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Journal Name

ARTICLE

Surface-dependent magnetic behavior of α -Fe₂O₃ quasi-cubes induced by Mg²⁺ ions

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Uniform α -Fe₂O₃ quasi-cubes with high-index facets exposed were controlled synthesized through a simple hydrothermal method by Mg²⁺ ions as structure-directing agents. The as-prepared α -Fe₂O₃ quasi-cubes are bound by (012), (10-2), and (1-12) facets with edge length of about 200 nm and dihedral angle of 86°. In the reaction system, Mg²⁺ ions would undertake the structure and surface director and adsorbed to α -Fe₂O₃ high energy surface and induce α -Fe₂O₃ 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 α -Fe₂O₃ 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 synthesize 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 formic acid and ethanol.^[3] Li and coworkers demonstrated that the unusually high-index {112} crystal planes of Co₃O₄ nanosheets are more reactive than the basic {001} planes of Co₃O₄ nanocubes and {011} planes of Co₃O₄ nanobelts for methane combustion.^[1] However, according to thermodynamics principles, during the crystal growth, high-index facets usually have fast growth rates and ultimately disappear while low-index facets can exist for its slow growth rates. So it's really a big challenge for scientists to synthesize nanocrystals bound by high-index facets. Up

to now, many efforts have been made to synthesize nanomaterials bound by high-index facets. Since the 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,^[6-9] there are few reports about the metal ions in controlling the shape and surface of nanostructures.^[10,11]

Hematite α -Fe₂O₃ 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.^[12-15] Diverse shape and morphology of iron oxide nanocrystals such as wires,^[16] tubes,^[17] rings,^[18] rods,^[19] disks,^[20] polyhedrons,^[21] dendrites,^[22] hollow spheres,^[23] and urchin-like structures^[24] were successfully synthesized. The surface status of α -Fe₂O₃ is very sensitive to the reaction systems and it is very difficult to obtain α -Fe₂O₃ particles enclosed by high-index facets. Up to now, the reports about high-index facets exposed α -Fe₂O₃ are very few. Yin *et. al* prepared high-index facets exposed tetrakaidehedra and oblique parallelepiped α -Fe₂O₃ 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 octodecahedral structure enclosed by (101) and (111) planes according to the concentration of F⁻ anions.^[21]

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Wu *et. al.* synthesized α -Fe₂O₃ oblique and truncated nanocubes through a facile one-step solvothermal method in the presence of oleylamine, acetylacetone and oleic acid.^[25] Liu *et. al.* have synthesized different shape and high-index facets exposed α -Fe₂O₃ nanocrystals using metal ions (Zn²⁺, Cu²⁺, Ni²⁺, Al³⁺) as structure-inducing agents.^[4,10,26] In this study, α -Fe₂O₃ quasi-cubes with high-index facets exposed were controlled synthesized by using metal ions Mg²⁺ 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 α -Fe₂O₃ quasi-cubes show surface-dependent magnetic behavior. The α -Fe₂O₃ 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(NO₃)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 transmission 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 α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV. X-ray photoelectron spectroscopy (XPS) was collected on a PHI 5000 VersaProbe X-ray photoelectron spectrometer, using monochromatized Al K α 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 Mg²⁺ was prepared by hydrothermally treating the mixture of Fe(NO₃)₃ and ammonium solution with metal salts of MgCl₂. Fig. 1 presents XRD pattern of the as-prepared sample. All the diffraction peaks can be indexed to the hexagonal phase of α -Fe₂O₃ (JCPDS 84-0311) and no characteristic peaks of impurities can be detected, indicating that relatively pure α -Fe₂O₃ 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 Fe2p_{3/2} and Fe2p_{1/2} corresponding to 710.9 and 724.2 eV with a shakeup satellite at ~ 719 eV, characteristic of Fe³⁺ in α -Fe₂O₃. 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 α -Fe₂O₃ product controlled by Mg²⁺ ions is relatively pure α -Fe₂O₃ powder. In this reaction system, Mg²⁺ ions may be just as structure-directing agents.

Fig. 3a-c show scanning electron microscope (SEM) and transmission electron microscope (TEM) images of

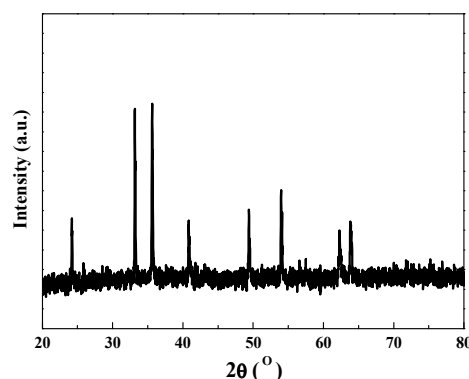


Fig. 1 XRD pattern of the obtained sample.

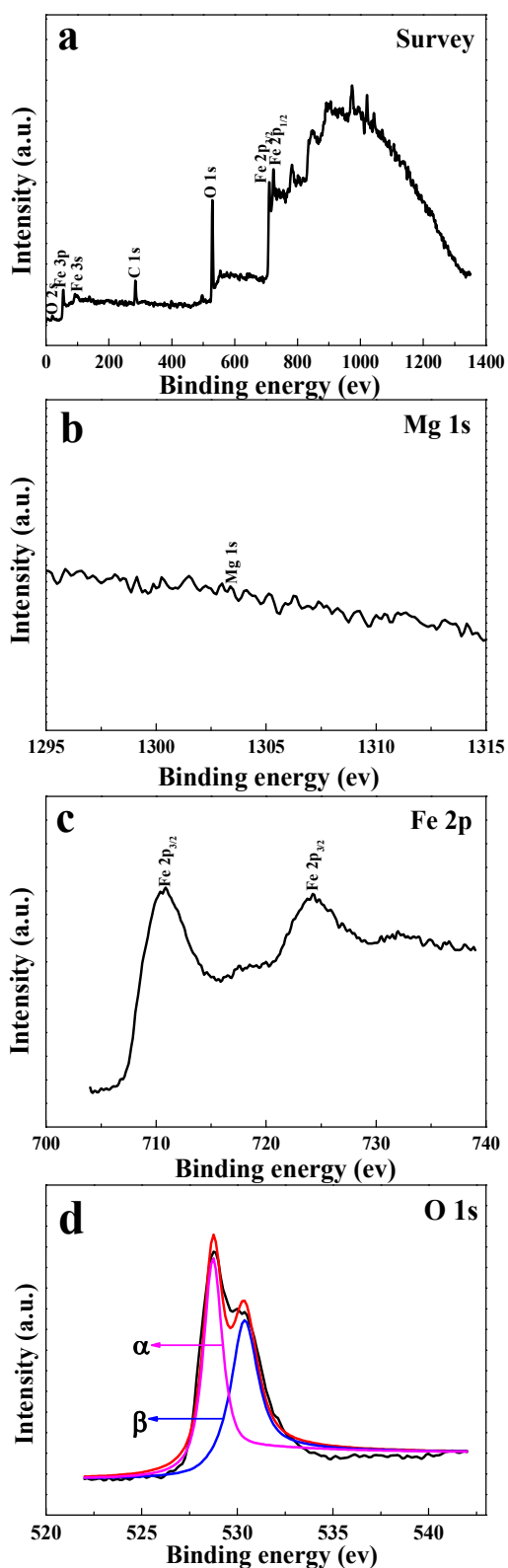


Fig. 2 XPS spectra of the obtained sample.

the obtained α -Fe₂O₃ sample controlled by Mg²⁺ 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 α -Fe₂O₃, respectively. Similar results can be obtained from the SAED pattern. Thus, the HRTEM image of the α -Fe₂O₃ quasi-cubes is projected from the [2-21] zone axis of a single crystal of hexagonal phase α -Fe₂O₃ 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 Fe³⁺ for α -Fe₂O₃ nanoparticles synthesis and Mg²⁺ ions can't precipitate in ethylenediamine solution, so in another one system, ethylenediamine take the place of ammonium solution, as shown in Fig. 4, the as-synthesized sample is also quasi-cubes with edge

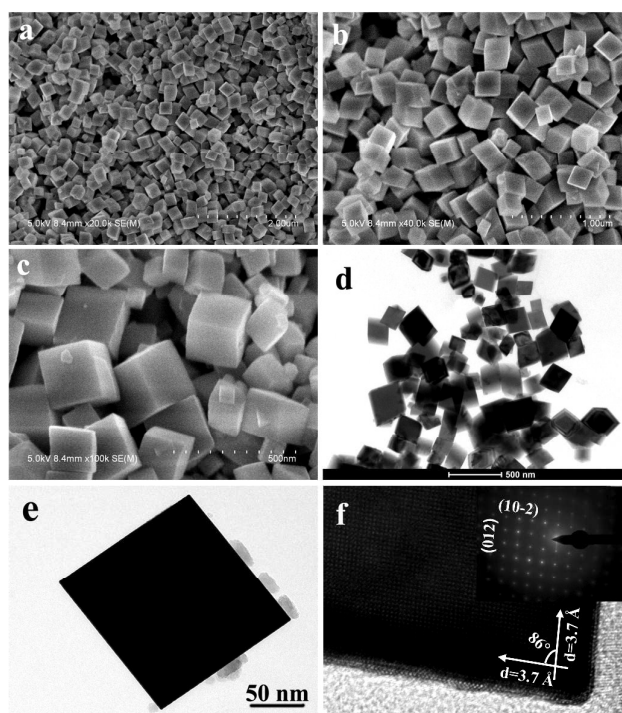


Fig. 3 (a-c) SEM images, (d, e) TEM images, (f) HRTEM image and SAED pattern (inset) of the obtained sample.

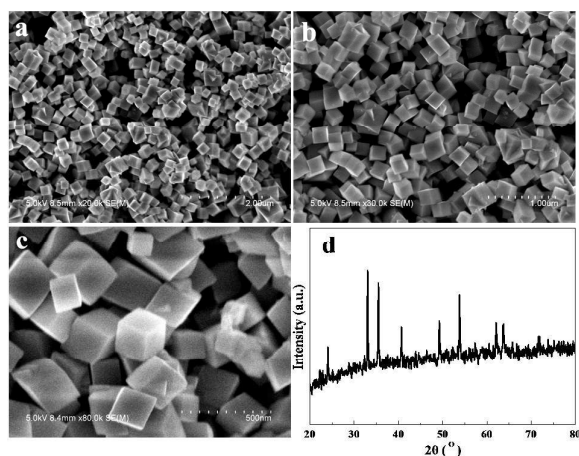


Fig. 4 (a-c) SEM images, (d) XRD pattern of the sample using ethylenediamine as basic source.

length of about 200 nm have dihedral angle near 90° and XRD pattern shows it is the hexagonal phase of $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS 84-0311).

In the reaction system, Mg^{2+} ions may be the reason for the formation of $\alpha\text{-Fe}_2\text{O}_3$ quasi-cubes bound by high-index facets. Without the addition of MgCl_2 , when only the mixture of $\text{Fe}(\text{NO}_3)_3$ and ammonium solution was hydrothermally treated, as shown in Fig. 5a and b, only irregular $\alpha\text{-Fe}_2\text{O}_3$ particles can be obtained. Without the addition of MgCl_2 , when the mixture of $\text{Fe}(\text{NO}_3)_3$ and ethylenediamine solution was hydrothermally treated, as shown in Fig. 5c and d, only $\alpha\text{-Fe}_2\text{O}_3$ nanorods can be obtained. When $\text{Mg}(\text{NO}_3)_2$ substituted for MgCl_2 , the obtained product is also $\alpha\text{-Fe}_2\text{O}_3$ 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 $\alpha\text{-Fe}_2\text{O}_3$ nanocubes with high-index facets exposed but not the anions (Cl^- or 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_2O_4 nanoparticles (Fig. 7d), which indicate at the first time the MgFe_2O_4 nanoparticles emerged (Fig. 7a). As time going, MgFe_2O_4 can react with excessive ammonium solution to form $\alpha\text{-Fe}_2\text{O}_3$ 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_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$ exist. In this system, $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals were cubic form and with high-index faced exposed as shown in Fig. 3, MgFe_2O_4 nanoparticles were irregular form. Time going to 24h,

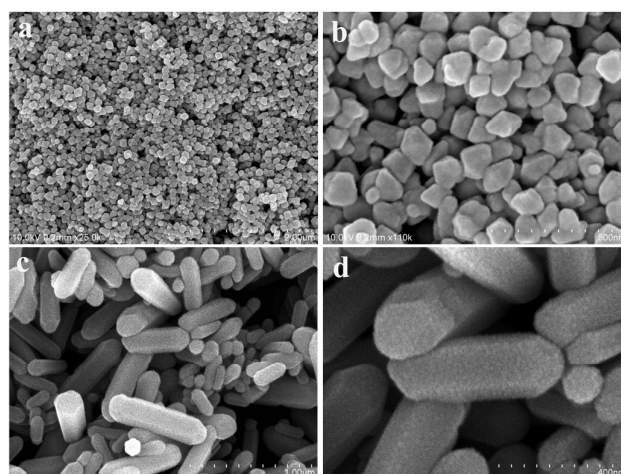


Fig. 5 SEM images of the $\alpha\text{-Fe}_2\text{O}_3$ crystals prepared without the addition of Mg^{2+} ions using different basic source (a, b) ammonia, (c, d) ethylenediamine.

there are almost all cubic nanocrystals and $\alpha\text{-Fe}_2\text{O}_3$ component. In the reaction system, metal ions would undertake the structure and surface director. It would be adsorbed to $\alpha\text{-Fe}_2\text{O}_3$ high energy surface and induce $\alpha\text{-Fe}_2\text{O}_3$ 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 $\alpha\text{-Fe}_2\text{O}_3$ 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 $\alpha\text{-Fe}_2\text{O}_3$ quasi-cubes controlled by Mg^{2+} ions. Bulk $\alpha\text{-Fe}_2\text{O}_3$ 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))

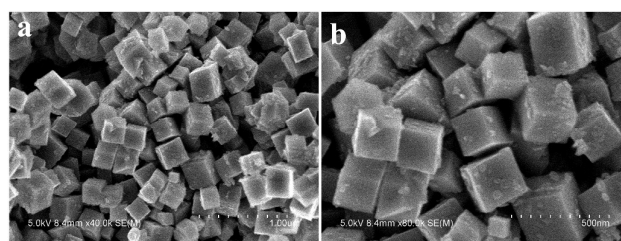


Fig. 6 (a) low magnification SEM image and (b) high magnification SEM image of the sample controlled by different Mg^{2+} ion source $\text{Mg}(\text{NO}_3)_2$.

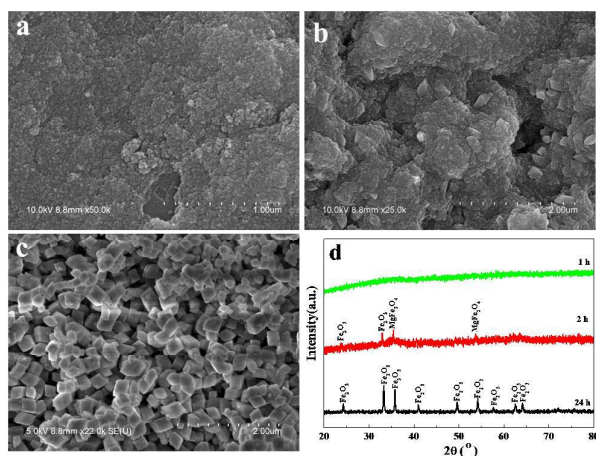


Fig. 7 SEM images (a) 1 h, (b) 2 h, (c) 24 h, and (d) XRD patterns of the samples prepared under hydrothermal conditions at 160 °C for different times.

of the α - Fe_2O_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 α - Fe_2O_3 quasi-cubes do not undergo a process like Morin transition with the temperature decreasing. According to the previous report, the magnetism of α - Fe_2O_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.^[4, 7, 27] The FC-ZFC curves in Fig. 8a suggest that unlike the bulk α - Fe_2O_3 powders, the α - Fe_2O_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 α - Fe_2O_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 α - Fe_2O_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 α - Fe_2O_3 quasi-cubes have a loop both at 300 K (Fig. 8b) and 2 K (Fig. 8c). The α - Fe_2O_3 quasi-cubes is in a weak ferromagnetic

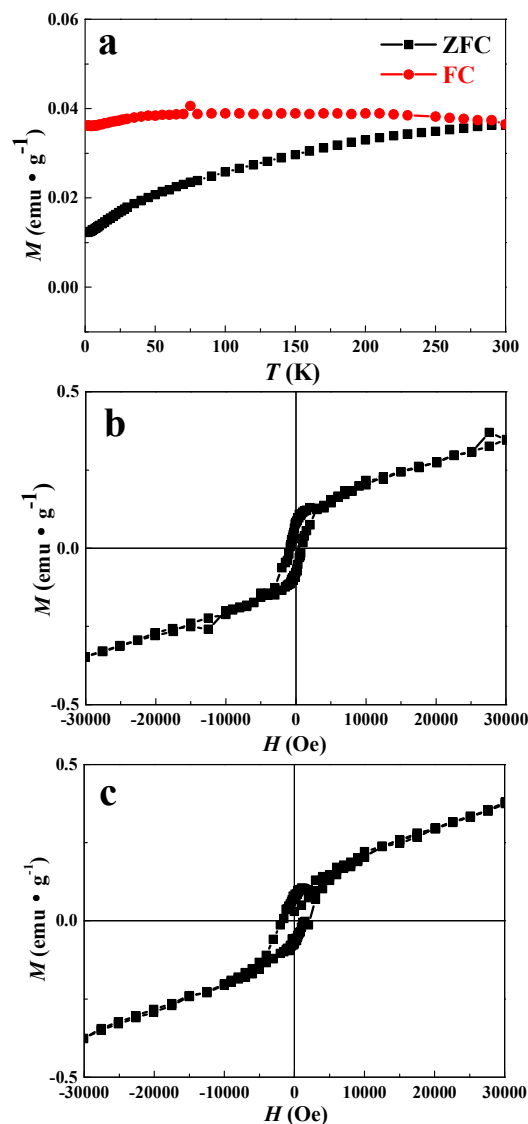


Fig. 8 (a) ZFC/FC and (b, c) M - H curves at 300 K and 2 K of the α - Fe_2O_3 quasi-cubes controlled by Mg^{2+} ions.

state at 300 K with a coercive field of approximately 350 Oe and a remanent magnetization of $8.2 \times 10^{-2} \text{ emu} \cdot \text{g}^{-1}$, and 2 K is also in a weak ferromagnetic state with a coercive field of approximately 1500 Oe and a remanent magnetization of $7.7 \times 10^{-2} \text{ emu} \cdot \text{g}^{-1}$, consistent with that from the FC-ZFC curves. Although to reach a clear conclusion requires further investigations, the α - Fe_2O_3 quasi-cubes might be defect ferromagnetic both at room temperature and low temperature.

Conclusions

In summary, α -Fe₂O₃ quasi-cubes with high-index facets exposed were controlled synthesized by Mg²⁺ ions as structure-directing agents. The quasi-cubes with the angle of about 86° bound by (012), (10-2), and (1-12) facets. Magnetic measurements testify that the quasi-cubes display surface-dependent magnetic behavior. The α -Fe₂O₃ 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.

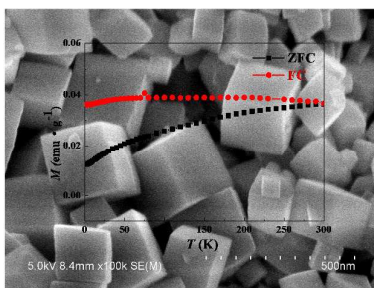
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Colour graphic:



High-index facets exposed α -Fe₂O₃ quasi-cubes were controlled synthesized by Mg²⁺ ions, which show surface-dependent magnetic behavior.