Supporting Information

Multimetallic Post-Synthetic Modifications of Copper Selenide Nanoparticles

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General Methods and Materials

Copper(II) sulfate pentahydrate (CuSO₄·5H₂O, > 98%), selenium dioxide (SeO₂, > 99.9%), gold(III) chloride trihydrate (HAuCl₄·3H₂O, \geq 99.9%), silver nitrate (AgNO₃, > 99.0%), mercury(II) nitrate monohydrate (Hg(NO₃)₂·H₂O, \geq 99.99%), potassium tetrachloroplatinate(II) (K₂PtCl₄, 98%), potassium tetrachloropalladate(II) (K₂PdCl₄, 99.99%), polyvinylpyrrolidone (PVP, average molecular weight 3.5 kDa), and L-ascorbic acid (> 99%), were purchased from Sigma Aldrich (St. Louis, MO). Deuterium oxide (D₂O, 99.9%) was purchased from Cambridge Isotope Laboratories, Inc. (Tewskbury, MA). All chemicals were used as received with no additional purification unless otherwise noted. NANOpure (> 18.2 MΩ cm, Thermo Fisher Scientific, Waltham, MA) water was used in the preparation of all solutions. Prior to use, all glassware and Teflon stir bars were washed in aqua regia and rinsed with copious amounts of water prior to oven drying.

Caution: aqua regia is highly toxic and corrosive and should only be used with proper personal protective equipment and training. Aqua regia should be handled inside a fume hood only. $Hg(NO_3)_2 \cdot H_2O$ is a toxic salt and is fatal if swallowed, in contact with skin or inhaled. It should only be handled with proper PPE and in a fume hood only.

Synthesis of Water Dispersible PVP-Capped Cu_{2-x}Se NPs

Cu_{2-x}Se NPs were synthesized using a modified ambient condition, room temperature, seed mediated procedure.^{1, 2} First, 3.5 kDa PVP (concentrations ranging from 5 to 35 mM) was dissolved in 10 mL of water prepared in a scintillation vial equipped with a Teflon-coated stir bar. 500 µL of 0.25 M SeO₂ agueous solution was added to the PVP solution followed by a rapid injection of 200 µL of 1.15 M aqueous ascorbic acid solution to promote the nucleation of selenium seeds, as indicated by color change of the solution from clear to bright orange. After stirring at 450 rpm for 10 minutes, 500 µL of 0.50 M CuSO₄ aqueous solution was added to the orange Se seed solution, followed by another quick injection of 300 µL of 1.15 M aqueous ascorbic acid solution. After 10 seconds, the solution turned dark brown. The solution was allowed to stir for approximately 15 hours during which the solution turned dark green. The Cu_{2-x}Se NP product was purified via centrifugation. First, the as-synthesized NPs were transferred to a 50 mL Falcon tube and diluted with water. The NP solutions were centrifuged in an Eppendorf 5804 centrifuge with a fixed angle rotor (FA-45-6-30) (Eppendorf, Inc., Hauppauge, NY) at a force of 16.639 rcf at 25 °C for 10 min. The resulting supernatant was carefully removed and the soft NP pellet was resuspended in approximately 50 mL of H₂O for additional centrifugation. This washing procedure was repeated 2 more times.

Post Synthetic Addition of M on Cu_{2-x}Se NPs (M = Ag, Au, Hg, Pt) (Step 1)

The secondary metal addition on purified Cu_{2-x}Se NPs was performed using modified ambient condition, room temperature procedure similar to the cation exchange and metal deposition protocols published by our group previously.^{3, 4} First, purified Cu_{2-x}Se NPs were dissolved in H₂O to make a concentrated stock. UV-vis-NIR spectroscopy was used to determine a concentration of approximately 70 optical density (O. D.) at the LSPR peak maximum at approximately 1100 nm. 2mL of such NP solution was prepared in a scintillation vial equipped with a Teflon-coated stir bar (see Supporting Information for details on NP concentration estimate). 5.60 mL of 2.0 mM aqueous solution of secondary

metal salt (e.g. HAuCl₄ for Au, etc.) was added to the NP solution followed by an injection of 5.60 mL of 1.6 M aqueous ascorbic acid solution, where the solution turned dark brown. The solution was allowed to stir for approximately 15 hours where the solution turned dark brown-green. As determined by ICP-OES and extinction spectroscopy reported previously,³ the molar ratio of secondary metal to Cu present within the NP lattice is 2:1.

The composite NP product was purified via centrifugation. First, the as-synthesized NPs were transferred to a 50 mL Falcon tube and diluted with water. The NP solutions were centrifuged in an Eppendorf 5804 centrifuge with a fixed angle rotor (FA-45-6-30) (Eppendorf, Inc., Hauppauge, NY) at a force of 16,639 rcf at 25 °C for 10 min. The resulting supernatant was carefully removed and the soft NP pellet was resuspended in approximately 50 mL of H₂O for additional centrifugation.

Post Synthetic Addition of M_2^{X+} on M_1 -Cu_{2-x}Se NPs ($M_2^{X+} = Ag^+$, Au^{3+} , Hg^{2+} , Pt^{2+}) (Step 2)

The purified M₁-Cu_{2-x}Se NPs was dissolved in H₂O to make a concentrated stock (50 O. D. at the LSPR peak maximum (approximately 1100 nm) determined by UV-vis-NIR spectroscopy; a slightly lower O.D. is used to account for the LSPR dampening). 2 mL of such M₁-Cu_{2-x}Se solution was prepared in a scintillation vial equipped with a Teflon-coated stir bar. 5.60 mL of 1.6 M aqueous ascorbic acid solution was added to the composite-NP solution followed by an injection of 5.60 mL of 2.0 mM aqueous solution of secondary metal salt (M₂^{X+}). The solution was allowed to stir for approximately 15 hours where the solution turned dark brown-green. The ternary-composite NP product (M₁-M₂-Cu_{2-x}Se) was purified via centrifugation. First, the as-synthesized NPs were transferred to a 50 mL Falcon tube and diluted with water. The NP solutions were centrifuged in an Eppendorf 5804 centrifuge with a fixed angle rotor (FA-45-6-30) (Eppendorf, Inc., Hauppauge, NY) at a force of 16,639 rcf at 25 °C for 10 min. The resulting supernatant was carefully removed, and the soft NP pellet was resuspended in approximately 50 mL of H₂O for additional centrifugation.

Post Synthetic Simultaneous Addition of M_1^{X+} and M_2^{Y+} on Cu_{2-x} Se NPs ($M^{X/Y+} = Ag^+$, Au^{3+} , Hg^{2+} , Pt^{2+})

2 mL of 70 O.D. purified Cu_{2-x}Se solution was prepared in a scintillation vial equipped with a Teflon-coated stir bar. 5.60 mL of 1.6 M aqueous ascorbic acid solution was added to the NP solution followed by a simultaneous injection of 2.8 mL of 4.0 mM of each aqueous solution of secondary metal salts, where the solution turned dark brown. The solution was allowed to stir for approximately 15 hours where the solution turned dark brown. The solution was allowed to stir for approximately 15 hours where the solution turned dark brown-green. The ternary composite NP product (M₁-M₂-Cu_{2-x}Se) was purified via centrifugation. First, the as-synthesized NPs were transferred to a 50 mL Falcon tube and diluted with water. The NP solutions were centrifuged in an Eppendorf 5804 centrifuge with a fixed angle rotor (FA-45-6-30) (Eppendorf, Inc., Hauppauge, NY) at a force of 16,639 rcf at 25 °C for 10 min. The resulting supernatant was carefully removed, and the soft NP pellet was resuspended in approximately 50 mL of H₂O for additional centrifugation.

All purified ternary-composite NPs were then characterized by HRTEM, STEM-EDS, and PXRD.

A note on selected reducing agent to metal ion ratios:

In the current report, our reagent ratios were motivated by a cascade effect, beginning with the ratio of ascorbic acid to metal ion added. For MD metals (M_{MD}) lower ratios of ascorbic acid to metal ion led to competing galvanic replacement reactions with the Cu₂₋ xSe NPs themselves, resulting in hollow particles that were depleted in Cu. Therefore, we used a high ratio (800x) of ascorbic acid to metal ion in order to avoid competing redox processes. The maximum solubility of ascorbic acid in water is ~1.7 M, and therefore the maximum concentration of metal we could add while maintaining this 800x ratio was 2 mM of metal ion (1.6 M ascorbic acid added).

High Angle Annular Dark Field (HAADF) Imaging and Scanning Transmission Electron Microscopy Energy Dispersive X-ray Spectroscopy (STEM-EDS)

All samples were prepared for TEM by drop casting an aliquot of purified solution (diluted 1:100 with water) onto carbon film-coated 200 mesh nickel TEM grids (Ted Pella, Inc., Redding, CA) for STEM-EDS analysis. The collection of EDS elemental maps and linescans were performed on a Thermo Fisher Titan Themis Cs-Corrected Microscope with an accelerating voltage of 200 kV (NanoScale Fabrication and Characterization Facility, Petersen Institute of NanoScience and Engineering, Pittsburgh, PA). Images were analyzed using Velox 2.13 for drift correction during acquisition and processing data. EDS elemental maps were post-filtered using Velox software using Gaussian blue.

Powder X-Ray Diffraction (PXRD)

Purified samples of Cu_{2-x}Se NPs, Au-, Ag-, Pt-, and Hg-containing composite NPs were lyophilized using a LabConco Freezone 6 Lyophilizer (Department of Chemistry, University of Pittsburgh) to obtain dry powders. The NP powders were packed in 0.50 mm capillary tubes (Hampton Research, Aliso Viejo, CA) and flame sealed for PXRD characterization. PXRD patterns were collected on a Bruker X8 Prospector Ultra (Department of Chemistry, University of Pittsburgh) at 45 kV, 0.65 mA equipped with a IµS micro-focus Cu K α X-ray source (λ = 1.54178 Å) with a scan speed of 0.5 s/step from 12.00-108.00° with a step size of 0.02°. Pd-containing composite NPs were dropcasted on a glass microscope slide (Fisher Scientific) and characterized using a Bruker AXS D8 Discover XRD (Nanoscale Fabrication and Characterization Facility, Petersen Institute of NanoScience and Engineering, Pittsburgh PA) at 40 kV, 40 mA for Cu K α X-ray source (λ = 1.5406 Å) with a scan speed of 3 s/step from 20 to 80° with a step size of 0.02°. All spectra were baseline corrected with respect to the spectrum of the amorphous glass background.

Ultraviolet-Visible-Near Infrared (UV-vis-NIR) Extinction Spectroscopy

The extinction spectra of Cu_{2-x}Se NPs were collected using a Cary 5000 UV-vis-NIR spectrophotometer (Agilent, Inc., Santa Clara, CA). Purified NPs were suspended in 1 mL of D₂O and placed in 1 cm quartz cuvettes (Hellma, Inc., Plainview, NY). The spectra were recorded from 1800 nm to 300 nm at a scanning rate of 1010 nm/min, with a grating and detector changeover occurring at 800 nm and a source changeover occurring at 290 nm. Spectra were baseline corrected with respect to 1 mL of D₂O for Cu_{2-x}Se NPs.



Figure S1. Representative STEM-EDS maps and HAADF images of Cu_{2-x}Se NPs after post-synthetic simultaneous addition of Ag and Au, where Cu K α , Se L β , Ag L α , and Au L α signals are represented in red, blue, green, and yellow respectively.



Figure S2. Representative STEM-EDS maps and HAADF images of Cu_{2-x}Se NPs after post-synthetic sequential Ag \rightarrow Au addition, where Cu K α , Se L β , Ag L α , and Au L α signals are represented in red, blue, green, and yellow respectively.



Figure S3. Representative STEM-EDS maps and HAADF images of Cu_{2-x}Se NPs after post-synthetic sequential Au \rightarrow Ag addition, where Cu K α , Se L β , Ag L α , and Au L α signals are represented in red, blue, green, and yellow respectively.



Figure S4. Representative STEM-EDS maps and HAADF images of Cu_{2-x}Se NPs after post-synthetic simultaneous addition of Ag and Pt, where Cu K α , Se L β , Ag L α , and Pt L α signals are represented in red, blue, green, and yellow respectively.



Figure S5. Representative STEM-EDS maps and HAADF images of Cu_{2-x}Se NPs after post-synthetic sequential Ag \rightarrow Pt addition, where Cu K α , Se L β , Ag L α , and Pt L α signals are represented red, blue, green, and yellow respectively.



Figure S6. Representative STEM-EDS maps and HAADF images of Cu_{2-x}Se NPs after post-synthetic sequential Pt \rightarrow Ag addition, where Cu K α , Se L β , Ag L α , and Pt L α signals are represented in red, blue, green, and yellow respectively.



Figure S7. Representative STEM-EDS maps and HAADF images of Cu_{2-x}Se NPs after post-synthetic simultaneous addition of Hg and Pt, where Cu K α , Se L β , Hg L α , and Pt L α signals are represented in red, blue, green, and yellow respectively.



Figure S8. Representative STEM-EDS maps and HAADF images of Cu_{2-x}Se NPs after post-synthetic sequential Hg \rightarrow Pt addition, where Cu K α , Se L β , Hg L α , and Pt L α signals are represented in red, blue, green, and yellow respectively.



Figure S9. Representative STEM-EDS maps and HAADF images of Cu_{2-x}Se NPs after post-synthetic sequential $Pt \rightarrow Hg$ addition, where Cu K α , Se L β , Hg L α , and Pt L α signals are represented in red, blue, green, and yellow respectively.



Figure S10. Representative STEM-EDS maps and HAADF images of Cu_{2-x}Se NPs after post-synthetic simultaneous addition of Hg and Au, where Cu K α , Se L β , Hg L α , and Au L α signals are represented in red, blue, green, and yellow respectively.



Figure S11. Representative STEM-EDS maps and HAADF images of $Cu_{2-x}Se$ NPs after post-synthetic sequential Hg \rightarrow Au addition, where Cu K α , Se L β , Hg L α , and Au L α signals are represented in red, blue, green, and yellow respectively.



Figure S12. Representative STEM-EDS maps and HAADF images of Cu_{2-x}Se NPs after post-synthetic sequential Au \rightarrow Hg addition, where Cu K α , Se L β , Hg L α , and Au L α signals are represented in red, blue, green, and yellow respectively.

Size Distributions of Particles and Deposition Islands

The size distributions of the core particle and metallic island deposits were analyzed using over 200 particles for each sample. Sizes are represented below both in histogram and table form for reader convenience.



Figure S13. Histograms of size distribution of core NP and deposition island for Au-Ag addition.

Table S1. Size distribution of core nanoparticle (diameter) and length of deposition island (length).

	Diameter (nm)	Length (nm)
Simultaneous Ag-Au	42.1 ± 3.7	18.1 ± 3.9
Seq Ag → Au	41.4 ± 3.8	17.3 ± 5.3
Seq Au → Ag	41.7 ± 4.1	15.7 ± 4.9



Figure S14. Histograms of size distribution of core NP and deposition island on Ag-Pt addition.

Table S2. Size distribution of core nanoparticle (diameter) and length of deposition island (length).

	Diameter (nm)	Length (nm)
Simultaneous Ag-Pt	55.4 ± 7.2	16.7 ± 4.1
Seq Ag → Pt	53.3 ± 5.7	18.6 ± 5.1
Seq Pt → Ag	55.4 ± 6.7	20.1 ± 5.6



Figure S15. Histograms of size distribution of core NP and deposition island on Hg-Pt addition.

Table S3. Size distribution of core nanoparticle (diameter) and length of deposition island (length).

	Diameter (nm)	Length (nm)
Simultaneous Hg-Pt	51.4 ± 7.9	15.9 ± 5.4
Seq Hg → Pt	52.8 ± 7.7	15.7 ± 5.7
Seq Pt → Hg	57.6 ± 6.1	18.7 ± 4.9





Table S4. Size distribution of core nanoparticle (diameter) and length of deposition island (length).

	Diameter (nm)	Length (nm)
Simultaneous Hg-Au	56.4 ± 5.6	20.0 ± 6.9
Seq Hg → Au	59.4 ± 7.0	18.4 ± 6.2
Seq Au → Hg	59.5 ± 5.4	24.1 ± 6.7

Extinction Spectra



Figure S17. Extinction spectra of Ag-Ag(A), Ag-Pt(B), Hg-Pt(C), Hg-Au(D) additions to Cu_{2-x}Se in D₂O.

Lattice Mismatch Calculations

All calculations of lattice symmetry were done according to the following formula,⁵

$$f = \frac{\propto_{Host} - \propto_{Growth}}{\propto_{Host}} \times 100$$

Where, f is the percentage lattice mismatch, \propto_{Host} is the lattice parameter of the host particle and \propto_{Growth} is the lattice parameter of the particle growing on it. (*N. B.* For non-cubic crystal systems, we consider each facet individually) The table below summarizes the lattice constant of Cu_{2-x}Se extracted experimentally from PXRD data and each metal extracted from the CRC Handbook of Chemistry and Physics.⁶

Table S5. The lattice symmetries and lattice parameters of the relevant metals and metal selenides.

	Lattice Symmetry	Lattice Parameters (nm)		
		а	b	С
Au	FCC	0.4065	0.4065	0.4065
Pt	FCC	0.4079	0.4079	0.4079
Cu _{2-x} Se	FCC	0.5700	0.5700	0.5700
HgSe	FCC	0.6085	0.6085	0.6085
Ag ₂ Se	Orthorhombic	0.4333	0.7764	0.7062
CuAgSe	Orthorhombic	0.4105	0.4070	0.6310

Table S6. The lattice mismatch calculations of the metals with the metal selenides.

	Cu _{2-x} Se	₂-xSe HgSe		Ag₂Se			CuAgSe	9
			а	b	С	а	b	С
Au	28.7%	33.2%	6.1%	47.6%	38.6%	0.1%	0.97%	35.6%
Pt	31.0%	35.5%	9.5%	44.4%	49.47%	3.6%	4.4%	37.8%

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Figure S18. Percentage of total NP population incorporating at least one of the added metals into the Cu_{2-x}Se (termed "modified" here, dark purple) compared to particles which did not incorporate any of the metals added (termed "unmodified" here, light purple). Over 150 particles are measured across at least 3 experimental replicates for each synthesis. Although not referred to specifically in the main text, this representation is helpful to visualize that for all metal combinations and synthetic routes studied, over 75% of particles undergo post-synthetic modification, and in many cases, the fraction is over 90% of NPs.



Figure S19. Percentage of NPs containing only the MD metal (blue), only the CE metal (yellow) and both CE and MD metals (green), measured over 150 particles across at least 3 experimental replicates for all syntheses.



Figure S20. Percentage of NPs containing only the CE metal (red/orange) and both CE and MD metals (light green/green) with partial CE in red/green and full CE in orange/light green, measured over across at least 3 experimental replicates. Each of the populations of CE only and both metals incorporated have been normalized for ease of comparison.

Table S7. Summarized Metal Selenide Properties for Predicting/Explaining Multimetallic

 Island Composition.

Metal Selenide	Lattice Symmetry ^a	Bond Dissociation ^a Enthalpy (BDE) (KJ/mol)	Solubility Product ^b (K _{sp})
Cu _{2-x} Se	Cubic	255.2	~10 ⁻⁵²
HgSe	Cubic	210.0	~4x10 ⁻⁵⁹
AgSe CuAgSe	Orthorhombic	-	3x10 ⁻⁵⁴

^aAll values are calculated from their lattice constants provided either in the CRC Handbook of Chemistry and Physics (ed. 92, Section 4–145 to 4–152) or their PXRD references and compared with the Cu_{2-x}Se experimentally observed lattice constant (5.7 Å).⁶ ^bValues are taken from the references.⁷



Figure S21. Line scans for sequential $Pt \rightarrow Hg$ addition, with varying amount of Hg relative to Cu and Pt, in the metal island.

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