Chem. Pap. (2017) 71:339–346
DOI 10.1007/s11696-016-0076-5

ORIGINAL PAPER

Electroless deposition of silver on poly(3, 4-ethylenedioxythiophene): role of the organic ions used in the course of electrochemical synthesis

Vasilena Karabozhikova[1] · **Vessela Tsakova**[1]

Received: 1 April 2016 / Accepted: 9 June 2016 / Published online: 7 December 2016

Abstract The electroless deposition of silver is studied on poly(3, 4-ethylenedioxythiophene) (PEDOT) layers synthesized in the presence of excess of perchlorate ions with and without the addition of two organic dopants: dodecylsulfate (DDS) or polystyrenesulfonate (PSS). Silver deposition is carried out at the expense of oxidation of the pre-reduced PEDOT layers using either Ag^+ cation or $[AgEDTA]^{3-}$ complex anion solutions. The amount of deposited silver is monitored by voltammetric stripping. The type of the metal deposit is imaged by SEM. It is found that there are marked differences between the three types of PEDOT with respect to the amount of deposited silver and size distribution of the metallic species. In both silver plating solutions, the largest amount of silver is deposited on PEDOT/DDS, followed by PEDOT/PSS and PEDOT/ClO_4^-. These results are discussed in the context of possible structural difference of the three types of PEDOT layers. The comparison between the silver deposits obtained in the two silver plating solutions shows finer dispersion and larger amount of the metallic phase obtained in the presence of the silver complex anions. This solution presents a better opportunity to obtain homogeneous distribution of silver crystalline species on the PEDOT surface.

Keywords PEDOT · Silver · PSS · SDS · Perchlorate · Chemical deposition

Introduction

Metal-modified conducting polymers (CPs) are still in the focus of numerous investigations due to the wide scope of possible application ranging from solar cells and batteries to electrocatalytic and sensing devices. Metal deposition on CPs may be accomplished in a number of different ways including chemical and electrochemical approaches (Tsakova 2010), such as polymerization in the presence of pre-synthesized metal nanoparticles, one-pot chemical synthesis of metal-CP composites, metal electrodeposition or chemical electroless metal deposition in the presence of dissolved reductant species on pre-deposited CP layers, and finally metal electroless deposition at the expanse of CP oxidation. The latter approach is most closely related to the nature and structural, physical and chemical properties of the CP material.

Conducting polymers may take different interconvertible oxidation states, and therefore provide the possibility for chemical (electroless) deposition of metals. Metal ion reduction occurs at the expense of the transition from lower to higher oxidation state of the CP material. The CP initial oxidation state may be controlled either through acid–base or doping/dedoping processes. Investigations have been carried out in both homogeneous (chemically produced suspensions) and heterogeneous (electrodeposited or solution-cast CP layers and membranes) systems. The supported CP layers are frequently used in an electrochemical environment and their oxidation state is controlled by applying corresponding electrode potentials.

The electroless deposition which combines spontaneous oxidation of the initially reduced CPs and oxidation of metal ions is a complex process involving diffusion of metal ions inside the porous polymer structure and also ingress/expulsion of doping ions (different than the metal

✉ Vessela Tsakova
tsakova@ipc.bas.bg

[1] Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

ones) and solvent molecules to compensate the charges arising at the oxidized polymer chains. Therefore, the structural properties, the type of intrinsic ionic and solvent transport of the CPs are expected to have an influence on the final characteristics of the metal deposit. Most of the studies in this field concern the deposition of noble metals such as Au (Smith et al. 2003; Wang et al. 2007; Scheffer et al. 2008; Sheffer and Mandler 2009; Kondratiev et al. 2011; Fedorczyk et al. 2014), Ag (Ivanov and Tsakova 2005; Zhang et al. 1995; Song and Shiu 2001; Stejskal et al. 2009; Stejskal 2013; Wang et al. 2007; Ocypa et al. 2006; Mack et al. 2011; Tolstopyatova et al. 2014), and Pd (Abrantes and Correia 1995; Mourato et al. 2006; Huang et al. 1998; Ilieva et al. 2006; Lim et al. 2001; Mourato et al. 2004; Eliseeva et al. 2009) with equilibrium potentials that are positive enough with respect to the potentials of the oxidation transitions in most CPs, e.g., polyaniline (PANI), polypyrrole (PPY) or PEDOT.

The correlation between CP properties and the characteristics of the metal deposit obtained by electroless process at the expense of the CP oxidation is seldom addressed, see e.g., (Wang et al. 2007). It is well known that the type of doping ions used in the course of CP synthesis has a marked influence on the structural and transport properties of CPs. Therefore, the aim of this work is to study the electroless deposition of silver on PEDOT layers produced in the presence of perchlorate ions with the addition of two organic dopants: dodecyl sulfate (DDS) or polystyrene sulfonate (PSS). PEDOT/ClO_4^- (without organic dopants) are also studied as reference layers. Bearing in mind the importance of the ionic transport in the course of the electroless deposition, two types of silver ions (silver cations and silver-ethylenediamine-tetraacetate (EDTA) complex anions) are used for the metal plating.

The Ag/PEDOT system is chosen due to the recent interest for this material in solar cells (Iwan et al. 2015; Kim et al. 2016), electrochromic devices (Namboothiry et al. 2007), sensing applications (Balamurugan and Chen 2009; Park et al. 2012), SERS substrates (Dogan et al. 2012), etc. Silver is known also as an antimicrobial agent and becomes easily combined with polymeric materials (Dallas et al. 2011; Kucekova et al. 2013).

Experimental

The electrochemical experiments were carried out in three-electrode set-up by means of PGSTAT 12 Autolab potentiostat/galvanostat (Eco Chemie, Utrecht, the Netherlands) equipped with GPES software (Eco Chemie, Utrecht, the Netherlands). A glassy carbon disk with surface area $S = 0.08\ cm^2$ and a platinum plate were used as working and counter electrodes, respectively. The reference electrode was saturated mercury/mercury sulfate (Hg/Hg_2SO_4/0.5 M K_2SO_4) electrode (MSE). In this paper, all potentials are referred to MSE ($E_{MSE} = 0.66$ V vs standard hydrogen electrode). Argon gas was used to remove dissolved oxygen from the electrolyte solutions.

Electrochemical polymerization of EDOT was performed at constant potential $E_a = 0.38$ V in aqueous solutions of 10 mM EDOT and 0.5 M $LiClO_4$. Three types of PEDOT layers were obtained in the absence or the presence of 34 mM organic anionic dopants-sodium PSS or sodium DDS. The PEDOT coatings obtained in the presence of the two organic dopants will be further denoted by PEDOT/PSS and PEDOT/DDS, respectively, whereas the coatings obtained in absence of organic dopant will be denoted by PEDOT/ClO_4^-. In all three polymerisation solutions, PEDOT layers with polymerization charges of 4 mC were synthesized and used further for electroless deposition of silver. The voltammetric behavior of the polymer-coated electrodes was measured in 0.4 M $HClO_4$ solution.

The electroless deposition of silver was carried out at pre-reduced PEDOT layers. The electrochemical reduction was accomplished at constant potential at −0.62 V in supporting electrolyte (0.4 M $HClO_4$) for 15 min. At this reduction potential PEDOT remains in the high conducting state. The reduced PEDOT-coated electrodes were transferred in the silver plating solution consisting of either 10 mM $AgNO_3$ and 0.4 M $HClO_4$ or 10 mM $AgNO_3$, 0.02 M $Na_2C_{10}H_{14}O_8N_2$ (NaEDTA) and 0.5 M KNO_3. In the latter solution, the silver species form $[AgEDTA]^{3-}$ anionic complexes. The equilibrium potentials of silver in these solutions are $E^0 = -0.002$ V vs MSE for Ag^+ and $E^0 = -0.040$ V vs MSE for $[AgEDTA]^{3-}$. The time for silver electroless precipitation was set at 50 s. After each silver deposition experiment silver was dissolved in 0.4 M $HClO_4$ by applying several voltammetric scans with scan rate 5 mV/s at potentials more positive than the equilibrium potential of Ag.

The surface morphology of the various Ag-precipitated PEDOT layers was examined by scanning electron microscope Jeol 6390 equipped with Inca Oxford EDX analyzer.

Results and discussion

Potentiostatic current transients measured in the course of polymerization (Fig. 1) show that addition of small amount of organic dopants (PSS or DDS) in the aqueous perchlorate solution has a strong influence on the polymerization kinetics with both organic anions slowing down the polymerization process. The effect is particularly strong for the dodecyl sulfate ions which are expected to impart

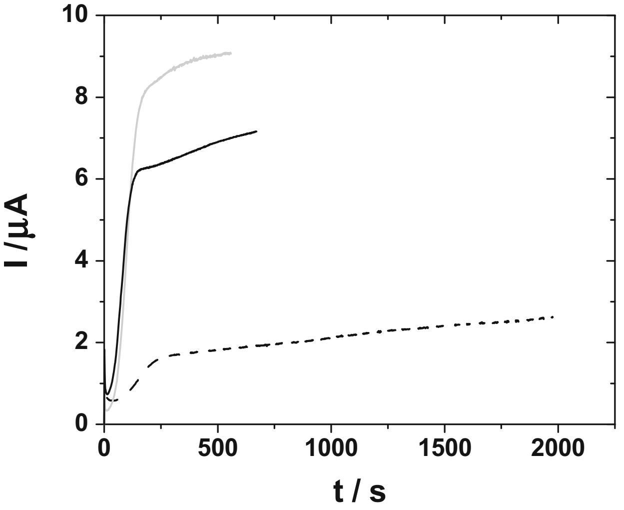


Fig. 1 Potentiostatic current transients measured in the course of polymerization of EDOT in ClO_4^-- (*full gray line*), PSS- (*full black line*) and DDS-containing (*dashed line*) solutions

hydrophobic properties to the growing PEDOT surface. PSS polyanions are expected to play the role of a template for the growing PEDOT chains, but their accommodation in the growing polymer structure may cause delay in the polymerization process. It is not clear to what extent the organic dopants become incorporated in the PEDOT structure in the presence of the excess of perchlorate ions in the solution. Nevertheless, based on the strong influence on the polymerization kinetics it should be expected that they have a marked influence on the polymer layer structure both at the micro and molecular level.

At the microscopic level a difference in the surface morphology of the layers was already established (Tsakova et al. 2015) with PEDOT/DDS having more compact morphology in comparison to PEDOT/PSS layers. The latter are characterized with larger surface roughness. The fine polymer structure at the molecular level is not so easy to be assessed. An indirect and somewhat speculative way would be to consider the difference in the steady state (plateau) currents of the polymerization curves. This difference indicates that diffusion should be excluded as factor controlling the polymerization reaction. In such a case, the steady state current should depend on the number of growth sites (i.e., the number of growing polymeric chains) and the charge transfer kinetics. Assuming that the electron transfer for monomer oxidation does not depend on the environment (i.e., the presence of a small amount of organic anions in a large excess of inorganic anions) the difference in the steady state currents should be attributed to different number of already formed polymeric chains. If this is so, the lower the plateau current, the lower the number of growing chains. To reach the same polymerization charge at lower number of growing chains, longer chains should be formed. If assuming that the plateau of the polymerization curve is proportional to the number of growing polymer chains the smallest number of longest chains should be found in the PEDOT/DDS case while the largest number of chains with correspondingly smallest length should be characteristic for the PEDOT/ClO_4^- case.

Furthermore, the possible immobilization of negatively charged organic ions within PEDOT may also lead to differences in the ionic transport in the course or oxidation/reduction of the three different kinds of polymer coatings. Our former studies of the electrooxidation of ascorbic acid and dopamine (Filjova et al. 2013), and acetaminophen (Tsakova et al. 2015) on these three types of PEDOT layers have already shown marked influence of the doping ions used in the course of polymerization on their electrocatalytic properties. All above mentioned factors may provide conditions for different distribution of the electroless deposited metal particles both in the bulk and at the surface of the different types of PEDOT layers.

The electroless deposition of silver on the three types of PEDOT was followed by monitoring the open circuit potential (OCP) of the working electrode after dipping the pre-reduced polymer-coated electrode in the silver plating solution.

Figure 2 shows OCP transients measured in solutions of Ag^+ and $[AgEDTA]^{3-}$ complex anions. A steep increase in OCP is observed in the case of the Ag^+-containing solution, whereas a slower kinetics is observed for the $[AgEDTA]^{3-}$ case. The three types of PEDOT behave in a similar way in the presence of Ag^+ and have an almost constant steady state final OCP. In the $[AgEDTA]^{3-}$ solution, the PEDOT/DDS and PEDOT/ClO_4^- have a more negative steady state OCP as should be expected for the $Ag/[AgEDTA]^{3-}$ in comparison to the Ag/Ag^+ equilibrium potential. Surprisingly, the steady state OCP of PEDOT/PSS remains one and the same in the silver cations and silver complex anions solution. This means that PEDOT/PSS becomes involved in the establishment of a mixed potential that is no longer the equilibrium potential of the Ag/dissolved Ag ions couple and the involvement of a third type of Ag-containing species should be discussed. It is known that sodium becomes exchanged by silver in cross-linked polystyrene sulfonate cation exchangers (Vaslow and Boyd 1966). More recently complexes of PSS with silver were used to obtain Ag/PSS nanocomposites (Girard et al. 2013). In the case of PPY, another polysulfonic acid (poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) was used as both doping species for PPY and complex formation agent for silver (Ignatova et al. 2003). It was suggested that once bound into a complex within the polymer layer, Ag^+ ions remain incorporated in the PPY/PAMPS structure upon reversible reduction/oxidation. In addition, in the case of PEDOT/PSS even if it is

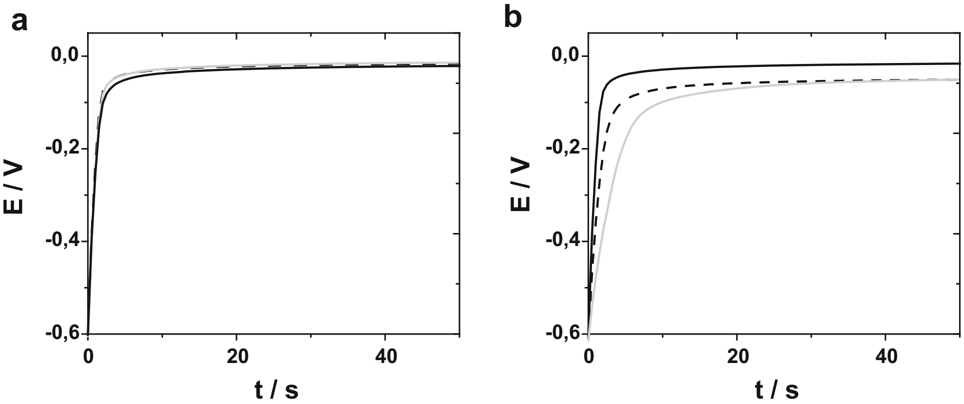


Fig. 2 OCP transients measured in **a** Ag^+ and **b** $[AgEDTA]^{3-}$ solutions at PEDOT/PSS (*black full line*), PEDOT/DDS (*black dashed line*), and PEDOT/ClO_4^- (*gray full line*) layers

only partially doped with PSS such an effect of Ag-complexation may be expected.

The amount of deposited silver was monitored by voltammetric stripping in acidic solution by several scans. Figure 3 shows the first dissolution voltammetric scan for the three types of layers after electroless deposition completed in Ag^+ and $[AgEDTA]^{3-}$ solutions. It is obvious that in both silver plating solutions the largest amount of silver is deposited on PEDOT/DDS, followed by PEDOT/PSS and PEDOT/ClO_4^-. The subsequent voltammetric scans have shown that although the main amount of silver becomes dissolved in the first scan for all studied specimens, residual amounts of silver are traced also in the second, third and even fourth stripping scans (Fig. 4). It is worth noting that a small reduction peak (at about −0.2 V) is found in the back scan of the voltammograms which may indicate to redeposition of silver originating from silver ions that could not diffuse away and became trapped inside the polymer structure in the former part of the potential scan. In all cases, the silver deposit obtained from the $[AgEDTA]^{3-}$ solution (Fig. 4b) becomes more easily dissolved than the one obtained from Ag^+ solution (Fig. 4a). This observation may imply that in the case of the silver complex ions a preferential deposition of the metal deposit close to the outmost polymer solution interface takes place.

SEM images taken at the surface of the six different PEDOT specimens are shown in Fig. 5. These images were taken in secondary electrons imaging (SEI) mode which results in morphological imaging contrast. Parallel imaging was also completed in back scattered electron mode which results in chemical contrast in the imaging. The comparison between both types of imaging (not shown here) revealed that the brightest features found in the SEI images are silver particles. They often decorate protruding morphological features of the polymer structure. In general, the observation showed that in all cases when silver electroless deposition was completed from Ag^+ solution (Fig. 5a, c, e), large silver crystals are found on the surface together with a big amount of smaller silver particles. The visible amount of deposited silver corresponds roughly to the electrochemically determined sequence with PEDOT/DDS showing the largest Ag amount and PEDOT/ClO_4^- the smallest. It could be argued that reduction of the silver cations proceeds easily on a small number of active sites on the PEDOT surface. Once the first silver nuclei appear they grow further by consuming the electrons provided by the

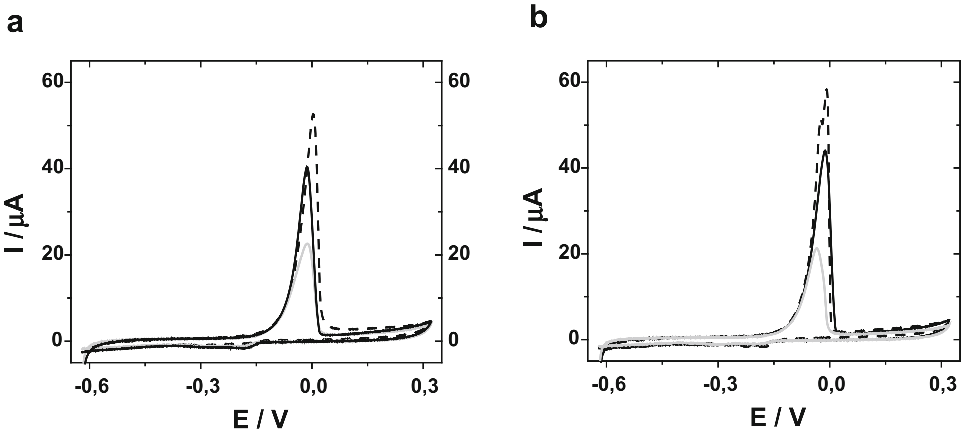


Fig. 3 First voltammetric scan of silver stripping measured after electroless deposition from **a** Ag^+ and **b** $[AgEDTA]^{3-}$ solutions at PEDOT/PSS (*black full line*), PEDOT/DDS (*black dashed line*), and PEDOT/ClO_4^- (*gray full line*) layers

Fig. 4 Silver charge obtained in consecutive stripping scans after electroless deposition from **a** Ag^+ and **b** $[AgEDTA]^{3-}$ solutions at PEDOT/DDS (*filled circle*), PEDOT/PSS (*filled square*), and PEDOT/ClO_4^- (*filled triangle*) layers

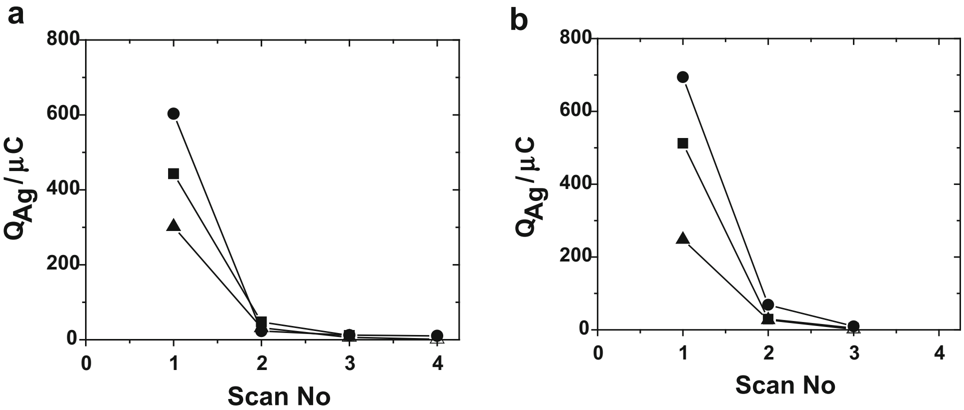
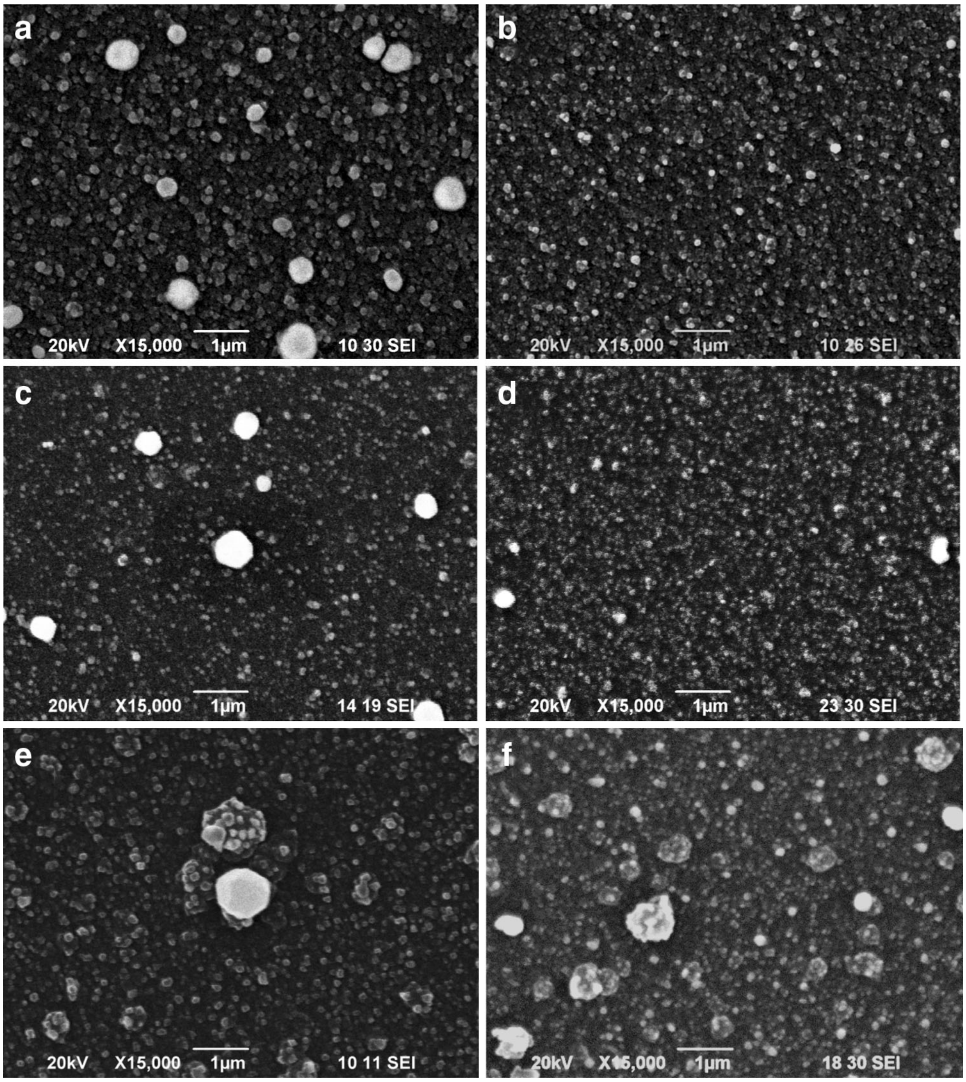


Fig. 5 SEM images of PEDOT/DDS (**a**, **b**), PEDOT/PSS (**c**, **d**) and PEDOT/ClO_4^- (**e**, **f**) layers obtained after electroless silver deposition in Ag^+ (**a**, **c**, **e**) and $[AgEDTA]^{3-}$ (**b**, **d**, **f**) containing solutions



surrounding PEDOT chains that become gradually oxidized. The number of initial active sites is the largest for PEDOT/DDS followed by PEDOT/PSS and PEDOT/ClO_4^-. In fact, this should mean that PEDOT/DDS is highly homogeneous with respect to redox sites and transfer of charge which corresponds with the suggested availability of longer PEDOT chains. On the other extreme is PEDOT/ClO_4^- which seems to be less reactive and to

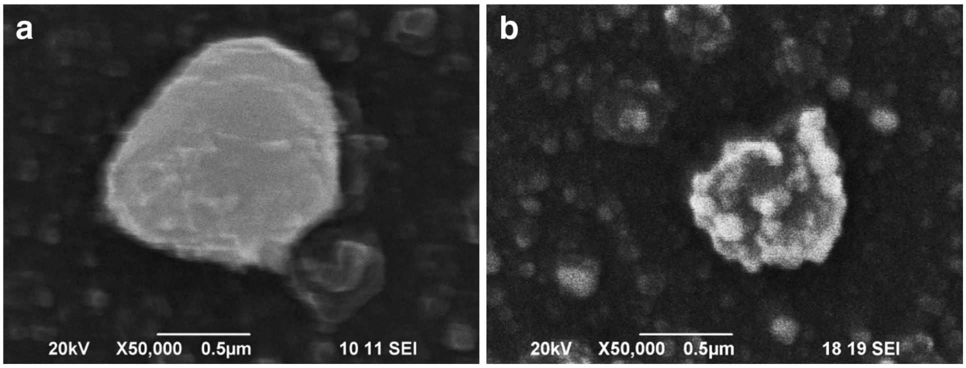


Fig. 6 SEM of individual silver-coated features observed at PEDOT/ClO_4^- layers after electroless deposition in Ag^+ (**a**) and $[AgEDTA]^{3-}$ (**b**) containing solutions

Table 1 Amount of silver deposited at the three types of PEDOT layers

PEDOT layer	$\Sigma Q_{Ag}/\mu C$	
	Ag^+	$[AgEDTA]^{3-}$
PEDOT/DDS	649	772
PEDOT/PSS	501	546
PEDOT/ClO_4^-	342	240

transfer sluggishly electrical charge. Shorter PEDOT chains may be in the origin of this lack of capacity for transferring charge across the layer and between the chains. Therefore, only some protruding well-conducting polymer globules (see Fig. 6) become coated by the metal phase. In addition, the type of metal deposit on this type of PEDOT seems not to be influenced by the source of metal reduction (Fig. 5e, f).

For the remaining two types of PEDOT (/DDS and/PSS), the plating from the $[AgEDTA]^{3-}$ complex anions results in a more homogeneous distribution of small mostly equally sized silver particles on the polymer surface (Fig. 5b, d) again with largest Ag amount for PEDOT/DDS and smallest for PEDOT/PSS. It is known that the use of metal anion complexes for metal plating results in smaller crystal grains of the metal deposit due to inhibited growth of the already formed silver clusters. Such an effect should be operative also for the electroless deposition on PEDOT providing a larger number of silver crystals. The bigger amount of silver deposited from the $[AgEDTA]^{3-}$ in comparison to the Ag^+ solution (Table 1) shows that the deposition of larger number of smaller evenly distributed crystals from the complex anion solution allows for a better consumption of the intrinsic PEDOT oxidation charge before the establishment of the steady state OCP. A possible explanation for this effect is that the large micrometer-sized crystals deposited in the Ag^+ solution might be finally in contact with the underlying substrate and consume electrons directly from the electrode thus involving completely different pathways for the polymer layer oxidation. Furthermore, it could be also argued that the diffusion within the polymer structure of the larger $[AgEDTA]^{3-}$ (in comparison to Ag^+) ions is impeded and their reduction occurs preferentially at or close to the polymer solution interface.

Conclusions

The investigations on the electroless deposition of silver on PEDOT layers obtained in the presence of excess of perchlorate ions and the addition of two different organic anions (DDS or PSS) show a marked effect of the doping ions on the electroless deposition process. The electroless deposition of silver occurs in a potential interval corresponding entirely to the high conducting state of PEDOT. In the course of oxidation of the polymer structure within this potential interval the amount of oxidized monomeric units, and therefore the amount of positive charges along the polymeric chains increases and involves transport of charge compensating ions. The metal ions reduction proceeds from the very beginning at highly conducting polymer chains which are expected to provide the opportunity for an easy transfer of electrons across the polymer layer. Nevertheless, there are marked differences between the three types of PEDOT used in this investigation mainly with respect to the amount of deposited silver (Figs. 3, 4). These differences are commented in terms of the different polymer morphology and the possibility for a change in the mean PEDOT chain length depending on the organic additives used in the polymerization solution. The latter hypothesis needs to be supported by further investigations on the conjugations length of the PEDOT chains obtained in the presence of the different anions. Largest amounts of silver with the most homogeneous distribution of the metal phase over the polymer surface are observed for the PEDOT/DDS case where the polymerization rate was found to be the slowest (Fig. 1). The latter could be due to the growth of a lower number of polymer chains that for a given polymerization charge will finally end with larger mean length. A better conjugation and charge distribution and transfer could be expected in this case. On the opposite, PEDOT/ClO_4^- layers show the fastest polymerization (Fig. 1) with expected large number of growing chains and small mean length. This may be in the origin of the poor conversion of charge between reducing metal ions and oxidizing polymer chains. PEDOT/PSS layers take an intermediate position which is, however, closer to the behavior of PEDOT/DDS (Fig. 4).

As found before for the case of PANI (Ivanov and Tsakova 2005), the use of silver anion complexes instead of silver cations for the metal plating results basically in a finer metal deposit (larger number of crystals with smaller size) (Fig. 5), which may be ascribed to reduced growth rate of the initially formed silver crystalline species. Nevertheless, the structural peculiarities of the different PEDOT layers induced by the presence of the organic doping ions in the polymerization solution continue to be the major factor controlling the amount of deposited metal (Table 1).

The present investigations show a first insight into the role of doping ions-induced characteristics of the conducting polymer layers for the metal electroless process driven at the expense of polymer chains oxidation. Further experiments directed to PEDOT layers obtained in the presence of only one type of doping ions, either PSS or DDS (in the absence of perchlorate or other inorganic ions) should be completed to reveal the role of massively immobilized anionic species on the electroless deposition process.

Acknowledgements The authors acknowledge the financial support of Bulgarian Academy of Sciences under Program for career development of young scientists (Project DFNP-18/20.04.2016). The SEM pictures are obtained with the kind assistance of Dr. S. Piroeva (Laboratory for Electron Microscopy at Institute of Physical Chemistry, Sofia).

References

Abrantes LM, Correia JP (1995) Polymer Films Containing Metal Particles-Noble Metals in Polyaniline. Mater Sci Forum 191:235–340

Balamurugan A, Chen SM (2009) Silver nanograins incorporated PEDOT modified electrode for electrocatalytic sensing of hydrogen peroxide. Electroanalysis 21:1419–1423

Dallas P, Sharma VK, Zboril R (2011) Silver polymeric nanocomposites as advanced antimicrobial agents: classification, synthetic paths, applications, and perspectives. Adv Colloid Interface Sci 166:119–135

Dogan Ü, Kaya M, Cihaner A, Volkan M (2012) Ag nanostructures on a poly(3,4-ethylenedioxythiophene) film prepared with electrochemical route: A controllable roughened SERS substrate with high repeatability and stability. Electrochim Acta 85:220–227

Eliseeva SN, Malev VV, Kondratiev VV (2009) Electrochemical properties of composite films based on poly-3,4-ethylenedioxythiophene with inclusions of metallic palladium. Russ J Electrochem 45:1045–1051

Fedorczyk A, Ratajczak J, Czerwinski A, Skompska M (2014) Selective deposition of gold nanoparticles on the top or inside a thin conducting polymer film, by combination of electroless deposition and electrochemical reduction. Electrochim Acta 122:267–274

Filjova DG, Ilieva GP, Tsakova VT (2013) Electropolymerization of poly(3, 4-ethylenedioxythiophene) layers in the presence of different dopants and their effect on the polymer electrocatalytic properties. Oxidation of ascorbic acid and dopamine. Bulg Chem Commun 45:196–201

Girard J, Brunetto PS, Braissant O, Rajacic Z, Khanna N, Landmann R, Daniels AU, Fromm KM (2013) Development of a polystyrene sulfonate/silver nanocomposite with self-healing properties for biomaterial applications. C R Chim 16:550–556

Huang SW, Neoh KG, Shih CW, Lim DS, Kang ET, Han HS, Tan KL (1998) Synthesis, characterization and catalytic properties of palladium-containing electroactive polymers. Synth Metals 96:117–122

Ignatova M, Labaye D, Lenoir S, Strivay D, Jerome R, Jerome C (2003) Immobilization of silver in polypyrrole/polyanion composite coatings: preparation, characterization, and antibacterial activity. Langmuir 19:8971–8979

Ilieva M, Tsakova V, Erfurth W (2006) Electrochemical formation of bi-metal (copper–palladium) electrocatalyst supported on poly-3,4-ethylenedioxythiophene. Electrochim Acta 52:816–824

Ivanov S, Tsakova V (2005) Electroless versus electrodriven deposition of silver crystals in polyaniline: Role of silver anion complexes. Electrochim Acta 50:5616–5623

Iwan A, Boharewicz B, Tazbir I, Sikora A, Zboromirska-Wnukiewicz B (2015) Silver nanoparticles in PEDOT: PSS layer for polymer solar cell application. Int J Photoenergy 764938:1–9

Kim H, Veerappan G, Wang DH, Park JH (2016) Large area platinum and fluorine-doped tin oxide-free dye sensitized solar cells with silver-nanoplate embedded poly(3,4-ethylenedioxythiophene) counter electrode. Electrochim Acta 187:218–223

Kondratiev VV, Pogulaichenko NA, Tolstopjatova EG, Malev VV (2011) Hydrogen peroxide electroreduction on composite PEDOT films with included gold nanoparticles. J Solid State Electrochem 15:2383–2393

Kucekova Z, Kasparkova V, Humpolicek P, Sevcikova P, Stejskal J (2013) Antibacterial properties of polyaniline–silver films. Chem Pap 67:1103–1108

Lim VWL, Kang ET, Neoh KG (2001) Electroless plating of palladium and copper on polypyrrole films. Synth Metals 123:107–115

Mack NH, Bailey JA, Doorn SK, Chen CA, Gau HM, Xu P, Williams DJ, Akhadov EA, Wang HL (2011) Mechanistic study of silver nanoparticle formation on conducting polymer surfaces. Langmuir 27:4979–4985

Mourato A, Viana AS, Correia JP, Siegenthaler H, Abrantes LM (2004) Polyaniline films containing electrolessly precipitated palladium. Electrochim Acta 49:2249–2257

Mourato A, Wong SM, Siegenthaler H, Abrantes LM (2006) Polyaniline films containing palladium microparticles for electrocatalytic purposes. J Solid State Electrochem 10:140–147

Namboothiry MAG, Zimmerman T, Coldren FM, Liu J, Kim K, Carrol DL (2007) Electrochromic properties of conducting polymer metal nanoparticles composites. Synth Metals 157:580–584

Ocypa M, Ptasinska M, Michalska A, Maksymiuk K, Hall EAH (2006) Electroless silver deposition on polypyrrole and poly(3,4-ethylenedioxythiophene): The reaction/diffusion balance. J Electroanal Chem 596:157–168

Park E, Kwon OS, Park SJ, Lee JS, You S, Jang J (2012) One-pot synthesis of silver nanoparticles decorated poly(3,4-

ethylenedioxythiophene) nanotubes for chemical sensor application. J Mater Chem 22:1521–1526

Scheffer M, Martina V, Seeber R, Mandler D (2008) Deposition of gold nanoparticles on thin polyaniline films. Isr J Chem 48:349–357

Sheffer M, Mandler D (2009) Control of locally deposited gold nanoparticle on polyaniline films. Electrochim Acta 54:2951–2956

Smith JA, Josowicz M, Janata J (2003) Polyaniline-gold nanocomposite system. J Electrochem Soc 150:384–388

Song FY, Shiu KK (2001) Preconcentration and electroanalysis of silver species at polypyrrole film modified glassy carbon electrodes. J Electroanal Chem 498:161–170

Stejskal J (2013) Conducting polymer-silver composites. Chem Pap 67:814–848

Stejskal J, Trchová M, Brožová L, Prokeš J (2009) Reduction of silver nitrate by polyaniline nanotubes to produce silver–polyaniline composites. Chem Pap 63:77–83

Tolstopyatova EG, Pogulyaichenko NA, Kondratiev VV (2014) Synthesis and electrochemical properties of composite films based on poly-3,4-ethylenedioxythiophene with inclusions of silver particles. Russ J Electrochem 50:510–516

Tsakova V (2010) Metallic-Based Nanocomposites of Conductive Polymers. In: Eftekhari A (ed) Nanostructured conductive polymers. Wiley, New York, pp 289–340

Tsakova V, Ilieva G, Filjova D (2015) Role of the anionic dopant of poly(3,4-ethylenedioxythiophene) for the electroanalytical performance: electrooxidation of acetaminophen. Electrochim Acta 179:343–349

Vaslow F, Boyd GE (1966) Thermodynamic properties in the exchange of silver with sodium ions in cross-linked polystyrene sulfonate cation exchangers. J Phys Chem 70:2295–2299

Wang HL, Li W, Jia QX, Akhadov E (2007) Tailoring conducting polymer chemistry for the chemical deposition of metal particles and clusters. Chem Mater 19:520–525

Zhang AQ, Cui CQ, Lee JY, Loh FC (1995) Interactions between polyaniline and silver cations. J Electrochem Soc 142:1097–1104