Research Article

Improved Visible Light Photocatalytic Activity for TiO₂ Nanomaterials by Codoping with Zinc and Sulfur

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S/Zn codoped TiO₂ nanomaterials were synthesized by a sol-gel method. X-ray diffraction, UV-vis diffuse reflectance spectroscopy, transmission electron microscopy, photoluminescence spectroscopy, and X-ray photoelectron spectroscopy were used to characterize the morphology, structure, and optical properties of the prepared samples. The introduction of Zn and S resulted in significant red shift of absorption edge for TiO₂-based nanomaterials. The photocatalytic activity was evaluated by degrading reactive brilliant red X-3B solution under simulated sunlight irradiation. The results showed S/Zn codoped TiO₂ exhibited higher photocatalytic activity than pure TiO₂ and commercial P25, due to the photosynergistic effect of obvious visible light absorption, efficient separation of photoinduced charge carriers, and large surface area. Moreover, the content of Zn and S in the composites played important roles in photocatalytic activity of TiO₂-based nanomaterials.

1. Introduction

Photocatalysis, emerging as a potential technique owing to its valuable utilization of solar energy in environmental purification, has been paid increasing attention. In order to search effective photocatalysts, semiconductor investigation is progressing rapidly. A series of semiconductor materials, such as WO₃ [1], ZnO [2], TiO₂ [3], CdS [4], Bi₂VO₄ [5], SnO₂ [6], ZrO₂ [7], and BiWO₆ [8], have been used in photocatalysis. Among these semiconductor photocatalysts, anatase TiO₂ is especially attractive because of its nontoxicity, low cost, and long-term stability. However, the efficiency of anatase TiO₂ is far from satisfactory thanks to the high recombination rate of photogenerated electron-hole pairs and wide bandgap of 3.2 eV, which limits the effective use of solar energy.

In recent years, intense works have been devoted to improve the optical response of TiO₂ under visible light irradiation, including doping TiO₂ with metal/nonmetal ions and decorating TiO₂ with metals, semiconductors, and polymers. For example, N-doped TiO₂ [9], In-doped TiO₂ [10], Ag@TiO₂ [11], SnS₂/TiO₂ [12], and polymer/TiO₂ nanocomposites [13] have been demonstrated to exhibit

photoactivity upon visible light irradiation. Among these methods, metal ion doping is especially attractive due to introducing additional electronic states within the bandgap of TiO₂, thereby extending the range of light absorption to the visible region. However, the kind of doping metals has an influence on photocatalytic activity for TiO₂-based materials. Di Paola et al. have reported a series of transition metal ions, such as Co, Cr, Cu, Fe, Mo, and V, can accelerate recombination of the photoinduced charge carrier, leading to poor photoactivity for TiO₂-based materials [14]. It is now well accepted that suitable metal ions for doping TiO₂ require not only improvement in light absorption but also high quantum efficiency of photoinduced charge carrier. Some previous reports have demonstrated TiO₂ doped with rare earth metal ions, such as La³⁺, Ce³⁺, Er³⁺, Pr³⁺, Gd³⁺, Nd³⁺, and Sm³⁺, exhibits high visible light photocatalytic activity [15, 16]. In addition, nonmetal elements, such as N and S, are also effective dopants for improving the photoactivity of TiO₂. In these cases, they act as electron donors or acceptors in the forbidden band of TiO₂ to induce absorption in the visible region [17, 18]. Moreover, it is worth noting that codoped TiO₂ with metal and/or nonmetal ions, which could further enhance visible light activity of TiO₂ due

to the synergistic effect, has been highlighted [19–21]. Niu et al. has elucidated Fe/S codoped TiO_2 nanomaterials for the photocatalytic degradation of phenol under visible light irradiation [19]. Hamadani et al. reported In/S codoped TiO_2 and Cr/S codoped TiO_2 present highly improved visible light photocatalytic activity compared to pure TiO_2 [20, 21]. To the best of our knowledge, the utilization of S/Zn codoped TiO_2 as a visible light photocatalyst has not been adequately investigated.

Herein, we present the fabrication and characterization of a series of S/Zn codoped TiO_2 nanomaterials. Such a modification provides a broadening optical window for effective light harvesting and high quantum efficiency of photogenerated electron-hole pairs. As a result, the nanomaterials are anticipated to exhibit good photocatalytic activities under visible light irradiation.

2. Experimental Section

2.1. Materials. Absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$, AR), tetrabutyl titanate (TBOT, CP), acetic acid (CH_3COOH , AR), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR), thiourea ($\text{CH}_4\text{N}_2\text{S}$, AR), reactive brilliant red X-3B, and nitric acid (HNO_3 , GR, 65 wt%) were used without further purification.

2.2. Preparation of S/Zn Codoped TiO_2 Nanomaterials. S/Zn codoped TiO_2 nanomaterials were prepared as follows. Firstly, a sol-gel solution, denoted by solution A, was prepared by dispersing 17 mL of TBOT and 0.2 mL of HNO_3 into 40 mL of $\text{C}_2\text{H}_5\text{OH}$ under vigorous stirring for 30 min. Another solution, denoted by solution B, was prepared by mixing 6 mL of deionized water, 5 mL of CH_3COOH , and different amounts of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CH}_4\text{N}_2\text{S}$ in 20 mL of $\text{C}_2\text{H}_5\text{OH}$. Subsequently, solution B was added dropwise into solution A under vigorous stirring at room temperature. After the reaction mixture was further stirred for 2 h, the solution was aged for 48 h at room temperature and the precursor gel was obtained. Finally, the gel was dried at 100°C for 6 h and grinded and calcined at 500°C for 2 h in air at ramp rate of $5^\circ\text{C}/\text{min}$. For comparison, Zn doped TiO_2 and pure TiO_2 photocatalysts were also prepared under the same condition.

In this case, a series of Zn doped TiO_2 nanomaterials with different nominal mole ratios of Zn:Ti (0.01:1, 0.02:1, 0.03:1, 0.04:1, and 0.05:1) and S/Zn codoped TiO_2 photocatalysts with different nominal mole ratios of S:Zn:Ti (0.12:0.04:1, 0.14:0.04:1, 0.16:0.04:1, 0.18:0.04:1, and 0.20:0.04:1) were synthesized under the abovementioned procedure. And they were denoted by ZT-1, ZT-2, ZT-3, ZT-4, ZT-5, SZT-1, SZT-2, SZT-3, SZT-4, and SZT-5, respectively.

2.3. Characterization. X-ray powder diffraction (XRD) analysis was measured by a Shimadzu XRD-6100 diffractometer with $\text{Cu K}\alpha$ radiation, operating at 40 kV and 100 mA. The diffraction data was recorded for 2θ values between 20° and 80° and the scanning rate was $8^\circ/\text{min}$. Ultraviolet-visible (UV-vis) diffuse reflection spectroscopy (DRS) was recorded on a spectrophotometer (Lambda 35, Perkin-Elmer

Corporation, USA) with an integrating sphere and 2 nm spectral resolutions at room temperature in the range of 200–800 nm, and BaSO_4 was chosen as a reference. The morphology of the products was observed using transmission electron microscopy (TEM, JEM-2000EX JEOL, Japan), operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were taken with a VG ESCALAB 250 spectrometer equipped with a monochromatic Al $\text{K}\alpha$ radiation source (1486.6 eV), and C 1s (284.6 eV) was used as a reference. The photoluminescence (PL) measurements were carried out using a Perkin-Elmer LS 55 fluorescence spectrophotometer. BET surface areas of the samples were measured using JW-BK222 specific surface area analyzer. Energy dispersive X-ray spectroscopy (EDS, Oxford INCA) was also used for elemental analysis of the samples. The Fourier transformed infrared spectroscopy (FTIR) was performed on a Perkin-Elmer Spectrum 10 FTIR spectrophotometer.

2.4. Measurement of Photocatalytic Activity. The photocatalytic activity of the as-prepared samples was evaluated by measuring the degradation rate of X-3B solution at room temperature and comparing the results with the activity of the commercial P25. The photocatalytic reaction was carried out using a magnetically stirred quartz reactor at 30°C . For a typical photocatalytic experiment, 200 mg of photocatalyst was added to 200 mL X-3B solution with an initial concentration of 20 and 40 mg/L in quartz reactor and stirred in the dark for 20 min to get an adsorption-desorption equilibrium before being placed under a 350 W xenon lamp and irradiated with continuous stirring. The suspensions were collected every 20 min and centrifuged immediately to separate the photocatalyst particles. The X-3B concentration was determined by monitoring the absorbance at $\lambda_{\text{max}} = 537 \text{ nm}$ by using a 721B spectrophotometer.

3. Results and Discussion

3.1. XRD Analysis. The phase structure and crystallinity of Zn doped TiO_2 and S/Zn codoped TiO_2 samples were investigated by XRD. As shown in Figure 1, the strong diffraction peaks correspond well to the peaks of anatase TiO_2 for all the samples. No peaks assigned to ZnO and ZnS were detected. It is probably due to the low Zn and S content in the samples. It should be noted that the full width at half maximum peak of doped TiO_2 is larger than that of undoped TiO_2 , suggesting that the particle size of doped TiO_2 is smaller than that of undoped TiO_2 .

3.2. EDS, XPS, and IR Analysis. EDS analysis was performed to better understand chemical composition of the obtained materials. EDS spectra of ZT-4 and SZT-3 are shown in Figure 2. It can be clearly seen that the signals for Zn are present in Zn doped TiO_2 nanomaterials; Zn and S signals also appear in the EDS spectrum of S/Zn codoped TiO_2 , illustrating the existence of Zn and S. For further confirming the existence of Zn and S, XPS has also been performed. Figure 3(a) displays the XPS survey spectrum of the same sample. The main elements are Ti, Zn, O, and S with sharp

FIGURE 1: XRD patterns of (A) undoped TiO₂, (B) ZT-1, (C) ZT-2, (D) ZT-3, (E) ZT-4, and (F) ZT-5 in (a) and (A) SZT-1, (B) SZT-2, (C) SZT-3, (D) SZT-4, and (E) SZT-5 in (b).

FIGURE 2: EDS spectra of (a) ZT-4 and (b) SZT-3.

photoelectron peaks, in good agreement with the EDS result. Figures 3(b), 3(c), and 3(d) display the XPS spectrum of Ti 2p, Zn 2p, and S 2p, respectively. The spectrum in Figure 3(b) shows two peaks locating at 458.0 and 464.1 eV, which are attributed to the spin-orbit splitting of Ti 2p_{3/2} and Ti 2p_{1/2}, respectively, in good agreement with those of titanium (IV) dioxide [22]. As shown in Figure 3(c), the binding energy values of Zn 2p_{3/2} and Zn 2p_{1/2} are observed at 1021.5 and 1044.7 eV, indicating that the Zn element could be in +II state bonding with oxygen [23]. From Figure 3(d), it could be observed that the S 2p peak is located at about 169 eV. This peak can be deconvoluted into two overlapping peaks at 168.3 and 169.4 eV, which is attributed to the S (+VI). The S (+VI) may be adsorbed on the surface of TiO₂ in the form of SO₄²⁻ ions [17]. This can be demonstrated by IR characterization. As shown in Figure 4, the peaks at 1142 and 1055 cm⁻¹, ascribed to SO₄²⁻ coordinating to Ti⁴⁺ and forming Ti–O–S bond [20], are observed on the spectrum for S/Zn codoped TiO₂. Based on the above observation, Zn and S elements should be doped into TiO₂ by the sol-gel method.

3.3. TEM Analysis. The textures of undoped TiO₂, Zn doped TiO₂, and S/Zn codoped TiO₂ were characterized by TEM. As shown in Figure 5(a), undoped TiO₂ are composed of small nanoparticles with the diameter in the range of 15–30 nm. However, both Zn doped TiO₂ and S/Zn codoped TiO₂ consist of small nanoparticles, which are uniform with the main diameter of approximately 14 and 11 nm, respectively. It is attributed to the presence of Zn and S in the composites, which can inhibit the growth of TiO₂ nanoparticles [20, 23]. The d-spacing of the lattice fringe (Figure 5(d)) is measured to be 0.35 nm, corresponding to the (101) plane of anatase TiO₂, indicating well crystalline TiO₂ nanoparticles are formed in this case.

3.4. DRS Analysis. The photoabsorption abilities of the samples were probed with UV-visible (UV-vis) diffuse reflectance spectroscopy (DRS). As shown in Figure 6, because of the interband electronic transitions, the onset of the absorption spectrum of pure TiO₂ represents a strong and broad absorption feature in the UV region. Furthermore, in comparison

FIGURE 3: The XPS core level binding energy in SZT-3. (a) An overview XPS spectrum of the sample; (b) Ti 2p spectrum; (c) Zn 2p spectrum; and (d) S 2p spectrum.

FIGURE 4: FTIR spectra of (A) undoped TiO₂ and (B) SZT-3.

FIGURE 5: TEM images of (a) undoped TiO₂, (b) ZT-4, and (c) SZT-3 and (d) high-resolution TEM (HRTEM) image of SZT-3.

with pure TiO₂, there is a considerable red-shift of absorption edge in the visible light region for the Zn doped TiO₂ and S/Zn codoped TiO₂. Particularly, S/Zn codoped TiO₂ exhibits a large red-shift than Zn doped TiO₂. According to previous report [24], the absorption of UV light in TiO₂ is ascribed to the excitation of O 2p electron to Ti 3d level. Due to Zn doping, a new electronic state is introduced in middle of the TiO₂ bandgap, as a result, giving rise to the red-shift in the bandgap. For S doping, S 2p states can interact with O 2p states of TiO₂, leading to a charge transfer between the dopant and the conduction and/or valence band [21]. Thus, S/Zn codoped TiO₂ nanomaterials present further red-shift of absorption edge. Accordingly, the obtained doped TiO₂ nanomaterials may exhibit high photochemical activity under visible light irradiation.

3.5. PL Analysis. The PL spectra from the recombination of photoexcited free carriers are shown in Figure 7. Obviously,

FIGURE 6: The UV-vis absorption spectra of (a) SZT-3, (b) ZT-4, and (c) undoped TiO₂.

FIGURE 7: Photoluminescence spectra of (a) undoped TiO_2 , (b) ZT-4, and (c) SZT-3.

TABLE 1: Specific surface area of the samples determined by BET equation.

Sample	Specific surface area ($\text{m}^2 \text{g}^{-1}$)
Undoped TiO_2	3.27
ZT-4	23.4
SZT-3	28.8

Zn doped TiO_2 presents much lower PL intensity than pure TiO_2 , implying that Zn doping suppresses the recombination of electrons and holes. This result is in accordance with Xie's report, in which Zn doped TiO_2 not only promotes the charge separation but also delays the charge recombination [23]. Furthermore, the S/Zn codoped TiO_2 has a greater decline in PL intensity, indicating that S/Zn codoped TiO_2 nanomaterials have higher separation efficiency of the photoinduced electrons and holes compared to Zn doped TiO_2 . It is ascribed to the fact that oxygen vacancies and/or defects, generated by S introduction, can capture the photoinduced electrons [25].

3.6. Photocatalytic Activity Analysis. The photocatalytic activity of the prepared samples was determined by photocatalytic degradation of X-3B solution under simulated sunlight irradiation. Figures 8(a) and 8(b) show photocatalytic activity of various Zn doped TiO_2 and S/Zn codoped TiO_2 photocatalysts under simulated sunlight irradiation, respectively. It can be seen that the optimum molar ratio of Zn in Zn doped TiO_2 is 4%, while that of S in S/Zn codoped TiO_2 is 16%. Figure 8(c) presents the photocatalytic activity of ZT-4, pure TiO_2 , P25, and SZT-3, respectively. It is obvious that SZT-3 shows the highest photocatalytic activity, while pure TiO_2 presents the lowest photocatalytic activity. In this case, the degradation rate of X-3B solution with SZT-3 could reach 74.6%, whereas those of ZT-4 and pure TiO_2 are 61.2% and 43.6%, respectively.

Since the surface areas of photocatalysts play important roles in the photocatalytic activity, N_2 adsorption/desorption analysis for pure TiO_2 , ZT-4, and SZT-3 has also been performed (Table 1). This observation indicates that both ZT-4 and SZT-3 have large surface area, which is beneficial to dye adsorption during photocatalytic process. On the basis of DRS, PL, and N_2 adsorption/desorption studies, the improved photocatalytic activity for the modified TiO_2 can be attributed to the photosynergistic effect of obvious visible light absorption, efficient separation of photoinduced charge carriers, and large surface area. In addition, Zn doping can also significantly decrease the amount of trap states, facilitating electron transport and charge separation [23]. However, it should be noted that Zn doping can also act as the recombination centers for the photogenerated electrons and holes, inhibiting the photocatalytic activity. Thus, the optimal dopant amount of Zn is 4%. Further introducing S to the Zn doped TiO_2 , the recombination of the photogenerated charge carriers can be restrained by S element, which can act as a hole trap [20]. Therefore, the charge carriers with a long lifetime make the sample exhibit higher photocatalytic activity. In addition, doping with both Zn and S increases the light absorption owing to extending the absorption to the visible range. In combination with the above results, it could be concluded that the photocatalytic activities of modified TiO_2 catalysts under simulated sunlight were greatly enhanced compared with those of pure TiO_2 , which could be ascribed to the photosynergistic effect of obvious visible light absorption, efficient separation of photoinduced charge carriers, and larger specific surface area.

Figure 9 shows the UV-vis absorption spectra of X-3B solution before and after simulated sunlight irradiation for different exposure periods with SZT-3. The characteristic absorption band of X-3B at 537 nm diminished quickly and became quite weak after 180 min under simulated sunlight irradiation.

4. Conclusions

In summary, S/Zn codoped TiO_2 nanomaterials were prepared by a sol-gel method. This method allows for the successful doping of Zn and S into anatase TiO_2 . The absorption spectrum of S/Zn codoped TiO_2 nanomaterials displays a red-shift to visible light region. The results show that S/Zn codoped TiO_2 possesses better photocatalytic activity than Zn doped TiO_2 and P25, due to enhanced separation efficiency of photoinduced electron-hole pairs and light absorption. Considering their high photocatalytic activity, the S/Zn codoped TiO_2 nanomaterials are promising photocatalysts for application in degradation of dye wastewater.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

FIGURE 8: (a) Photocatalytic degradation curves of X-3B over different samples. The initial concentration of X-3B solution was 20 mg/L for (a) and 40 mg/L for (b) and (c).

FIGURE 9: UV-vis absorption spectra of a X-3B solution before and after simulated sunlight irradiation for different times in the presence of the SZT-3 sample.

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