

Purifying behavior of photocatalytic TiO₂ anodized in nitrate ion containing solution

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Abstract: Mesoporous titanium dioxide films were fabricated on titanium plates by micro-arc oxidation method. To increase the photocatalytic activity of the films, NH₄NO₃ was added to the H₂SO₄ solution, and anodizing was carried out at high voltages using a DC power supply. The crystal structure, chemical composition, surface morphology and the optical property of the films were investigated by XPS, XRD, UV-VIS spectroscopy and SEM. The photocatalytic activity of the films was evaluated by the decomposition of aniline blue, and the activity of the films for the degradation turned out to be improved by the additives to the electrolyte solution. The enhanced photocatalytic activity might result from the increased porosity and nitrate ion incorporation into the anodic films by micro arcing, and thereby the TiO₂ layer might exhibit an improved absorption property for the visible light.

Key words: photocatalysis; TiO₂; anodizing; nitrate ion; micro-arc oxidation

1 Introduction

TiO₂ photocatalysts are attractive and promising materials due to their excellent properties such as high photocatalytic activity, stability, and non-toxicity. Especially, the high photocatalytic activity of TiO₂ has received much attention, therefore it has been applied in various fields such as purification of air and water[1], splitting of water into hydrogen[2], biocompatibility[3] and dye-sensitized solar cells[4]. To improve photocatalytic efficiency, tremendous efforts have been made in recent years. However, the application of TiO₂ films has been limited due to the large band gap. As known, the band gap energy, around 3.2 eV, only allows TiO₂ to absorb ultraviolet(UV) light, which accounts for about 4% of the whole solar spectrum[5]. For narrow band gap, a great deal of efforts have been made to prepare doped TiO₂ films by various methods. One popular approach is to dope nonmetal element into TiO₂. For example, ASAHI et al[6] successfully introduced a new approach to broaden the photoresponse of TiO₂ by doping with nitrogen. Other nonmetal elements such as C[7] and F[8] were also investigated by some researchers. Many techniques for producing the nanocrystalline TiO₂

films have been reported, including sol-gel processing, ion beam assistant deposition, chemical vapor deposition and vacuum plasma spraying. A newly developed electrochemical oxidation method is called micro-arc oxidation(MAO).

In this work, for the purpose of photocatalytic improvement, the electrochemical doping of nitrogen into the anodic TiO₂ layer on Ti substrate was attempted in H₂SO₄ solution with the addition of nitrate ion, and the characteristics of anodic titania films were examined. The photocatalytic activity of the anodized TiO₂ films has been evaluated from decomposition of aniline blue, and the relation between the photocatalytic activity and the electrolytic parameters of anodization time and voltage was discussed.

2 Experimental

Commercial grade pure titanium (99.5%) was used for anodic oxidation. The specimen was degreased in acetone, chemical polished in HF, HNO₃, H₂SO₄, and then washed. After the pretreatment, the titanium oxide films for photocatalytic application were prepared by anodizing in the mixture solution of 1.5 mol/L H₂SO₄+ 0.5 mol/L NH₄NO₃. The observation and the analysis of

the anodic titanium films were carried out using SEM, XPS and XRD, and the diffused reflectance of the film was measured by using an UV-Vis spectrophotometer. Photocatalytic efficiencies were evaluated by the degradation rate of aniline blue.

3 Results and discussion

Fig.1 shows the cross-sectional SEM images of the TiO_2 film anodized in $\text{H}_2\text{SO}_4+\text{NH}_4\text{NO}_3$ mixture solution. The film thickness was measured to be 0.5 and 1.4 μm for the anodizing times of 10 and 60 min at 180 V, respectively, and also 0.6, 0.9 and 1.4 μm for anodizing

voltages of 100, 120 and 180 V for 60 min, demonstrating that the film thickness increases with increasing anodizing time and voltage.

Fig.2 indicates the X-ray diffraction(XRD) patterns for the anodic titania films according to anodizing conditions. The anatase phase is revealed in the XRD results in early stage of anodization, also showing titanium peak from the titanium substrate. As the anodic reaction time increases, the X-ray peak intensities of anatase phase gradually increase. And the anatase appears to be the major phase of anodic films compared with the rutile; on the other hand, the brookite is not detected.

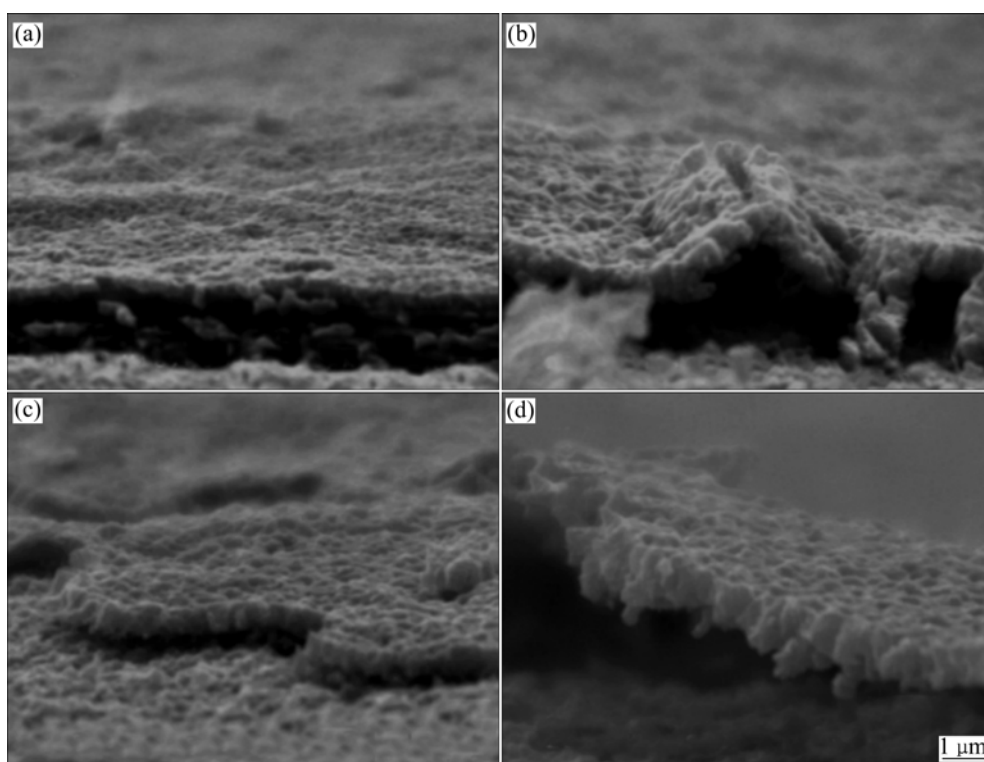


Fig.1 Cross sectional morphologies of anodic TiO_2 films for various anodizing voltage and time: (a) 100 V, 60 min; (b) 120 V, 60 min; (c) 180 V, 10 min; (d) 180 V, 60 min

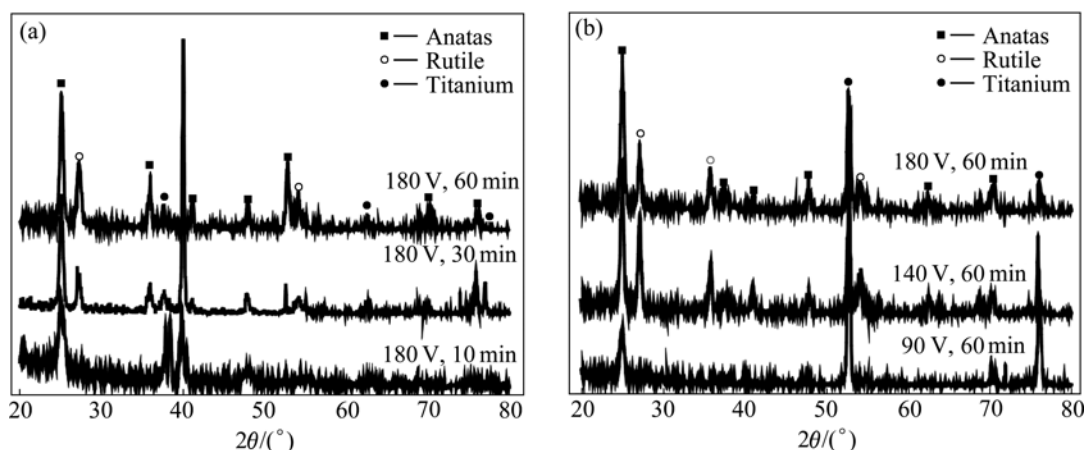


Fig.2 X-ray diffraction patterns of TiO_2 film according to anodizing time (a) and voltage (b)

Fig.3(a) illustrates the XPS wide scan spectrum of an anodic TiO₂ layer formed at 180 V. Regarding the spectrum peaks about the chemical state of the anodic TiO₂ surface, it was reported that the O 1s originating from the TiO₂ layer has a typical binding energy of 530.3 eV, while the binding energies of organic oxygen containing species and the oxides of several other metals are generally in the range of 532–534 eV[9]. The major O 1s binding energy is shown in Fig.3(a) at 530.3 eV, which is supposed to be originated from the TiO₂ layer. The XPS spectrum of N 1s is shown in Fig.3(b), in which the peaks are situated at 408.1 and 403.0 eV, and can be assigned to NO₃⁻ species[10]. It is indicated that NO₃⁻ has been incorporated into the TiO₂ layer during the anodization.

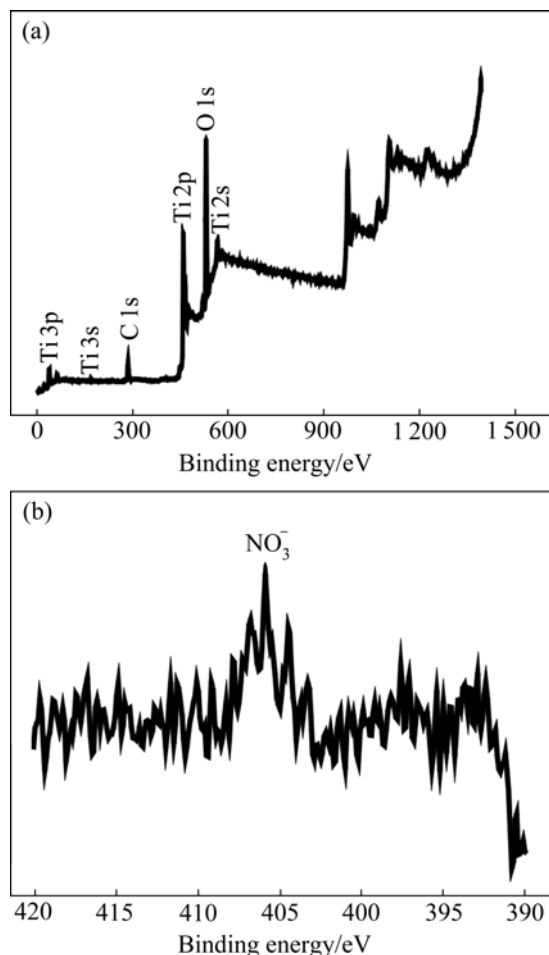


Fig.3 XPS spectra of anodic titania film formed at 180 V in 1.5 mol/L H₂SO₄+0.5 mol/L NH₄NO₃ solution: (a) XPS spectrum of wide scan; (b) N 1s

The optical response of the films has been characterized using UV-Vis spectroscopy. Fig.4 shows UV-Vis diffuse reflectance spectra of anodized TiO₂ films. The absorption edge for the TiO₂ film anodized in 1.5 mol/L H₂SO₄+0.5 mol/L NH₄NO₃ occurs at 415 nm, and band gap E_g is calculated by the formula[11]:

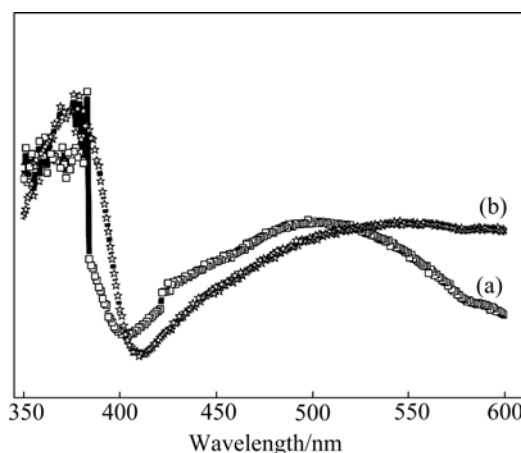


Fig.4 UV-Vis diffuse reflectance spectra of TiO₂ film anodized in 1.5 mol/L H₂SO₄ (a), and 1.5 mol/L H₂SO₄+0.5 mol/L NH₄NO₃ (b)

$$E_g = \frac{hc}{\lambda} = \frac{1239.8}{\lambda} \quad (1)$$

where E_g is the band gap (eV) of the specimen; λ is the cut-off wavelength of the spectrum (nm); h is the Plank's constant; c is the velocity of light. In this study, λ is chosen as the wavelength corresponding to the intersection point of the vertical and horizontal parts of the spectra. The band gap energy is calculated to be 2.98 eV. However, since the undoped TiO₂ specimen presents an onset of absorption edge around 401 nm, it can be suggested that the doping of nitrate ion affects light absorption characteristics of TiO₂. Therefore, it is predicted that the ion doping causes a red shift in the band gap transition, followed by expanding the wavelength response range of the TiO₂ to visible region and increasing the number of photogenerated electrons and holes to participate in the photocatalytic reaction.

Fig.5 exhibits the photocatalytic efficiency of the

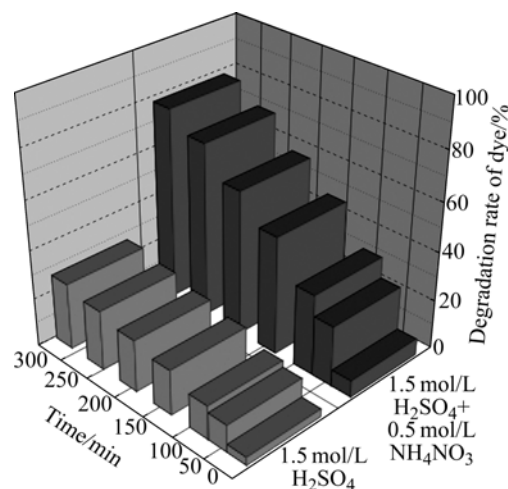


Fig.5 Photocatalytic degradation rate of aniline blue on anodic TiO₂

anodic TiO₂ films for the decomposition by irradiation of Hg lamp. The dye degradation rates of the TiO₂ anodized in 1.5 mol/L H₂SO₄ show 13.83% and 27.18% for the anodizing time of 1 h and 3 h, respectively, while the corresponding dye removal rates for the anodic solution with additive NH₄NO₃ are 33.01% and 78.40%, respectively. This results are in agreement with the diffuse reflectance spectra as shown in Fig.4, and support the idea that the doping of NO₃⁻ ions affects the photocatalytic activity of the film, resulting in preferable photocatalytic property compared with the undoped TiO₂ film.

To determine the reaction order, the dye decomposition rates on anodic TiO₂ film are summarized in Table 1. As the initial concentration of aniline blue increases from 3.125 to 25.000 μmol/L, the initial rate after 60 min of Hg lamp irradiation increases from 4.37×10^{-4} to 4.072×10^{-3} μmol/(L·s), and the initial rate increases with the same rate to the concentration of aniline blue. These results indicate that the reaction order for the dye decomposition is first dimension[12]. Therefore, the kinetic constants during the degradation of aniline blue can be calculated by the first order reaction rate, and rate constant is 1.58×10^{-4} μmol/(L·s).

Table 1 Reaction rate of dye decomposition after irradiation for 1 h for TiO₂ films

Initial dye concentration of aniline blue/(μmol·L ⁻¹)	Resultant concentration after 60 min/(μmol·L ⁻¹)	Initial rate/(μmol·L ⁻¹ ·s ⁻¹)
3.125	1.572	4.370×10^{-4}
6.250	3.588	9.970×10^{-4}
12.500	7.676	2.132×10^{-3}
25.000	14.658	4.072×10^{-3}

Anodizing condition: 1.5 mol/L H₂SO₄+0.5 mol/L NH₄NO₃, 180 V, 60 min.

4 Conclusions

1) The anodic titanium oxide film for photocatalytic activity was synthesized by anodic oxidation in acid solution, and the surface characteristics of anodic TiO₂ layer were evaluated.

2) The major structure of the films is anatase, and the surface morphology exhibits a porous structure, but there are differences in the morphology and thickness according to the anodic time and voltage.

3) From the analysis of chemical states of the anodic film using XPS, nitrate ions were observed in the anodic film, which is suggested to be infiltrated from the

electrolyte into the oxide layer during anodic process.

4) The corresponding dye removal rates of the TiO₂ films anodized in the additive NH₄NO₃ containing solution show an improved absorption property for the visible light, and outstanding photocatalytic activity compared with the undoped TiO₂ films.

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