



Enhanced activity of bismuth-compounded TiO₂ nanoparticles for photocatalytically degrading rhodamine B solution

Jia Wang, Liqiang Jing*, Lianpeng Xue, Yichun Qu, Honggang Fu

The Laboratory of Physical Chemistry, School of Chemistry and Material Sciences, Heilongjiang University, Harbin, 150080, PR China

ARTICLE INFO

Article history:

Received 21 December 2007
Received in revised form 27 February 2008
Accepted 27 February 2008
Available online 4 March 2008

Keywords:

TiO₂
Nanoparticle
Compounding bismuth
Charge separation
Photocatalysis

ABSTRACT

TiO₂ nanoparticles compounded with different amounts of bismuth were prepared by a sol-gel method, and the effects of compounding bismuth on the phase transformation, photoinduced charge separation and photocatalytic activity for degrading rhodamine B solution were mainly investigated, along with enhancement mechanism of photocatalytic activity of TiO₂ nanoparticles by compounding bismuth species. It can be confirmed that, by means of X-ray diffraction (XRD), surface photovoltage spectroscopy (SPS) and ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS), compounding bismuth can extend the optical response, and effectively inhibit the phase transformation process from anatase to rutile, consequently greatly improving the anatase crystallinity so as to promote the photoinduced charge separation. These factors are responsible for the increase in the photocatalytic activity of TiO₂ compounded with an appropriate amount of bismuth species.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Among various oxide semiconductor photocatalysts, TiO₂ has been proven to be one of the most suitable materials for widespread environmental applications because of its several attractive features, such as chemical and biological inertness, stability against photocorrosion, non-toxicity, high redox ability and less cost. In the last two decades, the fundamental and application researches on TiO₂ photocatalysis have been extensively documented [1–4]. Generally speaking, the separation and recombination of photoinduced charge carriers are in competing process, and the photocatalytic reaction is effective only when photoinduced electrons and holes are trapped on the surfaces, respectively. Although a great many of works about semiconductor photocatalysis have been published, the detailed photocatalytic mechanisms and factors affecting the photoactivity are still needed to explore further.

It has well been recognized that there are two bottleneck drawbacks associated with TiO₂ photocatalysis, namely, high charge recombination rate in itself and low efficiency for utilizing solar light, which would greatly hinder the commercialization of this technology. To overcome the above two problems, many attempts have been made to increase the utilization of visible light and enhance the separation situation of charge carriers. Among those

attempts, compounding or doping transitional metal is one of the most efficient methods. There have been many papers published about TiO₂ photocatalysts compounded or doped with Zn, Sn, Cu, Si, Ca, Al, Mn, Fe, Ni, V, Ag, rare-earth metal, etc. [4–13]. However, relative few papers about TiO₂ compounded or doped with Bismuth (Bi) species have reported up to now [11–17]. Rengaraj et al. reported that doping Bi could improve the photocatalytic activity of TiO₂, attributed to the increase in the efficiency of charge separation on the basis of the photoluminescence quenching. However, to the best of our knowledge, systematic studies on effects of compounding Bi on the phase transformation and the photoinduced charge separation by means of SPS measurement, together with their relationships with the photocatalytic activity, have never been reported so far. The SPS, which is a kind of action spectroscopy based on optical absorption, is an effective tool to investigate the photophysics of excited states generated by adsorption in the aggregate state, providing some important information, surface states and charge separation and/or recombination [9,10].

In the present work, the photocatalytic activity of TiO₂ nanoparticles is improved by compounding an appropriate amount of Bi species, and the activity enhancement is mainly attributed to the increase in the photoinduced charge separation situation based on the SPS analysis, resulting from the high crystallinity and the Bi-O polyhedral acting as electron trapping centers, as well as to the visible response. Moreover, it can be suggested that the SPS measurement be used to preliminarily evaluate the photocatalytic activity of the resulting TiO₂ quickly. This work will be valuable for the practical application of TiO₂ photocatalysts, and also help

* Corresponding author. Tel.: +86 451 86608616; fax: +86 451 86673647.
E-mail address: jinglq@hlju.edu.cn (L. Jing).

us understand the photophysical and photochemical processes of nanosized semiconductor well.

2. Experimental

All the used reagents are of analytical grade without further purification, and the deionized water is employed to prepare the solutions in our experiments.

2.1. Preparation of materials

The TiO₂ nanoparticles were prepared by a sol-gel process [8]. In a typical process, 5 mL of Ti(OBu)₄ was dissolved in 5 mL of absolute C₂H₅OH to produce Ti(OBu)₄-C₂H₅OH solution. Meanwhile, 5 mL of water and 1 mL of HNO₃ (67%) were added to another 20 mL of absolute C₂H₅OH in turn to form an ethanol-nitric acid-water solution. After the two resulting solutions were stirred for 30 min, respectively, the Ti(OBu)₄-C₂H₅OH solution was slowly added dropwise to the ethanol-nitric acid-water solution under vigorously stirring to carry out a hydrolysis. Then, a semitransparent sol was gained after continuously stirring for 1 h. Subsequently, the sol was dried at 60 °C in the air for about 24 h to produce dry gel powder after grinding. Finally, TiO₂ nanoparticles were obtained by calcining the dry gel precursor at certain temperature for 2 h. To synthesize Bi-compounded TiO₂ samples, the desired amount of Bi(NO₃)₃ was dissolved in an appropriate amount of ethanol-nitric acid-water solution prior to the hydrolysis. The remaining procedures were the same as described above.

2.2. Characterization of materials

The crystalline phases of the samples are analyzed by X-ray powder diffraction (XRD) using a Model D/MAX-IIIIB diffractometer made by Japanese Science Co., equipped with CuK α radiation ($\lambda = 0.15406$ nm). An accelerating voltage of 30 kV and an emission current of 20 mA were employed.

The samples are observed with a JEOM-1200EX transmission electron microscope (TEM).

The surface composition and elemental chemical state of the samples are examined by X-ray photoelectron spectroscopy (XPS) using a Model VG ESCALAB apparatus with MgK α X-ray source. The pressure is maintained at 6.3×10^{-7} Pa. The binding energies are calibrated with respect to the signal for adventitious carbon (binding energy = 284.6 eV). Relative quantitative analysis is carried out with the sensitivity factors supplied by this instrument.

The Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of the samples are recorded with a Model Shimadzu UV2550 spectrophotometer.

The Surface photovoltage spectroscopy (SPS) measurement of the samples is carried out with a home-built apparatus that had been described in detail elsewhere [10,18]. The powder samples are sandwiched between two ITO glass electrodes, and the change of surface potential barrier between in the presence of light and in the dark is SPS signal. The raw SPS data are normalized with a Model Zolix UOM-1S illuminometer made in China.

2.3. Evaluation of photocatalytic activity of materials

Rhodamine B (RhB) has commonly been used as a dye, especially for paper, and as a reagent for antimony, bismuth, cobalt, niobium, gold, manganese, mercury, molybdenum, tantalum, thallium and tungsten. However, it has been found to be potentially toxic and carcinogenic. Thus, the RhB solution is chosen as a model pollutant to evaluate photoactivity of the as-prepared TiO₂. The degradation intermediates were not determined. The experiment was carried out in a 200 mL quartz photochemical reactor, open to air, hav-

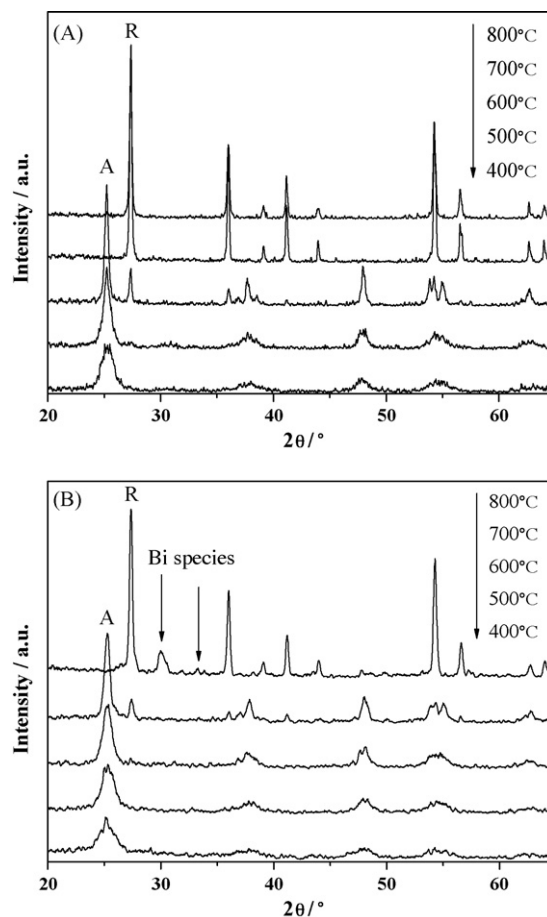


Fig. 1. XRD patterns of un-compounded (A) and Bi-compounded (B) TiO₂ calcined at different temperature.

ing the shape of a vertical cylinder. The light was provided from a side of the reactor by a 150 W GYZ220 fluorescence high-pressure Hg lamp made in china without filter, which was placed at about 20 cm from the reactor. The RhB solution initial concentration was equal to 10 mg/L, and the treated total volume was 100 mL under continuously stirring. The solution was first stirred for 20 min after 0.1 g of TiO₂ samples was added into the reaction system, it has been shown that this period was sufficient to reach the adsorption equilibrium, then began to illuminate. The RhB concentrations at different reactive times were measured with a Model Shimadzu UV2550 spectrophotometer according to the optical characteristic absorption at the wavelength of 553 nm of RhB solution after centrifugation.

3. Results and discussion

3.1. Measurements of XRD, TEM and XPS

The XRD peaks at $2\theta = 25.28$ and $2\theta = 27.48$ are often taken as the characteristic peaks of anatase (1 0 1) and rutile (1 1 0) crystal phase, respectively [8]. The percentage of anatase in the samples can be estimated from the respective integrated XRD peak intensities using the quality factor ratio of anatase to rutile (1.265), and the crystallite size can also be determined from the broadening of corresponding X-ray spectral peak by Scherrer formula [19]. Fig. 1 shows the XRD patterns of un-compounded (A) and 3 mol% Bi-compounded (B) TiO₂ nanoparticles calcined at different temperature.

From Fig. 1A, it can be seen that there is main anatase phase in the TiO₂ nanoparticles calcined at the temperature of lower than 600 °C, and the anatase crystallinity and crystallite size can increase as the thermal treatment temperature rises based on the intensities of characteristic XRD peaks. After calcination at 600 °C, a certain amount of rutile phase begins to appear. When the calcination temperature is equal to or higher than 700 °C, TiO₂ has completely been transformed into the rutile phase. It can be demonstrated that the temperature between 500 and 700 °C is the phase transformed temperature for the anatase to rutile [20].

As for Bi-compounded TiO₂ (Fig. 1B) samples, it can be confirmed that the phase transformation begins to take place at 700 °C, and the anatase phase has fully disappeared after calcination at 800 °C. On the condition of the same thermal treatment temperature, the Bi-compounded TiO₂ sample has larger anatase content and smaller crystallite size than those of corresponding TiO₂ un-compounded with Bi. The above results imply that compounding Bi has a great inhibiting effect on the phase transformation process. Thus, the crystallinity of anatase TiO₂ can be raised by compounding Bi. In general, the increase in the crystallinity of anatase TiO₂ is favorable to enhance the photocatalytic activity of TiO₂ [21]. The as-prepared Bi-compounded TiO₂ sample calcined at 700 °C, with about 15 nm anatase crystallite size, has a mixed phase composition of 82% anatase and 18% rutile, whose phase composition is similar to that of the internationally commercial P25 TiO₂. The P25 usually exhibits high photocatalytic activity, which is commonly recognized to be due to its mixed phase composition. Therefore, it can be predicted that the resultant TiO₂ compounded with Bi by thermal treatment at 700 °C have good photocatalytic performance because of its high anatase crystallinity and its mixed phase composition.

It should be noted that the XRD peaks of Bi-compounded TiO₂ do not shift a little, compared with un-compounded TiO₂, indicating that Bi does not come into the lattices to substitute partly Ti, which is possibly because of the larger radius of Bi³⁺ (0.096 nm) than that of Ti⁴⁺ (0.068 nm) during the process of soft chemical preparation. In addition, the phases related to Bi species in TiO₂ calcined at 800 °C are examined. After calcination at 800 °C, Bi₁₂Ti₂₀O₂₀ or Bi₄Ti₃O₁₂ is easily formed [22,23].

X-ray photoelectron spectroscopy with a high sensitivity is an effective method to investigate the surface composition and chemical states of solid samples. The two as-prepared TiO₂ samples compounded with 3% Bi by thermal treatment at 600 °C and 700 °C is tested by means of XPS method, and their XPS spectra are shown in Fig. 2. The XPS peak positions of Bi4f_{7/2} (Fig. 2A) and Ti2p_{3/2} (Fig. 2B) are at about 158.5 and 458.5 eV, respectively, demonstrating that the main chemical valences of Bi and Ti in the two samples are +3 and +4, respectively, according to the method principle and handbook of the XPS instrument. The two O1s XPS spectra are wide and asymmetric, demonstrating that there are at least two kinds of O chemical states according to the binding energy range from 530.1 to 533.0 eV, including crystal lattice oxygen (O_L) and hydroxyl oxygen (O_H) with increasing binding energy [24,25]. Thus, the O1s XPS spectrum is fitted to two kinds of chemical states with the Origin software by Gaussian rule. The O_L XPS signal is attributed to the contribution of Ti–O in TiO₂ crystal lattice, and its peak position is at about 530.0 eV. The O_H XPS is close related to the hydroxyl groups resulting mainly from the chemisorbed water, and its peak position is at about 531.5 eV. According to XPS analysis, it can be shown that the atomic number ratio of Bi and Ti is close to 3: 100, which corresponds to the desired amount of Bi, illustrating that Bi is uniformly dispersed into the TiO₂ samples.

Based on the above results of XRD and XPS, for the Bi-compounded TiO₂ calcined at the temperature below 800 °C, Bi should exist as the main chemical form of lots of Bi₂O₃ clusters,

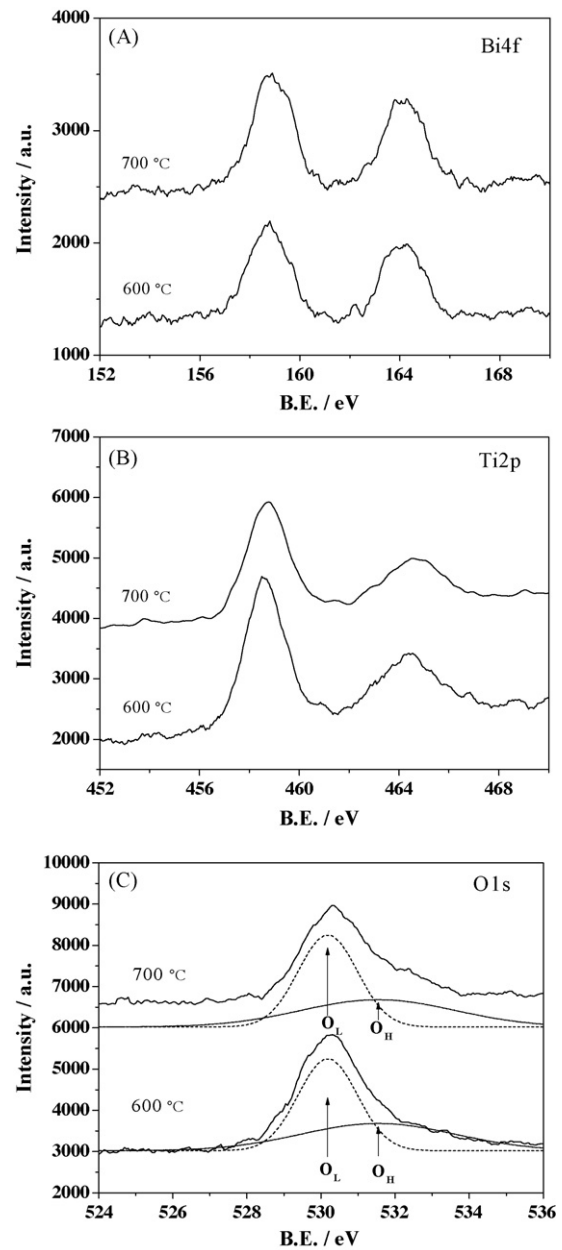


Fig. 2. XPS spectra of Bi4f (A), Ti2p (B) and O1s (C) of Bi-compounded TiO₂ calcined at 600 °C and 700 °C.

and be uniformly dispersed among the TiO₂ crystallites, further producing the Bi₂O₃–TiO₂ composite nanoparticles. Since Bi₂O₃ is dispersed uniformly among anatase crystallites, it should enhance the phase transformation temperature by suppressing the anatase crystallite contacts during the thermal treatment [24].

Fig. 3 shows the TEM images of TiO₂ nanoparticles un-compounded (A) and compounded with 3 mol% Bi (B) by thermal treatment at 600 °C. It can be seen that the both samples display similar sphere, with the average particle size of about 30 and 20 nm, respectively, demonstrating that compounding Bi can inhibit the growth of TiO₂ nanoparticles, which is in accordance with XRD characterization.

3.2. Measurements of DRS and SPS

Fig. 4 is the DRS spectra of TiO₂ nanoparticles calcined at 600 °C and 3% Bi-compounded TiO₂ nanoparticle calcined at 700 °C. Since

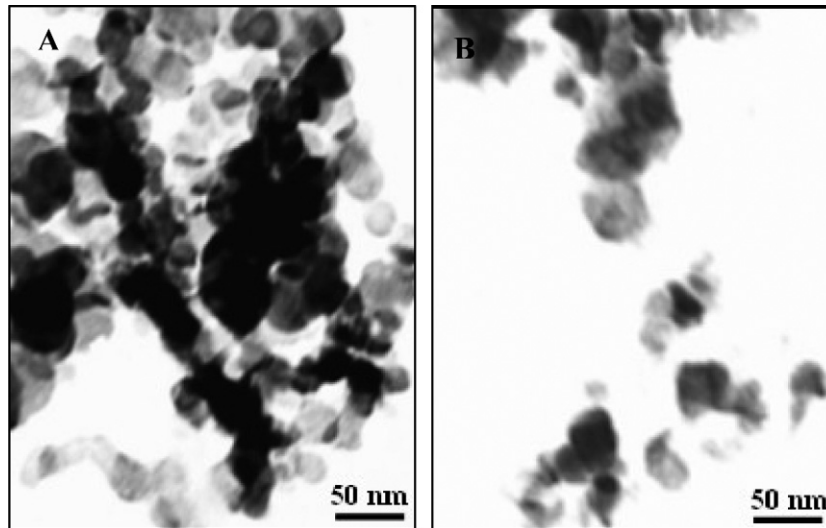


Fig. 3. TEM images of un-compounded (A) and Bi-compounded (B) TiO_2 .

the two samples have similar phase composition based on the above XRD analysis, their DRS spectra are similar. However, by comparison, it can be found that there is much less reflection (more absorption) at the wavelength range from 420 to 470 nm in the Bi-compounded sample, which can be attributed to Bi species.

The surface photovoltage (SPV) method is a well-established contactless and non-destructive technique for semiconductor characterization that relies on analyzing the difference of surface photovoltage after and before irradiating, further effectively reflecting the information about the separation and recombination of photoinduced charge carriers. Fig. 5 shows the SPS responses of different amount of Bi-compounded TiO_2 calcined at 700°C and un-compounded TiO_2 calcined at 600°C . For the obvious SPS peak at about 345 nm in the all four samples (Fig. 5), it can be attributed to the electronic transition from the valence band to conduction band ($\text{O}_{2p} \rightarrow \text{Ti}_{3d}$) according to the DRS spectra and TiO_2 energy band structure [25]. On the basis of the above XRD analysis, it can be expected that the four samples in Fig. 5 have similar phase composition. However, their SPS intensities are distinct. As the Bi amount increases, the SPS responses become strong. When the Bi content is 3%, the highest SPS response appears. However, after continuously increasing Bi amount, the SPS response begins to become weak inversely. This indicates that compounding an appropriate amount of Bi can enhance the SPS response so as to further promote photoinduced charge separation, which is possibly explained by the

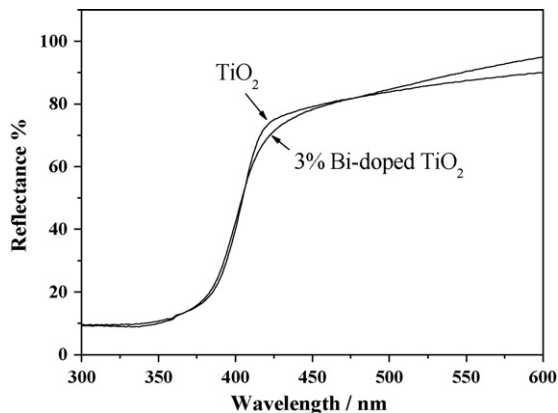


Fig. 4. UV-vis DRS spectra of un-compounded TiO_2 calcined at 600°C and Bi-compounded TiO_2 calcined at 700°C .

following three aspects. The first aspect is related to the increase in the crystallinity resulting from compounding Bi. The second aspect is because of the formation of $\text{Bi}_2\text{O}_3\text{-TiO}_2$ composite nanoparticles, in which the photoinduced electrons in the conduction of TiO_2 can easily transfer to the conduction of Bi_2O_3 according to their band structure. The third aspect is due to the Bi-O polyhedral, which can act as electron trapping centers so as to hinder electron-hole pair recombination [25]. However, compounding an excess amount of Bi can possibly affect the optical absorption of TiO_2 , which is responsible for the decrease in the SPS response.

In addition, it should be noted that a weak SPS response appears at about 425 nm in the TiO_2 compounded with Bi, especially for that with high amount of Bi, which is possibly ascribed to the existence of Bi_2O_3 . This is favorable to extend optical response of TiO_2 and to induce visible-driven photocatalytic reactions.

3.3. Measurement of photocatalytic activity

The photocatalytic activity of different content Bi-compounded TiO_2 nanoparticles can be evaluated by the degradation of RhB solution. From Fig. 6, it can be seen that the photocatalytic activity of TiO_2 nanoparticles can be improved by compounding an appropriate content of Bi. On the basis of the above analyses, the enhanced photocatalytic activity can be attributed to the higher charge separation rate, mainly resulting from the high crystallinity and Bi_2O_3 coupling, and to the extent of optical absorption. When the Bi

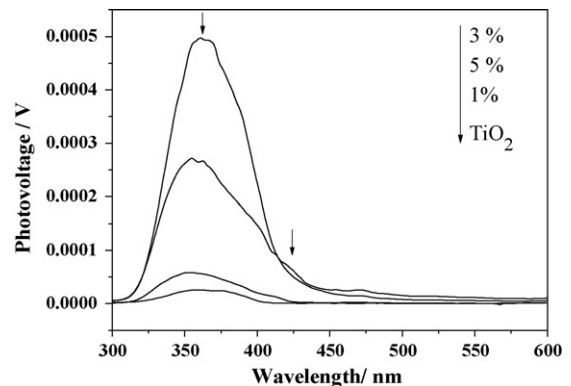


Fig. 5. SPS responses of different amount of Bi-compounded TiO_2 calcined at 700°C and un-compounded TiO_2 calcined at 600°C .

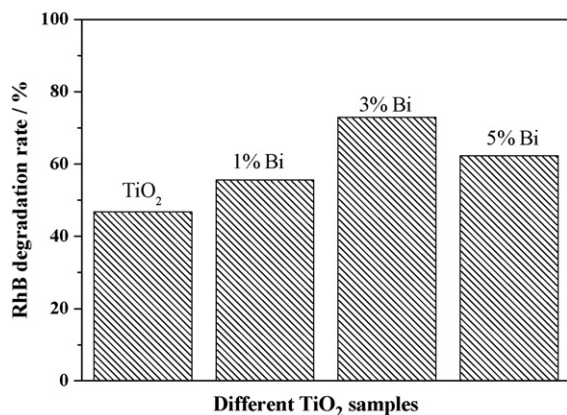


Fig. 6. Photocatalytic degradation rate of RhB solution on different content of Bi-compounded TiO₂ calcined at 700 °C and un-compounded TiO₂ calcined at 600 °C.

content is 3%, the Bi-compounded TiO₂ sample exhibits higher photocatalytic activity. If the Bi content continuously increases, the photocatalytic activity begins to go down inversely. Interestingly, the order of the photocatalytic activity is the same as the order of the SPS intensity.

4. Conclusions

Based on the above systematic research, several conclusions can be drawn as follows. Compounding Bi can inhibit the phase transformation from anatase to rutile so as to improve the crystallinity of anatase TiO₂, and can produce Bi₂O₃-TiO₂ composite nanoparticles. These results in the enhancement in the photoinduced charge separation and the extent of optical absorption, which are responsible for the increase in the photocatalytic activity of TiO₂ samples compounded with an appropriate amount of Bi species. Moreover, it can be suggested that for Bi-compounded TiO₂, the stronger is the SPS response, the higher is the photocatalytic activity.

Acknowledgements

This work is supported by the National Nature Science Foundation of China (no. 20431030 and 20501007), the program for New Century Excellent Talents in universities (NCET-2007-0259), the Key Project of Science & Technology Research of Ministry of Education of China (no. 207027), the Science Foundation for Excellent Youth of Heilongjiang Province (JC200701) and the Science and Technology Project of Education Bureau of Heilongjiang province of China (no. 11511283), for which we are very grateful.

References

[1] N. Serpone, E. Pellizzetti, *Photocatalysis: Fundamental and Applications*, Wiley Publisher, 1989, p. 1.

- [2] M.A. Fox, M.T. Dulay, Heterogeneous photocatalysis, *Chem. Rev.* 93 (1993) 341–357.
- [3] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chem. Rev.* 95 (1995) 69–96.
- [4] A.L. Linsebigler, G.Q. Lu, J.T. Yates, Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results, *Chem. Rev.* 95 (1995) 735–758.
- [5] M.I. Litter, Heterogeneous photocatalysis: transition metal ions in photocatalytic systems, *Appl. Catal. B* 23 (1999) 89–114.
- [6] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *J. Photochem. Photobiol. C* 1 (2000) 1–21.
- [7] M.V. Shankar, S. Anandan, N. Venkatchalam, B. Arabindoo, V. Murugesan, Fine route for an efficient removal of 2, 4-dichlorophenoxyacetic acid (2,4-D) by zeolite-supported TiO₂, *Chemosphere* 63 (2006) 1014–1021.
- [8] L.Q. Jing, B.F. Xin, F.L. Yuan, Effects of surface oxygen vacancies on photophysical and photochemical processes of Zn-doped TiO₂ nanoparticles and their relationships, *J. Phys. Chem. B* 110 (2006) 17860–17865.
- [9] Y.H. Lin, D.J. Wang, Q.D. Zhao, M. Yang, Q.L. Zhang, A study of quantum confinement properties of photogenerated charges in ZnO Nanoparticles by surface photovoltage spectroscopy, *J. Phys. Chem. B* 108 (2004) 3202–3206.
- [10] L.Q. Jing, Z.L. Xu, J. Shang, X.J. Sun, W.M. Cai, H.G. Fu, Review of surface photovoltage spectra of nano-sized semiconductor and its applications in heterogeneous photocatalysis, *Sol. Energy Mater. Sol. C* 79 (2003) 133–151.
- [11] J.H. Xin, S.M. Zhang, G.D. Qi, Preparation and characterization of photocatalysts, *React. Kinet. Catal. Lett.* 86 (2005) 291–298.
- [12] X.H. Xu, M. Wang, Y. Hou, Preparation and characterization of Bi-doped TiO₂ photocatalyst, *J. Mater. Sci. Lett.* 21 (2002) 1655–1656.
- [13] C.M. Whang, J.G. Kim, H.J. Hwang, Photocatalytic properties of the transition metal doped TiO₂ powder prepared by sol-gel process, *Key Eng. Mater.* 280–283 (2005) 647–650.
- [14] S. Rengaraj, X.Z. Li, *Chemosphere* enhanced photocatalytic reduction reaction over Bi³⁺-TiO₂ nanoparticles in presence of formic acid as a hole scavenger, *Chemosphere* 66 (2007) 930–938.
- [15] S. Rengaraj, X.Z. Li, P.A. Tanner, Z.F. Pan, G.K.H. Pang, Photocatalytic degradation of methylparathion – an endocrine disruptor by Bi³⁺-doped TiO₂, *J. Mol. Catal. A* 247 (2006) 36–43.
- [16] J. Georgieva, S. Armyanov, E. Valova, Enhanced photocatalytic activity of electro-synthesised tungsten trioxide-titanium dioxide Bi-layer coatings under ultraviolet and visible light illumination, *Electrochem. Commun.* 9 (2007) 365–370.
- [17] K. Sunahara, J. Yano, K. Kakegawa, Preparation of Bi₄Ti₃O₁₂ Particles by Crystallization from glass, *J. Eur. Ceram. Soc.* 26 (2006) 623–626.
- [18] L.Q. Jing, B.F. Xin, F.L. Yuan, B.Q. Wang, K.Y. Shi, W.M. Cai, H.G. Fu, Deactivation and regeneration of ZnO and TiO₂ nanoparticles in the gas phase photocatalytic oxidation of *n*-C₇H₁₆ or SO₂, *Appl. Catal. A* 275 (2004) 49–54.
- [19] Q.H. Zhang, L. Gao, J.K. Guo, Effects of calcination on the photocatalytic properties of nanosized TiO₂ powders prepared by TiCl₄ hydrolysis, *Appl. Catal. B* 26 (2000) 207–215.
- [20] L.Q. Jing, X.J. Sun, B.F. Xin, B.Q. Wang, W.M. Cai, H.G. Fu, The preparation and characterization of La doped TiO₂ nanoparticles and their photocatalytic activity, *J. Solid State. Chem.* 177 (2004) 3375–3382.
- [21] J.G. Yu, H.G. Yu, B. Cheng, X.J. Zhao, J.C. Yu, W.K. Ho, The Effect of Calcination Temperature on the Surface Microstructure and Photocatalytic activity of TiO₂ thin films prepared by liquid phase deposition, *J. Phys. Chem. B* 107 (2003) 13871–13879.
- [22] W. Feng Yao, X. Hong Wang, Hong Xu, Photocatalytic property of bismuth titanate Bi₁₂TiO₂₀ crystals, *Appl. Catal. A* 243 (2003) 185–190.
- [23] W.F. Yao, H. Wang, X.H. Xu, S.X. Shang, Y. Hou, Y. Zhang, M. Wang, Synthesis and photocatalytic property of bismuth titanate Bi₄Ti₃O₁₂, *Mater. Lett.* 57 (2003) 1899–1902.
- [24] J. Zhang, M. Li, Z. Feng, J. Chen, Can Li, UV Raman spectroscopic study on TiO₂. I. Phase transformation at the surface and in the bulk, *J. Phys. Chem. B* 110 (2006) 927–935.
- [25] L.Q. Jing, H.G. Fu, B.Q. Wang, Effects of Sn dopant on the photoinduced charge property and photocatalytic activity of TiO₂ nanoparticles, *Appl. Catal. B* 62 (2006) 282–291.