Preparation and Magnetic Properties of Parallelepiped α-Fe₂O₃ Nanoparticles

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ABSTRACT: Parallelepiped α-Fe₂O₃ nanoparticles with a narrow size distribution were was successfully synthesized by hydrothermal method. The structural and morphological properties of α-Fe₂O₃ nanoparticles were characterized by X-ray diffract meter (XRD), Scanning electron microscope (SEM), and transmission electron micrograph (TEM). The magnetic behavior of the Parallelepiped α-Fe₂O₃ nanoparticles was investigated, the results showed that The parallelepiped nanoparticles possessed the lower remanent magnetization and coercivity than other α-Fe₂O₃ particles with similar size, indicating its potential application in superparamagnetic materials.

1 INTRODUCTION

As an important and thermodynamically stable crystallographic phase of iron oxide, α-Fe₂O₃ has been widely used in commercial and industrial applications, including pigments [1], catalysts, purification [2], magnetic materials [3], sensors [4], lithium ion battery [5], solar energy conversion and water splitting [6]. Many efforts have been focused on the controllable preparation of α-Fe₂O₃ nanoparticles with various geometries and exposed surfaces, due to the properties of the α-Fe₂O₃ crystals are largely determined by external exposed surfaces. For example, the tetrakaiadekahedral α-Fe₂O₃ nanoparticles which bound by (012), (102) and (001) facets disappear ferromagnetism at temperatures lower than Tm [7]. In order to synthesis α-Fe₂O₃ nanocrystals with different morphologies and different exposed facets, the choice of appropriate adsorption ions or ligands was shown to be the most important for controlling the exposed surface as well as the crystal shape of the obtained nanocrystals. Usually, organic polymers which are soluble under normal temperature and pressure are chosen as adsorption and disperser reagent for the preparation of α-Fe₂O₃ with different morphologies, such as tetrabutylammonium bromide (TBAB), polyvinylpyrrolidone (PVP) [8] and sodium carboxymethyl cellulose (CMC) [7]. The influence of organic compounds and oxygen vinyl polymers on α-Fe₂O₃ particles morphologies were systematically investigated by Kandori etc [9, 10]. Meanwhile, inorganic anions with selective adsorption capability were also used to change the growth behavior of α-Fe₂O₃ particles, such as Wang obtained α-Fe₂O₃ dendritic micro-pines with the growth along six crystallographically equivalent [100] directions in the presence of CN⁻ [11]. Jia described that the shape of the α-Fe₂O₃ nanorings is mainly regulated by the adsorption of H₂PO₄⁻ ions on faces parallel to [001] direction during the nanocrystal growth, and the hollow structure is given by the preferential dissolution of the α-Fe₂O₃ along the [001] direction due to the strong coordination of the SO₄²⁻ ions [12]. The magnetic property of above mentioned (100), (001), (101) and (102) planes were tested, and the influence of adsorption ions or ligands on above low surface energy facet were investigated. However, few reports were referred to adsorption ions or ligands which influence α-Fe₂O₃ morphologies on (104) facet, and special magnetic property and sensing capacity of parallelepiped α-Fe₂O₃ which only exposed (104) facet was not still reported.

In the present work, we described a simply method to produce highly-dispersed parallelepiped α-Fe₂O₃ which exposed only by (104) facet, and their special magnetic property was investigated. We used triphenylphosphine to prepare α-Fe₂O₃ without soluble organic agents and dispersants added. At high temperature and pressure, the triphenylphosphine obviously had the coordination and dispersion effect for the formation of α-Fe₂O₃ particles. The as-synthesized α-Fe₂O₃ showed lower remanent magnetization and coercivity than others which were reported in literatures [13, 14].
2 EXPERIMENTAL

All chemicals were analytical grade and used without further purification. A typical experiment was as follows: 9.0×10^{-2} mM triphenylphosphine was added to an 80 mL aqueous solution of 9.0×10^{-1} mM FeCl_3·6H_2O under stirring, keeping the molar ratio of triphenylphosphine to Fe^{3+} was 10%. The solution was subsequently transferred into a 100 mL autoclave, sealed, and maintained at 220 °C for 24 h. After that, the autoclave was cooled to room temperature gradually. The red precipitates were collected by centrifugation, and then washed with deionized water and ethanol in an ultrasonic bath. The cycle was repeated three times, and finally dried in a desiccator at 60 °C for 4 h. the morphology comparative experiments were similar to the procedure described above except for the molar ratio of triphenylphosphine to Fe^{3+} was changed to 0%, 2.5%, 5%, and 20%.

X-ray powder diffraction (XRD) spectrum of the products was acquired by a Philips X’Pert PRO SUPER X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation (λ= 1.5418 Å). Morphology of the sample was examined by scanning electron microscopy (SEM, X-650) and transmission electron micrograph (TEM, Hitachi H-600). Selected area electron diffraction (SAED) patterns were obtained on high-resolution transmission electron microscope (HRTEM, JEOL-2010). Magnetic hysteresis loops of the samples were measured by superconducting quantum interference device (SQUID, MPMS-XL5).

3 RESULTS AND DISCUSSION

The size and morphology of the parallelepipied α-Fe_2O_3 particles which obtained at 10 mol% triphenylphosphine were examined by SEM and TEM (Fig. 2). Seen from Fig.2a, the sample consists of more than 80% parallelepipided nanoparticles with a narrow size distribution. It seems like there are three kinds of particles could be observed in Fig.2b,2c and 2d. Fig. 2b shows the particle of rhombus shape, in which the obtuse angle is about 115° and the length of each edge is about 60 nm. Fig. 2c shows a hexagonal particle with equal edge length. Fig. 2d illustrates the different situation from Fig. 2b and 2c. Actually, only one kind of particles exists in these images, i.e. parallelepipided particles. Three kinds of particles present in the TEM images because of the different orientations of the particles, and the corresponding inset in each figure show the detailed situation. Similar phenomena also can be found in some other literatures, for instance nanodisks of Cu and CuS [15, 16]. On the basis of above SEM and TEM analysis, it can conclude that most of the α-Fe_2O_3 particles are of parallelepipded shape, which have six same rhombic faces with obtuse angle is about 115° and the length of each size is near 60 nm.

Figure 1. XRD patterns of the product formed with 10 mol% triphenylphosphine.

Fig.1 shows the XRD patterns of the product synthesized by the typical experiment, seen from which the characteristic peaks are consistent with the standard data of the parallelepipded α-Fe_2O_3 (JCPDS 33-0664). The strong and sharp diffraction peaks mean the high crystallinity of the products.

Figure 2. SEM and TEM images of rhombohedral α-Fe_2O_3 particles obtain with 10 mol% triphenylphosphine.

Figure 3. Morphologies of rhombohedral α-Fe_2O_3 particles by HRTEM, the inset of (a) is SAED pattern.

HRTEM was used to provide more information about the microstructure and morphology of the parallelepipded α-Fe_2O_3 particles. Fig. 3a shows a typical parallelepipded α-Fe_2O_3 particle and its corresponding SAED patterns (inset of Fig. 3a). The
diffraction spots can be attributed to (110), (0-14), (104) planes and/or their equivalent planes under the incident electron beam along the [-441] direction. Besides, the sharp diffraction spots also reveal the single crystalline nature of the synthesized particle. Fig. 3b displays the HRTEM image of the obtuse corner of parallelepiped particle. The lattice spacing are 0.251 nm, 0.269 nm and 0.269 nm, which agree well with (110), (104) and (0-14) planes, respectively. The angle in the bottom of particle is 115.8° (Fig. 3a), which is very close to the angle between (104) and (0-14) crystal planes (115.2°). The angle value and particle edge image confirm that the side facets are parallel to the (104) and (0-14) crystal planes, which fit well with the results from the SAED pattern (inset of Fig.3a). According to the SAED analysis, the incident electron beam is [-441] projection, thereby the surface parallel to the background should be (-114) plane on the basis of reciprocity law. That is to say, the rhombohedra particles have three equivalent planes and these three facets all belong to the {104} family.

In the α-Fe₂O₃ shape evolution process, the ratio of ligands to precursor played the most important role [17]. To better understand the formation and shape evolution processes of the synthesized parallelepiped α-Fe₂O₃ nanoparticles, different molar ratio of triphenylphosphine to Fe³⁺ ions had been investigated. The morphologies of corresponding products were investigated by SEM in Fig. 4. Without adding triphenylphosphine, the distribution of particles was irregular and seriously aggregative (Fig. 4a), and the grain size was 100 nm~200 nm. When the amount of triphenylphosphine was 2.5 mol%, well dispersed spherical particles were obtained in Fig. 4b, and the particle size was reduced to around 60 nm. With increasing the triphenylphosphine to 5 mol%, the shape of the product changed from sphere to polyhedron (Fig. 4c). Fig. 2a shows a typical SEM image of α-Fe₂O₃ particles, which was obtained by increasing the amount of triphenylphosphine to 10 mol%. It can be seen that the uniform parallelepiped α-Fe₂O₃ nanoparticles with a narrow size distribution have formed. Further increasing the amount of triphenylphosphine to 20 mol% (Fig. 4d), the particles shape was still parallelepiped but the particle size became irregular (40-70 nm).

On the basis of above-mentioned SEM results, it can be concluded that the shape and size of α-Fe₂O₃ nanoparticles varied obviously with the concentration of triphenylphosphine. The effects are as follow: first, it is well known that the triphenylphosphine molecule has a phosphorus atom and three benzene rings. The phosphorus atom can provide isolated pair of electrons to coordinate with positive ion. The surface of α-Fe₂O₃ particles is covered by adsorbed hydroxyl in solution, and the (104) plane possesses the highest hydroxyl density of 5.3 nm⁻², including singly, doubly and triply coordinated hydroxyl groups [18]. When synthesized parallelepiped α-Fe₂O₃ nanoparticles in acid solution (pH=2.7), these hydroxyls are protonated and most active with phosphorus atom to adsorption. The adsorption capacity and density is bigger on (104) than on other planes, which restrain the crystal growth along [014] and lead to particle surface enclosed by {104} family facet. Besides, when triphenylphosphine was adsorbed on the surface of α-Fe₂O₃ particles, the effect of steric hindrance and electron cloud on the three benzene rings will prevent crystal from getting close to each other. This leads to the well dispersion of the synthesized parallelepiped α-Fe₂O₃ nanoparticles. At last, adsorption and dispersion effects are coexistence, but the main effect changed from adsorption to dispersion with the increase of triphenylphosphine, and the morphology of particles is transferred from aggregated particles to smaller nanocrystals. It reveals that the particle shape strongly depends on the triphenylphosphine adsorption onto α-Fe₂O₃ particles.

Because of the role of anisotropy in magnetism, the shape of magnetic materials is a crucial factor in affecting their magnetic behavior [19]. It is worthy to note that the particles in Fig. 2a and Fig. 4b have different shape, while the particles in Fig. 4b and Fig. 4d are different in size. Therefore, the magnetic hysteresis measurements of the three
Typical α-Fe$_2$O$_3$ particles were carried out to investigate the effects of particle size and morphology on the α-Fe$_2$O$_3$ magnetic properties (Fig. 5). Fig. 5a, 5b and 5c present the hysteresis loops of spherical, parallelepiped and un-uniform parallelepiped α-Fe$_2$O$_3$ particles, which are shown in Fig. 2a, Fig. 4b, and Fig. 4d respectively. In these curves, no saturation of the magnetization as a function of the field is observed up to the maximum applied magnetic field for all three samples. The magnetizations at the maximum applied magnetic field of 1 T (Mmax) are 0.45, 0.48, and 0.47 emu/g, respectively. The uniform parallelepiped α-Fe$_2$O$_3$ nanoparticles which enclosed by (104) plane have lower coercivity than other α-Fe$_2$O$_3$ particles and the corresponding coercivities are 549.60 Oe, 2.05 Oe and 13.87 Oe (inset table of Fig. 5), respectively. The uniform parallelepiped α-Fe$_2$O$_3$ nanoparticles which enclosed by (104) plane have lower coercivity than other α-Fe$_2$O$_3$ particles, and also possess better paramagnetic properties than bulk α-Fe$_2$O$_3$ (0.11 emu/g) or smaller α-Fe$_2$O$_3$ nanoparticles (8.70×10$^{-3}$ emu/g) at 300 K [20]. It is known that the coercivity depends on several possible factors, including crystallinity, size, structure, surface disorder, morphologies, etc. The lower remanent magnetization and coercivity of parallelepiped α-Fe$_2$O$_3$ particles may be attributed to the six equivalent exposed (104) plane surfaces, which improve them to magnetizing in directions along their easy magnetic axes [21]. In addition, well dispersion particles have more single domain than multidomain, which can also decrease remanence and coercivity [22].

4 CONCLUSIONS

In summary, parallelepiped α-Fe$_2$O$_3$ nanoparticles with a narrow size distribution (60 nm) were synthesized, and the uniform nanoparticles were encosed by six equivalent (104) planes. The influence of triphenylphosphine on the morphology of α-Fe$_2$O$_3$ nanocrystals and their magnetic properties was studied. Triphenylphosphine played multiple roles and acted as both coordinating and structure-directing agent in the synthesis process. Magnetic hysteresis measurements demonstrated that the α-Fe$_2$O$_3$ nanostructures showed structure-dependent magnetic properties. The parallelepiped particles with (104) facet had a very lower Mr and Hc compared with other α-Fe$_2$O$_3$ products of similar size, and indicating its potential application in superparamagnetic materials.

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REFERENCES