Supporting Information:

Sn Cation Valency Dependence in Cation Exchange Reactions Involving Cu$_{2-x}$Se Nanocrystals

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Size distribution analysis

![Size distribution analysis](image)

**Figure S1.** Size distributions of pristine Cu$_{2-x}$Se and exchanged Cu$_{0.66}$Sn$_{0.33}$Sn (or Cu$_2$SnSe$_3$) and SnSe NCs along with their average sizes calculated from corresponding TEM images presented in Figure 1 and 3 of the main text.

Crystal structure of Cu$_{2-x}$Se and Cu$_{0.66}$Sn$_{0.33}$Se phases and their site occupancy

Both cubic Cu$_{2-x}$Se and Cu$_{0.66}$Sn$_{0.33}$Sn (or Cu$_2$SnSe$_3$) phases exhibit an fcc arrangement of Se anions with the isometric basis vectors on a generic Se atom forming Se1 sites with multiplicity 4 and occupancy 1. The Se anion sublattices of the two phases form polyhedral sites in the structures: two cation sites with different coordination occur, namely tetrahedral at (0.25; 0.25; 0.25) with multiplicity 8 and non-tetrahedral at (0.3333; 0.3333; 0.3333) with multiplicity 32.

In Cu$_{2-x}$Se both tetrahedral (Cu1, red spheres in Fig S2) and non-tetrahedral (Cu2, orange spheres in Figure S2) sites are partially filled by Cu with an occupancy of 0.8 and 0.03, respectively. In Cu$_2$SnSe$_3$, only the tetrahedral sites (Cu/Sn1) occur. They exhibit multiplicity 4 and they are characterized by mixed filling in Cu and Sn, with occupancy of 0.67 and 0.33, respectively.
Figure S2. Atom structure models of cubic Cu$_{2-x}$Se and Cu$_2$SnSe$_3$ phases describing the crystal sites arrangement within the unit cells, characterized by four unit formula along two different zone axes. Note the fcc structure of Se anions sublattice (Se1 = Se sites, blue spheres) in both structures, the Cu sites with tetrahedral (Cu1, red spheres) and non-tetrahedral (Cu2, orange spheres) coordination in cubic Cu$_{2-x}$Se (left part of panels A and B) and the presence only of tetrahedral sites Cu/Sn1 with mixed Cu/Sn occupancy in Cu$_2$SnSe$_3$ (right part of panels A and B). Atom structure models showing coordination tetrahedra built around the tetrahedral Cu1 sites of both structures were added for better clarity in the bottom part of the two panels of the figure.
Elemental analysis by energy dispersive X-ray spectroscopy (EDS)

The elemental analysis was performed in STEM-EDS mode using a 0.7 nm wide electron probe. In all the analyses, the solutions were drop-cast on carbon-coated ultrathin Au grids and an analytical double tilt holder equipped with a low background beryllium tip was used. This setup was chosen in order to avoid interference and spurious signals coming from the holder and the standard ultrathin Cu grids during the spectral acquisitions.

In order to assess the homogeneous composition of the NCs during the cation exchange process from Cu$_{2-x}$Se to Cu$_{0.66}$Sn$_{0.33}$Se, EDS spectra were acquired in spot mode in different regions (central and peripheral) of each analyzed NC (see the examples of Figure S3). By comparing the averaged values obtained by EDS “spot” measurements recorded on whole single NCs, as well as on large groups of NCs, with the chemical results obtained by ICP (see Table below), the homogeneous distribution of Sn$^{4+}$ ions in the NCs was proven.

| SAMPLE                | Chemical quantification |          |          |
|----------------------|-------------------------|----------|----------|
|                      | EDS (spot)              | EDS (group) | ICP      |
| PARENT Cu$_{2-x}$Se | Cu$_{1.86}$Se          | Cu$_{1.99}$Se | Cu$_{1.96}$Se |
| INTERMEDIATE I       | Cu$_{1.20}$Sn$_{0.19}$Se | Cu$_{1.21}$Sn$_{0.16}$Se | Cu$_{1.2}$Sn$_{0.2}$Se |
| INTERMEDIATE II      | Cu$_{0.94}$Sn$_{0.26}$Se | Cu$_{0.90}$Sn$_{0.26}$Se | Cu$_{0.9}$Sn$_{0.3}$Se |
| FINAL Cu$_{0.66}$Sn$_{0.33}$Se | Cu$_{0.66}$Sn$_{0.31}$Se | Cu$_{0.58}$Sn$_{0.28}$Se | Cu$_{0.66}$Sn$_{0.33}$Se |
**Figure S3.** Representative high angle annular dark field (HAADF) scanning TEM (STEM) images of Cu$_{2-4}$Sn$_3$Se NCs. The collected spots for EDS spectra are indicated with colored dots going from 1 to 4 (a, Intermediate I) and from 1 to 2 (b, Intermediate II). Corresponding EDS spectra acquired in spot mode are shown below each HAADF-STEM image. In the EDS spectra, the main peaks of Se (Lα, 1.393 keV), Sn (Lα, 3.443 keV) and Cu (Kα, 8.036 keV), used for the chemical quantification, are indicated. The Lα peak of Cu (0.932 keV) is also reported in the spectra together with the Mα and Lα peaks of Au (2.123 keV and 9.704 keV, respectively), originating from the grid.
Epitaxial symmetry relationships for Cu$_{2-x}$Se/SnSe heterostructures

The interface between Cu$_2$Se (space group Fm$_3$m, JCPDS card 79-1841) and SnSe (space group Pnma, JCPDS card 48-1224) of Cu$_{2-x}$Se/SnSe heterostructures was analysed in order to find possible epitaxial symmetry relationships. The interface was aligned according to the following symmetry relationships:

$$\text{Cu}_2\text{Se } (1\overline{1}1)/\text{SnSe}(201)$$

$$\text{Cu}_2\text{Se } [-1\overline{7}2]/\text{SnSe }[-112]$$

with the first term representing the interface alignment and the second one the vector alignment. Thus, it was possible to calculate the actual lattice mismatch ($m$) between average lattice spacings of the two phases along a given direction. The mismatch parameter was defined from the average lattice spacings of phase 1 and 2 ($d_1$ and $d_2$, respectively) as:

$$m = 2\times |d_1 - d_2| / (d_1 + d_2)).$$

The Fourier analysis of the HRTEM images of well oriented heterostructures was performed by means of filtered 2D-Fast Fourier Transform (FFT) and proved the alignment of the epitaxial-related domains (see figure S4). A noticeable angular distortion between the 220 spots of Cu$_{2-x}$Se and -511 of SnSe was observed and it can be attributed to distortions in the anionic framework caused by the partial cation exchange of Cu$^+$ ions with Sn$^{2+}$ ions.

| Commensurate lattice mismatches $m$ |
|-------------------------------------|
| Cu$_{2-x}$Se //SnSe                | m          |
| [1-11]/[201]                       | 2.9%       |
| [-112]/[-1-72]                     | 0.8%       |
| [220]/[-511]                       | 10.2%      |
Figure S4. (left) HRTEM image of a representative Cu$_{2-x}$Se/SnSe epitaxial heterostructure where different domains are pictured in false colors (green and red respectively). (right) FFT patterns of Cu$_{2-x}$Se in green ([112] zone axis) and SnSe in red ([1-72] zone axis).

As shown from in the left panel of Figure S4, there is a visible angular distortion between the (220) planes of Cu$_{2-x}$Se and the (-511) planes of SnSe, which is also affected by a lattice mismatch higher than 10%, as reported in the previous table. Thus the epitaxial relationship characterizing our heterostructure can been defined as imperfect.
Polycrystalline and cubic SnSe NCs in the cation exchange process with Sn$^{2+}$ ions

**Figure S5.** HR-TEM images of (a) a polycrystalline Cu$_{2-x}$Se/SnSe heterostructure exhibiting different domains (Cu$_{2-x}$Se in green, SnSe in red and light blue) and (b) two fully exchanged SnSe NCs. In this last figure the NC in the top exhibits lattice spacings compatible with the cubic SnSe phase (space group Fm-3m, ICDD 01-089-4781) and the bottom NC shows two distinct domains (both red and blue correspond to two different SnSe domain) with lattice spacings compatible with orthorhombic SnSe (space group Pnma, ICDD 01-089-0233). Scale bars in both images are 5 nm. (c) A typical x-ray diffraction pattern collected from a dropcast solution of SnSe NCs obtained in a cation exchange process with Sn$^{2+}$ ions. The corresponding bulk reflections of orthorhombic SnSe (ICDD 01-089-0233) and cubic SnSe (ICDD 01-089-4781) phases are reported. The low intensity of the peaks corresponding to the cubic SnSe phase is directly related to the very small percentage of cubic SnSe NCs.
Cation exchange with Sn$^{2+}$ ions: *in situ* approach

**Figure S6.** HR-TEM images of representative NCs after the *in situ* cation exchange reaction, exhibiting lattice spacings compatible with (a) Cu$_{0.66}$Sn$_{0.33}$Se (space group F-43m, JCPDS card 65-7524), cubic SnSe (space group Fm-3m, JCPDS card 89-4781) and (b) orthorhombic SnSe (space group Pnma, JCPDS card 48-1224). (c) STEM-EDS chemical mapping and (d) image of a representative group of NCs, obtained by measuring the Sn L$\alpha$, (3.443 keV) and Cu K$\alpha$, (8.036 keV), edges, showing the distribution of Cu and Sn in the sample. (e) X-ray diffraction pattern and (f) Raman spectrum obtained from the dropcast solution of NCs produced by the *in situ* approach. While by x-ray diffraction measurements only the orthorhombic SnSe phase was detected, in the Raman spectrum it possible to see the main signals of the SnSe phase at 110 and 155 cm$^{-1}$ together with a shoulder at about 180 cm$^{-1}$ that we ascribe to the Cu$_2$SnSe$_3$ phase.

Cation exchange with Sn$^{4+}$ ions at high temperature

As a control experiment we performed a cation exchange reaction with Sn$^{4+}$ ions at 200°C. In this experiment, after quenching the Cu$_{2x}$Se NCs synthesis, the crude reaction mixture was heated to 100°C. At this point a solution of 0.4mmol of SnAc$_2$Cl$_2$ in ODE (4ml) and DDT (1ml), prepared in the glove box at 130°C, was transferred into the reaction flask together with 2ml of TOP. After the injection the
temperature of the reaction was allowed to reach 200°C for 10 minutes. The NCs were then washed twice by precipitation with addition of methanol followed by redissolution in toluene. As confirmed by ICP and XRD analysis, the product of the exchange were orthorhombic SnSe NCs showing a different morphology with respect to their parent Cu$_{2-x}$Se NCs (see Figure S7).

Figure S7. (a) Low resolution TEM image of the resulting SnSe NCs. (b) X-ray diffraction pattern obtained from the dropcast solution of the produced SnSe NCs. The corresponding bulk reflections of SnSe (ICDD 01-089-0233) are reported.
X-ray diffraction study of Cu$_{2-x}$Se NCs films.

Additional XRD measurements were carried on Cu$_{2-x}$Se NCs films in order to explain why in a typical 2theta/omega XRD acquisition the intensity ratio of the (111)/(220) reflections from Cu$_{2-x}$Se NCs does not match with what expected from the bulk Cu$_{1.75}$Se pattern (see discussion below). A Cu$_{2-x}$Se film was prepared by drop-casting a solution of NCs onto zero-background silicon wafer. Two different scan methods, with the use of parallel beam optics, were performed on the very same sample:

- Symmetric 2theta/omega scan: both angles of incident and diffracted beam against the sample surface are the same.
- Asymmetric 2theta scan: the incident X-ray beam is kept at a small angle ($\omega = 3^\circ$) while only the detector on 2theta axis is scanned to record diffraction intensities.

The collected XRD patterns are shown in Figure S8. As it is possible to see in Figure S8a (and in Figures 1d and 3d of the main text), in a typical 2theta/omega scan the intensity ratio of the (111)/(220) reflections from Cu$_{2-x}$Se NCs films (at roughly 27° and 45°, respectively) is much higher than that from the bulk Cu$_{1.75}$Se pattern. Being the crystal habit of our Cu$_{2-x}$Se NCs isotropic (i.e. cuboctahedral)\textsuperscript{1} we exclude any effect arising from an anisotropic growth of the NCs. The most probable explanation would be then that Cu$_{2-x}$Se NCs tend to form clusters, while being dropcast on the silicon wafer, that exhibit a preferential orientation. This is supported by our XRD measurements at small angle (on the very same film) in which all the observed reflections have intensities that are well matching with the bulk Cu$_{1.75}$Se ones (see Figure S8b). In this experimental configuration, in fact, the clusters of NCs with a preferential orientation are not in Bragg regime diffraction anymore and the observed XRD pattern arises from the randomly oriented NCs.
Figure S8. X-ray diffraction patterns obtained from the same Cu$_{2.5}$Se NCs film using (a) a symmetric 2theta/omega scan and (b) an asymmetric 2theta scan. The corresponding bulk reflections of Cu$_{1.75}$Se (ICDD 01-075-2714) are presented, highlighting the (111) and (220) reflections.

References

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