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Room temperature chemical synthesis of highly oriented PbSe nanotubes based on negative free energy of formation

B.R. Sankapal[a,*], R.D. Ladhe[a], D.B. Salunkhe[a], P.K. Baviskar[a], V. Gupta[b], S. Chand[b]

[a] *Thin Film and Nano Science Laboratory, Department of Physics, School of Physical Sciences, North Maharashtra University, Jalgaon 425 001 (MS), India*
[b] *Organic and Hybrid Solar Cell, Physics of Energy Harvesting Division, Dr. K.S. Krishnan Marg, National Physical Laboratory, New Delhi 110012, India*

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ABSTRACT

The sacrificial template free chemical synthesis of PbSe nanotubes at room temperature has been performed by lead hydroxination from cadmium hydroxide nanowires. This process was based on the ion exchange reaction to replace Cd^{2+} with Pb^{2+} ions from hydroxyl group followed by replacement of hydroxyl group with selenium ions. The reaction kinetics was accomplished due to more negative free energy of formation and thus the difference in the solubility products. The formed nanotubes were inclusive of Pb and Se with proper inter-chemical bonds with preferred orientations having diameter in tens of nanometer. These nanotubes can have future applications in electronic, optoelectronics and photovoltaic's as well.

1. Introduction

PbSe is an attractive semiconductor material from IV to VI group with narrow band gap (0.28–0.4 eV) and large dielectric constant ($\varepsilon_\alpha = 24$), high optical sensitivity, good magnetic, and electrical properties. It exhibits a large Bohr excitonic radius (46 nm), it is eight times larger than CdSe with nearly identical Bohr radii for the electron (23 nm) and hole (23 nm), and small effective masses for each (<0.1 m_0). Due to this the size quantization effects are pronounced in PbSe nanomaterial rather than the bulk. Furthermore, PbSe has six or eight mixing of energy band gaps and mixing of valance band which exhibits a strong confinement. Also, both carriers are strongly confined, allowing their electronic structure to be tuned by changing nanotubes/nanowire diameter and it exhibits high electron, hole mobilities and high absorption coefficient near IR region [1,2]. However, formation of such a long nanotubes/nanowires with high aspect ratio is advantageous in the manufacturing process for more complexed nanostructure devices. Furthermore, it provides more efficient charge transport over large distances between the individual wires/tubes and its versatile application for optoelectronic devices [3–5].

In recent years, the significant interest has been directed towards the growth of nanotubes/nanowires of PbSe. For this, the 'bottom-up' approach has been mostly employed for the chemical synthesis. This should be categorised into two ways as: (i) the use of hard templates, which physically confine the size and shape of the growing nanoparticles, and (ii) the use of capping agents during nanoparticle growth to control its direction and dimension [6]. In this concern, the pioneer work on PbSe was reported by Koh et al. for the synthesis of single crystal nanowire at high temperature (190–250 °C) [7], the thermoelectric properties of PbSe nanowire annealed at 200 °C has been reported by Liang et al. [8]. Hull and Zhu et al. have described the branching confinement of PbSe nanowires [9,10] and Bierman et al. showed the effect of hydrogen gas on PbS and PbSe nanowire deposited by CVD technique [1]. Jung et al. showed the confinement of PbSe wire deposited by r.f. magnetron sputtering on silicon substrate [11]. Many attempts have been made for the synthesis of PbSe nanomaterials based on either the use of sophisticated methodology, use of templates, capping agents or at high temperature synthesis. With this regards, the search for the cost effective, simple wet chemical synthesis at room temperature under milder conditions has rapidly gaining momentum. Obviously, developing the effective and environmentally friendly routes to fabricate large area nanotubes at a low cost is facing challenges.

The present article emphasis on the template free room temperature chemical synthesis of highly oriented PbSe nanotubes from $Cd(OH)_2$ nanowires on glass substrate which is reported elsewhere [12]. This was performed through the controlled precipitation of reaction kinetics based on the principle of solubility products through the formation of lead hydroxination as an

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* Corresponding author. Tel.: +91 257 2257474; fax: +91 257 2258403.
E-mail addresses: brsankapal@rediffmail.com, brsankapal@gmail.com (B.R. Sankapal).

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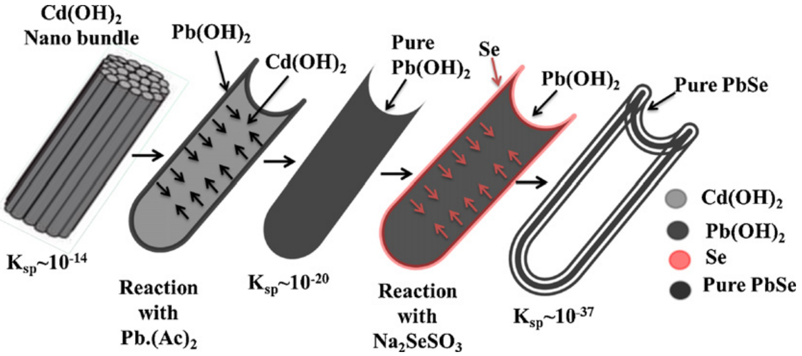

Fig. 1. Graphical representation of cation exchange (conversion) process for the formation of PbSe nanotubes.

intermediate step. The structure, morphology and composition analysis were performed and the results are discussed.

2. Experimental

All chemicals were analytical grade and used as received without further purification. All aqueous solutions were prepared in double distilled water. A typical synthesis of PbSe nanotubes using simple wet chemical route is as follows: (i) the formation of the $Cd(OH)_2$ films consisting of nanowires on the glass substrate at room temperature as reported elsewhere [12]. In short, the aqueous solution containing 100 mM $CdCl_2$ was complexed with 25% ammonia with constant stirring. Initially, a white precipitate was observed and subsequently dissolved back in the solution for further addition of ammonia (pH ~ 13). A cleaned glass substrate was immersed vertically in the reaction bath making an angle of 45 degree with the wall of the beaker. The overall assembly was kept at room temperature (27 °C) for 18 h resulting in the direct growth of $Cd(OH)_2$ nanowires on the glass substrate. After the deposition, substrate was rinsed smoothly in double distilled water and dried in air, afterwards it is used for further process, (ii) for the cation-exchange reaction from $Cd(OH)_2$ to $Pb(OH)_2$, the $Cd(OH)_2$ coated glass substrate was immersed in the 100 mM lead acetate solution for overnight (10–12 h), then taken out from solution, rinsed with double distilled water and dried in air. (iii) The room temperature sacrificial elemental transformation of $Pb(OH)_2$ into PbSe was performed by dipping $Pb(OH)_2$ substrate in aqueous 100 mM solution of selenium ion source (Na_2SeSO_3) at room temperature. After 20 h, the color of the film was changed from white to dark purple with localized selenization of $Pb(OH)_2$ resulting in the formation of pure PbSe material.

3. Growth mechanism

The simple experimental growth mechanism of PbSe nanotubes formation is as follows: the $Cd(OH)_2$ nanowires were grown through a simple wet chemical route. Solutions containing cadmium ions give white precipitates upon meeting sufficient OH^- ions in solution as long as K_{sp} of $[Cd^{2+}]\,[OH^{2-}]$ is greater than the K_{sp} value of $Cd(OH)_2$ (2×10^{-14}) at room temperature. However, $Cd(OH)_2$ is not always the final product, since hydrated cadmium ion complexes ($n[Cd(H_2O)p]^{2+}$) were transferred to cadmium hydroxide [$Cdn(OH)_2n$] through the stepwise replacement of water molecules in the hydrated cadmium ion complexes by hydroxide groups. This process is usually referred to as "olation" and offers the intermediate cadmium complex $[Cdn(OH)m(H_2O)np-m](2n-m)^+$ as shown in Eq. (1).

$$CdCl_2 + NH_3 + 2H_2O \rightarrow Cd(OH)_2 + NH_4Cl + HCl \tag{1}$$

As $Cd(OH)_2$ possesses solubility product value ($K_{sp} = 2 \times 10^{-14}$) more positive than the solubility product value ($K_{sp} = 10^{-20}$) of $Pb(OH)_2$ leading to replacement of Cd^{2+} with Pb^{2+} ions resulting in the formation of $Pb(OH)_2$ without altering the morphology. In another way, the free energy of formation of $Pb(OH)_2$ is more negative than that of $Cd(OH)_2$. The resulting ion exchange reaction is as follows

$$Cd(OH)_2 + Pb(Ac)_2{\cdot}3H_2O \rightarrow Pb(OH)_2 + Cd(Ac)_2 + 3H_2O \tag{2}$$

When the final product reacts with selenium ions source, inter diffusion of Se^{2-} ions occurs through the $Pb(OH)_2$ films, the outer covering layers of PbSe begin to form towards the inner side by replacing hydroxyl group with selenium ions until complete conversion. This was easily observed by naked eye due to change in color from white [$Pb(OH)_2$] to purple dark [PbSe]. This transformation is possible due to more negative solubility product of PbSe ($K_{sp} = 10^{-37}$) than that of $Pb(OH)_2$ ($K_{sp} = 10^{-20}$). Complete transformation was confirmed by different reaction time with selenium ion source by means of structural characterization at each step (not shown). It has also been suggested that the hydroxide cluster can act as a catalyst. In this case, selenide formation will occur preferentially at the surface of Pb sites rather than nucleate separately in the solution. The reaction for the formation of PbSe from $Pb(OH)_2$ is summarized as follows

$$Pb(OH)_2 + Se^{2-} \rightarrow PbSe + H_2O + 1/2O_2\uparrow \tag{3}$$

The schematic representation of ion exchange process from $Cd(OH)_2$ to $Pb(OH)_2$ to PbSe based on solubility product is depicted in Fig. 1.

4. Characterizations

The crystal structure of the films was investigated using X-ray diffractometer (Miniflex, Rigaku) using monochromatic CuK_α radiation ($\lambda = 1.5406$ Å) in the scanning angles between 20 to 80°. The surface morphology of the films was examined using scanning electron microscopy (SEM: Zeiss EVO MA-10). The energy dispersive X-ray analysis (EDAX) was investigated with an energy dispersive X-ray spectroscopy (EDAX: OXFORD INCA ENERGY 250 unit) coupled with SEM. The microstructural characterization of highly oriented PbSe surface (nanotubes) at higher magnifications and reciprocal space analysis was carried out using high resolution transmission electron microscope (HR-TEM: FEI Tecnai G2 F30 STWIN at 300 keV).

5. Results and discussion

An effective and versatile simple wet chemical route has been employed for a cation/anion-exchange reaction which is illustrated as an efficient way to "proxy" nanostructures without altering the morphology. The large solubility product (K_{sp}) difference is a key reference for the direct cation/anion exchange process. This reaction of nanocrystals occurs when K_{sp} value of goal product is more negative than that of reactant (used precursors), then spontaneous conversion into another kind of more stable nanocrystal. This approach opens up a new access to design and prepare nanotube which is difficult to achieve at room temperature through simple wet chemistry. Furthermore, the room temperature synthesis offers relatively slow growth rate and it is consistent to