

Synthesis of Metastable Wurtzite CuInSe₂ Nanocrystals

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The ever increasing demand for energy resources continues to drive the development of cost-effective and high efficiency photovoltaic devices.¹ The I–III–VI family of semiconductors, including CuInS₂, CuInSe₂, and CuIn_xGa_{1–x}Se₂, have band gaps that match well with the solar spectrum, have large absorption coefficients and good photostability, and avoid the use of overly toxic elements.² Thin films of I–III–VI semiconductors have been used as the active layer for high efficiency solar cells, with CuIn_xGa_{1–x}Se₂-based solar cells demonstrating power conversion efficiencies of nearly 20%.³ One of the ways to decrease the cost of these devices is to use solution-derived I–III–VI semiconductor nanocrystals as the active layer, which is advantageous because solution-phase routes are less energy intensive and have the potential for scalability, and nanocrystal suspensions can easily be deposited via spin-coating or printing methods.⁴

The tetragonal chalcopyrite phase of CuInSe₂ is thermodynamically preferred at room temperature.⁵ In the bulk, chalcopyrite CuInSe₂ possesses a desired band gap of $E_g \approx 1.04$ – 1.10 eV, with a reported Bohr exciton radius of 10.6 nm.⁶ A number of solution-phase routes to high-quality chalcopyrite CuInSe₂ nanocrystals have been reported over the past few years.^{6a,7} Since elemental stoichiometry, morphology, and crystal symmetry are known to influence the optoelectronic properties of semiconductor nanocrystals, it is of interest to explore new kinetically controlled pathways to unusual metastable crystal phases. Recently, the hexagonal wurtzite

(wz) phase of CuInS₂ nanocrystals was discovered by Yang and Lu.^{8a} In the bulk, wz-CuInS₂ is a high-temperature phase stable between 1045 and 1090 °C, where the copper and indium cations randomly share common lattice sites. Because wz-CuInS₂ nanocrystals are accessible at room temperature,⁸ it follows that other types of I–III–VI nanocrystals may exist in nonchalcopyrite phases at room temperature. Indeed, Hillhouse and Agrawal have recently shown that nanocrystals of the metastable sphalerite phase of CuInSe₂ can be synthesized.^{6a} Herein, we report the first example of the wurtzite phase for CuInSe₂ nanocrystals.

Diorgano dichalcogenides have shown recent utility as facile and low temperature chalcogen sources for semiconductor nanocrystal syntheses.^{8d,9} Here, CuInSe₂ nanocrystals were synthesized by injecting a solution of diphenyl diselenide into a hot solution of CuCl and In(acac)₃ in oleylamine and heating to 180 °C for 3 h. The resulting CuInSe₂ nanocrystals form stable suspensions in common organic solvents, such as hexanes and toluene. The powder X-ray diffraction (XRD) pattern of the CuInSe₂ nanocrystals prepared by this procedure did not match the diffraction patterns for previously reported chalcopyrite CuInSe₂ nanocrystals⁷ or those in the JCPDS database (JCPDS no. 00-040-1487). A diffraction pattern was simulated starting from the wz-ZnSe crystal structure and substituting the Zn²⁺ lattice positions with a 50/50 occupancy probability of Cu⁺ and In³⁺ cations (see Supporting Information). The simulated and experimental diffraction patterns match well (Figure 1), signifying that these CuInSe₂ nanocrystals possess a wurtzite crystal structure. Differences in intensity between the simulated and experimental diffraction patterns can be explained by some degree of preferred orientation of the nanocrystals, which is corroborated by selected area electron diffraction (vide infra). Lattice parameters of $a = 4.08$ Å and $c = 6.69$ Å were calculated from the experimental diffraction pattern for the wz-CuInSe₂ nanocrystals. The major diffraction peaks can be indexed to the (100), (002), (101), (102), (110), (103), (112), and (202) reflections of the simulated wurtzite crystal structure. The (200) and (211) reflections for chalcopyrite CuInSe₂ at 31° and 36° 2θ, respectively, are distinct in position from the wurtzite CuInSe₂ diffraction peaks and are noticeably absent in the diffraction pattern. Likewise, the (200) diffraction peak for cubic Cu₂Se at 31° 2θ

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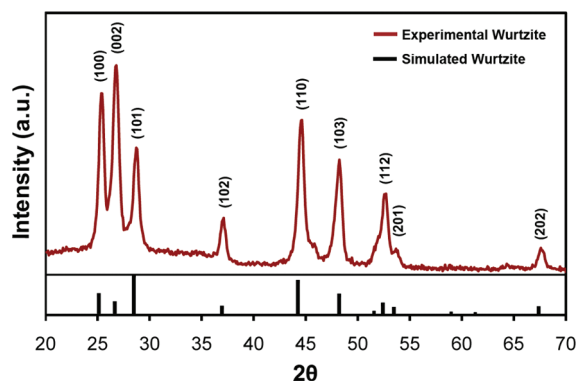


Figure 1. Experimental and simulated XRD patterns of wurtzite–CuInSe₂ nanocrystals.

(JCPDS no. 00-006-0680) and (090)/(620) diffraction peaks for hexagonal Cu₂Se at 40° 2θ (JCPDS no. 00-047-1448), which are also distinct, were not observed.

It was found that specific reaction control is necessary to synthesize wz-CuInSe₂. When an equal volume of squalane (i.e., a noncoordinating solvent) was substituted for oleylamine under otherwise identical conditions, the tetragonal chalcopyrite phase of CuInSe₂ was produced (see Supporting Information, Figure S3). This suggests that the presence of oleylamine has an influence on phase determination. Similar phenomena have recently been observed; that is, primary amines have been shown to influence the formation of wurtzite ZnS, CdSe, and CuInSe₂ nanocrystals.^{8d,10} It is thought that amine coordination to the metal cations has a kinetic effect on structure determination. In addition to amine, the use of diphenyl diselenide as a selenium source was also necessary for the production of wurtzite nanocrystals. Use of elemental selenium under otherwise identical conditions at 180 °C resulted in chalcopyrite CuInSe₂ in addition to Cu₂Se impurities (see Supporting Information, Figure S4). Interestingly, thiourea has been used to form wz-CuInSe₂ nanocrystals in the presence of an amine;^{8c} however, the analogous reaction with selenourea yielded chalcopyrite CuInSe₂ nanocrystals rather than the wurtzite phase.^{7a} Thus, the rate of selenium transfer from diphenyl diselenide appears to be just right to kinetically access the metastable wurtzite phase at 180 °C.

The as-synthesized wz-CuInSe₂ nanocrystals are poly-disperse with a mean diameter of 29.9 ± 6.6 nm, as determined by transmission electron microscopy (TEM) analysis (Figure 2). The lattice parameters calculated from selected area electron diffraction (SAED) patterns of several randomly chosen regions of the CuInSe₂ nanocrystals agree with the lattice parameters calculated from the XRD pattern for wz-CuInSe₂. Also, no other crystal phases were observed by SAED analysis. A high-resolution TEM image of an apparent single crystalline particle with the (002) lattice planes displayed (*d* = 0.33 nm) is shown in Figure 2b. Energy dispersive X-ray

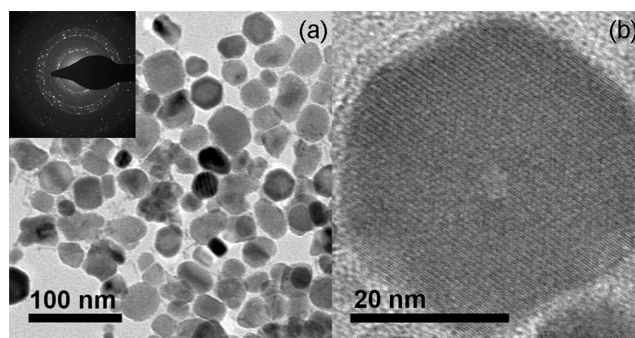


Figure 2. (a) Low-res TEM micrograph of CuInSe₂ nanocrystals with representative SAED pattern displayed as inset. (b) High-res TEM micrograph of an individual CuInSe₂ nanocrystal.

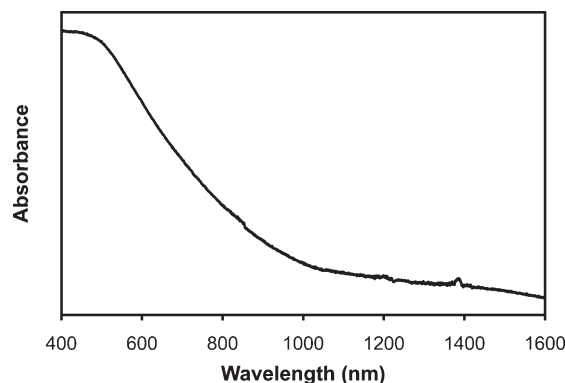


Figure 3. Visible-NIR absorption spectrum of the wurtzite–CuInSe₂ nanocrystals. The small features from 1200 to 1400 nm are related to absorption from cyclohexane.

spectroscopy was used to analyze the elemental composition of the wz-CuInSe₂ nanocrystals (see Supporting Information, Figure S6). Analysis of 10 randomly selected areas gave an average Cu:In:Se composition of 0.31:0.22:0.47. This experimentally determined Cu_{1.32}In_{0.94}Se_{2.00} elemental stoichiometry is consistent with a Cu_{*x*}In_{*y*}Se_{0.5*x*+1.5*y*} stoichiometry (within experimental error), and deviation from the ideal CuInSe₂ stoichiometry is made possible because Cu⁺ and In³⁺ cations share lattice positions in the wurtzite structure.^{8a} In the related system where wz-CuInS₂ nanocrystals were synthesized using a dialkyl disulfide in oleylamine, it was thought that the slight stoichiometric excess of copper in the nanocrystals resulted from copper nucleating faster than indium and sulfur.^{8d} It is possible that a similar phenomenon is observed here. X-ray photoelectron spectroscopy (XPS) was used to confirm elemental oxidation states for the CuInSe₂ nanocrystals (see Supporting Information, Figure S7). The Cu 3p_{3/2} peak at 931.8 eV matches well with the reported binding energy for Cu⁺ in CuInSe₂, while the In 3d_{5/2} peak at 444.2 eV is representative of In³⁺ in CuInSe₂.¹¹ Finally, an asymmetric peak at 53.8 eV is representative of the Se 3d binding energy for lattice Se^{2−}.¹¹

The wz-CuInSe₂ nanocrystals absorb strongly through the entire visible and into the near-IR region of the spectrum (Figure 3), resulting in the black color of the

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material. The band gap of the wz-CuInSe₂ nanocrystals was determined from the onset of the visible-NIR absorption spectrum to be $E_g = 1.19$ eV, while bulk chalcopyrite CuInSe₂ has a reported band gap between 1.04–1.10 eV.⁶ The reported Bohr exciton radius of 10.6 nm for CuInSe₂ suggests that smaller nanocrystals are needed to observe significant quantum confinement effects.⁶

For the first time, a solution-phase synthesis of wz-CuInSe₂ nanocrystals was described. The keys to wz-CuInSe₂ formation include the use of an amine solvent and facile selenium transfer from a diselenide at relatively low temperatures. This metastable phase may have important implications in photovoltaic device performance and heterojunction formation with wz-CdS overgrowth layers.¹² Future work will focus on controlling the size

and shape of the CuInSe₂ nanocrystals and incorporating them into a functional photovoltaic device.

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Supporting Information Available: Simulation of wz-CuInSe₂ diffraction pattern; indexed SAED pattern; XRD patterns for the squalane and selenium control reactions; additional high-res TEM; EDX spectra; XPS spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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