

Synthesis of Nanoporous TiO₂ Thin Films for Photocatalytic Degradation of Methylene Blue

M. Estrada¹, C. Reza¹, J. Salmones^{2,*}, J.A. Wang², M.E. Manríquez¹, J.M. Mora³,
M.L. Hernández², A. Zúñiga¹ and J.L. Contreras⁴

¹Laboratorio de Investigación en Físicoquímica y Materiales, Departamento de Ingeniería Química Industrial, ESIQIE, Instituto Politécnico Nacional, UPALM, Col. Zacatenco, 07738 México D.F., México.

²Laboratorio de Catálisis y Materiales, ESIQIE, Instituto Politécnico Nacional, UPALM, Col. Zacatenco, 07738 México D.F., México.

³Departamento de Ingeniería Metalúrgica y Materiales, ESIQIE, Instituto Politécnico Nacional, UPALM, Col. Zacatenco, 07738 México D.F., México.

⁴División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana Azcapotzalco, Av. Sn. Pablo 180, Col. Reynosa, C.P. 02200, México D.F., México.

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Abstract: This work reports a structure and photocatalytic activity of nanoporous titania (TiO₂) thin films by an anodizing approach. X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM) studies showed that tetragonal anatase was the main phase in the thin films that consisted of countless disordered nanopores in the order of 10 to 15 nm. In the photocatalytic degradation of methylene blue, the titania thin films showed a good photocatalytic activity. 82.2 % methylene blue could be photodegraded by titania thin films with UV radiation. XPS results indicate that during the degradation of methylene blue, some Ti³⁺ may be partially oxidized to Ti⁴⁺ in the TiO₂ films and the surface hydroxyls directly participate in the reaction. Our nanoporous titania thin films is commensurable to Degussa-25 TiO₂ powders because the latter requires filtration in each treatment; it is also much superior to the direct photolysis approach with respect to photoactivity.

Keywords: Nanoporous thin film; anodization; TiO₂; methylene blue; photocatalysis.

1. INTRODUCTION

Nowadays, there are different prospective approaches in the treatment of residual liquids containing a wide spectrum of chemical pollutants with various concentrations [1]. Among those approaches, photocatalysis has come attractive for the degradation of organic pollutants in water [1, 2]. It is noted that semiconductor materials like titania are widely applied in the photodegradation processes because of their great activity and chemical stability [3]. In many applications, titania powders are used as catalyst, however, titania exhibit several disadvantages due to problems like separation of the catalyst from the suspension, and the existence of aggregates or agglomerates in the suspension that usually lead to the reaction rate slow [4]. This can be avoided if films or coatings

of the active material are supported in a substrate, although the active area of the material is partly reduced [5].

Porous films of metal oxides can be produced by using different synthetic methods such as sol-gel [6], solvothermal [7] and chemical vapor deposition [8], and anodizing [9]. Titania film has been proved to resist corrosion and have been applied in photocatalysis, biomedical implants, and environment purification [10]. In the anodizing method, electrolytes have been used in the synthesis of titania films in HF, NH₄F, H₃PO₄ and HCl solutions [10]. It has been proven that structure of the films can affect strongly on their physicochemical properties [11-13].

In the present work, we report an anodizing method for synthesis of TiO₂ thin films with surfaces consisting of many disordered nanopores and aggregates with irregular flakes structures. The titania thin films were used for photodegradation of methylene blue with low concentration. Results show that anodizing method

*To whom correspondence should be addressed:

Email: jose_salmones@yahoo.com.mx,

Phone: +52 5557296000 ext 55241, Fax: 52 55 55862728

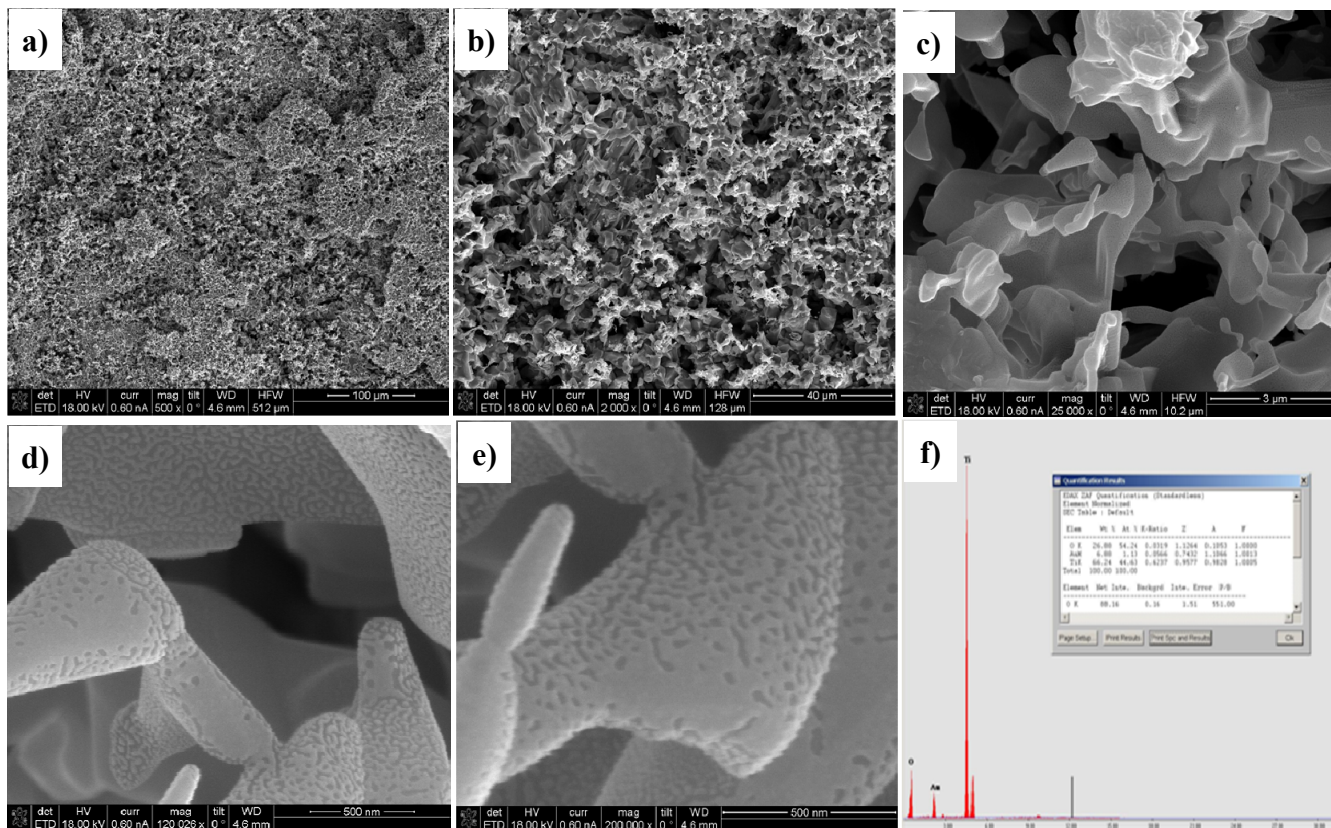


Figure 1. Top view of a titania film at different amplifications. a) 1000X; b) 4000X; c) 13000X; d) 50000X; e) 200000X; f) EDS Analysis.

(positive polarization) is a simple and high efficient method with low cost for the synthesis of nanoporous thin films.

2. EXPERIMENTAL PROCEDURE

Titanium templates (3 cm × 1 cm) with a purity of 99.99 % obtained from Aldrich were used as electrodes for the anodizing process. These Ti templates were carefully polished using fine sand paper in order to eliminate obvious roughness [14]. Then they were immersed into an aqueous solution of 0.7 vol % hydrofluoric acid as electrolytic solution, for anodizing 6 hours until the thin film was formed. A power source from Consort EV243 was used which can supply current 0.01 A and voltage 40 V. The TiO₂ thin film was washed with water and dried in air for use.

Micrographs of the TiO₂ thin film were obtained with a high resolution scanning electron microscope of field emission gun (SEM-FEG) (FEI Co. model Nova 200). This microscope has 2 nm of resolution. Voltages from 15 to 18 keV in the secondary electrons mode with amplifications from 6000X to 300000X and a work distance of 5.2 mm were used.

Micrographs were obtained with an atomic force microscope from Veeco, USA model Multimode. Contact mode at ambient temperature was used. Nanoscope 7.3 software was applied in order to display and analyzed the micrographs.

X-ray diffraction patterns were obtained using a D8 focus diffractometer at constant voltage of 35 kV and current of 25 mA, scanning from 20 to 120 degrees, at 2 degrees per minute in the

thin film modality.

Raman spectra were obtained with a micro RAMAN spectrophotometer from Confocal-Labram model HR800. An argon ion laser beam of 780 nm wavelength with a power of 0.5 mW was focused on the titania samples.

XPS spectra were obtained with a Thermo Scientific k-alpha with an X-ray beam, and a detector of photoelectrons. These samples were analyzed in a work area of 400 μm² under vacuum condition (pressure $P = 10^{-7}$ torr).

The synthesized films were immersed into a flask containing 60 ml of an aqueous solution of 15 ppm methylene blue. Radiation was made with UV lamps with wavelengths from 345 to 400 nm at T = 25°C. First, absorbance of known concentration solutions of methylene blue was obtained, and then these solutions were irradiated with UV light for 5 hrs. 5 ml samples were taken every 30 min and their absorbance was measured. By this way the degradation of methylene blue was monitored and the photocatalytic activity was evaluated. In photolysis, TiO₂ Degussa-25 as catalyst was used as reference in order to compare the photocatalytic behavior with titania films. UV-vis analyses were performed using a Perkin Elmer spectrophotometer at wavelength of 665 nm.

3. RESULTS AND DISCUSSION

A set of SEM micrographs of titania films are shown in Figure 1. It was observed that the surface of the film is rather rough with disordered arrangements varying from 3 to 5 μm. Many aggregates

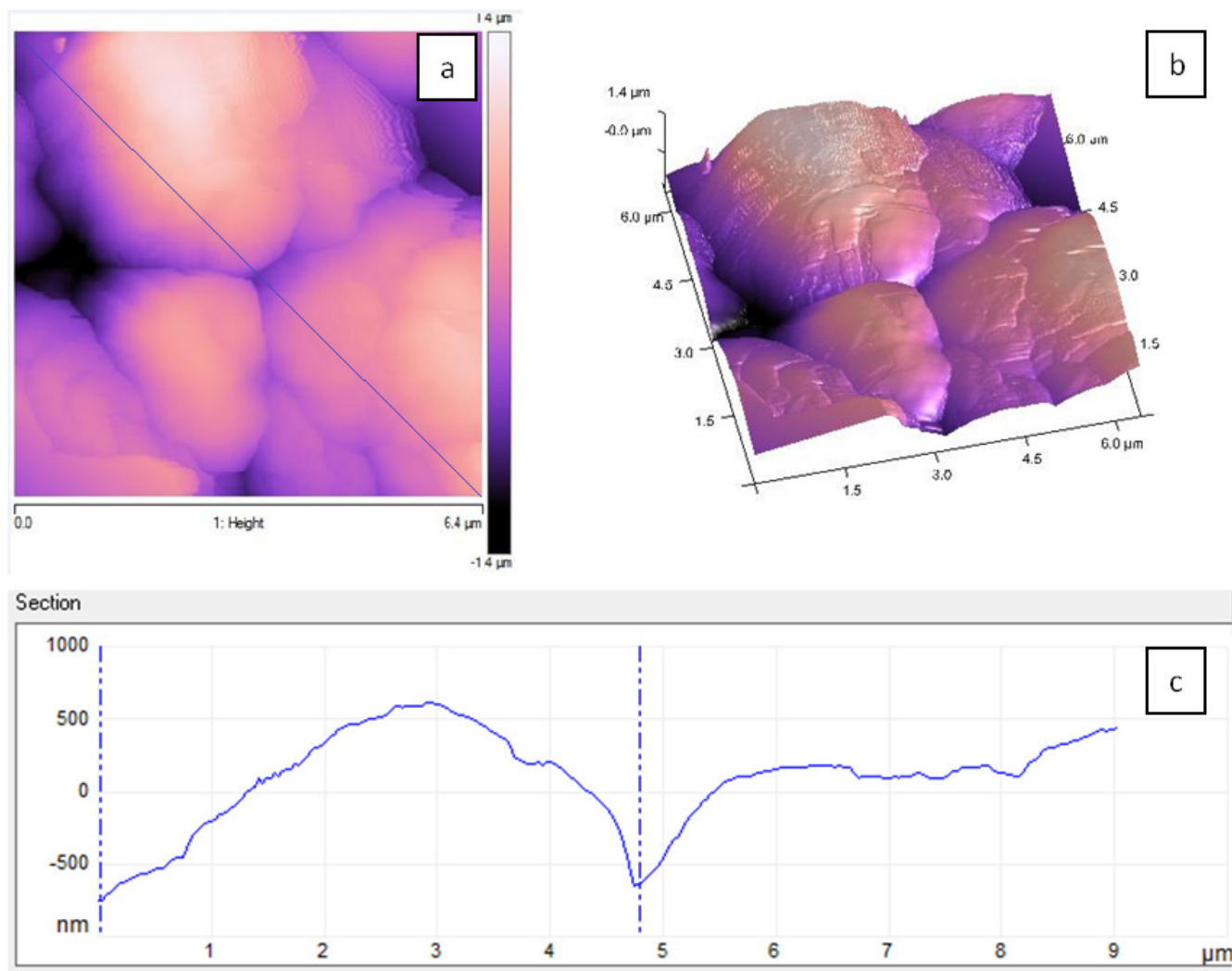


Figure 2. Micrographs obtained by AFM of the titania films. a) top view; b) side view; c) Mapping of a titania film surface.

with irregular flakes-like structures were formed. However, it is possible to observe that the film consists of several very small pores with diameters in the order of 10 to 15 nm. To obtain the elemental information of the film composition, the EDS analysis of a characteristic point of the film was applied as shown in Figure 1, where a 66.2 wt % of titanium and 26.9 wt % of oxygen together with carbon element were detected.

A nanoscope analysis method was employed to measure some parameters of roughness of the sample. AMF images show that titania films have surface with low arrangement and agglomerates that create variation in the highs (Figure 2 a-b). By using the section option, a mapping of the sample was performed in order to know its topography in two dimensions. An estimated of the roughness was obtained by taking into account the higher and lower points in each image. A line describing the topography of a titania film is in Figure 2 c (it was obtained from figure 2 a), which confirms that some variations were presented in the film due to the formation of agglomerates.

The crystalline structure and phase component of the titania

films were studied by using X-ray diffraction analysis. Titania films mainly consist of anatase phase and it has a growth direction (004) as shown in Figure 3 (JCPDS Card 21-1272) [15]. The crystallite size is very small because the peak was rather wide [16]. The lattice cell parameters $a = b = 3.777 \text{ \AA}$, and $c = 9.501 \text{ \AA}$ with the angles $\alpha = \beta = \gamma = 90^\circ$ which correspond to a tetragonal structure of anatase phase.

The Raman spectroscopic technique was also used to analyze the surface species of the film. Figure 4 exhibits an intense band at 148 cm^{-1} and three strong bands at 638 , 516 and 397 cm^{-1} . These are characteristic bands of typical anatase phase [17], in good agreement with the XRD analysis.

According to the UV-vis spectrum (not shown), the band energy or band gap (E_g) was determined. A value close to 3.3 eV was obtained, which is slightly higher than the value of 3.2 eV for anatase phase reported in the literature [18, 19]. The difference between our value and the reported data in the literature is probable due to an optical effect.

XPS measurements were made in order to study the chemical

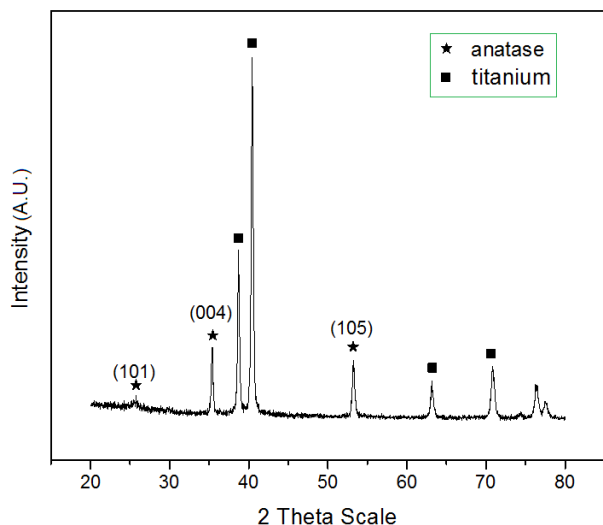


Figure 3. X-ray diffractogram patterns of the titania film.

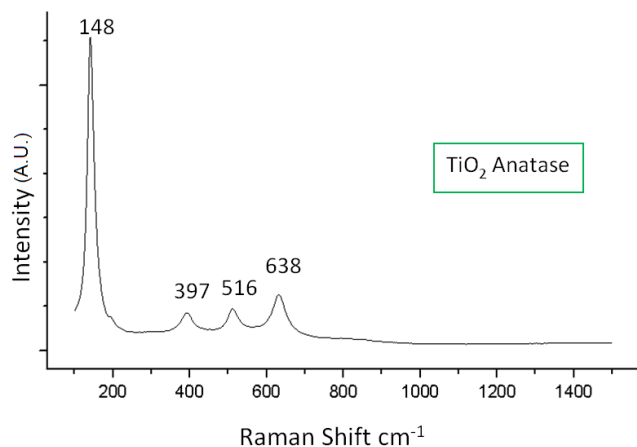


Figure 4. A Raman spectrum of a titania film.

states of each element of the titania film. The survey spectrum of XPS is shown in Figure 5. The O_{KLL} , Ti_{LMM} , C_{KLL} and N_{KLL} Auger peaks and XPS spectra peaks of Ti, O, C and trace N were identified for TiO_2 film. Figure 6 shows the binding energy (BE) of Ti_{2p} and O_{1s} XPS patterns before and after the reaction. All the peaks are located the same position as reported for the bands corresponding to pure TiO_2 [20-22]. Ti_{2p} bands indicate that a stoichiometric TiO_2 with low concentration of structural defects was obtained in the synthesis.

In the XPS spectra of the Ti_{2p} patterns, it is observed that the band $Ti\ 2p_{3/2}$ at 458.0 eV shifts to 459.4 eV after the degradation reaction. It is known that the binding energy of $Ti\ 2p_{3/2}$ electrons in trivalent state is shifted to lower binding energies by approximately 1.0-2.0 eV with respect to that of the tetravalent state [23]. This result indicates that Ti^{3+} ions in the thin film were partly oxidized to Ti^{4+} during the degradation procedure. Another band with greater intensity is observed at approximately 532 eV and it represents the oxygen species related to hydroxyls on the TiO_2 surface. The grade of hydroxylation is important in the dye degradation process be-

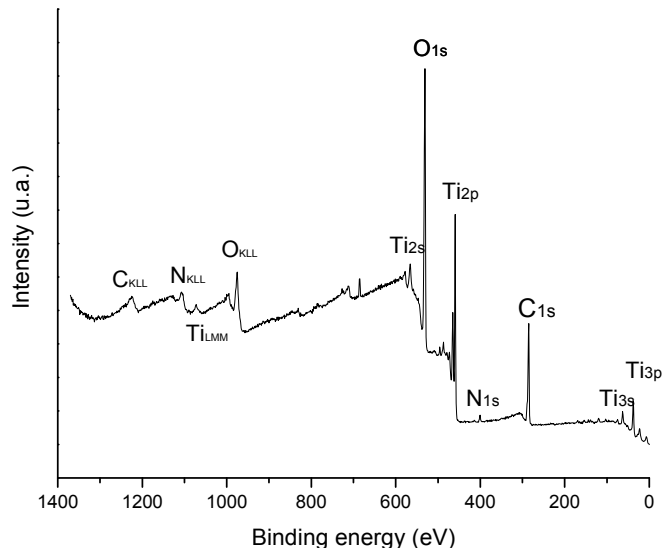


Figure 5. A general XPS spectrum.

cause when an $h\nu$ energy is directed on the TiO_2 , a pair of electron-holes might be generated, these electron-holes may induce free radicals generation both in the aqueous media and on the TiO_2 surface. Therefore, the high degree of surface hydroxylation of the TiO_2 surface may indicate a better photoactivity in the degradation reaction. A difference in intensity in O_{1s} patterns was observed in Fig. 6b in comparison with Fig. 6a. The band at 532 eV shows a significant decrease compared to that before the reaction. This band refers to the O present in the hydroxylated surface of titania. Because the reaction takes place in both aqueous solution and on the TiO_2 surface, many OH groups attached to the surface of TiO_2 participates in the reaction, resulting in a significant decrease of the intensity of the band at 532 eV.

Figure 7 shows the conversion profiles of methylene blue after being radiated with titania films in the presence of H_2O_2 . Three films were evaluated with radiation, achieving an 82.2 % of mineralization in 5 hrs. Photodegradation profiles of methylene blue with two reference systems are also presented in Figure 7, the first case was the use of 0.03 g of titania Degussa P-25 as catalyst in the presence of H_2O_2 and radiated for 5 hrs; the second case was the photolysis profile of methylene blue without catalyst only in the presence of H_2O_2 radiated for 5 hrs. It is clear that our nanoporous titania films are capable of photodegradation 82.2 % of methylene blue in 5 h which is lower than that obtained with Degussa-25 in the same condition. However, filtration operation is no necessary to separate the catalysts from the mixture by using our titania thin film. Our method is much superior to the direct photolysis using H_2O_2 alone which was capable of degradation only 19.1% methylene blue.

The $\ln(C/C_0)$ plots were constructed as a function of degradation time is shown in Figure 8, and straight lines indicated the linear behaviors, fitting well with the first order of reaction. The slopes of these lines were related to the apparent reaction constant k . The mineralization degree of the methylene blue after 5 h of degradation calculated as methylene blue conversion and the apparent reaction constants are reported in Table 1 for each test.

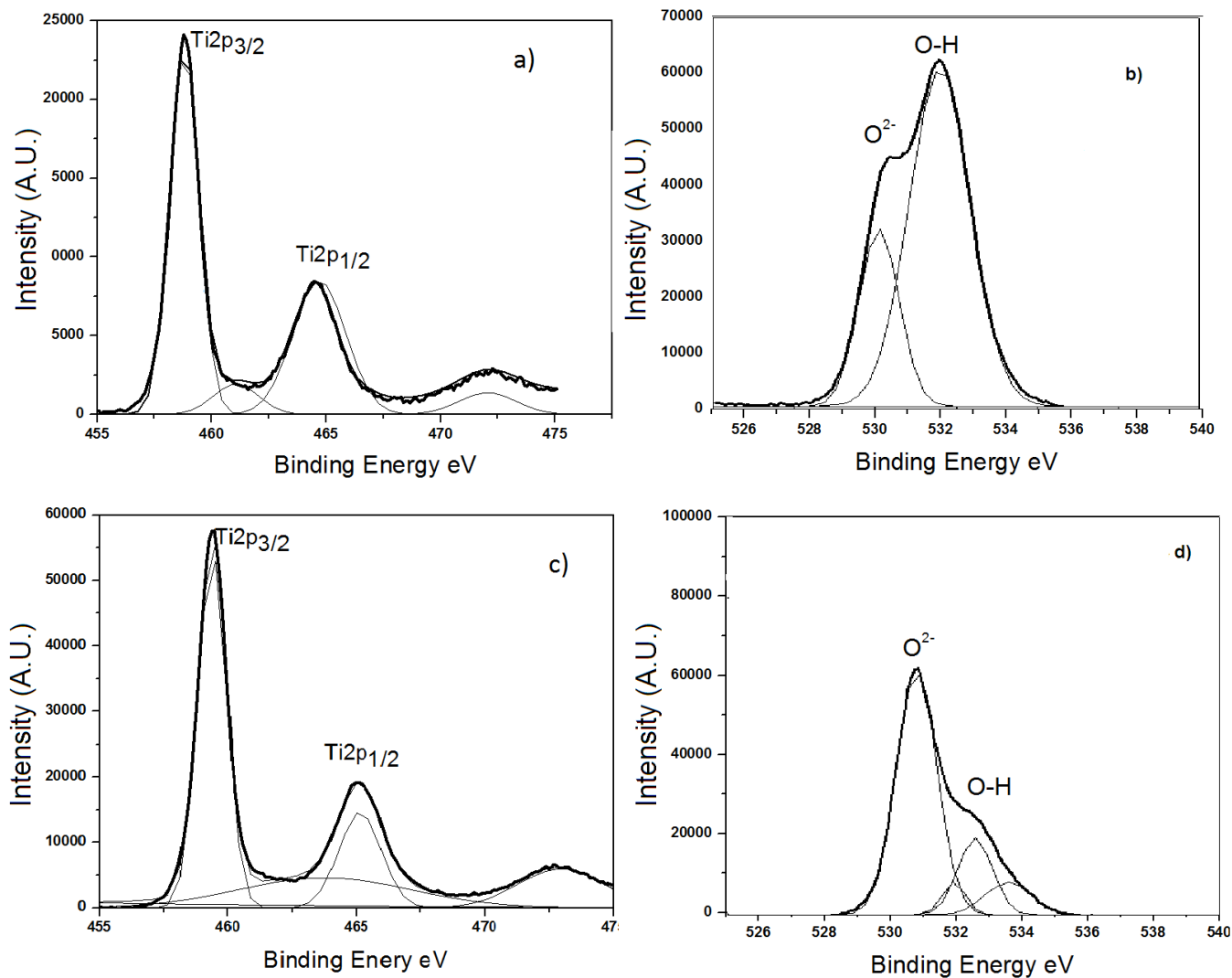


Figure 6. Ti2p and O1s XPS spectra of titanium. (a) before reaction; (b) after reaction.

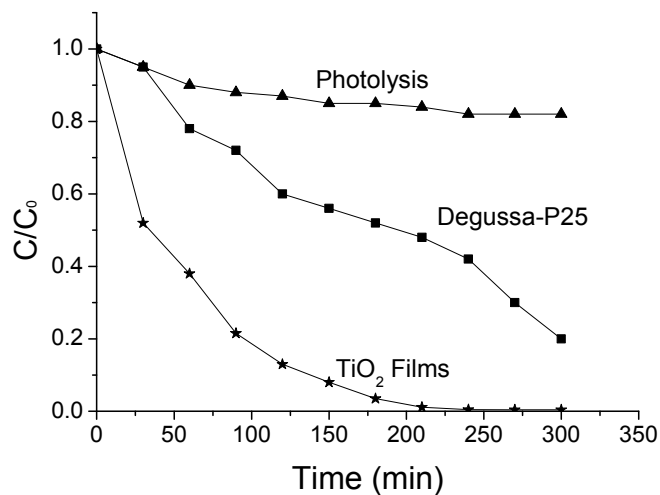


Figure 7. Methylene blue conversion as a function of reaction time.

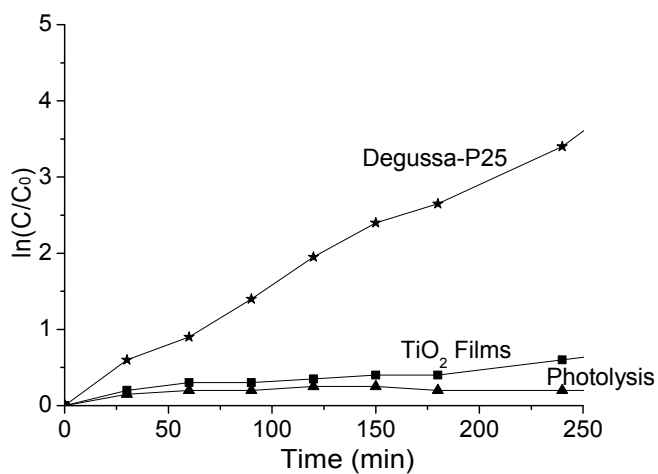


Figure 8. ln(C/C₀) as a function of reaction time.

4. CONCLUSIONS

Nanoporous titania thin films can be synthesized by using Ti template by a simple and economical anodizing method. Structural characterization shows that titania thin films are chiefly composed of tetragonal anatase phase with many nanopores. XPS results indicate that during the photodegradation of methylene blue, some of Ti^{3+} ions may be oxidized to Ti^{4+} in the TiO_2 films and the surface hydroxyls directly participate in the degradation reaction. These nanoporous titania thin films are capable of photodegradation 82.2 % of methylene blue which is competitive with Degussa-25 in the same condition, but without filtration to separate the catalysts. It is also much superior to the direct photolysis using H_2O_2 which was capable of degradation only 19.1% methylene blue.

5. ACKNOWLEDGMENTS

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