CURRENT - VOLTAGE CHARACTERISTICS OF POLYMETHYLTHIOPHENE/TiO$_2$ NANOCOMPOSITE CELLS

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SUMMARY

Titanium oxide nanoparticles (TiO$_2$) were combined with polymethylthiophene (PMT), giving nanocomposites in core-shell structure via chemical polymerization. In this work, the current - voltage characteristics of sandwich cells composed from such nanocomposite have been studied. For these investigations films of nanocomposites were prepared by electrophoretic deposition (EPD).

I - INTRODUCTION

Conducting polymer nanocomposites are rather prepared with interesting properties and application potentials [1 - 4]. Recently, such nanocomposites have been studied by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and photocurrent measurements [2 - 4]. In last paper, photo-electrochemical properties of PMT/TiO$_2$ nanocomposite layers were reported [5]. The photocurrent spectra measured in electrolyte was performed at several bias potentials, discovering the separate photoelectrochemical signals from TiO$_2$ (n-type semiconductor) and from PMT (p-type semiconductor). In sandwich cells, the photocurrent spectra showed the signals of p-n junction at 450 nm. In this work, current - voltage characteristics of such films are presented in order to study photoelectrical and electrical properties the cells fabricated from the PMT/TiO$_2$ nanocomposites.

II - EXPERIMENTAL

1. Preparation of PMT/TiO$_2$ nanocomposites and sandwich cells

Nanocomposites were prepared as described in Refs. [2 - 4]. The amount of PMT (5.3%) in the composites was calculated from the data of the thermogravimetrical measurements (performed with a thermobalance, METTLER TG 50). For *photoelectrical measurements* in solid state, sandwich cells of ITO/composite/aluminium were prepared. Composite layer was electrophoretically deposited on ITO and then a top electrode of gold was deposited using vacuum deposition. For photocurrent measurements in electrolyte (containing a redox couple I$_3^-$/I$^-$ in CH$_3$CN with a Pt counter electrode), layers of PMT/TiO$_2$ nanocomposite were electrophoretically deposited on ITO plates.

2. Material characterization

Photoelectrical measurements were made with an electrometer Keithley 236 and a Xenon lamp (Mỹller-Elektronik, P = 150 W).

III - RERULTS AND DISCUSSION

1. Current - voltage curves of solid cell

Current - voltage curves (in the dark) of a solid Au//PMT/TiO$_2$//Al cell in a range of ±4 V are shown in Fig. 1. The typical Schottky diode behaviour is explained by the fact that gold formed an Ohmic contact while aluminium formed a blocking contact with the composite, similar to [6]. Inset of Fig. 1 shows I/V characteristics on a semi-logarithmic scale. The rectification ratio of 10^2 (at ±4 V) was found.

According to [7], the rectification in a p/n junction can be explained: An n-type semiconductor contains mobile negative charges (electrons) and an equal concentration of fixed positive charges (ionized donors). Meanwhile, a p-type semiconductor contains mobile positive charges (holes) and fixed negative charges (ionized acceptors). With the two regions in contact, the mobile electrons and mobile holes can flow across the heterojunction and recombine together, resulting in the n-type region with a net positive charge and in the p-type region with a net negative charge. Thus, a field that was established has a direction in opposes with the further flow and brings the Fermi level in the n and p region to the same level. The band bending connected with the charging of the interface is shown in Fig. 2 (I). If a positive potential is applied to the p region and a negative potential to the n region, the effect is as shown in Fig. 2 (II). The potential barrier between two regions is lowered and the forward currents of both holes and electrons are greatly increased. The current arising from the generation of minority carriers remains the same and so there is a net flow of current across the junction with contributions from both holes and electrons. If the p region is made negative with respect to the n region, the potential barrier becomes much higher and the forward flow drops to a very low value for both kinds of carriers Fig. 2 (III).

From plotting in the semi-logarithmic scale under forward bias, four different regions can be distinguished as indicated in Fig 3. First, there is the ideal diode region (0.3 - 0.75 V) where the diode junction quality is quantified using its ideal factor, n. The ideal factor can be obtained from the equation (1) [8]:

$$n = \frac{q}{2.303.B.T} \cdot \frac{1}{slope} \qquad (1)$$
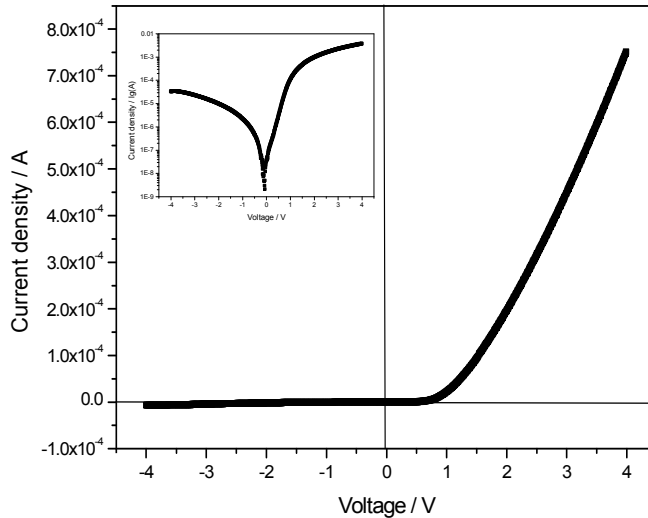
Where the slope of the current – voltage curve

Figure 1: Current-voltage curve of the Au//PMT/TiO$_2$//Al cell
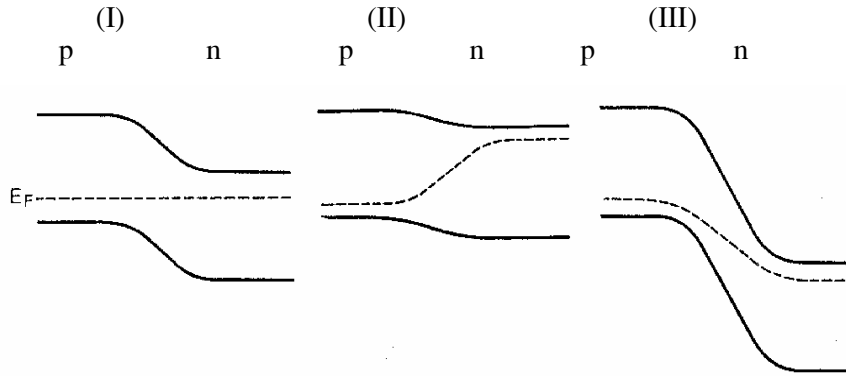(Inset: on a semi-logarithmic scale)

Figure 2: p/n junction: I) equilibrium condition II) forward bias and III) reverse bias [7]

in the semi-logarithmic scale is in units of V/decade; q is the electronic charge; B is the Boltzmann's constant and T is the temperature (in degree Kelvin). In the study, n of 4.4 is calculated, quite different from the ideal junction (n = 1, [8]). This is due to the presence of non-ideal effects. It can be explained by the soft structure of the deposited composite layer as well as by the bad contact between the composite particles and the electrode surface. On the left of the ideal diode region, there is a region where the current is dominated by the trap-assisted recombination in the depletion region. On the right of the ideal diode region, the current becomes limited by high injection effects and by the series resistance. High injection occurs in a forward biased p-n diode when the injected minority carrier density exceeds the doping density. High injection will therefore occur first in the lowest doped region of the diode since that region has the highest minority carrier density. For higher forward bias voltages, the current is not exponentially longer increase with voltage. However, it still increased linearly due to either the contact resistance between the metal and the semiconductor or the resistively of the semiconductor, or the series resistance of the connecting wires, or both. These four regions can be observed in almost p-n diodes although the high-injection region rarely occurs, as the series resistance tends to limit the current first.
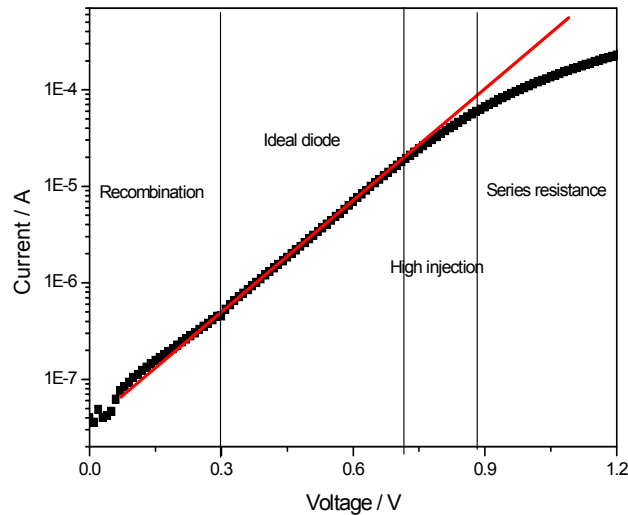

Figure 3: Current-voltage characteristic of a Au//PMT/TiO$_2$//Al cell under forward bias
(data from Fig. 1)

Current-voltage characteristics of a solid state ITO//PMT/TiO$_2$//Al cell tested both in the dark and under illumination through ITO using a Xenon lamp (150 W) are shown in Fig.4. In this case, the short circuit current (J_{SC}) and the open circuit voltage (V_{OC}) were 0.87 μA.cm^{-2} and 0.2 V, respectively.

2. Current - voltage curves of cell in electrolyte

Current-voltage characteristics of a photoelectrochemical PMT/TiO$_2$ cell in the I$_2$/I$_3^-$ electrolyte system recorded both in the dark and under light illumination through ITO are shown in Fig. 5. In the dark, the current remains relatively constant in a range of (-0.4 V) - (+ 0.8 V).

During illumination, a cathodic photocurrent is observed at cathodic potentials. It indicates that the neutral PMT behaves as a p-type semiconductor. The short circuit current (J_{SC}) and the open circuit voltage (V_{OC}) are
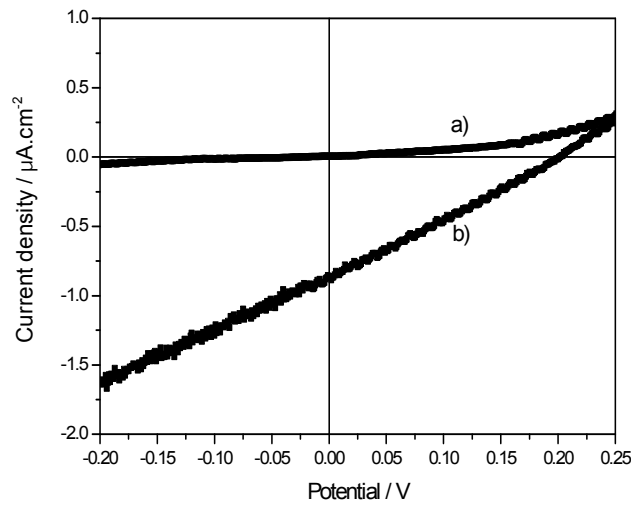

Figure 4: Current-voltage characteristic of the solid ITO//PMT/TiO$_2$//Al cell: a) in the dark and b) under illumination
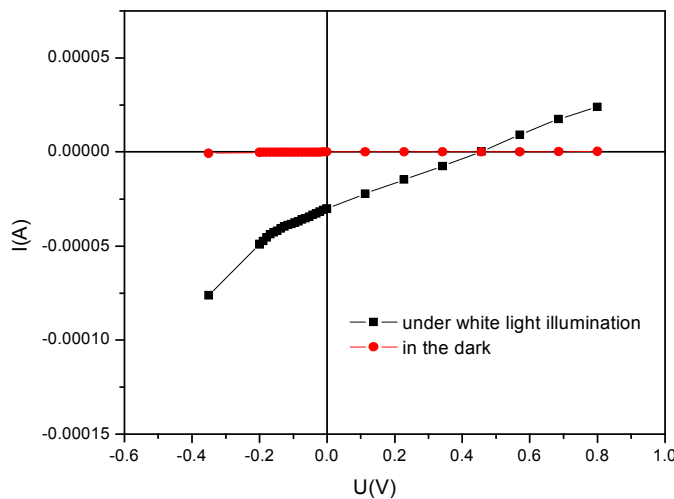

Figure 5: I/V characteristic of photoelectrochemical PMT/TiO$_2$ (5.3%) cell deposited on ITO in the I$_2$/I$_3^-$ electrolyte

determined to be 0.06 mAcm^{-2} and 0.45 V, respectively. The fill factor (FF) for the cell, which is a measure of the squareness of the out put characteristic, is calculated to be 0.5 [9]. Obviously, these values are higher than in the case discussed above (solid cell). This indicates that the high resistance of the solid cells was leading to low photocurrents. This result also explained why the ideal junction of p-n diode calculated above was high (n = 4.4).

3. Cyclic voltammetry

Fig. 6 shows the CV curves of PMT/TiO$_2$ nanocomposite layers deposited on platinum at 20 V. The onset potential of oxidation was 0.4 V$_{SCE}$, the observed anodic peak in vicinity of potential of PMT was + 0.7 V$_{SCE}$, both in agreement with values published in the literature [10]. The value of onset oxidation potential was very near with that of open circuit voltage showed in Fig. 5. The anodic peak current-density decreased from 0.65 µA.cm^{-2} in the first cycle to 0.6 µA.cm^{-2} in the 10 th cycle. The reduction potential of PMT was + 0.65 V$_{SCE}$. As in the case of the polythiophene/TiO$_2$ composites [2 - 4], the TiO$_2$ core showed no electrochemical activity.
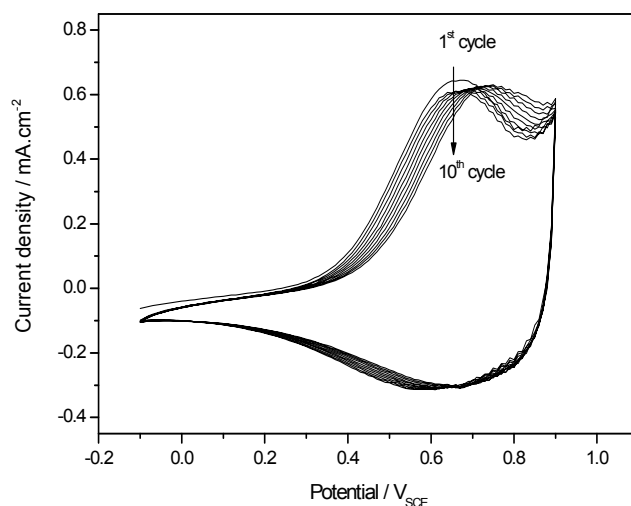

Figure 6: Cyclovoltammogram of PMT/TiO$_2$ composite layer prepared by EPD on platinum

IV - CONCLUSIONS

Thin films of polymethylthiophene/titanium oxide nanocomposites were prepared by electrophoretic deposition. Obtained films were applicable for the investigation of photoelectrochemical and electrical properties of the nanocomposite. The electrochemical behaviour of the composite layers was investigated by cyclic voltammetry. The reversible and stable redox behaviour of polymethylthiophene was obtained. The oxidation potential of polymethylthiophene (+ 0.4 V$_{SCE}$) was determined by cyclic voltammetry.

A sandwich cell composed of polymethyl-thiophene/titanium dioxide nanocomposite layer between ITO and Au electrodes was developed. The behaviour of a p/n diode was investigated. The ideality factor of the diode was 4.4. It shows that the film was not perfectly compact leading its resistance was high. However, the photoelectrochemical behaviour of the cells was still obtained in the I$_2$/I$_3^-$ electrolyte.

Investigations showed that the electrophoretic deposition is a suitable process to prepare stable films of the polymethyl-thiophene/titanium dioxide composite materials. However, the composite preparation and the deposition process were not optimized. Nevertheless, it is a promising procedure to prepare photoelectrically active devices composed from conducting polymer composites.

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