Thin Films with Photoresponse Modulation

Klusoň, Petr
2012

THIN FILMS WITH PHOTORESPONSE MODULATION

P. Klusoň[a], M. Morozová[a], P. Dzik[b], M. Veselý[b], L. Kubáč[c]

[a] ICPF of Academy of Sciences of the Czech Republic, Rozvojova 135, 165 02 Prague 6, Czech Republic. (kluson@icpf.cas.cz)
[b] Faculty of Chemistry, Brno Technical University, Purkyňova 464/118, 612 00 Brno, Czech Republic.
[c] Centre for Organic Chemistry Ltd., VUOS Pardubice, Rybitvi 296, Rybitvi 533 54, Czech Republic.

The presented work focuses on the generation of thin films formed of organised metal oxide nanoparticles with an inherent electrochemical end-function. The functionality requires the basic nanostructured materials to be "predefined" by means of special methods used for their preparation [1,2]. In this respect the piezoelectric jet printing of ionic liquids templated nanoparticles has been chosen [2,3]. Attention was paid to the self-assembly for yielding aggregates of variously structured room temperature ionic liquids (ILs). Potentially their coexistence with assemblies of non-ionic surfactants to form multicomponent templating superclusters will be also surveyed. This approach, together with the utilisation of piezoelectric jet printing, is understood as the basis for generating functional nanoparticulate materials in the form of thin films. Such systems are believed to be highly useful as parts of advanced electro-analytical photonic sensors [3]. Their utilisation is focused on trace detection of highly toxic chemicals in the environment, protection elements, etc. The functionalities of the developed materials toward the expected use are tested in the special opto-electrochemical module. Combination of the piezoelectric jet deposition with the template clusters and superclusters has not yet been reported yet.

Majority of current materials are typically structurally inhomogeneous. The physical and chemical processes associated with their primary functions take place on the surface which contains many defects. Molecular templating principles may assist in production of structures which are closely similar to idealized, theoretically designed materials. Independently of the types of new materials, the most important point concerns pathways that are capable to yield them. Among suitable approaches molecular templating have dominated in the recent past. These building components are usually nanometric, monodisperse, and the variety of their shapes and interactions enables the formation of an amazing range of architectures (and functionalities). One of the very efficient strategies is the reverse micelle templating. It has been pioneered during the last 12 years and it has received intensive international attention. The ionic liquid templating is the next step which was first described only recently. Its combination with the proposed deposition piezoelectric jet technique is completely new idea.

Nanoscale templated metal oxide thin films undoubtedly appertain to the most extensively studied materials due to their optical and electrochemical properties [4,5]. Their photo-induced properties arise from the semiconductor nature, especially from the ability of the light quantum absorption followed by the charge carrier generation. In order to produce metal oxide thin layer layers, the liquid sol containing also the templating bodies, and confining nanoparticles, must be coated onto a substrate. Various coating techniques have been used for this purpose, such as dip-, spin- or spray-coating. Recently a new promising deposition technique has appeared. The novel approach is usually termed piezoelectric jet material deposition or shortly material printing. In this case the ink is the specially formulated liquid purposed for transporting functional components onto the substrate surface. This technique brings the possibility of direct patterning, i.e. the fabrication of 2D patterns on the substrate without the need of any mechanical or optical masking. Material printing has been already employed for the deposition of variety functional materials [2,3].

Many metal semiconducting oxides materials reveal photoelectrocatalytic activity toward oxidation of various organic compounds. This process might be in principle used also for detecting organic substances in aqueous solutions based on monitoring steady-state photocurrents. It is known that, e.g., at the anatase TiO_2 nanoporous electrode the potential bias changes the rate-determining step from electron migration in the film at low potentials to photohole capture at relatively high potentials. When the applied potential bias is sufficient, the steady-state photocurrent obtained reflects exclusively the rate of the photohole capture (scavenging) at the metal oxide surface. A typical model compound for such experiments is oxalic acid, but in principle it might be any organic matter dissolved in water, even at very low concentrations [3-5].

The work has been particularly focused on characterisation of photoexcitation properties of thin TiO_2 layers produced by means of the sol-gel method carried out in the reverse micelle environments formed of structurally different surfactant molecules. Those surfactants were of the non-ionic type from the group generally referred to as Tritons X. The core of the micelle was utilised as a reaction space for hydrolysis of the Ti alkoxide molecules and for the parallel – consequential step, polycondensation of the forming intermediates. The Tritons molecular templates varied in the length of their hydrophilic oxyethylene chains. These variations may affect the size, morphology, shape and structure of the resulting particles of TiO_2. Structural characterisation was understood here as an essential part of the work and it comprised AFM, SEM, TEM, XRD, UV-Vis, the surface wettability tests and volumetric adsorption measurements [4,5]. The central point of this research was focused on the evaluation of the photoexcitation properties of the produced thin films. Photoelectrochemical and photocatalytic experiments were designed and performed as the tools to achieve this goal. Photoexcitation properties were characterised particularly with help of the cyclic voltametry, linear voltametry, amperometry and OCP. Generally, the ability of the produced nanoparticulate films to generate the photocurrent upon illumination with well-defined UV spectral line was followed. In parallel a simple photocatalytic test based on degradation of acid orange 7 model compound was also performed. Very easy and stable photoexcitation depending on the used molecular templates and also on some structural and morphological properties of the layers was found. Such features are of great advantage when constructing effective sensors and protecting elements based on the light to current conversion.

References

[1] P. Kluson, S. Hejda, M. Hejdova, J. Krysa: A genuine way to mimic the solar-light conditions in UV driven heterogeneous photocatalytic reactions, Reaction Kinetics, Catalysis and Mechanisms 104 (2011) 273.

[2] M. Morozova, P. Kluson, J. Krysa, P. Dzik, M. Vesely, O. Solcova: Thin TiO_2 films prepared by inkjet printing of the reverse micelles sol-gel composition, Sensors and Actuators 160 (2011) 371.

[3] M. Morozova, P. Kluson, J. Krysa, Ch. Gwenin, O. Solcova: Oxalic acid sensors based on sol–gel nanostructured TiO_2 films, J. Sol-Gel Sci. Technol. 58 (2011) 175.

[4] S. Kment, Z. Hubicka, P. Kluson, J. Krysa, H. Kmentova, J. Olejnicek, M. Slater, L. Jastrabik: Photo – Electrochemical Properties of Hierarchical Nanocomposite Structure: Carbon Nanofibers / TiO_2 /ZnO Thin Films, Catal. Today 161 (2011) 8.

[5] S. Kment, H. Kmentova, P. Kluson, J. Krysa, Z. Hubicka, V. Cirkva, I. Gregora: Notes on the photo-induced characteristics of transition metal-doped and undoped titanium dioxide thin films, J. Colloid Interface Sci. 348 (2010) 198.