

## CTAB-controlled Synthesis of One-dimensional Selenium Nanostructures

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(Received April 14, 2004; CL-040408)

Selenium nanowires, nanorods, and nanotubes have been successfully synthesized in aqueous solution by using cetyltrimethyl ammonium bromide (CTAB) as the soft template. The synthesis is performed by controlling CTAB concentration and temperature.

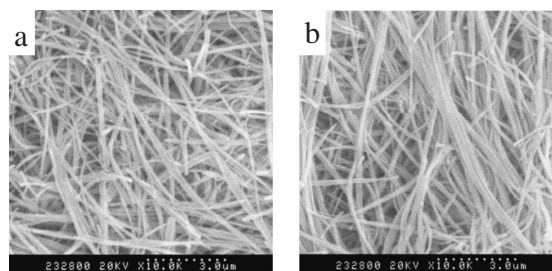
One-dimensional (1-D) selenium (Se) nanostructures have high photoconductivity<sup>1</sup> and would provide new opportunities in fabricating nanoscale optoelectronic devices.<sup>2</sup> On the other hand, the 1-D Se nanostructures may be used as templates for the construction of other 1-D nanostructures which are technologically important materials.<sup>3,4</sup> Thus, the synthesis of 1-D Se nanostructures has aroused considerable interest. Especially, some chemical methods, because of their low cost and potential application for large-scale production, have been actively explored to process Se into 1-D nanostructures.<sup>5-7</sup>

CTAB is a cationic surfactant that could favor the formation of 1-D nanostructures.<sup>8</sup> Recently, SnS, ZnO, and Ag 1-D nanostructures have been prepared with CTAB.<sup>9-11</sup> In this paper, CTAB was firstly used as the soft template for the synthesis of 1-D Se nanostructures. By controlling CTAB concentration and reaction temperature, Se nanowires, nanorods, and nanotubes were prepared. Especially, there is no report about the study of Se nanotubes that were firstly obtained.

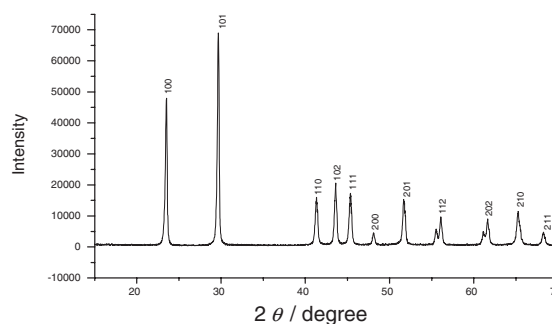
Typically, our experiments were carried out as follows. First, the 2.0 mL of 1 M selenious acid was mixed with 20.0 mL of 0.06 M CTAB aqueous solution. (Alcohol or NaBr was also added into reaction solution for the study of mechanism). Then 4.0 mL of 1 M ascorbic acid solution was added into selenious acid/CTAB mixture at 80 °C (and under ultrasound). After the reaction solution was aged for 3 h, the products were separated from the reaction solution by centrifugation, washed by alcohol and deionized water, and then characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Figure 1a shows the SEM images of the products as-prepared. From the images, it can be seen that uniform Se nanowires with the diameter from 80 to 100 nm (the length up to 200 μm) were obtained. The crystallization and the purity of Se nanowires were studied by XRD that was performed using a Japan Rigaku D/max-RA X-ray diffractometer with graphite monochromatized Cu Kα<sub>1</sub> radiation ( $\lambda = 0.15406$  nm). A scanning rate of 10°/min was applied to the XRD patterns in the  $2\theta$  range of 15–70°. As shown in Figure 2, all the diffraction peaks could be indexed as the trigonal phase of Se. The lattice constants were calculated as  $a = 0.436$  nm,  $c = 0.496$  nm which correspond well to those of the trigonal phase ( $a = 0.434$  nm,  $c = 0.495$  nm) reported in literature.<sup>12</sup> The XRD pattern indicates that the nanowires was a single phase of well-crystallized trigonal Se.

When the ultrasonic irradiation was used at 80 °C, Se nano-



**Figure 1.** SEM images of the Se nanowires obtained: (a) at 80 °C for 3 h; (b) at 80 °C under ultrasound for 1 h.



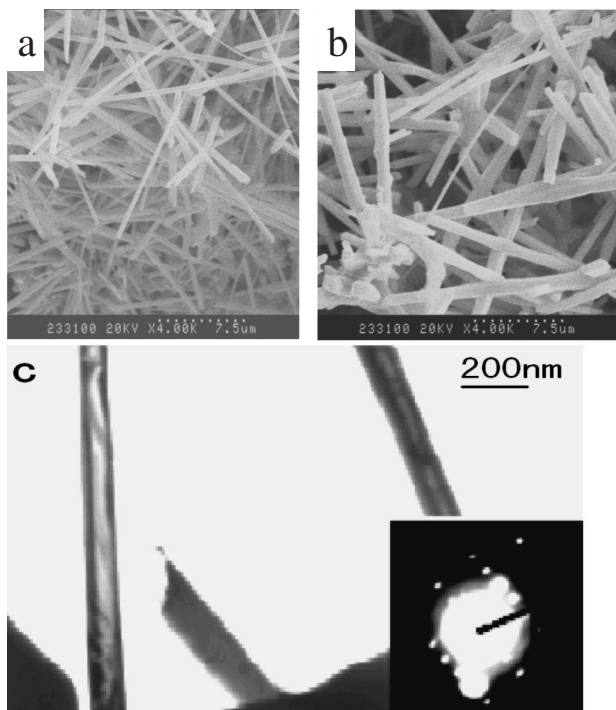
**Figure 2.** XRD patterns of Se nanowires.

wires in bundle were obtained with high yields (as shown in Figure 1b). This result can be explained as follows.<sup>6,13</sup> First, ultrasonic irradiation can dramatically increase reactivity, induce the transformation of amorphous Se to trigonal Se, and improve the yield of products. Second, ultrasonic irradiation may effectively remove the surface coating and cause the agglomeration of Se nanowires. Both the effects resulted in the formation of bundle Se nanowires.

The boost of temperature could speed up the progress of reaction and favor the formation of Se nanowires. When the temperature was increased from 80 to 100 °C, Se nanowires as shown in Figure 1a were obtained within 20 min. At room temperature, it would take several months to get the same products.

It had been shown that CTAB concentration played the major role in determining Se product morphology. With the increase of CTAB concentration, the shapes of Se products changed from spherical nanoparticles to linearly aligned spherical nanoparticles, nanowires and nanorods. Moreover, the diameter of nanorods increased with the boost of CTAB concentration. When CTAB concentration increased up to 0.6 M, some Se nanotubes with thick nanorods were obtained (as shown in Figure 3).

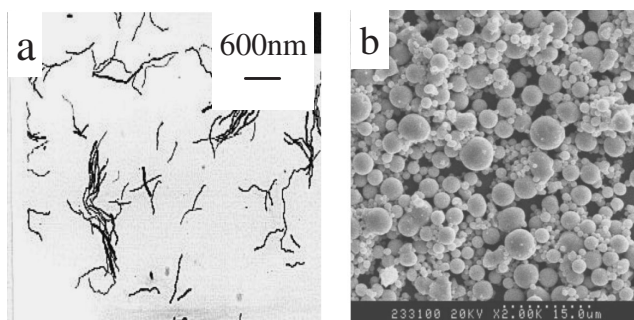
The mechanism about the influence of CTAB concentration on Se product morphology could be speculated as follows. Be-



**Figure 3.** SEM and TEM images of products obtained in different CTAB concentration: (a) 0.08 M; (b) 0.60 M; (c) 0.60 M. Inset in (c) shows an ED pattern of individual Se nanotube.

fore the addition of ascorbic acid solution, the  $\text{SeO}_3^{2-}$  ions with negative charges could be combined with cationic CTAB molecules by electrostatic force. When the ascorbic acid solution was added,  $\text{SeO}_3^{2-}$  ions were reduced to elemental Se in situ. In low CTAB concentration solution, there were spherical micelles or no micelles. Thus the products were linearly aligned spherical nanoparticles whose formation belongs to the directional aggregation mechanism of Se nanoparticles induced by both charge and steric effects of CTAB. With the increase of CTAB concentration, nanowires, or nanorods were produced since the anisotropy of CTAB itself may enhance the anisotropic characteristic of trigonal Se and favor the axis orientation growth of 1-D Se nanostructures. Furthermore, in high CTAB concentration solution, larger seeds were firstly produced because the surface tension of solution (that is, the energy needed to form a new phase) was largely reduced by CTAB. As a result, thick Se nanorods were produced on larger seeds. Se nanotubes may be formed on the soft templates of rod-like CTAB micelles.

This speculation was supported by further experiments. The length of Se nanowires became gradually shorter with the addition of alcohol into CTAB solution, which means the destruction of CTAB function by alcohol (as shown in Figure 4a). Although NaBr could favor the formation of rod-like micelles in CTAB solution,<sup>8</sup> the spherical nanoparticles were only obtained in high NaBr concentration (as shown in Figure 4b). The result could be explained that the inducement of CTAB for the axial orienta-



**Figure 4.** TEM and SEM images of the products obtained in: (a) 50% alcohol; (b) 1.5 M NaBr.

tion growth of 1-D Se nanostructures was weakened by NaBr because  $\text{Br}^-$  ions could tamper the combination of  $\text{SeO}_3^{2-}$  ions with cationic CTAB molecules by electricity field effect.

In summary, we have presented a novel practical approach to the large-scale synthesis of Se nanowires and nanorods by using CTAB as the soft template in aqueous solution. Especially, Se nanotubes were firstly obtained. The synthesis process is simple and controllable. The only requirement is the selection of an appropriate CTAB concentration and a proper temperature.

This work was supported by the National Natural Science Foundation of China (No. 90206037, 20075010), and Doctoral Fund of National Education Ministry of China (No. 20010284030).

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