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HYDROTHERMAL SYNTHESIS OF CHALCOGENIDE SnS NANORODS: LATTICE VIBRATIONS AND OPTICAL PROPERTIES

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Metal chalcogenides have attracted significant interest for the researchers having their potential application in superconductor devices. Tin sulfide (SnS) nanorods have been synthesized with the combination of $SnCl_2$ and Na_2S solutions. Stoichiometries ratio of 1:4 of $SnCl_2·2H_2O$ and $Na_2S.9H_2O$ solutions were used as main ingredients. Hydrothermal method was used for the preparation of single-crystalline monodispersed stannous sulfide (SnS) nanorods having a diameter of 413 nm and length up to 2.37 micrometer. The resultant nanorods were characterized using XRD, FESEM, PL and Raman spectroscopy techniques. Elemental composition was measured through EDS. Three modes 83.3, 163.1 and 220 cm^{-1} were observed by Raman spectroscopy, which were consistent with nano orthorhombic SnS herzenbergite phase.

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1. Introduction

Materials with low-dimensional structures have more benefits compared with other energy materials due to their high surface reactivity and extraordinary access to the material– material interface. In particular, one-dimensional materials have shown excellent behavior in their electrical, magnetic and optical properties in comparison with their bulk properties.

Recently, metal chalcogenides have attracted significant interest and are still the subject of intense investigation for the researchers owing to their potential application in optical, electronic and superconductor devices [1–3]. Due to the versatile coordinating characteristics of tin and sulfur, Tin sulfide is one of the most important chalcogenide showing a variety of phases, such as SnS, SnS_2, Sn_2S_3, Sn_3S_4, and SnS_3 etc. Among these materials, tin monosulphide (SnS) has been found to be one of the promising IV-VI semiconductor materials due to their important properties and potential applications. It belongs to the group of layered semiconductors having orthorhombic structures as deformed NaCl structure along c-axis, where the Sn and S atoms are tightly bonded with a layer by weak van der Waals forces [4]. SnS exhibits p- type conduction and the acceptor levels are created by double-ionized tin vacancies. An excess of tin changes the type of conductivity of SnS from p- to n- type [5]. SnS is reported to have a direct band gap of about 1.3-1.5 eV and an indirect band gap of 1-1.3 eV which depends on the condition of preparation. It has the high absorption coefficient of 10^4 cm^{-1} [6, 7].

Tin monosulfide (SnS) has attracted more attention of researchers owing to its interesting properties and potential application in photoconductors [8], near-infrared detector [9], holographic

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recording systems [10], and photovoltaic materials with high conversion efficiency [11]. To date, many methods were developed to fabricate SnS with different morphologies, including nanoparticles [12], fullerence-like nanoparticles [13], layered nanocrystallites [14, 15], nanorods [16], nanowires [17], and nanobelts [18].

Recently, stannous sulfide (SnS) nanostructures like nanoparticles, nanoflowers, nanofibers, nanoflakes, nanosheets and nanorods have been prepared by various synthesis routes, such as solvothermal method [19], hydrothermal method [20, 21], aqueous solution method [22] and polyol route [23]. Zubair et al. investigated the single crystalline SnS nanorods using the hydrothermal growth technique. They calculated that length of the as-grown tin (II) sulfide nanorod was 1-2 µm, width was about 80 nm and thickness was few nanometers [24]. Nanorods and nanosheets of tin sulfide (SnS) were synthesized by a novel thioglycollic acid (TGA) assisted hydrothermal process. The diameter of the SnS nanorods varied within 30–100 nm [25].

In the present work novel self-assembling nanorods-based crossed architectures of stannous sulfide (SnS) have been successfully fabricated using template-free hydrothermal synthesis under facile conditions. The physical and chemical structure of the as-prepared SnS nanorods were characterized. Furthermore, the phonon modes Raman spectroscopy and the photoluminescence of SnS nanorods will be discussed.

2. Experimental details

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 solvent. In a typical synthesis, 0.226 g of $SnCl_2.2H_2O$ and 0.91 g of Na_2S were dissolved ultrasonically in 20 ml of ethylene glycol (EG) respectively. Stoichiometric ratio of 1:4 $SnCl_2{\cdot}2H_2O$ and $Na_2S.9H_2O$ solutions was used for precipitation. The $SnCl_2$ solution was added drop wise in the Na_2S solution under magnetic stirring. The solution turns dark brown with the addition of $SnCl_2$ solution. The final participation transferred into a 40 ml Teflon-lined stainless autoclave. The autoclave was placed in the oven at a temperature of 250^{o}C for 24 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 7 h.

Sample Characterization

The identification of crystal structure was performed by a Rigaku D/MAX-RB X-ray diffractometer (XRD) using Cu-Kα rad (λ = 1.54056 Å). Elemental composition and structural characterization of the as-synthesized SnS powder were analyzed by energy dispersive analysis (EDS) (INCA X-MAX 50, England), field emission scanning electron microscopy (Zeiss Ultra 55, Germany). Confocal Raman micro-spectroscopy (Horiba Jobin Yvon HR 800 Raman spectrometer France, with a 532 nm wavelength as excitation source) was used to analyze phonon modes of as-synthesized SnS nanorods.

3. Results and discussion

The morphology of the as-prepared SnS nanorods was initially 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 tin sulfide. These synthesized SnS nanorods are well shaped and randomly oriented over the copper tape. Fig. 1(c, d) shows the diameter of about 413 nm and a length of about 2.37 um of a singles SnS nanorod. 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 the herzenbergite stannous sulfide nanorods with parameters a = 0.4329 nm, b = 1.1192 nm, c = 0.3984 nm and $\alpha = \beta = \gamma = 90$ (JCPDF Cards 39-0354). Moreover, no signals from other materials such as SnS_2, Sn_3S_4 etc. are observed in the spectra.

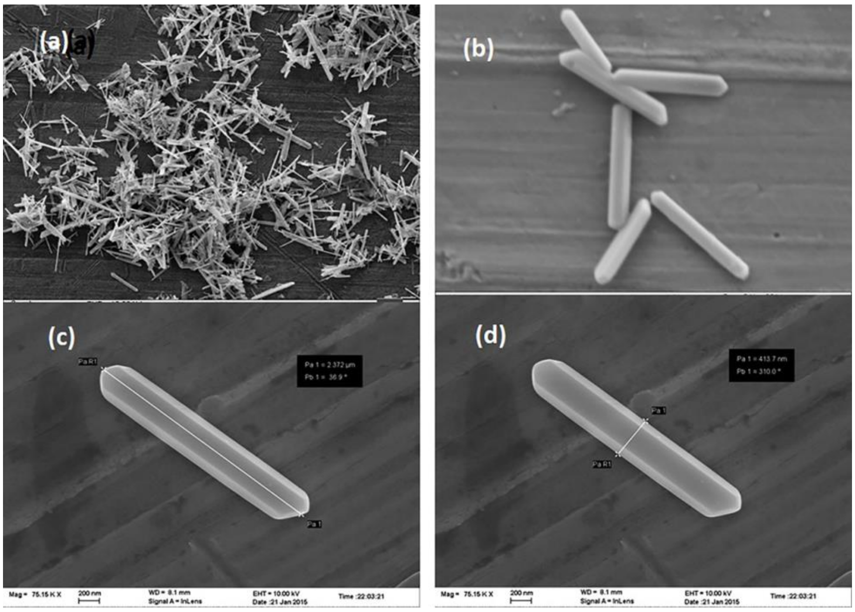

Fig. 1. (a) low magnification and (b-d) high magnification FESEM images of the as-synthesized SnS nanorods

The strong and sharp diffraction peaks indicate that the product is well crystallized. The XRD peaks indicated that the average crystalline size is in the range of 40–60 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. These results ratify the pure configuration of SnS without any impurities such as other binary sulfides and oxides. Furthermore, structural and vibrational modes of the as-prepared nanoparticles were measured by Raman spectroscopy. Raman spectroscopy is one of the advanced techniques to examine the compositions and chemical states. Fig. 3 (a) indicates the Raman spectrum of the as-prepared tin sulfide nanorods. The dominant Raman peaks are at 83.3, 163.1 and 220 cm^{-1}. The lattice vibrations at 83.3 and 163.1 cm^{-1} correspond to B_2g and the peak at 220 cm^{-1} correspond to Ag mode of SnS nanorods. The results are in good agreement with the reported literature [26]. Fig. 3 (b) shows the photoluminescence (PL) emission spectrum of the as-synthesized SnS nanorods.

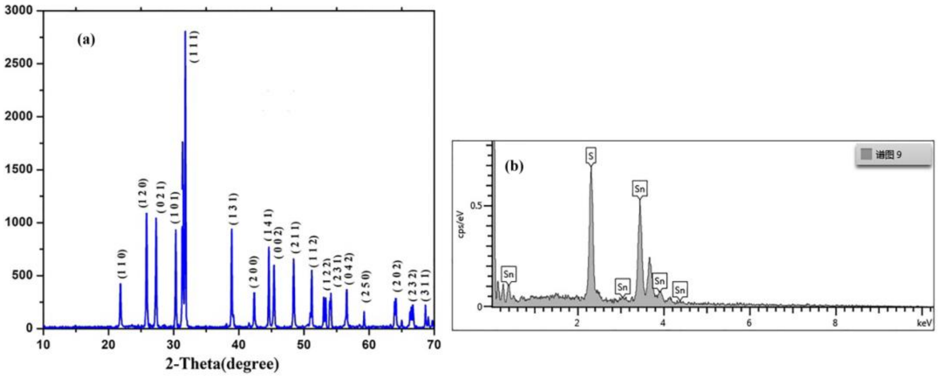

Fig. 2. (a) X-ray diffraction pattern (XRD) and (b) EDS spectrum of as-prepared SnS nanorods

The photoluminescence (PL) spectrum consists of one strong narrow emission at 478 nm. The absence of emission from trap states suggests the stoichiometric nature of SnS nanorods, without a surface excess of Cd2+ or S2+ vacancies. The luminescence at 478 nm may be attributed to a higher level transition in SnS crystallites. It has been reported that this kind of band-edge lumi3nescence arises from the recombination of excitons or from trapped electron-hole pairs [27].

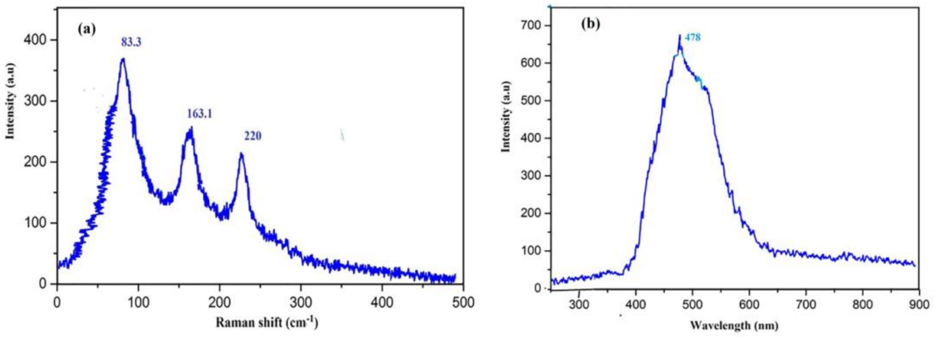

Fig. 3. (a) Raman s9pectra of the SnS (b) photoluminescence (PL) spectrum of the as-synthesized SnS nanoparticles

4. Conclusions

In summary, the chalcogenide SnS nanorods were successfully prepared by a low temperature hydrothermal method. XRD pattern, SEM images, EDS spectrum reveal that the product is composed of well crystallized SnS nanorods. Three vibrational modes of Raman spectrum and a strong peak of the photoluminescence (PL) spectrum confirm the formation of tin sulfide nanostructure. $SnCl_2/Na_2S$ mol ratio of the reactants and hydrothermal temperature are critical for hydrothermal synthesis of the SnS nanorods.

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