

Short communication

Hydrothermal synthesis of S-doped TiO₂ nanoparticles and their photocatalytic ability for degradation of methyl orangeHua Tian^{a,b}, Junfeng Ma^{a,c,*}, Kang Li^d, Jinjun Li^b^a College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266003, China^b Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China^c State Key Lab. of Green Building Materials, China Building Materials Academy, Beijing 100024, China^d Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266071, China

Received 28 February 2008; received in revised form 7 March 2008; accepted 2 May 2008

Available online 15 July 2008

Abstract

A simple synthesis route to nanocrystalline S-doped TiO₂ photocatalysts by a hydrothermal method at 180 °C was developed and the photocatalytic activity of the obtained powders for the degradation of methyl orange was studied. The products were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The phase composition (anatase/rutile ratio) and the photocatalytic activity of the final materials were found to be markedly influenced by the amount of the incorporated sulphur. On increasing the S-dopant amount, the anatase/rutile ratio and the photocatalytic activity of the as-prepared powders increased.

Crown Copyright © 2008 Published by Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Nanoparticles; TiO₂; S-doped; Hydrothermal synthesis

1. Introduction

Since the discovery of photocatalytic water splitting on TiO₂ single-crystal electrodes by Fujishima and Honda in 1972 [1], TiO₂ has been proved to be an excellent catalyst in the photocatalytic degradation of organic pollutants because it is effective, photostable, cheap, non-toxic and easily available [2]. However, most investigations have to be carried out under ultraviolet (UV) light [3–5] since TiO₂ photocatalyst shows relatively high activity and chemical stability under UV light. Therefore, solar light cannot be fully utilized. In the past decades, many efforts have been made for the visible-light sensitization of TiO₂. Doping is one of the typical approaches to extend the spectral response of a wide band gap semiconductor to visible light, where some metal ions can be used as a dopant [6–8]. However, photocatalytic activity of most of these catalysts decreases even in the UV region because the doped materials suffer from a thermal instability or an increase in the carrier-recombination centers [9]. Recently, some groups

reported results on the substitution of non-metal elements such as nitrogen (N) [10], fluorine (F) [11] and sulphur (S) [12] for oxygen (O) in TiO₂. These anion-doped TiO₂ photocatalysts showed good photocatalytic activity under visible light. Especially, introducing S at the O sites could significantly modify the electronic structures of TiO₂ because S has a larger ionic radius compared with N and F [13].

In previous reports, S-doped TiO₂ photocatalysts were prepared mainly by calcining materials containing titanium at high reaction temperatures [13–14]. More recently, Li et al. [15] reported that sulphur could be doped into titania by treating TiO₂ precursor (xerogel) under supercritical conditions in CS₂/ethanol fluid at 280 °C. It is well known that the hydrothermal method is a promising approach for the preparation of different classes of inorganic materials in a nanocrystalline state [16], but there have been few reports on the hydrothermal synthesis of S-doped TiO₂ nanoparticles.

In the present work, we report a simple method to synthesize nanocrystalline S-doped TiO₂ photocatalysts, which involve hydrothermal treatment of aqueous solutions of TiCl₄ and thiourea at a relatively low temperature of 180 °C. The obtained products have different morphologies and excellent photocatalytic activities for degradation of methyl orange.

* Corresponding author. Tel.: +86 10 51167477; fax: +86 10 65761714.

E-mail address: majunfengcbma@yahoo.com.cn (J. Ma).

2. Experimental

2.1. Preparation for nanocrystalline S-doped TiO₂ photocatalysts

TiCl₄ and CS(NH₂)₂ both analytical grade, were used as starting materials. In a typical synthesis, 0.711 g CS(NH₂)₂ and 2 ml of TiCl₄ were mixed with 68 ml of distilled water. The mixture was poured into a Teflon-lined stainless autoclave with 100 ml capacity. The autoclave was then sealed and heated up to 180 °C, and kept for 20 h, then cooled to room temperature naturally. Finally, the product was separated by centrifugation, and washed with distilled water and alcohol for several times, then dried at 70 °C for 3 h. The sample was labeled as 0.5% S-TiO₂, which 0.5% refers to the S/Ti molar ratio. Similarly, 1.0, 1.5% S-TiO₂ and pure TiO₂ samples were also prepared by repeating the above procedure. Pure TiO₂ sample was prepared without adding CS(NH₂)₂.

2.2. Apparatus

The photocatalytic degradation reactions were performed in a 500 ml Pyrex glass beaker under irradiation of a 400 W high pressure Hg lamp (Shandong Huamei Lighting Co., Ltd.) with a maximum emission at about 365 nm. The methyl orange concentration was analyzed by UV–vis spectroscopy using a 723 spectrophotometer (Shanghai Spectrum Instruments Company). X-ray diffraction (XRD) patterns were obtained using a D/max-rB X-ray diffractometer (Rigaku, Japan). The X-ray source was Cu K α radiation. A transmission electron microscope (JEM-1200 EX TEM) was used to observe the morphology and particle size of the as-prepared photocatalysts.

2.3. Photocatalytic experiments

Photocatalytic degradation reaction experiments were carried out by degrading methyl orange in water (its initial concentration was 20 mg/l). The schematic diagram of the photocatalytic reactor is shown in Fig. 1, it consists of two parts: a 500 ml Pyrex glass beaker and a 400 W high pressure Hg lamp that was parallel to the Pyrex glass beaker. The reaction temperature was kept at 25 °C by using a water circulation.

Reaction suspensions were prepared by adding 0.35 g of the as-prepared S-doped TiO₂ powders into 350 ml methyl orange aqueous solution. Prior to irradiation, each suspension was sonicated for 15 min to establish adsorption–desorption equilibrium in a dark. The suspension containing methyl orange and the photocatalyst was then irradiated under the UV light, and the photocatalytic reaction timing started.

At a given time interval, analytical samples were sequentially taken from the reaction suspension, and filtered through multilayer 0.2 μ m millipore filter. Then the filtrate was analyzed by UV–vis spectroscopy using a 723 spectrophotometer at its maximum absorption wavelength of 464 nm.

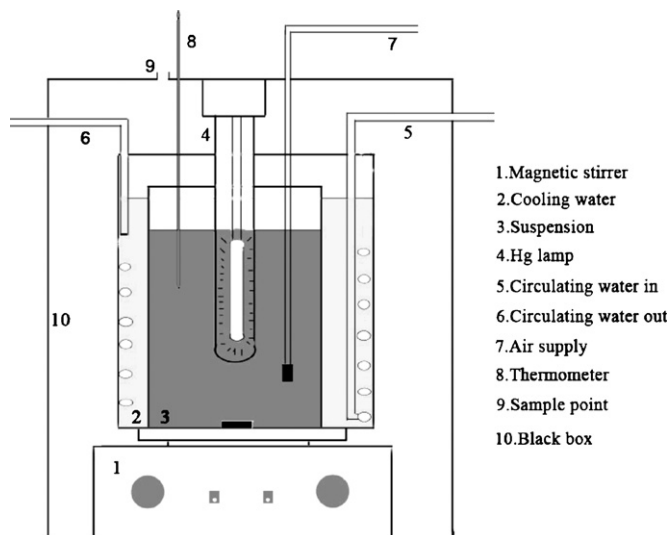


Fig. 1. Schematic diagram of the photocatalytic reactor.

3. Results and discussion

Fig. 2 shows XRD patterns of the S-doped TiO₂ photocatalysts hydrothermally synthesized at 180 °C with different S-doped amount. All of the samples consist of anatase and rutile phases and no other phases can be found. Compared with pure TiO₂, the 0.5% S-TiO₂ mainly shows the reflections corresponding to the rutile phase, and a trace amount of anatase phase. However, on further increasing the amount of the incorporation of S, the anatase phase gradually increases. It means that the ratio of anatase to rutile in the S-doped TiO₂ photocatalysts is strongly affected by the S dopant amount.

Fig. 3 presents TEM micrographs of the S-doped TiO₂ photocatalysts obtained by the hydrothermal method at 180 °C. It is evident that both 0.5% S-TiO₂ and 1.0% S-TiO₂ mainly consist of nanorods while 1.5% S-TiO₂ consists of spherical

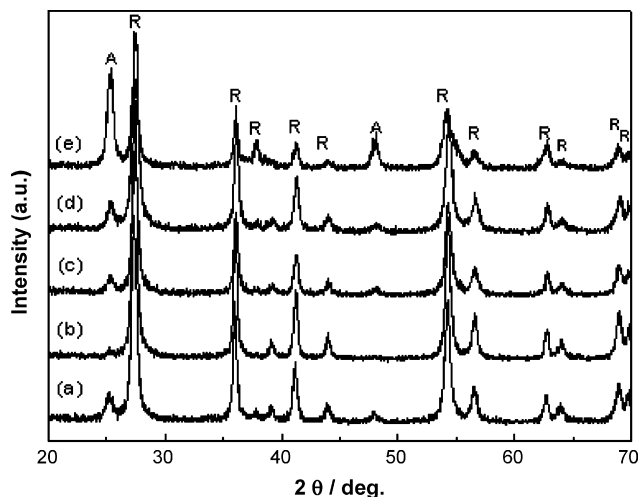


Fig. 2. XRD patterns of the pure TiO₂ and S-doped TiO₂ photocatalysts obtained by the hydrothermal method at 180 °C for 20 h: (a) TiO₂, (b) 0.5% S-TiO₂, (c) 1.0% S-TiO₂, (d) 1.5% S-TiO₂ and (e) 2.0% S-TiO₂. (R) rutile; (A) anatase.

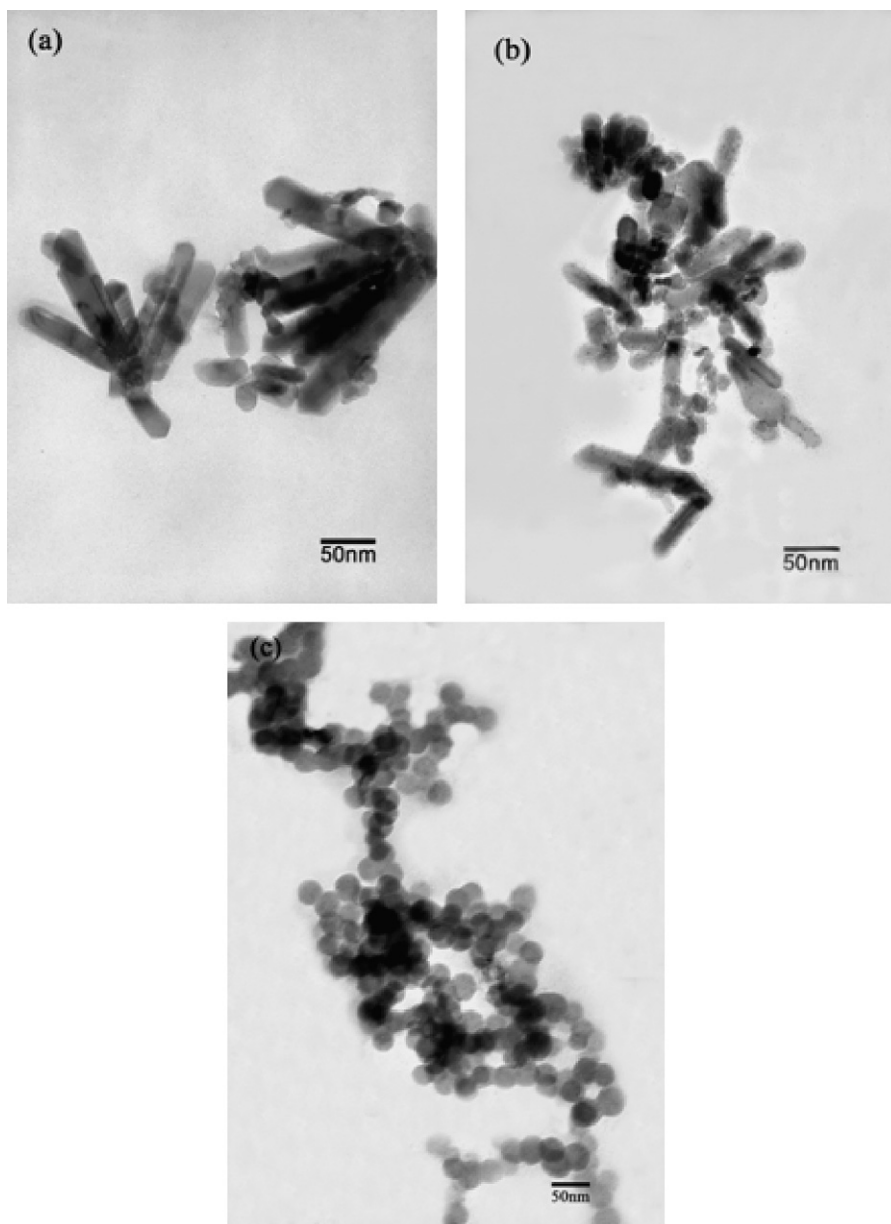


Fig. 3. TEM photographs of the S-doped TiO_2 photocatalysts obtained by the hydrothermal method at 180°C for 20 h: (a) 0.5% S- TiO_2 , (b) 1.0% S- TiO_2 and (c) 1.5% S- TiO_2 .

nanoparticles. It seems that increasing the incorporated amount of S would modify the morphology of the S-doped TiO_2 photocatalysts and reduce their particle sizes. When the amount of S increases from 0.5 mol% to 1.5 mol%, the nanorods of the S-doped TiO_2 photocatalysts with a diameter of about 30 nm and length of 100–150 nm can be completely changed to spherical nanoparticles of about 30 nm diameter.

The photocatalytic degradation of methyl orange was investigated by determining the remaining concentration of methyl orange [17] at various time intervals. Fig. 4 shows that the present photocatalytic degradation of methyl orange approximately follows zero order kinetics under UV irradiation [18]. Both 1.0% S- TiO_2 and 1.5% S- TiO_2 samples showed to be more photoactive than undoped TiO_2 , and 1.5% S- TiO_2 exhibits

the best photocatalytic activity, approximately 96% methyl orange being degraded in 40 min. The photocatalytic degradation reaction is a complicated process, which would be influenced by the particle size, morphology, and phase/chemical composition of photocatalysts. A smaller particle size and a larger surface area would facilitate the increase of the photogenerated electrons [19–20], and anatase/rutile mixtures have the high photonic efficiency, like commercial P25 [21], or other samples prepared as thin films [22]. As shown in Figs. 2 and 3, 0.5% S- TiO_2 sample is almost composed of a single phase of rutile and has the larger particle size, so it shows lower photocatalytic activity. When the incorporated amount of S increases, anatase/rutile mixture phases exist and the particle size decreases in the S-doped TiO_2 photocatalysts.

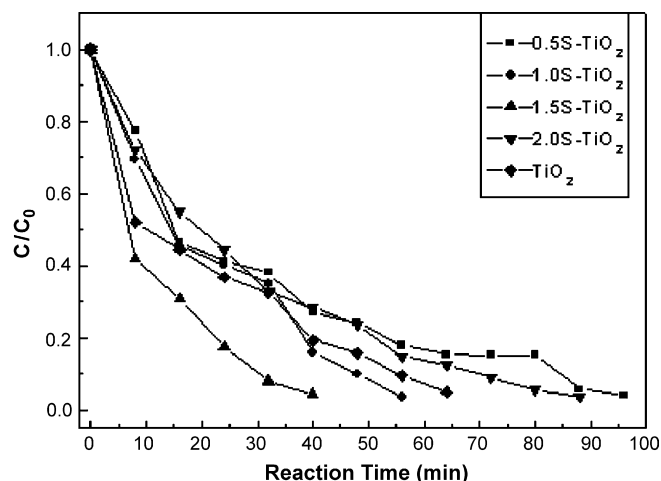


Fig. 4. Methyl orange degradation under UV irradiation (initial concentration of the methyl orange = 20 mg/l and catalyst = 1 g/l).

The combination of decreased particle size with S-dopant effect in 1.5% S-TiO₂ sample results in its higher photocatalytic activity.

Therefore, introducing S into TiO₂ could not only modify the ratio of the anatase to rutile phase, but also control the crystallization and development of the S-doped TiO₂ photocatalysts so as to improve the performance of TiO₂.

4. Conclusions

S-doped TiO₂ photocatalysts at a nanometer scale could be successfully synthesized at 180 °C by a hydrothermal process. The particle size and morphology, and phase/chemical compositions of the S-doped TiO₂ photocatalysts were strongly dependent on the amount of S incorporation in TiO₂. 1.5% S-TiO₂ sample with a spherical morphology and about 30 nm diameter has the best photocatalytic activity.

References

- [1] K. Honda, A. Fujishima, Electrochemical photocatalysis of water at a semiconductor electrode, *Nature* 238 (1972) 37–38.
- [2] L. Gao, Nano-sized TiO₂ Photocatalyst Materials and its Applications, Chemical Industry Press, 2002, pp. 104.
- [3] M. Kang, S.Y. Lee, C.H. Chung, S.M. Cho, G.Y. Han, B.W. Kim, K.J. Yoon, Characterization of a TiO₂ photocatalyst synthesized by the solvothermal method and its catalytic performance for CHCl₃ decomposition, *J. Photochem. Photobiol. A* 144 (2001) 185–191.
- [4] I. Mazzarino, P. Piccinini, L. Spinelli, Degradation of organic pollutants in water by photochemical reactors, *Catal. Today* 48 (1999) 315–321.
- [5] L.F. Zhang, T. Kanki, N. Sano, A. Toyoda, Development of TiO₂ photocatalyst reaction for water purification, *Sep. Purif. Technol.* 31 (2003) 105–110.
- [6] P.N. Kapoor, S. Uma, S. Rodriguez, K.J. Klabunde, Aerogel processing of MTi₂O₅ (M = Mg, Mn, Fe, Co, Zn, Sn) compositions using single source precursors: synthesis, characterization and photocatalytic behavior, *J. Mol. Catal. A* 229 (2005) 145–150.
- [7] A. Fuerte, M.D. Hernández-Alonso, A.J. Maira, A. Martínez-Arias, M. Fernández-García, J.C. Conesa, J. Soria, G. Munuera, Nanosize Ti–W mixed oxides: effect of doping level in the photocatalytic degradation of toluene using sunlight-type excitation, *J. Catal.* 212 (2002) 1–9.
- [8] B. Sun, E.P. Reddy, G. Smirniotis, Effect of the Cr⁶⁺ concentration in Cr-incorporated TiO₂-loaded MCM-41 catalysts for visible light photocatalysis, *Appl. Catal. B* 57 (2005) 139–149.
- [9] W.Y. Choi, A. Termin, M.R. Hoffmann, The role of metal ion dopants in quantum-sized TiO₂: correlation between photoreactivity and charge carrier recombination dynamics, *J. Phys. Chem.* 98 (1994) 13669–13679.
- [10] S. Mozia, M. Tomaszewska, B. Kosowska, B. Grzmil, A.W. Morawski, K. Kalucki, Decomposition of nonionic surfactant on a nitrogen-doped photocatalyst under visible-light irradiation, *Appl. Catal. B* 55 (2005) 195–200.
- [11] A. Hattori, M. Yamamoto, H. Tada, S. Ito, A promoting effect of NH₄F addition on the photocatalytic activity of sol–gel TiO₂ films, *Chem. Lett.* 8 (1998) 707–708.
- [12] T. Ohno, T. Mitsui, M. Matsumura, Photocatalytic activity of S-doped TiO₂ photocatalyst under visible light, *Chem. Lett.* 32 (2003) 364–365.
- [13] T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, Band gap narrowing of titanium dioxide by sulfur doping, *Appl. Phys. Lett.* 81 (2002) 454–456.
- [14] T. Ohno, M. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui, M. Matsumura, Preparation of S-doped TiO₂ photocatalysts and their photocatalytic activities under visible light, *Appl. Catal. A* 265 (2004) 115–121.
- [15] H.X. Li, X.Y. Zhang, Y.N. Huo, J. Zhu, Supercritical preparation of a highly active S-doped TiO₂ photocatalyst for methylene blue mineralization, *Environ. Sci. Technol.* 41 (2007) 4410–4414.
- [16] K. Byrappa, M. Yoshimura, Handbook of Hydrothermal Technology, William Andrew Publishing, 2001, pp. 875.
- [17] M.L. Zhang, T.C. An, X.H. Hu, C. Wang, G.Y. Sheng, J.M. Fu, Preparation and photocatalytic properties of a nanometer ZnO–SnO₂ coupled oxide, *Appl. Catal. A* 260 (2004) 215–222.
- [18] J.F. Zhu, W. Zheng, B. He, J.L. Zhang, M. Anpo, Characterization of Fe–TiO₂ photocatalysts synthesized by hydrothermal method and their photocatalytic reactivity for photodegradation of XRG dye diluted in water, *J. Mol. Catal. A* 216 (2004) 35–43.
- [19] F. Fresno, J.M. Coronado, D. Tudela, J. Soria, Influence of the structural characteristics of Ti_{1–x}Sn_xO₂ nanoparticles on their photocatalytic activity for the elimination of methylcyclohexane vapors, *Appl. Catal. B* 55 (2005) 159–167.
- [20] R. Anpo, T. Shima, S. Kodama, Y. Kubokawa, Photocatalytic hydrogenation of propyne with water on small-particle titania: size quantization effects and reaction intermediates, *J. Phys. Chem.* 91 (1987) 4305–4310.
- [21] R.I. Bickley, T. González-Carreño, J.S. Lees, L. Palmisano, R.J.D. Tilley, A structural investigation of titanium dioxide photocatalysts, *J. Solid State Chem.* 92 (1999) 178–190.
- [22] T. Kawahara, Y. Konishi, H. Tada, N. Tohge, J. Nishii, S. Ito, A patterned TiO₂(anatase)/TiO₂(rutile) bilayer-type photocatalyst: effect of the anatase/rutile junction on the photocatalytic activity, *Angew. Chem. Int. Ed.* 41 (2002) 2811+.