One-Pot Synthesis of New-Phase AgInSe₂ Nanorods

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In the past decade, the recognition of the strongly size- and shape-dependent physical−chemical properties of inorganic materials at the nanoscale[1] has stimulated efforts toward the synthesis of nanocrystals in a systematic and controlled manner.[2] To date, many colloidal semiconductor, magnetic, and noble metal nanocrystals with interesting properties differing from those of the bulk materials have been successfully synthesized.[3]

The potential applications of I−III−VI chalcopyrites for nonlinear optical devices and photovoltaic solar cells have long been recognized and studied.[4] AgInSe₂, a semiconductor with a band gap of 1.19 eV, is a ternary analogue of CdSe which has been used for a number of electronic devices.[5] Extensive studies on the electrical and optical properties of AgInSe₂ have been carried out.[6] So far, most of the studies are confined to bulk and thin film AgInSe₂ due to the limitation of the available synthetic methods.[7]

In this communication, we report a novel one-pot synthesis of close to monodispersed, one-dimensional (1D) AgInSe₂ nanorods (as shown in Figure 1) in which the single-source precursor is thermally decomposed in mixed amine and thiol solution. In addition, the morphology of the nanoparticles has been turned from a 1D rodlike structure to close to sphere-shaped nanoparticles. Usually tetragonal or cubic AgInSe₂ are the thermodynamically stable products in most of the syntheses.[8] Our synthetic method yields a previously unknown orthorhombic phase, AgInSe₂, which is isostructural with the well-known AgInS₂ (JCPDS-00-025-1328) phase. The synthesized nanoparticles can be dispersed freely in organic solvents such as toluene, CHCl₃, or hexane.

Previously, we have demonstrated that metal selenocarboxylates are good single precursors to prepare metal selenide nanoparticles.[9] We also found that amine could lower the thermal decomposition temperature of the precursor and facilitate the formation of nanoparticles at low temperature.[9b] Oleylamine (OA) and dodecanethiol (DT) have been widely used as surfactants for synthesizing various nanoparticles, and they are often reported as reagents that promote the anisotropic growth of nanoparticles.[10] Hence, we choose OA and DT as our reaction medium for synthesizing AgInSe₂ nanoparticles.

In a typical experiment, 0.03 mmol (50 mg) of [(PPh₃)₂AgIn-(SeC{O}Ph)₄][11] was added to a flask containing both OA (1.10 mL, 3.37 mmol) and DT (0.81 mL, 3.37 mmol). The precursor dissolved immediately and formed a black solution. This solution was then degassed for 15 min in a vacuum and heated to 185 °C in an oil bath for 17 h in an Ar atmosphere. At the end of the reaction, a black precipitate was found at the bottom of the flask. A small amount of toluene and a large excess of EtOH were added to the reaction solution, and AgInSe₂ nanocrystals were separated from the reaction solution by centrifugation. The nanocrystals were washed with EtOH, dried in a desiccator, and used for structural
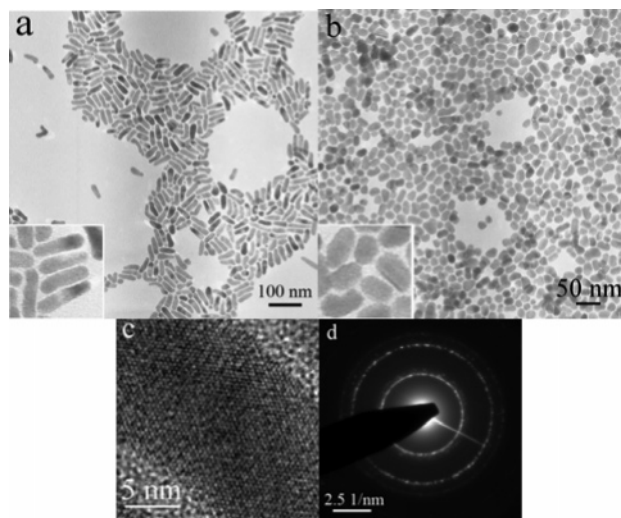

Figure 1. Low-magnification TEM images of (a) AgInSe₂ nanorod, (b) AgInSe₂ nanocrystal. (c) HRTEM micrograph showing the crystal lattice of an individual nanorod. (d) SAED pattern of AgInSe₂ nanorod.

characterization by X-ray powder diffraction (XRPD) and transmission electron microscopy (TEM).

As demonstrated in Figure 1a, the synthesized AgInSe₂ nanoparticles form a 1D rodlike structure. The synthesized nanorods are close to monodispersed with dimensions of (50.3 ± 5.0) nm × (14.5 ± 1.8) nm (measured from the TEM images based on 350 nanorods). The average aspect ratio of the synthesized nanorods is 3.5 ± 0.6. Figure 1c shows a HRTEM micrograph of an individual nanorod where the lattice fringes show that the nanoparticles are well crystallized. It is observed that the nanorods do not grow on a preferred axis. As the reaction temperature is increased to 250 °C, only irregularly shaped AgInSe₂ nanoparticles are obtained after 2 h of heating as shown in Figure 1b. It is likely that the precursor is less stable in the amine solution at high temperature and that less monomer is available to promote the anisotropic growth of nanocrystals.[2a] We found that both DT and OA are equally important in the synthesis of AgInSe₂ nanorods. By heating the precursor in OA alone, irregularly shaped AgInSe₂ particles (resembling melted particles) are obtained with unidentified impurities as indicated from their XRPD pattern. In the case of heating with DT alone, only bulk AgInSe₂ is obtained.[11] FTIR and EDX analysis confirmed that the majority of the surface of the nanorods is capped by OA with a slight amount of DT.[11] Thus, we propose that the OA acts as both activating agent[9b] and capping agent. As for DT, it may guide the particles to grow in a 1D manner. The growing mechanism of the nanorod is under investigation. When OA is replaced with an equal amount of hexadecylamine (HDA), identical AgInSe₂ nanorods are obtained.[11] This shows that the morphology of the AgInSe₂ nanocrystals is governed by the DT. When the reaction time is shortened from 17 to 1.5 h, small

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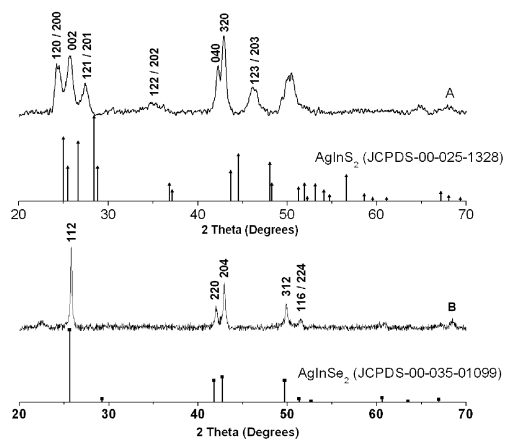
Figure 2. (A) XRPD pattern of AgInSe$_2$ nanorods obtained from OA and DT at 185 °C. (B) Bulk AgInSe$_2$ obtained from pyrolysis of the precursor.

nanorods mixed with polyhedron-shaped AgInSe$_2$ nanoparticles are obtained as shown in the TEM image.[11] To our surprise, the diameter of the nanorods remains unchanged on prolonged heating.

An XRPD pattern of the synthesized AgInSe$_2$ nanorods and the bulk AgInSe$_2$ (synthesized by pyrolyzing the precursor in a vacuum) is shown in Figure 2. The broadening of the diffraction peaks is characteristic of nanoparticles. As mentioned earlier, 12 types of AgInSe$_2$ have been reported.[8] However, the XRPD patterns of the synthesized AgInSe$_2$ nanorods do not match any of the patterns of the reported AgInSe$_2$ structures, not even that of the most common tetragonal AgInSe$_2$ (JCPDS-00-035-01099). Careful examination of the XRPD pattern reveals that it resembles the XRPD pattern of orthorhombic AgInS$_2$ with a consistent shift of the peaks to low angles. By using the cell parameters of orthorhombic AgInS$_2$ as a reference, we have calculated a new set of cell parameters for the synthesized AgInSe$_2$ nanorods.[11] With the new set of parameters, all the diffraction peaks can be indexed accordingly, as shown in Figure 2. Hence, the synthesized nanorods are a new phase of AgInSe$_2$ that is isostructural with the known orthorhombic AgInS$_2$.

This could be rationalized if the surfactants adjust the chemical environment in such a way that the relative stability of one phase over another can be reversed.[12] For example, Xiao et al. have demonstrated that a high-temperature phase ZnS nanocrystal can be obtained at low temperature through colloidal synthesis.[12b] A close inspection of randomly selected areas of the AgInSe$_2$ nanorods by HRTEM revealed that all the samples are uniform and have similar SAED patterns (Figure 1d) consistent with their XRPD patterns. XPS and EDX analyses of the synthesized nanorods show the 1:1 stoichiometry between Ag and In but slightly less Se than expected, which is consistent with the EDX results of some reported I−III−VI calcopyrites.[13] This could be due to the increase of the surface-to-volume ratio when the particles become smaller, which corresponds to a larger number of stabilizing thiol- or amine-capping groups on the particle surface relative to the number of Se atoms in the particle core.[11,13] On the other hand, a sulfur-containing surfactant could serve as a sulfur source in the colloidal synthesis.[14] If sulfur is diffused into the core to form AgInSe$_{2-x}$S$_x$, then shifting of the XRPD peaks to the right is expected for the alloy materials when the amount of DT is increased in the preparation.[15] However, no shifting of the XRPD peaks is observed as the molar ratio of DT to precursor is increased from 20 to 100. When DT is replaced by tri-*n*-octylphosphine oxide or tri-*n*-octylphosphine in the syn-

thesis, a mixture of orthorhombic (minor) and tetragonal (major) phases of AgInSe$_2$ is observed in the former case, and impurities are formed together with the orthorhombic phase product in the latter case.[11]

To summarize, we have synthesized close to monodispersed AgInSe$_2$ nanorods at 185 °C in a thiol and amine medium. For the first time, orthorhombic AgInSe$_2$ has been synthesized, and this new material may inherit some interesting electronic properties from its isostructural analogue, AgInS$_2$. The good solubility of the synthesized AgInSe$_2$ nanorods opens a venue for studying the novel properties of this material, e.g., third-order nonlinear optical properties, and it also allows one to utilize the nanoparticle in many applications, e.g. fabrication of polymer thin films containing discrete nanocrystals. Finally, the work reported here demonstrates that perfect matching of two or more surfactants might be the key to obtaining high-quality nanocrystals for many novel materials. This method may be applicable to other important I−III−VI semiconductor nanocrystals such as AgGaSe$_2$ and AgGaS$_2$.

Supporting Information Available: Synthesis of the precursor, cell data, IR, EDX, and XPS analyses of AgInSe$_2$ nanorods, XRPD patterns, and TEM images of AgInSe$_2$ nanoparticles synthesized from various experimental conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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