Research Journal of Nanoscience and Engineering
Volume 3, Issue 1, 2019, PP 1-4
ISSN 2637-5591

Synthesis, Characterization and Photocatalytic Activity of Strontium (II)-Doped Titanium Dioxide Powders

Chien-Hsin Yang[a], Yi-Chyun Hsu[b], Wen-Churng Lin[b,*]

[a] *Department of Chemical and Materials Engineering, National University of Kaohsiung, Kaohsiung 81148, Taiwan*
[b] *Department of Environmental Engineering, Kun Shan University, Tainan 71070, Taiwan*

***Corresponding Author:** Wen-Churng Lin, Department of Environmental Engineering, Kun Shan University, Tainan 71070, Taiwan E-mail: linwc@mail.ksu.edu.tw*

ABSTRACT

Titanium dioxide powders modified with specific metal or metal oxide could be used as photocatalyst with visible light activity. In this work, different concentration of strontium (II) doped TiO_2 photocatalyst powders were prepared from alkoxide solutions containing polyethylene glycol (PEG) via the sol–gel method and by calcination of a mixture of $SrCl_2{\cdot}6H_2O$ and titanium dioxide sol solution. And they were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Brunauer – Emmett–Teller (BET)-specific surface area, transmission electron microscopy (TEM), and Ultraviolet–Visible (UV-Vis) spectroscopy.

Sr^{2+}-doping in the TiO_2 decreases the crystal grain size, increases the specific surface areas of powders, extends the absorption to visible light regions, and exhibits the vis-photocatalytic activity for methylene blue (MB) degradation. Appropriate content of Sr^{2+}-doping is an effective means to improve the photocatalytic activity of TiO_2 for MB degradation under visible light irradiation.

Keywords: *Titanium Dioxide, Sol-gel, Visible light, Photocatalyst*

INTRODUCTION

A semiconductor is characterized by a filled valence band and an empty conduction band. When it is irradiated with light of sufficient energy corresponding to or exceeding its band gap, an electron is promoted into the conduction band, leaving a hole in the valence band. The electrons and holes are good reductants and powerful oxidants, respectively, and they can initiate redox reactions on the semiconductor surface [1]. Titanium dioxide was one of the most widely studied photocatalytic semiconductors in the past decades, because of its excellent capability of degrading a large variety of environmental contaminants such as organics, bacteria, viruses. Although TiO_2 has a great potential to be used for water purification and air remediation, only the ultraviolet light can be used due to its wide bandgap, which is less than 5% of the solar energy reached the earth surface. Furthermore, the efficiency of photocatalytic reactions is limited by the high recombination rate of photo induced electron–hole pairs formed in photocatalytic processes. Many studies have been devoted to the improvement of photocatalytic efficiency of TiO_2, such as depositing noble metals [2-5] and doping metal or nonmetal ions [6-9]. Generally, the introduction of doped ions can result in the formation of a doping energy level between the conduction and valence bands of TiO_2. In principle, it should be possible for doped TiO_2 to extend its absorption into the visible region effectively. In this work, TiO_2 doped with different amounts of Sr^{2+} was realized by sol–gel method. A systematic characterization was conducted. The photo degradation of methylene blue was chosen as a model reaction to evaluate the photocatalytic activity of prepared samples and the effects of Sr^{2+}-doping on the activity were also discussed.

EXPERIMENTAL SECTION

Preparation of Sr-TiO_2 Photocatalysts

Sr^{2+}-doped TiO_2 photocatalyst powders were prepared by sol-gel method using titanium tetraisopropoxide (TTIP) and strontium chloride as the precursors, iso-propanol (IPA) as the solvent, acetylacetone (AcAc) as the stabiliser, polyethylene glycol (PEG) as the structure -

directing agent, and hydrochloric acid (HCl) as a catalyst. The typical preparing process was as follows: Added 10 ml TTIP, 6.86 ml AcAc, and 20 ml IPA sequentially into a Pyrex reactor under magnetic stirring; then added sequentially 1 g PEG, 2 ml 2 N HCl, and the required amount of cupric nitrate. Finally 5 ml deionized water was added drop-wise into the above solution with a burette under stirring. The resultant alkoxide solution was kept refluxing at the temperature of 50–60 °C for 2 h, resulting in the titania sol. After the consecutive procedures of drying, calcination, and grinding, the desired photocatalysts were obtained. For convenience sake, the samples were labeled as m Sr-TiO_2, where “m” refers to the molar percentage concentration of Sr^{2+}. For example, a sample labeled as 0.01 Sr-TiO_2, which implied the sample had been doped with 1 mol% Sr^{2+}. For comparison, pure TiO_2 was also prepared without adding strontium chloride in the same way.

Characterization of Samples

The surface chemical states of the Sr-TiO_2 powders was detected by X-ray photoelectron spectroscopy (XPS) (Ulvac-Phi, Model ES 650). The crystalline phase for the photocatalyst powders obtained was identified by an X-ray diffractometer (XRD) (Rigaku, Rint-2000). The specific surface area of the as-prepared Sr-TiO_2 powders was determined by a BET analyzer (Micromeritics, ASAP 2101), and the surface morphologies and particle size were observed by a transmission electron microscopy (TEM) (Philips, CM-200). A spectrophotometer (Hitachi, U-3010) equipped with an integrating sphere was used to record the UV-Vis absorption spectra of the powder samples.

Evaluation of the Photocatalytic Activity of Sr-TiO_2.

The photocatalytic degradation of MB in water was carried out in a double-walled cylindrical Pyrex glass reactor. The reactor was equipped with water circulation in the outer jacket in order to maintain a constant temperature of 25 °C. A 300 ml of 20 ppm MB solution and 0.1 g photocatalyst powders were introduced into the reactor. The visible light irradiation (>380 nm) was achieved by cutting off the UV radiation of a 23 W fluorescent lamp with a glass filter (ZUL0400, Asahi Spectra Co.). Before irradiation the suspension was stirred in the dark for 1 h to reach adsorption equilibrium. The concentration of aqueous MB was sampled once per hour and determined with a UV-Visible spectrophotometer.

RESULTS AND DISCUSSION

Characterization of Samples

The presence of Ti 2p, O 1s, and Sr 3d signals in the XPS spectra of the Sr^{2+}-doped TiO_2 sample demonstrated the as-synthesized powders consist of Ti, O, and Sr elements. Fig. 1 shows the high-resolution Sr3d spectrum of the 0.005Sr-TiO_2 powders. The peak centered at 135.2 eV, which accorded with the results observed by Reddy *et al.* [10].

The XRD patterns of 0.01 Sr-TiO_2 powders calcined at different temperatures for 2 h are shown in Fig. 2. As seen, some of anatase transformed into rutile in the powder while the sample was calcined above 800 °C. To prevent the Sr^{2+}-doped TiO_2 photocatalyst from forming rutile crystal and losing its decomposition ability to pollutants, the temperature of 750 °C was adopted as the selected calcination temperature in the subsequent preparation experiments. Furthermore, no peaks due to various Sr species were detected in Fig. 2, which suggests that Sr species were uniformly dispersed in TiO_2 powder.

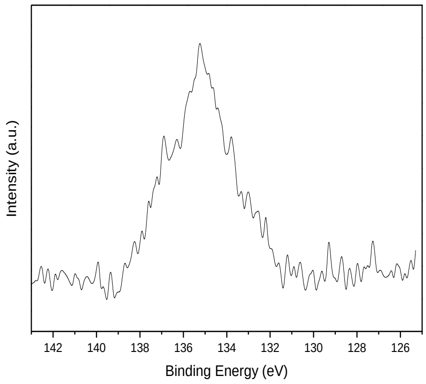

Fig1. *Sr 3d XPS spectrum of the 0.005Sr-TiO_2 powders.*

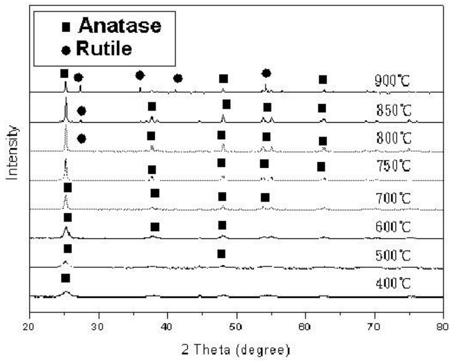

Fig2. *XRD patterns of 0.01Sr-TiO_2 calcined at different temperature.*

Fig. 3 shows the TEM micrographs of some as-prepared samples calcined at 750 °C. From the TEM images, we can find the morphologies of these samples present anomalistic sphericity and the particle size range of the Sr^{2+}-doped TiO_2 is about 10–40 nm whereas the particle size of undoped pure TiO_2 particles obtained from the same preparation conditions is 50–80 nm. The crystallite size of Sr^{2+}-doped TiO_2 decreases as compare pure TiO_2 calcined at the same temperature. Crystallite size decrease of Sr^{2+}-doped nanoparticles leads to the increase of specific surface areas. The specific surface areas of the Sr^{2+}-doped TiO_2 powders obtained in this work are 9.2–18.3 m^2g^{-1} from BET analyses, while that of undoped TiO_2 is around 8.5 m^2g^{-1}. A close observation reveals that the surface areas of Sr^{2+}-doped samples are always larger than that of undoped TiO_2. There is no doubt that the increase of surface area of Sr^{2+}-doped samples is due to the decrease of the grain size, which is consistent with the results of TEM.

The UV-Vis absorption spectra of the samples show that the onset of absorption is shifted to longer wavelengths (red shift) with increasing Sr^{2+} content in the TiO_2 matrix. Moreover, the spectra exhibit a progressive increase in absorbance with an increase in Sr content. It can be concluded that Sr modified TiO_2 extends its absorption into the visible region effectively.

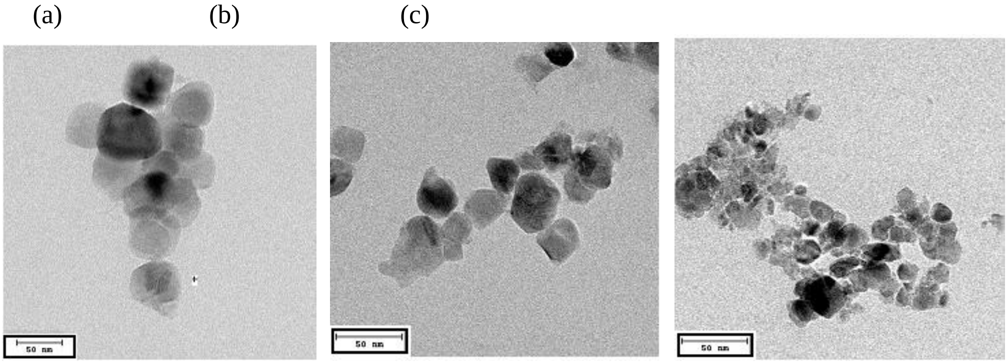

Fig3. *TEM images of: (a) undoped TiO_2; (b) 0.005Sr-TiO_2; (c) 0.05Sr-TiO_2*

Evaluation of Photocatalytic Activity

Table 1 shows the photocatalytic degradation rate ($(C_o\text{-}C)/C_o \times 100\%$, where C_o and C represent the initial concentration and the reaction concentration of MB at any time, respectively.) of MB in water over Sr^{2+}-doped TiO_2 photocatalysts with different Sr^{2+} dopant content after 10-hour visible light irradiation. It can be found that the degradation rate of MB is decreased with increase in Sr^{2+} dopant content. Over 0.005Sr-TiO_2, the degradation rate is the highest, which could be attributed to the appropriate amount of oxygen vacancies and doped Sr^{2+} ions on the surface layer of TiO_2 can effectively capture the photoinduced electrons. While in more Sr^{2+} dopant content (> 0.5 mol%), the excessive oxygen vacancies and Sr species can become the recombination centers of photoinduced electrons and holes. Meanwhile, excessive strontium oxides can cover the surface of TiO_2, leading to decrease in the photocatalytic activity of photocatalyst.

Table1. *Photocatalytic degradation rate of MB on different Sr^{2+}-doped amount TiO_2 under visible light irradiation.*

Sample	0.005Sr-TiO_2	0.01Sr-TiO_2	0.05Sr-TiO_2	0.09Sr-TiO_2	0.2Sr-TiO_2
Degradation rate	0.3975	0.3419	0.2407	0.2129	0.1239

CONCLUSIONS

Different concentration of strontium (II) doped TiO_2 had been successfully synthesized through the sol-gel method. XRD results confirmed the formation of pure anatase phase of TiO_2 in all samples. The increase of Sr^{2+} doping inhibited the particle growth, increased the specific surface areas of powders. Strontium ion in TiO_2 may change the band gap between conduction and valence bands. Thus, Sr^{2+}-doped titania acquires the capability of absorbing visible light and shows a red-shift in the UV-Vis spectra. The results of photocatalytic reaction indicate that the Sr^{2+}-doped TiO_2 has higher activity than pure TiO_2 under visible light irradiation. In our experiment condition, 0.5 mol% Sr^{2+}-doped TiO_2 exhibited a significant vis-photocatalytic activity for MB degradation.

REFERENCES

[1] X. Yang, C. Cao, K. Hohn, L. Erickson, R. Maghirang, D. Hamal, K. Klabunde, J. Catal. 252 (2007) 296–302.

[2] B. Sun, A.V. Vorontsov, P.G. Smirniotis, Langmuir 19 (2003) 3151–3156.

[3] H. Einaga, T. Ibusuki, S. Futamura, Environ. Sci. Technol. 38 (2004) 285–289.

[4] S. Kim, W. Choi, J. Phys. Chem. B 106 (2002) 13311–13317.

[5] T.G. Schaaff, D.A. Blom, Nano. Lett. 2 (2002) 507–511.

[6] A. Patra, C.S. Friend, R. Kapoor, P.N. Prasad, Chem. Mater. 15 (2003) 3650–3655.

[7] J. Premkumar, Chem. Mater. 16 (2004) 3980–3981.

[8] J.D. Bryan, S.M. Heald, S.A. Chambers, D.R. Gamelin, J. Am. Chem. Soc. 126 (2004) 11640–11647.

[9] M. Mrowetz, W. Balcerski, A.J. Colussi, M.R. Hoffmann, J. Phys. Chem. B 108 (2004) 17269–17273.

[10] B.M. Reddy, K.J. Ratnam, P. Saikia, G. Thrimurthulu, J. Mol. Catal. A 276 (2007) 197–204.

Citation: *Chien-Hsin Yang, Yi-Chyun Hsu, Wen-Churng Lin, "Synthesis, Characterization and Photocatalytic Activity of Strontium (II)-Doped Titanium Dioxide Powders", Research Journal of Nanoscience and Engineering, vol. 3, no. 1, pp.1-4, 2019.*