Synthesis of Novel Selenium Tubular Structure

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Tubular selenium has been synthesized successfully by reducing selenious acid with ascorbic acid in the presence of primary amines ($C_nH_{2n+1}NH_2$ with $10 \leq n \leq 16$) at room temperature.

The discovery of carbon nanotubes in 1991[1] has greatly initiated intense experimental and theoretical interest in such tubular structures. Tubular materials are envisaged for potential applications in the synthesis of designed catalysts, photonic band gap materials, chemical separations media and as selective adsorbents.[2,3] However, most considerable efforts have been placed on the materials commonly having sheetlike (layered) structural features, such as carbon-based substances,[4] sulfide,[5] and nitride.[6] It is still a challenging field for chemists or materialists to prepare tubular crystals from materials without sheetlike building blocks.

Selenium is well-known for photoelectrical and semiconducting properties. It is used as rectifiers, solar cells, photographic exposure meters, and xerograph. Selenium also has a high reactivity towards a wealth of chemicals that can be potentially exploited to convert selenium into other functional materials. For example, Ag_2Se could be prepared by reacting single crystalline selenium with $AgNO_3$ aqueous solution.[7] Recently, Abdelouas and his co-workers synthesized selenium nanowires by the use of protein cytochrome c_3 to reduce selenate.[8] Iris et al. reported the work on preparing nanostructured mesoporous selenium films by electrodeposition.[9] Gao's research group synthesized hollow sphere selenium nanoparticles by in-situ template interface reaction.[10] Xie et al. synthesized selenium tubular single crystals by solvothermal route.[11] Of very late, Gates et al. prepared trigonal selenium nanowires by aging amorphous selenium in the dark.[12] This synthetic process involved one-dimensional anisotropic growth on seeds of trigonal selenium that were generated in the same reaction solution through homogeneous nucleation, selenium atoms being provided continuously through the slow dissolution of amorphous colloidal selenium particles. It was of great interest to develop a solution phase route to prepare trigonal selenium tubular structures. We have indeed found it feasible to obtain tubular selenium by a simple solution-phase route.

In this communication, selenious acid was used as selenium precursor and ascorbic acid as reductant. The use of ascorbic acid in the synthesis originates from the previous study. First, the reaction between selenious acid and ascorbic acid was mild. Second, no by-product was introduced into the system, which may influence the interaction between selenium atom and long chain primary amine. A typical procedure is as follows. 0.360 g of ascorbic acid was introduced into 30 mL aqueous solution containing 0.128 g of selenious acid and 1.0 g of primary amine ($C_nH_{2n+1}NH_2$ with $10 \leq n \leq 16$) at temperature 10 °C, then the mixture was heated to 80 °C and kept at this temperature for 30 min. The white turbid mixture quickly became brick red, then slowly turned into gray black. All the steps above were performed under magnetic stirring. Finally, the resultant sample was centrifuged, washed with distilled water and absolute alcohol, and then dried in air before further characterization.

The crystal structure and composition of the obtained sample were analyzed by X-ray diffraction (XRD) on a Japan Rigaku D/MAX-2400 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å), at a scanning rate of 0.02° s^{-1} in the 2θ range of 20° to 80°. Figure 1 shows a typical XRD pattern for as-obtained sample. All the diffraction peaks, within experimental error, have a one-to-one correspondence to those of the bulk trigonal selenium (JCPDS card no. 06-362). The morphology and size were characterized by a JSM-5600LV scanning electron microscope. Figures 2A and B displayed hollow tubes with inner and external diameter of ca. 0.8 µm and 2 µm, and length of 10 µm. Some irregular spherical agglomerates were also observed. The yield of the tubular selenium was ca. 30%.

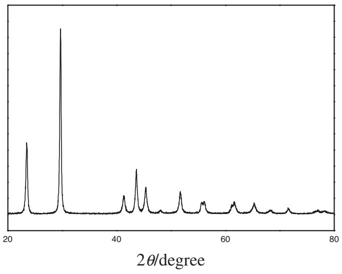

Figure 1. XRD pattern for selenium sample prepared at 80 °C.

Though the exact growth mechanism is still under investigation, our experiment results indicated that the one dimensional characteristics of the helical chains in the trigonal phase and the chain length of primary amine both played important roles in the formation of tubular structure. There have been some evidences through extensive and careful observations. For example, the coexistence of some unclosed structure in a single tubular selenium, as shown in Figure 2C, indicated that the growth of tubular selenium can not be determined by the rolling mechanism as the formation of WS_2 nanotubes.[13] Secondly, the unclosed tube in Figure 2D, in a way, also is helical. It seems feasible that this microscopic helicity could be reflected in the macroscopic helicity.

It is rational to believe primary amines will readily chelate selenium atom, since selenium is soluble in ethylenediamine. To understand the role of amine in the tubular formation, we designed a series of related experiments to test it. In order to weaken or eliminate the interaction between amine and selenium, 1 mL of 6 M hydrochloric acid was introduced into the reaction system. The resultant selenium displayed pure spherical

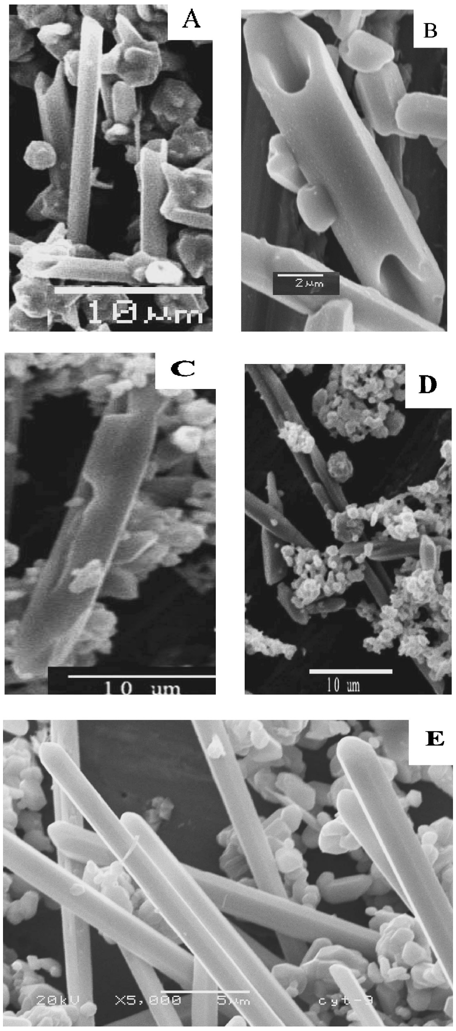

Figure 2. SEM images of (A) selenium tubes prepared in the presence of *n*-decylamine; (B) the magnification of an individual selenium tube; (C) tubular selenium with some unclosed place; (D) unclosed tube show helical; (E) selenium rods prepared in the presence of *n*-octylamine.

morphology. It was believed that intense coordination between amine (Lewis base) and hydrochloric acid might influence interaction between amine and selenium dissolved in water. It was also found that trigonal selenium nanorods were obtained as shown in Figure 2E, when we substituted long chain amines ($C_nH_{2n+1}NH_2$, $10 \leq n \leq 16$) with short chain amines ($C_nH_{2n+1}NH_2$, $n < 10$), while the other conditions were kept constant.

In summary, we have succeeded in preparing selenium tubular structure. We believe that this synthetic strategy, using the helicity of materials to synthesize tubular structure, is potentially extendable to prepare other tubular inorganic materials. Intensive investigation is under progress in our lab oratory.

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