JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 5, May 2007, p. 1403 - 1406

TiO_2 thin films prepared by spray pyrolysis deposition (SPD) and their photocatalytic activities

L. ANDRONIC, S. MANOLACHE, A. DUTA*
The Centre: Product Design for Sustainable Development,
Transilvania University of Brasov, Eroilor 29, Brasov, Romania

Titanium dioxide thin film of controlled particle size distributions was prepared using the spray pyrolysis deposition (SPD) process. The size and morphology of the titania particles exhibits strong dependency on the preparation conditions. The performance of the TiO_2 thin film was examined for the photocatalytic oxidation of organic dyes (methyl orange, methylen blue). The material characterization of the TiO_2 films was performed using X-ray diffraction (XRD), Scanning Electronic Microscopy (SEM). The optical absorption and the thickness of the films were measured using a UV–VIS spectrophotometer. Transmittance spectra of the thin films were measurements and energy band gaps were determined from the analysis of subtle features of the measured absorption coefficient. The optical stability of TiO_2 thin film deposited by SPD was examined at various pH-values considering the future utilisation of the TiO_2 thin film as catalyst in wastewater treatment. The catalyst activity demonstrated strong dependence on pH and on the structure of the dyes.

(Received November 14, 2006; accepted April 12, 2007)

Keywords: TiO_2, Spray Pyrolysis Deposition, Optical Band Gap, Photo-catalytic activity

1. Introduction

Photocatalytic oxidation technology based on TiO_2 has been proved effective for the degradation and mineralization of the organic dyes, [1-3] and is one of the environmental cleaning technologies. The photocatalytic advanced process is initialed by UV irradiation that induces the band-band excitation of TiO_2 to form conductive electrons and valence holes.

The titanium oxide exists in three different crystal structures: rutile, anatase and brookite, [4]. Commonly rutile and anatase are used in photocatalysis, with anatase showing a higher photocatalytic activity.

TiO_2 thin films have received great attention in recent years because of their excellent optical and electrical properties. However, the anatase TiO_2 phase has band gap energy (Eg) of 3.2 eV, [5], and requires light below 390 nm to create an electron–hole pair.

It is knows that the environmental condition can be variable and the pH can influence the chemical stability of the thin film.

Our work is focused on the synthesis and the evaluation of the stability properties of TiO_2 thin films deposited, by spray pyrolysis deposition. The investigation involves the comparison of removal efficiency among solution of methyl orange (anionic dye) and methylen blue (cationic dye) at different pH.

2. Experimental

2.1. Synthesis of TiO_2 thin film

The nanoporous TiO_2 layer were deposited by Spray Pyrolysis Deposition (SPD) using titanium(IV) izopropoxide, ($Ti[OCH(CH_3)_2]_4$, TTIP, 99.999%, Sigma-Aldrich) as precursor, acetyl acetone, (2,4 pentadione, 99+%, $CH_3COCH_2COCH_3$, AcAc, Aldrich) as stabilizer and absolute ethanol (C_2H_5OH, EtOH, J.T. Baker) as solvent. The deposition is done on the heated glass substrate at 400 °C in open atmosphere at a height of 25 cm using air as carrier gas at 1.2 bars and spraying sequences of 60 seconds. After spraying, the samples are annealed in air at 450 °C for six hours.

The deposition substrate, TCO, was cleaned by successive immersion in ethanol and acetone in an ultrasonic bath.

2.2 Characterisation of TiO_2 thin film

The morphology of TiO_2 thin film was studied using a Scanning Electron Microscope (SEM, Jeol JS M-5800LV).

The XRD measurements (Bruker D8 Advance Diffractometer) were used to evaluate the crystal structure of the films.

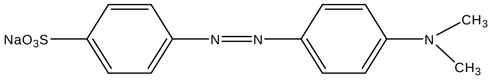
Reflectance and absorbance measurements were recorded in the range of 200–800 nm, using a UV - Visible spectrophotometer (Perkin Elmer Lambda 25 UV/VIS), allowing the calculus of the thickness and band gap of the titania film.

2.3. Photocatalytic degradation of organic dyes

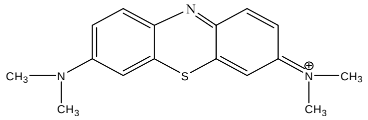
The photodegradation reactor is a static cylindric flask of 500 mL, open to air. The photodegradation reactor was equipped with three F18W/T8 blacklight tubes (Philips), placed annular to the photoreactor. Each of the tubes emitted a broad range of UVA light, typically 340–400 nm, with λ_{max} (emission) = 365 nm. The mean value of the radiation flux intensity, reaching the middle of the reacting suspension, measured with a digital Luxmeter (Mavolux 5032 C/B USM), was measured to be 3 Lx.

The photocatalyst (TiO_2 thin film) was immersed in the dyes solution, under stirring with a magnetic stirrer. The samples were exposed to illumination up to 360 minutes. Before irradiation, the solutions were stirred for 30 min in dark, to ensure the adsorption-desorption equilibrium of the solution with the photocatalyst.

Methyl orange (MO) and methylene blue (MB), were chosen as the target compounds; their structure are given in equations (1,2):



(1)



(2)

The photocatalytic degradation of methyl orange and methylene blue was determined by UV–Vis spectrometry (Perkin Elmer Lambda 25 UV/VIS) through indication of color bleaching. After 360 min of irradiation, the absorbance is registered at λ_{max} that is 460 nm for methyl orange, respectively, 660 nm for methylen blue. The concentration of the dyes solution was 7.8125 mg/L and the pHs from 3 till 10. The pH was obtained by adding different amounts of 0.1 M HCl or NaOH.

3. Results and discussion

3.1. Characterisation of TiO_2 thin film

The SEM micrograph shown in Fig. 1 indicates a lighly porous structure in the nanocrystalline TiO_2 film. The pores have linear extents of around 300 nm, and hence their sizes are similar to the dimension of the grain aggregates.

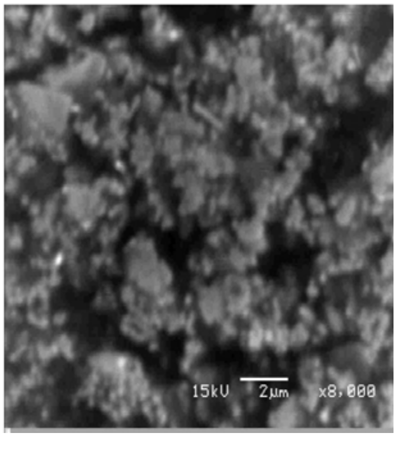


Fig. 1. SEM of nanoporous TiO_2 thin film.

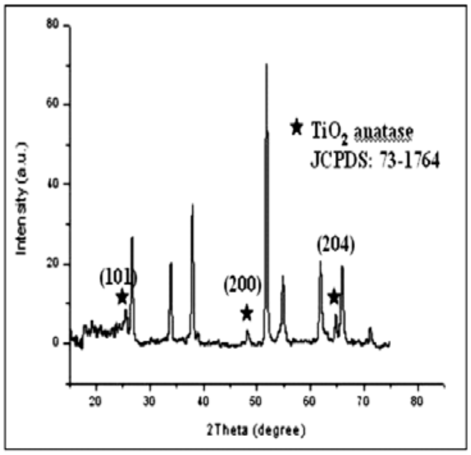


Fig. 2. XRD of nanoporous TiO_2 thin film.

The X-ray diffraction patterns show that the TiO_2 film contains only anatase, which is well known as the most suitable structure for the photocatalysis, Fig. 2. The unmarked peaks represent the TCO substrate.

3.2. Optical characterisation of TiO_2 thin film

Using the optical transmittance spectra, the absorption coefficient and the band gap of TiO_2 film were evaluated. The absorption coefficient was calculated using the equation:

$$\alpha = \ln(1/T)/t \tag{3}$$

where T is the transmittance and t the thickness of the film. The thickness of the film was evaluated from de UV spectrum and the average value corresponds to 340 nm for nanoporous TiO_2 thin film. The bandgap energy was obtained by plotting the optical absorption, $(\alpha h\nu)^2$ vs. the photon energy, ($h\nu$), and extrapolating the linear portion of the curve to $(\alpha h\nu)^2 = 0$, Fig. 3.

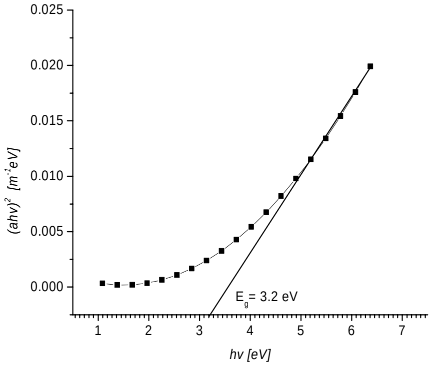


Fig. 3. Band gap energy of nanoporous TiO_2 thin film

Titanium oxide film absorbs appreciably at wavelengths less than 390 nm (which corresponds to a band-gap energy of 3.2 eV).

3.3. Influence of pH on chemical stability of TiO_2 thin film

The pH influences at the same time the surface state of titania and the ionization state of the dyes molecules. The potential at zero charge of TiO_2 surface i $pH_{pzc} = 6.80$, [6]. For pH values higher than the pH_{pzc}, the surface becomes negatively charged and it is the opposite for $pH < pH_{pzc}$, according to the following equilibrium:

$$\mathrm{Ti-OH + H^+ \leftrightarrow Ti-OH_2^+} \tag{4}$$

$$\mathrm{Ti-OH + OH^- \leftrightarrow Ti-O^- + H_2O} \tag{5}$$

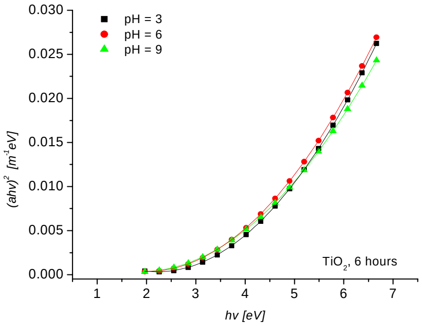


Fig. 4. Optical stability of thin film after 6 hours

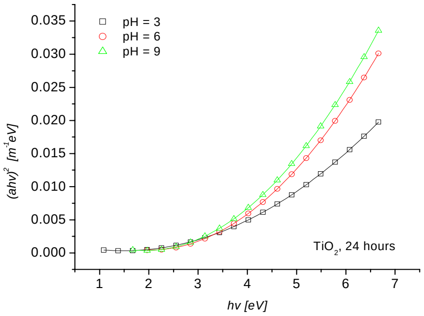


Fig. 5. Calculation of E_g in TiO_2 nanostructured film after 24h.

The absorption analysis shows o high stability of the band gap (E_g = 3.2 eV) after 6 hours for all values of the pH, Fig. 4. The TiO_2 films present slight modification in the band gap value after 24 hours on immersion in different electrolyte solutions, but the most stable thin film is that immersed in solution with pH = 6, Fig. 5.

3.4. Influence of pH on photocatalytic activity of TiO_2 thin film

The pH value is by far the major factor influencing the rate of the of photocatalytic process, [7].

The photocatalytic degradation of aqueous MO and MB are used as reference reactions to compare the photocatalytic activity of the TiO_2 thin film.

Since dyes are degraded at different pH values in real colored effluents, comparative experiments were performed at different pH values. The absorption spectra for both dyes are presented in Fig. 6, were A is the absorbance after 360 min of illumination and A_0 is the absorbance of blank solution.

The pH influences the adsorption property of organic compounds and their dissociating state in solution. The adsorption of MB on TiO_2 surface and the corresponding photodegradation is maximum at higher pH (pH~9) and in the case of MO most adsorption and photodegradation occurs at lower pH (pH~3) as shown in Fig. 7. This might be related to the amphoteric behavior of the TiO_2 semiconductor.

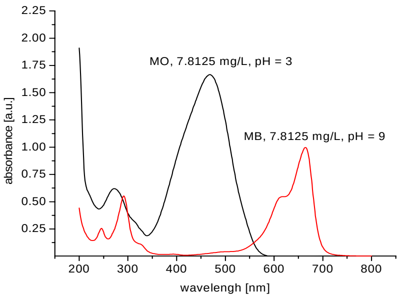


Fig. 6. Absorption spectra for dyes

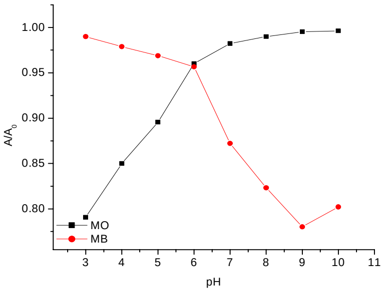


Fig. 7. Influence of pH on the MO and MB photodegradation

At higher pH, electrostatic interactions between the negative TiO_2 surface and MB cations lead to strong absorption and enhances degradation rate. In the acid pH there was a poor adsorption, because the TiO_2 surface and MB are both positively. Therefore, for MB, decrease in pH causes decrease in degradation rate.

So, when pH = 3 a strong rate of photobleaching of MO on the thin film is observed as a result of the electrostatic attraction of the positively charged TiO_2 with the dye.

4. Conclusions

The photocatalytic degradation of various organic dyes, illuminated by UV lamps, has a promising result when using titanium dioxide coated on substrate.

Titanium dioxide thin film of controlled particle size distributions was prepared using the spray pyrolysis deposition (SPD) process.

The optical study proves the presence of reversible chemical changes for titanium oxide for different pH and the absorption analysis show high chemical stability at pH = 6 after 24 hours.

The photocatalytic degradation of methyl orange and methylen blue in aqueous solutions was realized with the nanoporous TiO_2 thin film. The pH of the solution can influence rate of dyes photobleaching. In the TiO_2-photocatalysed oxidation of dyes, the optimum photodegradation pH was found pH = 3 for MO and pH = 9 for MB.

The UV- assisted photocatalytic device showed a potential application for photobleaching organic dyes in wastewater.

References

[1] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Herrmann, Applied Catalysis B: Environmental **39**, 75(2002).
[2] N. Guettaı, H. Ait Amar, Desalination **185**, 427 (2005).
[3] J. M. Wu, and T.W. Zhang, Journal of Photochemistry and Photobiology A: Chemistry **162**, 171(2004).
[4] A. K. Sharma, R. K. Tareja, U. Willer, W. Schade, Appl. Surf. Sci. **206**, 137(2003).
[5] F. Y. Oliva, L. B. Avalle, E. Santos, O. R. Cámara, Journal of Photochemistry and Photobiology A: Chemistry, 146, 175(2002).
[6] J. Zhao, H. Hidaka, A. Takamura, E. Pelizzetti, N. Serpone, Langmuir **9**, 1646(1989).
[7] J. Herrmann, Catalyst Today **53**, 115 (1999).

---

*Corresponding author: a.duta@unitbv.ro