

Influence of V^{5+} Ions on Photocatalytic Activity of TiO_2 Films Prepared by Micro-plasma Oxidation Method

Shao Zhongcai, Jiang Haitao, Yang Li, Wei Shouqiang

Shenyang Ligong University, Shenyang 110159, China

Abstract: Microporous titanium dioxide thin films have been fabricated on titanium plates by the micro-plasma oxidation method with the electrolyte of $Na_3PO_4+Na_2B_4O_7$. The influence of V^{5+} ions addition in the electrolyte on the photocatalytic activities was investigated. A kind of typical textile industry pollutant (methylene blue) was used to evaluate the photo-catalytic activity of the films. The results showed that this activity of the films had been improved by adding V^{5+} ions into the electrolyte solution. The removal of methylene blue reaches 90% for 60 min when V^{5+} ions addition concentrate is 0.3 g/L. X-ray diffraction, scanning electron microscopy and atomic force microscopy techniques were applied to characterize the modified films. Experimental results show that the improvement in activity was related to the forming of titanium dioxide lattice distortion, which could accept more photoexcited holes and produce more strong surface free radicals to oxidate adsorptive molecules.

Key words: microarc oxidation; ion doping; titanium dioxide; photocatalytic activity

TiO_2 is the most widely used photocatalyst for effective decomposition of organic compounds in air and water under irradiation of UV light with wavelength shorter than that corresponding to its band gap energy. Recently, TiO_2 has been extensively studied because of its moderate band gap, high photocatalytic activity, wider range of processing procedures, and its excellent chemical and photochemical stability^[1-3]. 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 photo-catalytic materials. In this context, TiO_2 thin films have recently gained much attention as useful photocatalysis. A few papers^[4,5] have reported the preparation of TiO_2 photocatalytic thin films with microarc oxidation (MAO). 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 aluminum, titanium, magnesium and zirconium^[6]. 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^[7,8].

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^[9-11]. In previous work^[4], TiO_2 thin films with photocatalytic activity have been grown on titanium plates by MAO method in the electrolyte solution. In this paper, V^{5+} ions of different concentrate were added into the above electrolyte during the MAO process. The objective of this research was to investigate the effect of V^{5+} ions in the electrolyte on the structural property, the surface morphology and the photocatalytic activity of the films prepared with MAO. Methylene blue was used to evaluate the photooxidation

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Corresponding author: Shao Zhongcai, Ph. D., School of Environmental and Chemical Engineering, Shenyang Ligong University, Shenyang 110159, P. R. China, Tel: 0086-24-24680345, E-mail: zhongesh@163.com; Jiang Haitao, jiangtao04522@163.com

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efficiency of the films under UV (Ultraviolet) irradiation.

1 Experimental

1.1 Preparation of TiO₂ thin films

Test sample using pure titanium, cut into 20 mm×20 mm×0.5 mm was used as standard sample, each sample surface was polished with 800# and 1000# abrasive paper, rinsed with distilled water, then washed with acetone ultrasonically and cleaned deionized water, and dried in desiccators. A stainless steel container was used as cathode. A 25 kW MAO coating deposition equipment of unit designed and built in the authors laboratory was used for the coating deposition. The anode was immersed in the center of the electrolyte cell. The electrolytes consisted of Na₃PO₄+Na₂B₄O₇ and different concentration NH₄VO₃ (0, 0.1, 0.3, 0.5 g/L) solution, respectively. The electrolyte was continuously circulated in the reaction chamber made of non-conductive material. The bath temperature was maintained at 20-30 °C with the help of an external heat exchanger. TiO₂ thin film had higher photocatalytic activity when the current density was 0.1-0.3 A/cm², the voltage was 320 V and oxidation time was 10 min. So, in this work, the above process parameters were kept constant.

1.2 Characterizations of TiO₂ thin films

Crystalline structure of the produced films were examined Using D/max-rB X-ray diffraction (XRD) with a Cu K α source. Surface morphology and roughness of the produced films was characterized by using Scanning Electron Microscopy (SEM) and atomic force microscopy (AFM). The AFM operates in contact mode in air. A SiN triangular micro-cantilevers (Olympus) with pyramidal tips were used, which has force constant of 42 N/m and resonance frequency of 300 kHz.

1.3 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 MAO was determined by measuring the degradation of methylene blue solution. Samples were immersed into 10 ml of a 5 mg/L methylene blue solution. The solution was stirred continuously and constantly supplied with air during the reaction. The UV light was irradiated for 180 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. Methylene blue had maximum absorbance at the wavelength of 665 nm in the Ultraviolet-Visible spectrometry. The change of methylene blue concentration with the irradiation time was measured by a UV spectrophotometry at the wavelength of 665 nm.

2 Result and Discussion

2.1 Variation of cell voltage against time in the MAO process

Fig.1 shows the change of voltages with time in the V⁵⁺ addition electrolyte of Na₃PO₄+Na₂B₄O₇, during the MAO 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 300 V within the 3 min. The increase rate of voltage is faster with the V⁵⁺ addition electrolytes than that with pure one and increases with the concentration of V⁵⁺ ion. This indicates that the increase of V⁵⁺ ion concentration favors the breakdown of barrier film and implies that the films prepared with V⁵⁺ addition electrolytes have different characterization of structure.

2.2 Surface morphology of ceramic coatings of addition V⁵⁺ ions

Fig.2 and Fig.3 depicts the SEM photographs and AFM images of the films (TiO₂, V/TiO₂). It can be seen from SEM photographs magnified by 2000 times that the surfaces of the microarc films are mesoporous. Compared with pure TiO₂, the surface grain size and the density of V/TiO₂ pores increase, which could improve the photo-catalytic activity of the films because more mesopores can produce more reactive sites to absorb and oxide pollutants.

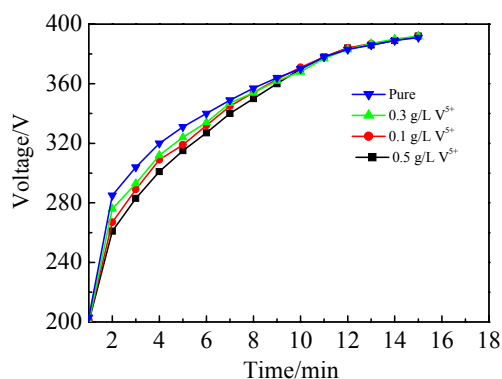


Fig.1 Effect of V⁵⁺ addition on voltages during the micro-plasma oxidation

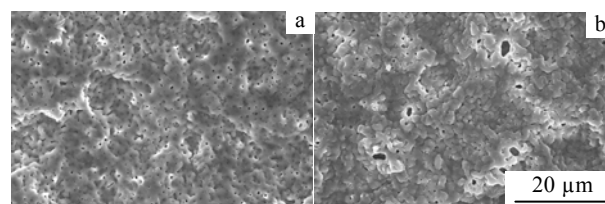


Fig.2 SEM images under different condition: (a) TiO₂ and (b) V/TiO₂

In parallel to the SEM photographs, AFM images for the above two kinds of films are shown in Fig.3 as well. These images verify that the V/TiO₂ film is much deeper than pure TiO₂ which is consistent with the SEM results. The value of the mean roughness and the maximum height of projections can be obtained directly from these AFM images. The roughness of the TiO₂ films is 42.89 nm and that of the V/TiO₂ films is 60.46 nm, while maximum heights of projections on the films are 300.61 and 410.78 nm, respectively. The above results indicate that the roughness of the films increase when V ions were doped into the electrolyte solution, which enable the film surfaces to better absorb and decompose organic compounds.

2.3 Structural analysis of the prepared films

The XRD patterns of the films prepared in the V⁵⁺ addition electrolytes of Na₃PO₄+Na₂B₄O₇ are shown in Fig.4. 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 TiO₂ and Ti. Secondly, it can be also seen that content of anatase TiO₂ increases with the V⁵⁺ addition concentration from XRD peaks of anatase TiO₂ 24.5°.

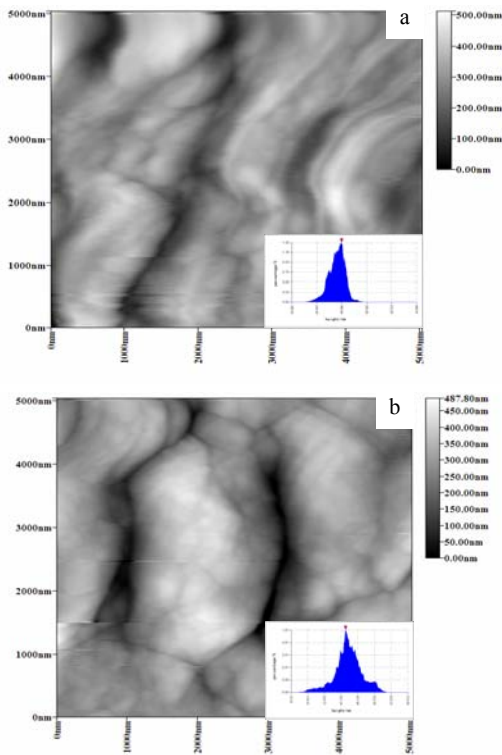


Fig.3 AFM images of films prepared with the V⁵⁺ addition electrolyte: (a) pure and (b) 0.3 g/L

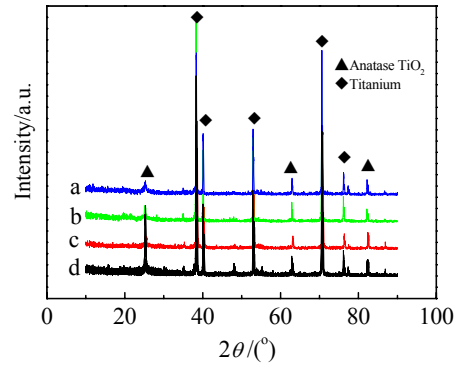


Fig.4 XRD patterns of films prepared with the V⁵⁺ addition electrolyte: (a) pure, (b) 0.1 g/L, (c) 0.3 g/L, and (d) 0.5 g/L

2.4 Photocatalytic activity of the films

Degradation of methylene blue over the produced films and without film irradiated by UV light was shown in Fig.5. As shown in Fig.5, photodegradation rate of methylene blue without the film is very lower than that with the films, and the photodegradation efficiencies of the films produced in different addition concentration of V ion are different. Less addition of V ion in the electrolyte makes the increase of the photocatalytic activity of the films. When the addition concentration is 0.3 g/L, the produced film achieves the faster photodegradation of methylene blue. The removal of methylene blue using the film with UV irradiation of 30 min (as shown in Fig.6) reaches 90%, which is 40% higher than the film produced with pure electrolyte.

As shown in Fig.6, the produced TiO₂ film exhibits optimum photocatalytic activity when the addition concentration of V ion is 0.3 g/L. As V ion is added into the electrolyte during the MAO process, the TiO₂ 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 TiO₂ films.

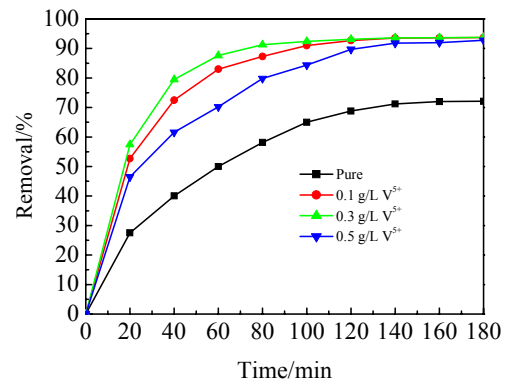


Fig.5 Effect of V⁵⁺ ion addition on the removal of methylene blue

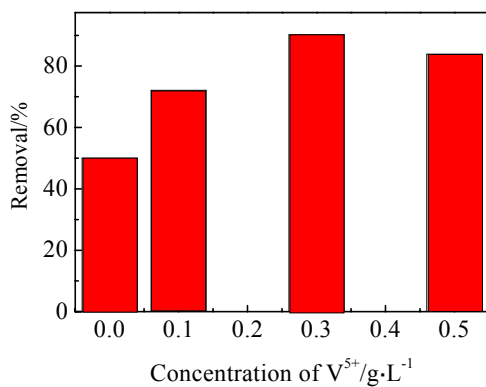


Fig.6 Removal of rhodamine B using the films prepared with the V addition electrolyte for 1.0 h

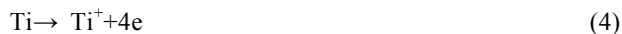
In the MAO process, At first, OH⁻ and VO³⁻ anions are generated due to ionization of the sodium three-phosphate and sodium vanadate salts in the water as shown below:



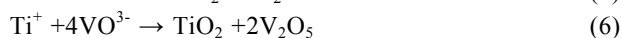
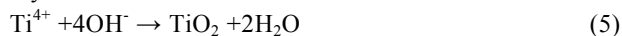
and



When the potential is applied (at the beginning time of the MAO process), titanium substrate, which is connected to the positive pole of the rectifier as anode, involves an oxidation reaction over the anode surface as below:

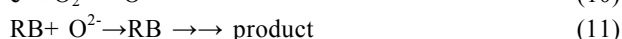


Simultaneously, the OH⁻ and VO³⁻ anions move toward the anode surface because of the strong electrical field between anode and cathode, and react with the Ti cations on the vicinity of the anode:



At the same time, large amounts of O₂ and H₂ bubble appear on the surface of the anode and cathode, respectively [12]. As the applied potential increases, the bubbles on the surface of the anode break, generating large amount of energy and low temperature plasma. The high-energy plasma accelerates the electrochemical reaction, and facilitates the MAO process.

Vanadia-titania porous layers were successfully synthesized by micro-arc oxidation process for the first time. Whereafter the photo-catalytic activity of each films produced by MAO was examined by measuring the degradation of methylene blue dye solution. A general mechanism for heterogeneous photo-catalysis on TiO₂ under UV irradiation is shown as [1-5]:



Upon excitation, a conduction-band electron and a valence band hole separate. Then the hole initiates an oxidative reaction while the electron initiates a reductive reaction if recombination does not occur. Organic compounds are believed to be destroyed through direct oxidation by the trapped holes or to be attacked by hydroxyl groups [13,14]. Sclafani and Herrmann have found that metal oxides with more structure defects on surface could ionosphere oxygen as O⁻ species, which can cause hole trap reaction and produces more OH⁻ radical [15]. So, the above lattice distortion can reduce the recombination rate of e⁻/h⁺ pairs and produce more OH⁻ radical, which will have a positive influence on the photo-catalytic activity of the films. When the V⁵⁺ dopant concentration is 0.3 g/L, the lattice distortion of TiO₂ is maximal. Therefore, the film has higher photo-catalytic activity, which is consistent with the results of the photo-catalytic degradation experiments. However, when the concentration of V⁵⁺ increase above 0.3 g/L reach 0.5g/L, degradation efficiency of the produced films decrease instead. It is likely to form the V₂O₅ on the surface of TiO₂ particles when doping V is more, which could decrease the quantity of vanadium entering into the TiO₂ lattice, reduce the distortion, and counteract the photoreaction. Because the amount of V₂O₅ in the films is very small, so the V₂O₅ phase cannot be detected by XRD. Another reasonable explanation ascribes to the more doping V, which is deleterious to the separation of electron-holepairs. It acts as a recombination centre leading to a shorter lifetime of the electron-holepairs. In order to improve the photo-catalytic activity of the TiO₂ film, further tests and explanation are actually underway.

3 Conclusion

TiO₂ films have been prepared with V⁵⁺ addition electrolyte of Na₃PO₄+Na₂B₄O₇ using MAO oxidation method. The produced TiO₂ films exhibit higher photocatalytic activities when the Fe ions addition concentration is 0.3 g/L in the electrolyte. And removal of methylene blue is up to 90% for 60 min under the irradiation of UV light, which is 50% higher than the film produced with pure electrolyte. The increase activity is related to change in the lattice parameters and surface structure caused by V⁵⁺ substitution.

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