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THIN SOL-GEL TiO_2 FILMS PREPARED BY INKJET PRINTING – PHOTOELECTROCHEMICAL PROPERTIES

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Abstract

This study reports the structural and electrochemical properties of the deposited TiO_2 layers prepared by means of the templated sol-gel method by the inkjet printing. The layer morphology and material properties were in detail investigated by optical microscopy, SEM, AFM as well as Raman spectroscopy and XRD analysis. The photo-excitation properties of the TiO_2 layers and the ability of their photocurrent generation were studied by electrochemical methods.

Keywords: Titanium oxide, Sol–gel, Inkjet printing, Photocatalysis, Photo-electrochemistry

Introduction

The thin layers of semiconductor oxides have recently evoked a great interest in the field of sensors, optical electrodes or solar cells. As generally known, the photo-induced properties arise 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 is a promising semiconductor widely used in the field of the advanced oxidation processes and the photoelectrochemical sensing due to its excellent efficiency to generate the electron-hole pairs.

Nowadays, a variety of deposition techniques for the thin layers creation from the liquid precursors exist. A new promising method is called inkjet material deposition or shortly material printing. This method proved to be very elegant and clean technique for the liquid sol deposition. The basic principles consist in the precisely deposited tiny droplets of a low-viscosity liquid onto a substrate by means of piezoelectric print head, which is similar principle to conventional inkjet printing. This technique also brings the possibility of direct patterning.

Experimental

The most commonly used method for the nanostructured materials with highly uniform nanoparticles preparation is sol-gel technique utilizing the molecular templates. The sol-gel method is based on hydrolysis followed by polycondensation of titanium alkoxide (TIOP) in the core of reverse micelles, where a small amount of water is involved. The micelles are formed by surfactant Triton X 102 in the nonpolar environment of xylene. Prepared sol is loaded into the adapted experimental inkjet printer equipped (Fujifilm Dimatix 2830) with the piezoelectric print head. Then small droplets are ejected from the print head and fall onto the conducting ITO glass. The glass plates with printed layers were dried in an oven at 110° C for 30 min and then the samples were thermally treated by calcination at 450° C for 4 hours.

The structure properties of the prepared layers were studied by series of characterization methods involving AFM, SEM, XRD, Raman and UV-Vis. Photo-induced electrochemical behaviour of TiO_2 electrode was performed at room temperature in the three-electrodes Pyrex

cell by means of electrochemical methods. A saturated Ag/AgCl electrode and a platinum plate were used as the reference and the auxiliary electrodes, respectively. The exposed area of the working TiO2/ITO electrode was irradiated by monochromatic light and the photoelectrochemical response was monitored by a computer-controlled Voltalab 10 PGZ-100 potentiostat. For all electrochemical experiments 0.1 M water solution of Na_2SO_4 was used as a working electrolyte.

Results and discussion

The crystallographic form of the pure anatase was detected by XRD analysis and confirmed by Raman spectroscopy. The particle size of anatase was estimated at 8 ± 1 nm. The layer thickness was determined by optical methods (NanoCalc and SEM images) and also by X-ray reflectivity (XRR). The layer thickness linearly increases and for 3 layers the value is approximately 340 nm (Fig. 1). The surface morphology was characterized by AFM analysis and the relative surface roughness expressed as RMS factor (3.7 nm) showed relatively smooth surface. The layers also possess very good transparency and mechanical stability. Nevertheless, some heterogeneity in the layer thickness reflected in the light interference was macroscopically visible. The UV–Vis absorption spectra of the ink-jet printed layers were measured for variable number of deposited layers. Only negligible shift of the absorption edge to the higher wavelengths with increase of the layer thickness was detected. The position of absorption edge was located at 350 nm.

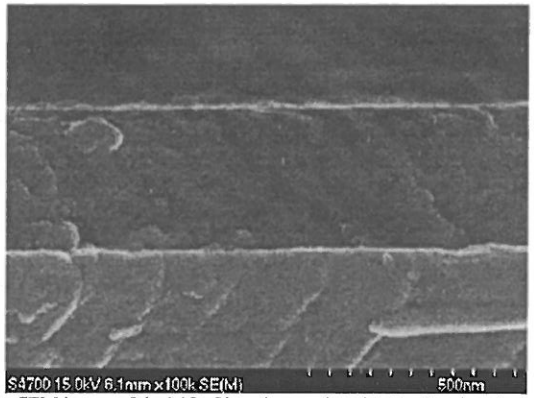

Fig. 1: SEM image of the TiO_2 film edge produced in 3 printed cycles.

The photo-excitation properties of the TiO_2 layers were measured by linear voltammetry, amperometry and open circuit potential (OCP). The dependence of the generated current density (recalculated to IPCE values) on the linear increasing potential is illustrated in Fig. 2. This linear voltammogram represents polarization curves of the ink-jet printed TiO_2 film electrode with different number of printed layers. The curves provide information of the layers efficiency to generate current upon irradiation and the efficiency to respond fast and repeatedly to the light signal. The influence of the film thickness which depends on the number of printing cycles is evident. The obtained IPCE values increase with the number of printed layers.

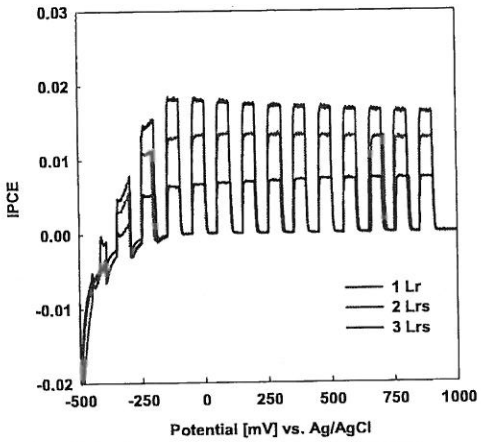

Fig. 2: The polarization curves of the printed TiO2 layers.

The amperometry measurements (Fig. 3) express the ability of the ink-jet printed TiO_2/ITO electrode to produce the measurable photocurrent values in the 5 min irradiation interval at constant potential 0.6 V. All measured samples embodied the very sharp maximum of the reached IPCE values. This current peak appears immediately at the first moment under the light. 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 decrease is assigned to their recombination. The influence of the printed cycle number is evident; the IPCE values increase again with increasing thickness of the prepared layers.

The photopotential (Eoc) decay was also measured. Figure 4 represents the dependence of the changing potential values on time. 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 *Eoc* values in the UV light period correspond to the steady state concentration of the not recombined electrons. The influence of the printed layers number can be seen - the amount of accumulated electrons in the TiO_2 nanostructure electrode depends on the layer thickness. Generally, the higher thickness of the TiO_2/ITO layers electrode, the higher photopotential values.

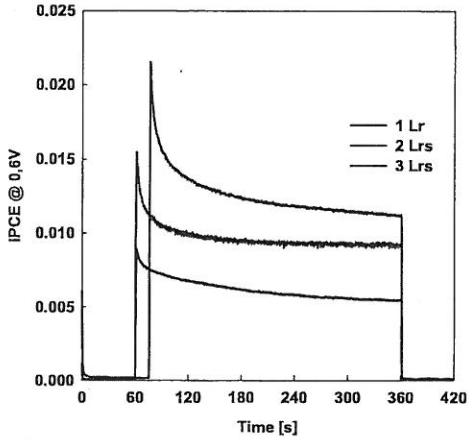

Fig. 3: Photocurrent-time behaviour of the prepared TiO_2/ITO anodes.

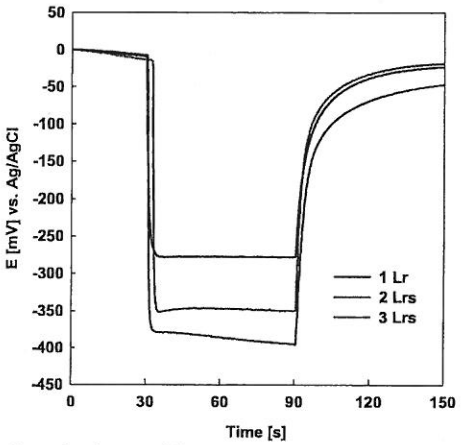

Fig. 4: Open circuit potential measurements

Conclusions

It was proved that prepared TiO_2/ITO electrodes (TiO_2 thin layers on ITO glass used as photoanode) are stable and possess good photoinduced properties. 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 photo-electrochemistry for detection of the semiconductor oxides photoactivity. This study clearly proved the possibility of production of transparent functional thin layers deposited on the conductive substrate by inkjet printing from the liquid sol utilized the reverse micelles system.

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EFFECT OF PREPARATION PARAMETERS ON THE PROPERTIES OF SPRAYED TiO_2 LAYERS

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Abstract

This work deals with the photocatalytic activity of TiO_2 films prepared by spraying of sol-gel precursors and colloidal suspension of TiO_2 particles. Photocatalytic activity was investigated using 2,6-dichloroindophenol model ink. It was found that layers prepared by spraying method of water suspension show minimal photocatalytic activity compared to layers prepared by sol-gel. Optimal conditions for the preparation of sol-gel method were found (distance 29 cm, spraying velocity 12.5 cm/s, substrate temperature 22 °C).

Keywords: titanium dioxide, photocatalysis, spray-coating, sol-gel, colloidal suspension

Introduction

Preparation of thin films is the most frequently used application of sol-gel method. Dip-coating and spin-coating are commonly used for the deposition of thin films. These methods, however, have several disadvantages as specific requirement to the size and shape of the substrate, non-economical use of precursors and complicated transition to large scale application. The method of layer deposition by spraying removes most of these requirements. Therefore we have dealt with this methodology in more detail.

The layers were prepared by two different techniques: (i) from the alcohol solution of TiO_2 precursor using sol-gel method and (ii) from the aqueous suspension of TiO_2 nanoparticles. The conditions for the preparation of homogeneous transparent photocatalytically active layers were optimized. Three parameters were controlled during the preparation of the layers: i) substrate temperature during spraying (22 °C, 100 °C), ii) movement rate of spray head (7 cm/s, 12.5 cm/s, 22 cm/s) and iii) distance of spray head from the substrate (25 cm, 29 cm) [1].

Experimental

Preparation:

For the preparation of TiO_2 layers by sol-gel method the following procedure was used. Titanium tetraisopropoxide (TiP) was mixed with isopropyl alcohol (IPA, p.a.) and then acetylacetone (AcAc SigmaAldrich) and hydrochloric acid (HCl, 36%, p.a.) was added [2]. Sol was applied by spraying on the substrate (soda lime glass) then annealed at temperature 500 °C (heating rate 2°C/min; time 120 min).

For the preparation of layers from the aqueous suspensions of TiO_2 the following procedure was used. Suspension was prepared from $TiOSO_4$ solution cooled to 0°C with addition of 25% NH_4OH to pH 8 and further addition of 65% HNO_3 to pH 1.5. Afterwards the solution was stirred at 70°C for 90 minutes. Concentration of TiO_2 anatase nanoparticles (5-10 nm) was ≈ 2.3 g/l. Aqueous suspension was deposited by spraying on the substrate (soda lime glass) and dried at room temperature

Characterization:

Crystalline structure was determined by X-ray diffraction (Seifert - XRD 3000; Panalytical HighScore Plus). Macrostructure of layers was investigated by optical microscope (Axio Scope Zeiss.A1). The thickness of layers was calculated from layer mass using the density of anatase and the geometric surface area. The photocatalytic activity of films was determined using the model ink containing dye 2,6-dichloroindophenol (DCIP) [3]. Thin film