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Recent developments in synthetic approaches to transition metal phosphide nanoparticles for magnetic and catalytic applications

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ABSTRACT

Recent advances in synthetic methods have led to the preparation of a wide array of transition metal phosphide nanoparticles, and characterization of these materials has provided insight into nanoscale magnetic and catalytic properties. This review highlights advances in the field that have been made since the time of the last review [S.L. Brock, S.C. Perera, K.L. Stamm, Chem. Eur. J. 10(2004)3364–3371]. Synthetic methods include solvothermal, solution-phase arrested precipitation, metal nanoparticle conversion, and phosphate reduction. Magnetic properties of FeP, Fe_2P and MnP nanoparticles and nanorods (among others), and recent data on thiophene hydrodesulfurization catalyzed by discrete, unsupported Ni_2P particles, is presented. Finally, the future prospects for the field are discussed.

1. Introduction

Transition metal phosphides are a class of compounds that exhibit a range of properties of fundamental and commercial interest, depending on their phase. For example, Fe_3P is a ferromagnet with a high transition temperature ($T_C = 692$ K) [1], whereas FeP_2 is a small bandgap semiconductor [2]; orthorhombic MoRuP is a superconductor ($T_C = 15$ K) [3], the filled phosphide skutterudites (e.g., $CeFe_4P_{12}$) exhibit promising thermoelectric properties [4], and Ni_2P is among the most active catalysts for hydrodesulfurization (HDS) [5]. These properties are often augmented on the nanoscale, providing an impetus for developing synthetic methods that enable preparation of discrete nanoparticles with control of size, shape and phase. In 2004, the last time transition metal phosphide nanoparticles were reviewed [6], very few methods had been explored for synthesis of transition metal phosphide nanoparticles other than solvothermal syntheses and reduction of phosphate salts on high surface area supports, with the latter method focused on generating catalytic materials for HDS. What little research was being conducted on discrete phosphide nanoparticles prepared by solution-phase methods was focused largely on main group metals, such as InP and GaP [7]. The 4 years that have elapsed since the last review have seen considerable advances in synthetic methods for transition metal phosphide nanomaterials, and these have enabled the magnetic and catalytic properties to be evaluated in some detail. The present review will describe recent advances in the synthesis of transition metal phosphide nanomaterials, with emphasis on discrete (unaggregated and unsupported) phases. The current understanding of the size- and phase-dependent magnetic properties will be discussed, as will the potential for discrete phosphide nanoparticles to address key factors in HDS catalyst activity. Many of the phases that have been studied most extensively, and therefore form the bulk of this review, fall into two main structure types, the MnP and Fe_2P structure types. These are illustrated in Fig. 1.

2. Synthetic approaches

Synthetic strategies for making metal phosphide nanostructures are taking a new face as various methodologies are discovered and used. In addition to describing advances in solvothermal methods, new approaches for preparing discrete nanoparticles, including arrested precipitation reactions and transformation of discrete metal particles to phosphides, will be presented. Finally, methods such as sonochemistry, confinement in carbon nanotubes (CNT), and reduction in templates, will be discussed.

2.1. Solvothermal methods

Solvothermal routes are less popular than they were several years ago for making transition metal phosphide nanoparticles

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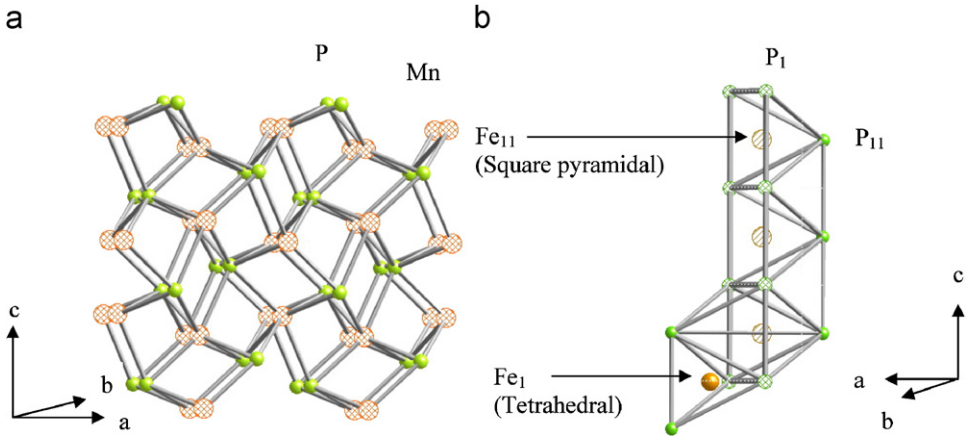

Fig. 1. Illustration of the structure types for (a) MnP (FeP, CoP) and (b) Fe_2P (Ni_2P) and relevant phosphides that crystallize in these structure types. The MnP structure type can be viewed as a distorted (orthorhombic) variant of the hexagonal NiAs structure type [39]. The Fe_2P structure type consists of a hexagonal arrangement of canals of alternating filled and empty square pyramids and tetrahedra pairs. The Co_2P structure (not shown) has the same local structure as Fe_2P, but the canals form a zig-zag stacking arrangement, resulting in an orthorhombic lattice [58].

[6], and few new phases have been reported. However, this approach has been exploited to make new particle and aggregate morphologies, including dendrites and hollow spheres and tubes. Reaction of nickel sulfate with yellow phosphorus in glycol/water at 180 °C yields dendritic nanostructures of Ni_2P [8], whereas a similar reaction with $CoCl_2$ in aqueous ammonia at 220 °C yields Co_2P nanorods [9]. In both cases, the anisotropic structures appear to grow from large, micron-sized spheres, consistent with a similar growth mechanism for the two cases that involves transformation of discrete nanoparticles to large aggregates (spheres), growth of rods from the spheres, transformation of rods into dendrites, and growth of dendrites at the expense of spheres [8]. Discrete nanoparticle aggregation has also led to micron-sized hollow spheres and tubes of Cu_3P [10] and Co_2P [11] and likely plays a role in $Ni_{12}P_5$ hollow sphere formation using CTAB as a structure directing agent [12]. The mechanism of formation of hollow structures in systems that do not have structure directing surfactants remains unknown, but has been postulated to arise from bubble formation during the course of the reaction [11]. Solvent phase separation may provide an alternate explanation, but no convincing evidence is put forth for any mechanism.

2.2. *Synthesis of nanorods and spherical particles from injection/slow heating of molecular precursors*

Despite their promise, solvothermal reactions suffer from a number of drawbacks when it comes to nanoparticle synthesis. Most notably, the products are lacking in monodispersity and are aggregated, rather than disperse, making it difficult to study their size-dependent physical properties. For this reason, there has been considerable focus on adapting methods used to make monodisperse quantum dots, such as CdSe, to transition metal phosphides. Originally applied to FeP and MnP spherical nanoparticles [6,13,14], a host of new phases have been prepared by this approach in the last 4 years. The general method involves reaction of metal and phosphorus precursors at high temperature and in a coordinating solvent, such as trioctylphosphine oxide (TOPO). Thus, discrete 4.7 ± 0.7 nm particles of FeP were prepared by reaction of $Fe(acac)_3$ with $P(SiMe_3)_3$ in TOPO at 260 °C [13], whereas 5.1 ± 0.5 and 6.7 ± 0.3 nm MnP particles were prepared by reaction of $Mn_2(CO)_{10}$ with $P(SiMe_3)_3$ at 220 and 250 °C, respectively [14]. Subsequently, it has been shown that many metal precursors are sufficiently reactive to confiscate phosphorus from considerably less reactive sources than $P(SiMe_3)_3$, such as trioctylphosphine (TOP), and even tetradecylphosphonic acid (TDPA). The use of strongly coordinating solvents, such as TOP, also facilitates formation of anisotropic structures by allowing high reagent concentrations that favor anisotropic growth in crystals where the crystallographic planes have different chemical potentials. As noted in Table 1, and described below, this approach has been successful in preparing nanorods and wires of a range of metal phosphides.

Discrete nanorods of iron phosphides were independently reported by three groups in 2004. The groups of Hyeon and Liu exploited the reaction of $Fe(CO)_5$ with TOP to prepare Fe_2P [15] and FeP nanorods [16], respectively; whereas the group of Chi used pre-reacted $(\eta^4\text{-}C_6H_8)Fe(CO)_3$ with TOP, presumably proceeding via iron nanoparticle intermediates, to prepare FeP nanorods [17]. The specific factors that govern which phase will form remain unclear, although both the solvent system and the temperature of the reaction are presumed to play a role. Thus, Hyeon obtained Fe_2P when using oleylamine (OA) and octylether (OE) as solvents at temperatures of 300 °C [15], whereas TOPO at much higher temperatures (360 °C) leads to FeP [18]. In contrast to reactions with $P(SiMe_3)_3$, reactions with TOP require higher temperatures (>300 °C) due to the fact that more energy is required to break the P–C bond, a necessary step in the liberation of active phosphorus from TOP, than the P–Si bond of $P(SiMe_3)_3$.

As indicated above, one critical factor related to nanorod/wire formation is maintaining a high concentration of reagents in solution. This can be achieved by starting with a high concentration (facilitated by strong binding ligands), sequential injection of additional precursor aliquots over the course of the reaction to maintain the concentration, or continuous injection of reagents. The Hyeon method applies continuous injection, and the length of the rods is related to the rate of the injection. Hyeon and co-workers have also employed this method for the formation of FeP, MnP, Co_2P and Ni_2P nanorods [18]. Intriguingly, the correlation between the length of the rods/wires and the injection rate depends on the identity of the metal. Thus, faster rates of injection lead to longer rods in the case of MnP, but shorter rods for Fe_2P [18]. This may be related to the relative reactivity of the metal complexes.

Nanorods prepared by high temperature injection appear to form as single crystals, although the growth direction has not been established in every case. Hyeon and co-workers report that MnP and Co_2P nanorods grow perpendicular to the (002) planes (i.e., along *c*), FeP nanowires grow perpendicular to the (013)