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Highly ordered CuSbS2 nanotube arrays: Controlled synthesis and electrochemical properties

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1. Introduction

Copper-based chalcogenide ternary semiconductors have received interest in various applications such as light emitting diodes [1], hydrogen evolution [2], and solar cells [3]. Suitable band gap [4], high absorption coefficient of $\alpha > 10^4 \text{cm}^{-1}$ [5], tunable hole concentration [6], hole mobility of 49 cm$^2$/Vs$^{-1}$ [5], low toxicity, cost-efficiency and earth abundance [7] have made CuSbS$_2$ an attractive material for solar absorber in sustainable and scalable photovoltaics, solar energy conversion and optoelectronics applications [4,8]. Due to the influence of morphology and size of the semiconductor nanostructures on their optoelectronic properties, and consequently the device performance, several approaches have been investigated to achieve different shapes of CuSbS$_2$ particles. So far, brick-, spherical-, and rod-shaped particles have been reported for this material using various methods [7,9-11]. Although one-dimensional nanostructures such as nanotubes (NTs) of several materials have attracted great interest due to their distinctive properties in optoelectronic device applications [12], this morphology has not yet been studied for CuSbS$_2$. Among the different methods for producing well aligned and uniform NTs, template method is one of the most efficient ones. Anodic aluminum oxide (AAO) templates with an ordered porous structure are highly suitable media to grow one-dimensional nanostructures. Nanostructures are formed in a controllable way within the ordered pore arrays of the template [13]. Further, these templates are thermally stable and can be used in high temperature reactions like hot-injection method. Therefore, in this study, CuSbS$_2$ nanotubes were fabricated using the template method and hot-injection synthesis. The nanotube structures can be detached from the template using an etchant, which preferentially attacks the template and leaves the nanotubes intact. Furthermore, addition of dichlorobenzene (DB), which has a lower boiling-point than the commonly used oleylamine (OLA), is proposed in this paper as a compound solvent mixture. This solvent mixture provided the required agitation thereby avoiding mechanical stirring and thus protecting the fragile template.

2. Experimental

For the preparation of CuSbS$_2$ NT arrays, a 200 nm AAO template, 44.54 mg CuCl, 102.65 mg SbCl$_3$, and a mixture of 3 ml OLA and 4 ml DB were placed in a 50 ml three-neck flask. The flask was sonicated for 30 min, to dissolve the precursors and push the liquid into the AAO pores. The solution was then backfilled with nitrogen for 30 min, and then heated gradually to 150 °C. The temperature was further increased, and at 200 °C the mixture began to boil. Injection of sulfur precursor with a ratio of 3:1 to metal precursors (sulfur powder in OLA), was performed at 240 °C and the reaction time was about 1 h. The solution was then allowed to completely cool down, and the AAO template containing NTs was separated from the mixture and washed with distilled water and ethanol. The template was dried in air for further characterization. Fig. 1a explains the developed approach to produce nanotube arrays using the AAO template. Measurements and characterization techniques are provided in the Supplementary Material.

Keywords:
CuSbS$_2$
Energy levels
Mott-Schottky
Nanotube

CuSbS$_2$ nanotubes (NTs) were prepared via a hot-injection method using an anodic aluminum oxide (AAO) template, and a mixture of oleylamine (OLA) and dichlorobenzene (DB) as solvent. Structural characterization of the powder indicated formation of high purity well-aligned CuSbS$_2$ NTs with an average diameter of 200 nm and an average wall thickness of 40 nm. Optical and electrochemical characterizations indicated that the obtained CuSbS$_2$ NTs exhibit p-type conductivity with a suitable band gap (1.53 eV), as well as valence band (VB), and conduction band (CB) positions, comparable to conventional materials utilized in solar cell.

**Featured Letter**

**Highly ordered CuSbS$_2$ nanotube arrays: Controlled synthesis and electrochemical properties**

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**ABSTRACT**

CuSbS$_2$ nanotubes (NTs) were prepared via a hot-injection method using an anodic aluminum oxide (AAO) template, and a mixture of oleylamine (OLA) and dichlorobenzene (DB) as solvent. Structural characterization of the powder indicated formation of high purity well-aligned CuSbS$_2$ NTs with an average diameter of 200 nm and an average wall thickness of 40 nm. Optical and electrochemical characterizations indicated that the obtained CuSbS$_2$ NTs exhibit p-type conductivity with a suitable band gap (1.53 eV), as well as valence band (VB), and conduction band (CB) positions, comparable to conventional materials utilized in solar cell.

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3. Results and discussion

Fig. 1b shows the XRD pattern of CuSbS$_2$ NTs. All the diffractions present in the XRD pattern can be attributed to the standard reference pattern of orthorhombic CuSbS$_2$ (ICSD No. 98-017-1051, space group Pnma; a = 6.018 Å; b = 3.7958 Å; c = 14.495 Å). No other phases were observed, confirming the purity of the CuSbS$_2$ sample. Moreover, broadening of the XRD peaks indicates a nanometer scale crystalline size. The Raman peak at 330 cm$^{-1}$ (Fig. S1) and no Raman peaks of impurity phases confirmed the formation and the purity of the chalcostibite phase.

SEM images in Fig. 2a-c show the AAO template containing CuSbS$_2$ nanotubes and Fig. 2d-f show extracted nanotubes. As it is evident from Fig. 2e and f, after template removal a large-scale array of highly ordered dense nanotubes remain without collapse. The obtained NTs are straight and parallel to each other and there is a good shape uniformity. The average diameter of the NTs is around 200 nm and the average wall thickness is about 40 nm, which is predictable according to size of the template. The well-aligned CuSbS$_2$ nanotubes can provide a direct and facile pathway for high-speed and low-loss electron transport [14], and thus result in higher efficiency of nanocrystalline solar cells when used as a photoanode material.

Fig. 3a depicts the diffuse reflectance data (inset of Fig. 3a) and band gap calculation. Band gap calculation results indicate a direct band gap of 1.53 eV and an indirect one of 1.32 eV. The small difference between these values suggests that the CuSbS$_2$ NTs can have both indirect and direct band gaps [15], while the majority of literature suggests that it is a direct band gap material [16]. This observation indicates that changing the morphology of the particles to a tubular structure with a wall thickness of 40 nm has no significant influence on the bandgap in comparison to the platelet-shaped particles having a similar thickness around 40 nm [7]. Photoluminescence (PL) spectrum in Fig. 3b exhibits an emission peak at 840 nm, emitting from the direct electron–hole recombination of band transition, which is equivalent to 1.48 eV. This value is in good agreement with the results obtained from UV–Vis data.

In order to investigate the compatibility of valence band and conduction band positions of the CuSbS$_2$ NTs with other conventional materials utilized in solar cells, and estimate the type of the conductivity and majority carrier concentration, we performed cyclic voltammetry (CV) analysis and Mott-Schottky (M–S) measurements. Energy levels, including CB and VB, can be calculated from the onset of reduction and the onset of oxidation potentials in the CV curve directly (inset of Fig. 4a). The VB position can also be estimated from the flat band potential ($V_{fb}$) value of the M–S plot. According to the CV curve analysis, CB and VB positions were estimated to be $-3.60$ eV and $-5.16$ eV, respectively. These values demonstrate a direct electronic band gap of 1.56 eV, which confirms that electrochemical band gap is comparable to the optical one achieved from the Tauc estimation. $V_{fb}$, p-type conductivity, and carrier density were evaluated by linear regression of the linear part of the M–S plot in Fig. 4a fitted to the equation:

$$A^2 = \frac{2}{\epsilon_k \epsilon_r e N_D} \left( V - V_{fb} - \frac{kT}{e} \right)$$

where $\epsilon_0$, $\epsilon_s$, $e$, and $N_D$ are vacuum permittivity, semiconductor dielectric constant, electron charge, and carrier density, respectively. $V$ and $V_{fb}$ are the applied potential and the flat band potential, $k$ is the Boltzmann constant, $T$ is the experiment temperature, $C$ is the space charge capacitance, and $A$ is the surface area of the working electrode. Negative slope of the linear regression confirms the p-type conductivity of CuSbS$_2$ NTs. $V_{fb}$ was estimated from the extrapolation of the x-axis intercept and it is about $0.76$ V vs NHE. Fermi level of p-type semiconductors is assumed to be about $0.1$ V more negative than the VB. Therefore, VB position is around $0.86$ V vs NHE and $-5.30$ eV vs vacuum level. This value is very close to that obtained from the CV curve. Comparing the VB and CB values with the energy levels of conventional materials used in solar cells and considering the p-type conductivity of NTs results in the schematic comparison of the energy band positions of CuSbS$_2$ NTs with ZnO, TiO$_2$, MAPbI$_3$ (PRV1), and (FAPbI$_3$)$_{0.85}$ (MAPbBr$_3$)$_{0.15}$ (PRV2) depicted in Fig. 4b. Here, MA and FA refer to methylammonium and formamidinium, respectively, and PRV refers to perovskite. The energy level positions of CB and VB were found to describe suitable band positions for injection of electrons from CuSbS$_2$ NT CB to titanium dioxide [17] and zinc oxide [18] CBs and holes from (PRV1) and (PRV2) [19] VBs to CuSbS$_2$ NT VB (Fig. 4b). Dielectric constant of CuSbS$_2$ was considered to be 17.02 [20] and a carrier concentration of $6.55 \times 10^{18}$ cm$^{-3}$ was calculated from the slope of linear fitting.

4. Conclusions

In summary, it is shown that high-quality p-type CuSbS$_2$ nanotubes can be successfully synthesized using an anodic aluminium oxide template and a hot injection processing route. The average diameter of the synthesized CuSbS$_2$ NTs was around 200 nm and their wall thickness about 40 nm. Calculation of the band gap and estimation of the valence and conduction band positions revealed that these nanotubes are proper candidates for application as a hole transport material and an absorber in solar cells.
CRediT authorship contribution statement

Shima Moosakhani: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Validation, Visualization, Writing - original draft, Writing - review & editing.

Hamidreza Daghigh Shirazi: Investigation, Writing - original draft, Writing - review & editing.

Simo-Pekka Hannula: Funding acquisition, Project administration, Supervision, Validation, Writing - review & editing.
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editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2021.130486.

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