



Size-controlled hydrothermal synthesis of SnS₂ nanoparticles with high performance in visible light-driven photocatalytic degradation of aqueous methyl orange

Yong Cai Zhang^{a,*}, Zhen Ni Du^a, Kun Wei Li^b, Ming Zhang^a

^aKey Laboratory of Environmental Material and Environmental Engineering of Jiangsu Province, College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China

^bFood and Agriculture Standardization Institute, China National Institute of Standardization, 4 Zhichun Road, Haidian District, Beijing 100088, China

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ABSTRACT

A simple hydrothermal method was developed for the size-controlled synthesis of SnS₂ nanoparticles, using common and inexpensive SnCl₄·5H₂O and thioacetamide as the reactants and 5 vol.% acetic acid aqueous solution as the solvent. The structure, composition and optical property of the obtained products were characterized by X-ray diffraction, transmission electron microscopy, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, Brumauer–Emmett–Teller (BET) surface area analysis and UV–vis diffuse reflectance spectra, and their possible formation mechanism was proposed. Besides, their photocatalytic properties were tested by degrading methyl orange in distilled water (20 mg/l) under visible light ($\lambda > 420$ nm) irradiation. It was found that SnS₂ nanoparticles synthesized under the appropriate hydrothermal conditions not only exhibited high visible light-driven photocatalytic activity, but also had good photocatalytic stability.

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1. Introduction

Recently, there has been an increasing interest in the application of semiconductors as photocatalysts to degrade organic pollutants, which are harmful to the environment, hazardous to human health, and difficult to degrade by natural means [1–25]. TiO₂ is by far the most studied photocatalyst, in view of its low cost, high activity for many photocatalytic reactions, excellent chemical and photochemical stability, and good biocompatibility [1–9]. However, it is only active under ultraviolet light irradiation due to its wide band gap (3.2 eV), not responding to visible light ($\lambda > 400$ nm) which is the main component (about 46%) in solar light [10]. In order to make full use of solar energy, it is necessary to develop visible light-sensitive semiconductor photocatalysts [10–25].

The semiconducting metal sulfides usually have light-absorbing capability in the visible and short-wavelength near-infrared regions, which enable them to work as a class of promising sensitizers for TiO₂ [14–19] or visible light-driven photocatalysts [20–25]. Among the sulfide semiconductors, CdS, which has a band gap of about 2.4 eV, is currently the focus of significant attention [22–24]. However, CdS itself is detrimental to human health and the

environment due to its high toxicity. SnS₂ is a CdI₂-type layered semiconductor with a band gap of about 2.2 eV [25], which is a little smaller than that of CdS. It is non-poisonous, inexpensive, chemically stable in acid and neutral aqueous solution, and thus has great potential to be an efficient visible light-driven photocatalyst [25]. However, to our knowledge, the information about the photocatalytic performance of SnS₂ is still rare so far [15,25,26]. Besides, because the structures, properties and applications of semiconducting materials have close relation to their preparation methods and preparation conditions, it is also desirable to design alternative routes and optimize reaction conditions for obtaining SnS₂ nanomaterials with better photocatalytic activity and stability.

Hydrothermal method is a simple and low cost wet chemical process that has been widely used to synthesize semiconducting nanomaterials [27–29]. It not only can induce the formation of well-crystallized products at low temperatures (generally below 200 °C), but also has the ability of controlling the size and shape of the resultant products [27–29]. Herein, we report a size-tunable hydrothermal synthesis of SnS₂ nanoparticles using common and inexpensive SnCl₄·5H₂O and thioacetamide as the reactants and 5 vol.% acetic acid aqueous solution as the solvent, simply by varying the reaction temperature and the initial amount of thioacetamide. The structure, composition and optical property of the resultant products are characterized by X-ray diffraction (XRD),

* Corresponding author. Tel.: +86 0514 87962581; fax: +86 0514 87975244.

E-mail address: zhangyc@yzu.edu.cn (Y.C. Zhang).

transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), Brumauer–Emmett–Teller (BET) surface area analysis and UV–vis diffuse reflectance spectra, and their possible formation mechanism is proposed. Furthermore, their photocatalytic properties are tested in the degradation of methyl orange (MO) in distilled water under visible light ($\lambda > 420$ nm) irradiation.

2. Experimental

All the reagents used were of analytical grade and purchased directly from Sinopharm Chemical Reagent Co., Ltd.

2.1. Synthesis

The powders of 0.005 mol $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 0.01–0.02 mol thioacetamide were weighed into a Teflon-lined stainless steel autoclave of 50 ml capacity, then 40 ml of 5 vol.% acetic acid aqueous solution was added in with stirring (the stirring was kept for a while until a homogeneous solution was formed). The autoclaves containing the reaction solutions were sealed and maintained at 120–180 °C for 12 h, then cooled naturally to room temperature. The as-formed yellow precipitates were filtered, washed with distilled water and ethanol, and finally dried in vacuum at 100 °C for 3 h.

For the convenience of description, the SnS_2 products synthesized under different conditions were hereinafter called as “ SnS_2 -(a)”, “ SnS_2 -(b)” and “ SnS_2 -(c)”, etc. as shown in Table 1.

2.2. Characterization

XRD patterns of the as-products were recorded on a German Bruker AXS D8 ADVANCE X-ray diffractometer. EDS measurements were conducted on a Japan Hitachi S-4800 field emission scanning electron microscopy. TEM images were taken on a Holland Philips Tecnai-12 transmission electron microscopy. High-resolution transmission electron microscopy (HRTEM) images were taken on an American FEI Tecnai G2 F30 S-TWIN field-emission TEM. XPS measurements were performed on an American Thermo-VG Scientific ESCALAB 250 XPS system with Al $K\alpha$ radiation as the exciting source, where the binding energies were calibrated by referencing the C 1s peak (284.6 eV) to reduce the sample charge effect. UV–vis diffuse reflectance spectra were obtained on a Japan Shimadzu UV-3101PC ultraviolet–visible–near infrared spectrophotometer, using BaSO_4 as reference.

2.3. Photocatalytic tests

Photocatalytic properties of the as-synthesized products were studied by following their catalytic decoloration of MO aqueous solution (20 mg/l) under visible light ($\lambda > 420$ nm) irradiation. For comparison, flowerlike CdS nanostructure (which was prepared

by a solvothermal method, according to the procedure reported by Di et al. [22]), “200-0 SnS_2 ” (which was synthesized by heating the mixture of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and excess S powders in air from room temperature to 200 °C, combined with a subsequent washing treatment [25]) and Degussa P25 TiO_2 were also tested under the same conditions.

The photocatalytic experiments were carried out in a homemade photochemical reactor [25], which includes mainly four parts: light source system including an 1000 W Xe lamp, ($\lambda > 420$ nm) cut-off filters and cooling attachments such as air pump and electric fan; reactor (two-layer Pyrex glass bottles of 400 ml capacity, and the space between the two layers is filled by circulating water to cool the reactor); magnetic stirrer; and temperature controller. In each experiment, the distance between the Xe lamp and the reactors was set to be 10 cm, and the reaction temperature was 25 °C. Prior to illumination, 300 ml of MO aqueous solution containing 0.3 g of photocatalyst was magnetically stirred in the dark for 1 h to achieve the adsorption/desorption equilibrium between the photocatalyst and MO. During illumination, about 4.0 ml of suspension was taken from the reactor at an interval of 10 min and centrifugated to separate the photocatalyst. The supernatant solution was analyzed by a Japan Shimadzu UV-2550 UV–vis spectrophotometer at the maximum absorption wavelength of MO (462.0 nm).

3. Results and discussion

3.1. Structure

Fig. 1a–f shows the XRD patterns of the products derived from hydrothermal reaction between $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and different amounts of thioacetamide in 5 vol.% acetic acid aqueous solution at 120–180 °C for 12 h. All the obtained products display only the characteristic XRD peaks of hexagonal phase SnS_2 (JCPDS card no. 23-677). Using the well-known Scherrer formula based on the half-width of their (0 0 1) peak, the particle sizes of SnS_2 -(a–f) are calculated and shown in Table 1.

The TEM images of SnS_2 -(a–f) are shown in Fig. 2. As can be seen, the morphologies of the obtained SnS_2 products turn from irregular nanoparticles into nanoplates with the increase of temperature from 120 to 180 °C. The particle sizes of SnS_2 -(a–f) observed by TEM are also summarized in Table 1. Although there is some difference between the particle sizes derived from TEM and Scherrer formula due to the shape and aggregation effects of the obtained SnS_2 nanoparticles, the size-changing trends inferred from these two kinds of methods agree with each other (Table 1): the sizes of the obtained SnS_2 nanoparticles generally become larger with the increase of reaction temperature, but decrease when more initial amounts of thioacetamide are used, while the other synthesis conditions remain the same. These phenomena may be explained by the different effects of reaction temperatures and initial amounts of thioacetamide on the nucleation and crystal growth processes of SnS_2 under the hydrothermal conditions, as discussed later in Section 3.3.

3.2. Composition

The compositions of SnS_2 -(a–f) were determined by EDS, whose results are listed in Table 1. It can be seen from Table 1 that SnS_2 -(a–f) are all made of only two component elements, Sn and S. But, the ratios of Sn to S in these products vary slightly. Generally, the products synthesized using more initial amounts of thioacetamide or at higher reaction temperatures (while the other synthesis conditions are identical) are less deficient in S, and have compositions closer to the stoichiometry of SnS_2 .

Table 1

The abbreviated names and properties of the SnS_2 products synthesized under different conditions (TAA = thioacetamide; SA = surface area; the superscript ^S and ^T denote the sizes/thicknesses obtained by the Scherrer formula and TEM, respectively).

Names	TAA (mol)	T (°C)	Composition	Size (nm)	BET SA (m^2/g)	E_g (eV)	$k \times 10^2$ (min^{-1})	R^2
SnS_2 -(a)	0.01	120	$\text{SnS}_{1.75}$	$8\text{--}23^{\text{T}}$; 10^{S}	104.5	2.25	5.94	0.990
SnS_2 -(b)	0.015	120	$\text{SnS}_{1.85}$	$5\text{--}20^{\text{T}}$; 8^{S}	143.3	2.15	2.89	0.996
SnS_2 -(c)	0.01	150	$\text{SnS}_{1.83}$	$12\text{--}46^{\text{T}}$; 14^{S}	63.5	2.23	3.50	0.992
SnS_2 -(d)	0.01	180	$\text{SnS}_{1.86}$	$22\text{--}142^{\text{T}}$; 34^{S}	31.3	2.16	3.14	0.984
SnS_2 -(e)	0.015	180	$\text{SnS}_{1.90}$	$16\text{--}65^{\text{T}}$; 20^{S}	58.3	2.12	2.55	0.988
SnS_2 -(f)	0.02	180	$\text{SnS}_{1.94}$	$7\text{--}46^{\text{T}}$; 16^{S}	68.4	2.12	2.19	0.996

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