Journal of Alloys and Compounds 664 (2016) 476–480

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Morphology-controllable synthesis and enhanced photocatalytic activity of ZnS nanoparticles

Lixiong Yin, Dan Wang, Jianfeng Huang*, Liyun Cao, Haibo Ouyang, Xiang Yong

School of Materials Science and Engineering, Shaanxi University of Science and Technology, Xi'an, Shaanxi 710021, China

ARTICLE INFO

Article history:
Received 26 November 2014
Accepted 29 October 2015
Available online 3 November 2015

Keywords:
ZnS
Nanostructured materials
Photocatalytic activity
Chemical synthesis

ABSTRACT

Well crystallized cubic sphalerite phase ZnS micro/nanocrystallites with controllable morphologies were successfully prepared by a facile and efficient microwave hydrothermal method. The syntheses were carried out by varying the Zn/S molar ratios. The phase compositions, morphologies and optical properties of the as-prepared samples were characterized by X-ray diffraction, scanning electron microscopy and UV–vis diffuse reflectance spectroscopy. Results show that with Zn/S molar ratio ranges from 2:1 to 1:2, the morphology of the prepared ZnS micro/nanocrystallites changed obviously. ZnS nanoparticles with good dispersibility prepared at Zn/S molar ratio of 1:2, which average size is about 20 nm, shows high photocatalytic activity to degrade Methyl orange (MO). The degradation efficiency of ZnS nanoparticles reaches 97.4% under UV irradiation for 20 min. The good ultraviolet absorbing ability and big specific surface area of ZnS nanoparticles are believed to have a positive impact on improving the final degradation rate and degradation efficiency of MO in our research.

1. Introduction

Environmental pollution coming from organic pollutants and toxic waste water has drawn more and more attention in recent years [1–3]. Now increasing interest of heterogeneous photocatalysis for the treatment of recalcitrant and toxic pollutants present in the wastewater has been aroused [4,5]. Because of high efficiency, commercial availability and high chemical stability, the semiconductor photocatalysis is considered as one of the most promising environmental pollution remediation processes [6]. The process of heterogeneous photocatalysis is a kind of advanced oxidative process. It is based on electron-hole pairs created in semiconductor materials by the absorption of photons, which can further generate free radicals such as hydroxyl in the system to redox compounds absorbed on the surface of photocatalysts [7,8].

ZnS as an important II–VI semiconductor material with the band gap energy (Eg) of 3.6 eV, has been studied extensively as active photocatalysts owing to its high energy conversion efficiency and the relatively negative redox potential of its conduction band [9,10]. To enhance the photocatalytic activity of ZnS, extensive researches have been performed by controlling the morphology [11], crystallinity [12], and surface area [13]. In addition, considered the size effects originate primarily from the size quantization in nanoscale that can change the band gap of semiconductor and size-related surface characteristics such as surface area and defects, ZnS nanoparticles with big specific area have gained continues attentions [14]. The development of facile, cost-effective template-free methods suitable for the large-scale synthesis of ZnS nanoparticles with good dispersibility is of great importance and challenge for their industrial applications [13].

Many recent literature have reported that hydro/solvothermal method [6,15], chemical vapor deposition [16], precipitation method [17] and thermal decomposition [18] were widely used to prepare ZnS. It has been demonstrated that hydrothermal method is the most effective in fabricating well crystallized ZnS [6]. However, it takes long time to synthesize ZnS by traditional hydrothermal method, so in this paper we propose a facile and efficient microwave hydrothermal method to prepare morphology-controlled ZnS micro/nanocrystallites by just adjusting the Zn/S molar ratios in the reaction system. The prepared ZnS micro/nanocrystallites with multistage micro/nanospheres and nanoparticles morphologies exhibit different optical and photocatalytic properties. The influence of different Zn/S molar ratios on the structure and photocatalytic activity of ZnS was particularly investigated. Different kinds of dyes: anionic (Methyl orange), cationic (Rhdamine B) and neutral (Neutral red) dyes were used to

* Corresponding author.
E-mail address: huangjfsust@126.com (J. Huang).

http://dx.doi.org/10.1016/j.jallcom.2015.10.281
0925-8388/

test the photocatalytic response property of the prepared ZnS nanoparticles. Moreover, the photocatalysis degradation reaction kinetics of MO, which catalyzed by the as-prepared ZnS micro/nanocrystallites was also researched in this paper.

2. Experiment

Analytical $Zn(NO_3)_2 \cdot 6H_2O$, thioacetamide (TAA), $NH_3 \cdot H_2O$ and HNO_3 were used as raw materials without any purification. First, 25 mmol $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved into 50 mL H_2O, then 12.5 mmol, 25 mmol and 50 mmol TAA were added with magnetic stirring to form the precursor solutions, respectively. The pH value of the reaction solutions were adjusted by $NH_3 \cdot H_2O$ (Wt% = 10%) and HNO_3 (0.5 mol L^{-1}) to be 7.00. The precursor solutions were transferred to 100 mL Teflon-lined stainless steel autoclaves with the filling capacity of 50% and maintained in an MDS-10 microwave hydrothermal system at 170 °C with the operating power of 400 W for 2 h. After the system terminated and cooled down to room temperature, the precipitants were centrifuged and washed by distilled water and anhydrous ethanol for several times. Afterwards, these precipitants were finally dried in vacuum drying oven at 60 °C for 3 h.

The crystalline microstructure of the as-prepared powder was characterized by a powder X-ray diffraction (XRD, Rigaku D/max-2000) with Cu Kα radiation (λ = 0.15406 nm) at 40 kV and 40 mA in the 2θ range of 10°~60°. The morphology of the sample was observed by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Acceleration voltage: 3 kV). UV–vis diffuse reflectance spectrum of the sample was measured by Shimadzu UV-2450 UV–vis spectrophotometer.

Photocatalytic activities of the prepared ZnS micro/nanocrystallites were evaluated by photocatalytic degradation of 10 mg L^{-1} Methyl orange (MO), Rhdamine B (RhB) and Neutral red (NR) aqueous solution. The photocatalytic activity tests were carried out by employing a BL-GHX-V photocatalytic reactor (Xi'an, BILOBN, Co. Ltd.) with a 300 W mercury lamp as UV light source. The loading amount of catalysts was 0.5 g L^{-1}. Before illumination, the suspensions of dyes with catalysts were magnetically stirred in the dark for 30 min, after dispersing in an ultrasonic bath for 5 min, to ensure the establishment of an adsorption–desorption equilibrium between catalysts and dyes. Then, the solution was exposed to a 300 W mercury lamp under magnetic stirring. By the irradiation time prolong, 6 ml of the solution was collected by centrifugation each 5 min. The concentrations of the remnant dyes in the collected solution were monitored by UV–vis spectroscopy (Unico UV-2600). In the process of photocatalytic reaction, the degradation efficiency of dyes was calculated by Eq. (1):

$$\text{Degradation efficiency } (\%) = (1 - C_t/C_0) * 100\% \quad (1)$$

Where C_0 represents the initial concentration of dye aqueous solution and C_t represents the concentration of dye aqueous solution after different minutes of UV irradiation.

3. Results and discuss

3.1. Phase analysis

Fig. 1 shows the XRD patterns of the samples prepared at different Zn/S molar ratios range from 2:1 to 1:2. All the diffraction peaks of the as-prepared samples shown in Fig. 1 can be readily indexed to the pure typical cubic sphalerite ZnS (JCPDS No.05-0566). Main reflection peaks of ZnS become sharper with the Zn/S molar ratio varies from 2:1 to 1:2, which indicates that excessive S^{2-} is good to improve the crystalllinity of ZnS.

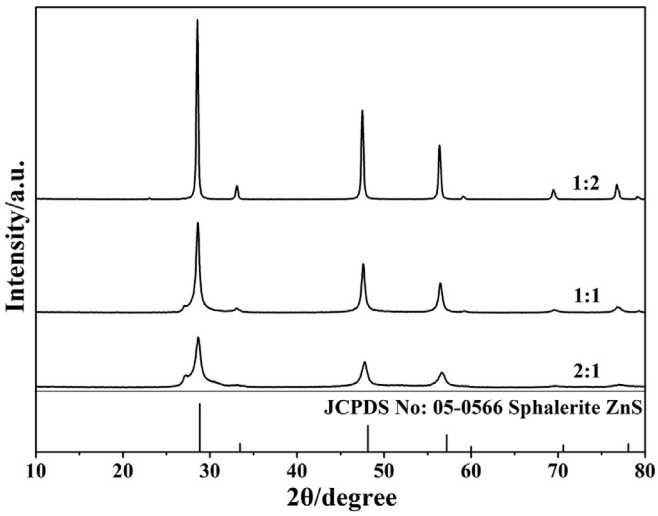

Fig. 1. XRD patterns of the samples prepared at different Zn/S molar ratios.

3.2. Morphological analysis

SEM images of the as-prepared ZnS micro/nanocrystallites are shown in Fig. 2. It can be obviously observed that the morphologies of ZnS prepared at Zn/S molar ratio varies from 2:1 to 1:1 are spheres with different sizes and surface morphologies. ZnS nanoparticles with uniform size and good dispersibility were achieved at Zn/S molar ratio of 1:2. With the increase of TAA, the concentration of S^{2-} increased, the size of the samples gets smaller. This suggests TAA play an important role in the morphology control of ZnS micro/nanocrystallites.

TAA can release mass S^{2-} in short time, which can easily react with Zn^{2+} to form ZnS crystal nucleus. Fig. 3 displays the schematic diagram of the possible growth pattern of ZnS micro/nanospheres and nanoparticles prepared at different Zn/S molar ratios. When S^{2-} is insufficient (Zn/S molar ratio equals 2:1), ZnS microcrystallites with microspheres morphology, which average diameter is about 1.2 μm were prepared. The surfaces of the microspheres were covered by small nanorods. In this case, ZnS microsphere may be assembled by small nanorods in the growth and crystallization process. ZnS nanocrystallites prepared at Zn/S molar ratio equals 1:1 with the morphology of multistage nanospheres, which average diameter is about 500 nm, were assembled by a lot of irregular nanoparticles. This means, when Zn/S molar ratio is according with the stoichiometric ratio to form ZnS, the ZnS crystal nucleuses competitively grow to be nanoparticles and random aggregation to assemble form nanospheres to decrease the higher surface energy of the nanoparticles. When S^{2-} is excessive (Zn/S molar ratio equals 1:2), mass ZnS crystal nucleuses formed to grow and crystallize of ZnS nanoparticles, which average size is only about 20 nm.

3.3. Optical and photocatalytical properties

The UV–visible diffuse reflection spectra of the as-prepared ZnS micro/nanocrystallites are shown in Fig. 4. It can be seen that there exists a strong absorption edge below 350 nm for all samples. The steep shape of the spectra indicates that the samples have good absorption property of ultraviolet. The absorption band edge of the samples prepared at Zn/S molar ratio of 1:2 is red-shift with the enhanced optical absorbing ability, which may be attributed to their smaller sizes.