Preparation of Single-crystalline Selenium Nanowires in the Presence of Ethylenediaminetetramethylenephosphonic Acid

Yun Lei, Lide Yao, Yuping He, Shiquan Wang, Richeng Yu, and Bingsuo Zou*
Nanoscale Physics and Device Laboratory, Beijing National Laboratory for Condensed Matter Physics,
Institute of Physics, Chinese Academy of Sciences, Beijing 100080, P. R. China

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Selenium nanowires have been synthesized by using 2-mercaptoethylamine-depleted CdSe nanoparticles as selenium source and ethylenediaminetetramethylenephosphonic acid as chelating agent. The products were characterized by X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, and UV–vis spectrophotometry. The result shows that the selenium nanowires are single crystals grown along the [001] direction of hexagonal lattice. The optical measurement shows a blue shift relative to the bulk hexagonal selenium, and the optical bandedge might be attributed to the interchain interactions within a hexagonal selenium crystal.

One-dimensional (1D) nanostructures, such as nanowires, nanotubes, nanorods, and nanobelts, have attracted growing interests on their synthesis, characterization, and applications because of their unique optical, electrical, and mechanical properties.[1] Selenium atoms tend to form helical chains through covalent bonding, and helical chains can be readily packed into a hexagonal lattice through van der Waals interactions. So the crystallization for generating 1D structure tends to occur along [001] direction favoring the stronger covalent bonds over the relatively weak van der Waals forces. Several synthesis methods for 1D selenium nanostructures have been reported in the literature. Notable examples include a solution-phase approach via the reduction of selenious acid with excess hydrazine,[2,3] a hydrothermal process with polycrystalline selenium powders,[4] a physical vapor deposition process of selenium powders with copper plates as substrates or Si powders as catalyst,[5,6] and a carbothermal chemical vapor deposition route via evaporation of an active carbon and selenium powder mixture.[7] The above-mentioned methods are conventional approaches to fabricate 1D nanostructures of hexagonal selenium nanowires (NWs), but vapor deposition routes involve high temperature procedure accompanied with a constant flow of inert gas, and solution-phase approaches are limited by their tendency to form unstable colloidal particles owing to the absence of any stabilizing ligands. So it remains a great challenge to develop mild solution routes to selenium NWs with an appropriate chelating agent capable of transformation of atoms or ions from unstable precursors to a stable crystalline product. In this manuscript a continuous transformation of selenium NWs from CdSe NPs using ethylenediaminetetramethylenephosphonic acid (EDTMP) and 2-mercaptoethylamine (MA) is reported.

2-MA-stabilized CdSe NPs were prepared using a synthetic route reported earlier.[8] The prepared CdSe NPs were washed with water and ethanol several times and redispersed into 11.5 mM EDTMP solutions at pH of 9.0. The solutions containing CdSe NPs and EDTMP were incubated in dark environment under 40 °C for 3 days and then were gradually elevated to 60 °C for 2 days. A gradual change of color from red to dark-red and gray indicated that CdSe NPs were transformed into selenium NWs. The detailed influences of temperature on the diameters of selenium NWs were examined and given in Supporting Information (1).

It has been demonstrated that excess stabilizers together with cadmium ions form complex on the surface of the CdSe particles and the layer of cadmium stabilizer complex can be considered as a shell, preventing NPs from oxidizing.[9] When the prepared NPs were washed with water and ethanol several times, the shell of cadmium stabilizer complex was partially removed, and the bare CdSe particles were exposed to the air. The standard redox potentials for Se^{2-}/Se and O_2/OH^- are -0.924 and 0.401 V, respectively, which makes the oxidation of Se^{2-} thermodynamically possible in the presence of oxygen. However, the activation energy of molecular precursors releasing from stabilizer-depleted particles is expected to be quite low, which obviously cannot satisfy the requirement in the transformation from CdSe NPs to selenium NWs. Thus, other driving forces are needed in this reaction system. The gradually increasing temperature provides energy to promote the dynamic transformation process and facilitates the lateral and longitudinal growth. Moreover, EDTMP is a strong chelating agent towards cadmium ions, and as a derivative of ethylenediamine it tends to form a stable complex with selenium atoms. The resulting complex intermediate including Cd and Se can promote the oxidation of Se^{2-} and further lead to the anisotropic growth of selemium NWs. The proposed mechanism[10] for stimulating the oxidation can be described as following:

$$\mathrm{CdSe} + \mathrm{H_2EDTMP^{2-}} \rightarrow \mathrm{CdSe(EDTMP)^{4-}} + 2\mathrm{H^+}, \quad (1)$$

$$\begin{aligned} &2\mathrm{CdSe(EDTMP)^{4-}} + \mathrm{O_2} + 2\mathrm{H_2O} \rightarrow \\ &2\mathrm{Se} + 2\mathrm{Cd(EDTMP)^{2-}} + 4\mathrm{OH^-}. \quad (2) \end{aligned}$$

The typical X-ray diffraction (XRD) pattern of the prepared sample is shown in Figure 1. No impurities such as selenium oxides or allotropes of selenium can be found in the pattern.

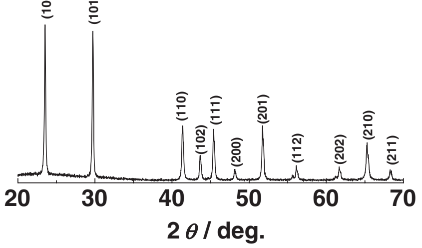

Figure 1. XRD pattern of the synthesized selenium nanowires supported on a glass slide. All peaks could be indexed to the hexagonal selenium.

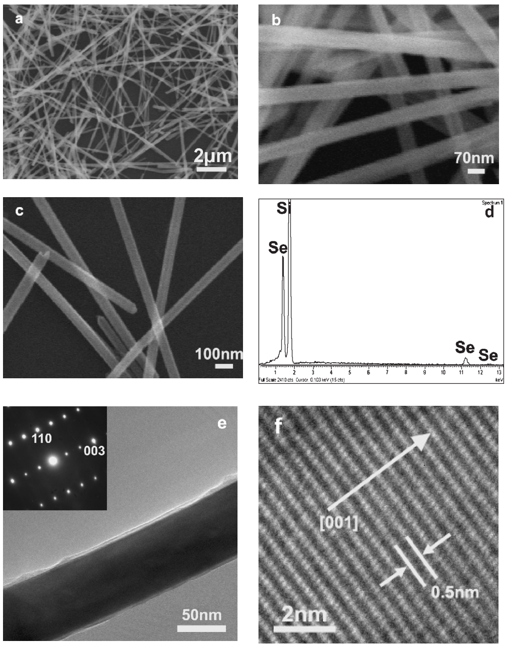

Figure 2. Selenium NWs prepared with 2-MA-depleted CdSe nanocrystals. The sample was incubated in dark environment under 40 °C for 3 days and then were elevated to 60 °C for 2 days. (a–c) SEM images of the prepared selenium NWs. (d) Energy dispersion X-ray spectroscopy of selenium NWs. (e) TEM image of an obtained nanowire (inset: SAED pattern of a single selenium nanowire). (f) Corresponding HRTEM image of a selenium nanowire.

All of the peaks could be indexed as the hexagonal selenium according to the stand card (JCPDS 06-0362) with the lattice parameters $a = 0.4366$ and $c = 0.4953$ nm.

The scanning electron microscopic (SEM) images illustrated in Figures 2a, 2b, and 2c reveal the general morphology of selenium NWs prepared with 2-MA-depleted CdSe NPs. It can be seen that the products consist of NWs ranging from 40 to 80 nm in width and several micrometers in length. No trace of CdSe NPs was observed in the SEM images, indicating a 100% conversion efficiency of CdSe NPs to selenium NWs. The chemical composition of the NWs was investigated by energy dispersion X-ray spectroscopy (EDX) in Figure 2d. Only selenium peaks were observed from the samples, confirming that these NWs were pure selenium. The silicon detected in the EDX measurement was from a silicon wafer that the selenium NWs were placed on, and no O, C, or P peaks was detected (like no O, C in the Figure 7A of ref. 3). A typical transmission electron microscopic (TEM) image of an obtained selenium nanowire is shown in Figure 2e. The inset of Figure 2e shows a selected area electron diffraction (SAED) pattern obtained along $[\bar{1}10]$ zone axis of an individual nanowire, indicating that each nanowire is a single crystal grown along [001] direction of hexagonal lattice. The single crystallinity and growth direction are also supported by high-resolution transmission electron microscopic (HRTEM) observation. The HRTEM image shown in Figure 2f further demonstrates a single-crystalline structure with 0.5 nm lattice spacing, corresponding to the (001) interplanar distance of hexagonal selenium NWs.

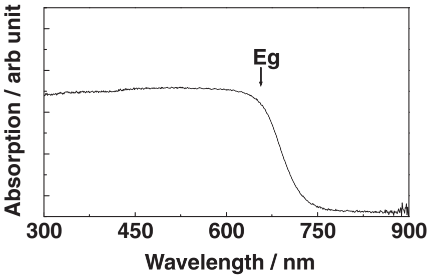

Figure 3. UV–vis absorption spectrum of selenium nanowires.

The synthesized hexagonal selenium NWs were further characterized by UV–vis absorption spectroscopy (Figure 3), which was transformed from the reflectance spectroscopy. The optical measurement with optical edge at 655 nm suggested that the hexagonal selenium is a semiconductor with a band gap of 1.89 eV, which is slightly blue-shifted relative to bulk hexagonal selenium of 1.6 eV. Since the optical bandedge above 530 nm might be solely attributed to interchain interactions perpendicular to the c axis, the energy of 1.89 eV might be ascribed to the interchain interactions within a hexagonal selenium crystal.

In summary, single-crystalline nanowires of hexagonal selenium have been synthesized using stabilizer-depleted CdSe NPs in the presence of ethylenediaminetetramethylenephosphonic acid. This facile, low-temperature solution-phase approach to fabricate 1D nanostructures involves the chelating agent to induce the anisotropic growth, which may be potentially extended to other functional materials with highly anisotropic structures.

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