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# Phase-Controlled One-Dimensional Shape Evolution of InSe Nanocrystals

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Received August 21, 2006; E-mail: sson@skku.edu

Nanocrystalline metal selenide semiconductors have attracted considerable attention because of their size-dependent optical and electrical properties. The shape dependence of these properties has prompted the development of synthetic routes for anisotropic nanomaterials.[1] Among the many metal selenides known, indium selenide has been recognized as a promising material for photovoltaic applications such as solar cells.[2] Accordingly, there has been considerable effort directed at the phase-selective preparation and fabrication of this material. Most research has been confined to the bulk material or to thin films due to limitations with available synthetic routes. The synthetic difficulty encountered with InSe arises from the limited accessibility range of InSe within the In−Se phase diagram.[3]

Usually, InSe has a hexagonal phase (B in Figure 1) and forms a layered structure.[4] InSe can be used as a binary source for preparing diverse ternary derivatives ($MInSe_2$, M = Cu, Ag), which are also promising optoelectric materials.[5] Their common phases are tetragonal as shown in Figure 1A. Interestingly, cubic-phase InSe (C in Figure 1) is quite rare not only in the bulk state but also in nanosized materials.[6] Nanosized InSe has been the subject of a few reports.[7] However, as far as we aware, there is no report on colloidal InSe nanowires. This paper reports the one-dimensional shape evolution of cubic InSe nanocrystals through phase control.

The key strategy of the phase-controlled synthesis of InSe nanowires is the use of the *poor solubility* of Se powder in oleylamine. Se powder is most often used as the Se source in the synthesis of metal selenide nanocrystals. In solution-phase synthesis, one of the technical problems with Se powder is its poor solubility in common solvents, including conventional surfactants with long hydrocarbon chains.[8] Several smart methods for the in situ generation of secondary soluble Se sources have been developed. For example, trialkylphosphine selenide can be generated by dissolving Se powder in trialkylphosphine.[9] In a preliminary solubility test, it was found that Se powder is insoluble in oleylamine at <205 °C and begins to dissolve rapidly to form a yellow color just above this temperature. On the basis of this observation, two different synthetic routes were designed in this study: increase in the reaction temperature above 205 °C *with and without dissolving selenium beforehand*. In the latter case, one can speculate that Se powder can function as a Se source above 205 °C.

In a typical synthesis, 0.10 g (0.45 mmol) $InCl_3$ and 0.043 g (0.54 mmol) Se powder was added to 9 mL of well-dried oleylamine at 110 °C, and the reaction temperature was increased rapidly to 215 °C. At this temperature, the reaction mixture was stirred for 5 h. After cooling to room temperature, the reaction mixture was poured into a methanol solution. The chocolate-brown precipitates were retrieved by centrifugation. As shown in Figure 2a, the TEM image of the synthesized nanocrystals showed one-dimensional wires, 7.8 nm in diameter and ~5 μm in length. Additional TEM images (please refer to Figure S1 in the Supporting Information) show well-packed nanowires, which verify the monodispersion of their diameters. Energy dispersive X-ray analysis (EDX) attached to a field emission scanning electron microscope (FE-SEM) revealed the synthesized indium selenides to have a In/Se ratio of 1:1 (Figure 2b). Interestingly, the powder X-ray diffraction pattern (XRPD) was clearly indexed to cubic-phase InSe (Figure 2c).

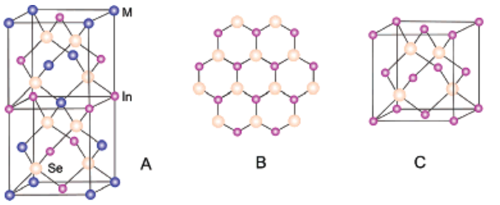

***Figure 1.*** Structures of (A) tetragonal $MInSe_2$, (B) hexagonal InSe, and (C) cubic InSe.

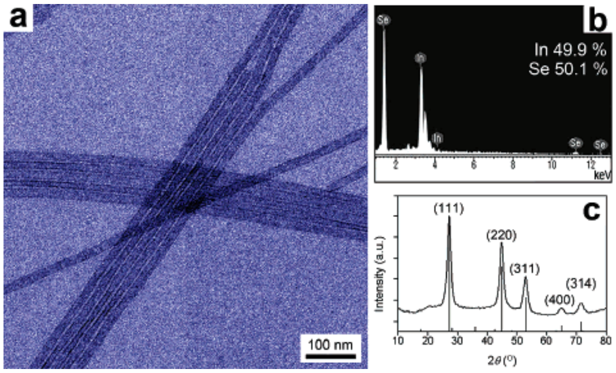

***Figure 2.*** (a) TEM image, (b) EDS spectrum, (c) powder XRD pattern of cubic InSe nanowires with 7.8 nm diameter.

The diameter of the nanowires could be controlled by varying the amount of Se. Thinner (2.5-nm diameter) and longer (~10 μm) wires were formed when the amount of Se was increased to 0.054 g (0.68 mmol) (Figure 3e). A decrease in the amount of Se (0.036 g, 0.46 mmol) caused the formation of thicker (16-nm diameter) and shorter (62 nm length) nanorods (Figure 3f). The concentration of Se can affect the evolution of the shape of nanocrystals because each crystal plane has a different chemical reactivity for Se.[10] In our case, an adequate Se supply appears to encourage the growth in the length direction. A HR-TEM was used to determine the growth direction of the nanowire. As shown in Figure 3d, the nanowires grew in the direction of the (111) lattice plane which is the most common elongation direction in the cubic structure.[11,12]

Although it is not common, there have been a significant number of reports on the one-dimensional (1D) cubic-phase nanomaterials.[12] Time-chasing TEM studies of 2.5-nm diameter nanowires were carried out to obtain information on the growth mechanism of this system. When the reaction was quenched at 200 °C, the precipitates contain almost no detectable particles. The sample taken at 215 °C

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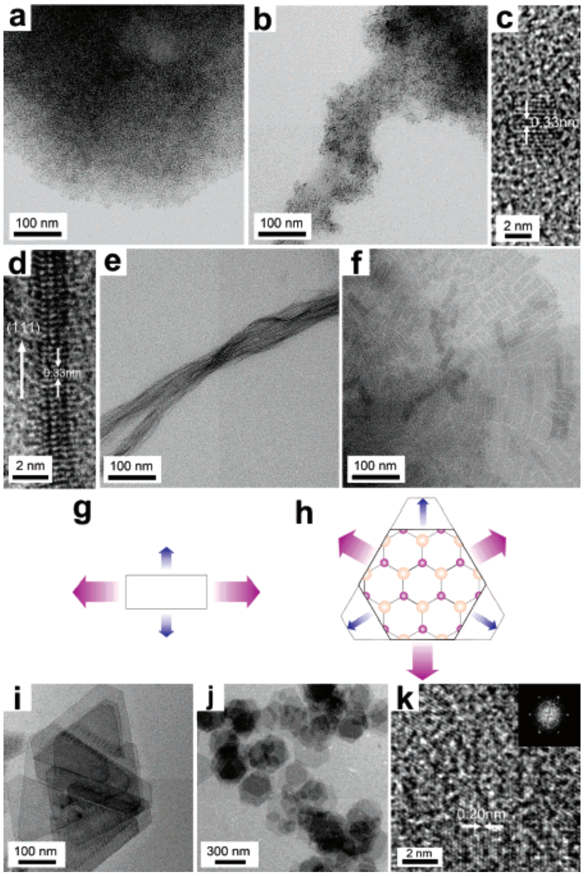

***Figure 3.*** Time-chasing TEM studies of 2.5-nm diameter cubic nanowires: immediately at 215 °C (a), after 2 h (b), after 5 h (e); HR-TEM images of small rods (c) and nanowires (d); TEM image of cubic InSe nanorods, 16-nm in diameter (f). Cartoons explaining growth direction of nanowire (g) and nanoplates (h): violet color shows an enhanced growth direction by sufficient Se supply. TEM images of hexagonal phase InSe; triangular (i) and hexagonal (j) nanoplates; HR-TEM image of hexagonal InSe nanoplates (k).

showed 2.5 nm × 5.0 nm sized small rods (Figure 3a). Their somewhat broad XRPD pattern matched perfectly with the cubic phase. The HR-TEM image of the small rods also clearly showed a 0.33 nm *d*-spacing along the length of the wires (Figure 3c). After 2 h aging, the formation of nanowires with small rods could be observed (Figure 3b). Five hours later, there were only wires (Figure 3e). During growth, there appeared to be a dramatic change in length, and there was no change in the diameter of the wires. Similarly sized nanorods were observed in the early stages and after 4 h. Therefore, oriented attachment can be a more reasonable growth mechanism. There have been recent explanations on the formation of cubic-phase nanowires by dipole-induced oriented attachment.[13]

Figure 3(i−k) shows the control experiments showing the formation of 2D hexagonal phase InSe nanoplates.[14] The main difference in the experimental conditions from those of cubic InSe nanowires was that Se was dissolved in oleylamine before temperature increase, which decreased the formation temperature of nanocrystals.[15] After heating the Se powder (0.054 g, 0.068 mmol) in oleylamine (9 mL) above 250 °C, the solution was cooled to 110 °C. $InCl_3$ (0.10 g, 0.45 mmol) was then added, and the reaction temperature was increased rapidly to 215 °C. The TEM images of precipitates showed 263-nm triangular plates with a 1.8-nm thickness (Figure 3i). Their XRPD pattern was indexed as the hexagonal phase of InSe (JCPDS No. 75-1008). Fast Fourier transformation (FFT) of the HR-TEM clearly shows the hexagonal phase (inset in Figure 3k). EDX analysis by FE-SEM also supports the 1:1 stoichiometric ratio of In to Se. Interestingly, hexagonally shaped nanoplates were obtained when the concentration of the reactants was increased (Figure 3j). As shown in Figure 3h, the structure projecting through the 00l plane of the hexagonal phase has two types of growth directions which are known to have a different reactivity toward the supply of Se.[10] One direction can grow faster with insufficient Se. However, two directions can grow equally with sufficient Se. Therefore, the increased amount of Se changed the shape of the synthesized nanoplates from triangular to hexagonal.

Low-temperature kinetically controlled synthesis is widely used to obtain 1D metal selenide nanocrystals because this reaction condition can differentiate the reactivity of each crystalline plane.[16] In this report, comparatively, obtaining an appropriate high reaction temperature for formation of nanocrystals using poor solubility of Se powder in oleylamine induced the generation of the unusual cubic phase of InSe to form nanowires. The highly monodisperse diameters of the wires could be controlled by varying the amount of Se. It is believed that this experimental condition can be extended to phase-selective solution-phase synthesis of other metal selenides. The physical properties such as conductivity and optical properties of the cubic InSe nanowires are currently under investigation.

**Acknowledgment.** This work was supported by the Hydrogen Energy R&D Center, a 21st Century Frontier R&D Program, funded by the Ministry of Science and Technology of Korea. K.H.P. thanks the Korea Research Foundation Grant (MOEHRD) (KRF-2005-005-J11901).

**Supporting Information Available:** Experimental details, additional TEM images, and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0660711