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Novel single source precursor for synthesis of Sb_2Se_3 nanorods and deposition of thin films by AACVD: Photo-electrochemical study for water reduction catalysis

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ABSTRACT

A new complex, *tris*(selenobenzoato)antimony(III) has been synthesized by a facile route and the structure determined by single crystal X-ray crystallography. The complex was used as a single source precursor to synthesize Sb_2Se_3 nanorods by the hot injection method whereas Sb_2Se_3 thin films were deposited on glass substrates by the Aerosol Assisted Chemical Vapour Deposition (AACVD) technique. The as synthesized nanorods and thin films were then characterized by powder X-ray diffraction, electron microscopy, Raman and UV/Vis spectroscopy. AACVD of the complex produced highly crystalline and pure Sb_2Se_3 thin films between 400 and 500 °C. The shape of Sb_2Se_3 crystallites are generally in the form of wires or thin plates, sometimes forming leaf-like structures uniformly spread on the entire substrate. The size and shape of these crystallites with their stoichiometry was found to be dependent on the deposition temperature. Sb_2Se_3 nanorods were tested for photo-electrochemical (PEC) water reduction catalysis. When simulated solar light was illuminated at the Sb_2Se_3/FTO surface, cathodic photocurrents were generated for H_2 generation. At open circuit potential (OCP) photo-cathodic current generated with the Sb_2Se_3/FTO electrode was in the range of -44.8 to $-52.1\ \mu A{\cdot}cm^{-2}$.

1. Introduction

Absorber materials such as, copper indium gallium sulfide, cadmium telluride and organic-inorganic hybrid perovskites (for example, $CH_3NH_4PbI_3$) have achieved remarkable device efficiencies (Jeon et al., 2014; Aamir et al., 2017a, 2017b, 2017c, 2018). However, the high cost of gallium/indium, the toxicity of lead and cadmium and instability of perovskite materials are important factors which limit their use at the industrial scale. Similarly, copper zinc tin sulfide (CZTS) has been introduced as a cost effective and environment friendly material but the complexity created by defects and rigorous control over the phase and stoichiometry of these materials, are serious obstacles for their large scale fabrication (Chen et al., 2013; Barkhouse et al., 2012). Nontheless, binary metal chalcogenides are potential candidates for the energy applications with promising efficiencies (Zhou et al., 2018; Yue et al., 2018; Li et al., 2018; Haghighi et al., 2018).

Antimony selenide belongs to V_2VI_3 binary metal chalcogenide materials (V = Sb, Bi or As; VI = S, Se or Te), which are an important class of semiconducting materials with anisotropic structures which find applications in photovoltaics and thermoelectric materials (Arivuoli et al., 1988; Chen et al., 1997; Suarez et al., 1998). Sb_2Se_3 is a direct band gap (approximately 1.1–1.3 eV) semiconductor that crystallizes in the orthorhombic system (pbnm space group) and is isomorphic with Bi_2S_3 and Sb_2S_3. The band gap of Sb_2Se_3 is lower than that of Sb_2S_3, but is comparable to the Bi_2S_3 (Vogel et al., 1994). The far infrared study indicates that the Sb_2S_3 is polar, Bi_2S_3 is slightly polar, whereas, Sb_2Se_3 is non-polar (Petzelt and Grigas, 1973). It is considered a relatively non-toxic and earth abundant material with an excellent light absorption coefficient ($> 10^5\ cm^{-1}$ at short wavelength) (Filip et al., 2013; Patrick and Giustino, 2011). It is also cost effective and can be easily scaled up as a light absorber in thin film solar cells. In addition, Sb_2Se_3 based solid state cells (Zhou et al., 2015) and photo electrochemical cells (Sankapal and Lokhande, 2001) exhibit high performance which attracts attention to its photo- response activity.

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The structure of Sb_2Se_3 is composed of infinite $(Sb_4Se_6)_n$ chains stacked together along the [0 0 1] direction and connected by strong Sb−Se covalent bonds, whereas the chains are held together by weak Van der Waals forces. Structural anisotropy is an interesting aspect of Sb_2Se_3 which introduces features that are difficult to achieve by simple particle size manipulation. A small variation in shape may have a significant effect on the desired properties (Gonzalez-Valls and Lira-Cantu, 2010; Pu et al., 2014). For instance, a dramatic increase in the efficiency of dye sensitized solar cells was observed by using vertically aligned nanorods (Patrick and Giustino, 2011; Que et al., 2014). Recently, anisotropic nanomaterials such as nanorods and/or nanosheets have found increased interest due to their applications in photovoltaic and thermoelectric devices (Wi et al., 2014; Sun and Greenham, 2006; Zhao et al., 2015).

Similarly, in order to enhance the efficiency of nanomaterials and facile deposition of thin films, various single molecular precursors have been designed, for efficient control over size and morphology (Hussain et al., 2015a, 2015b, 2015c; Khan et al., 2016a, 2016b, 2017; Memon et al., 2015; Akhtar et al., 2015; Khan et al., 2018; Nyamen et al., 2012). However, there are only a few reports on the use of single source precursors for the synthesis of Sb_2Se_3 nanostructures or thin films. Some of the common selenium based complexes used for the deposition of metal selenide nanoparticles or thin films are dialkyldiseleno phosphates (Lin et al., 2007; Chang et al., 2007), 2-pyridyl selenolates (Sharma et al., 2010), and selenophosphinate precursors (Nguyen et al., 2006). Sb_2Se_3 was also synthesized by alkylselenostibines and selenourea complexes (Benjamin et al., 2015; Maiti et al., 2011). However selenostilbines require toxic metal alkyl compounds for their synthesis, phosphorus based complexes may lead either to phosphorus contamination or formation of an entirely different phosphate product (Wi et al., 2014). Similarly, diselenocarbamate precursors has been used for metal selenide thin films but the synthesis requires the use of highly toxic carbon diselenide (CSe_2).

The development of reliable and efficient strategies for artificial photosynthesis is an intensive research focus over the last decade. Water splitting using nanostructures avoiding precious metals such as platinum, gold and ruthenium is highly desirable to meet the competitive market demands. The development of materials with surface chemistry that can have better charge carrier life times and electrical capabilities is very significant for H_2 production from water (Azevedo et al., 2016; Walter et al., 2010). Many metal oxide based nanostructures are explored for PEC studies but elemental nanostructures are not common due to very small band gaps and fast electron-hole recombination. Metal selenides are well known electocatalysts for hydrogen evolution reaction but their PEC properties are not well explored Zou and Zhang, 2015. Sb_2Se_3 is abundant in the geosphere and have attractive thermoelectric and electrical conductivity properties. However, their solar water splitting properties have not been sufficiently explored.

Herein, we report an efficient synthesis of a new complex *tris*(selenobenzoato)antimony(III), its single X-ray structure, and use as single source precursor for the synthesis of the Sb_2Se_3 nanoparticles by the hot injection method and deposition of highly crystalline thin films by AACVD. Sb_2Se_3 nanorods were also used as low cost nanomaterials for the photoelectrochemical (PEC) production of H_2 from water under sunlight illumination.

2. Experimental

2.1. Materials

The reagents and solvents *i.e.* $SbCl_3$, $NaBH_4$, benzoyl chloride, elemental selenium and ethanol were purchased from Sigma Aldrich and were used as such.

2.2. Synthesis of tris(selenobenzoato)antimony(III) complex

NaHSe was prepared by adding ethanolic solution of $NaBH_4$ (0.5 g, 12.0 mmol in 15.0 mL ethanol) into ethanolic solution of metallic Se powder (0.5 g, 6.0 mmol, in 15.0 mL) under inert conditions using a Schlenk line at room temperature. The reddish solution becomes colourless within 5 min. of stirring indicating the formation of NaHSe. Benzoyl chloride (0.89 g, 6.0 mmol) was then added dropwise into the freshly prepared NaHSe solution. The colour of the solution changed from colourless to yellow, indicating the formation of the seleno benzoate ligand. The stirring was continued for a further 15 min, after which $SbCl_3$ (0.48 g, 2.0 mmol of in 15.0 mL ethanol) was added dropwise while stirring. A dark yellow precipitate was formed which was filtered. The dried complex was then recrystallized from the THF solution to give yellowish crystalline needles. Elemental analysis Calc: (%) for $C_{21}H_{15}O_3SbSe_3$: C 37.42, H 2.24, Sb 18.07; Found: C 37.41, H 2.20, Sb 17.97.

2.3. Synthesis of Sb_2Se_3 nanorods

The synthesis of Sb_2Se_3 nanorods was carried out by injecting a dispersion of antimony selenobenzoate complex in 1-octadecene (ODE) (0.25 g, 0.37 mmol, 3.0 mL) into 10.0 mL of preheated oleylamine (OLA) at 200 °C. The color of the solution changed instantly from light yellow to brownish black, indicating the formation of nanoparticles. The stirring was continued for 1 hour at 200 °C. The heating was stopped and the solution was allowed to cool to around 60 °C, at which point 30.0 mL of 1:1 mixture of methanol and acetone was added. The product was obtained as a black precipitate which was separated by centrifugation and washed three times with acetone.

2.4. Thin films of Sb_2Se_3 by AACVD

Thin films of antimony selenide were deposited on borosilicate glass substrates (approx. 1 × 3 cm). The substrates were cleaned ultrasonically in nitric acid, distilled water and finally in acetone. The setup for aerosol assisted chemical vapour deposition comprises of a carbolite tube furnace and ultrasonic equipped humidifier (deurer living LB44) for generation of aerosol. For deposition of thin films, 0.2 g (0.3 mmol) of precursor was dissolved in 20.0 mL THF in 100 mL two necked round bottom flask and placed in water bath above the piezoelectric modulator of an ultrasonic humidifier. Six glass substrates were placed into the reactor tube, which was inserted into the tube furnace. A gas inlet was attached to one neck of the flask for flow of carrier gas and the other neck was attached to the reactor tube containing the substrates by reinforced tubing. The aerosol was generated by an ultrasonic humidifier and was carried towards the heating zone of the furnace with the help of carrier gas (argon) at a flow rate of 200 sccm. Thermally induced decomposition of the precursor took place on heated surface of the substrates and resulted in the deposition of Sb_2Se_3 thin films.

3. Characterization

Microanalysis was performed using a Thermo Scientific Flash 2000 Organic Elemental Analyzer. Thermogravimetric analyses were performed using a Mettler-Toledo TGA/DSC. The X-ray diffraction was performed using a Bruker D8 Discover Diffractometer using CuKα radiation (λ = 1.54178 Å), in a 2Θ range from 10° to 70°. The data collected was used to determine the lattice parameters and crystal phase. TEM and HRTEM images were collected on a Talos F200X at 200 kV using a FEI ceta camera. Scanning electron microscopy (SEM) was carried out using a Philips XL30 FEG SEM. Energy-dispersive X-ray (EDX) spectroscopy was performed using a DX4 detector. All samples were carbon coated using an Edwards coating system E306A prior to SEM analysis. Raman spectra were measured using a Renishaw 1000