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Electrosynthesis and properties of poly(3-methylthiophene-pyrrole) composites

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ABSTRACT

Poly(3-methylthiophene/overoxidized pyrrole) (PMT/OPPy) composites were electrochemically prepared by simultaneous polymerization of 3-methylthiophene and pyrrole, which were added together at a 10:1 concentration ratio into a non-aqueous medium (acetonitrile). The films were characterized by cyclic voltammetry, spectroscopic (FTIR, UV-VIS, and photocurrent) and current-voltage measurements, and with atomic force microscopy (AFM). The PMT/OPPy films exhibited intermediate characteristics than those seen for the homopolymers, OPPy and PMT, but with PMT as the predominant element of the PMT/OPPy composition. Optical, morphological, and electrical properties of the OPPy, PMT, and PMT/OPPy films were compared aiming toward application in optoelectronic devices and sensors.

KEYWORDS

Composites; conducting polymers; optoelectronic devices; polypyrrole

Introduction

Conjugated polymers have been applied in sensors and optoelectronic devices mainly because they are easily solution-processed allowing one to produce large area displays with tunable optoeletronic properties [1,2]. These polymers have been usually prepared as thin films by electrochemical methods of synthesis, allowing one to combine favorable mechanical, optical, and electrical properties.

The possibility of combining properties of interest by using two or more conjugated polymers has aroused interest in composites, such as polyaniline-polypyrrole [3], polypyrrole-functionalized polypyrrole [4], and polypyrrole-polythiophene [5,6]. The current for the oxidation of pyrrole and thiophene has been controlled during the electrosynthesis at lower concentrations of pyrrole (when compared with that of thiophene). This protocol is a useful approach for obtaining films at oxidation potentials far apart from those of each individual monomer, and under milder conditions. Among the composites of interest, it should be mentioned as poly(3-methylthiophene) polypyrrole) (PMT/PPy), which can be obtained by simultaneous electrosynthesis of PMT and PPy.

PPy is stable in the doped (conducting) form, and can be electrochemically prepared at relatively low potentials in aqueous or non-aqueous media [7,8]. A specific type of PPy has also been electrochemically prepared, so-called overoxidized PPy (OPPy), which behaves as

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a non-conducting, ion-exchange permselective membrane in biosensors aiming at preventive approach of interfering species [9]. PMT films, on the other hand, have been usually electrochemically obtained at high positive potentials in non-aqueous media [10,11]. Due to many favorable characteristics, such as adhesive properties, and absorption coefficient, electrical conductivity as well as stability in air, PMT has been frequently applied as active layer in photodiodes and photovoltaic devices [11,12]. Our contribution here was to prepare and characterize PMT/OPPy composites by comparing properties with those from the homopolymers, PMT and OPPy films.

Experimental

All electrochemical experiments were carried out by using a VersaStat II PAR potentiostat/galvanostat, a three-electrode glass cell with an Ag/AgCl reference electrode, and a Pt plate as the counter electrode. Saturated calomel electrode (SCE) was also used as reference when in aqueous solutions. The OPPy, PMT, and OPPy-PMT films were electrochemically obtained on Pt or ITO working electrodes (plates with 1.0 cm^2). The ITO electrodes were cleaned in ultrasonic bath in ethanolamine (20% v/v) for 30 min, aqua regia for 10 min, and then, isopropanol at 80 °C for 15 min; after that, they were dried with nitrogen.

The films were electrodeposited at a fixed potential in acetonitrile containing 0.05 mol L^{-1} tetrabutylammonium perchlorate (TBAP), and similar results were obtained in acetonitrile and 0.1 mol L^{-1} $NaClO_4$. The monomer concentrations were chosen as 0.1 mol L^{-1} 3-methylthiophene (or pyrrole) for the preparation of PMT (or OPPy) films, and 0.1 mol L^{-1} 3-methylthiophene and 0.01 mol L^{-1} pyrrole (10:1 composition) for the preparation of PMT/OPPy films. The amount of water in acetonitrile was 32 ppm before adding molecular sieves treated at 300 °C–400 °C for at least 24 h before use. All films were dedoped by applying a reduction potential of −0.2 V for 5 sec before proceeding with any electrochemical experiment.

The films were used as active layers in photodiodes by fabricating a single-layer configuration: ITO/PPy/Al, ITO/PMT/Al, and ITO/PMT/OPPy/Al. Al overlayers with 100 nm of thickness were vacuum evaporated on the top of the polymer films, which were previously electrodeposited on ITO electrodes. Current density vs. voltage (*J*–*V*) curves were obtained with a Keithley 2400 picoamperimeter/voltage source. The photocurrent spectra (current density vs. wavelength) were obtained under illumination with a Xenon lamp 450 W model 69921 (Thermo Oriel) connected to a Thermo Oriel 69920 monocromator in a vacuum chamber.

Fourier transform infrared spectroscopy (FTIR) and Ultraviolet–visible spectroscopy (UV-VIS) measurements were carried out using a Nexus 470 FT-IR spectrophotometer and a U-2001 Hitachi UV-VIS spectrophotometer, respectively. Atomic force microscopy (AFM) micrographs were acquired in a Digital Inst. Nanoscope 3A multimode microscopy in the tapping mode for films obtained at 1.8 V in acetonitrile and 0.1 mol L^{-1} $NaClO_4$. The images were analyzed with Digital Inst. Software.

Results and discussion

The strategy used here for preparing uniform, stable poly(3-methylthiophene)-overoxidized polypyrrole (PMT/OPPy) films was to apply, for a short polarization time (10 sec), a fixed potential of +2.1 V, which showed to be a potential value high enough to oxidize both monomers, pyrrole (which, in particular, becomes overoxidized at this value of potential), and 3-methylthiophene. Individually, we verified that the oxidative polymerization of pyrrole

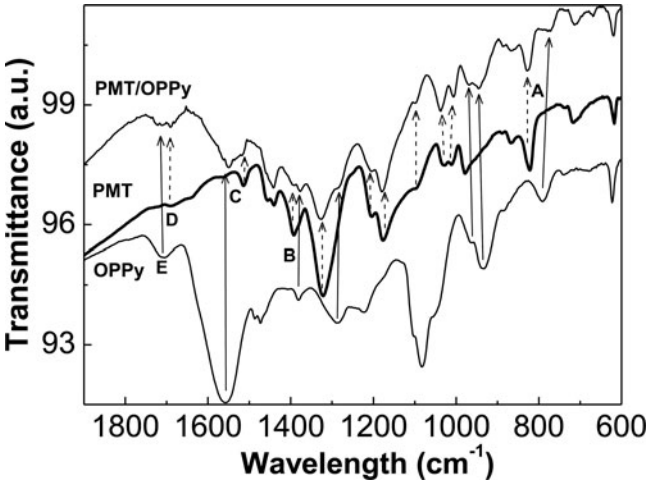

Figure 1. Infrared spectra for the PMT/OPPy, PMT, and OPPy films.

in a non-aqueous medium (acetonitrile) initiates at 0.6–0.8 V, and of 3-methylthiophene, at 1.4–1.8 V.

Applied potentials as higher as +1.8 V or +2.1 V yielded, at the end of the experiment, uniform and visibly thick films, with both overoxidized PPy and PMT contributing to the formation of the PMT/OPPy film, as it will be shown in a step further. As related to the concentration of pyrrole, we selected a value 10 times lower than that of 3-methylthiophene. In this case, at this concentration ratio, the current decayed exponentially under anodic polarization, indicating a diffusion-controlled process for polymerization of pyrrole, meanwhile 3-methylthiophene is continuously oxidized at the electrode/solution interface.

The FTIR spectra of the OPPy, PMT, and PMT/OPPy films are shown in Fig. 1.

There are remarkable differences in the spectrum of the PMT/OPPy film (obtained at +2.1 V) by comparing to those obtained for the OPPy and PMT films. Two most noticeable features are marked as A and B in the spectra of PMT/OPPy (Fig. 1) at about 800 cm^{-1} and 1400 cm^{-1}. The peaks (in A) appear isolated at 774 cm^{-1} and 827 cm^{-1} for the OPPy and PMT films, respectively, and together, at 791 cm^{-1} and 822 cm^{-1} for the PMT/OPPy film. The first peak can be assigned to α-substituted five member heterocyclic compounds, such as in PPy [13], and the second one, to out-of-plane C-H bending of thiophene rings [14]. In B, two peaks can be noticed in the spectrum of the PMT/OPPy film, at 1376 and 1392 cm^{-1}; but, for the OPPy and PMT films, they appear separately at 1381 and 1392 cm^{-1}, respectively, as assigned to the bond deformations of -CH_3 groups from PMT and -C-H groups from PPy. Additional peaks can be assigned to the presence of both PPy and PMT incorporated in the PMT/OPPy structure, and they are defined in Fig. 1 by the letters B, C, and D. Overoxidation of a PPy structure can be confirmed in both spectra, for the OPPy and PMT/OPPy films, due to the presence of a band at 1700–1710 cm^{-1} (letter E in Fig. 1), which is assignable to carbonyl groups in OPPy [15].

Figure 2 shows the voltammetric responses of the OPPy, PMT, and PMT/OPPy films in a monomer-free solution; these films were obtained at the same applied potential (+2.1 V) and polymerization time (10 sec). The voltammetric responses of the PMT and PMT/OPPy films are very close, indicating that PMT can be considered as the predominant element of the PMT/OPPy composition. Besides, higher values of current were noticed for the PMT/OPPy film due to a higher redox activity.

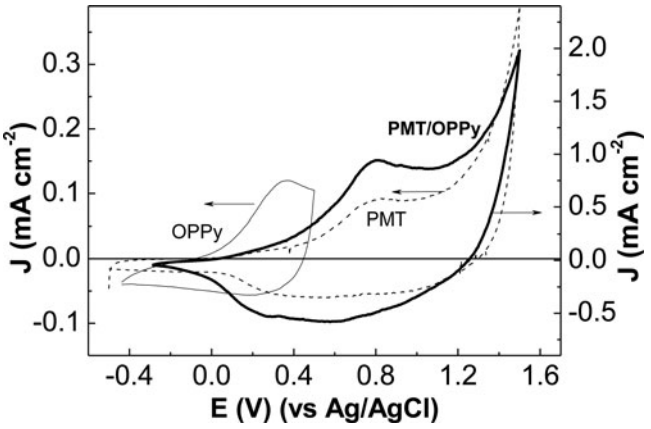

Figure 2. Cyclic voltammograms for the OPPy, PMT, and PMT/OPPy films in 0.1 mol L^{-1} tetrabutylammonium perchlorate in acetonitrile; scan rate = 30 mV s^{-1}.

The anodic polarization of polymer films, such as PPy, in a monomer-free solution can be explained in terms of anion incorporation into the film structure, which yields a swelled structure under positive potentials. Following a reverse cathodic polarization, expulsion of anions takes place toward the electrolyte solution, when the film structure becomes shrink, more compact. The presence of a broad anodic peak in Fig. 2 indicates a relatively slow process of anion incorporation into the films (*p*-type doping). This process is followed by a less effective movement of anions leaving the films in order to keep electroneutrality for densely packed, compact films, which, therefore, also explains why small currents are seen in the reserve, cathodic scan.

The films studied here showed to be unstable at negative ranges of potentials, that does not allows one to directly measure the values of reduction potentials (E'_{red}). However, from the values of E'_{ox} (oxidation potential onset), it was possible to estimate the values of ionization potential (IP) for these films, following a methodology described in the literature [16]. The values of IP were correlated directly to the values of electron affinity, EA, by means of an empirical relationship based on both theoretical and experimental approaches (effective valence shell Hamiltonian calculations and electrochemical measurements): IP = (E'_{ox} + 4.4) eV, and EA = (E'_{red} + 4.4) eV, where E'_{ox} and E'_{red} are onset potentials for oxidation and reduction, and taken from cyclic voltammetry experiments [17]. When the values of E'_{red} cannot be experimentally measured, it is a common practice to estimate the values of EA from subtracting the values of band gap, E_g [18,19]. However, the values of E_g may vary considerably, according to the method used for their calculation, types of samples, and media used; besides, if these values are either optically (from absorbance measurements) or electrochemically measured, they can be truly different [20]. The values of IP for OPPy, PMT, and PMT/OPPy were estimated taking into account data from Fig. 2, and they are also shown in Table 1.

Table 1. Oxidation potential onset (E'_{ox}), energy gap (E_g), ionization potential (IP), absorption onset (λ′), and electron affinity (EA) for the OPPy, PMT, and PPy/PMT films.

	OPPy	OPPy/PMT	PMT
E'_{ox} (V)	0.07	*0.36*	0.43
E_g (eV)	2.10 ± 0.01	*1.92 ± 0.02*	1.96 ± 0.01
IP (eV)	4.47	*4.76*	4.83
λ′ (nm)	589 ± 5	*646 ± 8*	632 ± 2
EA (eV)	2.56 ± 0.07	*2.95 ± 0.05*	3.08 ± 0.04

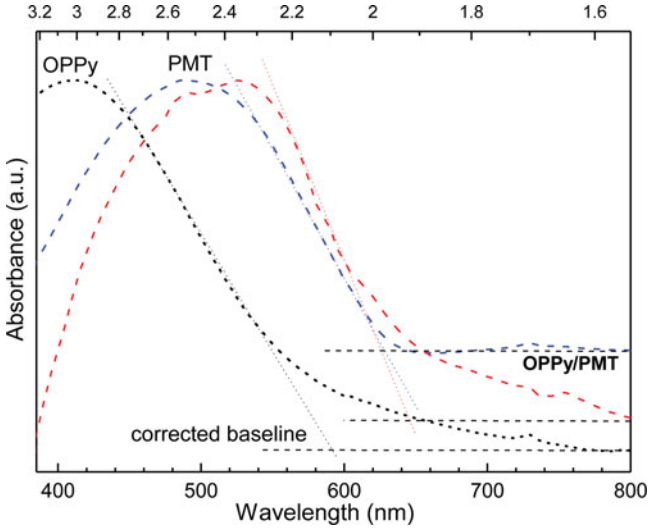

Figure 3. UV-VIS spectra for the OPPy, PMT, and OPPy/PMT films.

Figure 3 shows the UV-VIS spectra for the OPPy, PMT, and PMT/OPPy films, where it can be seen a unique, strong, broad band at 410 nm, 490 nm, and 527 nm, respectively, due to a typical π–π^* transition of conjugated polymers. The absorption onsets (λ_{edge}) were determined for these films from the cross points of the absorption onset line with the corrected baselines (see dashed lines in Fig. 3). The values for λ_{edge} were converted to the optical bandgap (E_g), in eV, as shown in Table 1, and they are an agreement with the values of bandgap theoretically calculated for PPy and PMT [21–23]. Table 1 summarized the results obtained, which clearly reveal that the optical parameters for the PMT/OPPy film are intermediate from those obtained for the OPPy and PMT films.

The films were also prepared by using a single-layer ITO/polymer/metal photodiode configuration: ITO/PPy/Al, ITO/PMT/Al, and ITO/PMT/OPPy/Al. Figure 4(a) shows the current–voltage (*J*--*V*) curves recorded in the dark; the photocurrent spectra were obtained under illumination from the top side (ITO electrode side), Fig. 4(b).

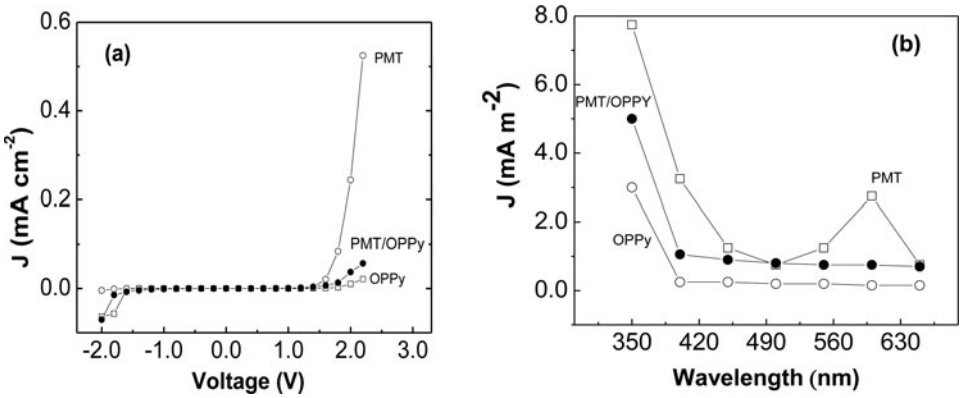

Figure 4. (a) *J*–*V* and (b) *J*-wavelength curves for the ITO/OPPy/Al, ITO/PMT/Al, and ITO/ OPPy/PMT/Al devices.

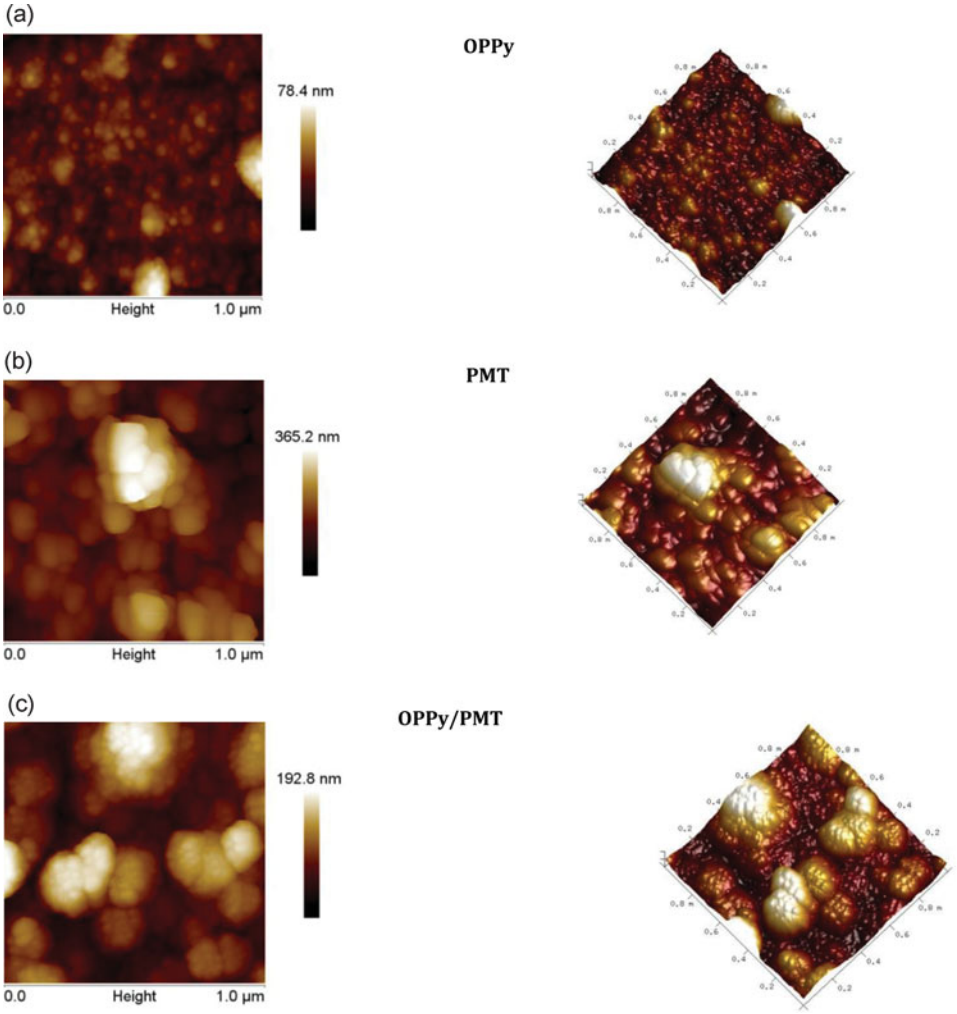

Figure 5. AFM images for the (a) OPPy, (b) PMT, and (c) OPPy/PMT films.

In the *J*–*V* curves, it was obtained a zero-current region from −1.5 V to +1.5 V, and a current, which sharply increased in the forward bias, in particular for the PMT film. Corroborating the results reported here, these data indicated that the PMT/OPPy film exhibits an intermediate behavior between those seen for the homopolymer films, PPy and PMT, joining properties that are interesting for potential application in devices and display applications.

The atomic force microscopy (AFM) images for the OPPy, PMT, and OPPy/PMT films are shown in Fig. 5 with different morphologies according to data from Table 2.

The root mean square (RMS) roughness for the OPPy/PMT film was 35.80 nm, which is intermediate value between those obtained for the OPPy film, 9.52 nm, and the PMT film,

Table 2. AFM parameters obtained for the OPPy, PMET, and OPPy/PMT films.

	OPPy	PMT	OPPy/PMT
Root mean square (RMS) roughness	9.52	57.30	35.80
Occupied/total area ratio (%)	8.33	51.80	29.40
Grain morphology (nm)	39.88 ± 0.10	113.64 ± 0.50	210.21 ± 0.30

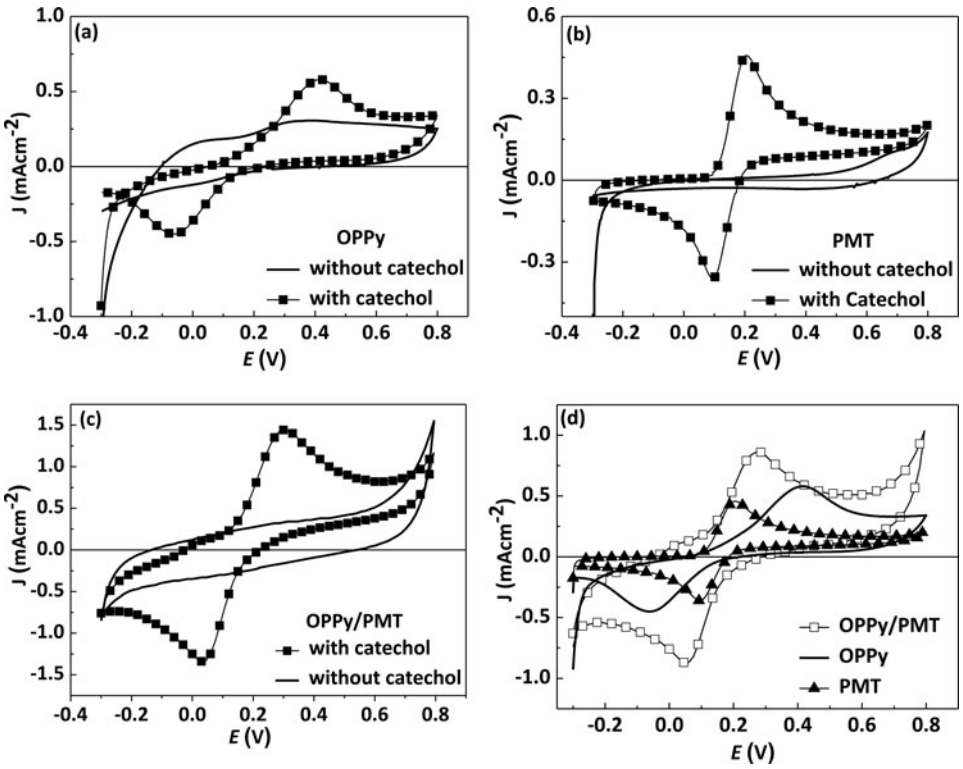

Figure 6. Cyclic voltammograms for: (a) OPPy, (b) PMT, and (c) OPPy/PMT films in phosphate buffer solution, pH 7.0, without and with 0.1 mol L^{-1} catechol; scan rate = 50 mV s^{-1}; (d) comparative results.

57.30 nm. In the first case, Table 2 indicates that smaller grains are distributed uniformly over the surface of the OPPy film; for PMT films, they appear as larger grains (higher surface area), and for the OPPy/PMT film, as agglomerates with different grain sizes (higher grain morphology). The analysis in Table 2 also provides the values of occupied area and total area ratios, and grain morphology.

The films were also analyzed in the presence of a phenolic compound aiming at biosensor application. The voltammetric responses of the PPy, PPy/PMT, and PPy/PMt films were obtained in phosphate buffer solution, pH 7.0, without and with the presence of 0.1 mol L^{-1} catechol (Fig. 6) up to reach a lower positive potential, +0.8 V, in a blank solution (without adding the monomer).

All films showed better current signals when in the presence of catechol; and for the OPPy/PMT film, it is evident how the current signal increases and has intermediate values than those seen for the OPPy and PMT films. The redox process seen in Fig. 6 indicates the reversible oxidation and reduction process of catechol between −0.2 V and +0.8 V, and it seems an interesting response when biosensors are aimed to be fabricated.

Conclusions

The electropolymerization of 3-methylthiophene and pyrrole at high positive potentials on ITO and Pt electrodes yields an overoxidized PPy structure in a composite with a predominant PMT. Since the concentration of 3-methylthiophene was higher than that of pyrrole (10:1), the electrochemical oxidation of 3-methylthiophene predominates for defining the PMT/OPPy

composition, as it was verified by using spectroscopic techniques (FTIR and UV-VIS). The PMT/OPPy film exhibited a higher average energy band gap than that measured for the PMT films. The search for novel polymer materials indicates that all these steps of characterization are helpful, although changes made such as oxidation potentials applied during the electrosynthesis and, also, composition of each comonomers, may yield differences in their optical and morphological properties.

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