

Optimization of Experimental Parameters in preparing Multinopororous TiO₂ Thin Films by the Anodic Oxidation Method

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ABSTRACT

The anodic oxidation method has been applied to the preparation of multinopororous TiO₂ thin films. The experimental parameters, including the electrolyte nature, oxidation voltage, and oxidation time have been carefully controlled. Their influence on the structure, morphology and photocatalytic activity of the prepared TiO₂ films has been evaluated by measuring the current density. The result showed that there was a relatively wide range of preparation conditions, and the internal relationship between the structure and the photocatalytic properties of the TiO₂ films was analyzed.

KEYWORDS

Titanium films, anodic oxidation, multinopororous films, photocatalytic activity.

1. Introduction

In the most recent research devoted to water purification, TiO₂-mediated photolytic catalysis is considered as an advanced oxidation process, which produces highly degrading hydroxyl radicals (HO[•]). These radicals generated in solution are strong oxidative species, responsible for the oxidation of organic pollutants present in waste water.¹⁻⁶

When one molecule of the TiO₂ catalyst (band gap 3.2 eV) is exposed to light whose energy exceeds the energy of the band gap of the semiconductor, an electron (e⁻) is promoted from the valence band (VB) to the conduction band (CB), leaving behind a hole (h⁺) in the valence band. Therefore, a portion of the photo-excited electron-hole pairs diffuse onto the surface of the catalyst. The charge-carriers (e⁻ and h⁺) produced are trapped at the surface of the semiconductor and take part in the chemical reaction. The holes can oxidize organic pollutants present in water, since they can react with water in a one-electron oxidation step to produce the highly reactive hydroxyl radical (HO[•]).



The use of TiO₂ in wastewater treatment is limited, due to its low energy conversion efficiency of less than 5%. Indeed, the majority of the photogenerated charge carriers (e⁻ and h⁺) undergo recombination before they reach the surface of TiO₂ where they can interact with the adsorbed molecules. Because of this recombination, up to 90% of the generated carriers are lost within 10⁻⁹ s after their production. The percentage of charge carrier recombination thus has a major effect on the photocatalytic efficiency of TiO₂. It was also reported that as the grain size of TiO₂ decreases, the probability of charge carrier recombination also decreases, thus resulting in an improvement of the TiO₂ photocatalytic properties.⁷

Furthermore, the use of porous materials has proved advantageous in this respect. Indeed, well-defined porous structures

have a higher surface area which offers a special environment for the degradation of the organic pollutants. Additionally, materials with porous morphology allow faster diffusion of reactive oxygen species, and in this case, the organic substrates are adsorbed within the catalyst surface where they are efficiently degraded.⁸⁻⁹

For the application of TiO₂ in the field of wastewater detoxification, the semiconductor photocatalyst powder is usually dispersed in a liquid suspension. After the degradation process under UV light, the TiO₂ powder remaining suspended in the water has to be removed by centrifugation or by filtration, and this is costly.

By contrast, a TiO₂-fixed-system needs no such operation and continuous wastewater treatment becomes more practical. Several investigators have dealt with the development of procedures for catalyst immobilization on a substrate (solid support). TiO₂ molecules have been fixed to a variety of surfaces: glass,¹⁰ silicon,¹¹ clays,¹² organic polymers,¹³ thin films,¹⁴ concrete,¹⁵ alumina,¹⁶ and carbon.¹⁷ However, in most of these methods, the desired TiO₂ electrodes were fabricated by pasting a slurry of TiO₂ on a substrate, drying the pasted slurry for a time long enough to remove substantially all of the liquid and to stabilize the mechanical binder, thereby providing a TiO₂ structure.

In the present work, a titanium (Ti) metal sheet is used as the starting material to produce titanium dioxide on the surface of Ti metal by anodic oxidation. The process, also called 'micro arc oxidation' (MAO), produces the anodic titania film with a good adhesion with the titanium substrate, higher specific surface area, and good chemical stability, which enable its application as a photocatalyst for the degradation of organic pollutants in waste water purification. Therefore, the TiO₂ produced is immobilized on a Ti metal substrate. For this purpose, the Ti sheet is made the anode by connecting it to the positive terminal of a direct current (DC) power supply. The cathode consists of a carbon rod, because carbon is inert in the anodizing bath. At a constant anodization current, when a voltage is applied, the titanium substrate surface is expected to react with water and form an oxide layer on the titanium metal surface.

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Table 1 Selected anodizing parameters for the production of TiO₂ thin films in H₂SO₄ electrolyte.

H ₂ SO ₄ /mol dm ⁻³	100 V		130 V			150 V		
	8 min	11 min	5 min	8 min	11 min	5 min	8 min	11 min
0.5	A ₈	A ₁₁	B ₅	B ₈	B ₁₁	C ₅	C ₈	C ₁₁
1.0	D ₈	D ₁₁	E ₅	E ₈	E ₁₁	F ₅	F ₈	F ₁₁
2.0	G ₈	G ₁₁	H ₅	H ₈	H ₁₁	I ₅	I ₈	I ₁₁

The aim of this paper was to select the best experimental conditions for producing multinanoporous TiO₂ thin films (anatase) with a higher pore density, smaller TiO₂ size and suitable photocatalytic properties. The multinanoporous morphology is needed because the pores could act as adsorption centres and so help improve the photocatalytic activity.¹⁸

2. Experimental

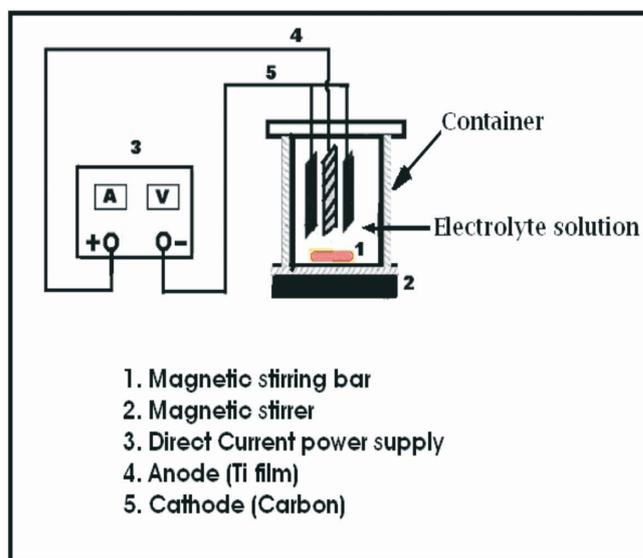
To prepare TiO₂ thin films by anodic oxidation, H₂SO₄ and NaOH were selected as electrolytes. Titanium substrates were prepared from titanium plates of 0.5 mm thickness containing Ti (≥97 %), N (≤0.012 %), C (≤0.02 %), Si (<0.04 %), and Fe (≤0.06 %). They were cut into pieces of dimensions 7.5 × 1 cm² and were cleaned in chloroform and etched in hydrofluoric acid (4 % w/w) for a period from 0.5 to 1 min, depending on the required surface structure. They were rinsed in distilled water, then in acetone before being dried and analyzed.^{19–20}

Electrodes of TiO₂ were prepared by anodic oxidation at room temperature by varying different parameters as listed in Table 1 where samples were labelled depending on the fixed experimental conditions. The current density was fixed to about 15–20 mA cm⁻² for the preparation of these electrodes. The direct current (DC) power supply (150 V – 5 A) was used to adjust the anodization voltage, under a potentiostatic regime. Sulfuric acid H₂SO₄ (or sodium hydroxide NaOH) of different concentrations was used as electrolyte. Three different values of oxidation voltages were chosen (100, 130 and 150 V). The H₂SO₄ concentrations selected were 0.5, 1.0 and 2.0 mol dm⁻³. The anodization time was varied from 5 to 11 min. After anodization, the products obtained were characterized with different analytical methods.

Since anodization is an exothermic process which leads to electrolyte heating, the solution was magnetically stirred during the oxidation process in order to maintain the temperature constant and thereby prevent local heating of the produced oxide film. Moreover, stirring the solution affects the rate at which electroactive molecules in the bulk solution are brought to the electrode surface by mass transfer. The experimental setup for the anodic oxidation is illustrated in Fig. 1.

To quantify the effect of the electrolyte nature in the production of TiO₂, another experiment was designed at room temperature in alkaline electrolyte solution (NaOH) at two different concentrations (0.1 and 0.2 mol dm⁻³). The oxidation voltage was fixed at 130 V and the anodization time to 5 min. In the same way, acidic electrolyte solutions of H₂SO₄ with respective concentrations of 0.1, 0.2, 0.5, 0.8 and 1.0 mol dm⁻³ were used at the same anodizing conditions to compare the efficiency of the prepared TiO₂ electrodes. The experimental conditions are listed in Table 2.

The photocatalytic properties were investigated by using 0.2 mol dm⁻³ methanol solution as an organic pollutant model in the presence of sodium sulfate (0.3 mol dm⁻³) as a supporting electrolyte because of its high conductivity which can be translated into little or almost no ohmic resistance between the reference electrode and the working electrode so that the measured current can be considered as due exclusively to the

**Figure 1** Typical experimental set-up for the anodic oxidation process.**Table 2** Selected electrolytes and concentrations used in the preparation of TiO₂ thin film electrodes.

Sample label	Electrolyte	Concentration/mol dm ⁻³
J ₁	NaOH	0.1
J ₂	NaOH	0.2
S ₁	H ₂ SO ₄	0.1
S ₂	H ₂ SO ₄	0.2
S ₅	H ₂ SO ₄	0.5
S ₈	H ₂ SO ₄	0.8
S ₁₀	H ₂ SO ₄	1.0

diffusion of the CH₃OH solution at the electrode surface.²¹

The Pyrex cell containing the CH₃OH solution was externally irradiated with a 125 W high pressure mercury UV lamp (model GGZ-125, λ = 365 nm) provided by 'Shanghai Yaming Lamps Factory'. A cooling fan was used to prevent overheating of the solution in the Pyrex cell. The system was placed over the designed compartment covered by an aluminium foil.

All photoelectrochemical experiments were performed by using a computer-controlled EG&G Princeton Applied Research (PAR, model 273A) potentiostat. For this purpose, three electrodes were required for the measurement: the working electrode made of a TiO₂ film, the counter electrode made of a platinum sheet (Pt) and a stable reference electrode (the saturated calomel electrode, SCE). All potentials were quoted with respect to the SCE. The measurement was made with CH₃OH (0.2 mol dm⁻³) and H₂SO₄ (0.3 mol dm⁻³). The photocurrent densities were measured first in the dark and then under UV illumination. The potentiostat was used to fix a constant applied bias of 0.5 V, and the current densities generated were recorded.

Table 3 Photocurrent densities*, I_{UV} (mA cm^{-2}) of the TiO_2 films prepared in H_2SO_4 electrolyte under different conditions (refer to Table 1).

$\text{H}_2\text{SO}_4/\text{mol dm}^{-3}$	100 V		130 V			150 V		
	8 min	11 min	5 min	8 min	11 min	5 min	8 min	11 min
0.5	3.3 ± 0.2	3.0 ± 0.2	4.8 ± 0.3	5.7 ± 0.3	4.9 ± 0.3	5.7 ± 0.3	3.3 ± 0.2	3.0 ± 0.2
1.0	3.8 ± 0.2	3.3 ± 0.2	6.5 ± 0.3	4.0 ± 0.2	3.8 ± 0.2	4.2 ± 0.2	0.4 ± 0.02	0.4 ± 0.01
2.0	2.7 ± 0.1	2.4 ± 0.1	3.8 ± 0.2	3.5 ± 0.2	3.1 ± 0.2	0.4 ± 0.02	0.3 ± 0.02	0.3 ± 0.01

* Values represented as mean \pm standard deviation.

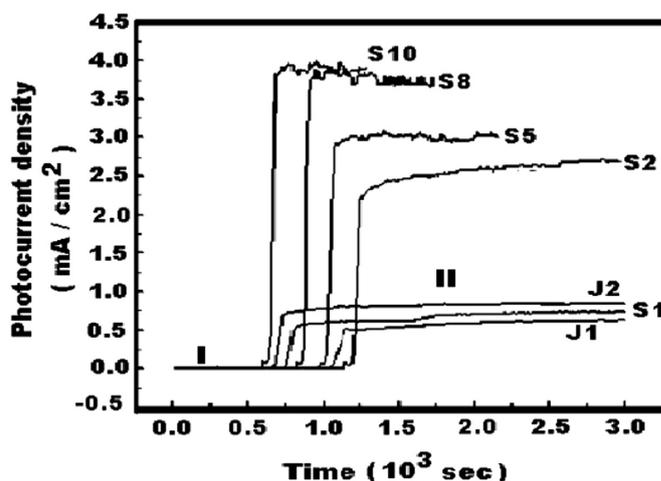
3. Results and Discussion

The photocurrent densities obtained with only H_2SO_4 as electrolyte, and when using NaOH and H_2SO_4 as electrolytes are respectively listed in Table 3 and Fig. 2 respectively.

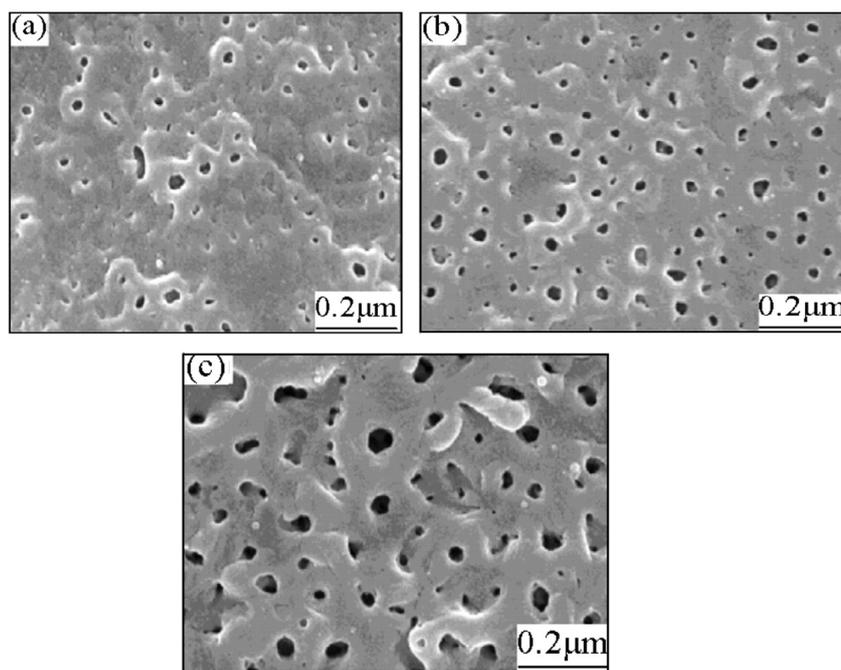
From Table 3, it can be seen that the electrodes prepared at 130 V exhibited higher values of photocurrent densities compared to those obtained with the electrodes prepared at 100 V and 150 V. The values of current densities for electrodes prepared at 130 V varied in the range between 3.1 mA cm^{-2} and 6.5 mA cm^{-2} . The maximum value of the current density measured is designated I_{UV} . By fixing the anodization time to 5 min and the H_2SO_4 electrolyte concentration to 1.0 mol dm^{-3} , the photocurrent obtained for sample E_5 was the highest and a value of $I_{UV} = 6.5 \text{ mA cm}^{-2}$ was obtained.

From Fig. 2 and Table 2, one can observe that the films of TiO_2 prepared in alkaline solutions (J_1 and J_2) exhibited smaller values of the current density (less than 1.0 mA cm^{-2}). However, for the series of TiO_2 films prepared in acid electrolyte (S_1, S_2, S_5, S_8 and S_{10}), a significant increase in current density was observed.

This result indicates that the photoelectrochemical properties of TiO_2 prepared in acid electrolyte depend significantly on the concentration of H_2SO_4 . Additionally, the photoelectrochemical properties of TiO_2 depend on the nature of the electrolyte used. Other researchers reported that the photocatalytic activity of TiO_2 can be greatly enhanced for films prepared by sulphuric acid treatment.^{22–24} Our experimental results agree well with the reported observation.

**Figure 2** Photocurrent densities of the TiO_2 thin film electrodes (prepared according to Table 2): (I) in the dark; (II) under UV irradiation.

To find out about the surface morphology of the prepared TiO_2 films, a scanning electron microscope (model: JSH-6700F FE-SEM) equipped with an EDAX X-ray micro analyser was used. The SEM micrographs of the samples prepared in $0.5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$, by fixing the anodization time to 11 min and by varying the anodization voltage from 100 V to 150 V are shown in Fig. 3.

**Figure 3** SEM micrographs of the surface morphology of the TiO_2 electrodes prepared in $0.5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ (anodization time 11 min) by varying the anodization voltage, (a) 100 V (b) 130 V and (c) 150 V.

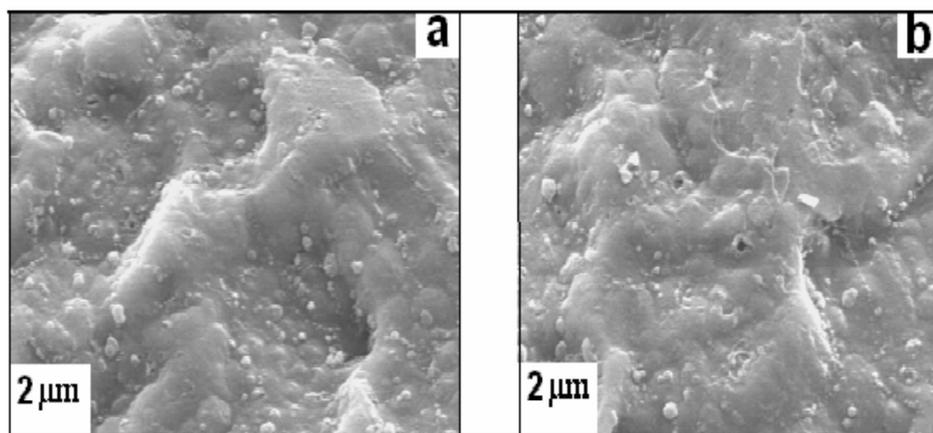


Figure 4 SEM morphologies of TiO₂ thin films prepared by anodic oxidation using NaOH as electrolyte (oxidation voltage: 130 V), (a) 0.2 mol dm⁻³ NaOH, and (b) 0.5 mol dm⁻³.

From Fig. 3, it can be observed that the film prepared at 100 V has more superficial pits with smaller pore density and pore diameter. The surface of the TiO₂ film prepared at 130 V has a higher pore density and the pores are uniformly distributed. Although the film prepared at 150 V has a higher pore density, the pore diameter increased compared to the films prepared at 130 V and 100 V. The experimental result shows that the surface morphology largely depends on the anodization voltage, in agreement with the literature.²⁵ From the surface morphology and the photoelectrochemical properties of the electrodes prepared in 0.5 mol dm⁻³ H₂SO₄ with an anodization time of 11 min, it was concluded that the anodization voltage of about 130 V could be the most suitable for preparing a TiO₂ film with good photocatalytic properties. As a further piece of information, it is worth noticing that there were no pores formed on the surface of the film when anodizing was carried out at low voltages, i.e. at 60, 80, and 90 V (the corresponding micrographs are not shown here).

Figure 4 is related to the surface morphology of a TiO₂ film prepared with NaOH as electrolyte.

From Fig. 4, it is observed that at low NaOH concentration and room temperature, the porous layer of the TiO₂ film could not be produced on the titanium sheet. The films produced in this way are characterized by a rather rough surface and they are not multiporous compared to those prepared in H₂SO₄ electrolyte. This suggests that the electrolytic medium plays a significant role on the surface morphology of TiO₂ prepared by anodic oxidation.

To find out about the crystallinity of the produced electrodes (A₁₁, B₁₁ and C₁₁; refer to Table 1), the XRD of these samples was recorded. The XRD patterns of the prepared TiO₂ electrodes after anodization at different experimental conditions are shown in Fig. 5.

From Fig. 5, it can be seen that the film prepared at 100 V is mainly amorphous (neither anatase nor rutile could be detected). By increasing the anodization voltage to 130 V, the crystallization significantly increased. A strong peak related to anatase could be observed. Finally, when the oxidation voltage further increased to 150 V, a mixture of anatase and rutile could be observed. The experimental results demonstrated that the structure of the prepared TiO₂ films responds sensitively to changes in voltage during anodizing of the titanium metal sheet. Therefore, in order to prepare TiO₂ with anatase structure, it is necessary to fix the anodization voltage to 130 V. Figure 6 describes the XRD spectra of the electrodes J₂, S₂, S₅ and S₁₀ TiO₂ thin films (see Table 2).

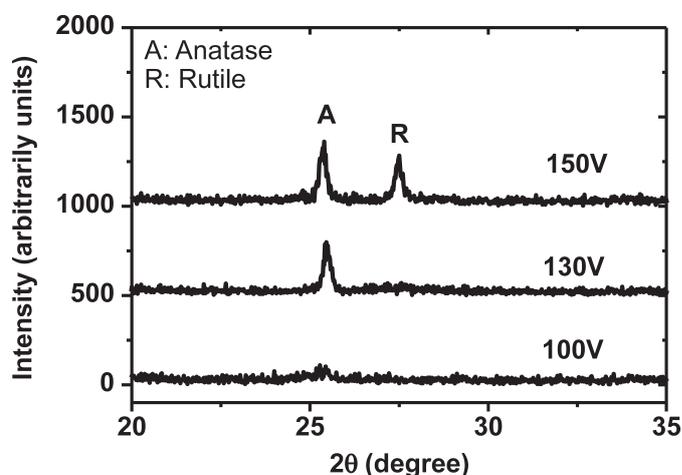


Figure 5 X-ray spectra of samples A₁₁, B₁₁ and C₁₁ (electrolyte 0.5 mol dm⁻³ H₂SO₄; anodization time 11 min; temperature 25 °C; current density 15–20 mA cm⁻²). Results were obtained by using Cu K_α radiation ($\lambda = 1.54178 \text{ \AA}$).

From Fig. 6, it can be seen that sample J₂ prepared in NaOH (0.5 mol dm⁻³) was mainly amorphous. For the samples prepared in acid electrolyte (S₂, S₅ and S₁₀), it is observed that, by increasing the H₂SO₄ concentration, the crystallization of TiO₂ significantly increased and a strong peak related to anatase was observed (see sample S₁₀ where H₂SO₄ concentration is 1.0 mol dm⁻³). This result indicates that the nature and the concentration of the

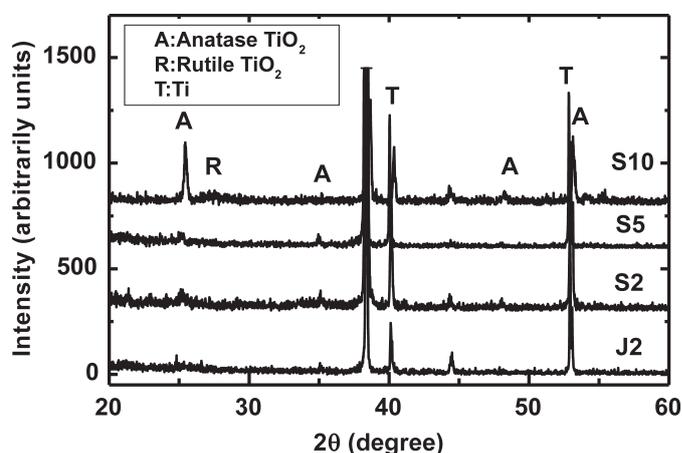


Figure 6 X-ray spectra of samples J₂, S₂, S₅, and S₁₀ TiO₂ thin films.

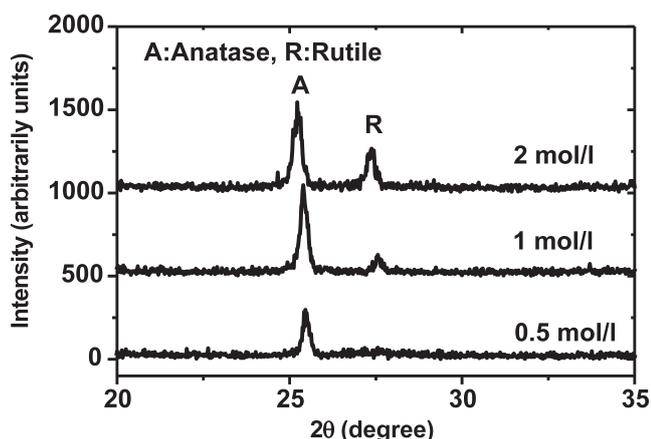


Figure 7 X-ray spectra of TiO₂ films prepared at 130 V, 11 min anodization time, H₂SO₄ concentration at 0.5 mol dm⁻³, 1 mol dm⁻³ and 2 mol dm⁻³; temperature 25 °C; current density 15–20 mA cm⁻². Results were obtained using Cu K_α radiation ($\lambda = 1.54178 \text{ \AA}$).

electrolyte used in the production of TiO₂ films plays an important role in its crystallization. The films prepared in NaOH display an amorphous structure, while those prepared in H₂SO₄ are crystalline.

From the surface morphology and the photoelectrochemical properties of the electrodes prepared in H₂SO₄ (0.5 mol dm⁻³) with an anodization time of 11 min, it was concluded that the anodization voltage of 130 V was the most appropriate for preparing electrodes with good photocatalytic properties.

Another experiment was run to investigate the influence of the H₂SO₄ concentration on the production of TiO₂ thin films. For this purpose, the voltage was fixed at 130 V, the time set to 11 min and three concentrations of H₂SO₄ selected (0.5, 1.0 and 2.0 mol dm⁻³).

Figure 7 displays the XRD spectra related to the TiO₂ films prepared under these different H₂SO₄ concentrations.

From Fig. 7, it can be seen that the TiO₂ prepared in 0.5 mol dm⁻³ H₂SO₄ is crystalline and mainly in the anatase form whereas TiO₂ prepared in 1.0 mol dm⁻³ H₂SO₄ consists mainly of anatase with some traces of rutile. When the concentration was increased to 2.0 mol dm⁻³, the TiO₂ produced was a mixture of anatase and rutile. The amount of rutile increased with increasing H₂SO₄ concentration. The photocurrent of the prepared TiO₂ film also decreased as shown in Table 3. This result indicates that the photocatalytic activity depends significantly on the crystallinity of the TiO₂ film prepared, and on the amount of rutile present in the sample. The sample prepared with 1.0 mol dm⁻³ H₂SO₄ exhibited a higher value of the photocurrent density, in good agreement with the result reported by other researchers who observed that a mixture of anatase and a small amount of rutile leads to a higher catalytic activity compared to a single crystal of anatase.^{26–28}

Finally, the effect of the anodization time on the preparation of TiO₂ thin films was investigated. For this purpose, the oxidation voltage was fixed to 130 V, the concentration of H₂SO₄ to 1.0 mol dm⁻³, and three anodization times selected (5, 8 and 11 min) as shown in Tables 2 and 3.

From Table 3, it can be seen that the photocurrent obtained for sample E₅ was the highest with a value $I_{UV} = 6.5 \text{ mA cm}^{-2}$. An increase in the anodization time showed a significant decrease in the photocurrent densities (refer to samples E₈ and E₁₁ in Table 1). Moreover, the crystallinity of sample E₁₁ (prepared in 1.0 mol dm⁻³ H₂SO₄, 130 V and 11 min) was mainly constituted of anatase TiO₂ with small traces of rutile. The particle size calcu-

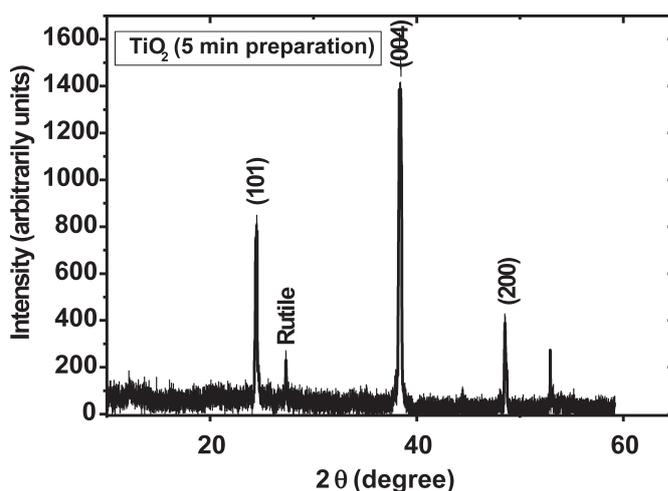


Figure 8 X-ray spectra of sample E₅ (TiO₂ film preparation conditions: Anodization voltage: 130 V, electrolyte: H₂SO₄ 1.0 mol dm⁻³; anodization time: 5 min; temperature: 25 °C; current density: 15–20 mA cm⁻²). Results obtained using Cu K_α radiation ($\lambda = 1.54178 \text{ \AA}$).

lated from the XRD spectrum by using the Scherrer formula was about 23 nm.^{29–30} Figure 8 shows the XRD spectrum of the TiO₂ prepared under the same conditions except that the oxidation time was fixed to 5 min (sample E₅).

The size of TiO₂ prepared in 5 min was evaluated by using the Scherrer formula, and the average size calculated from the peak (101) at 2θ of 25.28 °C related to anatase is about 14.6 nm. This means that the TiO₂ film produced in 1.0 mol dm⁻³ H₂SO₄, 5 min after the anodization at 130 V has the smallest diameter compared to those prepared at 8 and 11 min. This result indicates that the anodization time fixed in the production of TiO₂ plays an important role in its photocatalytic activity.

4. Conclusion

From the above results, it appears that, in order to prepare multinanoporous TiO₂ films with good photocatalytic properties, the best experimental conditions for anodization would be as follows: 130 V for the anodization voltage, 5 min for the anodization time, and 1.0 mol dm⁻³ for the H₂SO₄ electrolyte concentration.

Compared with conventional techniques like plasma spray or sol-gel, the present work shows that the nanostructure of the TiO₂ films (with diameter size less than 100 nm) can be easily obtained at lower cost by electrochemical oxidation on a titanium metal substrate. Furthermore, the structures and morphologies of the TiO₂ films can be controlled according to the anodizing conditions. The easy control of microstructures of the anodic film should be a major advantage for many technical applications especially in wastewater treatment.

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