This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
A Solvothermal Transformation from α-Fe₂O₃ Nanocrystals to Fe₃O₄ Polyhedrons

Liqiao Chen, a,b,# Qingfeng Xiong, c Wenlin Li, c Junpeng Li, c and Xuan Yu a

High-dispersed Fe₃O₄ polyhedrons have been fabricated through a solvothermal transformation of α-Fe₂O₃ nanocrystals. The shapes, sizes, and surface characteristics of Fe₃O₄ polyhedrons can be facilely controlled. The growth route is confirmed as the process of "dissolution-reduction-recrystallization". The saturation magnetization of as-prepared Fe₃O₄ is up to 102.2 emu/g.

Magnetite (Fe₃O₄) is attracting growing interest due to its great potential for many useful applications, such as magnetic fluids 1 and microwave absorption,2 magnetic resonance imaging (MRI),3,4 drug delivery,5,6 catalytic and lithium storage properties.6,7 In recent years, micro- and nanoparticles for Fe₃O₄ with specific facets attracted considerable attention due to their abundant size- and shape-dependent physical and chemical properties.8,9 In addition, surface characteristics of Fe₃O₄ strongly affect its properties and applications.10,11

As we know, fabrications of monodisperse Fe₃O₄ particles are often difficult due to its strong magnetism, especially for micrometer size Fe₃O₄ crystals, the as-obtained products are often with aggregation and wide size distribution even in the present of surfactants or complexing agents.12,13 In order to obtain high quality Fe₃O₄ crystals and prevent the aggregation of particles,13 metal–organic iron precursor such as Fe(acac)₃ or Fe(CO)₅ are usually used, and / or designed the reaction in an organic medium, such as EG, oleic acid,6,8,10,14 which increase the costs and bring off environmental issue, also render the surface of as-obtained samples be dirty. The dirty surfaces affect its properties and bring some difficulty for subsequent remove or surface modification.15

In addition, from a phase transformation viewpoint, Fe₃O₄ also can be obtained by reducing of Fe₂O₃ or oxidizing of Fe elemental. Fe₂O₃ nanoparticles are also synthesized by reduction phase transformation from γ-Fe₂O₃ nanoparticles in organic solvent.16 Microsized Fe₃O₄ with peanutlike morphology is successfully prepared from FeCO₃ with the same morphology via direct-sealed thermal decomposition.17 Zhang etc. researched structural evolution and characteristics of the phase transformations between α-Fe₂O₃, Fe₂O₃ and γ-Fe₂O₃ nanoparticles under reducing and oxidizing atmospheres.18 All the processes adopted a solid phase reaction under high-temperature, and many defects and impurities inevitably existed in the as-obtained crystals through these routes.

Herein, we find a novel solvothermal route to synthesize Fe₃O₄ polyhedrons through adopting only two reagents (See ESI†). That is α-Fe₂O₃ nanocrystals19 can transform into Fe₃O₄ only in present of N₂H₄-H₂O (See ESI†), and no any other agent, surfactant and additive is brought. The detail condition is listed as table 1.

Table 1. The experimental condition synthesized Fe₃O₄ polyhedrons

<table>
<thead>
<tr>
<th>Sample 1#</th>
<th>Precursor</th>
<th>N₂H₄-H₂O</th>
<th>Water</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe₂O₃ nanoparticles</td>
<td>4 mL</td>
<td>2 mL</td>
<td>220 °C</td>
<td></td>
</tr>
<tr>
<td>Sample 2#</td>
<td>α-Fe₂O₃ nanoparticles</td>
<td>4 mL</td>
<td>2 mL</td>
<td>220 °C</td>
</tr>
<tr>
<td>Sample 3#</td>
<td>α-Fe₂O₃ nanoparticles</td>
<td>4 mL</td>
<td>2 mL</td>
<td>180 °C</td>
</tr>
<tr>
<td>Sample 4#</td>
<td>α-Fe₂O₃ nanoparticles</td>
<td>4 mL</td>
<td>no</td>
<td>220 °C</td>
</tr>
<tr>
<td>Sample 5#</td>
<td>α-Fe₂O₃ nanoparticles</td>
<td>4 mL</td>
<td>4 mL</td>
<td>220 °C</td>
</tr>
</tbody>
</table>

The powder X-ray diffraction patterns (pXRD) of as-synthesized Sample 1# in Figure 1a match well with JCPDS card No. 89-3854 for cubic Fe₃O₄ with a = b = c = 8.395 nm, confirming that all of products are cubic-structure iron oxide. However, it is difficult to distinguish the γ-Fe₂O₃ and Fe₂O₃ phases only from the XRD patterns due to their similarity. X-ray photoelectron spectroscopy

P. R. China. E-mail:chenq118@126.com; Tel: +86 580 2262589.

State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China.

State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals, Kunming Institute of Precious Metal, Kunming 650106, P. R. China.

Electronic Supplementary Information (ESI) available: Experimental Section, pXRD and SEM image of α-Fe₂O₃ nanoplates and nanoparticles were used as the precursor to synthesize Fe₃O₄ polyhedrons. See DOI: 10.1039/xx000000x

This journal is © The Royal Society of Chemistry 20xx

CrystEngComm, 20XX, XX, X-X | X
(XPS) analysis (Figure 1b) was carried out to further ascertain the phase of the synthesized typical sample 1#. The binding energies relating to Fe 2p$^{1/2}$ and Fe 2p$^{3/2}$ are about 710.8, 725.2 eV, respectively, no satellite peak between the peaks of Fe 2p$^{1/2}$ and Fe 2p$^{3/2}$ are observed, indicating that the as-synthesized sample is composed of Fe$_3$O$_4$, which are in good agreement with those of Fe$_3$O$_4$ reported in the literature.$^{20}$ Therefore, XPS results also confirm the structure and phase of as-synthesized Fe$_3$O$_4$ products. The atom ratio of the product is determined as Fe (35.51%), O (64.49%) using XPS analysis. The oxygen content is higher than that of both Fe$_3$O$_4$ and α-Fe$_2$O$_3$. On one hand, it is probably because oxygen atoms are as the terminal atom layer for iron oxide crystals, which results in a higher oxygen detecting value near to the crystals’ surfaces, on the other hand, it is also because the clean surfaces easily adsorb oxygen in the air. From the SEM image in Figure 1c, we can see that the product consists of highly dispersed decahedral microcrystals and the sizes of crystals are about 5 μm with narrow size distribution. The selected area electron diffraction (SAED) pattern, High-resolution transmission electron microscopy (HRTEM) and corresponding fast Fourier transformation (FFT) image verify that the as synthesized sample is cubic phase of structure, and the regular SAED patterns and clear Lattice fringes show the as-obtained powders are with high crystallinity (Figure 1d, 1e, 1f).

Further, other experiments were operated to study the size tune and shape evolution of Fe$_3$O$_4$ crystals by controlling some facile experimental conditions. Herein, the effect of α-Fe$_2$O$_3$ precursor was firstly studied. Interestingly, the sizes of Fe$_3$O$_4$ decahedrons reduce to about 2.5 μm when α-Fe$_2$O$_3$ nanoparticles (See ESI†, figure S1b) are chosen as precursor (figure 2a). As our previous report and the following discussion, the side surface edges α-Fe$_2$O$_3$ nanoparticles gradually redissolve and “a mass transport” takes place to change into nanoparticles, which show the α-Fe$_2$O$_3$ nanoparticles easier to redissolve during solvothermal process than its nanoparticles. Herein, we speculate that the fast growth rate results in the formation of the small sizes of Fe$_3$O$_4$ decahedrons because the quick redissolving rates of the platy α-Fe$_2$O$_3$ could fast the growth rates of Fe$_3$O$_4$ polyhedrons. So the sizes of Fe$_3$O$_4$ polyhedrons can be controlled by very facile method in this route. The shape of Fe$_3$O$_4$ polyhedrons can change from decahedron into octahedron in the aging temperature low to 180 °C (figure 2b). As we all know, Fe$_3$O$_4$ octahedrons surrounded by eight (111) facets, and dodecahedral crystals are exposing the {110} basal surfaces. The growth rate of crystals will slow when the reaction temperature decrease from 220 °C to 180 °C, which favours the forming of low energy octahedron morphology. Specially, the surface smoothness of Fe$_3$O$_4$ polyhedrons is different if the aging happen at the different concentration of N$_2$H$_4$·H$_2$O. The surfaces of Fe$_3$O$_4$ decahedrons are rough (figure 2c) at the high concentration of N$_2$H$_4$·H$_2$O, and their surfaces are smooth and the edge profiles are clear (figure 2d) at the low concentration of N$_2$H$_4$·H$_2$O as the reaction medium. The experimental results show that, even in the absence of any surfactants and other additives, the shapes, sizes, and surface characteristics of Fe$_3$O$_4$ polyhedrons can facilely control through adopting the route designed in this paper.

![Figure 1. pXRD (a), Fe 2p XPS (b), SEM image (c), TEM (d), SAED pattern from the white square in figure 1d (e), HRTEM and FFT (f) of the as-obtained sample 1# of Fe$_3$O$_4$ crystals.](image)

![Figure 2. SEM images of the Fe$_3$O$_4$ polyhedrons obtained in different condition, (a) sample 2#, (b) sample 3#, (c) sample 4#, (d) sample 5#.](image)
To find out growth mechanism on this interesting evolution route, Herein, the growth process of this route was continuously monitored through collecting the samples from the different curing times, and the phase and morphology were characterized by pXRD. SEM and TEM (figure 3, figure 4).

At reaction times of 1 h, the X-ray diffraction patterns of as-obtained powders are similar to that of α-Fe₂O₃ precursor, and all peaks indexed to a rhombohedral α-Fe₂O₃ (PDF#No.33-0664) without any Fe₃O₄ peaks (figure 3). At reaction times of 2 h, pXRD peaks almost be indexed to the cubic phase of Fe₃O₄ and only weak diffraction peaks of α-Fe₂O₃ can be indexed (marked as "**"), which shows cubic phase of Fe₃O₄ have grown at this time. Prolong the reaction times to 6 h, the diffraction peaks of the cubic Fe₃O₄ are very strong and all of the diffraction peaks indexed α-Fe₂O₃ cannot be identified in figure 3. This indicates there is no α-Fe₂O₃ nanoparticle in the collected sample, or their contents are too low to be detected by XRD method, also maybe some exist as amorphous phase.

![Diffraction Patterns](image)

Figure 3. pXRDs of samples obtained at different aging time, the bars are from JCPDS Card No. 89-3854 for spinel structured Fe₃O₄ and No. 33-0664 for α-Fe₂O₃ diffraction peaks.

Seen from SEM and TEM (inset) image in Figure 4a, 4b, the structures of the particles after aging 1 h almost have no difference with α-Fe₂O₃ precursors (Figure 5a), but some micrometer size of products begin to appear, which should be the as-synthesized Fe₃O₄ particles. Some nanoparticles become smaller and the microparticles turn into regular polyhedrons when the reaction times prolong to 2 h (figure 4c, 4d). Prolong the reaction times to 6 h, it is difficult to find out the nanoparticles in the low magnification SEM images (figure 4f), although some nanoparticles can still be “fortunately” found in a certain place in high-magnification SEM image, and their sizes almost reduce to less 10 nm. The TEM image further identifies that the sample is composed from some little nanocrystals (figure 4e (inset)). To further clarify the shapes and structures of the products, HRTEM and FFT are implemented and the results are shown in figure 4g, 4h. The diffraction pattern of the small nanoparticle is indexed as α-Fe₂O₃. According to these experiment results that α-Fe₂O₃ precursors gradually get small and till completely disappear, herein, we can speculate that the graduate dissolving process of α-Fe₂O₃ precursors should exist in the synthesizing route of Fe₃O₄ polyhedrons.

![Structures](image)

Figure 4. The structures of samples obtained at different aging times, high-magnification SEM image and TEM (inset) (a) 1 h, (c) 2 h, (e) 6 h, low-magnification SEM image, (b) 1 h, (d) 2 h, (f) 6 h. HRTEM (g) from the zone of white square in figure 4e and FFT (h).

The dissolving process of α-Fe₂O₃ precursors can also be further demonstrated according to our previous experimental phenomenon. Therein, the as-synthesized nanoparticles (Figure 5a) was added to 10 mL of distilled water. After aging at 180 °C for 7 days, the resultant nanocrystals appear with quite different final shapes (Figure 5b). The edges of the nanoparticles after aging tend to be round, the nanoparticles themselves tend to be thicker, and the diameters tend to be smaller (Figure 5b). We proposed that there is a mass transport from side surfaces to basal surfaces. That is, the side surfaces gradually dissolved and the mass was gradually transported to the basal top (or bottom) (0001) surfaces during the aging stage in water. The results also support our statement about...
dissolving phenomenon of α-Fe₃O₄ precursors.

Figure 5. SEM image of α-Fe₃O₄ nanopltes, before aging (a), and after aging (b) at 180 °C for 7 days in the water.

So, in this paper, it can be speculated that partly Fe (III) from the dissolving of α-Fe₃O₄ nanoparticles is reduced by N₂H₂·H₂O into Fe (II) during "a mass transformation", then recrystallize into cubic Fe₃O₄ particles. Xu etc. fabricated 50-facet Fe₃O₄ polyhedron through FeCl₃·6H₂O as precursor, and they speculated the formation of Fe₃O₄ particles through the reduction of the possible intermediate phase of Fe₂O₃·H₂O nucleation of the Fe₃O₄ nuclei and oriented aggregation of the primary nanocrystals. Our experimental phenomena clearly confirm the transformation ways as "dissolving of α-Fe₃O₄ phase-reduction-recrystallization" process. In this route, the growth of crystal is much slower than traditional precipitation methods, so it is favorable to form regular polyhedral shapes. From a crystallographic viewpoint, Fe₃O₄ has a cubic inverse spinel structure with oxygen anions forming a face-centered-cubic (FCC) close-packed structure. As a FCC crystal, a general sequence of surface energies may hold, γ(111) < γ(100) < γ(110), which indicates that the Fe₃O₄ crystals usually exist with {111} lattice planes as the basal surfaces. So the regular octahedron surrounded by eight {111} facets is easy to be obtained through this route. Usually, some high-energy polyhedron morphology can be obtained under some severe conditions. In this paper, the strong and high concentration reducing agent, along with high temperature can provide a severe reducing environment, which result in the existing of high-energy Fe₃O₄ decahedrons.

Finally, the magnetic properties of iron oxide nanocrystals were conducted at 300 K. Figure 6a, 6b shows the hysteresis loops of the samples of α-Fe₃O₄ nanopltes and nanoparticles. The weak ferromagnetic behaves and the effects of shape anisotropy on magnetic property have been discussed in our precious paper. Figure 6c, 6d shows the magnetic hysteresis loop of Fe₃O₄ decahedrons (Samples 1#) and octahedrons (Samples 3#) at 300 K. It can be found that both of the samples are ferromagnetic despite small coercivities (Hc) and remanent fields (Mr). The saturation magnetization (Ms), remanent magnetization (Mr), and coercivity (Hc) of the as-prepared Fe₃O₄ decahedrons are 95.6 emu/g, 9.63 emu/g and 86.9 Oe, respectively. Accordingly, the three values of Fe₃O₄ octahedrons are 102.2 emu/g, 2.17 emu/g and 14.3 Oe, respectively. The low coercivities imply that the as-synthesized Fe₃O₄ nanoparticles are soft magnets. Interestingly, the saturation magnetization of both samples is higher than that (84.5 emu/g) of commercial magnefine powder and those reported Fe₃O₄ micro-octahedrons. The great increase suggests the as-grown Fe₃O₄ nanocrystals possess high magnetic moment, which should benefit from the increase of magnetic moment as a result of the noncollinear spin structure originated from the pinning of the surface spins and the clean surface. The values of Hc and Mr increase from 14.3 to 86.9 Oe, and from 2.17 to 9.63 emu/g, respectively as the particle shapes change from decahedrons to octahedrons, which might be as the result of their stronger magnetic anisotropy. The magnetic properties of materials are influenced by many factors, not only size, also crystallinity, surface structure, and so on. However, the higher saturation magnetizations for these two samples make this route deserve to further study and explore their possible industrial applications.

Figure 6. Magnetization-hysteresis (M-H) loops of α-Fe₃O₄ precursors (a) nanopltes, (b) nanoparticles, and as-prepared Fe₃O₄ samples (c) Samples 1#, (d) Samples 3#. The inset is the enlarged ones in the range of -0.3 and 0.3 KOe.

In conclusion, we adopted α-Fe₃O₄ as precursor to realize the growth of Fe₃O₄ polyhedrons. The transformation process from Fe₃O₄ to cubic Fe₃O₄ is confirmed through "dissolution-reduction-recrystallization". The reaction system in this method is simple and the as-obtained samples are dispersed with a clean surface due to only the addition of hydrazine hydrate, without any other surfactants or reagents. This route not only provides the convenience for the research of growth mechanism, also provides a practical method to controllably prepare high quality iron oxides and some other iron-based compounds. Fe₃O₄ polyhedrons obtained through this route show very high saturation magnetization.
This work is financially supported by National Natural Science Foundation of China (No. 51261008).

Notes and references