Synthesis and Properties of Nd-doped TiO_2 thin films by sol-gel dip-coating method

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Abstract TiO_2 thin films doped with neodymium(Nd) in the range from 0 at.% to 10at. % were prepared on glass substrates by sol-gel dip-coating method. Water contact angle on the Nd-doped TiO_2 films were measured by contact angle analyzer. The water contact angle measurement result showed that the hydrophily of the films improved when the Nd^{3+} concentration increased to 5 at.%. The photocatalytic activity of the undoped and Nd-doped TiO_2 thin films were investigated by the degradation of methylene blue under high-voltage mercury lamp. The results showed that 5 at.% Nd-doped TiO_2 thin film exhibited the highest photocatalytic efficiency.

1 Introduction

TiO_2 is a broad band gap (3.2 eV) semiconductor materials. TiO_2 have many excellent properties, such as non-toxicity, good chemical stability, good optical properties, photocatalyst, as well as biocompatibility(1-3). In recent years, the application of TiO_2 have been extend to dye sensitized solar, gas sensors, optical coatings, self-cleaning surface and biomedical materials(4-7).

One way to improve the properties of TiO_2 materials was coupling it with other semiconductors or metallic oxide. Fakhouri H. et al. (4) prepared TiO_2/TiN bilayer thin films. The photocatalytic properties were enhanced comparing signal layer TiO_2 films. Li C. et al.(8) found that the optical and photoelectrochemical properties were improved by using Ag_2O/TiO_2 double layer thin films. Another way to improve the properties of TiO_2 thin film was doping nonmetal or metal ions. Nonmetal (such as N(9),C(10)) and metal (such as Fe(5),Nb(3, 11, 12),Sm(13),Hg(14),Mn(15), et al.) ions doping TiO_2 thin films have been widely studied. The properties, especially optical and photocatalytic were improved.

Nd-doped TiO_2 films have been reported by many researchers. The photocatalytic properties were improved for Nd-doped TiO_2 thin film(16-19) and the mechanical properties were enhanced by Nd ions doping(20). However, the effect of Nd^{3+}-doping on the wettability and potocatalytic activity of TiO_2 thin films by sol-gel dip-coating method have not been elaborated.

Ion doping TiO_2 thin films can be prepared by CVD(1, 21), PVD(18, 22) and sol-gel(5) . Among them, sol-gel method have advantages such as ease of fabrication large area film,

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precise chemical composition control and reduced sintering temperature. In this paper, TiO_2 thin films doped with various Nd^{3+} ions (from 0 % to 10 at.%) were fabricated on glass substrates by sol-gel dip-coating. The effect of Nd^{3+} doping on the wettability and photocatalytic property of TiO_2 thin films were discussed in detail.

2 Experiment

The titania sols were prepared by mixed tetrabutyl titanate ($Ti(C_4H_9O)_4$, 98 wt.%), alcohol (CH_3CH_2OH, >99 wt.%) and concentrated nitric acid (HNO_3, 65~68 wt.%) with the mole concentration was 1:20:1.5. The detail process of preparing TiO_2 sols can be found elsewhere[23]. Neodymium was added to the TiO_2 sols in the form of neodymium oxide with five different mole ratio: 0 (undoped), 3, 5, 8, and 10 at.%. The undoped and Nd-doped sols were aged for 24h.

The absorbance spectra of the undoped and Nd-doped TiO_2 sols were shown in Figure1(a). Compared to the undoped TiO_2 sol, several absorbance peaks were found for Nd-doped TiO_2 sols. This may be ascribed to the 4f energy levels of neodymium ions. The absorption of photo can lead to electron transition between the energy levels, which displaying absorbance peaks. The intensity of the absorbance peak increased linear with Nd^{3+} concentration (shown in Figure 1(b)). It is consistent with Bouguer-Lambert-Beer law. The glasses substrates were cleaned in acetone, alcohol and distilled water respectively by supersonic purifier. The film deposition was carried out on glasses substrates by sol-gel dipping-withdrawing at 2000μm/s. The wet films were dried at 150°C for 30 mins and annealed at 500°C for 1h in air.

The wettability of the sol-gel films were tested by the water contact angle at room temperature. The photocatalytic activities of the undoped and Nd-doped TiO_2 thin films were evaluated by the degradation of methylene blue solution (2mg/L) under high-voltage mercury lamp. The photodegration were described by $(C_0\text{-}C)/C_0$, where C_0 and C are the initial absorbance and different reaction time absorbance at 654 nm.

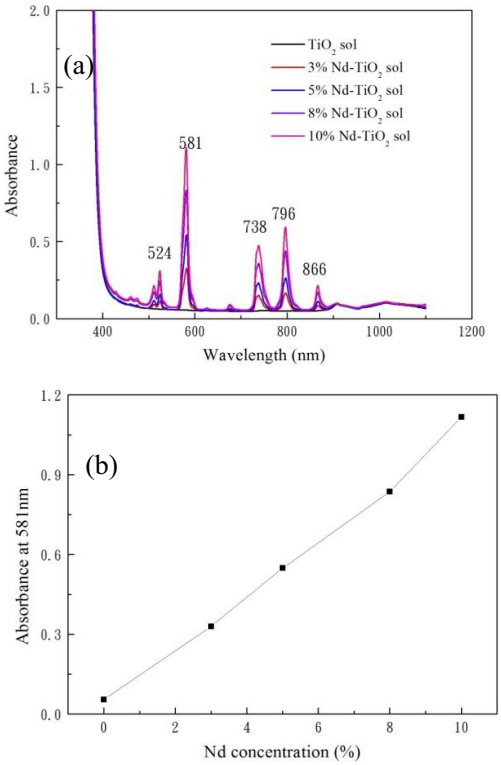

Figure 1 Absorbance spectra of undoped and Nd-doped TiO_2 sols (a) and the intensity of absorbance at 581 for different Nd^{3+} concentration (b)

3 Result and discussion

The wettability behavior of the films is important for photocatalytic activity, self-clean properties and biocompatibility. The water contact angle of uncoated, TiO_2 thin film coated and Nd-doped TiO_2 thin film coated glass substrates were measured. The contact angle images were exhibited in Figure 2. The contact angle of TiO_2 thin film (37.8°) was smaller than the uncoated glass substrates (53.4°), which indicating the TiO_2 thin film prepared by sol-gel method has hydrophily. The contact angle of 3 at.% Nd-doped TiO_2 thin film (36.7°) was similar to the undoped TiO_2 thin film. However, when the Nd^{3+} doping concentration exceeding 5

at. %, the contact angle decreased obviously (about 12 °-16 °). The improvement of the hydrophilic property for high content Nd^{3+} (>5 at.%) doping TiO_2 thin film may be ascribed to the varieties of the microstructure and chemical composition. The XRD results (will be published elsewhere) showed that the Nd^{3+} doping worsen the crystallization of TiO_2. The increasing of amorphous phase proportion and residual organics in Nd-doped TiO_2 thin film may enhance the hydrophilic property. Hydrophilic films can improve the self-clean and photocatalytic efficient. When Nd-doped TiO_2 films used as biomaterials, the improved hydrophilicity can promote the cell growth and proliferation, which is related to the biocompatibility[25].

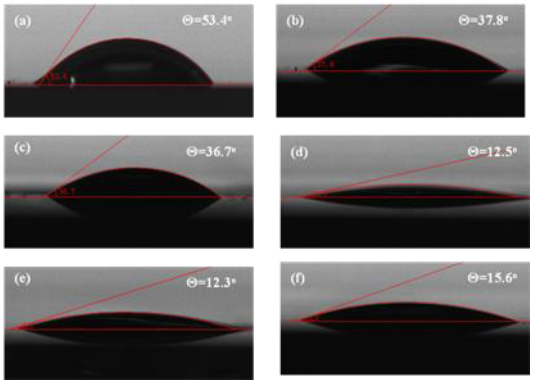

Figure 2 Water contact images of (a) glass substrate, (b) TiO_2 / glass, (c) 3 %Nd- TiO_2 / glass, (d) 5%Nd-TiO_2 / glass, (e)8%Nd- TiO_2 / glass and (f) 10 %Nd-TiO_2 / glass

The photocatalytic activity of TiO_2 thin films with different neodymium concentration was given in Figure 3. The degradation rate increase with the increasing of irradiation time. The effect of Nd^{3+} doping on the improvement of photocatalytic activity was obviously. As shown in Fig.6, the photocatalytic activity of 5 at.% Nd-doped TiO_2 films was higher than others under the same condition. Anatase TiO_2 and larger surface area are beneficial to photocatalytic activity. The increasing of Nd^{3+} ions doping decreased the grain size and reduced the proportion of anatase phase. In addition, good hydrophilicity also helps to improve the photocatalysis. The coordination of the reasons lead to 5 at.% Nd-doped TiO_2 thin film performed the best photocatalytic activity.

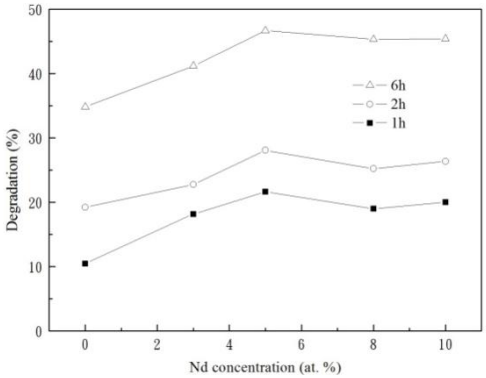

Figure 3 Photocatalytic activity of TiO_2 thin films with different neodymium concentration

4 Conclusion

Nd-doped TiO_2 films were successfully prepared by sol-gel dip-coating method. Wettability and photocatalysis of undoped and Nd-doped TiO_2 thin films were investigated. The concentration of Nd ions effect the wettability and photocatalysis . When the Nd^{3+} concentration exceeding 5 at.%, the hydrophilic of the films was improved obviously. The 5 at.% Nd-doped TiO_2 thin film performed the best photocatalytic activity under the same experiment condition.

Acknowledgements

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