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Enhanced photocatalytic degradation properties of nitrogen-doped titania nanotube arrays

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Abstract: Nitrogen-doped TiO_2 nanotubes array were synthesized to improve the photocatalytic efficiency by annealing the anodized titania nanotubes with ammonia at 500 ℃. Detailed structural analysis revealed that the nitrogen-doped titania nanotubes are of highly ordered structure, and exhibit a decreased phase transformation temperature compared with those that are not doped, as evidenced by the decrease in full width at half maximum (FWHM) of the (110) peak of rutile phase and the occurrence of the typical Raman peaks of rutile phase at 196, 235, 442, 610 cm^{-1}. According to the photocatalytic degradation of methyl orange under visible light irradiation, the nitrogen-doped TiO_2 nanotubes exhibit enhanced photocatalytic efficiency compared with their non-doped nanotubes, which might be a result of either the nitrogen doping induced band gap narrowing or the synergistic effect produced by both nitrogen and fluorine dopants.

Key words: TiO_2; nanotubes; nitrogen-doping; photocatalytic degradation

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1 Introduction

Though being regarded as one of the most efficient and environmentally benign photo-catalysts for photo-degradation of various pollutants, TiO_2 exhibits intrinsic drawbacks which severely limit its widespread technological applications. One of the most fatal drawbacks stems from the wide band gap of TiO_2, which requires ultraviolet irradiation for photocatalytic activation. While ultraviolet light accounts for only a small fraction of the solar energy, resulting in a photonic efficiency of less than 10% for TiO_2 in most degradation processes[1].

To improve its photocatalytic performance under visible light irradiation, metal-doped TiO_2 has been widely studied over the past decades[2], and TiO_2 is doped with different metal ions like alkaline earth (Ca^{2+}, Sr^{2+} and Ba^{2+})[3], Fe^{3+}[4], Cr^{6+}[5], Co^{3+} [6], Mo^{5+} [7], and rare earth cations (La^{3+}, Ce^{3+}, Er^{3+}, Pr^{3+}, Gd^{3+}, Nd^{3+}, Sm^{3+})[8] using different preparation techniques. The main objective of doping is to induce a batho-chromic shift (i.e. a decrease of the band gap or introduction of intra-band gap states, which results in more visible light absorption). However, many controversial results were reported in literatures since even the method of doping leads to different morphological and crystalline properties of the photo-catalyst, and the shift of the absorption edge in metal-ion doped systems may have a complex origin, from either homogeneous substitution of Ti^{4+} or segregated M_xO_y clusters[9−10]. Later, it was shown that the desired band gap narrowing of TiO_2 can be better achieved by using nonmetal ionic dopant species to obtain nonmetal-doped TiO_2 systems such as carbon-[11], nitrogen-[12], boron-[13], fluorine-doped [14], and co-doped[15−17] photo-catalysts. These nonmetal ion doped catalysts may be more appropriate for extending the photocatalytic activity of TiO_2 into the visible region than metal cation doping methods, because their impurity states are near the valance band edge and their roles as recombination centers may be minimized [18].

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In this case, we have combined the structural and spectral analysis of nitrogen-doped TiO_2 nanotubes used in the photo-degradation procedure. We have recently reported the promoted phase transformation of anatase TiO_2 to rutile when being annealed under rather low temperature as a result of the incorporation of nitrogen dopant. In the present work, we try to improve the photocatalytic activity of TiO_2 nanotube by nitrogen doping procedures and evaluate its photo-catalytic activity upon degradation of methyl orange under visible light irradiation.

2 Experimental

2.1 Materials and preparation

Titanium foil (Alfa Aesar, 0.25 mm thick, 99.95%) was used as the substrate for the growth of the oxide nanotube arrays. All the reagents of phosphoric acid (H_3PO_4), hydrofluoric acid (HF), concentrated ammonia ($NH_3{\cdot}H_2O$), and methyl orange were of analytical-grade, and purchased from commercial market without further purification. And all the aqueous solutions were prepared with de-ionized water obtained using a Milli-Q Reagent Water System (Millipore, Bedford, MA, USA).

Prior to the anodization, the titanium foils were chemically polished in aqueous solution of 1% HF and 0.5% H_3PO_4 for 2 min, rinsed with de-ionized water, and dried in nitrogen flow. The pretreated titanium foil was anodized by using platinum foil as cathode in an electrolyte containing 0.5% HF and 0.5% $NH_3{\cdot}H_2O$ with the bias voltage of 20 V at 25 ℃ for 20 min. After being anodized, specimens were rinsed with de-ionized water immediately and dried under nitrogen gas flow. To obtain nitrogen doped titania nanotube arrays, the as-anodized foils were first immersed in concentrated aqueous ammonia solution for 30 min, and then blow-dried and annealed at 500 ℃ in ammonia atmosphere with a flow rate of 40 cm^3/min for 30−120 min. The non-doped titania nanotubes were also annealed at the same temperature in oxygen atmosphere for comparison.

2.2 Characterization

The surface morphologies of the doped TiO_2 nanotube array were observed by a FEI SIRION 200/INCA OXFORD model field emission scanning electron microscopy (FE-SEM), and the crystallinity of the samples was performed by X-ray diffraction (XRD) using a PHILIPS PW3040/60 diffractometer. Raman spectra were collected at room temperature with a Raman spectrometer (Renishaw−2000) operating with the 514 nm line of an Ar^+ laser (Coherent Innova 90C−4) in backscattering geometry in the range of 100−1 000 cm^{-1}.

The photocatalytic activity of nitrogen-doped and undoped titania nanotubes under visible light was evaluated by degrading methyl orange in a photo-reactor irradiated by a 150 W OSRAM xenon lamp equipped with a solid sheet filter of cutoff wavelength at 415 nm. A slice of nanotube thin film with dimensions of 1 cm × 3 cm was immersed into 250 mL aqueous solution of 2 mg/L methyl orange, perpendicular to the xenon lamp. The photo-reactor was then covered with aluminum foil to prevent unfavorable irradiation during preheating the xenon lamp, and the solution in the photo-reactor was magnetically stirred for 30 min to reach the absorption/desorption equivalence of the dye molecules on the sample surface. The concentration of methyl orange during photocatalytic degradation process was determined by the absorbance value at the wavelength of 473 nm, using a Shimazu UV−3000 spectrometer (UV-Vis).

3 Results and discussion

3.1 Morphology of specimen

Fig.1 shows the top-view SEM morphologies of the undoped and nitrogen-doped TiO_2 nanotube arrays prepared by anodizing titanium in hydrofluoric acid containing aqueous solution, followed by a heat-treatment at 500 ℃ for 2 h. Both the undoped and nitrogen-doped TiO_2 consist of nanotube arrays with a tube diameter of 60−80 nm and a wall thickness of about

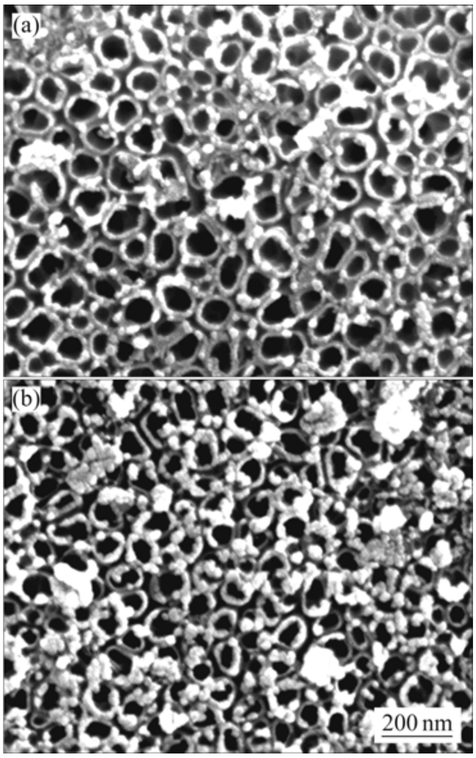

Fig.1 SEM images of undoped (a) and nitrogen-doped (b) TiO_2 nanotubes

20 nm, and most of the pore mouths of nanotube are open on the top of the layer. Although the titania nanotube array architecture was reported to disrupt after annealing because of the appearance of oxidation and grain growth in the underlying titanium foil at high temperatures[19], the well ordered architecture maintained after the heat-treatment at 500 ℃ for 2 h in our research. However, tiny clusters formed on the top of the nitrogen-doped nanotubes after annealing in the ammonia atmosphere, which consist of ammonium chloride derivatives as affirmed by EDS analysis.

3.2 Structure and vibrational spectra

Fig.2 shows the XRD patterns of the undoped and nitrogen-doped TiO_2 nanotubes annealed at 500 ℃ for 30 min, as well as that of the as-grown specimen without any thermal treatments. The as-grown TiO_2 thin-film exhibits an amorphous structure except for the existence of typical diffraction peaks of metallic titanium, indicating that the crystallization process of TiO_2 is unlikely to occur without thermal treatment. For the undoped sample annealed at 500 ℃, three weak diffraction peaks appear at 25.43°, 48.10° and 27.61°, in well accordance with the (101) and (200) peaks of anatase titania and (110) peak of rutile titania, indicating the formation of tiny crystalline phases of both anatase and rutile after a thermal treatment at 500 ℃. The nitrogen-doped titania nanotubes show no obvious difference from the undoped ones in the diffraction peak positions of anatase (101) and rutile (110), and the main crystalline phase is also metallic Ti, indicating that only farthing of nitrogen is incorporated and their effect on the crystal lattice is still impalpable. In comparison with that of the undoped specimen, the XRD pattern of the nitrogen-doped specimen exhibits increased peak intensity and decreased FWHM in the rutile (110) peak and an additional (210) peak of rutile, suggesting that nitrogen doping may have facilitated the phase transition of titania nanotube to rutile at low annealing temperatures, which has been reported elsewhere[20].

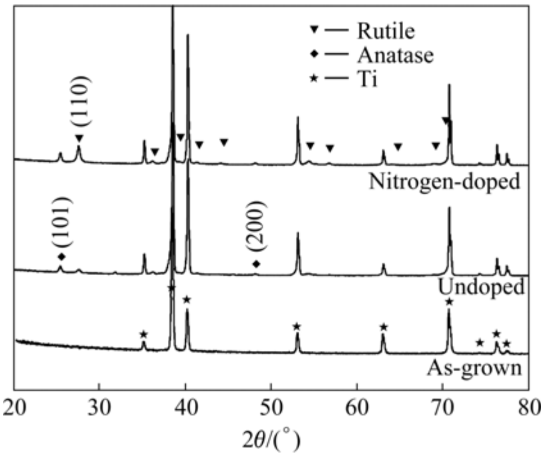

Fig.2 XRD patterns of undoped, nitrogen-doped and as-grown TiO_2 nanotube thin films

Fig.3 shows the Raman spectra of nitrogen-doped and undoped TiO_2 nanotubes annealed at 500 ℃, while the inset shows the Lorentzian fittings of the spectral features of nitrogen-doped specimen ranging from 380 to 750 cm^{-1}. For undoped TiO_2 nanotube thin film annealed at 500 ℃, the Raman scattering peaks appearing at 143, 196, 395, 514, 637 cm^{-1} are identified as $E_g^{(1)}$, $E_g^{(2)}$, B_{1g}, A_{1g}/B_{1g}, $E_g^{(3)}$ vibration modes of anatase phase[21]. The emergence of a slight Raman peak at 442 cm^{-1}, which is identified as E_g mode of rutile, confirms the coexistence of rutile with anatase in undoped thin film annealed at 500 ℃, in consistent with the XRD analysis previously discussed.

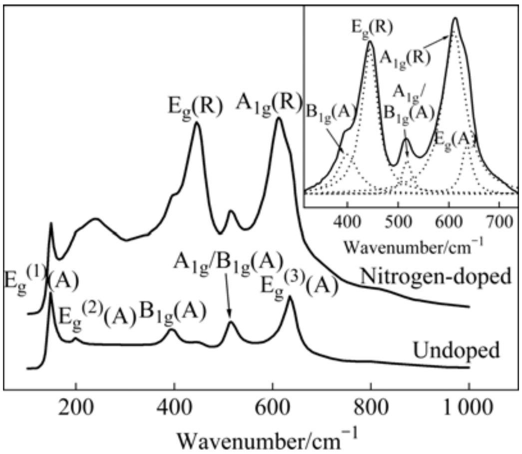

Fig.3 Raman spectra of undoped and nitrogen-doped TiO_2 nanotube annealed at 500 ℃

For nitrogen-doped sample annealed at 500 ℃, the Raman peaks at 442 and 610 cm^{-1} are confirmed as E_g and A_{1g} fundamental processes of crystalline rutile phase. Besides, a broad Raman scattering band occurs at 235 cm^{-1}, which is suggested to be a combination line concerned with the second-order scattering and disorder effects[22−23].

The apparently enhanced Raman scattering signals of rutile phase in the Raman spectrum of the nitrogen-doped nanotube in comparison with that of the undoped sample indicate that nitrogen-doping may have facilitated the phase transition of titania nanotube to rutile at low annealing temperatures, in accordance with XRD analysis. Furthermore, the Raman peaks are broadened appreciably for the nitrogen-doped TiO_2 nanotube arrays with respect to the undoped TiO_2 nanotube films. Since the atomic radius of nitrogen is slightly larger than that of oxygen, the nitrogen doping may lead to compressive stress and eventually cause the broadening of vibrating mode, which has been observed in phosphorus-doped titania[24].

3.3 Photocatalytic activity

Fig.4 shows the photocatalytic decomposition curves of methyl orange under visible light irradiation catalyzed with nitrogen-doped and undoped samples. A blank test curve with no photo-catalyst employed is also given for comparison. Since there is an iso-absorptive point at 473 nm in the range of pH=2−12 because of isomeric equilibrium of methyl orange, the concentration of methyl orange during photocatalytic degradation process was determined by the absorbance value at this wavelength to eliminate the influence of pH value on the absorption and hence on the concentration of methyl orange. The blank test confirms that methyl orange is only slightly degraded under intensive visible light in the absence of catalyst, while photo-catalyzed tests show obvious influence in the decomposition profiles. Both photo-catalyzed degradation procedures, as evidenced by their corresponding evolution curves, exhibit an obvious increase in the decomposition rate under irradiation of visible light in comparison with the result of the blank test, while the abrupt decrease in dye concentration before its exposure to the xenon lamp is caused by the absorption of dye molecules on the surface of the nanotubes. Since F-doped TiO_2 nanostructures have been reported to form in the presence of HF by mild wet chemical process[25], the unexpected visible photocatalytic activity for undoped titania thin film observed in this experiment is regarded to be caused by the incorporation of fluorine species during either anodizing or annealing, which may promote the formation of surface oxygen vacancies during surface photochemical process as reported by YU et al[26]. Fluorine impurity may lead to visible photocatalytic activity by the formation of surface oxygen vacancies during surface photochemical process, which can strongly modify the surface band structures with the appearance of intragap states and can lead to the formation of radical species by adsorbing molecular oxygen on the site[27]. Moreover, the photo-catalytic activity of the nitrogen-doped titania nanotube thin film is obviously higher than that of the undoped one, which may be induced either by the influence of nitrogen doping for band gap narrowing or by the synergistic effect produced by both nitrogen and fluorine dopants. Even though fluorine species is less possible to enhance the absorbance of TiO_2 in visible region, the role of nitrogen for band gap narrowing is evident and widely accepted, and the synergistic effect of both nitrogen and fluorine dopants for the visible light photocatalytic activation could not be excluded[28]. Further experiments still need to be performed, however, to determine the mechanism of enhanced visible light induced photocatalytic activity.

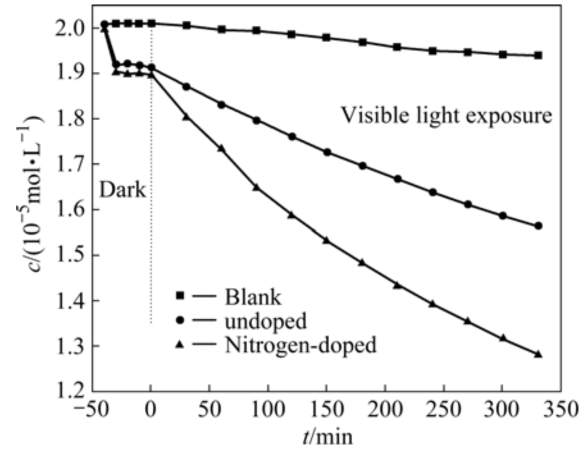

Fig.4 Photocatalytic degradation curves of methyl orange under visible light exposure

4 Conclusions

1) Nitrogen doped TiO_2 nanotubes were synthesized successfully by thermal treatment of the anodized TiO_2 in ammonia-containing atmosphere at 500 ℃. SEM observation confirmed that highly ordered TiO_2 nanostructure maintained after the nitrogen doping process.

2) XRD analysis and Raman spectra indicated that nitrogen doping may have facilitated the phase transition of titania nanotube to rutile, and both the nitrogen-doped and the undoped titania nanotubes showed the coexistence of anatase and rutile crystalline phases.

3) The nitrogen-doped titania nanotube exhibited enhanced photocatalytic properties under visible light irradiation. We assumed that either the nitrogen doping induced band gap narrowing or the synergistic effect produced by both nitrogen and fluorine dopants could be responsible of this improved photo-catalytic activity.

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