Supporting Information

Tailoring Cu^+ for Ga^{3+} Cation Exchange in $Cu_{2-x}S$ and $CuInS_2$ Nanocrystals by Controlling the Ga-Precursor Chemistry

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1. Figures referenced from the main text

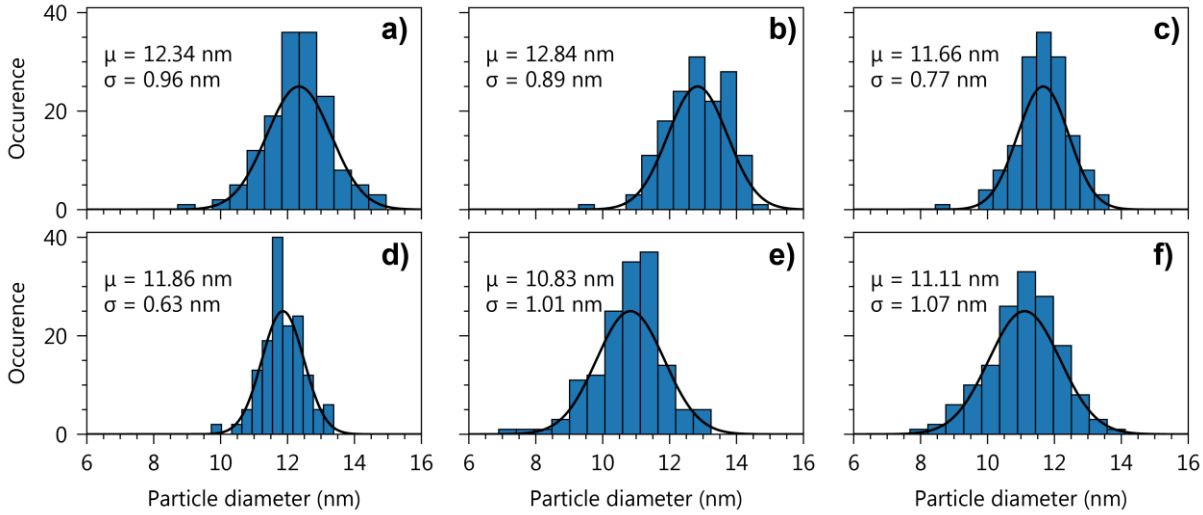

Figure S1. Histograms of particle diameters measured using transmission electron micrographs, of (a) the parent $Cu_{2-x}S$ nanocrystals; and the product nanocrystals obtained after reaction with: (b) $InCl_3$-TOP at 100 °C, (c) $GaCl_3$-TOP at 100 °C, (d) $GaCl_3$ at 30 °C, (e) $GaCl_3$-TPP at 100 °C and (f) $GaCl_3$-DPP at 100 °C. Black curves represent the corresponding Gaussian distributions, plot using the average (μ) and the standard deviation (σ) of the measured particle diameters. For each sample 150 particles were measured.

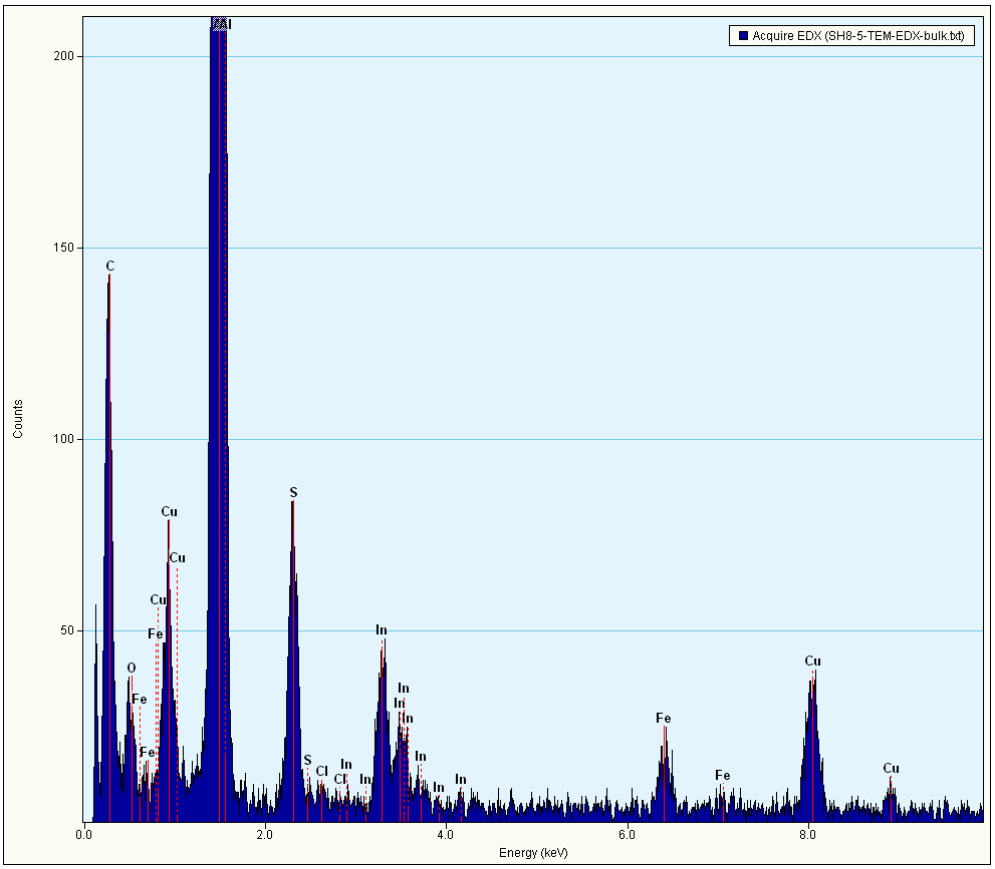

Figure S2. Energy-dispersive X-ray Spectrum (EDS) of $Cu_{1.03}In_{0.81}S_2$ (CIS) bifrustum nanocrystals, obtained after reaction of $Cu_{2-x}S$ nanocrystals with $InCl_3$-TOP. Quantification of the spectrum revealed a Cu:In ratio of 1.00:0.79. The spectrum was acquired on a large region containing hundreds of nanocrystals. The aluminium grid used in the measurement causes the peak at around 1.5 keV.

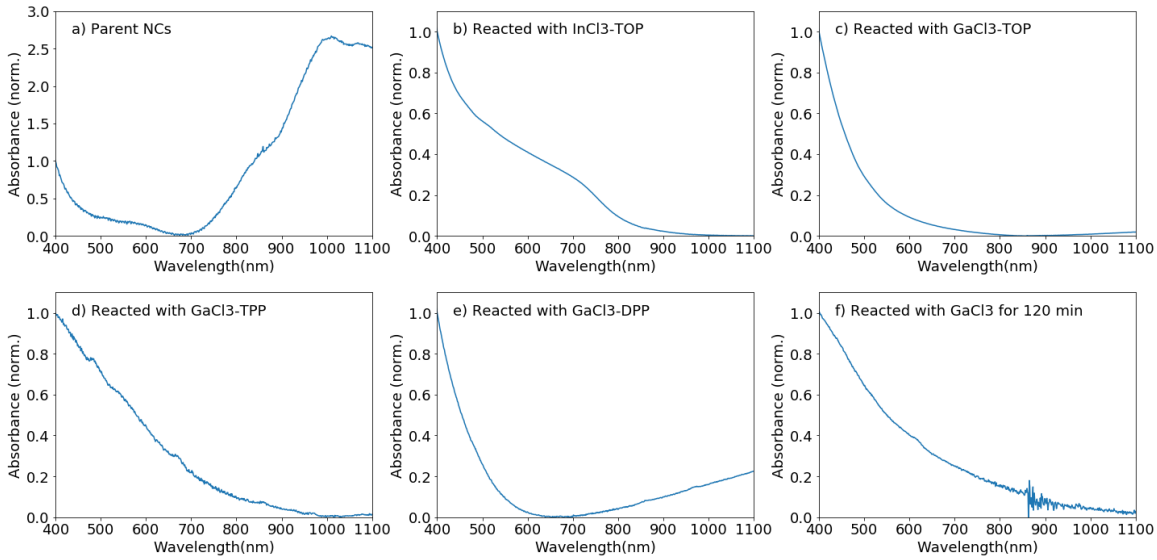

Figure S3. Absorption spectra of (a) the parent $Cu_{2-x}S$ nanocrystals; and the product nanocrystals obtained after reaction with: (b) $InCl_3$-TOP at 100 °C, (c) $GaCl_3$-TOP at 100 °C, (d) $GaCl_3$-TPP at 100 °C, (e) $GaCl_3$-DPP at 50 °C and (f) $GaCl_3$ at 30 °C. Each spectrum was corrected for background absorption, by subtracting a constant background, then normalized to the absorbance at 400 nm.

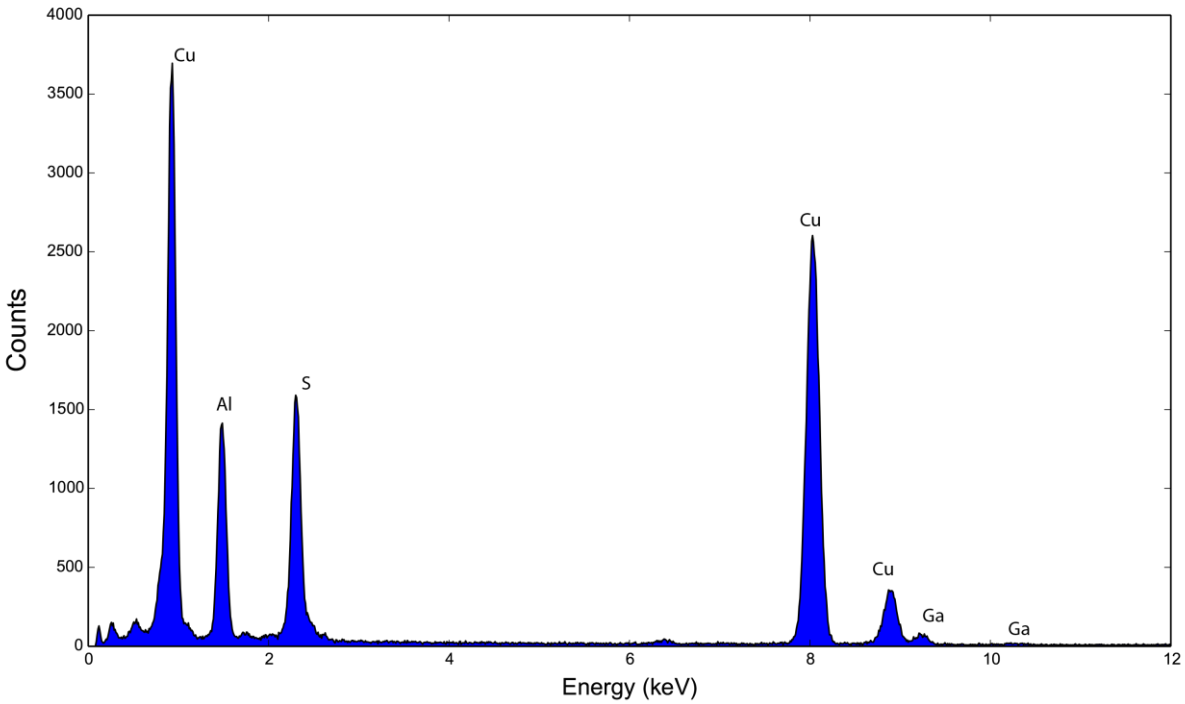

Figure S4. EDS of $Cu_{1.99}Ga_{0.04}S$ nanocrystals, obtained after reaction of $Cu_{2-x}S$ nanocrystals with $GaCl_3$-TOP. Quantification of the spectrum revealed a Cu:Ga ratio of 1.00:0.02. The spectrum was acquired on a large region containing hundreds of nanocrystals. The aluminium grid used in the measurement causes the peak at around 1.5 keV.

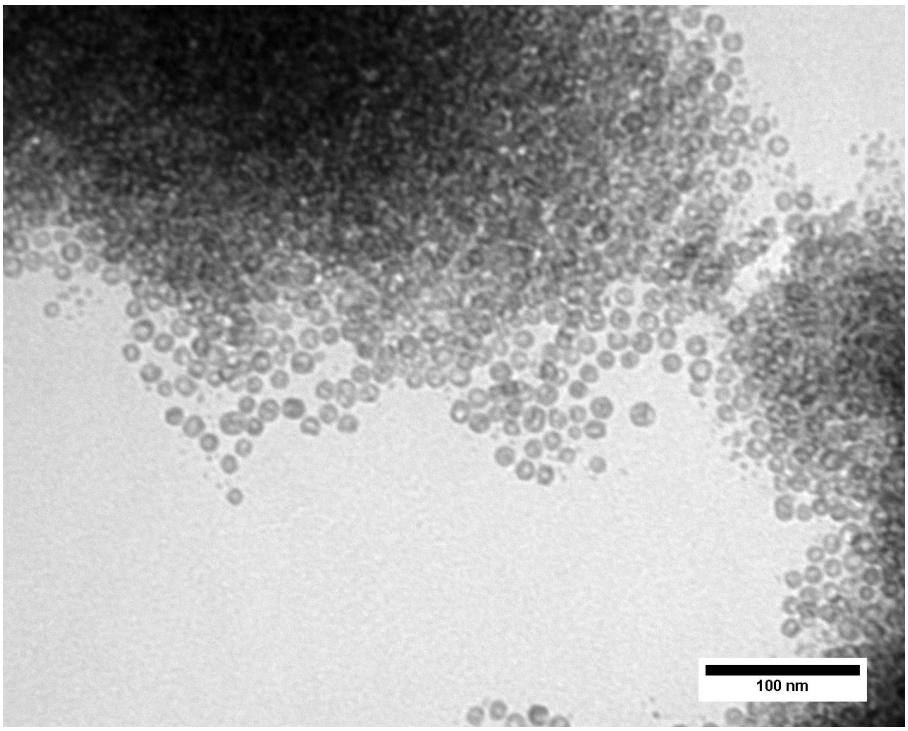

Figure S5. TEM image of $Cu_{2-x}S$ nanocrystals, after reaction with $GaCl_3$ at 100°C overnight.

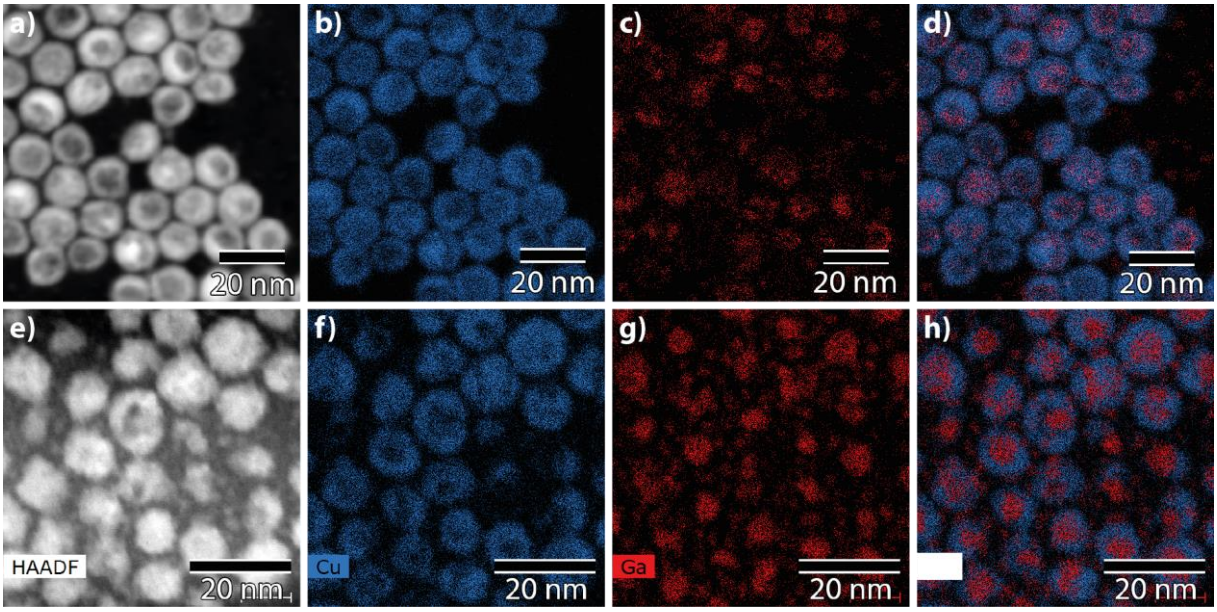

Figure S6. (a) HAADF-STEM micrograph and EDS elemental maps of (b, blue) Cu, (c,red) Ga and (d) Cu and Ga, of $Cu_{2-x}S$ nanocrystals after reaction with $GaCl_3$ for 120 min. (e) HAADF-STEM micrograph and EDS elemental maps of (f, blue) Cu, (g,red) Ga and (h) Cu and Ga, of $Cu_{2-x}S$ nanocrystals after reaction with $GaCl_3$ for 300 min.

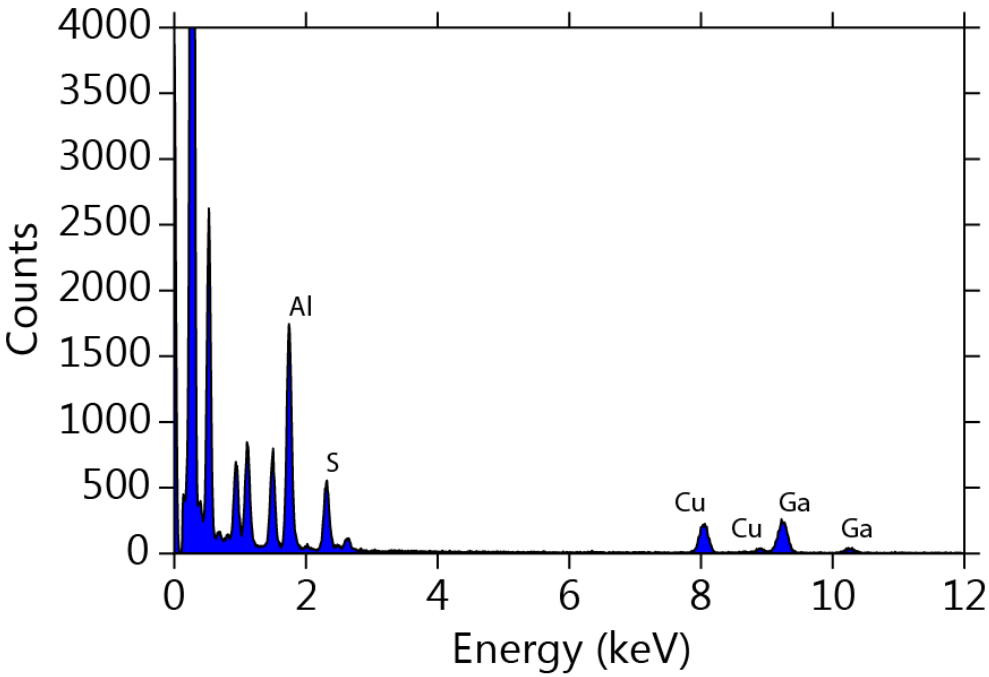

Figure S7. EDS of CGS nanocrystals, obtained after reaction of $Cu_{2-x}S$ nanocrystals with $GaCl_3$-TPP. Quantification of the spectrum revealed a Cu:Ga ratio of 1.00:1.38. The spectrum was acquired on a large region containing hundreds of nanocrystals. The aluminium grid used in the measurement causes the peak at around 1.5 keV.

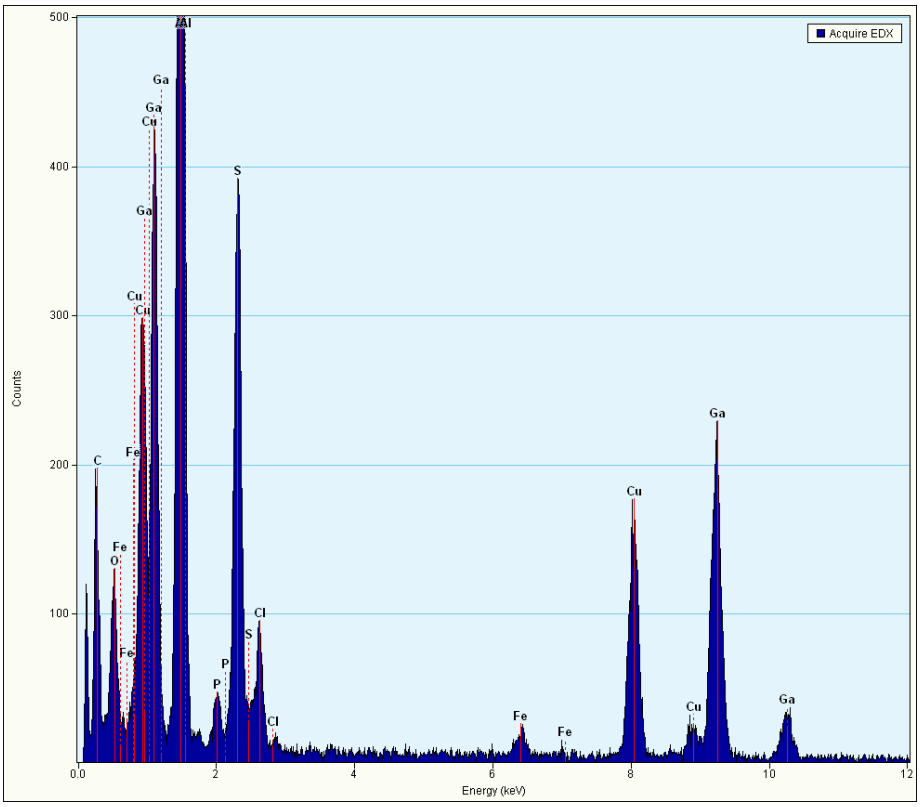

Figure S8. EDS of CGS nanocrystals, obtained after reaction of $Cu_{2-x}S$ nanocrystals with $GaCl_3$-DPP. Quantification of the spectrum revealed a Cu:Ga ratio of 1.00:1.48. The spectrum was acquired on a large region containing hundreds of nanocrystals. The aluminium grid used in the measurement causes the peak at around 1.5 keV.

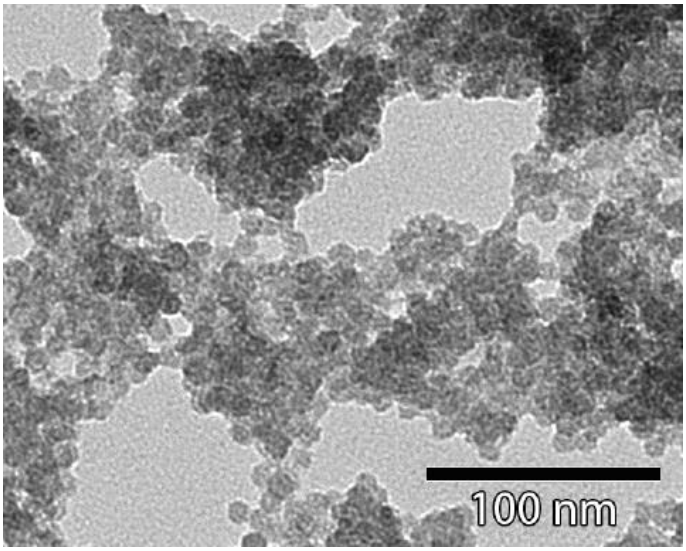

Figure S9. TEM image of agglomerated CGS nanocrystals, obtained after reaction of $Cu_{2-x}S$ nanocrystals with $GaCl_3$-DPP.

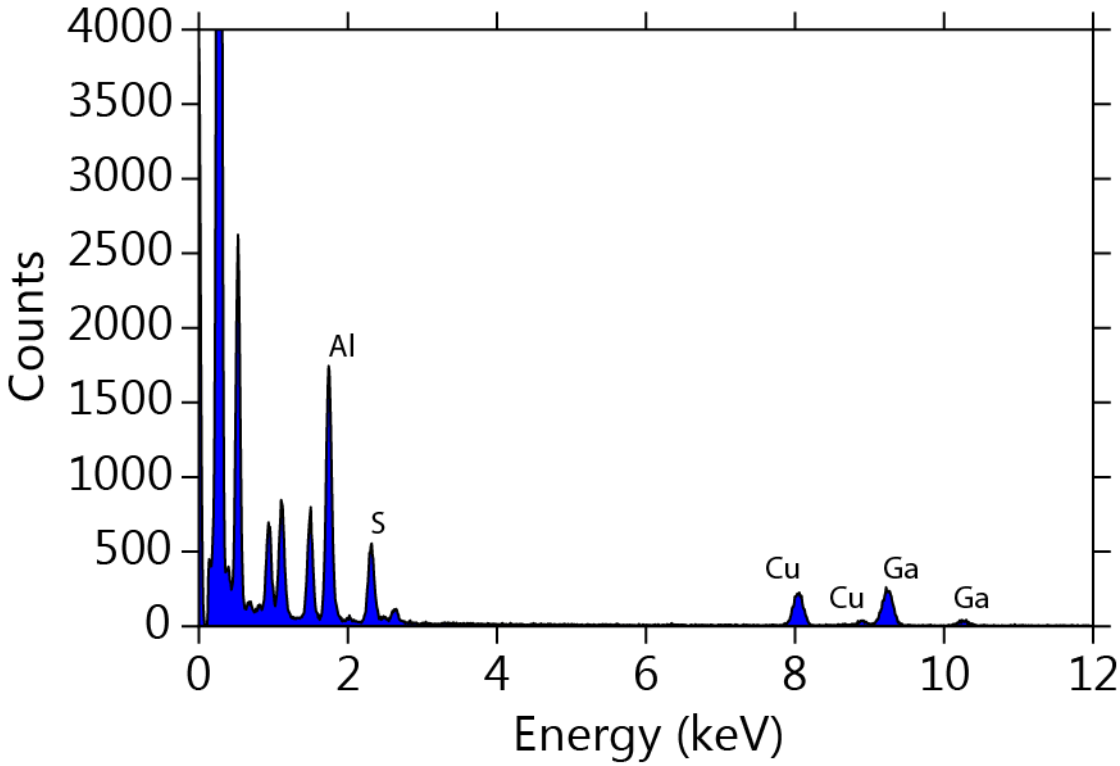

Figure S10. EDS of CGS nanocrystals, obtained after reaction of $Cu_{2-x}S$ nanocrystals with $GaCl_3$-DPP under milder reaction conditions (reaction temperature of 50°C) and in the presence of oleylamine ligands. Quantification of the spectrum revealed a Cu:Ga ratio of 1.00:0.62. The spectrum was acquired on a large region containing hundreds of nanocrystals. The aluminium grid used in the measurement causes the peak at around 1.5 keV.

2. Description of calibration of electron-diffraction (ED) patterns

Calibration of the measured ED patterns was performed by measuring the ED pattern of a gold reference sample (Agar S106). The two-dimensional pattern was then reduced to one dimension using the method described in the Experimental section. The known lattice distances of gold in real space, *d*, were transformed into distances in reciprocal space, *q*, using the equation $q=2\pi/d$ (Table S1).

Table S1. Lattice planes of cubic close packed gold, with the corresponding real-space lattice spacings *d*, obtained from JCPDS PDF-card 00-004-0784. The corresponding lattice space in reciprocal space, *q*, was calculated using $q=2\pi/d$.

Lattice plane	*d* (Å)	*q* (nm^{-1})
{111}	2.355	26.68
{200}	2.039	30.82
{220}	1.442	43.57
{311}	1.230	51.08

The measured peak maxima (in pixels) were plotted versus *q* (in nm^{-1}) and fit with a linear equation with an intercept at the origin. The resulting slope (in $nm^{-1}pixel^{-1}$) was used as calibration constant (or "camera constant") to convert the horizontal axis of the data from units of pixel into units of nm^{-1}.

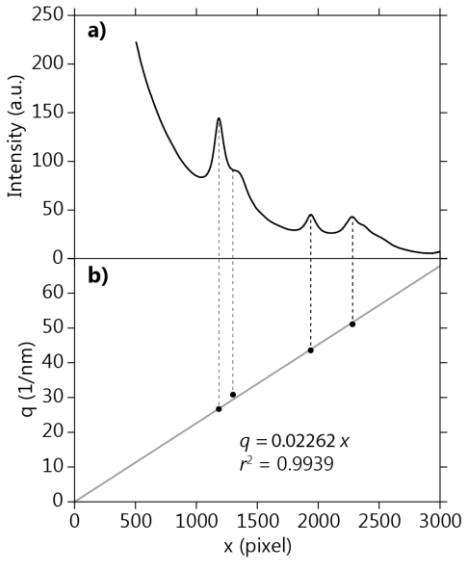

Figure S11. (a) Rotationally averaged electron-diffraction pattern of a gold reference sample and **(b)** the measured peak maxima plot versus the corresponding reciprocal space lattice spacings *q*. The resulting data points were fit using a linear equation with an intercept at the origin. The obtained slope was used as calibration constant. Dotted lines serve as guide to the eye.

This calibration procedure was performed for every ED measurement session. Comparison of the peak positions in the ED pattern of $CuInS_2$ nanocrystals (calculated using the calibration constant) to those in an XRD diffractogram of the same sample shows an excellent agreement (Figure S12)**,** indicating that the ED pattern calibration method used in our work is successful.

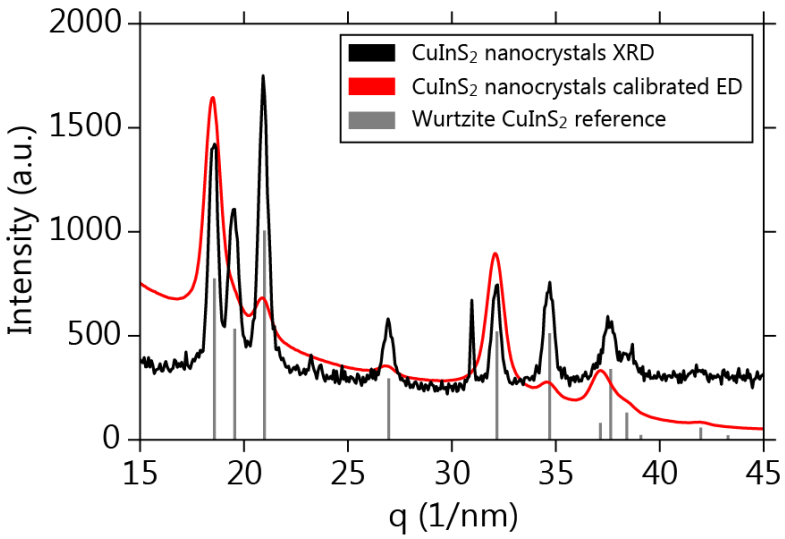

Figure S12. (black) X-ray diffraction (XRD) pattern of $CuInS_2$ (CIS) nanocrystals, (red) calibrated electron-diffraction pattern of the same sample and (gray) reference bars for the wurtzite CIS crystal structure. The XRD pattern was recorded using a Bruker D2 Phaser, equipped with a Cu Kα X-ray source (λ = 1.54184 Å). The horizontal axis of the resulting pattern was converted from 2ϑ (units of degrees) into q (units of 1/nm) using the equation $q = 4\pi \sin(\vartheta)/\lambda$. Reference bars were obtained from JCPDS PDF-card 01-077-9459.