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

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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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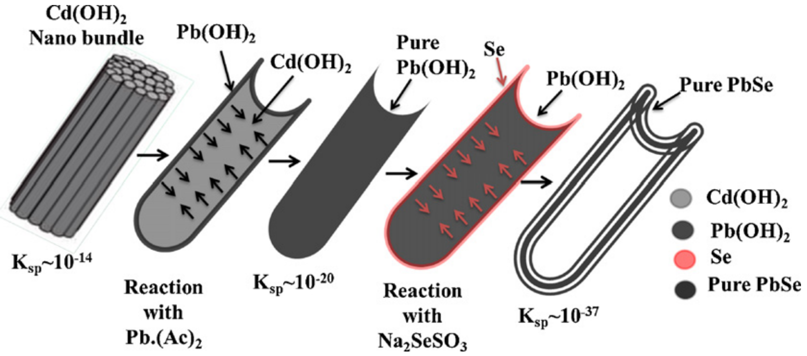

Fig. 1. Graphical representation of cation exchange (conversion) process for the formation of PbSe nanotubes.

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).

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

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

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

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

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

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

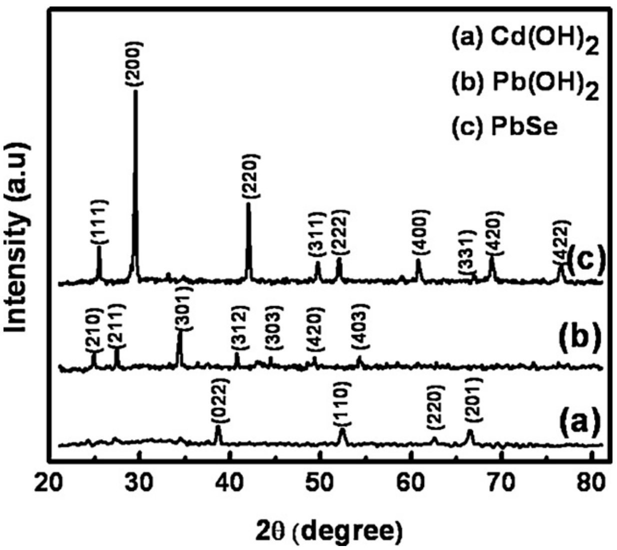

Fig. 2. X-diffraction patterns of (a) $Cd(OH)_2$, (b) $Pb(OH)_2$, and (c) PbSe nanotubes on the glass substrates.

the formation of PbSe nanotubes. Probably, the initial nucleation centers are sheltered on the substrates, not allowing the growth at other places, allowing extension of initially grown materials unlike to formation of large crystal first, from which the nanotubes are nucleated via heterogeneous nucleation with a variety of orientations. The stronger bond between cation and anion in prehistoric nanocrystal should be impaired or substituted through special organization of two compounds. The ligand could complex with target Pb^{2+} with Se^{2-} ions, this associate a strong coupling between cation and anion at room temperature through the solution chemistry in which the outside and inside phase of material can provide a driving force between them due to the chemical potential difference. In this process, $Pb(OH)_2$ nanowire may provide efficient pathways for diffusion of Se^{2-} ions and leave the OH^- ions from impaired phase resulting in the formation of pure PbSe nanotubes. These explorations significantly increase the scope of the methodological application in the field of nanostructures preparation. Herein, the current work further advances our understanding about the cation and anion-exchange reaction in the employment for achieving PbSe nanotubes.

The crystal structure, peak positions, and confirmation of phase for as deposited $Cd(OH)_2$, its intermediate conversion to $Pb(OH)_2$ material and its complete conversion of PbSe nanotube has been carried out using X-ray diffraction (XRD) technique. Fig. 2 shows the XRD patterns of $Cd(OH)_2$ nanowire, $Pb(OH)_2$ and corresponding converted PbSe on the glass substrates. The tiny peaks observed for $Cd(OH)_2$ correspond to (0 0 2), (1 1 0), (2 2 0) and (2 0 1) planes with $a = 3.494$ Å with hexagonal crystal structure (JCPDS card 31-0228). This shows the simple way for the template free formation of $Cd(OH)_2$ nanowire grown on glass substrates (Fig. 2a). The complete conversion of $Cd(OH)_2$ to $Pb(OH)_2$ can be seen by XRD patterns with diminished peaks of $Cd(OH)_2$ with emerged peaks of $Pb(OH)_2$ corresponding to tetragonal crystal structure (JCPDS card 77-1895, $a = 6.022$ Å) (Fig. 2b). The XRD pattern in Fig. 2c shows complete removal of hydroxide phase with selenium resulting in to

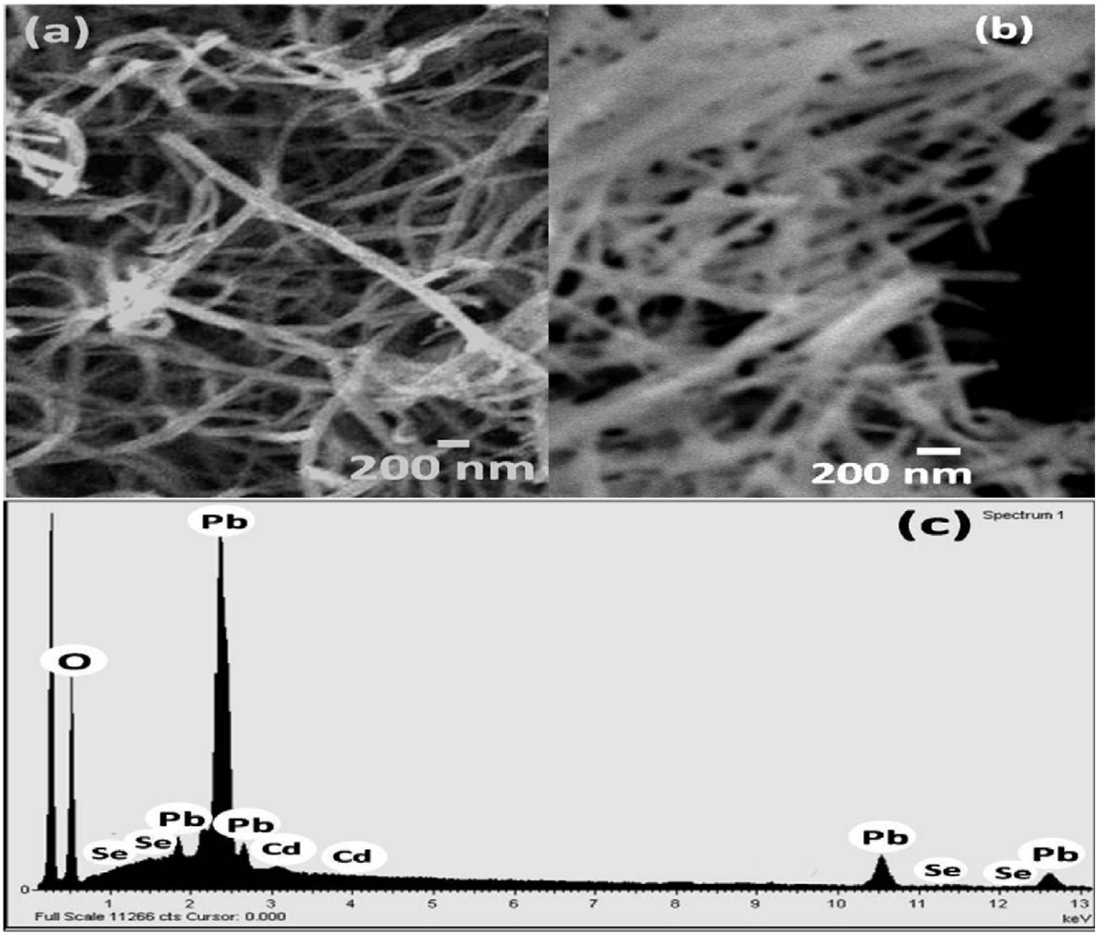

Fig. 3. Scanning electron micrograph of (a) $Cd(OH)_2$ and (b) PbSe nanotubes, and (c) shows the energy dispersive X-ray analysis of PbSe nanotubes.

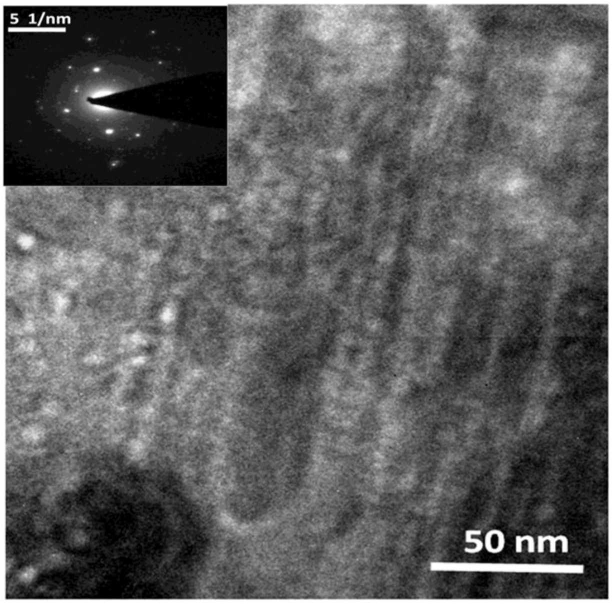

Fig. 4. Transmission electron micrograph of PbSe nanotubes. Inset shows Fourier transform image of PbSe nanotubes.

complete conversion of $Pb(OH)_2$ to PbSe with (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 1 1), (4 2 0), and (4 2 2) planes with preferred orientation along (2 0 0) plane corresponds to cubic crystal structure (JCPDS card no. 78-1903, $a = 6.121$ Å). It is more fascinating that the Cd component disappears and intensities of Pb become stronger, and shows the room temperature conversion into PbSe nanotubes based on ion exchange reaction. The diffraction peaks are in good agreement with the literature data for hexagonal $Cd(OH)_2$ [13] and cubic PbSe [14,15]. Fig. 3a shows the surface morphology of template free grown $Cd(OH)_2$ nanowire on the glass substrate and the surface morphology of converted PbSe clearly shows the PbSe nanotubes with length more than micron and average diameter of 30–50 nm (Fig. 3b). We strongly believe that such development of nanotubes is artifact of this method where there is neither branching between two nanotubes nor formation of gigantic structure during the cation/anion exchange process. However, the confirmation of the final product PbSe was performed using energy dispersive X-ray analysis (EDX) spectra as shown in Fig. 3c as it depicts the elemental composition of PbSe. The spectrum shows strong evidence for Pb and Se along with oxygen from the surface contamination which is unavoidable in the chemically deposited films. Small content of Cd (0.01 wt%) cannot be excluded entirely which might be due to porous network morphology resist for the complete removal of small content of Cd that adhere somewhere inside the film. Fig. 4 shows transmission electron microscopy (TEM) image of PbSe at higher magnification. The clear distinction can be made for the structure composed of nanotubes with one end closed and another end open inside the network of highly oriented structure with diameter of about 20–40 nm. From the Fourier transform, the corresponding selected area of electron diffraction pattern yields inter planer spacing of 3.9 Å representing (2 0 0) plane with cubic crystal structure. This supports to cubic structure observed by XRD studies with preferred orientation.

6. Conclusions

Simple, inexpensive and room temperature chemical route has been successfully employed for the synthesis of highly oriented PbSe nanotubes from $Cd(OH)_2$ nanowires through lead hydroxination as intermediate step. This was based on more negative free energy of formation and thus the difference in their individual solubility products. Strong orientation is observed along (2 0 0) plane with cubic crystal structure for PbSe without branching between two nanotubes and avoiding formation of gigantic structure during the cation/anion exchange process. The controlled growth of one dimensional highly oriented nanotubes may significantly expand the range of applications and will open up new research opportunities to use these nanotubes as building blocks in nanotechnology based devices.

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