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Communications to the Editor

A Solution-Phase Approach to the Synthesis of Uniform Nanowires of Crystalline Selenium with Lateral Dimensions in the Range of 10−30 nm

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This paper describes a solution-phase route to uniform nanowires of selenium, in which colloidal particles of amorphous (*a*-) Se were converted into wires of trigonal (*t*-) Se, with diameters in the range of 10−30 nm and lengths up to hundreds of micrometers. We selected solid selenium as the focus of this effort because this material exhibits a unique combination of many interesting and useful properties:[1] for example, a relatively low melting point (~217 °C), a high photoconductivity (~8×10^4 S/cm), and a high reactivity toward a wealth of chemicals that can be exploited to convert selenium into other functional materials such as ZnSe and CdSe.[2] Selenium has also been of tremendous importance in a wide variety of commercial applications that range from Xerox machines to rectifiers.[1] As one has experienced with other indirect gap semiconductors such as silicon, the availability of selenium nanostructures with low dimensionalities should be able to bring in new types of applications or to enhance the performance of the currently existing devices as a result of quantum-sized effects.[3]

Chemical approaches may provide a more promising approach to nanostructures than conventional methods in terms of cost, throughput, and potential for large-scale production.[4] Unfortunately, the capability and feasibility of most chemical methods are limited by their tendencies to form zero-dimensional (0D) structures such as colloidal particles and nanocrystallites.[5] Physical templates (e.g., channels in porous materials or scaffolds self-assembled from surfactants or block-copolymers) are often required in order to generate 1D nanostructures such as tubules, wires, or rods.[6] Nevertheless, a number of chemical approaches have been demonstrated for producing 1D nanostructures without the use of any physical template. Most of these methods were based on vapor−solid (VS) and vapor−liquid−solid (VLS) reactions, and nanostructures that have been successfully generated using these methods include carbon nanotubes and their derivatives,[7] nanowires of metals and semiconductors,[8] and nanowhiskers of a variety of inorganic substances.[9] Solution-based procedures were also demonstrated for producing nanowires of Si and III−V semiconductors, albeit their mechanisms were similar to that of the VLS method.[10] All of these chemical methods have one thing in common: the use of exotic, dual-functional nanocrystallites of metals that served as catalysts and seeds for the growth of nanostructures with 1D morphologies. The approach we described herein also involved the growth of 1D nanostructures on nanocrystallites, but the seeds were generated in situ in the solution through a solution−solid-phase transition.

The first step of our approach involved the formation of selenium in an aqueous solution through the reduction of selenious acid (H_2SeO_3, Aldrich, 99.999%) with excess hydrazine (N_2H_4, Aldrich, 98%) by refluxing this reaction mixture at 100 °C:[11]

$$H_2SeO_3 + N_2H_4 \rightarrow Se\,(\downarrow) + N_2\,(\uparrow) + 3H_2O$$

A brick-red color immediately appeared in the solution, indicating the formation of *a*-Se that existed in the form of spherical colloids with sizes around 300 nm.[11a] When this solution was cooled to room temperature, the small amount of selenium dissolved in the solution precipitated out as nanocrystallites of *t*-Se.[12] Our TEM studies suggested that it was these nanocrystallites of *t*-Se that served as the seeds for the growth of nanowires in the next step. Due to the absence of stabilizing agent, the spherical colloids underwent aggregation and rupturing (as a result of Rayleigh instability[13]), and finally became irregular colloids with a broad distribution in size that ranged from ~100 nm to ~1 μm.[14] When this dispersion that contained a mixture of colloids of *a*-Se and nanocrystallites of *t*-Se was aged in darkness at room temperature, the colloids of *a*-Se would slowly dissolve into the solution due to their higher free energies as compared to the seeds of *t*-Se. This dissolved selenium subsequently grew as crystalline nanowires on the seeds. In this solid−solution−solid transformation, the morphology of the final products was determined by the anisotropic nature of the building blocks—that is, the 1D characteristics of the infinite, helical chains of selenium in the trigonal phase. The diameters of the nanowires were largely defined by the lateral dimensions (i.e., perpendicular to the *c*-axis) of the seeds, and an increase in the aging time only led to the formation of more nanowires and wires with longer lengths.

We have characterized the selenium nanowires using a number of techniques. Our EDS measurements indicate that these nanowires were made purely of selenium.[14] The XRD and Raman scattering spectra obtained from these nanowires suggest that the selenium existed in the trigonal phase.[14] We have further examined

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(12) Since selenium is always labeled as insoluble in the handbooks and texts, we are unable to calculate the amount of selenium that will be precipitated out from the solution when its temperature is reduced from ~100 to ~20 °C.

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(14) See the Supporting Information for details.

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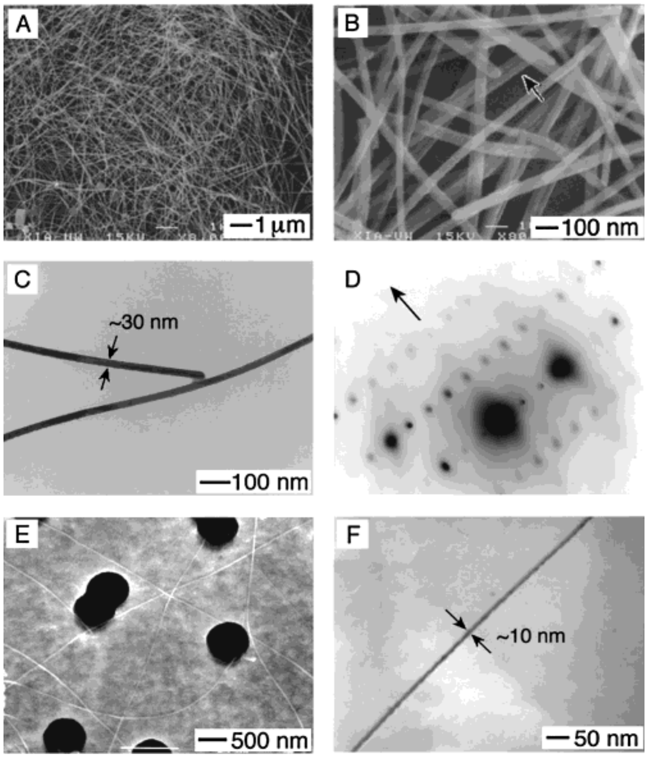

Figure 1. (A, B) SEM images of Se nanowires that had a mean diameter of 32 nm and a standard deviation of 5 nm. The solid selenium was formed in situ as spherical colloids by refluxing selenious acid (0.04 M) with an excess amount of hydrazine (0.75 M) at 100 °C for ∼10 min, followed by quenching with twice the amount of water. The solution cooled to room temperature in ∼20 min. This colloidal dispersion was then aged in the dark at room temperature for 10 days. As indicated by an arrow in (B), some of the nanowires aggregated into bundles in the solution or during the preparation of SEM sample. This may explain why some of the nanowires look wider than the others. (C) The TEM image of two nanowires that had diameters of ∼30 nm. These wires were taken from the same sample as in (A), but diluted by 20 times. (D) The electron diffraction pattern obtained by focusing the e-beam on the middle portion of an individual Se nanowire. This diffraction pattern indicates that the Se nanowires were crystallized in the trigonal phase, with their helical chains of Se atoms packed parallel to each other along the longitudinal axis of each wire. (E, F) The SEM (E) and TEM (F) images of selenium nanowires that were prepared using a procedure similar to that in (A), except that the refluxing temperature was 90 °C. The solution was diluted by 20× with water and filtered through a gold-coated polymeric membrane (Nucleopore, Corning). These nanowires had a mean diameter around 10 nm. The black circles in (E) are holes in the gold-coated membrane.

the morphologies and structures of these Se nanowires using SEM and TEM.[14] In Figure 1A and B show the SEM images of a typical, as-synthesized sample of selenium nanowires. These SEM images indicate the uniformity in lateral dimensions, the straightness along the longitudinal axises, the level of perfection, and the copiousness in quantity that we could routinely achieve for this synthetic system. Figure 1C gives a blow-up TEM image, which also shows the faced end of one selenium nanowire. Figure 1D shows a typical electron diffraction pattern of the nanowires that was obtained by focusing the beam on an individual nanowire. The 2-fold, rotational symmetry associated with this pattern indicates that these Se nanowires had predominantly grown along the [001] direction.[15] Lattice constants calculated from this diffraction pattern also match those of the trigonal phase, with the helical chains of Se atoms parallel to the *c*-axis. Because the diffraction patterns taken from various regions of an individual nanowire were essentially the same, it could be concluded that the Se nanowires synthesized using the present procedure were single-crystalline in structure.

The lateral dimensions of these selenium nanowires were found to strongly depend on the temperature at which the solution had been refluxed. Figure 1 E and F show the SEM and TEM images of selenium nanowires that were obtained from a solution refluxed at ∼90 °C. These nanowires had a uniform, cross-sectional diameter of ∼10 nm. We believe that a variation in the refluxing temperature had changed the amount of selenium dissolved in the solution and thus the sizes of nanocrystallites that subsequently served as seeds for the wire growth.

In summary, we have demonstrated a practical approach to the large-scale synthesis of nanowires of crystalline selenium that had uniform lateral dimensions in the range of 10−30 nm. The chemical reaction we used here is not new and has been previously studied by a number of groups for producing spherical colloids of *a*-Se.[11] Abdelouas et al. have recently tried to use a similar reaction to synthesize Se nanowires, but their products were chainlike aggregates of nanoparticles of monoclinic Se, rather than single-crystalline wires of trigonal Se as we have obtained here.[16] Since no exotic seeds (e.g., metal colloids) were used in our process, the two ends of each nanowire were free of any particulate material.[17] The absence of kinks or other related defects on our *t*-Se nanowires should make these 1D nanostructures particularly useful in fabricating electronic, optical, or electromechanical nanodevices.[18] In addition, the Se nanowires synthesized using this method can also be potentially converted into 1D nanostructures of other functional materials (e.g., CdSe and ZnSe) by reacting with appropriate elements or compounds.[2]

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Supporting Information Available: Three figures showing spectra (EDS, XRD, and Raman data), a schematic outline for nanowire growth and supporting SEM and TEM images for our proposed mechanism; a detailed procedure for SEM and TEM sample preparation were also described (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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