

Research Article

Preparation of Crystalline Sn-Doped TiO₂ and Its Application in Visible-Light Photocatalysis

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Sn-doped TiO₂ nanoparticles were prepared by the vapor transport method of water molecules and characterized by XRD and XPS analyses. The TEM images indicated that as-prepared samples were highly dispersed nanoparticles with a small and uniform size below 20 nm, as it would effectively control the rate of hydrolysis of Ti⁴⁺ by adjusting the flow speed of water vapor. Meanwhile, the photocatalytic properties of Sn-doped TiO₂ were tested, and the results showed that doping an appropriate amount of Tin would improve the photocatalytic activity of TiO₂ by enhancing the separation rate of photogenerated electrons and holes on the surface of TiO₂. In addition, the calcination temperature and Tin content had an important influence on the photocatalytic activity of TiO₂. When the mix ratio of Sn:Ti reached 1%, and the nano-Sn-TiO₂ sample was calcined at 400°C, it showed the best photocatalytic activity.

1. Introduction

TiO₂ has been considered as the most promising semiconductor photocatalyst [1–6] because of its high stability, low cost, and innocuity. However, it is only sensitive to UV light due to its large band gap (3.2 eV) [7], along with the relatively high electron-hole recombination rate [8, 9], which impedes its application. In order to use solar energy more efficiently, most of the investigations have been focused on preparing TiO₂ sensitive to visible light during the past several years [10–13]. Thus far, many ionic dopants in different valence states have been investigated, including both metallic ions (e.g., Ca²⁺, Sr²⁺, Ba²⁺, Al³⁺, Ga³⁺, Cr³⁺, Fe³⁺, Co³⁺, Ce³⁺, Ln³⁺, Sn⁴⁺, Zr⁴⁺, Nb⁵⁺, Mo⁵⁺, Sb⁵⁺ and Ta⁵⁺) and nonmetallic ions (e.g., N³⁺, C⁴⁺, S⁴⁺, F⁻, Cl⁻, and Br⁻) [14–17]. Particularly, TiO₂ doped with Sn has been proved to be an effective method and widely studied.

Preparations of Sn-doped TiO₂ photocatalysts focus on several methods such as sol-gel [18–21] and hydrothermal syntheses [22, 23], and chemical vapor deposition [24]. Among them, chemical vapor deposition needs special equipment. The other methods have a common ground that the reaction was performed in aqueous solution, and so, it is necessary for all of them to adjust the pH value of the solution to avoid rapid hydrolysis of Ti⁴⁺.

In this paper, Sn-doped TiO₂ was prepared by the vapor transport method of water molecules. It would effectively control the rate of hydrolysis of Ti⁴⁺ by adjusting the flow speed of vapor. In addition, isoamyl acetate was added as dispersant and it would be used circularly by spinning evaporation.

2. Experiments

2.1. Preparation of Sn-Doped TiO₂ Nanoparticles. In all experiments, deionized water was used. All of the chemical were analytical grade.

Sn-doped TiO₂ nanoparticles were prepared by water molecule transport method. Typically, 8 mL of tetrabutyl titanate, 40 mL of isoamyl acetate and 0.053 g of stannous chloride were mixed together in a flask. Air pump was turned on to transport air at a rate of 40 L·min⁻¹. A small quantity of water vapor was carried with the air from a beaker with water to the flask containing the mixture. Then, Ti⁴⁺ ions hydrolyzed slowly to form a white emulsion under ceaseless stirring for 1 h. After the reaction, isoamyl acetate was collected by spinning evaporation and used circularly. To obtain Sn-doped TiO₂ nanoparticles in which the mole ratio of Sn is about 1%, the precipitation was filtered,

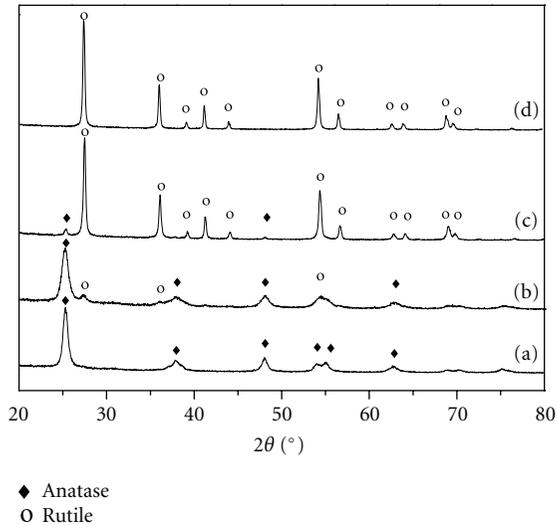


FIGURE 1: XRD patterns of samples (Sn proportion is 1%) annealed at different temperatures (a) 300°C; (b) 400°C; (c) 500°C; (d) 600°C.

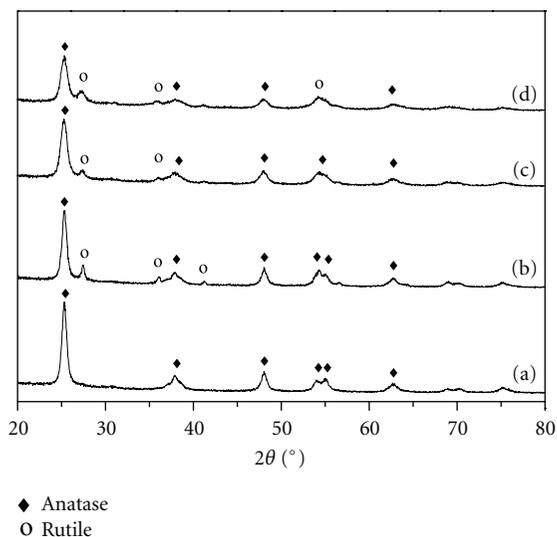


FIGURE 2: XRD patterns of samples with different Sn proportions annealed at 400°C (a) 0%; (b) 0.5%; (c) 1%; (d) 5%.

washed by distilled water, and sintered at 300–600°C for 2 h. Samples with different Sn proportions could be obtained by repeating the former steps, adding corresponding amount of stannous chloride. The Sn proportions mentioned here are all theoretical molar ratios of Sn:Ti in samples. The actual values were detected by EDS tests.

The pure and Sn-doped TiO₂ were designated as P-x and D-x, respectively, where “x” is the annealing temperature.

2.2. Characterization of the Samples. The crystalline phase was determined by X-ray diffraction (D/Max-IIIIC, Shimadzu) instrument with Cu K α radiation ($\lambda = 0.15406$ nm). The morphological feature and size of the product were observed by TEM (H600A-II, Hitachi). The analysis of

element content of the doping system was done with XPS (ESCALAB 250, Thermo) and EDS (Quanta 200FEG, FEI) spectra. The photocatalytic activity of the samples was monitored on a 2550Z UV-Vis-NIR spectrophotometer.

2.3. Photocatalytic Activity. The photocatalytic activity of Sn-doped TiO₂ was evaluated by methylene blue degradation performed in XPA series instrument with a closed gas-circulating system and an inner irradiation quartz reactor. A 500 W xenon lamp was selected as the visible light source, and between the xenon lamp and reactor was inserted a cut filter (ZJB 420) to eliminate light of wavelength <420 nm. The flow rate of air was kept at a constant value of 500 mL·min⁻¹. In a typical experiment, 0.08 g of Sn-doped TiO₂ was dispersed in 250 mL of methylene blue (10 mg·L⁻¹) solution. The actual effect of photocatalytic activity by chemical reaction was studied by maintaining the solutions in dark for 1 h before irradiation. At given irradiation time intervals, the samples (5 mL) were taken out every 15 min and analyzed by UV-Vis spectrophotometer. The percentage of degradation was calculated via the formula $(1 - A_i/A_0) \times 100\%$, where A_0 is the absorbance of original methylene blue solution before irradiation and A_i is the absorbance of methylene blue solution measured every 15 min in the process of photodegradation.

3. Results and Discussion

3.1. Characterization of Sn-Doped TiO₂ Nanoparticles. Figure 1 shows the XRD patterns for Sn-doped TiO₂ (1% for Sn) prepared with different annealing temperatures. The sample D-300 exhibits an anatase crystal structure (Figure 1(a)), while the sample D-600 is absolute rutile (Figure 1(d)). With increase of the annealing temperature, it turns to anatase gradually (Figures 2(b) and 2(c)). Hence, the lowest phase transition from anatase to rutile can take place at around 400°C for Sn-doped TiO₂, which is about 150°C lower than that for pure TiO₂ (550°C) [7]. No characteristic peaks of metal Sn or SnO₂ can be detected, because Sn was doped in TiO₂ in a small quantity and it was not enough to be detected.

The impact of different Sn proportions on the crystal phase of TiO₂ was investigated by XRD and the results were showed in Figure 2. Compared with the pure TiO₂ (Figure 2(a)), all of the Sn-doped TiO₂ ((Figures 2(b), 2(c), and 2(d)) annealed at 400°C exhibited rutile crystal structures partially, which further proved the doping of Sn would debase the phase transition temperature of TiO₂.

The average sizes of samples D-400 (containing Sn 0, 0.5, 1, 5%) are 7.9, 12.0, 8.9, and 8.2 nm estimated by Scherrer formula. The corresponding percentage (Y) of rutile in the mixed crystal phase were 0, 25.3%, 27.9%, and 32.5%, calculated by the formula $Y = (1 + 0.8 I_A/I_R)^{-1}$ [25], where I_A and I_R are the diffraction peak intensity of anatase ($2\theta = 25.3^\circ$) and rutile ($2\theta = 27.4^\circ$), respectively. It was proved that more presence of Sn⁴⁺ facilitated the transformation of TiO₂ from anatase to rutile under the same temperature.

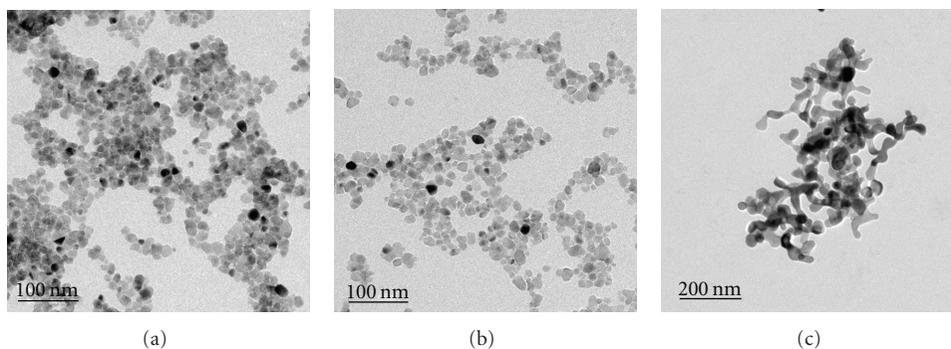


FIGURE 3: TEM images of different samples: (a) P-400; (b) D-400; (c) D-500.

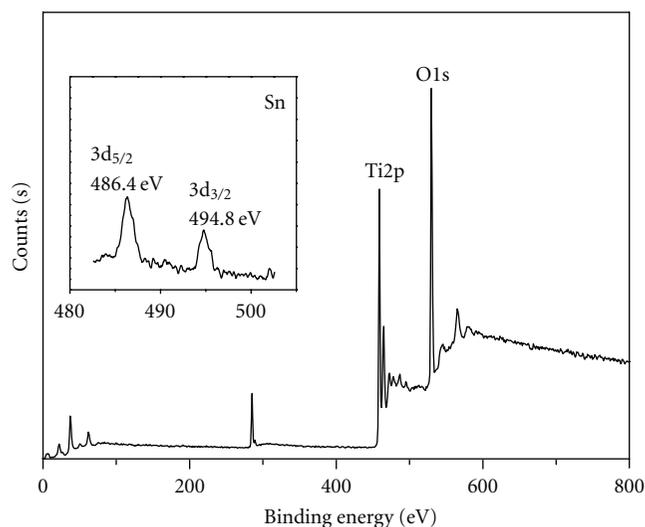


FIGURE 4: XPS survey spectrum of Sn-doped TiO_2 nanocomposite.

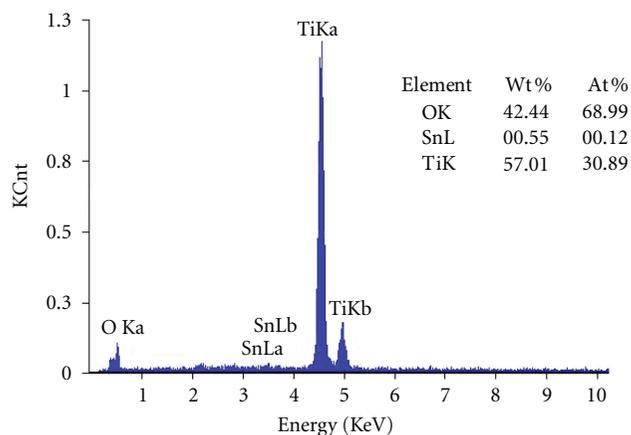


FIGURE 5: The typical EDS pattern of Sn-doped TiO_2 .

Figure 3 displays the TEM images of P-400 (Figure 3(a)), D-400, (Figure 3(b) and D-500 (Figure 3(c)). It could be observed that both P-400 and D-400 were nanoparticles with a uniform diameter of about 10 nm, implying doping Sn had no influences on the morphology and size of TiO_2 .

Sample D-500 was highly agglomerated with the particles of about 20 nm in size. It is consistent with the common sense that the crystal would grow bigger with the increase of the temperature.

XPS analysis was performed to further study the existing states of Sn^{4+} in TiO_2 . Figure 4 shows the survey spectrum of D-400 and inset is the Sn3d XPS spectrum. The doublet peak (486.4 and 494.8 eV) in the Sn3d XPS spectrum is ascribed to $\text{Sn}3d_{5/2}$ and $\text{Sn}3d_{3/2}$ of the substitutional Sn^{4+} dopants in the lattice, since the peak position of $\text{Sn}3d_{5/2}$ (486.4 eV) is located between that of SnO_2 (486.6 eV) and metallic Sn (484.4 eV) [26]. The radius of Sn^{4+} and Ti^{4+} ions are 0.071 and 0.068 nm, respectively. They are so close that it is easy for Sn^{4+} to replace Ti^{4+} in the lattice of TiO_2 . The XPS analysis proved this perfectly.

The actual content of dopant Sn was tested by EDS analysis, and a typical EDS spectrum was showed in Figure 5 (D-400, Sn proportion is 0.5%, theoretically). Quantification of the EDS peaks gives the atomic ratios of Sn:Ti to be about 0.39%, 0.77%, and 3.34%, corresponding to the theoretical molar ratios of 0.5%, 1%, and 5%, respectively. It could be observed that there were some differences between the actual and theoretical values, mainly because some Sn was wasted in filter washing process. In addition, the quantification of the CO_2 absorbed on the surface of the samples was probably another reason.

3.2. Photocatalytic Activity. We chose methylene blue (MB) as model dye to evaluate the photocatalytic activity of the photocatalysts under visible light irradiation, and the results were shown in Figures 6 and 7. Figure 6 showed the effects of the annealing temperature on the photodegradation of MB. As can be seen, the sample D-400 performed the best photocatalytic efficiency. On one hand, with the increase of the temperature, grain size increased and the specific surface area decreased, which is responsible for the depress of photocatalytic activity of Sn-doped TiO_2 . On the other hand, under lower temperature, TiO_2 phase conversion was not sufficient, and it is difficult for Sn to dope into the TiO_2 lattice to form shallow electron traps, which resulted in the lower photocatalytic activity.

Figure 7 showed the effects of the different dosage of Sn^{4+} on the photodegradation of MB under visible light.

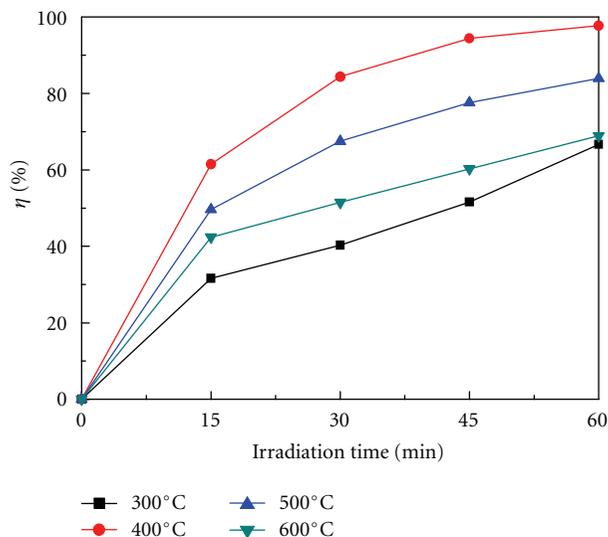


FIGURE 6: The effect of different annealing temperature on the degradation of MB under visible light.

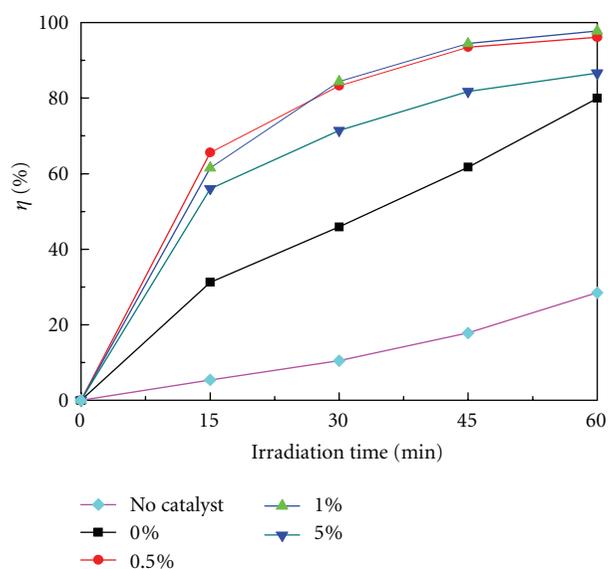


FIGURE 7: The effect of different dosages of Sn^{4+} on the degradation of MB under visible light.

Compared with the pure TiO_2 (sample P-400, Figure 6(a)), all of the samples D-400 exhibited a better photocatalytic activity. When tin dopant increases to 1% (Figure 6(c)), its photocatalytic activity reaches the maximum. Further increasing the tin dopant to 5% (Figure 6(d)) resulted in a decrease of its photocatalytic activity.

Photocatalytic activity mainly depended on the recombination rate of photogenerated electrons and holes produced in the course of photodegradation of MB under visible light. SnO_2 and TiO_2 are both wide band gap semiconductors. Although the band gap of SnO_2 (3.8 eV) is wider than that of TiO_2 (3.2 eV), the Fermi level of SnO_2 is lower than that of TiO_2 [27, 28]. It means that the photogenerated

electrons may easily transfer from TiO_2 to SnO_2 , but not to recombine with the photogenerated holes on the surface of TiO_2 immediately. Consequently, more and more holes are present on the surface and take part in the reactions of oxidizing OH^- and H_2O into hydroxyl radicals. Hydroxyl radicals would be finally responsible for the degradation of pollutants into H_2O and CO_2 . Doping an appropriate amount of Tin would improve the photocatalytic activity of TiO_2 , however, excessive amount of Sn^{4+} would induce the recombination of photogenerated electrons and holes, which resulted in the decrease of photocatalytic activity of TiO_2 [18].

4. Conclusion

Sn -doped TiO_2 nanoparticles were prepared by the water molecule transport method without adjusting the pH value of the solution. XRD results proved that the doping of Sn would debase the phase transition temperature of TiO_2 . The effects of Sn dopant on the photocatalytic activity of TiO_2 nanoparticles were evaluated by the photodegradation of methylene blue under visible light. Results showed that doping an appropriate amount of Tin would improve the photocatalytic activity of TiO_2 by enhancing the separation rate of photogenerated electrons and holes on the surface of TiO_2 . Among all of the samples, TiO_2 doped with 1% of Sn , annealed at 400°C , manifested the best photocatalytic activity.

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