Synthesis of $CuInSe_2$ Nanocrystals with Trigonal Pyramidal Shape

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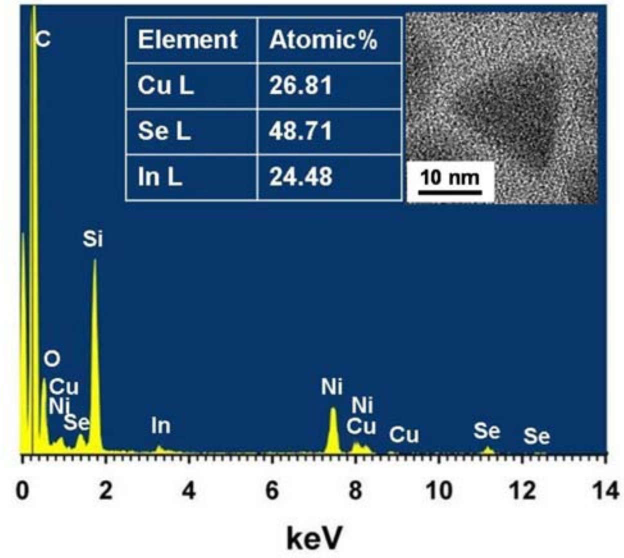
Supporting Information

Experimental Details

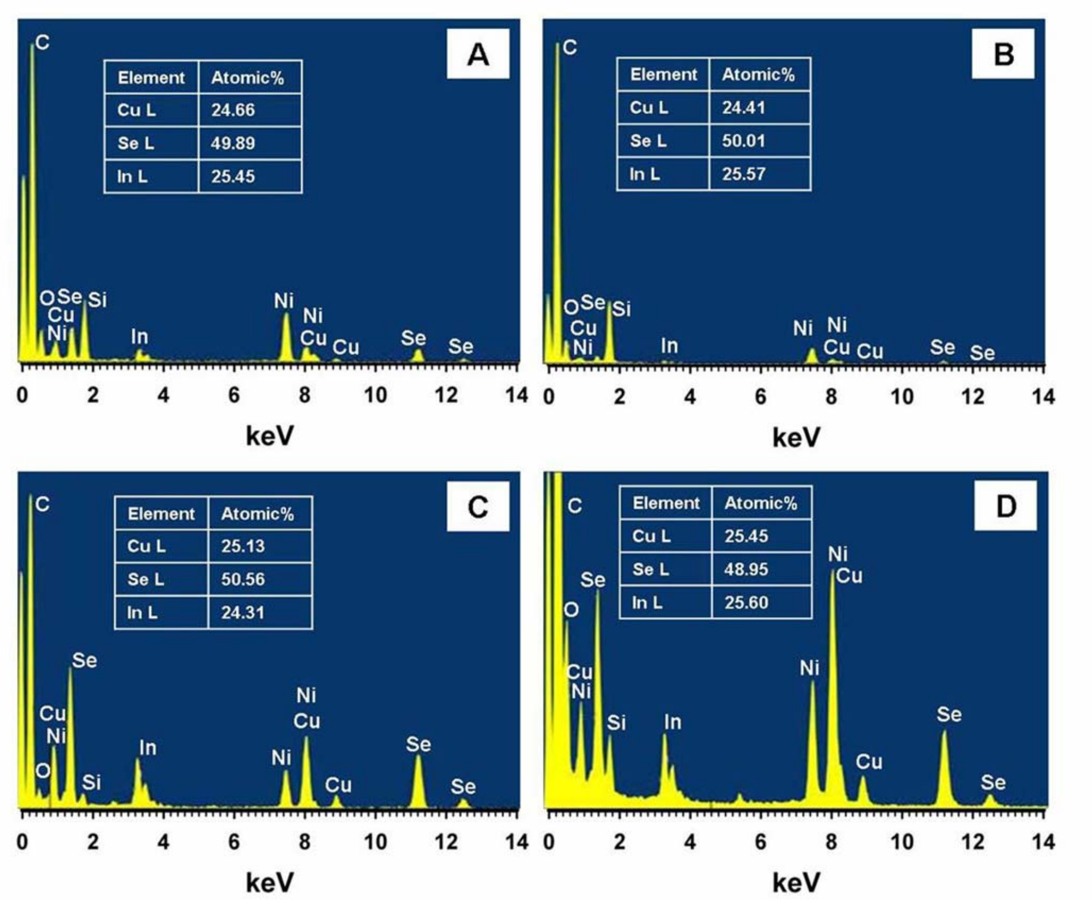
Nanocrystal Synthesis. Copper(I) chloride (CuCl, Aldrich, 99.995+ %) and indium(III) chloride ($InCl_3$, Aldrich, 99.999 %), selenourea (99+ %, STREM; 99.9+ %, ACROS), oleylamine (Fluka) were purchased and used as received. In a typical synthesis, a mixture of 0.05 g of CuCl (0.5 mmol of Cu), 0.11 g of $InCl_3$ (0.5 mmol of In), and 10 mL of oleylamine is vigorously stirred and degassed in the reaction flask for 30 minutes at 60 ºC by pulling vacuum on the Schlenk line. The mixture is then heated to 130 ºC under nitrogen for 10 minutes. During heating, the solution turns from blue to yellow, indicating the formation of oleylamine complexes with Cu and In. Meanwhile, the selenium reactant solution is prepared by dissolving 0.123 g of selenourea (1.0 mmol) in 1 mL of oleylamine at 200 ºC under nitrogen on a Schlenk line. This In/Cu/oleylamine reactant solution is cooled to 100ºC and the selenium reactant solution is added by syringe. Immediately after injection of the Se reactant, the reaction mixture is heated to 240 ºC at a rate of 15 ºC/min. After 1 hour, the nanocrystals are removed from the heating mantle and allowed to cool to room temperature. 30 mL of ethanol is then added to precipitate the nanocrystals, followed by centrifugation at 7000 rpm for 3 minutes. The supernatant is discarded. The nanocrystals redisperse in a variety of non-polar organic solvents, including chloroform, hexane, and toluene. Prior to characterization, dispersions are typically centrifuged again at 7000 rpm for 5 min to remove inadequately capped nanocrystals. A typical reaction yields ~120 mg of $CuInSe_2$ nanocrystals.

Materials Characterization. TEM images were acquired using either a Phillips EM280 microscope operated at 80 kV or a JEOL 2010F microscope equipped with a field emission gun operated at 200 kV. TEM samples were prepared by drop-casting nanocrystals dispersed in chloroform onto carbon-coated nickel TEM grids (200-mesh, Electron Microscopy Sciences). The JEOL 2010F is equipped with an Oxford EDS detector, which was used for elemental analysis of the nanocrystal composition. XRD was performed with (~200 μm thick nanocrystal films on quartz substrates using a Bruker-Nonius D8 Advance powder diffractometer with Cu Kα radiation (λ = 1.54 Å). Diffraction patterns were obtained at a scan rate of 12 deg / min in 0.01 deg increments for 12 hr, rotating the sample at 15 deg / min. Room temperature UV-visible absorbance spectra were collected on a Varian Cary 5000 Scan spectrophotometer.



Element	Atomic%
Cu L	26.81
Se L	48.71
In L	24.48

Figure S1. Cu:In:Se ratios of the $CuInSe_2$ nanocrystals measured by EDS. The inset shows a TEM image of a nanocrystal with composition measured by EDS as an example. In the EDS data, the Ni, C and Si signals are from the nickel grid, the carbon support and the background in the TEM.



A

Element	Atomic%
Cu L	24.66
Se L	49.89
In L	25.45

B

Element	Atomic%
Cu L	24.41
Se L	50.01
In L	25.57

C

Element	Atomic%
Cu L	25.13
Se L	50.56
In L	24.31

D

Element	Atomic%
Cu L	25.45
Se L	48.95
In L	25.60

Figure S2. Additional EDS data for four different $CuInSe_2$ nanocrystals.

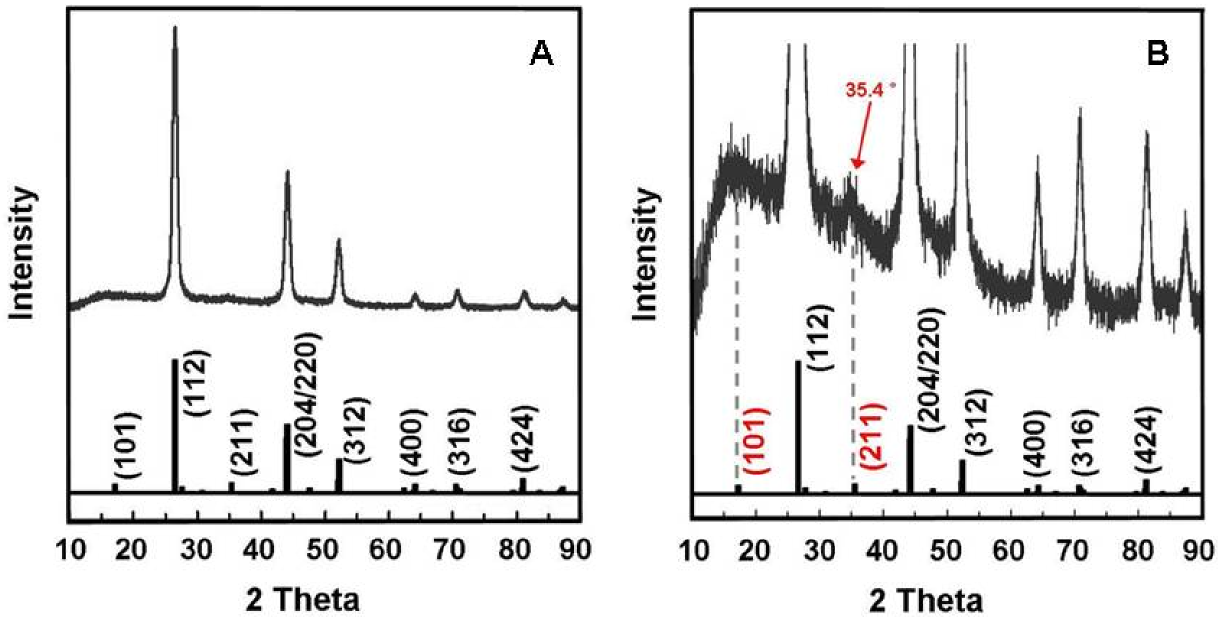


Figure S3. XRD patterns obtained from the $CuInSe_2$ nanocrystals. The data in (A) is plotted on a log scale in (B) to enhance the (101) and (211) peaks.

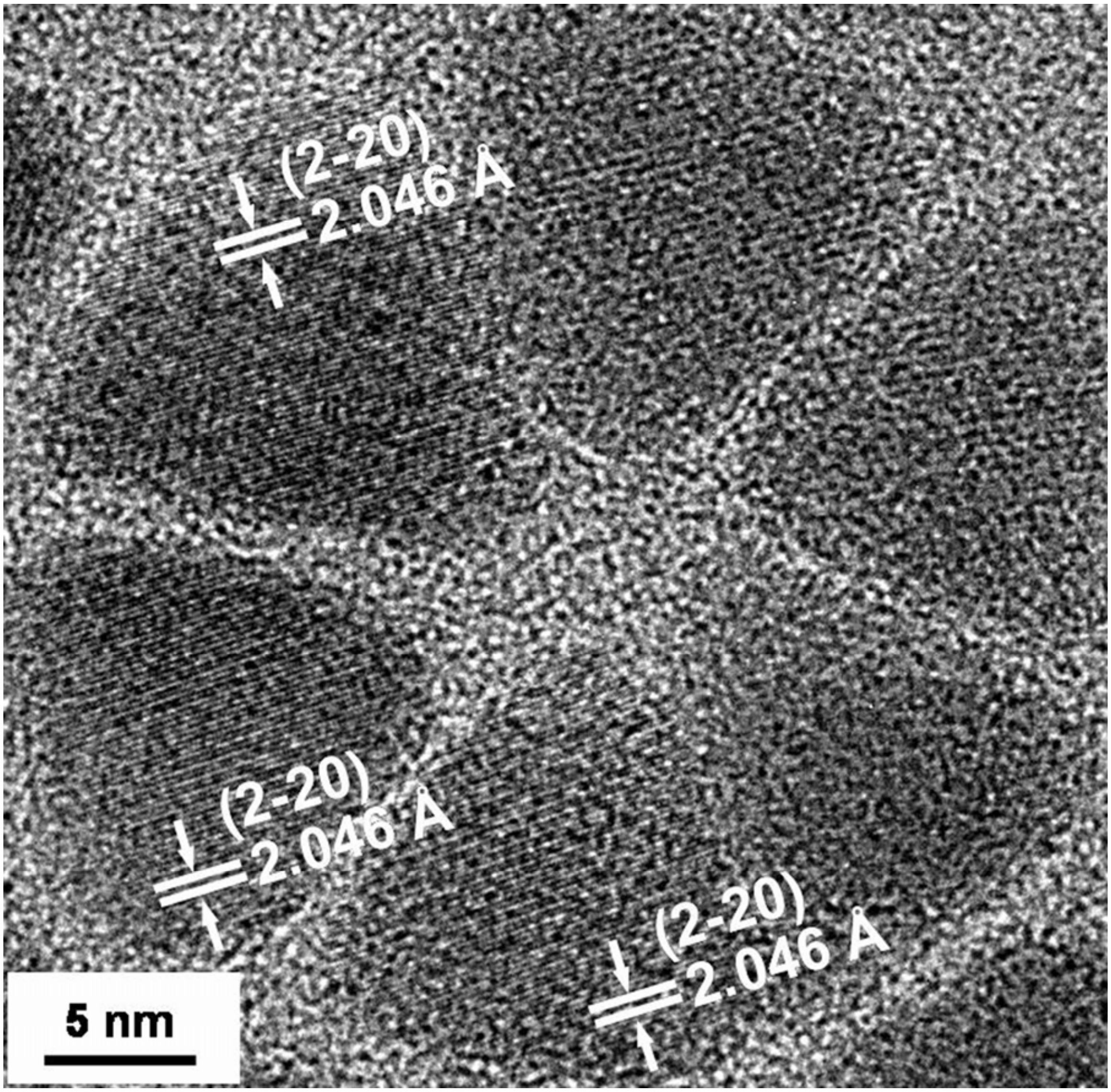


Figure S4. HRTEM image of ordered $CuInSe_2$ nanocrystals. The nanocrystals are all lying on the substrate on (114) facets with the same crystallographic orientation with respect to their triangular shape.

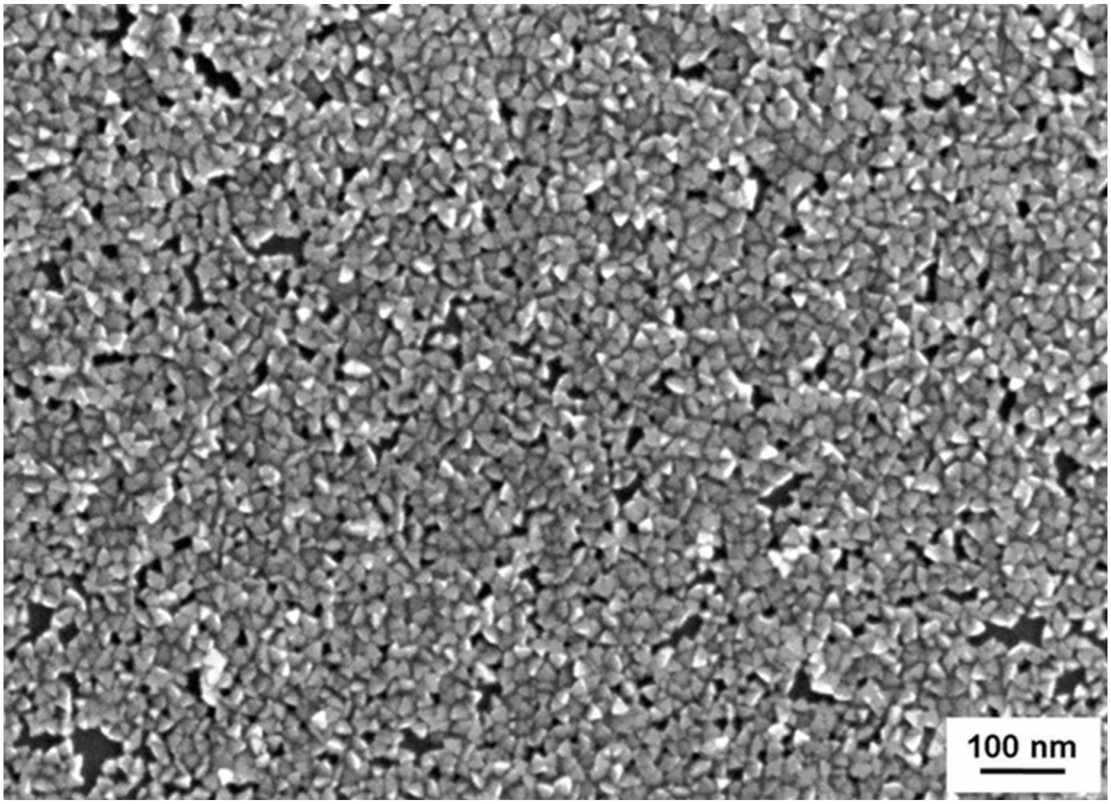


Figure S5. SEM image of CuInSe$_2$ nanocrystals on a SiO$_2$-coated Si substrate. The image was acquired with a Zeiss Supra 40 VP SEM at a working voltage of 10 kV and working distance of 8 mm.

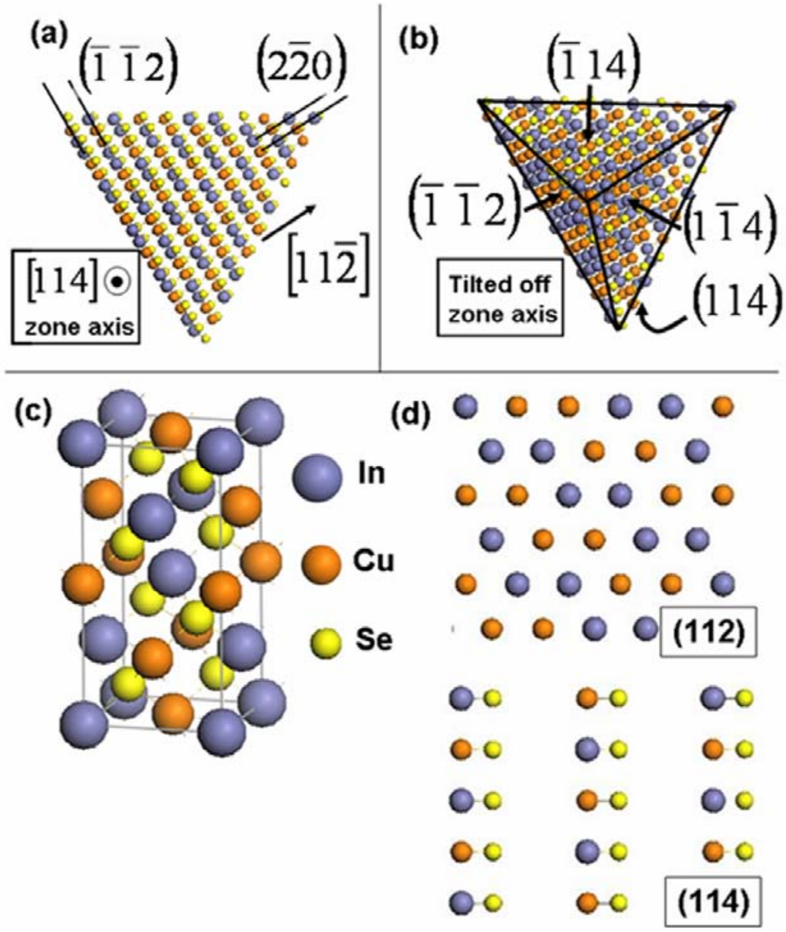


Figure S6. Crystallographic models of a $CuInSe_2$ nanocrystal with trigonal pyramidal shape (a) viewed down the [114] zone axis like the nanocrystals imaged by TEM image in Figure 2 and (b) viewed slightly off the [114] zone axis to illustrate the three-dimensional shape of the nanocrystal and its (-1-12) and (-114) and (1-14) faceted surfaces; (c) the unit cell of chalcopyrite (tetragonal) $CuInSe_2$; and (d) the (112) and (114) surfaces of $CuInSe_2$.

Oleylamine etching of $CuInSe_2$ nanocrystals.

Etching of the $CuInSe_2$ nanocrystals was observed when they were dispersed in the presence of excess amine. Nanocrystals did not etch when excess amine was not added to the dispersions. In a typical synthesis, the nanocrystals are precipitated with 30 mL of ethanol after the reaction, centrifuged, redispersed in a minimal amount of chloroform (a few mL) and reprecipitated with 30 mL of ethanol. This procedure removes the excess oleylamine that is not adsorbed to the nanocrystal surface. When nanocrystals purified using this procedure were stored as dispersions, the nanocrystals were stable, as shown in the TEM images in Figure S6b. After purification, if a drop of oleylamine (~ 2 μL) was added to the nanocrystal dispersion, the particles were observed to slowly dissolve over the course of days, as the TEM images show in Figure S6c. If the nanocrystals were not completely purified using the two precipitations after synthesis, then the nanocrystals were also observed to etch, but at a slower rate than when oleylamine was intentionally added in excess. The nanocrystals in the TEM images in Figure S6a were precipitated only once with only 10 mL of ethanol (followed by centrifugation). The blue color of the nanocrystal dispersions after 13 days (the picture below Figure S6a) indicates the formation of complexes comprising oleylamine and Cu (or In) atoms during aging, which is the byproduct of the etching process. XRD (Figure S7) of the partially-etched nanocrystals confirms that there is no phase change during the etching—the particles still exhibit chalcopyrite $CuInSe_2$ crystal structure.

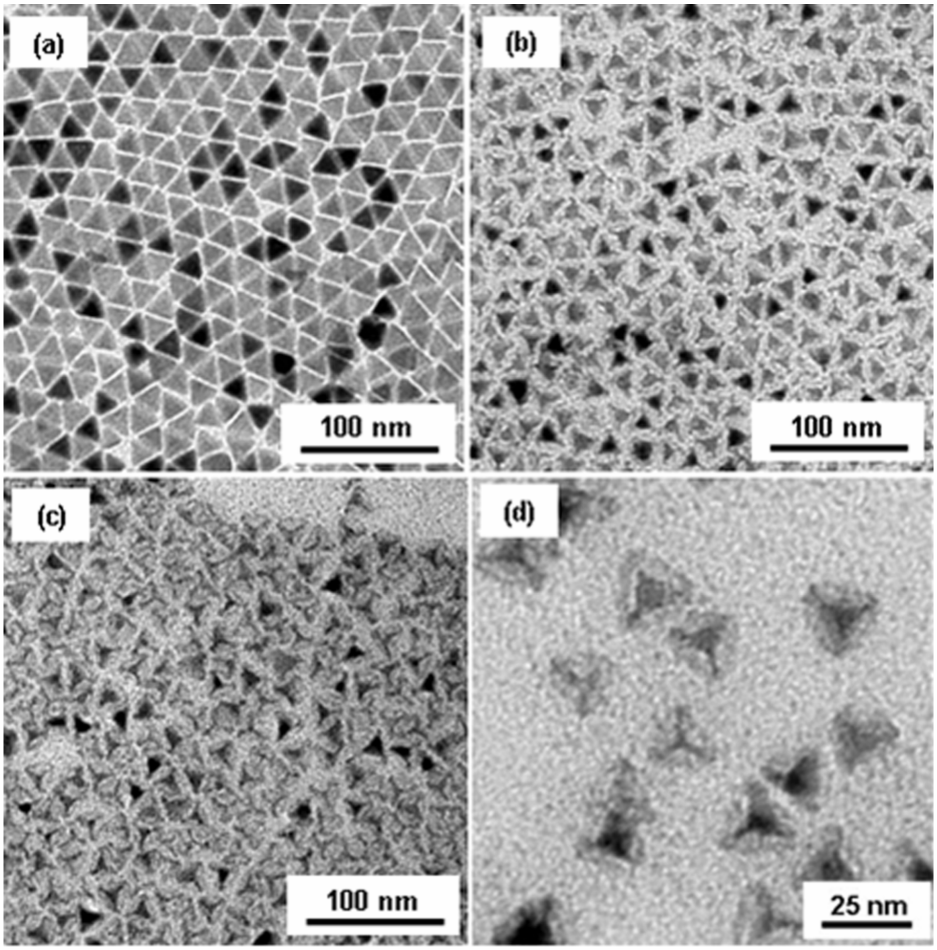


Figure S7. TEM images of $CuInSe_2$ nanocrystals after dispersing in chloroform at room temperature with excess oleylamine for (a) 1 day, (b) 9 days and (c,d) 13 days. The shape of the etched nanocrystals is consistent with a pyramidal shape.

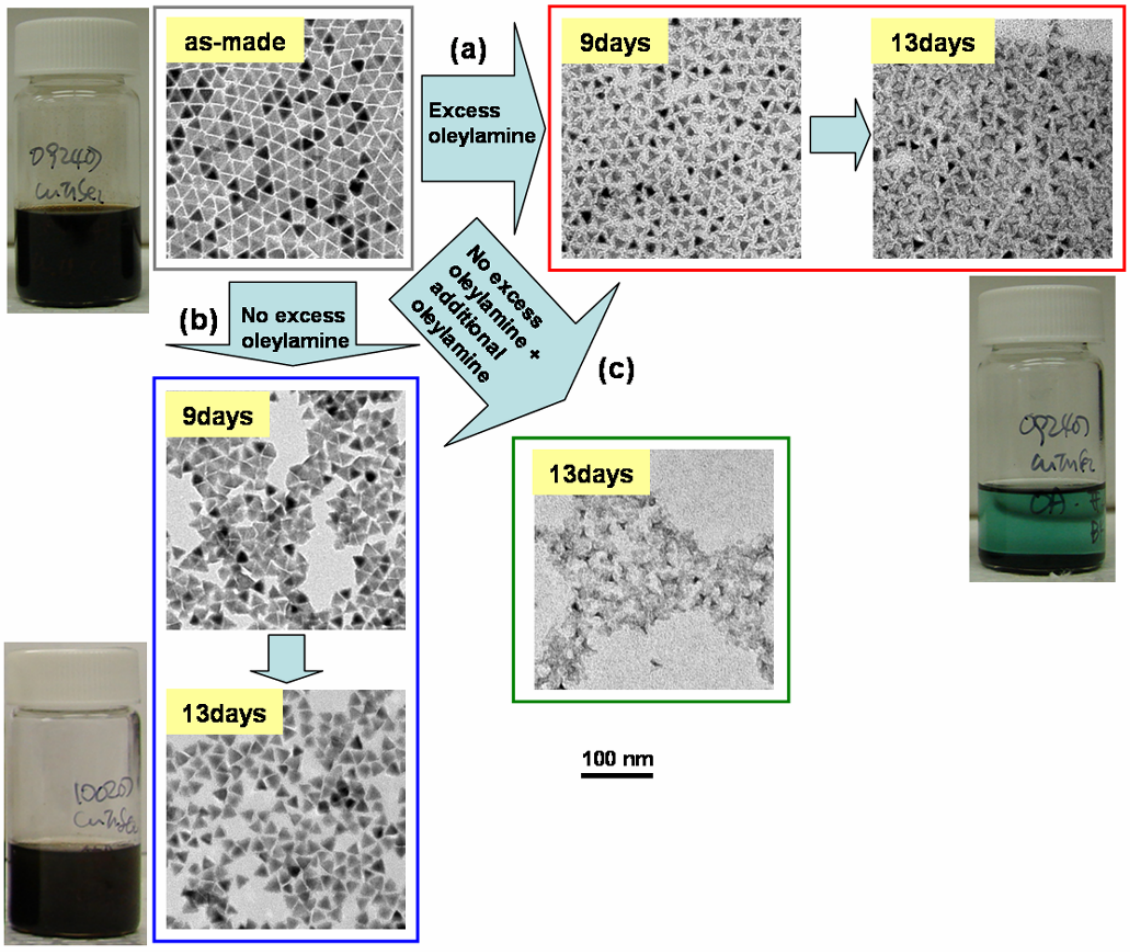


Figure S8. TEM images of CuInSe$_2$ nanocrystals after being stored in chloroform with varying amounts of excess oleylamine, as described in the text.

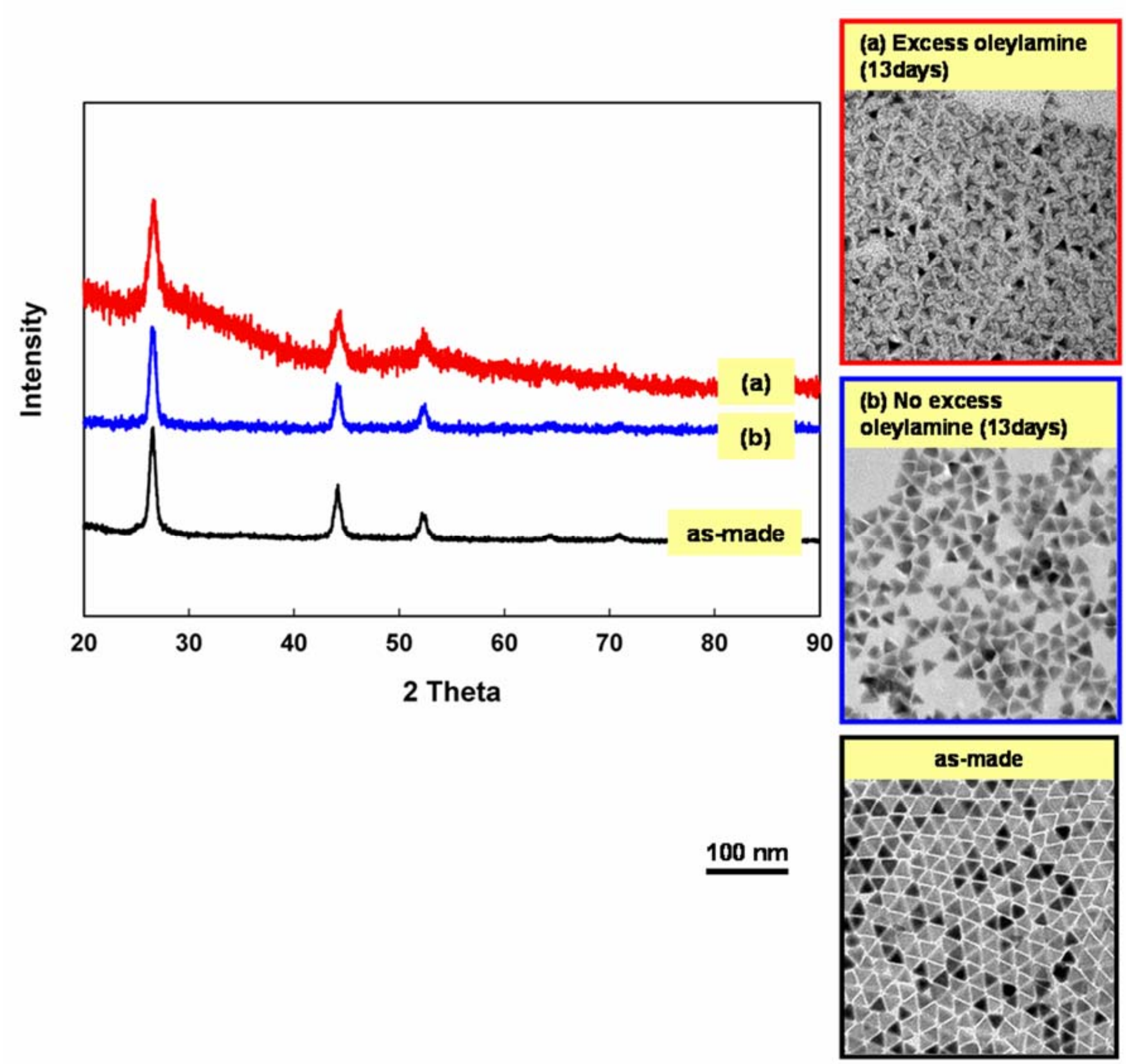


Figure S9. XRD patterns of etched $CuInSe_2$ nanocrystals: (a) shows the $CuInSe_2$ chalcopyrite XRD patterns of etched particles just as those of non-etched (b) or as-made particles.