Codoped Rutile TiO$_2$ as a New Photocatalyst for Visible Light Irradiation

Hongyan Liu and Lian Gao*

*State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics,
Chinese Academy of Sciences, Shanghai 200050, P. R. China*

(S, La$_2$O$_3$)-codoped rutile TiO$_2$ was synthesized by in situ hydrothermal method. The (S, La$_2$O$_3$)-codoped rutile TiO$_2$ treated at 200 °C exhibited the highest photocatalytic activities for degradation of methylene blue (MB) under visible light irradiation. The synergistic effects of S and a small quantity of La$_2$O$_3$ made the degradation rate of MB as high as 98.4%.

Titanium dioxide (TiO$_2$) is a promising material for the photodegradation of organics present in polluted water and air, and for the splitting water to produce H$_2$. However, because of its large band gap of 3.0–3.2 eV, only in the small UV fraction of solar light, about 2–4%, can be utilized. In recent years, many attempts to dope transitional metals into n-TiO$_2$[1] have been made in order to absorb light in the visible region of the solar spectrum. According to the pioneering works of Asahi et al.[2] some groups demonstrated the substitution of anion atoms such as nitrogen,[3] sulfur,[4] fluorine,[5] and carbon[6] for oxygen. Domen et al. reported the Ti-based oxynitrides[7] and Ti-based oxysulfide[8] as visible light irradiation photocatalysts. Therefore, the synergistic effects of rare earth elements and anions such as S and La in TiO$_2$ will maybe enhance highly the photocatalytic properties. Anatase with lower agglomeration and smaller particle size usually shows higher photocatalytic activity than that of rutile TiO$_2$ since rutile is normally prepared by calcination of anatase at high temperatures.[9] Because the band gap energy of anatase is so large that it only shows photocatalytic activities under UV light irradiation of wavelength <387 nm, corresponding to its band gap value of 3.2 eV.

In this study, a small quantity of lanthanum (0.03 mol %) and sulfur are codoped in rutile n-TiO$_2$. The high degradation rate of an organic compound reached to 98.4%. Compared to the S-doping and La-doping, respectively, the synergistic effect of S and La$_2$O$_3$ resulted in the highest photocatalytic activity under visible light irradiation.

Titanium tetrachloride (98%, TiCl$_4$) was used as a main starting material without any further purification. A titanium tetrachloride aqueous solution (0.8 mol/L) was mixed with thiourea (CS(NH$_2$)$_2$) at a molar ratio of 1:1 and 0.03 mol % La(NO$_3$)$_3$· 6H$_2$O, and in the presence of 1 mol % polyethylene glycol (PEG). The mixture solution was stirred in an ice-water bath and charged into a 100-mL teflon-lined stainless steel autoclave. The hydrothermal preparations were carried out at different temperatures for 2 h. The precipitated titanium oxide was repeatedly washed with distilled water to remove chloride ions, and then dried at 333 K in vacuum.

The XRD patterns (Figure 1a) show that the only phase is rutile without any impurity phases. Samples A, B, C, and D were undoped, S-doped, La$_2$O$_3$-doped, and (S, La$_2$O$_3$)-codoped TiO$_2$ by hydrothermal treatment, respectively. The crystallite sizes of the samples A, B, C, and D were determined to be 12, 17, 12, and

22 nm, respectively, from the half-width of the 110 peak by using the Scherrer equation ($t = 0.89\lambda/B\cos\theta$). Lattice parameters were calculated to determine whether the sulfur and lanthanum could enter the TiO$_2$ lattice, the cell volumes of undoped, S-doped, La$_2$O$_3$-doped, and (S, La$_2$O$_3$)-codoped TiO$_2$ are 62.21, 62.67, 62.44, and 62.44 Å^3, respectively. The S content of (S, La$_2$O$_3$)-codoped TiO$_2$ is about 0.504 mol % according to ICP analysis. S atoms could somewhat enter the TiO$_2$ lattice. In this experiment, the in situ hydrothermal synthesis made the La^{3+} either replace the Ti^{4+} site or go to the interstitial position, because the ionic radii value of doped La^{3+} is between those of Ti^{4+} and O^{2-} (1.132 Å), Sibu et al. found that some of La^{3+} ions replaced Ti^{4+} ions from the FTIR spectral analysis.[10] Because of the mismatch of the ionic sizes of Ti^{4+} and La^{3+} (0.68 and 1.016 Å, respectively), there is also a chance for the La^{3+} ions to go to the interstitial position.
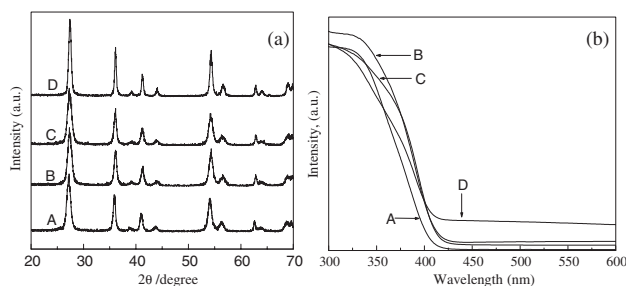

Figure 1. (a) XRD patterns, (b) UV–vis absorption spectra of samples prepared by hydrothermal treatment at 200 °C for 2 h. Samples A, B, C, and D were undoped, S-doped, La$_2$O$_3$-doped, and (S, La$_2$O$_3$)-codoped TiO$_2$, respectively.

The UV–vis absorption spectra of the samples are shown in Figure 1b, which were recorded on a Shimadzu Uv-3101PC spectrophotometer. Compared to the undoped TiO$_2$, the absorption edge is slightly shifted to the lower-energy region in the spectrum of the S-doped, La$_2$O$_3$-doped, and (S, La$_2$O$_3$)-coded TiO$_2$. Umebayashi et al. studied the band gap narrowing of titanium dioxide by sulfur doping.[4] When TiO$_2$ was doped with S, The S 3p states were somewhat delocalized, thus greatly contributing to the formation of valence band with the O 2p and Ti 3p states. Consequently, the mixing of the 3p states with valence band increases the width of the valence band itself. This result is a decrease in the band gap energy due to S doping. The absorption of (S, La$_2$O$_3$)-doped TiO$_2$ in the visible light region is stronger than that of S-codoped TiO$_2$, which is probably caused by the color of the lanthana-doped TiO$_2$.

Visible-light photocatalytic reactions were carried out to characterize the degradation rate of methylene blue (MB) in an aqueous solution. A 300-W medium pressure mercury lamp with a 400 nm cut off filter was used as visible light source. The sus-
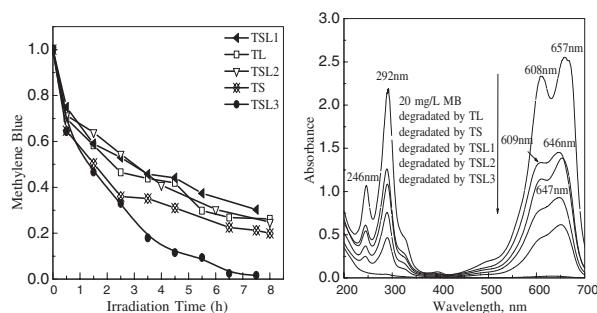
Figure 2. (a) The MB reduction rate as a function of visible-light irradiation time; (b) The UV–vis spectra of MB after degradation in aqueous photocatalyst under visible-light irradiation; TL and TS are La_2O_3-doped and S-doped TiO_2 treated at 200 °C; TSL1, TSL2, and TSL3 is (S, La_2O_3)-codoped TiO_2 treated at 150, 180, and 200 °C, respectively.

pension was stirred magnetically. 1.5-g photocatalyst powder was suspended in a 450 mL of 5.4×10^{-5} mol/L MB aqueous solutions and the absorption peak at 650 nm was monitored. Figure 2a showed that (S, La_2O_3)-codoped TiO_2 prepared by hydrothermal treatment at 200 °C exhibited a higher visible-light photocatalytic activity than S-doped and La_2O_3-doped TiO_2. The degradation of MB by S-doped TiO_2 and (S, La_2O_3)-codoped TiO_2 were significant before 2.5 h; but the photoactivities of S-doped TiO_2 decreased after 2.5 h. This was maybe because the intermediates are absorbed on the surface of S-doped TiO_2 and retarded further degradation of MB. After degradating MB, the color of S-doped TiO_2 powder changed into grayish-pink because of the intermediates absorbance. The average crystallite sizes of codoped TiO_2 treated at 150, 180, and 200 °C were 12, 17, and 22 nm, respectively. With the increasing temperature, the particle crystallization was increased; and the probability of the surface reaction of electrons and holes with MB molecules was increased. Thus, the photocatalytic activity of TSL3 is better than that of TSL1 and TSL2. The high activity of (S, La_2O_3)-codoped TiO_2 may be not only due to the contribution of S 3p states but the differences in the interactions between lanthana and TiO_2. According to the XPS results, the lanthanum ions were rich on the surface (1.7 atom %), which decreased the surface energy and inhibited the recombination of photoexcited carriers. Furthermore, at the surface of the powders, Ti atom is replaced by a lanthanum ion with a +3 oxidation state, creating a charge imbalance. The charge imbalance must be satiated; therefore, more hydroxide ions would be absorbed on the surface for charge balance. These hydroxide ions on the surface can accept holes generated by illumination and form hydroxyl radicals that oxidize absorbed molecules, preventing the recombination of electron-hole photogenerated. The Ti $2p_{3/2}$ binding energy of the (S, La_2O_3)-TiO_2 treated at 200 °C was found to be 457.7 eV, which is lower than that of pure TiO_2 (458.0 eV). The Pauling electronegativity value of Ti is 1.5 and that of La is 1.1,[11] which indicate the possibility of electron transfer from lanthanum to titanium in the Ti–O–La bond. This charge transfer makes Ti more electron-rich and lowers the Ti $2p_{3/2}$ core electron binding energy. Therefore, S-doping produces states in the band gap of TiO_2 which absorb visible light, and La_2O_3-doping inhibits the recombination of carriers. The synergistic effect of S and La_2O_3 leads to a highly efficient photoca-

talytic activity for the degradation of MB.

In this experiment, (S, La_2O_3)-codoped TiO_2 (TSL3) nearly completely mineralized the MB solution (Figure 2b); and no intermediates were observed. Photocatalyzed N-demethylation of MB occurs concurrently and some intermediates are derived from the N-demethylated MB.[12] According to earlier studies of Zhang et al.[12] absorption bands of N-demethylated analogs of MB in the visible range were seen at 648–655 nm for Azure B (blue color in aqueous solution), at 620–634 nm for Azure A (blue), at 608–612 nm for Azure C (blue), and at 602.5 nm for Thionine (first yields a blue color, then a violet solution). These characteristic bands were discernible in Figure 2b. The bands at 292 and 246 nm decreased significantly and no new bands appeared. This implied that fully oxidized form and any intermediates containing the phenothiazine are not present.

In summary, (S, La_2O_3)-codoped rutile TiO_2 photocatalyst prepared by in situ hydrothermal method at 200 °C has high efficient photocatalytic activities for degradation of MB under the visible light irradiation. It nearly completely mineralized the MB solution and no intermediates were observed. Although the co-doping quantity was small, the synergistic effect of S and La_2O_3 made the degradation rate of MB reach to 98.4%. It is expected that the codoped material could be used for cell conversion, catalysis, and electronic devices and the present method can be extended to other similar photocatalysts.

References
1   W. Choi, A. Termin, and M. R. Hoffmann, *J. Phys. Chem.*, **98**, 13669 (1994); H. Tsuji, H. Sugahara, Y. Gotoh, and J. Ishikawa, *Nucl. Instrum. Methods Phys. Res., Sect. B*, **206**, 249 (2003).
2   R. Asahi, T. Morikawa, T. Ohwaki, and Y. Taga, *Science*, **293**, 269 (2001).
3   H. Irie, S. Washizuka, N. Yoshino, and K. Hashimoto, *Chem. Commun.*, **2003**, 1298; T. Morikawa, R. Asahi, T. Ohwaki, A. Aoki, and Y. Taga, *Jpn. J. Appl. Phys.*, **40**, L561 (2001); S. Yin, Q. Zhang, F. Saito, and T. Saito, *Chem. Lett.*, **32**, 358 (2003).
4   T. Umebayashi, T. Yamaki, H. Itoh, and K. Asai, *Appl. Phys. Lett.*, **81**, 454 (2002); T. Ohno, T. Mitsui, and M. Matsumura, *Chem. Lett.*, **32**, 364 (2003); T. Umebayashi, T. Yamaki, S. Tanaka, and K. Asai, *Chem. Lett.*, **32**, 330 (2003).
5   A. Hattori, M. Yamamoto, H. Tada, and S. Ito, *Chem. Lett.*, **1998**, 707; K. Nukumizu, J. Nunoshige, T. Takata, J. N. Kondo, and M. Hara, *Chem. Lett.*, **32**, 196 (2003); J. C. Yu, J. Yu, W. Ho, Z. Jiang, and L. Zhang, *Chem. Mater.*, **14**, 3808 (2002).
6   H. Irie, Y. Watanabe, and K. Hashimoto, *Chem. Lett.*, **32**, 772 (2003); S. Sakthivel and H. Kisch, *Angew. Chem., Int. Ed.*, **42**, 4908 (2003).
7   A. Kasahara, K. Nukumizu, T. Takata, J. N. Kondo, M. Hare, H. Kobayashi, and K. Domen, *J. Phys. Chem. B*, **107**, 791 (2003).
8   A. Ishikawa, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, and K. Domen, *J. Am. Chem. Soc.*, **124**, 13547 (2002).
9   R. I. Bickley, T. Gonzalez-carreno, J. S. Lees, L. Palmisano, and R. J. Tilley, *J. Solid State Chem.*, **92**, 178 (1991).
10 C. P. Sibu, S. R. Kumar, P. Mukundan, and K. G. K. Warrier, *Chem. Mater.*, **14**, 2876 (2002).
11 H. Cheng, J. Ma, Z. Zhao, and L. Qi, *Chem. Mater.*, **7**, 663 (1995).
12 T. Zhang, T. Oyama, A. Aoshima, H. Hidaka, J. Zhao, and N. Serpone, *J. Photochem. Photobiol., A*, **140**, 163 (2001); T. Zhang, T. Oyama, S. Horikoshi, H. Hidaka, J. Zhao, and N. Serpone, *Sol. Energy Mater. Sol. Cells*, **73**, 287 (2002).