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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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Supporting Information

ABSTRACT: Controlling the composition and phase formation of bulk and nanoscale solids underpins efforts to control physical properties. Here, we introduce a powerful new chemical pathway that facilitates composition-tunable synthesis, post-synthesis purification, and precise phase targeting in metal chalcogenide systems. When metal selenides and sulfides react with trioctylphosphine (TOP) at temperatures that range from 65 to 270 °C, selenium and sulfur are selectively extracted to produce the most metal-rich chalcogenide that is stable in a particular binary system. This general approach is demonstrated for $SnSe_2$, FeS_2, $NiSe_2$, and $CoSe_2$, which convert to SnSe, FeS, Ni_3Se_2, and Co_9Se_8, respectively. In-depth studies of the Fe−Se system highlight the precise phase targeting and purification that is achievable, with PbO-type FeSe (the most metal-rich stable Fe−Se phase) forming exclusively when other Fe−Se phases, including mixtures, react with TOP. This chemistry also represents a new template-based nanoparticle "conversion chemistry" reaction, transforming hollow $NiSe_2$ nanospheres into hollow NiSe nanospheres with morphological retention.

For solid-state compounds, the chemical manipulation of composition is foundational for tuning physical properties, accessing desired structures, and influencing bonding characteristics for a diverse range of materials that includes thermoelectrics, catalysts, superconductors, semiconductors, battery materials, etc. For example, chemical de-intercalation of Na from Na_xCoO_2 facilitates tuning through various metallic, insulating, and magnetic states.[1] As a result, Na_xCoO_2 exhibits a wide range of composition-dependent properties, including superconductivity,[2] high thermopower,[3] and redox intercalation for battery electrodes.[4] Similarly, careful control of oxygen stoichiometry in the perovskite-type copper oxides permits tuning through various superconducting, electronic, and magnetic states.[5] Controlled chemical substitution in $ThCr_2Si_2$-type CaM_2P_2 (M = Fe, Co, Ni) phases modulates the P−P bond strength, which in turn leads to complex variations in the magnetic properties.[6]

In colloidal nanoscale solids, precise control over composition and phase is equally important. For example, the transport properties of quantum dot solids can be tuned by hydrazine-mediated doping,[7] and compositional tunability is critical for targeting optimal properties in nanoscale thermoelectric,[8] optical,[9] catalytic,[10] and magnetic materials.[11] Likewise, the ability to target one particular phase in a complex binary system is critical. For example, in the Fe−Pt system, the magnetic properties of $Fe_{1-x}Pt_x$ nanoparticles vary with x;[11] this range includes the distinct intermetallic compounds $FePt_3$, FePt, and Fe_3Pt. However, such phase targeting is not always straightforward in colloidal nanoparticle systems, particularly non-alloy systems that have multiple stable compounds.[12] Metal chalcogenides represent an important class of materials where this type of composition control and phase targeting is important, with direct applicability to quantum-confined semiconductors, phase change materials, thermoelectrics, superconductors, and materials for solar energy conversion.

Here, we describe a powerful new strategy for chemically manipulating the compositions and structures of nanoscale metal chalcogenides. Trioctylphosphine (TOP) is commonly used as a nanoparticle surface stabilizer,[13] a phosphorus source for chemical conversion,[14] and a chemical reagent in the form of TOP−X (X = S, Se, Te) complexes.[15] Here, we show that TOP can selectively extract selenium and sulfur from pre-made metal chalcogenides. The final products tend to be the most metal-rich stable compounds in each particular M−S or M−Se system, modulated by the concomitant ability of TOP to extract S and Se (driven by the large formation constants of the TOP−S and TOP−Se complexes) and the inability of TOP to reduce the M^{n+} in the chalcogenides to the zero-valent state. This chemistry has three important implications. First, selenium- or sulfur-rich metal chalcogenides can be chemically transformed into lower-chalcogen compounds via TOP extraction of Se or S; e.g., $NiSe_2$ and FeS_2 can be converted to Ni_3Se_2 and FeS, respecively. This allows a binary phase that is straightforward to synthesize by direct methods to be converted to a different binary phase that may be more challenging to synthesize directly. Second, impure samples containing mixtures of multiple metal chalcogenides can be purified by TOP extraction of Se or S, with the final product being the most metal-rich stable compound in the system. For example, mixed-phase samples containing $FeSe_2$ and Fe_3Se_4 can be converted exclusively to PbO-type FeSe, and samples of PbO-type FeSe containing small amounts of NiAs-type FeSe can be purified to exclusively the PbO-type polymorph. Third, preliminary evidence suggests that these reactions can proceed pseudomorphically; e.g., colloidal metal chalcogenide nanoparticles with pre-defined sizes and shapes can be transformed

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to derivative colloidal metal chalcogenide nanoparticles with morphological retention. Accordingly, this has the potential to add to the growing toolbox of "conversion chemistry" reactions for chemically transforming nanoparticle templates into derivative nanoparticle products.[16]

Figure 1 shows powder X-ray diffraction (XRD) data for several representative systems. Bulk-scale samples of the chalcogen-rich precursors $SnSe_2$ (CdI_2-type), FeS_2 (pyrite-type), $NiSe_2$ (pyrite-type), and $CoSe_2$ (marcasite-type) were synthesized by heating metal chloride salts and selenium or sulfur powder in tetraethylene glycol (see Supporting Information for details). After dispersing 20 mg of each ME_2 (E = Se, S) precursor in 12 mL of TOP via sonication and heating to appropriate temperatures (given in parentheses), the powder XRD patterns of the final products matched well with those of the most metal-rich stable chalcogenides in each binary system: SnSe (215 °C, Figure 1a), NiAs-type FeS (255 °C, Figure 1b), Ni_3Se_2 (225 °C, Figure 1c), and Co_9Se_8 (270 °C, Figure 1d). EDS analysis yielded compositions that were consistent with the stoichiometries expected for each of the compounds, within experimental error: $Fe_{0.55}Se_{0.45}$, $Fe_{0.55}S_{0.45}$, $Ni_{0.61}Se_{0.39}$, $Co_{0.55}Se_{0.45}$, and $Sn_{0.53}Se_{0.47}$. Our preliminary studies suggest that TOP can successfully extract Se and S from chalcogen-rich 3d transition metal and early p-block metal chalcogenides, but not from most 4d and 5d metal chalcogenides. This can be rationalized on the basis of oxidation states. The systems above involve either no change in oxidation state (e.g., FeS_2 with the S_2^{2-} anion to FeS with the S^{2-} anion) or two stable oxidation states for which reduction is relatively easy (e.g., $SnSe_2$ with Sn^{4+} to SnSe with Sn^{2+}). Early 4d and 5d transition metal systems, such as $MoSe_2$, contain S^{2-} and Se^{2-} (rather than S_2^{2-} and Se_2^{2-}) and are most stable for high oxidation states. Chalcogen extraction in these systems, for which the lower-valent and metal-rich products are not stable, would be difficult.

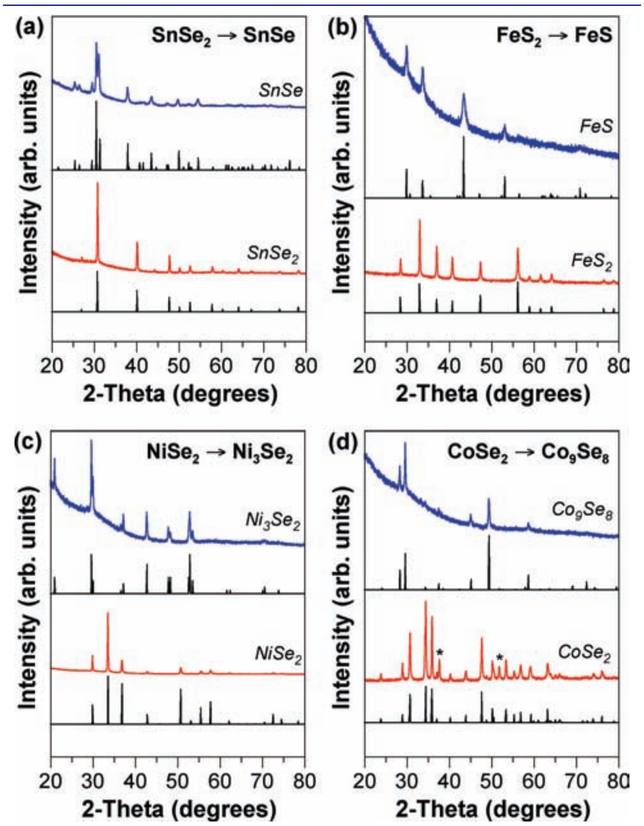

Figure 1. Powder XRD data showing TOP-mediated conversion reactions: (a) $SnSe_2 \rightarrow SnSe$, (b) $FeS_2 \rightarrow FeS$, (c) $NiSe_2 \rightarrow Ni_3Se_2$, and (d) $CoSe_2 \rightarrow Co_9Se_8$. For the $CoSe_2$ sample, two polymorphs coexist: cubic-$CoSe_2$ (marked with *) and orthorhombic-$CoSe_2$ (primary phase). In each panel, the red (bottom) and blue (top) XRD patterns correspond to the as-synthesized precursors and TOP-reacted products, respectively. The black patterns, shown below each experimental pattern, represent the corresponding simulated XRD data.

The Fe−Se system[17] provides an interesting application and extension of this chemistry. PbO-type FeSe, which exists only in a narrow composition window of 50.6−51.0% Fe,[18] is known to be superconducting at a very precise composition and with specific structural features.[19] NiAs-type FeSe, also a nominally 1:1 Fe−Se compound, exists in the composition window of 42.0−50.5% Fe[18] and is not superconducting. Figure 2a shows that NiAs-type FeSe fully converts to PbO-type FeSe when reacted with TOP at 180 °C. Similarly, when a sample of PbO-type FeSe that contains a small amount of a NiAs-type FeSe impurity is reacted with TOP at 180 °C, the product is exclusively PbO-type FeSe (Figure S1; see Supporting Information for experimental details). In addition to serving as a chemical purification pathway, this demonstrates that the most metal-rich stable chalcogenide product tends to form even when other stable compounds with very similar compositions exist. Interestingly, when an impure Fe−Se sample—one that contains a physical mixture of $FeSe_2$ and Fe_3Se_4—reacts with TOP at 180 °C, the product is also exclusively PbO-type FeSe

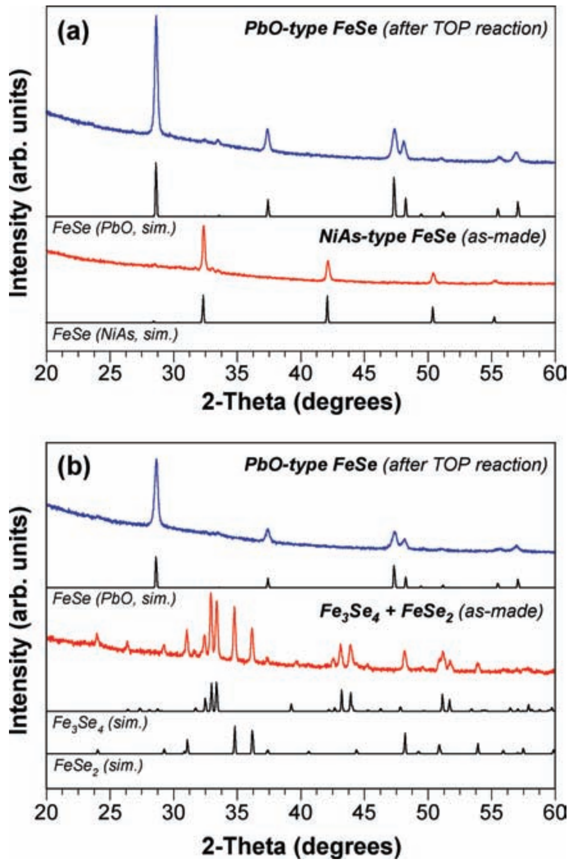

Figure 2. Powder XRD data showing the TOP-mediated conversion of (a) NiAs-type FeSe (bottom, red) to PbO-type FeSe (top, blue) and (b) a mixture of Fe_3Se_4 and $FeSe_2$ (bottom, red) to PbO-type FeSe (top, blue). Simulated XRD patterns are shown in black below the corresponding experimental data.

(Figure 2b). These results highlight both the precise phase targeting that is possible using this chemistry and the ability to purify mixed-phase samples by conversion to the desired compound. Our PbO-type FeSe samples are not superconducting, but we have not yet attempted to fine-tune the Se or Fe stoichiometry, as would be required to render them superconducting. Such studies are in progress.

This chemistry can also be successfully applied to colloidal nanostructures with morphological retention. Hollow nanospheres of $NiSe_2$ were synthesized by heating amorphous Se spheres and $NiCl_2$ in ethylene glycol to 170 °C, based on a literature report.[20] (See Supporting Information for details.) Figure 3a shows a representative transmission electron microscope (TEM) image of an ensemble of hollow crystalline $NiSe_2$ spheres, along with a selected area electron diffraction (SAED) pattern that confirms the $NiSe_2$ phase. After reaction with TOP at 65 °C, data from TEM and SAED confirm that the hollow $NiSe_2$ spheres convert to crystalline NiSe while retaining the size and morphology defined by the $NiSe_2$ template (Figure 3b). This demonstrates two important points. First, intermediate reaction temperatures can provide access to intermediate phases. The data in Figure 1c show that $NiSe_2$ converts to Ni_3Se_2 when reacted with TOP at 225 °C. However, $NiSe_2$ can be made to convert to NiSe instead by reaction at a lower temperature (65 °C, Figure 3b). Second, this provides preliminary evidence that chalcogen extraction via TOP can be considered as a viable nanoparticle "conversion chemistry" reaction,[16] in analogy to other classes of reactions that include galvanic replacement,[21] diffusion (including nanoscale Kirkendall effects),[22] ion exchange,[23] etc. Additional work is necessary to fully explore issues of size- and shape-dependent reactivity using this chemical conversion strategy, as well as its generality with respect to morphological retention across a wider range of systems.

In conclusion, we have demonstrated that TOP can be used for the phase-selective extraction of sulfur and selenium from metal chalcogenides. This represents a new low-temperature chemical strategy for manipulating the compositions and structures of solids,[24] and it also has applicability to phase-targeted nanoparticle synthesis, purificiation of multiphase samples, and pseudomorphic nanoparticle transformations. As such, it can be considered as a new addition to the growing toolbox of "conversion chemistry" reactions that transform nanoparticle templates into derivative nanoparticle products with morphological retention.

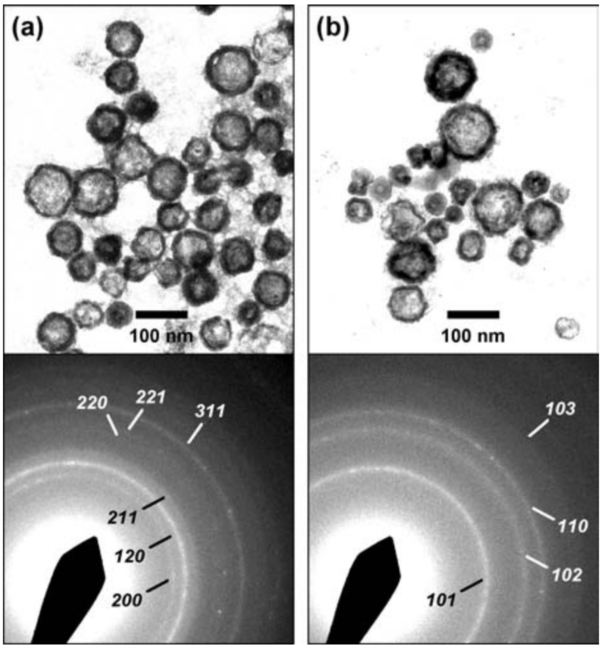

Figure 3. TEM images and SAED patterns for (a) hollow pyrite-type $NiSe_2$ nanosphere templates and (b) hollow NiAs-type NiSe nanosphere products after reaction with TOP at 65 °C.

ASSOCIATED CONTENT

Supporting Information. Complete experimental details and additional XRD data. This material is available free of charge via the Internet at http://pubs.acs.org.

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