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New electrode materials based on functionalized polypyrrole

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New functional electrode materials, based on polypyrrole, were prepared by potentiostatic electro-copolymerization of pyrrole with two different pyrrole monomers, functionalized with carboxylic group: 3-(1-pyrrolyl)-propanoic acid and 4-oxo-4(1*H*-pyrrole-3-yl)butanoic acid. The properties of the polymeric electrode materials depend mainly on the synthesis method, monomers ratio, reaction time, and the composition of the supporting electrolyte. The obtained materials were characterized by Fourier transform infrared spectroscopy and cyclic voltammetry measurements. The poly-(pyrrole-co-β-(1pyrrolyl) propanoic acid) copolymer, deposited on the surface of a glassy carbon electrode, was used as anchor for covalent immobilization of Toluidine Blue (TB), by coupling its aromatic amino group (position 3) with the carboxylic groups existing on the modified electrode. The covalent binding of TB onto the functionalized electrode surface results in a stable modified glassy carbon electrode, exhibiting a better electrochemical activity than that corresponding to poly-TB, obtained by TB electropolymerization on the same electrode surface.

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1. Introduction

Conducting polymers, due to their increasing use in the field of enzyme biosensors [1-3], have interesting properties, which make them very suitable for many and different biological, biomedical and analytical applications. Mainly, this kind of polymers can be exploited either as a self-supporting film or, alternatively, incorporated in a composite matrix together with a supporting material, an electroactive compound (redox mediator), and an ionic/molecular recognition receptor. In the last case, these systems are known as modified electrodes, exhibiting attractive electrocatalytic or selective recognition properties.

In recent years, chemical functionalization of conducting polymers has been extensively studied in order to improve their applications for energy storage systems, sensors, electrochemical displays and electrocatalysis. Among conducting polymers, functionalized polypyrrole has attracted a high interest because of the facility of molecular modification of the pyrrole monomer [4, 5]. Moreover, the polypyrrole films are attractive materials for obtaining modified electrode surfaces, due to their easy electropolymerization. In addition, functional groups can be included in the polypyrrole structure, inducing specific properties to the polymer. These new materials show a behavior resulting from the combination of the properties due to the conjugated backbone (electronic conductor properties) and to the presence of the functional group [6].

The main goal of this paper is to present the design and fabrication of two new functional electrode materials consisting of homo- and co-pyrrole polymers, having a carboxylic group attached to the pyrrole ring. A chemical approach involving two steps was used: (i) firstly, in order to obtain functionalized polypyrrole films, suitable pyrrole monomers were synthesized and electropolymerized onto the surface of a bare glassy carbon electrode; (ii) secondly, the compound of interest was covalently coupled, through its reactive group, to the functional groups existing on the electrode surface [7]. Thus, electrochemical copolymerization of pyrrole with 4-oxo-4(1*H*-pyrrole-3-yl)butanoic acid, 3-(1-pyrrolyl)-propanoic acid was carried out on the surface of a glassy carbon electrode, resulting in a modified electrode surface, covered with carboxylic functionalized polypyrrole. Subsequently, Toluidine Blue (TB), through its aromatic amino group (position 3), was covalently coupled to the carboxylic groups existing on the functionalized electrode surface. TB was selected as electroactive compound (redox mediator) because TB-modified electrodes show good electrocatalytic activity useful for amperometric detection of important analytes [8].

Fourier transform infrared (FT-IR) spectroscopy and electrochemical deposition techniques such as cyclic voltammetry, were combined in order to develop and test a more stable TB based glassy carbon modified electrode electropolymerized with functionalized polypyrrole.

2. Experimental

Chemicals. Acetonitrile (ACN), lithium perchlorate ($LiClO_4$), Toluidine Blue (TB), and pyrrole (Py) were purchased from Sigma (St. Louise, USA). 1-(3-

dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride (EDC) was obtained from Aldrich (Steinheim, Germany).

Cyclic voltammetry measurements were performed in phosphate buffer saline solution (0.1 M Na_2HPO_4, 0.1 M NaH_2PO_4, 0.1 KCl; pH 7). For TB immobilization a borate buffer solution (0.1 M H_3BO_3, 0.1 M $Na_2B_4O_7$; pH 9.1) was used. All reagents were of analytical grade. Solutions were prepared with deionized water obtained from a Milli-Q system, preceded by a reverse osmosis step, both from Millipore (Bedford, MA.)

Instrumentation. Cyclic voltammetry and potentiostatic electrolysis experiments were performed in a traditional three electrode system. A platinum wire was used as counter electrode, an Ag|AgCl/KCl_{sat} as reference electrode and glassy carbon as working electrode. All electrochemical experiments were carried out using a BAS 100 (Bioanalytical System, West Lafayette, IN, USA) electrochemical analyzer. The pH of the buffer solution was adjusted using a pH-meter (Radiometer, Denmark) equipped with a combined glass electrode.

Synthesis of monomers. Two different pyrrole monomers, with a carboxylic group placed on 3-position or on N-position, were synthesized. 4-Oxo-4(1*H*-pyrrole-3-yl)butanoic acid (3-Py) was prepared according to the procedure reported in the literature [9-11]. 3-(1-Pyrrolyl)-propanoic acid (N-Py) was synthesized using a procedure based on Blume's method [12]. ^{13}C-NMR spectra, FT-IR spectra confirmed the synthesis of both monomers [13]. The structures of the functionalized pyrrole monomers and the structure of TB are presented in Fig. 1.

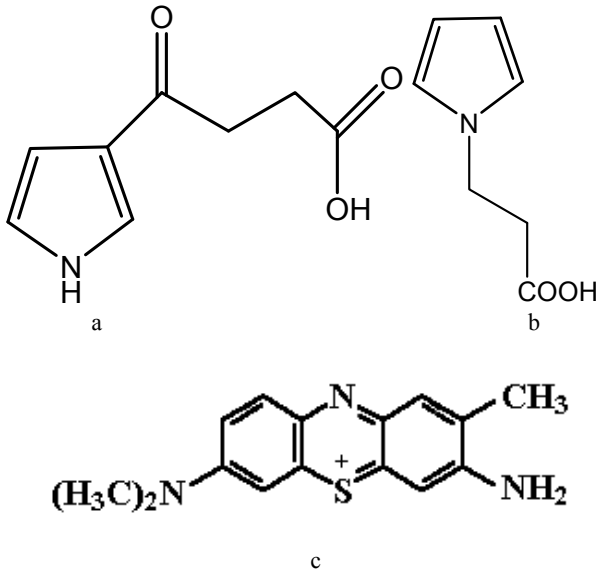

Fig. 1. The structure of pyrrole monomers 3-Py (A), N-Py (B) and TB (C).

Synthesis of homopolymers and copolymer films. Homopolymers [poly-(3-(1-pyrrolyl)-propanoic acid), (N-PPy) and poly-(4-Oxo-4(1*H*-pyrrole-3-yl)butanoic acid), (3-PPy)] and copolymers [poly-(pyrrole-co-3-(1pyrrolyl)-propanoic acid), P(Py-co-NPy) and poly-(pyrrole-co-(4-oxo-4(1*H*-pyrrole-3-yl)butanoic acid), P(Py-co-3Py)] were prepared. Before electropolymerization the solutions were de-gassed by bubbling argon.

The N-PPy and P(Py-co-NPy) were electropolymerized in acetonitrile solution, containing 0.1 M $LiClO_4$ and N-Py and Py monomers, at different concentrations and ratios. The electropolymerization was carried out potentiostatically (+1.08 V *vs.* Ag|AgCl/KCl_{sat}) for different reaction times. The 3-PPy and P(Py-co-3Py) were synthesized at a fixed potential (+0.75 V *vs.* Ag/AgCl/KCl_{sat}) in methanolic solution, containing 1 M H_2SO_4 and 0.1 M $LiClO_4$. After electrolysis all modified electrodes were washed with water. The synthesis parameters are presented in Table 1.

Table 1. Synthesis parameters of homo- and copolymer films.

Sample	Py conc. (M)	Substituted Py conc. (M)	Reaction time (s)
PPY	10^{-2}	0	200
N-PPY	0	10^{-2} (NPy)	200
3-PPY	0	10^{-2} (3-Py)	200
P(Py-co-NPy)1	$2\ 10^{-3}$	10^{-2} (N-Py)	20
P(Py-co-NPy)2	$2\ 10^{-3}$	10^{-2} (N-Py)	200
P(Py-co-NPy)3	$2\ 10^{-3}$	10^{-2} (N-Py)	600
P(Py-co-NPy)4	$6\ 10^{-3}$	$3\ 10^{-2}$ (N-Py)	200
P(Py-co-NPy)5	$2\ 10^{-2}$	10^{-1} (N-Py)	200
P(Py-co-NPy)6	$3.33\ 10^{-3}$	10^{-2} (N-Py)	200
P(Py-co-3Py)1	$2\ 10^{-3}$	10^{-2} (3-Py)	200

Imobilization of Toluidine Blue. Two different approaches were used to immobilize TB on the functionalized polypyrrole films: (a) oxidative electropolymerization; (b) covalent binding.

(a) Electropolymerization of TB was carried out on the surface of predeposited functionalized polypyrrole, according to the procedure previously reported by Karyakin *et al.* [14], by cycling the electrode potential during 20 scans, in the potential range between –0.6 and +0.8 V *vs.* Ag|AgCl/KCl_{sat} (scan rate, 50 mV s^{-1}; borate buffer solution (pH 9.1), containing 0.1 M $NaNO_3$ and 0.4 mM TB).

(b) The covalent attachment of TB was realized by coupling its aromatic amino group (position 3) to the carboxylic groups existing on the electrode surface. After polypyrrole electrodeposition, the functionalized films were washed with ethanol, dried and activated for 1.5 h using a 1% EDC solution in acetonitrile. After washing with 100 mM borate buffer (pH 9.1) the modified electrode was dipped into 0.4 mM TB solution and maintained for 5 h in a dark place.

Finally, careful washing with borate buffer was performed for both types of modified electrodes. The modified electrodes were stored at 4 °C, in a dark place.

3. Results and discussion

The functionalized copolymer films were investigated using cycling voltammetry, performed in a phosphate buffer solution (pH 7). Their cyclic voltammograms were compared to the voltammograms recorded for PPY and N-PPY homopolymers (Fig. 2). From Fig. 2 it can be seen that the copolymer response is intermediate between the responses of the homopolymers, indicating that the functionalized pyrrole monomer (N-Py) was incorporated in the copolymer films. Thus, it can be observed that the P(Py-co-NPy) copolymer films (curves c and d, Fig. 2) show a pair of quasi-reversible redox peaks, placed at +540 and +350 mV *vs.* Ag|AgCl/KCl_{sat}, while the P(Py-co-3Py) (curve e, Fig. 2) presents just an oxidation peak at +680 mV *vs.* Ag|AgCl/KCl_{sat}. For that reason, all further investigations on the effect of synthesis parameters concerned only the P(Py-co-NPy) copolymer.

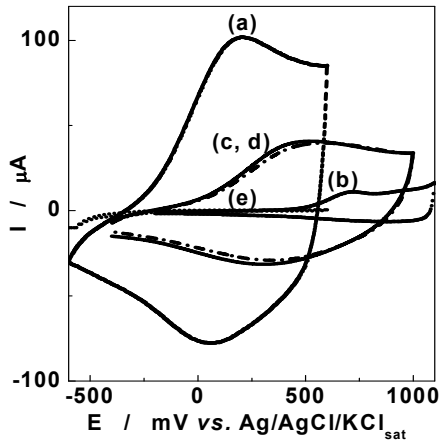

Fig. 2. Cyclic voltammograms of polypyrrole (a), N-Ppy homopolymer (b), P(Py-co-NPy) copolymer with Py:NPy ratio 5:1 (c) and 3:1 (d), and P(Py-co-3Py) copolymer (e). Experimental conditions: scan rate, 100 mV s^{-1}; supporting electrolyte, 0.1 M phosphate buffer (pH 7).

In order to observe the effect of the carboxylic group surface concentration on the voltammetric response of the copolymer film, two different ratios Py:N-Py 5:1 and 3:1 were used. From Fig. 2 (curves c and d) it can be noticed that the ratio between the pyrrole monomer (Py) and the functionalized pyrrole monomer (N-Py) has no significant effect on the electrochemical response of the modified electrodes. Probably, due to some steric impediments, a limitation of the insertion of the functionalized monomer in the copolymer structure occurs. Based on this result, a ratio of 5:1 between Py and N-Py was used in order to obtain copolymer films with good mechanical properties and high conductivity.

The effect of the synthesis conditions, *i.e.* the concentration level of the functionalized monomer and the reaction time, on the electrochemical response of the modified electrode, was examined keeping the ratio between Py and N-Py (Fig. 3) constant (equal to 5).

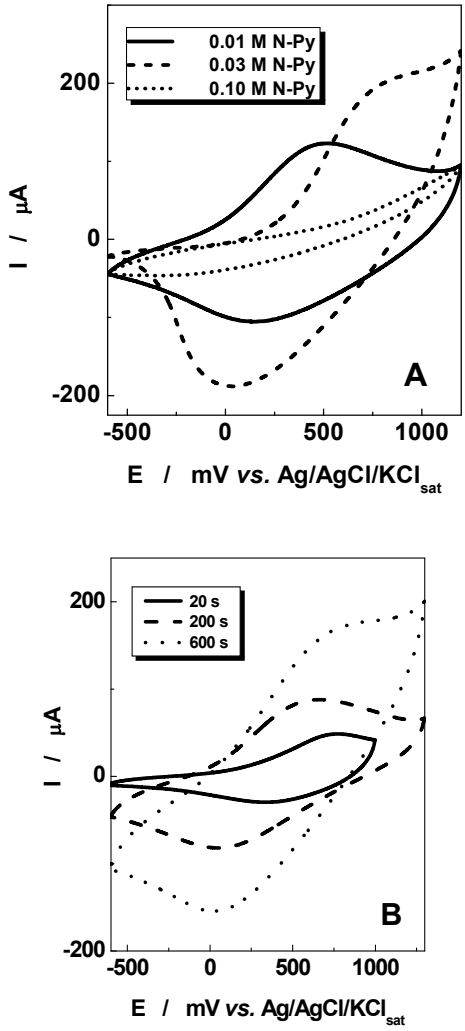

Fig. 3. Cyclic voltammograms of P(Py-co-NPy) copolymers: (A) different concentrations of monomers and (B) different polymerization times. Experimental conditions: scan rate, 100 mV s^{-1}; [Py]/[N-Py] = 5; supporting electrolyte, phosphate buffer, pH 7.

Based on the voltammetric response recorded for the modified electrodes obtained in different experimental conditions, the optimal parameters for the electrosynthesis of P(Py-co-NPy) copolymer films were: the concentrations of the monomers were; 10^{-2} M N-Py and 2 10^{-3} M Py and the reaction time was 200 s.

In order to confirm the formation of the P(Py-co-NPy) copolymer films on the glassy carbon electrode surface, Fourier transform infrared (FT-IR) spectroscopy measurements were used. FT-IR spectra recorded for N-PPy and P(Py-co-NPy), obtained using different ratios [Py]/[N-Py] are presented in Fig. 4.

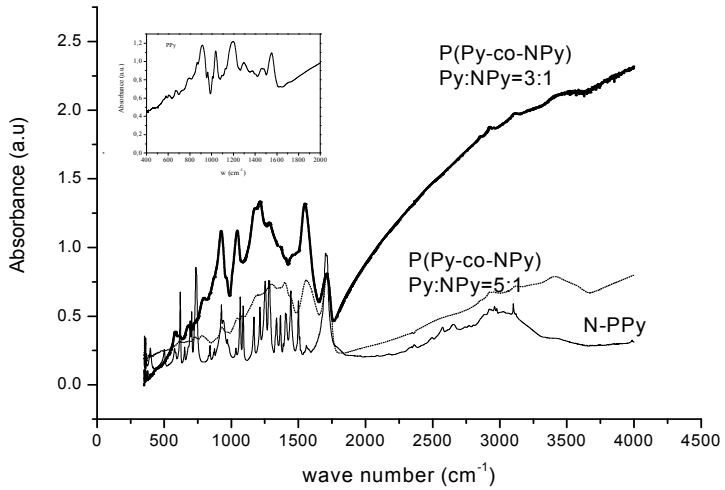

Fig. 4. FT-IR spectra for N-PPy and P(Py-co-NPy), obtained using [Py]/[N-Py] ratios of 3:1 and 5:1. Inset: IR spectra of PPY.

In Table 2 are presented the positions of the characteristic bands of the PPy, the N-PPy homopolymers and the P(Py-co-NPy) copolymer [15].

Table 2. The position of the absorption bands for homopolymers and copolymers.

PPy* ν (cm^{-1})	N-PPy ν (cm^{-1})	P(Py-co-NPy) ν (cm^{-1})		Characteristic vibrations
		3:1	5:1	
3440	3422	3443	3409	N-H and –OH-
-	1717	1710	1715	-C=O-
1552	-	-	-	C=C/C-C streaching
1465	1440	1543	1560	Ring breathing with contribution from C=C/C-C and C-N
1294	-	-	-	C-H in plane bending
1198	1251	1214	1295	Ring breathing
1037	-	-	-	C-H in-plane bending
914	-	-	-	Ring deformation
790	738	925	923	Ring deformation

*from ref. [14]

The band located at 1717 cm^{-1} in the spectrum of N-PPY, is characteristic to the –C=O- group and appears around the same value in the spectrum of P(Py-co-NPy). When the ratio [Py]/[N-Py] was 3:1, the band ascribed to the –C=O- group was more intense than that observed for the copolymer obtained with a ratio of [Py]/[N-Py] = 5:1. This finding suggests a higher density of carboxylic groups on the surface of the copolymer films. The copolymer spectrum shows significant changes for the intensity and the peaks position characteristic of the vibration of the Py ring. The position of these bands is correlated with the conjugation length of the polymer chain and the shift to higher frequencies indicates a decrease of the conjugation length for the copolymer, as compared to homopolymers [16**]**.

Toluidine Blue was immobilized on the surface of the polypyrrole modified electrode either by electro-polymerization or by covalent binding through its amino group.

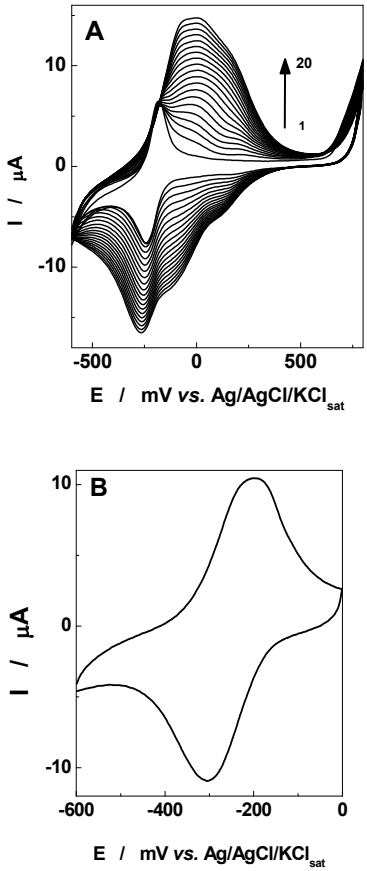

Fig. 5. Cyclic voltammograms corresponding to electropolymerized TB (A) and to the voltammetric response of TB covalently attached to P(Py-co-NPy) (B). Experimental conditions: scan rate, 50 mV s^{-1}; supporting electrolyte, (A) borate buffer (pH 9.1) and (B) phosphate buffer (pH 7).

Fig. 5A shows the cyclic voltammogram corresponding to the TB electropolymerization, performed by cycling the electrode potential during 20 scans, in the potential range between –0.6 and +0.8 V *vs.* Ag|AgCl/KCl_{sat}. In can be seen that, in the first cyclic voltammogram, the anodic peak is placed at –185 mV *vs.* Ag|AgCl/KCl_{sat} and the cathodic peak is located at –245 mV *vs.* Ag|AgCl/KCl_{sat}. This redox peaks pair was attributed to the redox activity of the monomeric form of TB. The peak currents intensities increase continuously during the successive potential scanning, indicating the continuous growing of the conducting poly-TB on the electrode surface. Unfortunately, when TB was immobilized by electropolymerization on the electrode surface, the resulting modified electrode exhibits a relatively unstable voltammetric response. Thus, after multiple electrode potential cycling in buffer solution, the color change in the electrode proximity proves that TB partially migrates in the electrolyte solution.

Fig. 5B shows the cyclic voltammogram of the modified electrode obtained after covalent attachment of TB through its aromatic amino group (position 3) and the carboxylic groups covering the electrode surface, activated by EDC. The pair of redox peaks of the TB covalently attached on P(Py-co-NPy) is similar with that recorded for electropolymerized TB (Fig. 5A): the anodic peak is located at -196 mV *vs.* Ag|AgCl/KCl_{sat} and the cathodic peak at -305 mV *vs.* Ag|AgCl/KCl_{sat}. This behavior suggests that in both cases, TB exists on the surface of the functionalized polypyrrole. Moreover, in the case of covalently bound TB the redox peak pair is better defined and the redox process involved in the electrode response is more reversible (smaller peak split) as compared with the electropolymerized TB.

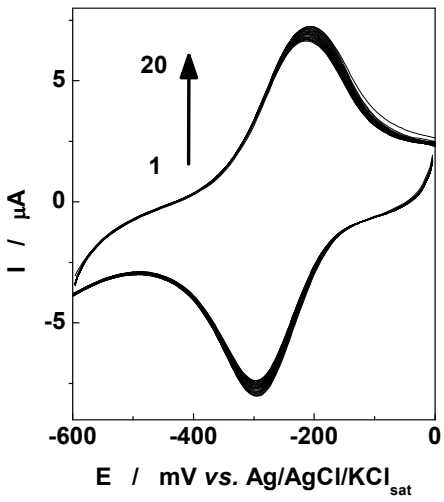

Fig. 6. Cycling voltammograms corresponding to the GC/P(Py-co-NPy)-TB modified electrode. Experimental conditions: scan rate, 100 mV s^{-1}; supporting electrolyte, 0.1 M phosphate buffer, pH 7.

As compared to the electropolymerized TB, the covalently immobilized TB on the functionalized polypyrrole surface results in a more stable electrode. Figure 6 shows the voltammograms corresponding proving the electrochemical stability of the covalently attached TB on the functionalized polypyrrole electrode surface [GC/P(Py-co-NPy)-TB]. Thus, by cycling the GC/P(Py-co-NPy)-TB modified electrode in phosphate buffer, no significant modification in the position and intensity of the peaks pair was observed. This indicates that, due to the covalent linkage formed between TB and the carboxylic group of the functionalized polypyrrole, a modified electrode with a high stability was obtained.

Work is in progress in order to prove the versatility of this method for immobilization of other redox mediators and to test their electrocatalytic effect for amperometric detection of important analytes for biomedical and biotechnological applications.

4. Conclusion

Two new modified electrodes based on copolymer films, containing pyrrole and functionalized pyrrole monomers were obtained. In order to optimize the copolymer preparation, the influence of the synthesis parameters on the electrochemical response, recorded for the corresponding modified electrodes, was investigated. The poly-(pyrrole-co-β-(1pyrrolyl) propanoic acid) copolymer, deposited on the surface of a glassy carbon electrode, was used as an anchor for covalent immobilization of Toluidine Blue (TB), by coupling its aromatic amino group (position 3) with the carboxylic groups existing on the modified electrode. The covalent binding of TB onto the functionalized electrode surface results in a stable modified glassy carbon electrode, exhibiting a better electrochemical activity than that corresponding to poly-TB, obtained by electropolymerization of TB on the same electrode surface.

Acknowledgments

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