

## SUPPORTING INFORMATION

# Phase-Selective Chemical Extraction of Selenium and Sulfur from Nanoscale Metal Chalcogenides: A General Strategy for Synthesis, Purification, and Phase Targeting

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### Materials

CoCl<sub>2</sub>·6H<sub>2</sub>O (98.0-102.0%), NiCl<sub>2</sub>·6H<sub>2</sub>O (99.95%), SnCl<sub>2</sub> anhydrous (99% min), FeCl<sub>3</sub> anhydrous (98%), sulfur powder (99.5%), selenium powder (99+%), hydrazine monohydrate, (98+%), and tetraethylene glycol (TEG, 99%) were purchased from Alfa Aesar. SeO<sub>2</sub> (99.9%) was purchased from Sigma Aldrich. Polyvinylpyrrolidone K30 (PVP, MW = 40,000), tri-n-octylphosphine (TOP, 85%), and oleylamine (40%) were purchased from TCI. Ethylene glycol (EG, 99.0%) was purchased from BDH.

### Characterization

Powder X-ray diffraction (XRD) data were collected on a Bruker Advance D8 X-ray diffractometer using Cu K $\alpha$  radiation. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were collected using a JEOL JEM 1200 EXII microscope operating at 80 kV.

### Synthesis of Chalcogenide Precursors

**Table S1.** Reaction conditions for the synthesis of chalcogenide precursors

Sample	Metal precursor (mg)	Chalcogenide powder (mg)	Solvent	Annealing temperature (°C)
FeSe (NiAs-type)	50.3 mg FeCl <sub>3</sub>	17.8 mg Se	oleylamine	303
FeSe (mixture)	53 mg FeCl <sub>3</sub>	21.3 mg Se	oleylamine	270
SnSe <sub>2</sub>	34 mg SnCl <sub>2</sub>	30.7 mg Se	TEG	210
FeS <sub>2</sub>	21.9 mg FeCl <sub>3</sub>	25 mg S	TEG	235
NiSe <sub>2</sub>	58.2 mg NiCl <sub>2</sub>	20.4 mg Se	TEG	170
CoSe <sub>2</sub>	46.9 mg CoCl <sub>2</sub>	46.9 mg Se	TEG	270

Appropriate precursors and solvent were placed in a 3-neck apparatus sealed using a condenser with an air-flow adapter on top, a thermometer adapter with mercury thermometer, and a 14/20 rubber septum. The 3-neck apparatus was then attached to a schlenk line and placed under vacuum for 30 minutes. The 3-neck apparatus was then placed under Ar and heated to the appropriate annealing temperature, and held there for 2 h. The reaction was then allowed to cool to room temperature. The precipitate was then quenched with an equal volume

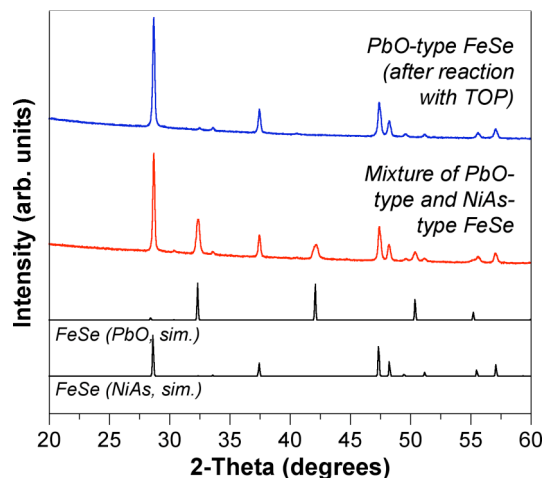
of ethanol or hexanes, depending on solvent, and centrifuged for 10 min at 12,000 rpm. The supernatant was decanted and the product was washed three times with ethanol or hexanes.

### ***Synthesis of NiSe<sub>2</sub> Hollow Spheres***

99.7 mg SeO<sub>2</sub>, 118 mg NiCl<sub>2</sub>·6H<sub>2</sub>O, 313.2 mg PVP, and 20 mL ethylene glycol were combined in a 3-neck apparatus sealed using a condenser with an air-flow adapter on top, a thermometer adapter with mercury thermometer, and a 14/20 rubber septum. The apparatus was then sonicated for 1 h to dissolve precursors. The 3-neck apparatus was then attached to a schlenk line and placed under vacuum for 30 min. The 3-neck apparatus was then placed under Ar, and 0.5 mL of hydrazine monohydrate was injected, causing the solvent to turn dark red. The solution was allowed to stir for 30 min. before heating to 160 °C, and held there for 1 h. The reaction was then allowed to cool to room temperature. The precipitate was then quenched with an equal volume of a hexanes and acetone mixture and centrifuged for 10 min at 12,000 rpm. The supernatant was decanted and the product was washed three times with ethanol.

### ***Reaction of Chalcogenides with TOP***

Precursors were dispersed in 12 mL TOP by sonication and then placed in a 3-neck apparatus sealed using a condenser with an air-flow adapter on top, a thermometer adapter with mercury thermometer, and a 14/20 rubber septum. The 3-neck apparatus was then attached to a schlenk line and placed under vacuum for 30 min. The 3-neck apparatus was then placed under Ar and heated to the appropriate annealing temperature, and held there for 1 h. The reaction was then allowed to cool to room temperature. The precipitate was then quenched with an equal volume of hexanes and centrifuged for 10 min at 12,000 rpm. The supernatant was decanted and the product was washed three times with ethanol, hexanes, and dichloromethane.



**Figure S1.** Powder XRD data showing the purification of a mixed-phase sample: a mixture of PbO-type and NiAs-type FeSe is converted to phase-pure PbO-type FeSe by reaction with TOP.