SUPPORTING INFORMATION

Exploiting Crystallographic Regioselectivity to Engineer Asymmetric Three-Component Colloidal Nanoparticle Isomers using Partial Cation Exchange Reactions

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Note: Reference numbers correspond to those documented in the main text.

Materials and Methods

Reagents

Octadecene [ODE, 90%, technical grade], oleylamine [OLAM, ≥98% (primary amine)], di-*tert*-butyl disulfide [97%], trioctylphosphine oxide [TOPO, ≥90%], *tert*-dodecanethiol [*t*-DDT, mixture of isomers 98.5%], 1-dodecanethiol [DDT, ≥98%], copper(II) chloride [$CuCl_2$, 97%], copper(II) nitrate trihydrate [$Cu(NO_3)_2{\cdot}3H_2O$, puriss. p.a. 99-104%], and zinc(II) chloride [$ZnCl_2$, ≥97% ACS reagent grade, anhydrous] were purchased from Sigma Aldrich. Trioctylphosphine [TOP, >85%] was purchased from TCI America. Benzyl ether [99%] was purchased from Acros Organics. Cadmium(II) acetate dihydrate [$Cd(OAc)_2$, 99.999% trace metals basis] was purchased from Alfa Aesar. All solvents, including hexanes, isopropanol [IPA], and acetone, were of analytical grade. All chemicals were used as received without further purification.

Synthesis of Roxbyite-type $Cu_{1.8}S$ spheres

Using a modification of a published procedure,[15,22] 341 mg $CuCl_2$, 47.2 mL OLAM, and 11.6 mL ODE were added to a 100-mL 3-neck round-bottom flask equipped with reflux condenser, thermometer, and rubber septum. The mixture was placed under vacuum, heated to 120 °C, and degassed for 30 minutes. After switching to an Ar flow, the mixture was heated to 200 ºC and degassed (under Ar flow) at this temperature for 60 minutes to remove gaseous side products formed during the dissolution of $CuCl_2$ in OLAM. The solution was then placed under an Ar blanket and cooled to 180 ºC. At 180 ºC, 8 mL of di-*tert*-butyl disulfide (under Ar) was rapidly injected, turning the clear yellow solution to turbid brown. Once the temperature stabilized at 180 ºC, the reaction was allowed to proceed for 40 minutes. The black/brown suspension was rapidly cooled by removing the heating mantle and placing the flask in a room-temperature water bath. The product was precipitated with a 1:1 mixture of IPA:acetone and collected by centrifugation. The particles were dispersed in hexanes and the precipitation/centrifugation process was repeated twice, until the centrifugate was clear and colorless. The resulting precipitate was dispersed in 10 mL hexanes (~6 mg/mL) for further use.

Synthesis of Roxbyite-type $Cu_{1.8}S$ rods

Using a modification of a published procedure,[22,30] 281 mg $Cu(NO_3)_2{\cdot}3H_2O$, 2.9 g trioctylphosphine oxide, and 15 mL ODE were added to a 100-mL 3-neck round-bottom flask equipped with reflux condenser, thermometer, and rubber septum. The mixture was placed under vacuum, heated to 80 °C, and degassed for 30 minutes. After switching to an Ar blanket, the contents of the flask were heated rapidly (within 5 minutes) to 180 ºC. When the temperature reached approximately 120 ºC, 7.5 mL of a 10:1 mixture of *tert*-dodecanethiol : dodecanethiol (under Ar) was rapidly injected as the temperature continued to increased. The reaction was allowed to proceed for 5 minutes at 180 ºC. The black/brown suspension was rapidly cooled by removing the heating mantle and placing the flask in a room-temperature water bath. The product was precipitated with a 1:1 mixture of IPA:acetone and collected by centrifugation. The particles were dispersed in hexanes and the precipitation/centrifugation process was repeated twice, until the centrifugate was clear and colorless. The resulting precipitate was dispersed in 6 mL hexanes (~6 mg/mL) for further use.

Synthesis of Janus CdS–$Cu_{1.8}S$ Spheres and End-Capped CdS–$Cu_{1.8}S$ Rods *via* Partial Cation Exchange with Cd^{2+}

Using a modification of a published procedure,[15,22] 245 mg $Cd(CH_3CO_2)_2{\cdot}2H_2O$, 8 mL OLAM, 2 mL ODE, and 15 mL benzyl ether were added to a 100-mL 3-neck round-bottom flask equipped with reflux condenser, thermometer, and rubber septum. The mixture was placed under vacuum,

heated to 100 °C, and degassed for 60 minutes. Meanwhile, the desired amount of $Cu_{1.8}S$ nanoparticle seeds (~12 mg for spheres, ~6 mg for rods) were dried and resuspended in 3 mL of TOP (under Ar). This dispersion was bath sonicated for 45 minutes. The Cd-OLAM solution was switched to a blanket of Ar and cooled to 50 ºC. The TOP/nanoparticle solution was then swiftly injected into the flask, and the reaction was allowed to proceed for 90 seconds. To quench the reaction, 8 mL of ice-cold acetone was introduced into the flask, which was then placed into an ice bath. Upon cooling to ~10 ºC, the particles were precipitated by the addition of IPA and collected by centrifugation. The particles were dispersed in hexanes and the precipitation/centrifugation process was repeated twice, until the centrifugate was clear and colorless. The resulting precipitate was dispersed in hexanes for further use.

Synthesis of Layered Sandwich ZnS–$Cu_{1.8}S$–ZnS Spheres and Multi-Stripe ZnS–$Cu_{1.8}S$–ZnS Rods *via* Partial Cation Exchange with Zn^{2+}

Using a modification of a published procedure,[15,22] 250 mg $ZnCl_2$, 8 mL OLAM, 2 mL ODE, and 15 mL benzyl ether were added to a 100 mL 3-neck round-bottom flask equipped with reflux condenser, thermometer, and rubber septum. The mixture was placed under vacuum, heated to 120 °C, and degassed for 60 minutes. After being placed under an Ar blanket, the solution was heated to 200 ºC and allowed to react for 30 minutes, forming a Zn-OLAM complex in solution. The solution was cooled to 100 ºC and degassed under vacuum for an additional 60 minutes. Meanwhile, the desired amount of $Cu_{1.8}S$ nanoparticle seeds (~12 mg for spheres, ~6 mg for rods) were dried and resuspended in 3 mL of TOP (under Ar). This dispersion was bath sonicated for 45 minutes. The Zn-OLAM solution was switched to a blanket of Ar and cooled to 50 ºC. The TOP/nanoparticle solution was then swiftly injected into the flask, and the reaction was allowed to proceed for 90 minutes. To quench the reaction, 8 mL of ice-cold acetone was introduced into the flask, which was then placed into an ice bath. Upon cooling to ~10 ºC, the particles were precipitated by the addition of IPA and collected by centrifugation. The particles were dispersed in hexanes and the precipitation/centrifugation process was repeated twice, until the centrifugate was clear and colorless. The resulting precipitate was dispersed in hexanes for further use.

Synthesis of Sandwich-Janus ZnS–($Cu_{1.8}S$–CdS)–ZnS Spheres and Janus-Stripe ZnS–(CdS–$Cu_{1.8}S$)–ZnS–(CdS–$Cu_{1.8}S$)–ZnS Rods *via* Secondary Cation Exchange with Cd^{2+}

Using a modification of the above procedure,[22] 75 mg $Cd(CH_3CO_2)_2{\cdot}2H_2O$, 1.6 mL OLAM, 0.4 mL ODE, and 7.5 mL benzyl ether were added to a 50 mL round-bottom flask equipped with reflux condenser, thermometer, and rubber septum. The heating/degassing profile was followed exactly as above. 2 mg of ZnS–$Cu_{1.8}S$ intermediate (either sandwich spheres or multi-stripe rods) were dried and dispersed in 1.5 mL TOP. Upon cooling to 50 ºC and introducing the particle/TOP solution, the reaction was allowed to proceed for 90 seconds. The workup procedure used above was repeated.

Synthesis of Janus-Sandwich CdS–(ZnS–$Cu_{1.8}S$–ZnS) Spheres and Multi-Stripe CdS–ZnS–$Cu_{1.8}S$–ZnS Rods *via* Secondary Cation Exchange with Zn^{2+}

Using a modification of the above procedure,[22] 50 mg $ZnCl_2$, 1.6 mL OLAM, 0.4 mL ODE, and 7.5 mL benzyl ether were added to a 50 mL round-bottom flask equipped with reflux condenser, thermometer, and rubber septum. The heating/degassing profile was followed exactly as above. 2 mg of CdS–$Cu_{1.8}S$ intermediate (either Janus spheres or segmented rods) were dried and dispersed in 1.5 mL TOP. Upon cooling to 50 ºC and introducing the particle/TOP solution, the reaction was allowed to proceed for 30 minutes. The workup procedure used above was repeated.

Synthesis of Multi-Stripe CdS–ZnS–(CdS–$Cu_{1.8}S$)–ZnS Rods *via* Tertiary Cation Exchange with Cd^{2+}

The preceding procedure (utilized for secondary cation exchange with Cd^{2+} on sandwich spheres and striped rods) was replicated, using approximately 1 mg of the multi-stripe CdS–ZnS–$Cu_{1.8}S$–ZnS dispersed particles. After injection of the seed particles in TOP, the reaction was allowed to proceed for 1 minute before being placed in an ice bath and worked up as detailed above.

Preliminary Solution Annealing Studies

To assess the stability of the heterostructured nanoparticles, 2 mg of particles from the samples shown in Fig. 2D and 2E were added to 5 mL of ODE in a 50-mL 3-neck round-bottom flask equipped with reflux condenser, thermometer, and rubber septum. The mixture was placed under vacuum, heated to 80 ºC, and degassed for 1 hour. The solution was placed under a blanket of Ar and subsequently heated to reflux (~315 ºC) for 5 hours of annealing. After cooling to room temperature, the particles were precipitated by adding IPA and then collected by centrifugation. The particles were dispersed in hexanes and the precipitation/centrifugation process was repeated. The resulting precipitate was dispersed in hexanes. After this solution annealing step, TEM imaging revealed no substantial change to either sample of heterostructured particles. This suggests that the reported structures are stable when heated in solution to temperatures higher than they were synthesized.

Characterization

Powder X-ray diffraction (XRD) data were collected on a Bruker D-8 Advance X-ray Diffractometer using Copper Kα radiation. Transmission electron microscopy (TEM) images were collected on a JEOL 1200 EX II microscope operating at 80 kV. High-resolution TEM (HRTEM) images were collected on an FEI Titan^3 G2 S/TEM equipped with spherical aberration correctors on the image and probe-forming lenses at an accelerating voltage of 200 kV. High angle annular dark field scanning TEM (HAADF-STEM) and STEM energy dispersive X-ray spectroscopy (STEM-EDS) maps were collected in the Titan using a beam current of ~0.15 nA. ES vision software (Emispec) was used for EDS data processing.

Element	***EDS Line***
Cu	Kα
Zn	Kα
Cd	L
S	Kα

Table S1. Mapped EDS lines used throughout the main text and supporting information figures.

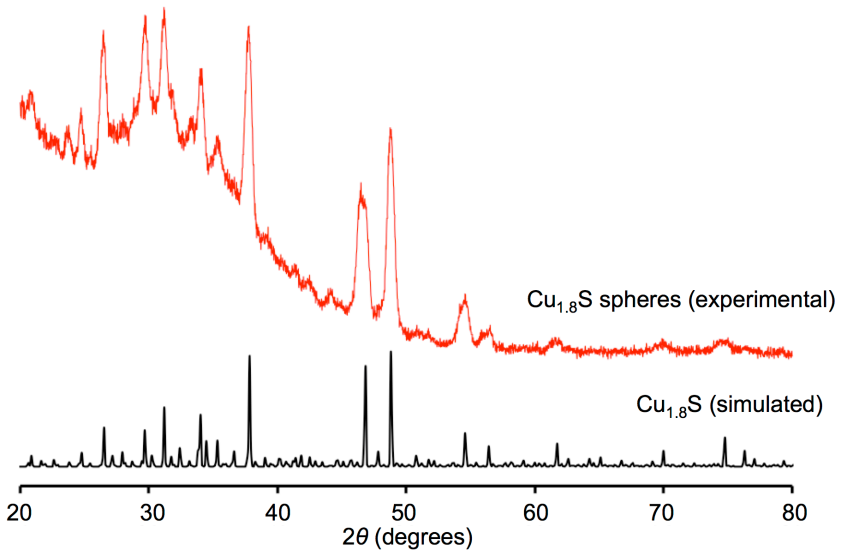

Figure S1. Powder X-ray diffraction (XRD) pattern for spherical $Cu_{1.8}S$ seed particles. A simulated pattern for roxbyite-type $Cu_{1.8}S$ is shown for reference.[27]

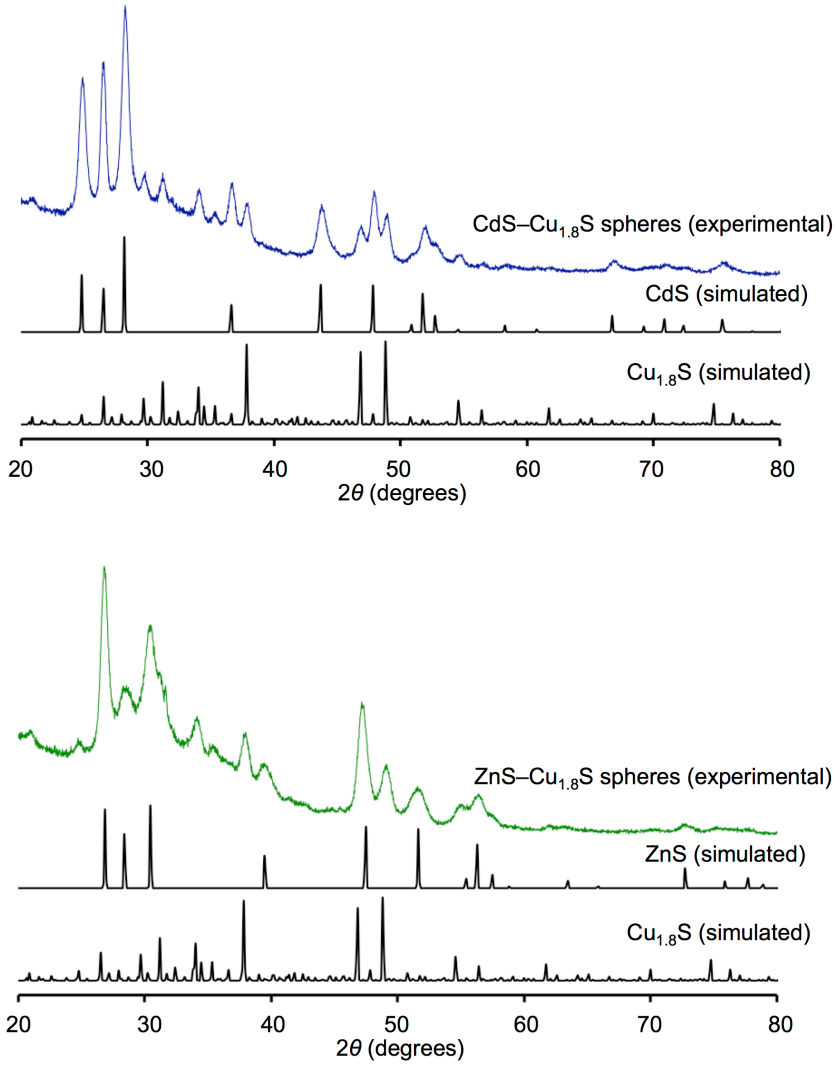

Figure S2. Powder X-ray diffraction (XRD) pattern for CdS–$Cu_{1.8}S$ Janus spheres (top) and ZnS–$Cu_{1.8}S$–ZnS sandwich spheres (bottom), demonstrating the preservation of the original roxbyite-type $Cu_{1.8}S$ structure along with the formation of the expected wurtzite-type metal sulfide through exchange. Simulated patterns for roxbyite-type $Cu_{1.8}S$ and wurtzite-type CdS and ZnS are shown for reference. [27,29]

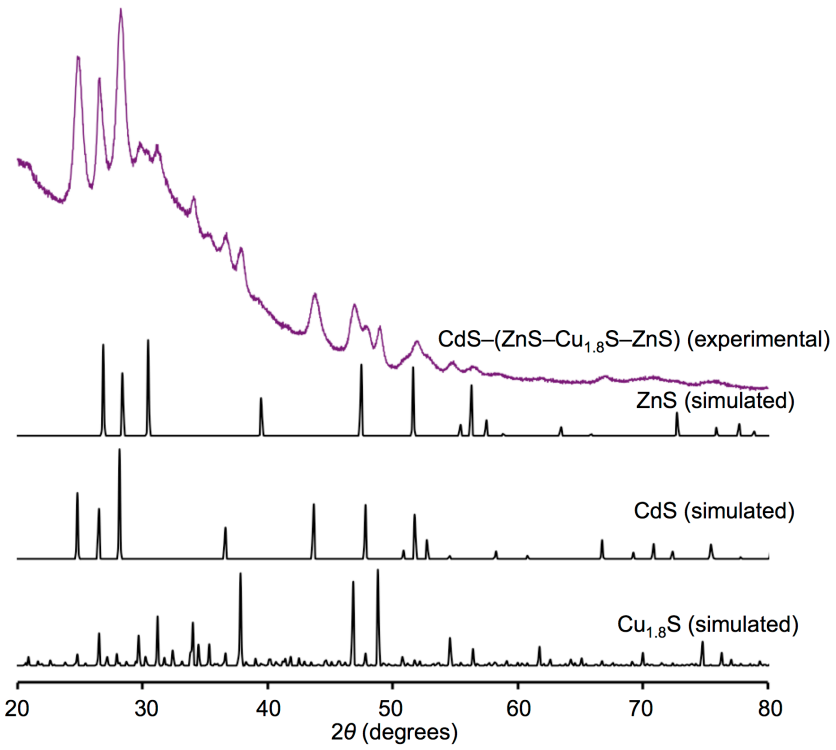

Figure S3. Powder X-ray diffraction (XRD) pattern for CdS–(ZnS–$Cu_{1.8}S$–ZnS) sandwich-Janus spheres, demonstrating the presense of the original roxbyite-type $Cu_{1.8}S$ structure along with both the expected wurtzite-type metal sulfides formed through sequential partial cation exchange. (The ZnS regions are small and also comprise only a small fraction of the overall particle, so the intensity of the ZnS phase is low.) Simulated patterns for roxbyite-type $Cu_{1.8}S$ and wurtzite-type CdS and ZnS are shown for reference. [27,29]

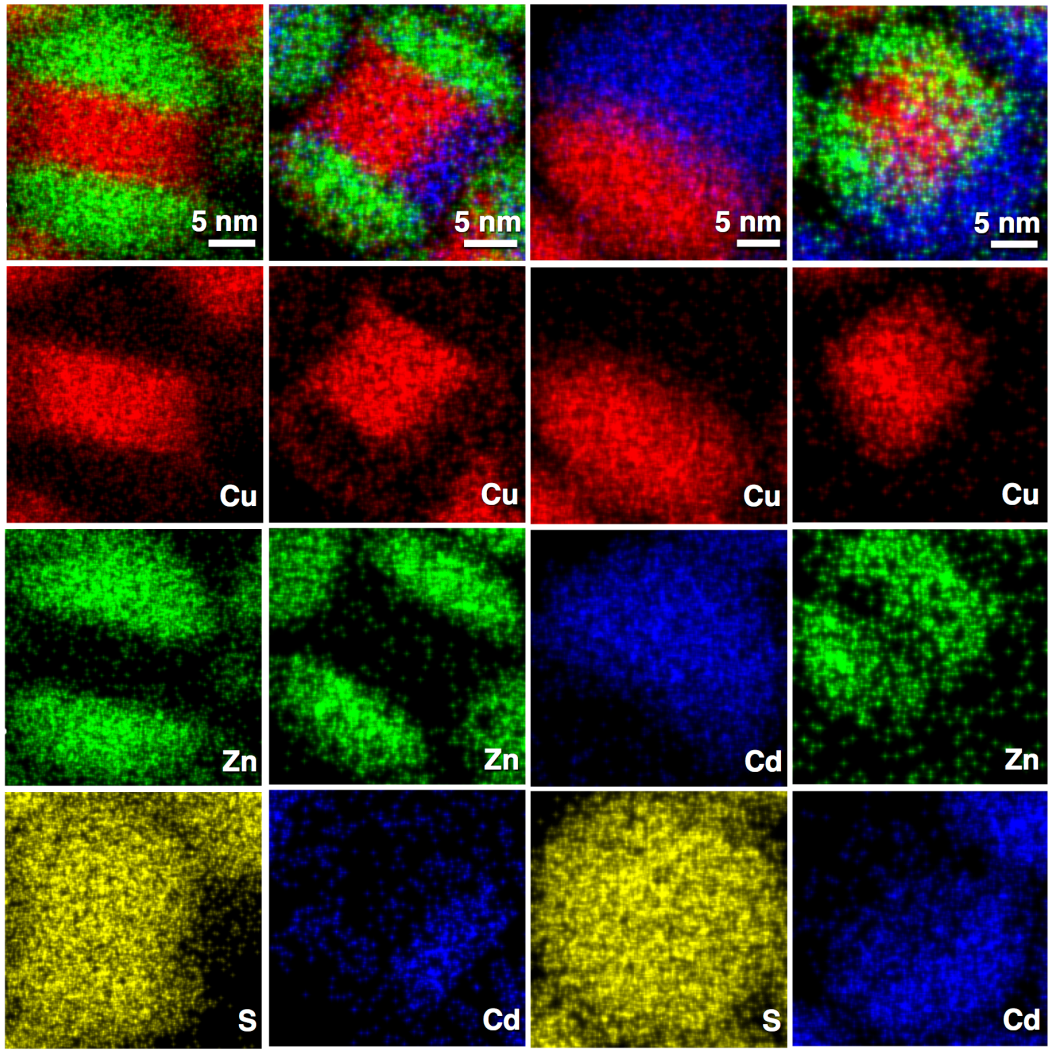

Figure S4. Single-element EDS maps for spherical particles shown in Figure 1, including ZnS–$Cu_{1.8}S$–ZnS sandwich particles, ZnS–(CdS–$Cu_{1.8}S$)–ZnS sandwich-Janus particles, CdS–$Cu_{1.8}S$ Janus particles, and CdS–(ZnS–$Cu_{1.8}S$–ZnS) Janus-sandwich particles.

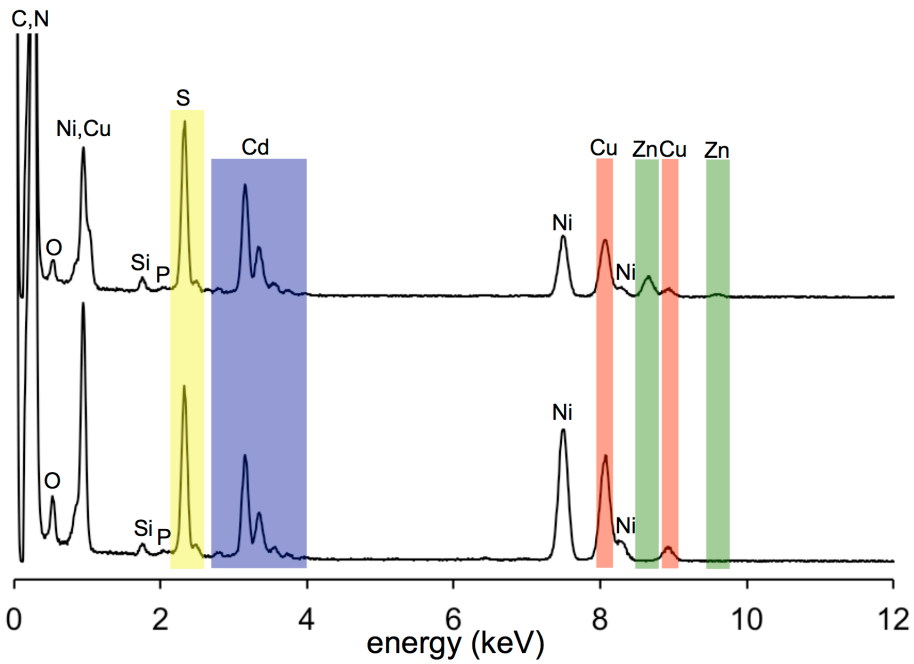

Figure S5. Correlated EDS spectra for the starting CdS–$Cu_{1.8}S$ Janus spheres (bottom) and the corresponding CdS–(ZnS–$Cu_{1.8}S$–ZnS) product (top), formed *via* partial exchange with Zn^{2+}. Both spectra are normalized to the intensity of the S Kα line (highlighted in yellow). The expected Zn signals (highlighted in green) appear in the product spectrum with a concomitant reduction in the intensity of the Cu signals (red), while the intensity of the Cd signals (blue) remain largely constant. The Si signal is adventitious. The Ni signal is from the Ni TEM grid.

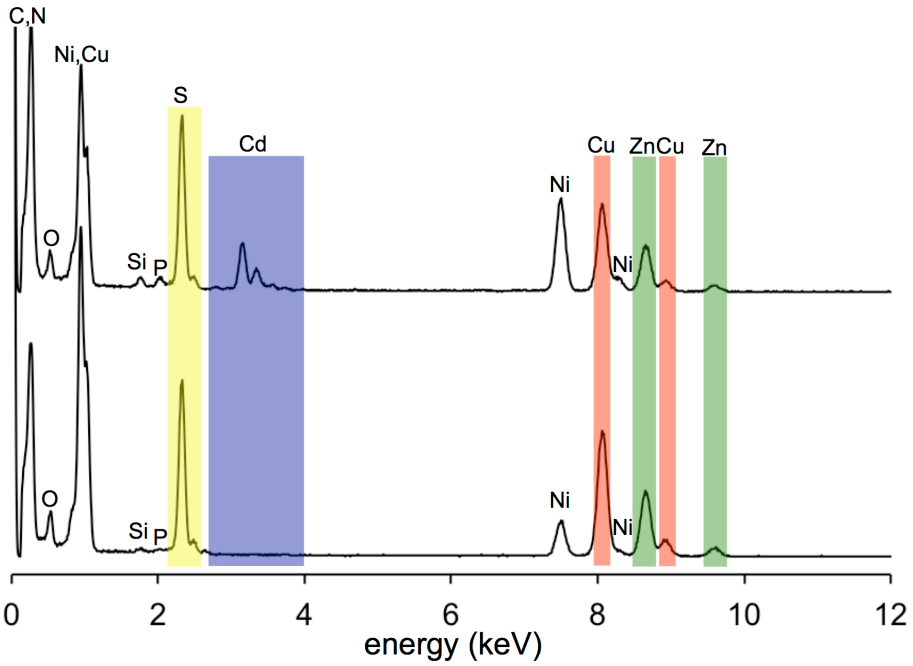

Figure S6. Correlated EDS spectra for the starting ZnS–$Cu_{1.8}S$–ZnS sandwich spheres (bottom) and the corresponding ZnS–(CdS–$Cu_{1.8}S$)–ZnS product (top), formed *via* partial exchange with Cd^{2+}. Both spectra are normalized to the intensity of the S Kα line (highlighted in yellow). The expected Cd signals (highlighted in blue) appear in the product spectrum with a concomitant reduction in the intensity of the Cu signals (red), while the intensity of the Zn signals (green) remain largely constant. The Si signal is adventitious. The Ni signal is from the Ni TEM grid.

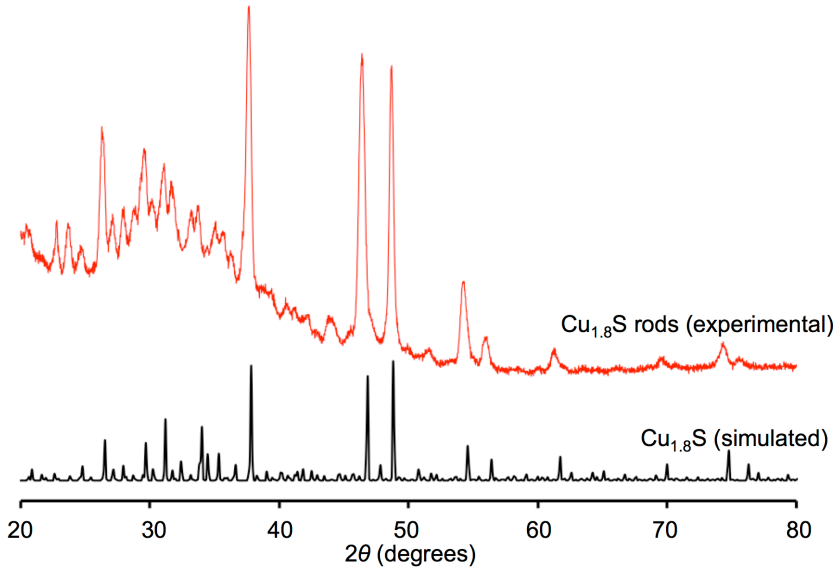

Figure S7. Powder X-ray diffraction (XRD) pattern for rod-like $Cu_{1.8}S$ seed particles. A simulated pattern for roxbyite-type $Cu_{1.8}S$ is shown for reference.[27]

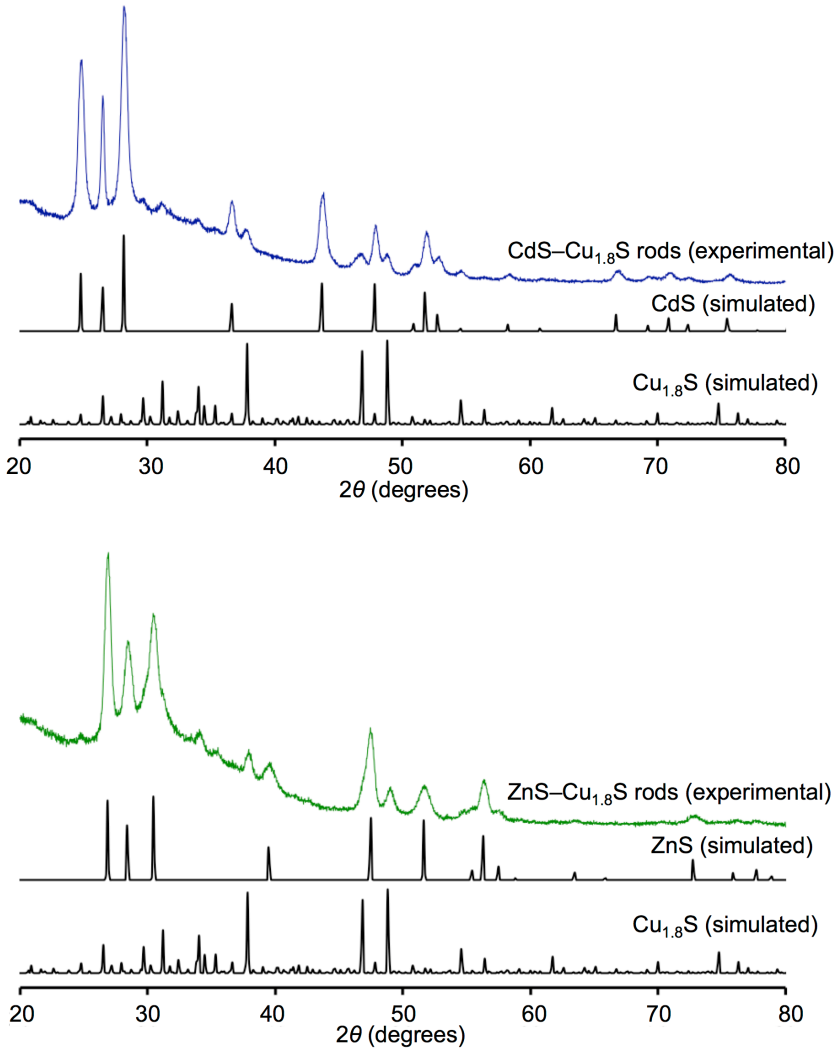

Figure S8. Powder X-ray diffraction (XRD) pattern for CdS–$Cu_{1.8}S$ Janus rods (top) and ZnS–$Cu_{1.8}S$–ZnS multi-stripe rods (bottom), demonstrating the preservation of the original roxbyite-type $Cu_{1.8}S$ structure along with the formation of the expected wurtzite-type metal sulfide through exchange. Simulated patterns for roxbyite-type $Cu_{1.8}S$ and wurtzite-type CdS and ZnS are shown for reference. [27,29]

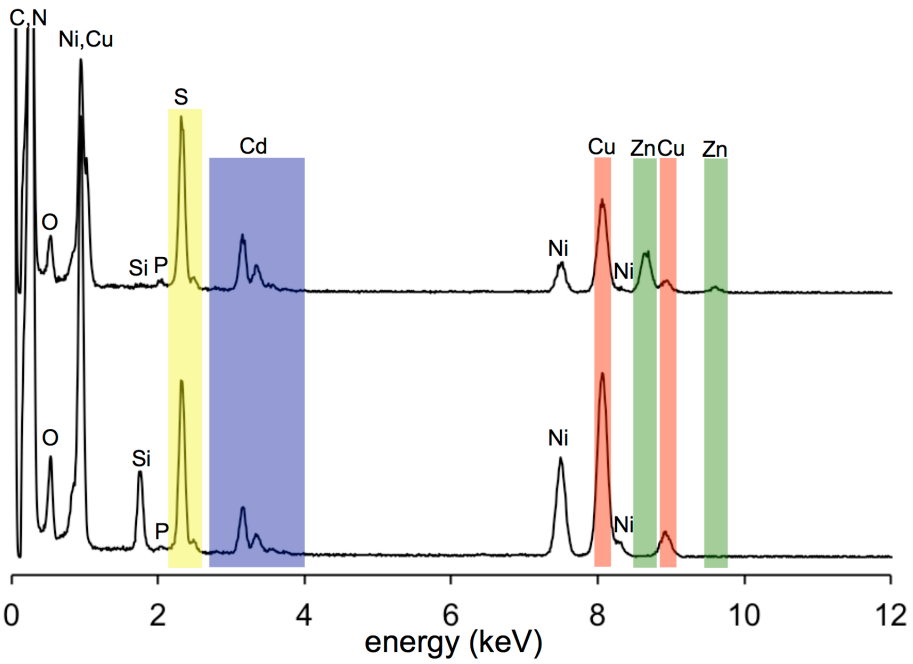

Figure S9. Correlated EDS spectra for the starting CdS–$Cu_{1.8}S$ end-capped rods (bottom) and the corresponding multi-striped CdS–ZnS–$Cu_{1.8}S$–ZnS product (top), formed *via* partial exchange with Zn^{2+}. Both spectra are normalized to the intensity of the S Kα line (highlighted in yellow). The expected Zn signals (highlighted in green) appear in the product spectrum with a concomitant reduction in the intensity of the Cu signals (red), while the intensity of the Cd signals (blue) remain largely constant. The Si signal is adventitious. The Ni signal is from the Ni TEM grid.

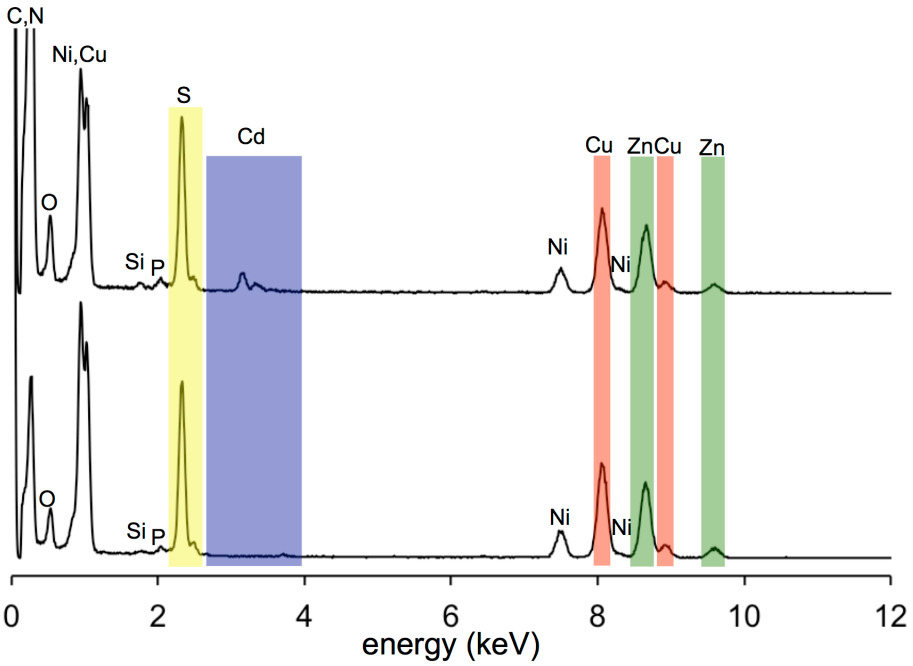

Figure S10. Correlated EDS spectra for the starting ZnS–$Cu_{1.8}S$–ZnS striped rods (bottom) and the corresponding ZnS–(CdS–$Cu_{1.8}S$)–ZnS–(CdS–$Cu_{1.8}S$)–ZnS product (top), formed *via* partial exchange with Cd^{2+}. Both spectra are normalized to the intensity of the S Kα line (highlighted in yellow). The expected Cd signals (highlighted in blue) appear in the product spectrum with a concomitant reduction in the intensity of the Cu signals (red), while the intensity of the Zn signals (green) remain largely constant. The Si signal is adventitious. The Ni signal is from the Ni TEM grid.

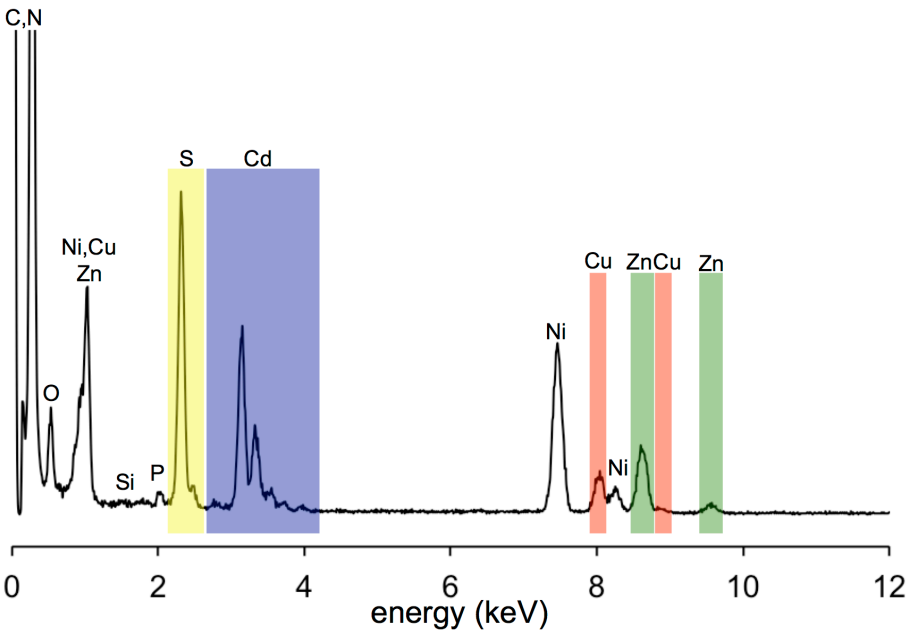

Figure S11. Correlated EDS spectrum for the multi-striped CdS–ZnS–(CdS–$Cu_{1.8}S$)–ZnS rods, formed *via* partial exchange of a CdS–ZnS–$Cu_{1.8}S$–ZnS rod with Cd^{2+}. The key signals for S, Cu, Zn, and Cd are highlighted in yellow, red, green, and blue, respectively. The Si signal is adventitious. The Ni signal is from the Ni TEM grid.