

# High-yield synthesis of selenium nanowires in water at room temperature†

Qing Li and Vivian Wing-Wah Yam\*

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High-quality t-Se nanowires were obtained in high yield via a facile and environmentally benign route in water at room temperature by using ascorbic acid as the reducing agent under the assistance of  $\beta$ -cyclodextrin.

One-dimensional (1D) nanostructures (e.g. wires, rods, ribbons and tubes) have received considerable attention owing to their distinct physical and chemical properties and potential applications in nanodevices.<sup>1</sup> Selenium, as an important elemental semiconductor, exhibits unique photoelectric and other promising properties, such as high photoconductivity ( $\sim 8 \times 10^4 \text{ S cm}^{-1}$ ), relatively low melting point ( $\sim 490 \text{ K}$ ), and it can be practically applied to solar cells, rectifiers, sensors, photographic exposure meters, xerography, and serves as an ideal candidate for generating other functional materials, such as ZnSe and CdSe.<sup>2</sup>

A number of methods have recently been demonstrated for making Se as 1D nanostructures. For example, Rao and co-workers synthesized trigonal Se (t-Se) nanorods and wires through a reaction of selenium powder with  $\text{NaBH}_4$  and the decomposition of  $[(\text{CH}_3\text{N})_4\text{Ge}_4\text{Se}_{10}]$ .<sup>3</sup> Abdelouas *et al.* employed protein cytochrome  $\text{C}_3$  to make selenium nanowires, accompanied by the formation of amorphous Se (a-Se).<sup>4</sup> Qi and co-workers generated 1D nanostructures of t-Se in micellar solutions of nonionic surfactants.<sup>5</sup> Xie and co-workers produced Se nanoribbons by a direct vapor deposition process.<sup>6</sup> Ren *et al.* synthesized Se nanowires through a physical transportation method by using Si as co-source material.<sup>7</sup> Particularly, Xia and co-workers did a series of elegant studies on the generation of 1D Se nanostructures with the use of hydrazine monohydrate as the reducing agent.<sup>8</sup> However, the search for simple, fast, low processing temperature, high-yield and environmentally benign methods to synthesize 1D nanostructures is still an on-going process and represents a major challenge.

In this communication, we demonstrate that the synthesis of Se nanowires can be realized in aqueous solution at room temperature by using ascorbic acid (vitamin C) as the reducing agent under the assistance of  $\beta$ -cyclodextrin. In this convenient approach, high-quality Se nanowires were obtained in high yield with neither exotic seed and toxic reagents nor complex equipment.

The chemical reaction involved in our method is as follows:



Center for Carbon-Rich Molecular and Nano-Scale Metal-Based Materials Research and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P.R. China.

E-mail: wwyam@hku.hk; Fax: (852) 2857 1586; Tel: (852) 2859 2153  
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The mixture changed rapidly from colorless to yellow, followed by an immediate formation of a brick-red suspension, indicating the formation of a-Se. The product was then re-dispersed in ethanol and aged for 2 hours before characterization.‡

X-Ray diffraction (XRD) was used to characterize the composition and structure of the product. All the reflections in the XRD pattern in Fig. 1A could well be assigned to a pure hexagonal phase of Se with lattice parameters  $a = 4.36 \text{ \AA}$  and  $c = 4.97 \text{ \AA}$  (JCPDS 06-0362). The (100) peak is more intense due to orientation effects. No XRD peaks arising from impurities could be detected, indicating that only elemental selenium grains with high crystallinity and purity were obtained.

The Raman spectrum gives further evidence confirming the trigonal phase. Fig. 1B shows a typical Raman spectrum of the as-prepared Se nanowires. Only one resonance peak at around  $238 \text{ cm}^{-1}$  was observed (no signals of the  $256 \text{ cm}^{-1}$  peak for monoclinic Se and the  $264 \text{ cm}^{-1}$  peak for a-Se), which is attributed to the vibration of helical selenium that only exists in the trigonal phase.<sup>8a,9,10</sup> This indicated that the as-prepared Se has a high quality crystallinity.

The chemical composition of the product was further checked with EDX. The spectrum (see ESI†) indicated that the products

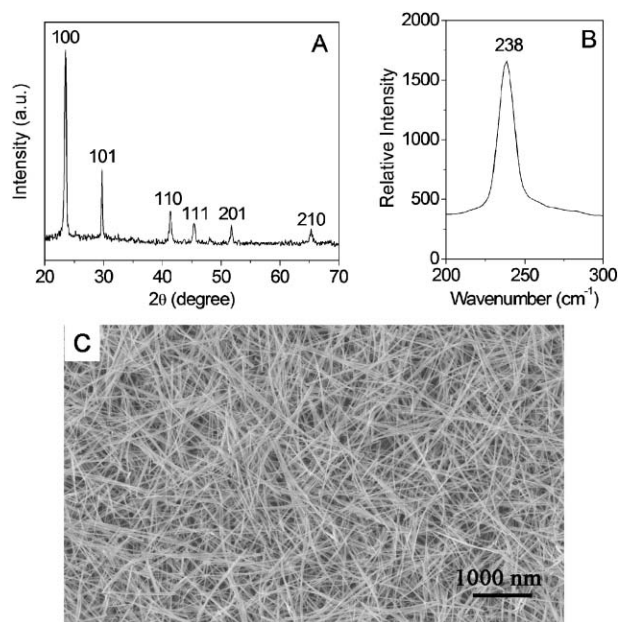


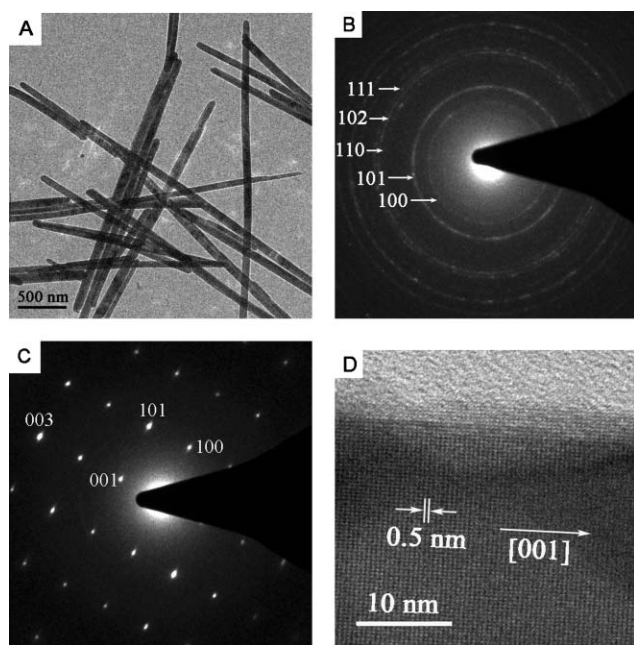
Fig. 1 (A) A typical XRD pattern of the obtained selenium nanowires. (B) Raman scattering spectrum of the Se nanowires. (C) FESEM image of the t-Se nanowires prepared in water at room temperature.

were pure selenium. The detected copper and carbon came from the carbon-coated copper grid upon which the products were deposited.

The morphologies and structures of the as-prepared Se nanowires were examined by scanning electron microscopy (SEM) techniques. Fig. 1C shows a representative low magnification SEM image of the collected product. It revealed the general morphology of the Se nanowires. Fig. 2A shows the typical TEM image of the as-prepared nanowires. It was found that an over 99% proportion of the sample dispersed on the copper grids showed nanowire structure with a mean diameter of  $65 \pm 15$  nm and lengths of over several micrometers, consistent with the SEM results.

The diffraction rings in the selected area electron diffraction (SAED) pattern (Fig. 2B) could be indexed as (100), (101), (110), (102) and (111) reflections, indicating the formation of hexagonal selenium, in agreement with the XRD result. The electron diffraction pattern taken on an individual Se nanowire is shown in Fig. 2C. The spots are slightly elongated as a result of the locally orientation-ordered structure, and the elongated direction was perpendicular to the long axis of the nanowires, suggesting that crystal orientation was along the [001] direction. The two-fold rotational symmetry in this diffraction pattern also confirms the assignment. The appearance of the (001) diffraction may be attributed to the double diffraction of the incident electron in the crystal.<sup>11</sup>

The preferred growth direction and the nature of the single crystallinity of the Se nanowire could be verified by the HRTEM image (Fig. 2D). The observed fringe spacing (0.5 nm) in this image agreed well with the separation for the (001) planes of t-Se, confirming that the as-prepared nanowires were structurally uniform single crystals with a growth direction of [001] (c-axis).



**Fig. 2** (A) Typical TEM image of the sample. (B) The corresponding electron diffraction pattern. (C) SAED pattern obtained from an individual wire. (D) HRTEM image obtained from the edge of an individual Se nanowire.

The continuous fringes demonstrate that the Se nanowires have a low defect density, indicating the high quality of the wires. The nanowires turned out to be very sensitive to longer time electron beam irradiation, in particular at high magnification. This was expected due to their relatively low melting point ( $\sim 490$  K).<sup>12</sup>

To investigate the growth process of these nanowires, the samples taken at various stages of the reaction were checked with FESEM (see ESI†). From these observations, the growth of Se nanowires in this approach appeared to go through a solid–solution–solid transformation mechanism.<sup>8a</sup> That is, the nascent a-Se gradually dissolved in ethanol solution to give a metastable solution, then from it the formation of t-Se crystallites took place. It has been reported that through different experimental parameters, the growth of nano/micro-structures with different morphologies, sizes, compositions, and microstructures could be controlled.<sup>13,14</sup> In this work, if water was used instead of ethanol for aging the a-Se, no nanowires of t-Se were formed. Thus ethanol appeared to serve as an important medium for the conversion and self-assembly of the initial a-Se to the t-Se nanowires. In addition, it has been found that the pH of the initial mixture of the solution influenced the final products significantly. When 1 M HCl or 1 M NaOH was used to adjust the pH of the solution mixture containing SeO<sub>2</sub> and  $\beta$ -CD, Se nanowires could be obtained in a broad range of pH ( $\text{pH} \leq 7$ ). When the pH exceeded 8, no precipitate emerged. In addition, an increase in the SeO<sub>2</sub> content would cause a decrease in the uniformity of the Se nanowires, whereas a higher ascorbic acid content would favour the formation of uniform wires. A shorter reaction time would also cause less uniform products. However, there appeared to be little influence on the uniformity of the nanowires when the reaction time exceeded 4 hours. With an elongation of aging time, the crystallinity of the product was found to increase and the wires would grow longer. However, when the transformation from a-Se to t-Se was completed, further extension of the aging time did not remarkably increase the size of the nanowires. In order to have a clear understanding of the shape and size control of 1D t-Se nanostructures, more in-depth studies are in progress.

In our experiment, when no  $\beta$ -CD was added, there was no Se nanowires precipitated from the solution. Instead, the product was isolated as irregular short Se rods. Though t-Se has a tendency to grow along the c-axis due to its inherent anisotropic structure<sup>15</sup> as well as from a thermodynamic perspective,<sup>12</sup> it is obvious that  $\beta$ -CD plays a key role in the process of nanowire formation. It is known that  $\beta$ -cyclodextrin ( $\beta$ -CD) is a torus-like macro-ring consisting of seven glucopyranose units. It is hydrophilic outside, but hydrophobic inside, rendering it water-soluble, and easy to form inclusion complexes with guest molecules.<sup>16,17</sup> In our system, the dimensions of the as-prepared Se nanowires were much larger than those of the  $\beta$ -CD cavity (0.78 nm),<sup>16</sup> indicating that the products were by no means included in the  $\beta$ -CD cavity. Herein, considering the rigidity and the –OH groups on the top and the bottom of  $\beta$ -CD, and the possible interaction of  $\beta$ -CDs with each other through hydrogen bonding to form a linear chain,<sup>15</sup> we speculate that selenium could be nucleated in such a restricted space provided by  $\beta$ -CD and finally assembled into wires. The exact mechanism for the formation of the Se nanowires in this system warrants further investigation.

In summary, we have developed a facile and environmentally benign route to the high-yield synthesis of t-Se nanowires.

$\beta$ -Cyclodextrin was found to play a key role in the process of crystal growth. We believe that this route is universal and can be potentially extended to the preparation of other 1D nanoscale inorganic materials. The Se nanowires prepared using this method may find potential use in the fabrication of electronic/optical nanodevices and as the templates to generate other one-dimensional functional nanomaterials.

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## Notes and references

‡ Typically, analytically pure  $\text{SeO}_2$  (0.05 g) and  $\beta$ -cyclodextrin (0.05 g) were added into a glass beaker containing distilled water (10 ml). The mixture was stirred for about 10 min to give a clear solution, which was promptly poured into another glass beaker containing ascorbic acid solution (10 ml, 0.028 M) under continuous stirring. The mixture changed rapidly from colorless to yellow, followed by an immediate formation of a brick-red suspension, indicating the formation of amorphous Se (a-Se). After reacting for 4 h, the product was collected by centrifugation and washed with distilled water and ethanol several times. Then it was re-dispersed in ethanol and allowed to age for 2 h without stirring. A color change from brick-red to metallic-gray was observed during this process. The final products (over 99% yield, according to the amount of  $\text{SeO}_2$  input) were collected for identification and characterization.

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