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Novel single source precursor for synthesis of Sb₂Se₃ 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 400-500 °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 $\text{Sb}_2\text{Se}_3/\text{FTO}$ surface, cathodic photocurrents were generated for H_2 generation. At open circuit potential (OCP) photo-cathodic current generated with the $\text{Sb}_2\text{Se}_3/\text{FTO}$ electrode was in the range of -44.8 to -52.1 $\mu\text{A}.\text{cm}^{-2}$.

Key words: AACVD, Nanorods, Sb_2Se_3 , Thin films, Water splitting

Introduction

Absorber materials such as, copper indium gallium sulfide, cadmium telluride and organic-inorganic hybrid perovskites (for example, $\text{CH}_3\text{NH}_4\text{PbI}_3$) have achieved remarkable device efficiencies.¹⁻⁵ 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.^{6, 7} Nonetheless, binary metal chalcogenides are potential candidates for the energy applications with promising efficiencies.⁸⁻¹¹

Antimony selenide belongs to V_2VI_3 binary metal chalcogenide materials ($\text{V} = \text{Sb}$, Bi or As ; $\text{VI} = \text{S}$, Se or Te), which are an important class of semiconducting materials with anisotropic structures which find applications in photovoltaics and thermoelectric materials.¹²⁻¹⁴ Sb_2Se_3 is a direct band gap (approximately 1.1-1.3eV) 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 .¹⁵ 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.¹⁶ It is considered a relatively non-toxic and earth abundant material with an excellent light absorption coefficient ($>10^5 \text{ cm}^{-1}$ at short wavelength).¹⁷ 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 cells¹⁹ and photo electrochemical cells²⁰ exhibit high performance which attracts attention to its photo- response activity.

The structure of Sb_2Se_3 is composed of infinite $(\text{Sb}_4\text{Se}_6)_n$ chains stacked together along the [001] 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.^{21, 22} For instance, a dramatic increase in the efficiency of dye sensitized solar cells was observed by using vertically aligned nanorods.^{18, 23} Recently,

anisotropic nanomaterials such as nanorods and/or nanosheets have found increased interest due to their applications in photovoltaic and thermoelectric devices.²⁴⁻²⁶

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.²⁷⁻³⁶ 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,^{37, 38} 2-pyridyl selenolates,³⁹ and selenophosphinate precursors.⁴⁰ Sb_2Se_3 was also synthesized by alkylselenostibines and selenourea complexes.^{41, 42} However selenostibines 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.²⁴ 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.^{43, 44} 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 electrocatalysts for hydrogen evolution reaction but their PEC properties are not well explored.⁴⁵ 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.

Experimental

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.

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.

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.

Thin films of Sb₂Se₃ by AACVD

Thin films of antimony selenide were deposited on borosilicate glass substrates (approx. 1 x 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 Sb₂Se₃ thin films.

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 CuK α radiation ($\lambda = 1.54178 \text{ \AA}$), 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 Micro-Raman System equipped with a 514 nm laser operating at 1 mW. UV–vis-NIR spectra were recorded using a PerkinElmer Lambda 1050 instrument, using quartz cuvettes with a path length of 1 cm.

Electrode preparation

PEC studies were carried out using fluorine doped tin oxide (FTO) conducting glass substrates. FTO substrates were ultra-sonicated, first in acetone and then in deionized water for 10 minutes each. A slurry of Sb_2Se_3 nanorods was made in *iso*-propanol and sonicated for 10 minutes. Two increments of 25 μL of the Sb_2Se_3 were drop casted over 1 cm^2 of the FTO glass substrate. The resulting $\text{Sb}_2\text{Se}_3/\text{FTO}$ electrode was then annealed at 80 $^\circ\text{C}$ for two hours to harden the substrate layer. 10 μL of 1% nafion solution was then drop casted over the Sb_2Se_3 layer to make it withstand during the PEC measurements. Once dried $\text{Sb}_2\text{Se}_3/\text{FTO}$ electrode was used for all subsequent PEC studies.

Experimental setup

A conventional three electrode cell was used for PEC studies with $\text{Sb}_2\text{Se}_3/\text{FTO}$ electrode as the working electrode, Ag/AgCl chloride (Saturated KCl) as reference electrode and platinum wire as an auxiliary electrode. The linear scan voltammetry (LSV) results are reported against the standard hydrogen electrode (SHE) by adding 0.197 V in all the measured results.⁴⁶ All three electrodes were placed in a 5.0 mL quartz cell containing 0.5 M sodium sulfate solution (pH 6.8) as an electrolyte. To remove any dissolved oxygen the cell solution was purged with nitrogen gas for 10 minutes prior to the PEC measurements.

A solar simulator equipped with a 150 W Xenon arc lamp (Model 16S-150, Solar Light Company Inc., Glenside PA 19038, USA) was used with a 1 sun light intensity. A mini μ -Autolab potentiostat, PGSTAT101 (MetrohAutolab.B.V.Kanaalweg, 29-G, Utrecht, The Netherlands) with NOVA 2.1 software was employed in all electrochemical experiments.

Single crystal X-Ray structure

Intensity data for complex $\text{C}_{21}\text{H}_{15}\text{SbSe}_3$ was collected by using graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$) on a Bruker Apex diffractometer. The structure was solved by direct methods and refined by full matrix least squares on F2. All calculations were carried out using the SHELXTL package. Further details can be found in supplementary data (Table S1).

Results and discussions

The synthesis of the antimony complex was carried out by modifying a method reported previously.⁴⁷ Our method excluded the use of sodium metal which is highly pyrophoric. We used NaBH₄ instead of metallic sodium and formed NaHSe in first step of reaction. The second step involved the reaction of NaHSe with benzoyl chloride to form the selenobenzoate. The reaction of selenobenzoate with the SbCl₃ in ethanol gave the *tris*(selenobenzoato)antimony(III) complex. Elemental and thermogravimetric analysis (TGA) were used to characterise the recrystallized product, whereas suitable crystals of antimony complex were also characterised by X-ray crystallography.

Crystal structure of *tris*(selenobenzoato)antimony(III)

The single crystal structure of the antimony complex belongs to the hexagonal R3 crystal system. The Sb atom is coordinated with three Se atoms of the selenobenzoato group and the overall geometry is based on a slightly distorted trigonal (Figure 1). The Sb(1)-Se(1) bond distance is 2.6019(12) Å while the C(7)-Se(1) distance is 1.931(13) Å. The Se(1)#1-Sb(1)-Se(1)#2 bond angle is 92.45(4)° with the C(7)-Se(1)-Sb(1) bond angle at 88.6(3)°. The structure is comparable to the thiobenzoate analogue of antimony as reported previously.⁴⁸

Thermogravimetric analysis

The TGA analysis indicates that the complex decomposed in three steps. The first step involves the major mass loss of ~36 % between the temperature range of 160 to 240 °C for antimony selenobenzoate, which is due to the loss of phenyl groups. The second step show a 14% weight loss which may be attributed to the loss of carbonyl groups, leaving behind the SbSe₃ fragment. The third step (13% weight loss) involved the conversion of SbSe₃ to Sb₂Se₃ via loss of some Se atoms.³⁸ The complete decomposition of the complex occurred at 390 °C giving the final residue of ~ 36.5% corresponding to the formation of Sb₂Se₃ respectively (Figure S1).

Sb₂Se₃ nanorods

The antimony selenide nanorods were prepared from *tris*(selenobenzoato)-antimony(III) in oleylamine at 200 °C. OLA not only acts as a capping agent and solvent

but also aids in the decomposition of the precursor.^{49, 50} The decomposition of selenobenzoate complex may follow a similar mechanism as suggested by Chin *et al.* for the decomposition of thiocarboxylate complexes in primary amines.^{51, 52} Vittal *et al.* also reported the synthesis of silver selenide nanoparticles and observed that the precursor decomposes easily at room temperature in the presence of a primary alkyl amine.⁵³ The primary amine behaves as a nucleation initiator and accelerates the decomposition of precursor. It separates the nucleation and growth steps, which is highly desired for obtaining monodispersed nanomaterials.⁵⁴

Structural characterization of Sb₂Se₃ nanorods

Figure 2(a) represents X-ray diffraction pattern of Sb₂Se₃ nanorods synthesized in OLA at 200 °C. The peaks match well with the orthorhombic antimony selenide phase (ICDD # 01-089-0821). There were no peaks indicating the presence of any impurities. The sharpness of the peaks is an indication of the high crystallinity of the nanorods. The intensity profile of the p-XRD pattern also matches well with the standard pattern, with highest intensity peak in (221) plane at 2 Θ value of 31.3°.

The TEM images show well defined Sb₂Se₃ nanostructures in the form of rods (Figure 2(c-d)) whose length is in the micron range. The preferential growth into rod-like morphology is largely determined by the anisotropic nature of the building blocks. The lattice fringes in the HRTEM image (Figure 2(b)) shows an interplanar spacing of 0.323 nm which corresponds to the (320) plane of orthorhombic Sb₂Se₃. Well defined discrete spots were observed by SAED (Figure 2(b), inset), which shows the single crystalline nature of the nanorods and it is in agreement with the sharp peaks observed in XRD spectrum. The EDX analysis (Figure S2) shows the presence of only antimony and selenium (the peaks for copper are attributed to the copper grid used for analysis), with Se in slight excess (1:1.58).

The structure of Sb₂Se₃ is composed of infinite long chains, extending parallel to the *c* axis with low symmetric environment of both Sb and Se atoms in the unit cell. The bonding within the chains is stronger and the chains are interconnected by comparatively weak atomic contacts between the chain fragments, which lead to the generation of a three dimensional orthorhombic structure (Figure 3). The nanorods and nanowires can be synthesized by cleavage of chain fragments from the bulk phase, due to the presence of

bonding anisotropy. The continuous chain like fragments which are connected to each other by weak forces, can easily break at higher temperature to give separate chain-like fragments. The injection temperature of 200 °C was high enough to break the weak inter-chain linkages and resulted in the formation of the nanorod morphology.

Sb₂Se₃ thin films

Sb₂Se₃ thin films were deposited on the glass substrates using THF solution of *tris*(selenobenzoato)antimony(III) complex. The precursor was soluble in solvents commonly used for AACVD, such as chloroform, toluene and THF. The thin films deposited using chloroform were poor in quality whereas toluene required increased deposition time. Therefore THF was chosen as the optimum solvent. The TGA showed that the complex decomposes completely around 390 °C, so the decomposition temperature was varied between 400 and 500 °C, using argon as a carrier gas with flow rate of 200 sccm. The deposited films at all temperatures were greyish black and the maximum deposition took place on the substrates which were placed in the middle to end of the quartz tube. The deposited thin films were uniform and moderately adherent.

The p-XRD pattern of the thin films deposited at 400, 450 and 500 °C, is shown in Figure 4. The peaks match well with the antimonselite (ICDD# 01-089-0821) phase. The pattern showed significant changes in the intensity of peaks depending on the deposition temperature. This change in intensity is more obvious along the (230) plane at $2\theta = 27.5$ which shows the decrease in peak intensity with an increase in deposition temperature. It appears as an intense peak at 400 °C and as a minor peak at 500 °C. A similar observation can be made for the (002) plane at $2\theta = 45.95$. These observations in p-XRD patterns indicate the significant impact of temperature on the shape and alignment of the particles along particular planes, which in turn can have a substantial effect on the thin film morphology. The width of the crystallites was estimated by Debye-Scherrer's equation. The approximate calculated width of the crystallites was observed to be 93 nm, 87 and 79 nm for films deposited at 400 °C, 450 °C and 500 °C respectively. The Scherrer equation is approximate and is more accurate for the stress free particles. However, in case of thin films, the lattice mismatch between the substrate and the deposited material, temperature and/or growth kinetics can induce stress, which may also contribute to peak broadness, hence, may not be a very accurate depiction of the width.^{55, 56}

The SEM images of the thin films deposited at 400 °C at different magnifications are shown in Figure 5(a-d). The images showed the deposition of rod-like structures with some randomly scattered leaf-like structures with varying sizes. Elemental mapping showed the antimony and selenium were distributed uniformly throughout the film (Figure 6(a-c)). The thin films were slightly selenium rich as a mean Se/Sb ratio of 1.67 was observed by EDX, which is close to the stoichiometric value of 1.50 (Figure S3 ESI†)

The deposition at 450 °C resulted in the formation of exclusively rod-like structures (Figure 5(e-h)). The size of the rods ranged from 20-30 µm. A magnified SEM image (Figure 5(h)) reveals that the thick rods were composed of several thin ribbon-like structures. A uniform distribution of elements in the film was confirmed by elemental mapping (Figure 6(d-f)). The growth of the films at 450 °C showed a significant change in the stoichiometric ratio of Se/Sb (1.58) as compared to those deposited at 400 °C (1.67) (Figure S4 ESI†). The films were selenium deficient at 400 °C but selenium rich at 450 °C.

The morphology of thin films at 500 °C revealed the deposition of nanoribbons (Figure 5(i-l)). This change in shape and size of crystallites was also indicated by the change in p-XRD peaks intensity. The thickness and the lengths of these ribbons ranged from 200- 220 nm (thickness) and 40-50 µm (length). Both thermodynamic and kinetic parameters play a role in the observed morphology, as at higher temperature along with thermodynamic stability, the rate of decomposition of the precursor also increases. As shown in Figure 3, the nanoribbons are linked with weak interactions which start to diminish with increase in temperature. The change in morphology of the deposited thin films can be explained on the basis of the interaction between chain fragments. At a deposition temperature of 400 °C the particles had large sizes, an increase in temperature to 450 °C resulted in the separation of fragments from each other. The deposition temperature of 500 °C was high enough to break the weak inter-chain linkages resulting in the formation of ribbon like morphology.

A further change in elemental stoichiometry was observed by EDX (Figure S5 ESI†) as the mean Se/Sb ratio was increased to 1.42, which shows further decrease of selenium in the deposited thin films. The elemental distribution in the thin films however was still uniform as shown in (Figure 6(g-i)).

Optical characterization of Sb₂Se₃ nanorods and thin films

The optical properties of the Sb₂Se₃ nanorod and thin films were determined by UV-Vis-NIR spectroscopy. The thin films were immersed in acetone and scratched with a spatula. The acetone dispersions of nanorods and thin films were well sonicated for an hour before analysis.

The absorption spectrum of well dispersed Sb₂Se₃ nanorods (Figure S6 ESI†) displayed a constant rising peak with continuous absorption. The band gap of the Sb₂Se₃ nanorods as determined by the Tauc plot is estimated to be 1.85 eV, (Figure 7(a)). Similarly, the sonicated solution of scratched thin films was used to obtain their absorption spectra (Figure S7 ESI†). The absorption for all thin films was observed in the Vis-NIR range. A sudden fall in absorption at wavelength of 860 nm was due to the transition from NIR to Vis-region. As such it is an instrumental artefact and has been observed previously.⁵⁷ The estimated band gap calculation for thin films indicates a successive blue shift with increase in temperature, *i.e.* 1.2, 1.32 and 1.46 eV for films deposited at 400, 450 and 500 °C respectively (Figure 7(b-d)). The blue shift in the band gap of both nanomaterials and thin films is in accordance with the reduced thickness of the nanorods in relation to the bulk.

The thin films were also characterized by Raman spectroscopy using a 514 nm laser excitation at 25 % power, and the peaks correspond well to those reported previously.⁵⁸ The vibrational modes (118 cm⁻¹, 188 cm⁻¹, 208 cm⁻¹ and 252 cm⁻¹) were present in all the thin films which show that the basic lattice structure was preserved during deposition at different temperatures (Figure 8). However, a prominent difference was observed in the relative intensities of the bands with change in the deposition temperature. At lower temperature (400 °C), all the vibrational modes are broad and the mode with comparatively higher intensity is present at 188 cm⁻¹, whereas at higher deposition temperatures (450, 500 °C) the bands become sharper and the vibrational modes at 188 cm⁻¹ and 252 cm⁻¹ showed almost equal intensity. The broadening of the band is related to the presence of stress or structural defects in scattering volume and shows low structural quality of the lattice.⁵⁹ The crystallinity of the material increased with increase in the deposition temperature so the intensity of the Raman bands. Similarly, a low intensity vibration mode at 371 cm⁻¹ was only observed at a high temperature of 500 °C which, along with the intensity of other bands, can be explained on the basis of preferential orientation of crystallographic planes in the nanoribbons.

Photo-electrochemical water reduction catalysis

Sb₂Se₃ nanorods were observed to exhibit cathodic photocurrents indicating their p-type nature. Figure 9(a) shows the chronoamperometric performance of the Sb₂Se₃/FTO photocathode, obtained at open circuit potential (OCP) as a function of time, under simulated sunlight illumination. Once the current response was stable, the light was cut off at regular intervals. It is obvious that when light was illuminated at the surfaces of the Sb₂Se₃/FTO electrode, significant cathodic currents were generated for H₂ generation. When the light was cut off, the photocurrent density instantaneously became negligible. This infers that the current generated was only due to the illuminated light and not to any intrinsic properties of the Sb₂Se₃ nanostructures.⁶⁰ For Sb₂Se₃/FTO, the photo-cathodic current generated was in the range -44.8 to -52.1 $\mu\text{A.cm}^{-2}$.

The LSV curves obtained with the Sb₂Se₃/FTO electrode is displayed in Figure 9(b). The enhancement in the cathodic current density was observed for the electrode over the entire potential range tested. With the Sb₂Se₃/FTO electrode, in dark the current density changed from -7.2 $\mu\text{A.cm}^{-2}$ at 0 V to -231.9 $\mu\text{A.cm}^{-2}$ at 0.6 V while with the same Sb₂Se₃/FTO electrode under simulated solar light the current density changed from -35.8 $\mu\text{A.cm}^{-2}$ at 0 V to -894.46 $\mu\text{A.cm}^{-2}$ at 0.6 V.

The factors, such as, crystallite size and/or morphology has a significant effect on PEC activity.^{61, 62} Generally, a small crystallite size can enhance the activity due to the higher surface area. Similarly, it is well known that the rod shaped morphology could give better catalytic activities compared to the spherical nanoparticles due to more atoms with unsatisfied valences present at the corners and the edges of the nanorods. The exposed facets in Sb₂Se₃ nanorods, were high energy planes *i.e.* (211), (221), (320) and (311), as determined by the higher intensity of these diffractions patterns. Nanorods also possess higher surface defects, which is an important factor in influencing the PEC activity. The surface defects have a positive effect on PEC activity by improving adsorption and surface activity. The intensity of such defects increases with the smaller crystallite sizes. Although, many other factors are also involved but enhanced surface activity and better segregation of electron and hole pairs due to increased defects in smaller crystallite sizes could be responsible for enhanced PEC activity.

The stability of the $\text{Sb}_2\text{Se}_3/\text{FTO}$ photocathode was also assessed under dark and sunlight illumination as displayed in Figure 9(c). The electrodes showed very stable response over 600 s of testing time. The dark current was very stable while a noisy photocurrent was observed due to H_2 evolution and accumulation of H_2 bubbles at surface of the electrode.⁶³ A small decrease in photocurrent response was observed over time, which could be recovered once solution was stirred to remove H_2 bubbles from the electrode surface. The photoresponse and stability of Sb_2Se_3 is better and comparable to many metal-oxide based nanostructures reported in the literature.^{44, 45, 64} Thus, the $\text{Sb}_2\text{Se}_3/\text{FTO}$ photocathode acted as efficient water reduction catalyst in neutral sodium sulfate solution and could be a promising candidate for cathodic water splitting applications. This also infers that the properties of Sb_2Se_3 can be tuned for their potential use in solar cell fabrication.

Conclusions

A facile one-pot synthesis of crystalline and stable antimony selenobenzoate complex at room temperature was reported in this study. The complex was suitable to be used as cost effective precursor for the preparation of Sb_2Se_3 nanorods and thin films by AACVD. The nanorods in OLA were synthesized well below the decomposition temperature of the complex as determined by TGA, suggesting that OLA is not only a capping agent but also catalyzes the decomposition of the precursors. For Sb_2Se_3 thin films, deposition temperature was found to have significant effect on the shape and preferred orientation of the particles, whereas a successive decrease in selenium was observed in thin films with increase in temperature. Hence, it is concluded that the alignment of the crystallites and stoichiometry in deposited thin films can be manipulated by judicious control on deposition temperature. Sb_2Se_3 nanorods showed significant photo-electrochemical catalytic properties for water splitting indicating the high potential of the material as a cheap source for the production of hydrogen from water. The synthetic route can be used for facile preparation of other metal seleno-benzoate complexes for metal selenide nanoparticles and thin films.

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Conflict of interest

Authors declare no conflict of interest.

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Figures

Fig. 1 X-ray structure of *tris*(selenobenzoato)antimony(III) ($C_{21}H_{15}O_3SbSe_3$) with selected bond lengths (Å) and angles ($^\circ$). Sb(1)-Se(1), 2.6019(12) Å, Se(1)#1-Sb(1)-Se(1)#2 92.45(4) $^\circ$.

Fig. 2 (a) p-XRD pattern of Sb_2Se_3 nanorods synthesized at 200 $^\circ C$, (b) HRTEM image and (inset) SAED pattern of nanorods, (c) and (d) TEM images of Sb_2Se_3 nanorods.

Fig. 3 (a) Crystal structure of antimony selenide showing “infinite chains” extending through the crystal (b) section of the infinite chain highlighting the different types of atomic contacts along c -axis, which connect the strongly bonded 1D chains.

Fig. 4 p-XRD of Sb_2Se_3 thin films deposited by AACVD on glass substrates at (a) 400 °C, (b) 450 °C and (c) 500 °C.

Fig. 5 SEM images of Sb_2Se_3 thin films deposited at (a-d) 400 °C, showing leaf like morphology, at (e-h) 450 °C, showing rods like morphology and at (i-l) 500 °C, showing wire like morphology.

Fig. 6 Elemental mapping of Sb_2Se_3 thin films deposited at (a-c) 400 °C, (d-f) 450 °C and (g-i) 500 °C, showing uniform distribution of antimony (red) and selenium (green) in the films.

Fig. 7(a) Estimated band gap for Sb_2Se_3 nanorods as determined by the Tauc plot and for thin films deposited at (b) 400 °C, (c) 450 °C and (d) 500 °C by AACVD.

Fig. 8 Raman spectra for Sb_2Se_3 thin films deposited at (a) 400 °C, (b) 450 °C and (c) 500 °C.

Fig. 9 (a) Chronoamperometric measurements with $\text{Sb}_2\text{Se}_3/\text{FTO}$ electrode at OCP using chopping 1 sun simulated illumination, (b) LSV curves (vs. SHE) with $\text{Sb}_2\text{Se}_3/\text{FTO}$ electrode in dark and under continuous 1 sun simulated illumination and (c) Chronoamperometric stability measurements with $\text{Sb}_2\text{Se}_3/\text{FTO}$ electrode at OCP in dark and under continuous 1 sun simulated illumination.