

Cellulose-Directed Growth of Selenium Nanobelts in Solution

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Received May 20, 2005. Revised Manuscript Received October 24, 2005

Elemental selenium nanobelts have been synthesized for the first time by a novel and mild solution method. The synthetic reaction was carried out with cellulose as both reducing and morphology-directing agents in solution under simple hydrothermal conditions at low temperature, which is quite different from the thermal evaporation/reaction process for nanobelts at high temperature. Some other mild biopolyhydric chemicals such as sorbitol and polygalacturonic acid, which are related to cellulose, have also been investigated under our synthetic conditions. When sorbitol and polygalacturonic acid were used as reducing agents, different one-dimensional (1D) nanostructures, simple cylindrical nanowires, and centipede-shaped 1D structures could be obtained. This method might bring a new, mild, and economical concept for the synthesis and construction of nanobelts, nanowires, and other kinds of 1D nanostructures.

1. Introduction

Nanoscale structures have attracted a great deal of attention because of their conspicuous physicochemical properties that differ markedly from those of bulk materials and potential for wide-ranging applications.^{1,2} Besides tubular structures,^{3,4} a variety of nanostructures have been synthesized, including cages,^{5,6} cylindrical wires,^{7–9} rods,^{10–12} cables,^{13,14} diskettes,¹⁵ springs,¹⁶ and more. Among them, one-dimensional (1D) nanomaterials are of extraordinary importance because of their special properties and potential applications in constructing nanoscale electronic and optoelectronic devices. A number of 1D nanostructures have been synthesized by many well-known routes such as vapor–liquid–solid growth,^{17,18}

a surfactant-assisted technique,^{19,20} and a hard template-limited approach.^{21,22} Recently, a newcomer of 1D nanomaterials, belt- (ribbon-)like nanostructure, which distinctly differs from solid nanowires and hollow nanotubes, has been successfully fabricated.²³ Because of the special morphology, there has been much speculation about the properties and potential applications of these nanostructures, which has initiated intense interest in the synthesis of such beltlike nanostructures.²⁴ Beltlike nanostructured oxides (ZnO, SnO₂, In₂O₃, and CdO) were first synthesized in 2001 by a thermal evaporation of oxide powders at high temperature (1000–1400 °C).²³ From then on, many kinds of nanobelts such as PbO,²⁵ Fe₂O₃,²⁶ ZnS,²⁷ Si,²⁸ Zn,²⁹ and Ge₃N₄³⁰ have been fabricated, but almost all are based on the thermal evaporation/reaction process at high temperature usually in the range 700–1400 °C with the exceptions of potassium titanate (K₂-Ti₈O₁₇) nanobelts³¹ by a basic hydrothermal route at low temperature and SiC nanobelts³² from SiCl₄, CH₃CH₂OH, and Li powder at 600 °C under pressure. Designing new

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approaches to develop new types of nanobelts or synthesize nanobelts under mild conditions is quite important for investigating the properties and applications of nanobelts.

Nonmetallic selenium is known as an important trace element for humans because of its great nutritional effects in biology, for example, protecting cells against free radicals from oxygen metabolism and strengthening the functions of the immune system.^{33,34} As an important semiconductor, selenium attracts even more attention in physical sciences as a result of its promising physical properties, such as the anisotropy of the thermoconductivity, superconductivity, catalytic activities to hydration and oxidation reactions, and high piezoelectric, thermoelectric, and nonlinear optical responses, and thus has been applied to a wealth of applications ranging from photocells, photographic exposure meters, and solar cells to semiconductor rectifiers.^{35–41} Furthermore, selenium also has a high reactivity toward other chemicals to convert itself into a series of functional materials such as CdSe, ZnSe, and Bi₂Se₃.^{42–45} It is reasonable to expect new or enhanced applications from 1D Se nanostructures. Recently, several approaches^{46–53} have been employed to fabricate selenium nanowires, including the use of cytochrome *c*3 as a reducing agent to obtain chainlike Se aggregates (rather than single crystalline Se nanowires),⁴⁶ with excess hydrazine as the reducing agent for single crystalline selenium nanowires under refluxing,⁴⁸ and chemical vapor deposition for Se nanowires with selenium powder as the reactant under flowing Ar gas.⁵¹ Zhang et al.⁵⁴ reported the synthesis of selenium nanoparticles in the presence of polysaccharides and the influences of temperature and ultrasonic on the morphology of selenium nanoparticles, in

which polysaccharides or modified polysaccharides were used as modifiers or stabilizers and ascorbic acid was used as the reducing agent to start the reaction. So far selenium nanobelts were just reported by a thermal evaporation route at high temperature (600 °C),⁵⁵ and no low-temperature method has been developed for the synthesis of selenium nanobelts in solution as we know. Developing a straightforward and mild method for 1D Se beltlike and wirelike nanostructures is of importance and still a challenge for materials scientists.

Cellulose and other biopolyols such as sorbitol and polygalacturonic acid are one kind of the most common biomolecules in our general life and have been used in diverse industries including pharmaceuticals, cosmetics, foods, textiles, and so forth. Although in the past decade some polyols have been successfully employed for the preparation of nanomaterials, such as ethylene glycol for silver nanoparticles,^{56–64} the biopolyols did not find their wide applications in the fabrication of nanomaterials. Herein, we demonstrate that cellulose, a safe and economical biopolyol, can be used as a reducing agent and morphology-directing agent for the synthesis of selenium nanobelts. It is the first report to the best of our knowledge for the synthesis of selenium nanobelts by using cellulose as a reductant in solution at low temperature. The synthetic reaction was carried out under simple hydrothermal conditions, which is quite different from the high-temperature evaporation/reaction process for nanobelts. Some other mild polyhydric chemicals such as sorbitol (alditol) and polygalacturonic acid (saccharic acid) related to cellulose are also investigated here for the synthesis of other 1D selenium nanostructures.

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2. Experimental Section

Materials. Anhydrous sodium selenite was purchased from A Johnson Matthey (Alfa Aesar) Co. Cellulose and starch were purchased from Research Chemicals Ltd. D-(–)-fructose, D-sorbitol, and α-lactose monohydrate were purchased from Sigma-Aldrich Co. Polygalacturonic acid and alginic acid were purchased from Sigma Chemical Co.

Synthetic Processes. The cellulose-induced synthetic process for selenium nanobelts is very easy and simple. In a typical procedure, 0.1 g of Na₂SeO₃ and 0.05 g of cellulose were dissolved in 10 mL of distilled water. No chemical reaction could be observed when the two chemicals were mixed at room temperature. The mixed solution was transferred into a Teflon-lined stainless steel autoclave and kept at 160 °C for 15 h without stirring. After cooling to room temperature, the product was collected. Solid and solution were

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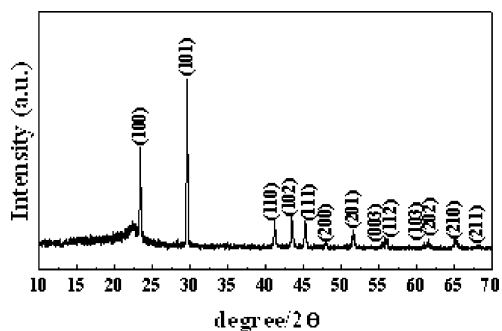


Figure 1. XRD pattern of the obtained selenium sample prepared with cellulose as the reducing agent.

separated by centrifugation and washed with distilled water and ethanol by centrifugation at 1000 rpm for ~ 10 min. The obtained powders were kept in ethanol at room temperature. The nanobelts could also form even if we changed the amount of cellulose and Na_2SeO_3 in a certain range, but the experimental conditions described above give out the best results. The sample kept in ethanol could be dried at room temperature to get powders, and the yield of the reductive reaction is about 85%.

X-ray Diffraction Measurements. The reaction products were deposited on slides and dried at room temperature for X-ray diffraction characterization using a Scintag diffractometer operated at a 35 kV voltage and 30 mA current with Cu $K\alpha$ radiation.

Transmission Electron Microscopy Measurements. The morphology, crystallinity, size, and organization behavior of selenium nanocrystals were determined by transmission electron microscopy, accompanied by selected area electron diffraction (SAED), carried out on a Philips 420 transmission electron microscope (TEM) operated at 120 kV and a JEOL-2010F high-resolution transmission electron microscope (HRTEM) operated at 200 kV. A small amount of the sample was dispersed in ethanol, and then a drop of this solution was deposited on an amorphous carbon film on a 300 mesh Cu grid for TEM observation directly.

UV/Vis Absorbance Spectroscopy Measurements. The optical properties of the obtained selenium crystallites were investigated by UV/vis absorbance spectroscopy using an Agilent 8453 UV/visible spectrophotometer. A small amount of the sample was dispersed in ethanol for UV/vis absorbance spectroscopy measurement.

3. Results and Discussion

Figure 1 shows the XRD pattern of the sample prepared with cellulose as the reducing agent confirming the realization of the crystalline selenium. All the strong peaks in this pattern can be indexed as hexagonal phase of selenium (Se, JCPDS, No. 6-362) with a low-intensity peak maybe due to stacking faults,^{65,66} which indicates that highly crystalline selenium grains have been successfully synthesized from selenite with the addition of cellulose under the hydrothermal conditions. Figure 2a shows a low-magnification TEM image of the obtained sample, revealing that the obtained selenium grains have 1D structure. The bending of these 1D nanostructures indicates that they are of beltlike (ribbonlike) morphology, which could be further confirmed by a TEM image with high magnification (Figure 2b) of a single

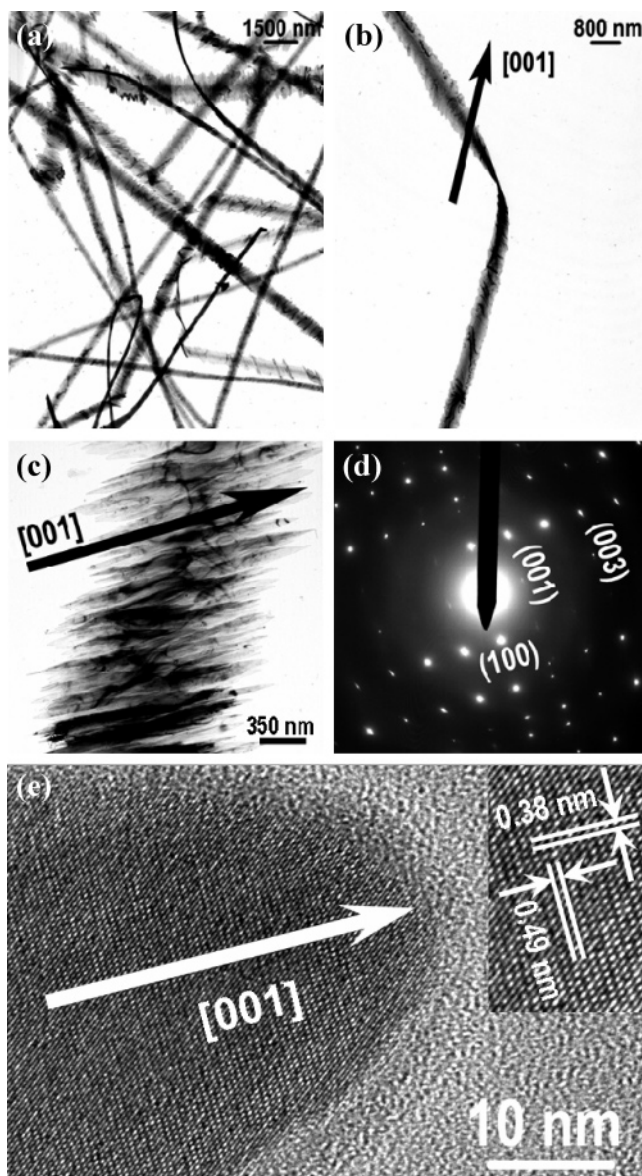


Figure 2. TEM images, SAED pattern, and HRTEM image of the obtained selenium sample prepared with cellulose as the reducing agent.

nanobelt. The widths of these nanobelts are not quite uniform ranging from 200 to 1500 nm, and their length are up to tens of micrometers. The thicknesses of these nanobelts are about tens of nanometers. The surfaces of the two sides of the nanobelts are not smooth and seem to have sawlike structures. The detailed structures of the nanobelts could be revealed more clearly by the magnified TEM image (Figure 2c). These sawlike nanobelts seem to be formed by the lateral connection of short needlelike nanorods. Its SAED pattern (Figure 2d) displays diffraction dots, instead of diffraction rings, which means that these nanobelts are single-crystal in nature. The nearest dot along the growth direction of needlelike nanorods could be indexed as (001), and that perpendicular to the growth direction of needlelike nanorods could be indexed as (100). This means that these needlelike nanorods might have a [001] preferred growth direction, and the nanobelt might have a [101] preferred growth direction. The crystallinity and structure of these nanobelts could be further confirmed by the HRTEM image. Figure 2e shows a

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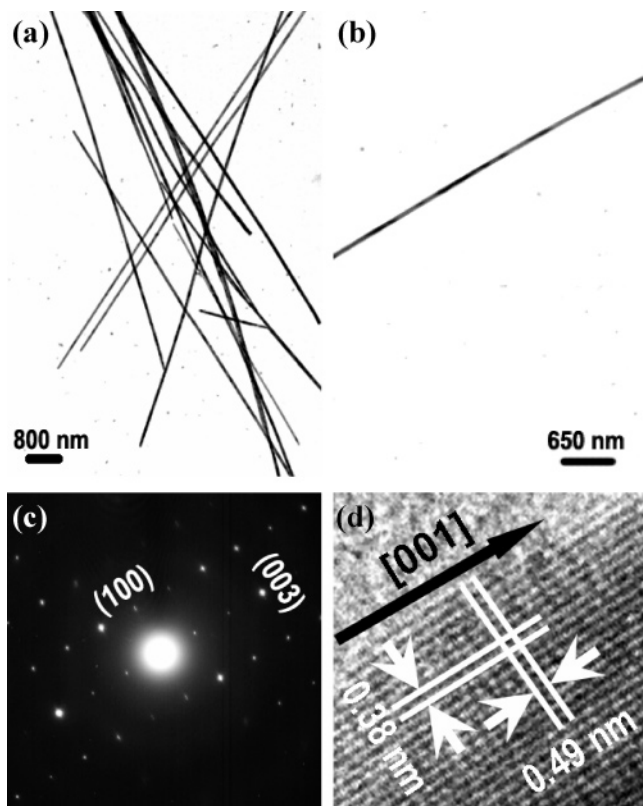


Figure 3. TEM images, SAED pattern, and HRTEM image of the obtained selenium sample prepared with sorbitol as the reducing agent.

HRTEM image of a needlelike rod in a nanobelt. The crystal planes (shown more clearly in the inset of Figure 2e), perpendicular and parallel to the needlelike rods, have the spacings of about 0.49 and 0.38 nm, which correspond to those of (001) and (100) planes, respectively. These results indicate that the nanobelts are of high crystallinity and the needlelike nanorods have a [001] preferred growth direction, consistent with those from the SAED pattern.

All of the above results show that, with the addition of cellulose, Se nanobelts can be formed from the selenite. In this process, cellulose is not only the reducing agent but also the morphology-directing agent. Although the exact mechanism of the nanobelt growth is quite difficult to know, it is reasonable to think that the property and the structure of cellulose are critical in the growth of nanobelts. The long chain and polyhydroxyl of cellulose could be a directing template for the growth of nanobelts assembled by needlelike nanorods. Thus, it might be reasonable to expect different functions from other polyhydric compounds for 1D Se nanostructures.

Sorbitol, the alcohol form of glucose, is a small molecular polyol. It is also a coordinating reagent and has relatively strong reducing ability, which might be useful for the growth of 1D selenium. To investigate this possibility, in our experiments, we replaced cellulose with sorbitol and found that crystalline selenium grains could also be obtained under hydrothermal conditions. Figure 3a shows the TEM image of the sample reduced by sorbitol, confirming that the formed selenium crystallites have wirelike morphology. However, they have cylindrical morphology with small diameters and smooth surface, quite different from those nanobelts. The

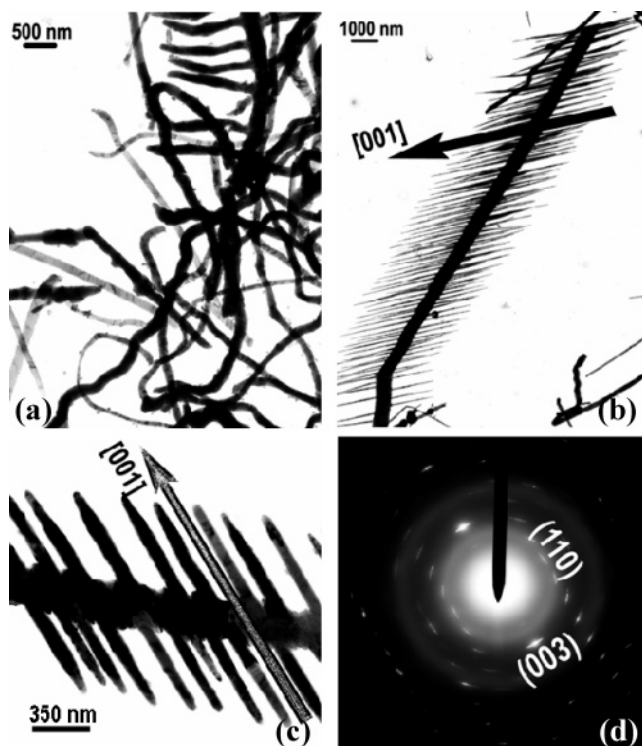


Figure 4. TEM images and SAED pattern of the obtained selenium sample prepared with polygalacturonic acid as the reducing agent.

average diameter is calculated to be ~ 60 nm, much smaller than the width of nanobelts, and the lengths are up to micrometers. Figure 3b shows the TEM image of a single nanowire of higher magnification. It can be seen clearly that the nanowire is in cylindrical morphology but not in beltlike shape and has a smooth surface instead of sawlike side surface. Its SAED pattern (Figure 3c) confirms that it is also single crystal in nature. According to the diffraction dots, the nanowire has a preferred growth direction of [001], similar to that of the needlelike nanorod. The HRTEM image (Figure 3d) further confirms the high crystallinity and the [001] preferred growth direction of the nanowire.

Polygalacturonic acid, a kind of polysaccharide from an orange, has also been investigated under our experimental conditions, and crystalline Se grains could be obtained from the selenite by using it as a reducing agent. The TEM image shown in Figure 4a confirms that the obtained Se sample has a 1D nanostructure. Interestingly, besides wirelike architectures, a novel centipede shape composed of dozens of parallelly aligned Se nanorods (Figure 4b,c), which is similar to the nanobelts assembled by needlelike nanorods, is also found. These 1D architectures are up to tens of micrometers long and several micrometers wide. Their feet are about tens of nanometers in width and up to few micrometers in length. The SAED pattern (Figure 4d) of the centipede-shaped architecture can be indexed as hexagonal selenium with single-crystal-like nature. The two diffraction spots perpendicular to each other in the SAED pattern could be indexed to (003) and (110), respectively, which indicates the feet of the centipede-shaped architecture might have a preferred growth direction of [001], similar to those of needlelike nanorods in nanobelts and the long nanowires obtained with sorbitol as an additive.

Other biopolyols such as fructose, lactose, alginic acid, and starch have also been investigated. By using these kinds of polyols as reducing agents, elemental selenium could also be obtained; however, they are in nonuniform and thick rodlike shapes.

The possible growth mechanism for these 1D nanostructured materials might be the simultaneous reduction and directed growth, which can be deduced from the fact that the obtained complex 1D structures (nanobelts and centipede-shaped structures) are single-crystal in nature. The crystal structure of selenium is highly anisotropic, and it has a tendency to grow along the [001] direction.⁶⁷ If the reduction reaction is not very fast, while the elemental selenium forms it tends to grow along the [001] direction to form nanorods. During the process, the directing function of long-chain polysaccharide cellulose might direct these short nanorods to grow along the long axis to form sawlike nanobelts. Energy dispersive spectrum (EDS) analyses on the nanobelts, the centipede-shaped structures, and the single nanowires show that there are only small amounts of carbon on them, and no great differences could be found between their EDS results. The elementary mapping results indicate that carbon amounts on the nanobelts, the centipede-shaped structures and the single nanowires are very low, and no relatively high amount of carbon could be detected on the interfaces of nanorods in the nanobelts and the centipede-shaped structures. These also suggest that the polysaccharides used in our experiments are not linking agents to simply aggregate the nanorods but growth-directing agents to direct the growth of selenium to form such special nanostructures, consistent with the SAED pattern results. The growth mechanisms for the different directing agents might be the same. But different structures of different molecules might lead to different morphologies. For polygalacturonic acid, the branched chains might not be beneficial to the close assembly of nanorods and lead to the formation of centipede-shaped structures. For small-molecule sorbitol the directing function along the long axis is not strong enough under our experimental conditions, and the self-growth of nanorods leads to the formation of single long nanowires with a smooth surface and preferred [001] growth direction.

UV/vis absorbance spectroscopy was also used to characterize the samples. Figure 5 shows the absorbance spectra of the obtained selenium 1D nanomaterials. The Se nanobelts prepared with cellulose show two peaks at about 380 and 630 nm, while the Se nanowires prepared with sorbitol show two absorbance peaks at about 440 and 610 nm. Comparatively, the Se nanostructures prepared with polygalacturonic

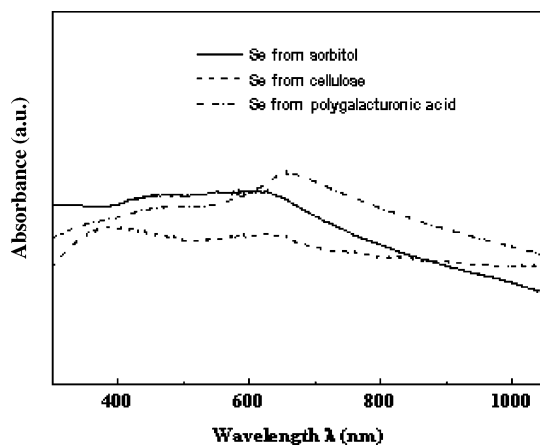


Figure 5. UV/vis absorbance spectra of the obtained selenium samples.

acid display a relatively weak peak around 450 nm and a strong absorbance peak at about 660 nm. The intensity change and the position shift of the absorbance peaks might be associated with the variation of the diameter and the assembly behaviors of 1D nanostructures. As previously reported, the optical property of Se could be adjusted by changing the synthetic conditions and, thus, the size and microstructure of the formed Se nanomaterials.⁴² The size and assembly effects of selenium 1D nanostructures might bring in new types of applications or enhance the performance of currently existing devices.

4. Conclusion

In this paper, Se nanobelts have been synthesized for the first time by a simple cellulose-reducing method at low temperature in solution, which is quite different from the thermal evaporation/reaction process for nanobelts at high temperature. The used cellulose serves not only as an effective reducing agent but also as a new morphology-directing agent for the selenium nanobelts from Na_2SeO_3 precursor powders. By replacing cellulose with other biopolyols, such as sorbitol and polygalacturonic acid, different 1D nanostructures, simple cylindrical nanowires and centipede 1D structures, could be obtained. This method might bring a new, mild, and economical concept for the synthesis and construction of nanobelts, nanowires, and other kinds of 1D nanostructures.

Acknowledgment. This work was supported by the NSF MRSEC under Grant DMR-0213623 and Huck Institutes of Life Sciences. TEM work was performed in the electron microscopy facility of the Materials Research Institute at Penn State University.

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