

Synthesis of Hollow Iron Nanoframes

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Magnetic nanocrystals have attracted tremendous attention from researchers in various disciplines, not only for fundamental size dependent magnetism but also for many technological applications.¹ In particular, magnetic nanoparticles with a hollow interior could find many biomedical applications. Most of hollow inorganic nanoparticles have been fabricated through template approaches.² Recently, hollow magnetic nanoparticles have been prepared directly through several synthetic strategies.³ In our continuous effort toward the designed synthesis of magnetic nanoparticles, we herein report on the synthesis of hollow iron nanoframes.

During the synthesis of iron nanocubes from the thermolysis of the Fe(II)-oleate complex,⁴ we noticed that solid nanocubes were sometimes transformed to hollow nanoframes. After many control experiments, we reasoned that residual sodium oleate was responsible for the formation of the nanoframes. We then systematically investigated the shape evolution during the thermolysis of the Fe(II)-stearate complex⁵ in the presence of sodium oleate. When iron(II) stearate (1.24 g, 2 mmol) dissolved in oleic acid (10 g) was heated to 380 °C with a heating rate of 5 °C·min⁻¹ and aged at that temperature for 2 h, uniform 23-nm-sized iron nanospheres with a slightly faceted shape were produced (Figure 1a). Electron diffraction, X-ray diffraction patterns, and high-resolution TEM (HRTEM) image revealed highly crystalline α -Fe structure with a very thin iron oxide layer on the surface (see Supporting Information (SI)). Various reducing agents, such as C, CO, and H₂, which were generated from the thermolysis of oleic acid, seemed to be responsible for the formation of metallic iron nanospheres.⁶ We adjusted the reaction temperature in between 300 and 400 °C, as the complete decomposition of oleic acid above 400 °C generated highly aggregated nanoparticles and oleic acid does not decompose below 300 °C.

Employing sodium oleate in the synthesis resulted in a remarkable change in the particle shape. When 0.1 g of sodium oleate was added to the above reactant mixture and heated at 380 °C for 1 h, 21-nm-sized nanocubes were generated (Figure 1b). Increasing the reaction time to 2 h resulted in primitive cubic structurelike nanoframes with an edge length of 21 nm (Figure 1c). HRTEM image (inset of Figure 1c) clearly showed their hollow interior. We employed long-chain erucic acid (CH₃(CH₂)₇CH=CH(CH₂)₁₁-COOH) to slow down the etching speed and consequently to get intermediate shaped nanocrystals. When 13 g of oleic acid and 2 g of erucic acid was used in the synthesis, 17-nm-sized nanocrystals with intermediate shape between solid nanocubes and hollow nanoframes were obtained (Figure 1d). Out-focused nanocrystals showed a thickness difference between their corners and centers, which is also evident in the HRTEM image (inset of Figure 1d). The (110) lattice in the HRTEM image showed that the nanocubes experienced (110)-facet selective etching. When the reaction mixture

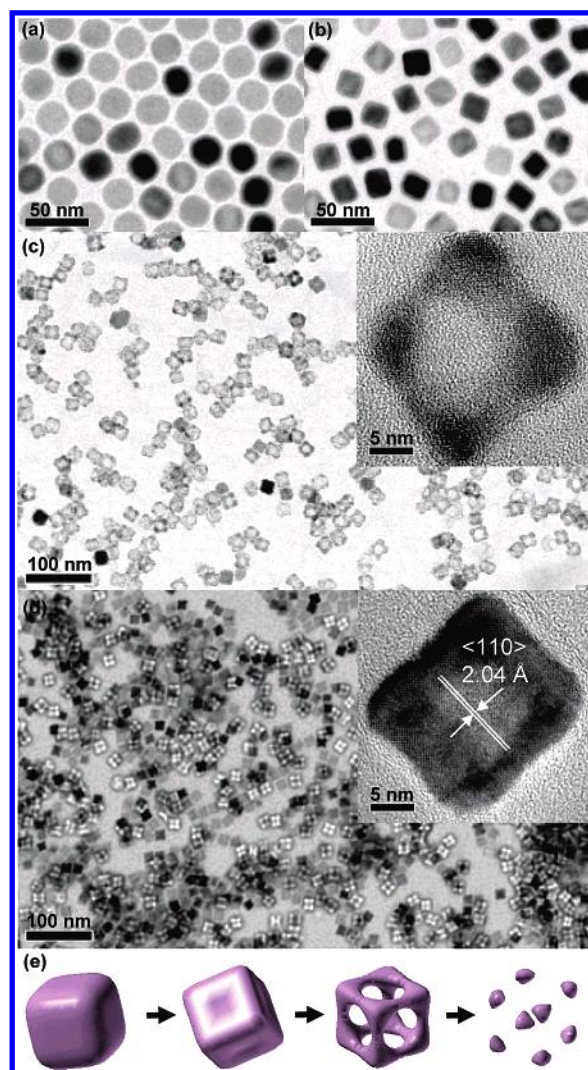


Figure 1. TEM images of the Fe nanoparticles: (a) 23-nm-sized nanospheres with slightly faceted shape; (b) 21-nm-sized solid nanocubes; (c) 21-nm-sized nanoframes (inset: HRTEM); (d) 17-nm-sized particles with intermediate shape between solid and hollow nanocubes (inset: HRTEM); (e) the overall shape evolution of the Fe nanoparticles.

was further aged at 380 °C for more than 3 h, small ~3 nm sized nanospheres, which originated from the dissociation of eight corners from the nanoframes, along with large particles of >50 nm were generated (Figure S4). The overall shape evolution is illustrated in Figure 1e.

We were able to control the dimensions of the nanoframes by varying the experimental conditions. For example, when an increased amount of oleic acid (15 g) was used, smaller 15-nm-sized nanoframes were obtained (Figure S5). When the heating rate

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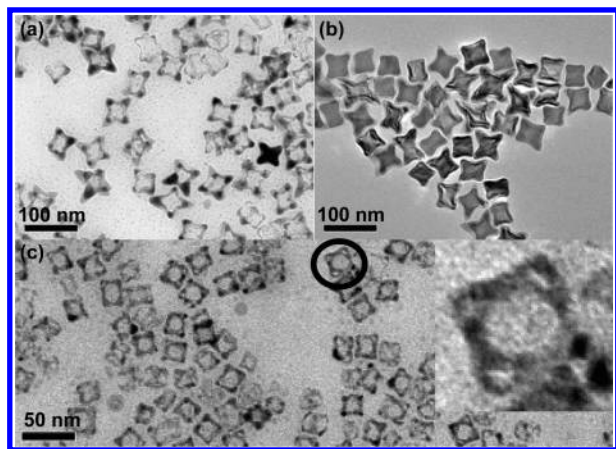


Figure 2. TEM images of (a) star-shaped hollow Fe nanoframes; (b) star-shaped solid Fe nanocubes; (c) oxidized nanoframes (inset: enlarged image).

was decreased to $2\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, larger star-shaped nanoframes ($>50\text{ nm}$) were generated (Figure 2a). On the other hand, when we performed the synthesis at this slow heating rate without using sodium oleate, similar-sized star-shaped solid Fe nanocubes were obtained, demonstrating that sodium oleate is critical for the formation of the nanoframes (Figure 2b).

We investigated the possible origin of the shape evolution. First of all, the Kirkendall effect⁷ does not seem to cause the formation of the nanoframes because neither inner island formation nor polycrystalline structure was observed in our current synthesis (Figure S6). Furthermore, oleate moiety in sodium oleate is not responsible for the formation of the hollow structure because the oleate moiety is also present in oleic acid, and the nanoframes can be obtained using sodium stearate. Therefore it is reasonable that the Na moiety in sodium oleate influenced the particle shape. Molten salt corrosion is assumed to be responsible for the etching of the Fe nanoparticles. Molten salts of Na (i.e., NaOH, Na_2O , etc.) are known to cause severe corrosion of metallic materials at high temperature, which is called “molten salt corrosion”.⁸ The corrosion can proceed continuously, as the corroded scale is soluble in the molten salt.^{8a} Sodium molten salts, which were derived from sodium oleate, seemed to bring about molten salt corrosion, leading to continuous etching of the Fe nanoparticles. Both the high reaction temperature and the byproducts from the decomposition of oleic acid might facilitate the formation of the molten salts, as it is known that Na species react with O_2 and H_2O to form molten salts at high temperature.^{8b} When we used NaOH (mp $322\text{ }^{\circ}\text{C}$) in the synthesis instead of sodium oleate, we were still able to produce Fe nanoframes (Figure S7). However, the reason that only (110) facet undergoes prominent etching is unclear yet. Presumably, adsorption or underpotential deposition⁹ of Na species might facilitate improved kinetics on Fe(110).

All the samples were readily oxidized when exposed to air. When we speed up the oxidation process by bubbling air in the solution containing the nanoframes, secondary hollowing process occurred at the corners of the nanoframes, probably through a mechanism similar to the Kirkendall effect⁷ (Figure 2c).

The temperature dependence of magnetization showed that all the samples exhibited blocking temperature higher than 380 K (Figure S8). However, as the nanocrystals became oxidized, a new transition at 120 K was observed, which could be attributed to the Verwey transition,¹⁰ indicating the presence of Fe_3O_4 . However, the coexistence of $\gamma\text{-Fe}_2\text{O}_3$ could not be excluded.¹¹ The nanoframes exhibited higher magnetization than that of the similar-sized solid nanospheres, conceivably caused by the increase of shape anisotropy.

However, detailed magnetic characterization was hampered by the rapid oxidation of the Fe nanocrystals.

In summary, we synthesized hollow Fe nanoframes from the thermal decomposition of the Fe(II)–stearate complex in the presence of sodium oleate and oleic acid. Sodium molten salts derived from sodium oleate seemed to be responsible for the formation of the nanoframes. The synthesized nanoframes are expected to be useful not only for the fundamental study on the nanoscale shape-dependent characteristics but also for many biomedical applications such as drug delivery.

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Supporting Information Available: Synthetic procedures, TEM, XRD, and SQUID data of the Fe nanocrystals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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