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Low-Temperature Solvothermal Synthesis of Phosphorus-Rich Transition-Metal Phosphides

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Transition-metal phosphides (MP_x) are well-known for their capability to form a wide variety of binary phases with compositions from metal-rich to phosphorus-rich (e.g., Cu_3P to MnP_4).[1] The differences in composition lead to a broad range of structural, electronic, magnetic, catalytic, and optical properties.[1,2] Phosphorus-rich MP_x phases have shown promise as reversible lithium-ion battery electrodes (mainly monoclinic NiP_2),[3] as thermoelectric materials (skutterudite CoP_3),[4] and as optical absorbers in photovoltaic cells (CuP_2 with 1.5 eV band gap).[5a] Most synthetic routes to phosphorus-rich metal phosphides involve the direct reaction of elements at high temperatures (~1000 °C); however, tin fluxes and chemical vapor transport methods can lower reaction temperatures to ~600 – 800 °C in special cases.[6] Phosphorus-rich MP_x phases have also been produced by high-energy ball-milling.[7b,8] For these materials to be widely useful, it is crucial to produce them in a variety of forms, for example, as thin films or dispersed nanoparticles. Phosphorus-rich phosphide synthesis is difficult since multiple binary phases with lower phosphorus content are often produced even when sufficient phosphorus is available for phosphorus-rich phases to form.[6a,8,9a] In this communication, we detail the facile, low-temperature, solvothermal synthesis of micro- and nanoparticles of three phosphorus-rich transition-metal phosphides (CoP_3, NiP_2, and CuP_2) using elemental molecular phosphorus (P_4).

While few synthetic routes to phosphorus-rich MP_x materials are known, a variety of syntheses to stoichiometric MP or metal-rich MP_x phases ($x < 1$) have been reported. Generally, transition-metal and main group metal phosphide syntheses include high-temperature reactions from the elements,[6,10] chemical vapor deposition,[5] solid-state and solvothermal metathesis reactions,[10] and other low-temperature solvothermal routes.[9,12] These and related routes frequently produce metal-rich MP_x as single crystals, microcrystalline powders, nanoparticulates, or thin films.[5–12]

Solvothermal reactions using elemental phosphorus have been reported to produce metal-rich MP_x nanoparticles at relatively low temperatures.[13,14] In one instance, a metal halide hydrate reacted with yellow P_4 in either ethylenediamine or dilute aqueous ammonia at 80–140 °C produced Co_2P, Ni_2P and Cu_3P.[13] Another reaction between anhydrous $CuCl_2$ and red phosphorus, which is more stable than white/yellow phosphorus, in superheated H_2O at 200 °C produced Cu_3P.[14] These syntheses generally used a high excess of phosphorus (~300%) to achieve complete reactions. Since the reaction environments were often not strictly anhydrous, it is likely that some phosphorus was lost to side reactions with water. This may be one reason why phosphorus-rich phases were not produced from aqueous solvothermal reactions using elemental phosphorus.

There are recent reports of anhydrous solvothermal reactions using trioctylphosphine or trimethylsilylphosphine as a phosphorus reagent that produce metal phosphides such as MnP and FeP.[12] Trialkylphosphine solvothermal reactions with reactive nanoparticulate or micrometer-sized metal particles below 360 °C produce a wide range of metal-rich

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Table 1. Data for Solvothermal Phosphorus-Rich MP_x Synthesis

target phase	MCl_2:P_4[a]	yield[a]	TGA loss[b]	MP_x analysis (M:P:Cl)[c]	annealed XRD (xtal size)[d]
CoP_3	1:0.93	82%	9.4%	1:2.97:0.04 (1:2.58:0.02)	cubic CoP_3 (99 nm)
NiP_2	1:0.67	85%	6.4%	1:2.45:0.15(1:2.13:0.06)	cubic NiP_2 (46 nm)
CuP_2	1:0.67	84%	8.6%	1:2.00:0.39 (1:1.86:0.01)	monoc. CuP_2 (102 nm)

[a] Molar ratio of reagents, yield based on MCl_2 used. [b] Weight loss during heating in argon from 25 °C to crystallization temp (350–500 °C). [c] Atomic ratios from EDS data for as-synthesized (annealed) products. [d] Calculated from XRD peak widths.

phosphides and selected phosphorus-rich MP_x phases (e.g., PdP_2 or PtP_2 and CuP_2/Cu_3P mixtures).[9]

Using carefully anhydrous solvothermal reaction conditions, we have synthesized several phosphorus-rich transition-metal phosphides (CoP_3, NiP_2, and CuP_2). The reaction of anhydrous, vacuum-dried divalent metal chlorides ($CoCl_2$, $NiCl_2$, and $CuCl_2$) with yellow molecular P_4 in rigorously dry superheated toluene was performed stoichiometrically as shown in eq 1. The proposed byproduct in this single exchange redox reaction is phosphorus trichloride.

$$3MCl_2 + [(3y + 2)/4]P_4 \rightarrow 3MP_y + 2PCl_3 \qquad (1)$$

In a typical experiment, the metal chloride and P_4 were combined under inert conditions with toluene in a stainless steel Parr reactor (see Supporting Information for experimental details). Reactions were first heated to 130 °C to ensure P_4 (mp 44 °C, bp 280 °C) reacted with the metal halide and did not transport out of solution (in toluene this occurs at ~140 °C) and then were heated to 275 °C and held for two days before being cooled to room temperature. All of the products recovered from these solvothermal reactions were fine black powders produced in good chemical yields based on the amount of metal halide used (Table 1).

The X-ray diffraction (XRD) patterns of the isolated CoP_3 and CuP_2 products were amorphous, but contained broad regions of diffraction intensity consistent with crystalline CoP_3 and CuP_2 peak positions. In contrast, the NiP_2 product's XRD pattern showed evidence of some poorly crystalline metal-rich Ni_2P along with broad peaks indicative of NiP_2 (see Supporting Information, Figure S1). Energy dispersive spectroscopy (EDS) analysis shows that the overall M:P ratios in the as-synthesized products are consistent with those targeted in the syntheses (MP_2 or MP_3) with varying degrees of chlorine residue (Table 1). All products were annealed in evacuated Pyrex ampoules for 15 h to improve crystallinity. For the NiP_2 and CuP_2 reactions, annealing at 350 °C (75 °C above synthesis temperature) was adequate to crystallize MP_2 phases, while the CoP_3 required a minimum temperature of 500 °C and showed greatly improved crystallinity after 600 °C annealing. The XRD patterns for the crystalline products along with calculated patterns based on their known structures are shown in Figure 1.[2a,15]

EDS analysis of annealed CoP_3 and CuP_2 shows that they are slightly phosphorus deficient while NiP_2 is slightly phosphorus rich, but all three have phosphorus contents within ~15% of their ideal values (Table 1), which is within EDS relative percent sampling error for particulate samples, and chlorine has dropped near detection limits (<2 wt %). While the as-synthesized NiP_2 product showed some initial crystallization of Ni_2P, there was sufficient phosphorus content in the bulk product to yield NiP_2 upon annealing. Solid-state spectroscopic investigations are in progress to determine the phosphorus chemical environment and microscopic metal distribution in the as-synthesized Ni−P materials. Thermogravimetric analysis (TGA) under flowing argon shows that most weight loss from as-synthesized phosphide products occurs near the crystallization temperatures, likely due to loss of surface bound organophosphorus halide (R_xPCl_y) species, consistent with lower P and Cl content after annealing (Table 1). Preliminary solid-state mass spectrometry analyses (EI-MS, heating to ~500 °C) on as-synthesized M-P products show HCl and P_n ($n \leq 4$) fragment evolution from all samples, in addition to PCl_3 and tolyl (C_7H_7) evolution from Co and Ni samples and metal halide clusters from Cu samples.

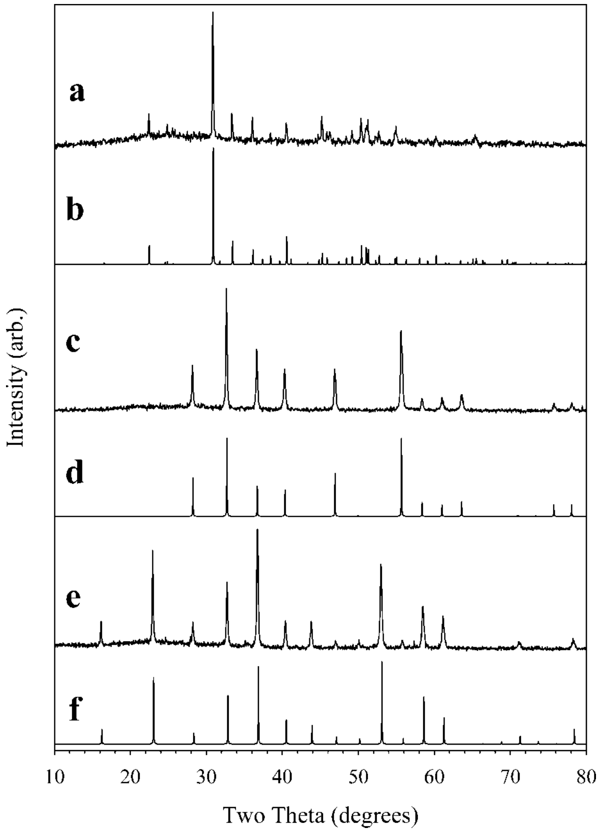

Figure 1. XRD patterns for (a) CuP_2 after 350 °C annealing, (b) calculated pattern for monoclinic CuP_2, (c) NiP_2 after 350 °C annealing, (d) calculated pattern for cubic NiP_2, (e) CoP_3 after 600 °C annealing, and (f) calculated pattern of cubic CoP_3.

Metal chlorides are typically hygroscopic but can be purchased as anhydrous reagents. We found that the as-purchased "anhydrous" metal halide reagents still contain surface water that is likely adsorbed during packaging and shipping. For the above MP_2 and MP_3 reactions to be

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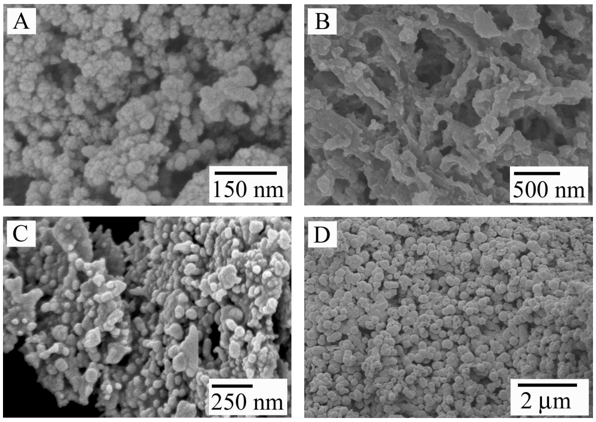

Figure 2. SEM images for (A) as-synthesized CuP_2, (B) CuP_2 annealed at 350 °C, (C) NiP_2 annealed at 350 °C, and (D) CoP_3 annealed at 500 °C.

successful using stoichiometric amounts of reactive yellow phosphorus, it was critical to vacuum-dry the as-purchased “anhydrous” metal chlorides. For example, the stoichiometric NiP_2 reaction using as-received anhydrous $NiCl_2$ produced solely metal-rich Ni_2P after annealing with a poor 15% yield. After the $NiCl_2$ was vaccuum-dried at 250 °C, the same solvothermal reaction produced NiP_2 after annealing with an 85% yield.

All three phosphorus-rich MP_x phases are part of a class of compounds called polyphosphides because they contain P_n^{x-} anion species with P−P bonds. Cubic skutterudite CoP_3 contains nearly square-planar P_4^{4-} rings, the cubic, pyrite-type NiP_2 contains P_2^{4-} “dumbbells”, and monoclinic CuP_2 contains fused P_{10}^{5-} rings that form infinite corrugated sheets.[1c,2a] The polyphosphide anions lead to diamagnetism in CoP_3 (Co^{3+}, d^6 low spin) and CuP_2 (Cu^+, d^{10}) and to Pauli paramagnetism in NiP_2 (Ni^{4+}, d^6 low spin).[6a,16]

Scanning electron microscopy (SEM) analysis revealed that the as-synthesized amorphous phosphides are aggregated spherical particles with a variety of sizes, with the largest being CoP_3 (∼150–250 nm), as compared to NiP_2 (∼50–100 nm) and CuP_2 (∼20–60 nm, shown in Figure 2A). After annealing, the CuP_2 nanoparticles form into a fused structure at 350 °C with ∼100–300 nm features (Figure 2B) that eventually grow into large micrometer sized plates by 500 °C (see Supporting Information, Figure S2). In contrast, the particles of NiP_2 (∼50–100 nm, Figure 2C) and CoP_3 (∼200–350 nm, Figure 2D) generally retain their shape, with some fused characteristics.

Our current working reaction model is that dissolved molecular P_4 attacks the metal halide that is either a solid microparticle or partially dissolved at elevated temperatures. This reaction may result in insertion of the P_4 into an M−Cl bond, forming a cluster intermediate, as was observed in trialkyl gallium reactions with white phosphorus.[17] The proposed reaction shown in eq 1 involves the eventual formation of toluene-soluble PCl_3 byproduct (mp = −94 °C, bp = 76 °C). Solution ^{31}P NMR analysis of the toluene supernatant after MP_x reactions showed the presence of several phosphorus-containing species, in addition to unreacted molecular P_4 at −520 ppm in all reaction filtrates. Surprisingly, PCl_3 (220 ppm) was a minor product, at best, and major peaks appeared near 175–180 ppm independent of the metal used. These peaks near 180 ppm are consistent with trivalent phosphorus species, such as $RPCl_2$ (e.g., $PhPCl_2$ at 166 ppm).[18] The CuP_2 product also showed minor peaks near 40 ppm that are near oxidized $RP(O)Cl_2$ chemical shifts (e.g., tolyl-$P(O)Cl_2$ at 35 ppm).[18b] The highly oxidized PCl_5 species (−80 ppm) was not detected in any reaction solution. The reactivity of PCl_3 with superheated toluene at 275 °C was examined to see if the harsh solvothermal MP_x reaction environment facilitates P−arene bond formation with HCl release. The ^{31}P NMR results from this experiment revealed PCl_3 as a minor component along with several peaks near 35 and 180 ppm. The pH of the solution was also acidic, which supports the formation of $RPCl_2$ or polymeric $R_zP_xCl_y$ species during the solvothermal synthesis. Additional experiments are underway to investigate the synthetic mechanisms and nature of intermediates associated with this stoichiometric solvothermal synthesis of phosphorus-rich metal phosphides.

Preliminary experiments with different reagent stoichiometries and solvent conditions suggest that these phosphorus-rich MP_x syntheses may be tailored to produce products with a wider variety of metal to phosphorus ratios. This work will be reported in a future publication. The effects of solvent and temperature on MP_x phase formation are unclear; however, the current study shows that rigorously dry anhydrous metal halide reagents and reactive molecular white/yellow phosphorus lead to controlled phosphorus-rich metal phosphide formation. Low-temperature annealing results in facile crystallization of phosphorus-rich MP_x products. This is the first report of the stoichiometric, high-yield, solvothermal synthetic formation of phosphorus-rich CoP_3, NiP_2, and CuP_2 nano/submicrometer sized particles.

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Note Added after ASAP Publication. There was an error in the second column heading of Table 1 in the version published ASAP March 25, 2008; the corrected version was published ASAP April 15, 2008.

Supporting Information Available: Experimental details, EDS data, XRD of Ni−P product, and SEM images of CuP_2 annealed to 500 °C (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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