

ELECTROCHEMICAL AND SURFACE CHARACTERIZATION OF COMPOSITE MATERIAL: POLYMER/ TiO₂ AND THIS APPLICATION

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RÉSUMÉ

In the present work, a composite material was electrochemically synthesized. This composite material was containing the monomers (terthiophene, sexithiophene) and semiconductor (TiO₂) particles, films obtained from (3T+6T) and titanium dioxide (TiO₂) at a platinum electrode or ITO glass electrodes (SOLEMS). The so obtained films were characterized using cyclic voltamperometry (CV), measurement, UV-visible, EDX, SEM to study their electrochemical properties. These modified electrodes can be used in various applications, such as light emitting diodes (LEDs) and photoelectrochemical applications such as the photovoltaic cells..

Keywords: composite materials, conducting polymer/semiconductor, cyclic voltamperometry (CV).

1. INTRODUCTION

Conducting polymer/semiconductor hybrids represent a novel class of materials for low-cost photovoltaic devices. The combination of p-type conducting polymers and n-type semiconductors is advantageous for the separation of the charges generated under illumination due to high electron affinity of the inorganic semiconductor and the relatively low ionization potential of the polymer [1-4].

Organic/inorganic polymer composite materials show a wide range of attractive potentialities to introduce original structural design in material sciences and to develop innovative derivative functions for device applications. Particularly, a hybrid associating an electronic conducting polymer and a semiconductor metal oxide is one of the most advantageous combinations for photo-electronic devices, including photovoltaics [5-7]

Most of the composite materials are based on TiO₂, which is chemically stable and has a long life-time of electron-hole pairs generated by optical excitation. At present, conductive polymers such as polyaniline and polypyrrole (PPy), polythiophene (PTH) [6-11], have attracted considerable attention due to their high absorption coefficients in the visible part of the spectrum, high mobility of charge carriers, and good environmental stability. Moreover, many conductive polymers are efficient electron donors and good hole transporters under visible light excitation. Therefore, conductive polymers are used as photosensitizers to modify TiO₂ nanoparticles and replace the dyes.

2 Experimental

In this study, dichloromethane (CH₂Cl₂) is used as solvent. The supporting electrolyte used is tetrabutylammonium perchlorate (TBAP) (Fluka product), which is a pure salt for analysis. This electrolyte is chosen because of its solubility in organic and aqueous solution, and of its electrochemical stability on a large

domain of potential. The reagents (Aldrich product) are: titanium dioxide (TiO_2) 99.9%, powder, as doping semiconductor, and terthiophene (3T),sexithiophene (6T) with 98% purity as monomer

3 Instrumentations

All the electrochemical measurements (cyclic voltammetry and electrochemical impedance spectroscopy) were performed with a Voltalab 402 type PGZ from RADIOMETER Analytical, coupled with a computer equipped with a software (voltmaster 4) which makes it possible to select the electrochemical technique and to fix the desired parameters.

A three electrodes cell was used to carry out electrochemical experiments: platinum working electrode (diameter 2mm), was used as working electrode for the deposition of composite: (P3T+6T+ TiO_2) films. For photoelectrochemistry and UV-vis characterization, ITO coated glass electrodes (SOLEMS) were used as working electrodes (surface of 2 cm^2), a platinum wire served as an auxiliary electrode, and a saturated calomel electrode (SCE) as reference and all the potential values referred to this electrode.

UV-vis spectroscopy measurements were performed on a SHIMADZU UV- spectrophotometer UV-1800, Japan, coupled with UV Probe software. AFM images were taken out using an apparatus Pico Scan 5.3 from Molecular Imaging. Scanning electron microscopy (SEM) and EDX measurements were carried out with a ZEISS ultra 55 microscope, the operating voltage used is 1 KV. The apparatus is coupled with energy dispersive X-ray spectroscopy (EDX). The EDX parameter are HV:10 KV and pulx:12.84 kcps. Were cps is the current gross count rate. The photoelectrochemical experiments were performed by used for cyclic voltammetry in a three electrode configuration cell at room temperature. The polymer and composite films were irradiated though the ITO side (substrate/electrode interface.). The cell was placed in a home-made optical bench consisting of a 100 mW cm^{-2} lamp polychromatic.

4 Results and discussion

a Electrochemical polymerization of composite material (P3T+6T) + TiO_2

Fig. 1 displays the electropolymerization of (terthiophene+sexithiophene) in the above mentioned conditions but in presence of TiO_2 . The formation and growth of composite material (P3T+6T)+ TiO_2 film. The oxidation peak of the film was slightly shifted to 1.48 V, indicating that the polymer hosts titanium oxide (TiO_2) particles which trapped in the polymer matrix during the electropolymerization process.

This is confirmed also by the increase of the courant intensity of oxidation and reduction of peaks with the increase of TiO_2 content (10^{-4} , 5.10^{-4} , 10^{-3} , 5.10^{-3} , 10^{-2} M) as shown in fig.1. The recording of the first voltammogram of each concentration at the platinum electrode, which was cleaned before each record and in presence a slight stirring, was carried out for a better homogeneity of the solution before each handling. Thus, during the positive potential scan, an anodic shoulder is observed at 1.48 V/SCE, which is characteristic of the terthiophene oxidation. So, during the negative potential scan, two waves located at 0.6 and 0.8 V/SCE are observed, attributed to the reduction of the formed polymer. The oxidation and reduction waves are seen to shift slowly towards higher voltages, when the TiO_2 is added to the solution [12, 13]. This confirms that the presence of TiO_2 influences the electrochemical behavior of terthiophene and sexithiophene, mainly on the kinetics of the process of polymer deposition on the electrode. So, the TiO_2 containing (P3T+6T) film grows faster compared to that obtained in the case of pure (P3T+6T) film formation.

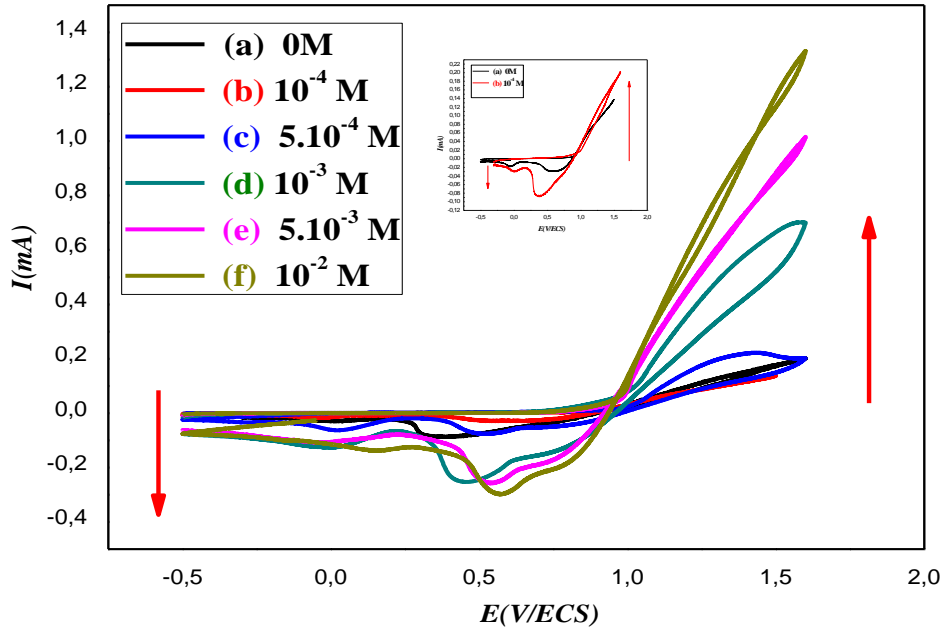


Figure 1 : Cyclic voltammograms during the polymerization of a composite film in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ (10^{-1} M) aqueous solution obtained for different concentrations of TiO_2 ($C = 0, 10^{-4}, 5 \cdot 10^{-4}, 10^{-3}, 5 \cdot 10^{-3}$ and 10^{-2} M), obtained with scan rate of 10 mV/s, over a potential range of -0.3 to 1.6 V/SCE by using a Pt electrode ($\varnothing = 2$ mm).

b UV-Vis spectroscopy of the modified P3T/ITO and (P3T+TiO₂)/ITO electrode¶

Fig. 2 shows UV-Vis absorbance spectra of (P3T+6T) and (P3T+6T) +TiO₂ films. For all the films, the peak at 453 nm is attributed to a $\pi \rightarrow \pi^*$ transition of the conjugated polymer [14]. The results for (P3T+6T) composite films containing different TiO₂ concentrations shows that addition of TiO₂ nanoparticles improves the absorbance. The increase in absorbance can be attributed to an increase in the active surface layer by introduction of TiO₂ nanoparticles. As a result, the (P3T+6T) +TiO₂ films have slightly broader absorbance peaks. This is in agreement with previous results reported by other researchers for composites based on (P3T+6T) [15]

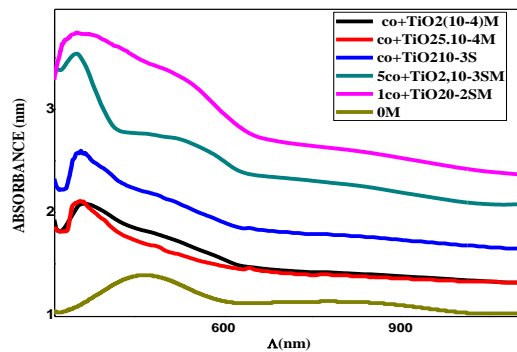


Figure 2: UV–visible absorbance spectra of (P3T+6T)/ITO and ((P3T++6T)+TiO₂)/ITO films, obtained for various contents of TiO₂ (0, 10⁻⁴, 5.10⁻⁴, 5.10⁻³, 10⁻³ and 10⁻² M).

c Morphological characterization of the (P3T+6T)/and composites film (P3T+6T)/TiO₂ by SEM and EDX

The SEM analysis revealed the morphology of the apparent surface of (P3T+6T) film electrodeposited on a ITO electrode, impregnated with titanium oxide nanoparticles (Fig.3 b) in comparison with the morphology of virgin P3T+6T without any modification as reference sample (Fig. 3a). The comparison of the two films surface images allowed to clearly observing the presence of titanium dioxide nanoparticles more or less dispersed at least on almost surface of the electrode with different sizes in the nanoscale and microparticles fixed to the porous structure of (P3T+6T) films [16].

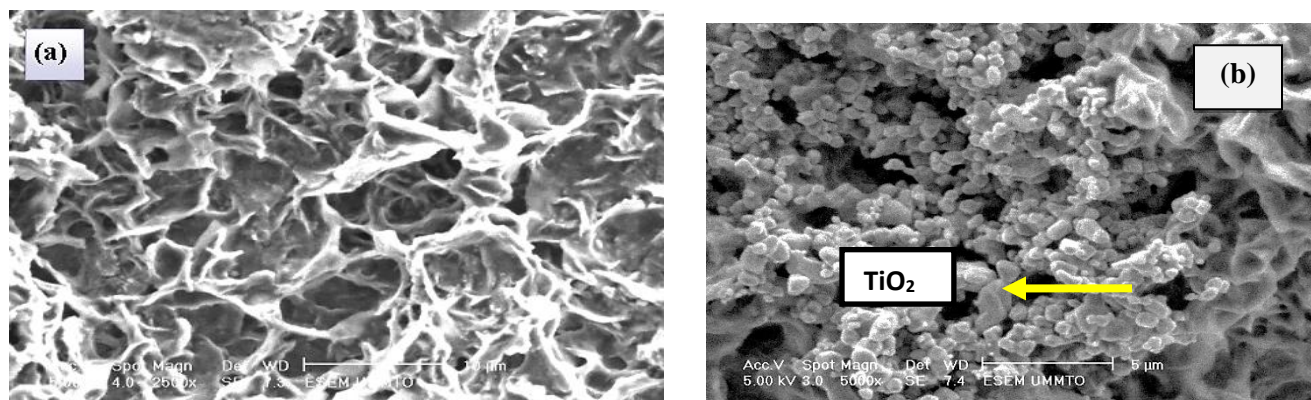


Figure 3: Micrographs of unmodified P3T+6T/ITO (a), and (P3T+6T+TiO₂)/ITO (b) films

The incorporation of titanium dioxide particles in the polymer is confirmed by EDX analysis, which showed the presence of the intense rays of titanium located at 4.60 and 0.20 keV [17] (Fig. 4). Also, the EDX spectrum of the electrochemically prepared composite film showed a carbon atom (C) and a sulfur (S) signals at 0.2 keV and 2.36 keV respectively, belong to the P3T+6T. The signals of chlorine (Cl) at 0.15 and 2.63 keV and oxygen (O) at 0.53 keV indicate that the P3T film was doped by perchlorate (ClO₄⁻) ions. These anions were produced from tetrabutylammonium perchlorate (TBAP), being used as supporting electrolyte. When we used the blades of ITO as a working electrode, we also observed two peaks at 3.28 keV and 0.4 keV of indium (In) and another at 1.75 keV of silicium (Si) which are specific to the substrate. The other elements (Hg, Na) are due to the presence of traces of impurities in titanium oxide. Thus, TiO₂ content in the composite film was confirmed by SEM and EDX analysis. Therefore, the TiO₂ particles can be incorporated in the polymer during the electropolymerization of terthiophene, which results in the pigmentation of the polymer film and the deposition of the composite (P3T+6T+TiO₂) on the electrode. Hence, interesting electrochemical properties are obtained, allowing the use of this composite as electrode material in the field of electrochemistry, photoelectrochemistry (material photoconductivity), electronic and electrocatalysis applications.

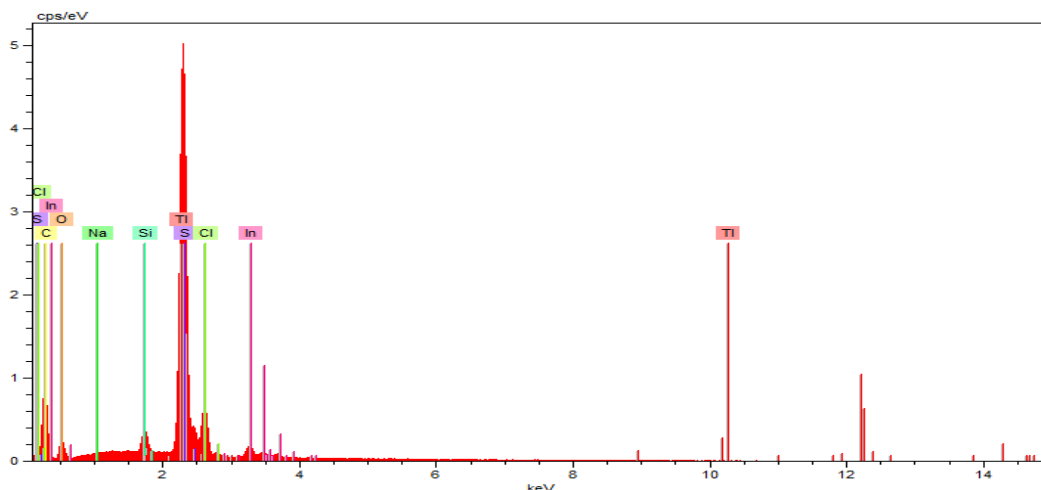


Figure 4: Micrographs and EDX analysis of unmodified (P3T+6T+TiO₂)/ITO

Photoelectrochemistry measurements

In order to test the photoelectrochemical performance of (P3T+6T) and (P3T++6T+TiO₂) as well as their hybrid with TiO₂, these films were used as a photoelectrode. Photocurrent measurements of these films were done in CH₂Cl₂/TBAP (10⁻¹ M) solution and in a three compartment photoelectrochemical cell. The polymer and the composite films were polarized at -400 mV. After stabilization of the current, the working electrode was irradiated with a polychromatic light at an intensity of 100 mW cm⁻². Fig.5 exhibits the plot of photocurrent versus bias voltage. The plots show that the polymer film presented a cathodic photocurrent peak immediately after irradiation. This response indicates that recombination processes are occurring into the film, probably due to the presence of charge carriers in the polymer bulk, mainly due to structural disorder. These results are in agreement with the conducting behavior of p-type polymers [18].

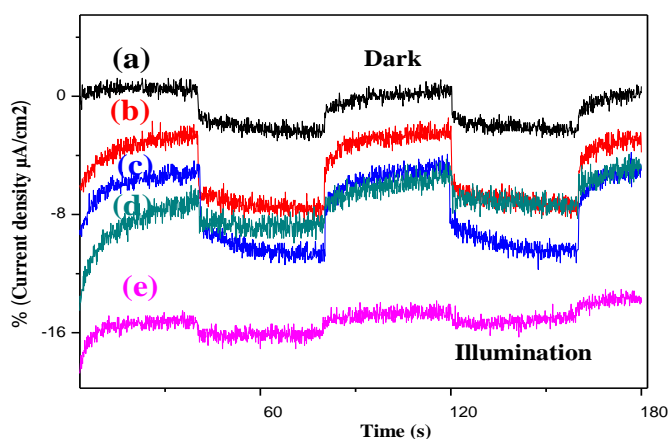


Figure 5: Current density-time plots of P3T+6T/ITO and (P3T+6T+TiO₂)/ITO films with different concentrations of TiO₂ (C = 0, 10⁻⁴, 5.10⁻⁴, 10⁻³, 5.10⁻³ and 10⁻² M), in CH₂Cl₂/TBAP (0.1 M) at a potential of -400 mV, observed on switching the light on and off for 100 mW.cm⁻² light intensity.

4 CONCLUSIONS

The analysis conducted on composite films, prepared from a (TiO₂) filled conjugated conducting polymer (P3T+6T), in a solvent electrolyte support system CH₂Cl₂/TBAP (10⁻¹ M) were performed by cyclic voltamperometry and Impedance Spectrometry. The study showed a variation of the cyclic voltamperogram shape when titanium dioxide was added to the polymer.

The presence of a semi-conducting species in the composite material was confirmed by Scanning Electron Microscopy (SEM), EDX. Consequently, the titanium dioxide particles can be incorporated in (P3T+6T) during the electropolymerization of (3T+6T), in presence a slight stirring. This leads to a pigmentation of the polymer film resulting in a composite material (P3T+6T)+TiO₂ deposited on the electrode surface.

The addition of (TiO₂) nanoparticles improved the photocurrent of (P3T+6T)+TiO₂ composite was higher than that of (P3T+6T) films without (TiO₂) Moreover, the photocurrent increased with the (TiO₂) concentration. Our results demonstrate that (TiO₂) nanoparticles improved the optical and photoelectrochemical properties of (P3T+6T) films.

This work conclusively provides a simple and efficient approach for making conductive polymer-immobilized quantum dot coatings of great importance in photovoltaic cells.

RÉFÉRENCES

- [1]. Be re z n ev S, Ko i s J , Go lo v ts o v I, O p ik AE , M el li ko v E (2006) Electrodeposited (Cu–In–Se)/polypyrrole PV structures. *Thin Solid Films* 512 :425–429
- [2]. Yanhu W, Dejin Z, Shenguang G, Lei G, Jinghua Y, Mei Y (2013) A novel microfluidic origami photoelectrochemical sensor based on CdTe quantum dots modified molecularly imprinted polymer and its highly selective detection of S-fenvalerate. *Electrochim Acta* 107:147–154
- [3] Wang R, Yan K, Wang F, Zhang J (2014) A highly sensitive photoelectrochemical sensor for 4-aminophenol based on CdS-graphene nanocomposites and molecularly imprinted polypyrrole. *Electrochim Acta* 121:102–108
- [4] Benhaddad L, Bernard MC, Deslouis C, Makhloufi L, Messaoudi B, Pailleret A et al (2013) Chemical synthesis of hollow sea urchin like nanostructured polypyrrole particles through a core–shell reduced oxime chemistry using a MnO₂ powder as oxidizing agent and sacrificial nanostructured template. *Synth Met* 175:192–199
- [5] A. Kar, Y.R. Smith, V.R. Subramanian, *Environ. Sci. Technol.* 43 (2009) 3260–3265.
- [6] G. Natu, Y. Wu, *J. Phys. Chem. C* 114 (2010) 6802–6807.
- [7] Y. Lin, H. Lee, *J. Hazard. Mater.* 179 (2010) 462–470.
- [8] G. Tsekouras, C.O. Too, G.G. Wallace, *Electrochim. Acta* 50 (2005) 3224–3230.
- [9] C. Zanardi, R. Scanu, L. Pigani, M.I. Pilo, G. Sanna, R. Seeber, N. Spano, F. Terzi, A. Zucca, *Electrochim. Acta* 51 (2006) 4859–4864.
- [10] F. Deng, Y. Li, Xu. Luo, Li. Yang, Xi. Tu, *Physicochem. Eng. Aspects* 395 (2012) 183–189.
- [11] M. Torrell, L. Md. R. Cunha, A. Kabir, M.I. Cavaleiro, F. Vaz. Vasilevskiy, *Mater. Lett.* 64 (2010) 2624–2626.
- [12] Y.S. Sohn, Y.R. Smith, V.R. Subramanian, M. Misra, *Appl. Catal. B* 84 (2008) 372–378.
- [13] G. Natu, Y. Wu, *J. Phys. Chem. C* 114 (2010) 6802–6807. *A Chem* 188 (2007) 364–370.
- [14] S.S. Kim, J. Jo, C. Chun, J.C. Hong, D. Kim Yu, *J. Photochem. Photobiol*
- [15] H. Derbal-Habak, C. Bergeret, J. Cousseau, J.M. Nunzi, *Sol. Energy Mater. Sol. Cells* 95 (2011) S53–S56.
- [16] Y. Lin, H. Lee, *J. Hazard. Mater.* 179 (2010) 462–470.
- [17] S. Abaci, B. Nessark, R. Boukherroub, K. Lmimouni, *Thin Solid Films* 519 (2011) 3596–3602. D. Verma, A. RangaRao, V. Dutta, *Sol. Energy Mater. Sol. Cells* 93 (2009) 1482–1487
- [18] A. Petrella, M. Tamborra, P.D. Cozzoli, M.L. Curri, M. Striccoli P. Cosma, G.M. Farinola, F. Babudri, F. Naso, A. Agostiano, *Thin Solid Films* 451–452 (2004) 64–68.