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Hydrothermal Synthesis, Characterization and Raman Vibrations of Chalcogenide SnS Nanorods

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Abstract: One dimensional nanostructure have been considered promising candidates for optoelectronics and energy storage devices. However, cost-effective approach for large-scale production using wet chemical method is still a big challenge. Here, single crystalline monodispersed stannous sulfide (SnS) nanorods in the range of 400nm to micrometer have been synthesized using solution-based method. The morphology of the prepared nanorods was controlled by tuning the parameters, including the concentrations of reagents, reaction time and temperature. The resultant nanorods were characterized using XRD, FESEM, and Raman spectroscopy techniques. Four vibrational modes 141 cm^{-1}, 165.3 cm^{-1}, 218 cm^{-1} and 289.6 cm^{-1} were observed by Raman spectroscopy, which is consistent with nano orthorhombic SnS herzenbergite phase.

1. Introduction

Last decade, the advancement in nanotechnology has been expanding rapidly and applying successfully in practical applications. Researcher have been paying attention to controlled shaped morphology of nanomaterials after growth, particularly solution-phase fabrication of one-dimensional nanostructures of binary semiconductors materials. Nanostructures of metal chalcogenides such as CdS, CdSe, ZnS, SnS, etc., have attracted considerable interest having their application in optical, electronic and superconductor devices [1, 2]. Narrow band gap IV–VI (IV = Sn, Ge, Pb; VI = S, Te, Se) semiconductors exhibiting infrared (IR) and near-infrared (NIR) optical activity have been extensively studied. Among them, tin chalcogenide based materials such as tin sulfide semiconducting nanomaterial has attained immense importance owing to its interesting potential applications such as photodetectors, optoelectronics, and data storage[3, 4]. SnS is a narrow bandgap semiconductor with an optical band gap of direct transitions 1.32–1.5 eV and indirect transitions 1–1.3 eV [5]. Additionally, it has the advantage that its constituent elements are abundant in nature and not possessing any health and environmental hazards. Also the orthorhombic herzenbergite modification of SnS possesses a layered structure consisting where the Sn and S atoms are tightly bonded in a layer and layers are bonded by weak Van der Waals forces [6] Importantly, SnS exhibits both the p- and n-type conduction depending on the concentration of tin [7]. The narrowband gap and the interesting structural property of SnS make it a potential candidate for solar absorber in thin film solar cell and near-infrared (NIR) detector [8, 9], as photovoltaic materials [10] and in holographic recording

medium [11]. Moreover, it has the advantage of its constituent elements being abundant in nature and not posing any health and environmental hazards. These phenomena demonstrate that SnS has appropriate electrical and optical features for use in solar cells [8].

Tin sulfides show a variety of phases, such as SnS, SnS_2, Sn_3S_4 and SnS, due to the versatile coordinating characteristics of tin and sulfur [12]. Nowadays, there is a great deal of current interest in the synthesis of nanostructures with specific nano-morphologies and structures [13–15]. Inorganic materials with different morphologies, which have the same chemical composition, may exhibit different properties [16]. In recent years, SnS nanostructures have been prepared by various methods, such as hydrothermal method [5], solvothermal method [17, 18], aqueous solution method [19], and polyol route [20].

In this paper, we developed a very simple solution based method for synthesis of large scale of SnS nanorods. A series of experiments are carried out to observe the growth mechanism of 1D SnS NRs. Phonon modes are calculated by Raman spectroscopy.

2. Experimental

2.1. Sample Preparation

All chemicals were of analytical grade (Beijing Chemicals Co., Ltd.) and were used without further refinement. Tin (II) chloride ($SnCl_2.2H_2O$) and sodium sulfide ($Na_2S.9H_2O$) were taken as tin and sulfur sources respectively, and ethylene glycol was used as a solvent. In a typical synthesis, 0.226 g of $SnCl_2.2H_2O$ and 0.678 g of Na_2S were dissolved ultrasonically in 20 ml of ethylene glycol respectively. The stoichiometric ratio of 3:1 $Na_2S.9H_2O$ and $SnCl_2 \cdot 2H_2O$ solutions were used for precipitation. The $SnCl_2.2H_2O$ solution was added dropwise in Na_2S solution under magnetic stirring. The solution turns to dark brown color with the addition of tin (II) chloride solution. The final participation transferred into 40 ml Teflon-lined stainless autoclave. The autoclave was placed in the oven at a temperature of 250^{o}C for 20 h and then cooled down naturally. Gray powder was collected and washed for several times with distilled water and ethanol to eliminate the impurities before drying at 70°C for 9 h.

2.2. Characterization

The identification of crystal structure was performed by X-ray diffractometer (XRD) using Cu Kα radiation (λ = 1.5406 Å)**,** with 2θ ranging from 10° to 650°. The elemental composition and structural characterization of the as-synthesized powder were analyzed by energy dispersive analysis (EDS) (INCA X-MAX 50, England), Scanning Electron Microscopy (SEM) (Zeiss-SUPRA55)**.** Confocal Raman micro-spectroscopy (Horiba Jobin Yvon HR 800 Raman spectrometer France) was used to analyze the phonon modes of as-synthesized SnS nanorods**.**

3. Results and Discussion

The morphology of as-prepared nanomaterial was firstly investigated by FE-SEM. Fig. 1(a, b) shows the low and high magnification FE-SEM images which demonstrate the high yield of 1D rod-like structure of SnS. These synthesized SnS nanorods are well shaped and randomly oriented over the copper tape. The crystallinity of SnS nanorods has the width of about 400 nm and the length is in several micrometers range. The crystal structures of the as-synthesized SnS nanorods were analyzed using X-ray diffraction as shown in Fig. 2(a). The crystal structures of the as-synthesized SnS nanorods were analyzed using X-ray diffraction as shown in Fig. 2(a). All the diffraction peaks are in good agreement with orthorhombic tin chalcogenide herzenbergite parameters a = 0.4329 nm, b = 1.1192 nm, c = 0.3984 nm and $\alpha = \beta = \gamma = 90^o$ (JCPDF Cards 39-0354). Moreover, no signals from other materials are observed in the spectra. The strong and sharp diffraction peaks indicate that the product is well crystallized. Debye–Scherrer formula is used to calculate the crystallite size of the particles which is in the range of 300–400 nm. Elemental composition of the SnS nanorods is

measured through EDS analysis as illustrated in Fig. 2 (b). The EDS spectrum has contained only Sn and S elements, which is in good agreement with the XRD result, which ratifies the pure configuration of SnS without any impurities such as other binary sulfides.

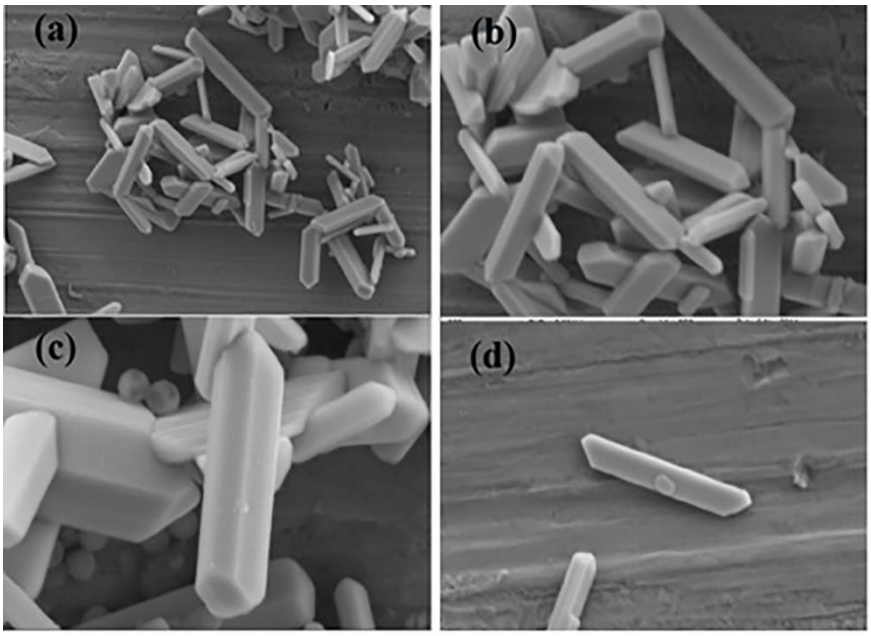
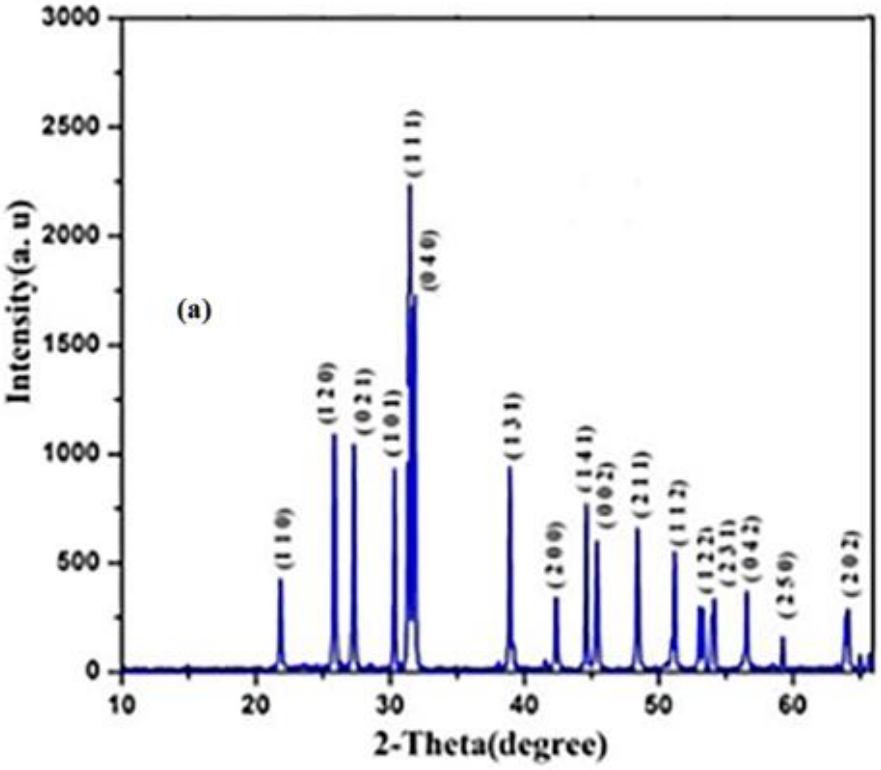


Figure 1. (a, b) Low magnification FESEM images of nanorods, **(c, d)** high magnification FESEM images of single SnS nanorod.



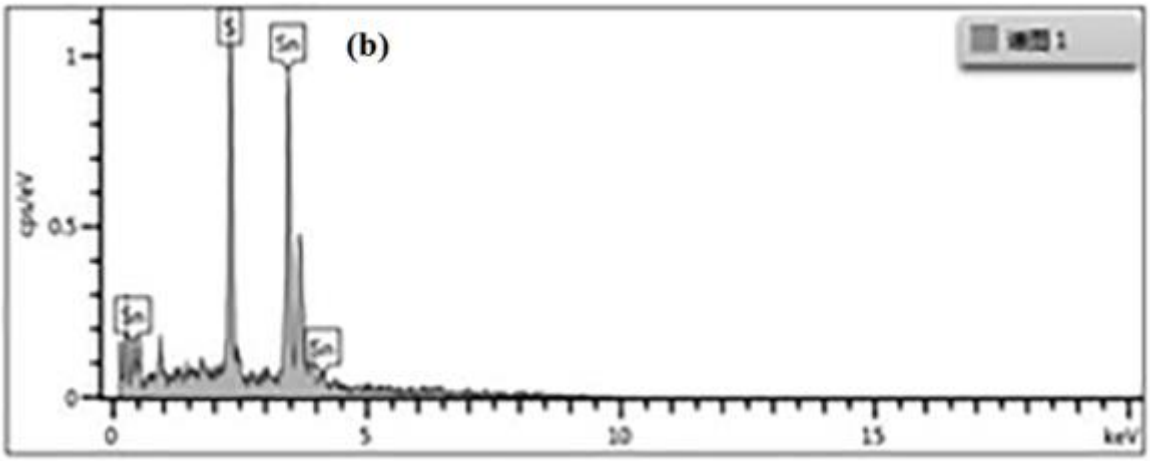


Figure 2. (a) X-ray diffraction pattern and **(b)** EDS spectrum of as-synthesized SnS nanorods.

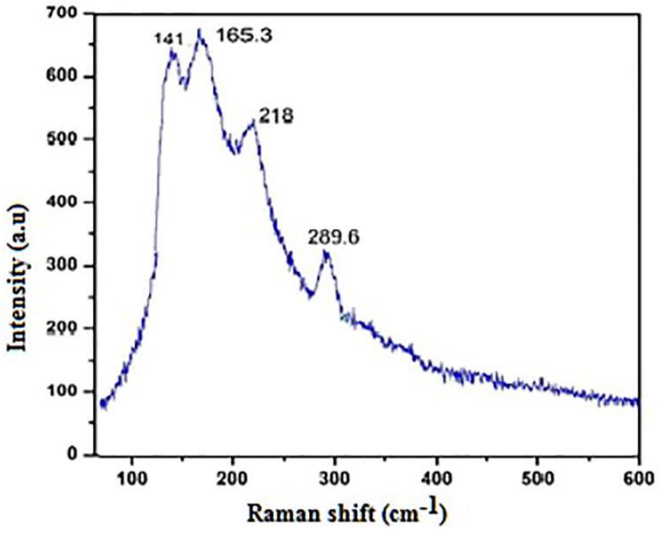


Figure.3. Raman spectrum of SnS nanorods at 373K.

Furthermore, structural and vibrational modes of the prepared tin monosulfide nanoparticles were measured by Raman spectroscopy. Raman spectroscopy is one of the advanced techniques to examine the compositions and chemical states. Fig. 3 indicates the Raman spectrum of the as-prepared SnS nanorods. The dominant Raman peaks are at 141 cm^{-1}, 165.3 cm^{-1}, 218 cm^{-1} and 289.6 cm^{-1}. The lattice vibrations at 141 cm^{-1} correspond to the B_{2u} mode, the peak at 165.3 cm^{-1} to the B_{3g} mode, the peak at 218 cm^{-1} to the A_g mode and the peak at 289.6 cm^{-1} to the B_{2g} mode of SnS nanoparticles at room temperature. Tin sulfide has 21 optical active modes of which 12 are Raman active modes, 7 are infrared active modes and 2 are inactive. According to the reported literature A_g, B_{2g} and B_{3g} are Raman active modes while B_{2u} is the infrared active mode of SnS nanostructure [21].these phenomena shows that the as-synthesized nanostructures are promising materials for energy storage applications and solar cells.

4. Conclusions

In summary, this paper presents synthesize of the single crystalline SnS nanorods using hydrothermal process. The FESEM results had exhibited that the length of prepared SnS nanorods was in the range of several micrometers, the width was about 300-400 nm and the average crystallite size was estimated

to be approximately 25 nm. Raman spectroscopy analyses indicated that the as-prepared nanorods mainly exhibit SnS phase. Such materials with controlled morphologies may exhibit a special performance in solar cell and energy storage applications.

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6. References

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