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Photo-electrochemical properties of ZnO and TiO_2 layers in ionic liquid environment

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ABSTRACT

Photoinduced electrochemical functionality of uniform TiO_2 and ZnO films prepared by sol–gel method, in the former case in the reverse micelle environment, was studied using a specific type of ionic liquids as electrolytes. The coating part was arranged as piezoelectric ink-jet printing. Ionic liquids could be regarded as nanostructured fluids with two distinctive kinds of spatial domain: one ionic, the other non-polar. The driving force for the segregation of the nonpolar chains is energetic. They are excluded from the cohesive network of positive and negative charges that is formed by the charged groups of the ions in close contact. If side-chains are too short they do not disturb the ionic network significantly and, they do not possess enough conformational freedom to adopt low energy configuration. By increasing the chain-length the role of its spatial arrangement becomes important. Such features must be reflected in their specific behaviour as electrolytes in the contact with photoactive semiconducting thin films. Attention was also paid to the correlation of the values of generated photocurrent densities in layers with the fluidity and conductivity of the used ionic liquids.

1. Introduction

In the past years endless number of ZnO, CeO_2, TiO_2, etc. based functional materials have been described. In terms of their photo-induced functionality two types of mutually dependent sub-functionalities must be always considered. The primary function is associated with the photo-induced generation of the hole–electron pair. If the particular material is identified as sufficiently effective in this manner it can be considered for the next step, for example as heterogeneous photocatalyst. Uniform functional films of nanoscopic metal oxides could be produced in many possible routines. One of such methods is the bottom-up generation of ordered structure nanoparticles in cores of reverse micelles [1,2]. The overall process is organized as the sol–gel method, the coating technique then as piezoelectric jet printing [3–6].

Undoubtedly titanium and zinc oxides are the most extensively studied transition-metal oxides. There are many possible applications that might be taken into account depending on their structural and functional features. Here we report on the possible utilization of various types of room temperature ionic liquids (RTILs) as electrolytes in the step of functional characterization of the produced nanoscopic ZnO and TiO_2 films. Hundreds of structurally different ionic liquids are currently available. However, the most commonly used are those with the imidazolium type of cation combined either with hexafluorophosphate or tetrafluoroborate counter ions. Another attractive group of ILs might be ranked among quaternary ammonium salts (QAS) [7]. Ionic liquids could be regarded as nanostructured fluids with two distinctive kinds of spatial domain: one ionic, the other non-polar. The driving force for the segregation of the nonpolar chains is believed to be energetic. They are excluded from the cohesive network of positive and negative charges that is formed by the charged groups of the ions in close contact [8,9]. If the side-chains are too short, they do not disturb the ionic network significantly and, also, they do not possess enough conformational freedom to adopt a low energy configuration. However, increasing the chain-length the role of its spatial arrangement becomes much more important. Obviously such features must be also reflected in their specific behaviour as electrolytes in the contact with photoactive semiconducting thin films [10–13].

To the best of our knowledge electrochemical interactions of these types of RTILs with the reverse micelles templated semiconducting nanoparticles have not been reported yet. Special attention was also paid to the correlation of the values of generated photocurrent densities in layers with the fluidity and conductivity of the used RTIL's.

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2. Experimental part

2.1. Layer's preparation

All TiO_2 and ZnO layers were prepared by means of the sol–gel method. The TiO_2 films were produced from titanium isopropoxide in the reverse micelles used as molecular templates at very low water to surfactant ratio. This modification allows generation of very uniform particles as specified in details elsewhere [1,2,14–16]. The method was previously optimized for piezoelectric ink-jet printing [3–6]. The ZnO films were prepared by standard sol–gel technique involving diethanolamine (DEA) (p.a., Penta, Czech Republic), zinc acetate dihydrate (ZA) (Sigma Aldrich) and propan-2-ol as solvent. The molar ratio between ZA and DEA was held at 1:1, and the concentration of ZA was $0.45\,\mathrm{mol\,L^{-1}}$. First propan-2-ol was mixed with ZA for 10 min to form a clear and transparent solution. Subsequently DEA was added to the solution and the arising sol was stirred for 5 min.

In both cases inkjet printer Fujifilm Dimatix 2830 was used for deposition of the liquid sols on substrates. The sol was loaded into the Dimatix ink tank and the Dimatix 10 pL printing head with the piezoelectric nozzles attached to the tank. This equipment was mounted into the Dimatix printer. As substrate the conductive ITO glass ($5–15\,\Omega\,\mathrm{cm^{-1}}$, Delta-Technologies Ltd., USA) and the soda-lime microscopic glass plates were used. In the case of TiO_2 layers drying (110 °C for 30 min) and calcination steps (450 °C for 4 h) were performed after each coating cycle. ZnO layers were treated by drying (110 °C for 30 min) and then calcined at 500 °C for 4 h. These conditions were already previously optimized [1,3–6,14–18].

2.2. Layers' structural and functional characterizations

The crystallographic form and the particle size of the TiO_2 and ZnO layers were determined by XRD analysis (Panalytical-MRD diffractometer with the Cu anode) and by Raman spectroscopy (Raman Dispersive Spectrometer Nicolet Almega XR). Surface properties of the layers were studied by SEM (Hitachi S4700) and AFM (Thericroscopes) microscopy techniques. Layers' thicknesses were evaluated from SEM images. Values of absorption edges were elucidated from UV–Vis spectra (Perkin-Elmer Lambda 35 equipped with a Labsphere RSA-PE-20 integration sphere).

The photo-induced properties of the TiO_2/ITO and ZnO/ITO electrodes in 0.1 M Na_2SO_4 solution as electrolyte were investigated by means of photo-electrochemical measurements under UV irradiation in the three-electrode Pyrex cell. Prepared films were used as working electrodes and they were irradiated with the light beam of the wavelength of 365 nm. A saturated Ag/AgCl electrode and a platinum plate were used as the reference and the auxiliary electrodes, respectively. The incident light intensity was measured by UV-meter (UV Light Meter UVA-365). The irradiation intensity was $0.4\,\mathrm{mW\,cm^{-2}}$ at 365 nm. Detailed description of the electrochemical set-up and the used electrochemical methodology were reported previously [19–21].

Initially a cyclic voltammetry (CV) was carried out. The CV was carried out from −200 mV to 1200 mV. The linear change of potential was $50\,\mathrm{mV\,s^{-1}}$. The next measurement was a linear voltammetry (LV) with the linear speed of potential change $10\,\mathrm{mV\,s^{-1}}$ and starting again at −200 mV. The light was switched on after 5 s and kept on for 5 s. Afterwards the light was switched off for the next 5 s. These periods were repeated until the potential hit the final value of 1200 mV against the saturated Ag/AgCl electrode. The next method was the amperometry at constant voltage of 0.6 V. In the first 30 s and the last 30 s the irradiation was switched off. Finally the OCP (open circuit potential) was performed. The OCP started with 30 s in the dark then the layers were irradiated for 60 s followed by 60 s of dark.

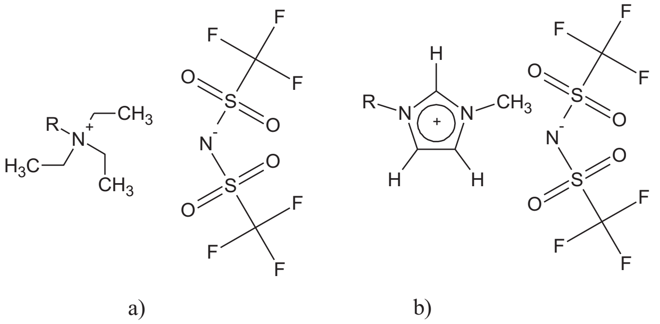

Fig. 1. (a) *N*-alkyl-triethylammonium bis(trifluoromethanesulfonyl) imides ($N_{[R,222]}Tf_2N$, R = 4, 8 and 12). (b) *N*-alkyl, *N′*-methylimidazolium bis(trifluoromethanesulfonyl) imides (RMIM Tf_2N, R = 2, 3 and 4).

Besides 0.1 M Na_2SO_4 specific types of ionic liquids were used as electrolytes [7]. Photo-electrochemical behaviour of the TiO_2/ITO and ZnO/ITO electrodes in the ionic liquid (RTIL) environment was monitored using the same sequence of electrochemical methods as for the Na_2SO_4 electrolyte. Molecular structures of the used ionic liquids are shown in Fig. 1. The ionic liquids differed in the number of carbons on the quaternary bonded nitrogen atom (QAS), and on nitrogen in imidazolium (RMIM). In Table 1 properties of ionic liquids employed to construct the Walden plot [22,23] are summarized. Tabled values were used to specify the current density by means of the dynamic viscosity and conductivity.

3. Results and discussion

3.1. Characterization of TiO_2 and ZnO thin layers

All prepared TiO_2 layers produced by piezoelectric inkjet printing possessed the crystallographic form of anatase (0 0 0 1 dominating orientation). The particle size was 6 ± 2 nm evaluated by the Scherrer equation, and 8 ± 2 nm and by the deconvolution method [24,25]. The only crystallographic form determined in the thin layers of ZnO was wurtzite with predominant 0 0 0 2 orientation. The particle size was 12 ± 2 (15 ± 2) (Table 2). For the surface morphology AFM analysis was employed. It provided information on the relative surface roughness expressed here as the rms factor (Table 2, Fig. 2.). All tested samples consisted of three layers (produced in 1–3 consecutive coating cycles as optimized previously [3–6,17]). The thicknesses of films were estimated from the SEM images (Fig. 2). It was found that the TiO_2 sample with same number of inkjet printed cycles revealed the thickness approximately of 340 nm, the ZnO layers were about 250 nm. Locations of absorption edges of nanoparticulate TiO_2/ITO and ZnO/ITO electrodes were evaluated from absorption spectra for TiO_2 and ZnO layers deposited on microscopic glass (Table 2). For TiO_2 the absorption edge was located around 365 nm with very sharp discontinuity, for ZnO it was determined at around 385 nm with less sharp increase of absorption.

3.2. Electrochemical properties in standard electrolyte environment

All prepared layers possessed very good photo-induced charge separation characteristics. Dependence of the generated current density on the linearly increased potential is illustrated in Fig. 3. The linear voltammetry plot represents the polarization curves of the ink-jet printed TiO_2 and ZnO film electrodes in $0.1\,\mathrm{mol\,L^{-1}}$ Na_2SO_4 solutions. These measurements proved their distinctive behaviour in the UV region, in which all layers reacted immediately and reproducibly to the illumination. Values of the generated