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Micelle-Mediated Synthesis of Single-Crystalline Selenium Nanotubes**

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Considerable attention has recently been directed towards one-dimensional (1D) nanostructures, such as wires, rods, belts, and tubes, owing to their unique physical and chemical properties and potential applications in nanoscale devices.^[1] In particular, much effort has been devoted to the controlled synthesis of inorganic nanotubes since the discovery of carbon nanotubes.^[2] A variety of inorganic nanotubes based on layered or pseudo-layered materials have been synthesized by

using high-temperature or hydrothermal processes; examples include boron nitride, metal dichalcogenides, metal dihalides, metal oxides and hydroxides, metal borates, as well as metals.^[3] Alternatively, nanotubes made from silica, alumina, silicon, and metals that do not possess a layered crystal structure have been fabricated by employing various templates such as porous membranes, carbon nanotubes, inorganic nanowires/nanorods, and organized assemblies of organic molecules,^[4] however, these nanotubes are usually either amorphous or polycrystalline. Notably, there are a few reports of single-crystalline nanotubes composed of semiconductors with non-layered structures. Single-crystalline GaN^[5] and Si^[6] nanotubes have been produced by epitaxial overgrowth against suitable nanowire templates using vapor deposition processes. Interestingly, single-crystalline tellurium nanotubes have been obtained via a solution-phase approach, i.e., the polyol process where ethylene glycol refluxed at 197 °C served as both solvent and reducing reagent.^[7] This soft solution processing strategy is promising but it still remains to be extended to inorganic materials other than tellurium. Therefore, it is a great challenge to develop new soft synthetic strategies that produce single-crystalline nanotubes from non-layered materials.

As an important elemental semiconductor, selenium shows many interesting properties, such as a relatively low melting point (~490 K), a high photoconductivity ($\sim 8 \times 10^4 \text{ S cm}^{-1}$), nonlinear optical responses, and a high reactivity toward a variety of chemicals, and it finds commercial applications in photovoltaic cells, rectifiers, mechanical sensors, photographic exposure meters, and xerography.^[8] Since the availability of 1D selenium nanostructures is expected to bring in new types of applications or to enhance the performance of the currently existing devices as a result of quantum-size effects, a number of synthetic methods have been developed to fabricate selenium nanorods and nanowires. Monoclinic selenium (m-Se) nanowires with a polycrystalline structure were obtained by using the protein cytochrome *c*₃ to reduce selenate (SeO_4^{2-}).^[9] Xia et al. synthesized single-crystalline trigonal selenium (t-Se) nanowires via the reduction of selenious acid (H_2SeO_3) with excess hydrazine by solution refluxing^[10] or sonochemical approaches.^[11] Subsequently, t-Se nanowires and nanorods were produced by the dismutation of Na_2SeO_3 under acidic condition^[12] or the solution-mediated transformation from Se powders.^[13] In addition, laser ablation and an evaporation and condensation process were used to prepare t-Se nanorods and nanowire networks, respectively.^[14] It is noteworthy that Xia et al. have successfully synthesized a variety of novel 1D nanostructures including Ag_2Se nanowires, CdSe nanotubes, and Pt nanotubes by templating against the obtained Se nanowires.^[15] However, to the best of our knowledge, there has been no report on the synthesis of uniform selenium nanotubes although large tubular single crystals of selenium were obtained under solvothermal conditions^[16a] and irregular or broken selenium nanotubes were produced through a hydrothermal process followed by sonication.^[16b] Here we describe a unique, facile, large-scale synthesis of single-crystalline t-Se nanotubes in micellar solutions of a

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non-ionic surfactant. It has also been demonstrated that novel Se nanobelts as well as Se nanowires can be produced under suitable conditions.

Selenium nanotubes were readily synthesized by the dismutation of Na_2SeSO_3 under acidic condition in micellar solutions of the surfactant poly(oxyethylene(23)) dodecyl ether ($\text{C}_{12}\text{E}_{23}$), which is a non-ionic surfactant with a low critical micelle concentration (cmc) in aqueous solution (typically $4 \times 10^{-5} - 2 \times 10^{-4} \text{ M}$).^[17] Figure 1 presents typical scanning electron microscopy (SEM) images and X-ray diffraction (XRD) pattern of the Se nanotubes obtained at a $\text{C}_{12}\text{E}_{23}$ concentration of 9.2 mM. As shown in Figure 1a, the product ex-

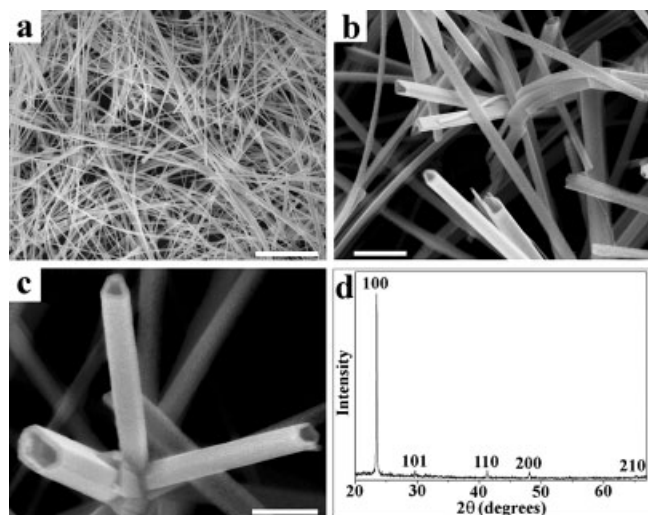


Figure 1. SEM images (a–c) and XRD pattern (d) of Se nanotubes obtained in micellar solutions of $\text{C}_{12}\text{E}_{23}$. [$\text{C}_{12}\text{E}_{23}$] = 9.2 mM, [HAc] = 44 mM. Scale bars: a) 5 μm , b) 1 μm , c) 500 nm.

hibits exclusively 1D wire-like nanostructures with diameters typically in the range 80–300 nm and lengths ranging from several micrometers to more than 100 μm . The hollow or tubular characteristic of the 1D nanostructures is revealed by an enlarged image (Fig. 1b). A high-magnification image of three nanotubes originated from a single knot (Fig. 1c) suggests that the tubes have a well-faceted prism morphology with a relatively uniform wall thickness (30–50 nm) and pseudo-hexagonal or pseudo-trigonal cross-sections, which is reminiscent of the reported hexagonally faceted, single-crystalline GaN ^[5] and t-Te ^[7] nanotubes, indicating the formation of single-crystalline t-Se nanotubes exhibiting {110} planes on the sides. The XRD pattern shown in Figure 1d demonstrates that the nanotubes are trigonal selenium and the abnormally intensified (100) peak is consistent with a preferential tube growth direction along the [001] direction. The related energy-dispersive X-ray spectroscopy (EDS) spectrum suggests that these nanotubes are made purely of selenium (Fig. S1, Supporting Information).

Figure 2a shows a TEM image of an individual nanotube clearly exhibiting a tubular structure. The selected-area elec-

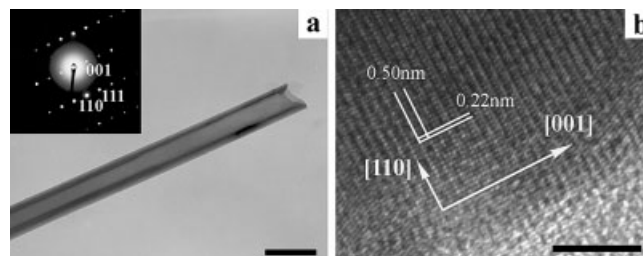


Figure 2. TEM (a) and HRTEM (b) images of Se nanotubes obtained in micellar solutions of $\text{C}_{12}\text{E}_{23}$. [$\text{C}_{12}\text{E}_{23}$] = 9.2 mM, [HAc] = 44 mM. Inset shows the corresponding ED pattern. Scale bars: a) 200 nm, b) 5 nm.

tron diffraction (ED) pattern related to the whole tube including the side wall can be indexed to the $[1\bar{1}0]$ zone axis of t-Se, suggesting that the whole nanotube is a single crystal grown along the [001] direction with the {110} planes on the tube sides. The single-crystallinity and structural integrity of the nanotubes are further demonstrated by the high-resolution transmission electron microscope (HRTEM) image of the tube edge (Fig. 2b), which is essentially the same as the HRTEM image obtained from the central part of the tube. The observed fringe spacings agree well with the spacings for the (001) and (110) planes of t-Se, respectively, confirming that the nanotubes are single crystals grown along the *c*-axis, i.e., the direction parallel to the helical chains of selenium atoms in t-Se.^[10]

It has been observed that the surfactant concentration plays a key role in the formation of the t-Se nanotubes and 1D t-Se nanostructures other than nanotubes can be obtained at different surfactant concentrations. As shown in Figure 3a,b, in addition to Se nanowires similar to those reported in the literature^[10–13], novel Se nanobelts were obtained at a smaller

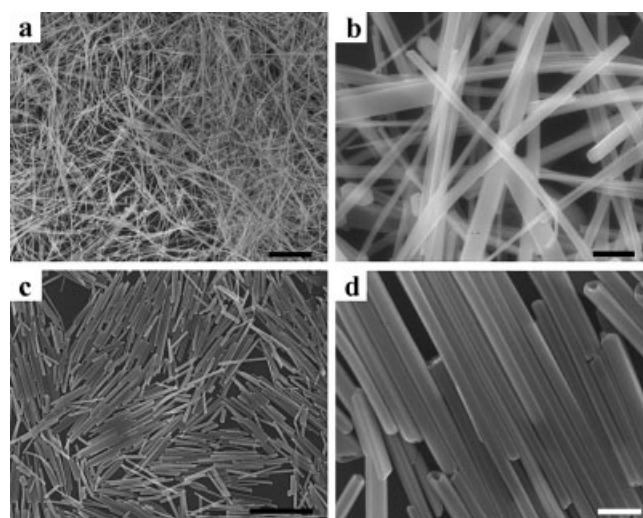


Figure 3. SEM images of 1D Se nanostructures obtained in $\text{C}_{12}\text{E}_{23}$ micellar solutions with varied $\text{C}_{12}\text{E}_{23}$ concentrations. [$\text{C}_{12}\text{E}_{23}$]: (a,b) 0.69 mM, (c,d) 18.4 mM. [HAc] = 44 mM. Scale bars: a) 5 μm , b) 500 nm, c) 5 μm , d) 500 nm.

$C_{12}E_{23}$ concentration (0.69 mM). Detailed SEM observations together with TEM images (Fig. S2, Supporting Information) suggest that the Se nanobelts, which have a thickness ~ 30 nm, widths up to 400 nm, and lengths as long as several tens of micrometers, coexist with the Se nanowires with diameters in the range 20–100 nm. On the other hand, if the $C_{12}E_{23}$ concentration was increased to 18.4 mM, relatively short Se nanotubes with wall thickness ~ 50 nm, outer diameters in the range 150–250 nm, and lengths in the range 3–7 μm were produced (Fig. 3c,d). It is worth noting that the nanotubes are reasonably uniform and they can be partly self-assembled into nematic two-dimensional arrays on the silicon wafer. In addition, it has been found that the acetic acid (HAc) concentration influences the morphology of the final products significantly. While short Se nanotubes were obtained at a lower HAc concentration, relatively uniform Se nanorods were produced at a higher HAc concentration (Fig. 4).

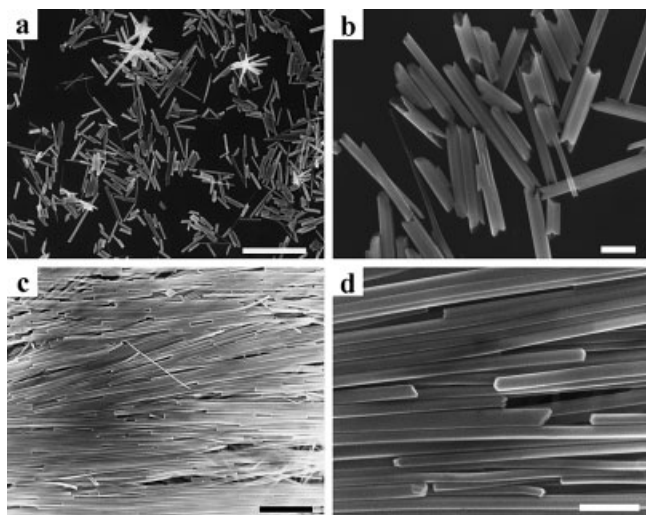


Figure 4. SEM images of 1D Se nanostructures obtained in $C_{12}E_{23}$ micellar solutions with varied HAc concentrations. [$C_{12}E_{23}$] = 9.2 mM, [HAc]: a,b) 22 mM, c,d) 88 mM. Scale bars: a) 5 μm , b) 500 nm, c) 2 μm , d) 500 nm.

The exact mechanism for the formation of the Se nanotubes in $C_{12}E_{23}$ micellar solutions is still under investigation. It has been documented that t-Se nanowires can grow spontaneously from t-Se nanocrystallites nucleated on the surface of amorphous selenium (a-Se) colloids due to the inherently anisotropic structure of t-Se.^[10,11] In the current situation, the extended polar shell of $C_{12}E_{23}$ micelles, which is filled with poly(oxyethylene) chains and entrapped water, may have a good ability to solubilize a-Se since a-Se shows an improved solubility in ethanol.^[11] Hence, in the solution, a-Se could mainly exist either as a-Se colloids in the solution or as a-Se solubilized in the polar shell of the $C_{12}E_{23}$ micelles. We believe that the $C_{12}E_{23}$ micelles could play an important role in controlling the distribution of a-Se in the solution and thereby lead to the formation of t-Se nanotubes following a mecha-

nism similar to that proposed for the t-Te nanotube formed through a polyol process.^[7] If the $C_{12}E_{23}$ concentration is too low, only a small amount of a-Se is solubilized in the micelles, resulting in the formation of t-Se nanowires or nanobelts probably due to the presence of a large amount of a-Se colloids (Fig. 5a). At a suitable $C_{12}E_{23}$ concentration, there are plenty of micelles and a large amount of a-Se is solubilized, resulting in a relatively small amount of a-Se colloids in the

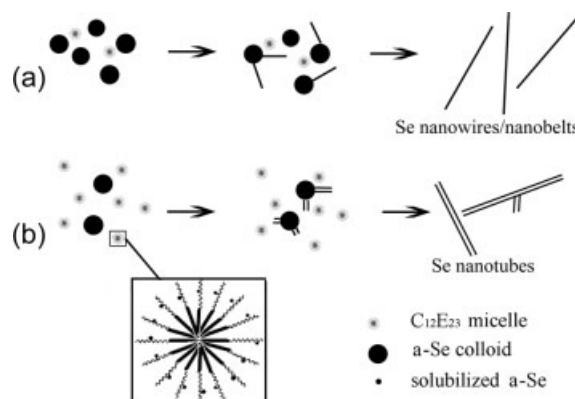


Figure 5. Schematic illustration of a possible mechanism for the micelle-mediated formation of Se nanowires/nanobelts (a) and Se nanotubes (b).

solution. The growth of t-Se nanowires through a solid–solution–solid process would be considerably limited and the continuous addition of Se atoms to the t-Se seeds would preferentially occur at the circumferential edges of hexagonally or trigonally faceted seeds, leading to the formation of t-Se nanotubes (Fig. 5b). The fact that Se nanotubes can only be obtained at relatively low HAc concentrations supports this mechanism as a high HAc concentration would lead to a fast formation of a large number of a-Se colloids in the solution. Therefore, the key to the success of this approach could be the use of the $C_{12}E_{23}$ micelles to control the concentration of a-Se in the solution.

In summary, large-scale synthesis of single-crystalline selenium nanotubes has been successfully realized for the first time by a novel micelle-mediated solution approach. This low-temperature soft chemical strategy is potentially extendable to other inorganic materials with anisotropic structures. The obtained Se nanotubes might be useful as templates to produce tubular nanostructures of other functional materials^[15] and as small containers for a variety of applications.

Experimental

Selenium nanotubes were synthesized by the dismutation of Na_2SeSO_3 under acidic condition in micellar solutions of the surfactant Brij-35 (poly(oxyethylene(23)) dodecyl ether, $C_{12}E_{23}$, Karl Roth, Germany). In a typical synthesis, a 0.2 M Na_2SeSO_3 solution was first prepared by stirring 0.2 M Se and 0.5 M Na_2SO_3 at approximately 70 °C for 24 h following the literature [18]. Then, 0.4 mL of 0.2 M Na_2SeSO_3 solution was mixed with 4.2 mL acidic solution containing

C₁₂E₂₃ (0.05 g) and HAc (0.2 mmol), resulting in an immediate appearance of red color in the solution, which indicated the formation of amorphous selenium (a-Se) [10]. The mixture was sonicated for 3 h in a normal ultrasonic bath, which was accompanied by an increase in temperature up to ~50 °C and a gradual color change from red to brown and cloudy, indicating a transformation from less stable a-Se to stable t-Se. The resulting solution was further aged for 2 h in darkness at room temperature and the solid product was collected by centrifugation. It was noted that although the sonication process accelerated the formation of selenium nanotubes, it was not a necessary condition for the nanotube formation and similar products could also be obtained without sonication but at higher temperatures (e.g., 80 °C). The final products were characterized by scanning electron microscopy (SEM, FEI STRATA DB235), transmission electron microscopy (TEM, JEOL JEM 200CX), high-resolution TEM (HRTEM, FEI TECNAI F30), and powder X-ray diffraction (XRD, Rigaku Dmax-2000).

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