

## Converting Metals into Phosphides: A General Strategy for the Synthesis of Metal Phosphide Nanocrystals

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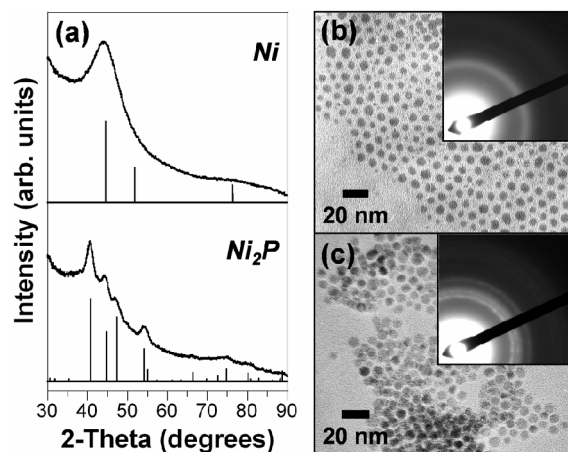
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Nanocrystalline transition metal phosphides are attractive candidates for advanced catalytic, electronic, and magnetic applications.<sup>1</sup> Furthermore, recent studies of their size-dependent physical properties have uncovered notable differences between bulk and nanoscale materials.<sup>1,2</sup> Thus, it is important to develop general synthetic approaches that yield nanocrystalline transition metal phosphides with careful control over both the composition and the morphology. A variety of methods have emerged for the synthesis of these materials, including solvothermal reactions,<sup>3</sup> decomposition of single-source precursors,<sup>4</sup> high temperature annealing of organometallic and solid-state precursors,<sup>5</sup> and the co-reaction of organometallic reagents with phosphines.<sup>2,6–8</sup> In particular, Brock,<sup>2,6</sup> Hyeon,<sup>8</sup> and Yang and Liu<sup>9</sup> have shown that high-quality 3d transition metal phosphide nanocrystals and nanowires can be obtained by thermal decomposition of metal–phosphine complexes that form in situ from the reaction of metal salts and trioctylphosphine (TOP), a common stabilizing agent.

Here we describe a new strategy for synthesizing nanostructures of transition metal phosphides. Unlike the previous methods that involve either direct combination of precursors or thermal decomposition of single-source precursors, our approach involves a different mechanism: the conversion of preformed metal nanoparticles into metal phosphides by solution-mediated reaction with TOP. By starting with metal nanoparticles as precursors, a large number of metal phosphide systems are accessible, including those with 4d and 5d transition metals that have not previously been reported as unsupported nanocrystals. Furthermore, nanostructures such as hollow spheres, which are not typically accessible using thermal decomposition reactions, can be easily made using a Kirkendall-type mechanism, which utilizes metal nanoparticles as reactive templates.

In a typical reaction, a metal acac salt dissolved in TOP is injected into a hot solvent (TOP, trioctylphosphine oxide, or octyl ether) at 300–360 °C. By collecting aliquots over time, we discovered that, unlike the previously reported pathways that involve the direct thermal decomposition of complexes formed between the metal acac salts and TOP, the formation of metal phosphide nanoparticles instead goes through a metal nanoparticle intermediate. (There are some key differences between our synthetic protocol and those used to form metal–TOP complexes; see details below and in Supporting Information.) For example, Ni<sub>2</sub>P nanocrystals can be synthesized by injecting a Ni(acac)<sub>2</sub>–TOP solution [27.5 mg Ni(acac)<sub>2</sub> in 1.0 mL TOP] into 2.00 mL of octyl ether at 290 °C and aging the solution at 300 °C for 2 h. When aliquots are taken close to 1 min after injection of the Ni(acac)<sub>2</sub>–TOP solution, Ni nanoparticles are observed via X-ray diffraction (XRD), transmission electron microscopy (TEM), and selected area electron diffraction (SAED). Building on this important observation, Ni nanoparticles can be made separately according to literature methods,<sup>10</sup> then isolated, washed, and re-dispersed in hot octyl ether with TOP to form Ni<sub>2</sub>P nanoparticles via a conversion mechanism.

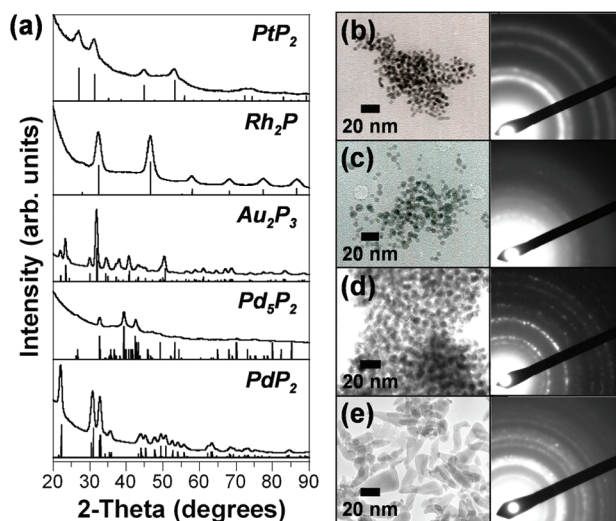


**Figure 1.** (a) Powder XRD data for Ni nanoparticles and Ni<sub>2</sub>P formed after their reaction with TOP; TEM/SAED data for (b) Ni nanoparticles and (c) Ni<sub>2</sub>P formed by reacting the particles in (b) with TOP.

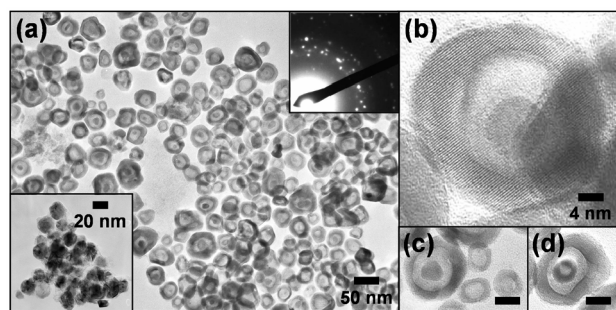
The Ni nanoparticles used as precursors (Figure 1a,b) are  $5.2 \pm 0.8$  nm, and the Ni<sub>2</sub>P nanoparticle products (Figure 1a,c) are  $5.6 \pm 0.8$  nm. The small but reproducible increase in average nanocrystal size (Figure S1) is roughly consistent with the volume expansion expected for the conversion of fcc Ni to Fe<sub>2</sub>P-type Ni<sub>2</sub>P via addition of phosphorus. This indicates that the relative size and dispersity of the metal nanoparticle precursors are maintained during the chemical conversion into metal phosphides.

In addition to Ni<sub>2</sub>P, other phosphides including PtP<sub>2</sub>, Rh<sub>2</sub>P, Au<sub>2</sub>P<sub>3</sub>, Pd<sub>5</sub>P<sub>2</sub>, and PdP<sub>2</sub> can be formed by analogous TOP-mediated conversion of the corresponding metal nanoparticles. Representative XRD, TEM, and SAED data are shown in Figure 2, along with TEM and SAED data for the Pt nanoparticles that are used as precursors for the formation of PtP<sub>2</sub>. Data for other metal nanoparticle precursors are shown in Figure S2. The Pd–P system is particularly noteworthy since it demonstrates that multiple phases can be accessed in the same system (Pd<sub>5</sub>P<sub>2</sub> and PdP<sub>2</sub>) simply by changing the reaction temperature and, thus, the amount of phosphorus incorporation. In addition, the formation of PdP<sub>2</sub>, as well as PtP<sub>2</sub> and Au<sub>2</sub>P<sub>3</sub>, is particularly interesting since these phases belong to a class of compounds called “polyphosphides”, which are phosphorus-rich phases that have P–P bonds. Polyphosphides can be difficult to synthesize as bulk-scale solids,<sup>11</sup> and they also have not been observed as products of low-temperature solution reactions. Thus, this nanoparticle conversion strategy provides a unified method for synthesizing a variety of 3d, 4d, and 5d transition metal phosphide nanoparticles, many of which have not been previously accessed by direct reaction of organometallic precursors with TOP.

By using metal nanoparticles as precursors, it is also possible to generate metal phosphide nanostructures that cannot easily form using other methods. Alivisatos and co-workers showed that Co



**Figure 2.** (a) Powder XRD data showing several transition metal phosphides that are accessible by reacting appropriate preformed metal nanoparticles with TOP; TEM and SAED images of (b) Pt nanoparticles, (c)  $\text{PtP}_2$  formed from (b), (d)  $\text{Rh}_2\text{P}$ , and (e)  $\text{PdP}_2$ .



**Figure 3.** (a) TEM images and SAED pattern of hollow  $\text{Ni}_2\text{P}$  spheres formed by reaction of 15–25 nm Ni nanoparticles (lower left inset) with TOP; (b–d) high-resolution TEM images showing hollow  $\text{Ni}_2\text{P}$  containing a floating core. Lattice fringes in (b) suggest that the hollow  $\text{Ni}_2\text{P}$  shells are single crystalline. Both dense (c) and hollow (d) cores are observed. The scale bars in (c) and (d) are 20 nm.

nanocrystals react with sulfur to form hollow  $\text{Co}_3\text{S}_4$  and  $\text{Co}_9\text{S}_8$  nanospheres via a nanoscale Kirkendall mechanism, which is facilitated by the different diffusion rates of two different chemical species.<sup>12</sup> In analogy, when we react 10–25 nm Ni nanocrystals (Figure 3a, inset) with TOP in octyl ether at 300 °C, hollow single-crystal  $\text{Ni}_2\text{P}$  nanospheres form (Figure 3a,b). TOP acts as a phosphorus source, which appears to diffuse into the Ni at a slower rate than the Ni diffuses out, forming hollow voids in the center. For the smaller nanocrystals (10–20 nm), the dominant products are completely hollow nanospheres (Figure 3c). However, for the larger nanospheres, material remains in the center of the hollow spheres (Figure 3b–d), in the form of either dense (Figure 3b,c) or hollow (Figure 3d) nanocrystals. It is difficult to discern at this point whether the encapsulated nanoparticles are Ni or  $\text{Ni}_2\text{P}$ . Further detailed studies, both synthesis and characterization, are in progress. Interestingly, this work hints at a size dependence to the formation of hollow nanocrystals since the smaller 5 nm Ni nanocrystals in Figure 1b produced dense  $\text{Ni}_2\text{P}$  nanospheres despite reactions that are carried out under identical conditions. A recent paper by Chiang (published after our work was submitted) also describes hollow

$\text{Ni}_2\text{P}$  nanospheres formed by reacting Ni nanoparticles with TOP,<sup>13</sup> although no sphere-in-sphere structures were reported.

In summary, through careful mechanistic studies, we have demonstrated that a variety of 3d, 4d, and 5d transition metal phosphide nanocrystals, including  $\text{Ni}_2\text{P}$ ,  $\text{PtP}_2$ ,  $\text{Rh}_2\text{P}$ ,  $\text{Au}_2\text{P}_3$ ,  $\text{Pd}_3\text{P}_2$ , and  $\text{PdP}_2$ , can be accessed by the solution-mediated reaction of preformed metal nanoparticles with TOP. In addition to its utility for accessing a wide range of transition metal phosphides using a highly robust and unified approach, various aspects of nanostructure (e.g., size, size dispersity, and hollow sphere formation) can be influenced by controlling critical aspects of the metal nanoparticle precursors. This is particularly important because robust methods exist for controlling the size and shape of single-metal nanoparticles,<sup>14</sup> and these can now serve as reactive templates for the formation of metal phosphides. Future work will focus on further generalizing this synthetic strategy, rigorously establishing the size dependence of reactivity with TOP, and exploring size- and shape-dependent properties.

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**Supporting Information Available:** Experimental details, additional XRD, TEM, and SAED data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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