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PHOTO-SENSITIVE LAYERS FORMED FROM POLYMETHYLTHIOPHENE/TiO_2 NANOCOMPOSITES

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SUMMARY

Nanocomposites of polymethylthiophene (PMT) and titanium dioxide nanoparticles (TiO_2) were prepared in core-shell structure, via chemical oxidative polymerization of methylthiophene in the presence of $FeCl_3$ catalyst. The electrophoretic deposition (EPD) technique was adopted to prepare the nanocomposite films on ITO plates. Then photoelectrochemical properties of the PMT/TiO_2 nanocomposite were investigated. Results showed the photo-sensitive properties of TiO_2 core (n-type semiconductor), PMT shell (p-type semiconductor) and their n-p junction.

I - INTRODUCTION

Inorganic nanoparticles of various nature and size can be combined with organic conducting polymers, giving nanocomposites with interesting physical properties and application potentials [1]. Nanocomposites in core-shell structure based on metal oxide core and conducting polymer shell are rather easy to chemically prepare even in large quantities [1]. However, the studies on the electrochemical properties of these materials are not easy because the preparation of the nanocomposite layers on conductive electrodes is very difficult. Hebestreit *et al.* managed to prepare the polythiophene (PTh)/TiO_2 nanocomposite layers on platinum plates by rubbing form pressed pellets [2]. However, the adhesion of the nanocomposite layers on the electrode was bad so that the photocurrent signal of these layers was small (in order of nA). Recently, the electrophoretic deposition (EPD) was adopted for preparation of thin films of conducting polymer/metal oxide nanocomposites of core-shell structure [3-6]. The photoelectrochemical properties of nanocomposite layers were investigated, indicating that conducting polymer shell is still electrochemically active after EPD even after high voltage applied during EPD. In the present work EPD was used to prepare layers of PMT/TiO_2 nanocomposites. The optical properties of such layers were studied by different methods.

II - EXPERIMENTAL

1. Preparation of PMT/TiO_2 nanocomposites and electrophoretic deposition

Composites were prepared following a procedure described in Ref. [3 - 6]. Size and morphology of the composite particles were published in Ref. [4 - 6], showing that TiO_2 nanoparticles were covered by conducting polymer shell with the thickness of some nanometers. EPD was done as described in Ref. [3 - 6]. In deposition procedure, conducting polymers was in reduced state.

3. Material characterization

Photoelectrochemical measurements were carried out with a Xenon lamp (Mueller-Elektronik, 1000 W) in combination with a Zeiss grating monochromator and a chopper as a light source, and a lock-in amplifier (5208, EG&G Princeton Applied Research) for the photocurrent detection. They were measured in a three-electrode cell containing 0.5 M $LiClO_4$ in acetonitrile. The saturated calomel electrode (SCE) and a platinum plate were used as the reference electrode and a counter electrode, respectively. For photoelectrical measurements in solid state, sandwich cells consisting of ITO//composite//aluminium were prepared. Composite layers were electrophoretically deposited on ITO and then a top electrode of aluminium for Schottky junction was deposited using vacuum deposition technique in Carl Zeiss Jena evaporator HBA 120/2 at vacuum of 1.10^{-2} Pa. The photoelectrical measurements were made under steady-state illumination conditions using a Xenon lamp (Mueller-Elektronik, 75 W) and a Jobin Yvon H25 monochromator, with a photodiode (EG&G HUV-1100 B) in the reference beam, in the serial connection of the sample, power supply (Keithley 230) and electrometer (Keithley 617).

III - RESULTS AND DUSCUSSION

The photocurrent spectra of deposited composite layer obtained at various bias potentials applied in the UV-Vis spectra region are shown in Fig. 1. The photocurrent spectra show a cathodic photocurrent maximum at the wavelength λ = 530 nm, corresponding with the optical absorption maximum of the reduced PMT. An additional cathodic shoulder near 400 nm was observed at the negative voltage bias, analogously to the results shown in Ref. [3 - 6], where it was ascribed to TiO_2 photoexcitation. However, the feature of p/n junction is not found from the photocurrent measurements in electrolyte.

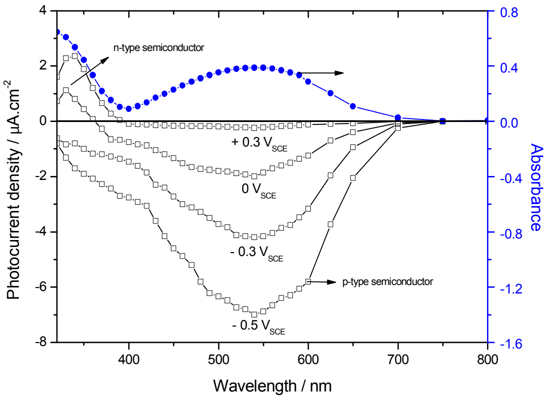

Figure 1: Photocurrent spectra of the PMT/TiO_2 composite (5.3% PMT) deposited on ITO at 20 V from a suspension of 5 gl^-

When a p-semiconductor is immersed into an electrolyte, the band bending appears at the semiconductor surface. If this surface is illuminated by light with energy hν > E_g (bandgap energy), the photogenerated holes move to the bulk of the semiconductor and the photoelectrons towards the surface. Subsequently, a reduction occurs at the semiconductor surface that is observed as a cathodic photocurrent. This photocurrent was described by Gọrtner and Butler [4, 5], in following equation:

$$i_{ph} = [e\Phi_0(1 - exp(-\alpha W_0(E-E_{FB})^{1/2})]/(1 + \alpha L_p) \quad (1)$$

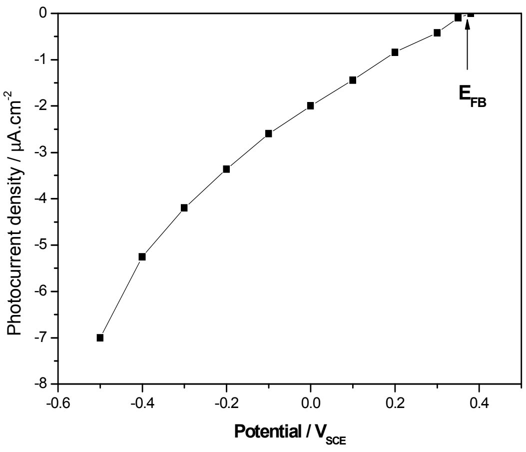

Figure 2: Photocurrent - potential dependence of the PMT/TiO_2 composite (5.3%) at 530 nm

From Eq. (1), the flatband potential, E_{FB}, can be obtained when plotting the photocurrent as a function of applied voltage, E (Fig. 2) for 530 nm excitation wavelength. The values $E_{FB} = 0.4$ V_{SCE} were found for the PMT/TiO_2 (5.3%) nanocomposite.

The photocurrent action spectrum measured at a fixed potential is a useful tool to determine the bandgap value of a semiconductor and the nature of the electronic transitions that is origin of the photocurrent. The bandgap energy, E_g can be determined through the linear $(i_{ph}h\nu)^2$ or $(i_{ph}h\nu)^{1/2}$ *vs.* hν plots [4, 5]. If the $(i_{ph}h\nu)^2$ vs. hν plot is linear the electron transition is direct. If $(i_{ph}h\nu)^{1/2}$ *vs.* hν plot is linear, on the contrary, the electron transition is indirect. Fig. 3 shows that a good linearity is observed for plot of $(i_{ph}h\nu)^2$ *vs.* hν. Obviously, the direct electron transition predominates. The extrapolated bandgap energy, $E_g = 1.9$ eV, is coincident with the one obtained from the absorption edge in the optical spectra and shows a good agreement with the values for PMT ($E_g = 1.9$ eV, Ref. [7]) and for PTh ($E_g = 2.0$ eV, Ref. [4, 5]).

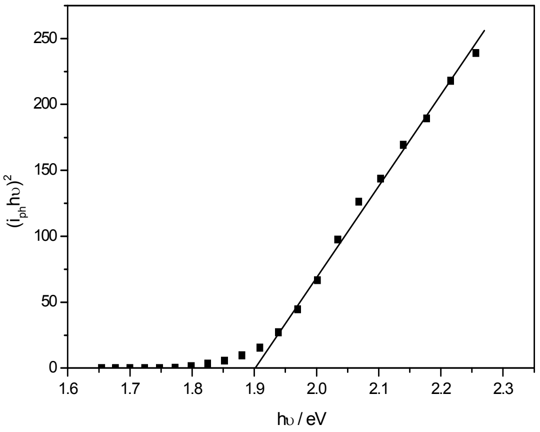

Figure 3: $(I_{ph}h\nu)^2$ vs. hν plot of PMT/TiO_2 (5.3%) for determining E_g^{di} of PMT

To study the photoelectrical properties in solid state, a PMT/TiO_2 (5.3%) composite film was electrophoretically deposited on an ITO electrode and completed with an aluminum layer, a top electrode that was deposited in vacuum. The short circuit photocurrent spectrum of such cell under vacuum (10^{-5} torr), compared with the UV-VIS optical absorption spectrum of the electrophoretically deposited layer, is shown in (Fig. 4).

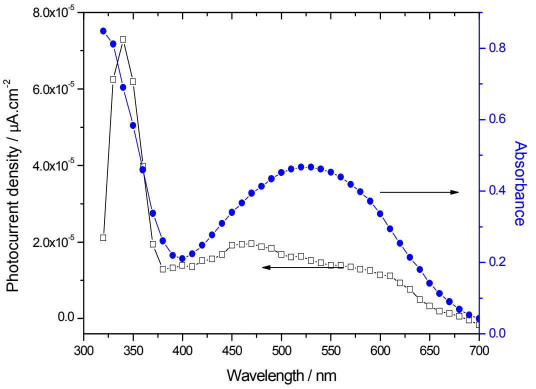

Figure 4: Short circuit photocurrent of a sandwich cell consisting of ITO // PMT/TiO_2 (5.3%) composite // Al

A shoulder at 600 nm belonged to the absorption of PMT and a peak in the UV region to the optical adsorption of TiO_2. A broad absorption, for photocurrent, maximum at 450 nm could be explained by the p/n heterojunction between TiO_2 core and PMT shell and the mechanism presented in Ref. [8]. An excitation formed from the photon absorption in the PMT shell dissociated into holes and electrons and were separated in the field inhomogeneity of the composite electrode structure.

The photocurrent generation in a p/n heterojunction is shown. In the prepared material, this process was complicated by the contacts within the composite particles as well as the contacts between particles and electrode. In comparison with the photocurrents measured in electrolyte, the cathodic absorption shoulder near 400 nm disappeared (Fig. 4).

For comparing the photocurrent spectra of the composites having various composition of PMT were presented in Fig. 5. Analogously to the results obtained in electrolyte, the photocurrents of the complete solid cells measured under vacuum depended on the amount of PMT. The values of the peaks at 340 nm increased and that of the peaks at 470 nm decreased with the decrease of the PMT content (Fig. 5). For composites with low amount of

PMT (1.2% and 1.9%), the shoulder at 600 nm disappeared. It showed that this peak belonged to PMT connecting directly with the ITO electrode (figures 4 and 5).

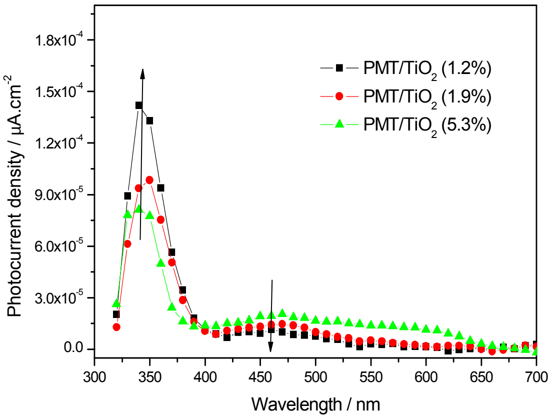

Figure 5: Short circuit photocurrents of sandwich cells consisting of ITO // PMT/TiO$_2$ composite // Al (measured under vacuum)

Short circuit photocurrents of sandwich cells consisting of ITO // PMT/TiO$_2$ composite // Al in the air and under vacuum were investigated. The photocurrent in the air was higher than that under vacuum. It could be explained by influence of the humidity and the oxygen in the air.

IV - CONCLUSIONS

The electrophoretic deposition was found to be a feasible method for the preparation of thin nanocomposite layers on conductive substrates. Obtained thin layers were applicable for the investigation of photoelectrochemical properties of the nanocomposite. The acquisition of the photocurrent spectra was performed at several bias potentials, discovering the separate photoelectrochemical signals from titanium dioxide and from polymethylthiophene (each compound represented different type of semiconductor). A direct transition (with bandgap energy, E_g = 1.9 eV) and a flatband potential (+0.4 V_{SCE}) for polymethylthiophene were obtained via photocurrent measurements. However, studies of the solid state cells showed n-p junction. The photocurrent intensity depended on the amount of the components in nanocomposites as well as the measurement condition.

The results from photoelectrochemical investigations show that the conducting polymer remains active after deposition. Therefore, the electrophoretic deposition is a suitable process to prepare stable films of the polymethylthiophene/titanium dioxide composite materials. So far the composite preparation and the deposition process were not optimized. Nevertheless, the qualities of the layers were sufficient for testing photoelectrically active devices. In the future, the conditions of the composite preparation must be improved for a best performance of possible applications.

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