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# Tin sulfide: Reduced graphene oxide nanocomposites for photovoltaic and electrochemical applications

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ABSTRACT

Nanocomposite thin films of tin sulfide (SnS) with graphene oxide (GO) and reduced graphene oxide (rGO) were prepared by spray deposition of tin sulfide nanocolloids mixed with graphene oxide. SnS nanocolloidal suspensions were synthesized by liquid phase pulsed laser ablation of a SnS target in isopropyl alcohol and dimethyl formamide. Spherical morphology and orthorhombic crystalline structure of the nanoparticles were determined by transmission electron microscopy. Graphene oxide was synthesized through a chemical pathway (Marcano's method) and was mixed with SnS nanocolloid. Thin films were deposited by spraying SnS nanocolloid as well as the GO mixed SnS on heated substrates. The thin films were post-annealed under vacuum to form reduced graphene oxide. Structure, morphology and optoelectronic properties of thin films formed at various conditions were determined by different techniques. Scanning electron micrographs showed porous film surface with GO/rGO net-like structures embedded in SnS nanoparticles. Photocurrent measurements at different illumination wavelengths and cyclic voltammetry using SnS:rGO as working electrodes showed improvement in the properties of graphene oxide incorporated SnS. A solar cell was fabricated using SnS:rGO thin film and the results obtained are promising.

## 1. Introduction

Tin sulfide (SnS), a p-type chalcogenide semiconductor, continues to attract the attention of researchers because of its versatile properties, low toxicity, earth abundance and cost considerations [1,2]. Due to its narrow direct (1.3 eV) and indirect (1.09 eV) bandgaps and high absorption coefficient, SnS finds applications in photovoltaics [3–6]. Several attempts have been made in the past to employ SnS as an absorber material in solar cell [5,7–9]. However, they lack noticeable efficiency and performance as dictated by the present requirements. They are also used as photodetectors and anode materials in storage devices [4,6,10–12]. Though the theoretical efficiency of SnS based solar cells is > 25% [7,8], the maximum reported value is 4.4% [9] for an ALD (atomic layer deposition) processed SnS solar cell. Nevertheless, ALD is a comparatively slow and expensive film fabrication technique and thus puts a barrier towards large scale production of cost effective solar cells [13]. The suitability of SnS for gas sensing applications was explored by several research groups [10,11,14,15]. Most of these properties originate from the layered orthorhombic structure and band gap of SnS semiconductor. Single crystal SnS nanowires [16,17] and SnS particles with morphologies like nanoflower [18], nanoribbons [4,6] and nanobelts [19,20] have been reported by different authors. SnS is a semiconductor having an ideal gap for photovoltaic (PV) applications. It is a good p-type absorber with an exceptional interlayer spacing (c = 0.4330 nm, space group *Pnma*). However, the low dark conductivity limits its use in PV and other optoelectronic applications.

Graphene is known for its excellent optical [21], electronic [22] and mechanical [23] properties. Graphene oxide (GO) can be produced by introducing oxygen defects in graphite [24]. Physicochemical properties of GO depend on factors such as microstructure, dopants, degree of

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oxidation/reduction and sheet size [25]. Reduced graphene oxide is obtained by removing oxygen from graphene oxide and thus possesses higher electronic conductivity than GO. Nanocomposites consisting of GO or rGO and semiconductors have proved their suitability and functionality for different applications [26–30]. Dye sensitized solar cell of 7.47% efficiency was reported using tin sulfide- reduced graphene oxide nanocomposite as the counter electrode [31]. Abundance of delocalized electrons in the conjugated sp2-bonded network in graphene related materials enhance the charge separation and their transport when nanocomposites of semiconductors and these materials are fabricated [32,33]. Properties such as conductivity, porosity and strength of the targeted material (in this case SnS:rGO) can be improved by introducing graphene in it [34]. P-type conductivity of SnS originating from the tin vacancies in the lattice which creates the acceptor levels [35], increases (transforming into a p + layer) when nanocomposite of SnS and rGO is fabricated and the result is a composite material with high electronic conductivity due to the synergistic effects. When incorporated in solar cells, this p + layer can improve the efficiency of the cell by enhancing the short-circuit current resulting from high and fast conduction through SnS:rGO network. In many cases, rGO acts as a conductive layer which enhances the transport of charge carriers generated in the semiconductor. In the case of solar cells, efficient charge carrier separation and high carrier life time are necessary for achieving high short circuit currents to improve cell conversion efficiencies [36].

PLAL is an emerging green technique to synthesize various kinds of nanoparticles (NPs) in a single stage process. Besides the NPs by PLAL possess high surface purity, the technique is scalable and offers high throughput [37]. Other advantages of this method include dispersion of the NPs by itself into the surrounding liquid medium by producing less or no chemical waste compared to other chemical synthesis techniques. Grisel et. al reported the influence of laser parameters and liquid media on size and morphologies of SnS NPs by PLAL [38]. Some authors showed appreciable efforts to obtain thin films from PLAL nanocolloids [39,40]. Ability to maintain the target composition same for the NPs as well as their thin films can be pointed out as the major advantage of this fabrication method where other benefits include less or no use of chemical reagents and lower temperature processing of the films, especially when primary alcohols are used as the solvent in PLAL. Spray deposition is a simple and cost effective thin film fabrication method useful to deposit thin films on large substrate area with practically no limitation on the film thickness [41]. Hence a combination of PLAL with spray technique can yield crystalline and phase pure thin films with interesting morphologies. Following that hypothesis, we have reported the synthesis and properties of SnS thin films deposited by spraying SnS nanocolloids obtained by PLAL [42]. In this case, SnS NPs were synthesized using a 532 nm, nanosecond pulsed Nd:YAG laser of frequency 100 Hz. Combining PLAL with spray technique is very promising for cost effective and simple production of nanocomposites which may help to reduce the fabrication costs of photovoltaic and opto-electronic devices considerably. The proposed technique is comparatively faster and produces lowest possible chemical wastages. Nanocolloids of SnS and GO were physically mixed and sprayed onto heated substrates to obtain SnS:GO thin films. A systematic study was carried out on the effects of different concentrations of GO on SnS thin films synthesized using the colloids in different liquid media and on the properties of pristine SnS, SnS:GO and SnS:rGO thin films. GO and rGO incorporated SnS thin films exhibited better optoelectronic and electrochemical properties than the pristine SnS films. A solar cell prototype was fabricated using SnS:rGO thin film absorber as a preliminary step towards the device fabrication employing the proposed method and a photoconversion efficiency of 2.32% is achieved.

## 2. Experimental

### 2.1. Synthesis of nanoparticles and thin films

Tin sulfide (SnS) nanoparticles were synthesized by pulsed laser ablation in liquid (PLAL) technique where the SnS target was irradiated using 1064 nm output from a nanosecond pulsed Nd:YAG laser of frequency 10 Hz and pulse width 10 ns. The target was immersed in a Pyrex 250 ml glass beaker containing an organic liquid (dimethyl formamide or isopropyl alcohol). The target was kept at the bottom of the beaker and the thickness of the liquid layer above the target was maintained at 3 cm for each liquid medium. Disk shaped commercial SnS sputter target of purity 99.99% was used as ablation target (2″ diameter and ¼″ thickness, supplied by Beijing Goodwill Metals, China). Organic solvents (isopropyl alcohol (IA) and dimethyl formamide (DMF)) used were of analytical grade and used as supplied without any further purification. Vertical configuration was used for the ablation experiment where the SnS target was irradiated from the top. The ablation was carried out for 5 min irrespective of the liquid medium. The laser fluence was 0.95 J/cm$^2$ for the synthesis of SnS NPs in isopropanol and DMF. During the ablation process, the target was linearly translated at a speed of 100 μm/s using a translation system to avoid deep ablation traces on the target as well as to reduce the effect of post irradiation on the synthesized NPs. After 5 min of ablation, the transparent liquids were changed to dark brown. Spray technique was employed to deposit thin films of SnS from the as synthesized nanocolloids. The term ‘spray technique’ is intentionally used instead of spray pyrolysis since no chemical reactions are expected to be carried out on the heated substrates for the relatively low temperatures used. The substrates were heated at temperatures 120 °C and 250 °C respectively for isopropyl alcohol and dimethyl formamide. Different substrate temperatures were applied depending on the boiling point of the solvents used in PLAL. Boiling point of DMF and isopropanol are 153 and 83 °C respectively, higher temperature is needed for the solvent evaporation for the nanocolloids in DMF compared to that in isopropanol. Moreover, the substrates were preheated for 10 min at the specified temperatures to improve the adhesion of the films on the substrates. The substrate to nozzle distance was kept fixed (27 cm) and the spray pressure (compressed air) was 0.75 kg/m$^2$. SnS thin films were fabricated by spraying the pristine SnS nanocolloids and SnS:GO thin films by a mixture of SnS nanocolloid and graphene oxide. Graphene oxide of concentration 4.3 g/l was synthesized following Marcano's method [43]. In a typical experiment, 1 g of graphite was placed in a mixture of concentrated $H_2SO_4$/$H_3PO_4$ (40:8 ml) and 5 g of $KMnO_4$ was added. The mixture was heated to 40 °C and stirred for 12 h. The reaction was cooled to room temperature and poured onto ice (150 ml) with 30% $H_2O_2$ (1 ml). The GO bright yellow dispersion was left overnight to complete potassium permanganate neutralization. GO was then separated by centrifugation. The solid material was first washed with an acidic solution of 50 ml of water and 100 ml of 30% HCl. The GO dispersion was finally washed by several centrifugation/redispersion cycles with deionized water until pH 6. The deposition of SnS:GO thin film was as follows: Different concentrations of GO viz. 0.1%, 0.5% and 1% by volume were added to the SnS in IA or SnS in DMF nanocolloids and stirred well for 30 min at room temperature. The solution mixture was kept in an ultrasonic bath for 5 min for better dispersion and then sprayed onto heated substrates under the same spray conditions used for pristine SnS film depositions. The spray system employed is a homemade one with a microcontroller-based movement and controlled air pressure and liquid flow. The spray nozzle (Model: 1/4JCO-SS + SU11-SS) was purchased from Spray Systems co., Mexico. The SnS:GO thin films obtained were darker than the bare SnS thin films due to the presence of GO. Pristine SnS and SnS:GO thin films were annealed at 380 °C for 1 h in vacuum to improve their crystallinity as well as for the reduction of GO to rGO (reduced graphene oxide) in the SnS:GO films.