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Photosensitive Layers of TiO_2/Polythiophene Composites Prepared by Electrodeposition

J. Pfleger,[*1] *M. Pavlík,*[1] *N. Hebestreit,*[2] *W. Plieth*[2]

[1] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
[2] Institute of Physical Chemistry and Electrochemistry, Dresden Technical University, Mommsenstr. 13, 01062 Dresden, Germany

Summary: We adopted an electrophoretic deposition method for the preparation of thin layers of insoluble composite nanoparticles composed of TiO_2 core and about 2 nm thick shell of polythiophene, prepared by oxidative polymerization of thiophene. The reduced form of TiO_2-polythiophene composite material was deposited on the conductive surface from an ultrasonically generated microdispersion. Varying the dispersion media, applied voltage and the electrode arrangement made it possible to control the quality and morphology of the films. Compact semitransparent films deposited on ITO electrodes, suitable for photoelectrical measurements, were obtained within short deposition times.

Keywords: electrodeposition; photoconductivity; polythiophene; thin films; titanium dioxide

Introduction

Since 1991, when O'Regan and Grätzel reported on a photoelectrochemical solar cell composed of a ruthenium dye-sensitized nanoporous titanium dioxide, achieving a photoelectrical conversion efficiency of about 10 % [1], many researchers have focused on the utilization of the heterojunction formed between a wide-band-gap inorganic semiconductor and organic visible light absorbing material for solar cell applications. Particularly, there is an increasing effort to overcome the limitations originated in utilization of the liquid electrolyte used in the original Grätzel-type solar cells by substituting it either with a solid electrolyte [2] or an amorphous organic hole-transporting material [3]. Combinations of ultrathin films of polythiophene (PT) and titanium dioxide (prepared chemically [4], electrochemically or by vapour deposition [5,6]) were also described, in which a p/n junction, formed between the

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TiO_2 film (n-type semiconductor) and the polythiophene film in the reduced state (p-type semiconductor), contributed to the creation and effective separation of charges upon illumination [7]. A nebulized vapour deposition method was reported recently [8], which enables the formation of nanoparticles of metal oxides and a simultaneous build-up of the charge transporting polymer network. The synthesis of hybrid organic/inorganic materials based on metal oxides and semiconducting polymers was also realized by the sol – gel process [9], and many further data about synthesis, properties and applications of nanocomposites, based on conductive or semiconductive polymers and various inorganic materials were reported [10].

Electrodeposition has evolved recently to a simple and effective method for fabrication of homogenous thin layers of insoluble materials, such as ceramics, with many possible applications. The electrodeposition, covering the conductive surface by a functional material in an applied electric field, brings, in addition to experimental simplicity, several remarkable advantages: good layer-forming control and fine regulation via optimization of many parameters (varying dispersion media, applied voltage, electrode type, etc.), guaranteed contact, perfect coverage of the electrode, and the possibility of preparation of very thin layers. Limitations in the use of the electrodeposition method are evident: only electrophoretically active, relatively stable dispersion-forming materials can be deposited and the substrates must be conductive.

Here we report on the application of the cathodic electrophoretic method as a possible method of the preparation of the solid-state photoelectrically sensitive cell based on the heterojunction between wide-band-gap titanium dioxide and polythiophene in the core-shell nanocomposite.

Experimental

Preparation of PT-coated TiO_2 nanoparticles: As a core we used a TiO_2 powder P25 (Degussa), with average particle size 21 nm and surface area 50 m^2/g, The polythiophene was prepared from fresh distilled thiophene (Aldrich – Chemistry, 99+ %) and anhydrous iron(III) chloride (Fluka Chemie, purum) [4,11].

An aliquot of 25 g TiO_2 (dried at 60 – 100 °C for 2 - 4 h) was dispersed together with 0.03 – 0.05 M thiophene in ca. 200 ml of chloroform (anhydrous, max. 0.03 % water, Merck) by stirring for a few minutes [4]. By this procedure, the oxide particles with thiophene adsorbed on the surface were obtained. To this dispersion, 50 ml of a saturated solution of 0.2 – 0.3 M iron(III) chloride in chloroform was added. After stirring for 1 - 2 h, the color of the mixture changed from gray to black and hydrogen chloride was produced. These changes were used for monitoring the reaction progress. At the end, the dispersion was filtered off and the dark gray product was dried. As a result, the oxide particles covered with the oxidized polythiophene shell were obtained. To obtain the reduced form of the polythiophene, iron chloride was extracted from the product by washing with methanol (2 - 4 h). During this procedure, the color changed from gray (oxidized state) to red (reduced state). Finally, the powder was dried at 60-80 °C for 2 - 3 h.

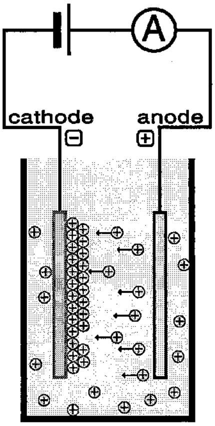

Figure 1. Schematic drawing of the typical anodic electrophoretic deposition setup.

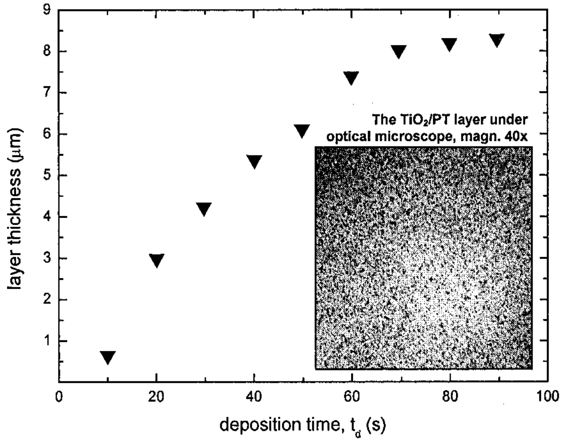

Figure 2. Dependence of the layer thickness on deposition time for TiO_2/PT particles (applied voltage 200 V, current limited to 0.1 mA).

The electrophoretic deposition was performed in the experimental setup shown schematically in Figure 1, consisting of the power supply in serial connection with an amperemeter and two electrodes inserted in the dispersion of particles in organic medium. The used power supply made it possible to work in the potentiostatic or galvanostatic mode. The dispersions were ultrasonicated before and stirred during the deposition.

The optical absorption spectra were obtained as diffusion reflection measured on pressed pellets prepared from the powder material or on films (thickness of several μm) electrodeposited on ITO substrates, using a Perkin Elmer 340 spectrophotometer equipped with an integration sphere.

The upper electrodes on the top surface of the deposited films were prepared by vacuum deposition. DC electrical conductivity was measured on pressed pellets using the van der Pauw method. The photoelectrical characteristics were measured under steady state illumination conditions using a Xe lamp (XBO 75) and a Jobin Yvon H25 monochromator, with a photodiode (EG&G HUV-1100B) in the reference beam, in the serial connection of the sample, a power supply (Keithley 230) and electrometer (Keithley 617). For the voltammetric measurements during the electrodeposition studies, the same electric devices were used.

Results and Discussion

Material characterization

The optical absorption spectrum of TiO_2/PT nanoparticles is given in Figure 4A as the Kubelka-Munk function. It consists of the optical absorption of TiO_2 nanoparticles with the absorption band E_g = 3.3 eV and the optical absorption of PT (E_g = 2.1 eV). The optical absorption of pure TiO_2 nanoparticles is shown for comparison.

The DC electrical conductivity obtained from measurements on pressed pellets in ambient atmosphere was $\sigma = 1.5 \times 10^{-6}$ S m^{-1}. Recalculated to the PT content in the composite (ca. 7 % by weight), this value corresponds to the conductivity of an undoped polythiophene.

Electrophoretic deposition

The dispersion systems containing TiO_2 nanoparticles, PT nanoparticles and TiO_2/PT composite nanoparticles in ethanol or butyl acetate, were tested for the possible preparation of thin layers on conductive substrates by the electrodeposition method in the experimental setup given in Figure 1. These dispersion systems differed in the electrodeposition ability as summarized in Table 1. The symmetric arrangement with both Ni electrodes was used in the electrodeposition studies. Generally, the nanoparticles based on TiO_2 were capable of electrodeposition in ethanol medium on the negative electrode only; no electrodeposition was observed on either cathode or anode when butyl acetate was used as a supporting medium, even at high electric potentials. The presence of the PT shell covering the TiO_2 nanoparticles surface caused an increase in the electrodeposition current by about one order of magnitude. On the other hand, no electrodeposition of the composite nanoparticles was observed in butyl acetate. The dispersion of neat PT behaved in opposite way. The polymer particles did not deposit in ethanol medium but the deposition in butyl acetate was observed, although at a high voltage exceeding 300 V and at a much lower deposition current, yielding only layers of poor quality. In this system, the dispersion stability was low, the dispersion tends to sedimentation, which suggests a smaller zeta potential of the nanoparticles.

Table 1. Summary of electrodeposition in various dispersion systems.

Material	**Electrodeposition media**	
	Ethanol	**Butyl acetate (+1% EtOH)**
TiO_2/PT particles	**DEPOSITION (cathodic)** $U > 30$ V, $I \sim 10^{-4}$ A	**NO DEPOSITION** $U \sim 300$ V, $I \sim 10^{-8}$ A
TiO_2	**DEPOSITION (cathodic)** $U > 30$ V, $I > 10^{-5}$ A	**NO DEPOSITION** $U \sim 300$ V, $I \sim 10^{-8}$ A
Polythiophene	**NO DEPOSITION** $U \sim 30$ V, $I \sim 10^{-4}$ A	**DEPOSITION (cathodic)** $U \sim 300$ V, $I \sim 10^{-6}$ A

The stability of the dispersion, electrophoretic mobility and the capability of coagulation and adhesion to the substrate have to be considered to discuss the electrophoretic deposition process. To achieve a stable dispersion of nanoparticles, their particulate surface charge is required. In nonaqueous dispersions, the dissociation/ionization of surface groups (electrostatic stabilization) and adsorption of ionic surfactants (electrosteric stabilization) are the only possible mechanisms for dispersion stabilization [12]. Oxide surfaces have a large concentration of surface amphoteric hydroxyl groups, which can react to yield both positively or negatively charged particles depending on pH of the medium [13]:

$$(M\text{-}OH)^0 + H^+ \rightarrow (M\text{-}OH_2)^+ \quad \text{at low pH}$$

$$(M\text{-}OH)^0 + OH^- \rightarrow (M\text{-}O)^- \quad \text{at high pH}$$

For the La, Zr or La oxides dispersed in ethanol, the three-step process of the surface charge stabilization was proposed [14]: (i) adsorption of ethanol molecules in undissociated form on the basic surface sites of the oxide particles, (ii) dissociation of ethanol molecules by H^+ transfer to the basic surface sites, and (iii) desorption of EtO^- anions. As a result, the nanoparticles are positively charged. In SiO_2 particles, the second step of the mechanism proposed above proceeds via the charge transfer from acid surface sites to ethanol, which yields the negatively charged particles. As can be seen from the results summarized in Table 1, the former mechanism explains the situation for TiO_2 as well as for PT-covered TiO_2 particles in ethanol medium.

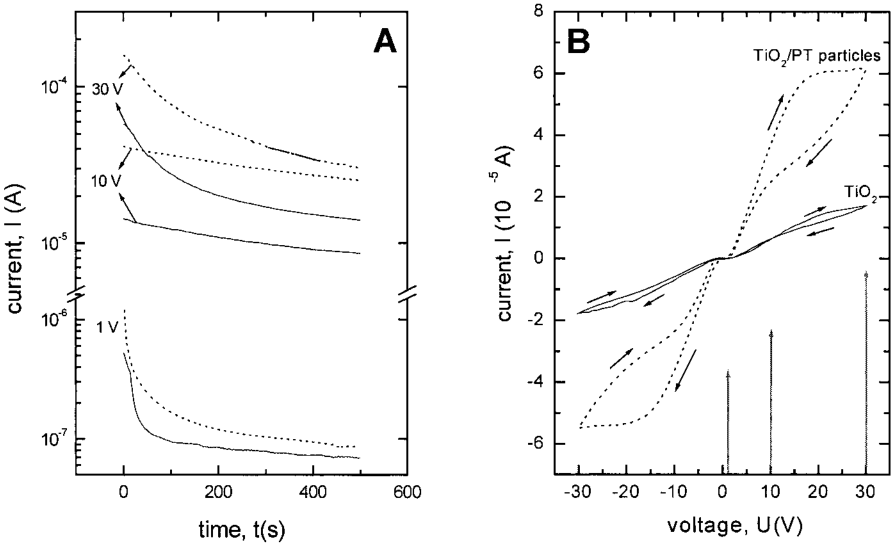

Figure 3. A. Relaxation of the electrodeposition current for a TiO_2/PT dispersion (dottted lines) and for TiO_2 particles (full lines) in ethanol after applying various voltages. **B.** Cyclovoltammetry of a TiO_2/PT dispersion (dotted line) and of neat TiO_2 (full line) in ethanol.

The layer formation by electrodeposition from the dispersion of TiO_2/PT nanoparticles in ethanol, under the constant current conditions (I = 0.1 mA, electrode distance 1 cm and area 0.5 cm^2) is shown in Figure 2. The deposition rate was decreasing with time, the thickness of the layer reached its saturation value at 8 μm within 80 s. The structure of the resulting layer is shown in the inset of Figure 2.

The time dependences of the electrodeposition of TiO_2/PT composite nanoparticles under the constant voltage conditions are shown in Figure 3A for the applied voltage 1, 10 and 30 V. The electrodeposition kinetics of neat TiO_2 nanoparticles is also shown for comparison. The starting concentration of nanoparticles in the dispersion was 14 mg/ml with the total amount of 500 mg in the volume, which allows to consider the deposition to take place under the constant concentration conditions.

The dependences of the electrodeposition current on the applied voltage for the same system as described above are presented in Figure 3B. It should be pointed out that the curves do not show the pure voltammetric behavior of the system, but reflect also a contribution of the growing layer to the total resistance in the electrical circuit. The symmetric shape of the voltammetric curves could be used as a proof of the electrophoretic mechanism of the deposition process: the nanoparticles preserve charge when deposited and the reversed electric field results in the stripping-off of the electrode and in the deposition on the opposite one. The UV-VIS optical absorption spectra of the electrodeposited composite nanoparticles did not show any observable optical absorption in the near-infrared region suggesting that the polymer did not undergo any oxidation during the electrodeposition process.

The observed time evolution of the electrodeposition current and its dependence on the applied voltage could be explained as follows. The deposition current is given by the product of nanoparticle concentration, electric field and reciprocal viscosity of the solvent. The electric field in the vicinity of the coated electrode has to exceed a certain threshold value to make the coagulation of the nanoparticles and their adherence to the electrode surface possible. In our case this threshold was ca. 5 V when the distance between the electrodes was 1 cm. During the deposition process, the growing layer forms an increasing resistance in the circuit on which the voltage drop occurs, which diminishes the driving force for the electrophoretic movement as well as for the particle coagulation on the surface of the growing layer. As a result, saturation of the layer thickness has been achieved.

Photoelectrical characteristics

We made an attempt to exploit the electrodeposition method for the fabrication of a photoelectrically sensitive hybrid polymer/inorganic solid cell based on the concept published recently [15]. In this type of the device, the photoelectrical conversion takes place on the interface between the TiO_2 core and PT shell of the composite particles, the bulk of the sample being sandwiched between two metal electrodes.

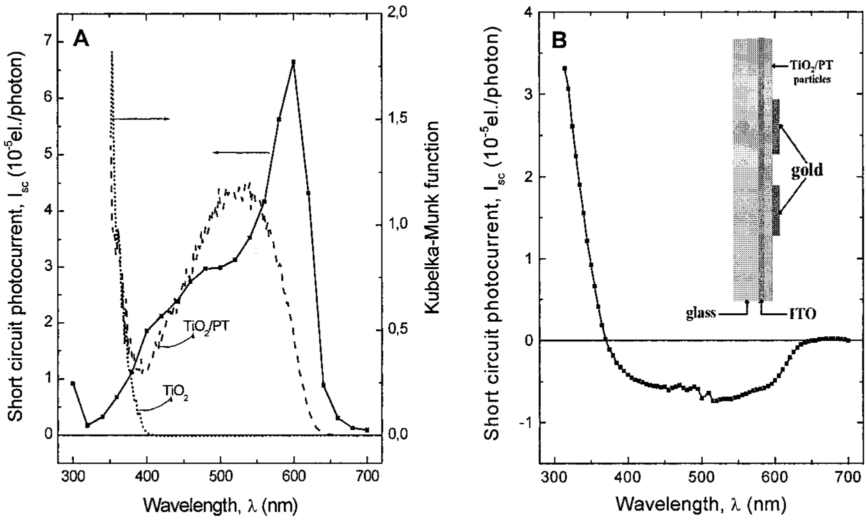

Figure 4. - **A.** Spectral dependence of the short-circuit photocurrent of TiO_2/PT samples measured in vacuum (10^{-3} Pa) - full line, UV-VIS absorption spectra of TiO_2/PT particles - dashed line, and neat TiO_2 - dotted lines. **B.** Spectral dependence of the short-circuit photocurrent of TiO_2/PT samples measured in air. Inset: sandwich structure of the sample under study.

The spectrum of the short-circuit photocurrent (I_{sc}) obtained on the samples of thickness 2 μm (for sample structure, see the inset of Figure 4B) at 10^{-3} Pa and room temperature is shown in Figure 4A, normalized to the incident photon flux. The sample was illuminated through the ITO electrode, the sign of the photocurrent refers to the top Au electrode. Compared with the optical absorption, the I_{sc} spectrum exhibits an antibatic behavior. It shows that the region near the ITO/polythiophene interface only weakly contributes to the free charge carrier photogeneration. This is in accordance with the mechanism in which the photogeneration takes place effectively in the bulk of the composite on the distributed p/n junction between TiO_2 and PT. The photogeneration in the visible region proceeds via the absorption of photons in PT shell. Because the LUMO level of the polymer is well above the TiO_2 conductance band, the photoexcited electron is transferred into the TiO_2 core leaving the hole in the polymer, through which it can move towards the top Au electrode, which forms with the polymer an Ohmic contact. The polymer thus works both as a photosensitizer and as a charge-transporting medium. This process is in agreement with the observed polarity of the Au electrode, which is positive upon illumination. In the UV spectral region, the photons are preferably absorbed by the TiO_2 core. Because the transfer of an electron from TiO_2 into PT is not energetically favorable, the charges recombine and do not contribute to the photocurrent.

The photoelectrical characteristics of the cell were found to be strongly dependent on ambient conditions. When the samples were exposed to the open atmosphere, the shape of the short-circuit photocurrent has changed dramatically as shown in Figure 4B. First, in the visible spectral region corresponding to the PT optical absorption, the direction of the photocurrent was reversed compared with the experimental conditions in vacuum, reaching a higher absolute value. Second, the photocurrent peak with opposite sign was observed for the wavelengths shorter than 380 nm, corresponding to the optical absorption of TiO_2. Also the charging/discharging effects were observed during the current-voltage characteristics measurements in the dark and under illumination. Similar behavior was found previously with photoelectrochemical cells composed of titanium electrode coated with the TiO_2/PT particles [16] or TiO_2/poly(bithiophene) bilayers [17] in $LiClO_4$/acetonitrile solution. The photocurrent was ascribed to the redox behavior of the PT (cathodic photocurrent) and TiO_2 (anodic peak). This suggests that the solid-state nature of the photoelectrical behavior of the cell under study measured in vacuum changed to the photoelectrochemical behavior upon the influence of ambient humidity.

Conclusions

The electrophoretic deposition was found to be a feasible way of preparing layers of insoluble polythiophene coated TiO_2 composite nanoparticles. Although the system was not optimized to achieve the best performance (e.g., neither adhesion promoter nor the binder was used in the electrodeposition), the quality of the layers was sufficient for the preparation of sandwich structures for photoelectrically active devices.

Acknowledgements

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[1] B. O'Regan, M. Grätzel, *Nature*, 1991, *353*, 737.
[2] F. Cao, G. Oskam, P.C. Searson, *J. Phys. Chem*, 1995, *99(47)*, 17071.
[3] U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer, M. Grätzel, *Nature*, 1998, *395*, 583.
[4] W. Plieth, N. Hebestreit, German patent announcement no. 19919261.8.
[5] L. Torsi, P. G. Zambonin, A. R. Hillman, D. C. Loveday, *J. Chem. Soc., Faraday Trans.*, 1993, *9*, 3941.
[6] K. Idla, O. Inganäs, M. Strandberg, *Electrochim. Acta*, 2000, *45*, 2121.
[7] S. Marchant, P. J. S. Foot, *J. Mater. Sci.: Mater. Electron.*, 1995, *6*, 144.
[8] C. L. Huisma, A. Goossens, J. Schoonman, Proceedings of the 17th Workshop on Quantum Solar Energy Conversion (QUANTASOL 2002), March 17-23, 2002, Rauris, Salzburg, Austria.
[9] J. Wen, G. L. Wilkes, *Chem. Mater.*, 1996, *8*, 1667.
[10] R. Gangopadhyay, A. De, *Chem. Mater.*, 2000, *12*, 608.
[11] J. Hofmann, M.S. Thesis, TU Dresden, 2000.
[12] J. Lyklema, *Adv. Colloid Interface Sci.*, 1968, *2*, 65.
[13] P. Sarkar, P.S. Nicholson, *J. Am. Ceram. Soc.*, 1996, *79*, 1987.
[14] G. Wang, P. Sarkar, P.S. Nicholson, *J. Am. Ceram. Soc.*, 1997, *80*, 965.
[15] D. Gebeyehu, C.J. Brabec, N.S. Sariciftci, D. Vaneneugden, R. Kiebooms, D. Vanderzande, F. Kienberger, H. Schindler, *Synth. Met.*, 2002, *125*, 279.
[16] N. Hebestreit, J. Hofmann, U. Rammelt, W. Plieth, *Electrochim. Acta*, 2002, accepted.
[17] U. Rammelt, N. Hebestreit, A. Fikus, W. Plieth, *Electrochim. Acta*, 2001, *46*, 2363.