

Selenium Nanotubes Synthesized by a Novel Solution Phase Approach

Hui Zhang, Deren Yang,* Yujie Ji, Xiangyang Ma, Jin Xu, and Duanling Que

State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027, People's Republic of China

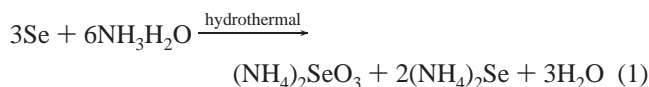
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In this communication, we demonstrate a new approach to well-controlled growth of Se nanowires and nanotubes, which comprises a hydrothermal process and a following sonication. The hydrothermal process was used to derive Se particles of trigonal phase. In the subsequent sonication, if the Se particles were large enough, they were first broken, and then aggregated along the circumferential edge of the gap thus forming Se nanotubes; conversely, the Se particles were not broken and then aligned into nanowires. The high-resolution transmission electron microscopy (HRTEM) proved that both the Se nanotubes and nanowires were single crystalline in nature and $\langle 100 \rangle$ oriented. Based on a series of the TEM observation, a phenomenological mechanism for the elucidation of the controllable growth of Se nanowires and nanotubes is presented.

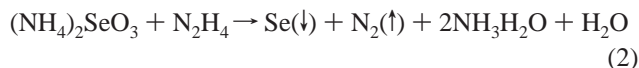
Since the discovery of carbon nanotubes in early 1990s, one-dimensional materials, such as nanowires, rods, or tubes, have attracted much attention due to their significant potential applications.^{1–5} Although most of the advanced methods, such as laser ablation and nanolithography, are capable of fabricating nanostructures with well-controlled sizes, the development of these methods into practical routes to derive large quantity and the low cost of nanostructures still requires great effort.⁶ Chemical methods, i.e., bottom up approach, provide a more promising direction to the synthesis of nanostructures due to low cost, high efficiency, and potential for large-scale production.^{7–11} Recently, most studies have been largely focused on the synthesis of layered structure compounds—for example, boron nitride, MX_2 ($\text{M} = \text{Mo}, \text{W}$), and graphite.^{12–15} Selenium is interesting for a spectrum of applications arising from its many interesting properties as follows: a high photoconductivity (about $8 \times 10^4 \text{ S}\cdot\text{cm}^{-1}$); a relatively low melting point (about 217°C); catalytic activity toward organic hydration and oxidation reaction; intrinsic chirality; high refractive indices and a large birefringence; relatively large piezoelectricity and thermoelectricity; nonlinear optical responses; and a high reactivity toward a wealth of chemicals that can be exploited to convert into other one-dimensional functional materials such as Ag_2Se and CdSe by chemical solutes.^{16,17} Furthermore, it is well-known that the trigonal selenium and tellurium nanowires and nanorods could be directly nucleated and grown from their aqueous solutions without use of any physical templates due to their crystal structures consisting of extended and helical chains. On the basis of this knowledge, Xia and co-workers have successfully fabricated chainlike building blocks materials (Se nanowires, Te nanotubes, and Se/Te alloy nanorods) via refluxing and sonochemical methods.^{18–22} However, these syntheses usually take too much time to grow appreciable quantities of nanostructures. More importantly, to our best knowledge, up to now, preparation of Se nanotubes is still a matter of question. Herein, we describe a solution-phase approach to controllable growth of single crystalline Se nanotubes and nanowires. A very interesting clue for the controllable

growth of Se nanotubes and nanowires has been preliminarily presented on the basis of the experimental results.

Different from Xia's work,¹⁸ we used Se powders as the Se source. The first step of our approach was the formation of selenide in an aqueous and ethanol mixed solution through the reaction of selenium with ammonia under the hydrothermal condition at 200°C :



After cooling to room temperature, a dark-red solution was found, which was different from the case reported in the previous work,¹⁸ because the product is not the a-Se spherical particles but the t-Se spherical particles formed by the following reaction:



Finally, the dark-red solution was placed in a glass beaker and sonicated for 30 min at about 40 kHz, with a power of 60 W. The solution became dark due to the formation of one-dimensional t-Se, which will be verified later.

Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and diffraction (both electron and X-ray) methods were used to characterize the Se nanostructures prepared sequentially by the hydrothermal process for 20 h and sonication for 30 min. The SEM image given in Figure 1a clearly displays the tube structure of Se and the size in lateral dimensions with width of about 200–500 nm. The solid walls of the Se nanotube with a considerably uniform thickness of about 50 nm and the straightness along the longitudinal axis can be further seen from the TEM image as shown in Figure 1b. The selected area electron diffraction (SAED) pattern inserted in Figure 1b manifests itself in sharp spots, implying the single crystallinity of the tube. The Se nanotubes were further characterized by an X-ray diffraction pattern (XRD) and high-resolution transmission electron microscopy (HRTEM). Figure 1c shows the XRD pattern of the Se nanotubes. All diffraction peaks can be indexed according to the trigonal Se with the lattice

* Tel: +86-571-87951667. Fax: +86-571-87952322. E-mail: mseyang@ dial.zju.edu.cn.

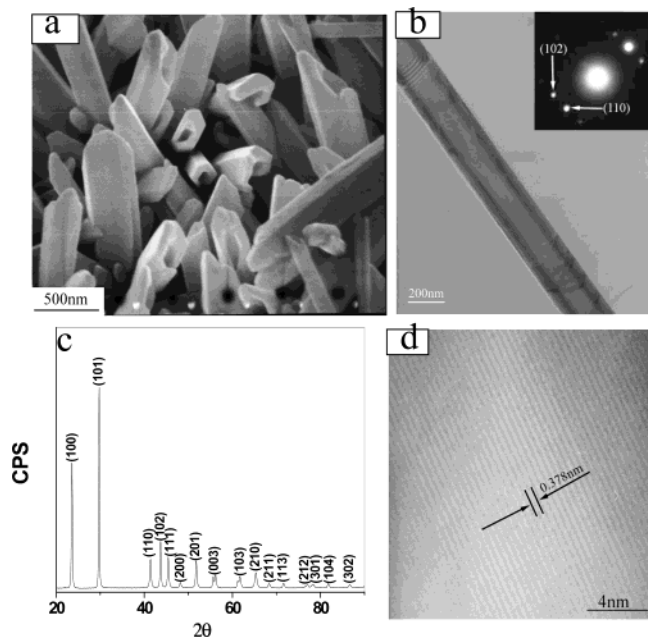


Figure 1. Characterizations of the Se nanostructures formed by the hydrothermal process for 20 h and the subsequent sonication for 30 min. (a) The typical SEM image of the Se nanostructures that exhibit tube-like structure. (b) TEM image of an individual Se nanotube. The SAED pattern (inset) indicated the single crystallinity of the nanotube. (c) XRD pattern of the Se nanotubes. All the diffraction peaks could be indexed according to trigonal Se. (d) HRTEM image of a part of the wall of a Se nanotube. The fringes with a spacing of 0.378 nm correspond to $\{100\}$ planes.

constants $a = 4.366 \text{ \AA}$, $c = 4.953 \text{ \AA}$, which is consistent with the values given in the standard card (JCPDS 06-0362). Compared to the standard card, the (100) peak in Figure 2a is much stronger, indicative of the $\langle 001 \rangle$ oriented growth of the trigonal Se nanotubes. Figure 1d shows the HRTEM image of the part of the wall of a Se nanotube, which reveals the clear fringes of $\{100\}$ planes with a lattice spacing of about 0.378

nm, indicating that the Se nanotube is single crystalline in nature with $\langle 001 \rangle$ orientation.

To substantially understand the growth mechanism of Se nanotubes, we investigated the evolution of Se nanostructures. Figure 2 shows the scenarios for the formation of Se nanotubes prepared by 20 h of hydrothermal treatment and subsequent sonication for different times. Figure 2a illustrates the sphere Se particles with diameters of about 200–500 nm formed by hydrothermal process. The corresponding SAED pattern implies that the Se particles are of trigonal phase, which is different from the a-Se particles prepared by the refluxing method reported in the previous work.¹⁶ After sonicating for 3 min, the larger Se particles in the size of about 500 nm were broken, which can be better seen in the corresponding enlarged picture. With the extension of the sonication, as shown in Figure 2c,d, the broken Se particles as the seeds subsequently aggregated along the circumferential edge of the gap. Because trigonal Se has a highly anisotropic structure, the growth direction is largely confined to the $\langle 001 \rangle$ direction, which is similar to the case of the growth of tellurium nanotube.²⁰ Note that the small Se particles adsorbed around the nanotubes (see Figure 2c,d). It is believed that these small Se particles were consumed by the continuing growth of the nanotubes. Finally, as the sonication proceeded long enough (about 30 min), as shown in the Figure 2e, the Se nanotubes without any adsorbed small particles were formed.

As a matter of fact, we found that the hydrothermal process time was a determining factor for the formation of a Se nanotube, given that the sonication time was long enough. In our experiment, it was determined that the Se nanotubes was formed when the hydrothermal process time was in the range 10–20 h, whereas Se nanowires other than nanotubes were formed when the hydrothermal process time was in the range 6–9 h.

Figure 3 shows the TEM images and XRD pattern of the Se nanowires prepared sequentially by the hydrothermal process for 6 h and the sonication for 30 min. Figure 3a shows the TEM

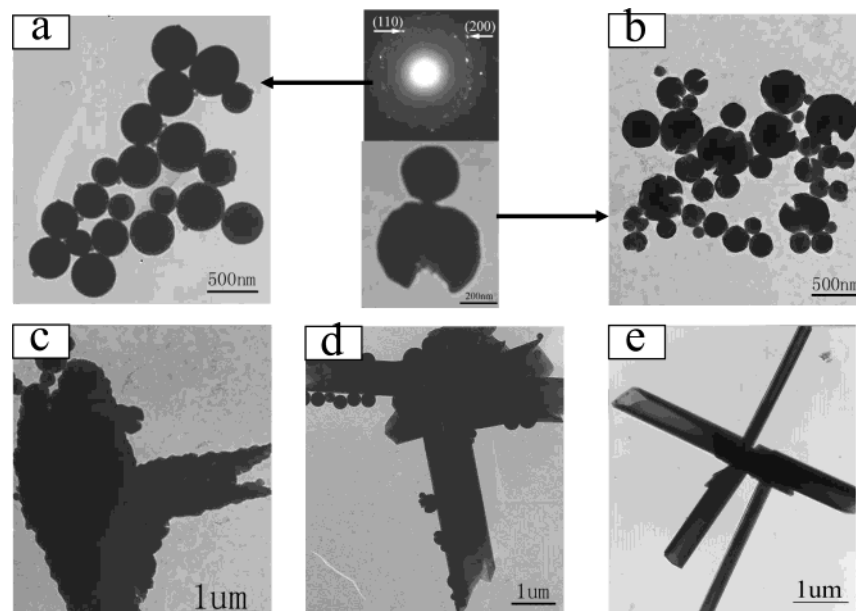


Figure 2. TEM images of Se nanostructures generated by the hydrothermal process for a fixed time of 20 h and the subsequent sonication for different times. (a) Sphere t-Se particles with the sizes of about 200–500 nm generated just by 20 h hydrothermal process. The SAED pattern is attached in the right picture. (b) The large Se particles were broken due to 3 min sonication, whereas the small particles were not broken. This case can be more clearly seen in the enlarged picture attached in the left of Figures 2b. (c) and (d) With the extension of sonication (6 and 9 min), the broken large particles aggregated into tubes along the specific direction while consuming the small particles. (e) Se nanotubes generated after 30 min sonication. Note that no small Se particles adsorbed around the tubes.

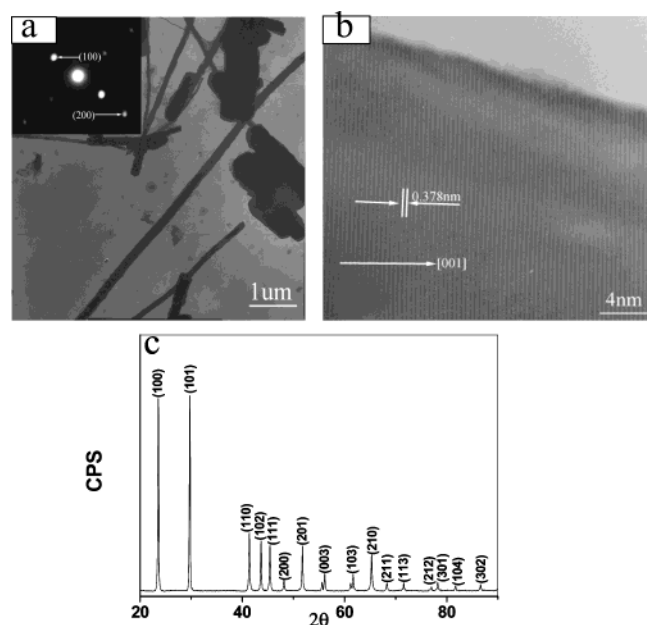


Figure 3. TEM image (a), HRTEM image (b), and XRD pattern (c) of the Se nanowires prepared by the hydrothermal process for 6 h and the subsequent sonication for 30 min.

image of the selenium nanowires. This TEM image shows the nanowires have the lateral dimensions in the range of about 50–200 nm. The SAED pattern (inset) taken from an individual Se nanowire manifests itself in sharp spots, implying that each wire is a single crystal. Figure 3b shows the HRTEM image of an individual Se nanowire, which reveals the clear fringes of {100} planes with a lattice spacing of about 0.378 nm, also indicating that the Se nanowire is single crystalline in nature with <001> orientation. Figure 3c displays the XRD pattern of Se nanowires, which is almost similar to that of the Se nanotubes, as described above.

The evolution of Se nanowires was also investigated in our study. Figure 4 shows the formation process of Se nanowires derived from a 6 h hydrothermal treatment and a subsequent sonication for different times. Due to the shorter hydrothermal treatment, the Se particles shown in Figure 4a were much smaller than those shown in Figure 2a. It is of interest that with the subsequent sonication, the Se particles were not broken but nearly aligned in a line, as shown in Figure 4b. Along with the sonication, much more Se particles aggregated into the nanowires, as revealed in Figure 4c. According to the information given by the HRTEM (Figure 3b), it is believed that the Se nanowires was also <001> oriented.

So far, it is clear that the Se particles formed by hydrothermal process will transformed into Se nanotubes or nanowires by sonication dependent on the size of particles, the reason for which is preliminarily derived below. During the sonication process, the ultrasonic sound waves radiate through the solution causing alternating positive and negative pressures in the liquid medium. Millions of microscopic bubbles form and grow in the negative pressure stage at the site of rarefaction and subsequently collapse and explode in the positive pressure stage, resulting in hot spots that are localized regions of extremely high temperature as high as 5000 K and pressure of up to ~1800 atm and the cooling rates can often exceed $\sim 10^{10} \text{ K s}^{-1}$.^{23,24} Therefore, during the sonication, the crystallized spherical Se particles of low melting point can be locally melted by the hot spots and then bound to each other, which is actually a recrystallization process. In this case, the crystal growth will proceed along the preferred orientation of the *c*-axis because

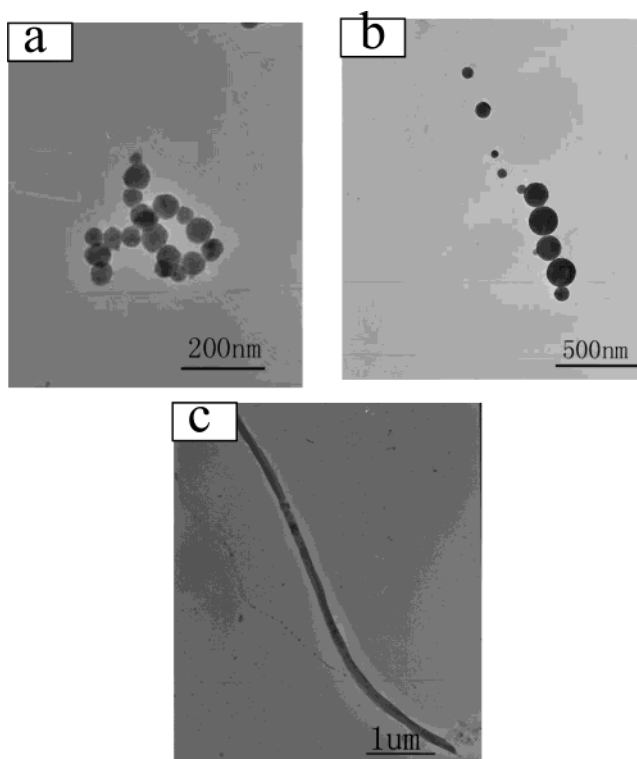


Figure 4. TEM image of Se nanostructures generated by hydrothermal process for a fixed time of 6 h and the subsequent sonication for different times. (a) Se particles with the sizes of about 30–50 nm were generated by just 6 h hydrothermal process. (b) The Se particles were well aligned due to 10 min sonication. (c) With the extension of sonication (30 min), the Se nanowires were generated by the aggregation of Se particles.

the Se particles are of a trigonal phase. Different from the phenomenon reported by Xia's group,¹⁸ in our experiment the crystalline Se spherical particles rather than amorphous ones formed by the hydrothermal process did not aggregate into a larger structure characterized by irregular morphologies during the sonication process but assembled into a one-dimensional nanostructure along a specific direction due to the nature of crystal growth of trigonal Se, as mentioned above. On the other hand, the Se particles will be destroyed by the hot spot and, obviously, the larger particles are much more susceptible in this way. Accordingly, the recrystallization of large Se particles will proceed along the circumferential edge of the broken particles' gap and thus generate a tube-like structure, whereas recrystallization of small Se particles that are not broken creates a wire-like structure.

In summary, we have demonstrated the formation of Se nanotubes by a solution-phase method that is composed of a hydrothermal process and subsequent sonication. The TEM investigation indicated that the hydrothermal process offered the t-Se particles, the size of which determined the morphology of the Se nanostructures formed in the subsequent sonication. The larger Se particles derived from the long time hydrothermal treatment were broken at the early stage of the sonication and then aggregated along the circumferential edge of the broken particles' gap, thus leading to the Se nanotubes formed by the extended sonication. However, the smaller Se particles obtained from the shorter time hydrothermal treatment were not broken in the beginning of the sonication, and therefore, the Se nanowires were formed by the extended sonication. Both the Se nanotube and nanowires are trigonal and <100> oriented, confirmed by XRD and TEM, respectively. It should be pointed out that the exact mechanism for the formation of Se nanotubes

and nanowires by the method presented herein should be further probed, which is now underway of our work. Importantly, the Se nanotubes might be useful as the templates to generate other one dimension functional nanomaterials.

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References and Notes

- (1) Iijima, S. *Nature* **1991**, 354, 56.
- (2) Duan, X.; Huang, Y.; Agarwal, R.; Lieber, C. M. *Nature* **2003**, 421, 241.
- (3) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, 291, 1947.
- (4) Huang, M. H.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Webber, E.; Russo, R.; Yang, P. *Science* **2001**, 292, 1897.
- (5) Han, W. Q.; Fan, S. S.; Li, Q. Q.; Hu, Y. D. *Science* **1997**, 277, 1287.
- (6) Xia, Y. N.; Rogers, J. A.; Paul, K.; Whitesides, G. M. *Chem. Rev.* **1999**, 99, 1823.
- (7) Jiang, Y.; Wu, Y.; Zhang, S.; Xu, C.; Yu, W.; Xie, Y.; Qian, Y. *J. Am. Chem. Soc.* **2000**, 122, 12383.
- (8) Kong, J.; Soh, H. T.; Cassell, A. M.; Quate, C. F.; Dai, H. *Nature* **1998**, 385, 878.
- (9) Liu, B.; Zeng, C. *J. Am. Chem. Soc.* **2003**, 125, 4430.
- (10) Manna, L.; Scher, E. C.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2000**, 122, 12700.
- (11) Bakkers, E.; Verheijen, M. *J. Am. Chem. Soc.* **2003**, 125, 3340.
- (12) Ren, Z. F.; Huang, Z. P.; Xu, J. W.; Wang, J. H.; Bush, P.; Siegal, M. P.; Provencio, P. N. *Science* **1998**, 288, 1105.
- (13) Suenaga, K.; Colliex, C.; Demoney, N.; Loiseau, A.; Pascard, H.; Willaime, F. *Science* **1997**, 278, 653.
- (14) Li, Y. D.; Li, X. L.; He, R. R.; Zhu, J.; Deng, Z. X. *J. Am. Chem. Soc.* **2002**, 124, 1411.
- (15) Remskar, M.; Mrzel, A.; Skraba, Z.; Jesih, A.; Ceh, M.; Demsar, J.; Stadelmann, P.; Levy, F.; Mihailovic, D. *Science* **2001**, 292, 479.
- (16) Henshaw, G.; Parkin, I. P.; Shaw, G. A. *J. Chem. Soc., Dalton Trans.* **1997**, 231.
- (17) Gates, B.; Wu, Y. Y.; Yin, Y. D.; Yang P. D.; Xia, Y. N. *J. Am. Chem. Soc.* **2001**, 123, 11500.
- (18) Gates, B.; Yin, Y. D.; Xia, Y. N. *J. Am. Chem. Soc.* **2000**, 122, 12582.
- (19) Gates, B.; Mayers, B.; Grossman, A.; Xia, Y. N. *Adv. Mater.* **2002**, 14, 1749.
- (20) Mayers, B.; Xia, Y. N. *Adv. Mater.* **2002**, 14, 279.
- (21) Gates, B.; Mayers, B.; Cattle, B.; Xia, Y. N. *Adv. Funct. Mater.* **2002**, 12, 219.
- (22) Mayers, B.; Gates, B.; Yin, Y. D.; Xia, Y. N. *Adv. Mater.* **2001**, 13, 1380.
- (23) Suslick, K. S. *Science* **1990**, 247, 1439.
- (24) Mason, T. J.; Lorimer, J. P. *Sonochemistry: Theory, Application and Uses of Ultrasound in Chemistry*; John Wiley and Sones, New York, 1988.