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Alcohothermal synthesis of flower-like ZnS nano-microstructures with high visible light photocatalytic activity

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ABSTRACT

Flower-like ZnS nano-microstructures have been successfully synthesized via the facile template-free alcohothermal method in an ethanol solution without any surface-active agents. The morphology and optical properties of the as-obtained samples have been characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM), UV–visible diffuse reflectance spectroscopy and photoluminescence spectra (PL). The photocatalytic experiments show that the flower-like ZnS presents excellent photocatalytic activity on the degradation of malachite green (98.2%) under visible light. The photocatalytic reusability was investigated up to six successive cycles and the flower-like ZnS still retains its activity about 80.1% of photodegradation ratio. Consequently, the flower-like ZnS can be employed as the efficient photocatalyst to treat the organic pollutants.

1. Introduction

With the growth of industrialization, environmental pollution caused by toxic organic compounds in wastewater has drawn more and more worldwide attention. Therefore, it is urgent to develop simple, cheap, safe and effective techniques to degrade the pollutants. Photocatalysis oxidation is one of the most promising techniques for alleviating the negative impact of environmental problems [1,2]. Most photocatalysts were successfully used for the degradation of various pollutants under UV irradiation [3,4]. Unfortunately, UV radiation accounts for only about 4%, compared to more than 50% of visible light in the solar spectrum. It is advantageous to use solar radiation as an abundant and inexpensive light source for photocatalysis [5]. Therefore, it is still a challenge for scientists to synthesize novel structural materials which are suitable for photocatalysis oxidation under visible light.

As an important direct wide-band gap semiconductor material, zinc sulfide (ZnS) has been applied in sensors, catalysis and optoelectronics, due to its excellent photoelectric conversion characteristics and luminescent properties [6,7]. The nontoxic ZnS nano-materials also present good photocatalytic activity on removal of hazardous materials [8–10]. In the past decades, much effort has been devoted to the preparation of morphology-controlled ZnS nanostructures, such as nanoparticles, nanorods, nanowires and nanosheets [10–13]. However, after environmental treatment, the separation of nanostructures from slurry type photocatalytic process is a big difficulty.

Compared with low dimensional nanostructures, the complex three-dimensional (3D) architectures constructed by nanoscale building blocks can possess more new properties because of their novel multidimensional framework. Recently, various 3D ZnS architectures have been successfully fabricated including mesoporous spheres, hierarchical spheres, urchin-like structures, cauliflower-like structure, and other complex 3D ZnS architectures [14–19]. However, organic surfactants or assisted small molecules are always used as templates or structure directing agents to control the growth of structures. Synthesis of novel 3D architectures of ZnS with a controllable morphology and favorable properties under facile conditions still remains an uphill task.

In this work, we report the synthesis of flower-like ZnS microstructures self-assembled with nanosheets via a simple one-step template-free alcohothermal route processing of $Zn(NO_3)_2$ and thioacetamide (TAA) starting materials in an ethanol solution. The visible light photocatalytic ability and reusability have been investigated for the flower-like ZnS microspheres.

2. Experimental

All the chemical reagents were of analytical grade and used without further purification. In a typical procedure, 5 mmol

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$Zn(NO_3)_2 \cdot 6H_2O$ and 5 mmol TAA were dissolved in 37.5 mL ethanol at room temperature under stirring for 30 min. The mixture was transferred into a Teflon-lined autoclave of 50 mL capacity and maintained at 120 °C for 5 h. After cooled to room temperature naturally, the as-formed precipitates were collected by centrifugation, washed with ethanol and distilled water for several times, and dried at 60 °C.

The morphology of the ZnS nano-microstructures was investigated by scanning electron microscope (SEM) (JSM-7500F). X-ray diffraction (XRD) patterns were recorded on the X'Pert PRO MPD diffractometer, configured with a Cu radiation X-ray source. The surface areas were determined by BET analysis on the basis of nitrogen adsorption isotherms measured at 77 K using a BELSORP-mini nitrogen adsorption apparatus. The optical properties were characterized by UV–visible diffuse reflectance spectra (PE Lambda850) and photoluminescence (PL) spectroscopy (Hitachi F-3600). The photocatalytic degradation of malachite green (MG) was presented in Supporting information. The absorbance of the dye was measured using a Shimadzu UV 1750 spectrophotometer.

3. Results and discussions

Fig. 1 shows the SEM images of various ZnS structures obtained in different alcohothermal reaction times (1, 3, 5 and 7 h). After 1 h, the aggregated nanoparticles can be fabricated as shown in Fig. 1a. The nanosheet structures are observed among the nanoparticles after 3 h. The flower-like microspheres with interwoven nanosheets are fabricated in 5 h, as shown in Fig. 1c. The active S^{2-} released from TAA reacts with Zn^{2+} to generate the ZnS nuclei, and nanoparticles can be obtained firstly. Afterwards, due to the polydispersity of the nanocrystals, small building block particles are involved in the Ostwald ripening process to form large nanosheets [14,20]. Finally, with the increasing number of nanosheets, they self-assemble to flower-like structure to decrease the surface energy. The schematic formation mechanism is shown in Scheme S1 (Supporting information). However, when the reaction time extended to 7 h, the large sphere-like aggregates can be fabricated (Fig. 1d). The three samples obtained from the different synthetic time are abbreviated as S1 (3 h), S2 (5 h), and S3 (7 h), respectively. In Fig. 1e, the XRD patterns of the samples (S1, S2 and S3) are shown with the similar diffraction peaks which present broad features, meaning small crystalline sizes. The intensity of the peaks changes with the increasing of reaction time. The XRD data from S3 is indexed as follows: peak (100) at 26.30°, (008) at 29.3°, (110) at 47.81°, which fit the peaks of hexagonal wurtzite ZnS exactly, similar to the case reported in the literatures [4,21]. Furthermore, the BET specific surface areas of the samples (S1, S2 and S3) are found to be 20.6, 29.2 and 13.7 $m^2\ g^{-1}$, respectively.

The optical properties were investigated by UV–visible diffuse reflectance spectra of ZnS (S1, S2 and S3) as shown in Fig. 2a. The wavelength distribution of the absorbed light is an important property of photocatalysts [22]. The samples show similar absorbance in the ultraviolet region which is located at about 340 nm. The higher absorbance indicates the better photoactivity of S2 and S3 as shown in Fig. 3a. The optical bandgap energy of the samples (see Fig. S1, Supporting information) is estimated to be about 3.5 eV (S1: 3.52 eV, S2: 3.50 eV and S3: 3.46 eV), which is smaller than the bulk wurtzite ZnS (3.77 eV) [6]. Since photocatalytic activity is related closely to the PL intensity and the recombination rate of photoexcited electrons and holes, the PL measurement of the flower-like ZnS (S2) was also performed as shown in Fig. 2b. When excited at 353 nm, S2 displays the maximum peak at 450 nm with the broad emission spectra in the range of 400–600 nm, which almost cover the whole visible region. The PL spectrum shows that flower-like ZnS can effectively generate excited electrons and holes during the photocatalytic reaction under visible light irradiation.

Fig. 3a shows the changes in MG concentration upon visible light irradiation in the presence of nano-microstructural ZnS.

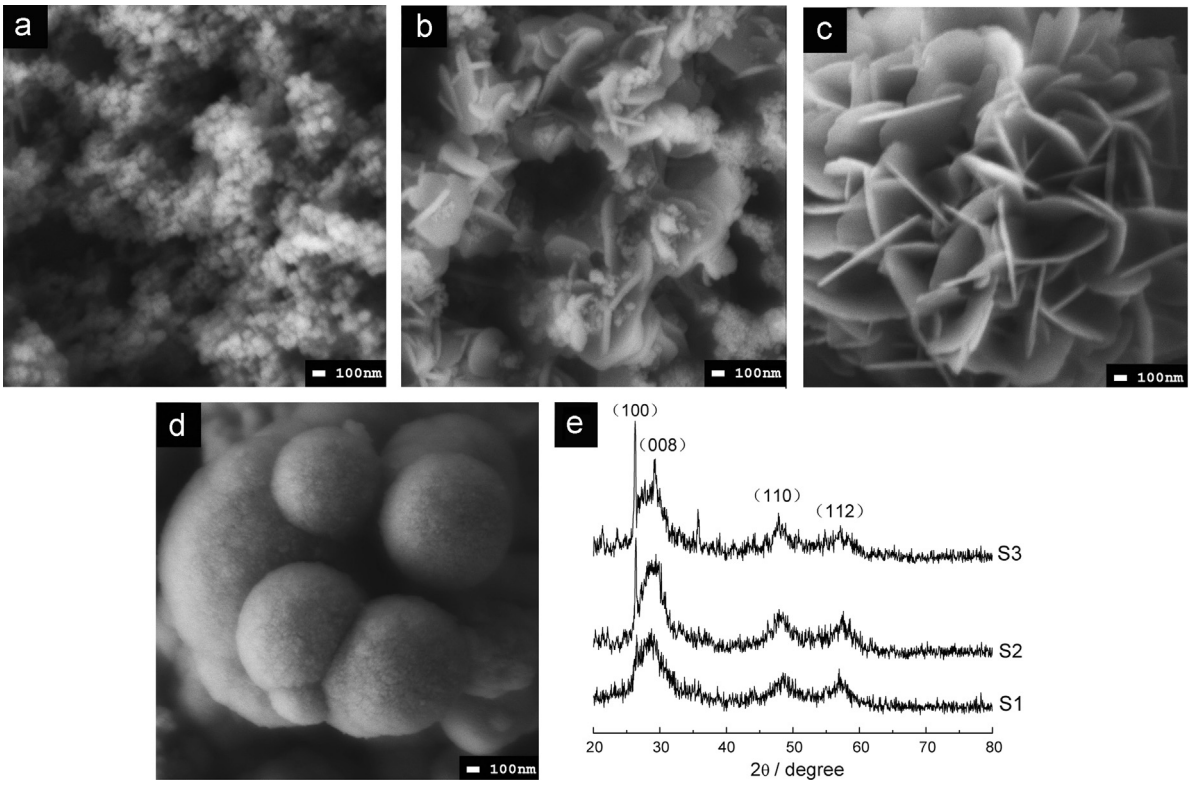

Fig. 1. SEM images of ZnS prepared for (a) 1 h, (b) 3 h, (c) 5 h, (d) 7 h, and (e) XRD spectra of nano-microstructural ZnS.