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Surface-dependent magnetic behavior of $\alpha$-Fe$_2$O$_3$ quasi-cubes induced by Mg$^{2+}$ ions

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Uniform $\alpha$-Fe$_2$O$_3$ quasi-cubes with high-index facets exposed were controlled synthesized through a simple hydrothermal method by Mg$^{2+}$ ions as structure-directing agents. The as-prepared $\alpha$-Fe$_2$O$_3$ quasi-cubes are bound by (012), (10-2), and (1-12) facets with edge length of about 200 nm and dihedral angel of 86°. In the reaction system, Mg$^{2+}$ ions would undertake the structure and surface director and adsorbed to $\alpha$-Fe$_2$O$_3$ high energy surface and induce $\alpha$-Fe$_2$O$_3$ nanoparticles to grow into quasi-cubic nanocrystals bound by high-index facets. Magnetic measurements testify that the quasi-cubes display surface-dependent magnetic behavior. The $\alpha$-Fe$_2$O$_3$ quasi-cubes have a splitting between FC curve and ZFC curve from the highest experimental temperature to lowest temperature and no Morin transformation occurs, indicating that they would be defect ferromagnetic control both at room temperature and low temperature.

Introduction

Surface status plays an important role in many physical and chemical processes such as heterogeneous catalysis, photo-catalysis, electrochemically catalysis, magnetic properties and gas sensing.[1-5] Until now, many efforts have been pay out to synthetize and study different exposed facets of micro/nano-materials. For example, Sun and coworkers certified that the single-crystal tetrahedral Pt nanocrystals enclosed by 24 high-index unusual facets such as {730}, {210}, and/or {520} surfaces show enhanced catalytic activity in electro-oxidation of small organic fuels of combustion.[6] Magnetic properties and gas sensing.[7] However, according to thermodynamics,[8] several species in the growth environment would play an important role during the crystal growth, therefore bring the additive to the reaction system may be an efficient method to prepare high-indexed facets exposed nanomaterials. Until now the most used additives are halogen ions, surfactants and support substrate,[9] there are few reports about the metal ions in controlling the shape and surface of nanomaterials.[10]

Hematite $\alpha$-Fe$_2$O$_3$ nanocrystals have been widely used in photo-, electro- and chemo-catalysis, magnetic devices, gas sensors, water splitting, supercapacitors and Li-ion batteries due to their excellent physical-chemical properties and low cost.[11-13] Diverse shape and morphology of iron oxide nanocrystals such as wires,[14] tubes,[15] rings,[16] rods,[17] disks,[18] polyhedrons,[19] dendrites,[20] hollow spheres,[21] and urchin-like structures[22] were successfully synthesized. The surface status of $\alpha$-Fe$_2$O$_3$ is very sensitive to the reaction systems and it is very difficult to obtain $\alpha$-Fe$_2$O$_3$ particles encased by high-index facets. Up to now, the reports about high-index facets exposed $\alpha$-Fe$_2$O$_3$ are very few. Yin et al prepared high-index facets exposed tetrakaidecahedra and oblique parallelepipeds $\alpha$-Fe$_2$O$_3$ using sodium carboxymethyl cellulose as structure-directing agents,[7] Lv et al synthesized a highly symmetric hexagonal bipyramidal dodecahedral structure enclosed by (101) crystal planes, an octododecahedral structure enclosed by (101) and (111) planes according to the concentration of F anions.[21]
Wu et al. synthesized \( \alpha\)-Fe\(_2\)O\(_3\) oblique and truncated nanocubes through a facile one-step solvothermal method in the presence of oleylamine, acetylacetone and oleic acid.\(^{125}\) Liu et al. have synthesized different shape and high-index facets exposed \( \alpha\)-Fe\(_2\)O\(_3\) nanocrystals using metal ions (Zn\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Al\(^{3+}\)) as structure-inducing agents.\(^{4,10,26}\) In this study, \( \alpha\)-Fe\(_2\)O\(_3\) quasi-cubes with high-index facets exposed were controlled synthesized by using metal ions Mg\(^{2+}\) as structure-directing agents through hydrothermally treated. The quasi-cubes looks like a cube but with the dihedral angle of about 86° bound by (012), (10-2), and (1-12) facets. Magnetic measurements testify that the \( \alpha\)-Fe\(_2\)O\(_3\) quasi-cubes show surface-dependent magnetic behavior. The \( \alpha\)-Fe\(_2\)O\(_3\) quasi-cubes have a splitting between FC curve and ZFC curve from the highest experimental temperature to lowest temperature and no Morin transformation occurs, indicating that they would be defect ferromagnetic control at room temperature and low temperature.

**Experimental Section**

In a typical procedure, the starting solution was prepared by mixing 0.05 g of magnesium chloride (Analytically pure) with 10 mL of 0.2 M Fe(NO\(_3\))\(_3\) solution under magnetic stirring. Then 10 mL of ammonia solution (25 %, analytically pure) was dropwise added. After 10 min of stirring, the mixture was transferred to a 50 mL Teflon-lined autoclave and sealed in it, kept at 160 °C for 48 h, and finally cooled to room temperature naturally. The product was collected by centrifugation (6000 rpm, 1 min), washed alternately by deionized water and ethanol, and dried in air under ambient conditions.

**Characterizations:** Scanning electron microscopy (SEM) characterizations were performed on Hitachi S-4800 at 5 kV. Transmission electron microscopy (TEM) images and high resolution transmissiom electron microscope (HRTEM) were obtained using a FEI Tecnai G2 F30 S-TWIN transmission electron microscope operating at 300 kV. Powder X-ray diffraction (XRD) patterns were collected using a Bruker D8 ADVANCE diffractometer with Cu K\(\alpha\) radiation (\(\lambda = 1.5406 \text{ Å}\)) at 40 kV. X-ray photoelectron spectroscopy (XPS) was collected on a PHI 5000 VersaProbe X-ray photoelectron spectrometer, using monochromatized Al Ka X-ray as excitation source. The binding energies were corrected for specimen charging by calibrating the C1s peak to 284.6 eV. Magnetic measurements were performed on a Quantum Design MPMS-XL-7T SQUID magnetometer with a maximum magnetic field of 30 kOe and the magnetic field reached up to 7 T.

**Results and discussion,**

The sample controlled by Mg\(^{2+}\) was prepared by hydrothermally treating the mixture of Fe(NO\(_3\))\(_3\) and ammonium solution with metal salts of MgCl\(_2\). Fig. 1 presents XRD pattern of the as-prepared sample. All the diffraction peaks can be indexed to the hexagonal phase of \( \alpha\)-Fe\(_2\)O\(_3\) (JCPDS 84-0311) and no characteristic peaks of impurities can be detected, indicating that relatively pure \( \alpha\)-Fe\(_2\)O\(_3\) product was got under the synthetic conditions. Because the synthesis system has Mg element, XPS was used to identify the content of Mg element, Fig. 2a demonstrated the spectra of the sample presence of Fe, Mg and O elements. The high resolution XPS spectra shown in Fig. 2b give the binding energies of Mg1s corresponding to 1303 eV with very weak intensity. Fig. 2c presents the binding energies of Fe2p3/2 and Fe2p1/2 corresponding to 710.9 and 724.2 eV with a with shakeup satellite at \(-719\) eV, characteristic of Fe\(^{3+}\) in \( \alpha\)-Fe\(_2\)O\(_3\). The peak of O1s at 528.6 eV is characteristics of oxygen in metal oxide, and the other at around 530.5 eV is assigned to crystal defect oxygen. Fe2p and O1s peak with strong intensity. The atomic concentrations of O1s, Fe2p and Mg1s obtained by XPS are 49.53%, 23.70% and 0 respectively, which indicate maybe there are very few Mg elements and below XPS detection limit, therefore it can’t detect Mg element in the sample and the \( \alpha\)-Fe\(_2\)O\(_3\) product controlled by Mg\(^{2+}\) ions is relatively pure \( \alpha\)-Fe\(_2\)O\(_3\) powder. In this reaction system, Mg\(^{2+}\) ions may be just as structure-directing agents.

Fig. 3a-c show scanning electron microscope (SEM) and transmission electron microscope (TEM) images of
the obtained $\alpha$-$\text{Fe}_2\text{O}_3$ sample controlled by $\text{Mg}^{2+}$ ions. As shown in Fig. 3a and b, the majority of the sample is quasi-cubes with edge length of about 200 nm. From the high-magnification SEM images shown in Fig. 3c, it can be seen that these quasi-cubes have dihedral angle of 86°. Fig. 3d-f show the sample's TEM images and HRTEM image with SAED pattern. The TEM images also confirmed that majority of the obtained sample has quasi-cubic shape with edge length of about 200 nm and dihedral angle of 86°. The HRTEM image shows two groups of facets with dihedral angle of 86° and both have the crystal plane spacing of about 3.7 Å, corresponding to be (012) and (10-2) planes of hexagonal phase $\alpha$-$\text{Fe}_2\text{O}_3$, respectively. Similar results can be obtained from the SAED pattern. Thus, the HRTEM image of the $\alpha$-$\text{Fe}_2\text{O}_3$ quasi-cubes is projected from the [2-21] zone axis of a single crystal of hexagonal phase $\alpha$-$\text{Fe}_2\text{O}_3$ and the other surface could be deduced to be (1-12).

As ethylenediamine is similar to ammonium solution, which also can as basic source to react with $\text{Fe}^{3+}$ for $\alpha$-$\text{Fe}_2\text{O}_3$ nanoparticles synthesis and $\text{Mg}^{2+}$ ions can’t precipitate in ethylenediamine solution, so in another system, ethylenediamine take the place of ammonium solution, as shown in Fig. 4, the as-synthesized sample is also quasi-cubes with edge

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Fig. 2 XPS spectra of the obtained sample.

Fig. 3 (a-c) SEM images, (d, e) TEM images, (f) HRTEM image and SAED pattern (inset) of the obtained sample.
length of about 200 nm have dihedral angle near 90° and XRD pattern shows it is the hexagonal phase of α-Fe$_2$O$_3$ (JCPDS 84-0311).

In the reaction system, Mg$^{2+}$ ions may be the reason for the formation of α-Fe$_2$O$_3$ quasi-cubes bound by high-index facets. Without the addition of MgCl$_2$, when only the mixture of Fe(NO$_3$)$_3$ and ammonium solution was hydrothermally treated, as shown in Fig. 5a and b, only irregular α-Fe$_2$O$_3$ particles can be obtained. Without the addition of MgCl$_2$, when the mixture of Fe(NO$_3$)$_3$ and ethylenediamine solution was hydrothermally treated, as shown in Fig. 5c and d, only α-Fe$_2$O$_3$ nanorods can be obtained. When Mg(NO$_3$)$_2$ substituted for MgCl$_2$, the obtained product is also α-Fe$_2$O$_3$ quasi-cubes as shown in Fig. 6. These results confirm that the existence of Mg$^{2+}$ ions are the main reason for the growth of α-Fe$_2$O$_3$ nanocubes with high-index facets exposed but not the anions (Cl$^-$/NO$_3^-$).

For further investigating the growth mechanism of quasi-cubes, experiments under different times have been carried out. Fig. 7 shows the SEM images and XRD patterns under different reaction time. When the reaction time is 1 h, there are only many unformed MgFe$_2$O$_4$ nanoparticles (Fig. 7d), which indicate at the first time the MgFe$_2$O$_4$ nanoparticles emerged (Fig. 7a). As time going, MgFe$_2$O$_4$ can react with excessive ammonium solution to form α-Fe$_2$O$_3$ and Mg$^{2+}$ ions in ammonium salt solution, Fig. 6b displays there are cubic nanocrystals form when time is 2h, XRD pattern shows there are MgFe$_2$O$_4$ and α-Fe$_2$O$_3$ exist. In this system, α-Fe$_2$O$_3$ nanocrystals were cubic form and with high-index faced exposed as shown in Fig. 3, MgFe$_2$O$_4$ nanoparticles were irregular form. Time going to 24 h, there are almost all cubic nanocrystals and α-Fe$_2$O$_3$ component. In the reaction system, metal ions would undertake the structure and surface director. It would be adsorbed to α-Fe$_2$O$_3$ high energy surface and induce α-Fe$_2$O$_3$ nanoparticles to grow into quasi-cubic nanocrystals bound by high-index facets. Based on these experimental results, we proposed a possible growth mechanism for the formation of α-Fe$_2$O$_3$ quasi-cubes as shown in Scheme 1 (Electronic Supplementary Information).

As known, the properties of nanomaterials depend greatly on the morphology and surface environment. In this work, we provide a probability to study the magnetic properties and the electro-catalytic activity of the high-index facet exposed α-Fe$_2$O$_3$ quasi-cubes controlled by Mg$^{2+}$ ions. Bulk α-Fe$_2$O$_3$ powders, with Morin transition temperature ($T_M$) of ca. 263 K, show parasitic ferromagnetism at room temperature and anti-ferromagnetism at low temperature.$^{[4]}$ Fig. 8a shows the magnetization-temperature curves (field-cooled under 100 Oe (FC) and zero-field-cooled (ZFC))
of the $\alpha$-Fe$_2$O$_3$ quasi-cubes. There is a splitting between FC and ZFC curves from the highest experimental temperature (300 K) to low temperature (2 K), suggesting that some spontaneous small magnetons maybe exist over the entire temperature range. The expected sharp drop at the Morin transition temperature does not occur, indicating that the $\alpha$-Fe$_2$O$_3$ quasi-cubes do not undergo a process like Morin transition with the temperature decreasing. According to the previous report, the magnetism of $\alpha$-Fe$_2$O$_3$ nanocrystals are intrinsic spin-canted ferromagnetism control and defect ferromagnetism control. The spin-canted ferromagnetism would undergo Morin transition to anti-ferromagnetic ordered state, while defect ferromagnetism is sensitive to structure and is changed with stress or heat and suppresses the Morin transition.\textsuperscript{[4, 7, 27]} The FC-ZFC curves in Fig. 8a suggest that unlike the bulk $\alpha$-Fe$_2$O$_3$ powders, the $\alpha$-Fe$_2$O$_3$ quasi-cubes are ferromagnetism at room temperature and low temperature, might be defect ferromagnetic control both at room temperature and low temperature. It can be assumed that the surface status of the $\alpha$-Fe$_2$O$_3$ quasi-cubes exposed by high-index facets with high energy in favor of the magnetons to maintain the spontaneous magnetization even at low temperature. To better study the magnetic behaviors of the $\alpha$-Fe$_2$O$_3$ quasi-cubes, Fig. 8b and c show the isothermal magnetic hysteresis measurements conducted at room temperature (300 K) and low temperature (2 K) with the field sweeping from -30 to 30 kOe. The magnetic behaviors of the $\alpha$-Fe$_2$O$_3$ quasi-cubes have a loop both at 300 K (Fig. 8b) and 2 K (Fig. 8c). The $\alpha$-Fe$_2$O$_3$ quasi-cubes is in a weak ferromagnetic state at 300 K with a coercive field of approximately 350 Oe and a remanent magnetization of $8.2 \times 10^{-2}$ emu·g$^{-1}$, and 2 K is also in a weak ferromagnetic state with a coercive field of approximately 1500 Oe and a remanent magnetization of $7.7 \times 10^{-2}$ emu·g$^{-1}$, consistent with that from the FC-ZFC curves. Although to reach a clear conclusion requires further investigations, the $\alpha$-Fe$_2$O$_3$ quasi-cubes might be defect ferromagnetic both at room temperature and low temperature.
Conclusions

In summary, \(\alpha\)-Fe\(_2\)O\(_3\) quasi-cubes with high-index facets exposed were controlled synthesized by Mg\(^{2+}\) ions as structure-directing agents. The quasi-cubes with the angle of about 86\(^\circ\) bound by (012), (10-2), and (1-12) facets. Magnetic measurements testify that the quasi-cubes display surface-dependent magnetic behavior. The \(\alpha\)-Fe\(_2\)O\(_3\) quasi-cubes have a splitting between FC curve and ZFC curve from the highest experimental temperature to low temperature and no Morin transformation occurs, indicating that they would be defect ferromagnetic control both at room temperature and low temperature.

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Notes and references


High-index facets exposed $\alpha$-Fe$_2$O$_3$ quasi-cubes were controlled synthesized by Mg$^{2+}$ ions, which show surface-dependent magnetic behavior.