



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

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Supporting Information

ABSTRACT: We studied cation exchange (CE) in core/shell $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ nanorods with two cations, Ag^+ and Hg^{2+} , which are known to induce rapid exchange within metal chalcogenide nanocrystals (NCs) at room temperature. At the initial stage of the reaction, the guest ions diffused through the Cu_{2-x}S shell and reached the Cu_{2-x}Se core, replacing first Cu^+ ions within the latter region. These experiments prove that CE in copper chalcogenide NCs is facilitated by the high diffusivity of guest cations in the lattice, such that they can probe the whole host structure and identify the preferred regions where to initiate the exchange. For both guest ions, CE is thermodynamically driven as it aims for the formation of the chalcogen phase characterized by the lower solubility under the specific reaction conditions.

Colloidal inorganic nanocrystals (NCs) are a testing ground for chemical and structural nanoscale transformations. Cation exchange (CE), e.g., has been studied in ionic NCs also as a means to implement current synthesis techniques.¹ An interesting aspect of CE applied to NCs is that its intermediate steps often consist of multidomain heterostructures. For example, partial CE performed on anisotropic NCs (i.e., nanorods, nanoplatelets, nanowires) can lead to heterostructures evidencing a replacement of cations only at the tips or in specific sections of the NCs.² Similarly, isotropic NCs can evolve into Janus-like or to core/shell structures when partially exchanged.³ Especially the Janus-like architectures appear to indicate that there exist regions on the surface of NCs acting as preferential entry points for cations, where the exchange is initiated and from which it proceeds to the remaining volume of the NC, so that both the interfacial energy and the elastic strain between the two different phases are minimized.^{2b} New insights into ion diffusion and CE reactions in NCs came from recent works on CE in CdSe NCs⁴ that demonstrated how Ag^+ ions, once incorporated in the NCs, could easily probe the whole NC lattice, via interstitial diffusion. As soon as a critical concentration of Ag^+ ions was reached, their mutual repulsion caused their segregation closer to the surface of the NCs, where the Ag^+ ions could start replacing Cd^{2+} ions. This was also proven in a recent work by optically monitoring the same reaction with single NC resolution.⁵ Therefore, while in CE reactions in NCs there could be multiple entry points for ions (virtually the whole NC surface), the actual exchange, initiated by ions that have already diffused in the particles, can start from a region inside the NC that does not

necessarily coincide with the entry point(s). This should be especially true when the guest ions are fast diffusing in the host lattice, so that they can quickly probe the whole NC in the quest for regions where it would be energetically more favorable for them to engage in CE reactions. Ideal NC samples on which to probe these hypotheses are represented by copper chalcogenide NCs, as the ones used in this work, since they are characterized by a large density of Cu vacancies that promote fast ion diffusion (through both interstitial and vacancy sites),⁶ facilitating CE with many different guest cations. These NCs can be easily fabricated, e.g., from the corresponding cadmium chalcogenide NCs (again by CE, see Supporting Information (SI) for details),^{2b-d,7} providing an ample set of samples, in terms of sizes, shapes and architectures, to start with. It is worth underlining that the Cu-chalcogenide NCs obtained through CE from Cd-chalcogenide NCs are normally characterized by a slight copper deficiency, due to the ease of formation of Cu vacancies, and as a direct consequence, they exhibit a localized surface plasmon resonance band (see Figure S1).^{2h,7a} As test cations, we chose Ag^+ and Hg^{2+} , as they have already been proven to induce CE in metal chalcogenides at room temperature conditions.^{2a,8} The different reactivities of the two cations were taken into account when choosing the appropriate feed ratios when performing CE reactions.

When Cu^+ cations in Cu_{2-x}S nanorods (NRs) were partially replaced by Hg^{2+} ions, the NRs evolved into multidomain structures, similar to what was observed by other groups when exposing CdS NRs or Cu_2S nanowires to Cu^+ or Ag^+ ions, respectively.^{2e,6,7b} This is seen in the high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images of Figure 1a,c, and in the compositional maps acquired via energy dispersive X-ray spectroscopy (EDS). In the Ag^+ case, the NRs were converted into a mixture of rods with a segmented structure and rods with ternary composition (see Figure 1b and selected area electron diffraction analyses in Figure S2). In some of the partially exchanged NRs, a slightly Ag-rich shell was also visible. The two cations, despite having similar ionic radii ($\text{Ag}^+ = 1.0 \text{ \AA}$ and $\text{Hg}^{2+} = 0.96 \text{ \AA}$ in tetrahedral coordination),⁹ seemed to behave differently: the Ag^+ ions appeared to probe the entire NR volume, while the Hg^{2+} ions were mainly engaged in reactions that started at the tips of the rods. We then extended this reaction scheme to core/shell $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs. A comparison of HAADF-STEM and EDS analyses of the initial sample with those after partial

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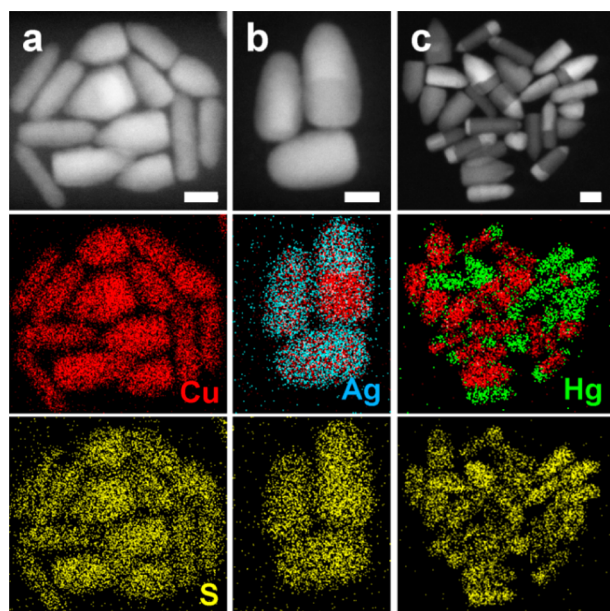


Figure 1. CE in Cu_{2-x}S NRs with Ag^+ and Hg^{2+} ions. HAADF-STEM images of representative groups of (a) pristine, (b) Ag^+ , and (c) Hg^{2+} partially exchanged Cu_{2-x}S NRs with the corresponding STEM-EDS elemental maps. Scale bars are 20 nm.

exchange indicated a selective replacement of Cu^+ ions in the selenide core region (see Figures 2 and S3, S4).

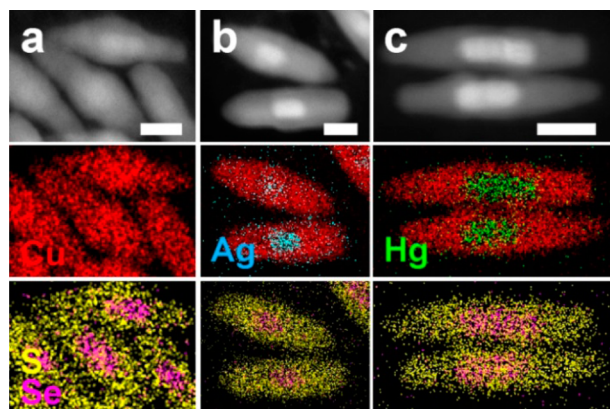


Figure 2. CE in $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs with Ag^+ and Hg^{2+} ions. HAADF-STEM images of groups of (a) pristine, (b) Ag^+ , and (c) Hg^{2+} partially exchanged $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs with the corresponding STEM-EDS elemental maps. Scale bars are 20 nm.

These findings were supported by elemental analyses (via STEM-EDS), which yielded a Hg/Se ratio of ~ 1 and a Ag/Se ratio of ~ 2 for the Hg-treated and Ag-treated NRs, respectively (Table S1). High-resolution TEM (HRTEM) images of partially exchanged $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs, with both Ag^+ and Hg^{2+} ions, reported in Figure S5, confirmed the selective ion replacement in the core region and, importantly, showed a continuous shell, exhibiting no cracks, surrounding the cores. The exposure of $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs to a higher amount of Ag^+ or Hg^{2+} ions led to an almost complete replacement of Cu^+ ions (see Figures S6, S7 and Table S1). The peculiarity of these results stands in the evidence that cation replacement in the Cu_{2-x}Se core must be preceded, both for Ag^+ and Hg^{2+} cations, by diffusion of cations through the Cu_{2-x}S shell. The structural transformations of the

core/shell $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs upon partial CE were monitored via X-ray diffraction (XRD). The XRD patterns of the pristine $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs (Figure 3c) were dominated

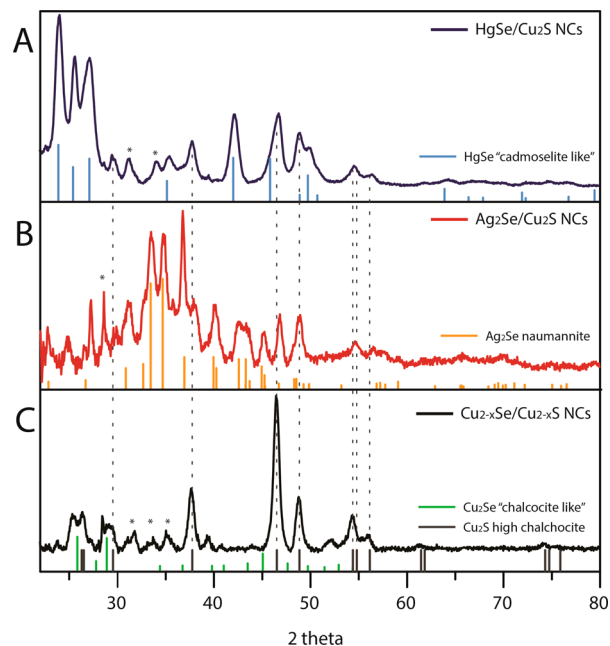


Figure 3. XRD patterns of (c) pristine, (b) Ag^+ , and (a) Hg^{2+} partially exchanged $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs, with bulk reflections of hexagonal Cu_2S (high chalcocite, ICDD 98-016-6578) and orthorhombic Ag_2Se (naumannite, ICDD 98-026-1822). Reflections of the Cu_2Se "chalcocite-like" phase are adapted from ref 7a. The Bragg peaks emerging after Hg^{2+} partial exchange correspond to the bulk reflections of hexagonal CdSe (cadmoselite, ICDD 96-901-6057). In all samples, other minor peaks (labeled with *) can be assigned to a substoichiometric tetragonal $\text{Cu}_{116}\text{S}_{64}$ phase (roxbyite, ICDD 96-901-5183), probably appearing due to slight oxidation of the NC films exposed to air during pattern acquisition.

by the hexagonal Cu_2S (high chalcocite) peaks, with other minor reflections ascribable to the metastable Cu_2Se "chalcocite-like" phase, as previously reported by us.^{7a} The XRD patterns of partially exchanged NRs, instead, evidenced in both cases the presence of high chalcocite Cu_2S , together with a second majority phase that, in the case of Ag^+ -treated NRs, could be indexed according to the orthorhombic Ag_2Se (naumannite) phase (see Figure 3b), while for the Hg^{2+} -treated rods, it could not be indexed to any known bulk HgSe or to any alloyed $\text{HgSe}_x\text{S}_{1-x}$ phase.

By extending the search to other known phases, these peaks could be well matched with the hexagonal CdSe (cadmoselite) structure (Figure 3a). Since no traces of Cd were detected by elemental analysis, the formation of a "cadmoselite-like" hexagonal HgSe phase is likely due to the topotactic replacement of Cu^+ ions with Hg^{2+} ions in the core region, with preservation of the hexagonal structure of the Se^{2-} anion sublattice. Overall, XRD analyses corroborated the preservation of the Cu_2S shell and, at the same time, the selective replacement of Cu^+ ions in the core region with Ag^+ or Hg^{2+} cations. By combining results from experiments on Cu_{2-x}S and on core/shell $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs, we can state that the initial step in the CE reactions is represented by the diffusion of the guest cations (Ag^+ and Hg^{2+}) in the NCs, most likely from multiple entry locations. In the $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs, the guest ions, after having diffused through the Cu_{2-x}S

shell and probed the whole NC volume, selectively replaced Cu^+ host ions within the Cu_{2-x}Se core. If one considers bond dissociation energies, CE involving Cu_{2-x}S or Cu_{2-x}Se NCs should not occur, since stronger Cu–S or Cu–Se bonds are broken to form weaker M–S and M–Se ($M = \text{Ag}, \text{Hg}$) bonds (Table 1). However, the overall energy balance includes also

Table 1. Bond Dissociation Energies (BDEs, expressed in kJ/mol) (from ref 11) and Solubility Product Constants (K_{SP} , at 25°C) of Different Metal Chalcogenides (from refs 1e and 12)

material	E = S		E = Se	
	BDE	K_{SP}	BDE	K_{SP}
Ag_2E	216.7 ± 14.6	6.3×10^{-50}	210.0 ± 14.6	3×10^{-54}
CdE	208.5 ± 20.9	1×10^{-28}	127.6 ± 25.1	4×10^{-35}
Cu_2E	274.5 ± 14.6	2.5×10^{-48}	255.2 ± 14.6	N.A.
HgE	217.3 ± 22.2	6×10^{-53}	144.3 ± 30.1	4×10^{-59}

solvation energies of the exchanging cations, which in most cases creates the actual driving force.^{1b} Since in these CE reactions no phosphine was used, and methanol was the only Lewis base promoting the exchange (see SI for details), the thermodynamic feasibility of CE can be tentatively rationalized by the trend in solubility product constants (K_{SP}) of the materials involved^{1e} (Table 1). It is known that a ionic solid with a relatively high K_{SP} can spontaneously transform, through CE, to another ionic solid with a lower K_{SP} . As Ag_2E and HgE ($E = \text{S}, \text{Se}$) are less soluble in polar solvents than the corresponding Cu_2E solids, the former are thermodynamically favored. Moreover, metal selenides are generally characterized by lower K_{SP} than their corresponding sulfides.¹⁰ Therefore, when both Cu_{2-x}Se and Cu_{2-x}S domains are exposed to an amount of guest cations that enables competition between the two, CE is more likely to occur in the metal selenide domain.

Also, the Cu_{2-x}Se core, compared to the Cu_{2-x}S shell, has a stronger tendency to form Cu vacancies, as found by us in a previous work by exposing the rods to oxidizing agents:^{8c} this led to the formation of hollow particles by coalescence of the Cu vacancies that had gathered in the Cu_{2-x}Se core. Here, it is possible that a larger density of Cu vacancies in the core would additionally favor the diffusion of guest cations in such region. Our experiments show that in “simple” Cu_{2-x}S rods, which lack such preferred region, the guest Hg^{2+} ions, after having likely probed the whole rod, found the outer surface layers and/or the rod tips as the most convenient regions to initiate exchange. For Ag^+ , this preference was less marked, since also particles with ternary composition were found (see Figure 1b).^{4b} These considerations may help elucidating how CE can proceed in NCs in which ions have high diffusivity: guest ions can diffuse in host NCs and target the preferred region where to initiate CE rather than necessarily replace original cations starting from the NCs surface, as commonly believed. This argument is supported by additional tests employing Au^{3+} ions as guests in core/shell $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs. Here too, partially exchanged samples evidenced a selective localization of Au ions in the core (see Figure S8). This was corroborated by STEM-EDS elemental analyses in which a Au/Se ratio of 0.7 was measured, suggesting the formation of a Au_{1-x}Se phase in the core region (Table S1).

These experiments were then benchmarked against CE on CdSe/CdS nanoheterostructures. In cadmium chalcogenide structures, where the density of vacancies is considerably lower than in Cu-based ones, ion diffusion proceeds mostly interstitially. When CdSe/CdS NRs were partially exchanged with Ag^+ ions,

no preferential exchange of the core was observed (see Figure S9). Instead, at the early stage of the CE process, Ag-containing domains started “decorating” the CdS outer layer, accompanied by the replacement of Cd^{2+} ions at the tips of the rods, producing heterostructures similar to the $\text{Ag}_2\text{S}/\text{CdS}$ NRs reported in the literature.^{2a} Also, in a previous work of ours, we studied CE involving CdSe/CdS octapod-shaped NCs with Cu^+ ions, in conditions that are similar to those of this work;^{2c} in that case too, the CE started at the extremities of the CdS pods and left the CdSe core unaltered. Furthermore, our data are in line with those of recent works where it was shown that partial exchange of core/shell CdSe/CdS nanoplatelets and NRs with Cu^+ ions resulted in a selective replacement of Cd^{2+} cations in the CdS shell.¹³ In the light of the data discussed on $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs so far, these results suggest that, in CdSe/CdS NRs, even if the thermodynamically preferred phases would be Cu_2Se and Ag_2Se (Table 1), the limited diffusivities of both the entering Cu^+ or Ag^+ cations and the exiting Cd^{2+} ions are mainly responsible for the preferential nucleation of the Cu_2S or Ag_2S phases at regions of the NCs close to their surface. We also ran control experiments starting from “inverted” core/shell $\text{Cu}_{2-x}\text{S}/\text{Cu}_{2-x}\text{Se}$ NRs, prepared by complete Cu^+ exchange on CdS/CdSe NRs (see SI).^{8c} When partial exchange with Ag^+ or Hg^{2+} ions was carried out on them, the replacement affected selectively the shell region (i.e., the Cu_{2-x}S phase), as shown in Figure 4

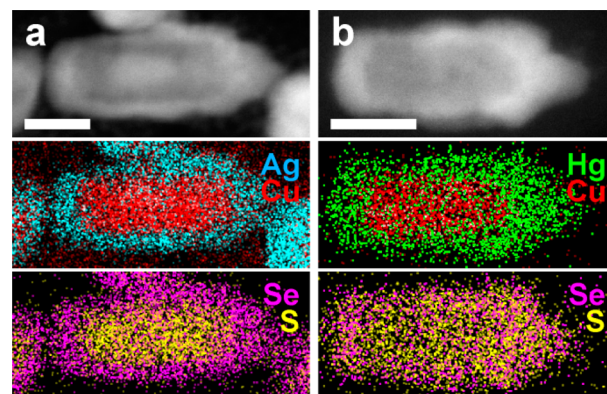


Figure 4. CE in “inverted” core/shell $\text{Cu}_{2-x}\text{S}/\text{Cu}_{2-x}\text{Se}$ NRs, with Ag^+ and Hg^{2+} ions. HAADF-STEM images of representative “inverted” NRs partially exchanged with (a) Ag^+ or (b) Hg^{2+} , along with the corresponding STEM-EDS elemental maps. The scale bars in the images are 20 nm.

(see also Table S1). It is interesting to notice that, in CE reactions involving Hg^{2+} ions, there was a substantial anion interdiffusion throughout the NRs (Figure 4b). This further proves that CE, affecting in this case mainly the shell region, represents only the final step of a series of events in which Hg^{2+} ions had previously probed extended regions inside the rods, in this case partially “dragging”, along their way, S^{2-} and Se^{2-} ions.

In yet another control experiment, a mixture of Cu_{2-x}S and Cu_{2-x}Se NCs, prepared by standard direct synthesis protocols and not via CE (see SI for details), was exposed either to Ag^+ or to Hg^{2+} ions. Here too, the experiments were run with Ag/Cu or Hg/Cu feed ratios that were insufficient to achieve a complete replacement of the copper ions, in order to trigger competition between the two different types of NCs toward CE (see SI for experimental details). In analogy with the experiments discussed above, CE selectively affected the Cu_{2-x}Se NCs rather than the Cu_{2-x}S ones (see Figure 5). These experiments rule out any

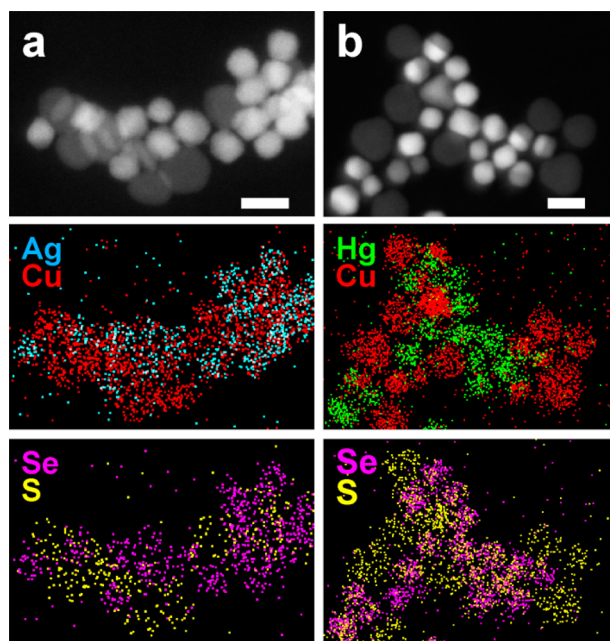


Figure 5. CE in a mixed population of Cu_{2-x}S and Cu_{2-x}Se NCs with Ag^+ and Hg^{2+} ions. HAADF-STEM images of groups of copper sulfide and copper selenide NCs exposed to (a) Ag^+ or (b) Hg^{2+} ions with the corresponding STEM-EDS elemental maps. The scale bar in each image is 20 nm.

potential influence of the preparatory history of the copper chalcogenide NCs (i.e., whether they were synthesized directly or they were prepared instead by CE) on their reactivity toward the guest cations.

In conclusion, we have shown that in partial CE involving core/shell $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs exposed to Ag^+ , Hg^{2+} , and Au^{3+} ions, a selective replacement of the core cations occurred. This selective CE is made possible by the high ion diffusivity in copper chalcogenides, as it allows guest cations to probe the whole structure and initiate the exchange in the core rather than in the shell. The overall process, on the other hand, is driven by thermodynamic factors which favor the formation of metal selenides over the corresponding sulfides in our reaction environment. Our hypotheses were supported by various control experiments. The ability to selectively transform the core in core/shell copper chalcogenide NCs offers an additional tool to tailor the topology and the chemical composition of colloiddally synthesized nanoparticles.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06379.

Details on chemicals, syntheses, reactions, structural and compositional characterization (PDF)

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Notes

The authors declare no competing financial interest.

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