

Research Article

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

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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 TiO₂ photocatalyst powders were prepared from alkoxide solutions containing Polyethylene Glycol (PEG) *via* the sol-gel method and by calcination of a mixture of SrCl₂·6H₂O 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.

Sr²⁺-doping in the TiO₂ 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 Sr²⁺-doping is an effective means to improve the photocatalytic activity of TiO₂ 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, and viruses. Although TiO₂ 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 photoinduced electron-hole pairs formed in photocatalytic processes. Many studies have been devoted to the improvement of photocatalytic efficiency of TiO₂, 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 TiO₂. In principle, it should be possible for doped TiO₂ to extend its absorption into the visible region effectively. In this work, TiO₂ doped with different amounts of Sr²⁺ 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 Sr²⁺-doping on the activity were also discussed.

Experimental Section

Preparation of Sr-TiO₂ photocatalysts

Sr²⁺-doped TiO₂ photocatalyst powders were prepared by sol-gel method using Titanium Tetra Isopropoxide (TTIP) and strontium chloride as the precursors, IsoPropanol (IPA) as the solvent, Acetylacetone (AcAc) as the stabilizer, 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°C to 60°C for 2 h, resulting in the titania sol. After the consecutive procedures of drying, calcination, and grinding, the desired photocatalysis were obtained. For convenience sake, the samples were labeled as m Sr-TiO₂, where “m” refers to the molar percentage concentration of Sr²⁺. For example, a sample labeled as 0.01 Sr-TiO₂, which implied the sample had been doped with 1 mol% Sr²⁺. For comparison, pure TiO₂ was also prepared without adding strontium chloride in the same way.

Characterization of samples

The surface chemical states of the Sr-TiO₂ powders were detected by X-ray Photoelectron Spectroscopy (XPS) (Ulvac-Phi, Model ES 650). The crystalline phase for the photocatalyst powders obtained

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was identified by an X-ray Diffract meter (XRD) (Rigaku, Rint-2000). The specific surface area of the as-prepared Sr-TiO₂ 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-TiO₂

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 Sr²⁺-doped TiO₂ sample demonstrated the as-synthesized powders consist of Ti, O, and Sr elements. Figure 1 shows the high-resolution Sr 3d spectrum of the 0.005 Sr-TiO₂ 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-TiO₂ powders calcined at different temperatures for 2 h are shown in Figure 2. As seen, some of anatase transformed into rutile in the powder while the sample was calcined above 800°C. To prevent the Sr²⁺-doped TiO₂ 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 Figure 2, which suggests that Sr species were uniformly dispersed in TiO₂ powder.

Figure 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 anomalous sphericity and the particle size range of the Sr²⁺-doped TiO₂ is about 10 nm to 40 nm whereas the particle size of undoped pure TiO₂ particles obtained

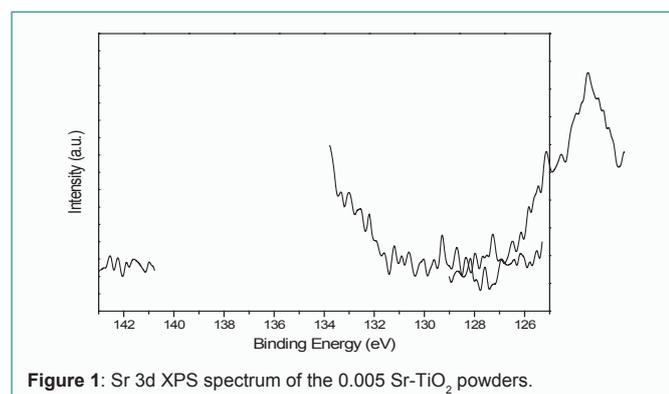


Figure 1: Sr 3d XPS spectrum of the 0.005 Sr-TiO₂ powders.

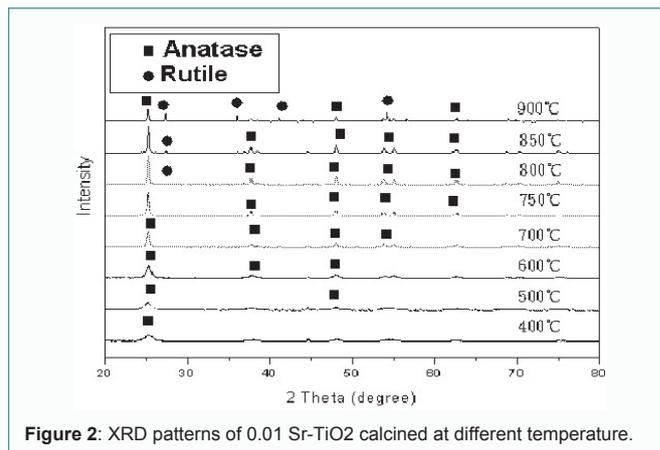


Figure 2: XRD patterns of 0.01 Sr-TiO₂ calcined at different temperature.

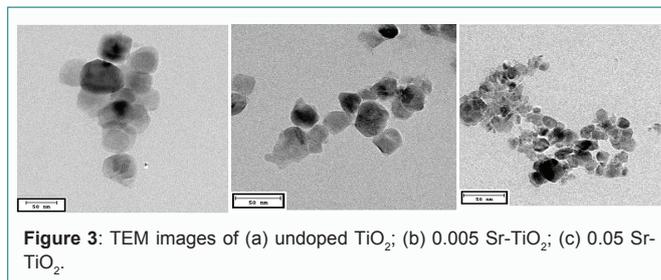


Figure 3: TEM images of (a) undoped TiO₂; (b) 0.005 Sr-TiO₂; (c) 0.05 Sr-TiO₂.

from the same preparation conditions is 50 nm to 80 nm. The crystallite size of Sr²⁺-doped TiO₂ decreases as compare pure TiO₂ calcined at the same temperature. Crystallite size decrease of Sr²⁺-doped nanoparticles leads to the increase of specific surface areas. The specific surface areas of the Sr²⁺-doped TiO₂ powders obtained in this work are 9.2 m²g⁻¹ to 18.3 m²g⁻¹ from BET analyses, while that of undoped TiO₂ is around 8.5 m²g⁻¹. A close observation reveals that the surface areas of Sr²⁺-doped samples are always larger than that of undoped TiO₂. There is no doubt that the increase of surface area of Sr²⁺-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 Sr²⁺ content in the TiO₂ matrix. Moreover, the spectra exhibit a progressive increase in absorbance with an increase in Sr content. It can be concluded that Sr modified TiO₂ extends its absorption into the visible region effectively.

Evaluation of photocatalytic activity

Table 1 shows the photocatalytic degradation rate $((C_0 - C)/C_0 \times 100\%)$, where C₀ and C represent the initial concentration and the reaction concentration of MB at any time, respectively) of MB in water over Sr²⁺-doped TiO₂ photocatalyst with different Sr²⁺ dopant content after 10-hour visible light irradiation. It can be found that the degradation rate of MB is decreased with increase in Sr²⁺ dopant content. Over 0.005 Sr-TiO₂, the degradation rate is the highest, which could be attributed to the appropriate amount of oxygen vacancies and doped Sr²⁺ ions on the surface layer of TiO₂ can effectively capture the photoinduced electrons. While in more Sr²⁺ 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 TiO₂, leading to decrease in the photocatalytic activity of photocatalyst.

Table 1: Photocatalytic degradation rate of MB on different Sr²⁺-doped amount TiO₂ under visible light irradiation.

Sample	0.005 Sr-TiO ₂	0.01 Sr-TiO ₂	0.05 Sr-TiO ₂	0.09 Sr-TiO ₂	0.2 Sr-TiO ₂
Degradation rate	0.3975	0.3419	0.2407	0.2129	0.1239

Conclusion

Different concentration of strontium (II) doped TiO₂ had been successfully synthesized through the sol-gel method. XRD results confirmed the formation of pure anatase phase of TiO₂ in all samples. The increase of Sr²⁺ doping inhibited the particle growth, increased the specific surface areas of powders. Strontium ion in TiO₂ may change the band gap between conduction and valence bands. Thus, Sr²⁺-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 Sr²⁺-doped TiO₂ has higher activity than pure TiO₂ under visible light irradiation. In our experiment condition, 0.5 mol% Sr²⁺-doped TiO₂ exhibited a significant vis-photocatalytic activity for MB degradation.

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