

Elemental Solvothermal Reaction To Produce Ternary Semiconductor CuInE₂ (E = S, Se) NanorodsYang Jiang,^{*,†} Yue Wu,[†] Xiao Mo,[†] Weichao Yu,[†] Yi Xie,^{†,‡} and Yitai Qian^{†,‡}

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The synthesis of nanostructure semiconductors has been of interest to material scientists and chemists because of their potential applications in recent years.^{1–4} I–III–VI₂ ternary semiconductor compounds such as CuInSe₂ and CuInS₂ with the chalcopyrite structure have been shown to be useful as nonlinear optical and direct energy gap materials.^{5,6} Previous synthesis routes proposed for CuInSe₂ and CuInS₂ include electrodeposition,^{7,8} high-pressure Se vapor treatment,⁹ H₂Se treatment of Cu–In alloys,¹⁰ ionized cluster beam technique,¹¹ metal organic chemical vapor deposition (MOCVD),¹² and reaction between CuCl₂, InCl₃, H₂SeO₃ in aqueous solution.¹³ However, these conventional routes usually need either a high temperature and long time or special devices, and some even require toxic reagents. Attention is currently focused on developing new methods for the preparation of nanoparticles and nanofilms.^{14,15} Herein we report a convenient method for the synthesis of CuInSe₂ and CuInS₂ nanorods from the elements under a solvothermal process.

Starting materials were analytical grade Cu, In, and Se powders. Ethylenediamine was used as solvent. In a typical synthesis, a 1:1:2 stoichiometric ratio of reactants (typically 0.0084 mol Cu, 0.0084 mol In, and 0.0168 mol Se) was added into a stainless steel autoclave. Ethylenediamine was then added until 80% of the autoclave's 30 mL capacity was reached. The sealed autoclave was heated at 280 °C for 48 h, then cooled to room temperature in the furnace naturally. The precipitate was filtered and washed several times with distilled water and absolute ethanol, then vacuum-dried at 70 °C for 6 h. The obtained sample was characterized by X-ray powder diffraction (XRD), using a Rigaku Dmax r-A X-ray diffractometer ($\lambda = 1.54056 \text{ \AA}$). TEM images and selected area electronic diffraction (SAED) patterns were taken with a Hitachi model H-800 transmission electron microscope. HRTEM images were obtained by using a JEOL 2010 electron microscope operated at 200 kV. X-ray photoelectron

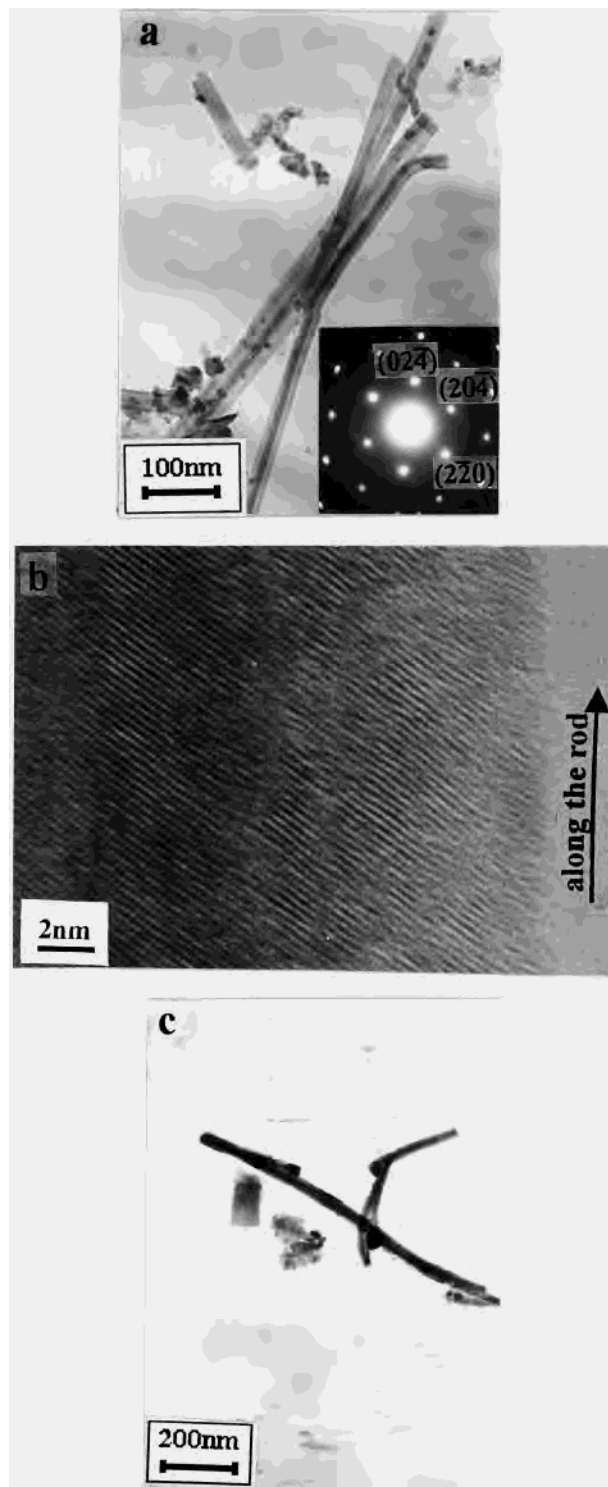


Figure 1. (a) TEM image of CuInSe₂ nanorods and corresponding SAED pattern along [221] zone axis. (b) HRTEM image of CuInSe₂ nanorod. (c) TEM image of CuInS₂ nanorods.

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spectra (XPS) was recorded on a VGESCALAB MK II X-ray photoelectron spectrometer, using nonmonochromatized Mg K α radiation as the excitation source.

The XRD patterns of the product can be indexed to the tetragonal phase CuInSe₂. The cell constants $a = 5.7396 \text{ \AA}$, $c = 11.5198 \text{ \AA}$ are near literature data (JCPDS card, no. 40-1487). The XPS spectra of CuInSe₂ show that the binding energies of Cu_{2p3}, Se_{3d5}, and In_{3d5} are 933.40, 54.25, and 444.45 eV, respectively. The molar ratio Cu/In/Se, according to the qualification of the peaks, is 1.000:0.944:1.946, close to the stoichiometry of CuInSe₂. TEM images of the sample show the main morphology of CuInSe₂ to be of a uniform nanorod (Figure 1a) with an average size of 12 nm \times 600 nm, and a few nanoparticles can also be seen. The electron diffraction pattern was taken from the selected area of the CuInSe₂ nanorod shown in Figure 1a with a convergent beam. The zone axis is 221 of the tetragonal phase CuInSe₂ ($c = 2a$), and the hexagonal spots can be indexed to (204), (024), (220), (204), (024), and (220). In the HRTEM image shown in Figure 1b the (201) lattice fringes appear with $d = 2.667 \text{ \AA}$, indicating the preferential orientation of the nanorods obviously.

In this electron-transfer reaction, liquid In plays an important role because the synthesis temperature is higher than the melting point of In (157 °C). Two of the three elements are dispersed homogeneously in the solvent ethylenediamine, and Se dissolves under the reaction conditions. At the reaction temperature, Se can react with In to form some In–Se compound dissolved in the liquid In. On the solid surface of Cu, Cu loses 2e and becomes Cu²⁺, then complexes with ethylenediamine to form [Cu(en)₂]²⁺. Cu²⁺ ions in the complex react at the growth site possibly with the In–Se compound dissolved in the liquid In. The existence of liquid In may motivate this electron-transfer reaction to grow whiskerlike CuInSe₂ crystals. This mechanism resembles that of the complex solution–liquid–solid (SLS) proposed for the growth of InP whiskers by the T. J. Trentler and W. E. Buhro groups,^{16,17} where the elements of the crystal phase are fed from a solution phase and pseudo-one-dimensional growth of the crystal phase from the flux liquid In after supersaturation is achieved. From our TEM image (Figure 1a), we also observed the bending

crystalline at the end of the nanorod, which was very similar to that in T. J. Trentler's report. To understand the SLS mechanism, InCl₃ was chosen as the reactant instead of In. Although the reaction of InCl₃, Cu, and Se also produced CuInSe₂, the products were nanoparticles. We also obtained nanoparticles of FeIn₂S₄ by reaction of InCl₃, Fe, and S.¹⁸ These results may further confirm that liquid In is critical to the growth process of the nanorods. To look at solvent effects, we substituted ethylenediamine with benzene and ethanol, keeping the other conditions constant. The XRD data indicated that in neither benzene nor ethanol a ternary selenide was produced. We attributed the need for ethylenediamine to its strong coordination capacity and its activation of the metal surface by removing the surface oxides, as reported by Ramli¹⁹ and Henshaw²⁰ in their investigations of low-temperature elemental metal reaction.

We also successfully synthesized crystalline CuInS₂ through this solvothermal technique by using S instead of Se. The XRD pattern of this tetragonal phase yielded cell constants $a = 5.5086 \text{ \AA}$, $c = 11.0264 \text{ \AA}$, close to the reported data (JCPDS card, no. 38-777). The TEM image (Figure 1c) indicated that CuInS₂ is also a nanorod with sizes of 20 nm \times 800 nm.

In summary, we have successfully synthesized CuInSe₂ and CuInS₂ nanorods by using a relatively simple and convenient elemental solvothermal reaction process. The effect of In and ethylenediamine on the growth process of the nanorods was also investigated. We expect this method to be useful for the synthesis of nanorods of other I–III–VI₂ sulfides or selenides.

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Supporting Information Available: XRD data for CuInS₂ and CuInSe₂ and XPS data for CuInSe₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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