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One-pot synthesis of magnetic iron phosphide nanoparticles

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ABSTRACT

A novel one-pot synthetic method to produce crystalline tri-octylphosphine (TOP) capped iron phosphide nanoparticles is reported here. Standard method of synthesizing FeP includes preparation of a precursor, sodium phosphide, which is finally reacted with ferric chloride (FeCl₃). The methods for synthesizing iron phosphide (FeP), reported so far, rely on the use of toxic red or yellow phosphorus to generate the precursor, Sodium phosphide (Na₃P). In present investigation, instead of red or yellow phosphorus, a relatively less toxic substance TOP and sodium metal (Na) have been used to yield Na₃P. The synthesized nanoparticles were fully characterized by X-ray diffraction pattern (XRD), Infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM) and superconducting quantum interference device (SQUID) analyses. The results showed that the synthesized FeP nanoparticles have the characteristic orthorhombic crystal structures, with the size \sim 10 nm and the coercivity 70 Oe at RT.

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Introduction

The transition metals phosphides specifically of Group VIII are well known in the literature like Group III-V phosphides such as Gallium phosphide (GaP) and indium phosphide (InP). The Group III-V phosphides are synthesized by the reaction of metals of Group III and phosphorus of Group V. Transition metal carbides and nitrides have shown significant applications in catalyzing various chemical reactions.^[1,2] Very few methodologies could be developed for the synthesis of metal phosphides due to implication of highly sensitive phosphorus sources. Although, transition metal phosphides, for instance, molybedum phosphide, nickel phosphide, cobalt phosphide, iron phosphide and tungsten phosphide have shown good catalytic properties in hydrotreating reactions. ^[3-6] Multiple synthetic routes have been developed for Ni₂P and MoP as reported by Phillips and Sawhill.^[7-9] Recently, magnetic metal phosphides nanostructures have gained popularity due to their potential applications in magnetic and electronic devices.^[6,10-15] These magnetic metal phosphides were synthesized by various techniques including thermal,^[16] sonochemical^[17] and solvothermal methods.^[18] Nanostructures of iron phosphide (FeP) orthorhombic, FeP₃ (tetragonal), Fe₂P (hexagonal/ orthorhombic), FeP (orthorhombic), FeP₂ (orthorhombic), and FeP₄ (orthorhombic) are found to exhibit different magnetic properties. The methodologies, reported to synthesize iron phosphides nanostructures, includes thermal decomposition of single source (iron & phosphorus) organometallic

precursors,^[19,20] and injection of metal nanoparticles-trioctyl phosphine complex into hot solution of trioctyl phosphine (TOP) and trioctyl phosphine oxide (TOPO) utilizing it as a surfactant for achieving nano-sized dimensions of the product.^[21-29] TOP has been extensively used as a source of phosphorus as well as co-solvent for the synthesis of metal phosphides. TOP can produce phosphorus by the catalytic cleavage of P-C bond in the presence of metal nanoparticles (Fe, Ni or In), either generated during the reaction or injected in the hot solution of TOP already prepared in another flask. Subsequently, free phosphorus, generated during the reaction, may form metal phosphides. This hypothesis of catalytic cleavage of P-C bond was proposed by Chen et al.for TOP-capped FeP nanoparticles.^[30] Similar hypotheses have also been proposed for the synthesis of InP^[31] and nickel phosphide (Ni₂P) nanoparticles.^[32] In addition, phosphorus pentachloride (PCl₅)^[33] was also used as a source of phosphorus for the synthesis of highly reactive sodium phosphide (Na₃P) by the reaction of the transition metal precursor to yield transition metal phosphide. Schaak and Henkes also synthesized iron phosphides nanoparticles by using iron nanoparticles and TOP under argon at high temperature and transferred this into n-hexadecylamine at high temperature.^[33] There are some reports that also utilized red or yellow phosphorus to synthesize Na₃P.^[18,31] Such methodologies require formidable challenges because of toxicity and difficulty in handling of the red or yellow phosphorus. Therefore, a route utilizing less toxic phosphorus precursor is required, Na₃P.

Sodium phosphide (Na₃P) synthesis was first reported by Alexandre Baudrimont in mid-19th century using phosphorus pentachloride (PCl₅) as the phosphorus source.^[33] Subsequently, various methods were reported based on the use of sodium metal and red or yellow phosphorus as the phosphorus source to yield Na_3P ^[15] to generate FeP. The very tedious method for the synthesis of Na₃P was reported by DiSalvo and coworkers by using sodium azide (NaN₃), titanium nitride (TiN), and Phosphorus with potassium iodide, halide flux under argon atmosphere at very high temperature in niobium (Nb) sealed tube and found single crystals of Na₃P as red-block.^[33] Toxicity of the chemicals used rendered these approaches difficult and challenging. The synthesis of Na₃P is also very challenging due to toxicity of TOP that may arise by the formation of phosphine gas as a by-product during the reaction in solution.

A simple method to synthesize Na_3P by reacting TOP and sodium metal, without the use of red or yellow phosphorus, has been proposed in this study. In this method, free phosphorus was generated by the reaction of Na and TOP *via* catalytic mechanism. The synthesized sodium phosphide was further reacted with FeCl₃ in the presence of TOP to yield FeP/TOP-NPs. This method avoids direct use of the red or yellow phosphorus and proposes a novel onepot synthetic route for the production of FeP/TOP-NPs.

Experimental

General

Tri-octylphosphine (TOP), anhydrous ferric (III) chloride (FeCl₃), sodium metal (Na), were purchased from Sigma-Aldrich (San Louise, USA). Toluene and methanol were purchased from J.T. Baker (Phillipsburg, NJ). The magnetic properties of iron phosphide were measured using a superconducting quantum interference device (SQUID) magnetometer with a maximum field of 20000 Oe. X-ray diffraction (XRD) measurements were performed using a Philips X'Pert-Pro diffractometer with Cu-K_{α} radiation with a wavelength of $\lambda = 1.5406$ Å. X-ray photoelectron spectra (XPS) were recorded with a PHI 5000 Versa Probe (Chigaski, Japan) XPS system. Transmission electron microscopy (TEM), Electron dispersion X-ray (EDX) and Selected area electron diffraction (SAED) of samples were performed ona JEOL JEM-2100F (Tokyo, Japan) that was operated at 200 keV. Dynamic light scattering (DLS) was performed at room temperature by using 35mW diode laser on a Brookhaven 90Plus (Holtsville NY) particle size analyzer. IR spectra were recorded on a Perkin-Elmer Spectrum (Massachusetts, USA) 100 series between 400 and $4000 \,\mathrm{cm}^{-1}$.

Synthesis of iron phosphide

In-situ Na₃P was prepared by mixing TOP (2.24 mL, 0.0072moles + 1.76 mL excess TOP) and sodium (0.5 gm,0.022moles) metal at 250 °C under argon atmosphere; the mixture was left for stirring at 280 °C for 2-3 it



Scheme 1. Schematic presentation of the synthesis of TOP capped FeP

turned black with green reflection color indicated the formation of Na₃P. During stirring, anhydrous FeCl₃ (0.5 g, 0.0031moles) dissolved in 4 mL TOP was slowly added to Na₃P mixture. The temperature was raised to 320 °C followed by constant stirring for 3-4 h under inert atmosphere. The mixture turned from greenish-black to black indicating completion of the reaction. After cooling of the reaction mixture to RT, methanol (75 mL) was slowly added to decompose the un reacted sodium metal; and then the mixture was centrifuged at 8000 rpm for 5 min. After the centrifuge, the obtained black pellet was re-dispersed in toluene (25 mL); and was re-precipitated by the addition of methanol (50 mL). The precipitate was separated by the centrifugation; subsequently pellet was washed with water (25 mL x 2) and finally with methanol and dried under vacuum.

Results and discussion

In this work, FeP nanoparticles were synthesized using TOP as a phosphorus source and a capping reagent to control the size of particles (Scheme 1). The availability of free phosphorus, generated during the reaction by the catalytic cleavage of P-C bond in the presence of Na metal, led to the formation of Na₃P at 280 °C under argon atmosphere. Na₃P, a highly reactive source of phosphorus, produced a black colored product upon reaction with FeCl₃.^[33]

The powder was examined by XRD to characterize the crystal structure of the synthesized FeP/TOP-NPs. The XRD pattern of the synthesized FeP/TOP-NPs is shown in Figure 1. The pattern showed all major peaks at 2θ values of 30.80 (002), 32.75 (011), 34.60 (200), 35.76 (102), 37.14 (111), 37.60 (201), 46.27(112), 46.92 (202), 48.36 (211), 50.34 (103), 55.98 (301) and 59.66 (020) degrees, which are characteristic features of crystalline planes of orthorhombic structure of FeP.^[18,26] A weak peak at an angle of 40.30 in XRD pattern (Figure 1) indicated the presence of trace Fe₂P. The orthorhombic XRD pattern matched well with the JCPDS (78-1443) data of FeP; the broadening of the Bragg's peaks indicating poor crystallinity of TOP capped nano sized FeP particles was also observed. The average thickness of grain is calculated by the Scherrer's equation (D = $0.9\lambda/\beta$

cos θ , where D = average thickness of grain in perpendicular to specific facet, λ = frequency of X-ray and β = FWHM at a selected 2θ) was found to be ~11.4 nm (Table 1).



Figure 1. XRD pattern of FeP/TOP-NPs prepared from Na_3P. Fe_2P phase is depicted by $^{\prime*\prime}$.

Table 1. Average grain thickness and lattice spacing of FeP/TOP-NPs calculated using Scherrer's formula.

hkl planes	2 θ (°)	θ (°)	FWHM	Lattice spacing (Å)	Average grain thickness (nm)
011	32.75	16.38	0.75	2.750	11.54
111	37.14	18.57	0.57	2.406	15.37
211	48.36	24.18	0.81	1.880	11.24
301	55.98	27.99	0.98	1.638	9.60
020	59.66	29.83	1.04	1.542	9.21

TEM images of FeP nanoparticles revealed a particle size below 10 nm (Figure 2a and b). The aggregates appearing in the images are due to the drying process of the powder on TEM grid. The majority of nanoparticles showed a spherical morphology while only few of them showed an elliptical shape. The diffused rings in the electron diffraction pattern indicated nano-crystalline nature of the product, which is consistent with the XRD data. Furthermore, elemental analysis by EDX confirmed the presence of Fe & P with the stoichiometric ratio of Fe: P (21.60: 21.10). The observed percentage of Fe was slightly more due to the presence of impurity of Fe₂P or Fe nanoparticles in the product. The particle size and size distribution of the synthesized FeP/ TOP-NPs measured by DLS showed average size 13.5 nm (Figure 3).

The XPS spectra of TOP capped FeP nanoparticles are shown in Figure 4. The high-resolution spectrum of FeP showed splitting in 2p3/2 & 2p1/2 of the binding energies 711 eV and 720 eV respectively.^[18,25] Similarly, the spectrum of P 2p3 showed two peaks one of lower energy at 129.5 eV that can be assigned to FeP and other one of higher energy at 133.5 eV ^[18,25] corresponding to the oxidized phosphorous due to oxidation of the surface of nanoparticles in presence of oxygen absorb form surrounding.^[9,19,34]

Infrared spectroscopy was employed to examine the presence of TOP capping around FeP nanoparticles where TOP was employed as a phosphorus source as well as a stabilizer to control the particle size. The IR spectra of TOP and the



Figure 2. TEM (a) HRTEM (b) SAED (c), and EDX (d) of FeP/TOP-NPs.



Figure 3. The particle size distribution of FeP/TOP-NPs as observed in DLS measurements.



Figure 4. XPS of FeP/TOP-NPs as prepared from Na_3P showed the binding energies of (a) Iron & (b) Phosphorus.

synthesized FeP/TOP nanoparticles are shown Figure 5. The characteristic IR absorption bands of TOP at 2852 and 2921 cm^{-1} (corresponding to -CH stretching); and at 1468and1376 cm⁻¹ (corresponding toCH₂ deformation) were observed in the spectrum. The other IR absorption bands, appearing at 1199, 1100 and 1036 cm⁻¹, were attributed to C-P stretching of TOP.^[25,35] Thus, it is evident from the IR data that all absorption bands attributed to TOP were observed in the analysis of the product confirming the proper capping of FeP nanoparticles by trioctylphosphine.

The temperature dependent magnetic properties of the FeP/TOP-NPs samples were measured by SQUID magnetometer. The results obtained in this study indicating super paramagnetic behavior and is typical for magnetic nanoparticles (Figure 6a).^[25,30] The higher blocking temperature







Figure 6. The magnetic properties of Iron phosphides measured by SQUID (a) Magnetization as a function of field at RT and the inset displays the field dependence of magnetization with coercivity 70 Oe for FeP/TOP-NPs. (b) The ZFC & FC curves measured with an applied magnetic field of 100 Oe.

(200 K) and irreversibility temperature (300 K) were observed for FeP that may be attributed to high aspect ratio (length/width) and greater thermal energy required to align disordered spin. The small hysteresis loop was observed at room temperature with a coercivity 70 Oe. Thus, the present results affirm that it is possible to obtain magnetism at

room temperature for a material showing antiferromagnetic nature at low temperature. However, the bulk iron phosphide does exhibit antiferromagnetic property, with a Neel temperature at 115 K,^[19,34] but contrary to that a ferromagnetic like behavior of FeP was also reported by Chen et al.^[30] The magnetization profile from the present results showed a small hysteresis loop indicating the presence of ferromagnetic traces in the product, which may be due to presence of a ferromagnetic material- Fe₂P. The presence of Fe₂P traces in the product was also supported by XRD (Figure 1) and EDX (Figure 3d). Furthermore, in order to estimate the blocking temperature of FeP/TOP-NPs, the zero-field cooling (ZFC) and field-cooling (FC) magnetization curves were measured at an applied field of 100 Oe in the temperature range of 0 to 350 K (Figure 6b). ZFC curve showed a maximum at T > 200 K, associated to the blocking temperature of the nanoparticles system and gradually dropped to zero at 350 K. However, ZFC and FC curves showed irreversible temperature at T > 300 K indicating the presence of a size distribution or nanoparticles aggregation. The blocking temperature depends on many factors such as the material total anisotropy (K) and the volume of the nanoparticles. Similar results have been reported where estimated blocking temperature was 140 K with an irreversible temperature at 233 K.^[30,36-40]

Conclusion

In conclusion, this study provides a simpler alternative route for the synthesis of Na_3P without the use of toxic red or yellow phosphorus, where reaction of TOP with Na metal led to the formation of Na_3P . Subsequently, Na_3P further reacted with iron chloride to form FeP/TOP-NPs along with Fe₂P traces. The phosphorus source was generated from TOP through the catalytic cleavage of P-C bond in the presence of Na-metal. Moreover, these FeP/TOP-NPs exhibited significant superparamagnetic properties, compared to their bulk counterparts.

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