

Copper-modified poly(3,4-ethylenedioxythiophene) layers for selective determination of dopamine in the presence of ascorbic acid: II Role of the characteristics of the metal deposit

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Abstract The present study focuses on the specific role of the number, size, and shape of copper crystals electrodeposited on poly(3,4-ethylenedioxythiophene) (PEDOT) layers for the electroanalytic determination of dopamine (DA). It is shown that the type of the metal deposit is significantly influenced by the thickness of the polymer layer and the type of copper ions plating solutions, e.g., copper sulfate or copper oxalate. By combining electrochemical measurements and scanning electron microscopic investigations, it is found that the loss of electroactivity for DA oxidation, established for Cu deposited on thick PEDOT layers (from copper sulfate solution), relates to the instability of small needle-like Cu crystals decorating the PEDOT surface in this case. Large (several micrometer-sized) copper crystals (as deposited on thin PEDOT layers from copper sulfate solution) are found to suffer surface destruction along the crystalline edges when exposed to electrochemical treatment in the presence of DA. Finally, smaller ($\sim 0.5 \mu\text{m}$) bulky crystals with a large surface coverage (up to 30%), as deposited from copper oxalate solution, are found to provide a stable and highly sensitive Cu–PEDOT composite material operating in the nanomolar DA concentration range. Differential pulse voltammetry measurements carried out in the 6 nM to 2 μM DA concentration range, in the presence of large excess (1 to 5 mM) of ascorbic acid, show two regions of linear response with different sensitivities, 9 nA nM⁻¹ and 0.313 $\mu\text{A} \mu\text{M}^{-1}$, respectively.

Keywords PEDOT · Conducting polymers · Copper · Dopamine · Ascorbic acid

Introduction

In the last years, the quantitative determination of dopamine (DA) by electrochemical methods has attracted considerable interest. Various materials, e.g., conducting polymers (CP) [1–15], overoxidized or de-activated CP [16–33], and metal nanoparticle-modified electrodes [34–41] have been investigated. Attempts have been made to combine the electrocatalytic properties of CP and metal particles [42–48] in order to achieve better sensitivity and selectivity for the DA oxidation reaction. In general, most of the studied electrode materials show sensitivity in the micromolar concentration range of DA, the main difference being the width of the concentration region for linear [amperometric, voltammetric, or differential pulse voltammetric (DPV)] response and the selectivity with respect to other organic compounds, e.g., ascorbic and uric acids. Typically concentration intervals of linear response for DA detection are found in the micromolar concentration range [14, 21, 25, 48]. In few cases, electrochemical detection in nanomolar concentration ranges has been also communicated [42, 43]. Although the selectivity, especially with respect to ascorbic acid (AA), is widely investigated, in most cases, there is scarce information on the electrochemical stability of the electrodes in the course of multiple measurements and thus on their feasibility for practical applications.

In the first part of this investigation [48], we have studied poly(3,4-ethylenedioxythiophene) (PEDOT)- and copper crystals-modified PEDOT-coated electrodes for the electrooxidation of AA and DA. The combination of Cu particles and PEDOT was chosen because both organic and inorganic component in this composite material show electrocatalytic activity for DA oxidation. The formation

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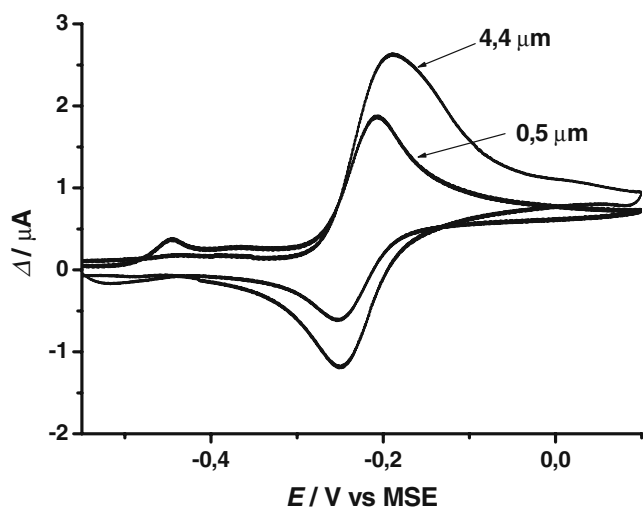
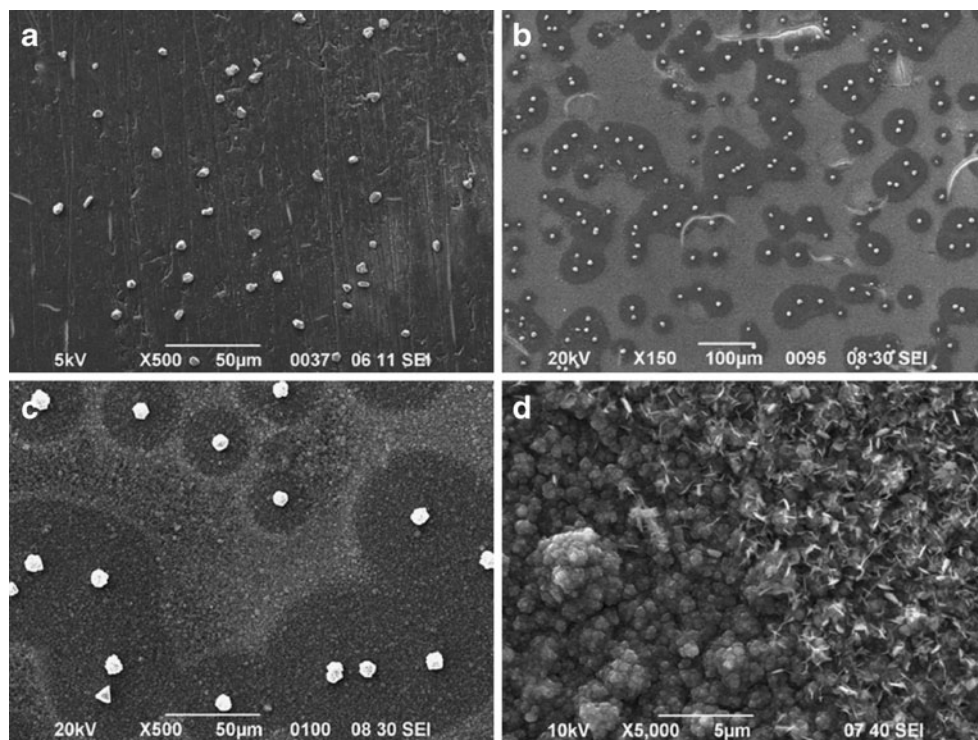


Fig. 1 Cyclic voltammetric curves (after background correction) measured in the presence of 2 mM DA in PBS at copper-modified PEDOT-coated electrodes with different thickness of the PEDOT layer 0.5 and 4.4 μm . $m_{\text{Cu}}=70 \mu\text{g cm}^{-2}$ (1500 s). $v=20 \text{ mV s}^{-1}$

of a Cu(II)-*o*-quinolate complex was suggested as promoter of the DA electrooxidation reaction [49]. By comparing the performance of PEDOT alone and Cu-modified PEDOT, it was shown that the Cu crystals promote the DA and suppress the AA oxidation reaction [48]. Thin PEDOT layers ($d=0.5 \mu\text{m}$) with electrodeposited copper crystals provided good stability and a linear DPV response in a wide concentration range (6 μM to about 200 μM) of DA

Fig. 2 SEM of Cu-PEDOT specimens obtained after Cu-deposition from CuSO_4 solution on a thin (a) and thick (b–d) PEDOT layer



in the presence of a large excess (1 mM concentration) of AA. These results were obtained with a rather low surface coverage of copper (about 0.3%) and relatively large, several micrometer-sized crystals. In the present investigation, we address the possibility to improve further the performance of the Cu-PEDOT material for DA oxidation by affecting the surface coverage, size, and crystallographic features of the electrodeposited copper crystals. The aim is to produce an electrochemically stable composite material that could provide a linear DPV response in a larger DA concentration range covering the span from several nanomolar to several micromolar concentrations of DA.

Experimental

All electrochemical measurements were performed in a three-electrode setup consisting of a platinum single crystal bead electrode sealed in glass with surface area $S=2.3 \times 10^{-3} \text{ cm}^2$, a platinum plate counter electrode, and a mercury/mercury sulfate reference electrode. Platinum plates ($S=2 \text{ cm}^2$) were used for preparing specimens for SEM observation. All potentials in the text are referred to the saturated mercury sulfate electrode (MSE; $E_{\text{MSE}}=0.66 \text{ V}$ vs standard hydrogen electrode). All solutions were de-aerated with argon before the onset of the electrochemical measurements.

The electrochemical measurements including cyclic voltammetry, DPV, chronoamperometry, and chronovoltammetry were performed by means of a computer-driven

potentiostat/galvanostat (Autolab PGSTAT 12, Ecochemie, The Netherlands).

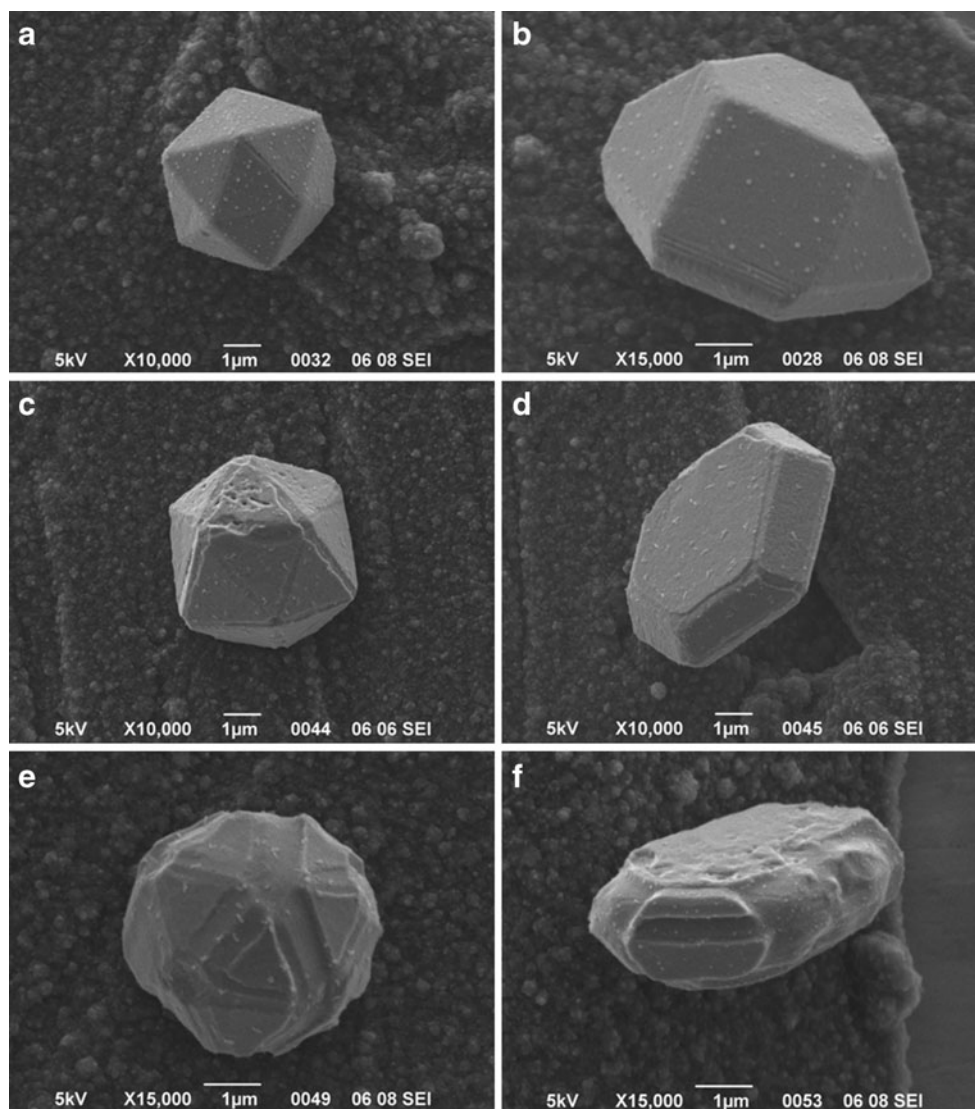
Each experimental series consisted of several steps performed consecutively in five electrochemical cells as described in details in our former investigation [48]. The basic steps in the experiments are briefly described below:

Electrochemical polymerization EDOT was carried out in an aqueous microemulsion [50, 51] consisting of 0.068 M 3,4-ethylenedioxythiophene (H.C. Strack GmbH, Germany), 0.04 M surfactant (polyoxyethylene-10-laurylether, Sigma), and 0.5 M LiClO₄ (Aldrich). Polymerization of EDOT occurred at constant anodic potential, $E_a=0.37$ V for different times. The polymerization charge passed during synthesis of PEDOT was used to estimate the thickness of the polymer layers on a 240 mC cm⁻² per 1 μm basis. PEDOT layers with two limiting thicknesses $-d=0.5$ μm (denoted further as thin) and $d=4.4$ μm (denoted further as thick) were investigated.

Copper was electrodeposited by applying a constant current, $i=-0.17$ mA cm⁻², in an aqueous solution consisting of either acidic solution of 0.033 M CuSO₄, and 0.5 M H₂SO₄, or close to neutral solution of 0.02 M CuSO₄, 0.06 M Na₂C₂O₄, and 0.344 M K₂SO₄, pH 6.5. In the second solution, the di-oxalate complex of copper [Cu(C₂O₄)₂]²⁻ (further denoted as CuOx₂) is the dominating species [52, 53]. The amount of copper deposited from both plating solutions was calculated by using the charge passed in the course of the galvanostatic experiment after exceeding the equilibrium potential of copper in the respective copper plating solution. ($E_{\text{CuSO}_4}=-0.400$ V and $E_{\text{CuOx}}=-0.547$ V). The electrodes obtained by using the copper oxalate solution for the metal electrocrystallization step will be further denoted as Cu_{ox}-modified PEDOT-coated electrodes.

The electroanalytic measurements were carried out in phosphate buffer solution (PBS), consisting of 0.1 M K₂HPO₄ and 0.1 M KH₂PO₄, (pH 7.0). The scan rate used

Fig. 3 Single Cu crystals deposited on a thin PEDOT layer using CuSO₄ solution. SEM images are taken after treatments in various solutions: **a, b** PBS; **c, d** 1 mM AA in PBS; **e, f** 1 mM AA and successive addition of 0.03 to 0.3 mM DA in PBS



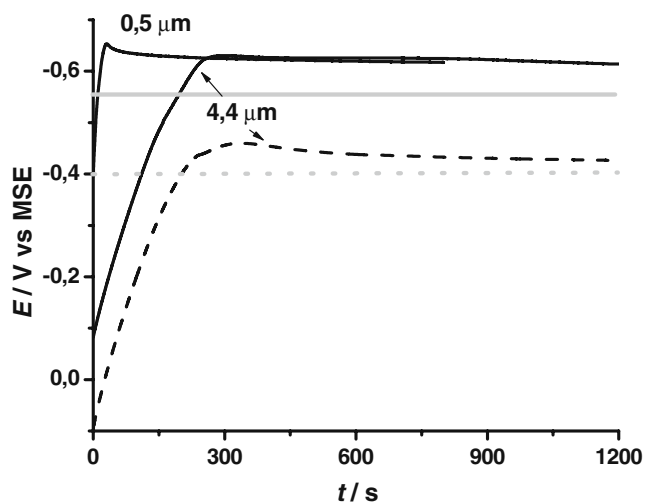
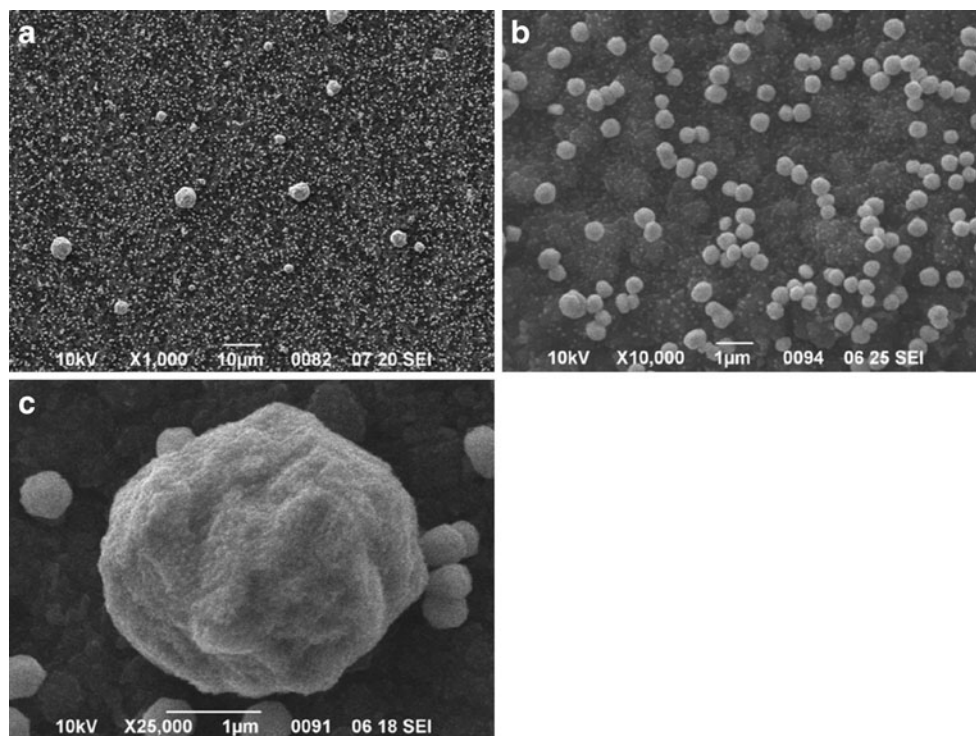


Fig. 4 Galvanostatic electroreduction curves measured in CuOx_2 solution ($i = -0.17 \text{ mA cm}^{-2}$) at thick and a thin PEDOT-coated electrodes (full black lines). For comparison the galvanostatic curve (dashed black line) obtained at the $4.4 \mu\text{m}$ PEDOT layer in CuSO_4 solution is also shown. The gray lines denote the values of the equilibrium potentials of copper in the corresponding solutions: CuOx_2 (full line) and CuSO_4 (dotted line)

for the voltammetric measurements was 20 mV s^{-1} . In several figures in this investigation, the voltammetric curves are presented after background correction, i.e., after subtraction of the reference voltammetric curve measured in PBS in the absence of DA. This allows for a better resolution of the DA redox currents. The parameters used for the DPV

Fig. 5 SEM of Cu–PEDOT specimens obtained after Cu-deposition from CuOx_2 solution on a thick PEDOT layer. The micrographs a–c show different magnifications



procedure were: modulation time 0.05 s , step potential 5 mV , and modulation amplitude 20 mV . The electrodes were pre-conditioned at -0.5 V for 30 s before each DPV run.

Electrochemical dissolution of the deposited copper crystals was carried out in $0.5 \text{ M H}_2\text{SO}_4$ by cycling the potential in the -0.6 to 0.0 V range at 5 mV s^{-1} . This final step of the experiment allowed estimating the amount of copper that remained on the electrode surface after the measurements performed in PBS in the absence and the presence of DA and AA.

Scanning electron microscopy (SEM) imaging of Cu-modified PEDOT-coated electrodes was accomplished by means of a JSM 6380 (JEOL) apparatus.

Results and discussion

Copper electrodeposition from copper sulfate solution

In our former study, it was established that at one and the same amount of electrodeposited copper thick PEDOT layer provide higher DA oxidation currents in comparison to much thinner PEDOT coatings (Fig. 1). Nevertheless the Cu-modified thick PEDOT-coated electrode was found to be electrochemically unstable, whereas Cu crystals deposited on a thin PEDOT layer could operate much better for DA oxidation.

SEM images of the copper deposit obtained on thin and thick PEDOT layers (Fig. 2) reveal very different character-

istics of the metal deposit. A relatively low number ($1.2 \times 10^5 \text{ cm}^{-2}$) of similar micrometer-sized crystals are detected on the thin PEDOT layer (Fig. 2a). On the thick PEDOT layer, there is a lower number ($1.2 \times 10^4 \text{ cm}^{-2}$) of large crystals that coexist with a dense population of needle-like crystals. The latter cover the whole surface area of the electrode (white contrast in Fig. 2b–d) with the exception of the dark circular zones arising around the big crystals. The needle-like crystals seem to be loosely bound to the polymer surface, and there are sharp limits between free (dark areas) and needle-like crystals occupied (white areas) zones on the electrode surface (Fig. 2d). This patterning of the electrode surface by metal crystals is very probably due to zones of reduced overpotential (or nucleation exclusion zones) arising around the crystals that have first nucleated on the electrode surface [54–56].

In order to understand the lack of stable electrochemical response of Cu-modified thick PEDOT coatings further, SEM observations were carried out after the electrodes were exposed to a two-step treatment: (1) several voltammetric scans in PBS and (2) several voltammetric scans in the presence of DA in PBS. The population of the Cu needles was not observed after this treatment. The repeated surface oxidation and reduction of the copper crystalline species that occurs at pH 7 within each voltammetric scan is very probably in the origin of the loss of the tiny crystals on the electrode surface. The loss of a large amount of copper was confirmed also by studying the amount of the dissolved metal after treatment in the DA containing PBS.

Although the bulky crystals obtained after copper deposition on thin PEDOT layers seemed to offer a stable surface, also, in this case, it was found that the oxidation reactions affect the crystalline surface. Three Cu-modified thin PEDOT specimens obtained under identical conditions were examined in SEM: (1) after several voltammetric scans in PBS (first specimen, Fig. 3a, b); (2) after several voltammetric scans in PBS and then DPV measurements in the presence of 1 mM AA (second specimen, Fig. 3c, d), and (3) after several scans in PBS and then DPV measurements in the presence of both AA (1 mM) and DA (0.3 mM; third specimen Fig. 3e, f). The copper crystals shown on the SEM micrographs in Fig. 3 are typical representatives found on the surfaces of the three specimens. Similar Cu crystals, characterized with pentagonal symmetry, were already observed in the case of copper electrocrystallization on metal substrates [57, 58]. Our experiments show that the treatment in PBS results in the formation of small humps on the large flat crystalline faces. The further treatments in AA and DA result in well-detectable destruction of the Cu crystals occurring preferentially at the crystalline edges. The effect is strongly expressed in the DA oxidation case. Nevertheless the massive crystals offer reasonable stability and provide the possibility to carry out DPV measurements in a large concentration range covering the micromolar region of DA [48].

Further optimization of the Cu–PEDOT system was sought in the possibility to increase the surface coverage with stable bulky Cu crystals. This aim was approached by using a different plating solution for the copper electrodeposition.

Copper electrodeposition from copper oxalate solution

In general, the use of metal anion complexes in electroplating results in the formation of metal deposits consisting of small crystalline grains. However, the nucleation stage in metal electrodeposition on a foreign substrate depends markedly on the surface properties of the electrode. Thus, for a given

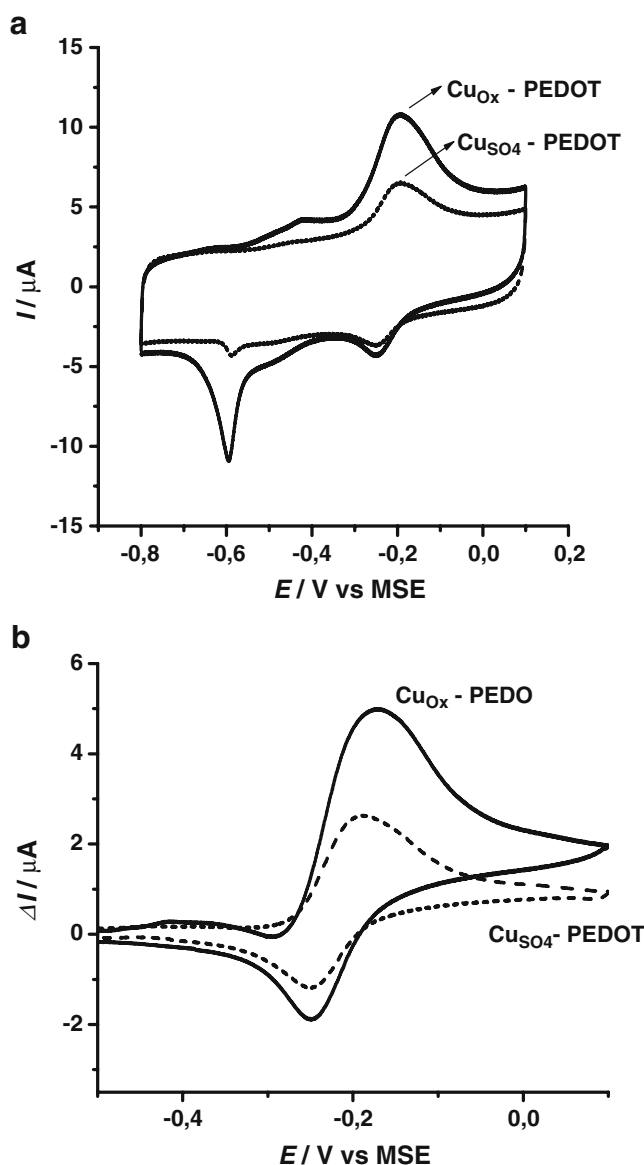


Fig. 6 Cyclic voltammetric curves measured in 2 mM DA in PBS at copper-modified PEDOT-coated electrodes obtained by copper deposition from CuOx_2 (solid line) and CuSO_4 (dashed line) solutions without (a) and with (b) subtraction of the corresponding background curves. $d_{\text{PEDOT}}=4.4 \mu\text{m}$, $m_{\text{Cu}}=70 \mu\text{g cm}^{-2}$, $v=20 \text{ mV s}^{-1}$

electrode use of various metal anion complex solutions may result both in a larger or a smaller number of initially nucleated crystals in comparison to the deposit obtained in the corresponding cation solution. Specifically, electrodeposition on CP layers by means of metal complex solutions may involve various additional effects, e.g., shift of the potential range for metal deposition and thus change in the oxidation state of the CP material, penetration of the metal complex anions in the CP layer for charge compensation, possible interaction of the complexing anions with the CP [59]. The use of copper oxalate solution for the electrocrystallization of Cu was based on our former experience with polyaniline layers [52] showing the possibility to increase considerably the number of copper crystals and to decrease their size by keeping the metal amount one and the same. Copper electrodeposition in PEDOT was extensively studied in previous investigations, but so far, only by using acid copper sulfate solutions [60–62].

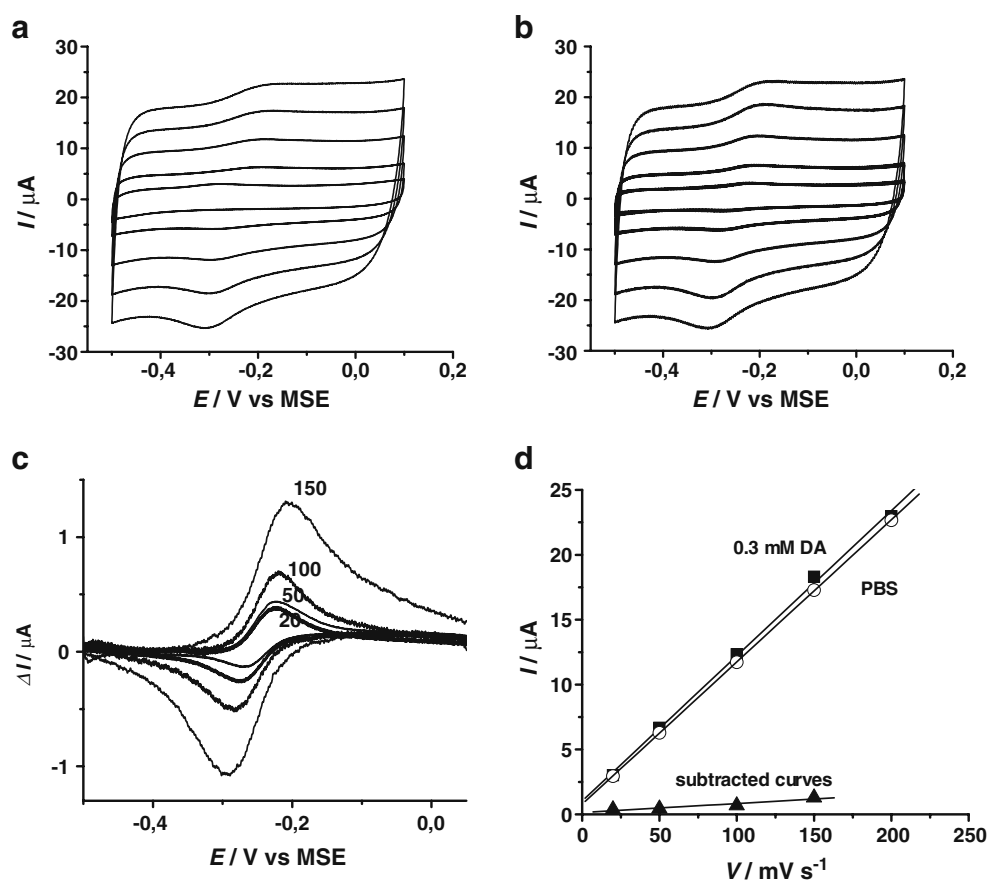
Figure 4 shows galvanostatic current transients obtained when using a copper oxalate solution for the deposition of Cu on thin and thick PEDOT layers. It is obvious that the nucleation and growth proceeds at higher overpotential in comparison to the CuSO_4 case. There is a difference in the maximal deviation from the equilibrium potential (i.e., the maximum overpotential) which is responsible for the nucle-

ation but the two transients coincide in a larger time interval showing that growth proceeds without inhibition on the thick polymer layer.

SEM images of the electrode surface obtained after deposition of Cu from copper oxalate solution on a thick PEDOT layer show a completely different type of the crystalline deposit (Fig. 5) in comparison to the copper sulfate case (Fig. 2b–d). There are again big (several micrometer-sized) crystals with about the same density ($1 \times 10^5 \text{ cm}^{-2}$) as in the copper sulfate case together with a large population ($1.54 \times 10^8 \text{ cm}^{-2}$) of much smaller ($0.5 \mu\text{m}$) bulky crystals that are homogeneously distributed and uniform in size and shape. The estimated surface coverage by copper, in this case, is about 30% and thus much higher than the one (about 0.3%) in the copper sulfate deposition case. The comparison of the copper crystalline deposit obtained on thin and thick PEDOT layers showed no essential difference. The number of crystals remained of the same order of magnitude in both cases.

Further investigations were directed to the comparison of DA oxidation on Cu-modified PEDOT-coated electrodes obtained on thick PEDOT layers by depositing one and the same amount of Cu but by using the two different copper plating solutions (Fig. 6). The voltammetric curves of DA oxidation measured at the electrode with the high population of bulky crystals showed about two-fold increase in the

Fig. 7 Scan rate dependence of the voltammetric curves measured at CuOx-modified PEDOT-coated electrodes in: **a** PBS and **b**, **c** 0.3 mM DA in PBS; **c** voltammetric curves after background correction; **d** scan rate dependence of the peak currents for the measurements in PBS (*open circle*), PBS+DA (*filled square*), and for the subtracted curves (*filled triangle*). $d_{\text{PEDOT}}=4.4 \mu\text{m}$, $m_{\text{Cu}}=70 \mu\text{g cm}^{-2}$, $v=20, 50, 100, 150,$ and 200 mV s^{-1}



oxidation peak currents (Fig. 6b). A further comparison was made between thin and thick PEDOT layers with one and the same amount of Cu deposited from copper oxalate solution. Higher DA and AA oxidation currents were obtained for the thick PEDOT layers thus showing that PEDOT has its own contribution to the electrocatalytic activity of the Cu_{ox}-PEDOT system. For this reason, in the further studies, Cu_{ox}-modified thick PEDOT layers were investigated.

The scan rate dependence of the voltammetric curves was measured in the absence and the presence of 0.3 mM DA in the PBS in the potential limits used for electroanalytic DPV measurements (Fig. 7a, b). For both series, the anodic peak currents were found to depend linearly on the scan rate (Fig. 7d). The voltammetric curves obtained after subtraction of the reference lines (i.e., the voltammetric curves measured in the absence of DA) show clearly that the peak position remains unaffected by the scan rate (Fig. 7c). This means that for the Cu_{ox}-modified PEDOT-coated electrode with 30% surface coverage of Cu the DA reaction is reversible in the 20 to 150 mV s⁻¹ scan rate limits and becomes limited by surface adsorption. A similar finding concerning the surface-limited DA oxidation was communicated in the case of edge plane pyrolytic graphite [63]. Based on the high electrocatalytic currents and surface-limited reaction established on the Cu_{ox}-modified thick PEDOT-coated electrode, it could be expected that they should provide a lower detection limit and higher sensitivity than the ones obtained so far.

DPV measurements on Cu_{ox}-modified PEDOT-coated electrodes

Figure 8a shows a series of DPV curves measured at a Cu_{ox}-modified thick PEDOT-coated electrode in PBS in the presence of 1 mM AA and various concentration of DA starting from 6 nM to 2 μM. The concentration dependence of the peak current (at about -0.3 V) shows a sensitive linear response in the 6 to 60 nM DA concentration interval and a second less sensitive linear region covering the 300 nM to 2 μM concentration range (Fig. 8b). A further DPV series was measured by fixing the DA concentration at the 12 nM DA level and increasing the concentration of AA from 1.2 to 4.7 mM (Fig. 9a). A linear response of the AA peak currents (at about -0.43 V) on AA concentration was observed (Fig. 9b). Then, at the 4.7 mM concentration level of AA, the DA concentration was gradually increased from the initial 12 to 69 nM (Fig. 9c). Figure 9d shows the concentration dependence of the DA DPV peaks from the two DA series and a repeated third control measurement in the nanomolar concentration range of DA. The two independent series measured at one and the same AA concentration (1 mM) show one and the same slope (0.009 μA nM⁻¹) in the I_{DPV} vs c_{DA} plot. The slope obtained in the same concentration range for a five-fold higher concentration of AA is somewhat higher

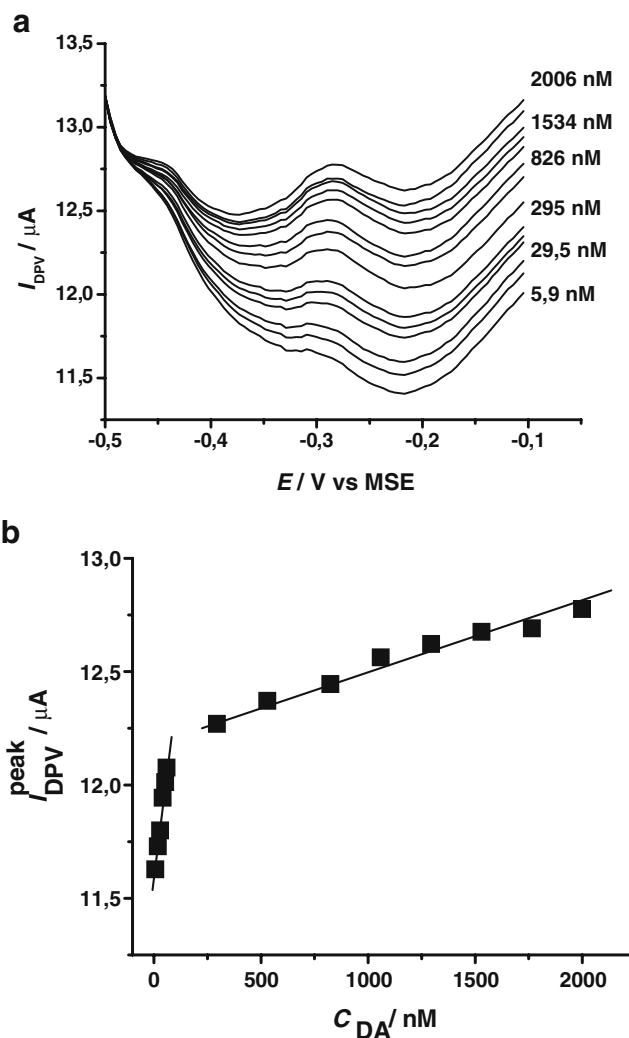


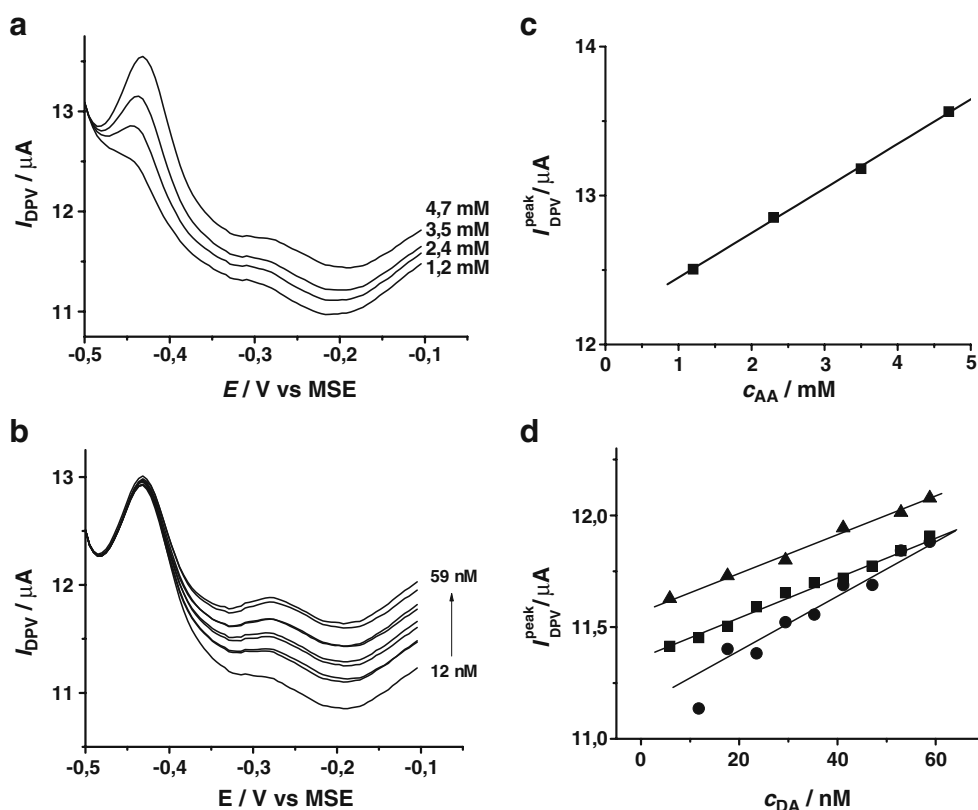
Fig. 8 DPV curves measured in PBS in the presence of 1 mM AA at different concentrations of DA from 6 to 2,006 nM at a Cu_{ox}-modified PEDOT-coated electrode (a) and concentration dependence of the DA oxidation peak (b). $d_{PEDOT}=4.4 \mu\text{m}$, $m_{Cu}=70 \mu\text{gcm}^{-2}$

(0.012 μA nM⁻¹). Thus, the investigated Cu_{ox}-modified thick PEDOT-coated electrodes have a very high sensitivity for DA in the nanomolar concentration range in the presence of a large excess of AA. The relative standard deviation for DA determination based on five measurements was found to be about 5%. The 3σ detection limit of DA was estimated to be 4 nM. The second linear region found in the 0.3 to 2.0 μM range (Fig. 8b) shows a lower slope (0.313 μA μM⁻¹) corresponding to a lower sensitivity for DA determination in the several micromolar concentration range.

Conclusions

The present investigation shows that the Cu-PEDOT system is a suitable candidate as sensing material for DA in the

Fig. 9 DPV curves measured in PBS at a Cu_{ox} -modified PEDOT-coated electrode: **a** in the presence of 12 nM of DA and different concentrations of AA from 1.2 to 4.7 mM; **b** in the presence of 4.7 mM AA and different concentrations of DA from 12 to 60 nM; **c** concentration dependence of the AA oxidation peak; **d** concentration dependence of the DA oxidation peaks obtained from three independent runs at 1 mM AA (filled square and filled triangle) and 4.7 mM AA (filled circle). $d_{\text{PEDOT}}=4.4 \mu\text{m}$, $m_{\text{Cu}}=70 \mu\text{g cm}^{-2}$



presence of excess of AA. Depending on the thickness of the PEDOT layer and the amount and type of electrodeposited copper crystals linear DPV response may be obtained in different concentration intervals. As was shown before [48], thin PEDOT layers and a small amount of copper crystals ($\sim 10^5 \text{ cm}^{-2}$ with surface coverage of about 0.3%) provide linear voltammetric response in a wide DA concentration interval in the micromolar range (7 to 200 μM) in the presence of millimolar concentrations of AA. The sensitivity in this case is 0.013 $\mu\text{A}/\mu\text{M}$ [48], and the reaction is diffusion limited. In the present study, it was demonstrated that optimization of the Cu–PEDOT system carried out by increasing drastically the number of crystals ($\sim 10^8 \text{ cm}^{-2}$), and their surface coverage (up to about 30%) respectively combined with the use of PEDOT with optimal thickness results in a highly sensitive material operating in the nanomolar concentration range. The Cu-modified PEDOT-coated electrodes show good stability in the cases when bulky crystals, well bound to the polymer surface become electrodeposited.

The high sensitivity for the DA determination in the nanomolar concentration range should relate to the formation of a $\text{Cu(II)}-o\text{-quinolate}$ complex and its role as promoter of the DA oxidation reaction. It is interesting to note that for the Cu_{ox} -PEDOT electrode with high copper surface coverage the DA oxidation reaction becomes

surface-limited in contrast to the diffusion limited reaction observed for the Cu-modified thin PEDOT with low copper content. This should be due to preferential adsorption of DA on the electrocatalytic copper surface as was assumed also for the case of DA oxidation on edge plane pyrolytic graphite [63]. The two linear regions with different slopes established in the Cu_{ox} -PEDOT case could relate to the occupation of different types of adsorption sites on the copper surface. A further interesting aspect of our study is the crystallographic anisotropy with respect to DA oxidation. It was demonstrated that large micrometer-sized euhedral copper crystals with pentagonal symmetry (as obtained from copper sulfate solution) suffer surface destruction along the crystalline edges upon exposure to DA. On the other hand, much smaller anhedral crystals obtained in the copper oxalate solution have seemingly a better stability when exposed to DA solution. These observations raise the question on the role of the crystallographic features of the metal crystals for their electrocatalytic performance and stability that need to be further explored.

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