

Nanoheterostructure Cation Exchange: Anionic Framework Conservation

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Abstract: In ionic nanocrystals the cationic sublattice can be replaced with a different metal ion via a fast, simple, and reversible place exchange, allowing postsynthetic modification of the composition of the nanocrystal, while preserving its size and shape. Here, we demonstrate that, during such an exchange, the anionic framework of the crystal is preserved. When applied to nanoheterostructures, this phenomenon ensures that compositional interfaces within the heterostructure are conserved throughout the transformation. For instance, a morphology composed of a CdSe nanocrystal embedded in a CdS rod (CdSe/CdS) was exchanged to a PbSe/PbS nanorod via a Cu₂Se/Cu₂S structure. During every exchange cycle, the seed size and position within the nanorod were preserved, as evident by excitonic features, Z-contrast imaging, and elemental line scans. Anionic framework conservation extends the domain of cation exchange to the design of more complex and unique nanostructures.

In ionic nanocrystals, especially transition metal chalcogenides, the cationic sublattice can be replaced with a different metal ion via a fast, simple, and reversible place exchange, altering the composition of the nanocrystal, while preserving its size and shape.^{1–7} It is generally assumed that, during such an exchange, the anionic framework of the crystal is conserved, while the cations, due to their relatively smaller size and higher mobility, undergo replacement. This has not, however, been experimentally proven or utilized, as only single-phase nanocrystals have so far been transformed using cation exchange. Preservation of the anionic framework during cation exchange would enable transformation of multicomponent nanoheterostructures, while conserving not only the nanostructure size and shape but also the compositional interface between the constituents. This would greatly extend the domain of cation exchange to the design of ever more complex nanostructures. In this Communication, we demonstrate that, indeed, the anionic framework is preserved during cation exchange and that this can be utilized for accessing customized nanoheterostructures.

The model heterostructure selected is a seeded rod consisting of a spherical CdSe nanocrystal embedded in a CdS nanorod.^{8–10} A unique functional feature of such a structural arrangement is the ability to design the relative band alignment of the two semiconductors across the interface, allowing independent tuning of the spatial distribution of electrons and holes along the elongated dimension.^{11–16} The seeded rod is a canonical example of a nanoheterostructure that allows customization of electronic properties for

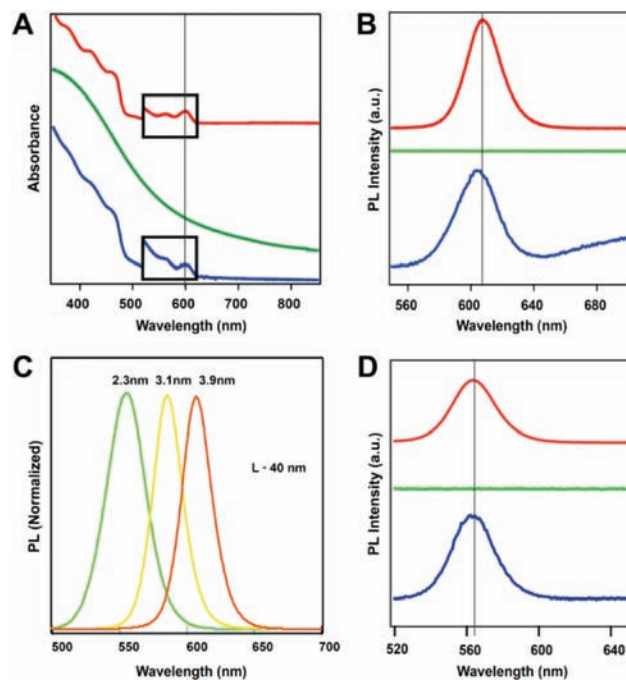


Figure 1. (A) Absorbance and (B) photoluminescence (PL) spectrum of a 40-nm long CdS nanorod with an embedded 3.9-nm CdSe nanocrystal (top), following complete exchange with Cu⁺ (middle) and back-exchange to Cd²⁺ (bottom). (C) Sensitivity of the PL peak position to the CdSe seed diameter. (D) PL spectrum of a seeded nanorod with a 2.3-nm CdSe nanocrystal embedded in a 40-nm long CdS rod (top), following Cu⁺ exchange (middle) and back-exchange to Cd²⁺ (bottom), showing recovery of the peak to the same position (within 0.5 nm) and fwhm (~17 nm) as the original nanorods.

applications such as force sensing,¹⁷ photocatalysis,¹⁸ optoelectronics,^{19–21} and quantum information technology.²²

A 40-nm long CdSe/CdS seeded nanorod synthesized with a 3.9-nm seed (Supporting Information) exhibits absorption features (Figure 1A) attributable to excitons in the CdSe seed (600 and 562 nm) and the CdS rod (460 nm) and strong photoluminescence (PL) due to exciton recombination in the seed (Figure 1B). Complete cation exchange of the nanorods with Cu⁺ results in the loss of CdS and CdSe excitonic features and the emergence of an absorption band edge at ~850 nm, typical of Cu chalcogenides (indirect bulk band gap ~1.2 eV). Back-conversion of the Cu₂Se/Cu₂S seeded rod to Cd²⁺ recovers all excitonic features of the original structure (Figure 1A, B, and D).

The PL peak maximum, due to the confined nature of the emitting exciton in the seed, is known to be highly sensitive to the seed diameter (Figure 1C). It is noteworthy that, following two cycles of exchange, the PL peak recovered with a similar position as that

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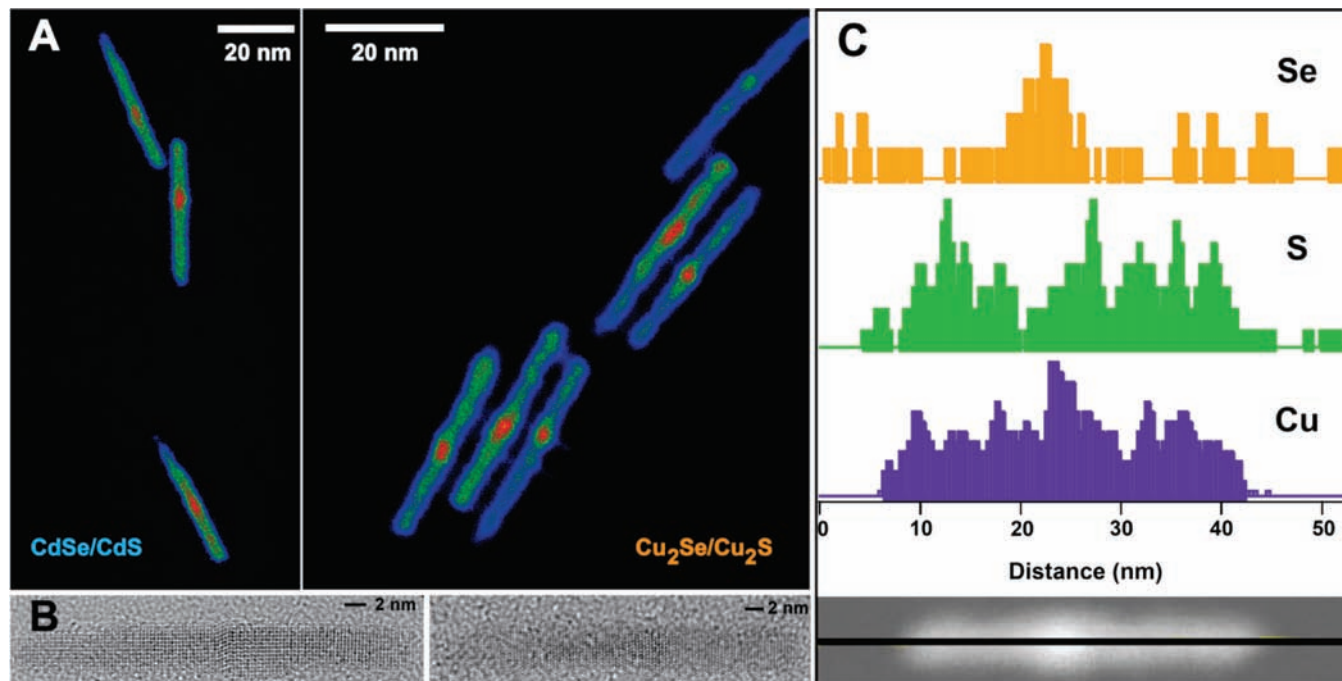


Figure 2. (A) High-angle annular dark-field image rendered as a pseudocolor map and (B) high-resolution transmission electron micrograph of CdSe/CdS (left) and Cu₂Se/Cu₂S (right) seeded rods. (C) Energy dispersive X-ray line scan across a representative Cu₂Se/Cu₂S nanorod. The position of the selenide seed in the EDS line scan agrees with the location of high Z-contrast in the HAADF image shown at the bottom. Line profiles of absolute intensity through the nanorods in (A) are shown in the Supporting Information.

of the initial nanorods. This indicates complete conservation of the selenide seed embedded in the sulfide rod throughout the forward and reverse transformations. Remarkably, this holds for a seed diameter as small as 2.3 nm (Figure 1D). For the 3.9-nm seed, the PL maximum position recovers to within 4 nm, indicating no more than a 4% size change (based on the trend in Figure 1C). However, a significant part of this shift may in fact be attributed to effects unrelated to a size change. For instance, back-exchange of the Cu₂Se/Cu₂S structure could result in a strained CdSe/CdS interface, especially in the case of the larger seed, leading to a blue shift in the recovered PL.^{17,23} In addition, the 3.9-nm seed is exposed to the surface/ligand environment, making it sensitive to dielectric changes in the ligand shell and increase in surface traps resulting from the cation exchange process,¹ possibly causing the shift and the broad trap emission at longer wavelengths in the recovered PL (Figure 1B). The 2.3-nm seed, in which case the sensitivity of its PL position to the external surface/ligand environment is expected to be minimal due to complete embedment in the rod, shows recovery of its PL maximum position to within 0.5 nm, implying insignificant size change. This demonstrates that the anionic framework is preserved during the exchange without significant mixing of the anions across the interface, allowing the original heterostructure morphology to be conserved.

High-angle annular dark-field (HAADF) and high resolution transmission electron microscopy (HRTEM) of the Cd and Cu seeded rods (Figure 2, Supporting Information) show that they maintain their size and shape during exchange. In HAADF images (Figure 2A), the selenide seed exhibits higher Z-contrast compared to the sulfide rod, allowing visualization of seed location. This is further supported by elemental dispersive X-ray (EDX) line scans across a representative rod (Figure 2C). This confirms that the position of the seed within the rod is conserved during the ionic transformation.

Anionic framework conservation allows access to new and unique heterostructures, otherwise difficult to make via colloidal synthesis.

For example, a structure with a PbSe nanocrystal embedded in a PbS rod has not yet been described in the literature. Such a structure would enable band gap engineering and tuning of electron/hole transport properties in the near-infrared (NIR) region, potentially

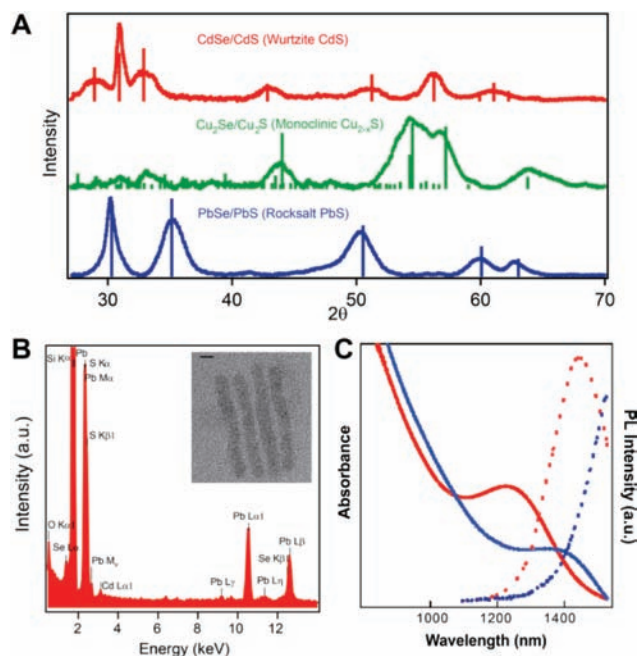


Figure 3. (A) X-ray diffraction pattern showing exchange of CdSe/CdS (top) to PbSe/PbS seeded rod with rock-salt structure (bottom) via Cu₂Se/Cu₂S with monoclinic crystal structure (middle). (B) Energy dispersive X-ray spectra and (inset) transmission electron micrograph of PbSe/PbS nanorods; scale bar: 5 nm. (C) Absorbance (solid) and photoluminescence spectra (dotted) of rods with a 3.9-nm (blue) and 2.3-nm (red) PbSe seed. Note that the PL detection sensitivity range is limited to 1550 nm.

useful for NIR photovoltaics, photodetectors,²⁴ and fluorescent imaging labels.

To demonstrate this example, we started with CdSe/CdS rods as templates and transformed them to a PbSe/PbS structure by two successive cation exchange steps: $\text{Cd}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Pb}^{2+}$ (Figure 3A). Here, we extend a procedure developed by Luther et al.⁵ where ligands are employed to create a disparity between the solvation of divalent (Cd^{2+} and Pb^{2+}) and monovalent cations (Cu^+).

EDX spectra (Figure 3B) and TEM (Figure 3B inset) confirm the formation of PbSe/PbS nanorods with size and shape preserved. The NIR spectrum (Figure 3C) exhibited by these nanorods is characteristic of the excitonic absorption of the PbSe seed,²⁵ coupled with contribution from the PbS nanorod.⁵ Consistently, a size-dependent excitonic absorption is seen for PbSe/PbS rods with two different seed diameters (3.9 and 2.3 nm). The exciton absorption of the PbSe seed is red-shifted (by 0.1 and 0.25 eV for larger and smaller seed, respectively) from the expected value for the corresponding bare PbSe,²⁵ consistent with embedment in a PbS matrix.^{21,26,27} The rods also show seed size-dependent NIR emission.

The phenomenon of anionic framework preservation in cation exchange can be generalized to achieve a wide gamut of design goals in nanoheterostructure synthesis. For instance, structures with multiple interfaces or complex topologies may be transformed with high ease and fidelity.

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Supporting Information Available: Details of CdSe/CdS rod synthesis with different seed diameters; cation exchange procedures; details of characterization (STEM, EDAX, XRD, optical spectra); seed position statistics for Cd and Cu seeded nanorods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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