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Single-Crystalline Nanowires of Ag_2Se Can Be Synthesized by Templating against Nanowires of Trigonal Se

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Template-directed synthesis represents a straightforward approach to generating one-dimensional (1D) nanostructures. In this approach, the template serves as a scaffold against which other materials are assembled with a morphology similar (or complementary) to that of the template. A variety of 1D templates have been successfully demonstrated for use with this process, and examples include channels in porous materials,[1] hexagonal assemblies of surfactants or block copolymers,[2] and 1D nanostructures synthesized using other chemical methods.[3,4] These templating processes, although very versatile, often led to the formation of polycrystalline 1D nanostructures that are limited in use for device fabrication or property measurements. Highly crystalline nanowires were only produced at temperatures around 800−1200 °C when carbon nanotubes were allowed to react with proper chemicals under carefully controlled conditions.[3] A template-directed process that could generate single-crystalline nanowires in the solution phase and at room temperature is yet to be demonstrated. Here we describe a template-directed reaction, in which single-crystalline nanowires of trigonal Se (*t*-Se) were quantitatively converted into single-crystalline nanowires of Ag_2Se by reacting with aqueous $AgNO_3$ solutions at room temperature. The single-crystalline 1D morphology of the wire-like templates was retained in the final products with high fidelity.

Silver selenide exhibits many interesting and useful properties.[5] Its high-temperature phase (β-Ag_2Se, >133 °C) is a superionic conductor that is useful as the solid electrolyte in photochargable secondary batteries. The low-temperature phase (α-Ag_2Se) is a narrow band gap semiconductor, and has been widely used as a photosensitizer in photographic films or thermochromic materials. α-Ag_2Se is also a promising candidate for thermoelectric applications because of its relatively high Seebeck coefficient (-150 μV/K at 300 K), low lattice thermal conductivity, and high electrical conductivity.[6] Large magnetoresistance has also been reported for a nonstoichiometric derivative of this solid.[7] It is reasonable to expect that the availability of Ag_2Se in the form of well-controlled nanowires could bring in new applications, and greatly enhance the performance of many currently existing devices as a result of their one-dimensionality.[8]

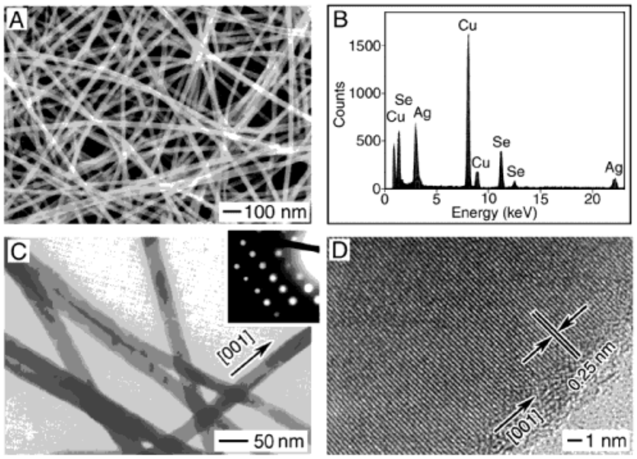

Figure 1. SEM (A) and TEM (C) images of uniform nanowires of Ag_2Se that were synthesized through a reaction between the 32-nm nanowires of *t*-Se and an aqueous solution of $AgNO_3$ at room temperature. The EDX spectrum obtained from these nanowires is given in (B). The strong signals for Cu came from the copper grid on which these Ag_2Se nanowires were supported. The inset gives a typical microdiffraction pattern that was obtained by focusing the electron beam on an individual wire. This low-temperature Ag_2Se has a tetragonal structure, and the longitudinal axis of each wire is along the ⟨001⟩ direction. The single-crystallinity of these wires was further confirmed by the high-resolution TEM image in (D).

Uniform nanowires of trigonal Se were synthesized using a previously reported procedure.[9] We could control the diameters of these nanowires from ~10 to 100 nm by varying the reaction conditions. During the templating process, the *t*-Se nanowires (as suspensions in water or supported on TEM grids) were allowed to react with an aqueous $AgNO_3$ solution at room temperature. The products were then examined by electron microscopy and X-ray diffraction (XRD). Figure 1 shows the SEM, TEM, and HRTEM images of Ag_2Se nanowires that were generated by templating against 32-nm nanowires of *t*-Se. The SEM and TEM measurements indicate that the wire-like morphology of the templates was retained with high fidelity during this solid−solution reaction. The phase and composition of the as-synthesized nanowires of Ag_2Se were analyzed using several other techniques. The XRD pattern indicates that these nanowires were crystallized in the tetragonal structure with lattice constants $a = b = 0.698$ nm, and $c = 0.496$ nm. The energy-dispersive X-ray (EDX) spectrum shown in Figure 1B also confirms the right stoichiometry for these Ag_2Se nanowires. The smooth surfaces and the uniform contrast observed along individual wires under TEM (Figure 1C) suggest that these as-synthesized nanowires of Ag_2Se were single-crystalline. The electron microdiffraction pattern (the inset of Figure 1C) obtained from the individual nanowires confirmed this hypothesis. The diffraction spots could be indexed as the tetragonal, low-temperature phase of Ag_2Se, with the longitudinal axis of each wire along the ⟨001⟩ direction. The HRTEM image shown in Figure 1D further supports our claim on the single-crystallinity of these Ag_2Se nanowires. The fringe spacing (~0.25 nm) observed in this image agrees well with the separation between the (002) lattice planes.

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(1) (a) Martin, C. R. *Science* **1994**, *266*, 1961. (b) Martin, B. R.; Dermody, D. J.; Reiss, B. D.; Fang, M. M.; Lyon, L. A.; Natan, M. J.; Mallouk, T. E. *Adv. Mater.* **1999**, *11*, 1021. (c) Zhang, Z.; Gekhtman, D.; Dresselhaus, M. S.; Ying, J. Y. *Chem. Mater.* **1999**, *11*, 1659.

(2) (a) Han, Y. J.; Kim, J.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 2068. (b) Mehnert, C. P.; Weaver, D. W.; Yin, J. Y. *J. Am. Chem. Soc.* **1998**, *120*, 12289. (c) Moller, K.; Bein, T. *Chem. Mater.* **1998**, *10*, 2950.

(3) (a) Dai, H.; Wong, E. W.; Lu, Y. Z.; Fan, S.; Lieber, C. M. *Nature* **1995**, *375*, 769. (b) Han, W.; Fan, S.; Li, Q.; Hu, Y. *Science* **1997**, *277*, 1287.

(4) Song, J. H.; Wu., Y.; Messer, B.; Kind, H.; Yang, P. *J. Am. Chem. Soc.* **2001**, 123, 10397−10398.

(5) Kobayashi, M. *Solid State Ionics* **1990**, *39*, 121.

(6) Ferhat, M.; Nagao, J. *J. Appl. Phys.* **2000**, *88*, 813.

(7) Xu, R.; Husmann, A.; Rosenbaum, T. F.; Saboungi, M. L.; Enderby, J. E.; Littlewood, P. B. *Nature* **1997**, *390*, 57.

(8) See, for example, (a) Hu, J.; Odom, T. W.; Lieber, C. *Acc. Chem. Res.* **1999**, *32*, 435. (b) Prokes, S. M.; Wang, K. L. Special issue in *MRS Bull.* **1999**, *24*, 13−19. (c) Dekker: C. *Phys. Today* **1999**, *May*, 22. (d) Frank, S.; Poncharal, P.; Wang, Z. L.; De Heer, W. A. *Science* **1998**, *280*, 1744.

(9) Gates, B.; Yin, Y.; Xia, Y. *J. Am. Chem. Soc.* **2000**, *122*, 12582.

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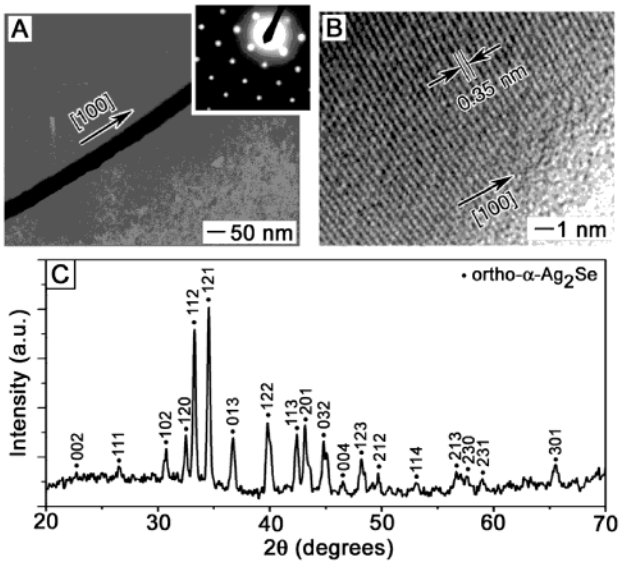

Figure 2. (A) The TEM image and microdiffraction pattern (inset) of a Ag_2Se nanowire whose diameter was ∼50 nm. The diffraction spots could be indexed as the orthorhombic structure; this assignment is further supported by the high-resolution TEM image shown in (B). (C) The XRD pattern of α-Ag_2Se nanowires that were synthesized by reacting 80-nm nanowires of *t*-Se with an aqueous $AgNO_3$ solution. The Ag_2SeO_3 phase had been removed by rinsing with hot water (∼90 °C).

Interestingly, we also found that the crystal structure of these single-crystalline nanowires of Ag_2Se strongly depended on their lateral dimensions: For wires with diameters $>\sim 40$ nm, an orthorhombic structure (with $a = 0.705$ nm, $b = 0.782$ nm, and $c = 0.434$ nm) was found to be more favorable. Figure 2A shows the TEM image of a Ag_2Se nanowire whose diameter was ∼50 nm. The inset shows a microdiffraction pattern observed for this nanowire, which could be readily indexed according to the orthorhombic crystal structure. This lattice structure was also in agreement with the HRTEM image shown in Figure 2B; and the fringe spacing observed in this image matched well with the separation between the (200) planes. Figure 2C shows the XRD pattern obtained from a sample that was synthesized by reacting 80-nm nanowires of *t*-Se with an aqueous $AgNO_3$ solution. In this case, the major products were orthorhombic, low-temperature phase Ag_2Se and monoclinic Ag_2SeO_3; and the Ag_2SeO_3 impurity had been selectively removed by rinsing with hot water. Both tetragonal and orthorhombic structures have been previously reported for low-temperature phase Ag_2Se, but the origin of these two different polymorphic forms was not clear.[10] The present observation suggested that the crystal structure was mainly determined by the lateral dimension of the nanowires (or the domain size of a polycrystalline thin film commonly involved in previous studies).

Although the exact transformation mechanism from *t*-Se to single-crystalline Ag_2Se is still not completely understood at this point, a plausible one is described below. As confirmed by the XRD studies (see the Supporting Information), the net reaction involved in this templating process can be presented as the following:

$$3\mathrm{Se}(s) + 6\mathrm{Ag}^{+}(aq) + 3\mathrm{H_2O} \rightarrow 2\mathrm{Ag_2Se}(s) + \mathrm{Ag_2SeO_3}(aq) + 6\mathrm{H}^{+}(aq)$$

We believe a minimal reorganization of the parent solid structure (topotactic characteristics) is the key to the formation of single-crystalline products from single-crystalline templates. When silver cations diffused into single-crystalline nanowires of *t*-Se,[11] the silver ions might catalyze a disproportional process of Se^0 into Se^{2-} and Se^{4+}. The Se^{4+} species then diffused out of the solid matrix and reacted with Ag^+ and H_2O to generate Ag_2SeO_3 in the aqueous medium around the templates. The Se^{2-} species combined with trapped Ag^+ to generate single-crystalline nanowires of Ag_2Se. Note that the lattice constant in the *c*- or *a*-axis was essentially unchanged during the formation of tetragonal or orthorhombic Ag_2Se, respectively. In particular, a change in the fringe spacing from 0.16 to 0.25 nm (as shown by the HRTEM images) indicates that only one layer of Se atoms (perpendicular to the *c*-axis) needs to be removed from each primitive lattice when the tetragonal Ag_2Se is formed. As a result, the atomic arrangement in the template might be largely unaffected during the course of this reaction, and one could obtain single-crystalline products by templating against single-crystalline nanowires. The topotactic characteristics of this process resembles many intercalation reactions that are well-documented for their minimal structural reorganization[12] but differs in that an additional product (in this case, Ag_2SeO_3) was also involved in this templating process.

In summary, we have described a template-directed reaction through which the morphology and single crystallinity of the template were both retained with high fidelity. This synthetic strategy might be extendible to other systems. *The only requirement seems to be that the reconstruction of the parent crystal lattice is kept minimal*. Since anions generally occupy most of the spaces of an inorganic solid, this requirement could be readily met by designing a system where the anions of the product will come directly from the template, rather than the gaseous or liquid reagents.

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Supporting Information Available: One figure showing the SEM, TEM, and HRTEM images of the starting nanowires of *t*-Se, a schematic illustration of the plausible mechanism, a XRD pattern of the as-synthesized products, and a description of the experimental procedure are also described (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Saito, Y.; Sato, M.; Shiojiri, M. *Thin Solid Films* **1981**, *79*, 257.

(11) Silver atoms were highly mobile at room temperature as suggested by an in situ TEM study: Giersig, M.; Ung, T.; Liz-Marzan, L. M.; Mulvaney, P. *Adv. Mater.* **1997**, *9*, 570.

(12) Rao, C. N. R.; Gopalakrishnan, J. *New Directions in Solid State Chemistry*; Cambridge University Press: Cambridge, 1997; p 482.