

Copper-modified poly(3,4-ethylenedioxythiophene) layers for selective determination of dopamine in the presence of ascorbic acid: I. Role of the polymer layer thickness

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Abstract The oxidation of ascorbic acid (AA) and dopamine (DA) is studied on non-modified and copper crystal-modified poly(3,4-ethylenedioxythiophene) (PEDOT)-coated electrodes. Both oxidation reactions are studied for different thickness of the polymer layers. For several microns thick PEDOT layers both PEDOT and Cu-modified PEDOT show the largest currents. A stable voltammetric response for AA oxidation is observed together with a linear dependence of the peak currents on concentration in the 0.3 to 6.0 mM range. For DA oxidation, however, a gradual loss of electroactivity is found with increasing number of voltammetric scans and concentration. This problem is overcome by using thinner (<1 μm) polymer layers. In the presence of both AA and DA, the Cu-modified PEDOT-coated electrodes provide better selectivity with respect to DA in comparison to non-modified PEDOT due to partial suppression of the AA oxidation currents. Thin PEDOT layers modified with electrodeposited Cu crystals show a stable and sensitive response for DA oxidation in the micromolar concentration range. A linear dependence of the voltammetric peak currents is found in a wide concentration range (from 6 to about 200 μM) of DA in the presence of a large excess (1 mM concentration) of AA. The sensitivity is 0.013 $\mu\text{A}\mu\text{M}^{-1}$.

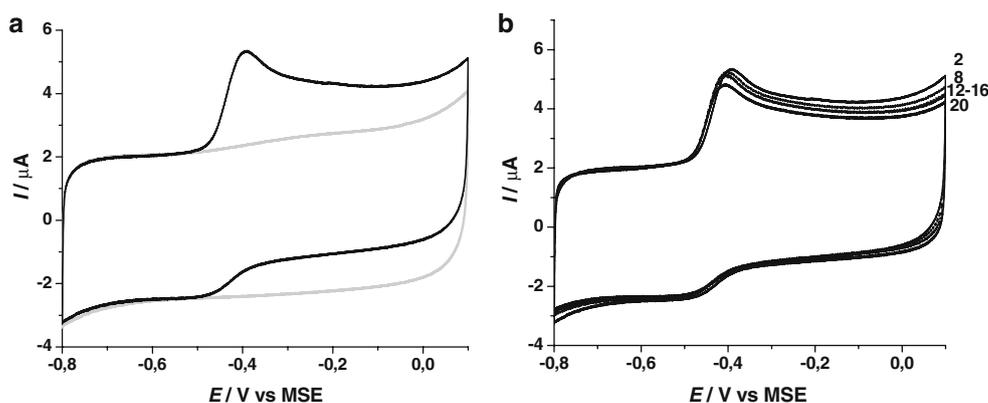
Keywords PEDOT · Conducting polymers · Copper · Dopamine · Ascorbic acid

Introduction

The first attempts to involve conducting polymer (CP) layers in electroanalytic applications started as early as 1986 with the work of Saraceno et al. [1] using polypyrrole-coated glassy carbon electrodes for resolving the voltammetric waves of ascorbic acid and dopamine oxidation. Few years later, poly(3-methylthiophene) (P3MET)-coated electrodes were used in voltammetric measurements on the oxidation of phenolic compounds and provided the possibility to eliminate passivation occurring otherwise on glassy carbon electrodes [2]. In general, CP-coated electrodes were expected to be able to promote interfacial electron transfer in a broad potential window opposed to redox mediators of the electron transfer that usually provide a narrow operation potential range [3]. Overcoming of surface fouling effects, typical for simple metal and glassy carbon electrodes, and improved selectivity in the presence of interfering moieties were also anticipated advantages of these types of modified electrodes. Selectivity was expected based either on electrostatic interactions between charged solutes or reaction intermediates and cationic fixed sites in oxidized CPs [1] or on selective size exclusion effects in the case of a permselective CP layers [4]. The field expanded rapidly into studies involving various CPs, i.e., P3MET [2, 3, 5–10], substituted poly(bi-thiophene) [11], polypyrrole [1, 3, 4, 7, 8, 12], polyaniline [3, 4, 7, 8, 13–17], polyphenylenediamine [18, 19], and more recently, poly(3,4-ethylenedioxythiophene) (PEDOT) [20–24] and covered a number of organic compounds of biological interest, e.g., ascorbic (AA) and uric acids, catecholes, catecholamines, NADH, etc. Attention was specifically focused on the selective determination of dopamine (DA) as an important biologically relevant

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Fig. 1 Voltammetric curves measured in the presence of 5 mM AA in PBS at a PEDOT-coated electrode: **a** first scan and reference line obtained in absence of AA; **b** 20 consecutive scans. ($d_{\text{PEDOT}}=4.4 \mu\text{m}$, $\nu=20 \text{ mV s}^{-1}$)



compound in the presence of other analytes, e.g., AA and uric acid that are simultaneously available in the biological probes. Sensitivities in the micromolar concentration range of DA in relatively narrow concentration intervals (typically 10 to 100 μM) were communicated in several cases, e.g., [10, 14, 15, 19, 21, 24].

Apart from non-treated CPs, overoxidized CP-coated electrodes were involved in these studies. Overoxidation resulted in partial destruction of the material and increase in the polymer film porosity and amount of negative charge over the polymer chains. The latter was expected to be favorable for attracting the positively charged DA species and repelling the negatively charged ascorbate species. Thus, mainly overoxidized polypyrrole [25–29] but also other overoxidized CPs [30–33] were found to have a high sensitivity for the determination of dopamine based presumably on a combination of electrostatic and size discrimination of DA against AA species [32]. In these studies, a linear response [usually from differential pulse voltammetry, (DPV), peak current measurements] was found typically in the several micromolars to 1 mM concentration range of DA [32]. A linear response in the nanomolar range (starting from 50 nM) in the presence of 0.3 mM AA was demonstrated in [31].

Further attempts to increase the sensitivity and selectivity of CP-modified electrodes for DA determination in the

presence of excess of AA involved CPs layers modified with Au [34–37] and Pd [38, 39] particles. Increased sensitivities for DA in comparison to the non-modified CPs were found in all studied metal-modified systems. In the Au nanoparticles–PEDOT case [34], a linear DPV response was documented in the 2 to 25 nM concentration range for DA (without AA) and in the 2–20 μM concentration range for DA in the presence of 1 mM AA. Well resolved DPV peaks were observed in three-component analyte solutions containing AA, DA, and uric acid for both Au–PEDOT [36] and Pd–PEDOT [38] systems. The role of the Au nanoparticle organic shell for the sensitivity and selectivity of the electrochemical response was discussed in [37]. It was demonstrated that negatively charged Au nanoparticles act as a sort of electrostatic shield towards negatively charged species, i.e., AA. Thus, use of metal particles modified CPs offered an alternative opportunity to affect markedly both the sensitivity and selectivity of the electrochemical response of DA in the presence of interfering species, AA including. The choice of the type of the metal particles and of their surface chemical state (e.g., type of stabilization shell) is substantial for the electrochemical performance of the hybrid metal particles–CP materials.

In the present investigation, copper particles modified PEDOT layers are used for studying the oxidation of DA in neutral solution. The choice of Cu is based on findings

Fig. 2 Voltammetric curves measured in the presence of 2 mM DA in PBS by using a PEDOT-coated electrode: **a** first scan and reference line obtained in absence of AA; **b** 20 consecutive scans. ($d_{\text{PEDOT}}=4.4 \mu\text{m}$, $\nu=20 \text{ mV s}^{-1}$)

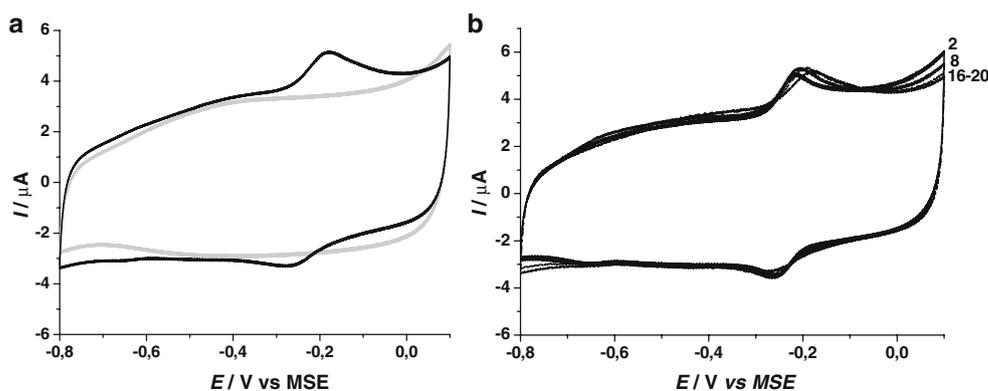
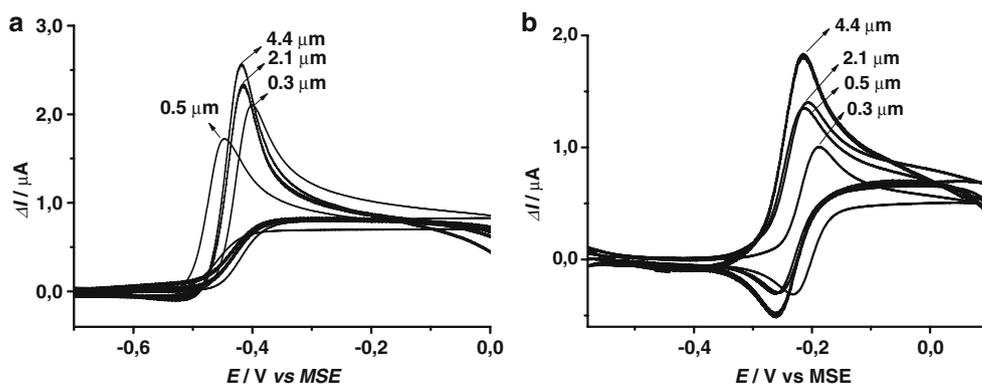


Fig. 3 Dependence of the voltammetric response on the PEDOT layer thickness measured in PBS in the presence of: **a** 5 mM AA and **b** 2 mM DA. ($\nu=20 \text{ mV s}^{-1}$)



showing that it acts as a suitable electrode for selective determination of *o*-diphenols in neutral solutions [40]. The formation of a Cu(II)-*o*-quinolate complex is suggested as promoter of the DA electrooxidation reaction [40]. Investigations on copper containing sol-gel electrodes have demonstrated a good resolution (by about 0.3 V) of the voltammetric peaks for dopamine and ascorbic acid oxidation and a high sensitivity for dopamine alone [41].

The aim of the present study is to explore the possibility to use the Cu-PEDOT system for electrochemical sensing of both DA and AA, separately, and together in the presence of large excess of AA with respect to DA. Series of measurements are first performed with non-modified PEDOT layers in order to be able to differentiate the contributions of the polymer layer and the metallic phase to the sensitivity and selectivity of the Cu-PEDOT system for the oxidation reactions. The role of the PEDOT layer thickness is explored for both AA and DA oxidation in order to find out the optimal conditions for the performance of the PEDOT and the Cu-PEDOT system. Special attention is paid to the stability and reproducibility of PEDOT and Cu-modified PEDOT-coated electrodes when carrying out series of measurements. These points have almost not been addressed in the literature concerning CP and metal-modified CP-coated electrodes involved in electroanalytic applications.

In a separate study [42], the attention is specifically focused on the possibility to optimize the Cu-PEDOT system with respect to sensitive and selective determination of dopamine by varying the characteristics (number, size, and shape) of the copper crystalline species deposited on the PEDOT surface.

Experimental

All electrochemical measurements were performed in a three-electrode set-up consisting of a platinum single crystal bead electrode with surface area $S=2.3 \times 10^{-3} \text{ cm}^2$, a platinum plate counter electrode and a mercury/mercury sulfate reference electrode. (The working electrode was prepared by melting a thin platinum wire in an oxygen flame and sealing it in a glass tube.) 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).

Fig. 4 **a** Voltammetric curves (after background correction) measured in PBS at different concentrations of AA by using a PEDOT-coated electrode, $\nu=20 \text{ mV s}^{-1}$; **b** concentration dependence of the peak currents measured by using of PEDOT (open circle) and Cu-PEDOT (filled square)-coated electrodes. ($d_{\text{PEDOT}}=4.4 \mu\text{m}$, $m_{\text{Cu}}=70 \mu\text{g cm}^{-2}$)

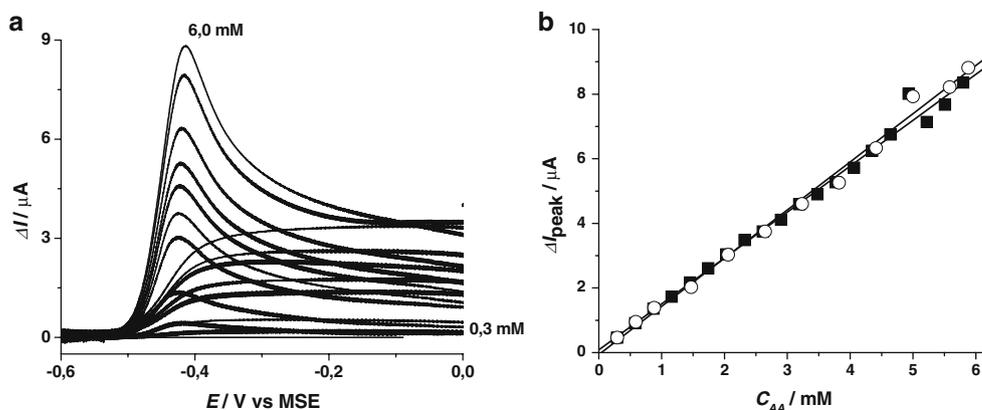
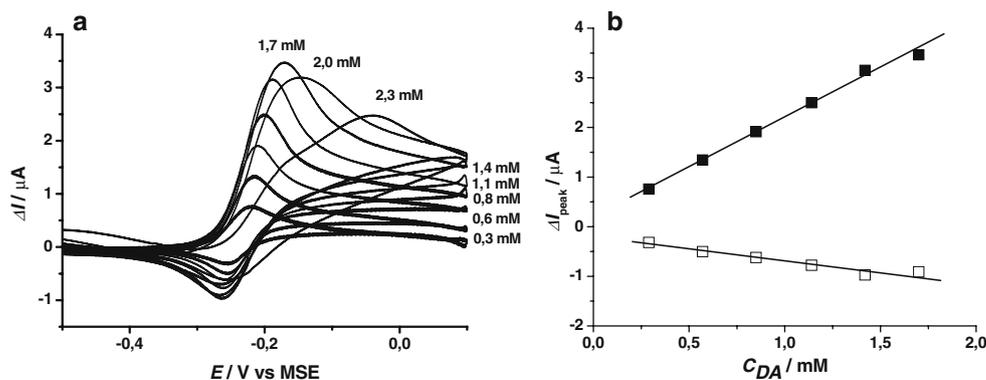


Fig. 5 a Voltammetric curves (after background correction) measured in PBS for different concentrations of DA at a PEDOT-coated electrode, $v=20 \text{ mV s}^{-1}$; **b** concentration dependence of the peak currents. ($d_{\text{PEDOT}}=4.4 \text{ }\mu\text{m}$)



Each experiment consisted of several steps performed consecutively in five electrochemical cells:

1. Electrochemical polymerization EDOT was carried out in an aqueous microemulsion [43–45], where polyoxyethylene-10-laurylether (Sigma) was used as micellar surfactant. The polymerization solution consisted of 0.068 M 3,4-ethylenedioxythiophene (H.C. Strack GmbH, Germany), 0.04 M surfactant, and 0.5 M LiClO_4 (Aldrich). Polymerization of EDOT occurred at constant anodic potential, $E_a=0.37 \text{ V}$ 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 $1 \text{ }\mu\text{m}$ basis.
2. After synthesis, the polymer-coated electrodes were transferred in acid supporting electrolyte (0.5 M H_2SO_4) for measurement of their voltammetric behavior in the potential window -0.73 – 0.32 V at 100 mV s^{-1} .
3. Copper was electrodeposited by applying a constant current, $i=-0.17 \text{ mA cm}^{-2}$, in an aqueous solution consisting of 0.033 M CuSO_4 and 0.5 M H_2SO_4 for two different times 800 and 1,500 s. Copper electrodeposition in PEDOT was extensively studied in our

previous investigations [45–48]. The amount of deposited copper was calculated by using the charge passed in the course of the galvanostatic experiment after exceeding the equilibrium potential ($E_{\text{Cu}^{2+}}=-0.400 \text{ V}$) of copper in the copper ions containing solution.

4. Voltammetric measurements in phosphate buffer solution (PBS), consisting of 0.1 M K_2HPO_4 and 0.1 M KH_2PO_4 , ($\text{pH}=7.0$), were carried out for all polymer or copper–polymer modified electrodes in absence of analytes in the buffer solution. These reference measurements were necessary for assessing the contribution of the current due to the intrinsic electroactivity of the PEDOT (or Cu–PEDOT) material in the buffer solution. Voltammetric curves were measured at 20 mV s^{-1} .
5. Cyclic voltammetry or DPV in the presence of DA and AA were carried out in PBS in the concentration range $6 \text{ }\mu\text{M}$ – 2 mM for DA and 0.3 – 6 mM for AA. The scan rate used for the voltammetric measurements was 20 mV s^{-1} . The parameters used for the DPV procedure were: modulation time 0.05 s, step potential 5 mV, and modulation amplitude 20 mV. The electrodes were conditioned at -0.5 V for 30 s.

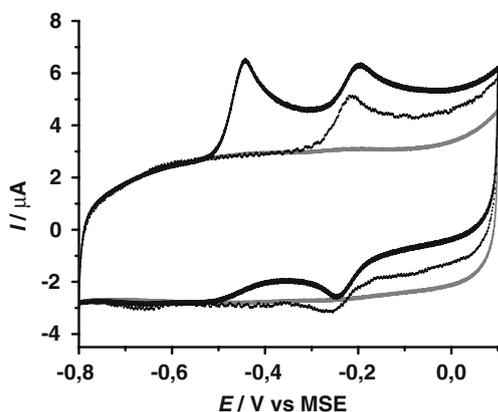


Fig. 6 Voltammetric curves measured at a PEDOT-coated electrode in PBS (gray line) and upon subsequent addition of 2 mM DA (dotted line) and 5 mM AA (full line). ($d_{\text{PEDOT}}=4.4 \text{ }\mu\text{m}$, $v=20 \text{ mV s}^{-1}$)

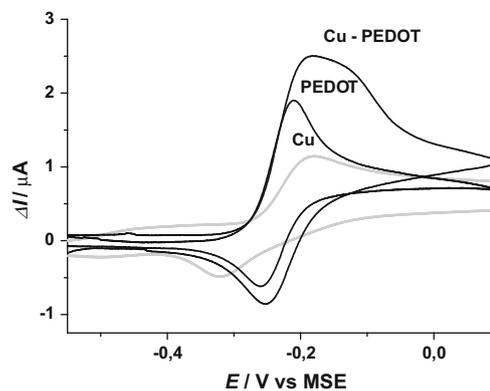


Fig. 7 Voltammetric curves measured in PBS with 1.7 mM DA by means of Cu- (gray line), PEDOT (dotted line), and Cu-modified PEDOT (full line)-coated electrodes. ($d_{\text{PEDOT}}=4.4 \text{ }\mu\text{m}$, $m_{\text{Cu}}=70 \text{ }\mu\text{g cm}^{-2}$, $v=20 \text{ mV s}^{-1}$)

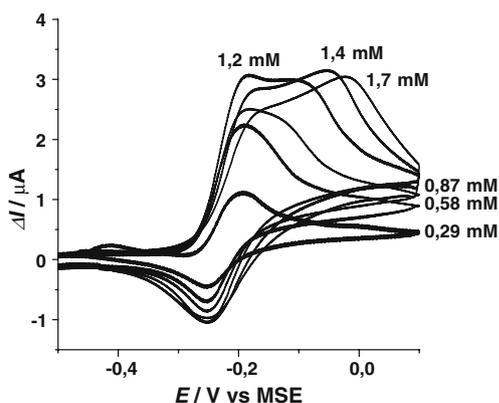


Fig. 8 Voltammetric curves (after background correction) measured in PBS for different concentrations of DA at a Cu-modified PEDOT-coated electrode ($d_{\text{PEDOT}}=4.4 \mu\text{m}$, $m_{\text{Cu}}=70 \mu\text{g cm}^{-2}$, $v=20 \text{ mV s}^{-1}$)

- Repeated measurements in PBS in the absence of analytes were carried out in order to follow the state of the polymer and Cu-modified polymer layers after exposure to DA and AA.

Results and discussion

Oxidation of AA and DA on PEDOT-coated electrodes

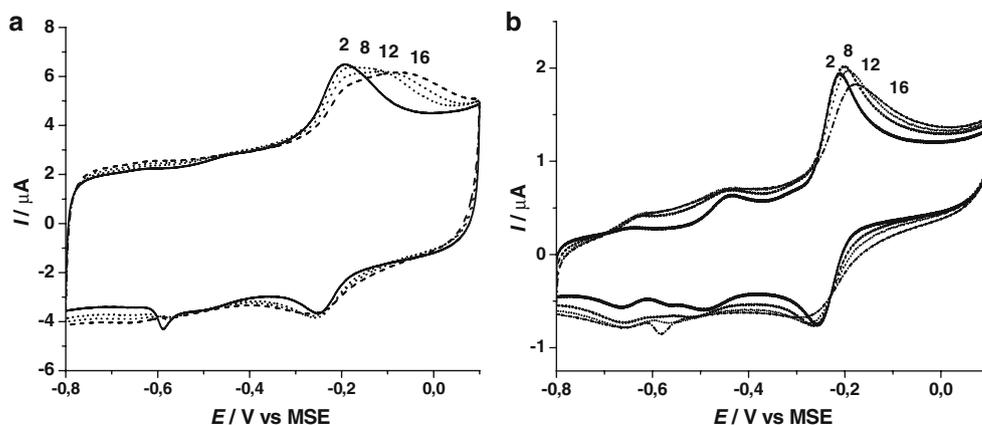
Figure 1a, b shows voltammetric curves measured in the presence of 5 mM AA using a PEDOT-coated electrode with 4.4 μm thickness of the polymer layer. The stability of the voltammetric response within 20 consecutive scans is shown in Fig. 1b. A similar series of measurements with the same thickness of the PEDOT layer is shown in Fig. 2a, b for 2 mM solution of DA. The figures show that the voltammetric peaks for AA and DA oxidation occurring at the PEDOT-coated electrodes are resolved by about 0.21 V. The stability in terms of height and position of the voltammetric peaks is reasonable within the first 20 scans.

In a further series of measurements, AA and DA oxidations were separately studied by using PEDOT-

coated electrodes with different thickness of the polymer layer ranging from 0.3 μm to about 5 μm . The comparison of the electrochemical response due to AA and DA oxidation is made by subtracting from each voltammetric curve measured in the presence of the analyte (AA or DA), the reference curve (for the corresponding PEDOT layer) measured in the buffer without analytes. The subtraction procedure provides the opportunity to follow clearly the voltammetric waves due to the oxidation of the analytes without interference of the intrinsic pseudocapacitive currents of PEDOT. Figure 3a, b shows the voltammetric waves due to AA (a) and DA (b) oxidation obtained by using PEDOT layers with different thickness. For both analytes, the thinnest (0.3 μm) PEDOT layer shows more positive potentials of the oxidation peaks and lower amplitudes due very probably to the non-compact coverage of the underlying platinum electrode by the PEDOT layer at this average thickness. Increase in the polymer layer thickness results in a fixed position of both voltammetric waves with respect to potential and a gradual increase in the peak heights. Saturation is reached for the 4.4- μm thick layer. Further considerable thickening of the PEDOT layer resulted in lower voltammetric peaks that were shifted again to positive potentials. For this reason, the 4.4- μm thick PEDOT layers were used for further studying the concentration dependence of the voltammetric response for AA and DA oxidation.

Figure 4a shows the voltammetric waves due to AA oxidation measured in the 0.3 to 6 mM concentration range of AA. A linear response (open circle in Fig. 4b) was found in the whole studied concentration interval with sensitivity of $1.5 \mu\text{A mM}^{-1}$. The evolution of the voltammetric waves with increasing DA concentration (Fig. 5a) shows, however, a very narrow linear concentration range (Fig. 5b) and a deterioration of the voltammetric curves with increasing concentration (and number of scans). Besides, it was found that, once employed in the DA-containing solution, the PEDOT-coated electrode showed additional electroactivity in

Fig. 9 Series of voltammetric scans measured in the presence of 2 mM DA in PBS at Cu-modified PEDOT-coated electrodes with different thickness of the polymer layer: **a** $d_{\text{PEDOT}}=4.4 \mu\text{m}$ ($m_{\text{Cu}}=70 \mu\text{g cm}^{-2}$) and **b** $d_{\text{PEDOT}}=0.5 \mu\text{m}$ ($m_{\text{Cu}}=84 \mu\text{g cm}^{-2}$). (The numbers of the corresponding scans are denoted in the plots, $v=20 \text{ mV s}^{-1}$)



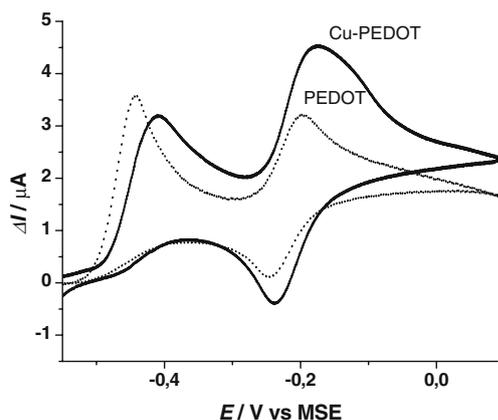


Fig. 10 Comparison of the voltammetric response (after background correction) measured in PBS in the presence of 5 mM AA and 2 mM DA by using PEDOT (dotted line) and Cu-modified PEDOT (full line) coated electrodes. ($d_{\text{PEDOT}}=4.4 \mu\text{m}$, $m_{\text{Cu}}=70 \mu\text{g cm}^{-2}$, $v=20 \text{ mV s}^{-1}$)

PBS (without DA) due very probably to irreversibly adsorbed electroactive reaction intermediates or products. The initial state of the PEDOT electrode could be partially recovered by continuously cycling the electrode in PBS solution. For that reason, after each measurement in DA-containing solution, the electrode was transferred back to PBS, without DA, in order to recover its initial state. Even in this way, the problem with the irreversible inhibition of the surface of thick PEDOT layers could not be overcome completely especially at the highest concentrations of DA studied.

The next step of our studies was to explore the voltammetric behavior of PEDOT in the presence of both AA and DA in PBS (Fig. 6). The resolution of the oxidation peaks became even larger (0.24 V), and the dopamine oxidation peak was influenced by the presence of AA due to a contribution of the AA oxidation currents in the dopamine oxidation potential region. Therefore, sensitive determination of DA in the presence of excess of AA required a suppression of the AA oxidation current.

Oxidation of AA and DA at Cu-modified PEDOT-coated electrodes

The Cu-modified PEDOT-coated electrode was first studied for AA oxidation in the absence of DA. A linear concentration dependence of the current peak was found in the 0.3 to 6 mM AA concentration range (filled square in Fig. 4b) with almost unchanged sensitivity ($1.3 \mu\text{A mM}^{-1}$).

The DA oxidation reaction was found to be enhanced at the Cu-modified PEDOT-coated electrode in comparison to PEDOT (Fig. 7). Unfortunately, the attempt to study the concentration dependence of DA oxidation through voltammetric curves (Fig. 8) showed the same effect of deterioration of the voltammetric waves with increasing DA concentration that was already observed for PEDOT alone. In fact, it was established that, in the course of continuous cycling at a constant concentration of DA, the Cu-modified PEDOT-coated electrode lacks stable response. The voltammetric curves showed a gradual shift of the peak to more positive potentials and broadening of the voltammetric wave (Fig. 9a). Nevertheless, the voltammetric behavior of the Cu-modified PEDOT in the presence of both AA and DA in the solution showed increased DA and suppressed AA oxidation currents (Fig. 10) by preserving the resolution of the voltammetric waves. Thus, the main problem remained the instability of the thick PEDOT layer with respect to its electrochemical response in dopamine-containing solution. To solve this problem, the thickness of the PEDOT layers was reduced down to about $0.5 \mu\text{m}$, thus reducing the contribution of PEDOT for both the oxidation currents of AA and DA and relying on the increased sensitivity for DA due to the presence of copper crystals. This turned out to be an advantageous approach that provided the possibility to solve the problem with stability (see Fig. 9b) and to carry out detailed series of measurements. By means of scanning electron microscopic investigations, it was found that the copper crystals obtained after electrocrystallization on thin

Fig. 11 Scan rate dependence of the voltammetric curves measured at Cu-modified PEDOT-coated electrode in the presence of 2 mM DA in PBS (a) and scan rate dependence of the anodic peak currents (b). ($d_{\text{PEDOT}}=0.5 \mu\text{m}$, $m_{\text{Cu}}=86 \mu\text{g cm}^{-2}$)

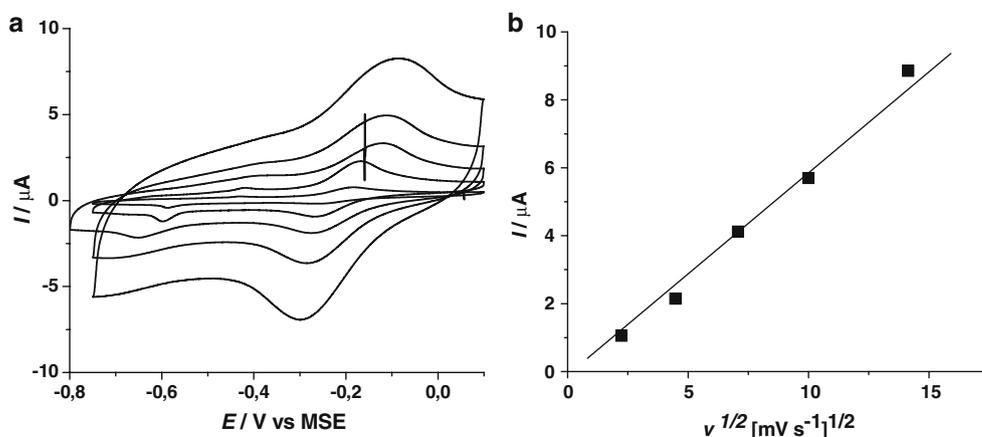
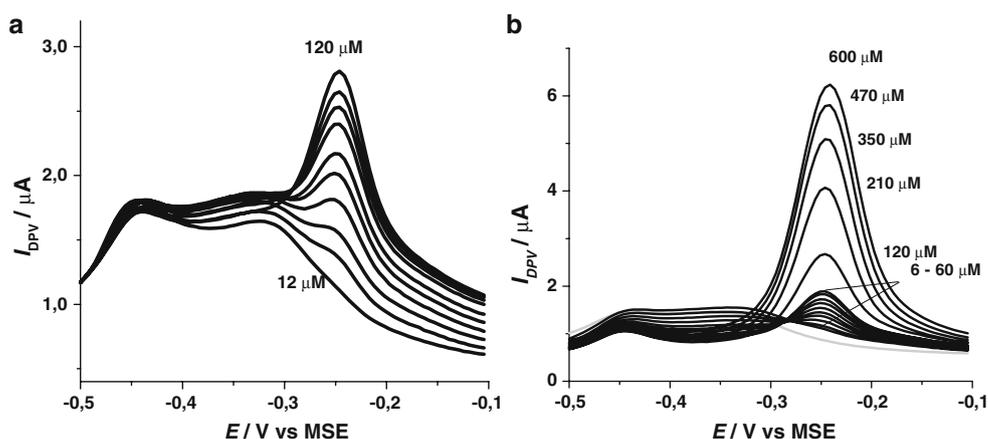


Fig. 12 DPV curves measured in the presence of 1 mM AA in PBS for different concentrations of DA at Cu-modified PEDOT-coated electrodes with different amounts of copper: **a** $m_{Cu} = 46 \mu\text{g cm}^{-2}$ and **b** $m_{Cu} = 86 \mu\text{g cm}^{-2}$. $d_{PEDOT} = 0.5 \mu\text{m}$



PEDOT layers have a surface density of $1.4 \times 10^5 \text{ cm}^{-2}$ and an average size in the several micrometer range.

Figure 11 shows the scan rate (v) dependence of the voltammetric peaks due to dopamine oxidation measured at a thin Cu-modified PEDOT layer. The obtained linear dependence of the peak currents on $v^{1/2}$ indicates that the reaction is controlled by diffusion limitations. The current peaks shift their positions with increasing scan rate (by about 60 mV per decade change in scan rate) thus pointing to an irreversible reaction.

The DPV method was further involved in the investigations in order to study the detection limit and linear concentration range for determination of DA. Figure 12a, b shows two series of DPV measurements carried out in the presence of 1 mM AA with Cu-modified thin (0.5 μm) PEDOT layers at two different amounts of the deposited copper—46 and 86 $\mu\text{g cm}^{-2}$. (The DPV curves shown in the figure correspond to the second measurement at each concentration and remain stable upon further measurements. The first DPV curve measured at given DA concentration usually gives higher currents.) The investigated concentration range of DA covers 6 to 590 μM . In both DPV series, the AA oxidation peak (at about -0.45 V) is strongly suppressed. Figure 13a, b shows the concentration dependence of the peak currents

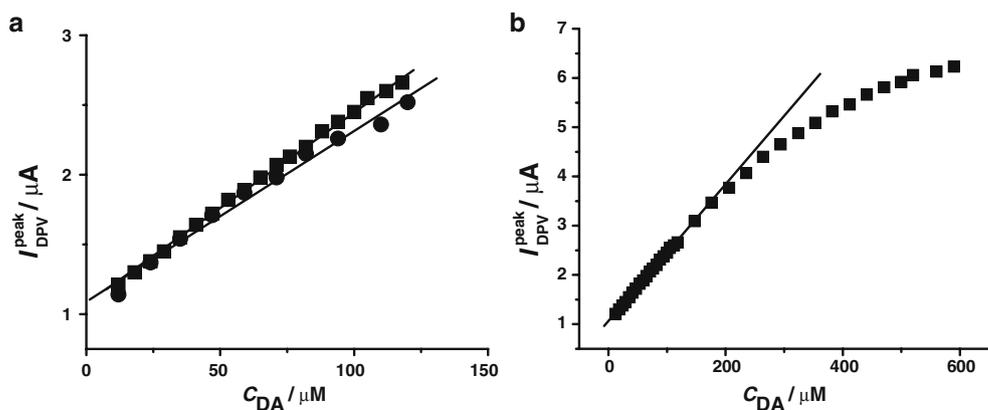
obtained in the different runs. It is seen that the amount of copper does almost not influence the DPV peak currents (compare squares and circles in Fig. 13b). A linear concentration dependence is found in the 6 to about 200 μM concentration range of DA. The sensitivity is $0.013 \mu\text{A} \mu\text{M}^{-1}$. The reproducibility of the results in the linear concentration range is satisfying, and the absolute values of the peak currents differ in the average within 5 % from experimental run to run.

Conclusions

The results presented so far demonstrate the possibility to involve Cu-modified PEDOT-coated electrodes for the selective determination of DA (in the micromolar concentration range) in the presence of excess (millimolar concentration) of AA. The studies carried out with single analytes (AA or DA) reveal some peculiarities of the PEDOT and the Cu-modified PEDOT-coated electrodes:

1. The oxidation currents of both AA and DA depend on the thickness of the PEDOT layers. An increase of the voltammetric peak currents by about 50% for AA and

Fig. 13 Concentration dependence of the DA oxidation peaks obtained in the presence of 1 mM AA in PBS: **a** results from two separate runs in the low concentration range, with different amounts of copper 46 $\mu\text{g cm}^{-2}$ (filled circle) and 86 $\mu\text{g cm}^{-2}$ (filled square); **b** results obtained in a large concentration range with $m_{Cu} = 86 \mu\text{g cm}^{-2}$, $d_{PEDOT} = 0.5 \mu\text{m}$



100% for DA is found when increasing the polymer layer thickness from 0.3 to 4.4 μm . Nevertheless, use of thick PEDOT layers for the DA oxidation results in strong inhibition of the reaction with increasing the concentration and the number of voltammetric scans. The latter effect compromises long series of measurements in the millimolar concentration range of DA.

- Thick PEDOT layers show a linear voltammetric response for AA in the millimolar (0.3 to 6 mM) concentration range and could be considered as a good sensing material for these species.
- The combination of Cu particles with PEDOT results in enhancement of the DA and suppression of the AA oxidation currents. This leads to increased sensitivity with respect to DA in the presence of AA without losing in selectivity (peaks potential resolution).
- Thin (0.5 μm) PEDOT layers modified with electro-deposited micrometer-sized Cu particles show a stable and sensitive response for DA oxidation in the micromolar concentration range. A linear dependence of the voltammetric peak currents is found in a wide concentration range (from 6 to about 200 μM) of DA in the presence of a large excess (1 mM concentration) of AA.

The presented results concerning sensitivity and width of the concentration range for linear DPV response are comparable with the best results obtained by using CP-modified electrodes. Nevertheless other types of electrodes, i.e., carbon ionic liquid electrodes [49], show superior performance in what concerns width of the DA concentration range (from 2 μM to 1.5 mM) for linear response. Moreover, simultaneous determination of DA, AA, and uric acid was demonstrated in human blood serum and urine samples [49]. The Cu–PEDOT electrode used in this study is limited to the micromolar DA concentration range. However, the experiments so far presented are obtained at fixed conditions for copper electrodeposition and do not address the possibility for further optimization of the electrochemical response by influencing the characteristics of the metal deposit. Investigations directed to the elucidation of this aspect of the Cu–PEDOT system and further possibilities to extend the concentration range for DA determination to lower limits are shown in a separate study [42].

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