

Rapid, high yield, solution-mediated transformation of polycrystalline selenium powder into single-crystal nanowires†

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Received (in Cambridge, UK) 3rd April 2003, Accepted 23rd June 2003

First published as an Advance Article on the web 3rd July 2003

Single-crystal selenium nanowires were successfully synthesized for the first time by a convenient solution-mediated transformation of polycrystalline powder, and characterized by SEM, XRD, TEM and HRTEM.

Selenium is an important elemental semiconductor with good photoelectric and semiconductor properties,¹ linear and non-linear optical properties such as photo-darkening and optical phase conjugation,² a relatively low melting point (~ 490 K), a photovoltaic effect and high photoconductivity ($\sim 8 \times 10^4$ S cm^{-1}), and a high reactivity toward a variety of chemicals that can be exploited to convert selenium into other functional materials.³ Hence, selenium has been used in photovoltaic cells, rectifiers, photographic exposure meters, and xerography.⁴ It is also an essential trace element for humans.⁵ Amorphous selenium (a-Se) with a mean particle size of 2 nm has been synthesized in aqueous solution by Dimitrijevic *et al.*,⁶ however, the solutions are subject to extreme photocorrosion and are stable for only a few days. Recently, Quintana *et al.*⁷ used a pulsed laser ablation technique to prepare amorphous selenium nanoparticles and deposited them on different substrates (glass, Au, Si). Johnson *et al.*⁴ synthesized amorphous and monoclinic selenium in a reverse micelle microemulsion. Trigonal selenium (t-Se) nanoparticles have been produced by colloidal precipitation, capping,⁸ physical adsorption through vapor phase diffusion,⁹ precipitation and subsequent evaporation of the solvent,² rf-co-sputtering,¹⁰ confinement in zeolite pores or cancrinite nanochannels,¹¹ γ -radiation of solution,¹² and crystallization of melt-quenched amorphous selenium.¹³

Recently, studies on one-dimensional (1-D) nanostructures – nanowires, nanorods or nanotubes – have received increasing attention due to their potential use as active components or interconnects in fabricating nanoscale electronic, optical, optoelectronic, electrochemical, and electromechanical devices.¹⁴ A number of methods have been developed to fabricate and assemble 1-D nanostructures, including nanolithographic techniques (*e.g.*, electron beam lithography, proximal probe patterning, X-ray patterning),¹⁵ and many low cost chemical methods (*e.g.*, vapor–solid(VS), vapor–liquid–solid(VLS), solution–solid(SS)). Abdelouas *et al.*¹⁶ used the protein cytochrome c_3 to reduce selenate (SeO_4^{2-}) to monoclinic selenium (m-Se) nanowires. Gao *et al.*¹⁷ used glutathione (GSH) to reduce sodium selenite in solution to get m-Se nanowires. Xia's group used direct solution refluxing¹⁸ and sonochemical¹⁹ approaches to get t-Se nanowires. Trigonal selenium nanorods have also been obtained by using laser ablation recently.²⁰

In this communication, single-crystal selenium nanowires are fabricated by direct conversion of polycrystalline selenium powder *via* a simple hydrothermal process. In a typical procedure, 0.06 mol Se powder (from Alfa Aesar, ~ 200 mesh, 99.999%), 0.2 mol NaOH and 30 mL HPLC grade water were put in a Teflon-lined stainless steel autoclave, stirred, then heated at 150 °C for 24 h, and cooled to ambient temperature over ~ 3 hours. The product was collected, washed (with

distilled water and ethanol), and dried at room temperature under vacuum. The morphology of the product was characterized by scanning electron microscopy (SEM) (JEOL JEM-6300 scanning electron microscope), transmission electron microscopy (TEM) (Philips CM12, with an accelerating voltage at 120 kV), and high-resolution TEM (HRTEM) (Topcon EM-002B, with an accelerating voltage at 200 kV). The crystallinity was investigated by powder X-ray diffraction (XRD) using a Rigaku Multiflex X-ray diffractometer at 40 kV and 40 mA.

Figure 1 shows the SEM images of the starting commercial selenium powder (A) and as-prepared single-crystal selenium nanowires (B). Fig. 1(A) shows the morphology of commercial selenium powder, an aggregate of micron-size polycrystals. After hydrothermal treatment, the morphology of selenium is completely transformed ($\sim 100\%$ yield) from powder to nanowires. The average diameter of the as-prepared nanowires is in the range of several tens to several hundreds of nanometers with a mean value situated around 300–400 nm. Figure 2 shows XRD patterns of the starting material (A) and the final, as-prepared Se nanowires (B). The observed peaks with 2θ values of 23.48°, 29.74°, 41.38°, 43.72°, 45.44°, 48.14°, 51.8°, 55.96°, 61.5°, and 65.38° correspond to diffraction from (100), (101), (110), (102), (111), (200), (201), (003), (103), and (210)

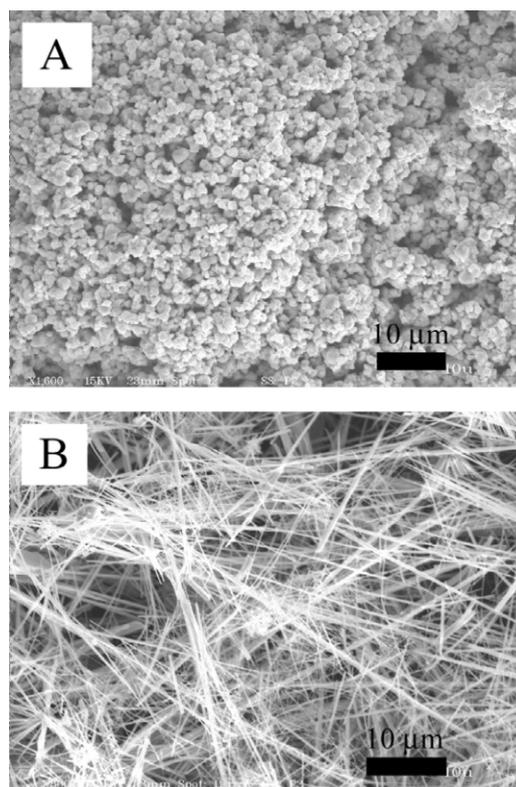


Fig. 1 SEM images of commercial poly-crystalline selenium powder (A) and as-prepared, single-crystal selenium nanowires (B); the scale bar is 10 μm .

† Electronic supplementary information (ESI) available: histogram of diameter distribution of as-prepared single-crystalline trigonal selenium nanowires. See <http://www.rsc.org/suppdata/cc/b3/b303755j/>

planes respectively. All of the diffraction peaks in the two patterns can be indexed with the trigonal phase of selenium.

In pattern B, the intensity of the (100) peak is much stronger than the other peaks. This indicates that the selenium nanowires grow preferentially along the [001] direction, the *c*-axis. This is also confirmed by HRTEM result.

Figure 3 shows the TEM results of as-prepared selenium nanowires. Fig. 3 (A) is a TEM image of representative selenium nanowires (diameter ~200 nm). The inset shows a selected area electron diffraction (SAED) pattern. The SAED pattern indicates that the selenium nanowires are single crystals. The single crystal morphology of the nanowires is corroborated by a high-resolution TEM image, Fig. 3 (B). The HRTEM image shows a fringe spacing (~0.5 nm) that agrees well with the spacing of the (001) lattice planes.

In order to understand the mechanism of the transformation of selenium from polycrystalline powder to single crystal nanowires, it is necessary to consider the factors influencing single crystal growth and the structure of the trigonal form of selenium. It is well known that the most important factor affecting single crystal growth in a solution is the solubility of the solute. In our experiment, selenium powder can be dissolved in NaOH solution to give a metastable, supersaturated solution by controlling the concentration of selenium. The growth of single-crystal selenium presumably takes place in the metastable, supersaturated solution²¹ or alternatively the nanowires are formed *via* precipitation on cooling.³ From a structural point of view, selenium consists of a helical chain of atoms with three atoms per turn and corresponding atoms in neighboring chains form a hexagonal network.¹⁸ The bonds between atoms on the same helix are covalent, whereas the “bonds” between chains are comprised of van der Waal’s type.²² From a thermodynamic perspective, the activation energy for *c*-axis direction of growth of trigonal selenium is lower than that of growth perpendicular

to the *c*-axis.²³ This means a higher growth rate along the *c*-axis and a lower one perpendicular to the *c*-axis to give selenium nanowires that grow preferentially along the [001] direction. This is in very good agreement with the abnormally strong intensity of (100) peak in XRD pattern (Fig. 2, pattern B) and HRTEM result (Fig. 3, B).

In summary, large-scale synthesis of single-crystal selenium nanowires has been successfully realized for the first time by a simple solution-mediated treatment of polycrystalline selenium powder. The mechanism of this transformation follows the dissolution–recrystallization mechanism.²¹ Growth of selenium single crystals along the *c*-axis, that is growth of the (100) face, is classified as the adhesive growth and crystal growth occurring perpendicular to *c*-axis is the layer-by-layer growth (accretion on the (001) face).²⁴ This method opens up a convenient and effective route to selenium single crystal nanowires in high yield.

This work is supported in part by the NASA University Research, Engineering and Technology Institute on Bio Inspired Materials (BIMat) under award No. NCC-1-02037. The authors would like to thank Dr Peter S. White for his help in XRD measurement, and Dr Wallace W. Ambrose for his assistance in EM measurements.

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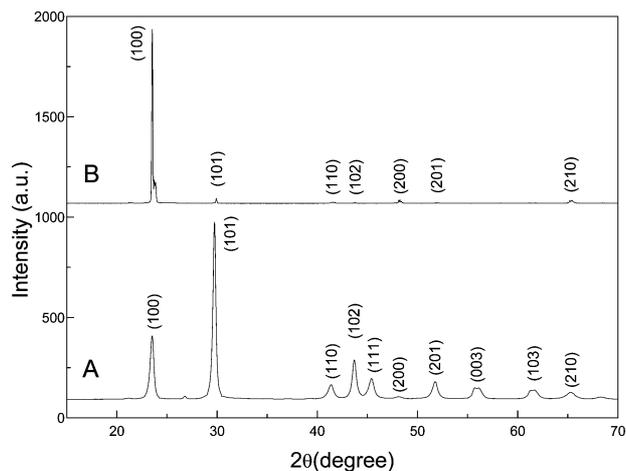


Fig. 2 XRD patterns of commercial selenium powder (A) and as-prepared selenium single-crystal nanowires (B).

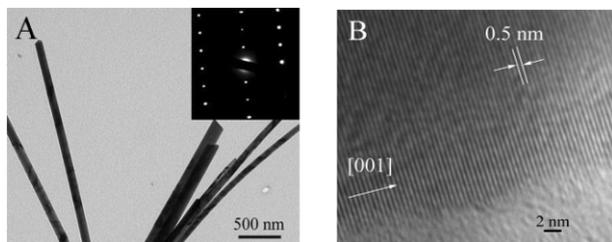


Fig. 3 (A) TEM image of as-prepared Se nanowires, the inset shows the SAED pattern of a single nanowire; (B) representative HRTEM image of as-prepared Se nanowires; the [001] direction is coincident with the nanowire axis.