Supporting Information for:

Selective Cation Exchange in the Core Region of Cu$_{2-x}$Se/Cu$_{2-x}$S Core/Shell Nanocrystals

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- **Transmission electron microscopy (TEM) analyses.** The samples were prepared by dropping dilute suspensions of nanocrystals (NCs) onto carbon coated aluminum grids. High-resolution TEM (HRTEM) imaging and energy-dispersive X-ray spectroscopy (EDS) analyses, the latter combined with high-angle annular dark field (HAADF) - scanning TEM (STEM) imaging, were carried out with a JEOL JEM-2200FS microscope equipped with a Schottky emitter working at an accelerating voltage of 200 kV, a CEOS spherical aberration corrector for the objective lens and a Bruker Quantax 400 system with a 60 mm² XFlash 6T silicon drift detector (SDD). The EDS spectra were quantified using the Cliff-Lorimer method for the Cu Kα, Se Kα, S Kα, Ag Lα, Cd Lα, Hg Lα, Au Lα peaks, and the reported STEM-EDS maps are obtained by integrating the intensities over the same peaks, except for Cd maps, where the Lβ peak was used. In case of EDS maps on partially Ag⁺-exchanged core/shell CdSe/CdS NRs, the Ag Lα and Cd Lβ peaks were integrated over a narrow range (55% of the peak area) due to partial superimposition of the respective peaks in the L series. Selected area electron diffraction (SAED) patterns were acquired using a FEI Tecnai F20T TEM (Schottky emitter, 200 kV) at constant camera length with the sample placed at the eucentric height and after carefully focusing the NC images. The camera length was calibrated using a nanocrystalline Au sputtered film on a standard C-covered Cu grid. The elaboration of SAED patterns (beam-stop removal, centering, azimuthal integration and background subtraction) was carried out using PASAD.¹

- **X-ray diffraction (XRD) measurements.** X-ray diffraction analysis was performed on a PANanalytical Empyrean X-ray diffractometer equipped with a 1.8 kW CuKα ceramic X-ray tube, PIXcel³D 2x2 area detector and operating at 45 kV and 40 mA. Specimens for the XRD measurements were prepared in a glove box by dropping a concentrated NCs solution onto a quartz zero-diffraction single crystal substrate. The diffraction patterns were collected in air at room temperature using Parallel-Beam (PB) geometry and symmetric reflection mode. XRD data analysis was carried out using HighScore 4.1 software from PANalytical.
- **Chemicals.** Triocylphosphine oxide (TOPO, 99%), Triocylphosphine (TOP, 97%), Sulfur powder (S, 99%), Selenium powder (Se, 99.99%), Copper(I) chloride (CuCl, 99.999% ), Mercury(II) bromide (HgBr₂, ACS) were purchased from Strem Chemicals. Octadecylphosphonic acid (ODPA, 99%) and Hexylphosphonic acid (HPA, 99%) were purchased from Polycarbon Industries. Cadmium oxide (CdO, 99.5%), Cadmium chloride (CdCl₂, 99.99%), Tetrakis(acetonitrile)copper(I) hexafluorophosphate ([Cu(CH₃CN)₄]PF₆, 99.99%), Oleylamine (Olam, 70%), 1-octadecene (ODE 90%), Silver nitrate (AgNO₃, 99.999%), Copper(II) chloride (CuCl₂, 99%), Gold(III) chloride (AuCl₃, 99%) were purchased from Sigma-Aldrich. Anhydrous methanol and toluene were purchased from Carlo Erba reagents.

- **Synthesis of CdS nanorods (NRs).** TOPO (3.0 g), ODPA (0.280 g), HPA (0.110 g), CdO (0.050 g) and CuCl₂ (0.006 g) were mixed in a 50 mL flask and degassed under vacuum at 130 °C for one hour. After that the solution was heated up to 300 °C under nitrogen and 1.5 g of TOP was injected into the flask. The temperature was then set to 350 °C and a S:TOP solution (prepared by dissolving 0.06 g of sulfur powder in 1.5 g of TOP) was injected into the flask to start the nucleation of the NCs. The NCs were allowed to grow for 10 minutes, after which the flask was rapidly cooled down to room temperature. After the synthesis, the NCs were washed by repeated precipitation with the addition of methanol and redissolution in toluene. Finally the NCs were dissolved in toluene.

- **Synthesis of CdSe NRs.** CdO (0.060 g) was mixed with TOPO (3.0 g), ODPA (0.280 g) and HPA (0.110 g) in a 50 mL flask, heated up to 130°C and exposed to vacuum for one hour. Then, under nitrogen, the solution was heated up to 300°C to dissolve the CdO. When the reaction mixture became optically clear and colorless, 1.5 g of TOP was injected into the flask. The temperature was then set to 350 °C and a Se:TOP solution (obtained by dissolving 0.15 g of selenium powder in 1.5 g of TOP) was injected into the flask to start the nucleation of the NCs. The NCs were allowed to grow for 7 minutes, after which the flask was rapidly cooled down to room temperature. The NCs were repeatedly precipitated with methanol and were eventually dissolved in toluene.
- Synthesis of core/shell CdSe/CdS NRs. In a typical synthesis of core/shell CdSe/CdS NRs via a seeded growth approach, adapted from ref \(^2\), CdO (0.060 g) and CdCl\(_2\) (0.006 g) were mixed in a flask together with TOPO (3 g), ODPA (0.280 g) and HPA (0.080 g) and degassed under vacuum for about one hour at 130\(^\circ\)C. The resulting solution was heated up to 300 \(^\circ\)C under nitrogen and, after the complete dissolution of the CdO precursor, 1.5 g of TOP was injected into the flask. The temperature was allowed to reach 350 \(^\circ\)C and a solution containing both the sulfur precursor and the CdSe seeds was quickly injected. Such solution was previously prepared by dissolving 0.060 g of sulfur powder in 1.5 g of TOP and adding 200 \(\mu\)L of a 400 \(\mu\)M solution of CdSe rods in TOP. The NCs were allowed to grow for 7 minutes, then the synthesis was quenched by removing the heating mantle and leaving the solution to cool down to room temperature. After a first precipitation with methanol, the NCs were redispersed in toluene.

- Synthesis of “inverted” core/shell CdS/CdS\(_x\)Se\(_{1-x}\) NRs. In a typical synthesis, according to the procedure published by our group,\(^3\) CdO (60 mg), CdCl\(_2\) (6 mg), HPA (80 mg), ODPA (290 mg) and TOPO (3 g) were mixed in a 25 mL flask and degassed under vacuum at 120 \(^\circ\)C for 1 h. The temperature was raised to 380 \(^\circ\)C under nitrogen and the initial red suspension transformed into a transparent solution. Then 2 mL of TOP were added to the solution and, once the temperature was recovered, 0.25 g of S:TOP solution (prepared in a glovebox by dissolving 90 mg of sulfur powder in 1mL of TOP) was injected into the flask and the reaction was allowed to run for 10 minutes. The temperature of the reaction vessel was then lowered to 350 \(^\circ\)C and 0.25 g of a Se:TOP solution (prepared in a glovebox by dissolving 72 mg of selenium powder in 1mL of TOP) was added. The reaction mixture was stirred at this temperature for an additional 5 minutes to allow the growth of the CdS\(_x\)Se\(_{1-x}\) shell around the CdS cores. The synthesis was quenched by cooling the solution down to room temperature and the final brown product was extracted with toluene and precipitated by addition of methanol. Eventually, the NCs were redispersed in toluene.

- Cation exchange on Cd-based NCs. Cu\(_{2-x}\)S bullets, core/shell Cu\(_{2-x}\)Se/Cu\(_{2-x}\)S NRs and “inverted” core/shell Cu\(_{2-x}\)S/Cu\(_{2-x}\)Se NRs were prepared through a complete cation exchange from Cd\(^{2+}\) to Cu\(^+\),
performed in a nitrogen-filled glovebox, following a procedure reported by Sadtler et al. In each experiment a Cu\(^+\) solution in methanol was prepared by dissolving 0.03 mmol of tetrakis(acetonitrile)copper(I) hexafluorophosphate in 5 mL of methanol. 0.01 mmol of Cd-based NCs were dispersed in 5 mL of toluene and then mixed with the Cu\(^+\) solution, under stirring for 5 minutes, at room temperature. The Cu/Cd atomic ratio all the experiment was 3. The exchanged NCs were precipitated through centrifugation and redispersed in toluene.

- **Direct synthesis of Cu\(_{2-x}\)Se NCs.** The synthesis of Cu\(_{2-x}\)Se NCs was carried out following a procedure previously reported by our group, with slight modifications. A mixture of Olam (3mL) and ODE (5mL) was degassed under vacuum in a reaction flask at 130°C for one hour, using a standard Schlenk line. Then the mixture was put under nitrogen flow and 1 mmol of CuCl, previously dissolved in 2 mL of degassed Olam in a nitrogen filled glovebox, was added into the reaction flask. The temperature was set to 310°C and a solution of Se (0.5 mmol) in Olam (3 mL) was rapidly hot injected into the reaction flask at 280°C. The overall reaction time after the injection was 15 minutes, after which the flask was rapidly cooled to room temperature. The NCs were precipitated with the addition of methanol and eventually redissolved in toluene.

- **Direct synthesis of Cu\(_{2-x}\)S NCs.** The synthesis of Cu\(_{2-x}\)S NCs was carried out following a published procedure. 100 mg of CuCl and 10 mL of Olam were loaded in a reaction flask and degassed at 130 °C for 2 h under vacuum. Then the mixture was put under nitrogen flow and the temperature was set to 240 °C, followed by the injection of a sulfur solution obtained by dissolving 32 mg of sulfur in 2 mL of degassed Olam. The overall reaction time was 10 minutes. The final product was precipitated by addition of methanol, centrifuged, and redispersed in toluene.

- **Cation exchange reactions involving Ag\(^+\), Hg\(^{2+}\) and Au\(^{3+}\) ions.** In a typical cation exchange reaction with Ag\(^+\) (or Hg\(^{2+}\) or Au\(^{3+}\)) ions, a solution of AgNO\(_3\) (or HgBr\(_2\) or AuCl\(_3\)) in methanol (1 mL) was mixed with a dispersion of Cu (or Cd)-based NCs in toluene at room temperature under nitrogen. After one minute the NCs were precipitated and finally redispersed in toluene.
In the case of Cu$_{2-x}$S NRs, we used a Ag/S feed molar ratio equal to 0.25 (the resulting NCs are shown in Figure 1b of the main text) and a Hg/S feed molar ratio of 0.5 (the resulting NCs are shown in Figure 1c of the main text). In experiments involving the core/shell Cu$_{2-x}$Se/Cu$_{2-x}$S NRs we used a Ag/Se feed ratio of 4 and a Hg/Se feed ratio of 10 for the partial cation exchange (the resulting NCs are shown in Figure 2 of the main text and in Figures S3-S4), while for the complete cation exchange process we used a Ag/Se feed ratio of 15 and a Hg/Se feed ratio of 20 (the resulting NCs are shown in Figure S6 and S7). In partial cation exchange experiments with gold ions a Au/Se ratio of 5 was used (the resulting NCs are shown in Figure S8). For the “inverted” core/shell Cu$_{2-x}$S/Cu$_{2-x}$Se NRs we used a Ag/Se feed ratio of 2.4 and a Hg/Se feed ratio of 1.2 for the partial cation exchange experiments (the resulting NCs are shown in Figure 4 of the main text). The results of the exchange reactions with core/shell Cu$_{2-x}$Se/Cu$_{2-x}$S NRs and “inverted” core/shell Cu$_{2-x}$S/Cu$_{2-x}$Se NRs have been summarized in Table S1. As regarding the CE on a mixed population of Cu$_{2-x}$S and Cu$_{2-x}$Se NCs the Ag/Se feed ratio we used was 1.5 while the Hg/Se one was 0.5 (the resulting NCs are shown in Figure 5 of the main text). In the case of core/shell CdSe/CdS NRs we used a Ag/Se feed ratio equal to 6 (the resulting NCs are shown in Figure S9) for partial exchange experiments.
Table S1. Results of the CE reactions between Cu-based NCs and Ag\(^{+}\), Hg\(^{2+}\) and Au\(^{3+}\) ions.

|                        | Exchange with Ag\(^{+}\) ions |                         | Exchange with Hg\(^{2+}\) ions |
|------------------------|-----------------------------|-------------------------|---------------------------------|
|                        | Ag/Se feed molar ratio      | Composition from EDS    | Hg/Se feed molar ratio          | Composition from EDS    |
| Cu\(_{2-x}\)Se/Cu\(_{2-x}\)S NRs | 4                           | Ag\(_{1.6}\)Se/Cu\(_{1.8}\)S   | 10                              | Hg\(_{0.9}\)Se/Cu\(_{2}\)S |
|                        | 15                          | Ag\(_{16.6}\)Cu\(_{0.7}\)S\(_{6.8}\)Se | 20                              | Hg\(_{7.2}\)CuS\(_{6.7}\)Se |
| “inverted” Cu\(_{2-x}\)S/Cu\(_{2-x}\)Se NRs | 2.4                         | Cu\(_{3.0}\)S/Ag\(_{1.6}\)Se   | 1.2                              | Cu\(_{1.0}\)S/Hg\(_{1.2}\)Se |

|                        | Exchange with Au\(^{3+}\) ions |
|------------------------|--------------------------------|
|                        | Au/Se feed ratio   | Composition from EDS    |
| Cu\(_{2-x}\)Se/Cu\(_{2-x}\)S NRs | 5                                       | Au\(_{0.7}\)Se/Cu\(_{2.1}\)S |

Figure S1. UV-Vis-NIR Absorption spectrum of core/shell Cu\(_{2-x}\)Se/Cu\(_{2-x}\)S NRs dispersed in TCE. The broad absorption peak with its maximum at about 1200 nm is ascribable to a localized surface plasmon resonance arising from the presence of Cu vacancies in the NCs.
Figure S2. Azimuthally integrated, background subtracted SAED patterns collected on (c) pristine, (b) Ag\(^+\) and (a) Hg\(^{2+}\) partially exchanged Cu\(_{2-x}\)S NRs (same samples as reported in Figure 1 in the main text). The corresponding bulk reflections of monoclinic Cu\(_2\)S (low chalcocite, ICSD 100333), monoclinic Ag\(_2\)S (\(\beta\)-Ag\(_2\)S, ICSD 182916) and trigonal HgS (cinnabar, ICSD 70054) are reported.
Figure S3. HAADF-STEM image of a representative group of Ag\textsuperscript{+}-partially exchanged core/shell Cu\textsubscript{2-x}Se/Cu\textsubscript{2-x}S NRs with the corresponding STEM-EDS elemental maps.
**Figure S4.** HAADF-STEM image of a representative group of Hg\(^{2+}\)-partially exchanged core/shell Cu\(_2\)\(_x\)Se/Cu\(_{2-x}\)S NRs with the corresponding STEM-EDS elemental maps.
Figure S5. HRTEM images of partial Hg$^{2+}$ (top, feed molar ratio Hg:Se=10) and Ag$^+$ (bottom, feed molar ratio Ag:Se=4) exchanged core/shell Cu$_{2-x}$Se/Cu$_{2-x}$S NRs. In both cases, the HRTEM images show that the nanocrystals are structurally defective, as they exhibit zinc-blende stacking faults (ZB SF) and twin boundaries (TB) formed due to the lattice misfit between core and shell materials (some of these defects are indicated in the Figure). In particular, a continuous shell clearly surrounds the cation-exchanged cores, with no cracks formed upon cation diffusion from the NC surface into the cores. In Hg$^{2+}$ case, the FFT pattern could not be indexed to any known bulk HgSe or to any alloyed HgSe$_x$S$_{1-x}$.
phase, but rather with the hexagonal CdSe (cadmoselite) structure, in analogy with the XRD data discussed in the main text. In the Ag\textsuperscript{+}-exchanged sample, the FFT of the shell material corresponds to monoclinic Cu2S (low chalcocite), due to a slight oxidation of the shell upon exposure to air.

Figure S6. HAADF-STEM image of a representative Ag\textsuperscript{+}-totally exchanged core/shell Cu\textsubscript{2-x}Se/Cu\textsubscript{2-x}S NRs with the corresponding STEM-EDS elemental maps.

Figure S7. HAADF-STEM image of a representative group of Hg\textsuperscript{2+}-totally exchanged core/shell Cu\textsubscript{2-x}Se/Cu\textsubscript{2-x}S NRs with the corresponding STEM-EDS elemental maps.
Figure S8. HAADF-STEM image of a representative Au$^{3+}$-partially exchanged core/shell Cu$_{2-x}$Se/Cu$_2$S NRs with the corresponding STEM-EDS elemental maps.

Figure S9. HAADF-STEM images of representative groups of Ag$^+$-partially exchanged core/shell CdSe/CdS NRs with the corresponding STEM-EDS elemental maps. The two different pictures show the evolution of the CE reaction: a) initial decoration of the NRs with Ag-based domains, b) successive formation of Ag$_2$S domains at the tips of the NRs. Scale bars are 20 nm.
Additional References

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