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THE INFLUENCE OF VARIOUS DEPOSITION TECHNIQUES ON THE STRUCTURAL AND PHOTOELECTROCHEMICAL PROPERTIES OF THE THIN TiO_2 FILMS

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The nanostructured electrode materials with uniform nanoparticles could be prepared by physical (PVD), physically-chemical (PECVD) or purely chemical methods. The sol–gel technique is the most common and successful method for the uniform nanoparticle preparation. This wet chemical method offers approaches to the synthesis of metal oxides with the controlled structure, morphology, particles sizes and even the chemical composition of the final material. Due to rheological properties of the liquid sol it is possible to create fibres by spinning or thin films by various deposition techniques. A number of articles concerning various deposition techniques of the thin layer preparation from liquid precursors have been reported [1-3]. Each of them refers to advantages and disadvantages of the applied method. The dip-coating belongs to the traditional and the widely used method of the thin layer preparation. It is based on dipping the substrate into the sol and pulling it out at constant and the well-defined speed. The layer thickness could be controlled by the pull-out speed, by the time interval which the substrate spends in a liquid and/or by the viscosity of the liquid sol. The spray-coating is the other elementary technique which applies liquid precursor on the substrate by the spray head with one three-axe system nozzle. The system is able to cover homogenously the large substrate areas by droplets of liquid solution. Usually, this technique is widely used in industry. Inkjet printing has appeared recently as a new way of the sol application. The inkjet print head contains an array of piezoelectric nozzles ejecting very small droplets of a low viscosity ink or other functional liquid. The possibility of a complete control over the deposition process parameters and precise patterning without the need of any mechanical or optical masking make this deposition method very appealing for the production of sensors, solar cells etc. This study is focused on comparison of the photo-induced conductivity of the thin TiO_2/ITO electrode deposited by three various deposition techniques (dip-coating, spray-coating and inkjet printing) on conductive ITO glass.

The thin TiO_2 layers were prepared by the sol–gel method using molecular templating, which allows a production of uniform particles in layers. The prepared thin layers were used as photoanode in the three-compartment electrochemical cell. The thin TiO_2 films were treated at 450° C and after calcination all samples possessed the crystallographic form of anatase. The surface properties of the calcined layers were determined by XRD, Raman spectroscopy, SEM, AFM, UV–Vis analyses and by the optical microscopy. The photo-induced properties of nanoparticulate TiO_2/ITO photoanode were studied by electrochemical measurements combined with UV irradiation. The relationship between surface structure and photo-induced conductivity of the nanostructured layers was investigated.

It was found that the used deposition techniques significantly influenced the structural properties of prepared layers; mainly, the formation of defects and their quantity in the prepared films. The type of created defects similarly as their amount and ratio of the surface/bulk defects in the prepared thin films play an important role in the photo-induced properties [4]. These defects probably arise from the means of the sol deposition on substrates similarly as from the sol volume presented on substrate at calcination. By choice of the liquid sol deposition method the surface/bulk defect concentration in layers can be controlled. It was proved that decreasing ratio of the bulk to surface defects improved the charge carriers (electron–hole pairs) separation efficiency. Thus, the photocurrent generation could be significantly enhanced. In general, it is obvious that structural properties, especially the surface morphology can significantly influence the local surface chemistry. To compare their photoelectrochemical properties TiO_2 layers supported on ITO glass were tested as TiO_2/ITO photoanode. All tested photoanodes possessed very good photo-induced properties; moreover, a very fast response to the light signal was proved even for the low light intensity. On the other hand, the observed differences in the reached IPCE values for the photoanodes prepared by dip-coating, inkjet printing and spray-coating were relatively low (Fig. 1).

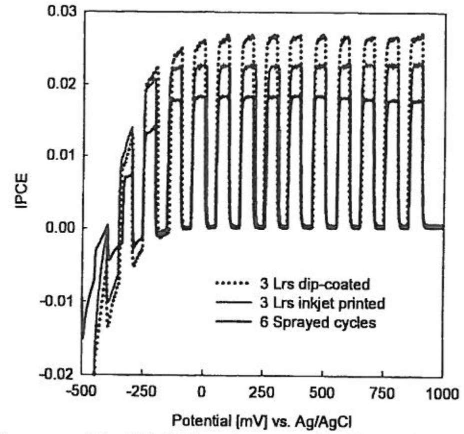

Fig. 1: The polarization curves of the TiO_2/ITO anodes prepared by dip-coating, inkjet printing and spray-coating techniques, scan rate 0.01 V/s, the incident light intensity 10 mW/cm^2

It can be summarized that each of the deposition techniques offers some advantages as well as disadvantages. The dip-coating method forms the best homogeneous thin film with minimum of the bulk defects and thus the highest IPCE values and the photogenerated current. The inkjet printing method also forms the homogeneous thin film with a low amount of the bulk defects and the high IPCE values. Moreover, this technique enables printing of the regular as well as the irregular patterns. The spray coating method reveals the rather lower IPCE values and the photogenerated current, but this method enables to cover any surface by the nanosized TiO_2 layers even if the area would be larger.

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