Nanorods

Novel Synthesis of Magnetic Fe$_2$P Nanorods from Thermal Decomposition of Continuously Delivered Precursors using a Syringe Pump**

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One-dimensional (1D) nanostructured materials, such as nanorods, nanowires, and nanotubes, have received tremendous attention because of their unique properties, which are derived from their low dimensionality and possible quantum confinement effects.[1] These 1D nanostructured materials have found application as the interconnects and functional blocks used in fabricating nanoscale electronic, magnetic, and optical devices.[2] The synthesis of nanostructured magnetic

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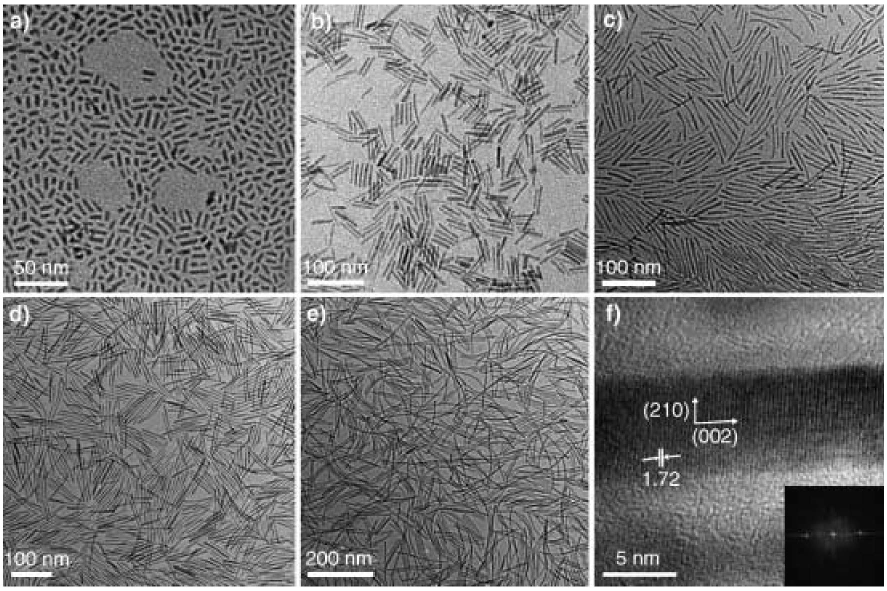

Figure 1. TEM images of iron phosphide nanorods. a) 3 × 12 nm, obtained by single injection; b) 5 × 43 nm, obtained by double injection; c) 5 × 88 nm, obtained using an injection rate of 10 mL h^{-1}; d) 6 × 107 nm, obtained using an injection rate of 5 mL h^{-1}; e) 6 × 290 nm, obtained using the injection rate of 3 mL h^{-1}; f) HRTEM image of a single iron nanorod from c) (inset: fast-Fourier transform (FFT) image originating from the lattice of the iron phosphide nanorods).

materials is a very important area of research, because of their applications in multi-tera-bit in^{-2} magnetic storage devices and in magnetic carriers for drug targeting.[3] So far, there have been several reports on the synthesis of discrete 1D magnetic nanostructured materials; for example the synthesis of iron nanorods through the oriented attachment of monodisperse spherical nanoparticles reported by our research group.[4] Alivisatos and co-workers reported the synthesis of cobalt nanodisks via the thermal decomposition of a cobalt carbonyl precursor.[5] Chaudret and co-workers reported the synthesis of cobalt nanorods[6] and nickel nanorods[7] from the high-temperature reduction of organometallic complexes. Metal phosphides are currently of great scientific interest in materials science and chemistry because of their important magnetic, electronic, and chemical properties.[8] For example, hexagonal iron phosphide and related materials have been intensively studied for their ferromagnetism, magnetoresistance, and magnetocaloric effects.[9] Consequently, it would be very interesting to understand the size- and shape-dependent characteristics of nanostructured metal phosphides. However there have only been a limited number of reports on the synthesis of nanostructured materials containing transition-metal phosphides. Recently, Brock and co-workers synthesized FeP and MnP nanoparticles from the reaction of iron(III) acetylacetonate and manganese carbonyl, respectively, with tris(trimethylsilyl)-phosphane at high temperatures.[10] Very recently, Liu and co-workers synthesized antiferromagnetic FeP nanorods via the thermal decomposition of a precursor/surfactant mixture solution.[11] Herein, we report on the synthesis of discrete iron phosphide (Fe_2P) nanorods from the thermal decomposition of continuously supplied iron pentacarbonyl in trioctylphosphane (TOP) using a syringe pump. To the best of our knowledge, this is the first report on the synthesis of 1D nanostructured materials using a syringe pump for the continuous delivery of precursors.

The current synthetic procedure is a modified version of the method developed by our group for the synthesis of monodisperse nanocrystals of metals, oxides, and sulfides, which employs the thermal decomposition of metal–surfactant complexes.[3a,12] We employed a syringe pump for the continuous supply of iron–phosphane complexes into a hot surfactant solution in order to induce one-dimensional growth.

In the first synthesis, 5 mL of the iron–phosphane (Fe–TOP) complex solution, prepared by mixing [$Fe(CO)_5$] (0.2 mL, 1.52 mmol) and trioctylphosphane (TOP; 10 mL), was added to a mixture containing octylether (10 mL) and oleylamine (2 mL) at 300 °C, in order to synthesize short iron phosphide nanorods that were, on average, 3 nm in diameter and 12 nm in length (Figure 1 a). When we injected 10 mL of the Fe–TOP complex solution (as two 5 ml portions in a "double injection", with an interval of 30 min between injections) into the surfactant solution at 300 °C, we were able to synthesize longer nanorods with average dimensions of 5 × 43 nm (Figure 1 b). After finding that longer nanorods were produced from the double injection of the Fe–TOP complex, we used a syringe pump for continuous delivery, in order to further control the length of the nanorods. A total of 10 mL of the Fe–TOP complex solution was continuously added to the surfactant solution at 300 °C using a syringe pump at controlled rates. Figure 1 c, d, and e show TEM images of 1D Fe_2P nanorods with sizes of 5 × 88, 6 × 107, and 6 × 290 nm, which were synthesized at injection rates of 10, 5, and 3 mL h^{-1}, respectively. The widths of these nanorods were almost identical. A high-resolution TEM image (Figure 1 f) shows that the nanorods grew along the [002] direction.

When 5 × 88 nm Fe_2P nanorods were slowly evaporated on a TEM grid, an extensive 3D hexagonal close-packed (hcp) superlattice was formed along the [002] direction (Figure 2). Very similar 3D-superlattice formation was observed in the case of cobalt nanorods.[6a] A high-magnification TEM image of the 3D superlattice array of Fe_2P nanorods revealed that an individual column was composed of at least four parallel nanorods (inset of Figure 2).

The formation of 1D nanorods seems to be caused by the cooperative effects resulting from the different binding capabilities of the two surfactants (TOP and oleylamine) and the intrinsically anisotropic hcp crystal structure of Fe_2P. To understand the role of the TOP surfactant in the growth of the nanorods, we systematically decreased the relative amount of TOP, while keeping all the other experimental parameters unchanged. When 8 mL of TOP (instead of 10 mL) was used in the synthesis, a mixture of products containing predominantly 5 × 70 nm-sized nanorods and a small amount of thicker 20 × 70 nm nanorods was generated.

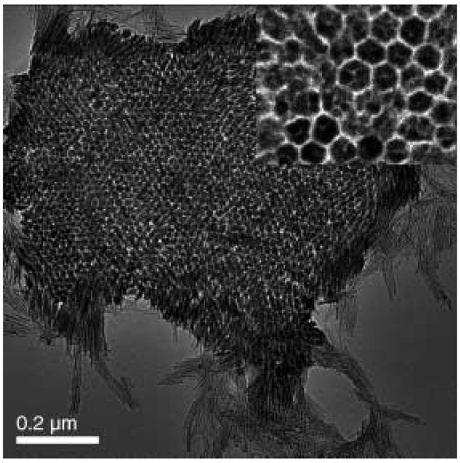

Figure 2. TEM image of self-assembled 5×88 nm nanorods with long-range order (inset: high-magnification TEM image of the 3D superlattice array of the Fe_2P nanorods).

When the amount of TOP in the stock solution was further decreased to 5 mL, near-spherical nanoparticles were generated (see Supporting Information). When less than 5 mL of TOP was used in the synthesis, an insoluble precipitate was deposited in the reaction vessel, due to extensive coalescence of the nanoparticles. The results demonstrate that a minimum amount of TOP is required for preferential growth along the [002] direction to occur from effective stabilization of the crystal faces perpendicular to the (002) plane.

Figure 3 shows the X-ray diffraction pattern of 5×88 nm Fe_2P nanorods. All of the diffraction peaks in the XRD pattern can be indexed with the hexagonal Fe_2P structure and no extra reflections were observed. Rietveld refinement of the XRD pattern also confirmed a hexagonal crystal structure with the space group $P\bar{6}2m$ (No. 189; see Supporting Information). It is well known that 1D nanocrystals grown along the [001] direction generally display 00*l* lines of maximum sharpness and wide *hk*0 reflections. The 002 reflection of the XRD pattern was sharpened, which indicated that growth of rod occurred along the *c* axis.

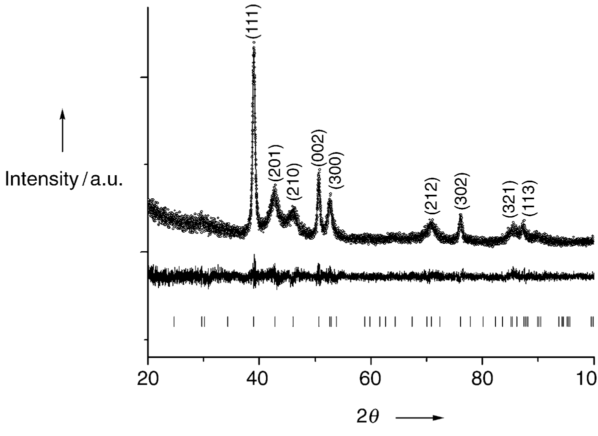

Figure 3. Observed, calculated, and difference XRD profiles for 5×88 nm Fe_2P nanorods using a Rietveld refinement.

We further tried to control the diameters of the nanorods by using different amine surfactants, since there have been few reports on the diameter-controlled synthesis of nanorods or nanowires.[13] When dioctylamine, octadecylamine, and hexadecylamine were used in the synthesis, with all the other reaction conditions remaining unchanged (injection rate = 10 mL h^{-1}), we were able to produce Fe_2P nanorods with sizes of 9×50, 18×75, and 5×160 nm, respectively (Figure 4).

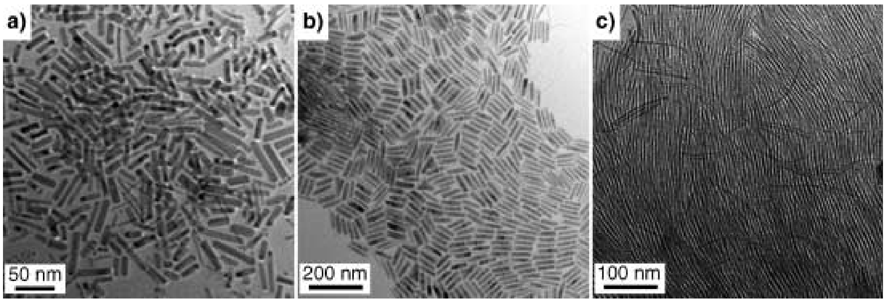

Figure 4. TEM images of nanorods obtained using a) dioctylamine; b) octadecylamine; c) hexadecylamine.

1D magnetic nanorods are expected to have a large magnetic anisotropy as a result of the anisotropy of their shape.[3,4,6] The temperature dependence of the magnetization was measured with zero-field-cooling (ZFC) and field-cooling (FC) procedures in an applied magnetic field of 100 Oe between 2 and 350 K using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS5XL). It was found that as the size of the samples increased, the blocking temperature increased and, at the same time, the coercive field value also increased, which is consistent with the Stoner–Wohlfarth theory on single-domain systems. The blocking temperatures are 120, 250, and 235 K for the 5×88, 6×107, and 6×290 nm samples, respectively (Figure 5). The data for the 6×290 nm sample was scaled down (by a factor of three) to allow a direct comparison of the data for all of the samples. We noted that the blocking temperature for the 6×110 nm sample was slightly higher than the bulk ferromagnetic transition temperature of Fe_2P ($T_c = 217$ K).[14] There are two possible reasons for this unusual observation: One possibility is that our sample might be richer in Fe than stoichiometric Fe_2P, or might even contain some pure Fe inside the nanorods. The other possibility for this enhancement may lie in the intrinsic effects of the Fe_2P nanorods. It is well known that the ferromagnetic transition of Fe_2P is very sensitive to variations in physical parameters, since it has strong ferromagnetic spin fluctuations, as observed by susceptibility and neutron scattering experiments.[14] On the other hand, energy dispersive X-ray spectroscopy (EDX) on the nanorods after removing the stabilizing surfactant revealed that the molar

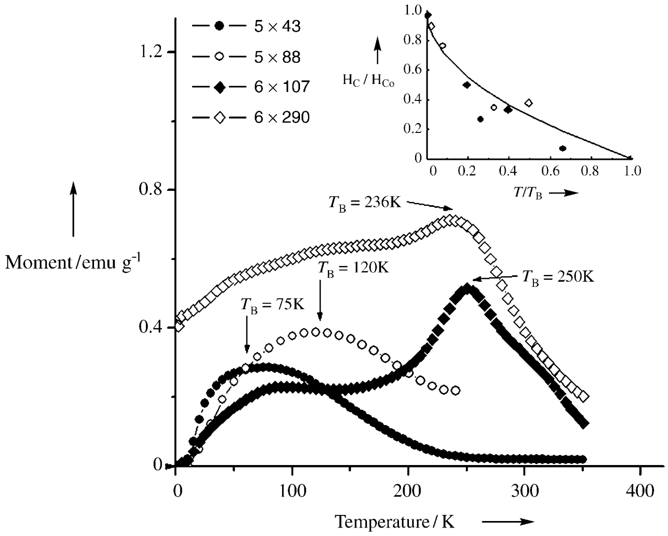

Figure 5. The temperature dependence of the ZFC magnetization for 5×43, 5×88, 6×107, and 6×290 nm nanorods. The arrows denote the blocking temperature for each sample. For the purpose of presentation, the data for the 6×290 nm nanorod was scaled down by a factor of three (inset: the normalized coercive field (Hc/Hc_0) as a function of normalized temperature (T/T_B) for each sample. The line is a theoretical curve for a single domain of fine particles).

ratio of Fe to P for all four different nanorods was higher than two, which implies the presence of pure iron in the nanorods. However, the pure iron phase or any other impurity was not observed in the high-resolution XRD pattern, as described previously. From these results, we conclude that a very small amount (less than 2% of the total volume, which is the resolution limit of the diffractometer used in the study) of pure iron or an Fe-rich phase (for example, Fe_3P; $T_c = 716$ K[15]) seems to be present in the nanorods. Another interesting point is the temperature dependence of the coercive field for the four different samples, as shown in the inset of Figure 5. The line in the inset is a theoretical curve for a single domain of fine particles: $Hc/Hc_0 = 1-(T/T_B)^{1/2}$, where Hc is the measured coercive field, Hc_0 is the estimated coercive field at $T = 0$ K, and T_B is the measured blocking temperature.[16] Although we acknowledge that the number of data points is rather small, it is fair to say that the temperature dependence of the measured coercive field for the four different samples can be reasonably explained by the simple theoretical curve representing a single domain of fine particles.

In summary, we have developed a new synthetic procedure for the production of magnetic Fe_2P nanorods with controllable sizes via the thermal decomposition of iron–phosphane complexes that are continuously delivered by using a syringe pump. The current synthetic procedure offers several very important features for the synthesis of 1D nanostructured materials. First of all, continuously delivering precursors with a syringe pump provides a new synthetic route for many other 1D nanostructured materials. Secondly, the size-controlled synthesis of 1D nanostructured materials has rarely been reported. With this technique, the diameters and lengths of the nanorods can be controlled by varying the experimental conditions, which is of great significance for their future applications, since the physical characteristics of the nanorods are highly dependent on their dimensions.

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