Research Article

Facile Synthesis and Special Phase Transformation of Hydrophilic Iron Oxides Nanoparticles

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Superparamagnetic iron oxide nanoparticles (SPIONs), γ -Fe₂O₃, with hydrophilic surfaces are fabricated in ethylene glycol solutions, without surfactant or additive, by solvothermal process from α -Fe₂O₃ nanoparticle as precursors. With the addition of a trace of hydrazine hydrate, the cubic phase Fe₃O₄ nanoparticles are obtained instead of γ -Fe₂O₃. The saturation magnetization value of γ -Fe₂O₃ nanoparticles is up to 74.3 emu/g. This study provides a low cost, safe, and universal route to serve as excellent biocompatibility magnetic core for future applications in biomedical, agriculture, and horticulture applications.

1. Introduction

Superparamagnetic iron oxide nanoparticles (SPIONs) attracted increasing attention due to their promising applications like tissue cryopreservation, magnetic resonance imaging (MRI), immunoassay, biomolecule separation, hyperthermia, and drug delivery [1–4]. All of these biomedical applications require the nanoparticles to have high magnetization values and hydrophilic surface and also nontoxicity and biocompatibility [5, 6].

Until now, various wet chemical processes such as coprecipitation, sol-gel, hydrothermal/solvothermal, thermal decomposition, electrochemical strategy, and ultrasonic chemistry have been extensively applied to prepare superparamagnetic nanoparticles [7–10]. Among these routes, different surfactants, such as oleic acid, are introduced to prevent the aggregation of nanoparticles; also toxic reagents such as Fe(III) glucuronate, Fe(acac)₃, or Fe(CO)₅ are usually used, which render the surface of as-obtained samples to be nonbiocompatible, and obstructed the further surface modification [4, 8, 11, 12].

Benefiting from previous study [13], we find a novel route to synthesize superparamagnetic iron oxide nanoparticles through α -Fe₂O₃ nanoparticles as precursor in this study, only in presence of ethylene glycol, without the presence of any other agents, surfactants, and additives. Herein, nanoscale γ -Fe₂O₃ particles were obtained using a smaller

particle size of α -Fe₂O₃ as precursors and the mild ethylene glycol as a solvent. This study provides excellent biocompatibility magnetic core for applications in biomedical, agriculture, and horticulture applications.

2. Experimental

α -Fe₂O₃ precursors were synthesized by the modified solvothermal method as previously reported [13]: 0.273 g of FeCl₃·6H₂O (0.1 mmol) was dissolved under vigorous magnetic stirring in ethanol (10.0 mL) and 2 mL of deionized water. Until completely dissolved, 0.6 g of sodium acetate was added while stirring. The mixture was sealed in a Teflon-lined stainless-steel autoclave (25 mL) and maintained at 160°C for 3 h for solvothermal crystallization. γ -Fe₂O₃ nanoparticles were synthesized by the following procedure: the samples were washed by distilled water and absolute ethanol then transferred to a Teflon-lined stainless-steel autoclave (25 mL) and sealed after adding 10 mL of ethylene glycol, and solvothermal processing was maintained at 180°C for 12 h. The resulting products were washed with water and alcohol several times and finally dried in a desiccator at 60°C for ca. 10 h.

Powder X-ray diffraction (XRD) was characterized by a Rigaku D/MAX 2200 diffractometer. Scanning electron microscopy (SEM) was taken with a FEI Quanta 400. TEM images were prepared on a JEM-2010HR transmission

FIGURE 1: pXRD (a), Fe 2p XPS (b), SEM (c), and TEM (d) of the as-prepared α -Fe₂O₃ precursors.

electron microscope. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250 spectrometer. The magnetic properties of the samples were measured at 300 K on a Quantum Design MPMS XL-7 SQUID magnetometer.

3. Results and Discussion

The powder X-ray diffraction patterns (pXRD) of as-prepared α -Fe₂O₃ precursor in Figure 1(a) match with JCPDS card number 33-0664 for rhombohedral α -Fe₂O₃ with $a = b = 0.5036$ nm and $c = 1.3749$ nm, confirming that the product is hematite. The weak peaks of XRD patterns probably foretold a very small crystal size or amorphous state of the final products. Figure 1(b) shows the XPS spectrum of as-prepared nanoparticles. The Fe_{2p}^{3/2} binding energy of 710.9 eV and the corresponding satellite peak at 719.5 eV, a result of charge transfer screening, can be solely attributed to the presence of Fe³⁺ of the solid samples, indicating that the as-synthesized sample is composed of α -Fe₂O₃ [14]. From the SEM and TEM image in Figures 1(c) and 1(d), we could see that the sample consists of nanoparticles with sizes of only less than 3 nm, which are greatly less than α -Fe₂O₃ in our previous work [13].

Then, the new structure were obtained by adding 10 mL of ethylene glycol into as-prepared α -Fe₂O₃ precursors, and solvothermal processing was maintained at 180°C for 12 h. The pXRD of as-synthesized typical sample in Figure 2(a) match well with JCPDS card number 39-1346 for cubic-structure iron oxide with $a = b = c = 8.395$ nm. However, it is difficult to distinguish the γ -Fe₂O₃ and Fe₃O₄ phases only from the XRD patterns due to their similarity of phase structures. The XPS spectrum is usually an important way to distinguish γ -Fe₂O₃ and Fe₃O₄ phase. The powder samples (Figure 2(b)) are similar to that of α -Fe₂O₃ precursors, and the satellite peak at 719.6 eV still exists, indicating that the as-synthesized sample is composed of γ -Fe₂O₃. The atom ratio of the product is determined as Fe (23.99%) and O (56.54%) using XPS analysis. The oxygen content is higher than that of both Fe₃O₄ and γ -Fe₂O₃. 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 the crystals surfaces; on the other hand, the clean surfaces easily adsorb oxygen in the air.

From the TEM image in Figure 2(c), we can see that the product consists of highly dispersed polyhedral nanoparticles

FIGURE 2: pXRD (a), Fe 2p XPS (b), TEM (c), and HRTEM (d) of the as-obtained γ -Fe₂O₃ nanoparticles.

and the sizes of particles are about 18 nm with narrow size distribution. The clear lattice fringes of nanoparticles in the high-resolution transmission electron microscopy (HRTEM) show the as-obtained powders with high crystallinity (Figure 2(d)).

In our previous report, the side surface edges α -Fe₂O₃ nanoplates gradually redissolved into nanoparticles through “a mass transformation” during solvothermal processing [13]. We could speculate that other iron oxides particles should be obtained if we tune some experimental conditions during “a mass transformation.” Herein, nanoscale γ -Fe₂O₃ was synthesized by using less than 3 nm or amorphous α -Fe₂O₃ as precursor in present of ethylene glycol.

However, if a trace of hydrazine hydrate was brought, the cubic phase Fe₃O₄ nanoparticles are obtained instead of γ -Fe₂O₃. We believe that the possible “intermediate” phase Fe₃O₄ forms during regrowth of γ -Fe₂O₃ or Fe₃O₄ crystals from α -Fe₂O₃ precursors, but the “intermediate” is unstable and fast converts into γ -Fe₂O₃ under the condition of high temperature and rich-oxygen [15]. If hydrazine hydrate is used at the same experiment conditions, the “intermediate” is maintained due to the strong reducing atmosphere, resulting in the final products of cubic Fe₃O₄ (Figure 3(a)); however, sizes of the products are still nanoscale (Figure 3(b)). Therefore, we can speculate that the reducing atmosphere in

the hydrothermal system determines the final phase of the iron oxides.

Finally, the magnetic characteristics of the prepared nanoparticles in the presence of magnetic field were measured using a vibrating sample magnetometer (VSM). Figure 4(a) shows the hysteresis loops at 300 K of as-prepared α -Fe₂O₃ precursor. It can be found that the saturation magnetization (Ms), remanent magnetization (Mr), and coercivity (Hc) are 13.6 emu/g, 0.016 emu/g and 92.6 Oe, respectively, showing soft ferromagnetic behaviour. Accordingly, the three values of as-synthesized γ -Fe₂O₃ nanoparticles are 74.3 emu/g, 2.86 emu/g, and 43 Oe, respectively. The low remanent magnetization and high saturation magnetization simply indicate that the as-synthesized γ -Fe₂O₃ nanoparticles are with good superparamagnetic property [9].

4. Conclusions

Our work offers a facile method to prepare biocompatible nanoparticles. Herein, we adopted α -Fe₂O₃ as precursor to realize the growth of γ -Fe₂O₃ nanoparticles, and Fe₃O₄ nanoparticles can also be obtained only with the addition of a trace of hydrazine hydrate. The as-obtained samples are dispersed in water with a clean surface. This route provides a practical method to controllably prepare high quality iron oxides

FIGURE 3: XPS (a) and TEM images (b) of the Fe_3O_4 polyhedrons obtained with the addition of a trace of hydrazine hydrate.

FIGURE 4: Magnetization-hysteresis (M-H) loops of $\alpha\text{-Fe}_2\text{O}_3$ precursors (a) and as-obtained $\gamma\text{-Fe}_2\text{O}_3$ samples (b); the inset is the enlarged ones in the range of -0.02 and 0.02 kOe.

for biomedical application. The magnetic measurement by VSM revealed that the prepared iron oxides exhibit excellent superparamagnetic behavior.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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