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Preparation of size-tunable SnS nanoparticles by a sonochemical method under multibubble sonoluminescence conditions

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ABSTRACT

SnS nanoaprticles have been synthesized by an environmentally benign sonochemical method under multibubble sonoluminescence conditions. First, SnS nanoparticles were prepared at room temperature by reacting $SnCl_2$ and thioacetoamide dissolved in ethylene glycol with various ethanolamines such as ethanolamine, diethanolamine, and triethanolamine. The sonochemical reactions were operated at 20 kHz and 220 W for 5 min. Depending on the kind and amount of ethanolamines, SnS nanoparticle sizes in diameter varied within 4–15 nm range. Depending on the SnS nanoparticle size, their bandgap changed from 1.46 to 2.0 eV. These nanoparticles were characterized by a UV–vis spectrophotometer, X-ray diffraction, and high-resolution transmission electron microscopy.

1. Introduction

Tin sulfide (SnS) is one of the most interesting materials since it has high potential in device fabrication with low cost due to its non-toxicity and easier availability of the constituent materials. It is an IV–VI layered semiconductor with orthorhombic or tetragonal crystal structures [1]. Moreover, Loferski theoretically proved that a maximum efficiency of 25% can be achievable for the SnS absorber solar cell [2]. Its direct bandgaps are reported to be in a wide range from 1.3 to 1.86 eV, depending on the synthetic methods [3].

Various nanoparticles have been studied because of their special physical and chemical properties and various applications in diverse fields. Because of such unique properties, SnS nanomaterials have been synthesized through various synthetic methodologies such as thermal decomposition with organo-tin sulfur containing precursors [4], tin and sulfur powder reaction in diethyleneglycoldimethylether (diglyme) [5], solvothermal route by the reaction between thiourea and $SnCl_2 \cdot 2H_2O$ in organic solvent [6] or between $SnCl_2 \cdot 2H_2O$ and KSCN in ethylene glycol (EG) [8], and refluxing $SnCl_2 \cdot 2H_2O$ and thiourea in EG [7]. However, there are only a few reports that presented the synthetic method for the preparation of SnS nanoparticles less than 10 nm in size. Hickey et al. fabricated SnS nanoparticles of around 7 nm size using the air sensitive organometallic complex $Sn[N[(SiCH_3)_3]_2]_2$ as a tin precursor and thioacetamide as sulfur prercursor with trioctylphosphine (TOP) and oleic acid (OA) as surfactants [9]. Liu et al. reported the synthesis of around 6 nm SnS nanoparticles using $SnCl_2$ and $[(CH_3)_3Si]_2S$ in oleylamine (OLA) [10], and Ning et al. prepared 5 nm SnS nanoparticles through the reaction of $Sn_6O_4(OH)_4$ with thioacetamide in the presence of OA and OLA [12]. Xu et al. prepared SnS nanoparticles through a simple reaction with $SnBr_2$ and Na_2S in ethylene glycol with triethanolamine solvent [11].

Herein, we report a facile and simple sonochemical method to prepare SnS nanoparticles of 4–15 nm in size by using stable, cheap, and less toxic chemicals such as $SnCl_2$ and thioacetoamide (TAA), ethylene glycol, and ethanolamines.

2. Experimental details

Reagents: Most of the reagents and solvents were purchased from Sigma-Aldrich-Corporation and $SnCl_2$ and thioacetamide were used without further purifications. Ethylene glycol, ethanolamine, diethanolamine, and triethanolamine were heated at 120 °C in vacuum condition for 24 h and they were stored under inert atmosphere.

General procedures: Scheme 1 shows that the experimental apparatus has been published [13]. The sonochemical reaction system consists of a cylindrical quartz cell into which a 5 mm diameter titanium horn (Misonix XL2020, USA) is inserted. It was operated at 20 kHz and 220 W which is quite intensive compared to other typical ultrasound irradiation processes [14–16] and kept at 1.4 atm with argon gas. The temperature of the solution inside the cell was kept at around 20 °C by a circulating water bath,

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which was found to be the optimal condition for the nanoparticle synthesis process [13]. In a typical synthesis of homogeneous SnS nanoparticles, 0.5 mmol $SnCl_2$ with 1, 2, or 3 ml ethanolamines [ethanolamine (EA), diethanolamine (DEA), and triethnaolamine (TEA)] were simultaneously dissolved in 5 ml ethylene glycol. Also 0.5 mmol thioacetoamide for sulfur source was dissolved in 5 ml ethylene glycol. After mixing these two solutions, more ethylene glycol was added to 13 ml in total. The mixed solutions were sonochemically treated under the above multibubble sonoluminescence conditions for 5 min. Then, as-prepared SnS colloid was centrifuged in ethanol, washed with water and ethanol for several times, and dried in vacuum at room temperature for 12 h.

The SnS nanoparticles were characterized by X-ray powder diffractions (New D8-Advance/Bruker-AXS), a high resolution-transmission electron microscope (JEM-3010/JEOL), energy dispersive X-ray spectroscopy, and a UV–vis spectrophotometer (S-3100/SCINO). The SnS nanoparticles were treated with oleylamine for mono-dispersed TEM image analysis.

3. Results and discussion

The presence of ethanolamines was found to be very important for the size conrol in small size SnS nanoparticle syntheses. Pramanik et al. reported that TEA complexes with Sn^{2+} formed a chelate compound $[Sn(TEA)_n]^{2+}$ [17]. DEA and EA also formed complexes with tin, but these complexes were reported to be less stable than the TEA complexes [17]. This fact is very important in the control of SnS nanoparticle size. The stable complex form, $[Sn(TEA)_n]^{2+}$, tends to provide smaller size and uniform SnS nanoparticles. However, the unstable complex form, $[Sn(EA)_n]^{2+}$, tends to fabricate larger size and folded nanoparticles. Ying Xu et al. reported similar results about hydroxyl group effect; they used TEA, N-methyldiethanolamine (two hydroxyl group), and N,

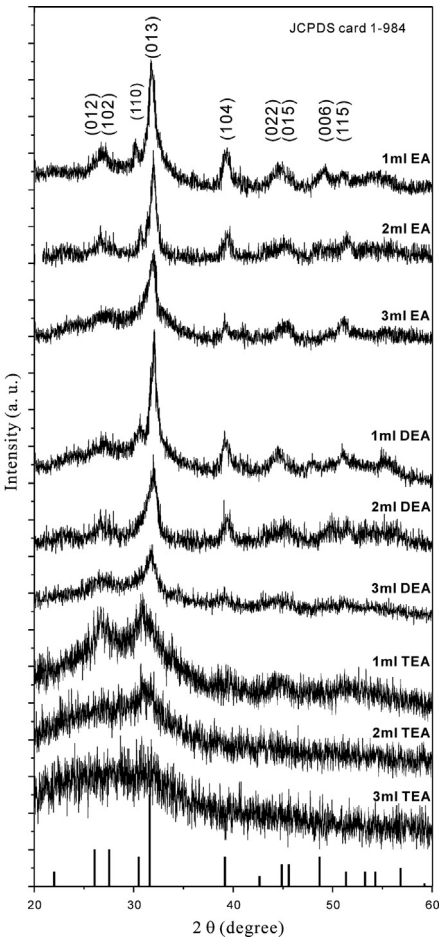
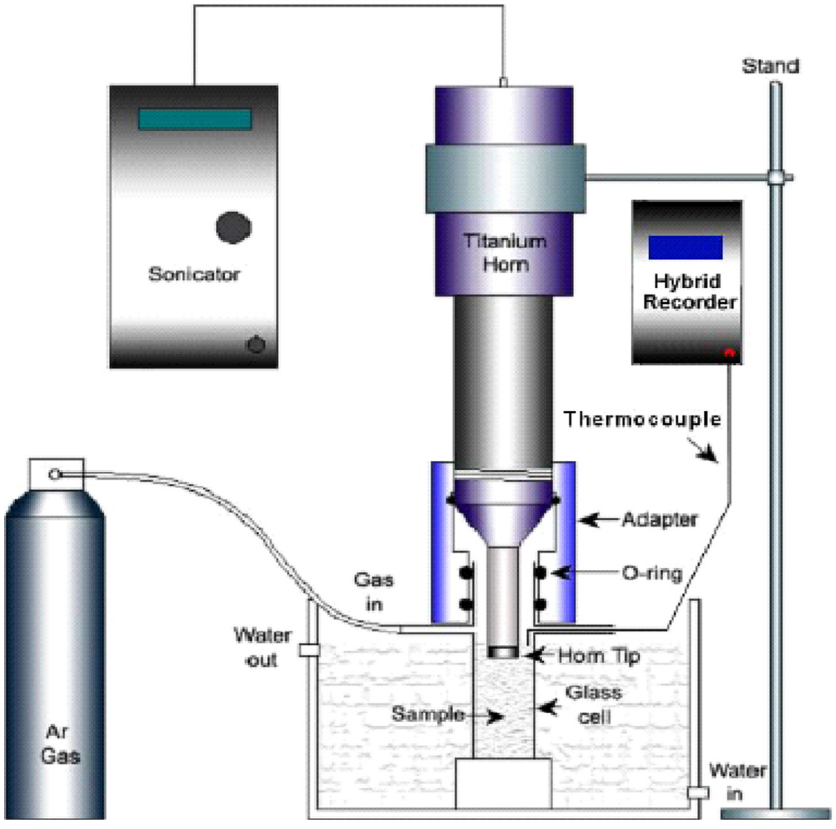


Fig. 1. XRD patterns of SnS nanoparticles.



Scheme 1. Experimental set-up for sonochemical experiment.