

Influence of Fe^{3+} ions on the photocatalytic activity of TiO_2 films prepared by micro-plasma oxidation method

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Abstract

Microporous titanium dioxide thin films have been fabricated on titanium plates by the micro-plasma oxidation method with the electrolyte of H_2SO_4 . The influence of Fe^{3+} ions addition in the electrolyte on the photocatalytic activities was investigated. The results reveal that titanium dioxide thin films produced with Fe^{3+} addition electrolyte exhibit higher photoactivity than pure electrolyte for the oxidation of rhodamine B. The removal of rhodamine B reaches 90% for 30 min when Fe^{3+} addition concentrate is 0.2 g/L. Experimental results of X-ray diffraction and atom force microscopy show that the increase in activity is related to change in the lattice parameters and cell volume.

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1. Introduction

In recent years, TiO_2 photocatalyst has attracted extensive attention, because it provides a promising strategy for cleaning polluted air or water [1,2]. However, the use of conventional power catalysts results in disadvantages of stirring during the reaction and of separation after the reaction. Preparation of the catalysts coated as thin films will make it possible to overcome these disadvantages and provide large reaction surface area, which are necessary for the practical application of photocatalytic materials. In this context, TiO_2 thin films have recently gained much attention as useful photocatalysis. A few papers [3,4] have reported the preparation of TiO_2 photocatalytic thin films with micro-plasma oxidation (MPO). This method is based on the anodic oxidation, which runs at potential above the breakdown voltage of the oxide film growing on the surface of metal anode, such as Al, Mg, Ti, Nb, and Zr [5]. The process consists of numerous simultaneous and uniform plasma discharges over the metal surface. The

advantages by this method are that uniform films are grown on the surface of metal substrate both with good adherence to substrates and with a number of micropores [6,7].

It is known that transition metal ions doped into catalysts can increase the quantum efficiency of the heterogeneous photocatalytic property by acting as electron (or hole) traps and by altering the e^-/h^+ pair recombination rate [8–10]. In previous work [3], TiO_2 thin films with photocatalytic activity have been grown on titanium plates by MPO method in the electrolyte solution of H_2SO_4 . So, in this paper, Fe^{3+} ions of different concentrate were added into the above electrolyte during the MPO process. The objective of this research was to investigate the effect of Fe^{3+} ions in the electrolyte on the structural property, the surface morphology and the photocatalytic activity of the films prepared with MPO. Rhodamine B was used to evaluate the photooxidation efficiency of the films under UV (Ultraviolet) irradiation.

2. Experimental details

2.1. Preparation of TiO_2 thin films

A high-purity (99.9%) titanium sheet was selected as anode, with a reaction area of $25 \times 10 \times 0.5$ mm. A stainless

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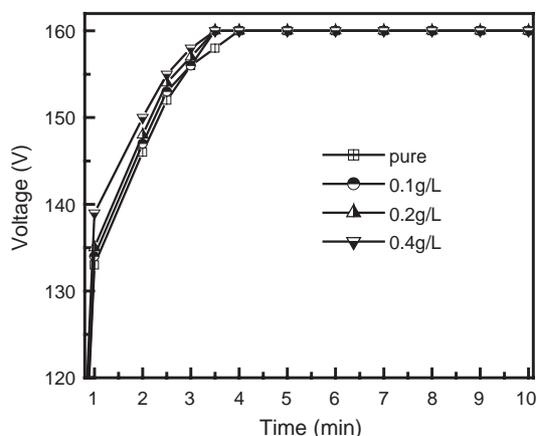


Fig. 1. Effect of Fe^{3+} addition on voltages during the micro-plasma oxidation.

steel container was used as electrolyte cell and cathode. The set-up scheme has been shown as presented in Ref. [4]. The anode was located in the center of the electrolyte cell. The electrolytes consisted of 0.5 M H_2SO_4 and different concentration $\text{Fe}_2(\text{SO}_4)_3$ (0, 0.1, 0.2, 0.4 g/L) solution, respectively. An electrical current was applied by using a laboratory-made direct current power supply with a maximum power of 3 kW. The MPO process was conducted in two stages, in which the galvanostatic anodization with a constant current density was first performed until a designated anode-to-cathode voltage was reached. Then the constant voltage was maintained until the end of oxidation, while the current was decreasing gradually. The temperature was controlled within the range (20 ± 0.2 °C) with a cold water jacket. The freshly generated film was then rinsed by distilled water and dried in a current of hot air. According to previous work [3], TiO_2 thin film had higher photocatalytic activity when the current density was 80 mA/cm^2 , the voltage was 160 V and oxidation time was 10 min. So, in this work, the above process parameters were kept constant.

2.2. Characterizations of TiO_2 thin films

Crystalline structure of the produced films were examined using D/max-r B X-ray diffraction (XRD) with a Cu $\text{K}\alpha$ source. Surface morphology of the produced films was characterized by NT-MDT P 47 atomic force microscopy (AFM). Composition of TiO_2 films were analyzed by X-ray photoelectron spectroscopy (XPS), using VG ESCALAB Mark II spectrometer with Al $\text{K}\alpha$ X-ray source.

2.3. Evaluation of photocatalytic property of the films

The bench-scale photoreactor system consisted of a cylindrical quartz cell with the size of 25 mm in diameter and 50 mm in height, a 20 W UV lamp with a maximum UV irradiation peak at 365 nm. The schematic diagram of photoreactor was presented in previous paper [4]. The photo-catalytic activity of each film produced by MPO was determined by measuring the degradation of rhodamine

B dye solution. Samples of 250 mm^2 were immersed into 10 ml of a 10 mg/L rhodamine B solution. The solution was stirred continuously and constantly supplied with air during the reaction. The UV light was irradiated for 150 min perpendicularly to the surface of the sample through the sidewall of the cylindrical quartz cell and the distance between the UV lamp and the film was 20 mm. Rhodamine B had maximum absorbance at the wavelength of 552 nm in the Ultraviolet–Visible spectrometry. The change of rhodamine B concentration with the irradiation time was measured by a UV spectrophotometry at the wavelength of 552 nm.

3. Results

3.1. Variation of cell voltage against time in the MPO process

Fig. 1 shows the change of voltages with time in the Fe^{3+} addition electrolyte of H_2SO_4 during the MPO process. It can be seen from Fig. 1 that all of the voltages fast increase within the initial 1 min, subsequently increase slowly, and then are up to 160 V within the 4 min. The increase rate of voltage is faster with the Fe^{3+} addition electrolytes than that with pure one and increases with the concentration of Fe^{3+} ion. This indicates that the increase of Fe^{3+} ion concentration favors the breakdown of barrier film and implies that the films prepared with Fe^{3+} addition electrolytes have different characterization of structure.

3.2. Structural analysis of the prepared films

XPS analysis is carried out to determine the chemical composition of the films before and after doping Fe^{3+} ions in the electrolyte. The XPS survey spectra of all films are shown in Fig. 2. It can be seen from Fig. 2 that the films consist of the element of Ti, O and S, and there is no Fe element in the doped

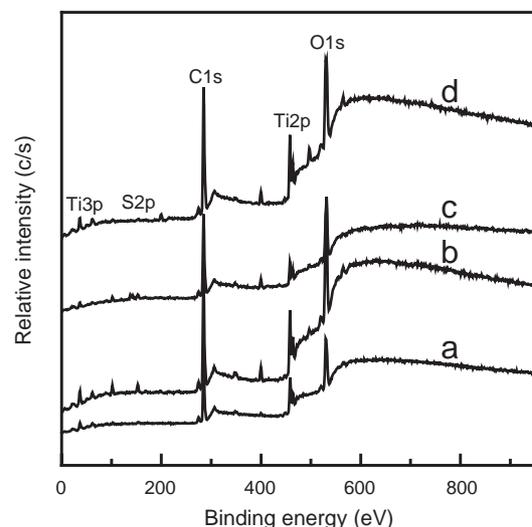


Fig. 2. XPS survey spectra for the surface of TiO_2 films prepared with the Fe^{3+} addition electrolyte. a) pure; b) 0.1 g/L; c) 0.2 g/L; d) 0.4 g/L.

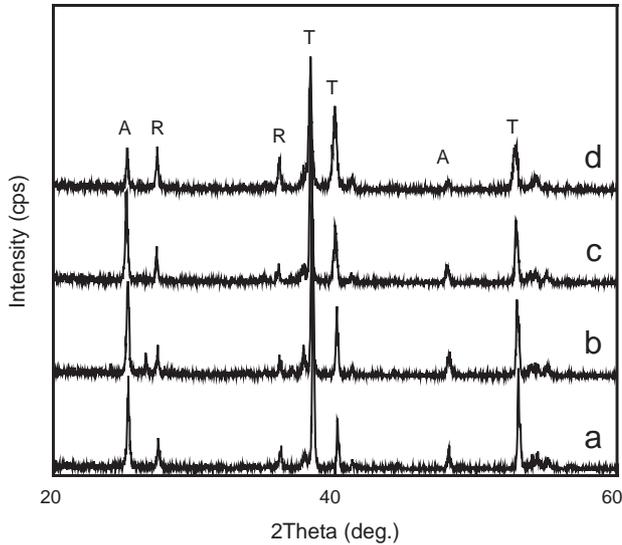


Fig. 3. XRD spectra of films prepared with the Fe^{3+} addition electrolyte. a) pure; b) 0.1 g/L; c) 0.2 g/L; d) 0.4 g/L.

films, which shows that Fe element in the electrolyte has not heavily enter into the films. A small quantity of S element comes from the electrolyte of H_2SO_4 .

The XRD patterns of the films prepared in the Fe^{3+} addition electrolytes of H_2SO_4 are shown in Fig. 3. First, as shown in the figure, there are many sharp peaks in the XRD patterns, which indicate that the prepared films have been well crystallized. According to Joint committee on power diffraction standard data cards, the films mainly consist of anatase and rutile TiO_2 . Secondly, it can be also seen that content of rutile TiO_2 increases with the Fe^{3+} addition concentration. Fig. 4 shows the enlarged XRD peaks of anatase TiO_2 plane (101). From Fig. 4, it is clear that the X-ray diffraction peaks of crystal plane (101) shift to lower diffraction angle with increasing concentration of Fe^{3+} ions.

The X-ray diffraction peaks of crystal plane (101) and (200) in anatase are selected to determine the lattice parameter of the

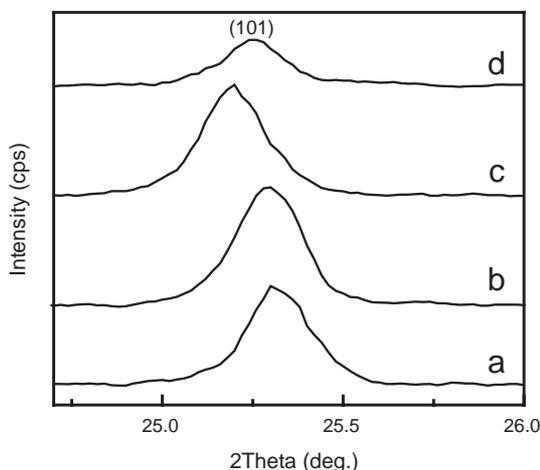


Fig. 4. X-ray diffraction peaks of crystal plane (101). a) pure; b) 0.1 g/L; c) 0.2 g/L; d) 0.4 g/L.

Table 1
Effect of Fe^{3+} ion concentration on lattice parameter and cell volume of anatase TiO_2

Fe^{3+} ions addition concentration (g/L)	$a=b$ (nm)	c (nm)	Cell volume (nm^3)
0	0.3783	0.9499	0.1359
0.1	0.3783	0.9553	0.1367
0.2	0.3792	0.9683	0.1392
0.4	0.3786	0.9614	0.1378

produced TiO_2 films. The lattice parameters are obtained by using the following equations:

$$\text{Bragg's law: } d_{(hkl)}^{-2} = \lambda / 2 \sin \theta$$

$$d_{(hkl)}^{-2} = h^2 a^{-2} + k^2 b^{-2} + l^2 c^{-2}$$

where $d_{(hkl)}$ is the distance between crystal planes of (hkl), λ is the X-ray wavelength, θ is the diffraction angle of crystal plane (hkl), hkl is the crystal plane index, and a , b , and c are lattice parameters (in anatase form, $a=b \neq c$).

The lattice parameters and cell volumes of TiO_2 catalysts are summarized in Table 1. According to Table 1, the cell volume and lattice parameters (a , b , and c) generally increase with increase of Fe^{3+} concentration in the electrolyte, and the

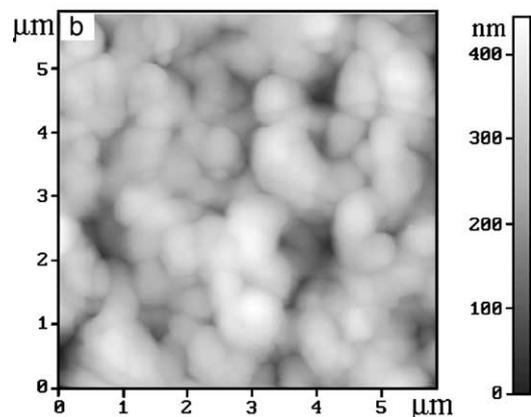
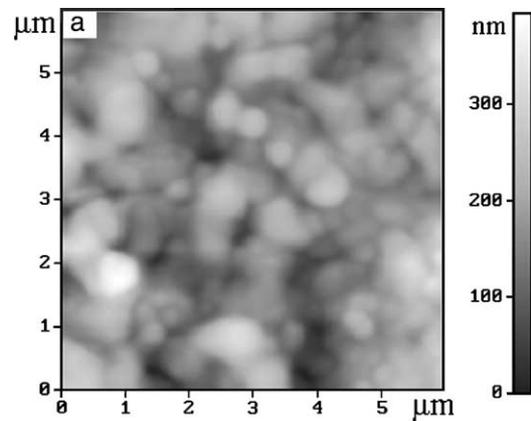


Fig. 5. AFM images of films prepared with the Fe^{3+} addition electrolyte. a) pure; b) 0.2 g/L.

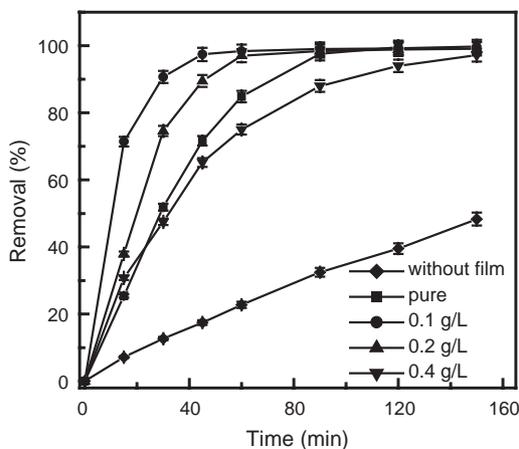


Fig. 6. Effect of Fe^{3+} ion addition on the removal of rhodamine B.

increase reaches the maximum at the Fe^{3+} addition concentration of 0.2 g/L.

3.3. Surface morphology of the films

Fig. 5 depicts the AFM images of the prepared films. It can be seen that the surface morphology of the micro-plasma oxidation films are microporous. The micropore of the film prepared with Fe^{3+} addition electrolyte is much deeper than that of the film prepared with pure electrolyte. In addition, the surface roughness (R_{rms}) of the film prepared with pure electrolyte is 54.2 nm, while that of film prepared with 0.2 g/L Fe^{3+} addition electrolyte is 72.3 nm.

3.4. Photocatalytic activity of the films

Degradation of rhodamine B over the produced films and without film irradiated by UV light was shown in Fig. 6. As shown in Fig. 6, photodegradation rate of rhodamine B without the film is very lower than that with the films, and the photodegradation efficiencies of the films produced in different addition concentration of Fe^{3+} ion are different. Less addition of Fe^{3+} ion in the electrolyte makes the increase of the photocatalytic activity of the films. When the addition concentration is 0.2 g/L, the produced film achieves the faster photodegradation of rhodamine B. The removal of rhodamine B using the film with UV irradiation of 30 min (as shown in Fig. 7) reaches 90%, which is 40% higher than the film produced with pure electrolyte.

4. Discussion

As shown in Fig. 7, the produced TiO_2 film exhibits optimum photocatalytic activity when the addition concentration of Fe^{3+} ion is 0.2 g/L. As Fe^{3+} ion is added into the electrolyte during the MPO process, the TiO_2 film formed may be different in both physical and chemical characteristics such as the phase constitution and surface area. We will discuss the effects of these physical and chemical changes on the photocatalytic activity of the TiO_2 films.

In the MPO process, a barrier film can be firstly formed on the metal surface in a certain electrolyte. When the voltage goes up and exceeds a critical value, the barrier film is broken and spark discharge appears. Although the life of each spark is very short, a plasma atmosphere is formed and the momentary temperature in these small discharge zone can increase very quickly and exceed 2000 °C in a short time [11]. Under this condition, oxygen molecules generated at the surface of anode can combine with titanium to form molting oxide. Then the materials are cooled rapidly by the surrounding electrolyte. Stabilized products are condensed onto the surface. This results in the formation of TiO_2 crystallite and pores on the surface, which corresponds to the fine sparks of sample surface in the process of oxidation.

The curve in Fig. 1 shows that a higher voltage can be obtained when Fe^{3+} ion is added into electrolyte. When the voltage becomes very high, a stronger electric field would appear, so the discharging sparks become bigger and their number increases on the surface of the electrode at the higher concentration of Fe^{3+} ion. It results in higher instantaneous temperature and bigger pores during the breakdown of coating. Thus the micropores' size and surface roughness increased when Fe^{3+} ion exists in the electrolyte, which is consistent with the result shown in Fig. 5. Their increase can improve the photocatalytic activity of the TiO_2 films because the micropores increase the specific surface area, which produces more reactive sites to absorb and oxidize pollutants.

It has been shown in Fig. 3 that rutile increases with the concentration of Fe^{3+} ion in the electrolyte. It is known that rutile is less effective than anatase as a photocatalyst for the oxidation of most organic compounds [12]. However, the photocatalytic activity of the TiO_2 film produced with Fe^{3+} addition electrolyte are still higher than that of pure electrolyte as shown in Fig. 6. It can be concluded that the rutile content in the produced films does not play a significant role in determining its photocatalytic activity.

We believe that a probable explanation for the enhanced photocatalytic activity of the TiO_2 films produced with the Fe^{3+} doped electrolyte is the structural defects induced by the introduction of ferrum into the TiO_2 lattice. Although there is

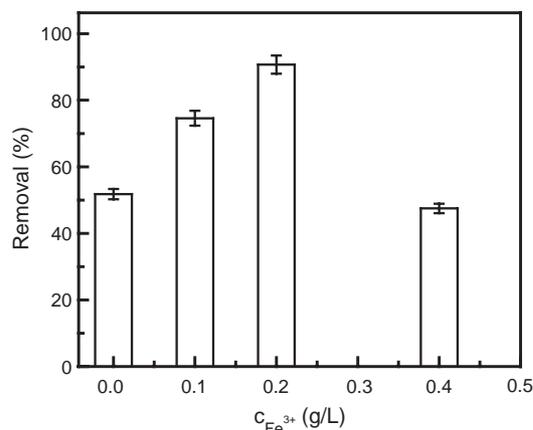


Fig. 7. Removal of rhodamine B using the films prepared with the Fe^{3+} addition electrolyte for 0.5 h.

no Fe element which appears in the XPS analysis, it can be the result of the few content of Fe element. As spark discharge produces momentarily high temperature during the MPO process, Fe^{3+} ion in the electrolyte can introduce into TiO_2 lattice during its formation, which results in the formation of structural defects. From Table 1 and Fig. 6, it is quite clear that the photocatalytic activities of TiO_2 films produced with Fe^{3+} addition electrolyte increase with increase of its lattice parameters and cell volume. The increase is caused by the size difference between titanium and ferrum. When Fe^{3+} (with an ionic radius of 0.064 nm) substitutes for Ti^{4+} (with an ionic radius of 0.068 nm) in the TiO_2 lattice, the TiO_2 film exists in a strained form with high lattice energy. It is suggested that some oxygen might escape from the surface of the lattice to trap the photogenerated holes. In addition, Sclafani and Herrmann have found that metal oxides with more structure defects on surface could ionosorb oxygen as O^- species, which were photoactive in mild oxidation reactions [13]. Compared with the basal trap reaction [14], the expanding lattice can cause other hole trap reaction via the following mechanism:



Where O_L^{2-} represents the oxygen species that escape from the surface of lattice.

The O^- species formed in reaction (1) may also oxidize water molecules adsorbed on the photocatalyst:



It is known that the dissociated atomic oxygen species formed in reactions 1 and 2 are able to attack the chemical bonds of surface adsorbed organic compounds, and the OH^\bullet radical is a powerful oxidizing agent capable of mineralizing the majority of organic pollutants [14,15]. So the enhanced photocatalytic activities of TiO_2 film produced with Fe^{3+} addition electrolyte can be explained by the presence of this addition pathway for the generation of hydroxyl radicals and highly reactive atomic oxygen species. Degradation efficiency is increased with addition of Fe-dopant, but it decreases by excessive Fe-dopant >0.2 g/L. Dopant Fe^{3+} ions suppress the electron–hole recombination as hole trapper and increase the generation of hydroxyl radicals, but excessive Fe atom fails to enter into the lattice. Therefore, the cell volume of the Fe-dopant TiO_2 of 0.4 g/L is not larger than that of 0.2 g/L (as shown in Table 1). In addition, excessive Fe^{3+} ions favor anatase to rutile phase transformation in TiO_2 (as shown in Fig.

3), which also decrease the photocatalytic activity. So, the produced film shows the highest photocatalytic activity when the Fe^{3+} ions addition concentration is 0.2 g/L in the electrolyte of H_2SO_4 .

5. Conclusion

TiO_2 films have been prepared with Fe^{3+} addition electrolyte of H_2SO_4 using MPO oxidation method. The produced TiO_2 films exhibit higher photocatalytic activities than that prepared in the pure electrolyte. The produced film shows the highest photocatalytic activity when the Fe^{3+} ions addition concentration is 0.2 g/L in the electrolyte. And removal of rhodamine B is up to 90% for 30 min under the irradiation of UV light, which is 40% higher than the film produced with pure electrolyte. The increase activity is related to change in the lattice parameters and surface structure caused by Fe substitution. It is proposed that the lattice O^{2-} and O^- ionosorbed on surface are responsible for the increased photocatalytic activities.

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