Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 42 (2016) 211–219

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Bandgap tuning and photocatalytic activities of $CuSe_{1-x}S_x$ nanoflakes

Shuaishuai Ni, Yanjie Su*, Zhe Ai, Jing Hu, Zhi Yang, Eric Siu-Wai Kong, Yafei Zhang*

Key Laboratory for Thin Film and Microfabrication Technology of the Ministry of Education, Department of Micro/Nano Electronics, Shanghai Jiao Tong University, Shanghai 200240, China

Received 8 June 2015; received in revised form 12 August 2015; accepted 18 August 2015
Available online 24 August 2015

Abstract

Hexagonal $CuSe_{1-x}S_x$ nanoflakes with 200–600 nm edge in length and 15–20 nm thick have been successfully synthesized via a concentrated alkaline hydrothermal method from CuCl, Se and S powders. Experimental results indicate that the reaction conditions such as NaOH concentration, reaction temperature, surfactant category and Cu source greatly affect the morphology of as-synthesized $CuSe_{1-x}S_x$ nanoflakes. Moreover, their bandgaps are tunable as a function of x (0.1–0.5), which can be easily realized by changing the ratio of Se/S in the starting mix. The photocatalytic degradation of organic methylene blue (MB) with $CuSe_{1-x}S_x$ and H_2O_2 addition under visible light irradiation has also been studied. Degradation time for the MB aqueous solution (2×10^{-5} M) was about 15 min for $CuSe_{1-x}S_x$ nanoflakes with different x values (0.1–0.5), indicating the excellent photocatalytic activities of the hexagonal $CuSe_{1-x}S_x$ nanoflakes.

Keywords: A. Powders: chemical preparation; B. Nanocomposites; C. Optical properties

1. Introduction

Among the copper chalcogenides, CuS and CuSe are two typical p-type semiconductors, which have potential applications in supercapacitors [1], Li-ion batteries [2], solar cells [3,4], gas sensors [5], medical devices [6,7] and photocatalysts [8–10] due to their excellent physical, chemical, electrical, biochemical and optical properties. Since the outstanding properties have a direct correlation with their micromorphologies [11,12], the controlled synthesis of copper chalcogenides is considered to be necessary before large-scale applications. Especially, the synthesis of flakes-like copper chalcogenides has attracted more and more attentions in recent years.

For instance, Basu et al. [13] have reported that CuS with hexagonally stacked plate morphology can be synthesized by employing copper (II) chloride, acetylacetone, sodium acetate, dichloromethane, ethanol, and sodium hydroxide as precursors via a modified hydrothermal method. Liu et al. [14] have synthesized hexagonal CuS nanoplatelets by using copper nitrate, potassium ethylxanthate, ethanol and hexadecylamine as raw materials, via a facile solution method. Li et al. [15] have reported a sonochemical-assisted method to synthesize α-CuSe nanoflakes with a direct bandgap of 2.2 eV, using elemental Se and $Cu(Ac)_2$ as precursors. Vinod et al. [16] have demonstrated a solution-phase synthetic route with a relatively low temperature reaction, using a single precursor and resulted in the surfactant-free growth of nanomaterials for preparing hexagonal CuSe nanoplatelets. In our earlier work [8], we synthesized pure CuSe with hexagonal nanoflake-like morphology via a concentrated alkaline hydrothermal method. However, very few reports about the synthesis and microstructure of $CuSe_{1-x}S_x$ have been published to date, especially for plate-like morphology.

For copper chalcogenide semiconductors, bandgap value is a critical factor and bandgap engineering of atomically thin two-dimensional nanomaterials is the key to their application in nanoelectronic and optoelectronic devices such as solar cells and light emitting diodes [17]. For example, Wang et al. [18] developed a facile one-pot method to synthesize monodispersed, ternary-alloyed

*Corresponding authors. Tel./fax: +86 21 34205665.
E-mail addresses: yanjiesu@sjtu.edu.cn (Y. Su), yfzhang@sjtu.edu.cn (Y. Zhang).

http://dx.doi.org/10.1016/j.ceramint.2015.08.092
0272-8842/

copper sulfide selenide ($Cu_{2-x}S_ySe_{1-y}$) nanocrystals with tunable bandgap. However, the morphology of $Cu_{2-x}S_ySe_{1-y}$ was also modified with the tuning of the bandgap and the molar ratio of Cu/(Se+S) does not equal to one. Moreover, there are few reports about $CuSe_{1-x}S_x$ nanomaterial with a tunable bandgap while having the same morphology.

In this paper, we successfully synthesized $CuSe_{1-x}S_x$ nanoflakes using the concentrated alkaline hydrothermal method, in which CuCl, Se and S powder are used as raw materials. We also investigated the difference among $CuSe_{1-x}S_x$ with different x values (x=0.1, 0.2, 0.3, 0.4 and 0.5). It is found that all as-synthesized $CuSe_{1-x}S_x$ nanoflakes have almost the same morphology. In addition, the bandgap value of $CuSe_{1-x}S_x$ nanoflakes can be tuned by changing the x values (0.1–0.5), which can be fulfilled by changing the molar ratio of Se/S in the raw materials. The MB degradation with $CuSe_{1-x}S_x$ and H_2O_2 addition has also been studied under visible light irradiation,. The experimental results indicate that as-synthesized $CuSe_{1-x}S_x$ nanoflakes have excellent photocatalytic activity.

2. Experimental

2.1. Materials

Polyvinyl pyrrolidone (PVP, M_W=1,300,000) and Se powder ($\geq$99.99% purity) were purchased from Aladdin Chemistry Co., Ltd. CuCl ($\geq$97% purity), cetyltrimethylammonium bromide (CTAB, $\geq$99% purity) and S powder ($\geq$99.5% purity) were purchased from Sinopharm Chemical Reagent Co., Ltd. NaOH ($\geq$96% purity) and 30% H_2O_2 aqueous solution were purchased from Shanghai Ling Feng Chemical Reagent Co., Ltd. All chemicals were analytical grade and used without further purification.

2.2. Synthesis of $CuSe_{1-x}S_x$ nanoflakes

$CuSe_{1-x}S_x$ (x=0.1, 0.2, 0.3, 0.4 and 0.5) nanoflakes have been synthesized by using a concentrated alkaline hydrothermal method. In a typical synthetic procedure of $CuSe_{1-x}S_x$ (x=0.3): first, 297 mg (3 mmol) of CuCl and 200 mg of PVP were dissolved into 25 mL NaOH solution (6–7 M) with stirring for 30 min to form a uniform solution. Second, 248.7 mg (3.15 mmol) Se powder and 43.5 mg (1.35 mmol) S powder were added into them with stirring for another 30 min to making the solution homogenous. Third, the above solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed and maintained at 110 °C with stirring for 2 h, and then cooled to room temperature. Finally, the black precipitate was separated and collected by centrifugation, and then washed with deionized water and centrifugation for several times before dried at 40 °C in vacuum. The typical procedures of $CuSe_{1-x}S_x$ (x=0.1, 0.2, 0.4 and 0.5) are similar to the above procedure (x=0.3), and the only thing to do is the change of the dosage of Se powder and S powder. And it is worth mentioning that the concentration of NaOH aqueous solution increases slightly between 6 and 7 M while the value of x varying from 0.1 to 0.5.

In order to investigate the influence of NaOH concentration, reaction temperature, surfactant category and Cu source on formation process of $CuSe_{1-x}S_x$ nanoflakes, the same experiment was repeated using NaOH concentration (5, 6, 7, 8, 10 and 12 M), reaction temperature (90, 100, 110 and 120 °C) and surfactant (PVP, CTAB) while other conditions were kept the same.

2.3. Characterizations

The scanning electron microscopy (SEM, Zeiss Ultra 55, Germany) and transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) were used to characterize the micro-structural morphologies of the as-synthesized $CuSe_{1-x}S_x$ nanoflakes. Oxford INCA energy-dispersive X-ray spectroscopy (EDS) was used to examine the chemical composition of $CuSe_{1-x}S_x$ nanoflakes. The crystal structure of the $CuSe_{1-x}S_x$ nanoflakes was examined by X-ray powder diffraction (XRD) using a 18 kW advanced X-ray diffractometer (D8 ADVANCE, Bruker, Germany) with Cu-Kα radiation (λ=0.154056 nm) at a scanning rate of $6^\circ\ min^{-1}$ in 2Theta (2θ) ranging from 20° to 80°. After the $CuSe_{1-x}S_x$ nanoflakes were dissolved in the deionized water by ultrasonic to form a homogenous solution, the optical properties of the as-synthesized $CuSe_{1-x}S_x$ nanoflakes were measured by using a UV−vis−NIR spectrophotometer (Perkin-Elmer Lambda750) at room temperature. The wavelength was 400–800 nm and the deionized water was the reference material.

2.4. Catalytic degradation of MB solution

The photocatalytic activities of the as-synthesized $CuSe_{1-x}S_x$ nanoflakes were investigated by degrading MB under visible light illumination. Here a Xe lamp (150 W power, 200–2500 nm wavelength) was used as the light source after filtering the UV light (under 400 nm) by an optical filter. So the light intensity used in the experiment was 20 mW/cm^2. The specific process was as follows: 10 mg $CuSe_{1-x}S_x$ nanoflakes were mixed with 40 mL MB solution (2×10^{-5} M). One-minute-ultrasonic was employed to disperse the $CuSe_{1-x}S_x$ uniformly. Then, the dispersion was stirred in the dark for 60 min to ensure the adsorption–desorption equilibrium. After that, 1 mL 30% H_2O_2 aqueous solution was added into the $CuSe_{1-x}S_x$–MB solution and the resulting solution was stirred under light irradiation. To investigate the stability of as-synthesized $CuSe_{1-x}S_x$ nanoflakes, recycling experiments were carried out. In the first cycle, 10 mg $CuSe_{0.7}S_{0.3}$ nanoflakes and 1 mL H_2O_2 were used to perform the MB degradation experiment. Then the $CuSe_{0.7}S_{0.3}$ nanoflakes were collected by centrifugation and dried at 40 °C in vacuum. In the second cycle, we used the $CuSe_{0.7}S_{0.3}$ nanoflakes collected in the first cycle to repeat the MB degradation experiment. The third and fourth cycles were the same by using the same $CuSe_{0.7}S_{0.3}$ nanoflakes.

3. Results and discussion

3.1. Characterizations of morphology and microstructure

Fig. 1 shows the SEM images of as-synthesized $CuSe_{1-x}S_x$ nanoflakes. It can be clearly seen that the as-synthesized $CuSe_{1-x}S_x$ have almost the same morphology of hexagonal