

Study on Photoelectric Properties of Surface TiO₂ Nanoparticles Doped with Sn⁴⁺ ion

Jianbin Xu^a, Haigang Xu^{b*}

^aSchool of Physics and Electronics, Henan University, Kaifeng 475004, China

^bDepartment of Automatic Control, Henan Institute of Technology, Xinxiang 453002, China
hndxflamezl@163.com

This paper prepares pure TiO₂ nanoparticles and TiO₂ nanoparticles doped with different tin contents using sol-gel method, characterizes the structure of the samples using XRD, UV-Vis and surface photovoltage spectroscopy (SPS), analyzes the effects of annealing temperature and Sn⁴⁺ doping amount on the surface photoelectric properties of TiO₂ nanoparticles, and discusses the mechanism of the effect of Sn⁴⁺ doping on the surface photoelectric properties of TiO₂ nanoparticles. The experimental results show that the tin ion doping can significantly increase the surface photovoltage of the TiO₂ nanoparticles, while 3 mol% is the optimal doping concentration for tin ion.

1. Introduction

Wide band-gap TiO₂ nanoparticles have been widely used in photocatalytic degradation of organic compounds (Hoffmann et al., 1995; Hagfeldt and Gratzel, 1995) and dye-sensitized solar cells (Try et al., 2000) due to their good chemical stability, photocorrosion resistance, non-toxicity, low cost and large specific surface area. In order to improve its performance, metal ion doping, surface precious metal deposition and wide-narrow semiconductor coupling are commonly used to modify it (Mills and Huntel, 1997; Martra, 2000). SPS is an effective method to study the transfer behavior of photogenerated carriers on the surface and interface of semiconductor nanomaterials, which can reveal the surface structure properties and surface states of semiconductor nanomaterials, as well as the composition and separation of photogenerated carriers (Jing et al., 2003; Jing et al., 2004), providing a strong basis for evaluating high-performance semiconductors. In this paper, pure TiO₂ nanoparticles and TiO₂ nanoparticles with different tin contents are prepared and the SPS is used to characterize the surface photoelectric properties of the samples.

2. Experiment

2.1 Reagent

All the reagents used in the experiment are pure analytical reagents available on the market, and the water used is deionized water.

2.2 Preparation of samples

The preparation method in References (Jing et al., 2003; Lv et al., 2010) is used. Add dropwise a certain amount of tetrabutyl titanate slowly to absolute ethanol with vigorous stirring, and then add a mixture of concentrated nitric acid, deionized water, and a small amount of anhydrous ethanol (volume ratio: 2:1:1). After natural aging for a period of time, dry the resulting sol to obtain a TiO₂ precursor. Finally, the precursor is annealed in a muffle furnace at different temperatures for 2 hours to obtain pure TiO₂ nanoparticles. Repeat the above process, and replace the deionized water with 1 mol%, 3 mol%, and 5 mol% SnCl₄ aqueous solution to prepare TiO₂ nanoparticles doped with different Sn⁴⁺ concentrations.

2.3 Sample characterization

The crystal structure of the film sample is characterized by DX-2500 X-ray diffractometer. The Cu K ray diffraction source is used, with a wavelength of 0.15406 nm, the test tube current of 35 mA, and the tube voltage of 30 kV. The optical absorption properties of the samples are analyzed using the Cary 5000 ultraviolet-visible-near infrared spectrophotometer of US Vary Company under the conditions of monochromatic Al K α radiation. The surface photoelectric properties of the samples are obtained by a self-assembled surface photovoltage spectrometer, and the corresponding data were normalized. The experimental principle and method are described in references.

3. Results and Analysis

3.1 XRD characterization

In Figure 1, the diffraction peak of $2\theta=25.3^\circ$ (101) is the characteristic peak of the anatase phase and the diffraction peak of $2\theta=27.4^\circ$ (110) is the characteristic peak of the rutile phase. No diffraction peaks related to SnO or SnO₂ other than TiO₂ are found. It is shown that there is no new heterozygous phase formation. The radius of Sn⁴⁺ is 71 pm and the radius of Ti⁴⁺ is 68 pm. There is no significant difference between the two.

Chapter 2 Figure 2 shows that pure TiO₂ nanoparticles are mixed crystal structure of anatase phase and rutile phase at 600°C, and TiO₂ nanoparticles with different tin contents are rutile phase at 600 °C, which further indicates that tin doping promotes the phase transformation of TiO₂ nanoparticles from anatase to rutile. According to the calculations with Scherrer Formula (Jaboyedoff et al., 1999), the average sizes of grain with content of 0 mol%, 1 mol%, 3 mol% and 5 mol% of tin at 600 °C are 27.7 nm, 22 nm, 18.8 nm and 18.4 nm, respectively.

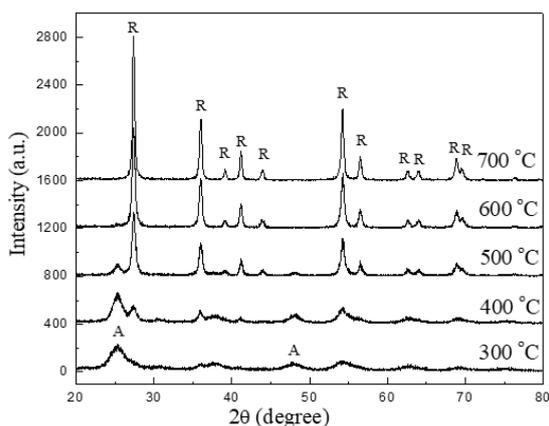


Figure 1: XRD pattern of pure and 5 mol% tin-doped TiO₂ nanoparticles

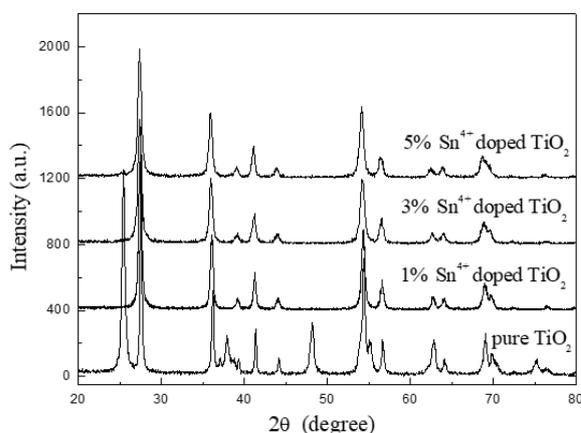


Figure 2: XRD pattern of pure TiO₂ nanoparticles and TiO₂ nanoparticles doped with different contents of tin at an annealing temperature of 600 °C

3.2 UV-Vis characterization

Figure 3 shows the function curve of wavelength and $F(R)$ of pure TiO_2 nanoparticles and TiO_2 nanoparticles doped with different tin contents at an annealing temperature of 600°C . The band gap is determined by the Kubelka-Munk equation $F(R)=(1-R)^2/2$ (Chao et al., 2003). The band gaps from a to d are 3.04 eV, 3.05 eV, 3.08 eV and 3.09 eV, respectively. That is, the band gap of the sample from a to d gradually increases, which may be due to the quantum size effect of the sample.

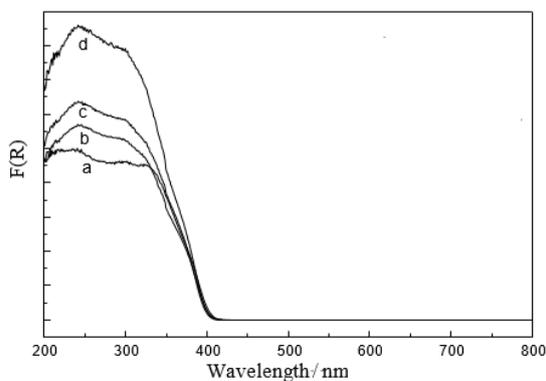


Figure 3: The function curve of wavelength and $F(R)$ of pure TiO_2 nanoparticles (wherein, a denotes the case without doping, b with content of 1mol% tin, c with content of 3mol% tin, and d with content of 5mol%tin)

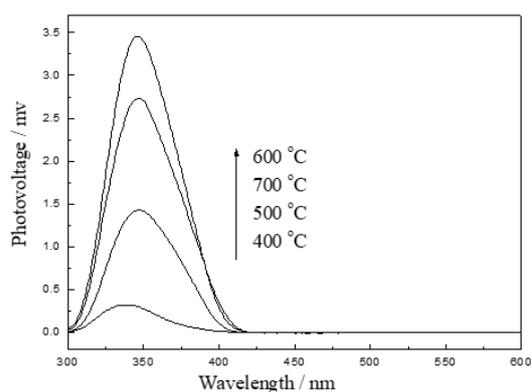


Figure 4: SPS of pure TiO_2 nanoparticles at different annealing temperatures

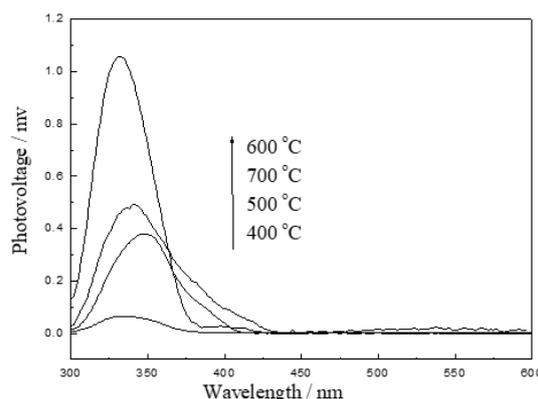


Figure 5: SPS of TiO_2 nanoparticles doped with 5mol % of tin at different annealing temperatures

3.3 SPS Characterization

As can be seen from Figure 6:

(1) The surface photovoltage intensity of both pure and tin-doped TiO_2 nano-particles increases with the annealing temperature, reaches the maximum at the annealing temperature of 600°C , and then decreases. For pure TiO_2 nanoparticles, this is mainly due to the mixed crystal effect of the sample as the annealing temperature increases. Furthermore, the increase of rutile content contributes to the separation of photogenerated carriers on the surface and reduces the recombination probability of electron-hole pairs. Thus the maximum is reached at 600°C , and the sample is completely transformed into rutile phase at 700°C , so that the separation efficiency of surface photogenerated carriers is decreased and the surface photovoltage intensity is decreased. For TiO_2 nanoparticles doped with 5mol% of tin, the increase of surface photovoltage intensity at 400°C and 500°C may be due to the increase of mixed crystal effect and rutile content. Interestingly, the sample at 600°C has completely transformed into the rutile phase, but the surface photovoltage intensity does not decrease and it is obvious that there is no mixed crystal effect at this time, which shows that the doping of tin ions may be the cause of the increase of surface photovoltage. At 700°C , the surface photovoltage intensity of the sample decreases, which may be related to the sharp drop in surface area caused by the sintering of the particles during high temperature processing.

(2) At various annealing temperatures, it is found that the surface photovoltage of tin-doped TiO_2 nanoparticles is stronger than that of pure TiO_2 nanoparticles, indicating that the doping of tin ions into the TiO_2 lattice obviously promotes the separation of photogenerated carriers on the surface of TiO_2 nanoparticles and improves the separation efficiency of surface photogenerated carriers.

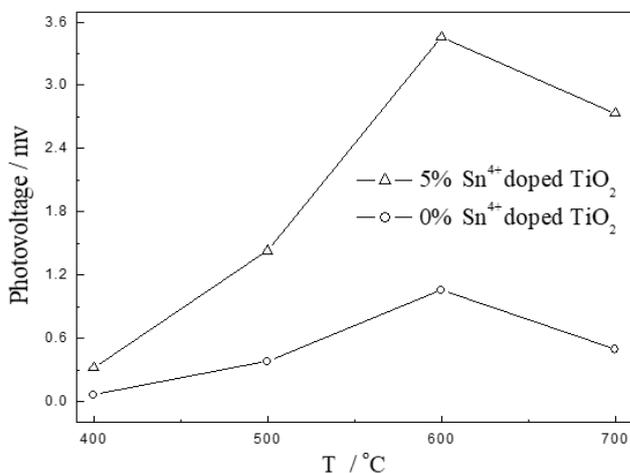


Figure 6: Comparison of surface photovoltage intensity of pure TiO_2 nano-particles and TiO_2 nano-particles doped with different tin contents at different annealing temperatures

Figures 7, 8 and 9 show the SPS of TiO_2 nanoparticles doped with different tin contents at annealing temperatures of 400°C, 600°C and 700°C. It can be seen from the figures that with the increase of tin content, the surface photovoltage of the sample shows a trend of rising first and then decreasing, but it is stronger than the surface photovoltage of undoped TiO_2 nanoparticles. The relationship between surface photovoltage intensity and concentration is: 3 mol% > 5 mol% > 1 mol% > undoped. It can be seen from the figure that the optimal doping concentration in this test is 3 mol%.

The surface photovoltage of tin-doped TiO_2 nanoparticles is stronger than that of undoped TiO_2 nanoparticles, suggesting that tin doping can promote the separation of photogenerated carriers on the surface of TiO_2 nanoparticles and remarkably increase the surface photovoltage of TiO_2 nanoparticles. Through analysis, it is believed that the reasons are as follows:

(1) When the annealing temperature is 400°C, combined with XRD, it is known that the undoped TiO_2 nanoparticles have a pure anatase phase structure, while the tin-doped TiO_2 nanoparticles have a mixed crystal structure, and there is no significant difference in the crystal grain size of the samples. The content of rutile in the mixed crystal with different doping concentration calculated by the formula of mass factor ratio is as follows: 1 mol%: 35.5%; 3 mol%: 48.8%; and 5 mol%: 42.5%. Therefore, the fact that the photovoltage of the surface of tin-doped TiO_2 nano-particles is stronger than that the undoped at 400°C may be due to the mixed crystal effect.

(2) At an annealing temperature of 600°C, combined with XRD, it is known that the undoped TiO_2 nanoparticles have a mixed crystal structure, and the tin-doped TiO_2 nanoparticles have all been converted to a rutile structure. The grain size of the sample does not differ significantly. The doping of excessive tin ions makes Sn^{4+} to become a recombination center for photoelectrons and holes, which reduces the separation efficiency of photogenerated carriers on the surface, thereby reducing the surface photovoltage at a doping of 5 % mol of tin. It is shown from the figure that the surface photovoltage intensity is the highest when the tin doping is 3 mol%, which indicates that 3 mol% is the optimal tin doping concentration.

(3) At an annealing temperature of 700°C, combined with XRD, it is known that both undoped and tin-doped TiO_2 nanoparticles have a rutile structure. There is little difference in grain size of samples. However, it can be seen from Figure 9 that the surface photovoltage intensity of tin-doped TiO_2 nanoparticles is still significantly greater than that of undoped TiO_2 nanoparticles and that when the tin doping is 3 mol%, the surface photovoltage intensity reaches its maximum, further suggesting that 3 mol% is the optimal tin doping concentrate.

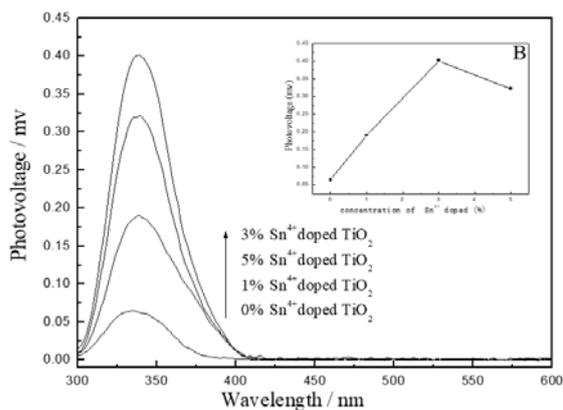


Figure 7: Surface photovoltage comparison of TiO_2 nanoparticles doped with different tin contents (molar concentration) at an annealing temperature of 400°C Figure B shows the change curve of surface photovoltage with different tin contents at 400°C

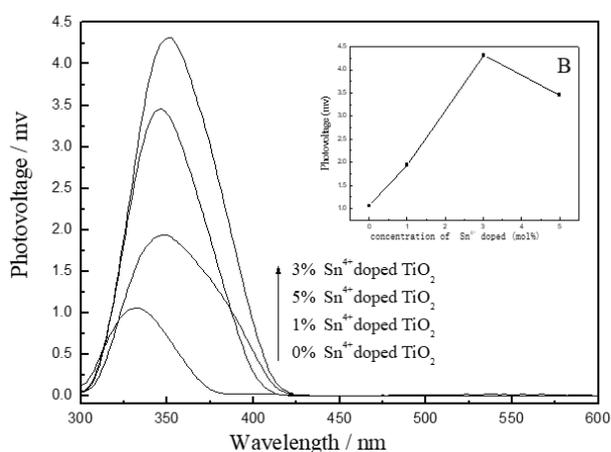


Figure 8: Surface photovoltage comparison of TiO_2 nanoparticles doped with different tin contents (molar concentration) at an annealing temperature of 600°C Figure B shows the change curve of surface photovoltage with different tin contents at 600°C

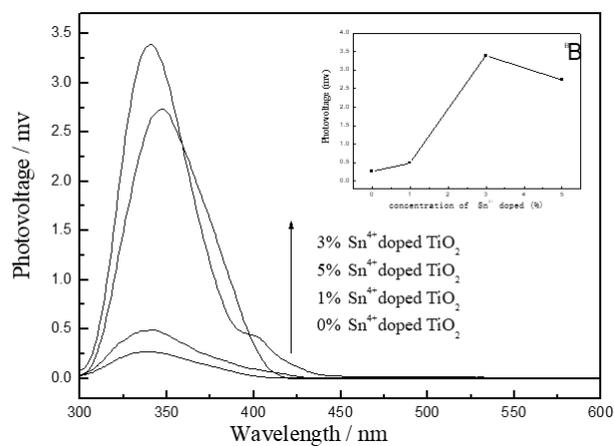


Figure 9: Surface photovoltage comparison of TiO_2 nanoparticles doped with different tin contents (molar concentration) at an annealing temperature of 700°C Figure B shows the change curve of surface photovoltage with different tin contents at 700°C

4. Conclusions

This paper prepares pure and TiO₂ nanoparticles doped with 1mol%, 3mol% and 5mol% of tin using sol-gel method, and characterizes the samples. The XRD results show that the doping of tin ions promotes the phase transition of TiO₂ nanoparticles from the anatase phase to the rutile phase and reduces the phase transition temperature. SPS test results show that the tin ion doping can significantly increase the surface photovoltage of the TiO₂ nanoparticles, while 3 mol% is the optimal doping concentration for tin ion.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (No.51205276)

Reference

- Chao H.E., Yun Y.U., Xing F.H., Larbot A., 2003, Effect of silver doping on the phase transformation and grain growth of sol-gel titania powder, *J Eur Ceram Soc*, 23(9), 1457-1464, DOI: 10.1016/S0955-2219(02)00356-4
- Hagfeldt A., Gratzel M., 1995, Light-induced redox reactions in nanocrystalline systems, *Chem Rev*, 95(1), 49-68.
- Hoffmann M.R., Choi W., Bahnemann D.W., 1995, Environmental Applications of Semiconductor Photocatalysis, *Chemical Reviews*, 95(1), 69-96.
- Jaboyedoff M., Kübler B., Thélin P.H., 1999, An empirical Scherrer equation for weakly swelling mixed-layer minerals, especially illite-smectite, *Clay Minerals*, 34(4), 601-617, DOI: 10.1180/000985599546479
- Jing L., Sun X., Cai W., Xu Z., Du Y., Fu H., 2003, The preparation and characterization of nanoparticle TiO₂/Ti films and their photocatalytic activity, *Journal of Physics & Chemistry of Solids*, 64(4), 615-623, DOI: 10.1016/S0022-3697(02)00362-1
- Jing L., Sun X., Shang J., Cai W., Xu Z., Du Y., Fu H., 2003, Review of surface photovoltage spectra of nano-sized semiconductor and its applications in heterogeneous photocatalysis, *Solar Energy Materials & Solar Cells*, 79(2), 133-151, DOI: 10.1016/S0927-0248(02)00393-8
- Jing L., Xin B., Yuan F., Wang B., Shi K., Cai W., Fu H., 2004, Deactivation and regeneration of ZnO and TiO₂ nanoparticles in the gas phase photocatalytic oxidation of n-C₇H₁₆, or SO₂, *Applied Catalysis A General*, 275(1), 49-54, DOI: 10.1016/j.apcata.2004.07.019
- Li F.B., Li X.Z., 2002, Photocatalytic properties of gold/gold ion-modified titanium dioxide for wastewater treatment, *Applied Catalysis A General*, 228(1), 15-27, DOI: 10.1016/S0926-860X(01)00953-X
- Lv Y., Ding Y., Zhou J., Xiao W., Feng Y., 2010, Preparation, Characterization, and Photocatalytic Activity of N, S-Codoped TiO₂ Nanoparticles, *Journal of the American Ceramic Society*, 92(4), 938-941, DOI: 10.1111/j.1551-2916.2009.02951.x
- Martra G., 2000, Lewis Acid and base sites at the surface of microcrystalline TiO₂ Anatase: relationships between surface morphology and chemical behaviour, *Applied Catalysis A*, 200(2), 275-283, DOI: 10.1016/S0926-860X(00)00641-4
- Mills A., Huntel S.L., 1997, An overview of semiconductor photocatalysis, *Journal of Photochemistry and Photobiology A*, 108(1), 33-35, DOI: 10.1016/S1010-6030(97)00118-4
- Try D.A., Fujishima A., Honda K., 2000, Recent topics in photoelectrochemistry: achievements and future prospects, *Electrochim Acta*, 45(15), 2363-2376, DOI: 10.1016/S0013-4686(00)00337-6