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Poly(3-methylthiophene)/palladium sub-micro-modified sensor electrode. Part II: Voltammetric and EIS studies, and analysis of catecholamine neurotransmitters, ascorbic acid and acetaminophen

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ABSTRACT

Promising voltammetric sensors based on the modification of Pt and poly(3-methylthiophene) (PMT) electrodes with Pd nanoparticles were achieved for the determination of catecholamine neurotransmitters, ascorbic acid and acetaminophen. Electrochemistry of the indicated compounds was studied at these electrodes and interesting electrocatalytic effects were found. Furthermore, simple, easily prepared one electrochemical step Pd-modified Pt electrode (Pt/Pd) is reported for the first time. Cyclic voltammetry (CV) and chronocoulometry (CC) were used for the determination of the apparent diffusion coefficients in different electrolytes at these electrodes and the values are in the range from 10^{-4} to 10^{-5} cm^2 s^{-1}. Furthermore, it was found that the method of polymer formation had a substantial effect on the synergism between the polymer film and the loaded metal particles towards the oxidation of dopamine (DA) in different supporting electrolytes. This was confirmed by the CV, CC and EIS (electrochemical impedance spectroscopy) as well as SEM (Scanning Electron Microscopy) results. Pt and PMT electrodes modified with Pd nanoparticles showed excellent results for the simultaneous determination of tertiary and quaternary mixtures of the studied compounds.

1. Introduction

Conducting polymers (CPs) are widely employed as coatings conferring the electrode systems antifouling properties and possibly activating electrocatalytic redox processes [1,2]. Among different CPs, PMT showed unusual characteristics towards the determination of catecholamine neurotransmitters compared to commonly used electrodes such as Pt, Au, glassy carbon, and chemically modified electrodes [3,4]. A step forward with respect to 'simple' modification with pristine CPs consist of the inclusion of metal functionalities inside the polymeric matrix, in order to further increase the performances of the resulting composite material. In particular, inclusion of noble metal nanoparticles (NPs), whose catalytic properties are well known [5], constitutes one of the most interesting possibilities. Similar composites based on polypyrrole and polyaniline have been recently reported [6–10]. Polythiophenes/NPs composites are even less studied [11–13]. Among polythiophenes, poly(3,4-ethylenedioxythiophene) (PEDOT) is presumably the most studied one but few recent papers are reported on PMT/NPs composites [14–16] in spite of its interesting properties. Among the reported conducting polymer–metal composites, platinum (Pt) is probably the most studied one. The fabrication and the subsequent characterization of palladium (Pd)-modified CP nanocomposites are not extensively reported in the literature [16,17]. On the other hand, the rate of charge or mass transport associated with redox reactions in modified films is commonly studied by determining the apparent diffusion coefficient (D_{app}) [18].

The development of voltammetric sensors for the determination of catecholamine neurotransmitters and specially dopamine (DA) has received considerable interest during the last few years [15]. They include dopamine (DA), epinephrine (E), and norepinephrine (NE). They play important roles in various biological, pharmacological and physical processes [19]. Recently, attention has been paid to develop a new generation of modified electrodes involving monolayers, conducting polymers and nanoparticles able to solve efficiently the problems encountered in the conventional unmodified electrodes.

Electrochemical impedance spectroscopy (EIS) is an effective technique for probing the features of chemically modified electrodes and for understanding electrochemical reaction rates [20,21]. EIS was used to characterize Pt-modified polyaniline (PAN) film in H_2SO_4 solution [22]. The results showed that compared with the pure polyaniline film|H_2SO_4 solution interface, the deposition of platinum in the polyaniline matrix greatly reduces the electrochemical charge transfer resistance (R_{ct}) in the platinum-modified polyaniline film|H_2SO_4 solution interface.

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In the first part of this work, we have reported the modification of PMT polymer films with Pd particles [16]. In this paper, the electrochemistry of dopamine and other catecholamine neurotransmitters as well as ascorbic acid, acetaminophen and some organic compounds at the Pd nanoparticles modified PMT electrode are considered. Different methods were used for the formation of PMT films and the deposition of Pd nanoparticles. The effect of supporting electrolyte on the electrochemistry of these compounds is addressed as well. CV and CC are used for the determination of the apparent diffusion coefficient values for these compounds at different electrodes and electrolytes as it gives some information about the kinetics of charge transfer during the redox reactions of these compounds. The effect of the method of polymer film formation on the synergism between the polymer film and the subsequently loaded Pd particles is thoroughly studied. CV, CC, SEM and EIS measurements were used to address this point. EIS was used to study the capacitance and resistance of the metal modified polymer composites. Finally, this novel modified sensor electrode is used for the simultaneous detection of tertiary and quaternary mixtures of these compounds.

2. Experimental

2.1. Chemicals and reagents

All chemicals were used as received without further purification. 3-Methylthiophene (distilled under rotary evaporation prior to use) tetrabutyl ammonium hexafluorophosphate (Bu_4NPF_6), acetonitrile (HPLC grade), hydroquinone, catechol, dopamine, epinephrine, norepinephrine, methyl-L-DOPA, p-aminophenol, acetaminophen, ascorbic acid, sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, perchloric acid, sodium sulfate, sodium nitrate, sodium chloride, and sodium phosphate were supplied by Aldrich Chem. Co. (Milwaukee, WI, USA). Palladium (II) chloride was supplied by Scherimg Kaul Paum AG, Berlin, Germany. Aqueous solutions were prepared using double distilled water.

2.2. Electrochemical cells and equipments

Electrochemical polymerization and characterization were carried out with a three-electrode/one-compartment glass cell. Experimental details can be found elsewhere [16]. All experiments were performed at 25 °C.

Electrochemical impedance spectroscopy was performed using a Gamry-750 system and a lock-in-amplifier that are connected to a personal computer. The data analysis software was provided with the instrument and applied non-linear least square fitting with Levenberg-Marquardt algorithm. All impedance experiments were recorded between 0.1 Hz and 100 kHz with an excitation signal of 10 mV amplitude.

2.3. Electrodeposition of the polymer film on Pt electrode and further modification with Pd particles

Two electrochemical methods were employed for the deposition of the polymer film from a solution of 0.05 M 3-methylthiophene and 0.05 M Bu_4NPF_6 in acetonitrile. In the first method (BE method) the potential applied between the platinum disc working electrode and the reference (Ag/AgCl) is held constant at +1.8 V for 30 s (the electrode is indicated Pt/PMT(BE)). The second alternative (CV method) is to vary the potential with time, namely 50 mV s^{-1}, between two potential limits, ca. $E_i = -0.1$ V and $E_f = +1.8$ V for 15 cycles (the electrode is indicated Pt/PMT(CV)).

Further modification with Pd particles involves the following: a polymer film is prepared and washed with doubly distilled water. This was followed by the electrochemical deposition of Pd particles from a solution of 2.5 mM $PdCl_2$ in 0.1 M $HClO_4$ by applying a double potential step (BE) or cyclic voltammetric program (CV) to the polymer. The double potential step conditions are ($E_i = -0.05$ V, $\Delta t_i = 30$ s, $E_f = +0.01$ V, $\Delta t_f = 300$ s). In the cyclic voltammetric (CV) method, on the other hand, the electrode is cycled between −0.25 V and +0.65 V at a scan rate of 50 mV s^{-1} for 25 cycles [16]. Moreover, Pd particles were also deposited directly over Pt electrode.

3. Results and discussion

3.1. Electrochemistry of DA at Pt/PMT/Pd-modified electrodes

Initial studies of the voltammetric behavior of DA were performed using cyclic voltammetry. Fig. 1(A) compares typical cyclic voltammograms of 5 mmol L^{-1} dopamine in 0.1 mol L^{-1} H_2SO_4 recorded at four different working electrodes (i.e. bare Pt, Pt/PMT(BE), Pt/PMT(BE)/Pd(BE), and Pt/PMT(BE)/Pd(CV) electrodes). At bare Pt electrode, a poorly defined oxidation peak was observed at 664 mV whereas at Pt/PMT(BE) electrode the potential shifts negatively to 543 mV. Further, an increase in peak current is also observed due to the improvements in the reversibility of the electron transfer processes and the larger real surface area of the polymer film. The porous structure of conducting polymer allows dispersing the metal particles into the polymer matrix and generates additional electrocatalytic sites [23–25]. The electrodeposition of Pd particles on the polymer film causes a remarkable

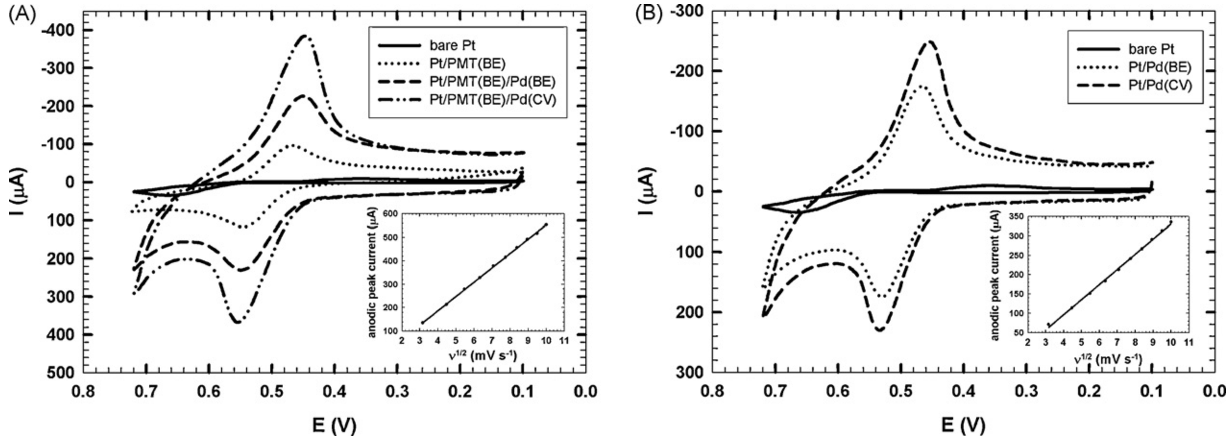

Fig. 1. Cyclic voltammetric behavior of 5 mmol L^{-1} DA/0.1 mol L^{-1} H_2SO_4 at: (A) bare Pt, Pt/PMT(BE), Pt/PMT(BE)/Pd(BE), and Pt/PMT(BE)/Pd(CV) electrodes. (B) Bare Pt, Pt/Pd(BE) and Pt/Pd(CV) electrodes. Scan rate = 50 mV s^{-1}. (Inset: relationship between the square root of scan rate and anodic peak current.)