

ELECTRONIC SUPPLEMENTARY INFORMATION

Orthogonal reactivity and interface-driven selectivity during cation exchange of heterostructured metal sulfide nanorods

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Materials and Methods

Chemicals

1-Octadecene [ODE, C₁₈H₃₆, Technical Grade, 90%], Oleylamine [OLAM, C₁₈H₃₇N, Technical Grade, 70%], Trioctylphosphine Oxide [TOPO, C₂₄H₅₁OP, ReagentPlus, 99%], 1-Dodecanethiol [DDT, C₁₂H₂₆S, ≥98%], tert-Dodecanethiol [t-DDT, C₁₂H₂₆S, Mixture of Isomers, 98.5%], Copper(II) Nitrate Trihydrate [Cu(NO₃)₂·3H₂O, 98%], Zinc(II) Chloride [ZnCl₂, Anhydrous, >97%], Cobalt(II) Chloride [CoCl₂, Anhydrous, >98%], Tetrakis(acetonitrile) Cu(I) hexafluorophosphate [97%], Methanol [MeOH, Anhydrous, 99.8%], and Octylamine [CH₃(CH₂)₇NH₂, 99%] were purchased from Millipore-Sigma. Dibenzyl Ether [C₁₄H₁₄O, 99%] was purchased from Acros Organics. Tri-n-octylphosphine [TOP, C₂₄H₅₁P, 85%] was purchased from TCI America. Cadmium(II) Chloride [CdCl₂, Anhydrous, 99.99%], Manganese(II) Chloride Tetrahydrate and [MnCl₂·4H₂O, 98.0–101.0%] were purchased from Alfa Aesar. All solvents, including toluene, acetone, ethanol [EtOH], and isopropyl alcohol [IPA] were of analytical grade. All chemicals were used as received without further purification.

Synthesis of Cu_{1.8}S Nanorods

Cu_{1.8}S nanorods were synthesized using a published procedure.¹ Briefly, Cu(NO₃)₂·3H₂O (843 mg), TOPO (8.7 g), ODE (45 mL), and distilled-OLAM (750 μL) were combined in a 250 mL, 3-neck flask equipped with a reflux condenser, gas flow adapter, thermocouple, rubber septum, and magnetic stir bar. This mixture was placed under vacuum, heated to 80 °C, and maintained for 30 minutes. The flask was then placed under a blanket of Ar after cycling with vacuum and Ar three times. A mixture of t-DDT:DDT in a 10:1 ratio (22.5 mL) was rapidly injected. The flask was then placed under Ar flow and the reaction temperature was increased to 180 °C within 5 minutes and held at 180 °C for 15 minutes before being cooled rapidly by removing the heating mantle and placing the flask into a room temperature water bath. The resulting product was precipitated by addition of a 1:1 mixture of IPA:acetone, followed by centrifugation and resuspension in toluene. The centrifugation / resuspension process was repeated once more before the nanoparticles were dispersed in toluene. This suspension was allowed to settle in a septum-capped vial overnight before the supernatant was decanted off and the final few milliliters of toluene were evaporated under vacuum. The resulting solid was carefully scraped into a powder and stored under ambient conditions for further use.

Preparation of Cation Exchange Solutions

Cation exchange solutions were prepared using a published procedure.^{1,2} Briefly, Benzyl ether (15 mL), ODE (2 mL), distilled-OLAM (8 mL), and the corresponding metal salt (see Table S1) were combined in a 50 mL 3-neck flask equipped with a reflux condenser, gas flow adapter, thermocouple, rubber septum, and magnetic stir bar. The reaction flask was placed under vacuum, heated to 100 °C, and held at this temperature for 60 minutes. The flask was then placed under Ar flow after cycling with vacuum and Ar three times, heated to the appropriate temperature (Table 4.1), and held at this temperature for the tabulated amount of time. The solution was then cooled to approximately 60 °C before being transferred by syringe to a 40 mL septum capped vial for storage under Ar (for Zn²⁺ and Cd²⁺ solutions) or used immediately (all other exchange solutions).

Table S1: Metal cation reagent, reaction temperature and time, and cation exchange concentration for each exchange solution used to make the multicomponent nanorods.

Cation Solution	Metal Reagent, Amount	Temperature Under Ar Flow (°C)	Time under Ar Flow (minutes)	[Exchange Solution] (mmol/mL)
Zn ²⁺	ZnCl ₂ , 250 mg	200	30	0.0734
Cd ²⁺	CdCl ₂ , 84.1 mg	200	30	0.0184
Co ²⁺	CoCl ₂ , 59.6 mg	200	30	0.0184
Mn ²⁺	MnCl ₂ ·4H ₂ O, 72.5 mg	180	30	0.0147

Synthesis of Janus Nanorods Using Partial Cation Exchange

Janus nanorods were synthesized using a modified published procedure.¹ Briefly, benzyl ether (7.5 mL), ODE (1 mL), and distilled-OLAM (4 mL) were combined in a 50 mL 3-neck flask equipped with a reflux condenser, gas flow adapter, thermocouple, rubber septum, and magnetic stir bar. This flask was placed under vacuum, heated to 100 °C, and held at this temperature for 30 minutes. The flask was then placed under an Ar blanket after cycling with vacuum and Ar three times and heated to 120 °C. During this time, 18 mg of the Cu_{1.8}S powdered nanorods were added to a septum capped vial, and evacuated and cycled with Ar and vacuum three times before being placed under a blanket of Ar. TOP (1.75 mL) and distilled-OLAM (0.25 mL) were added to this vial, and again cycled with Ar and vacuum three times before being placed under a blanket of Ar. This vial was sonicated for 45 minutes, and then swiftly injected into the surfactant-solvent mixture. The flask was immediately placed under vacuum and cycled with Ar and vacuum three time before being placed under a blanket of Ar. Once the nanorods were sufficiently suspended in the solution, the reaction was cooled to the temperature described in Table S2. A portion of a previously prepared exchange solution (see Table S2), described above, was then injected, and the flask was placed under vacuum immediately and then cycled with Ar and vacuum three times and placed under a blanket of Ar. The reaction was allowed to proceed for the allotted amount of time (Table S2) and then cooled to the next injection temperature, if applicable. The flask was then cooled to room temperature. The product was isolated through addition of a 1:1 IPA:acetone mixture (unless CoS is present in the nanorods, in which case, only IPA was used), followed by subsequent centrifugation and resuspension in toluene. The centrifugation / resuspension process was repeated twice before the final product was suspended in toluene for characterization.

Table S2: Reaction parameters for multicomponent nanorod samples.

Partial Cation Exchange	Volume for ~50% Exchange (mL)	Injection Temperature (°C)	Reaction Temperature (°C)	Reaction Time (minutes)
Zn ²⁺	0.43	120	120	15
Cd ²⁺	1.7	25	110	30
Co ²⁺	in excess	25	110	45
Mn ²⁺	in excess	25	100	10

Synthesis of Control Nanorods Using Complete Cation Exchange

Metal sulfide nanorods were synthesized using a modified published procedure.¹ Briefly, benzyl ether (7.5 mL), ODE (1 mL), and distilled-OLAM (4 mL) were combined in a 50 mL 3-neck flask

equipped with a reflux condenser, gas flow adapter, thermocouple, rubber septum, and magnetic stir bar. This flask was placed under vacuum, heated to 100 °C, and held at this temperature for 30 minutes. The flask was then placed under an Ar blanket after cycling with vacuum and Ar three times and heated to 120 °C. During this time, 18 mg of the Cu_{1.8}S powdered nanorods were added to a septum capped vial, and evacuated and cycled with Ar and vacuum three times before being placed under a blanket of Ar. TOP (1.75 mL) and distilled-OLAM (0.25 mL) were added to this vial, and again cycled with Ar and vacuum three times before being placed under a blanket of Ar. This vial was sonicated for 45 minutes, and then swiftly injected into the surfactant-solvent mixture. The flask was immediately placed under vacuum and cycled with Ar and vacuum three times before being placed under a blanket of Ar. Once the nanorods were sufficiently suspended in the solution, the reaction was cooled to the temperature described in Table S2. A portion of a previously prepared exchange solution equal to ~4 times the amount specified in Table S2 was then injected, and the flask was placed under vacuum immediately and then cycled with Ar and vacuum three times and placed under a blanket of Ar. The reaction was allowed to proceed for the allotted amount of time (Table S2) and then cooled to room temperature. The product was isolated through addition of a 1:1 IPA:acetone mixture (unless forming CoS, in which case, only IPA was used), followed by subsequent centrifugation and resuspension in toluene. The centrifugation / resuspension process was repeated twice before the final product was suspended in toluene for characterization.

Cu⁺ Exchanges on Janus and Control Nanorods

Exchanges using Cu⁺ were performed using a published procedure.³ Briefly, tetrakis(acetonitrile) Cu(I) hexafluorophosphate (100 mg) and anhydrous MeOH (5 mL) were mixed in a 20 mL septum capped vial under an inert atmosphere. In a separate 20 mL septum capped vial a magnetic stir bar, toluene (1 mL), and Janus nanorods (2 mg, in toluene) were mixed under Ar flow, and cooled to -77 °C using a dry ice/IPA slurry. A portion of the Cu⁺ exchange solution (see Table S3), equivalent to about 50% of the nanorod reagent, was then injected into the nanorod solution, and the reaction was allowed to proceed for 5 minutes at -77 °C, after which it was warmed to room temperature. (The exchange was carried out at -77 °C to slow the speed of exchange from about one second at room temperature to about a minute or two at -77 °C, which enabled aliquot studies and prevented over-exchange.) The product was isolated through centrifugation (without anti-solvent) and resuspended in toluene. The centrifugation / resuspension process was repeated twice, using a 1:1 mixture of IPA:acetone as an anti-solvent and a few drops of distilled-OLAM to help with resuspension, before the final product was suspended in toluene for characterization.

This procedure was then followed using the single component control nanorods instead of the Janus nanorods, and substituting 2 mL of Cu⁺ exchange solution for the volumes in Table S3. All other instructions in the procedure remained the same.

Table S3: Volumes of Cu⁺ exchange solutions needed to exchange ~50% of the Janus nanorod reagents.

Multicomponent nanorod reagent	Volume of Cu⁺ solution (mL)
ZnS–CdS	0.15
ZnS–MnS	0.20
ZnS–CoS	0.20
CdS–MnS	0.16

Characterization

Transmission electron microscopy (TEM) images were collected on a FEI Tecnai G2 XTWIN with a LaB₆ source operating at 200 kV. High angle annular dark field scanning TEM (HAADF-STEM) and STEM energy dispersive X-ray spectroscopy (STEM-EDS) element maps were collected on a FEI Talos F200X S/TEM at an accelerating voltage of 200 kV. ES vision software (Emispec) was used for EDS data processing. EDS lines for each element map shown in this work can be found in Table S4. Samples for TEM analysis were all drop-casted onto 400-mesh nickel TEM grids with a carbon/formvar film. MATLAB software was used to generate all plots in this work (MATLAB ver. R2020a).

Table S4: Elemental energy lines and color scheme used in the EDS maps and spectra for each sample in this work.

Element	Energy Line Mapped	Energy Line Value (KeV)	Color
Cu	K α	8.04	Red
S	K α	2.31	Light Grey
Zn	K α	8.63	Bright Green
Cd	L α	3.13	Medium Blue
Mn	K α	5.89	Gold
Ni	K α	7.47	Cyan
Co	K α	6.93	Lavender

Supplementary Figures

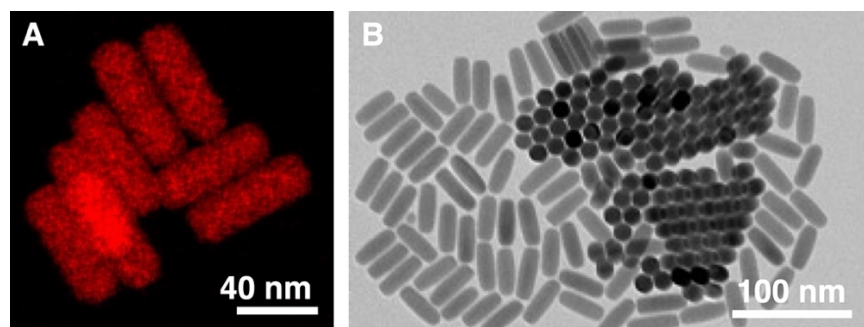


Figure S1. (A) STEM-EDS elemental map and (B) bright-field TEM images of Cu_{1.8}S nanorods. The Cu signal is indicated in red in (A).

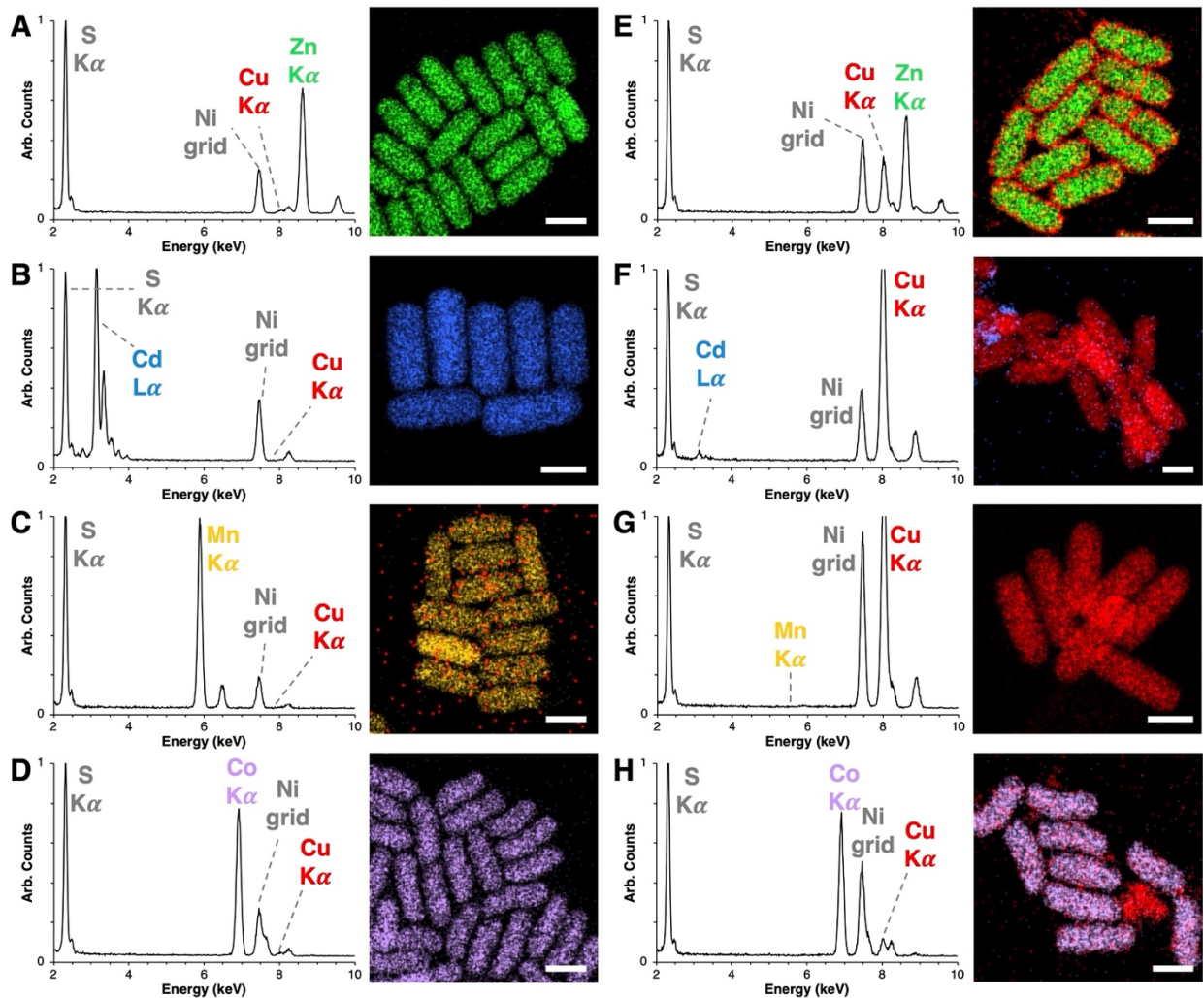


Figure S2. EDS spectral data and wide-field STEM-EDS elemental maps for each nanorod precursor and cation exchange product for the control studies from Figure 1: (A) ZnS, (B) CdS, (C) MnS, and (D) CoS nanoparticle precursors, and (E-H) the corresponding products following a Cu^+ back exchange. The energy lines used to generate the EDS maps in Figure 1 are indicated in each of these figure panels using the same color scheme: Zn is bright green, Mn is gold, Cd is blue, Co is lavender, and Cu is red. All scale bars are 25 nm.

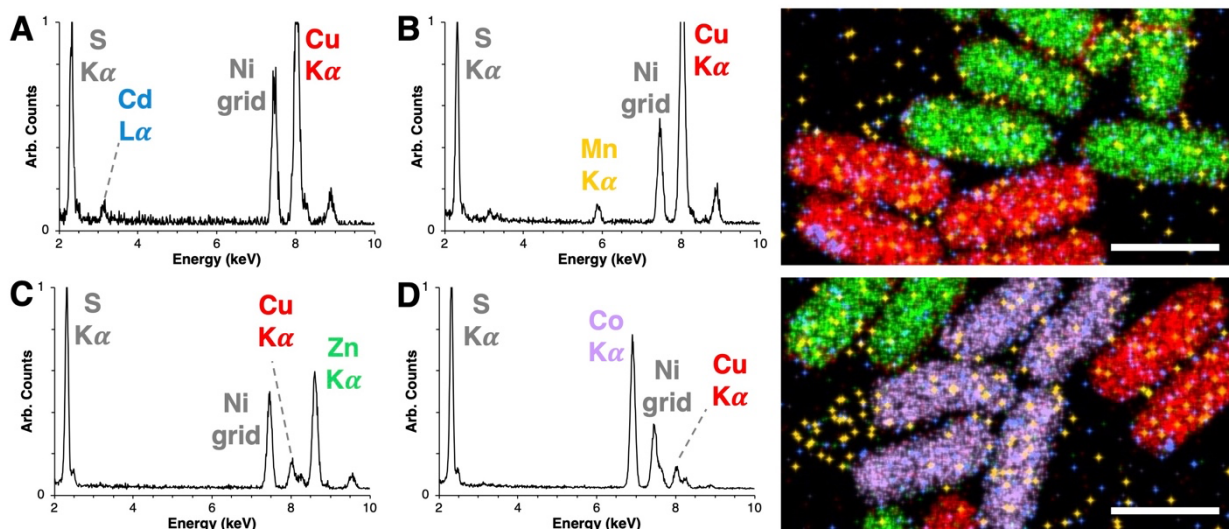


Figure S3. EDS spectra and wide-field STEM-EDS elemental maps corresponding to the STEM-EDS maps from a partial Cu^+ exchange on a physical mixture of the ZnS, CdS, MnS, and CoS nanorods from Figure 2. The energy lines used to generate the EDS maps in Figure 2 are indicated in each of these figure panels using the same color scheme: Zn is bright green, Mn is gold, Cd is blue, Co is lavender, and Cu is red. All scale bars are 30 nm.

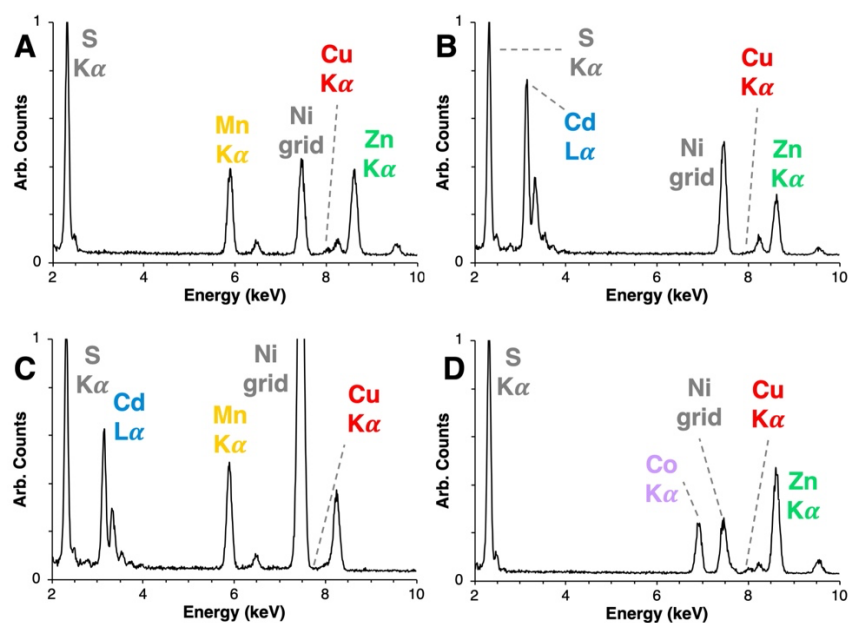


Figure S4. EDS spectral data from each Janus nanorod sample shown in Figure 3. The relevant energy lines that were used to map each element are indicated.

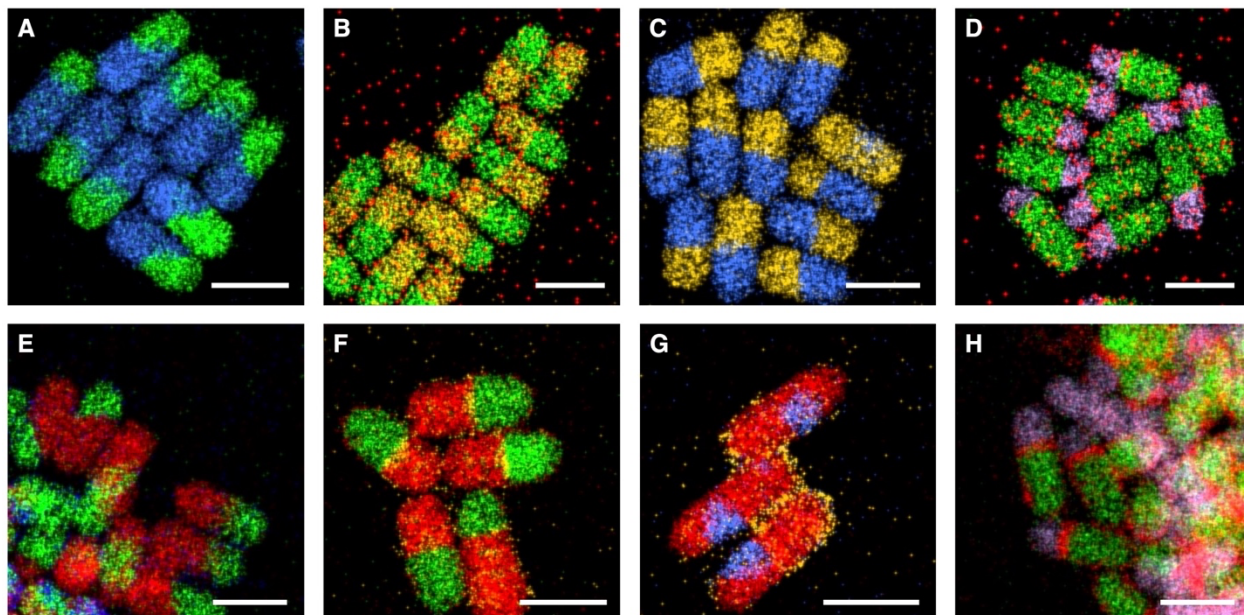


Figure S5. Wide-field STEM-EDS elemental maps for each Janus nanorod precursor and cation exchange product from Figure 3: (A) ZnS–CdS, (B) MnS–ZnS, (C) MnS–CdS, and (D) CoS–ZnS Janus nanorod precursors, and (E–H) the corresponding products following a partial Cu^+ back exchange. The energy lines used to generate the EDS maps in Figure 1 are indicated in each of these figure panels using the same color scheme: Zn is bright green, Mn is gold, Cd is blue, Co is lavender, and Cu is red. All scale bars 30 nm.

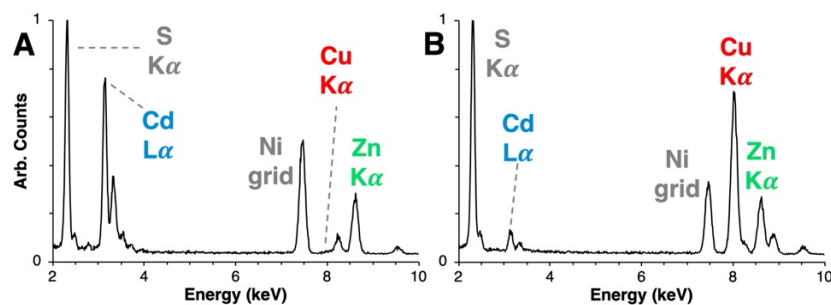


Figure S6. EDS spectra for (A) a ZnS–CdS Janus nanorod precursor, showing the presence of Cd and Zn signal and the absence of Cu signal in the precursor, and (B) the product of a partial Cu^+ cation exchange reaction, showing the presence of Cu and Zn signal and minimal Cd signal in the product where Cu^+ cations selectively exchanged for the Cd^{2+} cations.

References

1. Steimle, B. C.; Fenton, J. L.; Schaak, R. E. Rational Construction of a Scalable Heterostructured Nanorod Megalibrary. *Science* **2020**, 367, 418–424.
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3. Fenton, J. L.; Hodges, J. M.; Schaak, R. E. Synthetic Deconvolution of Interfaces and Materials Components in Hybrid Nanoparticles. *Chem. Mater.* **2017**, 29, 6168–6177.