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Electrochemical properties of TiO₂ electrode prepared by various methods

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Abstract

Thin transparent TiO₂ layers were created on the conductive ITO glass by means of the templated sol-gel technique and by the subsequent calcination at 450° C. The sol-gel method using molecular templating is based on a chemical process utilizing hydrolysis and polycondensation of metal alkoxides in the core of reverse micelles which allows a production of uniform particles in layers. The sol-gel method was chosen by reason of the sol-gel layers electrodes are transparent and possess very stable surface. For the preparation of the thin sol-gel TiO₂ films, numerous deposition techniques were applied. This contribution is focused on the study of structural and photo-electrochemical properties of the sol-gel nanostructured layers deposited by two various techniques (a dip-coating and an inkjet printing). The sol's viscosity, concentration, solvent volatility, speed of pulling etc. may influence the final structural properties of layers, such as film thickness, nanoparticles size and surface morphology. The surface properties were determined by XRD, Raman, SEM, AFM and UV-Vis analyses. Photo-induced electrochemical properties were measured by potentiodynamic methods in the three-compartment electrochemical cell. This Pyrex cell contained supporting electrolyte (0.1M Na₂SO₄) and the TiO₂/ITO electrode was used as a working electrode. As an UV source the polychromatic mercury lamp was employed and the wavelength of the incident light was focused by an interference filter on 365 nm.

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Keywords: Titanium dioxide, sol-gel, photoelectrochemistry, dip-coating, inkjet printing

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1. Introduction

Nanoscaled titanium dioxide (TiO_2) in thin layer or powder forms appertains to the most extensively studied semiconductors. This metal oxide is a promising semiconductor frequently used as a photocatalyst in the advanced oxidation processes (water or air purification) due to its non-toxicity, chemical stability, photocatalytic activity and low cost [1-4]. Especially, thin films as the nanostructured electrode materials have become very important in fields of photovoltaics, energy storage, sensing, photoelectrocatalysis etc. [5,6]. As generally known, the photoactivity arises from the semiconductor nature, especially from the ability of the light quantum absorption followed by the charge carrier generation. TiO_2 in crystallographic form of anatase has become an interesting candidate as an n-type photoanode due to its excellent efficiency to generate the electron-hole pairs [7,8].

Preparation of the nanostructured electrode materials with highly uniform nanoparticles has been investigated by many groups [9-11]. The most commonly used method is the sol-gel technique utilizing the molecular templates. The main advantage of this purely chemical method lies in a possibility of layer preparation under laboratory conditions as well as the possibility to tailor TiO_2 layer properties by varying preparation conditions. Nanoparticles with controlled chemical composition, size distribution, uniformity and dispersion can be readily synthesized using reverse micelles [12-14]. Layers prepared in this way possess usually highly transparency, surface homogeneity, size, structure uniformity and very high adhesion to substrate in comparison with the particulate layers.

Nowadays, a variety of deposition techniques for the liquids deposition, such as dip-, spin- or spray-coating, doctor blade, roller etc., has been appeared and each of them offers some advantages and disadvantages [15]. There are three traditional methods of thin layer preparation from liquid precursors: spin-coating, spray-coating and dip-coating. Dip-coating belongs to the traditional and widely used methods of the thin layer preparation. It is based on dipping the substrate into the sol and pulling it out at constant speed. Spray-coating is the other elementary technique which applies liquid sol on the substrate by the spray head with one three-axe system nozzle. And the last method spin-coating uses centrifugal force to form a film of liquid precursor [15-17]. As a new process of the sol application the ink-jet printing has been appeared. This technique proved to be very elegant and clean method for liquids deposition and direct patterning [18].

The sol viscosity, concentration, solvent volatility and the speed of pulling influence the resulting film thickness and structural properties. This contribution is focused on the study and the comparison of structural and photo-electrochemical properties of the sol-gel nanostructured TiO_2/ITO electrode deposited by dip-coating and inkjet printing.

2. Experimental

2.1. Layers preparation

Thin transparent TiO_2 layers were created on the one side of the conductive ITO glass (5–15 Ω , Delta-Technologies Ltd., USA) and on the soda-lime microscopic glass plates by means of the templated sol-gel technique and by the subsequent calcination at 450° C for 4 h. The sol-gel method using molecular templating is based on a chemical process utilizing hydrolysis and polycondensation of metal alkoxides in the core of reverse micelles which allows a production of uniform particles in layers. The reverse micelles were created by molecular templates TX 102 (Sigma-Aldrich) in the nonpolar environment of cyclohexane (Aldrich, 99.9%, HPLC grade) or xylene (p.a., Penta, Czech Republic). In the core of the created micelles a small amount of demineralised water was added. As titan precursor the titanium

isopropoxide (TTIP, 99.999%, Sigma–Aldrich) was used drop-wise. The sol-gel with cyclohexane was used for the dip- and spray- coating techniques. In the case of ink-jet printing the nonpolar environment has been changed to xylene by reason that cyclohexane disturbed the plastic print head [19].

The sol application was performed by laboratory dip-coater (ID-Lab coater 4). The substrate was dipped into the sol where it was kept for 30 s and then substrate was pulled with velocity 6 cm/min. After the each dip-coating cycle the samples were heat-treated. An adapted experimental inkjet printer Fujifilm Dimatix 2830 was used for preparation of the printed layers. Xylene sol was loaded into the Dimatix ink tank and the Dimatix 10 pL printing head with the piezoelectric nozzles was attached to the tank. Then this equipment was mounted into the Dimatix printer. Then small droplets (10 pL) were ejected from the print nozzles and they fall onto ITO glass. After the every new printed layer a gelling and drying step was performed [18].

2.2. Characterization

The deposited thin films were treated by calcination and the surface properties were determined by XRD (Panalytical-MRD laboratory diffractometer with the Cu anode), Raman spectroscopy (Raman Dispersive Spectrometer Nicolet Almega XR), SEM (Hitachi S4700), AFM microscope (Thericroscopes) and optical microscope equipped with Nikon D5000 digital camera. The layer thickness was evaluated by Ocean Optics USB4000 diode array photometer with fibre optic reflectance probe (NanoCalc). Values of absorption edges of layers were obtained from UV–Vis spectra (Perkin-Elmer Lambda 35 equipped with a Labsphere RSA-PE-20 integration sphere).

2.3. Photoelectrochemical measurement

Photoelectrochemical measurements were performed at room temperature in the three-electrode Pyrex cell by means of electrochemical methods. All potentials were referred to Ag/AgCl/KCl(sat) electrode, whereas a Pt sheet was used as a counter electrode. The exposed area of the working TiO₂/ITO electrode for UV illumination and photoelectrochemical reaction was 1 cm². Measurements were performed with a computer-controlled Voltalab 10 PGZ-100 potentiostat. For all electrochemical experiments 0.1 M solution of Na₂SO₄ in ultrapure water (0.06 μS cm⁻¹) was used as working electrolyte. A 500 W polychromatic lamp (Hg, LOT-Oriel) with a water filter was used for UV–Vis irradiation and the incident light beam was modified with an interference filter (Melles Griot) producing spectrally narrow flux of photons (365 ± 10 nm). The applied irradiance was measured with an UV sensor (UVA Light Meter) with intensity 10 mW cm⁻² in the most experiments. Obtained incident light intensity was recalculated to Incident-Photon-Current-conversion-Efficiency (IPCE). The layer photoexcitation properties were characterized by linear voltammetry, amperometry and open circuit potential (OCP) [20].

3. Results and discussion

3.1. Structural properties

Figure 1 (a and b) made by optical microscope illustrates the surface morphology of sample produced by dip-coating and ink-jet printing. As can be seen a visual appearance provided by the optical microscopy shown a homogenous layers with smooth surface without the higher extent of surface defects.

Nevertheless, some heterogeneity in the printed layer thickness reflected in the light interference was macroscopically visible.

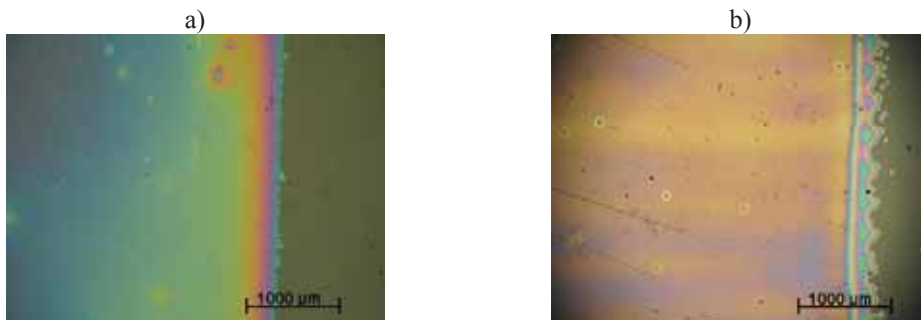
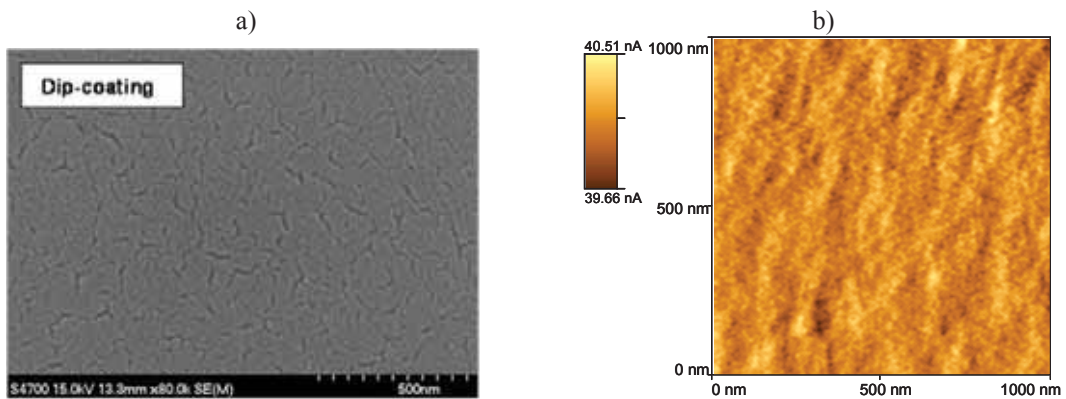


Fig. 1. The layer's surfaces as seen by optical microscopy (a) 1 dip-coated layer; (b) 1 inkjet printed layer

Figure 2(a, b) depicts the surface morphology of sample produced by the three ink-jet printed cycles and three dip-coated cycles recorded by SEM and AFM. The more detailed view at the surface morphology made by SEM shows a smooth porous surface without the higher extent of surface defects which corroborate the results from the optical microscopy. The relative surface roughness expressed as the roots mean square values (RMS) was studied by AFM. Very smooth surface (RMS factor < 1) was detected for the dip-coated layers.



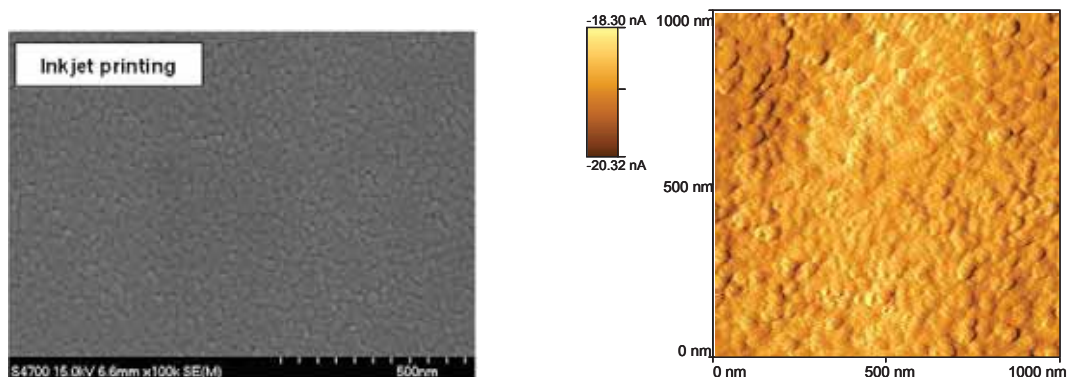


Fig. 2. The images of the 3 dip-coated and 3 inkjet printed layers surface as seen by (a) SEM and (b) AFM

The thin TiO_2 layers produced by various deposition methods possess the crystallographic form of anatase, which was determined by XRD analysis and confirmed Raman spectroscopy. The particles size in layer was obtained from the XRD diffraction lines and calculated by special method (Table 1). The layers thicknesses were investigated from images made by SEM and the absorption edge for both samples was determined from absorption spectra approximately at 355 nm.

Table 1. Characteristics of the produced layers

Layers	RMS factor [nm]	Particles size [nm]	Thickness of 3 layers [nm]	Eoc [mV]
Dip-coating	0,5	7	330	-460
Inkjet printing	3,6	8	340	-400

3.2. Photoelectrochemical properties

All prepared layers possess very good photoinduced properties. The dependence of the generated current density (recalculated to IPCE values) on the linear increasing potential is illustrated in Fig. 4. This linear voltammogram represents polarization curves of the three dip-coated and the ink-jet printed cycles TiO_2 film electrodes. The plot proves the ability of the layers to react on the UV light signal immediately and repeatedly. A very fast photo-response was a general property of all tested layers and represents an important feature that might be appreciated practically (fast response of a sensor). The generated photocurrents in the positive potential area were constant with time and reached characteristic plateau at every irradiated intervals. At negative potential (-400 mV) the photocurrents were also generated, however the values were lower and it can be seen the gradual growth to the constant level.

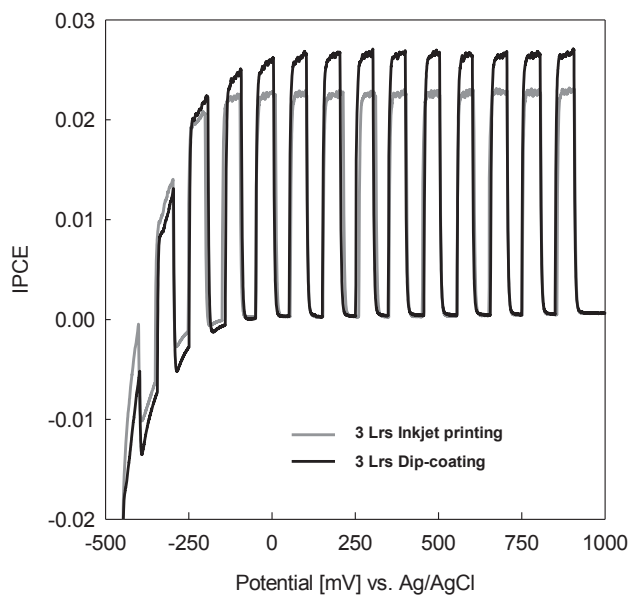


Fig. 4. The polarization curves of the coated and printed TiO_2 layers, scan rate 0.01 V s^{-1} , the incident light intensity 10 mW/cm^2

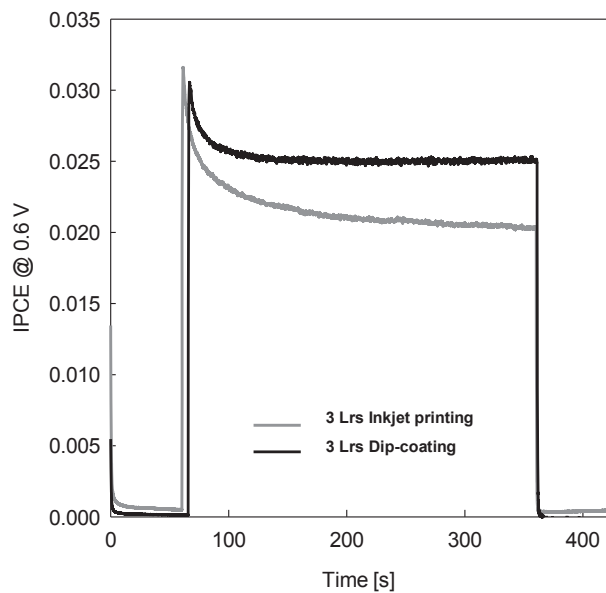


Fig. 5. Photocurrent-time behavior of the prepared TiO_2/ITO anodes. The incident light intensity was 10 mW/cm^2 , constant potential 0.6 V

The values of generated photocurrent were measured at constant potential (0.6 V) by amperometry measurement. This experiment shows the efficiency of the prepared TiO₂/ITO electrode to reach in the 5 min irradiation interval constant photocurrent. The obtained curves indicate the photocurrent-time behavior of the layers. The measured samples embodied the very sharp maximum of the reached IPCE values which was much obvious for the inkjet printed layers. This so called current peak appears immediately at the first moment of the irradiation. Further, the curves decrease very slowly to get a steady state values. The instantaneous increase of IPCE values means a rapid electrons-holes generation and separation at the space charge region. The decrease is assigned to their recombination.

The open circuit potential (OCP) represents the experiment focused on evaluation the kinetics of efficient separation of electrons and holes. The photopotential (E_{oc}) decay was measured and the obtained E_{oc} values are summarized in Table 1. Upon UV irradiation, the open circuit potential shifts immediately to more negative values which reflects rising of the major charge carriers (electrons) concentration. The potential regresses to the original values after the light is switched off. The constant E_{oc} values in the UV light period correspond to the steady state concentration of the not recombined electrons. The amount of photoexcited electrons reacts either with an electron scavenger (e.g. oxidisable species) or with the photogenerated holes or migrates through layers to the conductive substrate.

4. Conclusions

It was proved that the prepared TiO₂/ITO electrodes (TiO₂ thin layers deposited on ITO glass by dip-coating and inkjet printing technique and used as photoanode) are stable and possess good photoinduced properties. The structural properties, especially the surface morphology, and also the photoelectrochemical behavior, mainly the generated photocurrent values, are slightly different. The structural distinction was caused by the used deposition technique. In the photoelectrochemical measurement the differences are very negligible. The obtained electrochemical curves of layers reflect the ability to react on UV light signal by generation of the charge carriers. The electrochemical measurements confirmed the high potential of photoelectrochemistry for detection of the semiconductor oxides photoactivity.

5. Acknowledgements

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6. References

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