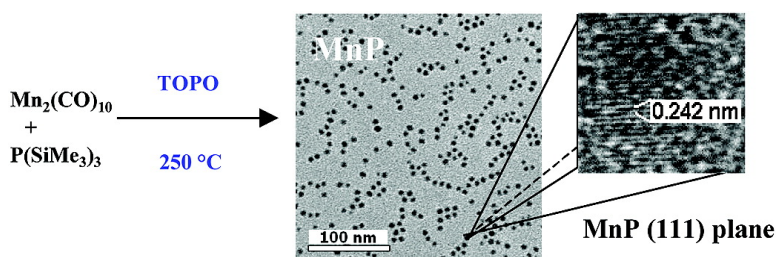## Communication

Synthesis of MnP Nanocrystals by Treatment of Metal Carbonyl Complexes with Phosphines: A New, Versatile Route to Nanoscale Transition Metal Phosphides

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Synthesis of MnP Nanocrystals by Treatment of Metal Carbonyl Complexes with Phosphines: A New, Versatile Route to Nanoscale Transition Metal Phosphides

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The successful implementation of nanotechnology in advanced devices is predicated on the ability to control structure, size, and composition on the nanoscale, and on a detailed understanding of how properties develop as material size and surface characteristics are adjusted. On the basis of this paradigm, ultraviolet nanolasers have been produced,[1] integrated FET arrays have been assembled from nanowires and demonstrated to perform logic functions,[2] and gold nanoparticle sensors have been developed for DNA and RNA detection.[3] However, to date, the types of materials investigated have been limited, with the majority of published work focused on metals or metallic alloys, main group pnictides (pnicogen = group 15 element) and chalcogenides (the III−V and II−VI semiconductors), and oxides (magnetic ferrites and binary semiconductors). As a class of compounds, the transition metal pnictides embrace a wide range of electronic, magnetic, and optical properties and remain an unexplored frontier on the nanotechnology landscape.[4] One area of particular interest is the possible role of manganese pnictide clusters in the reported ferromagnetism of some "spintronic" materials. Spintronic materials demonstrate spin-dependent electronic properties and can be formed by the homogeneous doping of transition metals (typically manganese) into III−V semiconductors.[5] However, phase segregation by manganese pnictide cluster formation is a notorious problem in these systems and, in some cases, is the likely source of the observed magnetic effects rather than the doped semiconductor phase.[6] Nevertheless, there has been no independent investigation of the effect of particle size on the properties of manganese pnictides.

Previous reports of transition metal pnictide nanoparticle syntheses are scarce.[7] Our earlier studies, focused on the phosphides, have demonstrated the successful synthesis of FeP nanoparticles by desilylation chemistry reactions between Fe(III) salts and tris-(trimethylsilyl)phosphine[8] as well as from the reduction of $FePO_4$ nanoparticulate precursors on surfaces.[9] Both of these methods, while potentially general, proved unsuccessful for the production of the related manganese phosphide phase.

Here, we report a new synthetic strategy for the rapid production of low polydispersity, highly crystalline transition metal phosphide nanoparticles; the specific application of this methodology for preparation (for the first time) of discrete MnP nanoparticles; and the magnetic characteristics of these particles as a function of size. This route involves the reaction of zerovalent transition metal carbonyl complexes with phosphines in coordinating solvents at moderate temperatures and appears to be general for a number of transition metals (demonstrated here for manganese, iron, and cobalt).

The treatment of $Mn_2(CO)_{10}$ with $P(SiMe_3)_3$ in trioctylphosphine oxide (TOPO)/myristic acid at elevated temperatures produced MnP as discrete nanoparticles (Figure 1A).[10] The broad reflections in
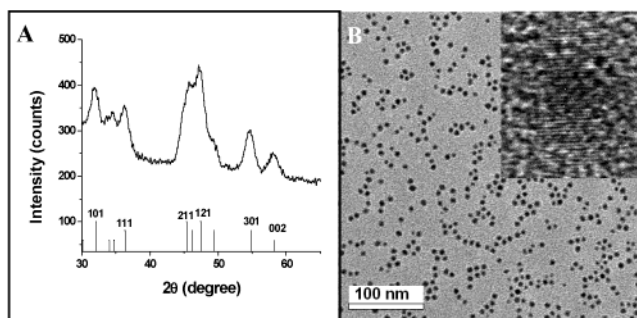

Figure 1. (A) The XRD pattern for MnP nanoparticles produced at 250 °C and matching orthorhombic MnP line diagram (JCDPS # 07-0384). (B) A corresponding TEM micrograph showing 6.7(3) nm MnP nanoparticles. Lattice fringes (inset) observed in a single particle are spaced at 0.242 nm and correspond to the (111) plane of MnP.

the X-ray powder diffraction pattern (XRD) are consistent with orthorhombic MnP and could not be successfully indexed on other manganese phosphide phases or likely byproducts (manganese metal, manganese oxide, etc.). Transmission electron microscopy clearly shows the formation of spherical particles with narrow polydispersity (less than 10% standard deviation, Figure 1B). These samples are achieved in a single precipitation step and in high yield (92%).[11] The size of the nanoparticles[12] can be adjusted to some extent by the temperature and time scale of the reaction. For example, MnP produced at 220 °C for 24 h had a size of 5.11 ± 0.48 nm, whereas a heating profile of 250 (18 h) followed by 220 (18 h) °C produced particles of diameter 6.67 ± 0.33 nm. The high degree of crystallinity in the particles is evident in the manifestation of lattice fringes in high-resolution electron micrographs (see Figure 1B, inset). No evidence of stacking faults or other crystal defects was detected. The particle nucleation and growth is also dependent on the activity of the metal: FeP nanoparticle formation from $Fe(CO)_5$ and $P(SiMe_3)_3$ requires higher temperatures (270 °C) and produces smaller particles (3.16 ± 0.34 nm) after heating for 48 h, whereas CoP nanoparticles form at still higher temperatures (320 °C) (Supporting Information).

In previously reported syntheses of nanoparticles of InP[13] and FeP,[8] for example, the role of $P(SiMe_3)_3$ is typically to provide a source of phosphide (P^{3-}) by a redox neutral desilylation pathway.[14] However, in our case, the phosphine is also a likely source of oxidizing equivalents.[15] This kind of reactivity between metals and phosphines has been reported at elevated temperatures,[7c,d,16] and recently the preparation of bulk aggregates of amorphous FeP by sonochemical reaction of $Fe(CO)_5$ with $P(CH_2CH_3)_3$ has been described.[17] Presumably, similar reactivity is occurring under our conditions, which in turn suggests that the silyl group may not be germane to metal phosphide formation. Indeed, preliminary results indicate that ordinary alkyl phosphines are equally effective in MnP
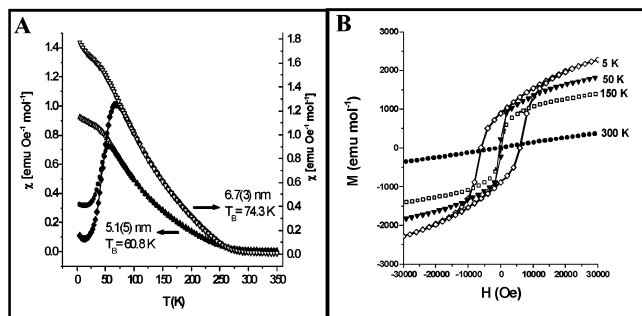

Figure 2. (A) Temperature dependence of the magnetization for field-cooled (open symbols) and zero-field-cooled (filled symbols) MnP nano-particles under an applied magnetic field of 500 Oe. (B) Corresponding variation of magnetization as a function of field for the 5.1(5) nm particles at various temperatures.

nanoparticle formation, thus expanding on the generality and usefulness of the method (Supporting Information).

The temperature dependence of the dc magnetization[18] indicates that the MnP nanoparticles order ferromagnetically just below 300 K, consistent with the reported ferromagnetic Curie temperature (T_c) of 291.5 K for bulk MnP.[19] The ordering is evident in the change in slope of the curves in the magnetization versus temperature data (Figure 2A) and the appearance of saturation behavior in the magnetization versus field data acquired below 300 K (Figure 2B). Below T_c, the particles display superparamagnetic behavior with the 5.1(5) nm spherical particles exhibiting a blocking temperature (T_B) of 60.8 K and the 6.7(3) nm particles exhibiting a higher T_B of 74.3 K (Figure 2A). T_B is identified by the location of the bifurcation between zero-field-cooled (ZFC) and field-cooled (FC) data and represents the temperature below which the super-paramagnetic particles are unable to relax within the time scale of the experiment.[20] As is typical of a superparamagnetic system, the coercivity (hysteresis) decreases as T_B is approached and drops to zero above T_B, as illustrated for the 5.1(5) nm MnP particles in Figure 2B. However, the hysteretic behavior in the field dependent magnetization data below 50 K is significantly different from the behavior of bulk (microcrystalline) MnP, which is reported to undergo a ferromagnetic to metamagnetic transition at this temperature.[19] Apparently, the metamagnetic phase is completely destabilized in the nanoparticles, and only ferromagnetic ordering occurs within the nanoparticles at all temperatures below T_c.

In conclusion, nanoparticles of MnP have been produced for the first time and are found to exhibit superparamagnetic behavior below T_c with no evidence of a metamagnetic transition, as is observed in bulk (microcrystalline) MnP. As such, nanoparticulate precipitates of MnP are a possible source of observed ferromagnetism in Mn-doped semiconducting phosphides. The synthesis was achieved by a new method in which zerovalent metal carbonyl complexes are treated with phosphines in coordinating solvents at $T \geq 220$ °C. This route appears to be generally suitable for the preparation of a number of metal phosphides (as illustrated here for MnP, FeP, and CoP) and can even employ less-reactive (and less expensive) alkylphosphines.

Supporting Information Available: TEM and synthesis data for MnP particles produced from an alkylphosphine, TEM and XRD data for 6.7(3) nm spherical MnP, XRD data for FeP and CoP nanoparticles, TEM image of FeP nanoparticles, and table of magnetic data for MnP nanoparticles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Calculated from ICP analysis of manganese precipitated as MnP nano-particles relative to the quantity employed in the synthesis.

(12) Nanoparticle size was determined by measuring the diameter of over 200 particles imaged by electron microscopy.

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