Improving the photo-degradation activity of SnS₂ under visible light by TiO₂ (rutile)

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Abstract

The nano-sized SnS₂ modified with rutile phase TiO₂ (SnS₂/TiO₂) was prepared through the hydrothermal treatment of TiCl₃ in the presence of SnS₂ at 160 °C for 4 h. The samples have been characterized by X-ray diffraction, X-ray photoelectron spectroscopy, scanning and transmission electron microscopy and UV–vis spectroscopy. The photodegradation of methyl orange has been investigated under the light irradiation of 360–600 and 400–600 nm by using the samples as photocatalyst. The results demonstrated that the photocatalytic activities of the as-prepared SnS₂/TiO₂ depended on the content of TiO₂, and that SnS₂/TiO₂ containing 26% TiO₂ displayed the optimum activity which was much larger than that of pure SnS₂ although the rutile TiO₂ had little activity for the degradation of methyl orange.

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1. Introduction

Recently, there has been considerable interest in the application of semiconductors as photocatalysts to clean environment and produce H₂ energy via splitting water. During the process the electron–hole pairs are separated upon irradiation of photons, and then the electrons or holes move to the surfaces and react with species adsorbed on the powders [1]. To date, it has been reported that the composite structure can enhance the photocatalytic activity of the semiconductor catalysts, and that the improved activity of the composites is largely attributed to the enhanced separation of photo-induced electrons and holes via interfacial charge transfer [2–5]. Hence, much effort has been devoted to develop composite semiconductors in order to maximize the utilization of solar energy and reduce the recombination of electron–hole [6].

SnS₂, a kind of n-type semiconductor with a bandgap of 2.18–2.44 eV, has good stability in acid and neutral aqueous solutions and some oxidative and thermal stability in air, which makes it a promising visible light-sensitive photocatalyst [7] or dye in photocell [8,9]. Anatase (3.2 eV) crystalline phase TiO₂ has been used widely due to its non-toxicity, inexpensiveness and considerable photo-stability [10]. Recently, it was revealed by some reports that rutile TiO₂ (3.0 eV) with a small size and large surface area can possess relatively higher photocatalytic activity [11–13] although anatase is usually more active than rutile [14]. Considering the appropriate matching degree of band potentials between SnS₂ and rutile TiO₂, SnS₂/TiO₂ composites with appropriate compositions will have higher visible light-driven photocatalytic activity than individual SnS₂ and TiO₂.

In this paper, SnS₂/TiO₂ composites are prepared by the hydrothermal method in the presence of SnS₂ and TiCl₃ aqueous solutions. It is proved that the degradation of methyl orange under visible light can be greatly improved when the optimum composite of SnS₂/TiO₂ (rutile) is used as catalyst.

2. Experimental

Materials: All reagents were of analytical grade and SnS₂ nanoparticles were synthesized according to literature [7]. The pure TiO₂ particles were synthesized by treating 1.0 mL TiCl₃ aqueous solutions in 10 mL distilled water at 160 °C for 4 h. SnS₂ powder (120 mg) was dispersed in distilled water, and then certain amount of TiCl₃ aqueous solution was dropped into the mixture under stirring. The mixtures were transferred into teflon-lined stainless steel autoclaves, and then the autoclaves were heated at 160 °C for 4 h in an oven. The final products were filtered, washed with distilled water several times, and then dried in a vacuum oven at 100 °C for 3 h. The composite containing 17, 23, 26, 29 and 33 wt% of rutile phase TiO₂ was defined as SnS₂/TiO₂-17, 23, 26, 29 and 33, respectively.

Characterization and tests: The morphologies of the samples were observed by using a scanning electron microscope (SEM, JEOL7010F) and transmission electron microscopy (TEM, JEOL2010). The XRD patterns were recorded on a Bruker D8 Advance X-ray
diffractometer (Cu Kα), and the X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALab 220i-XL spectrometer (VG Scientific, England) employing a monochromic Al Kα source at 1486.6 eV. The UV–vis diffuse diffraction spectra were obtained on a Thermo Scientific Evolution 220 UV–visible spectrophotometer.

Photocatalytic experiments were carried out by using MO (20.0 mg/L) solution as target under the 360–600 and 400–600 nm light irradiation. Before illumination, the mixture of MO (50.0 mL) and photocatalyst (10.0 mg) was magnetically stirred under darkness for 30 min to reach the adsorption/desorption equilibrium. Then the reactions were initiated by irradiating with a 200 W Xe lamp located 36 cm above the vessel; the temperature of the solution was kept at about 25 °C in the process of degradation. During the irradiation, 1.0 mL of the mixture under radiation was taken from the vessel at an interval of 5 or 10 min and was centrifuged at 12,000 rpm for 5 min to remove the catalyst particles completely. The concentration of MO solution was determined by a UV–vis spectrophotometer at the maximum absorption wavelength of 462.0 nm.

3. Results and discussion

From the SEM images (Fig. S1), it is difficult to get the shape and size of the particles for SnS2 and SnS2/TiO2, but it is clear that the pure SnS2 particles are flaky, and that the small TiO2 particles are assembled on the surface of SnS2 in the samples of SnS2/TiO2–26 (Fig. 1A and B). However, pure TiO2 particles synthesized from TiCl3 exhibit the size of several microns (Fig. 1C). These indicate that TiO2 can disperse on SnS2 well and the composites have been synthesized successfully. The XRD pattern shows the characterized diffraction peaks of pure SnS2 (Fig. 1(D-a)) while the XRD pattern of TiO2 (Fig. 1(D-g)) shows that the rutile TiO2 is synthesized in this approach but without the anatase phase. The XRD patterns of SnS2/TiO2 composites with various contents of...
TiO\textsubscript{2} possess the peaks corresponding to SnS\textsubscript{2} and TiO\textsubscript{2}. But it is found that the peaks of rutile TiO\textsubscript{2} in SnS\textsubscript{2}/TiO\textsubscript{2}-26 have relatively weaker intensity than the mixture of SnS\textsubscript{2} and TiO\textsubscript{2} with the same ratio (Fig. S3), which may be because the content of rutile TiO\textsubscript{2} in composite is less than that of mixture or because the particles of TiO\textsubscript{2} deposited on the surface of SnS2 have small size and poor crystallization.

The XPS spectra are recorded in order to clarify the interaction between the components (Fig. 2). The binding energy (BE) of Sn3d\textsubscript{5/2} (486.7 eV) for SnS\textsubscript{2}/TiO\textsubscript{2}-23 is higher than that for pure SnS\textsubscript{2} (486.6 eV), which may be due to some tin oxide (486.9 eV) formed during the preparation process which can cause the BE of Sn3d\textsubscript{5/2} to shift to higher region [15] compared with pure SnS\textsubscript{2}. Moreover, the BE of Ti2p\textsubscript{3/2} for SnS\textsubscript{2}/TiO\textsubscript{2} is located at 458.6 eV which is also higher than that of rutile TiO\textsubscript{2} (458.3 eV). The above-mentioned XPS results reveal that there are changes in the outer electron cloud density of Ti and Sn ions, and that the interaction between SnS\textsubscript{2} and TiO\textsubscript{2} in the composites is strong.

The UV–vis diffuse reflection spectra of the samples (Fig. 3) reveal that TiO\textsubscript{2} displays a strong absorption mainly below 400 nm while SnS\textsubscript{2} and SnS\textsubscript{2}/TiO\textsubscript{2} display light absorption in the wavelength range of 400–750 nm. It is found that the intensity of the absorption in the UV region decreases with the increase of TiO\textsubscript{2} in the composites (Fig. 3(A)). In order to confirm this...
phenomenon, the electron adsorption spectrum of SnS2/TiO2-26 (physical mixing) has been recorded and it shows stronger adsorption in the range < 450 nm and slightly weaker adsorption in the range of 450–750 nm than SnS2/TiO2-26, which is similar to the curve of 74% SnS2 spectrum + 26% TiO2 spectrum but with a relatively stronger absorption in the range of 400–750 nm (Fig. 3B). This may be because the content of rutile in SnS2/TiO2-26 is less than the mixture, or because the TiO2 dispersed on the surface of SnS2 exhibits a weaker absorption in the UV region than the sole TiO2 due to the small size.

From Fig. 4A and C, it is found that the degradation of MO almost does not take place when TiO2 is used as the photocatalyst under the irradiation of 360–600 nm (1.12%, 20 min) and 400–600 nm (1.16%, 40 min), while it is 59.4% at 20 min (360–600 nm) and 71.6% at 40 min (400–600 nm) when SnS2 is used as photocatalyst. However, the degradation rate is about 100% at 20 min under 360–600 nm and 40 min under 400–600 nm irradiation in the presence of SnS2/TiO2-23, 26 or 29. The photo-catalytic degradation of the organic pollutants follows the pseudo-first-order kinetic; the apparent reaction constant ($K_{app}$) can be obtained from the linear relationship between $\ln(C_0/C_t)$ and the reaction time. It is clear that the $K_{app}$ in the presence of SnS2 is about 0.048 min$^{-1}$ (360–600 nm) and 0.034 min$^{-1}$ (400–600 nm), and that the $K_{app}$ increases with the increase of TiO2 in composites initially. The $K_{app}$ reaches the maximum (0.12 min$^{-1}$ under 360–600 nm, 0.079 min$^{-1}$ under 400–600 nm) when the content of TiO2 is about 26% in the composite which is much larger than that of TiO2, and decreases when the content of TiO2 in the composites increases further. However, the degradation of the MO is about 96% at 40 min, and the $K_{app}$ is about 0.060 min$^{-1}$ under irradiation of 280–400 nm, which is smaller than that under the irradiation of visible light. So it can be concluded that among these obtained photocatalysts, SnS2/TiO2-26 reveals the most efficacious performance under the visible light. According to the above measurements, the higher degradation of MO caused by the composite under visible light may be ascribed to the matching band potentials of SnS2/TiO2 and efficient electron–hole separations via interface.

4. Conclusions

SnS2/TiO2 composites with different contents of TiO2 have been prepared via hydrothermal treatment of various amounts of TiCl3 aqueous solutions in the presence of SnS2 at 160 °C for 4 h. There are intense interactions between the components of the composites, and the activities of SnS2/TiO2 depend on the mass ratio of the components. Composite of SnS2/TiO2-26 possesses the optimum photocatalytic activity under UV–visible or visible light irradiation. The high visible light-driven activity makes it a kind of promising catalyst in the efficient utilization of solar energy for the treatment of some chemically organic dye.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2013.02.009.

References