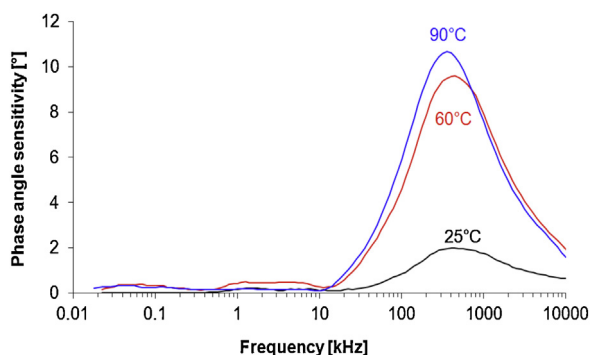


Fig. 9. Phase-angle sensitivity of NiPcTS to 1000 ppm of hydrogen.

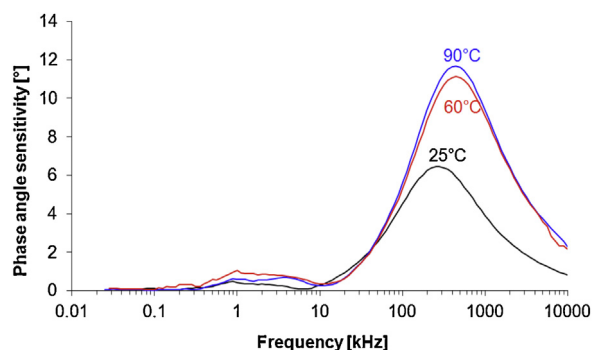


Fig. 10. Phase-angle sensitivity of NiPcTS to 100 ppb of ozone.

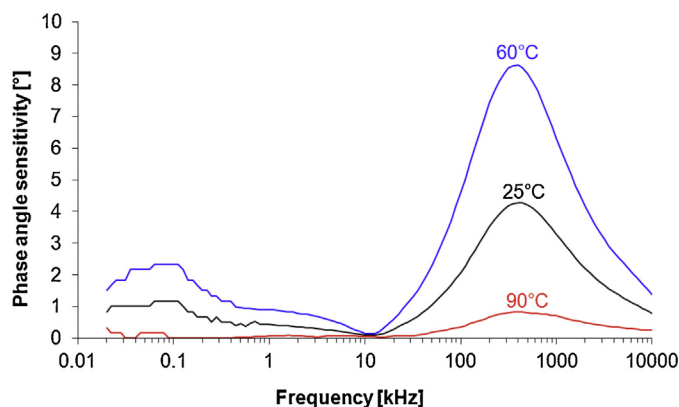


Fig. 11. Phase-angle sensitivity of CuPcTS to 1000 ppm of hydrogen.

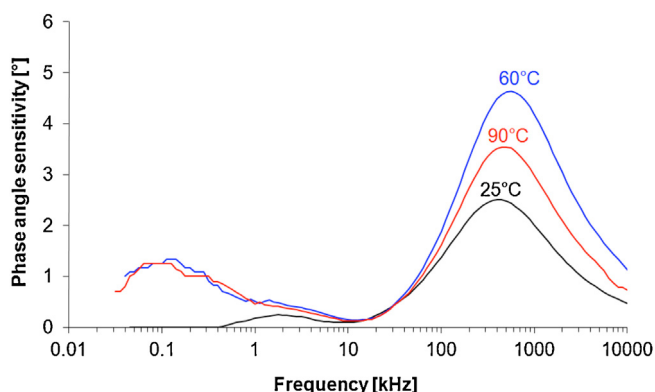


Fig. 12. Phase-angle sensitivity of CuPcTS to 100 ppb of ozone.

of ozone evaluated. The results are summarized in sequence of Figs. 9–12.

The sensors exhibit the highest phase-angle sensitivity (S_{pa} ranging from 5° to 12°) at approx. 500 kHz frequency of measuring signal in all cases. CuPcTS sensors have also secondary maximum in the vicinity of 100 Hz. As for temperature dependence of S_{pa} – the sensors were tested at operating temperatures 25–90 °C, because at higher temperatures reaction of MePcTS with atmospheric oxygen can start. There was also found certain low-temperature sensitivity – i.e. measurable sensor response at 25 °C.

4. Conclusions

Tetrasulfonated metal phthalocyanines were deposited by MAPLE method from dimethylsulfoxide matrix. It was proved that for energy density of laser radiation corresponding to ablation

threshold the molecular structure of the deposited material (i.e. MePcTS) remained preserved. The prepared layers have porous structure with large relative surface-properties suitable for sensor applications. The sensors based on deposited layers were successfully tested for detection of hydrogen and ozone; low temperature phase-angle sensitivity was observed ($S_{pa} = 2.5$ – 6.6° at the temperature of 25 °C), hence these sensors are able to operate at laboratory temperature. Also dynamic properties of sensors are satisfactory (response time $\tau_{90} \approx 30$ s, recovery time $\tau_{90}^* \approx 70$ s). One can also observe a typical feature of chemical gas sensors – recovery time is longer than response time. To our best knowledge the evaluation of phase-angle sensitivity has not been published by another group. There is a reference concerning “dc-sensitivity” of sulfonated/non-sulfonated cobalt phthalocyanine to ozone [13].

Acknowledgment

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Polypyrrole nanotubes: mechanism of formation

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This article presents a contribution to better understanding of the processes which take place during the synthesis of polypyrrole nanotubes using a structure-guiding agent, methyl orange. Polypyrrole was prepared by oxidation of pyrrole monomer with iron(III) chloride. In the presence of methyl orange, the formation of nanotubes was observed instead of the globular morphology. Two reaction schemes with reversed additions of oxidant and monomer have been tested and they show remarkable influence on the produced morphology. Nanotubes with circular or rectangular profiles and diameters from tens to hundreds of nanometres have been obtained. FTIR and Raman spectra were used to assess the molecular structure of polypyrrole and detect residual methyl orange in the samples. The conductivity of nanotubes compressed into pellets was as high as 68 S cm⁻¹. The mechanism of nanotubular formation starting at the nucleus produced with the participation of organic dye is proposed. The growth of a nanotube, however, proceeds in the absence of a template. An alternative mechanism for the formation of nanotubes, the coating of solid templates with a polypyrrole overlayer, is also discussed.

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Introduction

The last decade of conducting polymer research has been characterized by increasing interest in the control of their morphology at the nanoscale. Among them polypyrrole (PPy) and polyaniline (PANI) have been most studied. In particular, one-dimensional structures, such as nanorods, nanotubes or nanofibres are promising^{1–3} due to their possible uses in sensors,⁴ energy storage,⁵ electrocatalysis,⁶ electrorheology,⁷ electromagnetic interference shielding,⁸ and biomedicine,⁹ or in the conversion to nitrogen-containing carbon materials.¹⁰ They are better suited for the charge transport than globular forms and also their larger specific surface area is of benefit in many applications. More complex three-dimensional hierarchical morphologies have also been reported¹¹ but they are usually generated only by non-conducting aniline oligomers.

There are three basic approaches to the preparation of one-dimensional conducting polymer nanostructures: (1) hard-template methods using solid inorganic membranes or fibres for the deposition of conducting polymers,^{12–15} (2) soft-template methods employing supramolecular assemblies of auxiliary

organic substances, such as surfactant micelles^{16–18} or aggregates of dyes¹⁹ as structure-guiding agents^{20–22} and, finally, (3) polymer nanotubes or nanofibres can also be produced without any external template, as well documented for PANI.^{1,3,23} The preparation of uniform nanotubular or nanofibrillar morphologies in large quantities required for practical use, however, still remains an important research issue.

The principles underlying the formation of one-dimensional morphologies have to be similar for PANI and PPy. The preference of the PANI or PPy depends on the potential applications. While PANI displays acid–base transition associated with colour and conductivity changes, which is well applicable in sensors, PPy is usually preferred in biomedical uses, where the toxic hazards associated with aromatic amines are feared. PPy nanotubes have also higher conductivity compared with PANI analogues. For that reason, PPy has been used for the present study but its relation to PANI has also always been considered.

PPy, when prepared by the oxidation of pyrrole with inorganic oxidants, such as iron(III) salts, is obtained in globular morphology. An acidobasic indicator, methyl orange (MO), represents a simple and easily accessible structure-guiding agent in the preparation of PPy nanostructures. The synthesis of PPy in the presence of MO was for the first time introduced by Yang *et al.*,²¹ and resulted in nanotubes with inner diameter of 50 nm. The mechanism of PPy nanotubes formation was explained by creation of self-degraded template, a complex of iron(III) chloride with MO. The preparation of PPy nanotubes in the presence of MO has been later used many times.^{21,24–32} The morphology control of nanotubes was improved by using MO along with a cationic surfactant, hexadecyltrimethylammonium

^aFaculty of Chemical Engineering, Institute of Chemical Technology Prague, 166 28 Prague 6, Czech Republic. E-mail: martin.vrnata@vscht.cz; Fax: +420 220 444 334; Tel: +420 220 443 383

^bInstitute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

^cCharles University in Prague, Faculty of Mathematics and Physics, 180 00 Prague 8, Czech Republic

^dInstitute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg 199004, Russian Federation

bromide,³³ or anionic surfactant, sodium dodecyl sulfate.¹⁷ It has to be stressed that the use of surfactants alone does not promote the formation of nanotubes.^{34–36} Other one-dimensional PPy morphologies, such as nanofibres or nanoribbons, have been reported only rarely.¹⁸

MO has also been successfully used in the preparation of PANI nanotubes.^{24,37} It should be noted that such PANI syntheses were carried out in the presence of strong inorganic acid, such as hydrochloric acid. Under such acidity conditions, PANI is usually produced as nanofibres at high dilution of reactants,^{38,39} and only moderate acidity is preferred for the preparation of PANI nanotubes.¹ The presence of MO thus stimulates the nanotubular growth of PANI under the conditions where globular morphology is obtained in its absence.

In present contribution, we study the synthesis and morphology control of PPy nanotubes using a structure guiding agent, MO, without any additional auxiliary substances, such as inorganic acids or surfactants. Both MO sodium salt and corresponding acid form were tested. Two reaction schemes of synthesis differing in the sequence of reactant addition have been carried out at various MO concentrations. These experiments produce a basis for the formulation of the mechanism of nanotubular growth.

Experimental

Synthesis of PPy in the presence of methyl orange

Pyrrole (Sigma-Aldrich), iron(III) chloride hexahydrate (Sigma-Aldrich), and methyl orange, sodium 4-[4-(dimethylamino)phenylazo]benzenesulfonate (Fluka, Switzerland) were used as received. 4-[4-(Dimethylamino)phenylazo]benzenesulfonic acid (MO-A) was prepared from MO by ion-exchange technique using hydriodic acid.

PPy was prepared by the oxidation of pyrrole with iron(III) chloride hexahydrate in two ways differing in the sequence of reactants addition (Table 1). In the first reaction scheme (RS1), iron(III) chloride oxidant was added to MO solution, followed by the addition of monomer, pyrrole. In the second protocol (RS2), the additions of oxidant and monomer were reversed. In some cases, the simple mixing of all reactants has also been tested (RS3).

In a typical RS1 synthesis, 10 mmol iron(III) chloride hexahydrate was dissolved in 200 mL of 5 mM aqueous solution of MO, and a flocculate appeared immediately. The mixture was thermostatted at 5 °C, and then 0.7 mL of pyrrole was added drop-wise during two hours. The final molar concentrations of reactants thus were: 50 mM pyrrole, 50 mM iron(III) chloride hexahydrate, and 5 mM MO. Equimolar ratio of pyrrole and

oxidant was used in all experiments, and the mole ratio of MO and pyrrole, [MO]/[Py], was varied.

In a similar RS2 synthesis, 0.7 mL of pyrrole was added to 200 mL of 5 mM solution of MO. The solution was thermostatted to 5 °C. Then 10 mmol of iron(III) chloride hexahydrate was dissolved in 23 mL of water and added drop-wise in the course of two hours. The mixtures were gently stirred for 24 h.

In RS3 synthesis (listed in Table 1), 0.7 mL of pyrrole and 10 mmol of iron(III) chloride hexahydrate dissolved in 23 mL were simultaneously added to 200 mL of 2.5 mM solution of MO. The reaction mixture was thermostatted to 5 °C and gently stirred for 24 h.

PPy precipitate was separated by filtration, purified by Soxhlet extraction using acetone until the extracts were colourless, then washed with ethanol and dried at 40 °C in vacuum. As the reference sample, PPy was also prepared in the absence of MO.

Reaction intermediates

In order to investigate the role of structure-guiding agents in the formation supramolecular PPy structures, the reaction intermediates were isolated and analysed. In the reaction scheme RS1, the precipitate produced after mixing of MO with iron(III) chloride hexahydrate was separated by filtration. Such precipitate may act as a hard template in the subsequent synthesis of PPy. Its growth and morphology were directly observed *in situ* with an optical microscope Nikon Eclipse LV100D equipped with digital camera SONY DFW-SX910 and evaluated by means of image analysis using software NIS-Elements AR 3.20. No precipitate was produced in RS2 scheme after mixing MO with pyrrole, but it might be generated in the next step after the addition of an oxidant.

Characterization

The morphologies of PPy were observed by scanning (SEM) and transmission (TEM) electron microscopies using JEOL 6400 and JEOL JEM 2000FX microscopes, respectively. Fourier-transform infrared (FTIR) spectra of the powders dispersed in potassium bromide pellets have been registered with a Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC detector in the 650–4000 cm^{−1} wavenumber region. Raman spectra excited with an Argon-ion 514 nm laser were collected on a Renishaw inVia Reflex Raman spectroscopy. A Peltier-effect cooled CCD detector (576 × 384 pixels) registered the dispersed light. Room temperature conductivity of composites was measured on pellets compressed at 540 MPa by a four-point van der Pauw method using a Keithley 220 Programmable Current Source, a Keithley 2010 Multimeter as a voltmeter, and a Keithley 705 Scanner equipped with a Keithley 7052 Matrix Card.

Results and discussion

Morphology

Polypyrroles prepared at various concentrations of MO were obtained as nanotubes (Table 2, Fig. 1 and 2) and only exceptionally, at the lowest concentration of MO, a coexistence of

Table 1 Three reaction schemes used in the preparation of PPy

RS1:	MO + oxidant → intermediate solution + pyrrole → polypyrrole
RS2:	MO + pyrrole → intermediate solution + oxidation agent → polypyrrole
RS3:	MO + pyrrole + oxidation agent → polypyrrole

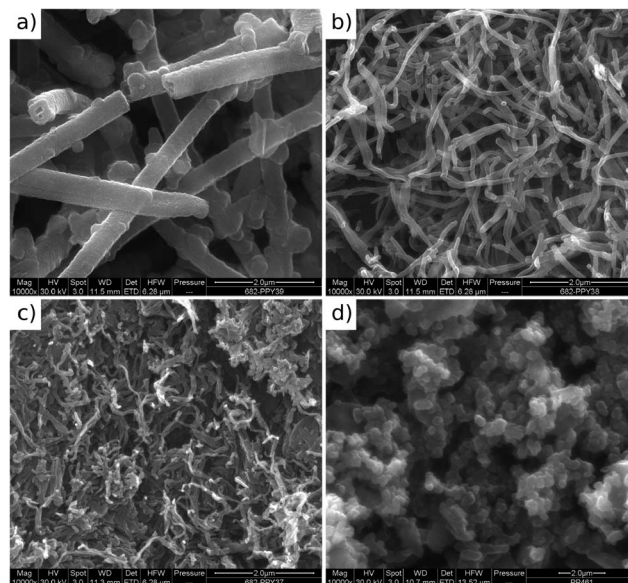
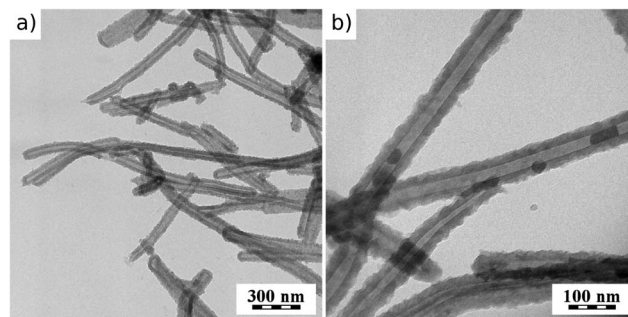
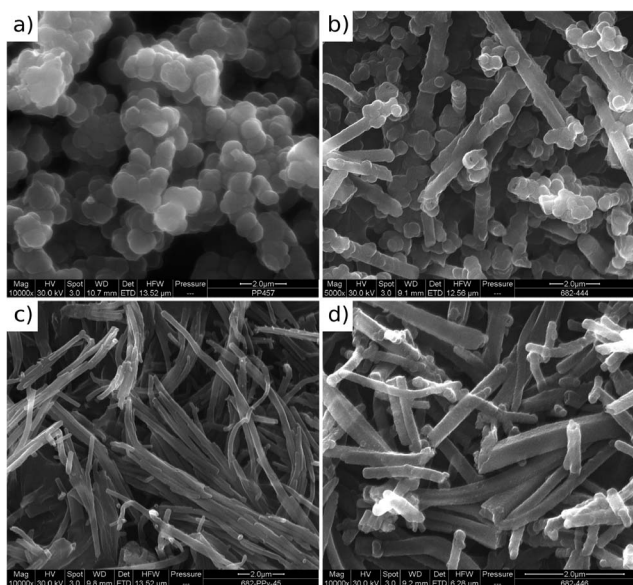
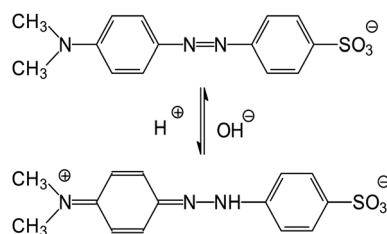
Table 2 Properties of PPy nanotubes prepared by the schemes RS1 or RS2 at various mole ratios [MO]/[pyrrole]^a

Scheme	[MO]/[pyrrole]	Profile	Diameter (nm)	Conductivity (S cm ⁻¹)
RS1	0.01	Rectangular	400–570	51.7
	0.05	Rectangular	190–310	48.7
	0.1	Rectangular	210–400	39.1
RS2	0.01	Rectangular	400–500	11.4
	0.05	Circular	60–110	67.8
	0.1	Circular	40–70	48.8
RS3	0.05	Circular	140–190	52.5

^a 50 mM pyrrole, 50 mM iron(III) chloride hexahydrate.

globular and nanotubular morphology was observed (Fig. 1b). Nanostructures prepared by the protocol RS1 had a larger diameter and always a rectangular profile; the RS2 protocol yielded much thinner nanotubes, often with circular profile. A typical length of nanotubes extends to several micrometres. Nanotubular morphology is confirmed by transmission electron microscopy, where the cavity inside the nanotubes is clearly visible (Fig. 3). Also simple mixing of both reactants in the presence of MO yielded nanotubular morphology. In the absence of MO, a globular morphology was obtained (Fig. 1a).

MO exists in two structural forms (Fig. 4). Under alkaline condition as a benzenoid anion, a sodium salt, under acidic condition as a protonated quinonoid structure. The former form is yellow, the latter form is red. When commercial sodium salt of MO was replaced in experiments with acid form of MO, no nanotubes have been obtained at all concentrations and in both protocols RS1 and RS2 (Fig. 2d).

**Fig. 2** RS2 protocol: the morphology of PPy prepared at the mole ratio [MO]/[pyrrole] = (a) 0.01, (b) 0.05, and (c) 0.1. (d) The morphology of the sample prepared with MO acid instead of MO sodium salt at [MO-acid]/[pyrrole] = 0.1 is shown for comparison.**Fig. 3** Transmission electron microscopy of PPy nanotubes (RS2 scheme, [MO]/[pyrrole] = 0.05); two magnifications. cf. Fig. 2b for scanning electron image.**Fig. 1** RS1 protocol: the morphology of PPy prepared at the mole ratio [MO]/[pyrrole] = (a) 0, (b) 0.01, (c) 0.05, and (d) 0.1.**Fig. 4** Two pH-dependent forms of MO. When dissolved in aqueous medium, the former is yellow, the latter is red. The transition between both forms occurs at pH range 3.1–4.4.

Intermediates

In the RS1 scheme, iron(III) chloride hexahydrate is dissolved in MO solution and the formation of a precipitate was observed, in

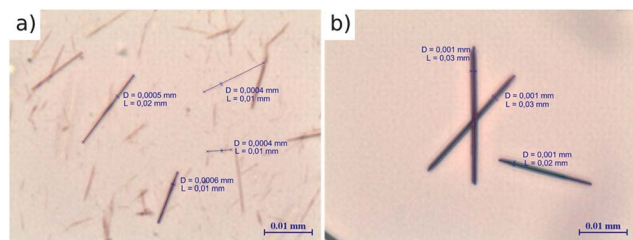


Fig. 5 Optical microscopy of objects produced after mixing the solutions of (a) MO with iron(III) chloride hexahydrate and (b) the solution of MO with hydrochloric acid solution, D = diameter; L = length.

the accordance with the literature.²⁴ The microcrystals were found, about 20 μm long and around 0.5 μm in diameter (Fig. 5a). The addition of iron(III) chloride to the solution will cause an increase in its acidity caused by the hydrolysis. A simple test, a mixing of MO and hydrochloric acid solutions, reveals that microneedles are also produced (Fig. 5b). This means that iron(III) ions need not directly participate in the formation of nanoneedles. This is indeed supported by observation that, when pyrrole is added to microneedles prepared in the presence of iron(III) chloride, no polymerization takes place. As the positive and negative charges are present in acid form of MO (Fig. 4), they are likely to produce ionic bonds leading to neutral dimers. As a result the acid form is much less soluble in aqueous medium compared with sodium salt. In this context, we may mention *o*-aminobenzenesulfonic acid which, despite the presence of sulfonic group, is practically insoluble in water due to the formation of similar ionic bonds.

This experiment demonstrates that MO is able to self-assemble to one-dimensional microrods. It is a question if they play any template role in the growth of PPy nanotubes. It has to be stressed that these objects appear only in the RS1 protocol when they are present *before* the polymerization of pyrrole starts. In the scheme RS2, they have not been observed but they may be produced *during* such polymerization. This difference could possibly account for the smaller diameters of nanotubes in the latter experiment (Table 2).

Molecular structure

Molecular structure of PPy nanotubes was analysed by two different vibration spectroscopic methods, by the FTIR and Raman spectroscopies (Fig. 6 and 7). In the infrared spectra of samples prepared by protocol RS1, only the spectrum of pure PPy is visible till the mole ratio $[\text{MO}]/[\text{pyrrole}] = 0.1$; at higher MO concentration, the features of this dye become apparent. In the cases of protocols RS2 and RS3, the peaks of MO have also been detected in the infrared spectra (Fig. 6a). In the Raman spectra, we detect the spectral features of MO for all concentrations of MO measured and for all protocols (Fig. 6b). In the infrared spectra MO is detected to be in its acid form, in the Raman spectra spectral features of acid form prevail.

The different results of both spectroscopies are connected with the different nature of these methods. The infrared spectroscopy is a bulk method, and its sensitivity increases with

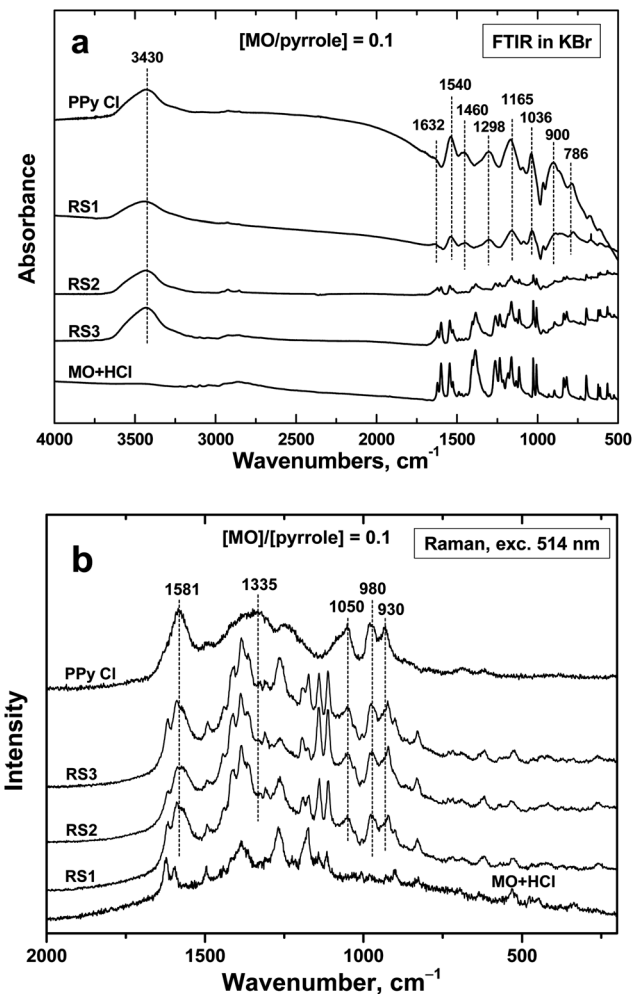


Fig. 6 FTIR (a) and Raman (b) spectra of PPy nanotubes prepared at mole ratio $[\text{MO}]/[\text{pyrrole}] = 0.1$ by the protocols RS1, RS2, and RS3. The spectra of globular PPy hydrochloride prepared in the absence of MO (PPy Cl) and of MO are shown for comparison.

amount of MO present in the sample. On the other hand, the Raman spectroscopy is based on scattering and, for that reason, it is surface sensitive, and in heterogeneous samples, such as PPy nanotubes, even a small amount of MO may be detected. The observed Raman intensity is also enhanced by a resonance effect of the excitation line used. In the case of protocol RS3 the concentration dependence of the infrared and Raman spectra on the mole ratio $[\text{MO}]/[\text{pyrrole}]$ is demonstrated in Fig. 7. It should be stressed, that the main bands of PPy nanotubes correspond well to the band of PPy prepared in absence of MO in both the infrared^{34,40} and Raman^{41,42} spectra (Fig. 6). Samples of composites were very difficult to disperse in potassium bromide pellets because of their compact stone-like structures. Absorption of the sample was very small and the measured spectra contained relatively high absorption bands in the region of stretching and bending vibrations of water molecules at about 3430 cm^{-1} and 1632 cm^{-1} respectively. Absorption of the samples prepared with mole ratios $[\text{MO}]/[\text{pyrrole}] = 0.01, 0.02$, and 0.05 was multiplied by a factor of 3 in Fig. 7a for better observation.

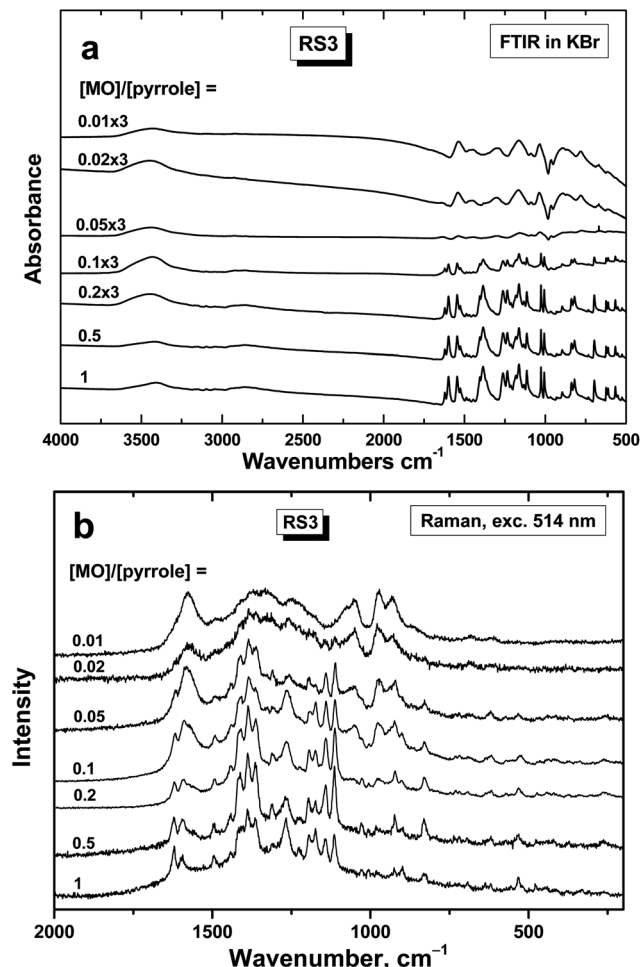


Fig. 7 FTIR (a) and Raman (b) spectra of PPy nanotubes prepared at various mole ratios $[MO]/[pyrrole]$ by the scheme RS3.

The peaks of MO observed in the infrared and Raman spectra of PPy nanotubes correspond most probably to the solid precipitated structures which are produced when MO interacts with iron(III) salts. Such MO thus does not need to be associated with the template that starts or guides the growth of PPy nanotubes. The potential MO template might have been separated in the course of purification of the samples and thus cannot be detected in the spectra.

Conductivity

The conductivity of PPy nanotubes is little dependent on the dimensions of nanotubes and varies between 11 and 68 $S\ cm^{-1}$ (Table 1) and it is comparable with the values published earlier on nanotubes, 20 $S\ cm^{-1}$ prepared in the presence of acid blue AS,⁴³ and 29–36 $S\ cm^{-1}$, for MO.^{30,31} Such values are regarded as high; they are four orders of magnitude higher compared with PANI nanotubes.⁴⁴ Conductivity was measured on pellets prepared by compression of PPy nanotubes. The mechanical properties of pellets were good, and preliminary tests indicate they are at least comparable to PANI analogues.⁴⁵ This is surprising, because globular PPy prepared in the absence of MO

cannot be compressed to pellets at all. Its conductivity was thus estimated only indirectly by measurement on both types of powders, and it is one order of magnitude lower compared with nanotubes.

There is additional feature of interest. The conductivity of PANI nanotubes is reduced from $10^{-2}\ S\ cm^{-1}$ to $10^{-9}\ S\ cm^{-1}$ after conversion of the salt to base with ammonium hydroxide solution.⁴⁴ With PPy nanotubes, the conductivity reduction under the same conditions is much smaller, from $10^1\ S\ cm^{-1}$ to $10^{-2}\ S\ cm^{-1}$, *i.e.* PPy nanotubes maintain a good level of conductivity even under alkaline conditions. This may be of interest for biomedical applications operating at physiological pH 7.4 as well as for alkaline energy sources.

General concept of morphology formation in conducting polymers

The model of nanostructures produced by conducting polymers is based on the concept of nucleates.¹ This model was proposed for PANI but it seems to be applicable also to PPy and related polymers. In the oxidative polymerization of aniline, aniline dimers to tetramers are gradually produced at first and they are called here as *nucleates*. Due to limited solubility of nucleates, they separate from aqueous medium, act as initiation centres and subsequently start the growth of polymer chains.⁴⁴ The *random aggregation* of nucleates followed by polymer-chain growth gives rise to the most common *globular morphology*. Nucleates adsorbed at interfaces immersed in the reaction mixture stimulate the growth of a *thin polymer film*.⁴⁶

One-dimensional morphologies, *nanofibres* (nanowires) and *nanotubes*, have often been reported both for PANI and PPy.^{1–3,47,48} For example, when the reaction mixture is diluted, the oligomeric nucleates self-assemble into a stack and subsequent growth of polymer chains produces a body of a nanofibre. Upon dilution of reaction mixture, the globular morphology thus converts to nanofibres under otherwise similar reaction conditions.⁴⁷ The formation of a nanotube requires an initial template object, assumed to be of cylindrical shape, or some rod-like crystallite. The nucleates assemble into stacks around this template, and subsequent one-dimensional spiral-like (helical) growth produces a nanotube.⁴⁹ It has to be stressed that the template is required only at the *start* of nanotubular growth.⁴⁹ The similar concept has been used for carbon nanotubes, where the role of a starting template is taken by a metal catalyst nanoparticle. The above model is supported by the observation that the thickness of polymer films produced on immersed substrates, radii of globules and nanofibres and the thickness of nanotubular walls are comparable, typically between 50 and 250 nm, possibly proportional to molecular weight of polymer chains. For the sake of completeness, it has to be mentioned that other models of nanotubular formation have been offered, self-curling of sheets^{50,51} being most pertinent alternative.

Polypyrrole nanotubes

The formation of PPy nanostructures should be discussed along with analogous PANI objects. PANI nanotubes are produced

spontaneously during the oxidation of aniline under moderate acidity conditions.⁴⁴ Phenazine-based aniline oligomers generated as reaction intermediates have been proposed to produce *internal* templates that guide nanotubular growth of PANI.⁴⁹ Such flat molecules, closely related to a mauveine dye,⁵² are expected to produce stacks stabilized by π - π interactions. No similar nucleates, however, are produced in the oxidation of pyrrole and nanotubular growth of PPy obviously requires some *external* starting template.

The formation of PPy nanotubes is subject to the presence of some dyes, such as MO,^{21,24-31} acid blue AS,⁴³ rhodamine B,⁵³ Prussian blue,²⁵ or methylene blue.⁵⁴ Many dyes are known to have an ability to self-assemble in the solution, as demonstrated by stacked J-aggregates or H-aggregates.⁵⁵ The organization of dye molecules manifests itself in a shift of absorption maxima in optical spectra and by its narrowing. It is proposed here, that such self-assembled dyes may act as starting templates (Fig. 8a,b) in the growth of PPy nanotubes. The aggregation of MO in aqueous media has been confirmed by electric impedance spectroscopy⁵⁶ and is supported by present experiments. Hydrophilic sulfonic group and large hydrophobic organic moiety containing azo group provide MO with features of surfactants that are known to produce supramolecular structures. PPy nanotubes have indeed been produced in the presence of surfactant, such as tetradecyltrimethylammonium bromide.¹⁷ The role of cylindrical micelles in the formation of nanotubes has also been proposed.⁵⁷⁻⁵⁹ In this case, the template would be a *soft* type, *i.e.* not a solid (Fig. 8a). The higher is the concentration of MO, the larger number of nanotubes is likely to be produced. The increase in the concentration of MO thus has to lead to either thinner nanotubes at the same mass of PPy produced. This trend is indeed demonstrated by the experiment (Table 2).

MO, however, may form insoluble products with iron^{25,27} or silver salts²⁵ that were used as oxidants of pyrrole. As demonstrated above (Fig. 5) and reported in the literature,²⁵ MO in the solutions of hydrochloric acid has limited solubility. Micro-needles are produced, and as they are growing they may act as *hard* nuclei (Fig. 8b). In such a case, nanotubes should have a rectangular cavity (Fig. 8b), or also a rectangular profile, if the starting template has a rectangular shape. Rectangular cavities in nanotubes have also been observed for PANI albeit with chemically different template.^{7,60,61} The assessment of the cavity profile has to be done with some care. The rectangular profile,

which is well visible with thicker nanotubes may not be discernible in thinner ones, which thus may appear as circular.

It is the important prerequisite that the hard templates are anisotropic. In the case of rectangular shape, the adsorption of oligomeric nucleates takes place on the *side* of templates, rather than on their *top* or *bottom*. For this reason, the concept of anisotropic stacked dye or J-aggregate fits better to the present concept than isotropic micellar forms.

The starting template of nanotubular growth are produced by the aggregation of dye molecules, which is controlled probably by diffusion-limited aggregation model.^{62,63} For that reason, they are uniform in size and also the inner diameter of nanotubes is comparable for all nanotubes in the concrete sample. The thickness of nanotubular walls was proposed to be proportional to the molecular weight of constituent polymer chains.¹

In the contrast to the *growth* of nanotubes, another way of their origin is feasible (Fig. 8c), and has to be considered as alternative. When insoluble one-dimensional objects, such as inorganic nanofibres, *e.g.*, manganese(IV) oxide,^{64,65} vanadium(V) oxide,^{27,66-69} titanium(IV) oxide¹⁵ or zinc(II) oxide,⁷⁰ or carbon nanotubes,⁷¹⁻⁷³ are present in the reaction mixture at the early stages of oxidation, such objects become coated with conducting polymer overlayer.^{13,66,68,71,72} Thin polymer films grow on any immersed substrate.⁴⁶ This is the typical *coating* of hard template. Such model has been proposed also for the MO which produces insoluble microrods with iron(III) chloride oxidant.²⁵ After the template is dissolved, polymer nanotubes are produced. This mechanism is quite different from nanotubular growth using the template for the start of growth only. Hard templates may either be introduced or may be produced *in situ* during the oxidation. The former situation is illustrated by the addition of vanadium oxide nanofibres, the latter by the formation of PPy microtubules deposited on crystals produced by the compounds present in the reaction mixtures.¹³ Rectangular profiles are typical for such syntheses.^{13,68} The template is removed after the synthesis, *e.g.*, by extensive washing with organic solvents, or by treatment with alkalis in the case of metal oxides.

In the procedure RS1, the solid precipitated structures are produced when MO interacts with iron(III) salts. These objects have sizes in micrometre range. In principle, they could be coated with PPy. The growth of PPy nanotubes with a diameter smaller than 200 nm, however, seems to be preferred²⁷ over the formation of much larger core-shell structures. In addition, nanorods would be produced by this mechanism, while we observe the formation of nanotubes that are definitely not straight (Fig. 2).

Conclusions

The oxidation of pyrrole with iron(III) chloride produces PPy in globular form. In the presence of MO, however, PPy nanotubes are generated. Their dimensions are dependent on the preparation protocol, *e.g.*, on the sequence of reactant addition. Nanotubes become thinner as the concentration of MO increases. Three protocols have been tested. The protocol RS2,



Fig. 8 (a) Soft or (b) hard templates (black) start the growth of PPy (green) nanotubes with circular or rectangular profile, respectively. (c) The core-shell nanotubular structure may be produced by coating of suitable hard templates with conducting polymers.

the gradual addition of an oxidant to a solution of pyrrole and MO, is best suited for the preparation of thin nanotubes with homogeneous distribution in size.

The mechanism based on the starting template produced by MO and followed by the growth of PPy nanotube is proposed. The cavity profile in thin nanotubes having a diameter 40–190 nm appears as circular; in thicker nanotubes the profile is rectangular. This suggests that the nucleus is solid-like rather than liquid. As the growth of the nanotube proceeds beyond the starting template, the nanotubes may become curved and have a high aspect ratio.

If suitable hard templates produced by the reaction intermediates are present in the reaction mixture, they may become coated with PPy. The nanotubes produced after the dissolution of the template would be thicker, straight, with a rectangular profile, and lower aspect ratio. In such cases, there is no nanotubular growth assumed above, and the mechanism of nanotube formation is different, based on the coating of substrates with a thin PPy film. It seems that, depending on the reaction conditions, both mechanisms may be applicable, but one of them dominates.

PPy nanotubes have conductivity as high as 68 S cm^{-1} , which is reduced after deprotonation in ammonia solutions to $10^{-2} \text{ S cm}^{-1}$. This means that they could be efficiently used in applications operating under physiological conditions, where the conductivity of other PPy forms or other conducting polymers, such as PANI, becomes too low.

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Polypyrrole salts and bases: superior conductivity of nanotubes and their stability towards the loss of conductivity by deprotonation

Jaroslav Stejskal,^{*a} Miroslava Trchová,^a Patrycja Bober,^a Zuzana Morávková,^a Dušan Kopecký,^b Martin Vršata,^b Jan Prokeš,^c Martin Varga^c and Elizaveta Watzlová^c

Polypyrrole nanotubes exhibit conductivity of tens S cm^{-1} which is one of the highest among the current conducting polymers. They are thus superior to the common globular form with the conductivity of units of S cm^{-1} or lower. The conductivity of both forms is reduced after treatment with alkalis but still remains high, units of S cm^{-1} and $10^{-2} \text{ S cm}^{-1}$, respectively. The deprotonation, which is responsible for conductivity reduction, is discussed on the basis of salt–base transition in polypyrrole. It is not fully reversible, and the reprotonation with acids recovers the conductivity only in part. The role of methyl orange, which was used to support the formation of nanotubes, is proposed to be similar to that of surfactants. FTIR and Raman spectroscopies prove that methyl orange is strongly bound to polypyrrole in its acid form, and an “insertion” mechanism is proposed to explain the resistance towards the deprotonation of nanotubes. The spectra also illustrate that the molecular structure of nanotubular polypyrrole is preserved even under highly alkaline conditions at a pH close to 14, where the globular form becomes damaged. Polypyrrole, especially in its nanotubular form, is of promise in applications requiring electrical conduction even under neutral or alkaline conditions, where other conducting polymers, such as polyaniline, lose their exploitable conductivity.

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Introduction

Conducting polymers, such as polypyrrole or polyaniline, find uses especially in energy storage devices and recently also in biomedical applications that exploit their intrinsic conductivity, responsivity, and electrochemical switching. They are popular because of their easy and economic preparation by the oxidation of corresponding monomers. Some of their applications, however, are limited by the pH at which conducting polymers are used. This applies especially to those operating under physiological or alkaline conditions, where the conducting polymer salts convert to non-conducting polymer bases. There are valued properties of such conducting polymers: (1) high conductivity, (2) stability towards the deprotonation and consequent loss of conductivity under alkaline conditions, (3) electrochemical activity, (4) responsivity to external stimuli, (5) catalytic and electrocatalytic properties, and (6) long-term environmental stability. The control and understanding of

their underlying molecular structure and morphology is an important goal.

The present study is focused on polypyrrole. The typical conductivity of polypyrrole prepared by the oxidation of pyrrole with iron(III) salts is $10^{-2} \text{ S cm}^{-1}$.¹ When the polypyrrole was prepared in the presence of surfactants, the conductivity was higher by about two orders of magnitude, and reached 3.1 S cm^{-1} for sodium dodecylbenzenesulfonate,¹ 9.9 S cm^{-1} for dodecylbenzenesulfonic acid,¹ 12.3 S cm^{-1} for sodium bis-(2-ethylhexyl)sulfosuccinate,² 26.1 S cm^{-1} for sodium dodecylbenzenesulfonate³ and 42 S cm^{-1} in the presence of sodium *n*-alkylnaphthalenesulfonate.⁴ The surfactants thus have a beneficial influence on the conductivity of polypyrrole.

The conductivity was reduced by several orders of magnitude when polypyrrole was converted to corresponding bases in ammonia solutions, and even more in sodium hydroxide solutions.^{1,5–11} The certain level of conductivity is still maintained even under strongly alkaline conditions. For example, the conductivity of globular polypyrrole, 0.012 S cm^{-1} , was reduced to $3.7 \times 10^{-5} \text{ S cm}^{-1}$ after treatment with 1 M ammonium hydroxide.¹² Similarly, the conductivity of globular polypyrrole sulfate was reduced from 0.24 S cm^{-1} to $3.8 \times 10^{-6} \text{ S cm}^{-1}$ after being immersed in 1 M ammonium hydroxide, and to $6.4 \times 10^{-10} \text{ S cm}^{-1}$ in 1 M sodium hydroxide.¹ The conductivity increased again after treatment with acid solutions but its recovery has not been complete.^{5,6,11} The deprotonation/

^aInstitute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic. E-mail: stejskal@imc.cas.cz^bFaculty of Chemical Engineering, University of Chemistry and Technology, 166 28 Prague 6, Czech Republic^cCharles University in Prague, Faculty of Mathematics and Physics, 180 00 Prague 8, Czech Republic

reprotonation cycle in polypyrrole was exploited in ammonia sensors,^{13–15} silver recovery¹⁶ and sodium-ion batteries.¹⁷ Such salt–base conversion imposes restrictions to some applications, *e.g.*, to textiles coated with conducting polymers that need to be washed.¹⁸ Both forms, a salt and a base, differ not only in conductivity but also in density and thermal conductivity,¹⁹ electron spin concentration²⁰ or the third-order optical non-linearity,²¹ and other electrical and optical properties.

When polypyrrole was prepared in the presence of a dye, such as methyl orange (MO), polypyrrole nanotubes were obtained^{12,22–24} instead of a classical globular morphology. The conductivity of nanotubular polypyrrole was of the order of tens S cm^{-1} ,^{23,25} *i.e.* considerably higher compared with the conductivity of the globular form. The preparation and application of polypyrrole nanotubes has therefore recently become a fast developing research direction,^{26–31} also due to the interesting nanostructured morphology. The conductivity of polypyrrole nanotubes decreased from 60 S cm^{-1} only to 0.012 S cm^{-1} after suspension in 1 M ammonium hydroxide,²³ *i.e.* nanotubes were still conducting under alkaline conditions.^{12,32} Similar trend was observed in the composites of polypyrrole nanotubes with silver.^{12,33} The high conductivity of polypyrrole nanotubes and its resistance towards the deprotonation and consequent loss of conductivity under alkaline conditions inspired the present study aimed at the discussion of salt–base transition in various forms of polypyrrole.

Experimental

Preparation of globular and nanotubular polypyrrole

Polypyrrole nanotubes were prepared by the oxidation of 0.05 M pyrrole with 0.05 M iron(III) chloride in the presence of 0.005 M of methyl orange. 3.35 g of pyrrole and 1.64 g methyl orange, sodium 4-[(4-dimethylamino)phenylazo]benzenesulfonate, were dissolved in water and the volume was adjusted to 0.5 L. 13.5 g of iron(III) chloride hexahydrate was similarly dissolved in water to 0.5 L of solution. Both solutions were mixed at room temperature to start the oxidation of pyrrole. Next day, polypyrrole precipitate was collected on filter, rinsed with 0.2 M hydrochloric acid, copious amounts of ethanol, and left to dry in air. For the purpose of present study, globular polypyrrole was prepared in the same manner, only in the absence of MO.

Deprotonation and reprotonation of polypyrrole

Polypyrrole hydrochloride obtained after preparation was deprotonated by immersion in excess of 1 M ammonium hydroxide. Weighed amount of polypyrrole in sintered glass filter was placed in ammonia solution and left at rest for 24 h. The filter was then removed, rinsed with ammonia solution, and ethanol. The mass of solids was determined after drying. The ammonia solutions were evaporated and the mass of collected solids, referred to below as a filtrate, was determined.

A part of the deprotonated polypyrrole was immersed again in excess of 1 M hydrochloric acid for 24 h to test the reprotonation ability. The solids were then collected, rinsed with acid

solution, and ethanol. After drying, the change in mass was evaluated.

Characterization

Room temperature conductivity was determined by a four-point method in van der Pauw arrangement using a Keithley 220 Programmable Current Source, a Keithley 2010 Multimeter as a voltmeter and a Keithley 705 Scanner equipped with a Keithley 7052 Matrix Card.

Energy-dispersive X-ray spectra (EDS) were recorded by Quantax 200 spectrometer with a XFlash 6|10 detector (Bruker Corp.) using 15 kV of accelerating voltage of primary electron beam in Mira LMH (Tescan) scanning electron microscope.

Fourier-transform infrared (FTIR) spectra of the powders dispersed in potassium bromide pellets were registered using a Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC detector in the $400\text{--}4000 \text{ cm}^{-1}$ wavenumber region.

Raman spectra were recorded on a Renishaw InVia Reflex Raman microspectrometer. The spectra were excited with a near infrared diode 785 nm laser. A research-grade Leica DM LM microscope with an objective magnification $\times 50$ was used to focus the laser beam on the sample placed on an X–Y motorized sample stage. The scattered light was analyzed with a spectrograph using a holographic grating 1200 lines per mm. A Peltier-cooled CCD detector (576×384 pixels) registered the dispersed light.

Results and discussion

Molecular structure

The molecular structures of protonated polypyrrole (polypyrrole salt) proposed in the literature somewhat vary but there is agreement on the structure of polypyrrole base obtained after deprotonation, which is composed of both the oxidized and reduced pyrrole constitutional units (Fig. 1).^{7,9,13} The localization of positive charges on polymer chain, as well as the presence of unpaired spins, polarons, detected by electron paramagnetic resonance, is still open to discussion. For the purpose of present study, the rearrangement of electrons within polypyrrole chain leading to the formation of charge carriers can be proposed (Fig. 2).

Conductivity

Polypyrrole exists as a conducting salt obtained after preparation and less conducting or insulating base (Fig. 1) produced by subsequent deprotonation after the treatment with alkalis.^{1,10,12} Both the level of conductivity and the resistance towards the deprotonation were improved when the polymerization of pyrrole was carried out in the presence of anionic surfactants, and the conductivity of polypyrrole increased by one or two orders of magnitude.^{1,34} The presence of anionic surfactants thus generally (1) increased the conductivity of polypyrrole and (2) improved the level of conductivity under alkaline conditions. Surfactant anions were proved to participate as counter-ions in polypyrrole (Fig. 1).^{1,9} The ionic bond responsible for the salt formation seems to be sterically protected by the hydrophobic



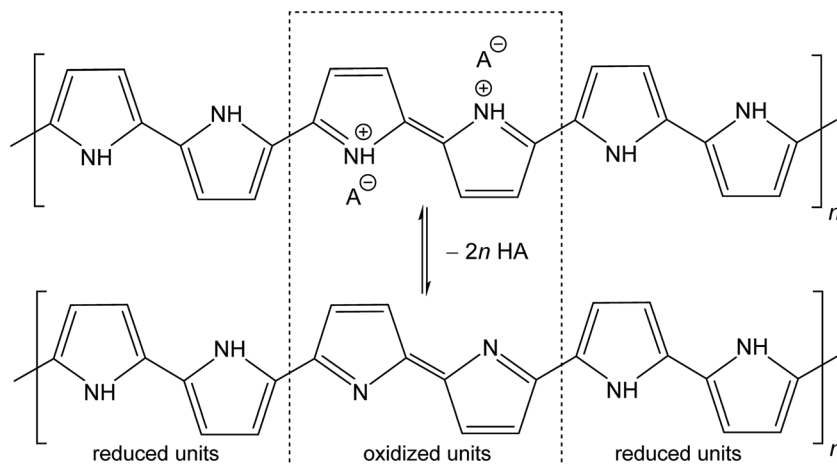


Fig. 1 Conducting polypyrrole salt converts to non-conducting polypyrrole base under alkaline conditions. HA is an arbitrary acid, A^- is a corresponding counter-ion, here chloride.

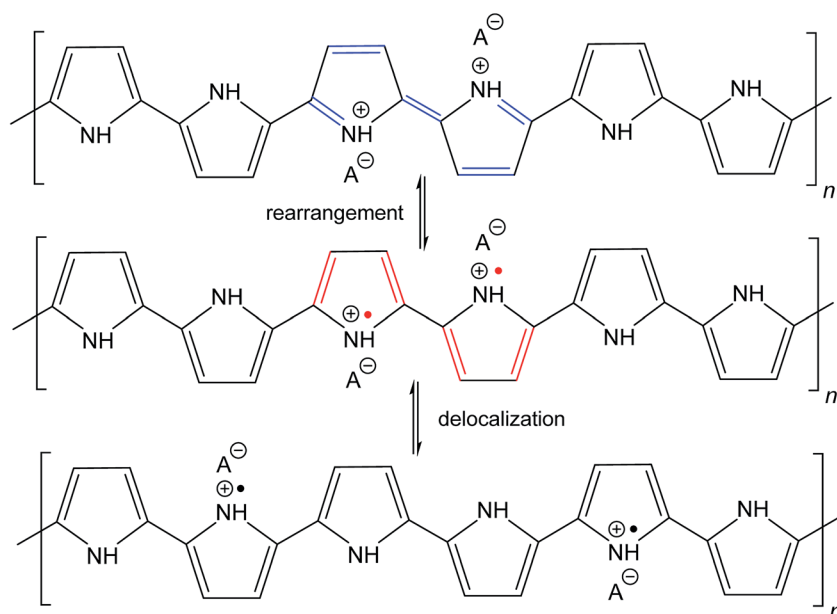


Fig. 2 The rearrangement of electrons in polypyrrole salt may generate bipolarons and finally polarons by delocalization over the polymer chain. Polarons act as charge carriers.

surfactant part from the direct access of alkalis, hydroxyl ions, thus reducing the extent of polypyrrole deprotonation to a corresponding base (Fig. 1).

The similar observation has recently been made when polypyrrole was prepared in the presence of MO dye (Fig. 3). The conductivity of polypyrrole hydrochloride was (1) considerably higher compared with the preparation in the absence of MO, and (2) the resistance to the loss of conductivity after treatment with alkalis was considerably improved (Table 1) as mentioned in the Introduction. In addition, the morphology distinctly changed from globular to nanotubular (Fig. 4). Nanotubes have also higher specific surface area,³² $55 \text{ m}^2 \text{ g}^{-1}$, than the globular form, $4.3 \text{ m}^2 \text{ g}^{-1}$.

We conclude that the dye has about the similar effect on the preparation of polypyrrole as a surfactant, but its performance with respect to conductivity is even better. In aqueous media, the classical surfactant, sodium dodecylbenzenesulfonate has a tendency towards the formation of micelles with a hydrophobic core composed of dodecyl substituents. In fact, MO is similarly composed of a large hydrophobic moiety and hydrophilic sulfonate group (Fig. 3). Both types of molecules thus can sterically protect the bonding of sulfonic group to nitrogen atoms in polypyrrole chain. The marked difference, however, consists in the molecule rigidity, which is flexible in the former case and stiff in the case of MO. While dodecylbenzenesulfonate would produce amorphous micellar aggregates, MO may be better suited to form more organized objects of



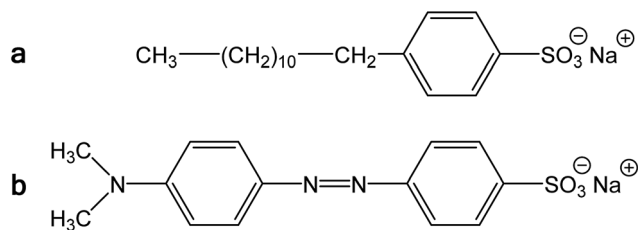


Fig. 3 (a) Sodium dodecylbenzenesulfonate and (b) methyl orange, sodium 4-[(4-dimethylamino)phenylazo]benzenesulfonate.

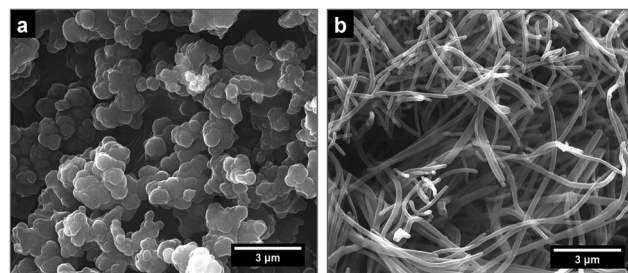


Fig. 4 Illustration of globular polypyrrole (left) and polypyrrole nanotubes (right).

liquid-crystalline type. The improved organization of polypyrrole chains, enforced already to the pyrrole monomers by surfactants, then leads to the improved conductivity of this polymer.

Nanostructures where polypyrrole chains are organized are expected to have improved conductivity, and brush-like chain-ordering in electropolymerized polypyrrole films may also serve as an example. The reported conductivity was $15\text{--}36\text{ S cm}^{-1}$,⁹ $26\text{--}28\text{ S cm}^{-1}$,⁷ $34\text{--}52\text{ S cm}^{-1}$,³⁵ and $\approx 100\text{ S cm}^{-1}$,⁶ *i.e.* three orders of magnitude higher compared with globular polypyrrole. The conductivity in the first case⁹ was reduced to 0.3 S cm^{-1} after treatment with 0.5 M sodium hydroxide at 100°C , *i.e.* the resistance towards the deprotonation in alkalis was also good.

Mass balance and elemental analysis

The deprotonation scheme (Fig. 1) has frequently been proposed for polypyrrole^{9,10,12,14,24,33,34,36} in the discussion of its properties. In the present case, the number of reduced polypyrrole units ($-\text{NH}-$ in base) is higher than the number oxidized polypyrrole units ($=\text{N}-$ in base) as assumed in early reports.^{9,13} The protonation of oxidized units is preferred to reduced units as confirmed in experimental studies.^{9,17} It should be noted that some papers consider also the protonation of amine groups.³⁷ The hypothesis that the current counter-ions are not only simply removed during deprotonation but replaced with hydroxide anions have also been proposed.²⁰

Generally, however, the deprotonation is associated with the reduction of mass.⁶ In the case of polypyrrole hydrochloride, the mass fraction of hydrochloric acid in polypyrrole salt calculated according to the formula in Fig. 1 is $15.8\text{ wt}\%$. The lower mass decrease by 9.4 and $9.1\text{ wt}\%$ were found in present experiment for globular and nanotubular polypyrroles, respectively (Table 1). If all acid were neutralized with ammonium

hydroxide, 1 g of polypyrrole hydrochloride should yield 232 mg of ammonium chloride. Ammonium chloride is indeed recovered as white crystals after evaporation of ammonium hydroxide solution, as identified by FTIR spectra below. Its quantity, however, is again lower, 173 and 130 mg per 1 g of globular and nanotubular polypyrrole salts. This means that either (1) a part of acid still remains attached to polypyrrole backbone and the deprotonation was not complete or (2) the amount of hydrochloric acid was smaller than that proposed. The former hypotheses seem to be supported by mass balance and elemental analysis by EDS.

The Cl/N atomic ratio expected by the proposed stoichiometry (Fig. 1) is $2/6 = 0.33$. EDS yields ratio 0.21 for globular form. This suggests that globular polypyrrole is protonated less than expected. After deprotonation with 1 M ammonia solution, the Cl/N ratios is reduced from 0.21 to 0.12 but not to zero, as expected for complete deprotonation. Only in stronger alkali, in 1 M sodium hydroxide, Cl/N ratio drops to 0.02 .

For polypyrrole nanotubes the Cl/N ratio was 0.30 , *i.e.* close to theoretical expectation, and the value was reduced to 0.03 after treatment with ammonia solution, again indicating agreement with the proposed deprotonation (Fig. 1). This atomic ratio may also be affected by the presence of methyl orange. Polypyrrole nanotubes contain in addition sulfur from the sulfonic groups in MO. The atomic S/N ratio 0.10 was reduced only to 0.06 after being exposed to ammonia solutions, and changed only marginally to 0.05 in 1 M sodium hydroxide. The former hypothesis of incomplete deprotonation is also supported by conductivity measurements that confirm still a good level of conductivity, 10^{-2} S cm^{-1} , and by the observation that the conductivity is further reduced after treatment with a stronger alkali, sodium hydroxide.³⁸

Table 1 Conductivity of polypyrrole before and after deprotonation in 1 M ammonium hydroxide (D), and after reprotonation in 1 M hydrochloric acid (R). The changes in mass of polypyrrole after deprotonation, the fraction of recovered ammonium salt, and the change in mass after reprotonation relative to the mass entering the reaction

	Conductivity (S cm^{-1})			Deprotonation loss, wt%	Ammonium salt, wt%	Reprotonation gain, wt%
	Original	D	R			
Globular	1.55	0.012	0.026	9.35	17.3	8.06
Nanotubes	49.8	1.42	3.64	9.13	13.0	9.69



The increase in mass after reprotonation of deprotonated samples with 1 M hydrochloric acid about compensates the loss after deprotonation (Table 1). The conductivity partly recovers for globular polypyrrole (Table 1). A similar deprotonation/reprotonation behavior was reported but the conductivity gradually decreased after each cycle.^{5,6} The literature on this process have been thoroughly reviewed.¹³ The recovery of conductivity in polypyrrole nanotubes has also never been complete. This is probably due to the damage of chain organization associated with mass loss and consequent volume reduction during deprotonation.

Infrared spectra during deprotonation

Infrared spectrum of the globular polypyrrole salt (spectrum G in Fig. 5a) exhibits the main bands which were previously described.^{1,10,32} The shape of the spectrum of polypyrrole after deprotonation with 1 M ammonium hydroxide changed³² (spectrum D). Absorption in the region above 1600 cm⁻¹

decreased and a weak band at 1700 cm⁻¹ appeared. It corresponds to the presence of carbonyl group previously attributed to the nucleophilic attack of water during the preparation.¹ The maximum of the band observed in the spectrum of the polypyrrole salt at about 1542 cm⁻¹ (C–C stretching vibrations in the pyrrole ring) shifted to 1553 cm⁻¹, which corresponds to the deprotonation of the pyrrole rings (spectrum D). The maximum of the band of C–N stretching vibrations in the pyrrole rings moved from 1455 to 1478 cm⁻¹. The broad band with a maximum at about 1305 cm⁻¹ (C–H or C–N in-plane deformation modes) remains at the same position. The maximum of the band associated with the breathing vibrations of the pyrrole rings observed at 1167 cm⁻¹ in the spectrum of polypyrrole salt is situated at 1180 cm⁻¹ in the spectrum of deprotonated polypyrrole. The peak at 1092 cm⁻¹ connected with N–H⁺ deformation vibrations only slightly shifted to 1096 cm⁻¹ after deprotonation. The sharp band at 1045 cm⁻¹ (C–H and N–H in-plane deformation vibrations) remains at the same position. The band at 905 cm⁻¹ (the C–H out-of-plane deformation vibrations of the ring) shifted to 912 cm⁻¹ wavelengths after deprotonation.

The shape of the spectrum of the sample obtained after reprotonation with 1 M hydrochloric acid (spectrum R) dramatically changed. It exhibits very small absorption caused by compact stone-like structure which was difficult to disperse in potassium bromide pellets. As a consequence the aliphatic impurities (detected at 2925 and 2856 cm⁻¹) and a relatively strong absorption bands in the region of stretching and bending vibrations of water molecules at about 3422 cm⁻¹ and 1633 cm⁻¹ coming from potassium bromide pellet were detected in the spectrum. Nevertheless, the main bands of protonated polypyrrole can be observed in the spectrum. The spectrum of the filtrate obtained after deprotonation (spectrum F) corresponds well to the spectrum of ammonium chloride, *viz.* N–H vibrations in ammonium cation, as it was expected in the Fig. 1.

Infrared spectra of the nanotubular polypyrrole (NT in Fig. 5b) and its deprotonated (D) and reprotonated (R) forms exhibit small absorption, which is a result of their compact stone-like structure and they were difficult to disperse in potassium bromide pellets. This may be connected with strong hydrogen bonding in the samples. In addition to the bands of aliphatic impurities (at 2925 and 2856 cm⁻¹) and of humidity (at 3440 and 1633 cm⁻¹), the band of carbonyl group at about 1722 cm⁻¹ can be detected. The main bands of polypyrrole are present in all spectra. The band of C–N stretching vibrations in the pyrrole rings observed at 1455 cm⁻¹ in the spectra of globular polypyrrole splits into two maxima at 1470 and 1443 cm⁻¹, similarly as it was observed in the presence of surfactants.¹ The maximum of the band connected with the breathing vibrations of the pyrrole rings observed at 1163 cm⁻¹ in the spectrum of polypyrrole nanotubes keeps the same position after deprotonation. Some small peaks in the spectra of deprotonated and reprotonated samples marked with asterisk correspond to the presence of methyl orange (spectrum MO).

Please note that MO is, except for some traces, absent in the spectrum of the filtrate obtained after deprotonation (spectrum F). This means that MO is not simply bound to

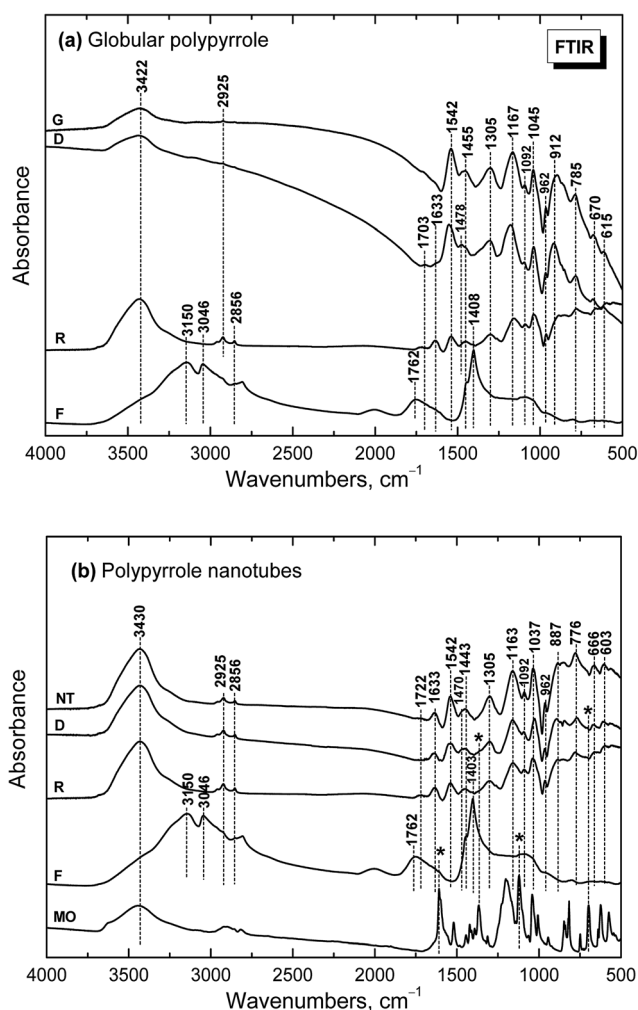


Fig. 5 Infrared spectra of (a) globular (G) and (b) nanotubular polypyrrole (NT) before and after deprotonation with 1 M ammonium hydroxide (D), and reprotonation with 1 M hydrochloric acid (R). Spectra of the solids collected from filtrate after deprotonation (F) and of neat methyl orange (MO) are included for comparison.



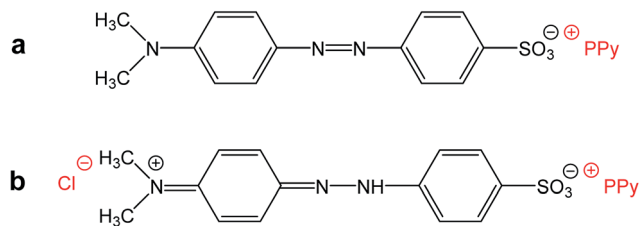


Fig. 6 (a) Methyl orange can act as a simple counter-ion in polypyrrole (PPy) or (b) it can be "inserted" into polypyrrole hydrochloride in its acid form.

polypyrrole in its yellow salt form (Fig. 3b) as a counter-ion (Fig. 6a), but might be "inserted" into polypyrrole salt in its red acid form (Fig. 6b). Such construction would explain the absence of MO in the filtrate after treatment with ammonia, and a consequent resistance of nanotubes towards the complete deprotonation associated with the loss of polypyrrole conductivity.

Raman spectra during deprotonation

Raman spectroscopy is a convenient tool for the study of structural bonding in conjugated polymers, such as polypyrrole. A formula of polypyrrole salt includes the oxidized and reduced units in its molecular structure (Fig. 1). In reality, we have to consider the presence of localized structural defects associated with polymer backbone which are connected with the existence of polarons (radical cations) and bipolarons (dications diradicals) (Fig. 2). They can be detected in the Raman spectra of protonated polypyrrole.

In the spectrum of globular polypyrrole salt (spectrum G in Fig. 7a) we observe the bands of C=C in-ring of C-C inter-ring vibrations and of the stretching vibrations in cation of the polypyrrole backbone with a maximum at 1598 cm⁻¹.^{39,40} The maximum of this band is shifted to 1607 cm⁻¹ in the spectrum of polypyrrole after deprotonation with 1 M ammonium hydroxide (spectrum D), which corresponds to the C=C backbone stretching vibrations in short conjugation length, a dication.³⁹ The band of C-C and C=N stretching skeletal vibrations is situated at 1492 cm⁻¹. This band is shifted to 1495 cm⁻¹ after deprotonation. The double peak observed in the spectrum of polypyrrole salt at about 1376 and 1333 cm⁻¹ corresponds to ring-stretching vibrations of pyrrole. The peak situated at the higher wavenumbers is assigned to the C-C ring stretching vibrations of oxidized polypyrrole. The second maximum was assigned to the neutral C-C ring stretching vibrations of reduced units.³⁹ This peak increased after deprotonation and it has been connected with less conducting polypyrrole.⁴¹ A shoulder at 1405 cm⁻¹ appeared in the spectrum of deprotonated polypyrrole which corresponds to the C-N stretching vibrations in the neutral units.³² The band of C-H antisymmetric in-plane bending vibrations with a maximum at about 1243 cm⁻¹ remained practically at the same position after deprotonation. In the double peak situated at 1088 and 1053 cm⁻¹ in the spectrum of polypyrrole salt, the higher peak is attributed to the C-H in-plane deformation vibrations in

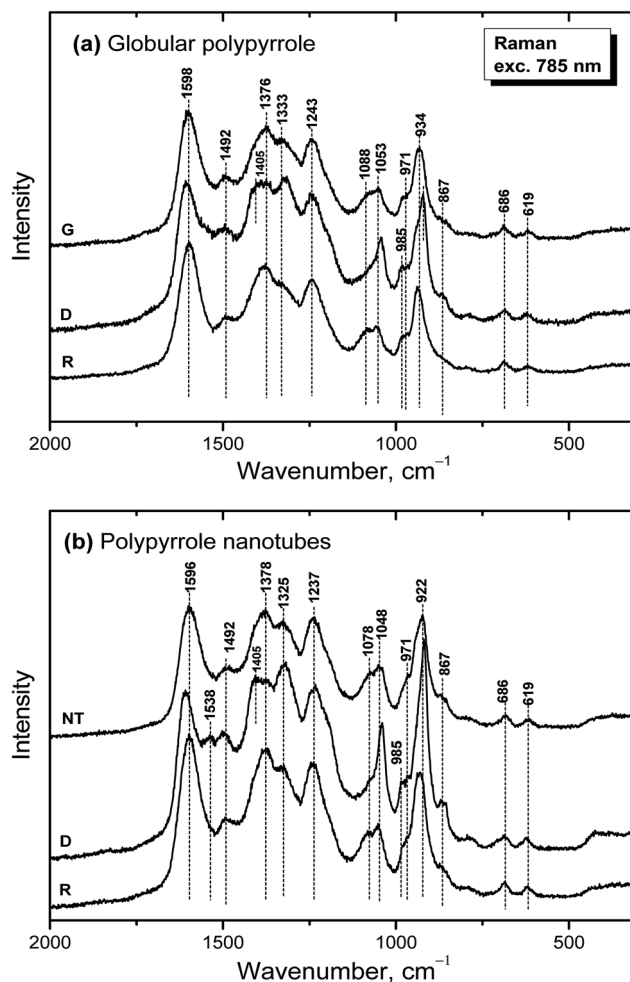


Fig. 7 Raman spectra of (a) globular (G) and (b) nanotubular (NT) polypyrrole before and after deprotonation with 1 M ammonium hydroxide (D), and reprotonation with 1 M hydrochloric acid (R).

radical cation units in protonated polypyrrole. The conductivity of polypyrrole is linked to the increase in intensity of this peak corresponding to oxidized polypyrrole units.⁴¹ The peak situated at lower wavenumber increased after deprotonation, and it is assigned to the C-H in-plane deformations in the neutral units of polypyrrole base³⁹ (Fig. 1). The peak at 971 cm⁻¹ in the spectrum of polypyrrole salt is attributed to the C-C ring deformation vibrations with radical cation.⁴⁰ It moved to 985 cm⁻¹ in the spectrum of deprotonated polypyrrole, and it belongs to the ring deformation in neutral units.³⁹ The band situated at 934 cm⁻¹ in the spectrum of polypyrrole salt moved to 922 cm⁻¹ after deprotonation and increased in intensity. It is assigned to the C-C ring deformation vibrations within dication unit.⁴¹ After reprotonation of deprotonated samples in the solutions of acids the Raman spectrum returns to the original state (spectrum R).

In the Raman spectrum of nanotubular polypyrrole salt we observe the same bands practically at the same positions as in the spectrum of globular polypyrrole (spectrum NT in Fig. 7b). This means that both forms have the identical molecular structure and differ in the organization of polymer chains. After



deprotonation of nanotubular polypyrrole, a new band located at 1538 cm^{-1} appears. It may be connected with an increase of the C=N stretching skeletal vibrations in deprotonated units (Fig. 1). The spectrum exhibits a higher increase in the intensity of the band of the neutral C-C ring stretching vibrations of reduced units situated at 1325 cm^{-1} and also of the band of the C-C ring-deformation vibrations with dication situated at 922 cm^{-1} than in case of globular polypyrrole. This may be connected with interaction between polypyrrole and MO. After reprotonation of the nanotubular polypyrrole with 1 M hydrochloric acid, we recognize the bands with intensities corresponding to the protonated polypyrrole salt (spectrum R). The bands of neat MO are not observed in the Raman spectra measured with near-infrared diode 785 nm excitation laser.

The dependence of conductivity on pH

The above discussion of deprotonation of polypyrrole with 1 M ammonium hydroxide (1.7 wt% NH_3) corresponded to the value of pH 11.6. The effect of the polypyrrole treatment with solutions of ammonium and sodium hydroxides of various concentrations in the pH range 10–14 on the conductivity has also been investigated (Fig. 8).

The conductivity of nanotubes treated with ammonia solution stays above 0.1 S cm^{-1} , even at 25% ammonia concentration and only a moderate decrease is observed as the ammonia concentration increased. The same trend was found for globular polypyrrole, only the conductivity was lower by about two orders of magnitude compared with nanotubes.

In the solutions of sodium hydroxide the conductivity of nanotubes was reduced as methyl orange was liberated and hydrolytic changes in the molecular structure of polypyrrole took place, as confirmed by spectroscopic method below. At pH > 13, the conductivity of both types of polypyrrole is comparable. Some conductivity was maintained even after the exposure of polypyrrole nanotubes to 5 M and 10 M sodium

hydroxide, *viz.* 5.1×10^{-6} and $1.2 \times 10^{-6}\text{ S cm}^{-1}$, *i.e.* at the level which is far from being negligible. Polypyrrole is thus suited even for the application operating at neutral or alkaline conditions where other conducting polymers, such as polyaniline, fail. It should be mentioned that the reprotonation of alkali-treated polypyrroles with acids does not recover the original conductivity, and the increase in conductivity is marginal, if any.

The dependence of infrared spectra on pH

When globular polypyrrole treated with alkali solutions in the pH range 10–14 is considered, the differences in the infrared spectra are relatively small (Fig. 9a). They correspond to the consecutive deprotonation of polypyrrole as pH increases. The maximum of the band of C–N stretching vibration in the pyrrole rings situated at 1478 cm^{-1} increased during deprotonation, the other maximum of this complex band at 1455 cm^{-1} is now well detected and a new shoulder at 852 cm^{-1} appeared in the spectra.

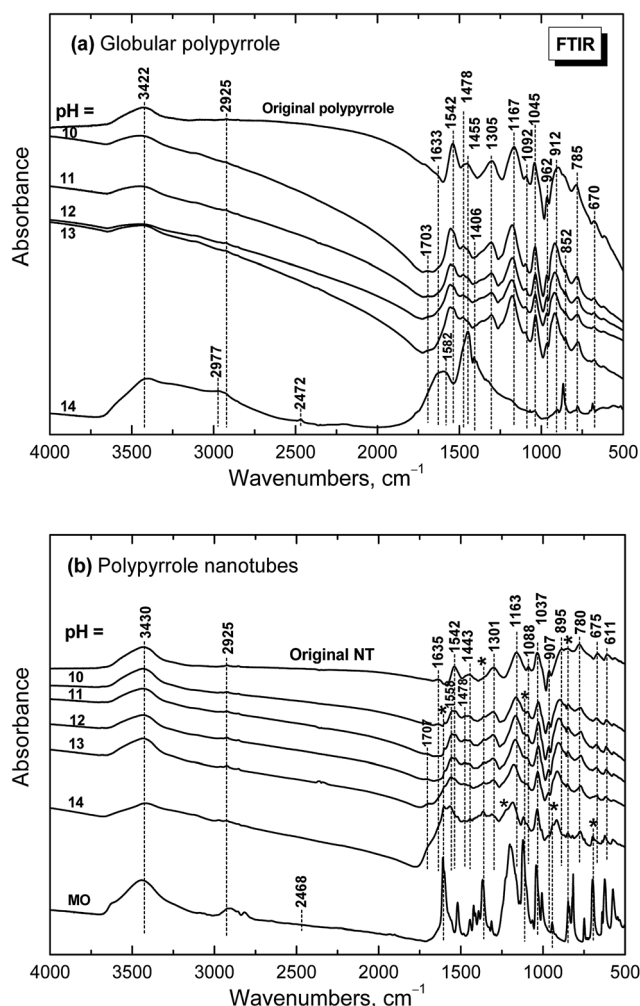


Fig. 9 Infrared spectra of (a) globular and (b) nanotubular polypyrrole before and after exposure to the media of various pH.

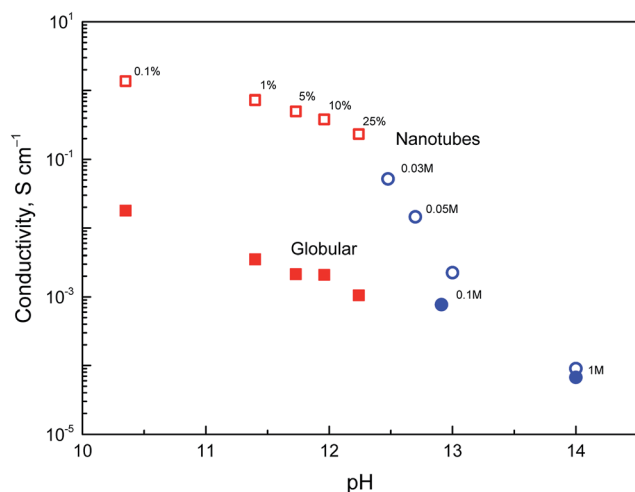


Fig. 8 Dependence of conductivity of polypyrrole nanotubes (open symbols) and globular polypyrrole (full symbols) on pH of deprotonation medium constituted by aqueous solution of ammonium hydroxide (wt%, squares) or sodium hydroxide (mol L^{-1} , circles).



Under strongly alkaline medium represented by 1–10 M sodium hydroxide with pH close to 14, the spectrum of polypyrrole dramatically changed, as the chemical changes in polypyrrole chain took place. A broad band with maxima at 3422 and 2977/2925 cm^{-1} and a new peak at 2472 cm^{-1} are observed in the spectrum. A broad band with maximum at 1582 cm^{-1} with a shoulder at 1633 cm^{-1} and a strong peak at 1455 cm^{-1} dominate in the spectrum. A sharp maximum located at 852 cm^{-1} is well observed. As it was shown in electrochemical experiments provided in alkaline medium, the potential needed for overoxidation of polypyrrole is significantly reduced⁴² and the formation of hydroxyl and carbonyl groups by nucleophilic attack takes place,⁴³ followed by alkaline hydrolysis to carboxylic salts and amines.^{42,44,45} All these products are also reflected in the present spectrum of polypyrrole exposed to strongly alkaline medium. The bands of original polypyrrole practically disappeared in the spectrum. Similar changes have previously been observed for electrochemical overoxidation of polypyrrole.^{45–47}

Infrared spectra of the nanotubular polypyrrole (spectrum NT in Fig. 9b) are well resolved as the samples are better dispersible in potassium pellets compared with globular form. The peaks of MO marked with asterisk increased during consecutive deprotonation with increasing pH. The main bands of polypyrrole are detected in all spectra till pH 13 as it was observed in the spectra of globular polypyrrole. The situation, however, is different when pH reaches the value close to 14. Contrary to the globular polypyrrole, in the case of nanotubular polypyrrole we observe well all the bands of polypyrrole (spectrum for pH 14 in Fig. 9b) on the background corresponding to the fully oxidized globular polypyrrole (spectrum for pH 14 in Fig. 9a). Some sharp peaks of MO in its salt form are well visible in the spectrum of polypyrrole (spectrum MO). This means that the chemical stability of polypyrrole nanotubes under strongly alkaline conditions is better compared with globular form. This may be due to the fact that MO remains, at least in part, incorporated in polypyrrole as proposed in Fig. 6.

The dependence of Raman spectra on pH

Raman spectra of globular polypyrrole excited with a 785 nm laser excitation line correspond to the above described spectrum of globular polypyrrole obtained after deprotonation with 1 M ammonium hydroxide (Fig. 7a) at pH 10–13 (Fig. 10a). Changes in the spectra follow the consecutive deprotonation of polypyrrole with increasing pH. The increase in the number of the C=N bonds in the neutral units is reflected in the new peaks appearing at 1548 cm^{-1} and 1410 cm^{-1} . In strongly alkaline medium with pH approaching 14, the spectrum dramatically changed as in the case of FTIR spectra. We observed a broad fluorescence band corresponding to the excitation of the overoxidized units of polypyrrole.

Raman spectra of alkali-treated polypyrrole nanotubes (spectrum NT, Fig. 10b) in the medium with pH 10–13 correspond to the spectrum of nanotubular polypyrrole obtained after deprotonation with 1 M ammonium hydroxide (Fig. 7). When pH reached the value 14, the bands at about 1495, 1405,

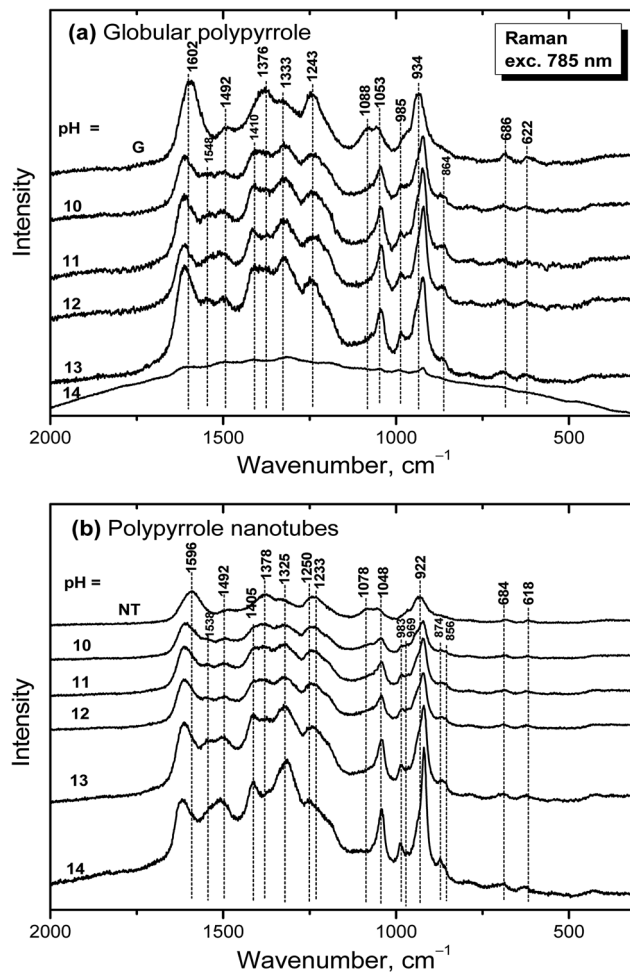


Fig. 10 Raman spectra of original (a) globular (G) and (b) nanotubular polypyrrole (NT) and after exposure to the medium of various pH.

1325, 1048, 983, 922 and 874 cm^{-1} increased. Contrary to the spectrum of globular polypyrrole, where no bands of polypyrrole have been detected, the spectrum of nanotubular polypyrrole preserved its features even after treatment with strongly alkaline medium. A fluorescence background corresponding to the presence of MO is present in the spectrum of polypyrrole.

Conclusions

The conductivity of globular polypyrrole salt was reduced from the units of S cm^{-1} to $10^{-2} \text{ S cm}^{-1}$ after treatment with 1 M ammonia solution at pH 11.6. The conductivity of polypyrrole nanotubes, 50 S cm^{-1} , was higher compared with globular form and after exposure to ammonia solution the conductivity dropped to the units of S cm^{-1} . This means that polypyrrole, in particular in its nanotubular form, retains most of its conductivity under moderate alkaline conditions, up to pH 13. This may be of importance for applications operating under physiological or in alkaline region. FTIR and Raman spectra prove that the molecular structure of globular polypyrrole is irreversibly damaged at pH 14. The conductivity of both polypyrroles is



further reduced under strongly alkaline conditions after treatment with 5 or 10 M sodium hydroxide solutions. The reprotonation of polypyrrole, *i.e.* the treatment by solutions of strong acids after exposure to alkalis, does not recover the original level of conductivity and the conductivity increase is only partial.

The model molecular structure expecting the protonation of each third polypyrrole constitutional unit, *i.e.* Cl/N = 0.33 atomic ratio for polypyrrole hydrochloride, reasonably well reflects the experimental reality. The polypyrrole was deprotonated only in part to polypyrrole base in ammonia solution. Methyl orange, which was used as a template in the preparation of nanotubes, stayed incorporated in polypyrrole and may take a role of counter-ions resistant to the deprotonation, similarly like surfactants reported in the literature. The “insertion” of acid form of methyl orange into polypyrrole hydrochloride is proposed to account for better conductivity and stability towards the deprotonation.

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Article

Polypyrrole Nanotubes and Their Carbonized Analogs: Synthesis, Characterization, Gas Sensing Properties

Jitka Kopecká ¹, Miroslav Mrlík ², Robert Olejník ², Dušan Kopecký ^{1,*}, Martin Vrnáta ¹, Jan Prokeš ³, Patrycja Bober ⁴, Zuzana Morávková ⁴, Miroslava Trchová ⁴ and Jaroslav Stejskal ⁴

¹ Department of Physics and Measurements, University of Chemistry and Technology Prague, Prague 6 CZ-166 28, Czech Republic; Jitka.Kopecka@vscht.cz (J.K.); martin.vrnata@vscht.cz (M.V.)

² Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, Zlin CZ-760 01, Czech Republic; mrlík@ft.utb.cz (M.M.); olejník@ft.utb.cz (R.O.)

³ Faculty of Mathematics and Physics, Charles University in Prague, Prague 8 CZ-180 00, Czech Republic; jprokes@semi.mff.cuni.cz

⁴ Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague 6 CZ-162 06, Czech Republic; bober@imc.cas.cz (P.B.); moravkova@imc.cas.cz (Z.M.); trchova@imc.cas.cz (M.T.); stejskal@imc.cas.cz (J.S.)

* Correspondence: kopeckyd@vscht.cz; Tel.: +420-220-443-351

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Abstract: Polypyrrole (PPy) in globular form and as nanotubes were prepared by the oxidation of pyrrole with iron(III) chloride in the absence and presence of methyl orange, respectively. They were subsequently converted to nitrogen-containing carbons at 650 °C in an inert atmosphere. The course of carbonization was followed by thermogravimetric analysis and the accompanying changes in molecular structure by Fourier Transform Infrared and Raman spectroscopies. Both the original and carbonized materials have been tested in sensing of polar and non-polar organic vapors. The resistivity of sensing element using globular PPy was too high and only nanotubular PPy could be used. The sensitivity of the PPy nanotubes to ethanol vapors was nearly on the same level as that of their carbonized analogs (i.e., ~18% and 24%, respectively). Surprisingly, there was a high sensitivity of PPy nanotubes to the *n*-heptane vapors (~110%), while that of their carbonized analog remained at ~20%. The recovery process was significantly faster for carbonized PPy nanotubes (in order of seconds) compared with 10 s of seconds for original nanotubes, respectively, due to higher specific surface area after carbonization.

Keywords: polypyrrole nanotube; carbon nanotube; carbonization; functionalized nanotube; heptane detection

1. Introduction

Since carbon nanotubes (CNTs) appeared to be very attractive for volatile organic compounds detection, many research groups focused on the development of the various sensors [1–7]. It was observed that especially defects and/or impurities, such as heteroatoms, present in nanotubes are responsible for their detection ability, since they modify generally low chemical interaction of CNTs with gas or vapor analytes [2,8]. The neat CNTs are able to detect only molecules with electron-donating (e.g., NH₃) or electron-accepting (e.g., NO₂) properties, but, in general, for the detection of such weakly absorbed molecules on the surface their change of the resistance (i.e., sensitivity) is small [9]. On the contrary, the functionalized nanotubes exhibit higher molecular reactivity, therefore the development of new carbonaceous materials with controlled morphology is a promising research direction in sensing

applications [10–14]. Polypyrrole (PPy) is also known to be a promising material for gas sensors detecting vapors of organic solvents [15]. Another interesting aspect is represented by the possibility to study properties of PPy-based sensors by impedance spectroscopy [16].

Conducting polymers, such as PPy [17–19], have been shown to produce nitrogen-containing carbons when exposed to temperature above 600 °C in an inert atmosphere. It is important to stress that the morphology is retained during this process but the specific surface area is likely to increase. An extensive review concerning the carbonization of these two polymers has recently been published [20].

Polypyrrole is usually prepared by the oxidation of pyrrole with iron(III) salts [21,22] or ammonium peroxydisulfate [23]. Polypyrrole typically has a globular morphology [21]. When prepared in the presence of so-called structure-guiding agents, such as methyl orange, PPy is obtained as nanotubes [19,24–29]. It is of interest if the difference in nano-scale morphology, globular or nanotubular, would be reflected in sensing applications.

In present study, globular and nanotubular PPy has been prepared and subsequently converted to nitrogen-containing CNTs by exposure to elevated temperature in an inert atmosphere. The vapor response of both the original and carbonized PPy was investigated for two organic solvents, polar ethanol and non-polar *n*-heptane, by using evaluation of resistance changes.

2. Materials and Methods

2.1. Preparation

Globular PPy was prepared by chemical polymerization of pyrrole monomer with iron(III) chloride hexahydrate at equimolar ratio in water. Molar concentrations of both reactants were 422 mM, total volume of reaction mixture was 379 mL. The stirred reaction mixture was kept at 5 °C for 24 h. The precipitated PPy was separated by filtration, rinsed with water and acetone, and dried at 40 °C in vacuo.

Polypyrrole nanotubes were synthesized in similar manner in the presence of structure-guiding additive, methyl orange, and sodium 4-[4-(dimethylamino)phenylazo]-benzenesulfonate. 200 mL of 2.5 mM solution of methyl orange in distilled water and 700 µL of pyrrole were mixed. Then solution of 10 mmol iron(III) chloride hexahydrate dissolved in 23 mL distilled water was added drop-wise during two hours. Both solutions were cooled to 5 °C before mixing and kept at this temperature afterwards. Molar concentrations of reactants thus were 45 mM pyrrole, 45 mM iron(III) chloride hexahydrate, and 2.2 mM methyl orange. After 24 h, precipitated PPy nanotubes were isolated by filtration, and purified by Soxhlet extraction using acetone until the extract was colorless. Polypyrrole nanotubes were dried as above. Both samples were converted to PPy bases [30] by overnight immersion in excess of 1 M ammonium hydroxide, rinsed with acetone, and dried.

2.2. Carbonization of Polypyrrole

Thermogravimetric analysis was used at first as an analytical tool of PPy carbonization. This was performed in 50 cm³·min^{−1} nitrogen flow at a heating rate of 10 °C·min^{−1} with a TGA 7 Thermogravimetric Analyzer (Perkin Elmer, Waltham, MA, USA). A comparative experiment in air has also been done.

In a preparative carbonization, 5 g of PPy nanotubes or globular PPy bases were heated in an inert nitrogen atmosphere to 650 °C in an electric oven. The selection of this particular temperature was made according previous experiments on polyaniline and PPy. In case of polyaniline it follows from the evolution of the infrared and Raman spectra that after carbonization at 650 °C, the G and D bands characteristic of a carbon material are well developed and the residue of the sample is close to 60 wt %. It has been proven also for nanotubular PPy derived carbon nanotubes [20]. When the carbonization temperature was lower, the carbonization was not complete. At higher temperatures, the yield of carbonized product is substantially reduced.

The heating was switched on, and the temperature increased at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ rate. After the target temperature was reached, the heating was switched off, and the residue was left to cool down in the flowing nitrogen stream.

2.3. Characterization

Infrared spectra in the range of $400\text{--}4000\text{ cm}^{-1}$ were recorded at 64 scans per spectrum at 2 cm^{-1} resolution using a fully computerized NEXUS 870 FTIR Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with DTGS TEC detector (Thermo Fisher Scientific). Samples were dispersed in potassium bromide and compressed into pellets. Raman spectra excited with a diode 785 nm laser were collected on a Renishaw inVia Reflex Raman spectroscopy. A research-grade Leica DM LM microscope (Leica Microsystems, Wetzlar, Germany) with an objective magnification $50\times$ was used to focus the laser beam. The scattered light was analyzed by the spectrograph with a holographic grating $1200\text{ lines mm}^{-1}$. A Peltier-effect cooled CCD detector (576×384 pixels) registered the dispersed light. To avoid degradation of the samples by the laser beam, a reduced beam power was always used. Transmission electron microscope (TEM) JEOL JEM 2000 FX (JEOL, Tokyo, Japan) and scanning electron microscope (SEM) JEOL 6400 (JEOL, Tokyo, Japan) were used to assess the morphology. Specific surface area was determined by nitrogen adsorption using a Gemini VII 2390 Analyzer (Micrometrics Instruments Inc., Norcross, GA, USA).

Room temperature conductivity of PPy nanotubes was determined on pellets compressed at 700 MPa by a four-point method in the van der Pauw arrangement using a Keithley 220 Programmable Current Source, a Keithley 2010 Multimeter (Keithley Instruments, Solon, OH, USA) as a voltmeter and a Keithley 705 Scanner (Keithley Instruments) equipped with a Keithley 7052 Matrix Card (Keithley Instruments). The conductivity of globular PPy and carbonized PPy was estimated on powders placed between two conducting pistons by two-probe method with applied pressure of ca. 23 kPa and using a Keithley 6517 electrometer (Keithley Instruments).

2.4. Vapor Response

Polypyrrole nanotubes, both original and carbonized form, were dispersed in 50 mL of deionized water containing 0.1 M of sodium dodecyl sulfate (SDS) surfactant (Sigma Aldrich, St. Louis, MO, USA) and 0.14 M of 1-pentanol (Sigma Aldrich), respectively. The concentration of nanotubes in the suspension was 0.3 wt %. The suspension was homogenized in an ultrasonic apparatus (UZ Sonopuls HD 2070, Bandelin, Germany) for 5 min at ca. $50\text{ }^{\circ}\text{C}$. Polypyrrole nanotube networks were prepared by vacuum filtration of suspension through nonwoven polyurethane membrane, composed of polyurethane straight fibers with average diameter $0.14 \pm 0.09\text{ }\mu\text{m}$. The fibers' surface was smooth and the main pore size was around $0.2\text{ }\mu\text{m}$. Thus, prepared network on polyurethane support was rinsed several times with deionized water and methanol. After drying, this composite structure was tested as a layer sensitive to volatile organic compounds when exposed to the vapors of *n*-heptane and ethanol (having nearly the same vapor pressure at room temperature but with different polarity). For sensitivity testing, laboratory air was used as the reference gas. Aqueous suspensions of globular PPy in 0.4 wt % concentration were similarly prepared and processed.

The stripes $5 \times 20\text{ mm}^2$ made of active components deposited on polyurethane supports were placed on a planar holder with copper electrodes fixed on both sides of the stripe by a screw mechanism. Time-dependent electrical resistance was measured along the specimen length by the two-point technique using a multimeter Keithley 6517B (Keithley Instruments) during adsorption (analyte-on phase) and desorption (analyte-off phase). The holder with the specimen was transferred into an air-tight conical flask containing saturated vapors of the respective solvent at atmospheric pressure and $25\text{ }^{\circ}\text{C}$. Under these conditions, the saturated vapor of ethanol has a concentration of 7.7 vol % and the corresponding value for *n*-heptane is 6.0 vol %. After 6 min of measurement the holder was removed from the flask and, for the next 6 min, the sample resistance was measured in laboratory air in the desorption mode until steady state. The sensitivity of sensors, a relative change in

resistivity is defined as $S [\%] = (R_g - R_a) / R_a \times 100$, where R_a is the resistance in air under laboratory conditions and R_g is the resistance of the specimen exposed to organic vapor.

3. Results and Discussion

The classical preparation of PPy yields a product with globular morphology [21] (Figure 1a left). Its carbonization proved that the morphology is retained when this process is carried out in an inert atmosphere (Figure 1a right). The introduction of methyl orange to the reaction mixture results in a dramatic change in polymer morphology, and PPy nanotubes are obtained instead (Figure 1b left). The cavity inside the nanotubes is demonstrated by using transmission electron microscopy (Figure 2).

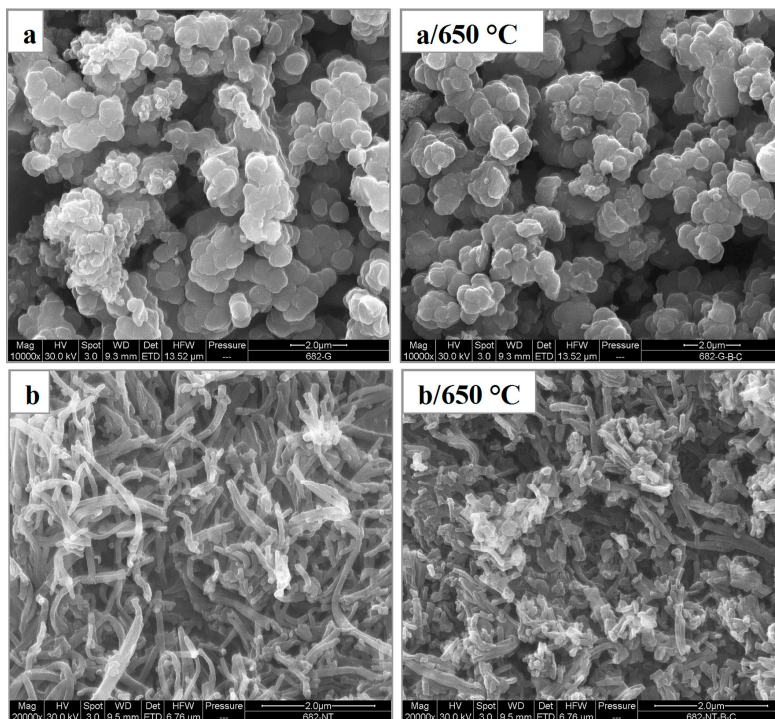


Figure 1. Scanning electron micrographs of (a) original globular polypyrrole and (b) polypyrrole nanotubes. They are depicted before- (left column) and after- carbonization at 650 °C (right column).

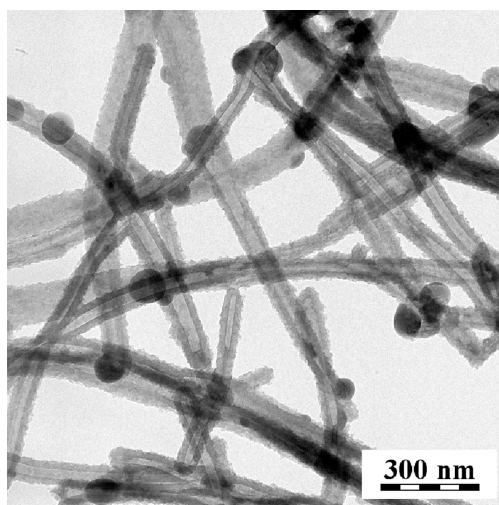


Figure 2. Illustration of nanotubular morphology by transmission electron microscopy.

The nanotubular structure is damaged but not destroyed after carbonization (Figure 1b right). The shrinkage is the consequence of the loss of mass during the exposure to elevated temperature (Figure 3).

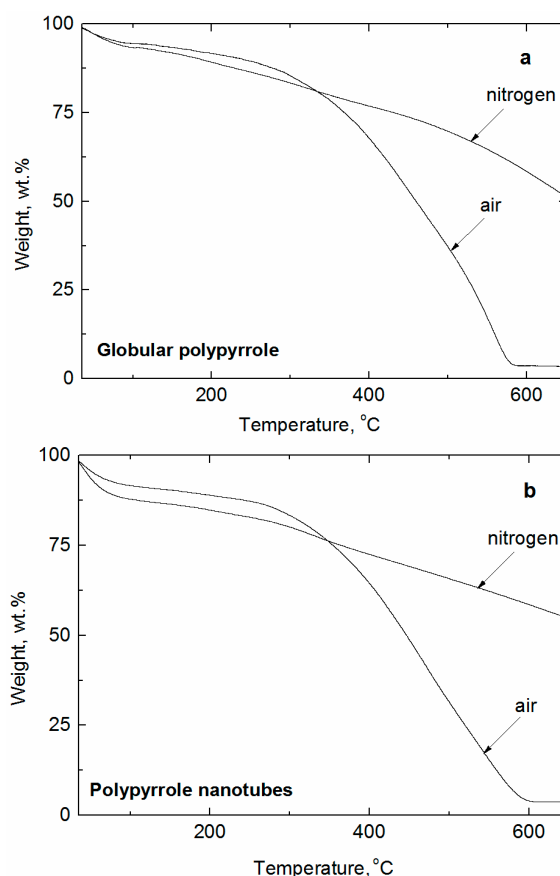


Figure 3. Thermogravimetric analysis of (a) globular polypyrrole and (b) polypyrrole nanotubes in air and in nitrogen.

The conductivity of PPy obtained by oxidative polymerization of pyrrole with iron(III) chloride is usually around units $\text{S}\cdot\text{cm}^{-1}$ [31,32]. In the presented case, the conductivity of globular PPy was of the order of $10^{-2} \text{ S}\cdot\text{cm}^{-1}$ (Table 1). By changing the morphology from globules to nanotubes, the conductivity increased to $60 \text{ S}\cdot\text{cm}^{-1}$. After the deprotonation with ammonium hydroxide the conductivity decreases by several orders of magnitude due to conversion of conducting PPy to less conducting PPy base. Polypyrrole bases have originally been intended for the application in electrorheology [33–35] but, for that purpose, the conductivity of the nanotubular form was too high. For that reason, the samples have been tested in the present study for sensing properties, where the level of conductivity is suitable.

Table 1. Conductivity and specific surface area of globular and nanotubular PPy salts, bases, and their carbonized analogs.

Sample	Conductivity ($\text{S}\cdot\text{cm}^{-1}$)			Specific Surface Area ($\text{m}^2\cdot\text{g}^{-1}$)		
	Salt	Base	Carbonized Base	Salt	Base	Carbonized Base
PPy nanotubes	60 ^a	6.7×10^{-2} ^a	6.7×10^{-6}	75	63	211
Globular PPy	0.011	3.4×10^{-5}	1.4×10^{-7}	26	25	150

^a Measured on pellets compressed at 530 MPa pressure. Pellets could not be prepared from other samples. Their conductivity was estimated in a powdered state. Such conductivities are usually one to two orders of magnitude lower compared with those of the pellets.

3.1. Analytical Carbonization

To get a deeper insight into the process of carbonization, thermogravimetric analysis was performed both in air and nitrogen atmosphere. The analysis in air illustrates the complete destruction of PPy between 550 °C and 600 °C (Figure 3a). There is no significant difference in the thermal stability between globular and nanotubular forms of PPy. A residue of ≈ 5 wt % is most likely represented by iron oxides produced from the oxidant, iron(III) chloride.

In inert nitrogen atmosphere, however, the residue is in both cases above 50 wt % at 650 °C. Also here, there is no substantial difference in the stability of globular and nanotubular PPy (Figure 3b). This is logical, because the thermal stability is established by molecular, rather than supramolecular, structure.

3.2. FTIR Spectroscopy

3.2.1. Polypyrrole Bases

Infrared spectra of granular and nanotubular PPy bases (Figure 4) are close to each other and correspond well to the spectra of PPy bases described in the literature [23]. We observe a broad absorption band at wavenumbers above 2000 cm^{-1} , and the band at about 1700 cm^{-1} which corresponds to the presence of a carbonyl group formed by the nucleophilic attack of pyrrole by water during the preparation [21,23]. The band at 1572 cm^{-1} is assigned to C–C stretching vibrations in the pyrrole ring, the band at 1475 cm^{-1} to C–N stretching vibration in the ring. A broad band attributed to C–H or C–N in-plane deformation modes with a maximum at 1300 cm^{-1} is well detected in the spectra. In the region of the C–H and N–H in-plane deformation vibrations from 1250 to 1000 cm^{-1} , we observe a maximum at 1170 cm^{-1} in the spectra of PPy base. The bands corresponding to the C–H and N–H in-plane deformation vibrations are situated at 1030 cm^{-1} and to C–C out-of-plane ring-deformation vibrations at 965 cm^{-1} . The C–H out-of-plane deformation vibrations of the pyrrole ring (at about 907 cm^{-1}) and of the C–H out-of-plane ring deformations (at about 776 cm^{-1}) are present in the spectra of the PPy base.

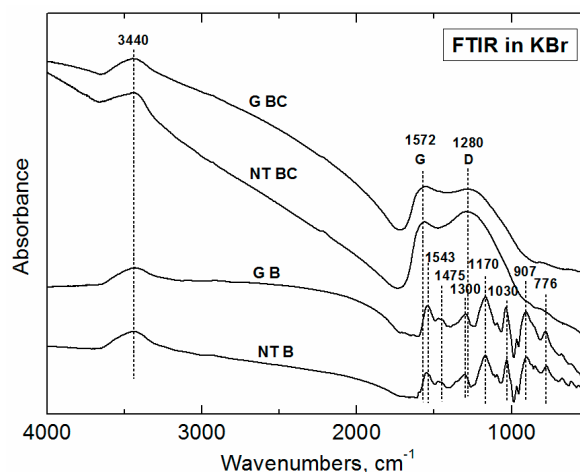


Figure 4. FTIR spectra of original globular (G) and nanotubular (NT) polypyrrole bases before (B) and after (BC) carbonization.

3.2.2. Carbonized Materials

In the FTIR spectra of carbonized PPy bases, we observe a local maximum at 1572 cm^{-1} , and a broad band with a maximum at about 1280 cm^{-1} . The first band emerged from the C–C stretching vibrations in the pyrrole ring, the second from the C–N in-plane deformation modes. The shape of the spectra is close to that of the spectra of a carbon-like material with the Raman-active D and G bands,

which are usually inactive in FTIR spectra. In disordered samples, however, they become IR-active because of symmetry-breaking of the carbon network, but they are rather weak and the spectra are flat and almost featureless.

3.3. Raman Spectroscopy

3.3.1. Polypyrrole Bases

Raman spectroscopy is well suited to characterize the progress of carbonization (Figure 5). Raman spectra of powdered samples have been recorded with excitation wavelength 785 nm. The spectra of globular and nanotubular PPy bases differ in elevated intensity and narrower shape of the band located at 930 cm^{-1} (C–H out-of-plane deformation vibrations of dication-bearing unit [36]), the presence of band at 1555 cm^{-1} , and a shoulder around 1415 cm^{-1} in the case of nanotubular PPy. The PPy base bands are located at 1615 cm^{-1} (C=C stretching in the pyrrole ring), 1495 cm^{-1} (C=N stretching vibrations in the pyrrole ring), 1390 cm^{-1} (C–H and N–H bending), 1330 cm^{-1} (C–C stretching of neutral units), 1245 cm^{-1} (antisymmetric C–H bending), 1045 cm^{-1} (in-plane ring-deformation vibrations) with a shoulder at 1090 cm^{-1} (C–H, N–H and out-of-plane ring-deformation vibrations), 980 cm^{-1} (C–C deformation vibrations in neutral rings), 687 cm^{-1} , and 617 cm^{-1} (ring-deformation vibrations).

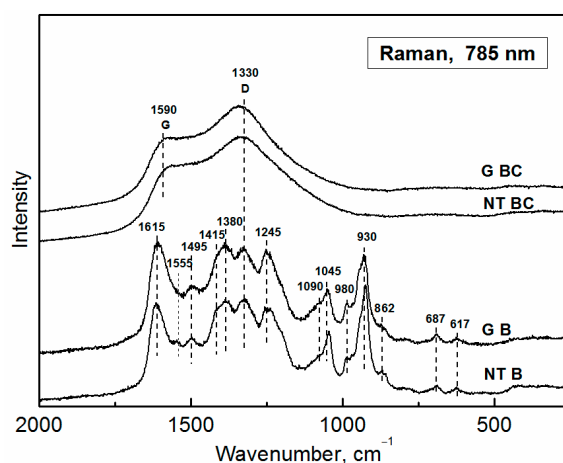


Figure 5. Raman spectra of original globular (G) polypyrrole bases and polypyrrole nanotubes (NT) before (B) and after carbonization (BC).

3.3.2. Carbonized Materials

In the Raman spectra of carbonized PPy the band at 1590 cm^{-1} (emerged from the C=C stretching vibrations of the pyrrole ring) and the broad band centered at 1330 cm^{-1} (emerged from the C–C stretching vibrations of the pyrrole ring) can be observed. These bands can be considered as G-band (“graphitic” band, C=C stretching vibrations of any pair of sp^2 sites) and D-band (“disorder” band, breathing of aromatic rings activated by any defect including a heteroatom), bands defined for graphitic material [37] and proved to be usable for nitrogen-doped graphitic material. The spectrum corresponds to a disordered nitrogen-containing graphitic material.

3.4. Vapor Response

In the case of globular PPy samples, the resistivity of the prepared materials was too high, thus the vapor response properties of corresponding sensors were not measurable. The response properties of both PPy nanotubes as well as their carbonized forms were obtained (Figures 6 and 7). When detecting ethanol vapors (Figure 6), the sensitivity (i.e., a relative increase in resistance) of both nanotubular samples differs only slightly (i.e., 18% for non-carbonized PPy and 24% for a carbonized analog).

When detecting *n*-heptane (Figure 7), the significantly better sensitivity of 110% was determined for the original PPy nanotubular base, while the carbonized ones exhibit only a 20% response. The high sensitivity to *n*-heptane is remarkable because typical values reported in the literature for detection of alkanes are of the order of units of a percent [38]. We can speculate that the high sensitivity of as-synthesized PPy to *n*-heptane is connected with the reduction of humidity level in the sample and consequent increase in its resistivity. Another interpretation of this phenomenon can be made according to basic theory of sensing mechanisms on conducting polymers [39–42]: Doping and undoping play key roles in the sensing mechanism of conducting polymer based sensors. Their doping level can be altered by transferring electrons from or to the sensitive layer. All π - or σ -electron donating gases can be detected. Our analyte (*n*-heptane) probably acts as an σ -electron donor.

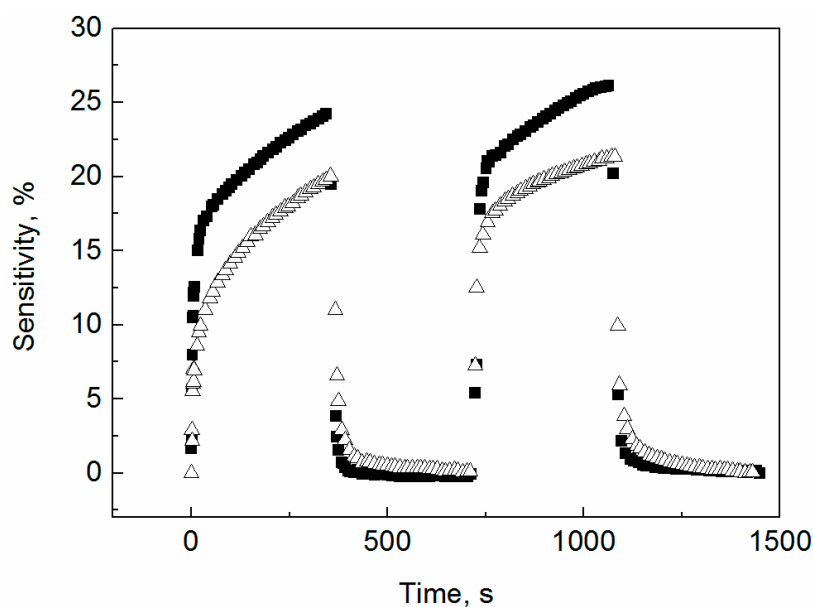


Figure 6. The response profile during two adsorption/desorption cycles in the presence of ethanol (7.7 vol %) for (Δ) polypyrrole nanotubes and ($\blacksquare$) carbonized polypyrrole nanotubes.

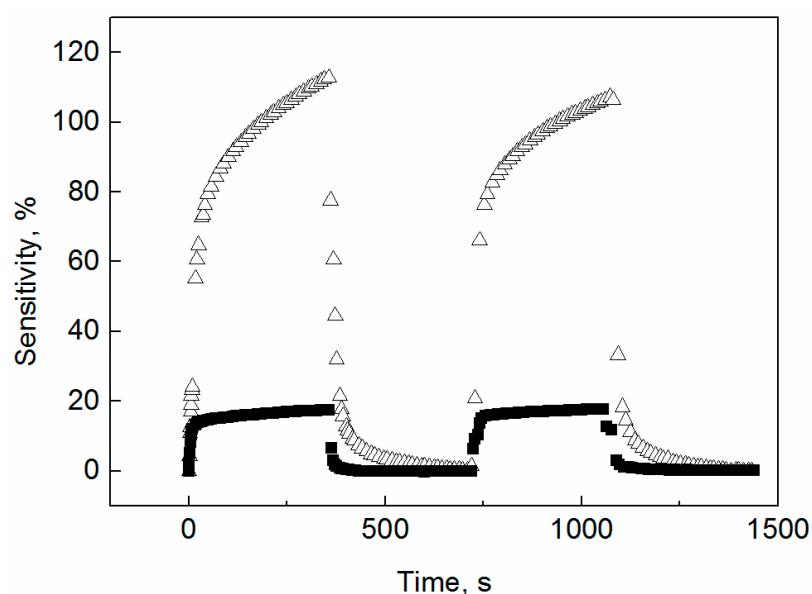


Figure 7. The response profile during two adsorption/desorption cycles in the presence of *n*-heptane (6.0 vol %) for (Δ) polypyrrole nanotubes and ($\blacksquare$) carbonized polypyrrole nanotubes.

There is still one important trend observable (Figures 6 and 7), a significantly faster response of carbonized nanotubes on the change of the vapor environment especially in recovery process for both investigated solvents. This is probably due to structural changes during carbonization which are connected with increasing material porosity.

To determine the detection limit for ethanol and *n*-heptane, we can take into account a conventional definition that the minimum detectable signal (i.e., detection limit) of a sensor should be calculated as a value of input quantity which causes change of output quantity three times higher than it is the effective noise of output quantity. When evaluating the meta-data for Figures 6 and 7, we observed that the level of noise of sensor output is lower for carbonized polypyrrole nanotubes than for as-prepared polypyrrole nanotubes (this is a positive aspect of the former sensors). With respect to meta-data and the above-mentioned definition the detection limits were calculated as follows: 3000 ppm of ethanol on carbonized PPy nanotubes; 5000 ppm of ethanol on PPy nanotubes; and 10,000 ppm of *n*-heptane on carbonized PPy nanotubes; 5000 ppm of *n*-heptane on PPy nanotubes.

A comparison of our sensitivity results with those found in the literature is included in Table 2. It is limited to detection of two relevant classes of compounds—alkanes and alcohols—on PPy nanotubes or their carbonized analogs. We have converted various expressions of sensitivity reported in original references to a quantity defined as the relative change in the resistivity, $S = (\Delta R/R_0) \times 100$ [%].

Table 2. Overview of sensitivity of sensors based on PPy nanotubes, nitrogen-containing carbons, and MWCNT. The detected analytes are alkanes and alcohol vapors.

Sensor Design		Detection Conditions			
Sensitive Material	Analyte	Concentration	S (%)	Temp./Hum. (°C)/(% RH)	References
Sensors of this work					
PPy nanotubes deprotonated	ethanol	saturated vapors at 25 °C	18	25/0	This work
	<i>n</i> -heptane		110		
PPy nanotubes carbonized	ethanol		24		
	<i>n</i> -heptane		20		
Polypyrrole based sensors ^a					
PPy/sulfate	propane/butane	1040 ppm	55	27/35	[39]
PPy/Cl [−]	hexane	-	0.8	100/0	[38]
	methanol		5		
PPy/ClO ₄ [−]	<i>iso</i> -butanol		15.5		
	ethanol		10.4		
	<i>iso</i> -propanol		15.8		
	<i>n</i> -pentanol		11.2		
PPy/PF ₆ [−]	<i>iso</i> -butanol	saturated vapors at 25 °C	0.5	25/0	[15]
	ethanol		3.2		
	<i>iso</i> -propanol		0.6		
	<i>n</i> -pentanol		1.1		
PPy/CF ₃ SO ₃ [−]	<i>iso</i> -butanol		3.0		
	ethanol		7.5		
	<i>iso</i> -propanol		4.4		
	<i>n</i> -pentanol		1.3		
PPy/camphorsulfonate	<i>iso</i> -butanol		6.1		
	ethanol		5.8		
	<i>iso</i> -propanol		5.7		
	<i>n</i> -pentanol		5.1		

Table 2. Cont.

Sensor Design		Detection Conditions			References
Sensitive Material	Analyte	Concentration	S (%)	Temp./Hum. (°C)/(% RH)	
PPy/ <i>p</i> -toluenesulfonate	methanol ethanol	-	18 10	-	[40]
PPy/3-nitrobenzenesulfonate	methanol ethanol		11 6		
Nanostructured PPy/ClO ₄ [−]	methanol ethanol <i>n</i> -propanol <i>iso</i> -propanol	11% wt. of VOC in <i>n</i> -hexane	2.9 0.58 0.22 0.18	120/0	[41]
Nanostructured PPy/ <i>p</i> -toluenesulfonate	methanol ethanol <i>n</i> -propanol <i>iso</i> -propanol		1.5 0.75 – –		
PPy/PCP ^a	methanol ethanol	–	7 7	–/0	[42]
PPy/PEO	methanol ethanol		3.5 5.5		
PPy/PMMA	methanol ethanol		65 20		
PPy/PVAL	methanol ethanol		14 14		
PPy/PVAc	methanol ethanol		27.5 37.5		
CNT based sensors					
MWCNT	<i>iso</i> -pentane methanol	saturated vapors at 25 °C	20.3 13.6	25/60	[3]
MWCNT/PMMA	<i>iso</i> -pentane methanol		12.6 14.7		
MWCNT/PMMA	methanol hexane	saturated vapors at 25 °C	429 –	–/0	[4]
Surface modified MWCNT/PMMA	methanol hexane		4500 –		
MWCNT	<i>iso</i> -pentane methanol	saturated vapors at 25 °C	20.6 12.9	25/60	[5]
Oxidized MWCNT	<i>iso</i> -pentane methanol		12.0 46.6		

^a Definition of abbreviations: PCP—polycaprolactone, PEO—poly(ethylene oxide), PMMA—poly(methyl methacrylate), PVAL—poly(vinyl alcohol), PVAc—poly(vinyl acetate), MWCNT—multi-wall carbon nanotubes, CVD—chemical vapor deposition, VOC—volatile organic compounds.

For alkanes detected on PPy (Table 2), there is reported detection of 1040 ppm of propane/butane with sensitivity 55% [39], and an unknown concentration of hexane with sensitivity 0.8% [38]. In the present case, it was 60,000 ppm of *n*-heptane with sensitivity 110%. As for alkanes detected on carbon nanotubes, only response to the saturated vapor is reported (i.e., 905,000 ppm at 25 °C) of *iso*-pentane which yielded sensitivity of 20.3%, 12.6%, 20.6%, and 12% at various conditions [3]. The present result is 60,000 ppm of *n*-heptane with sensitivity of 20%.

As for alcohol vapors detected on PPy, there are mainly responses reported to vapors saturated at 25 °C (their concentration is in the order of 10,000–100,000 ppm) in dependence on the number of carbon

atoms in the alcohol molecule. The sensitivity varies from 0.22% to 37.5% [15,38,40–42]. The present result is 18% for 77,000 ppm of ethanol. As for alcohol vapors detected on carbon nanotubes—for saturated methanol vapor there was reported sensitivity from 12.9% to 46.6% [3,5]—one paper presents significantly higher sensitivity, i.e., 429% and 4500% for saturated methanol vapor [4], while the result of this study is 24% for 77,000 ppm of ethanol.

To conclude, the preliminary results related to detection of *n*-heptane are significantly better than the average of those reported elsewhere. When comparing the response to alcohol vapors, there is a wide range of sensitivities; and they should be assessed case-by-case. The values obtained in this study are approximately in the middle of interval of reported sensitivities [3,5]. The detection of both alkanes and alcohol vapors will be the subject of our further systematic research.

4. Conclusions

During the oxidation of pyrrole with iron(III) chloride, globular morphology of PPy is transformed to nanotubes by addition of methyl orange. PPy bases obtained after deprotonation convert to nitrogen-containing carbon by heating to 650 °C in inert atmosphere. The original morphology is preserved after carbonization. Conductivity of PPy was reduced after the conversion to bases as well as after subsequent carbonization. The conductivity of globular form becomes too low for the application in sensors. The nanotubular PPy base, however, was demonstrated to respond to ethanol or *n*-heptane vapors by the change in resistivity. The sensitivity of the original nanotubular base to *n*-heptane reached 110%, which is a unique result, and even the carbonized analog maintained a 20% sensitivity. The recovery was faster in the carbonized PPy. Organic vapor may reduce the humidity in the samples and thus cause a consequent increase in the resistivity.

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Author Contributions: Jitka Kopecká and Dušan Kopecký synthesized PPy nanotubes; Patrycja Bober prepared and characterized carbonized samples; Jan Prokeš measured electrical conductivities of all samples; Zuzana Morávková and Miroslava Trchová provided IR and Raman spectra; Miroslav Mrlík and Robert Olejník prepared sensors and measured sensitivities; Martin Vršata discussed material properties and discussed and wrote the sensor part; Jaroslav Stejskal contributed to data evaluation and manuscript preparation.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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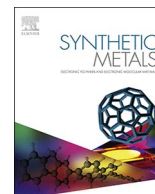
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Optimization routes for high electrical conductivity of polypyrrole nanotubes prepared in presence of methyl orange

Dušan Kopecký^{a,*}, Martin Varga^b, Jan Prokeš^b, Martin Vršná^a, Miroslava Trchová^c, Jitka Kopecká^a, Marek Václavík^d

^a Department of Physics and Measurements, Faculty of Chemical Engineering, University of Chemistry and Technology, Prague, 166 28 Prague 6, Czech Republic

^b Faculty of Mathematics and Physics, Charles University, 180 00 Prague 8, Czech Republic

^c Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

^d Department of Chemical Engineering, Faculty of Chemical Engineering, University of Chemistry and Technology, Prague, 166 28 Prague 6, Czech Republic

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ABSTRACT

The synthesis of polypyrrole nanotubes using methyl orange as a structure guiding agent is a popular method for obtaining electrically conductive material of nanostructured morphology. This work presents certain route of chemical synthesis, where the experimental conditions were optimized in order to obtain a material with high conductivity (up to 91.6 S cm^{-1}) and specific surface area (up to $67.6 \text{ m}^2 \text{ g}^{-1}$) via modification of two parameters: a) the methyl orange concentration (from 0.5 mM to 25 mM) and b) the polymerization temperature (from -5°C to 35°C). The synthesized material was then characterized by scanning electron microscopy, energy X-ray dispersive spectroscopy, nitrogen physisorption, Fourier-transform infrared and Raman spectroscopies and measurement of electrical conductivity. It was found, that the concentration of methyl orange in polymerization solution strongly influences both the diameter (ranging from 60 to 900 nm) and the shape (circular or rectangular cross-section) of synthesized polypyrrole nanotubes. Moreover, while at low concentrations of methyl orange in the native liquor the resulting nanotubes are accompanied by globular form of polypyrrole, at higher concentrations the composite of polypyrrole nanotubes with acidic form of methyl orange is produced. The detailed mechanism of methyl orange role during the polymerization process was explained in terms of behaviour of planar aromatic sulfonic acids. As for the polymerization temperature, it has stronger influence on the morphology than on the chemical composition of resulting polypyrrole nanotubes. Finally, we report a universal relation – a power law describing dependency of electrical conductivity on nanotube diameter for this class of materials.

1. Introduction

Polypyrrole nanotubes (PPy-NTs), prepared using methyl orange (MO) as a structure guiding agent, have recently attracted considerable attention by properties superior to their granular counterpart (PPy-G) [1]. This particular synthesis excels due to its simplicity, effectivity and possibility to tune the outer diameter of nanotubes in nano- or micro-metric scale. Since the first experiments made by Yang et al. [2] in 2005, these PPy-NTs were successfully tested in a variety of applications: as a material for sensors, [3,4] supercapacitors and batteries [5–9], aerogels [10], synthetic absorbents [11], antioxidants [12,13], reducing agents [14], catalysts [15], photocatalysts [16], or conducting fabrics [17].

The synthesis of PPy-NTs using MO usually proceeds by chemical

way, but analogous, electrochemical synthesis by anodic oxidation of pyrrole monomer was also reported [18]. In a typical chemical synthesis, an oxidant is mixed with MO water solution resulting in formation of fibrous flocculant. Subsequently, the pyrrole monomer is added dropwise. Iron(III) chloride (FeCl_3) is a first choice oxidant for this kind of polymerization, but ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) [19], iron (III) nitrate ($\text{Fe}(\text{NO}_3)_3$) [3,20], silver nitrate (AgNO_3) [20], or iron(III) sulphate ($\text{Fe}_2(\text{SO}_4)_3$) [21] can be also used.

According to generally accepted theory, the fibrous flocculant is created by the complex of MO-iron(III) chloride and serves as a self-degraded reactive template during the polymer synthesis [2,22]. Nevertheless, the detailed survey of the polymerization process [23] has shown that the reverse synthesis procedure, where MO is mixed with pyrrole followed by slow addition of oxidant also leads to PPy-

* Corresponding author.

E-mail addresses: kopecyk@vscht.cz, kopecyk.dusan@gmail.com (D. Kopecký), jprokes@semi.mff.cuni.cz (J. Prokeš), trchova@imc.cas.cz (M. Trchová), Marek.Vaclavik@vscht.cz (M. Václavík).

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NTs, although the flocculant intermediate is not created during the reaction. Therefore, the seeding mechanism of PPy-NTs formation, which emphasizes the role of MO aggregates (dimers or oligomers) formed in an aqueous solution [24], has been also proposed [23]. The hypothesis of the seeding mechanism is supported by the fact that using the pyrrole dimer, *i.e.* 2,2-bipyrrole (which serves as a homogeneous polymerization site instead of MO dimers) leads also to the similar PPy nanostructures, although no flocculant is created during the polymerization [25,26].

It is worth to note that MO as a structure-guiding agent also stimulates formation of nanotubes of other conductive polymers – polyaniline and polythiophene [22,27].

The supramolecular nature of PPy-NTs provides new or more pronounced material features among whose the most valuable are the increased electrical conductivity and large specific surface area. The increased electrical conductivity and large specific surface are desirable in many applications like in supercapacitors [6], sensors [4] or in cryogels substituting for instance polyaniline which has been mainly employed so far [28]. From this perspective, it is essential to reveal the influence of various synthesis conditions on both properties. In the previous studies it was found that the template-to-monomer ratio [23] and the type of oxidant [21] affects the final diameter and the conductivity of nanotubes. In the present study we focus on the structure-property relationship and optimization of synthesis and processing conditions in order to increase the electrical conductivity and the specific surface area of PPy-NTs. For this purpose, we selected a wide range of two experimental parameters: MO concentrations ranging from 0.5 to 25 mM and polymerization temperatures ranging from -5 to 35 °C.

2. Material and characterization

2.1. Synthesis

Pyrrole (Sigma-Aldrich), iron(III) chloride hexahydrate (Sigma-Aldrich), methyl orange *i.e.* (4-[4-(Dimethylamino)phenylazo]benzenesulfonic acid sodium salt; Fluka, Switzerland), ethanol (Penta, Czech Republic), acetone (Penta, Czech Republic) were used as received. PPy-NTs were prepared by the oxidation of the pyrrole monomer with iron (III) chloride in the presence of MO as a structure-guiding agent, according to the previously published procedure [23].

At the beginning, the solution of MO in deionized water was prepared. The initial concentration of MO varied with each reaction so as to create ascending concentration series of 0.5; 1; 1.5; 2.5; 3.5; 5; 10; 25 mM. Totally five temperature series were created; the individual reaction solutions were tempered to -5 ; 5; 15; 25; 35 °C, respectively. In the next step, after tempering, the pyrrole monomer was added into the MO solution and mixed using a stirrer. After 15 min, a concentrated solution of the oxidizing agent, *i.e.* iron(III) chloride hexahydrate, was added dropwise into the solution. The monomer to oxidant molar ratio was 1:1 (*see the note to the molar ratio selection in Supporting information*) and it was kept constant for all the syntheses. A black precipitate started to be formed immediately after the addition of oxidant, but the whole reaction mixture was kept tempered and under constant stirring for 24 h to ensure that all reactants have properly reacted (*see an example of the reaction in Supporting information*). Black precipitate of PPy-NTs was filtered after 24 h and purified by Soxhlet extraction using acetone. The purified black powder was dried in vacuum at 40 °C for several days.

2.2. Characterization

The morphology and chemical composition of samples were studied by scanning electron microscopy (SEM) using the Mira 3 LMH (Tescan) microscope at 3 kV of accelerating voltage and energy-dispersive X-ray spectroscopy (EDX) using Quantax 200 with XFlash 6|10 detector (Bruker) with the resolution of 127 eV and 15 kV of accelerating voltage, respectively.

The surface area of the PPy-NTs powders was evaluated by nitrogen physisorption using Quantachrome NOVA 2200e surface area analyser. The powders (50–200 mg per sample, depending on its morphology) were vacuum degassed at 140 °C at least 12 h and subsequently, adsorption-desorption isotherms (77 K) were measured. The specific surface area of the samples was calculated using Brunauer–Emmett–Teller (BET) theory.

Fourier-transform infrared (FTIR) spectra of powdered samples dispersed in potassium bromide and compressed into pellets were measured using Thermo Nicolet NEXUS 870 FTIR Spectrometer with DTGS TEC detector in 400 – 4000 cm^{-1} wavenumber region. Raman spectra were recorded with Renishaw InVia Reflex Raman microspectrometer using near infrared diode 785 nm laser excitation line. A research-grade Leica DM LM microscope was used to focus the laser beam. The scattered light was analysed with a spectrograph using holographic grating 1200 lines mm^{-1} . The Peltier-cooled CCD detector (576×384 pixels) registered the dispersed light.

Polypyrrole powders were compressed (at *ca.* 530 MPa) to the pellets of 13 mm in diameter and 0.5–1 mm thick. Their electrical conductivity was then measured by the four-point van der Pauw (VDP) method. The experimental set-up consisted of Keithley 220 programmable current source, Keithley 2010 multimeter as a voltmeter, and Keithley 705 scanner equipped with Keithley 7052 matrix card (*see Supporting information – the note to measuring current selection*).

The tensiometer Lauda TD1 was used for measurement of surface tension of MO solution at different concentration by Du Noüy ring method.

3. Results and discussion

Two synthesis conditions, *i.e.* a) concentration of MO and b) polymerization temperature, were varied in order to modify the PPy-NTs structure, diameter, specific surface area, chemical composition and electrical conductivity. Preliminary results from this area we reported in the recent paper [23]. To carry out more comprehensive research, we varied the concentration of MO in the native liquor from 0.5 to 25 mM and the temperature of synthesis from -5 to $+35$ °C. Hence a large set of data was obtained and subsequently, some generalized consequences among *synthesis conditions* $\leftrightarrow$ *the PPy structure and chemical composition* $\leftrightarrow$ *electrical conductivity of the polymer* could be formulated. Moreover, a universal relation between *electrical conductivity* and *nanotube diameter* of PPy-NTs has been proposed.

3.1. The effect of methyl orange concentration on properties of PPy-NTs

Firstly, we studied the effect of MO concentration (0.5–25 mM) on the above named properties of PPy. The partial results are summarized in Fig. 1 and in Fig. 2.

3.1.1. Structure and diameter of synthesized PPy nanotubes

Observation of the synthesized PPy-NT structure and evaluating the diameter of nanotubes by SEM have revealed some interesting facts.

Both the rectangular and the circular cross-sections of synthesized nanotubes are present (Fig. 1). Their diameter strongly depends on MO concentration. As can be seen from Fig. 2(i), in the interval of 0.5–3.5 mM the diameter of PPy-NTs decreases monotonously with rising concentration of MO in the reaction solution. For 5 mM and 10 mM concentration the diameter remains almost constant. The highest concentration, *i.e.* 25 mM of MO, was not included into Fig. 2(i), as the material produced under such conditions possesses rather compact, stone-like structure with barely visible contours of nanostructures.

The average diameter of the biggest tubes is in the range from 360 to 560 nm for 0.5 mM of MO, while the smallest tubes have the diameter between 65 and 85 nm for concentrations starting from 3.5 mM of MO. On the other side, the spatial density of created nanotubes

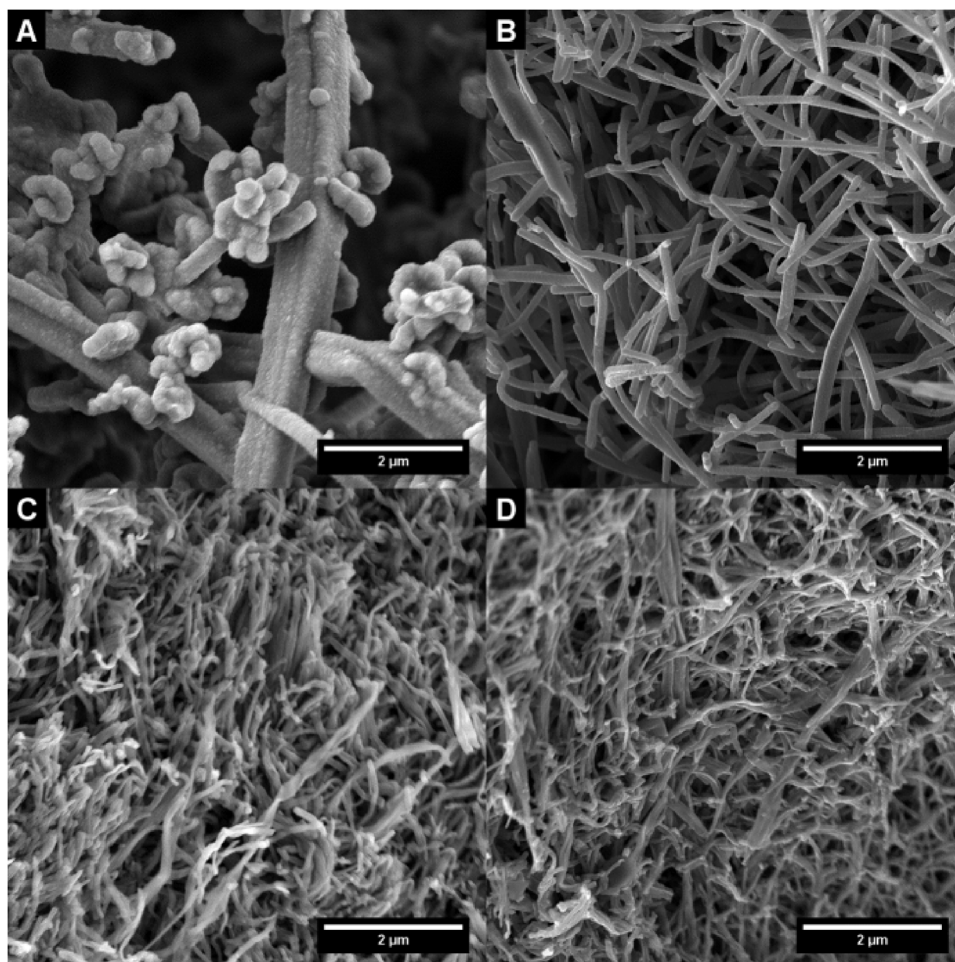


Fig. 1. The morphology of synthesized PPy-NTs in relation with the initial concentration of MO: The structure of PPy synthesized with A) 0.5 mM, (rectangular cross-section); B) 1.5 mM, (circular cross-section); C) 3.5 mM, (circular cross-section); D) 10 mM of MO, (circular cross-section); at polymerization temperature equal to 5 °C observed by SEM.

throughout the volume of synthesized PPy increases with increasing concentration of MO. These phenomena support the explanation of PPy-NTs formation *via* the seeding mechanism reported by Kopecká et al. [23]. The smaller is the concentration of MO, the smaller is the number of MO seeds in the volume – this circumstance allows the nanotubes to grow to larger diameters. At 0.5 mM the relative lack of MO, when compared with concentration of the iron (III) chloride oxidant, even leads to the partial occurrence of PPy-G in the product, as apparent from Fig. 1A.

These results comply with [2,19,22,29], where all reactions were made only in the presence of flocculant. Based on our results, it can be additionally stated that the presence of the fibrous MO flocculant in a reaction solution is not the essential condition to obtain PPy-NTs. Also it seems that the biggest diameter of PPy-NTs is observed in the area of the smallest MO concentration (0.5 mM), where the formation of MO-iron(III) chloride template of the equivalent size would be suppressed due to stoichiometric reasons. Moreover, different synthesis conditions allow creation of two possible shapes of nanotubes – either of the circular or the rectangular cross-section. The complete overview of relationships between the diameter and the concentration of MO and also between the diameter and the temperature (discussed in the part 3.2.1), can be found on a 3D graph in Supporting information, see Fig. 1S.

3.1.2. The elemental analysis

The results of the EDX elemental analysis of synthesized PPy-NTs are summarized in Fig. 2(ii). There is presented the content of sulphur and chlorine in synthesized samples. The motivation for focusing on these two elements is following: the only source of sulphur in the reaction mixture is MO and the only source of chlorine is iron(III) chloride. As both MO and chloride ions can act as counter-anions to PPy

backbone-polycation, the content of chlorine and sulphur in a resulting material could be the measure of a protonation degree of synthesized PPy.

From Fig. 2(ii) it is apparent that with increasing concentration of MO in the reaction mixture the content of sulphur monotonously increases from ca 0.3 at.% to ca 2.8 at.%. On the contrary, the content of chloride ions have higher variance, but when we calculate for each concentration of MO the average from values corresponding to distinct temperatures, we obtain monotonous decrease from ca 3.2 at.% to ca 0.5 at.%. Thus we can presume that with increasing concentration of MO in the reaction mixture the chlorine counter-anions are replaced with the MO counter-anions. What is significant, the hypothetical sum of dopants, *i.e.* sulphur and chlorine, slightly decreases till approx. 3.5 mM of MO and sharply increases above this MO concentration (valid for syntheses at –5; 5; 15; 25 °C; at 35 °C this trend is fuzzy), see Fig. 4S in Supporting information.

However, this hypothetical outstanding protonation level observed for concentrations above 3.5 mM of MO is not followed by corresponding increase of electrical conductivity. According to our opinion, the reason for this fact is connected with a specific behaviour of MO at higher concentrations.

According to Kendrick et al. [24] MO creates stacked dimers at concentrations from 0.1 mM to 2 mM and oligomers at above 2 mM (at 25 °C). Moreover, our measurement of the surface tension of the MO solution at different concentrations (at 7 °C) has shown a rapid decrease in the range of 0.05–2 mM and only a slow decrease between 2 and 10 mM (see Supporting information, Fig. 5S). This can be connected with continuous creation of MO structures stacked by π - π interaction (dimers, oligomers) whose influence on surface tension is proportional to their size.

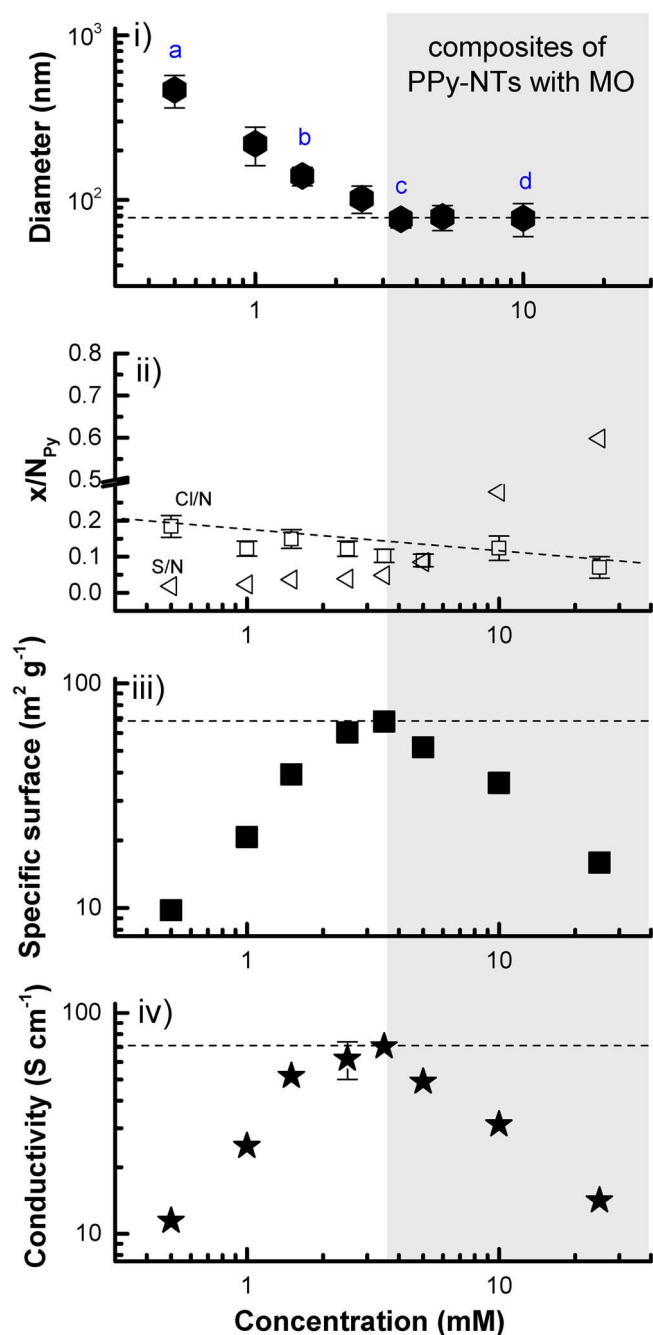


Fig. 2. Selected properties of synthesized PPy-NTs in the relation with variable concentration of MO in native liquor: nanotube diameter (i), chlorine and sulphur content (ii), specific surface area (iii) and electrical conductivity (iv). The data were obtained at polymerization temperature equal to 5 °C. Note: For better orientation in graph the error bars of the sulphur content are displayed only in Supporting information, Fig. 3S.

Therefore, we can speculate, that the presence of, at least, MO dimers is determinative for propagation of PPy polymerization into the supramolecular nanostructure. Nevertheless, the incorporation of MO into the PPy chain as counter anions at high concentrations of MO is probably connected with the incorporation of additional MO molecules which are stacked together by reacting with a MO counter anion. This inevitably leads to creation of a composite of PPy-NTs and MO. Moreover, according to Takagishi et al. [30] the interaction of MO with a polycation, *i.e.* protonated PPy-NTs in aqueous solution, is characterized by a simultaneous effect of electrostatic attractive forces between the oppositely charged ionic groups and repulsive forces between water molecules and hydrophobic parts of MO. Hence the role of MO as

a dopant of PPy-NT in syntheses with a higher concentration of MO, can be simply suppressed by the stronger role of MO as a composite component.

This opinion of ours is supported by several other facts. Firstly, at higher concentrations (more than 5 mM) of MO, one can observe red-dish crystals scattered in a bulk of PPy-NT; this means that MO is present in its acidic form in higher amount. Further, the presence of MO in the acidic form was confirmed by FTIR (see the part 3.1.3) starting from the concentration 3.5 mM and thirdly, the electrical conductivity of a material reaches its maxima also near 3.5 mM of MO, and steadily decreases thereafter (see the part 3.1.5).

It should be also noted, that according to these results, the Soxhlet process using acetone, regardless of the time duration, is not efficient enough to break all bonds among stacked MO molecules (occurred at high concentration) and to release them out of the PPy-NTs bulk.

3.1.3. Results of FTIR and Raman spectroscopy

3.1.3.1. Infrared spectra. Infrared spectra of the samples may be divided into two groups. In the first group (the concentration of MO 0.5; 1; 1.5; 2.5 mM) we can observe the well distinguished bands of PPy described previously in the Refs. [31,32] (Fig. 3). The bands observed at 3438 and 1628 cm^{-1} in the spectrum of PPy-NTs synthesized at 0.5 mM of MO belong to water molecules coming from potassium bromide pellets. The positions of maxima of the main bands (1539 cm^{-1} of C–C stretching vibrations in the pyrrole ring, at 1476 cm^{-1} C–N stretching vibrations in the pyrrole rings, at 1305 cm^{-1} C–N stretching vibrations, at 1165 cm^{-1} of the breathing vibrations of the pyrrole rings, at 1093 cm^{-1} connected with N–H⁺ deformation vibrations, and at 903 cm^{-1} of the C–H out of plane deformation vibrations of the ring) correspond to slightly deprotonated PPy [33]. This deprotonation can be a result of the decreasing level of chloride ions (acting as dopants; see Fig. 2(ii)) with the increasing MO concentration in syntheses when we accept the limited role of MO ions as dopants of PPy-NTs (see the part 3.1.2). In the spectrum of PPy-NTs synthesized at 1 mM of MO we detect the peak at 1761 cm^{-1} which corresponds to the stretching vibrations of a carbonyl group. The samples of PPy-NTs synthesized at 1.5 and 2.5 mM were difficult to disperse in potassium bromide pellets, which is caused by their consistence. For the second group of samples (3.5; 5; 10; 25 mM of MO) the peaks of MO in its acidic form are dominating in FTIR spectra (Fig. 3).

3.1.3.2. Raman spectra. Raman spectra of the samples may be divided into the same two groups as in the case of infrared spectra. In the

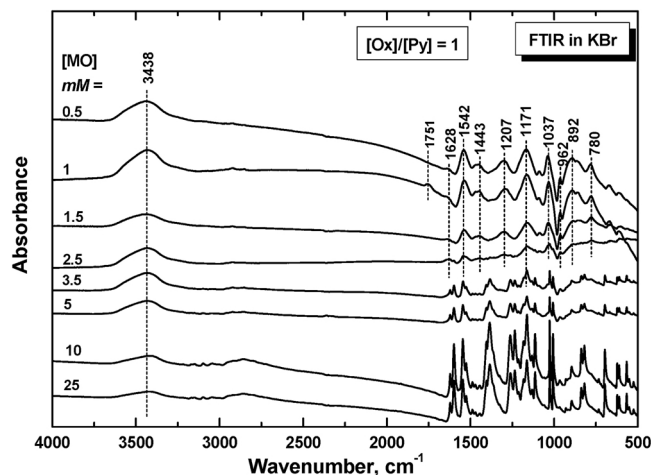


Fig. 3. FTIR spectra of PPy-NTs prepared in the presence of various molar concentrations of MO (the temperature of synthesis 5 °C).

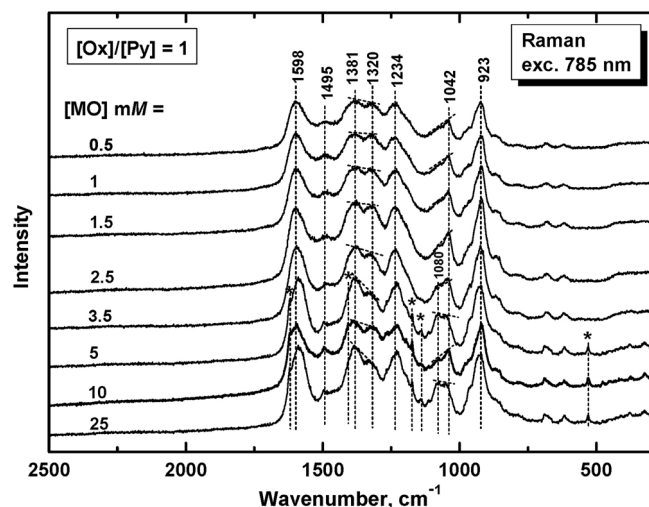


Fig. 4. Raman spectra of PPy-NTs prepared in the presence of various molar concentrations of MO (temperature of synthesis 5 °C).

spectra of the first group (concentration of MO 0.5; 1; 1.5; 2.5 mM) we can distinguish only the bands of PPy described previously in the Ref. [34] (Fig. 4). We observe the band of the stretching vibrations in the cation of PPy backbone with the maximum at 1598 cm^{-1} , the band of C–C and C=N stretching skeletal vibrations 1492 cm^{-1} , the double peak at about 1376 and 1333 cm^{-1} , the band of C–H antisymmetric in-plane bending vibrations with a maximum at about 1243 cm^{-1} , the double peak situated at 1088 and 1053 cm^{-1} , and the peak at 922 cm^{-1} assigned to the C–C ring deformation vibrations within a dication unit. The position of these bands corresponds to the slightly deprotonated samples [33]. In the Raman spectra of the second group of samples (concentration of MO 3.5; 5; 10; 25 mM) we detect the area in which the peaks of MO in its acidic form are prevailing (not shown in Fig. 4), and the area where the bands of PPy are dominating. The spectra measured in these areas still contain some peaks of MO (marked with asterisks in Fig. 4). The shape of the bands corresponds to the protonated form of PPy [33]. Products are thus inhomogeneous at micrometer size. The same we have recently observed in [35], where we also detected the areas rich in PPy, at which the spectrum of PPy in the slightly deprotonated form prevails, and areas rich in MO, where mostly MO is detected and the peaks of protonated PPy were observed. The different protonation state of PPy nanotubes observed in the Raman spectra for two different groups of samples may be explained by the resonance character of the Raman scattering. The spectra obtained with the laser excitation at 785 nm , which falls into the electronic absorption band of polaron, correspond especially to the surface of the PPy nanotubes. In the first group of samples the Raman spectra corresponds to the slightly deprotonated surface of the samples. In the second group the spectra correspond to PPy nanotubes which are in contact with dyes close to their surface.

3.1.4. The specific surface area

The shape of all physisorption isotherms (see Supporting information, Fig. 6S), regardless of the MO concentration, follows Type II isotherms as defined by IUPAC and this is in accordance with the previously published result measured on PPy-NTs synthesized at 2.5 mM of MO (at 5 °C). [34] At lower concentrations of MO (0.5 – 3.5 mM) the specific surface area of PPy-NTs increases by more than one order of magnitude and it is accompanied by the decrease of their diameter (see Fig. 2(iii)). On the contrary, at higher concentrations of MO, i.e. 5 , 10 and 25 mM , the specific surface area of the synthesized composite decreases, while the diameter of PPy-NTs stagnates. The maximum specific surface area was achieved at 3.5 mM of MO (at 5 °C) reaching the value approx. $67.6\text{ m}^2\text{ g}^{-1}$, which is much lower than that of common absorbents (an

activated carbon ~ up to thousands of $\text{m}^2\text{ g}^{-1}$) but better than previously published results on PPy-NTs ($57.5\text{ m}^2\text{ g}^{-1}$) [34] or polyaniline nanotubes ($34.6\text{ m}^2\text{ g}^{-1}$) [36].

Another meaningful detail – the shape of the dependence of the specific surface area vs. the concentration of MO is almost identical with the one displaying the conductivity vs. the concentration of MO (compare Fig. 2(iii) and (iv)).

Once again, the decreasing level of specific surface area above 3.5 mM of MO is probably the result of the increasing level of MO composite component (see the full explanation in the following part 3.1.5.).

3.1.5. The electrical conductivity

We have found the non-monotonic dependence of the electrical conductivity of PPy on the concentration of MO (Fig. 2(iv)). Moreover, the ratio of nanotubular to globular component in the sample is increasing up to the state with prevailing nanotubular form. In the recent study [21], both internal order and conductivity of PPy-NTs oxidized with iron(III) chloride was found to be higher than that in the case of granular polymer. Therefore, with the increasing content of nanotubes the overall conductivity increases, despite the lower protonation level (represented by the amount of chloride dopants). Clearly, for achievement of the highest conductivity it is desirable to reduce the content of PPy-G as much as possible.

Moreover, we can discuss the extent, to which the increasing electrical conductivity has correlation with decreasing diameter of nanotubes (Fig. 2(i)). The answer to this question is probably more complex, because (beside the nanotubular form) the nature of dopants and composite components incorporated in the PPy-NTs chain play also the essential role (see the discussion below). In the following text we present the evidence which confirms such a correlation (see the part 3.2.3.).

The small spherical chloride counter anion prevails in PPy-NTs synthesized at low concentrations of MO. When the concentration of MO in syntheses increases, the amount of chloride ions is decreasing and the amount of MO planar aromatic molecules (no matter if incorporated as counter anions or as the composite component) is increasing (Fig. 2(ii)). This has major impact on mechanical properties of the material in the macroscopic scale: At low concentrations of MO, the synthesized PPy is a soft, feather-like material, prone to compression into pellets; in the middle range of concentrations the corresponding PPy-NTs resemble sand particles and at higher concentrations it has the compact, stone-like structure. This effect was confirmed by experiments with X-ray scattering on PPy doped by different spherical or planar dopants [37]. Small spherical dopants promote an isotropic, i.e. disordered, molecular organization in PPy, while large planar aromatic molecules (like MO) prefer higher level of orientation and thus formation of denser material. At the same time, more oriented material, i.e. material with higher content of planar molecules, exhibits higher electrical conductivity because of higher material compactness, resulting in lower distances of PPy chains in comparison with PPy containing small spherical dopants. This behaviour is valid until the excessive concentration of MO reaches certain critical value, after which the suppressing effect of the composite component on electrical conductivity prevails. In our case, the breaking point is around 3.5 mM of MO.

It is worth to note, that the similar character of dependency of electrical conductivity on concentration of dopants was found in case of sulfonic acids with a planar aromatic ring [38] with the structure reminiscent of MO [33].

3.2. Variation of the polymerization temperature and its effect on properties of PPy-NTs

3.2.1. The dependency of the PPy-NTs diameter on the temperature

The temperature of synthesis has a significant impact on the PPy-

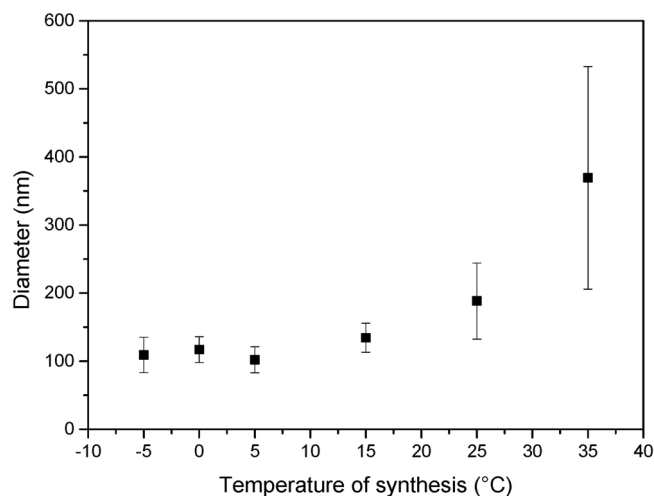


Fig. 5. The diameter of synthesized PPy-NTs in relation with the temperature of synthesis (concentration of MO 2.5 mM).

NTs diameter. As follows from Fig. 5, the higher is the temperature of synthesis, the bigger is the diameter of PPy-NTs and the higher is content of PPy-G component in the material. PPy-NTs synthesized between -5 and 5 °C (the concentration of MO 2.5 mM) has almost constant value of the diameter at around 100 nm. The elevated temperatures increase this diameter up to more than 350 nm at 35 °C.

In our opinion there are two possible reasons for such behaviour. Firstly, MO dimers and oligomers tend to dissolve at higher temperatures as π - π interactions are relatively weak. Thus the final concentration of polymerization sites is lower with the same mechanism of growth as in case of low concentrations of MO (see results and the discussion in the part 3.1.1). Secondly, higher temperatures promote faster polymerization kinetics and – thanks to this fact – polymerization proceeds more frequently in the space located out of existing seeds (on laboratory glass, existing tubes etc.) thus resulting in globular form of PPy. Both phenomena probably act simultaneously and it is difficult to determine the dominant one.

Variable experimental conditions investigated in our experiments (the temperature of synthesis together with concentration of MO) create certain area of “allowed” combinations suitable for syntheses of PPy-NTs. This area is displayed on the 3D graph in Supporting information (Fig. 1S).

3.2.2. EDX

No particular temperature dependence was found for the content of chlorine and sulphur in the synthesized polymer. Hence the variations of chlorine and sulphur are below the measurement error of EDX spectrometer (see error bars in Supporting information Fig. 2S and 3S). From this fact we conclude that the temperature has stronger influence on the supramolecular structure of PPy (Fig. 5) than on its chemical composition. Such a result is very important when evaluating dependence of the electrical conductivity on the synthesis temperature (see the next part 3.2.3).

The complete overview of measurements of chlorine and sulphur content in dependence on concentration of MO and temperature of synthesis can be found in Supporting information Fig. 2S and Fig. 3S, respectively.

3.2.3. The dependency of the electrical conductivity on the temperature and the concentration of MO

The facts presented in part 3.1.5 revealed that the presence of PPy-G, content of MO (as single counter-anions or the composite component) and nanotube diameter of PPy-NT have strong influence on electrical conductivity of the final product although it is difficult to

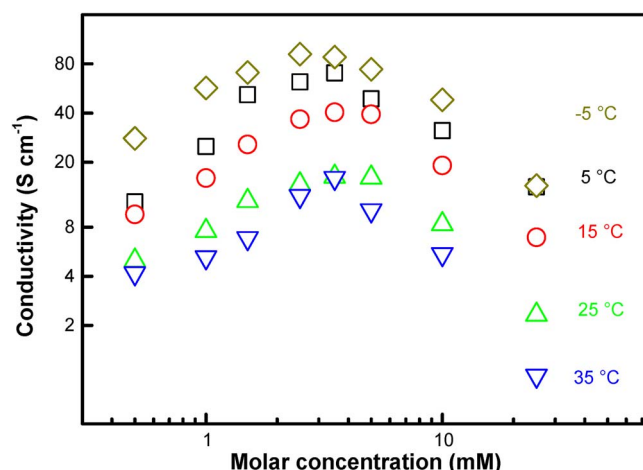


Fig. 6. The dependence of the PPy-NTs electrical conductivity on the MO concentration for various temperatures of the synthesis.

separate individual contributions. The situation seems to be clearer in case of the temperature dependence. From Fig. 6 it can be concluded that the higher is the temperature of the synthesis, the lower is the electrical conductivity of produced polymer. This statement is of course limited to investigated range of temperatures (from -5 °C to 35 °C), as the behaviour under lower sub-zero temperatures could be more complex due to necessity of using anti-freezing agents.

Moreover, when we consider the negligible dependence of elemental composition (see the part 3.2.2) on temperature and also the strong dependence of the neat nanotubular state and the nanotube diameter on the temperature (Fig. 5), we can conclude that the temperature of the synthesis strongly influences electrical conductivity by changing both the occurrence of the neat nanotubular state and the diameter of nanotubes.

Combining the information from Figs. 5 and 6 we can obtain the dependence of the conductivity on the nanotube diameter (Fig. 7). The increased conductivity with the reduced nanotube diameter has been reported many times [1,39,40]. One of the reasoning of this phenomenon is in the enhanced molecular and supramolecular order [39] although enhanced order itself may not necessarily lead to higher conductivity [41]. The plot of conductivity against nanotube diameter (Fig. 7 left) is particularly important, since we could add another system, e.g. PPy-NTs synthesized without MO (in a porous polycarbonate membrane) [39], for comparison. As a result, we found the same functional dependence regardless of synthesis conditions. Moreover, its power law form is reported for the first time and it seems that this class of materials exhibits the universal exponent equal to 0.7. On the other hand, we can see that the “strength” of this dependence (expressed as the variable A) varies with both the method of synthesis and the polymerization temperature. Regarding the former aspect, when using hard template synthesis, one obtains a better result [39].

Moreover, it is remarkable that we could not prepare thinner nanotubes than ca. 65 nm under fixed conditions (i.e. polymerization time, monomer to oxidant ratio, type of oxidant etc.) that we have chosen, by reducing temperature below -5 °C (which is near the freezing point of polymerization solution). Regarding the later aspect we observed the Arrhenius dependence of A on the temperature with the activation energy E_A about 0.31 eV. From this point of view, the limitation of nanotube thickness can be overcome by lowering the synthesis temperature. It should be noted, however, that the impact of sub-zero temperatures to the properties of a synthesized material still needs to be properly investigated. From the preliminary results it seems that using anti-freezing agents (e.g. methanol [39]) does not lead to highly conducting PPy-NTs when MO is employed.

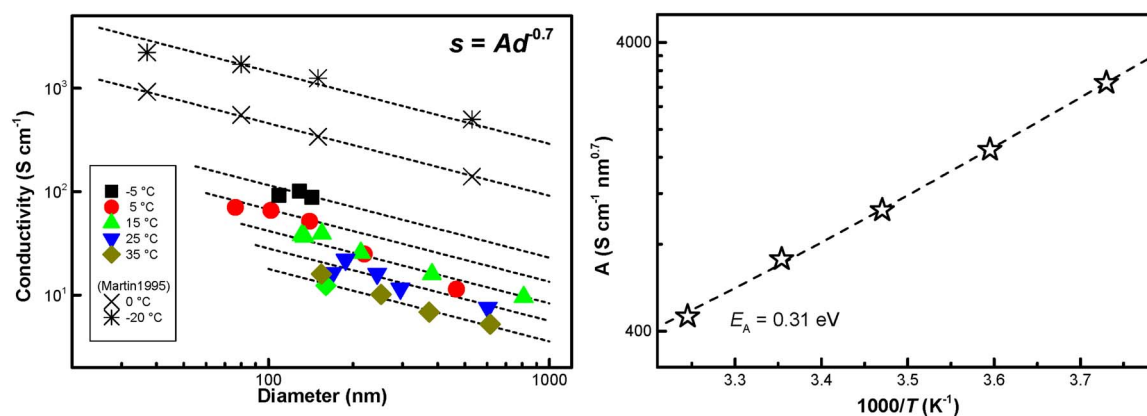


Fig. 7. The dependence of the conductivity on the nanotube outer diameter (left) for PPy-NTs synthesized with MO (this work) and PPy-NTs synthesized in nanoporous polycarbonate templates [39] at various temperatures of the synthesis. The Arrhenius plot of pre-factor A with the activation energy E_A for PPy-NTs with MO.

4. Conclusions

We have found a non-monotonic dependence of electrical conductivity of PPy-NTs on concentration of MO. The maximum conductivity was achieved with a concentration of MO that provides creation of the neat nanotubular state of PPy, while the other concentrations of the structure guiding agent lead either to its mixture with the less conducting PPy-G or to the composite with insulating stacked molecules of MO. Moreover, this conductivity maximum is perspective also from the point of the maximal specific surface area of the material.

The evaluation of the elemental composition, FTIR and Raman spectra have brought the new insight on the effect of MO as the counterion and the composite component in the PPy backbone. With the increasing concentration of MO in the reaction solution also the amount of MO in its acidic form present in PPy backbone increases. At the same time more nanotubes of the lower diameter are generated till the specific breaking point is achieved. After this point the bulk of the material is filled with MO molecules in the acidic form and creates the composite.

No particular dependence was found in case of elemental composition vs. temperature. It seems that stronger effect on the electrical conductivity has the occurrence of neat nanotubular state. On the other side, it was observed a strong dependency between the electrical conductivity and the temperature. From this point, the most perspective PPy-NTs seem to be synthesized at low temperatures (5 °C) or even subzero temperatures (−5 °C). There are also signs, that even lower temperatures will lead to higher electrical conductivities, although some technical obstacles must be overcome in future.

Finally, the power law describing the dependency of the PPy-NTs electrical conductivity on the diameter was found. It seems to be valid generally for all PPy-NTs nanotubes regardless of a synthesis method.

Acknowledgements

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Appendix A. Supplementary data

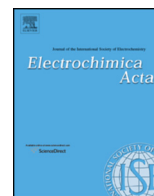
Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.synthmet.2017.06.004>.

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Amino-substituted Tröger's base: electrochemical polymerization and characterization of the polymer film



Tatiana V. Shishkanova^{a,*}, Martin Havlík^{a,b}, Vladimír Král^{a,b}, Dušan Kopecký^c, Pavel Matějka^d, Marcela Dendisová^d, Vladimír M. Mirský^e

^a Department of Analytical Chemistry, University of Chemistry and Technology Prague, 16628 Prague 6, Technická 5, Czechia

^b First Faculty of Medicine, Charles University in Prague, Kateřinská 32, 121 08 Prague 2, Czechia

^c Department of Physics and Measurements, University of Chemistry and Technology Prague, 16628 Prague 6, Technická 5, Czechia

^d Department of Physical Chemistry, University of Chemistry and Technology Prague, 16628 Prague 6, Technická 5, Czechia

^e Department of Nanobiotechnology, Institute of Biotechnology, Brandenburgische Technische Universität Cottbus-Senftenberg, 01968 Senftenberg, Germany

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ABSTRACT

The amino-substituted coumarin derivative of Tröger's base (CTB) was electrochemically polymerized on the surface of gold electrodes. The obtained polymer films were characterized by SEM, Raman spectroscopy, cyclic voltammetry and *in-situ* conductometry. Spectroscopic analysis indicates that the polymerization of CTB takes place via oxidation of the aniline fragment of CTB molecule, similar to the polymerization of aniline. The similarity of the polymer backbone to that of the polyaniline is also confirmed by the influence of potential on the film's conductivity, however the conductivity of the new material is in principle lower than that of polyaniline. SEM shows that the polymer forms a thin layer with a thickness of ~100 nm. Possible applications of the new material as an artificial receptor for aromatic analytes containing carboxy-group are proposed.

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1. Introduction

The deposition of thin polymeric layers using electrochemical polymerization is a field of increasing interest in electrochemical research and industry. Such films are applied in wide range of fields as chemical sensors [1] and biosensors [2], corrosion protection [3] and antistatic coatings [4], electrochromic devices [5,6] or catalysts [7]. The formation of these films using electrochemical polymerization provides a simple way to control the thickness of the polymer film. Varying the polymerization parameters enables the structural properties of the films to be modified [8]. Electrochemical polymerization performed in a few steps can be used for the formation of polymeric multilayers with different functions [9]. Electrochemical polymerization on arrays provides the possibility of electrical addressation [10,11] and subsequent high-throughput analysis [12].

Polyaniline, easily manufactured by the polymerization of aniline, is one of the most studied and applied polymers [1,13]. It has a high conductivity which can be controlled by pH, oxidation/

reduction, dopants. Electrical control of its spectral properties led to its applications in electrochromic devices. Changes in its physical properties due to the binding of various analytes enables its intensive applications in various types of chemical sensors including electrochemical transistors [14,15], potentiometric chemosensors [16–18] or sensors with integrated affinity control [19]. But the applications of polyaniline can be extended essentially by its chemical modification [20]. It can be done by carbonization [21] or by the introduction of defined functional groups [22–24]. One direction of such modification includes the introduction of chemical groups with a high affinity to defined compounds. A number of such polymers with a receptor, specifically calixarene [25], boronic acid [26], tetrahydroquinoline C5a [27], porphyrins [28,29], phthalocyanine [30], and α -D-mannose [31] were described. An introduction of specific recognition sites into the PANI skeleton is a way to achieve improved selectivity to some defined analytes. Wilcox et al. have demonstrated that the polyaniline glycopolymers selectively bind Concanavalin A and should have potential applications as sensors for proteins or microbes [31].

Recently an application of Tröger's base (TB) derivatives as binding blocks for supramolecular chemistry and molecular recognition was discussed [32]. Unique properties of TB such as

* Corresponding author.

E-mail addresses: shishkat@yahoo.com, tatiana.shishkanova@vscht.cz (T.V. Shishkanova).

rigidity, V-shape, possessing hydrophobic cavity, as well as its relatively high redox- and chemical stability, are generating interest in this compound among the scientific community. We have reported the synthesis of amino-substituted TB also containing a coumarin group (CTB) (Fig. 1) and described its possible application in potentiometric sensing [33]. A goal of this work is to characterize the thin films formed by electrochemical polymerization of this compound on gold electrodes. This was done by a combination of spectroscopic (Surface-enhanced Raman scattering – SERS spectroscopy) and electrochemical techniques (cyclic voltammetry and *in-situ* conductometry).

2. Experimental

2.1. Reagents

The synthesis of CTB was described in [33]. All chemicals were of analytical grade and were used without further purification: tetrabutylammonium tetrafluoroborate (TBATFB) (Sigma-Aldrich, Germany), aniline (99%, Sigma-Aldrich, Germany), ammonium peroxydisulfate (APS) (Lachema, Czech Republic), coumarin (Sigma-Aldrich, Germany), acetonitrile (ACN) (99.5%, Sigma-Aldrich, Germany). Inorganic salts, acids and hydroxides were from Lachema (Czech Republic). All aqueous solutions were prepared using deionized water additionally purified with an ELGA system.

2.2. Preparation of electrodes

2.2.1. Electrochemical measurements

Thin-layer gold electrodes were fabricated on the surface of a glass wafer by sputtering 150-nm thick gold structures using a Ti/W adhesion layer. The electrode geometry was described in [14]. The reference and counter electrodes were an Ag/AgCl saturated electrode and Pt wire, respectively. Before polymer deposition, the surface of the working electrodes was washed with acetone, ethanol, water, treated with piranha solution (1:3 v:v mixture of H₂O₂ (30%) and H₂SO₄ (98%)), rinsed thoroughly with water and dried under an air flow.

2.2.2. Spectroscopic measurements

The SERS-active gold electrodes were prepared by electrolysis from the [Au(CN)₂][−] electrolyte using a two-electrode arrangement with a Pt plate cathode and Au spiral anode; precise electrochemical conditions are described in [34]. The cyanide ions were then removed by boiling in persulfate solution. Electrochemical polymerization of CTB was performed on the freshly prepared Au SERS-active electrode surface.

2.3. Synthesis of polymeric films from amino-substituted Tröger's base

Polymeric films were prepared using chemical and electrochemical polymerization of CTB. Electrochemical polymerization was performed in the standard three-electrode configuration. The gold electrodes were used as the working electrodes. An Ag/AgCl saturated electrode and Pt wire acted as the reference and counter electrodes, respectively. The polymerization was performed in the prepared solution by mixing 0.6 mg CTB, 65.8 mg TBATFB and 20 μ L 0.1 M HCl solution in water and 2 mL acetonitrile. The electrode potential was swept repeatedly between 0.0 and 1.2 V vs. Ag/AgCl at a scan rate of 50 mV s^{−1}. These SERS-active gold electrodes coated with polymeric CTB film were used for the SERS measurements. The chemical polymerization of CTB was performed in a mixture of 2 mL CH₃CN and 20 μ L 0.1 M HCl in water by the addition of APS to an APS/CTB molar ratio of 1.25. The reaction mixture was incubated for 24 h at 25 °C. The formed dark brown precipitate was collected for FTIR–ATR spectroscopic characterization.

2.4. Characterization of electrochemically and chemically generated polymeric films

2.4.1. Spectroscopic measurements

The spectra of monomeric CTB were collected using FTIR–ATR and FT-Raman spectroscopy. Infrared spectra were measured with a Thermo Nicolet 670 Nexus FTIR spectrometer equipped with an MCT detector using ATR on a ZnSe crystal by the accumulation of 256 scans with 4 cm^{−1} resolution. The spectrum of the monomeric CTB was measured from the pressed pellets, while the spectra of the polymeric CTB were obtained from the precipitate after complete solvent evaporation. The Raman spectra of the monomer were collected using an Equinox 55/s FT-NIR spectrometer (Bruker, Germany) with an FRA 106/s FT Raman module (Bruker, Germany). The source of the irradiation was a Nd:YAG laser (Coherent, USA) with 1064-nm excitation. The FT-Raman spectrometer was equipped with a Ge detector cooled with liquid nitrogen. 1024 scans at 4-cm^{−1} resolution and 300 mW laser power were collected for one spectrum; the final spectrum was an average of 30 accumulations.

Surface-enhanced Raman scattering (SERS) spectroscopy was performed at excitation wavelengths of 1064, 785 and 633 nm with a Renishaw InVia Reflex Raman microspectrometer equipped with a HeNe laser (633 nm, 0.7 mW), diode laser (785 nm, 10 mW) and a microscope with a 100 $\times$ objective and X–Y–Z motorized sample stage. 10 measurements with 10 s integration time were used for one spectrum, 10 spectra were averaged.

Scanning electron microscopy (SEM) was performed with a Mira 3 LMH electron microscope (Tescan company). The Schottky

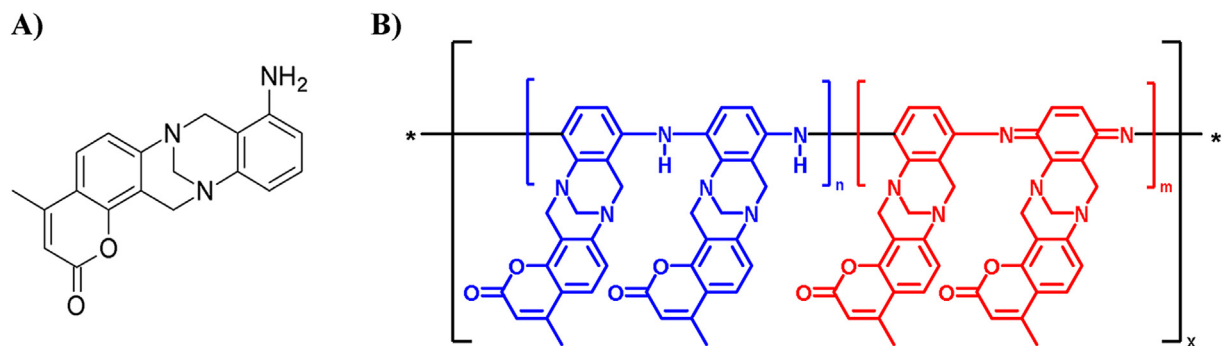


Fig. 1. Chemical structure of amino-substituted coumarin derivative of Tröger's base (CTB) (A) and suggested structure of its polymer (B).

emitter of the electron microscope used 1 kV of accelerating voltage with an emission of 170 μ A. Magnification of the sample was 20 000 $\times$. The secondary electrons were detected by the detector of Everhart-Thornley type.

2.4.2. Electrochemical measurements

Electrochemical measurements were performed by an Autolab PGSTAT20 computer-controlled potentiostat (EcoChemie, The Netherlands). Cyclic voltammetry was performed in three-electrode configuration. Gold electrodes, an Ag/AgCl saturated electrode and a Pt wire acted as the working, the reference and the counter electrodes, respectively. *In-situ* conductivity measurements were performed using the simultaneous two- and four-point measurement (s24)-technique [35]. The values of $1/G4$ characterize the value of the polymer resistance between two adjustment measurement electrodes, while the value of $1/G2$ includes the polymer resistance through about three times larger length of the polymer layer and two contact resistances. The details are presented in [36]. The measurement time was 3.4 s per data point. Within this time, the resistance value was calculated from the current difference of two opposite voltage pulses. The value of the contact resistance was obtained from simultaneous two- and four-point measurement according to the approach described earlier in [36–38].

3. Results and discussion

3.1. Cyclic voltammetry

The derivative of Tröger's base used in our work (CTB) includes a coumarin group and an amino group. To understand the possible involvement of these groups in electrochemical polymerization, a comparison was made of cyclic voltammograms in the supporting electrolyte without any additional substances (Fig. 2A), with coumarin (Fig. 2B), with aniline (Fig. 2C) and with CTB (Fig. 2D). The data obtained in the supporting electrolyte and in the supporting electrolyte with coumarin are almost identical. The observed influence of coumarin on the anodic peak relating water oxidation does not indicate any intrinsic electrochemical activity of coumarin [39]. The voltammetric curves obtained in the presence of aniline (Fig. 2C) demonstrate oxidation waves at $\sim +1.02$ V corresponding to the formation of cation radicals [40]. The cyclic voltammograms of CTB (Fig. 2D) were observed to be very similar to that of substituted aniline, but with some shift of the peaks corresponding to the doping/dedoping of the material [41]. The peak currents decreased within the first few cycles. The similarity of the CV curves for aniline (Fig. 2C) and for CTB (Fig. 2D) enables us to suggest that under such conditions CTB can also be polymerized through its amino group, via the same mechanism as aniline. This supposition was verified using the spectroscopic measurements (please, see “3.3. Vibrational spectroscopic studies”). The shift of electrochemical activity in the anodic direction may be caused by the influence of Tröger base protonation under the electropolymerization conditions.

3.2. Scanning electron microscopy

The formation of polymer films of CTB on the electrode surface due to potential cycling (Fig. 2D) was confirmed by SEM measurements. Fig. 3 shows comparison of interface between gold electrode and substrate uncoated (Fig. 3A) and coated (Fig. 3B) by thin polymeric film with thickness of approximately ~ 100 nm.

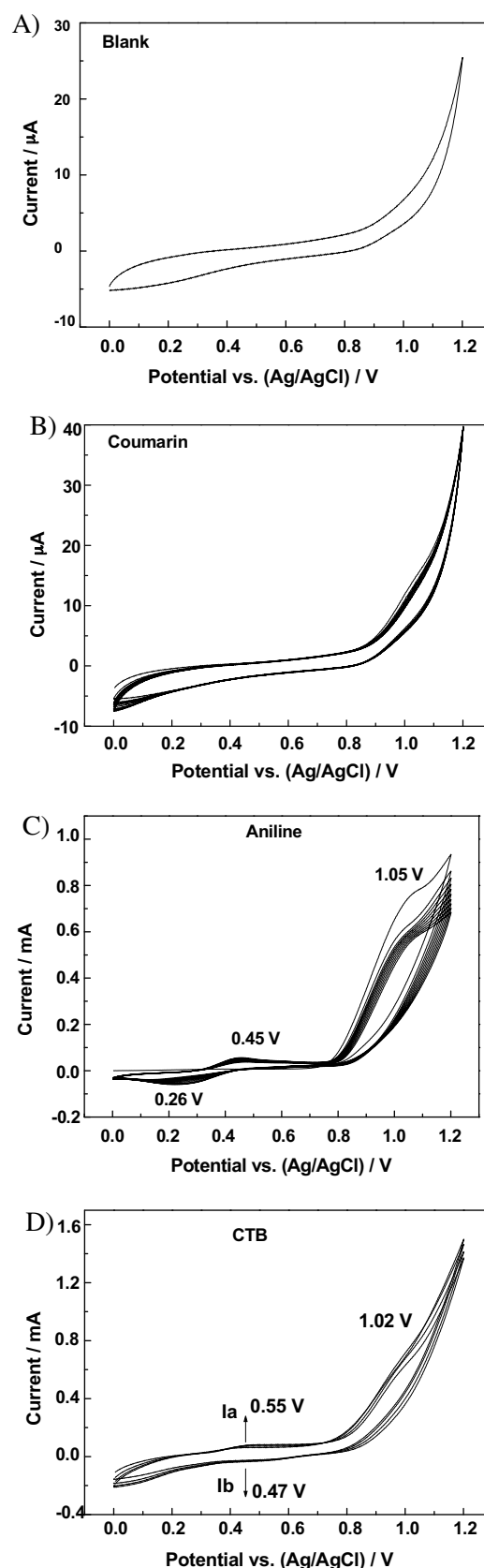


Fig. 2. Comparison of cyclic voltammograms obtained in the supporting electrolyte before (A) and after the addition of 0.001 M coumarin (B), 0.001 M aniline (C) and 0.001 M amino-substituted coumarin derivative of Tröger's base (CTB) (D).

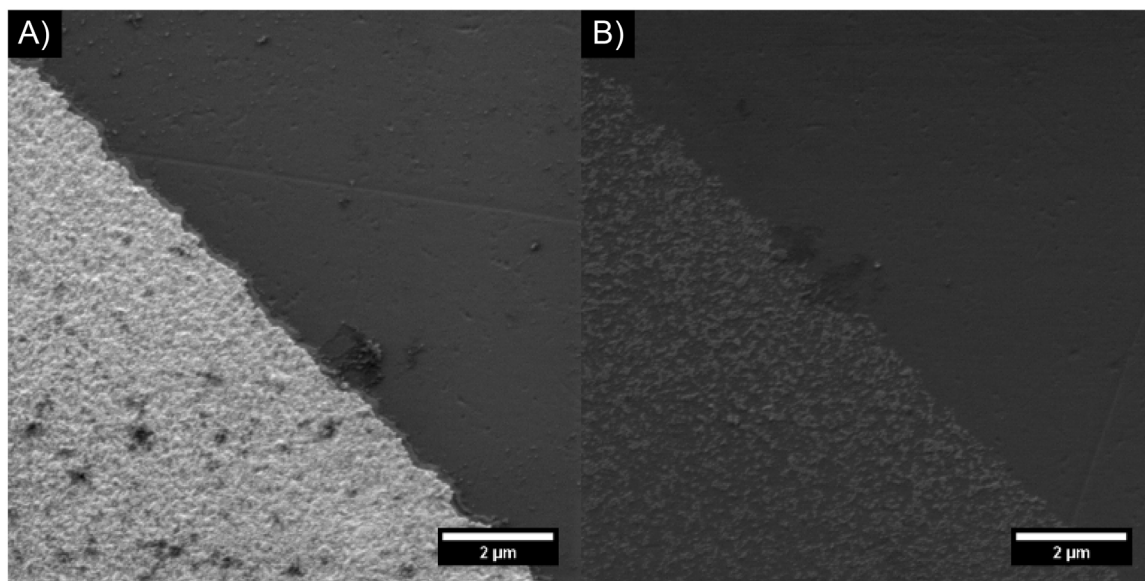


Fig. 3. Gold electrode – substrate interface uncoated (a) and coated (b) with polymeric film electrochemically generated from amino-substituted coumarin derivative of Tröger's base. Image obtained during scanning electron microscopy measurements.

3.3. Vibrational spectroscopic studies

In this part of our study, we focused on how to adsorb the polymeric film onto the gold surface. Firstly, the CTB monomer was characterized by FTIR and Raman spectroscopic techniques (Fig. 4) which confirmed the presence of functional groups. The stretching and bending vibration modes characteristic of the aliphatic and aromatic parts are observed in both the Raman and IR spectra, while the band of the NH group was observed at 3358 cm^{-1} in the IR spectrum. The carbonyl stretching vibrational mode was found with different intensities in the IR and Raman spectra of CTB monomer at 1712 and 1718 cm^{-1} , respectively.

Secondly, Raman studies of the polymeric film were carried out using three different excitation laser lines at 633, 785 and 1064 nm. As can be seen from Fig. 5, which shows the SERS spectra of poly (CTB) on the Au surface, the excitation wavelength used strongly affected the observed spectral patterns. It should be noted that the

bands assigned to coumarin and TB were observed in all cases independently of the applied excitation wavelengths. However, the selection of excitation wavelength significantly influenced the band intensity ratios. The stretching aliphatic modes were the most enhanced at 633-nm excitation, while the stretching C—C vibrations of the aromatic ring were the most enhanced at near-infrared excitation. The band of the carbonyl group (observed for the monomer at ca. 1718 cm^{-1}) was not observable with any of the excitations used. It was hypothesized that the carbonyl group is oriented in a parallel to the surface and therefore is inactive for surface-enhanced techniques. The out-of-plane modes of the aromatic ring, for example represented by the band at ca. 472 cm^{-1} were enhanced at 785 and 633 nm. The changes in the band intensity ratios could be caused by both the disorder of molecules on the surface and by the contribution of molecular resonance in the SERS signal. From the SERS spectra shown, it is obvious that the optimal excitation wavelength in terms of maximum signal

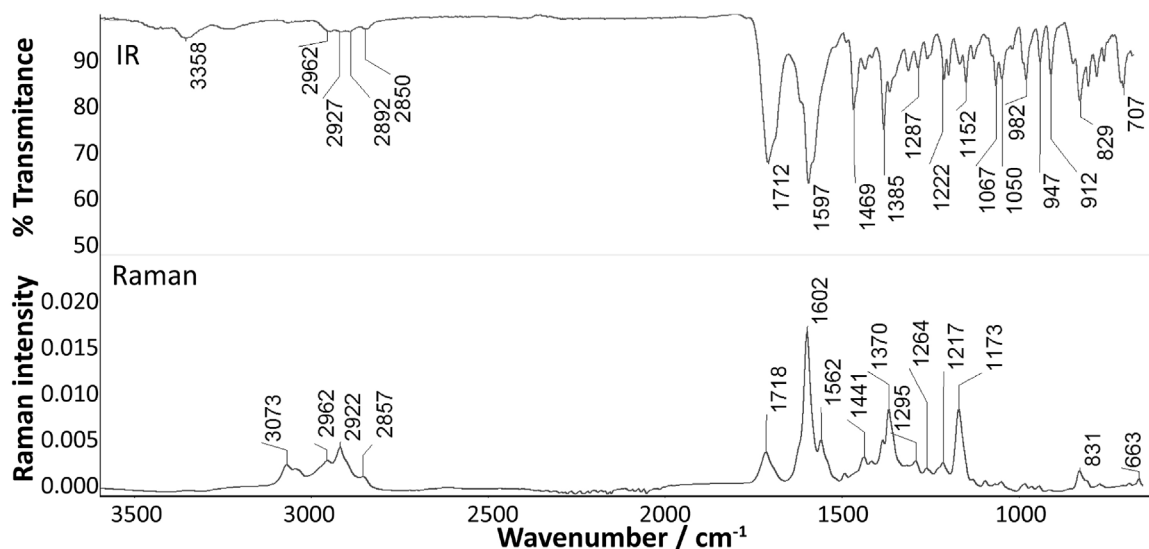


Fig. 4. FT-IR (above) and FT-Raman (below) spectrum of amino-substituted coumarin derivative of Tröger's base monomer.

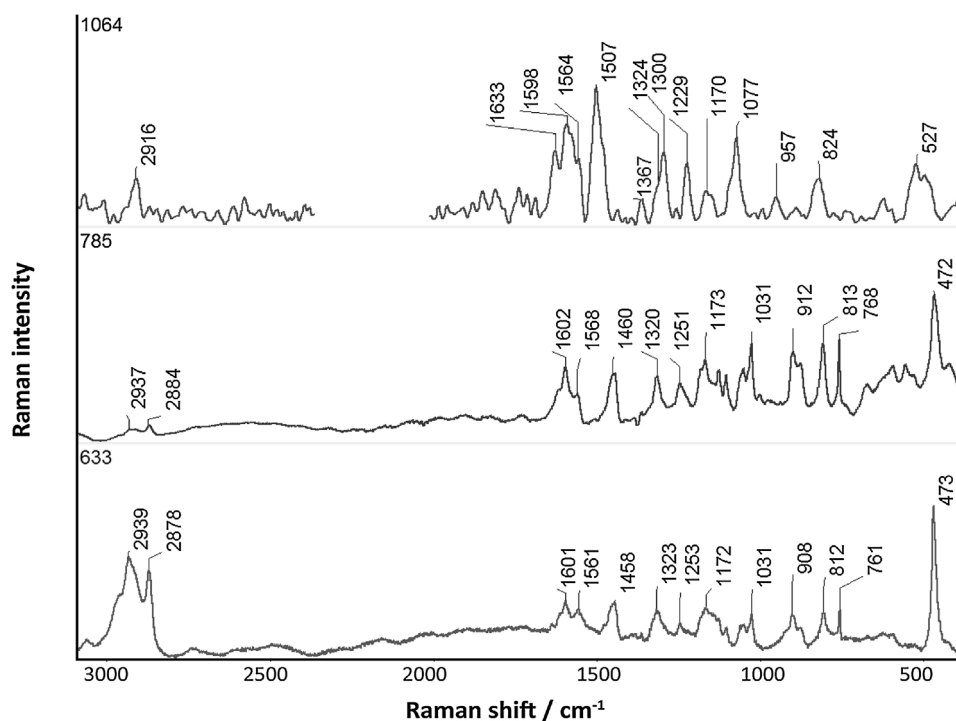


Fig. 5. SERS spectra of poly(CTB) adsorbed onto Au electrode at excitation wavelength of 1064, 785 and 633 nm.

enhancement (mainly contributed by plasmon resonance) is 633 nm, which was used for the polyaniline study by Trchova et al. [42].

Looking for the characteristic bands of polyaniline, we observed maxima at ca. 1600 cm^{-1} ($\text{C}=\text{C}$ vibration in a quinonoid ring), 1640 cm^{-1} (in the spectrum obtained using 1064 nm excitation, this appeared to be the band typical for deprotonation). The bands at about 1450 cm^{-1} assigned to $\text{C}=\text{N}$ vibrations in the quinonoid ring are similar to ones which corresponds head-to-tail coupling in PANI chain. Other bands at ca. 1320 cm^{-1} missing in normal Raman spectrum were assigned to the $\text{C}\sim\text{N}^+$ stretching vibration according to [42]. Excitation at the edge of the visible and near-infrared region 785 nm is not optimal because the region of stretching vibrations at about 3000 cm^{-1} is outside the effective plasmonic enhancement. The 1064-nm excitation was used for comparison, and because the monomer was studied using this excitation (another excitation (in the visible region) could not be used for studying the monomer because of the intense luminescence signal of the coumarin derivative).

From the structure of CTB is obvious that both the coumarin unit and Tröger's base can "lay" on the electrode surface (Fig. S1, Supplementary Materials). If the CTB was adsorbed via Tröger's base the spectra had to be different. We would observe bands of NH_2 group and more intensive in-plane modes from two aromatic systems. The coumarin part would lose the conjugated system and the used different excitation wavelengths (effects of molecular π electronic and plasmonic electron resonances) would not such effect on the different enhancement. Accordingly to the SERS experiments and selection rules for the surface-enhanced techniques (the most enhanced modes are perpendicular to the surface), the molecules are adsorbed to the surface via the coumarin unit. The in-plane vibrational modes of the coumarin unit (at ca. 1067, 1050, 1031 cm^{-1}) are the less enhanced while the out of plane modes (at ca. 824, 813, 768 cm^{-1}) are the most enhanced. The contribution of Tröger's base is less significant. The scheme of this possible adsorption is on Fig. S2 (Supplementary Materials). The proposed orientation is further supported by an apparent effect of

the selected excitation wavelength which influences the electronic resonance of the conjugated π electron systems located in the coumarin unit and contributes to the wavelength-dependent difference of bands enhancement related to contribution of molecular and plasmonic electron resonances.

Comparing the literature data [42,43] and our experimental results, we can conclude that polymerization occurs through the aniline group. The SERS measurements showed that the carbonyl group of the coumarin unit does not participate in the polymerization process, but is able to interact with the gold surface due to the conformation of the polymeric backbone.

3.4. In-situ conductometry

In-situ conductivity measurements were complicated by the relatively high resistance of the polymer film, which was in many cases above the maximal limit of our set-up ($\sim 20\text{ MOhm}$) for reliable quantitative analysis. Specifically, under some conditions quantitative measurements were possible while under other conditions it was only possible to obtain qualitative data and to observe some trends in the behavior of the conductance of polymerized CTB. Fig. 6A shows the influence of pH on electrical conductance. There is a trend of increasing conductivity with pH decrease, which is similar to the behavior of polyaniline. In addition, the poly(CTB) showed the potentiometric pH dependence with the sensitivity -51 mV/decade from pH 2 up to pH 9 (Fig. S3, Supplementary Materials). The ratio between G4 and G2 is ~ 10 , this indicates a contribution of contact resistance into the value measured by two-point technique. Conductivity depends on ideal conjugation of PANI systems, which is in our case disrupted by presence of sterically demanding substituent. Recently it has been reported that alkyl substitution decreases the conductivity of substituted PANIs [44]. It is therefore reasonable to expect that the conductivities of the substituted PANIs will be decreased with increasing size of substituent. This observation is again consistent with reported data that next substituent on the aniline core decreases the conductivity of corresponding substituted PANI. In

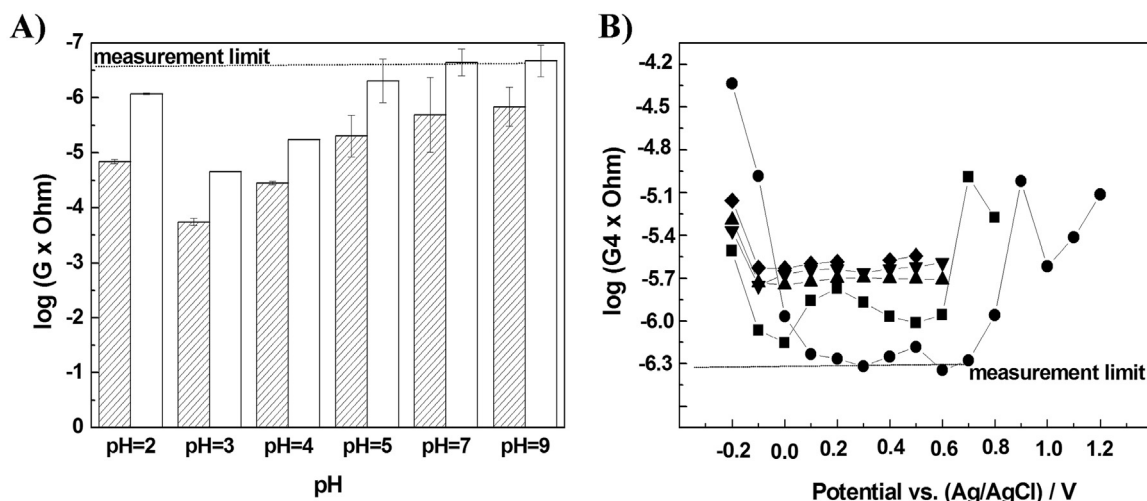


Fig. 6. Influence of pH (A) ($n = 4$, where n is the number of tested electrodes) and potential (B) on conductivity of polymeric CTB film measured in 0.1 M phosphate buffer at pH = 7 in the presence of 0.2 M NaCl applying simultaneously two (G2)- (right open columns) and four (G4)- (left shaded columns) point measurements technique.

the case of the poly(CTB), polymer contains disubstituted aniline core (alkyl and dialkylamino groups). The dependence of the conductivity of the film of polymerized CTB on the applied potential is shown in Fig. 6B. The conductivity increases sharply at a potential below -0.1 V and at anodic potentials above $+0.6$ V. Such behavior is very close to the properties of polyaniline films [19]. Therefore, the data on the *in-situ* conductivity measurements of polymerized CTB confirm the suggestion that the polymerization leads to the formation of a polymeric structure similar to PANI. It was further demonstrated that the value of the polymer conductance increases essentially due to the interaction of the polymer film with benzoic acid and derivatives of mandelic acid, which are important as markers for neuroblastoma [45]. However, a more detailed analysis of its chemosensitive properties towards benzoic acid and derivatives of mandelic acid will be published elsewhere.

4. Conclusions

Here we have presented an investigation of a polymer film obtained by the electrochemical and chemical polymerization of the coumarin derivative of amino-substituted Tröger's base. The spectroscopic results indicate on primary adsorption of coumarin unit onto the electrode surface and participation of aniline unit in the formation of a polymer film. The film has thickness of ~ 100 nm. The formation of a polymer film is similar to the polymerization of aniline. The obtained pH-dependence of conductivity of poly(CTB) might suggest the presence of basic groups in the polymeric film able to protonate. The electrochemical and conductivity properties of the formed polymer film were similar to the PANI film, but the resistance was much higher. The observed influence of benzoate and derivatives of mandelic acid on the film resistance indicates a possible analytical application of this new material. The development of electrochemical detection of derivatives of mandelic acid which are low molecular metabolites of tumor marker is very desirable [45] and is in progress in our laboratory [33].

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2016.12.061>.

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PAPER

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Synthesis of silver-anchored polyaniline–chitosan magnetic nanocomposite: a smart system for catalysis

Mohamad M. Ayad,^{ID}*^{ab} Wael A. Amer,^{ID}^a Mohammed G. Kotp,^a Islam M. Minisy,^{ID}^a Ahmed F. Rehab,^a Dušan Kopecký^c and Přemysl Fitl^c

A simple route was employed for the fabrication of a polyaniline (PANI)–chitosan (CS)–magnetite (Fe₃O₄) nanocomposite (PANI–CS–Fe₃O₄) via the *in situ* polymerization of aniline in the presence of CS using anhydrous iron(III) chloride as an oxidizing agent. The magnetic character of the nanocomposite results from the presence of iron oxide nanoparticles, which were formed as side products during the synthesis of the PANI–CS nanocomposite. The synthesized PANI–CS–Fe₃O₄ nanocomposite was fully characterized using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), energy dispersive X-ray (EDX), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and vibrating sample magnetometry (VSM). The reduction of silver nitrate by the synthesized nanocomposite enables the anchoring of silver (Ag) nanoparticles onto its surface. The catalytic properties of the Ag-decorated nanocomposite (Ag@PANI–CS–Fe₃O₄) toward the reduction of 4-nitrophenol was investigated using sodium borohydride as a reducing agent.

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1. Introduction

In recent years, noble metal nanoparticles have attracted remarkable attention in different fields of human activities such as thermal therapy, optoelectronics, biological imaging, sensors, biomedicine, energy conversion and catalysis^{1–5} due to their extraordinary chemical, physical and biological properties. The properties and hence the efficacy of these metal nanoparticles depend mainly on their size.^{6–8} Furthermore, there is a growing interest in developing nanoparticles for the catalysis of different types of reactions due to their high specific surface as well as the catalytic performance, which was found to gradually increase with decreasing nanoparticle size.^{6,9} Silver nanoparticles are especially important due to their relative abundance, low cost, high electrical and thermal conductivity, high resistance to oxidation and antimicrobial effects, resulting in their application in the textile industry, food additives, plastics and packaging and for medical instruments and burn dressings.¹⁰ On the other hand, silver nanoparticles have a disadvantage in their aggregation leading to large size aggregates; hence low catalytic efficiency is obtained. To prevent their aggregation,¹¹ researchers aim their efforts to reduce silver nanoparticles on the surface of different

conducting polymers or their nanocomposites such as polyaniline (PANI)–graphene nanocomposite.¹²

Chitosan (CS) is one of the most popular natural biopolymers and is considered to be the second most widespread polymer in nature after cellulose. CS is a linear β-1,4-linked polysaccharide and it is the product of chitin deacetylation.¹³ CS is a cationic polymer that possesses chelating ability due to the presence of active amino and hydroxyl functional groups. The ultimate properties *e.g.* non-toxicity, good water permeability, high mechanical strength, adhesion, biocompatibility, biological activities such as induced disease resistance in plants and antimicrobial effect¹⁴ were the motivation for the application of CS in different fields such as medicine, pharmaceutical industry, food production, plant growing and chemical engineering.^{13,15–17} Despite all these good and attractive properties, CS has relatively poor stability and thus its nanocomposites with other polymers of high stability (such as conducting polymers) were fabricated to make way towards new possible applications.^{17–21}

Recently, conducting polymers such as PANI, polypyrrole, polyacetylene, polyethylene dioxythiophene have been studied by many researchers in different fields as a result of their π-conjugated structures and promising properties.^{22–24} PANI has a special position among these polymers due to its unique properties such as ease of preparation, high conductivity, chemical and environmental stability under ambient conditions, low operational voltage in addition to its unique redox properties^{25,26} which result in directing the research in the last

^aChemistry Department, Faculty of Science, Tanta University, Tanta 31527, Egypt.
E-mail: mohamad.ayad@ejust.edu.eg; Fax: +20 3 4599520; Tel: +20 3 4599520

^bSchool of Basic and Applied Sciences, Egypt-Japan University of Science and Technology, New Borg El-Arab City, Alexandria 21934, Egypt

^cDepartment of Physics and Measurements, Faculty of Chemical Engineering, University of Chemistry and Technology, 166 28 Prague, Czech Republic

years, to use PANI for different applications especially as catalyst supports.^{27–33}

Researchers face a great problem during the separation of the products from the reaction medium; the traditional routes were filtration or centrifugation (especially for nanometer-scaled materials), which are time and energy consuming.^{34,35} Magnetic separation is one of the most promising techniques in separation that has excellent advantages over other methods including high speed, accuracy, ease of control as well as simplicity.³⁶ Recently, a magnetic chitosan–polypyrrole–magnetite nanocomposite was prepared and employed as an impressive adsorbent of an anionic dye from aqueous solution.³⁷

In this work, a facile one step method for the preparation of magnetic nanocomposite (PANI–CS–Fe₃O₄) using PANI, CS and magnetite (Fe₃O₄) is presented. Subsequently, this nanocomposite acts as a reducing agent for silver nitrate to get silver nanoparticles anchored onto its surface.^{31,38} The synthesized magnetic nanocomposite (Ag@PANI–CS–Fe₃O₄) was fully characterized *via* different analysis techniques including FTIR, XRD, SEM, TEM and EDX. The catalytic effect of the synthesized nanocomposite was examined for the reduction of one of the most hazardous and toxic nitroaromatic compounds (4-nitrophenol (4-NP)), which are widely used in different industries.³⁹

2. Experimental

2.1. Chemicals

Aniline (Adwic, Egypt) was distilled twice over zinc dust.⁴⁰ Acetic acid (Adwic, Egypt), chitosan (Acros, USA, molecular weight: 100 000–300 000), anhydrous FeCl₃ 98% (SISCO, India), NaOH pellets (Loba Chemie, India) were used as received. Sodium boron hydride (NaBH₄) (Johnson Matthey, UK), silver nitrate (BDH, UK), 4-nitrophenol (4-NP) (Sigma Aldrich) were used without further purification. Double distilled water was used for all preparations.

2.2. Synthesis of PANI

PANI was fabricated according to the previous protocol reported by Ayad *et al.*⁴¹ Briefly, 0.05 M of aniline monomer was dissolved in 50 mL of 0.1 M HCl with stirring till complete dispersion and homogeneity. 50 mL of anhydrous FeCl₃ solution (0.154 M) was added dropwise to the aniline solution with stirring for 3 hours. The resulting PANI was washed 3 times by distilled water then it was finally washed with methanol. The polymer was left to dry at 50 °C overnight.

2.3. Synthesis of PANI–CS–Fe₃O₄ nanocomposite

The synthesis of PANI–CS–Fe₃O₄ nanocomposite was performed according to the procedures reported by Ayad *et al.*¹⁶ 1 g of CS was dissolved into 100 mL of 2% v/v acetic acid then 0.5 mL of aniline monomer was added. The resulting solution was left under stirring for 1 hour to homogenize it. In an ice bath, 2.51 g of anhydrous FeCl₃ was added to the mixture and left under mechanical stirring overnight. 25 mL of 0.5 M NaOH solution was added dropwise to the mixture. The resulting product was collected and washed several times with distilled water and

ethanol. Eventually, the product was dried in an oven at 50 °C overnight.

2.4. Synthesis of Ag nanoparticles@PANI–CS–Fe₃O₄ nanocomposite

PANI–CS–Fe₃O₄ nanocomposite was added to 50 mL of 0.1 M NH₄OH for full deprotonation, then it was washed with distilled water. 0.2 g of the previously deprotonated PANI–CS–Fe₃O₄ nanocomposite was added to 50 mL of 3 mM of AgNO₃ under mechanical stirring for 3 hours. The product was washed with distilled water and ethanol several times. Finally, it was dried at room temperature for 2 days.

2.5. Catalytic activity of Ag@PANI–CS–Fe₃O₄

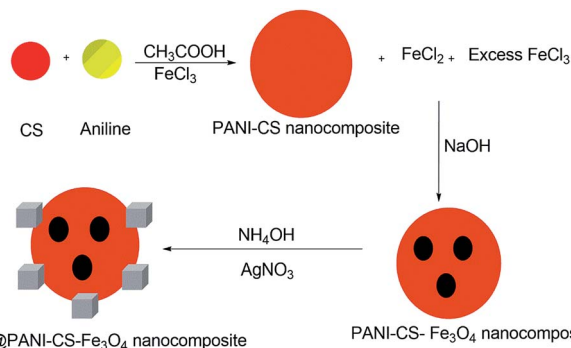
In a well stoppered quartz cuvette, 2.5 mL of 7 mM of alkaline solution of 4-NP was added to 1 mg of Ag@PANI–CS–Fe₃O₄ nanocomposite and the UV-VIS absorption spectra were recorded. Afterwards, 0.5 mL of 10 mg mL^{−1} of NaBH₄ was added to the previous solution and the reaction progress was followed by measuring the UV-VIS absorption spectra over time.

2.6. Characterization

XRD patterns of the prepared samples were measured by X-ray diffractometer (GNR APD-2000 PRO) with CuK α radiation (40 kV, 30 mA) in the step scan mode. Elemental composition of the prepared samples was determined by EDX spectrometer (Bruker Quantax 200 with XFlash 6|10 detector) at 15 kV of accelerating voltage. A Bruker Tensor 27 FTIR (with the frequency range of 4000–400 cm^{−1}) was used to record functional groups and also to record the finger print regions in different steps of the nanocomposite preparation. SEM images were captured on Tescan Mira 3 LMH at accelerating voltage of 30 kV. TEM (JEM-2100F) at 200 kV was used for morphology measurements. UV-VIS absorption spectra were recorded using UVD-2960 (Labomed Inc.) spectrometer. Magnetic properties were measured by vibrating sample magnetometer (VSM) on physical property measurement system (Quantum Design).

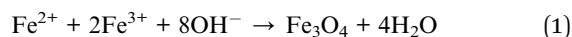
3. Results and discussion

Two steps-based simple method was used for synthesizing Ag@PANI–CS–Fe₃O₄ nanocomposite. *In situ* chemical polymerization of aniline was performed using FeCl₃ as an oxidant in presence of CS. During polymerization, iron(III) chloride was reduced into iron(II) chloride. In addition, sodium hydroxide solution was added to the previous solution to produce hydroxides of Fe²⁺ and Fe³⁺ ions [Fe(OH)₂ and Fe(OH)₃], which resulted in the formation of Fe₃O₄ nanoparticles (as shown in Scheme 1) that grants the nanocomposite with magnetic character.¹⁶ The classical synthesis of Fe₃O₄ *via* co-precipitation method in pH range between 8 and 12 was followed through reaction of stoichiometric ratio of 2 : 1 (Fe³⁺/Fe²⁺) ions as ascribed in eqn (1).⁴² The inclusions of magnetic Fe₃O₄ particles facilitate the separation process. NH₄OH was used to make and ensure the deprotonation process of PANI–CS–Fe₃O₄ nanocomposite in order to activate the lone pair of electrons located



Scheme 1 The formation mechanism of Ag@PANI-CS- Fe_3O_4 nanocomposite.

at amino, imino and hydroxyl groups in polyaniline and chitosan which facilitates the coordination of Ag ions onto these basic active sites.



Generally, reducing agents such as hydrazine and sodium citrate were used for anchoring silver nanoparticles over some surfaces.⁴³ These reductants may cause many problems such as toxicity of a product.⁴⁴ In the present study, silver ions were reduced *via* PANI to silver nanoparticles onto the nanocomposite surface.⁴⁵ Furthermore, CS has an affinity toward silver ions as a result of its primary amines and hydroxyl groups which chelates with the metal cation.⁴⁶

The chemical structures of PANI, CS, and the magnetic nanocomposite PANI-CS- Fe_3O_4 before and after anchoring the silver nanoparticles were investigated by measuring their FTIR spectra. Fig. 1 shows the comparison of the FTIR spectra of PANI-CS- Fe_3O_4 (Fig. 1C) and Ag@PANI-CS- Fe_3O_4 (Fig. 1D) with the FTIR spectra of PANI (Fig. 1A) and CS (Fig. 1B). The main peaks of PANI appear at 1571 cm^{-1} , 1472 cm^{-1} , 1301 cm^{-1} , 1121 cm^{-1} and 803 cm^{-1} (Fig. 1A) which are attributed to nitrogen quinone (Q) structure, benzene ring (B) structure vibration, C-N stretching vibration, in plane C-H vibration and out-of-plane C-H bending vibrations, respectively.^{33,47,48} The saccharide structure of CS biopolymer is represented by the peaks at 3440 cm^{-1} , 1655 cm^{-1} , 1372 cm^{-1} , 2861 cm^{-1} , 1155 cm^{-1} and 1070 cm^{-1} (Fig. 1B) that are related to its stretching NH_2 groups, bending NH_2 , vibrational alcoholic groups C-OH, bending C-OH, anti-symmetric bending of C-O-C bridge and vibrational C-O, respectively.^{18,49} The FTIR spectrum of PANI-CS- Fe_3O_4 nanocomposite (Fig. 1C) exhibits broadening between 3435 cm^{-1} and 2826 cm^{-1} which indicates the hydrogen bond interaction between PANI and CS.^{18,50} Moreover, the disappearance of CS band at 1654 cm^{-1} (Fig. 1B) accompanied by appearance of new one at 1636 cm^{-1} for PANI-CS- Fe_3O_4 nanocomposite (Fig. 1C) is an effective indication for the interaction between PANI and CS.¹⁶ In addition, presence of pristine magnetite is usually associated with presence of two peaks at 580 cm^{-1} and 464 cm^{-1} .^{51,52} In Fig. 1C, the new peaks at 595 cm^{-1} and 449 cm^{-1} support the presence of magnetite and

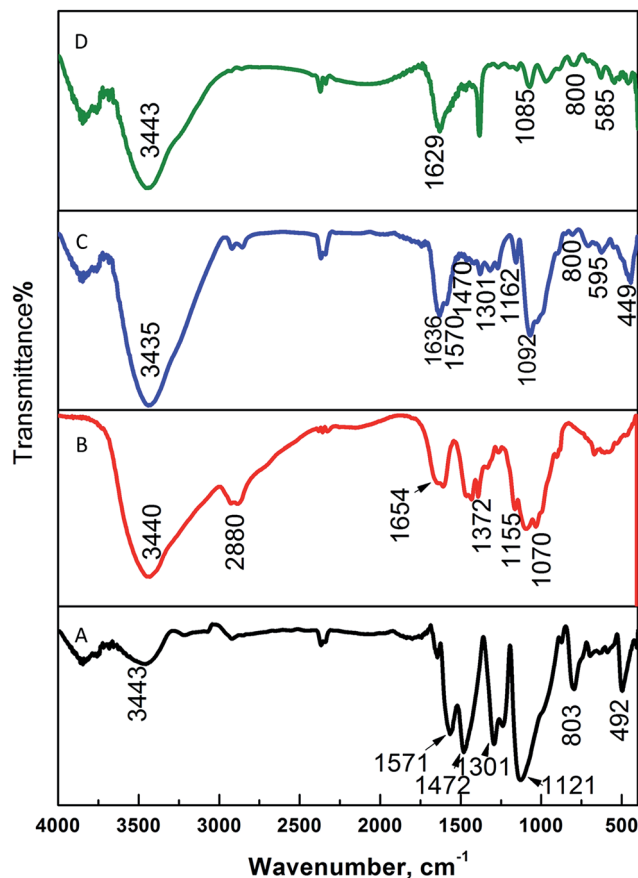


Fig. 1 FTIR spectra of PANI (A), CS (B), PANI-CS- Fe_3O_4 nanocomposite (C), and Ag@PANI-CS- Fe_3O_4 nanocomposite (D).

are related to vibrational Fe-O bond.^{51,53} The shifting of the magnetite peaks from that of parent magnetite peak indicates the interaction of magnetite with PANI and CS particles. Track D shows the finger print of track C with small shift of NH and OH peaks position from 1636 cm^{-1} and 3435 cm^{-1} (Fig. 1C) to 1629 cm^{-1} and 3343 cm^{-1} (Fig. 1D) due to silver metal reduction its deposition over PANI-CS- Fe_3O_4 nanocomposite. The wave-number shift caused by anchoring silver was observed in the literatures by many authors.^{46,54} Therefore, FTIR suggest good

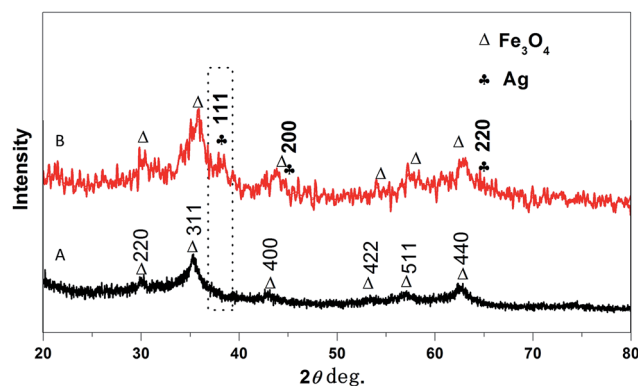


Fig. 2 XRD patterns of the prepared PANI-CS- Fe_3O_4 (A) and Ag@PANI-CS- Fe_3O_4 (B) nanocomposites.

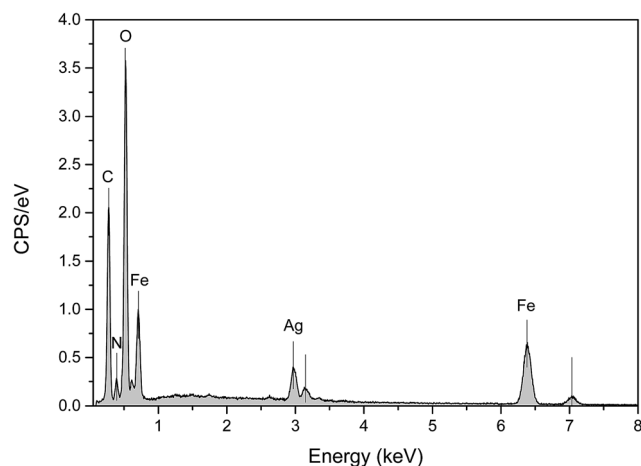


Fig. 3 EDX of Ag@PANI-CS-Fe₃O₄.

Table 1 Average of elements masses in the Ag@PANI-CS-Fe₃O₄ nanocomposite

Element	Mass norm. %		Average
Measurement no.	1	2	
Oxygen	39.609918	38.52287	39.07
Iron	28.744685	33.317434	31.03
Carbon	21.980049	18.941147	20.46
Silver	6.1181148	6.8474	6.48
Nitrogen	3.5472337	2.3710902	2.96
	100	100	100

interaction between CS and PANI, the presence of magnetite and the deposition of silver metal nanoparticles on the PANI-CS-Fe₃O₄ nanocomposite.

X-ray diffraction (XRD) helps to identify the crystallinity and phase of the product. Fig. 2A exhibits the XRD pattern of the prepared nanocomposite PANI-CS-Fe₃O₄ which represents the diffraction patterns of Fe₃O₄ that can be indexed to (*h k l*) reflection peaks of [220], [311], [400], [422], [511] and [440] at 2θ equivalent to 30.2°, 35.74°, 43.12°, 53.51°, 57.19° and 62.78°, respectively for face centered cubic (FCC) phase of magnetite.^{53,55,56} Track B represents PANI-CS-Fe₃O₄ nanocomposite after formation of silver nanoparticles over its surface. Three main diffraction lines were observed at 2θ of 38.2°, 44.1° and 64.5° that can be indexed with (*h k l*) crystallographic planes to [111], [200] and [220], respectively and related to FCC silver crystals.^{57–59} These XRD data match with FTIR spectra and therefore they prove the presence of magnetite and silver nanoparticles on the PANI-CS-Fe₃O₄ nanocomposite.

The EDX spectra of Ag@PANI-CS-Fe₃O₄ nanocomposite were measured to identify the chemical composition (Fig. 3). The analysis result reveals the presence of oxygen, iron, carbon, silver and nitrogen. The average of mass percentages of the elements were determined and calculated twice and then cited in Table 1.

The morphology and the size distribution of the nanocomposite were determined using the SEM technique. Fig. 4A shows the typical SEM image of Ag@PANI-CS-Fe₃O₄ nanocomposite. The image reveals the nanostructure of the synthesized nanocomposite and the spherical shape of the Fe₃O₄-Ag

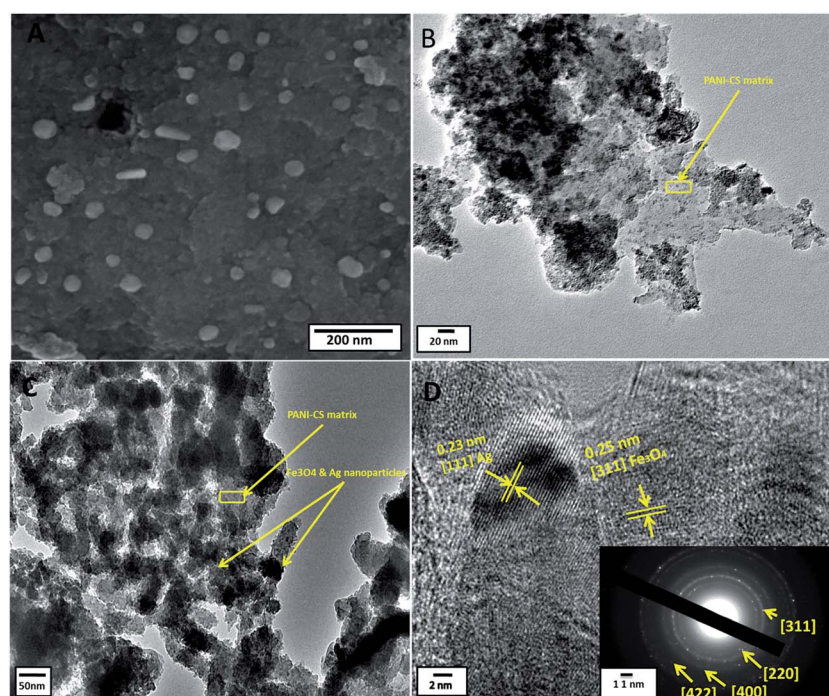


Fig. 4 SEM of Ag@PANI-CS-Fe₃O₄ nanocomposite (A), TEM images of PANI-CS-Fe₃O₄ nanocomposite (B) and Ag@PANI-CS-Fe₃O₄ nanocomposite (C), and HRTEM of Ag@PANI-CS-Fe₃O₄ nanocomposite (D). The inset shows SAED of Ag@PANI-CS-Fe₃O₄ nanocomposite.

nanostructures (without aggregation) on PANI-CS matrix with particle size of about 30–50 nm.

The structure features of Ag@PANI-CS-Fe₃O₄ nanocomposite were investigated *via* the TEM technique. The TEM image of PANI-CS-Fe₃O₄ nanocomposite (Fig. 4B) shows the dispersion of Fe₃O₄ nanoparticles through PANI-CS matrix with low aggregation at high magnification. Fig. 4C is the TEM image of Ag@PANI-CS-Fe₃O₄ nanocomposite; it shows uniform distribution of Fe₃O₄-Ag nanostructures accompanied with low aggregation to some extent. The typical HRTEM image of Ag@PANI-CS-Fe₃O₄ nanocomposite (Fig. 4D) shows that the nanoparticles are crystalline as the lattice fringes spacing are 0.25 nm, which is consistent with the crystal structure of Fe₃O₄,⁶⁰ and also 0.23 nm revealing the crystal structure of Ag nanoparticles.⁶¹ The inset image exhibits the selected area *via* electron diffraction (SAED) of Ag@PANI-CS-Fe₃O₄ nanocomposite, which shows arrays with bright circles confirming the crystallinity of these nanoparticles that is consistent with the data obtained from XRD.

Vibrating sample magnetometer (VSM) system was used to investigate the magnetic properties of the synthesized nanocomposite. Fig. 5 shows non-coercive force property or remanence values at room temperature indicating the ferromagnetic property of PANI-CS-Fe₃O₄@Ag nanocomposite. Saturation mass magnetization (M_s) of the Ag@PANI-CS-Fe₃O₄ nanocomposite observed from Fig. 5 is 0.4 emu g⁻¹ so Ag@PANI-CS-Fe₃O₄ nanocatalyst can be separated easily from the reaction medium by applying external magnetic field.

The reduction reaction of 4-NP to 4-aminophenol (4-AP) was selected as an example for testing the catalytic activity of Ag@PANI-CS-Fe₃O₄ nanocomposite. 4-NP can be reduced through NaBH₄ (the hydrogen source for reduction reaction) as a reducing agent to 4-AP. Without catalyst, the color of 4-NP does not change with time. Therefore, noble metals or their nanocomposites are required as catalysts to accelerate the transfer of electrons from the electron donor (BH₄⁻) to 4-NP as the acceptor and in this case the reduction reaction ends in few minutes.³⁹ The catalyzed reduction reaction was followed easily

via UV-VIS spectrophotometry since 4-NP has a characteristic absorption peak at 400 nm under alkaline conditions. The reduction of 4-NP to 4-AP is accompanied by change of the intense yellow color of 4-NP into colorless 4-AP solution with emergence of another peak at 310 nm, which is related to 4-AP as shown in Fig. 6.⁶² Furthermore, the reduction in the concentration of 4-NP can be found by following the decrease of

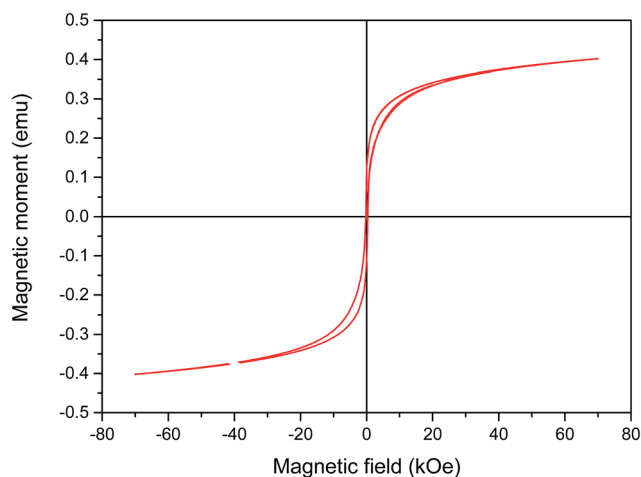


Fig. 5 Magnetic hysteresis loop (M-H) of Ag@PANI-CS-Fe₃O₄.

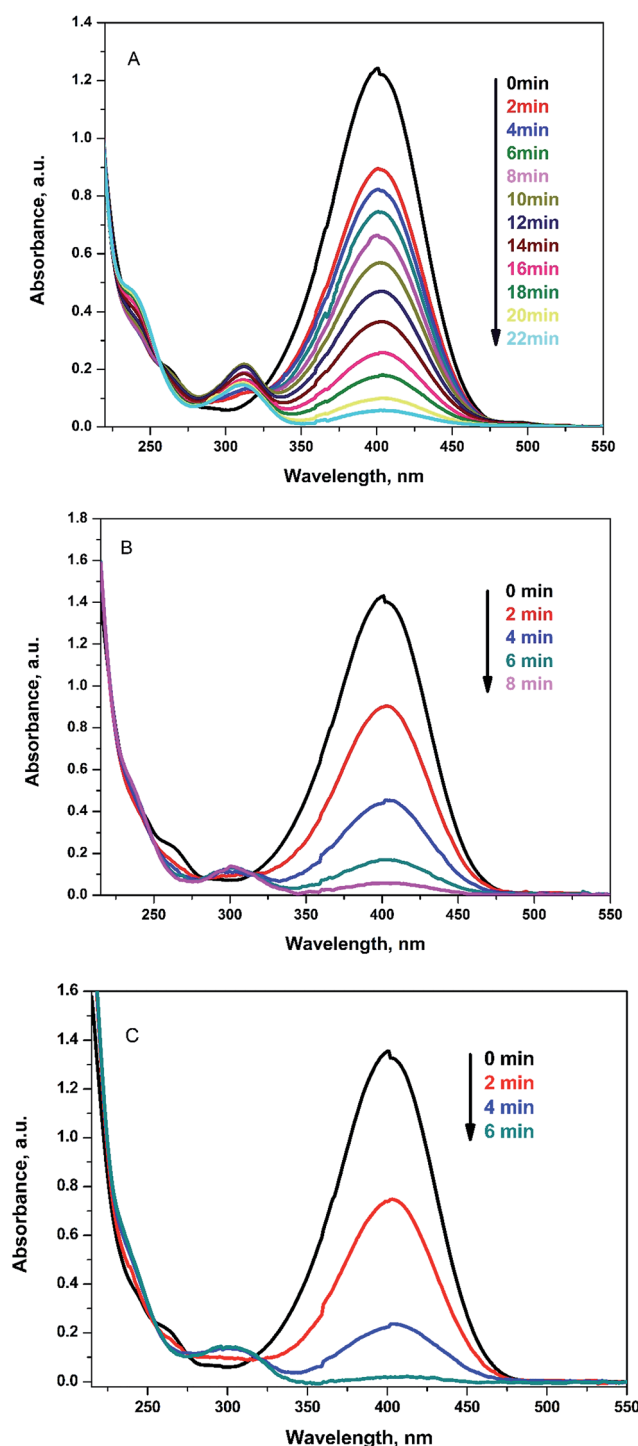


Fig. 6 UV-VIS spectra for reduction of 4-NP to 4-AP by NaBH₄ using 1 mg (A), 2 mg (B), 3 mg (C) of Ag@PANI-CS-Fe₃O₄ as a catalyst.

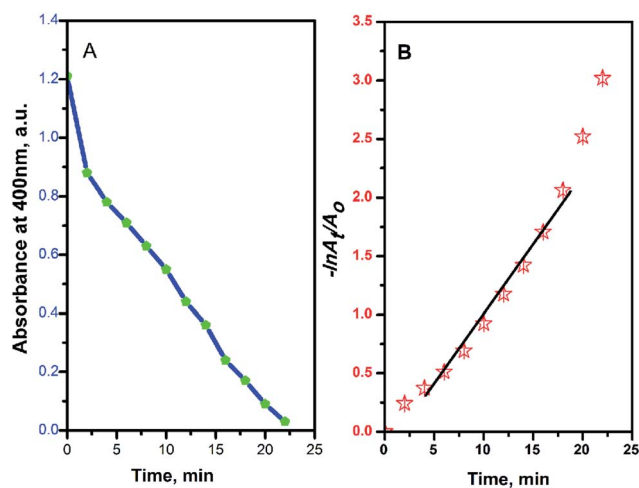


Fig. 7 Absorbance at 400 nm (A) and $-\ln A_t/A_0$ (B) versus the reduction reaction time of 4-NP by NaBH_4 using $\text{Ag@PANI-CS-Fe}_3\text{O}_4$ nanocomposite as a catalyst.

absorbance at 400 nm over time as shown in Fig. 6A. 1 mg of $\text{Ag@PANI-CS-Fe}_3\text{O}_4$ nanocomposite was used in the first period of the catalysis test and the reaction was ended within 22 min as shown in Fig. 6A and 7A. On using 2 mg and 3 mg of the

fabricated catalyst, the reaction finished after only 8 min and 6 min, respectively as presented in Fig. 6B and C.

Due to the high concentration of the reducing agent NaBH_4 compared to 4-NP, pseudo first order assumption was applied to calculate the kinetic rate of this reduction reaction.^{39,63} Fig. 7B shows the linear relation between $-\ln A_t/A_0$ over time, where A_0 is the initial absorbance and A_t is absorbance at time t , to confirm the pseudo first order assumption.

Various metals anchored onto variety of substrates with their kinetic rates calculated from pseudo first order assumption were ascribed in Table 2. By comparing our system with other data reported for other systems in the literature, it can be found that a very small amount (1 mg) of $\text{Ag@PANI-CS-Fe}_3\text{O}_4$ nanocomposite (as compared to large amounts of other substrates) shows a very high catalytic efficacy toward the reduction of 4-NP as well as its ease of separation. This high catalytic activity may be attributed to the small size of silver nanoparticles that are uniformly distributed through the $\text{PANI-CS-Fe}_3\text{O}_4$ nanocomposite, which usually leads to high catalytic activity.

Low catalyst dose with high catalytic efficiency results from the presence of chelating sites in both PANI and CS represented in amino groups as well as hydroxyl groups which are entrapping more Ag nanoparticles leading to an increase in anchoring Ag metal onto a small weight of the catalyst. The ease of

Table 2 Comparison of Ag nanoparticles anchored onto various substrates with their kinetic rates

Substrate	Dose	Conc. (mol L^{-1})	Reduction rate (10^{-3} s^{-1})	Ref.
Poly(amidoamine) dendrimer (G4)-Ag nanocomposite	10 (mmol dm^{-3})	0.3 cm^3 of 2 mmol dm^{-3}	0.59	64
Poly(propyleneimine) dendrimer (G4)-Ag nanocomposite	20 (mmol dm^{-3})	0.3 cm^3 of 2 mmol dm^{-3}	0.413	64
$\text{Fe}_3\text{O}_4/\text{SiO}_2$ -Ag	1 g	1.2×10^{-4}	7.67	65
Ag NPs-supported poly[N-(3-trimethoxysilyl)propyl]aniline	7.2 mg	1.5×10^{-3}	3.17	66
Ag@egg shell membrane	10 mg	3×10^{-3}	4.1	61
Ag@PANI-CS- Fe_3O_4	1 mg	7×10^{-3}	2.0	The present work

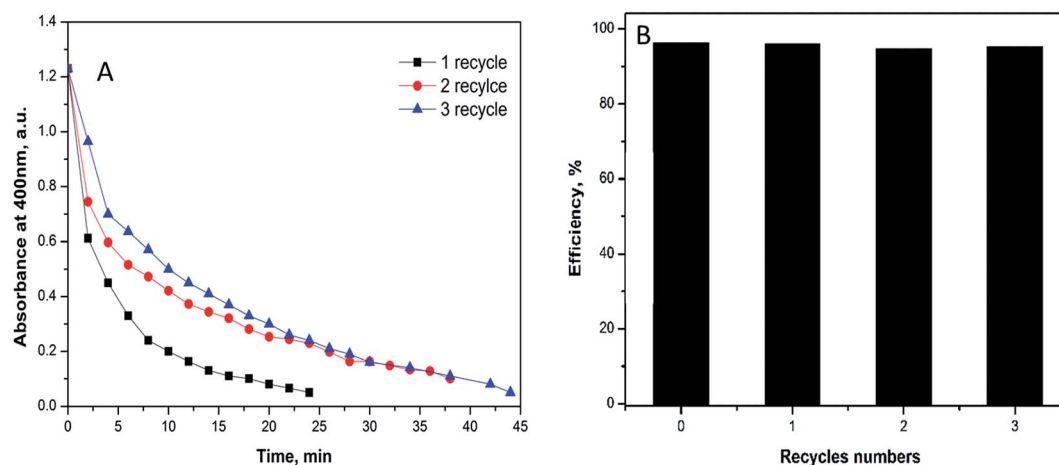


Fig. 8 Reusability of 1 mg of $\text{Ag@PANI-CS-Fe}_3\text{O}_4$ catalyst nanocomposite toward reduction of 4-NP via NaBH_4 as a reducing agent.

separation of the catalyst (magnetically) and the low catalyst dose (1 mg) as compared to other catalyst systems (as seen in Table 2) which results a high catalytic rate is the main reason for calling this system a smart system.

The recovery of the catalyst was tested using 1 mg of the fabricated catalyst under the similar above conditions. For the separation process, the substrate was exposed to magnetic field in the reaction cuvette and the produced aminophenol was drained quietly by syringe. The catalyst was recovered three times without great loss in the efficacy to prove that the catalyst is intact. In the first recycle, the reduction process ended at 25 min while the second and the third recycles last for 38 and 45 minutes, respectively (Fig. 8A). The time difference between the three recycles indicates the small decrease in the efficiency of the catalyst that could be attributed to the minor loss of the substrate during recycling.

The efficiency percentage (α) was calculated as reported by Zhang *et al.*⁶⁷ according to eqn (2):

$$\alpha = \frac{C_o - C_t}{C_o} \times 100\% \quad (2)$$

where, C_o is the initial concentration and C_t is the concentration at the termination stage. Fig. 8B represents efficiency percentages for 4 successive cycles with efficacy more than 95% in the fourth cycle. This means that the same amount of the catalyst can be used many times with negligible loss in the catalytic efficacy.

4. Conclusion

In summary, PANI-CS-Fe₃O₄ nanocomposite was successfully prepared through simple steps method. The prepared nanocomposite acted as a green surface that was decorated with silver nanoparticles. The role of the substrate (PANI-CS nanocomposite) lies in the reducing power of PANI and the availability of amino, imino and hydroxyl groups in PANI and CS which facilitates the coordination of Ag ions onto these basic active sites. The Ag-anchored nanocomposite was fully characterized by FTIR, XRD, EDX, SEM, TEM and VSM. These characterizations proved successful formation of Ag@PANI-CS-Fe₃O₄ nanocomposite with coarse particles of a spherical shape. The UV-Visible spectrophotometry technique proved good catalytic efficacy of the prepared nanocomposite towards reduction of 4-NP. The new as-prepared nanocomposite from conducting polymer (PANI) and natural one (CS) with silver nanoparticles can be considered an eco-friendly catalyst that is characterized by its ease of preparation as well as its magnetic character (for ease of separation) and thus Ag@PANI-CS-Fe₃O₄ can be considered a promising catalysis candidate for industry and other fields.

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The ageing of polypyrrole nanotubes synthesized with methyl orange

Martin Varga^{a,*}, Dušan Kopecký^b, Jitka Kopecká^b, Ivo Křivka^a, Jan Hanuš^a,
Alexander Zhigunov^c, Miroslava Trchová^c, Martin Vrnáta^b, Jan Prokeš^a

^a Faculty of Mathematics and Physics, Charles University, 180 00 Prague 8, Czech Republic

^b Department of Physics and Measurements, Faculty of Chemical Engineering, University of Chemistry and Technology Prague, 166 28 Prague 6, Czech Republic

^c Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

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ABSTRACT

The process of ageing of polypyrrole is accompanied by gradual changes in its chemical composition, protonation level and charge transport mechanism. Although these changes are often limiting for practical application of polypyrrole, they are still far from being understood. In our contribution, natural (*i.e.* ageing at room temperature) and accelerated ageing (at 120 °C) of polypyrrole nanotubes were studied. Natural ageing for about 3 year timespan lead to relative decrease of sample conductivity to about 0.2 of its initial σ_0 value. Accelerated ageing caused a dramatic decrease of 7 orders of magnitude after about 1000 h accompanied by partial deprotonation and backbone oxidation as confirmed by infrared, Raman and XPS spectroscopy and elemental analysis. Occurrence of crystalline domains was attributed to residual methyl orange and was not affected by ageing. The presence of methyl orange was found crucial for improving stability of sample conductivity; it caused about 4 orders of magnitude enhanced conductivity when compared with polypyrrole without methyl orange. In macroscopic scale the conductivity loss was found to be a spatially homogeneous process as revealed by electrical tomography. With increasing ageing time, besides gradual degradation on microstructural level, a qualitative change of charge transport mechanism was found.

1. Introduction

Nowadays, increasing number of applications of conducting polymers requires long-term stability of their physical properties, particularly electrical conductivity. Numerous studies have been carried out to investigate the decrease of conductivity in polypyrrole (PPy) during natural [1–5] or accelerated ageing at elevated temperatures [6–12]. Generally, stability of polymer depends on the material composition (*i.e.* presence and type of dopants) [5,6,13], and the ageing conditions (temperature, humidity, radiation, presence of oxygen, various solvents) [7,14–16]. However, the mutual relations among the synthesis conditions, polymer composition and conditions of ageing are still far from being understood. For instance, natural ageing of PPy doped with arylsulfonates was found to be much slower than expected from accelerated ageing tests [4]. This approach is useful for separation of the degradation factors.

The main phenomena taking place during the ageing process which have an impact on polymer conductivity are: loss of the dopant counterions and redistribution of the remaining ones along polymer chains. The chemical reasoning of these phenomena is

* Corresponding author.

E-mail address: martin.varga@mff.cuni.cz (M. Varga).

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based on the substitution reactions on the polymer, covalent bonding of counter-ions to polymer backbone (e.g. chlorination), oxidation and chemical cross-linking (e.g. ternary amines in polyaniline (PANI)) [17]. Other transitions could occur due to the loss of water or (in general) solvent molecules causing a change in the hydrogen bonding and subsequently in conductivity [13]. Besides the chemical changes, the conformational structure is also modified by thermal treatment [18]. However, mainly from a point of chemical kinetics, oversimplified correlations between induced chemical changes and conductivity loss were criticised [19]. A possible explanation of the conductivity decay was given using the concept of a heterogeneous corrosion-like process of disruption of conducting islands with simultaneous expansion of amorphous insulating phase [19]. In such case, although conductivity change was still mediated by chemical changes, the final kinetics of the process was altered. The knowledge of kinetics is therefore important for deeper understanding of overall ageing process.

Here we performed both natural and accelerated ageing tests for polypyrrole nanotubes (PPy-NT) prepared with methyl orange (MO) as a template [20]. We also compared the conductivity decay of PPy-NT with that of their template-free granular counterparts (PPy-G). The well-conducting nanotubular form containing well-ordered phase (close to metal-insulator transition) [21] was also found more stable in alkaline solutions than the granular one [22]. Information about the stability of electrical properties for nanotubular morphology of conducting polymers can be particularly important, since these 1D nanostructures have received much attention for their wide application potential in nanoelectronics [23]. Another emerging area for their application seems to be synthesis of three-dimensional soft conducting materials such as hydrogels well-suitable for biomedical applications [24,25]. While in synthesis of novel cryogels polyaniline is mainly applied so far [26], polypyrrole nanotubes can become the next candidate to fulfil this role.

In this work we study the changes of PPy-NT conductivity and charge transport mechanism during: (i) long-term natural ageing within three year timespan and (ii) accelerated ageing at 120 °C. The impact of accelerated ageing on morphology, crystalline structure, molecular structure and doping level of PPy-NT is investigated as well. Finally, kinetics for conductivity and chemical composition changes are determined.

2. Materials and characterization

2.1. Synthesis

Pyrrole (Sigma-Aldrich), iron(III) chloride hexahydrate (Sigma-Aldrich), and methyl orange *i.e.* (4-[4-(dimethylamino)phenylazo] benzenesulfonic acid sodium salt; Fluka) were used as received. Polypyrrole nanotubes were prepared by chemical oxidation of pyrrole with iron(III) chloride hexahydrate in the presence of structure-guiding agent methyl orange, MO, according to previously published procedure [20].

600 mL of 2.5 mM (1.5 mmol) aqueous solution of MO and 2.1 mL (30 mmol) of pyrrole were mixed and cooled to 5 °C. Then 8.12 g (30 mmol) of iron(III) chloride hexahydrate was dissolved in 69 mL of deionized water and subsequently added dropwise into the reaction solution. Thus, the molar concentrations of reactants in the reaction solution were 45 mM pyrrole, 45 mM oxidant, and 2.2 mM MO, respectively. We set the monomer to oxidant ratio to 1:1 although there are other studies suggesting other ratios for optimal synthesis of PPy; mainly to avoid a number of varying parameters keeping in mind that any significant effect on conductivity was not observed [27,28]. The reaction solutions were gently stirred for 24 h. PPy-NT were subsequently separated by filtration and purified by Soxhlet extraction using acetone to remove residual MO. Then the samples were rinsed with ethanol and dried at 40 °C in a vacuum oven. Common PPy-G was synthesized in analogous way without addition of MO; this sample serves as the reference for structural studies.

One part of the samples was then stored at ambient laboratory conditions (referred to as natural ageing), *i.e.* at temperature 25–30 °C, relative humidity about 30–35%, and not being protected from sunlight. It is worth to mention that any humidity control device or light source with controlled radiation were not used. The main idea was to study stability of samples during natural ageing. The second part of the samples – the artificially aged ones – was obtained only by their treatment at elevated temperatures in a PC controlled Heraeus-Vötsch VMT 07/35 thermostatic chamber (protected from daylight) at about 120 °C. Material was studied either in the form of powder or as compressed pellet (at *ca.* 530 MPa) of 13 mm in diameter and 0.3–1 mm in thickness. For quick comparison of samples with various composition we determined the degradation time of *ca.* 260 h (preliminary experiments have shown us that such time period is long enough to reveal differences in sample stability).

2.2. Characterization

The morphology of PPy was observed by scanning electron microscopy (SEM) using Mira 3 LMH (Tescan). Elemental analysis was measured by energy-dispersive X-ray spectroscopy (EDX) using Bruker Quantax 200 spectrometer with XFlash 6|10 detector (Bruker Corporation) with 15 kV of accelerating voltage.

Wide-angle X-ray Scattering (WAXS) experiments were performed using a pinhole camera (modified Molecular Metrology System, Rigaku) attached to a microfocused X-ray beam generator (Rigaku MicroMax 003) operating at 50 kV and 0.6 mA (30 W). The camera was equipped with removable and interchangeable Imaging Plate 23 × 25 cm (Fujifilm). Experimental setup covered the momentum transfer (q) range of 0.4–3.6 Å^{−1}, with $q = (4\pi/\lambda)\sin \theta$, where $\lambda = 1.54$ Å is the wavelength and 2θ is the scattering angle. Calibrations of the center and sample-to-detector distance were made using Si powder. The samples were measured in transmission mode – each of them for 60 min.

Fourier-transform infrared (FTIR) spectra of the powders dispersed in potassium bromide pellets were measured using a Thermo

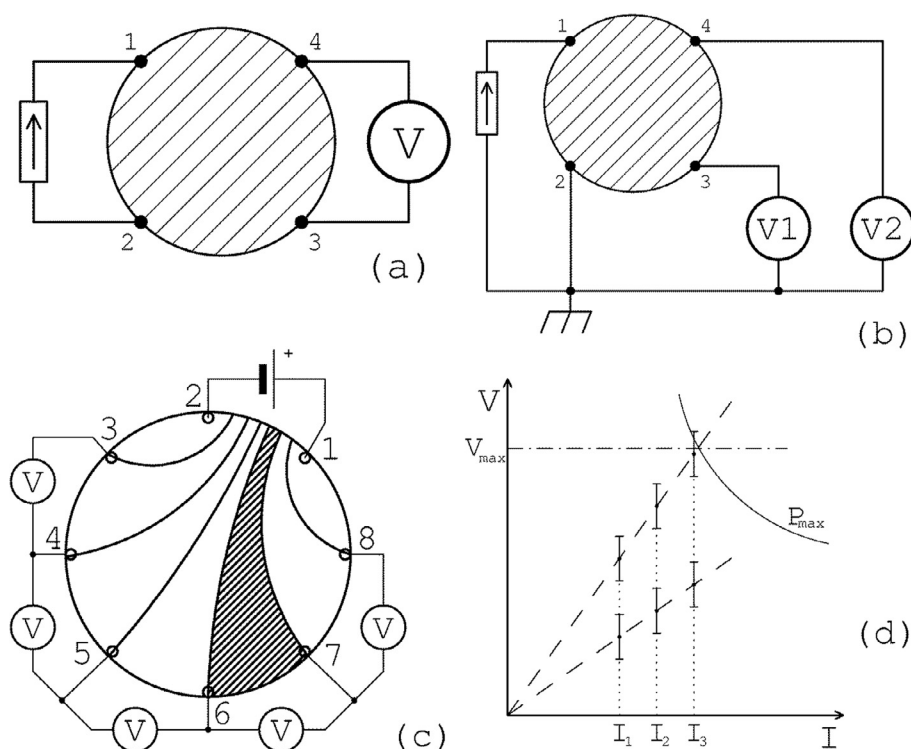


Fig. 1. Schemes for conductivity measurement by common four-point probe method configuration (a), the extended van der Pauw configuration for low conductivity measurements (b) and the eight-point probe electrical impedance tomography (c), and the criterion for selection of measuring currents (d).

Nicolet NEXUS 870 FTIR Spectrometer (Madison, WI 537 11) in an H₂O-purged environment with DTGS (Deuterated Triglycine Sulfate) detector in the wavelength range from 400 to 4000 cm⁻¹.

Raman spectra of the powdered samples were measured on a Renishaw InVia Reflex Raman micro-spectrometer. The spectra were excited with a diode 785 nm laser. A research-grade Leica DM LM microscope with an objective magnification $\times 50$ was used to focus the laser beam on the sample placed on an X-Y motorized sample stage. The scattered light was analysed by the spectrograph with holographic grating 1200 lines mm⁻¹. A Peltier-cooled CCD detector (576 $\times$ 384 pixels) registered the dispersed light.

X-ray photoelectron spectroscopy (XPS) was performed on powders placed into a XPS apparatus (Specs) using an Al K α X-ray source (Specs, XR-50) and hemispherical electron analyzer (Specs, Phoibos 100). Apparatus with samples was at least one day continuously pumped to achieve desirable high vacuum ($< 10^{-7}$ Pa). Correction to charging effects was done using the binding energy of 284.8 eV for the main peak in C 1s spectrum. Intensity in spectra of aged samples was normalized to corresponding peaks of non-aged sample.

We would like to emphasize that conductivity measurements have to be performed with care especially at high degradation level (low conductivity) to avoid errors and subsequent misinterpretation. Therefore, experimental methods are explained with more details as follows. Conductivity was measured by the four-point van der Pauw (VDP) method [29]. The most often used VDP configuration (Fig. 1a) can be negatively influenced by common mode currents flowing through the sample between floating low impedance terminals of the current source and the voltmeter, both devices being powered from electrical grid. The common mode interference thus prevents application of measuring currents lower than typically 10^{-8} A. The simple VDP configuration (Fig. 1a) was suitable only for samples with conductivity higher than ca. 10^{-4} S cm⁻¹. Modified configuration (Fig. 1b) can measure considerably lower conductivity [30]. The corresponding set-up consisted of a Keithley 6220 programmable current source, a Keithley 6485 picoammeter, a Keithley 2000 multimeter, a Keithley 706 scanner equipped with a Keithley 7152 low current matrix card, and two Keithley 6517B electrometers as high impedance voltmeters. In this configuration, common mode currents were reduced because low impedance terminals of all devices were not floating, but connected and grounded together. The voltage difference $V = V_2 - V_1$ between the two electrometers' preamplifier outputs was read by a common multimeter. All high impedance cables were triaxial and employed guarding technique; on high impedance terminal of a current source, the guarding reduces leakage currents and on terminals of electrometers it shortens the settling time necessary for steadying of measured voltage [30]. From the practical point of view, this set-up enabled us to measure conductivity down to 10^{-10} S cm⁻¹.

Temperature dependence of conductivity was measured on pellets by VDP method. The less conducting samples ($\sigma_{RT} < 10$ S cm⁻¹) were measured in a nitrogen cryostat (Janis VNF100) at temperature range ca. 70–315 K. The experimental set-up consists of a Keithley 220 programmable current source, a Keithley 2010 multimeter as a voltmeter, and a Keithley 705 scanner equipped with a Keithley 7052 matrix card. Measurements at extended temperature range, i.e. 5–315 K, were performed only for

well-conducting samples in a helium cryostat (CS210SX19 with coldhead DE-210S, Advanced Research Systems with a Lake Shore AC Resistance Bridge 372). During these measurements the samples were not placed in vacuum but in exchange gas to ensure a good thermal contact. Prior to all temperature scans, the pellets were kept in dynamic vacuum (10^{-2} – 10^{-2} Pa) for about 8 h to establish defined moisture of the material.

Electrical impedance tomography (EIT) can be used to construct a map of conductivity distribution [31]. The more electrodes, the higher is resolution of the map. As a compromise between resolution and measurement speed, pellets furnished with eight electrodes were used to collect EIT data [32]. The current was always applied through neighbouring electrodes and the voltage was measured successively from all other adjacent electrode pairs (Fig. 1c). For each position of source pair, five independent voltage values could be obtained. As the source pair can be alternated in eight positions, $8 \times 5 = 40$ voltage measurements was done on each sample. The experimental equipment for such measurement included a Keithley 238 current source, a Solartron-Schlumberger 7081 voltmeter and a Keithley 706 scanner equipped with four 7164D relay cards. The conductivity map was then constructed using algorithms based on the backprojection method [33,34].

Measuring currents should be as high as possible to minimize relative errors of voltages due to the noise. The limiting factors are the safe voltage limit $V_{\max}$ (high resistive samples) or maximum energy dissipated by Joule heating $P_{\max}$ (low resistive samples). Moreover, it is helpful to repeat VDP or EIT procedure using several current values spanning at least one order of magnitude which makes possible to verify that all measured voltages are directly proportional to the applied current. Only in that case it is correct to consider the measured resistivity as a current-independent value (Fig. 1d).

3. Results and discussion

3.1. Conductivity decay during natural and accelerated ageing

The naturally aged samples were stored at ambient conditions and measured from time to time. The relative change of conductivity during natural ageing for about three years (1076 days) at ambient storage conditions is depicted at Fig. 2a. It is worth to note that despite the statistical deviation (various sets) of the initial conductivity of up to 30 % from its mean value, about 65 S cm^{-1} , the relative decrease of conductivity during ageing was found to be the same. In order to characterize the time decay and to compare the stability of various materials, the half-life time $t_{0.5}$ defined as the ageing time required for conductivity to be halved from initial value σ_0 , $\sigma(t_{0.5}) = 0.5\sigma_0$, can be used [7,35]. For PPy-NT the $t_{0.5}$ value was estimated to be ca. 160 days. This is much higher than for PPy-G estimated to about 12 days [3] or about 11 days in our case. We also evaluated kinetics of degradation using stretched exponential time decay, $\sigma(t)/\sigma_0 \sim \exp\left[-\left(\frac{t}{\tau}\right)^n\right]$, which is widely accepted for ageing of conducting polymers. Although mostly used value of exponent is 0.5 [19,36–38], also others are theoretically justified [39,40]. However, we focus here mainly on relaxation time τ regardless of the value of exponent which was adjusted to produce a fair agreement with experimental data. The proper determination and interpretation of exponent requires much more detailed study and will be published elsewhere. In this case, we estimated value of the exponent to be 0.29 for both PPy-NT and PPy-G with one order of magnitude larger relaxation time for nanotubes. The results are summarized in Table 1.

At 120 °C a significant degradation within a reasonable experimental timeframe was observed (Fig. 2b). Within 1000 h (41 days) period the conductivity decreased of about 7 orders of magnitude. The difference between PPy-NT and PPy-G increased with ageing time. It should be noted that even poorly conducting samples were measured with VDP technique, in the extended mode (Fig. 1b). We again fitted the data with stretched exponential relaxation function. While for PPy-NT we obtained the exponent value equal to 0.5, for PPy-G it was only available for ageing time longer than tens of hours. Even though it would be in agreement with literature [19], we leave it here with $n = 0.32$ which describes the data better. The relaxation time for PPy-NT is two orders of magnitude higher than for PPy-G. The difference in stability is more pronounced for higher temperatures and longer degradation time. The results are again summarized in Table 1. While in both cases of degradation (both natural and artificial one) a stretched exponential was found, a detailed temperature dependence of relaxation time should be studied to compare the respective kinetic processes involved in those two ageing modes. Such detailed study will follow. We also compared degradation of the material in pellet and in powder form. Two main differences were observed. The former ones were generally prone to formation of highly resistive surface layer (and thus their results are difficult for interpretation) while the latter ones were found to be more degraded in bulk (Fig. 2c) as the larger material surface was subjected to degradation process. Finally, we studied the effect of MO concentration applied at synthesis (and its residual content) on stability of sample conductivity. Other properties on such samples were studied elsewhere [41]. Here we determined the degradation time to be about 260 h to compare values for various samples. We can see difference in stability of sample conductivity more than four orders of magnitude favouring high MO content (Fig. 2d). The presence of MO residuals in samples and its impact are discussed below.

As the extensive degradation takes place during accelerated ageing, the artificially aged samples were further used for structural investigations. Moreover, for deeper insight into ageing process, the mapping of heterogeneity of conductivity was employed on macroscopic scale by means of EIT.

3.2. Effect of ageing on charge transport

Charge transport mechanism was studied for selected samples, both naturally and artificially aged, by means of measurement of temperature dependence of conductivity. The type and parameters of charge transport models depend on various factors related to

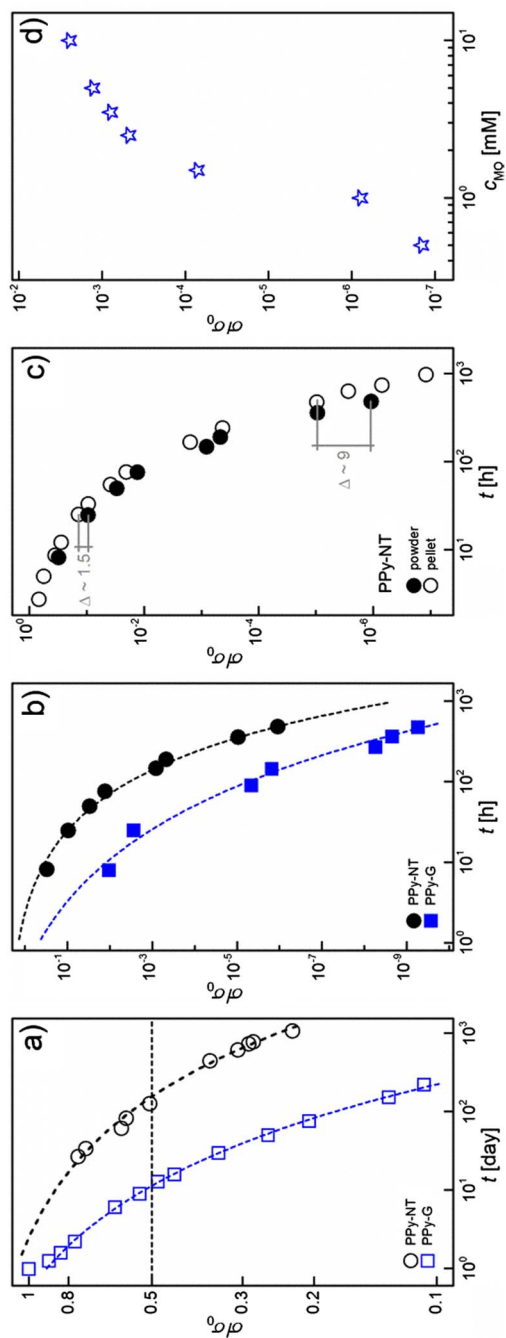


Fig. 2. Relative change of conductivity of (a) naturally aged PPy-NT and PPy-G in pellet form and the value of $0.5\sigma_0$ (dashed line), (b) artificially aged PPy-NT and PPy-G at 120 °C in powder form, (c) PPy-NT at 120 °C in powder and pellet form, (d) PPy (in pellet form) with various MO content at 120 °C and 260 h.

Table 1

Fitted parameters of stretched exponential relaxation for naturally and artificially aged (at 120 °C) PPy-NT and PPy-G .

Sample	Natural ageing		Artificial ageing	
	PPy-NT	PPy-G	PPy-NT	PPy-G
τ [h]	3800	160	2.2	0.022
n	0.29	0.29	0.5	0.32

level of doping, homogeneity, disorder, etc. [42]. Tracking the changes in charge transport induced by ageing can shed more light on the nature of ageing mechanism.

Here we evaluated the preliminary results according to two different models suggested in our previous work on charge transport in PPy [21]:

$$\frac{1}{\sigma(T)} = \frac{1}{aT^\gamma} + \frac{1}{\sigma_0^I \exp\left(-\left(\frac{T_0^I}{T}\right)^{0.25}\right)}, \quad (1)$$

$$\sigma(T) = \sigma_0^{II} \exp\left(-\left(\frac{T_0^{II}}{T}\right)^{0.5}\right) + \sigma_0^{III} \exp\left(-\frac{T_0^{III}}{T}\right). \quad (2)$$

The *Model 1* (Eq. (1)) represents a serial connection of well-ordered areas in the vicinity of metal-to-insulator transition (the closer to insulator part, the higher γ) with disordered regions where 3D variable hopping prevails. The *Model 2* (Eq. (2)) stands for a parallel connection of another hopping model (Q1D or 3D between polaronic clusters) and simple activated transport of Arrhenius type. All regions in both models are geometrically weighted; this is included in prefactors a , σ_0^{I-III} . The detailed analysis is far beyond the scope of the current paper. Here we focus on transition between these two models and change of parameters related to internal order, doping level, etc. represented by adjustable parameters T_0^{I-III} .

The results for temperature dependence of conductivity and their fits to theoretical models are summarized at Fig. 3. We also add plots of the so-called reduced activation energy, i.e. $d \ln(\sigma(T))/d \ln(T)$, which were successfully used to improve determination of model. First we plotted a referential sample which was found to follow the *Model 1* [21], here with attribute of 34 days of natural ageing. Two more samples could be fitted with the same model, the naturally aged one for 471 d and the artificially aged one for 5 h at 120 °C. For the samples artificially aged for 50 or 120 h the *Model 2* was more appropriate. Moreover, ‘disorder’ parameters in both models increase with ageing time (Table 2). Without going into details, we can deduce that ageing introduces gradual degradation on microstructural level up to qualitative change in charge transport mechanism. Subsequently, the degradation in conducting areas continues. Even though MO gives morphology to PPy and enhances its stability, we can see that (after thermal treatment) the original well-ordered internal structure of PPy is not preserved and the charge transport is then the one characteristic for strongly-disordered materials such as pristine PPy-G [21]. To better understand the influence of ageing on the character of charge transport, particularly on change of physical parameters, a detailed separate study is needed and will be published elsewhere. It should be emphasized that since artificial ageing can be used to systematically prepare samples with desired conductivity/internal order, it is beneficial

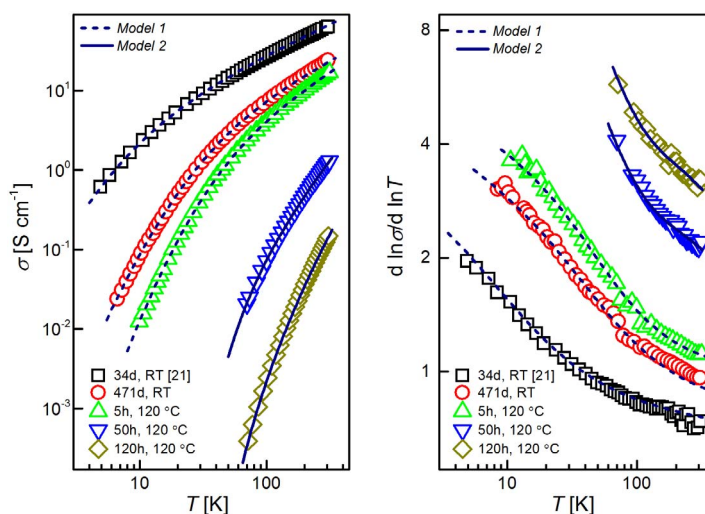


Fig. 3. Temperature dependence of conductivity (left) and reduced activation energy (right) of various aged samples with corresponding fits of model 1 (Eq. (1)) and model 2 (Eq. (2)).

Table 2

Fitted parameters of charge transport models (Eqs. (1) and (2) for various naturally and artificially aged (at 120 °C) PPy-NT.

Ageing conditions	Model 1				Model 2			
	α [S cm ⁻¹ K ^{-γ}]	γ	σ_0^I [S cm ⁻¹]	T_0^I [K ⁻¹]	σ_0^{III} [S cm ⁻¹]	T_0^{II} [K ⁻¹]	σ_0^{III} [S cm ⁻¹]	T_0^{III} [K ⁻¹]
34 d, RT	1.3	0.74	6.4×10^3	3.4×10^4	–	–	–	–
471 d, RT	0.36	0.78	1.3×10^4	2.0×10^5	–	–	–	–
5 h, 120 °C	0.075	0.98	5.3×10^4	5.4×10^5	–	–	–	–
50 h, 120 °C	–	–	–	–	152	8.0×10^3	0.72	260
120 h, 120 °C	–	–	–	–	104	1.4×10^4	0.077	400

technique for charge transport studies [19]. Hence, these two studies are rather complementary.

3.3. Conductivity mapping by electrical tomography

During accelerated ageing, each sample was scanned using the EIT procedure, which provides a map of the electrical conductivity distribution on the area of a sample. Fig. 4 shows several snaps from a time development sequence of the conductivity distribution recorded from the PPy-NT sample aged at 120 °C during *ca.* 16 days. Time interval between individual snaps is approximately 16 h. On the very beginning the sample shows almost uniform conductivity distribution. More ragged profiles together with marked decrease of mean conductivity can be observed later (the density of contour lines is 50 lines per decade in the whole range of logarithmic scale). It can be seen that both the evolution of non-uniformity and the conductivity decrease rate correlate with the ageing time.

3.4. Infrared and Raman spectroscopy

Infrared spectroscopy was employed in order to track chemical changes during accelerated ageing. Absorption bands in FTIR spectra of PPy-NT before ageing (Fig. 5) exhibited very small intensity in comparison with PPy-G, which was caused by its compact stone-like structure difficult to disperse in potassium bromide pellets. It may be connected with strong hydrogen bonding in the sample. The measured spectra contain relatively strong absorption bands in the region of stretching and bending vibrations of water molecules at about 3427 cm⁻¹ and 1644 cm⁻¹, respectively. However, the main bands of PPy-G can be well distinguished practically at the same positions in the spectrum of PPy-NT. They were described in Refs. [28,43]. Some very weak peaks of MO can be identified in the spectrum of PPy-NT. After ageing at 120 °C during 119 h, the positions of the main peaks of PPy remained unchanged, but their intensities varied. The intensity of the peaks of MO slightly increased, they are marked with asterisk (Fig. 5). The shape of the spectrum is close to the spectrum of the PPy deprotonated with 1M NH₄OH (PPy base) described in Ref. [44]. It correlates with decrease of conductivity. Absorption in the region above 1600 cm⁻¹ decreased and a weak band at 1711 cm⁻¹ appeared. It corresponds to the presence of carbonyl group, in that case attributed to the nucleophilic attack of water during the preparation [43]. After ageing during longer time periods (119 h, 242 h, 480 h, and 962 h) the samples were generally much better dispersible in the pellet which may be connected with loss of water and disappearing of hydrogen bonds. The corresponding spectra dramatically

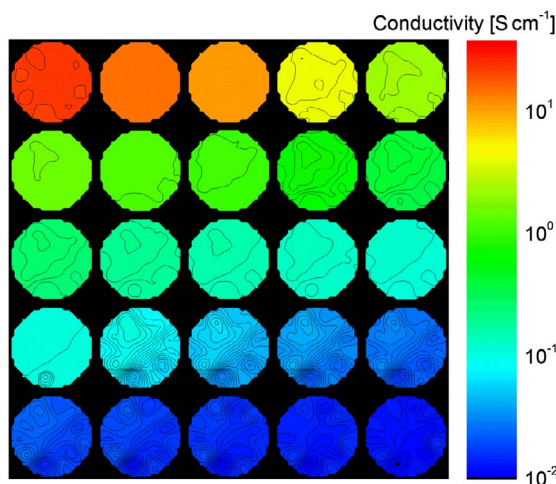


Fig. 4. Electrical tomography maps of spatial distribution of conductivity for PPy-NT sample during accelerated ageing at 120 °C. Total time is 16 days. Time interval between snaps is approximately 16 h.

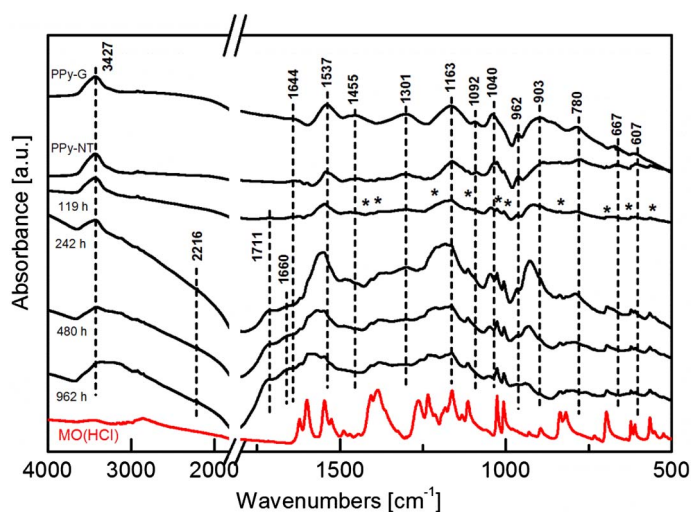


Fig. 5. FTIR spectra of PPy-NT before and after ageing (119 h, 242 h, 480 h, 962 h). Spectra of non-aged PPy-G and of MO(HCl) are included. Peaks related to MO are marked with asterisks.

changed (Fig. 5). The intensity of the peaks attributed to MO increased with heating. It should be stressed that MO is present in the samples in its acidic form MO(HCl) [20]. The maxima of the bands observed in the spectrum at about 1537 cm^{-1} (C–C stretching vibrations in the pyrrole ring), at 1163 cm^{-1} (the region of the C–H and N–H in plane deformation vibrations) and at 903 cm^{-1} (the C–H out of plane deformation vibrations of the ring) shifted to higher wavenumbers after heating. The same shift has been observed in the spectra after deprotonation in Ref. [44]. The heating causes a relative decrease of the band at 1455 cm^{-1} (C–N stretching vibration in the ring), of the broad band with maximum at about 1300 cm^{-1} (C–H or C–N in-plane deformation modes) and of the band at 1030 cm^{-1} (C–H and N–H in-plane deformation vibrations) [44]. The intensity of the band at 1711 cm^{-1} belonging to the vibrations of carbonyl group and of the band situated at 1660 cm^{-1} dramatically increased. A very weak peak of N=C=O vibrations appeared at 2216 cm^{-1} . These attacks of oxygen on polymer backbone probably lead to decrease in average conjugation length and thus decrease of conductivity [2].

Raman spectroscopy is an adequate tool to study the molecular structure and the doping level of conducting polymers. We have used the laser excitation wavelength 785 nm because it is not in resonance with the energetic transitions in MO and so the spectral features of PPy can be clearly displayed. The Raman spectrum of the original PPy-NT (Fig. 6) is very close to the Raman spectrum of PPy-NT salt [44]. The band of C=C stretching vibrations of PPy backbone with the maximum situated at 1598 cm^{-1} , whose position is characteristic for the oxidation state of PPy [45], remained practically at the same position in the spectra of all aged samples (Fig. 6). After ageing, the Raman spectra exhibit the fluorescence background of MO. As the Raman scattering is a surface-sensitive method, it may be connected with migration of MO from the bulk to the surface of the samples during heating. It should be stressed that the structure of free elapsed MO may be different from MO interacting with PPy in nanotubes. Intensity of the band with maximum at 1498 cm^{-1} (C=N and C–C stretching vibrations) increased during heating. This band was slightly shifted to higher

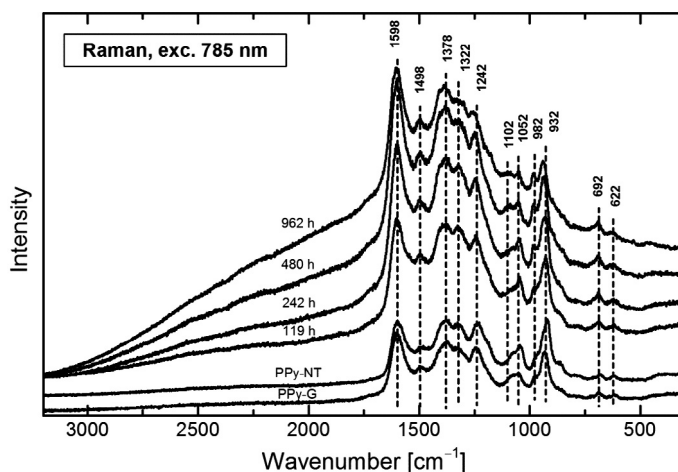


Fig. 6. Raman spectra of original PPy-NT before and after (119 h, 242 h, 480 h, 962 h) ageing and the spectrum of non-aged PPy-G measured with 785 nm laser excitation line for comparison.

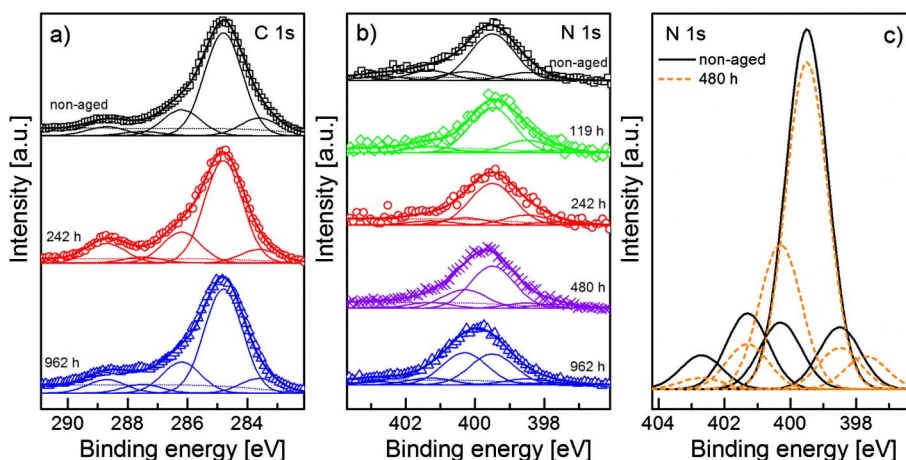


Fig. 7. XPS spectra of C 1s (a) and N 1s (b) of PPY-NT before and after (119 h, 242 h, 480 h, 962 h) ageing with deconvolution (see text) and envelope fits. Detailed plot of deconvoluted N 1s spectra for untreated and aged (480 h) samples (c).

wavenumber during ageing which may be connected with the deprotonation of the samples. It correlates also with appearing of a shoulder at about 1416 cm^{-1} in the spectra of heated samples which belongs to the increased C–N stretching vibrations in the neutral units. The two peaks situated at 1378 and 1322 cm^{-1} are assigned to the ring stretching vibrations of PPY. The first one belongs to the oxidized and more conducting PPY and the second one to the ring stretching vibrations of deprotonated units [45]. The relative ratio of these two bands in aged PPY remained almost unchanged after ageing which indicates that at least partial protonation was maintained. After ageing, the peaks at 1242 cm^{-1} (antisymmetric C–H deformation vibrations) and at 932 cm^{-1} (ring deformation vibrations in dication units) shifted to the higher wavenumbers in the spectra of samples aged for 242–962 h (Fig. 6). The double peak at about 1102 and 1052 cm^{-1} belongs to the C–H out of plane deformation vibrations. The relative intensity of these peaks corresponds to the deprotonated PPY [45]. The intensity of the sharp peak of the ring deformation vibrations of neutral units situated at 982 cm^{-1} increased in the spectra of the samples heated for 242–962 h. The ring deformation and out of plane C–C deformation vibrations are connected with the peaks situated at 918 and 864 cm^{-1} .

3.5. X-ray photoelectron spectroscopy

Ageing effect of PPY-NT studied with XPS enabled us to qualitatively track the changes at the surface of the samples. Deconvolution of PPY spectra of N 1s and C 1s was done using Gaussian functions with constant width and positions according to literature [46–48]. All spectra of C 1s (Fig. 7a) were found to be quite similar and except main C_{α} and C_{β} peaks (284.8 eV , 283.6 eV) in PPY backbone, three oxygen-containing groups C=N/C–O, C=O and O–C=O at about 286.2 eV , 287.5 eV and 288.8 eV , respectively, were identified [46]. Only a slight increase in relative intensity of C=N/C–O, C=O groups was observed. It should be stressed that XPS is an extremely surface-sensitive method and certain contamination of sample surface could not be avoided. More information could be extracted from N 1s spectra (Fig. 7b and c). The spectrum of non-aged sample is composed from typical peaks of protonated PPY of C–N⁺, C=N⁺ and –NH– situated at 401.1 eV , 402.7 eV and 399.7 eV , respectively [46], peak at 398.5 eV often attributed to pyridine-like N [49,50] and peak at 400.3 eV which probably comes from azo-group in MO [51,52]. After ageing we found lower relative intensity coming from protonated species. Moreover, a small peak at 397.7 eV attributed to deprotonated species –N= in PPY [47] appeared in aged sample (Fig. 7c). Our results are consistent with the picture of incomplete deprotonation caused by alkaline solutions [48]. Significant increase of the peak intensity at 400.3 eV can be related to migration of MO species to the surface during ageing. All these findings are in agreement with FTIR and Raman spectra. Finally, Cl 2p spectra were unfortunately too noisy for any analysis and hence only rough estimate for chlorine content to be about 0.2–1.2 at.% was done. The sulfur content was estimated to 0.5–1.4 at.%. This again confirms that the MO species are present at the surface of sample.

3.6. Elemental analysis

Up to this point we identified the chemical changes in PPY-NT during ageing, such as increase of carbonyl groups, partial deprotonation and MO migration to surface, with an aid of spectroscopic methods. In this section we correlate these qualitative trends with results of elemental analysis determined from EDX. As for the content of distinct elements (reported in at.%) we can distinguish three different trends (Fig. 8); (i) contents of nitrogen ($\approx 17\%$) and sulfur (coming solely from MO, $\approx 1\%$) remain constant throughout the whole ageing period; (ii) content of oxygen continuously increases from ca. 7% to ca. 19%; (iii) content of chlorine coming from oxidant decreases from initial $\approx 3.5\%$ to final $\approx 1.2\%$. From all these results one can deduce that (i) the chemical ageing of PPY is not accompanied by release of nitrogen in the form of volatile compounds and, moreover, amount of MO in PPY also remains constant, (ii) while the initial oxygen content could be attributed mostly to gas chemisorbed to PPY surface (as the ageing process is carried out at 120°C , we can avoid the influence of increased chemisorption at elevated temperature), the significantly increasing

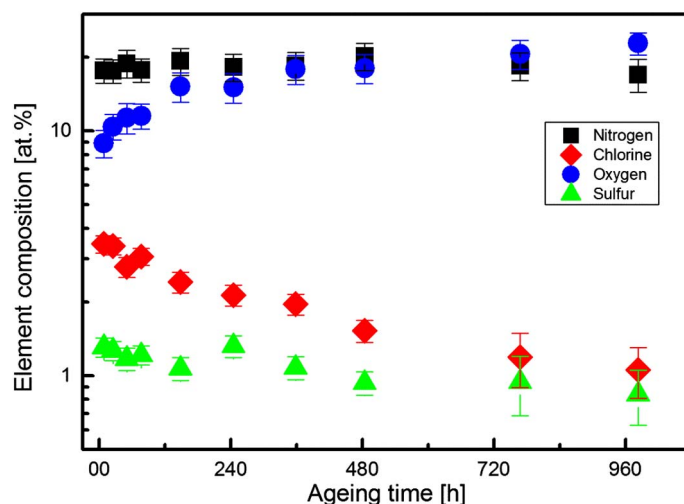


Fig. 8. Effect of ageing at 120 °C on elemental composition of PPy-NT determined by energy-dispersive X-ray spectroscopy.

content of oxygen can be explained by carbonylation of PPy heterocycles in agreement with results of Raman/FTIR/XPS spectroscopies (Fig. 5, Fig. 6), and finally (iii) chlorine is released from the polymer, e.g. in a form of gaseous HCl [35] or NH_4Cl [10].

3.7. Morphology

Morphology of prepared PPy-NT was investigated by SEM. Randomly entangled nanotubes with circular profile of diameter ≈ 85 –120 nm were observed (Fig. 9). To investigate the effect of ageing on change of morphology, the extremal conditions were selected, i.e. prolonged ageing for ca. 978 h at 120 °C. Nevertheless, they did not cause any remarkable damage (such as cracks) of nanotubular morphology.

3.8. Wide-angle X-ray scattering

We observed several crystalline reflections in WAXS spectra of PPy-NT (Fig. 10) along with two broad amorphous halos characteristic for PPy-G [53–55]. It is known that (using templating) it is possible to obtain organized structure [56]. On the other hand, the nanostructured PPy was found to be completely amorphous unless containing residual MO-Fe complexes [57]. Molecules of MO themselves are known to form the triclinic structure [58]. Observed peaks can be divided into two groups related to MO in a salt form and acidic form, respectively. Presence of these two forms is in agreement with spectroscopic results. While the former form of MO comes into reaction, the latter must be formed during polymerization. It should be noted that the total crystallinity of samples varies significantly with various batches, while the conductivity remains practically the same. While the crystalline structure itself is not responsible for enhanced conductivity and better conductivity stability in case of PPy-NT, we again observe traces of residual MO remaining in samples that can be responsible for such enhancement.

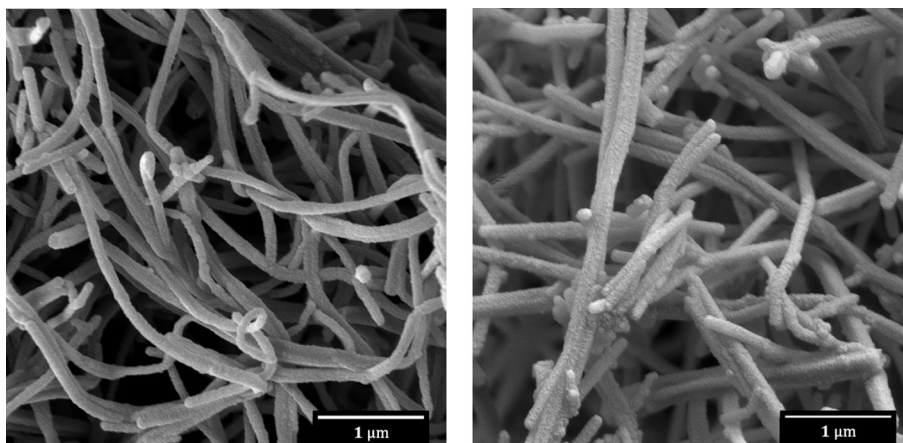


Fig. 9. Morphology of as-prepared polypyrrole (left) and polypyrrole aged at 120 °C for ca. 978 h (right) as probed by SEM.

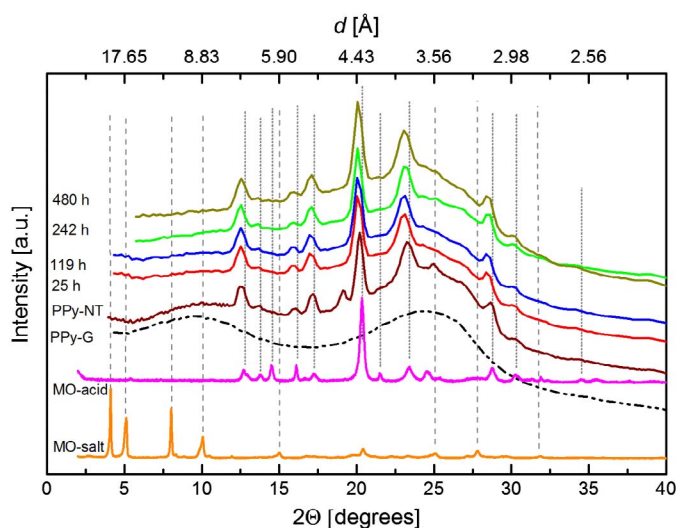


Fig. 10. Effect of ageing at 120 °C on crystalline structure of PPy-NT. WAXS spectra of PPy-G and MO in salt and acid forms are included for comparison.

3.9. Composition-conductivity relationship and increased stability

From the above mentioned results of chemical analyses we assume two phenomena having the major impact on conductivity, (a) chlorine decrease (partial deprotonation) and (b) increase of oxygen (due to backbone oxidation via formation of carbonyl groups). In order to have a quantitative estimate of their extent, we can express the content of both chlorine and oxygen as their ratio to nitrogen originating only from PPy (Fig. 11), i.e. after subtraction of MO contribution (three nitrogen atoms per one atom of sulfur). For simplicity, in the following reasoning we consider the ratio Cl/N as a protonation (doping) level. Even though we could not exclude molecules of MO from being co-dopants [59], they would only cause a shift of the doping level to higher values without the change of general trend, since the content of residual MO was found to be constant (Fig. 8). Interestingly, conductivity of PPy-NT decreases within the period of 0–980 h continuously (Fig. 3), while Cl/N ratio seems to saturate at 0.067. We fitted the data using simple exponential relaxation ($n = 1$ in the expression for stretched exponential function) with relaxation time 266 h. This value is two orders of magnitude higher than relaxation time for conductivity change. Beside decrease of protonation level, oxygen content increases, which was interpreted as an increase of occurrence of carbonyl groups. The observed decrease of conductivity has therefore (at least) two reasons: (a) decreasing concentration of charge carriers in backbone (polarons and bipolarons) connected with decrease of Cl/N ratio; (b) increasing concentration of the sites with destroyed conjugation in backbone influenced by occurrence of carbonyl groups. Indeed, increase of C=O groups during ageing of PPy was well correlated with conductivity decay [2]. Finally, decrease of content of water in PPy-NT is likely to occur but probably only at initial stages of ageing at elevated temperature. Moreover, the effect of water on conductivity of PPy-NT was found rather unimportant [60]. While all induced changes in structure and conductivity during accelerated ageing are monotonous, one can be tempted to assume a rather simple conductivity-structure relationship.

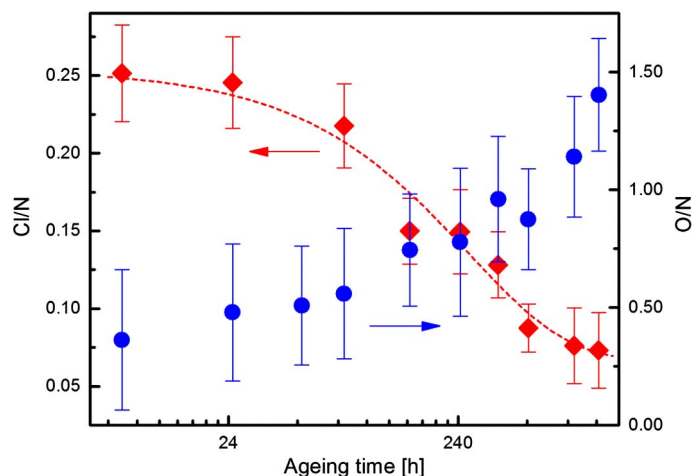


Fig. 11. Effect of ageing at 120 °C on the protonation level expressed as chlorine to nitrogen ratio (diamonds) and increase of oxygen to nitrogen ratio (circles) in sample. Fit of exponential decay of Cl/N (dash).

However, this approach fails for two reasons (i) it is inconsistent for naturally aged samples, where, despite the lack of systematic study, Cl/N and O/N for these samples were found to be in range 0.10–0.25 and 0.29–1.33, respectively, *i.e.* covering almost whole range of vertical scales in Fig. 11 for accelerated ageing but exhibiting only modest conductivity decay; and (ii) the kinetics is different for composition and conductivity changes. Therefore, one should be very careful when making direct link between total composition and conductivity variations. More relevant information on this issue could be obtained from both detailed kinetics and detailed charge transport mechanism studies which will follow. From our preliminary results on charge transport we deduced that internal degradation within conducting domains at some point leads to its dramatic change. Such changes could be barely attributed only to the overall changes in composition.

The relationship between morphology (granular/nanotubular), content (and form) of residual MO on one side and material conductivity, and its stability on the other side seems to be very complex. For instance, it was found that PPy-NT, when synthesized with FeCl₃, contains a highly doped and highly ordered phase and conductivity is thus enhanced, but this improvement is dependent on used oxidant [21]. Apart from morphology difference, PPy-NT always contains residual MO. The content of MO generally influences a lot of properties (conductivity, morphology, specific surface). These are studied elsewhere but – as an important note – we mention here that part of MO can be in the form of counter anions incorporated to PPy and part of electroneutral MO molecules (dependent on concentration) remained stacked together by reacting with the above mentioned counter anions [41]. Such conglomerates could be more stable than just single molecules of dopants. Further, we can assume that enhanced stability of PPy-NT is due to the presence of the sulfonic group, SO₃[−], known for its assurance (mostly bonded to an aromatic ring) of better stability in conducting polymers [4,13,35,61]. It can be viewed in a similar manner as also for some surfactants, *e.g.* dodecylbenzene sulfonic acid [5]. Moreover, enhanced stability of PPy-NT against alkaline media (*i.e.* against deprotonation) was also attributed to presence of MO [22]. Finally, MO itself can be regarded as an organic semiconductor albeit with very low conductivity $\approx 10^{-9}$ S cm^{−1}, but showing good thermal stability upon heating [58]. Nevertheless, MO itself does not ensure that the well-ordered and well-conducting PPy domains are completely protected from thermal degradation (as shown in charge transport evaluation).

4. Summary

We studied both natural and accelerated ageing of highly conducting polypyrrole nanotubes, which turned out to be more stable than their common granular counterparts. Natural ageing for about 3 year timespan (1076 days) lead to relative decrease of PPy conductivity to about 0.2 of its initial value (σ_0). Accelerated ageing at 120 °C caused dramatic decrease of conductivity to be by 7 orders of magnitude after about 1000 h (41 days). Comparing conductivity change and relaxation time for nanotubular and globular forms of PPy, we found nanotubes to be an order of magnitude more stable material, and thus promising for applications.

For selected samples we evaluated changes in charge transport mechanism. We observed gradual degradation of material related to disruptions at microstructural level and (at some point) to change in type of charge transport mechanism; a well-ordered material close to metal-insulator transition shifted to a strongly disordered material. From a macroscopic point of view, conductivity loss was a spatially homogeneous process, at least at beginning stages, as revealed by electrical tomography.

Alongside with the significant changes in conductivity during accelerated ageing, structural properties were investigated. Two of them, supramolecular and crystalline (given by MO) structure were left unaffected by elevated temperatures. On the other hand, chemical composition was changed since partial deprotonation (loss of dopant) and oxidation (formation of carbonyl groups) were observed. A higher stability of electrical conductivity of nanotubular polypyrrole comparing to globular one was attributed to residual presence of MO containing stabilizing SO₃[−] group. During ageing, MO was found to migrate to the material surface while its amount was almost constant. We found monotonic increase of stability about 4 orders of magnitude with increasing MO content used during PPy-NT synthesis.

We found that composition as an integral quantity is not the key factor in conductivity degradation. For instance, before the apparent changes in composition during accelerated ageing are even noticeable, the substantial degradation of electrical properties takes place, regarding to the two orders of magnitude difference in relaxation time for composition and conductivity, respectively. Further detailed studies of both the degradation kinetics and charge transport mechanism could be beneficial for deeper understanding of underlying ageing processes. We believe that further effort in material synthesis/modification should focus on dopant stabilization, anti-oxidative protection and inhibition of growth of internal disorder.

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