

Ordered Mesoporous Films of TiO₂ as Highly Efficient Photocatalysts for Clean Environment

Jiří Rathouský*, Vít Kalousek* and Christine Walsh**

*J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic, jiri.rathousky@jh-inst.cas.cz

**SOPRA SA, Bois-Colombes, France

ABSTRACT

We have developed a low-cost procedure for the deposition of mesoporous films of TiO₂, which is based on spraying a sol containing titanium alkoxide, concentrated HCl, a suitable block-copolymer serving as a structure directing agent and a solvent, the viscosity of the spraying sol and the conditions of spraying being precisely adjusted in order to achieve uniform coverage of the surface. The thickness of the films can be readily controlled by varying the number of deposited layers, their porosity being homogeneous and their surface area and pore volume increasing practically linearly with the increasing number of deposited layers. The mesoporous films of TiO₂ are highly promising photocatalysts for the oxidation of NO at low concentrations and the removal of liquid layers deposited on their surface.

Keywords: TiO₂, mesoporous layers, spray-coating, photocatalysis, nitric oxides, self-cleaning surfaces

1 INTRODUCTION

At present we are faced with the consequences of the pollution of the municipal cities atmosphere and the soiling of the external surfaces of building structures. Another very important general issue in a vast range of technologies is the requirement to render the surface of a number of products self-cleaning or at least easy-to-clean. Such distinguishable properties would substantially enhance the utility value of the products and would help improve the cleanness of the environment and the quality of life.

Photocatalytic oxidation is a promising technology for the purification of air. Its main advantage over other oxidation treatments is the ability to degrade pollutants at ambient pressure and temperature from the direct absorption of light. [1,2] Providing the surfaces of objects both large and small with a finish, which is photocatalytically active and exhibits stable illumination-induced superhydrophilicity, is a promising route how to render them self-cleaning or easy-to-clean. The layer should be active enough to decompose the solid or liquid deposits or to convert them to such a form, which is easy to remove, typically to smaller oxygenated organic compounds, which can be easily washed off.

Due their unique properties, the anatase crystalline films with developed 3D mesoporosity are photocatalysts of choice for the environmental applications. [3,4] In recent years, a generalized sol-gel procedure for the preparation of large-pore mesoporous films of metal oxides has been developed, which is based on a mechanism that combines evaporation-induced self-assembly (EISA) of a block copolymer with complexation of molecular inorganic species enabling to prepare mesoporous films with good mechanical, optical and transport properties. [5,6]

Mesoporous films of TiO₂ are especially effective when the photodecomposition mechanism is based on the surface-adsorbed reactants. The amount of adsorbed substances is increased due to the large surface area, which enhances their decomposition. Further the mesoporosity will ensure fast transport of O₂ and H₂O, which are viable for the photocatalytic degradation of deposits. This transport is often significantly hindered by the compact layer of the dirt.

The films are usually deposited by dip- or spin-coating, these procedures, however, being often technologically inconvenient and rather costly due to the shape and size of the object to be coated. In a recent review, Sanchez *et al* suggested that EISA is compatible also with spray coatings without providing any experimental data. [7] In the present communication we report a low-cost procedure, which is based on the spraying of a sol containing titanium alkoxide, concentrated HCl, a suitable block-copolymer serving as a structure directing agent and a solvent, the viscosity of the spraying sol being precisely adjusted in order to achieve uniform coverage of the surface. These layers will be shown efficient in the photocatalytic oxidation of NO and photocatalytic decomposition of layers of a model fatty dirt, namely oleic acid.

2 RESULTS AND DISCUSSION

2.1 Preparation

The sol for the spraying was prepared by mixing 5 g of Pluronic P123, 56 mL of 1-butanol, 14.4 mL of titanium ethoxide and 10.2 mL of concentrated hydrochloric acid, followed by dilution with 1-butanol in the ratio ranging from 1:100 to 20:100. The diameter of the orifice in the spray-gun, the air pressure and the width of the sprayed area were carefully optimized. The glass slides, on which the sol was deposited, were preheated at 70 °C. After spraying, the layers were aged at room temperature and controlled humidity for 24 hours and afterwards calcined at 350 °C for 3 hours.

2.2 Morphological and Structure Properties

The films obtained were characterized by a number of physic-chemical techniques, such as profilometry, thin film refractometry, transmission and scanning electron microscopies, X-ray diffraction, UV/VIS spectroscopy, krypton adsorption at 77 K and ellipsometric porosimetry.

The variation in the preparation conditions has shown that the concentration of the sol used for spraying is one of the decisive processing parameters, medium dilution ranging from 5 to 10:100 being preferable.

Scanning and transmission electron microscopy images show the films are homogeneous without any substantial distortions, the pores not exhibiting any long range ordering (Fig. 1). The profilometric study of a number of films has shown that the thickness achieves ca 250 nm per layer, increasing approximately linearly with the number of layers for repeated deposition. The films exhibit the very good adhesion to the support.

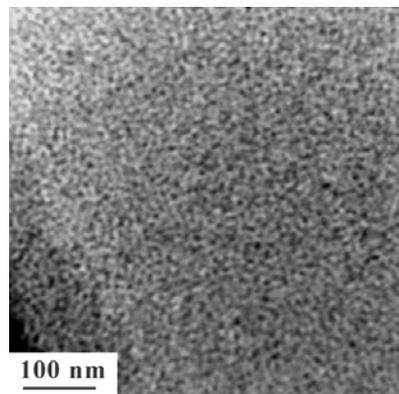


Fig. 1 TEM image of a mesoporous film of TiO₂

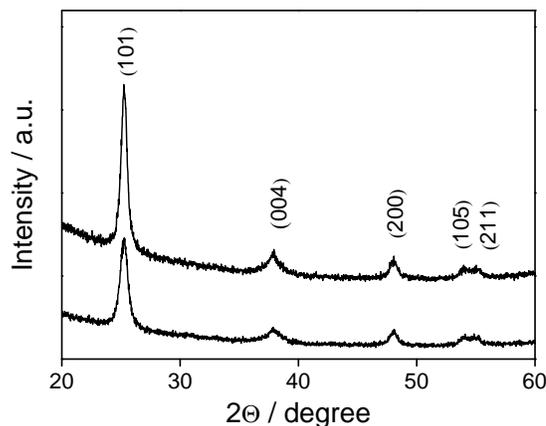


Fig. 2 X-ray diffractograms for two typical films

The X-ray diffractograms show that the films contain anatase nanoparticles besides some proportion of amorphous titania (Fig. 2). The absorption edge in UV/VIS spectra for 1- to 3-layered films is blue shifted in comparison with bulk anatase (optical band gap of 3.2 eV). The shift depends on the number of layers, decreasing

with the increasing number of layers, which is due to the sintering caused by calcinations after deposition of each layer (i.e., the 3-layered film was calcined three times). For example the 1- and 2-layered films exhibit optical band gap of 3.35 and 3.33 eV, respectively.

For a deeper insight into the properties of these films it is crucial to reliably determine their texture properties and to understand the sorption of gas-phase molecules within their complex porous system. In this study, physical adsorption of Kr and ellipsometric porosimetry were effectively combined to elucidate the texture and adsorption properties of mesoporous TiO₂ films.

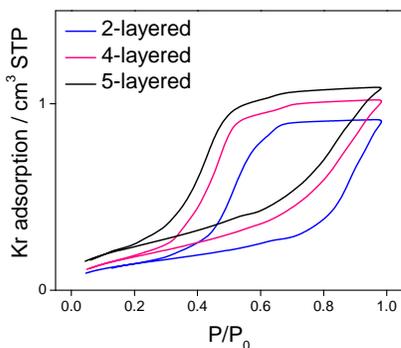


Fig. 3 Adsorption isotherms of Kr at 77 K on a series of films with different number of layers

The information on the pore size and pore volume was obtained from Kr isotherms by analyzing the shape of the hysteresis loop and the limiting adsorption at saturation pressure as well as by comparison of the adsorption on the samples under study with that on well-defined reference materials (Fig. 3). The specific surface area related to cm² of the support achieves 78, 150 and 222 cm²/cm² for one-, two- and three-layered films, respectively. Clearly the surface area increases practically linearly with the increasing number of coatings. Similarly, the specific pore volume calculated from the limiting adsorption for the plateau at P/P₀ close to 1 increase more or less regularly with the number of layers. The values are 0.293, 0.359 and 0.483 mm³/cm² for one-, two- and three-layered films, respectively. Ellipsometric porosimetry provided information on the porosity of films (about 40 %) and the pore size

distribution, which was found narrow centred at 8-10 nm.

2.3 Photocatalytic performance

The self-cleaning performance of mesoporous TiO₂ films was tested by following the decomposition of a layer of oleic acid. Oleic acid was deposited by dip-coating its 10% heptane solution. The samples were illuminated with a UV light (365 nm, 2.0 mW/cm²), the photocatalytic decomposition of oleic acid being followed by measuring the decrease in the contact angle for water, which is expected proportional to the degree of its degradation, i.e. its transformation into more hydrophilic compounds, such as acids with shorter chains, aldehydes, alcohols, as well as to gaseous products (CO₂, H₂O), which leads to the exposure of the hydrophilic TiO₂ surface

Fig. 4 shows the originally hydrophobic layer of oleic acid is gradually removed or converted to hydrophilic products, which are easy to remove by washing.

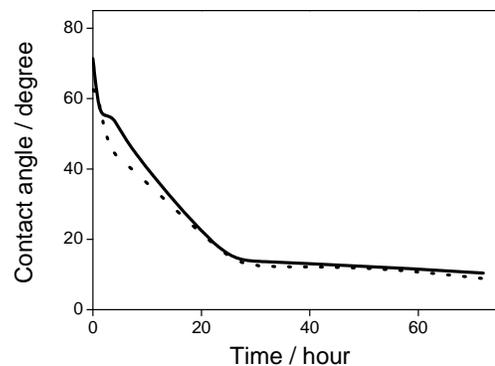


Fig. 4 Photocatalytic decomposition of a thin layer of oleic acid on two selected typical films. The decrease in the contact angle for water is proportional to the extent of the decomposition of oleic acid.

The experimental set-up for the photocatalytic tests in the gaseous phase consisted of a gas supply part, the photoreactor, and a chemiluminiscent NO-NO_x gas analyzer. The gaseous reaction mixture was prepared by mixing streams of dry air (1500 mL/min), wet air (1500 mL/min, relative

humidity of 100 %) and 50 ppm NO/N₂ (approx. 6 mL/min), in order to obtain a final concentration of NO of 100 ppb at a relative humidity of 50 %. The photoreactor was illuminated by four 8 W black lights, the UV light intensity achieving 1 mW/cm².

In its photocatalytic oxidation, adsorbed NO molecules react first with OH• or HO₂• radicals to form adsorbed HNO₂, which is further photooxidized to NO₂. NO₂ is either desorbed or converted to HNO₃. The degree of conversion to HNO₃ depends on the residence time of NO₂ in its adsorbed state, which is substantially enhanced by the porosity of the employed photocatalyst. The surface of the photocatalyst was first equilibrated with the gaseous 1 ppm NO/water vapour/air mixture. Afterwards, the illumination was started. The conversion of NO equals

$$\text{NO conversion (\%)} = ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}) \times 100 / [\text{NO}]_{\text{in}},$$

where [NO]_{in} and [NO]_{out} are the NO concentration at the inlet and at the outlet of the photoreactor, respectively.

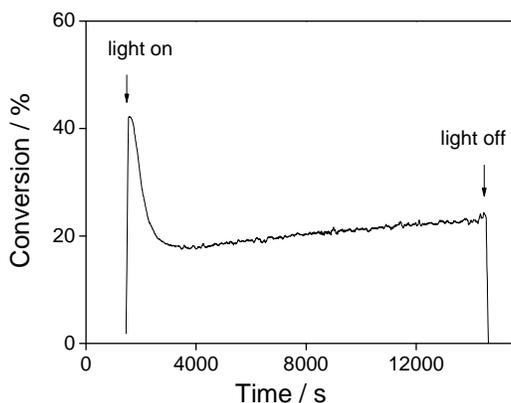


Fig. 5 Photocatalytic decomposition of NO on a typical film

Fig. 5 shows the characteristic time response – very fast increase in the conversion following immediately after switching on the light. This fast increase is followed by a decrease in conversion efficiency, the final steady state conversion of ca 20 % being practically independent on the thickness of the film. The deactivation observed is

likely due to the formation and deposition of nitric acid on the surface, as the photocatalytic activity was restored by rinsing the layers with water.

3 CONCLUSIONS

In summary, mesoporous films of TiO₂ prepared by the low-cost spraying procedure are highly promising photocatalysts for the removal of liquid layers deposited on their surface, which is due to the increased diffusion of O₂/H₂O owing to the 3D-porosity. A commercial non-porous film tested at the same condition exhibited much lower photocatalytic activity. Therefore they are serious candidates for the creation of effective self-cleaning surfaces, as they can be easily produced with high reproducibility by a versatile spraying procedure.

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REFERENCES

- [1] S. Devahasdin, C. Fan jr., K. Li, D.H. Chen, *J. Photochem. Photobiol. A: Chem.* 156, 161, 2003.
- [2] K. Hashimoto, K. Wasada, N. Toukai, H. Komonami, Y. Kera Y., *J. Photochem. Photobiol. A: Chem.* 136, 103, 2000.
- [3] F. Bosc, D. Edwards, N. Keller, V. Keller, A. Ayral, *Thin Solid Films* 495, 272, 2006.
- [4] J. Tschirch, D. Bahnemann, M. Wark, J. Rathouský, *J. Photochem. Photobiol. A: Chem.* 194, 181, 2008.
- [5] P. Yang, D. Zhao, D.I. Margolese, B.F. Chmelka, G.D. Stucky, *Nature* 396, 152, 1998.
- [6] C.J. Brinker, Y.F. Lu, A. Sellinger, H.Y. Fan, *Adv. Mater.* 11, 579, 1999.
- [7] C. Sanchez, C. Boissiere, D. Grosso, C. Lanerty, L. Nicole, *Chem. Mater.* 20, 682, 2008.