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PHOTOCATALYTIC DECOLORISATION OF SELECTED ORGANIC DYES BY MESOPOROUS TiO_2 THIN FILMS

A. Zarubica[1], M. Vasic[1], M. Marinkovic[1], N. Stojkovic[1] and J. Nedeljkovic[2]

[1]*Faculty of Science and Mathematics, University of Nis, Visegradska 33, 18000 Nis, Serbia*
[2]*Vinca Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia*

ABSTRACT
The mesoporous TiO_2 films were prepared by dip coating technique combined with the evaporation-induced self-assembly method using selected polymer templates. Influence of specific surface area, pore size, (nano)crystal structure and morphology of TiO_2 films on the photocatalytic behaviour was investigated. In addition, particular process parameters were considered in decolorisation of organic dyes, such as: thickness of TiO_2 films, initial concentration of selected pollutants and number of reaction cycles.

INTRODUCTION

One of the major global problems is water pollution. The large amount of organic dyes used in textile manufacturing processes and other industries represents an increasing environmental danger owing to their toxic, carcinogenic and mutagenic nature [1].

Due to their numerous favorable properties TiO_2 thin films have been commonly used photocatalysts for degrading a wide range of organic pollutants. Several techniques and preparation process parameters can be used in order to obtain photocatalyst with the desired properties.

The evaporation-induced self-assembly method [2-4] using various titania precursors and templating polymers has been used in order to prepare mesoporous TiO_2 films. It is proposed and shown that the type of polymer template has a substantial influence on the porosity of the final material [5].

The aim of this study was to investigate the photocatalytic activity of homogenous and crack-free TiO_2 films with templated mesoporosity, prepared by using two different polymers (Pluronic F127 and PSM02). In this paper photocatalytic decolorisation of methylene blue (MB) and crystal violet (CV) was used in order to test photocatalytic activity of the TiO_2 thin films as a function of porosity, crystallinity, particle size, and thickness (catalyst dosage).

EXPERIMENTAL

Templated TiO_2 thin films were prepared by using silicon wafers as substrates. Precursor solutions for dip coating were prepared using $TiCl_4$ dissolved in dry ethanol under an inert atmosphere. An alcohol-water mixture containing either Pluronic F127 or PSM02 polymer was added and molar ratio between $TiCl_4$ and F127 was adjusted to 1 : 0.001, while the molar ratio between $TiCl_4$ and PSM02 was 1 : 0.01. These solutions were stirred at room temperature for 24 hours and the addition of deionized water led to a molar ratio between selected solution constituents $TiCl_4$: EtOH : H_2O = 1 : 30 : 10. The TiO_2 films were deposited onto silicon substrates by dip coating combined with the evaporation-induced self-assembly method. Calcination of the TiO_2 films was carried out at 450 °C for 15 min. The physico-chemical characterization of the catalysts were conducted using textural (BET), structural (XRD) and morphological (SEM/TEM) analyses. Photocatalytic efficiency of mesoporous TiO_2 thin films was tested in the decolorisation reactions of MB and CV over a broad range of initial concentrations and reaction cycles. Changes in concentrations of organic dyes were monitored by using UV/VIS spectra. Catalyst dosage in each photocatalytic test was 28±2 mg. The organic dyes, like methylene blue and crystal violet, were selected as model pollutants in photocatalytic test reaction. In order to establish the equilibrium of potential sorption process, thin films were tested during 12 h. The UV lamp (ROTH Co.) characterized with following working features: 16W, 2.5 mW/cm^2 and λ_{max} = 366 nm was used.

RESULTS AND DISCUSSION

BET surface areas of TiO_2 films obtained by the dip coating technique in the presence of F127 and PSM02 templates after calcination at 450 °C are shown in Table 1. The characteristics of pore system in titania thin films can be related to the applied preparation method, used polymer template and titania precursor, calcination temperature and finally substrate surface properties. The specific surface area may have a significant effect on the photocatalytic efficiency of titania thin films [5]. The TiO_2 film templated with F127 exhibits BET surface area of 48 m^2/m^2 and pore size up to 10 nm, while titania based thin film with PSM02 poses BET surface area of 20 m^2/m^2 with pores of 22 nm in size (Table 1). In accordance with developed pore system and larger BET surface area, TiO_2 film templated with F127 has shown higher efficiency in photocatalytic decolorisation of selected organic dyes comparing with titania based film templated with PSM02 (Fig. 3). The XRD analysis (Fig. 1) indicated the presence of TiO_2 in anatase crystal phase with a small amount of nonstoichiometric Ti_2O_3. The crystallite size of anatase phase, calculated by Scherrer's equation, was found to be 12 nm (Table 1). The XRD pattern of TiO_2 film was recorded exclusively for the film of an adequate thickness to obtain reliable data (TiO_2 - F127, thickness of 270 nm). It is expected that the crystal phase composition of TiO_2 - PSM02 film, after the calcination at the same temperature (450 °C), is also crystalline and characterized with high amount of anatase crystal phase.

Table 1. Textural and structural properties of titania thin films

Photocatalyst – polymer	BET surface area (m^2/m^2)	Average pore size (nm)	Crystal phases	Crystallite size (nm)
TiO_2 – F127	48	10	TiO_2 anatase / Ti_2O_3	12
TiO_2 – PSM02	20	22	/	/

FE-SEM micrographs, the top view, show that TiO_2 film prepared by using PSM02 polymer as a template, leads to formation of crack-free mesoporous TiO_2 films with larger pores (20-22 nm) (Fig. 2b) compared to the films prepared by using Pluronic F127 polymer (8-10 nm) (Fig. 2a).

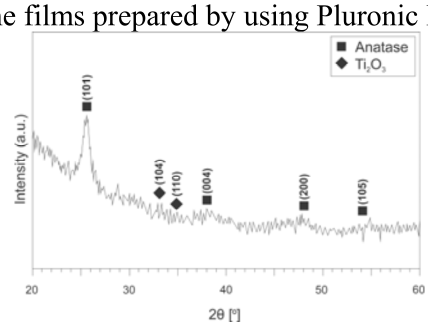

Figure 1. The XRD pattern of TiO_2-F127 thin film with thinckness of 270 nm [5]

The images of cross-section of the TiO_2 films prepared by using PSM02 polymer indicated the elliptical shape of pores, and a lower level of their interconnectivity. On the other hand, the polymer Pluronic F127 used for film preparation resulted with a cubic-like porosity in the titania film surface with interconnected mesopores ordered in a short range.

a) b)

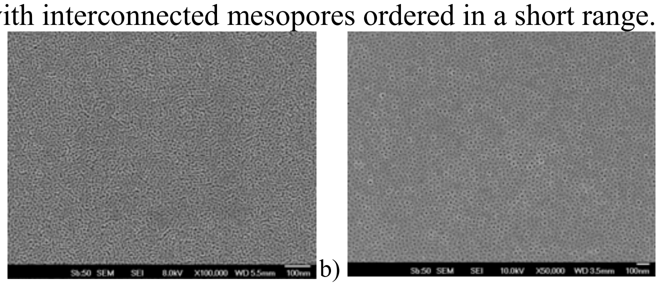

Figure 2. FE-SEM images of ordered mesoporous titania thin films templated with different polymer matrices: a) F127,

BET specific surface area, pore size and level of pores connectivity all together affect photocataytic activity of titania thin films. It can be observed that photocatalytic decolorisation process of selected dyes is the most effective when thicker mesoporous TiO_2 films (higher catalyst dosage) with larger specific surface area (TiO_2-F127, 48 m^2/m^2) was used. Also, under the same experimental conditions, the photocatalytic degradation of MB is faster compared to the degradation of CV (Fig. 3). Most likely, this effect is a consequence of different structures of the organic dyes.

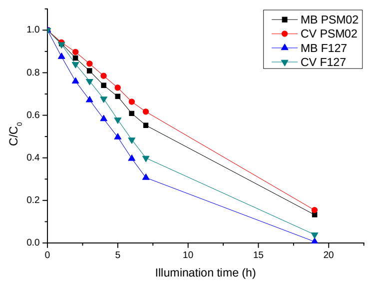

Figure 3. Decolorisation kinetics of MB and CV using mesoporous titania thin films (TiO_2 - F127 and TiO_2 - PSM02)

CONCLUSION

The dip coating technique was proved to be effective and relatively simple technique to obtain desired morphology of ordered mesoporous TiO_2 thin films. Complete degradation/decolorisation of the selected organic dyes was achieved. The obtained kinetic data of photodegradation reactions were correlated with the properties of TiO_2 thin films (specific surface area, pore size and shape, and crystallite size).

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REFERENCES

[1] J.R. Dominguez, J. Beltran, O. Rodriguez, Catal. Today, 2005, 101, 389-395.
[2] B. Smarsly, D. Grosso, T. Brezesinski, N. Pinna, C. Boissiere, M. Antonietti, C. Sanchez, Chem. Mater., 2004, 16, 2948-2952.
[3] J.M. Wu, M. Antonietti, S. Gross, M. Bauer, B.M. Smarsly, Chem. Phys. Chem., 2008, 9, 748-757.
[4] J. Tang, Y.Y. Wu, E.W. McFarland, G.D. Stucky, Chem. Commun., 2004, 14, 1670-1671.
[5] A. Zarubica, M. Vasic, M.D. Antonijevic, M. Randjelovic, M. Momcilovic, J.Krstic, J. Nedeljkovic, Mater. Res. Bull., 2014, 57, 146-151.