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Cu(In_{1-x}Ga_x)S₂ nanocrystals and films: low-temperature synthesis with size and composition control†

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We demonstrate a single-step X-ray irradiation process that yields high-quality Cu(In_{1-x}Ga_x)S₂ nanocrystals in colloidal solutions, with complete control of size and composition. Thin films produced by drop-casting exhibit high-quality photoresponse, confirming that our process is suitable for microelectronics applications.

Photovoltaic technology is partly oriented towards quantum-confinement devices¹⁻³ based on semiconductor nanocrystal films. Cu(In_{1-x}Ga_x)Se₂ (CIGS)⁴⁻⁷ has emerged as a leading candidate with respect to other materials.⁸⁻¹³ Its advantages include high photovoltaic efficiency and several other aspects.¹⁴ High-quality CIGS nanocrystals in colloidal solution, suitable for thin film production, can be obtained with wet-chemistry approaches.^{15,16}

Still, CIGS is not immune from problems. An interesting alternative is Cu(In_{1-x}Ga_x)S₂ that can better match the solar spectrum with a direct gap tunable from 1.43 eV ($x = 0$) to 2.45 eV. Furthermore, the replacement of Se by S is highly desirable since it would decrease the environmental impact and the large-scale production costs.¹⁷

The practical use of Cu(In_{1-x}Ga_x)S₂ requires effective fabrication techniques for nanocrystal-based thin films, with full control of the composition that determines the optical and electrical properties.¹⁸ The preferred approach is to synthesize nanocrystals in a colloidal solution, to be used as a printable ink. The technical requirements include homogeneity in the nanocrystal composition and size and stability of such

characteristics throughout the fabrication process. One must specifically avoid, in the nanocrystals and in the final films, secondary phases such as Cu₂S–In₂S₃.^{19,20}

We present here an effective solution: a fabrication process based on irradiation of the precursor solution with intense X-rays from a synchrotron source. Among the possible chemical procedures,²¹⁻²⁷ we selected the reaction of elemental sulfur^{4,26} with Cu, Ga, and In salts. In fact, elemental sulfur is inexpensive and stable, and therefore preferable to other S sources.²¹⁻²⁷ The composition is accurately controlled by tuning the precursor solution composition.²⁸⁻³² X-ray irradiation causes a fast reduction that completely eliminates the composition inhomogeneities and yields nanocrystals with narrow size distributions, controlled by the irradiation time.

X-ray irradiation had been already tested for CuGaS₂ nanocrystals.³³ We were motivated to extend it to quaternary compounds in this family by the difficulties in controlling the composition with other methods.³⁴⁻³⁶ Specifically, previous approaches mostly relied on expensive organometallic single source precursors. Other irradiation methods based on microwaves³⁶ or ultraviolet light³⁷ required long exposure times, undesirable for large-scale production. Furthermore, they thermally activate the reactions, making it difficult to produce uniform-size nanoparticles.

We found that X-ray irradiation eliminates the above problems. The products, single-phase nanocrystals of uniform size, disperse well in toluene and can be deposited as uniform, crack-free thick films on glass and metal substrates.

Prototype photovoltaic devices were fabricated with this approach. Their photovoltaic response is stable and reproducible.

One marked advantage of our fabrication technique is temperature: the entire process takes place at room temperature, including thin film fabrication. This makes it suitable for other kinds of substrates, notably polymers.

Experimentally, the nanocrystals synthesized by irradiating the precursor solution with intense X-rays are described in detail in the ESI.†

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† Electronic supplementary information (ESI) available: Synthesis and experimental details, XPS spectra, SEM images, and the corresponding size distribution of the Cu(In_{1-x}Ga_x)S₂ nanocrystals. See DOI: 10.1039/c3nr00264k

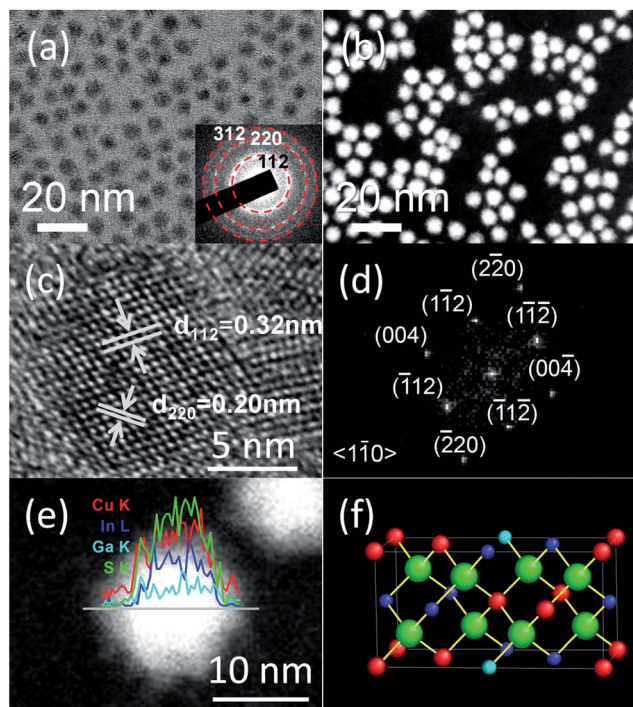


Fig. 1 (a) TEM image of $\text{Cu}(\text{In}_{0.73}\text{Ga}_{0.27})\text{S}_2$ nanocrystals. Inset: indexed SAED pattern. (b) HAADF-STEM image of typical 8 nm $\text{Cu}(\text{In}_{0.73}\text{Ga}_{0.27})\text{S}_2$ nanocrystals. (c) HRTEM image and (d) corresponding FFT of a single $\text{Cu}(\text{In}_{0.73}\text{Ga}_{0.27})\text{S}_2$ nanocrystal projected in the $\langle 110 \rangle$ direction. (e) STEM-EDS line scan along a single ~ 10 nm $\text{Cu}(\text{In}_{0.73}\text{Ga}_{0.27})\text{S}_2$ nanocrystal. (f) Structural model of the nanocrystal lattice projected along the (010) direction. Crystal structure: indium (blue) cations and gallium (cyan) cations occupy the tetrahedral sites of the chalcopyrite structure; sulphur anions and copper cations are shown in green and red.

The first characterization concerned the nanocrystal size. Fig. 1a and b show TEM and dark-field scanning transmission electron microscopy (DF-STEM) images of nanocrystals from a 0.3 Ga/(Ga + In) ratio solution, synthesized by X-ray irradiation for 5 minutes. The nanocrystals have near-spherical shapes with an average diameter ≈ 8.5 nm and a size deviation of 4.3 nm. TEM images and size distributions for Ga/(Ga + In) ratios of 1.0, 0.9, 0.7, 0.5, 0.1 and 0.0 are shown in Fig. S1 of the ESI.†

In all cases, the nanocrystals were found to be near-spherical, with narrow size distributions and good crystalline

character. The mean sizes for the above molar ratios are 6.8 ± 3.2 nm, 7.2 ± 2.9 nm, 7.5 ± 2.4 nm, 8.5 ± 2.1 nm, 8.7 ± 4.3 nm, and 9.9 ± 3.6 nm (Table 1).

The crystalline character of the nanocrystals is demonstrated by their SAED patterns – see the inset of Fig. 1a. Other phases are not observed and the nanoparticle composition appears uniform.

Fig. 1c and d show high-resolution TEM (HRTEM) images and the corresponding indexed fast Fourier transform (FFT) of a single nanocrystal projected in the $\langle 110 \rangle$ direction. These lattice images indicate again nanoparticles with good crystalline structure and no symptoms of an inhomogeneous internal composition. In Fig. 1e, a STEM-EDS line scan through the center of a single ~ 10 nm nanocrystal from a 0.3 Ga/(Ga + In) ratio reveals Cu, In, Ga, and S over the entire width, with an average Cu/In/Ga/S composition of 0.98/0.73/0.27/2.02, close to the 1.0/0.7/0.3/2.0 target. Fig. 1f shows the crystal structure.

XPS results for oleylamine-capped nanocrystals from a 0.3 Ga/(Ga + In) ratio are presented in ESI Fig. S2.† ESI Fig. S2a† reveals that the Cu 2p binding energy is in good agreement with reported values for CuInS_2 nanocrystals,²³ suggesting a copper valence state of +1. ESI Fig. S2b† shows the In 3d peaks consistent with a +3 valence. ESI Fig. S2c† shows the Ga 3d spectrum, in agreement with the literature.³⁸ In ESI Fig. S2d,† the S 2p peak includes the S $2p^{3/2}$ (161.5 eV) and S $2p^{1/2}$ (162.8 eV) components and indicates a -2 valence, characteristic of sulfide (*i.e.*, S bound to copper or indium).

Powder XRD patterns of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ nanocrystals are presented in Fig. 2, together with those of CuInS_2 and CuGaS_2 nanocrystals. These results support the formation of single-phase $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ nanocrystals and demonstrate their crystal structure to be tetragonal chalcopyrite. At $x = 0$, the XRD data correspond to chalcopyrite CuInS_2 (JCPDS no. 85-1575). As the Ga content increases, the diffraction peaks gradually shift toward higher 2θ angles due to the decrease in lattice spacing. At $x = 1$, the XRD results correspond to chalcopyrite CuGaS_2 (JCPDS no. 85-1574).

The lattice parameters a and c of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ derived from XRD are listed in Table 1. The relationship between a and c and the Ga/(Ga + In) ratio is shown in Fig. 3a and Fig. 3b, respectively. Here, the Ga/(Ga + In) ratios obtained from EDS

Table 1 Composition, size, and optical band gap (E_g) of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ nanocrystals obtained by X-ray irradiation

Ga/(In + Ga) ^a	Cu% ^b	Ga% ^b	In% ^b	In + Ga	Estimated sizes ^c (nm)	Measured sizes ^d (nm)	a^e (Å)	c^e (Å)	E_g^f (eV)
1.0	24.32	25.81	0.00	25.81	6.6	6.8 ± 3.2	5.34	10.50	2.45
0.9	25.25	22.32	2.44	24.76	7.1	7.2 ± 2.9	5.36	10.60	2.27
0.7	24.52	17.11	7.75	24.86	7.3	7.5 ± 2.4	5.43	10.72	1.99
0.5	24.38	11.02	14.51	25.53	7.7	8.5 ± 2.1	5.46	10.93	1.75
0.3	25.71	5.01	19.53	24.54	8.1	8.5 ± 4.3	5.49	11.02	1.55
0.1	24.14	2.27	22.75	25.02	8.8	8.7 ± 4.3	5.51	11.07	1.45
0.0	24.25	0.00	25.65	25.65	9.7	9.9 ± 3.6	5.53	11.08	1.43

^a Feed molar ratio. ^b EDS measurements have an error of $\approx \pm 2$ atom%. ^c Estimated mean sizes from the (112) 2θ position of XRD. ^d Measured mean sizes based on manual counts of $\approx 10^3$ nanocrystals from TEM images. ^e The lattice parameters a and c were determined from XRD patterns. ^f Gap energies (E_g) were determined from UV-VIS-NIR spectra.

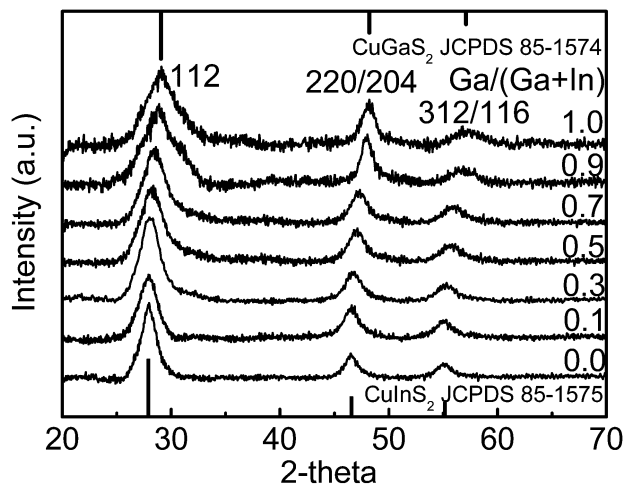


Fig. 2 XRD angular scans of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ nanocrystals for different Ga/(Ga + In) ratios.

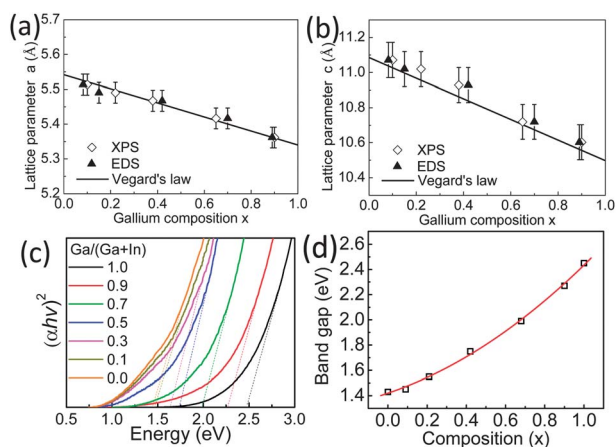


Fig. 3 Relationship between (a) the lattice parameter a or (b) the lattice parameter c and the x -value for $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ nanocrystals. (c) Optical absorption data of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ nanocrystals for different Ga/(Ga + In) ratios; (d) band gap as a function of x (determined by EDS).

correspond to the solid triangles, and those from XPS to hollow diamonds. The straight line shows Vegard's law. These results again support the conclusion that the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ nanocrystals contain a single phase.

The average sizes of the nanocrystals were estimated from the Scherrer equation assuming no microstrain. Taking microstrains into account, the size measured should be smaller than what was observed by TEM.³⁹ This is in fact what we find (see Table 1), suggesting that our nanocrystals do have microstrains. Both the average sizes estimated from XRD and those measured by TEM increase with the In content and reach a maximum for ternary CuInS_2 . This trend is in agreement with previous reports.^{4,6}

Absorption measurements of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ nanocrystals dispersed in toluene with varying gallium content highlight the ability to effectively select the band gap (Fig. 3c). The absorption threshold red-shifts with the In content, consistent with the

narrower CuInS_2 gap. The nanocrystals gap can in fact be tuned from 2.45 eV to 1.43 eV by controlling x , as shown in Fig. 3d. The relationship is nonlinear as for several other semiconductor alloys. For example, both bulk and nanocrystal $\text{CdSe}_x\text{Te}_{1-x}$ display a similar "optical bowing" linked to the 11% lattice mismatch.^{40,41}

Three factors contribute to this effect: different atomic size, the electro negativities of the ions, and the different lattice constants.^{42,43} Lattice mismatch (12%) should play a significant role in this case. To analyze this point, the gap vs. x curve was fitted using the modified bowing equation:

$$E_g = (1 - x)E_{g(\text{CuInS}_2)} + xE_{g(\text{CuGaS}_2)} - bx(1 - x),$$

where $E_{g(\text{CuInS}_2)}$ and $E_{g(\text{CuGaS}_2)}$ are CuInS_2 and CuGaS_2 gaps and b is the so-called "bowing parameter". We found a b -value of 0.48 eV, slightly larger than the reported values of 0.42 for $\text{Cu}_{1.0}\text{Ga}_x\text{In}_{2-x}\text{S}_{3.5}$.³⁶ The small difference is reasonable considering the difference in composition.

Finally, we performed (Fig. 4) preliminary photoresponse tests for thin films obtained by drop-casting from nanoparticle in toluene. Fig. 4b shows a smooth $\sim 1 \mu\text{m}$ thick film on a glass substrate with gold electrodes (interdigitated).¹² The nanocrystal film thickness could be controlled by varying the nanocrystal concentration in the solution, as shown in Fig. 4a. The drop-casting procedure worked well to deposit uniform, crack-free nanocrystal films. However, it was so far limited to a maximum thickness $\approx 2.5 \mu\text{m}$. Multiple dropping steps could increase the thickness, but cracks appear after thermal annealing (ESI Fig. S3†).

The current-voltage (I - V) curves, shown in Fig. 4c for $\text{CuIn}_{0.73}\text{Ga}_{0.27}\text{S}_2$, CuGaS_2 , and CuInS_2 nanocrystals, exhibit photoresponse. The current of $\text{CuIn}_{0.73}\text{Ga}_{0.27}\text{S}_2$ films at 5 V increases indeed from 9.2×10^{-6} mA in the dark to 1.4×10^{-5} mA under illumination.

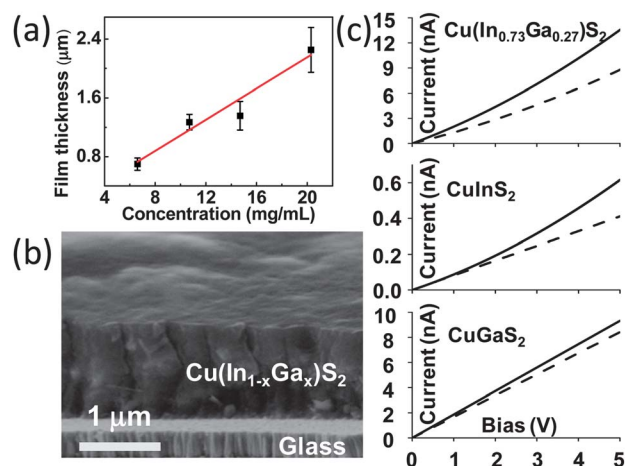


Fig. 4 Thin films obtained by drop-casting from our colloidal nanoparticle solutions in toluene. (a) Film thickness for different solution concentrations. (b) SEM image showing the cross-section of a $1.3 \mu\text{m}$ thick nanocrystal film on soda lime glass. (c) Photovoltaic response of the films: I - V curves of films built by drop-casting CuGaS_2 , CuInS_2 , and $\text{Cu}(\text{In}_{0.73}\text{Ga}_{0.27})\text{S}_2$ nanocrystals; the curves were taken in the dark (dashed lines) and under lamp illumination (solid lines).

In summary, We have successfully tested an X-ray irradiation method to produce $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ nanocrystals in colloidal solutions. Results from XRD and TEM, together with EDS and XPS, show that each nanocrystal has a single phase. The size distribution of nanocrystals is narrow. The optical gap and the lattice parameters depend on the composition, following the bowing equation and Vegard's law.

We also investigated the transport properties of drop-cast nanocrystal films on interdigitated electrodes, finding a clear photoresponse: a current increase by a factor of two from the dark to illumination. Thus, our method yields products suitable for photovoltaic device technology. Considering the advantages of the procedure, from low temperature to excellent size and composition control, these results constitute a significant technological advance in nanoparticle-based electronics.

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