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2011

Dostupný z <http://www.nusl.cz/ntk/nusl-155850>

Dílo je chráněno podle autorského zákona č. 121/2000 Sb.

Tento dokument byl stažen z Národního úložiště šedé literatury (NUŠL).

Datum stažení: 19.08.2024

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Acknowledgement

Dr. Urh Černigoj is acknowledged for his contribution in designing the photoreactor and formulating the sols. This research was supported by the Slovenian Research Agency and partly also by the Slovenian-Indian bilateral project "Application of different photocatalytic materials for efficient degradation of different industrial pollutants".

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THIN SOL-GEL TiO₂ FILMS PREPARED BY INKJET PRINTING – SYNTHESIS AND CHARACTERIZATION

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Abstract

An optimized reverse micelles sol-gel composition was deposited by inkjet direct patterning onto glass supports. Experimental "material printer" Fujifilm Dimatrix 2831 was used for sol patterning. Printing was repeated up to 4 times in wet-to-dry manner and photocatalytic coatings of various thickness were obtained after final thermal calcination. Basic material properties of prepared coating were studied by optical microscopy, electron and atomic force imaging, Raman, XRD and UV-VIS spectrometry. Photocatalytic activity was evaluated by dye and fatty acid degradation rate. Reverse micelles proved to be viable synthetic route for the preparation of titania coatings with even structure and their compatibility with inkjet direct patterning deposition was demonstrated.

Keywords: titanium dioxide, photocatalysis, reverse micelle, inkjet printing

Introduction

For the past 4 decades, titanium dioxide has been the subject on an intensive research. What was started by Fujishima and Honda's seminal report [1] on photoelectrochemical splitting of water on titanium dioxide electrodes, has gradually developed into a broad technological field of applied photocatalysis.

Undoubtedly, the sol-gel process definitely proved its benefits and potential as a viable route to fabrication of nanostructured coatings. However, the sol-gel chemistry is only one part of the story – in order to produce titania layers, the liquid sol formulation must be coated onto a substrate. Many different coating techniques have been proposed, such as dip-, spin- or spray-coating, doctor blade spreading, roller etc.[2] While all these techniques proved to be useful, they are buried by some inherent limitations. These include, but are not limited to: sensitivity to surface defects, limited coating area, ambient humidity interference, efficiency of precursor use. Fortunately, a new promising deposition technique has become available recently. The novel approach is usually termed inkjet material deposition or shortly material printing. The technique shares the basic principles with conventional inkjet printing, i.e. tiny droplets of a low-viscosity liquid are precisely deposited onto a substrate by means of thermal or piezoelectric printhead. In the case of material printing, the ink is a specially formulated liquid used for transporting a functional component onto the substrate surface.

This technique is very robust and outperforms the traditional ones in most aspects:

- Sensitivity to **surface defects** is strongly suppressed, because a defect is simply overprinted. In the worst cases it may eventually disrupt the layer homogeneity, but it certainly won't influence its surroundings.
- **Coating area** is limited solely by the printer design. Inkjet printers handling roll media of a meter width or rigid media of several square meters area are common nowadays in the printing industry. Such printers can be easily converted for printing functional liquids instead of original colored inks.

- **Environmental sealing:** The ink is kept in airtight tanks and tubing until printing so evaporation and humidity absorption is eliminated.
- **Efficiency of sol consumption:** A tiny fraction of the ink is consumed for print head cleaning and purging, but most of the ink is actually delivered to the substrate.
- The most important advantage this technique brings is 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 successfully employed for the deposition of a great variety of functional materials forming thin layers, various patterns 2D (arrays, gaps, sandwich) and even 3D structures. The authors of this paper have previously reported [3] the deposition of conventional sol-gel formulations based on tetraisopropoxy titanate and acetylacetone by a modified office inkjet printer equipped with piezoelectric print head (Epson R220). In this way they were able to prepare thin layers of TiO₂ with excellent optical properties and photocatalytic performance comparable to dip- or spin-coated layers. Thick multilayer coatings were printed with the help of poly(ethylene glycol) acting as viscosity modifying, templating and anticracking agent [4].

In this work, the authors summarize their further achievements concerning titania coatings deposited by inkjet printing. This paper briefly summarizes the key results of recent experiments employing original reverse micelles sol-gel dip-coated composition [5] later adopted for inkjet direct patterning of photocatalytic coatings. A following paper presented in this preceding discloses a summary on the photoelectrochemical properties of these coatings. Separate original research articles giving detailed information on the sol development, optimization the photoexcitation properties of the TiO₂ printed layers [6] as well as photocatalytic activity [7] have been published recently.

Experimental

The optimised sol formulation consisted of xylene, non-ionic surfactant Triton X 102, water and titanium isopropoxide (see [6] for details). Prepared sol was stored at room temperature in airtight bottles and was stable for 6 months at least.

Experimental inkjet printer Fujifilm Dimatix 2831 was used for sol deposition and patterning. Prepared sol was sonicated for 5 minutes and then loaded into a syringe. A 0.2 um membrane filter (Pall Corporation, USA) and a blunt needle were attached to the syringe luer port and the sol was filtered and filled into the Dimatix ink tank in once. A Dimatix 10 pL printing head was attached to the tank and mounted into the Dimatix printer. Since the sol is a true analytical solution and does not contain any solid components, the jetting performance was excellent and nozzle blockage was rarely observed.

Two sizes of soda-lime glass substrates were used for printing the sol: Standard microscopic plates (25x75 mm, Paul Marienfeld, Germany) and custom cut plates (50x50 mm, Merck, Czech Republic). Plates of both sizes were pre-treated by boiling in 9 M sulphuric acid for 1 hour in order to remove the surface sodium ions. Without such treatment, sodium ions would migrate [8] during the calcination process into the forming TiO₂ layer and could reduce the photocatalytic activity [9].

A simple rectangular pattern 20x20 mm and 40x40 mm were printed onto the microscopic and custom-cut plates, respectively. The printing process was repeated up to 4 times to obtain various thicknesses of the resulting TiO₂ layers: each printing phase was followed by a gelling and drying phase (30 min at 110 °C) The finished samples were then calcined in air for 4 hours at 450 °C.

Microphotographs of printed layers were recorded using Nikon Eclipse E200 optical microscope equipped with a Nikon D5000 digital camera and Nikon Camera Control Pro 2

software. Polarised light was used to enhance the interference-originating color of the printed layers. Captured raw images were conveniently processed and organised by Adobe Lightroom. Structural analysis of the prepared thin films was performed by Raman spectroscopy (Raman Dispersive Spectrometer Nicolet Omega XR), scanning electron microscope (Hitachi S4700, Tescan MIRA II LMU) and AFM microscope (Nigra Prima by NT-MDT). Diffuse reflectance UV-Vis spectra were recorded by Ocean Optics Redtide spectrophotometer with reflectance fiber probe.

Photocatalytic activity of prepared titania coatings towards solid organic matter was evaluated on the basis of fatty acid thin film degradation monitored by FTIR spectrometry. Stearic acid (SA) was used in this experiment. SA film was again deposited by inkjet printing: printing ink was prepared by mixing 1 ml of 0.1 molar solution of SA in toluene with 9 ml of isobutanol. This ink was filtered through 0.2 um membrane filter and loaded into a Dimatix ink tank. The tank was attached to a 10 pL print head and mounted into the Dimatix 2831 printer set to 20 um nozzle span. A single layer was printed onto previously prepared samples of TiO₂.

Results and discussion

Fig. 1 illustrates the visual appearance of prepared samples as seen in the optical microscope. The catalyst layers are smooth, glossy, clear and transparent, with a slight color tint originating from light interference. Cracking takes place in the thickest 4-layered sample and on the edges of other samples where the thickness is increased by edge effects.

SEM images at fig. 2 show the characteristic even porous structure free of defects. SEM cross-sectional images were also used to determine the layer thickness which is appr. 110 nm per single layer. AFM imaging revealed the globular structure originating from the micellar nature of sol. It is evident that the printed and calcined layer maintained the imprints of individual micelles very well. On the other hand, the globular surface topology is extremely regular with minimal vertical deviations and therefore contributes to the very high smoothness of the printed layer. RMS roughness of 3-layered sample was 3.7 nm. Raman spectroscopy and XRD was used to study the phase structure. Both confirmed pure anatase phase in all printed samples, details are discussed at [6]. Diffuse reflectance spectra of prepared samples are presented at fig. 4.

The photocatalytic activity towards solid fatty acid is strongly influenced by the layers thickness. Fig. 5 illustrates the kinetic data obtained from the stearic acid degradation experiments. Relative decrease in the integral peak area of FTIR absorption bands over the range 2700–3000 cm⁻¹ has been plotted as the function of irradiation time and corresponding exposure dose. Data were obtained from the averaging of 5 parallel batches whose deviations were well below 1 % making the error bars invisible. The pseudo-first order rate constants and their errors linear fitting are plotted in the figure inset.

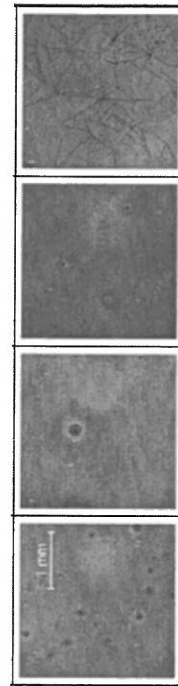


Fig. 1: Optical micrographs of printed titania layers, 1 – 4 layers, left to right

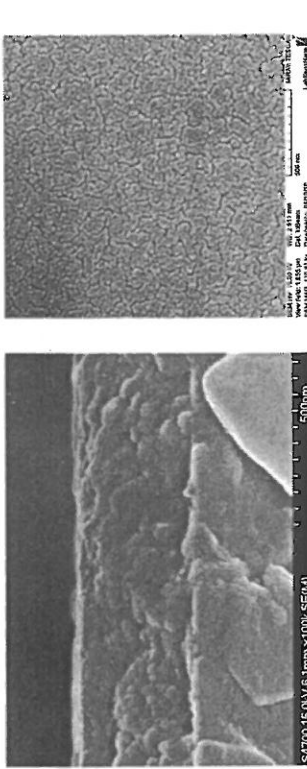


Fig. 2: SEM top view of printed photocatalyst (left) and the cross sectional view of 3 layered sample

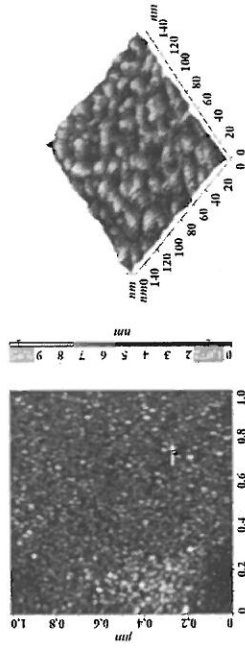


Fig. 3: AFM scans of printed photocatalyst single layer

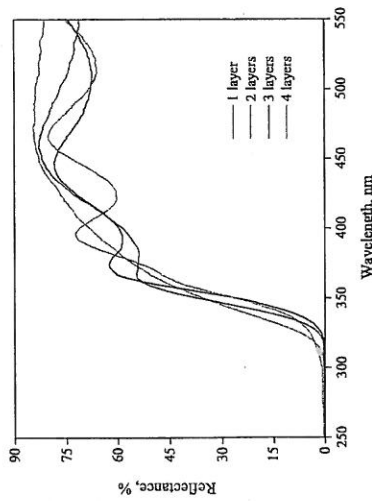


Fig. 4: Diffuse reflectance UV-VIS spectra of printed photocatalyst

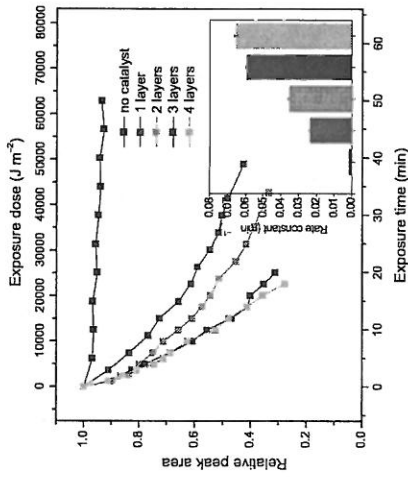


Fig. 5: Degradation of stearic acid

Conclusions

A reverse-micelle organotitanate sol composition was printed by experimental inkjet printer onto glass support. After thermal calcination, titania coating of various thickness were obtained. The coatings were smooth and transparent (with the exception of 4-layered samples which cracked significantly), consisting of pure anatase phase structure. SEM and AFM analysis revealed a well preserved globular surface topology with low surface roughness.

Direct patterning performed by piezoelectric inkjet printing proved to be an attractive method for depositing liquid formulations onto solid supports. It provides clean, efficient and highly repeatable way of coating. Moreover, it is easy to up-scale to coat large substrates by means of industrial large-format printers and at the same time it brings the possibility to produce 2D patterns with micrometer accuracy. These features make direct inkjet patterning one of the prominent deposition techniques for the quickly expanding field of printed electronics.

Acknowledgement

This work has been supported by projects 104/09/P165 and 203/08/H032 of the Czech Science Foundation. Authors also appreciate the work of Jana Chomoucká who provided SEM imaging at the LabSensNano laboratory of Faculty of Electrical Engineering and Communication, Brno University of Technology.

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