

New strategies for the synthesis of t-selenium nanorods and nanowires

Ujjal K. Gautam,^a Manashi Nath^a and C. N. R. Rao^{*a,b}

^aSolid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

^bChemistry and Physics of Materials Unit, CSIR Centre of Excellence in Chemistry, Jawaharlal Nehru Centre for Advanced Scientific Research Jakkur P. O., Bangalore 560 064, India. E-mail: cnrrao@jncasr.ac.in; Fax: (+91) 80-8462760

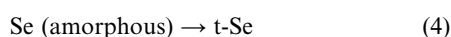
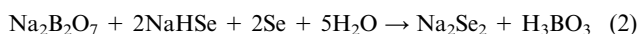
Received 17th July 2003, Accepted 5th September 2003

First published as an Advance Article on the web 16th September 2003

Two different strategies for the synthesis of t-selenium nanorods and nanowires are described, wherein the solution based method involves a reaction of selenium powder with NaBH₄ while the other employs the thermal decomposition of [(CH₃)₄N]₄Ge₄Se₁₀.

Selenium exhibits several useful properties such as high photoconductivity and catalytic activity and has commercial use in photocopiers and rectifiers.¹ It also undergoes an interesting amorphous to t-phase transition.² Nanorods of selenium of different diameters from 20 nm to several hundred nanometers have been prepared by laser ablation of selenium powder.³ Se nanowires have been prepared by refluxing selenous acid with N₂H₄.² Se nanorods are also prepared by the reduction of sodium selenate using cytochrome c₃.⁴ The solution methods generally yield amorphous selenium as the initial product which then transforms to t-selenium. Xie *et al.*⁵ have recently reported the spontaneous transformation of monoclinic Se microballs to trigonal nanorods in ethanol solution. In this communication, we describe a simple and novel solution based synthesis wherein selenium powder is first reacted with NaBH₄ to yield NaHSe⁶ in solution which then transforms to amorphous selenium.

In a typical room temperature reaction, 0.025 g (0.32 mmol) of selenium was mixed with 20 ml of deionized water in a three necked round bottom flask. 0.030 g (0.81 mmol) of NaBH₄ was added to this mixture and the flask was immediately purged with nitrogen gas in order to create an inert atmosphere. The entire selenium dissolves in water within 60 minutes giving rise to a clear colourless solution. The colour of the solution starts turning red thereafter. We propose the following reaction scheme for the formation of Se:



We see that in this method, selenide ion acts as the source of Se while the other methods reported in the literature use the oxyanions with a positive charge on Se as the source. The nascent selenium produced in step (3) imparts the wine red colour to the aqueous solution. On standing for a few hours the solution transforms into amorphous Se in colloid form. A small

portion of the dissolved selenium precipitates as the t-Se nanoparticles which act as nuclei to form one-dimensional nanorods. The amorphous Se colloid dissolves slowly as the nanorods increase in length. In the process, the red colour of the solution fades away and the dark selenium nanorods settle down.

In Fig. 1a, we show the SEM image of nanorods formed at 30 °C after 24 h. The diameter of the rods is around 150 nm. TEM images show rods of smaller diameters along with a majority of bigger ones (see the inset in Fig. 1a). Fig. 1b and the inset shows SEM images of the rods after 96 h and 15 days respectively. The rods grow in length with time while the diameters remain almost the same. The high resolution TEM (HRTEM) image shown in the in Fig. 1c reveals that the rods are single crystalline, devoid of crystallographic defects. The lattice spacing of 4.9 Å in the HREM image along the growth

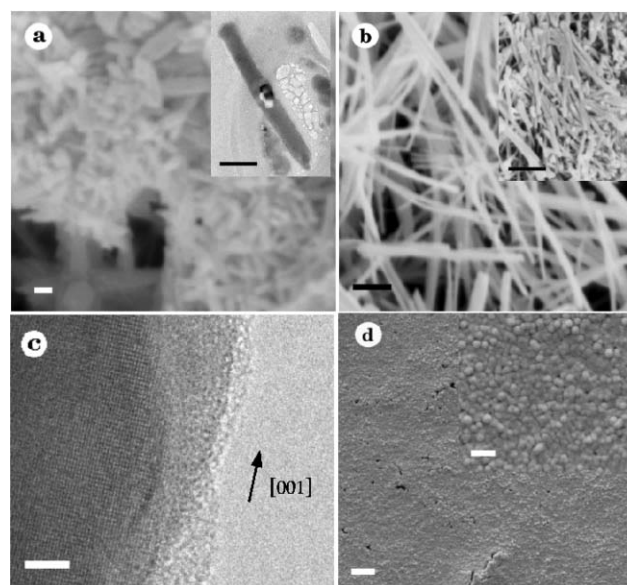


Fig. 1 SEM images of t-Se nanorods. (a) After 24 h (bar = 300 nm). The inset shows TEM image of one of the rods (bar = 200 nm). (b) After 96 h (bar = 500 nm). The inset shows SEM image of the nanorods after 15 days (bar = 1 µm). (c) The HRTEM image of one of the nanorods (bar = 5 nm). The growth direction is shown by an arrow. (d) Low magnification SEM image of a free standing film of t-selenium nanoparticles (bar = 1 µm). The inset is a high magnification SEM image of the same film (bar = 300 nm).

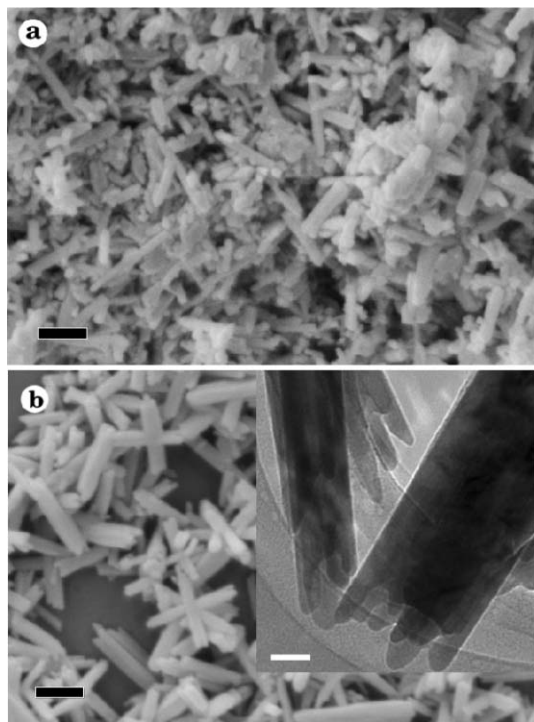


Fig. 2 SEM images of t-Se nanorods synthesized at (a) 0 °C (bar = 500 nm) and (b) at 30 °C after dilution. The inset is a TEM image showing a bundle of nanorods of diameter 20 nm (bar = 50 nm).

direction corresponds to the separation between the (001) lattice planes, showing thereby that the growth direction is along the *c* axis. Along with the nanorods, we observe the formation of nanoparticles of t-Se which assemble on the water surface to produce free-standing films of nanoparticles. Fig. 1d shows such a film which is intact upto several microns. We obtained shorter nanorods when the reaction mixture was quenched at 0 °C for 96 h (Fig. 2a). The diameter of the nanorods could be decreased by diluting the reaction mixture. Thus, 20 nm nanorods were obtained when the reaction mixture was diluted four times. These nanorods assemble in bundles as shown in Fig. 2b (see the TEM image in the inset of Fig. 2b).

The Se nanorods were characterized by powder X-ray diffractometer (XRD) as well as by Raman and X-ray photoelectron spectroscopy (Fig. 3). The powder XRD pattern could be indexed as the trigonal phase with the (001) peak being more intense due to orientation effects. The Raman band found at 239 cm^{-1} arises from the vibration of the helical Se chains.⁷ The absence of boron and sodium in the samples was confirmed by X-ray photoelectron spectroscopy, the peak at 55.2 eV corresponding to the Se⁰ (2p) level.

We have observed an interesting morphology of t-Se when the synthesis was carried out under hydrothermal conditions or in the presence of a capping agent. Use of polyvinylpyrrolidone leads to a flowery morphology (Fig. 4a). The magnified SEM image (see inset) shows non-homogeneous diameters of the rods. However, the reaction carried out under solvothermal conditions gives a scroll-type morphology, with a wall thickness of the order of 100 nm (Fig. 4b).

In addition to the above solution method, we have also found another way of obtaining t-Se nanowires based on the thermal decomposition of $[(\text{CH}_3)_4\text{N}]_4\text{Ge}_4\text{Se}_{10}$, prepared by the literature procedure.⁸ When this compound was thermally decomposed in a furnace at 600 °C under argon gas flow, a black product was obtained at the outlet of the reaction tube. The product contained nanowires of t-Se, as seen in the TEM image shown in Fig. 5a. The yield of the nanowires by this

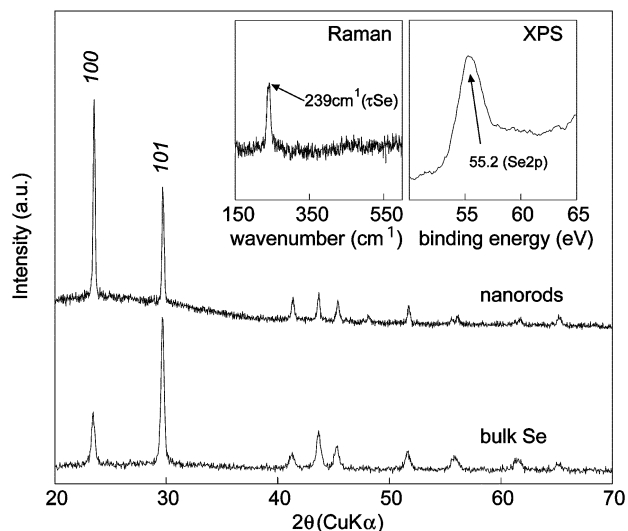


Fig. 3 Powder XRD patterns of t-Se nanorods and bulk selenium used as the starting reagent. In the inset, the Raman and XPS spectra of the nanorods are shown.

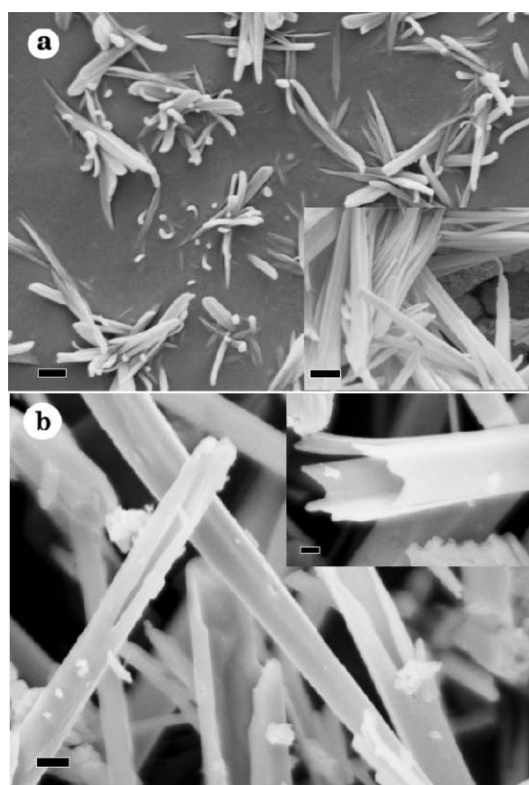


Fig. 4 SEM images of (a) PVP-capped selenium (bar = 1 μm). The inset is a magnified SEM image of one of the bundles (bar = 1 μm). (b) Scroll-type morphology of t-Se obtained under hydrothermal conditions (bar = 1 μm). The inset shows a high magnification SEM image of one of the scrolls (bar = 200 nm).

method is high, nearly 90%. The nanowires have diameters of 30 to 80 nm, and lengths of several microns. The layer separation of 3.8 Å estimated from the HRTEM image (Fig. 5b) matches the (101) layer separation of t-Se. The ED pattern shows the single crystalline nature of the nanowires and the spots could be indexed to (101) and (100) planes. From the HRTEM and ED patterns, it is concluded that the growth direction of the nanowires is along the *c* axis. The mechanism of formation of Se by this method involves the decomposition of the precursor to yield GeSe_2 and Se, the latter subliming

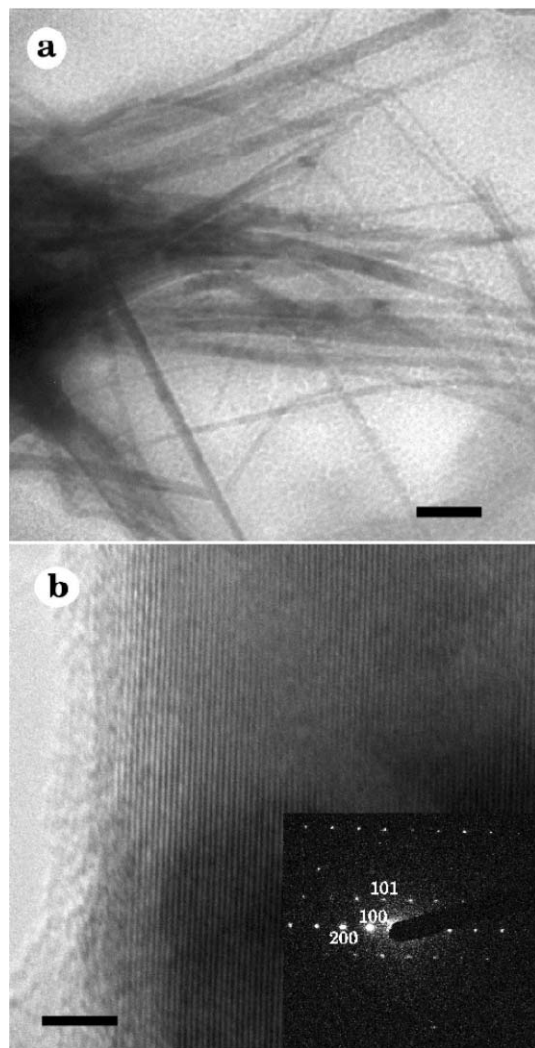


Fig. 5 (a) TEM image of the selenium nanowires obtained by the thermal decomposition of the precursor (bar = 100 nm). (b) HREM image of a nanowire (bar = 5 nm). The inset shows the ED pattern of a nanowire.

from the reaction product and collecting at the cooler zone of the reaction tube.

In conclusion, we have been able to synthesize t-Se nanorods and nanowires by two new independent procedures. The procedures are attractive because of their simplicity.

Acknowledgements

UKG thanks the Council of Scientific and Industrial Research, India for a senior research fellowship.

Notes and references

- 1 *Selenium*, R. A. Zingaro and W. C. Cooper, eds., Van Nostrand Reinhold, New York, 1974.
- 2 B. Gates, B. Mayers, B. Cattle and Y. Xia, *Adv. Funct. Mater.*, 2002, **12**, 219.
- 3 Z. Y. Jiang, Z. X. Xie, S. Y. Xie, X. H. Zhang, R. B. Huang and L. S. Zheng, *Chem. Phys. Lett.*, 2003, **368**, 425.
- 4 A. Abdelouas, W. L. Gong, W. Lutze, J. A. Shelnett, R. Franco and I. Moura, *Chem. Mater.*, 2000, **12**, 1510.
- 5 S. Y. Xie, C. F. Wang, X. H. Zhang, Z. Y. Ziang, Z. X. Xie, Z. Q. Tian, R. B. Huang and L. S. Zheng, *J. Mater. Chem.*, 2003, **13**, 1447.
- 6 D. L. Klayman and T. S. Griffin, *J. Am. Chem. Soc.*, 1973, **95**, 197.
- 7 G. Lucovsky, A. Mooradian, W. Taylor, G. B. Wright and R. C. Keejer, *Solid State Commun.*, 1967, **5**, 113.
- 8 H. Ahari, A. Garcia, S. Kirby, G. A. Ozin, D. Young and A. J. Lough, *J. Chem. Soc., Dalton Trans.*, 1998, 2023.