Sol-Gel Preparation of La Doped Strontium Titanate

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La doped strontium titanate was prepared using sol-gel method. Pure strontium titanate has larger particle size than the La doped samples. The produced substances in the samples varied in accordance to La doping content. The La doped strontium titanate might be composed of Sr_2TiO_4 , $\text{Sr}_{1.9}\text{La}_{0.1}\text{TiO}_{3.95}$, $\text{Sr}_{0.8}\text{La}_{0.2}\text{TiO}_3$ and a small per cent of TiO_2 with respect to La content. The doping of La can improve the activity of the materials when La content is between 2-7 %. The strontium titanate doped with more than 10 % La undergoes drastic activity declining. Adsorption rate of methyl orange on the two materials is not more than 3 % after 2 h. The doped strontium titanate has much improved activity than the sample without La doping. After 2 h of irradiation, methyl orange degradation rate is as high as 90.5 % on the 5 % La doped strontium titanate.

Key Words: La, Strontium titanate, Photocatalytic, Methyl orange.

INTRODUCTION

The aims of developing new photocatalyst and promoting activity of currently well studied materials are the two major research focuses. Perovskite structured composite metal oxides were well studied as a potential photocatalytic material due to high mobilization of charge carriers and the visible light responsible band structure^{1,2}. Strontium titanate is a kind of perovskite structured material, which has been widely used as an electronic ceramic in various industrial applications³. As a functional material, strontium titanate has good photocatalytic activity and suitable band edge (3.2-3.8 eV) and has been used in photocatalytic field such as photochemical cell⁴, photocatalytic water splitting⁵ and degradation of organic pollutants⁶.

In order to obtain strontium titanate with high purity and quality, recently many kinds of preparation methods have been investigated⁷⁻¹⁰. Metal ion doping is an effective method to improve activity of photocatalytic material. It is recognized that the doped metal ions can provide new energy level in the material and extend light responding spectrum^{11,12}. In this paper, tetrabutyl titanate and strontium nitrate were used as initial materials in a sol-gel process to prepare La doped strontium titanate. The main focus of this paper was to study effects of La doping on phase composition, structure and photocatalytic activity of the strontium-titanium.

EXPERIMENTAL

In this paper, La doped strontium titanate was prepared by a modified sol-gel method. 10 mL acetic acid was mixed

with 10 mL deionized water and then different amount of strontium nitrate and lanthanum chloride was dissolved in the former solution to obtain solution A, where molar ratio of $n(\text{Sr})/n(\text{Ti})$ was 1:1. 1.7 mL of tetrabutyl titanate was dissolved in absolute ethanol under magnetic stirring for 10 min to obtain solution B with volume ratio of $[\text{Ti}(\text{OC}_4\text{H}_9)_4]:(\text{C}_2\text{H}_5\text{OH}) = 1:45$. After that, solution B was dropped into warm solution A at a constant speed under continuous vigorous magnetic stirring. A small amount of ethylene glycol was added into the mixture acting as stabilizer. The mixture was kept under stirring until a sticky sol formed. After 24 h of ageing at room temperature, the sol was dried at 110 °C for 8 h to obtain a gel, followed by calcination of the gel at 800 °C for 3 h. The calcination products were grinded to obtain strontium titanate with different La doping content.

Characterization: Scanning electron microscope (SEM) images were taken on a HTACHI S-3400N scanning electron microanalyzer. The samples for SEM imaging were coated with a thin layer of gold film to avoid charging. The crystalline phases of the photocatalysts were measured by X-ray diffraction (XRD) with D/max-rB diffractometer using a $\text{CuK}\alpha$ radiation. FT-IR spectra of the samples were obtained using a Fourier transform infrared (FT-IR) spectrometer (WQF-410) with KBr pellets. The N_2 -adsorption and desorption of the samples were measured by F-Sorb 3400 specific surface area analytical instrument. Specific surface areas were calculated from N_2 desorption isotherms, according to BET equation.

Adsorption and photocatalytic activity: Prior to photocatalytic experiment, methyl orange adsorption on the photo-

catalyst in the dark was measured in the suspension of photocatalyst. 30 mL of 5 mg/L aqueous solution of methyl orange was mixed with 1000 mg/L photocatalyst in a 60 mL quartz reactor. The suspension was stirred magnetically for 25 min to reach adsorption equilibrium. After that, 5 mL of the suspension was taken out of the reactor and filtrated through a Millipore filter (pore size 0.45 μm) to remove the photocatalyst. Finally, absorbency of the solution was measured by a 721E spectrophotometer at the maximum absorption wavelength of methyl orange (468 nm).

Subsequently, photocatalytic activities were evaluated in the above mentioned photocatalytic reactor. A 20 W UV lamp was located at the top of the reactor with the distance of 5 cm. The lamp can irradiate UV light at wavelength of 253.7 nm with the intensity of 2200 mW/cm². The irradiation time in the subsequent experiments was set to 0.5 h if not indicated. The suspensions were filtrated through the Millipore filter before measuring.

RESULTS AND DISCUSSION

SEM images of strontium titanate doped with different content of La are shown in Fig. 1. The samples present various surface morphologies as the factor of La doping content. Although all the samples have fairly rough surface morphology, the pure strontium titanate has noticeable larger particle size than the La doped samples. Surface areas of the samples containing 0, 1, 5 and 15 % La are 9.0, 20.3, 36.0 and 22.3 m² g⁻¹, respectively. The particle size shrinkage with increasing La content leads to even rough surface morphology and high surface area, which is beneficial to adsorption and photocatalytic activity¹³.

Fig. 1. SEM images of strontium titanate doped with different content of La (a: 0 %, b: 1 %, c: 5 %, d: 15 %)

Fig. 2 illustrates XRD patterns of strontium titanate doped with different content of La. The substances in the produced samples varied in accordance to La doping content. When La content is 1 %, the XRD pattern is the same to that of pure strontium titanate. The samples are composed of Sr₂TiO₄ and TiO₂. As calculated using peak intensities of the two phases, volume percentages of the two phases are 84.5 and 15.5 %. The main substance in the samples is Sr₂TiO₄.

Fig. 2. XRD patterns of strontium titanate doped with different content of La

When La content increases to 5 %, diffraction peaks of Sr_2TiO_4 nearly disappear and a new substance $\text{Sr}_{1.9}\text{La}_{0.1}\text{TiO}_{3.95}$ takes place. A small amount of TiO_2 also exists in the sample. The volume percentages of $\text{Sr}_{1.9}\text{La}_{0.1}\text{TiO}_{3.95}$ and TiO_2 are 89.4 and 10.6 %, respectively. In the sample containing 15 % of La, another new substance, $\text{Sr}_{0.8}\text{La}_{0.2}\text{TiO}_3$ takes place of $\text{Sr}_{1.9}\text{La}_{0.1}\text{TiO}_{3.95}$. Low amount of La can enter the crystallite structure of strontium titanate and does not alter the structure of the material. However, excessive amount of La ions may substitute the Sr ions in the crystallite structure and makes changes to the perovskite structured material.

FT-IR spectra of the strontium titanate doped with different content of La are shown in Fig. 3. There is no adsorption after 2000 cm^{-1} , indicating that organic substances decomposed totally during high temperature calcination. The adsorption peak around 1560 cm^{-1} represents bending vibration of -OH in H_2O that was adsorbed on surface of the sample¹⁴. The adsorption peak situated at 1084 cm^{-1} is assigned to vibration of La-O and the peak at 1030 cm^{-1} is assigned to vibration of Sr-O bond. The adsorption peak appeared at 489 cm^{-1} can be ascribed to be bending vibration of Ti-O-Ti¹⁵. The results are in accordance to composition revealed by XRD analysis. As indicated before, the La doped strontium titanate are composed of Sr_2TiO_4 , $\text{Sr}_{1.9}\text{La}_{0.1}\text{TiO}_{3.95}$, $\text{Sr}_{0.8}\text{La}_{0.2}\text{TiO}_3$ and a small percent of TiO_2 . The La-O, Sr-O and Ti-O-Ti bonds are representatives of the produced substances.

Fig. 3. FT-IR spectra of strontium titanates doped with different content of La

The content of doped La has important influence on photocatalytic activity of the strontium titanate (Fig. 4). The doping of La can improve the activity of the materials when La content is between 2-7 %. The doped La can provide new energy level in the materials and extend the lifetime of photogenerated electrons and holes. The increasing surface area after La doping can also help on promoting photocatalytic activity. The reason is that the produced substances are different with the variation of La content. Obviously, these substances have different activity for degradation of methyl orange.

Fig. 4. Effect of La content in strontium titanate on the degradation rate of methyl orange

The strontium titanate doped with more than 10 % La undergoes drastic activity declining. This can be attributed to low activity of the produced $\text{Sr}_{0.8}\text{La}_{0.2}\text{TiO}_3$ and an other reason may be the crystalline defects produced at high La content^{16,17}. These defects can be the recombination center for charge carriers and reduce photocatalytic activity. The strontium titanate doped with 5 % La showed the optimum photocatalytic activity.

Photocatalytic activity of strontium titanate doped with 5 % La is compared with strontium titanate without La (Fig. 5). Adsorption rate of methyl orange on the two materials is not more than 3 % after 2 h. The doped strontium titanate has much improved activity than the sample without La doping. After 2 h of irradiation, degradation rate of methyl orange is as high as 90.5 % on the 5 % La doped strontium titanate.

Fig. 5. Effect of irradiation time on the decoloration rate of methyl orange

Conclusion

The effects of La doping in strontium-titanium on phase composition, structure and photocatalytic activity were studied. The samples present various surface morphologies as the factor of La doping content. The substances in the produced samples

varied in accordance to La doping content. The strontium titanate doped with 5 % La showed the optimum photocatalytic activity. The doped strontium titanate has much improved activity than the sample without La doping.

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REFERENCES

1. H.W. Eng, P.W. Barnes, B.M. Auer and M. Woodward, *Solid State Chem.*, **175**, 94 (2003).
2. H. Kato and A. Kudo, *Photochem. Photobiol. A*, **145**, 129 (2001).
3. E.M. Sbaolsky, A.R. Jmae, S. Kwom, S. Troler-McKinstry and G.L. Messing, *Appl. Phys. Lett.*, **78**, 2551 (2001).
4. K. Akuto and Y. Sakurai, *J. Electrochem. Soc.*, **148**, A121 (2001).
5. M. Avudaithai and T.R.N. Kutty, *Mater. Res. Bull.*, **22**, 641 (1987).
6. J.A.I. Joice, G. Ramya, R. Vaithiyanathan, R. Ramakrishnan and T. Sivakumar, *Asian J. Chem.*, **24**, 5766 (2012).
7. S. Zhang, J.X. Liu, Y.X. Han, B.C. Chen and X.G. Li, *Mater. Sci. Eng. B*, **110**, 11 (2004).
8. H.X. Liu, X.Q. Sun, Q.L. Zhao, J. Xiao and S.X. Ouyang, *Solid-State Electron.*, **47**, 2295 (2003).
9. J.S. Wang, S. Yin, M. Komatsu, Q.W. Zhang, F. Saito and T. Sato, *J. Photochem. Photobiol. A*, **165**, 149 (2004).
10. X.W. Wang, Z.Y. Zhang and S.X. Zhou, *Mater. Sci. Eng. B*, **86**, 29 (2001).
11. Y. Matsumoto, U. Unal, N. Tanaka, A. Kudo and H. Kato, *J. Solid State Chem.*, **177**, 4205 (2004).
12. H. Kadowaki, N. Saito, H. Nishiyama, H. Kobayashi, Y. Shimodaira and Y. Inoue, *J. Phys. Chem.*, **111**, 439 (2007).
13. Y. Qin, G. Wang and Y. Wang, *Catal. Commun.*, **8**, 926 (2007).
14. K.-D. Kim and T. Khalil, *J. Non-Crys. Solids*, **195**, 218 (1996).
15. Q. Li, H.J. Su and T.W. Tan, *Biochem. Eng. J.*, **38**, 212 (2008).
16. T. Ishii, H. Kato and A. Kudo, *Photochem. Photobiol. A*, **163**, 181 (2004).
17. M. Miyauchi, M. Takashio and H. Tobimatsu, *Langmuir*, **20**, 232 (2004).