Chalcogenide and Pnictide Nanocrystals from the Silylative Deoxygenation of Metal Oxides

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Abstract
Transition metal chalcogenide and pnictide nanocrystals are of interest for optoelectronic and catalytic applications. Here, we present a generalized route to the synthesis of these materials from the silylative deoxygenation of metal oxides with trimethylsilyl reagents. Specific nanophases produced in this way include Ni₃S₂, Ni₅Se₅, Ni₂P, Co₉S₈, Co₃Se₄, CoP, Co₂P, and heterobimetallic (Ni/Co)₉S₈. The resulting chalcogenide nanocrystals are hollow, likely due to differential rates of ion diffusion during the interfacial phase transformation reaction (Kirkendall-type effect). In contrast, the phosphide nanocrystals are solid, likely because they form at higher reaction temperatures. In all cases, simultaneous partial decomposition of the deoxygenating silyl reagent produces a coating of amorphous silica around the newly formed nanocrystals, which could impact their stability and recyclability.

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Chalcogenide and Pnictide Nanocrystals from the Silylative Deoxygenation of Metal Oxides

Chia-Cheng Lin, Shannon J. Tan and Javier Vela

Transition metal chalcogenides and pnictides have attracted much interest due to their catalytic and opto-electronic properties. These materials are active in the catalytic upgrading of conventional and bio-derived oils through hydrodesulfurization (HDS), hydrodeoxygenation (HDO), and hydrodenitrification (HDN) reactions. As an example, Ni2P has comparable activity to the Ni-Mo-S catalyst currently used for industrial HDS and HDN. Transition metal chalcogenides and phosphides are also active in water electrolysis. Late transition metal sulfides have been used for electrochemical evolution of oxygen and hydrogen. Ni3S2 is capable of selectively hydrogenating chloronitrobenzene. Furthermore, metal sulfides and phosphides have been employed in lithium ion and aqueous alkaline batteries and solar cells.

To fully understand and utilize these materials and their properties, efforts were devoted to developing synthetic strategies that generate high surface area versions with phase-, morphology- and size-control. Transition metal chalcogenides and phosphides are often made by chemical vapor deposition, solution phase decomposition of suitable molecular precursors, including metal-trioctylphosphine complexes and metal carbonyl- or acetylacetonate-alkyl phosphine and phosphide complexes. The resulting chalcogenide nanocrystals are hollow, likely due to differential rates of ion diffusion during the interfacial phase transformation reaction (Kirkendall-type effect). In contrast, the phosphide nanocrystals are solid, likely because they form at higher reaction temperatures. In all cases, simultaneous partial decomposition of the deoxygenating silyl reagent produces a coating of amorphous silica around the newly formed nanocrystals, which could impact their stability and recyclability.

1. Introduction

Transition metal chalcogenides and pnictides are of interest for optoelectronic and catalytic applications. Here, we present a generalized route to the synthesis of these materials from the silylative deoxygenation of metal oxides with trimethylsilyl reagents. Specific nanophases produced in this way include Ni3S2, Ni5Se5, Ni2P, Co9S8, Co3Se4, CoP, Co2P, and heterobimetallic (Ni/Co)-S. The resulting chalcogenide nanocrystals are hollow, likely due to differential rates of ion diffusion during the interfacial phase transformation reaction (Kirkendall-type effect). In contrast, the phosphide nanocrystals are solid, likely because they form at higher reaction temperatures. In all cases, simultaneous partial decomposition of the deoxygenating silyl reagent produces a coating of amorphous silica around the newly formed nanocrystals, which could impact their stability and recyclability.

2. Experimental

2.1 Materials

Cobalt(II) acetylacetonate (acac) (Co(MeCOCHCOMe)2), cobalt(II) acetate tetrahydrate (MeCOO)2Co·4H2O, Brij 58 (poly(ethylene glycol)hexadecyl ether), tetraethylorthosilicate (Si(OEt)4, TEOs), hexamethyldisilazane [(CH3)3SiNHsi(CH3)3, HMDS) and bis(trimethylsilyl) sulfide (Me2Si)2S, TMS2S) were purchased from Sigma-Aldrich; methanol, ethanol (absolute, 200 proof), 

Surface area, porous solid support in order to increase their stability and recyclability. Silica is a common support as demonstrated recently with metal phosphides, such as Pd5P3 or Ni2P/SiO2. Silylative defluorination and deoxygenation reactions are regularly used in the synthesis and deprotection of molecular inorganic and organic compounds. For example, they have been used in stoichiometric and catalytic C–F bond activation and hydrodefluorination. These reactions are driven by the formation of very strong Si–X bonds between silicon and a highly electronegative element, such as F (Si–F, 576 kJ/mol) or O (Si–O, 800 kJ/mol). Here, we explore the use of silylative deoxygenation of preformed metal oxide nanocrystals with trimethylsilyl precursors (TMSxE, where TMS = Me3Si and xE = 2S, 2Se, 3P) in order to synthesize nanocrystalline metal phosphides and chalcogenides (Scheme 1). Parallel in situ decomposition of excess trimethylsilyl precursor creates a protecting silica shell around the newly formed nanocrystals. Thus, this new methodology results in silica-encapsulated metal chalcogenide and phosphide nanocrystals in a simple, single step synthetic process.

Scheme 1. Silylative deoxygenation of metal oxides.

M2Ox + (TMS)xE ⇋ \( \frac{\Lambda}{\lambda} \) M2(Er)x + (TMS)xO

TMS = SiMe3, M = Co, Ni; E = 2S, 2Se, 3P
isopropanol (2-propanol), cyclohexane, aqueous ammonium hydroxide (28.54 wt%) and diethylamine from Fisher; nickel chloride hexahydrate (NiCl₂•6H₂O), trioctylphosphine (TOP), bis(trimethylsilyl)sulfide ((Me₃Si)₂S, TMS₂S) and tris(trimethylsilyl)phosphine ((Me₃Si)₃P, TMS₃P, 10 wt% in hexane) from Strem; oxalic acid from Alfa Aesar; oleylamine (2-octadec-9-enylamine), sodium borohydride (NaBH₄), de-ionized water (0.05 g, 2.78 mmol) and trioctylphosphine (TOP, 2 mL, 4.5 mmol) were added into the flask. After 10 min. The solid (particles) was re-dispersed in hexane and washed by precipitation and re-dispersion cycles (see above), and the solid products were analyzed by XRD and optical absorption (below). With bis(trimethylsilyl)sulfide. Performed under identical conditions as mentioned above for TMS₂S. With tris(trimethylsilyl)phosphine. Performed under similar conditions as mentioned above for TMS₃P, except that, due to the increased reactivity of TMS₃P, all glassware had to be surface passivated. Briefly, the oven dried Schlenk line was allowed to cool down under vacuum, and surface silanol groups were passivated by exposure to hexamethyldisilazane (HMDS) in a low-pressure chamber or desiccator. CAUTION: Trimethylsilyl reagents are toxic, very reactive and, in the case of TMS₂S, flammable and pyrophoric. Only well-trained personnel wearing approved personal protective equipment in an inert environment, such as a dry, oxygen-free glove box should handle these reagents. Silylative deoxygenation products were typically dispersed in organic solvents such as hexanes or toluene.

2.3 Structural Characterization

Powder X-ray diffraction (XRD) data were measured using a Rigaku Ultima IV diffractometer with a Cu Kα radiation source (40 kV, 44 mA). Sample percent composition was determined using PowderCell 2.4 (PCW) refined against standard XRD patterns. Nitrogen physisorption was measured on a Micromeritics ASAP 2020 surface area and porosimetry system. Samples were degassed at 100 °C under vacuum overnight prior to the analysis. Surface area was calculated with the Brunauer-Emmett-Teller (BET) method in the relative pressure range of 0.005 to 0.25 of adsorption data. Pore size distribution was calculated with the Barret-Joyner-Halenda (BJH) method. Transmission Electron Microscopy (TEM) was measured on an FEI Tecnai G² F20 field emission scanning transmission electron microscope (S/TEM) at 200 kV (point-to-point resolution <0.25 nm, line-to-line resolution <0.10 nm).

2.4 Spectroscopic Characterization

Solution-phase optical density (absorption + scattering) spectra (UV-Vis) were collected in toluene with a photodiode-array Agilent 8453 UV–Vis spectrophotometer. Solid state NMR data were collected with a Bruker Avance II 600 spectrometer at 119.2 MHz for ²⁹Si equipped with a 4 mm Bruker MAS probe spinning at 10 KHz. ²⁹Si DP-MAS NMR spectra were recorded with a pulse width of 4 µs and a recycling delay of 1 min. ²⁹Si NMR spectra were externally referenced to sioxane (δ = -9.6 ppm), and ²⁹Si isotropic chemical shifts reported against TMS (δ = 0 ppm).

3. Results and Discussion

Silylative deoxygenation of bare nickel oxide. Silylative deoxygenation of cubic, rock salt NiO nanocrystals with TMS₂S in trioctylphosphine (TOP) for 20 h at 130 °C results in a noticeable color change from light gray to black (Scheme 2a). This is consistent with the appearance of a broad light absorption hump in the 400-1000 nm region (Figure 1). Powder X-ray diffraction (XRD) is consistent with formation of Ni₃S₂ (Figure 2), indicating partial reduction of Ni(II) to Ni(I). Transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) show the newly formed Ni₃S₂ nanocrystals possess a distinct hollow morphology, with an overall average particle diameter of 36±7 nm and an average Ni₃S₂ ‘shell’ thickness of 8±2 nm. The latter is close to the average Ni₃S₂ single crystalline domain size of 13±3 nm calculated from XRD peak widths using the Scherrer equation (Table 1). The hollow Ni₃S₂ nanocrystals appear to be coated with an outer, amorphous silica (SiO₂) shell.
(Figure 3c). In fact, TEM of all nanocrystals produced by silylative deoxygenation reveals the presence of a lower contrast outer layer which originates from decomposition of excess trimethylsilyl reagent into amorphous silica (SiO2). This is confirmed by 29Si solid state (ss) NMR measurements. For example, the 29Si ssNMR spectra of Ni3S2/SiO2 and Co3S8/SiO2 (see below) show a broad resonance around -100 ppm, which is consistent with partly merging Q bands (Q2, Q3 and Q4)—see Supporting Information (SI).

**Scheme 2.** Silylative deoxygenations of NiO (unbalanced).

(a) NiO + (TMS)2S \[\Delta / \text{Ar} \] TOP \[\rightarrow\] Ni3S2/SiO2

(b) NiO + (TMS)2Se \[\Delta / \text{Ar} \] TOP \[\rightarrow\] Ni3Se4/SiO2

(c) NiO + (TMS)3P \[\Delta / \text{Ar} \] TOP \[\rightarrow\] Ni2P/SiO2

**Figure 1.** Solution-phase optical density of NiO nanocrystals before and after silylative deoxygenation.

**Figure 2.** Powder XRD patterns of NiO nanocrystals and the product of silylative deoxygenation with TMS2S. Reported XRD patterns for bulk rock salt NiO and heazlewoodite Ni3S2 are shown for comparison.

Silylative deoxygenation of NiO nanocrystals with TMS2Se in TOP for 20 h at 130 °C (Scheme 2b) results in a similar color change and chemical transformation (Figure 1). Powder XRD and TEM data reveal formation of hollow Ni3Se4 particles with total and shell dimensions of 36±7 nm and 7±2 nm, respectively. Thus, unlike the sulfide case, the oxidation state of Ni(II) remains unchanged in the product. As before, an amorphous SiO2 shell is clearly visible, which likely arises from thermal decomposition of excess silyl reagent.

Silylative deoxygenation of NiO nanocrystals with TMS3P in TOP for 250 °C for 17 h (Scheme 2c) results in a color change from light gray to dark gray, as evidenced by the appearance of a broad absorption between 500-900 nm (Figure 1). Importantly, control experiments in the absence of TMS3P unambiguously show that TOP does NOT act as a source of phosphide under the same reaction conditions. When TMS3P is added, powder XRD and TEM analyses confirm formation of ‘solid’ (not void/not hollow) Ni3P nanocrystals, with Scherrer and TEM diameters of 11±1 nm and 12±2 nm, respectively (Figures 4 and 5). Thus, Ni(II) is partially reduced to Ni3P. TEM and HAADF-STEM reveal the Ni3P nanocrystals are embedded inside an amorphous silica (SiO2) matrix. Thus, part of the driving force for silylative deoxygenation comes from formation of very strong Si-O bonds, not only in free TMS2O (Scheme 1), but also in the amorphous SiO2 overlayer coating the resulting particles (Scheme 2).
Figure 4. Powder XRD patterns of NiO nanocrystals and the product of silylative deoxygenation with TMS₂P. Reported XRD patterns for bulk rock salt NiO and Mn₂P-type Ni₃P are shown for comparison.

Figure 5. Representative bright field TEM (a) and HAADF-STEM (b) images of Ni₃P nanocrystals produced by silylative deoxygenation of NiO with TMS₂P.

Understanding hollow vs. solid nanocrystal formation. Formation of vesicle-like chalcogenide nanoparticles is consistent with a Kirkendall-type effect. Reactions at solid–liquid interfaces are affected by relative diffusion rates of the different ions involved. When the diffusion rate of the reacting (‘inner’) material (NiO) is greater than that of the newly produced (‘outer’) material (Ni₃S₂), a net outward mass flow results that is accompanied by an inward void or ‘vacancy’ flow; in the most extreme case, this can lead to shell cracking and fragmentation, leading to small nanoparticles (Scheme 3). During the first two interfacial silylative deoxygenation reactions above, the smaller oxide anion (O²⁻) diffuses out of the nanocrystal and onto its surface much faster than the heavier and larger sulfide anion (S²⁻) diffuses into the new lattice. Further, the highly oxophilic Si center in TMS₂Si is expected to act as an avid oxide sponge at the surface of the original NiO nanoparticles, accelerating the outward mass flow.

Scheme 3. Kirkendall-type hollowing and fragmentation during silylative deoxygenation of metal oxide nanocrystals.

The absence of similar voids in Ni₃P nanocrystals could be discussed in the context of several factors, including relative anion charge, size, polarizability, metal–element bond strength, specific lattice entropy, or reaction temperature. It is well known that diffusion of ions in solids increases as ionic size, charge and metal-element bond strength decrease. Thus, formation of voids in hollow nickel sulfides and selenides can be explained on the basis of the expected relative diffusion rates: O²⁻ > S²⁻ > Se²⁻. However, the absence of voids in nickel phosphide is counterintuitive based on the expected relative diffusion rates: O²⁻ > S²⁻ > P³⁻ (this would imply the nickel phosphide particles should have the most pronounced voids, which is not observed). Stronger nickel-phosphide bonds, or higher reaction temperature required for silylative deoxygenation, or both may explain the lack of voids in Ni₃P. In particular, the higher reaction temperatures could minimize or cancel out any differential diffusion rates of both outward-bound O²⁻ ions and inward-bound P³⁻ across the solid-liquid interface. Additionally, a higher reaction temperature could also cause any initially formed (and otherwise observable) void to collapse due to melting and coalescence of nanosized particles.

Silylative deoxygenation of bare cobalt oxides. Silylative deoxygenation of deep black Co₃O₄ nanocrystals with TMS₂S in TOP for 25 h at 130 °C (Scheme 3a) occurs without a significant color change. Powder XRD and TEM data show formation of a mixture of CoO and Co₉S₈, hollow nanocrystals (see SI). Thus, this reaction is accompanied by partial reduction of Co(III) to Co(II). Similarly, silylative deoxygenation of Co₃O₄ nanocrystals with TMS₂Se in TOP for 20 h at 130 °C (Scheme 3c) did not result in a significant color change. Powder XRD and TEM show formation of a mixture of CoO and Co₃Se₄, hollow nanocrystals (see SI). In contrast, silylative deoxygenation of CoO nanocrystals with TMS₂S in TOP for 20 h at 130 °C (Scheme 3b) results in a color change from brown to black, as evidenced by loss of the two 600 nm and 700 nm peaks in the solution-phase absorption spectrum (Figure 6a). Powder XRD and TEM show formation of hollow Co₉S₈ nanocrystals with an overall average particle diameter of 20±3 nm and an average Co₉S₈ shell thickness of 8±2 nm (Figures 7 and 8). The latter is close to the average Co₉S₈ single crystalline domain size of 6±1 nm calculated from XRD peak widths using the Scherrer equation (Table 1).

Scheme 4. Silylative deoxygenations of Co₃O₄ (unbalanced).

(a) Co₃O₄ + (TMS₂)S $\xrightarrow{\text{A/Ar TOP}}$ CoO/Co₉S₈/SiO₂
(b) CoO + (TMS₂)S $\xrightarrow{\text{A/Ar TOP}}$ Co₉S₈/SiO₂
(c) Co₃O₄ + (TMS₂)Se $\xrightarrow{\text{A/Ar TOP}}$ CoO/Co₉Se₄/SiO₂
(d) Co₃O₄ + (TMS₂)P $\xrightarrow{\text{A/Ar TOP}}$ CoP/SiO₂
Silylative deoxygenation of mixed-metal oxides. Having established the wide generality of silylative deoxygenation reactions from simple and readily available metal oxide precursors, we probed whether they could be applied to mixed-metal oxides. In particular, we questioned whether silylative deoxygenation could proceed at comparable rates for different metal ions, or if instead it would lead to phase segregation. To test this idea, we performed the silylative deoxygenation of NiCo2O4 nanocrystals with TMS2S in TOP for 16 h at 130 °C (Scheme 4a). This resulted in a color change from dark gray to black, as evidenced by the loss of 500 nm and 800 nm peaks in the solution-phase absorption spectrum (Figure 6b). Powder XRD, TEM and HAADF-STEM confirm the formation of hollow (Kirkendall-type) nanocrystals with general composition (Ni/Co)9S8 (Figure 10 and SI). To gain a deeper insight into this reaction, we performed energy dispersive X-ray spectroscopy (EDS) mapping, which reveals Co (K- and L-edge), Ni (K- and L-edge) and S (K-edge) are distributed homogeneously across particles (Figure 11). EDS elemental analysis of different areas containing several nanocrystals showed Co to Ni ratios between 8 and 5, which agrees with two well-known mixed-metal sulfide phases: NiCo8S8 and Ni3Co6S8 (Table 1). These results demonstrate that silylative deoxygenation of more complex, mixed-metal oxides can also occur without significant phase segregation.

Scheme 5. Silylative deoxygenations of mixed-metal and silica-coated metal oxides (unbalanced).

(a) \( \text{NiCo}_2\text{O}_4 + (\text{TMS})_2\text{S} \xrightarrow{\Delta/\text{Ar}} \text{TOP} \rightarrow \text{(Ni,Co)}_9\text{S}_8/\text{SiO}_2 \)

(b) \( \text{NiCo}_2\text{O}_4/\text{porous-SiO}_2 + (\text{TMS})_2\text{S} \xrightarrow{\Delta/\text{Ar}} \text{TOP} \rightarrow \text{Ni}_8\text{Co}_2\text{S}_8/\text{SiO}_2 \)

(c) \( \text{Co}_3\text{O}_4/\text{porous-SiO}_2 + (\text{TMS})_2\text{S} \xrightarrow{\Delta/\text{Ar}} \text{TOP} \rightarrow \text{Co}_2\text{O}_2\text{S}_2/\text{SiO}_2 \)
Figure 10. Powder XRD patterns of NiCo₂O₄ nanocrystals before and after silylative deoxygenation with TMS₂S. Reported patterns for several relevant oxides and sulfides are shown for comparison.

Figure 11. Registered HAADF-STEM/EDS images of the product of silylative deoxygenation of NiCo₂O₄ with TMS₂S. Scale bar = 50 nm.

Silylative deoxygenation of silica-coated metal oxides. Finally, we tested the feasibility of performing silylative deoxygenation of nanocrystalline metal oxides that are already contained in a protective silica matrix. NiO nanocrystals embedded in one-dimensional ‘solid’—non-porous—silica capsules (NiO⊂SiO₂) react with TMS₂S in TOP for 70 h at 130 °C (Scheme 4b) to give a mixture of Ni₃S₂/Ni₉S₈⊂SiO₂ (see SI). It is not surprising then, that silylative deoxygenation of embedded in porous silica shells (Co₃O₄/porous-SiO₂ core/shells) react with TMS₂S under similar conditions to give a mixture of Co₉S₈/SiO₂ (Figure 6b and SI). Thus, silylative deoxygenation of metal oxides generally produces—and proceeds through—high surface-area, silica coated nanomaterials, which could enable their use and recycling in catalytic and other technologically-relevant applications.¹⁰⁻²⁷

Conclusions

In summary, we have successfully demonstrated the versatility of utilizing trimethylsilyl reagents (TMSₓE) to transform preformed, nanocrystalline metal oxides (NiO, CoO, Co₃O₄, and NiCo₂O₄) into nanocrystalline metal chalcogenides and pnictides. Nanocrystalline phases produced via this silylative deoxygenation reaction include Co₅Se₈, Co₃Se₄, CoP, Co₅P, Ni₅S₂, Ni₃S₈, and Ni₃P. Nanocrystalline chalcogenide (sulfides, selenides) resulting from silylative deoxygenation possess hollow, vesicle like morphologies, whereas the nanocrystalline pnictides (phosphides) do not. Hollow morphologies can be explained on the basis of a nanoscale Kirkendall-type effect, arising from differential ion diffusion rates between ions in the reactant and product phases.

The silylative deoxygenation route presented here nicely complements other published methods that are available for the synthesis of metal chalcogenide and pnictide nanocrystals. All nanocrystalline chalcogenides and pnictides produced by silylative deoxygenation are surrounded by an outer amorphous silica layer, which could help in preventing agglomeration and degradation. Introduction of porosity within these shells may be accomplished by adding a surfactant during the silylative deoxygenation process. Successful silylative deoxygenation of the ternary, mixed-metal oxide NiCo₂O₄ with TMS₂S demonstrates that silylative deoxygenation can be performed from more complex precursors without significant phase segregation. This could enable the preparation of ternary systems, such as II-IV-VI semiconductors (e.g., CaTiS₃, BaZrS₃, CaZrSe₃) from well-known metal oxides, and for which traditional routes remain underdeveloped. Similarly, successful silylative deoxygenation of silica-encapsulated metal oxides bears potential in particle recycling and regeneration.

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References

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<td>NiO/Co&lt;sub&gt;3&lt;/sub&gt;SiO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>TMS&lt;sub&gt;2&lt;/sub&gt;S/130 °C/70 h/Ar</td>
<td>NiO (n.d.)&lt;sup&gt;d&lt;/sup&gt; + Ni&lt;sub&gt;3&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt; (n.d.)&lt;sup&gt;d&lt;/sup&gt; + Ni&lt;sub&gt;9&lt;/sub&gt;S&lt;sub&gt;4&lt;/sub&gt; (n.d.)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>n.d.&lt;sup&gt;g&lt;/sup&gt;</td>
<td>n.d.&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
<tr>
<td>11</td>
<td>Co&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;/SiO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>TMS&lt;sub&gt;2&lt;/sub&gt;S/130 °C/70 h/Ar</td>
<td>CoO (30%)&lt;sup&gt;j&lt;/sup&gt; + hollow Co&lt;sub&gt;3&lt;/sub&gt;S&lt;sub&gt;8&lt;/sub&gt; (70%)&lt;sup&gt;j&lt;/sup&gt;</td>
<td>CoO: 10±1 nm Co&lt;sub&gt;3&lt;/sub&gt;S&lt;sub&gt;8&lt;/sub&gt;: 5.7±0.3 nm</td>
<td>n.d.&lt;sup&gt;g&lt;/sup&gt;</td>
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<sup>a</sup>14.1±0.4 nm. <sup>b</sup>13±2 nm. <sup>c</sup>17±4 nm. <sup>d</sup>See Experimental for full details. <sup>e</sup>Co/P ratio determined by dividing three times the chemical amount of Co<sub>3</sub>O<sub>4</sub> over that of TMS<sub>2</sub>P (both in moles). <sup>f</sup>Determined by Powder Cell for Windows (PCW). <sup>g</sup>n.d. = Not determined. <sup>h</sup>Measures single crystalline domain size. <sup>i</sup>Outer diameter (total size). <sup>j</sup>Shell thickness (if hollow).
Transition metal chalcogenides and pnictides are interesting inorganic materials for optoelectronic and catalytic applications. We present a generalized synthesis route to transform preformed metal oxide nanocrystals into sulfides, selenides, or phosphide nanocrystals via silylative deoxygenation with highly reactive trimethylsilyl reagents. In all of the reactions studied, simultaneous decomposition of excess silyl reagent produces a protective, amorphous silica coating around the newly formed chalcogenide and pnictide nanocrystals.

TOC Synopsis:
Transition metal chalcogenides and pnictides are interesting inorganic materials for optoelectronic and catalytic applications. We present a generalized synthesis route to transform preformed metal oxide nanocrystals into sulfides, selenides, or phosphide nanocrystals via silylative deoxygenation with highly reactive trimethylsilyl reagents. In all of the reactions studied, simultaneous decomposition of excess silyl reagent produces a protective, amorphous silica coating around the newly formed chalcogenide and pnictide nanocrystals.