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Sonochemical Synthesis of Trigonal Selenium Nanowires

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This paper describes a solution-based method for the large-scale synthesis of selenium nanowires. Sonication was used as the driving force for both nucleation and dispersion. The trigonal Se seeds were formed during sonication and grew over the course of hours at the expense of the amorphous Se colloids in a process similar to Ostwald ripening. The resultant nanowires were typically single crystals of trigonal Se whose morphologies could be tuned by adjusting the reaction conditions. A variety of solvents are demonstrated for use with this process. We also demonstrate patterned growth of these nanowires on substrates to form extensive 2D networks and isolated clusters. The morphologies of the products were examined with a combination of microscopic and spectroscopic techniques.

Introduction

Solution-based methods provide an effective route to one-dimensional (1D) nanostructures. A variety of such procedures have been demonstrated to synthesize 1D nanostructures from a diversified range of metals and semiconductors.[1] Among these materials, chalcogens represent a class of interesting solids in which crystal structure provides the major driving force to direct anisotropic growth, i.e., the formation of nanowires. Trigonal Se (*t*-Se) has a remarkable crystal structure, consisting of infinite spiral chains of covalently bound Se atoms.[2] This inherent anisotropy makes Se an ideal candidate for generating 1D nanostructures without the need for templates or surfactants to induce and direct anisotropic growth.

Selenium has many intriguing physical and chemical properties.[3] Most well-known of these properties is perhaps its photoconductivity (0.8×10^4 S/cm), which has been exploited for xerography, rectification, and solid-state light sensing applications. Trigonal Se is intrinsically chiral and is also a well-known piezoelectric material with $d_{11} = 6.5 \times 10^{-11}$ C/N (~30 times larger than that of quartz). In addition, *t*-Se can be readily converted to chalcogenides through template-engaged reactions.[4] The availability of new low-dimensional nanostructures of chalcogens and chalcogenides may bring about new applications, or greatly enhance the performance of currently existing devices based on selenium as a result of quantum confinement.

Syntheses of Se as 1D nanostructures have been reported in the literature. For example, Lickes and co-workers synthesized rod-shaped Se hydrosols through heterogeneous nucleation on silver nuclei.[5] Moura and co-workers demonstrated the use of Cytochrome c_3 as a reducing agent to generate polycrystalline Se nanowires.[6] Loiseau and Pascard have generated nanostructures of Se by filling carbon nanotubes with molten Se.[7] Recently, Gao and co-workers generated 1D nanostructures of monoclinic Se using a solution phase method.[8] Our group has also demonstrated a solid-solution-solid (SSS) route for the generation of *t*-Se nanowires.[9] In this method, *t*-Se seeds were formed in a temperature-induced nucleation event. Nanowires grew over the course of weeks as material was slowly transferred from colloids of amorphous Se (*a*-Se) to the growing surfaces of *t*-Se nanocrystallites through an Ostwald ripening process.

To our knowledge, all of these syntheses of Se 1D nanostructures (including our own) were characterized by one or more of the following: elevated temperatures, long growth times, high pressures, low yields, and the presence of heterogeneous nuclei. This paper focuses on a new SSS route for the large scale synthesis of *t*-Se nanowires that was briefly discussed in a recent communication.[10] In this improved approach, sonication is used as the driving force for the nucleation of *t*-Se nanocrystallites in a procedure that was wholly accomplished *at room temperature, under ambient pressure, and without the use of exotic seeding materials*. Moreover, the synthesis could be carried out in a matter of hours to generate high-quality, single-crystalline

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nanowires of trigonal selenium. In this paper we examine the growth mechanism and the effect of solvents on the morphology of the products using electron microscopy. Another benefit of this sonochemical method is the potential for use in device fabrication. We have demonstrated new techniques for surface-patterning of nanowires using the SSS mechanism. The first step involved the self-assembly of the *a*-Se colloids. These colloids could then be immersed in an appropriate solvent and grown into arrays of discrete islands or fully interconnected two-dimensional (2D) networks.

Experimental Section

Materials. Selenious acid (H_2SeO_3, 99.999%) and hydrazine monohydrate ($N_2H_4{\cdot}H_2O$, 98%) were purchased from Aldrich (Milwaukee, WI). The water used in all syntheses was purified by passing through an 18- MΩ (E-Pure, Dubuque, IA) system. Track-etched membranes made of polycarbonate (Nucleopore, Whatman, Clifton, NJ) were used for filtration.

Synthesis of *a*-Se Colloids. Selenious acid (40 mL, 1 M) was added dropwise to 95 mL of 3 M hydrazine monohydrate in a plastic beaker at 0 °C and under constant magnetic stirring. The formation of colloids visibly progressed as the solution turned from water white, to pink/peach, to brick red. At 20 min, the solution was filtered over a 1-μm track-etched polymer membrane to collect the amorphous colloids. These *a*-Se colloids were rinsed with water (4 × 10 mL) and stored in a desiccator in the dark until they were used for the sonication step.

Formation of *t*-Se Nanowires in Solutions. In a typical procedure, 1−5 mg of *a*-Se colloids was added to a glass or plastic vial containing 1−4 mL of the solvent. The vial was sonicated for 15 to 25 s and then stored in the dark, allowing the nanowires to grow.

Formation of *t*-Se Nanowires on Substrates. In a typical procedure, *a*-Se colloids were sonicated as above and then immediately used for nanowire growth. Two methods were used to pattern the *a*-Se colloids: capillary flow and filling of cavities on the surfaces of solid substrates. For capillary flow, a few drops of the sonicated dispersion were deposited at the openings of 20-μm channels formed between a PDMS stamp and a silicon substrate. After the excess liquid had been dried with a paper towel, the sample was allowed to dry in air. Finally, the PDMS stamp was removed, and the substrate was submersed in ethanol or *n*-propanol in the dark for 12 h.

For filling cavities on the surface of a solid substrate, holes or channels were patterned in a Si or polymer substrate using conventional photolithography or replica molding. A few drops of the sonicated dispersion (or <1 mg of *a*-Se colloids) were placed on the patterned substrate and dried by air-flow. The colloids deposited on the surface were then wiped with a flat strip of PDMS to spread them into the recessed regions and to remove excess material from the raised regions. The substrate was then submersed in ethanol or *n*-propanol in the dark for 12 h.

Instrumentation. Sonication was performed using a Branson 1510 sonicator (Danbury, CT) that operated at 42 kHz, with an output of 0.15 W/cm^2 and a VC 750 Vibra-Cell variable output sonicator (Sonics and Materials, Newton, CT) equipped with an immersion microtip. The TEM images and electron diffraction patterns were taken using a JEOL-1200XII microscope operated at 80 kV. The SEM images were obtained using a Siron XL field-emission microscope (FEI, Hillsboro, OR) operated at 5−20 kV. All UV−visible and near-infrared extinction spectra were collected at room temperature with a Hewlett-Packard 8452A Diode Array UV−Vis spectrophotometer and a quartz cuvette with a path length of 5 mm. The XRD patterns were obtained using a Philips PW1710 diffractometer with Cu Kα radiation.

Results and Discussion

Formation of *t*-Se Nanowires. The fist step of this sonochemical route was the synthesis of *a*-Se colloids through the reduction of selenious acid with hydrazine in water:

$$H_2SeO_3 + H_2N_2H_2 \rightarrow a\text{-Se}\ (\downarrow) + N_2\ (\uparrow) + 3H_2O$$

This synthesis was originally developed by Gutbier and later modified by Kruyt and van Arkel.[11,12] In our previous studies,[9] *t*-Se nanocrystallites were formed when a refluxing aqueous dispersion of *a*-Se colloids was cooled, and nanowire growth occurred over the course of weeks. In the present synthesis we avoided this initial nucleation event by performing the colloidal synthesis at room temperature. For colloids synthesized at elevated temperatures, nucleation was avoided by filtering the *a*-Se colloids while the reaction mixture was still hot. All *a*-Se colloids were captured and dried on track-etched polycarbonate membranes. They were then redispersed in a suitable solvent, whereupon sonication was used to initiate nucleation of *t*-Se nanocrystallites. In the following step, material was transferred from *a*-Se colloids to the more stable *t*-Se seeds in a process similar to Ostwald ripening until all *a*-Se colloids had been consumed (over the course of 5 h).[13] This mechanism resulted in quantitative conversion of *a*-Se colloids into *t*-Se nanowires with narrowly distributed diameters as seen in Figure 1A. This SEM image shows a typical sample of *t*-Se nanowires synthesized in ethanol which exhibited hexagonal cross sections (67 ± 9 nm) and high aspect-ratios (>500:1). The reason this mechanism was so effective in generating uniform nuclei is the intense energy associated with sonication. Acoustic cavitation caused the growth and collapse of tiny bubbles within the liquid phase.[14] The concussive implosions of these bubbles generated transient localized hot spots with incredible temperatures and pressures (in excess of 5000 K and 500 atm). We believed that supersaturation and subsequent nucleation could occur within these localized spots of increased solubility.

In the past, sonication has been used extensively for the generation of zero-dimensional (0D) nanostructures.[15] In comparison, we note that examples of 1D nanostructures formed via sonication are far fewer in number, and the uniformity and monodispersity in size for these 1D structures still need to be improved. For example, Walton et al have synthesized microscale, tree-like crystals of WO_X which could be subsequently broken into nanoneedles through sonication.[16] More recently, Lee et al demonstrated the formation of hydrocarbon nanotubes and nanoscale onions through sonication-

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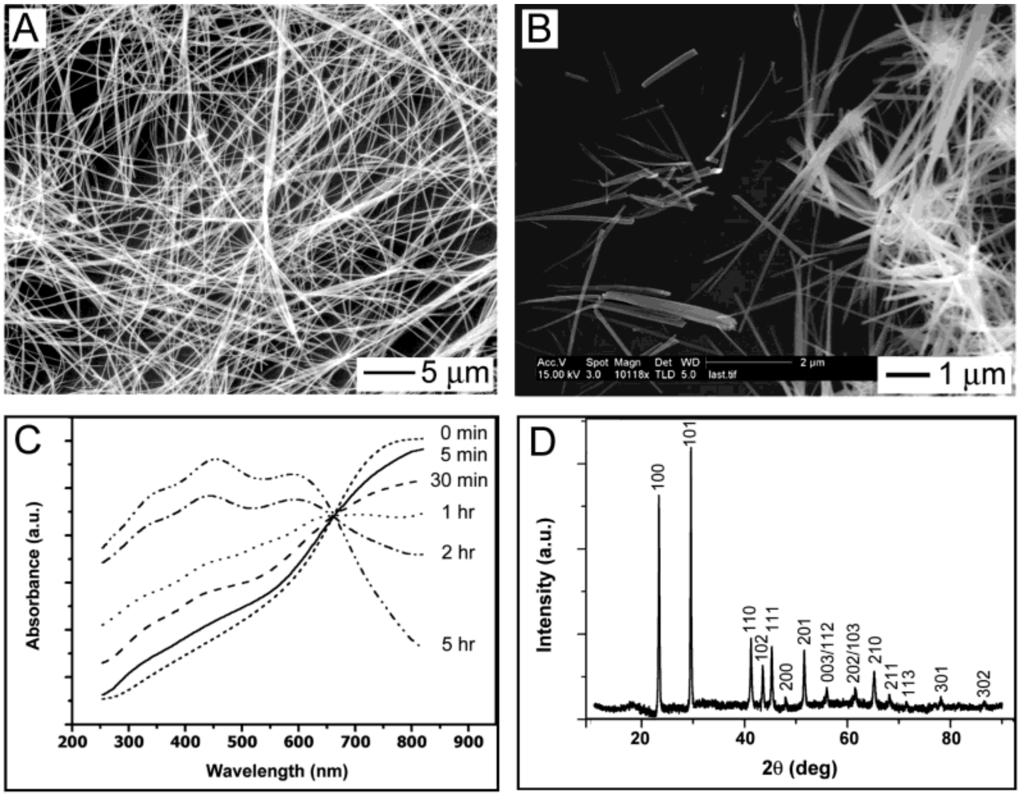

Figure 1. (A) SEM image of typical *t*-Se nanowires synthesized by sonication of *a*-Se in ethanol at room temperature. (B) SEM image of Se nanowires grown from *a*-Se colloids in ethanol without sonication. (C) UV−vis absorption spectra for a typical synthesis in ethanol. Spectra were taken at 0 min, 5 min, 30 min, 1 h, 2 h, and 5 h after sonication. The broad, low-energy peak (>700 nm) at early reaction times was attributable to the polydisperse *a*-Se. Characteristic peaks for *t*-Se appeared at higher energy wavelengths: 590, 452, and 354 nm. The spectra have been adjusted to fit an isobesic point at 650 nm. (D) XRD pattern for *t*-Se nanowires synthesized in ethanol. All peaks can be indexed to trigonal selenium.

induced templating processes.[17] Gedanken and coworkers have also demonstrated the use of sonochemical synthesis in forming needlelike nanostructures.[18] None of these studies were able to generate 1D nanostructures with relatively uniform diameters.

In our reactions, sonication was typically run for 15 to 25 s. Shorter times afforded incomplete dispersal so that aggregates of polydispersed nanowires were formed. It was also found that longer sonication times (>1 min) tended to result in shorter nanowires with irregular diameters. This was most likely due to the formation of a larger number of crystalline seeds, and an increase in solution temperature for the dispersion. It should be noted that sonication was not absolutely necessary for the nucleation of *t*-Se seeds. Figure 1B shows the typical SEM image of a product obtained without sonication. In this experiment, the *a*-Se colloids were simply dispersed in ethanol with vigorous shaking. The solubility and mobility of Se in ethanol was great enough that reorganization of the Se atoms (crystallization) would occur over a period of days. However, the products obtained using this method were polydisperse in both diameter and length. We believe that sonication at the outset of the reaction led to the concerted formation of relatively uniform nuclei. In comparison, shaking seemed to afford incomplete dispersal and piecemeal nucleation.

Sonication power did not have an appreciable effect on the overall size of the nuclei as long as the temperature of the reaction mixture was not significantly changed. For example, solutions were sonicated at low temperatures (0 °C) to increase the energy of the sonically induced implosions,[19] and there was negligible effect on the final diameters of the *t*-Se nanowires. However, at high amplitude settings (or excessively long sonication times), the growth solution began to heat up. If the ambient solution temperature was allowed to increase over 60 °C, the resultant products mainly consisted of aggregated clumps of Se and relatively short nanowires.

Monitoring the Growth of *t*-Se Nanowires. The progress of nanowire growth was conveniently followed using UV−vis spectroscopy (Figure 1C). In this case, the colloidal dispersion (in ethanol) was placed in a quartz cuvette after sonication and the cuvette was gently shaken before each spectrum was taken. The spectra could be qualitatively interpreted to show the transition from *a*-Se colloids to *t*-Se nanowires. Dauchot and Watillon have performed extensive studies on the optical properties of selenium sols.[20] They found that the extinction spectrum of a dispersion of *a*-Se colloids was highly dependent on the size and distribution of the particles. The absorption maximum $\lambda_{\max}$ was red shifted as particle diameter (ϕ) was increased (e.g., when

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Table 1. Comparison of t-Se Grown in Various Solvents

solvent	viscosity (cP)	low energy abs (nm)	high energy abs (nm)	structure	morphology
ether	0.224	650	450	crystalline	nanowires
methanol	0.54	630	450	crystalline	nanowires
ethanol	1.07	600	450	crystalline	nanowires
propanol	1.95	600	450	crystalline	nanowires
butanol	2.54	610	450	crystalline	slightly tapered nanowires
hexanol	4.58	630	*b*	crystalline	slightly tapered nanowires
2-propanol	2.04	645	415	crystaline	tapered nanowires
isobutanol	4.31	640	>415	crystalline	tapered nanowires
2-butanol	3.1	665	>415	crystalline	tapered nanowires
cyclohexanol	57.5	630	404	crystalline	tapered nanowires
ethylene glycol	16.1	(>690)	*b*	mixed amorph/crystalline	tapered nanowires
diethylene glycol	30.2	(>690)	*b*	mixed amorph/crystalline	tapered nanowires
triethylene glycol	50	(>690)	*b*	mixed amorph/crystalline	tapered nanowires
tetraethylene glycol	>60	(>690)	*b*	mixed amorph/crystalline	tapered nanowires
PEO (MW = 150)	>80	(>690)	*b*	crystalline	tapered rods
3-(dimethylamino)-propanol	>10	*a*	*a*	crystalline	non uniform microcrystals
2-methylamino-ethanol	>10	*a*	*a*	crystalline	non uniform microcrystals
18 MOhm water	0.89	(>690)	*b*	amorphous	no reaction
unsubstituted alkanes		(>690)	*b*	amorphous	no reaction
acetone	0.31	*a*	*a*	crystalline	polydisperse rods
chloroform	0.54	*a*	*a*	crystalline	polydisperse rods
aniline	2.03	*a*	*a*	crystalline	tapered rods
acetonitrile	0.37	*a*	*a*	crystalline	tapered rods
ethylenediamine				soluble	

[a] Unable to disperse and attain absorption spectra. [b] No peak observed.

$\phi = 40$ nm, $\lambda_{\max} \approx 290$ nm; when $\phi = 175$ nm, $\lambda_{\max} \approx 570$ nm). In addition, as the standard deviation (σ) of ϕ increased, the intensity decreased accompanied by broadening of the peaks. In our experiments, the spectrum had a maxima at ~775 nm at 1 min after sonication. This position is in agreement with the large particle size, up to 600 nm. The absence of fine structures in the spectra that were observed in studies of more monodisperse colloids is likely due to the large σ for ϕ. We expected that σ was further magnified due to sonication-induced disruption and aggregation of the colloids.

Despite aggregation, the emergence of distinct absorption bands associated with *t*-Se was evident in the early stages of the synthesis. At 5 min, these peaks began to grow in intensity. After 1 h, they were unmistakable. At 5 h, the reaction was complete. Maxima at 590 and 452 nm, and an inflection at 354 nm were evident, consistent with reflectivity measurements on *t*-Se single crystals.[21] It is worth noting that peaks above 530 nm can be solely attributed to interchain interactions perpendicular to the *c*-axis, as confirmed by Bogomolov et al in their studies of isolated polymer chains of Se and Te atoms formed in zeolite pores.[22] We therefore attributed the peak at 590 nm to interchain transitions. In Figure 1C, this peak is somewhat blue-shifted with respect to bulk *t*-Se due to size confinement effects in the plane perpendicular to the longitudinal axis.

The crystalline structures of the as-synthesized nanowires were confirmed by XRD. Figure 1D shows the XRD pattern of nanowires synthesized in ethanol. All the peaks could be indexed to *t*-Se. The crystallinity and purity of composition of these *t*-Se nanowires were further evidenced in electron diffraction and energy dispersion spectroscopy studies. The nanowires also appeared to be indefinitely stable for more than 14 months when stored as suspensions in solution and in the dark.

Influence of Solvent on Nanowire Growth. For the sonochemical synthesis, it was critical to select an appropriate solvent in which *a*-Se was soluble and *t*-Se was insoluble to allow for fast growth of *t*-Se nanowires. Nanowires were found to grow in a variety of solvents when combined with the sonication scheme. Table 1 gives a list of solvents that we have tested, classified by their functionality. Figure 2 shows the SEM images of some of the crystalline products from different solvents.

In general, alcohols gave the best results for nanowire growth—that is, highly anisotropic single crystals with relatively homogeneous diameters. The short chain primary alcohols (ethanol and propanol in particular) yielded long nanowires without taper (Figure 1A). As the length of the hydrophobic end of the alcohol was extended, the quality of the nanowires decreased. Secondary and tertiary alcohols could also be used to convert *a*-Se colloids to *t*-Se nanowires. However, these solvents induced tapered morphologies with triangular cross-sections. Figure 2A shows nanowires that were grown in cyclohexanol. Diols, specifically oligomers of poly(ethylene oxide), were also tested. Because of their high viscosities, these solvents required several weeks to grow nanowires. The products in all cases were mixtures of *a*-Se colloids and *t*-Se nanowires. For ethylene glycol, there was very little conversion of *a*-Se colloids to *t*-Se nanowires (<5% from SEM studies). For oligomers such as diethylene and triethylene glycol, there was 40−80% colloid conversion over the course of 1 week (Figure 2B). Long chain polymers such as 150-mers of poly(ethylene oxide) (PEO) also gave partial conversion from *a*-Se to *t*-Se.

Primary amines tended to form stable complexes with selenium atoms. Ethylenediamime, for example, would completely dissolve *a*-Se when sonicated. Rough, non-

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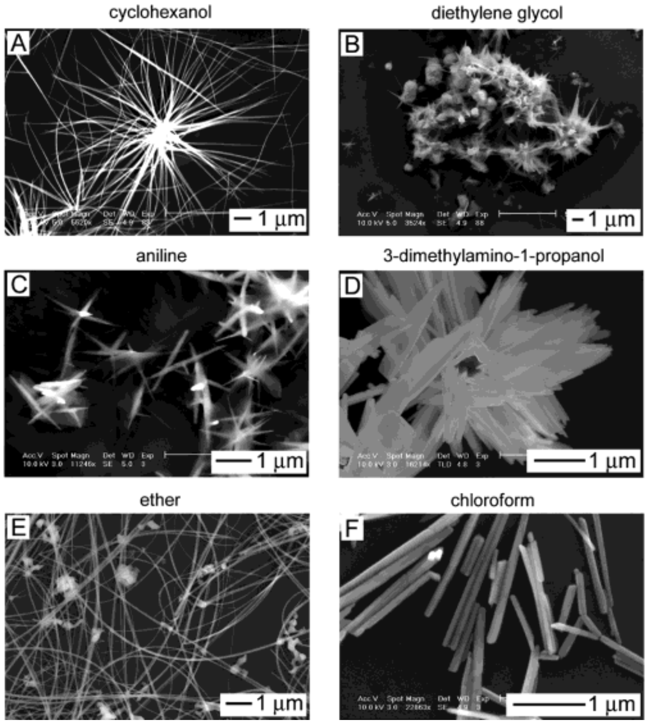

Figure 2. SEM images for typical sonochemical syntheses in a variety of solvents: (A) uniform nanowires from cyclohexanol; (B) partial conversion to tapered nanowires in diethylene glycol; (C) relatively uniform nanorods from aniline; (D) micrometer scale structures from 3-(dimethylamino)-1-propanol; (E) uniform, high aspect-ratio nanowires and nanocrystals from ethyl ether; and (F) polydisperse nanorods from chloroform.

uniform *t*-Se microcrystals could be precipitated out by adding water to the diamine solution. Sonication in aniline resulted in complete conversion of *a*-Se colloids to short, anisotropic rods of *t*-Se (Figure 2C). Solvents with both alcohol and amine functionality were also examined as potential solvents. The products for these syntheses were nonuniform microcrystals of *t*-Se (Figure 2D). Acetonitrile yielded nanowires that were similar to those synthesized in secondary alcohols. The *a*-Se colloids were stable in unsubstituted alkanes (such as hexane) and were not converted to the trigonal form. Sonication in ether produced exceptionally long and high quality nanowires of *t*-Se (Figure 2E), although a small amount of large micrometer-sized crystals were also produced. Chloroform and acetone both generated polydispersed *t*-Se nanorods with relatively low yields (Figure 2F).

Figure 3 displays electron microscopic images and diffraction patterns of nanowires grown in two different alcohols. This figure illustrates the difference in nanowires grown from primary versus secondary (and tertiary) alcohols. At low magnifications, the nanowires formed in *n*-propanol (Figure 3A) can be seen to exhibit higher aspect-ratios, and better flexibility than their counterparts formed in 2-propanol (Figure 3B). On closer inspection by TEM and electron microdiffraction, the nanowires for both samples were single crystals of *t*-Se oriented along the $\langle 001 \rangle$ axis. In the case of *n*-propanol (Figure 3C), the flexible nanowire had a hexagonal cross-section with no taper and uniform diameter on the order of ~20 nm. The stiff nanowire grown in 2-propanol (Figure 3D), displayed a tapered, triangular cross-section. The diameters of these *t*-Se nanowires could be as large as 120 nm in the middle and have tips with diameters <10 nm.

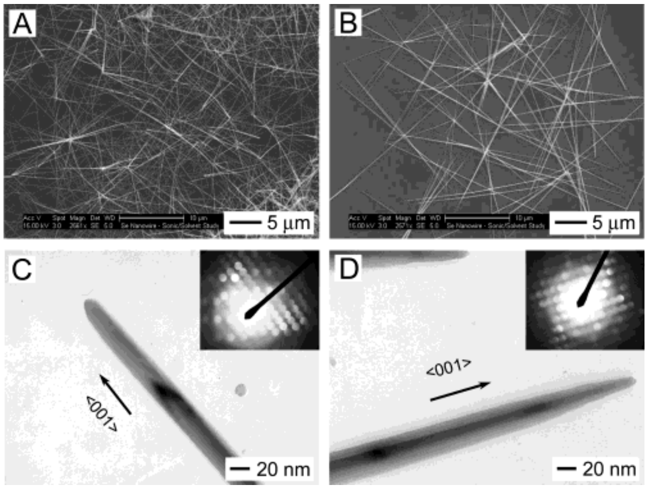

Figure 3. Low-magnification SEM images of a typical sample of *t*-Se nanowires synthesized sonochemically in (A) *n*-propanol and in (B) 2-propanol. The synthesis with *n*-propanol generated long flexible nanowires with hexagonal cross-sections. The synthesis with 2-propanol generated shorter, stiffer, tapered nanowires. TEM images of the nanowires from (C) *n*-propanol and (D) 2-propanol indicated that both syntheses generated single crystalline nanowires with the primary growth direction along the $\langle 001 \rangle$ axis.

Table 1 lists the absorption maxima for nanowires synthesized in several different solvents. Because the peaks above 530 nm could be solely attributed to interchain interactions within a given *t*-Se crystal, monitoring the position of the low-energy maxima was instructive. This is particularly true for the alcohols when comparing absorption maxima to morphology. The crystals with the highest degree of perfection, that is, those with perfectly hexagonal cross-sections and without taper, had high-energy interchain interactions at ~590 nm. This is indicative of the well-packed Se chains that can be seen in the ideal *t*-Se crystal structure. In a poor solvent, when atoms were less mobile, trapped defects led to the formation of a tapered morphology.[23] As the quality of the crystals decreased and they became more and more tapered, this peak was further red-shifted indicating weaker interchain interactions. We can conclude that ethanol and *n*-propanol were near-ideal solvents because both of them allowed for maximization of interchain forces (best chain packing).

Solvent viscosity also had an observable effect on nanowire growth. For example, the nanowires grown in ether (0.224 cP), Figure 2F, were >100 μm long. In cyclohexanol (57.7 cP), Figure 2A, the nanowires were ~6 μm long. In PEO (150-mer) with a viscosity >80 cP, the nanowires only grew to an average length of 1 μm. It should also be noted that in the latter two solvents the nanowires grew into star-shaped clusters as determined by the diffusion gradient around the *a*-Se colloids (diffusion length decreased with the increasing viscosity).

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In this study, we have limited the solvents to nonchiral systems. However, each nanowire of *t*-Se should be essentially a chiral crystal, composed entirely of L or R helices. Considering *t*-Se nanowires could be grown in such a wide variety of solvents, it is likely that a chiral solvent could also be used in the sonochemical synthesis. It is plausible that appropriate selection of a chiral solvent might lead to an enantioselective synthesis of *t*-Se nanowires.

Formation of 2D Networks of *t*-Se Nanowires on Solid Substrates. It is straightforward to deposit nanowires on a surface to generate random networks. On the other hand, to make solution-phase synthesis of nanowires useful in applications such as electronic devices and sensors, it will be necessary to develop methods for coordinating nanostructure growth or assembly into well-defined structures.[24] The SSS sonochemical system described here is promising in this respect. One of the major benefits of this sonochemical synthesis is the portability of its precursors. The *a*-Se colloids could be dried and assembled as desired, even after they had been sonicated. To initiate nanowire growth, one would simply need to add alcohol. Because the assembly of colloids has been well studied, there is a rich variety of techniques that could be used to generate complex ordered structures. Here we describe two methods that we have employed for the rational organization of *a*-Se colloids and subsequent growth of *t*-Se nanowire networks.

Figure 4A shows how *a*-Se colloids could be patterned on a surface using an elastomeric mold. The colloids could be pushed along the solvent front in micrometer-scale channels. When the solvent dried, the colloids would be left behind in ordered lines. When an alcohol was added, wires grew out of the colloids to form linear networks consisting of interconnected nanowires. Figure 4B and C show the typical results of this synthesis. In this case, the colloids were dispersed with sonication in a 1:2 ethanol−water mixture. A drop of this dispersion was placed at the opening of 20-μm channels in a PDMS stamp that was placed on a Si substrate. The dispersion was allowed to penetrate a short distance into the mold and then dried with a paper towel. Once dry, the PDMS stamp was removed, and the Si substrate (decorated with *a*-Se colloids) was submersed in *n*-propanol. The low magnification SEM image (Figure 4B), shows a linear network composed of nanowires (44 ± 7 nm in diameter), that is ∼50 μm and spans a distance >700 μm. Using this technique, it was possible to generate chainlike networks that spanned distances of several millimeters. The individual nanowires contained in such a network were relatively uniform and monodisperse in diameter, and tens of micrometers in length (Figure 4C).

Figure 5A shows a second schematic for generating patterned arrays of *a*-Se colloids. The scheme depicts how colloids could be pushed into the negative relief structures on a patterned surface. When an alcohol was added, nanowires grew out of the holes to form an interconnected network or isolated clusters of nanowires. In a typical procedure, colloids were sonicated in pure ethanol and immediately deposited onto a prepatterned silicon substrate. The surface was wiped multiple times (in all directions) with an elastomeric strip to press in the colloids and remove any excess. Figure 5B shows an optical microscopy (bright-field) image of the Si surface with *a*-Se colloids placed in periodic pyramidal holes (10 μm periodicity). This image clearly indicates that this technique was successful in removing the excess colloids while leaving the colloids behind in the cavities.

Figure 5C shows the SEM image of the same sample (Figure 5B) after it had been soaked in *n*-propanol overnight. The low-magnification SEM image suggests

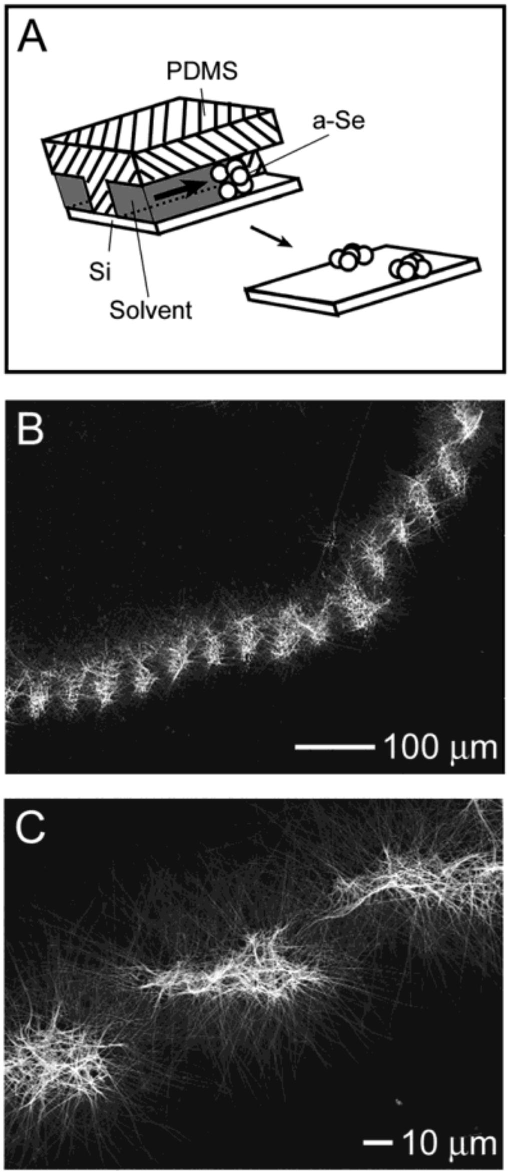

Figure 4. (A) Schematic for patterning *a*-Se colloids on a Si substrate by capillary flow in PDMS microchannels. The colloids were first pushed through the channels along the solvent front. When the solvent was dried and the PDMS was removed, clusters of *a*-Se colloids were deposited where the solvent front had stopped. The substrate was then submersed in *n*-propanol for 10 h. (B) Low- and (C) high-magnification SEM images show the quality of interconnected networks that could be obtained. Using this technique, serial networks >1 mm in length were generated.

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[24] See for example (a) Huang, Y.; Duan, X. F.; Wei, Q. Q.; Lieber, C. M.; *Science* **2001**, *291*, 630−633. (b) Vayssieres, L.; Rabenberg, L.; Manthiram, A. *Nano Lett.* **2002**, *2*, 1393. (c) Hermanson, K. D.; Lumsdon, S. O.; Williams, J. P.; Kaler, E. W.; Velev, O. D. *Science* **2001**, *294*, 1082. (d) Sapp, S. A.; Mitchell, D. T.; Martin, C. R. *Chem. Mater.* **1999**, *11*, 1183.

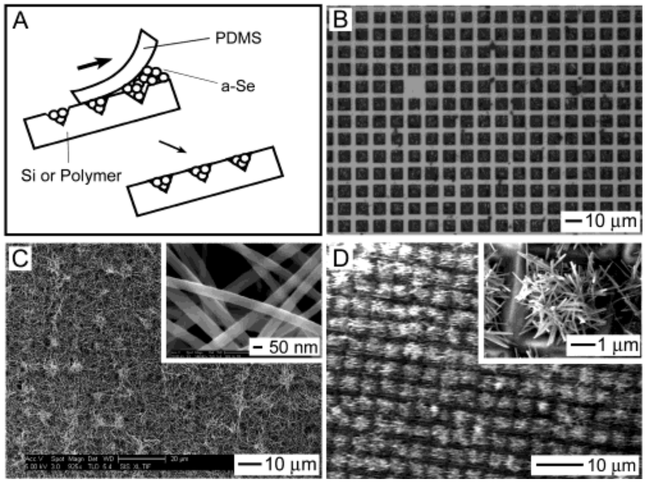

Figure 5. (A) Schematic for patterning *a*-Se colloids on a substrate by templating against relief structures on the surface. The substrate was patterned with conventional photolithography or replica molding. The *a*-Se colloids were deposited on the surface as a dry solid or in a dispersion immediately after sonication. The schematic shows how the colloids were pushed into depressions on the surface with a poly(dimethylsiloxane) (PDMS). (B) Bright field optical microscopy image showing colloids that had been wiped into holes in Si with $\sim$10 μm periodicity. Very little excess material remains outside of the holes. The unfilled square (top left) represents a defect in the pattern where no hole was etched. (C) SEM image of the same sample after it was submersed in *n*-propanol for 10 h. The surface was completely covered with an interconnected network of nanowires. The inset shows a blown-up SEM image. (D) SEM image of nanowires grown using this technique on a polymer substrate with 4-μm holes. In this case, the nanowires formed discrete clusters on the substrate because there was less growth material in the holes. The inset shows a blown-up SEM of the same sample.

that the substrate had been coated with a uniform 2D network of *t*-Se nanowires. The high-magnification SEM image (inset of Figure 5B) demonstrates the uniformity and level of perfection of these nanowires (57 ± 8 nm diameter, with lengths >5 μm). It was also possible to generate isolated islands of nanowires by placing fewer colloids into each cavity. Figure 5D shows the SEM image of nanowire clusters that were grown using a similar procedure, in pyramidal holes on polyurethane (4-μm periodicity). In this case the shallower holes contained less material, and the resultant nanowires were shorter. The continuity of the networks was tested through simple conductivity and photoconductivity tests. For a 2D network ($\sim$1 mm^2 in area) of *t*-Se nanowires on an insulating substrate, the conductivity increased by more than 100 times upon irradiation with visible light.

One advantage for these patterning procedures is that the colloids can be deposited on any substrate that can be subsequently soaked with the appropriate solvent. The patterns that we demonstrate here are of a low order of complexity. However, more complex patterns could be easily generated with the use of a variety of patterning techniques that include photolithography, shear flow, dewetting from surfaces modified with microcontact printing, and ink jet printing. It should also be possible to transform the nanowires in these networks into other interesting materials due to the relatively high reactivity of Se (e.g., to form chalcogenides or metals).[4] It is reasonable to expect that this approach could be used not only to grow photoconductive interconnects, but also to grow active components, suitable for use in device fabrication.

It should be noted that the sonochemical synthesis could also be used to form spongelike 3D networks. At high concentrations of colloids, the nanowires that grew out from the colloidal centers slowly expanded into an unfilled network structure. It was possible to generate porous networks ($>$1 cm^3) with densities $<5 \times 10^{-3}$ g/cm^3 in alcohol solutions. These networks were free-standing and fully interconnected, with less than a tenth of a percent filling-fraction (calculated on the basis of density of bulk *t*-Se, 4.8 g/cm^3). These networks could remain indefinitely stable in solutions, but would collapse when solvents were removed.

Conclusions

We have demonstrated the generation of *t*-Se nanowires through a sonication-induced SSS mechanism. We believe that this synthesis can be potentially extended to generate 1D nanostructures from other materials that include both semiconductors and metals. The major requirements seem to be the generation of a stable (or quasi stable) amorphous phase, and the selection of an appropriate solvent (i.e., a solvent capable of facilitating the transport of atoms or ions from the amorphous precursor to a more stable, crystalline product). For solid materials with isotropic structures, it might be necessary to add ligands or capping reagents to induce and direct the anisotropic growth. Because the *entire* process was carried out at ambient temperature and pressure, such a synthesis could be conveniently scaled up for high-volume production of 1D nanostructures. In addition, the synthesis was fast and clean (no byproducts), with nearly quantitative yields.

We have also demonstrated that this synthesis could be employed for the fabrication of 2D networks of nanowires supported on solid substrates. After sonication, the colloidal particles could be easily deposited as patterned arrays with techniques such as templating against molds, dewetting on surfaces modified with microcontact printing, and ink-jet printing. These colloids could then be grown into networks suitable for use as interconnects or active components for nanoscale electronic and optoelectronic devices. They should also be useful for the investigation of transport properties under 1D confinement.

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