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Large-scale synthesis of single-crystal CdSe nanowires through a cation-exchange route

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Abstract

Cation-exchange reaction between Ag^+ and Cd^{2+} was employed to transform single-crystal Ag_2Se nanowires into single-crystal CdSe nanowires as a case study of transformation from one chalcogenide to another one. The CdSe nanowires of ~30 nm in diameter had a wurtzite crystal structure and showed preservation of both the morphology and single crystallinity of the Ag_2Se nanowires. This synthetic route is useful in producing large quantities of CdSe nanowires with uniform diameters and exceptionally long lengths (>50 µm). © 2005 Elsevier B.V. All rights reserved.

1. Introduction

Nanowires have received ever-growing interest because of their fascinating properties and unique applications that cannot be obtained from nanoparticles or bulk solids [1]. As a key step towards realization of their potential in practical applications, it is necessary to develop synthetic routes capable of generating uniform nanowires in high volumes, together with controllable sizes, compositions, and single crystallinity.

Among various synthetic methods [1], templating against existing nanostructures offers a very powerful means to increase the compositional diversity of materials or to generate nanostructures that might be difficult or impossible to directly synthesize. For example, surface coating of nanowires could form nanocables and selective removal of the cores could produce nanotubes with different compositions [2–4]. Chemical reactions of nanowires with vapors of metal oxides produced nanowires made of various semiconductors [5–7]. Galvanic displacement between silver nanowires and salt precursors led to the formation of nanotubes made of noble metals such as Au, Pd, and Pt [8–10]. The high chemical reactivity of Se could be

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used to form chalcogenide semiconductors. Silver precursors have been exploited to completely transform nanowires of trigonal Se (t-Se) into Ag₂Se without changing the single crystallinity [11,12]. Also, t-Se nanowires could be partially transformed to Se@CdSe nanocables in a medium containing Cd²⁺ cations [13]. However, the reaction was limited to the surface of t-Se nanowires because disproportionation of elemental Se into Se²⁻ and SeO₃²⁻ was prohibited after insoluble CdSe nanoparticles completely covered the surface of t-Se nanowires. In the present work, we demonstrated that cation-exchange reactions could be used to transform Ag₂Se nanowires into other semiconductors on relatively large scales.

Recently, Könenkamp and coworkers [14,15] employed an anion-exchange reaction to convert ZnO tubular columns into ZnS and further transformed ZnS into Ag₂S and Bi₂S₃ through cation-exchange reactions. Alivisatos and coworkers [16] demonstrated that the cation-exchange reactions between Ag⁺ and Cd²⁺ were reversible for both Ag₂Se and CdSe nanorods and the morphology could be preserved. Most recently, we also showed that the reversible cation-exchange reactions between Ag⁺ and Cd²⁺ could be extended to spherical colloids on the mesoscale to produce polycrystalline colloids of Ag₂Se and CdSe [17]. The present work exploits the same cation-exchange reactions with a focus on the transformation of Ag₂Se

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nanowires into CdSe nanowires with preservation of both morphology and single crystallinity. In spite of extensive studies of CdSe in the nanostructured form [18–20], we note that there are only a limited number of reports on the solution-phase synthesis of single-crystal CdSe nanowires with uniform, controllable diameters [20–23].

2. Experimental

Selenious acid (H₂SeO₃, 99.99%), hydrazine monohydrate (N₂H₄ · H₂O, 55%), poly(vinyl pyrrolidone) (PVP, $M_w = 55000$), silver nitrate (AgNO₃, 99.9%), cadmium nitrate tetrahydrate (Cd(NO₃)₂ · 4H₂O, 98%,), tributylphosphine (C₁₂H₂₇P or TBP, 97%) were all purchased from Aldrich. Ethylene glycol (HOCH₂CH₂OH, EG, 99.9%) and methanol (99.8%) were obtained from Fluka and EMD, respectively. All chemicals were used as received.

Our synthesis began with single-crystal nanowires of t-Se, which served as templates to obtain Ag₂Se nanowires to be used in the Ag^+/Cd^{2+} cation-exchange process. The t-Se nanowires were synthesized using the sonochemical approach [24,25]. In a typical procedure, an aqueous solution of selenious acid (4.2 mL, 1 M) was added dropwise to an aqueous hydrazine solution (10 mL, 3 M) under magnetic stirring in a 50-mL round bottom flask. After 20 min, the spherical colloids of amorphous Se (a-Se) were filtered over 0.2 µm polymer membrane, rinsed with pure water (20 mL), and dried under ambient conditions. The a-Se colloids (0.1 g) were then added to a 200-mL beaker containing 100 mL of ethanol. The beaker were sonicated for 30 s (1510R-DTH, Bransonic) and then kept in dark at room temperature for 12 h to generate uniform t-Se nanowires. The t-Se nanowires were centrifuged, washed with ethanol twice, and dried under ambient conditions.

The t-Se nanowires (20 mg) were redispersed in 20 mL ethylene glycol by sonication (10 s) together with 0.1 g of PVP. Meanwhile, 60 mg AgNO₃ was dissolved in 1 mL ethylene glycol and the solution was added to the suspension of t-Se nanowires dropwise for 10 min at room temperature and under mild magnetic stirring. The color of the solution turned dark gray within 20 min, which indicates the transformation of nanowires from t-Se into Ag₂Se. The reaction was continued for 1 h to ensure complete conversion. The Ag₂Se nanowires were centrifuged and ethylene glycol was decanted.

After three rounds of repetitive centrifugation and washing with methanol, the Ag₂Se nanowires were dispersed by sonication (10 s) in 20 mL methanol and hosted in a 50-mL round bottom flask containing PVP (0.1 g). Cd(NO₃)₂ (1.0 g) was dissolved in pure water (0.3 mL) and added to the Ag₂Se nanowire suspension. At 50 °C, 20 μ L TBP was introduced and the reaction was allowed to proceed for 3 h. The color of the solution turned dark brown within 30 min, implying the conversion of Ag₂Se into CdSe. The CdSe nanowires were centrifuged and washed twice with methanol (20 mL) and further washed with pure water and ethanol.

SEM imaging was performed on Siron XL at an acceleration voltage of 5 kV. EDX was acquired using Genesis 2000 at an acceleration voltage of 15 kV. TEM images were obtained using a JEOL microscope (JEM 1200 EX II) operated at 80 kV. HRTEM images were taken on a JEOL 2010 LaB6 high-resolution transmission electron microscope operated at 200 kV. Powder XRD was performed on a Philips PW-1710 diffractometer.

3. Results and discussion

The chemical transformations were first characterized using energy dispersive X-ray spectra (EDX), as shown in Fig. 1. After conversion from t-Se into Ag₂Se nanowires, the peaks for Ag appeared in the range of 2.99–3.35 keV. From the atomic ratio (Ag = 66%, Se = 34%), the resultant nanowires were found to match the stoichiometry expected for Ag₂Se. Cation-exchange between Ag⁺ and Cd²⁺ resulted in the complete replacement of Ag peaks with Cd peaks (3.17–3.50 keV). The atomic ratio (Cd = 48%, Se = 52%) confirmed the stoichiometric conversion from Ag₂Se into CdSe.

Powder X-ray diffraction (PXRD) was employed to identify the crystal structure corresponding to each sample of nanowires (see Fig. 2). As shown in the previous study [25], the abnormal intensity of (001) peak in t-Se nanowires indicates that they predominantly grew along the $\langle 001 \rangle$ direction or *c*-axis. The lattice constants of t-Se nanowires were found to be a = 0.436 nm and c =0.495 nm. The Ag₂Se nanowires had an orthorhombic structure (β -phase) with lattice constants a = 0.433 nm, b = 0.706 nm, and c = 0.776 nm. No residual peak of t-Se indicated a complete conversion into Ag₂Se. The CdSe nanowires were crystallized in the wurtzite structure with a = 0.430 nm, b = 0.430 nm, and c = 0.701 nm, and the sample did not show any peak from β -Ag₂Se. The change of crystal structure was consistent with the results obtained



Fig. 1. EDX spectra taken from the nanowires. The CdSe nanowires were derived from Ag₂Se nanowires via cation-exchange process. The Ag₂Se nanowires were, in turn, formed by reacting t-Se nanowires with AgNO₃ in ethylene glycol. The peaks of Cd completely replaced the peaks of Ag after the transformation from Ag₂Se into CdSe.



Fig. 2. PXRD patterns taken from the nanowires made of t-Se, β -Ag₂Se, and CdSe. In the ion-exchange process, the orthorhombic structure of β -Ag₂Se was converted into the wurtzite structure of CdSe.

for the polycrystalline system, where spherical colloids of Ag_2Se were transformed into CdSe [17].

Fig. 3 displays SEM and TEM images of the nanowires: t-Se (A–B), β -Ag₂Se (C–D), and CdSe (E–F). The t-Se nanowires were uniform in thickness $(30 \pm 7 \text{ nm})$ and longer than \sim 50 µm. Some nanowires might look much thicker in the SEM image; they were bundles of nanowires formed during sample preparation. The electron diffraction in the inset of Fig. 3B suggests that the t-Se nanowires were single crystals. The transformation of t-Se into β -Ag₂Se nanowires slightly increased the thickness $(35 \pm 8 \text{ nm})$. Both SEM and TEM images did not show any kinks or other related defects within these wires. Electron diffraction patterns (see the inset of Fig. 3D) taken from different regions of an individual nanowire were essentially the same. This homogeniety in the crystalline structure and orientation implies that the β -Ag₂Se nanowires were also single crystals. Note that the reaction involved in the present work is different from our previous demonstrations where t-Se nanowires were reacted with AgNO₃ in water and the formation of Ag₂SeO₃ solid byproduct was inevitable [12]. When the solvent was switched from water to ethylene glycol, Ag⁺ cations were reduced to Ag atoms by ethylene glycol and subsequent reaction with Se(s) led to the formation of Ag₂Se without producing any byproduct [17]. In the conversion of Ag₂Se into CdSe, the use of TBP and an elevated temperature was crucial. The transformation did not take place without TBP or at room temperature. The resultant CdSe nanowires did not contain defects such as kinks as revealed by both SEM and TEM images. The electron diffraction pattern shown in Fig. 3F also suggests the single crystallinity of the as-synthetized CdSe nanowires. From SEM studies, CdSe nanowires were found longer than 50 µm, which is probably the longest CdSe nanowires reported so far [22,23]. However, it is worth pointing out that too much sonication (e.g., longer than 1 min) could easily break the nanowires making them shorter than $\sim 10 \,\mu m$ (with a random distribution in length).



Fig. 3. SEM (left) and TEM (right) images of nanowires: t-Se (A–B), β -Ag₂Se (C–D), and CdSe (E–F). The insets in the TEM images are electron diffraction patterns taken from individual nanowires. Note that the SEM images are on the same scale, as well as the TEM images. The SEM and TEM images did not show defects in CdSe nanowires and the diffraction pattern suggests that the CdSe nanowires are single crystalline.

The single crystallinity of β -Ag₂Se and CdSe nanowires was supported by HRTEM studies, as displayed in Fig. 4. The fringe spacing of 0.27 nm observed in Fig. 4A matched with the separation between the (112) planes of orthorhombic β -Ag₂Se. The fringe spacing of CdSe obtained from Fig. 4B was 0.36 nm, which corresponds to the separation between the (100) lattice planes. HRTEM analysis across individual nanowires further confirmed the absence of domain boundaries within each nanowire.

The preservation of single crystallinity in the the transformation from t-Se into β -Ag₂Se has also been observed and explained in our previous publications [11,12]. The lattice constant in the *a*-axis of t-Se matches with the *a*-axis of the orthorhombic lattice of β -Ag₂Se. As a result, the positions and arrangements of Se atoms in the t-Se lattice were largely unaffected during the transformation, facilitating the preservation of single crystallinity. For the transformation from Ag₂Se into CdSe, Alivisatos and coworkers showed that the Se anion sublattices of CdSe wurtzite structure also exhibit a topotactic relationship with the Se²⁻ anion sublattices of orthorhombic β -Ag₂Se. The *a*- and *b*-axis of orthorhombic β -Ag₂Se match with the *a*- and *c*-axis of wurtzite CdSe. This excellent superimposition could facilitate the in- and out-diffusion of Ag⁺ and Cd²⁺



Fig. 4. HRTEM images of β -Ag₂Se (A) and CdSe (B) nanowires. The insets show TEM images of the corresponding nanowires.

cations through the layers of Se^{2-} anions and resulted in the conversion of β -Ag₂Se into CdSe without causing substantial rearrangement for the Se²⁻ sublattice.

Alivisatos and coworkers also observed that the transformation were reversible and the morphology was kept for other pairs of chalcogenide semiconductors such as CdS and Ag₂S or CdTe and Ag₂Te [16]. These semiconductors have good topotactic relationship between each other, which makes the transformation easy and fast. The transformation will have a good chance to preserve the single crystallinity if the initial nanostructures are single crystals. They also mentioned that hexagonal CuSe and cubic PbSe nanocrystals could be produced from CdSe nanocrystals even though they do not have any topotactic relationship with wurtzite CdSe [26]. The limit in size and shape for preserving the single crystallinity in cation-exchange reactions between crystal structures having no topotactic relationship deserves further systematic studies. If single crystallinity is not a critical issue, cation-exchange reactions can greatly expand the scope of semiconductors prepared as well-defined nanostructures.

4. Conclusion

In summary, we have demonstrated that cation-exchange can be employed to transform one chalcogenide semiconductor into another one with feature sizes on the scale of \sim 30 nm. As a case study, we replaced Ag⁺ in Ag₂Se nanowires with Cd²⁺ to produce uniform CdSe nanowires with preservation of both morphology and single crystallinity. This approach provides an immediate advantage for the large-scale synthesis of CdSe nanowires as both t-Se and Ag₂Se nanowires can be easily prepared on the gram-scale [24,25]. These single-crystal nanowires might be useful in fabricating flexible electronic devices [27,28]. We also believe that the same strategy can be extended to other types of nanostructures and semiconductors.

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