Catalytic synthesis, characterization and magnetic properties of iron phosphide nanowires†

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We report on the synthesis of iron phosphide nanowires by thermal decomposition of \((\eta^4\text{-cyclohexadiene})\text{iron tricarbonyl}\) in the presence of TOP (tri-\(n\)-octylphosphine) and characterization of the products.

Nanostructured materials are attracting great research interest due to their application as catalysts of organic reactions, as gas sensors and as advanced materials in future optic, electronic and magnetic devices.1–3 Recently, the fabrication of Fe-containing magnetic nanomaterials including iron4, iron oxides5 and alloys such as FePt6 and FeCo7 became a very important issue in the potential application of their magnetic characteristics. Iron phosphide, FeP, a low-band gap semiconductor material with special magnetic properties, has traditionally been prepared by high-temperature reactions.8

Recently, Lukhart and Brock groups reported the preparation of FeP and FeP nanoparticles, respectively.9 Herein, we present the first example of synthesis of iron phosphide FeP nanowires by thermal decomposition of \((\eta^4\text{-cyclohexadiene})\text{-iron tricarbonyl}, (\eta^4\text{-C}_6\text{H}_8)\text{Fe(CO)}_3\) in the presence of \(n\)-octylphosphine oxide (TOPO) and \(n\)-octylphosphine (TOP) as the stabilizing surfactants. In addition, magnetic properties of these products have been investigated in this study.

The preparative procedure summarized in Scheme 1 is modified from the method for generation of Fe nanorods previously reported by Hyeon et al.9a Heating a mixture of 200 mg of \((\eta^4\text{-C}_6\text{H}_8)\text{Fe(CO)}_3\) and 5.0 g of TOP at \(\sim 340 ^\circ\) C under a nitrogen atmosphere for 30 min afforded a black solution. To this black mixture in TOPO, was added a set amount of \((\eta^4\text{-C}_6\text{H}_8)\text{Fe(CO)}_3\) (0 mg, sample A; 10 mg, sample B; 25 mg, sample C) in 50 ml of TOP and the solution was continuously heated at \(\sim 360 ^\circ\) C for 30 min. This step was repeated once. After the resulting black mixture was cooled to room temperature, excess acetone was added to produce a black precipitate. The black powder product was collected by centrifugation and can be re-dispersed in pyridine or \(n\)-hexane to form a homogeneous solution.

These products were characterized by transmission electron microscopy (TEM, JEOL JEM-3010), energy-dispersive X-ray spectroscopy (EDS, Noran Nodel Voyager 100 and Link EXL-II), inductively coupled plasma atomic emission spectroscopy (ICP-AES, Jarrell-Ash ICAP 9000), and X-ray powder diffraction analysis (XRD, Rigaku Rotaflex RTP 500RC). The resulting data are summarized in Table 1. TEM examination revealed that the majority of the products were nanowires with a diameter of about 5 nm and a length of several hundred nanometers. A TEM image of sample B is shown in Fig. 1a. EDS analysis showed a relatively high phosphorus content in this sample (Fig. 1b). A HRTEM image of a single wire is shown in Fig. 1c and demonstrates the crystalline nature of the nanowire.

A comparison experiment (sample D) conducted by reflux of the precursor in TOP for 1 h gave spherical nanoparticles whose EDS analysis exhibited a low phosphorus content (see ESI, Fig. S-4). ICP-AES analysis of the samples provided the Fe and P content (wt%). By subtraction of the weight percentage of C, H, O, and P in the surfactant TOPO, the Fe/P mole ratio in these samples can be calculated and data are listed in Table 1. Iron/phosphorus mole ratios close to one in samples A, B and C indicate the existence of FeP as the major component. Elemental analysis for sample D showed that it contained 98% Fe. XRD patterns for samples A, B and C show nine strong peaks, collected in Table 1. All the peaks are in good agreement with the reported values.10 These prove that polycrystalline FeP exists in the nanowires.

The magnetic properties of sample B have been investigated by a superconducting quantum interference device (SQUID, Oxford MagLab 2000). The temperature dependence of magnetization was measured in an applied magnetic field of 1000 Oe between 2 and 300 K using zero-field cooling (ZFC) and field-cooling (FC) procedures. The result shown in Fig. 2a is typical for magnetic nanoparticles.11 Much higher blocking (140 K) and irreversibility temperatures (233 K) were observed for sample B compared to sample D, probably caused by the high aspect ratio (length/width) and greater thermal energy needed to align the disordered spin. The magnetization hysteresis loop at 2 K is shown in Fig. 2b and exhibits a

† Electronic supplementary information (ESI) available: TEM images, EDS and XRD data for samples A–D. See http://www.rsc.org/suppdata/jm/b3/b311943b/
coercivity of about 4000 Oe and no saturation up to a magnetic field of 4 T.

A mechanism of formation of FeP nanostructures is proposed in Scheme 2. Reflux of \((\eta^4-C_6H_8)Fe(CO)_3\) in TOPO provided iron nanoparticles. Tri-n-octylphosphine was added to the solution and it coordinated to the iron particles first. Then, catalytic cleavage of P–C bonds in TOP occurred and P atoms formed on the surface of Fe particles. Diffusion of phosphorus atoms to the inside of the particles resulted in the

table below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe (wt%)</th>
<th>P (wt%)</th>
<th>Calc. C, H &amp; O ((\text{wt%}))</th>
<th>Calc. (P_{\text{sample}}) ((\text{wt%}))</th>
<th>Fe/P mole ratio</th>
<th>Composition and appearance (TEM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>28.9</td>
<td>20.8</td>
<td>50.3</td>
<td>16.4</td>
<td>0.98</td>
<td>FeP nanorods</td>
</tr>
<tr>
<td>B</td>
<td>21.8</td>
<td>17.1</td>
<td>61.1</td>
<td>11.8</td>
<td>1.02</td>
<td>FeP nanowires</td>
</tr>
<tr>
<td>C</td>
<td>22.8</td>
<td>17.5</td>
<td>59.7</td>
<td>12.3</td>
<td>1.03</td>
<td>FeP nanowires and nanorods</td>
</tr>
<tr>
<td>D</td>
<td>24.5</td>
<td>6.3</td>
<td>69.2</td>
<td>0.3</td>
<td>45.29</td>
<td>Fe spherical nanoparticles</td>
</tr>
</tbody>
</table>

The inaccuracy of ICP-AES is 3%. \(^a\) Calc. \(C, H \& O \text{ (wt\%)} = 100 - \text{Fe (wt\%)} - P \text{ (wt\%). Calc. } P_{\text{sample}}(\text{wt\%}) = P \text{ (wt\%)} - \left[ \text{Calc. } C, H \& O \text{ (wt\%)/355.67} \right] \times 30.97. \(^b\) ICCD-PDF No. 78-1443.

Fig. 1 (a) Transmission electron micrograph, (b) EDS data, and (c) high resolution transmission electron micrograph for sample B.

Fig. 2 (a) ZFC and FC magnetization vs. temperature at an applied magnetic field of 1000 Oe, and (b) magnetization hysteresis loop recorded at 2 K for sample B.
formation of FeP. Powdered FeP has been produced by the sonochemical reaction of Fe(CO)₅ and triethylphosphine via a similar pathway.¹²

Acknowledgements

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Notes and references


10 The diffraction pattern for FeP is obtained from ICCD-PDF No. 78-1443.
