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Preparation and characterization of silicone-oil-based γ-Fe_2O_3 magnetic fluid

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Abstract In this study, silicone-oil-based γ-Fe_2O_3 magnetic fluid was successfully prepared by thermal oxidizing of Fe_3O_4 magnetic nanoparticles, which were prepared by chemical co-precipitation with $FeSO_4{\cdot}7H_2O$ and $FeCl_3{\cdot}6H_2O$, and their surface was modified by oleate ligands. Silicone oil was used as carrier liquid and oleic acid was as surfactant for preparing γ-Fe_2O_3 magnetic fluid. It is found that the Fe_3O_4 nanoparticles surrounded by oleate ligands are not damaged during the thermal oxidizing. The shape of γ-Fe_2O_3 magnetic nanoparticles prepared is similar to spherical, and their mean size is about 10–20 nm, which has nothing obvious difference compared with Fe_3O_4. The saturation magnetization of γ-Fe_2O_3 magnetic fluid prepared is 14.25 $A{\cdot}m^2{\cdot}kg^{-1}$ and that of γ-Fe_2O_3 nanoparticles is 57.56 $A{\cdot}m^2{\cdot}kg^{-1}$. The needle of γ-Fe_2O_3 magnetic fluid is much bigger than that of Fe_3O_4 magnetic fluid under the same magnetic field, which shows better magnetic properties.

Keywords Fe_3O_4 magnetic particles; γ-Fe_2O_3 magnetic particles; γ-Fe_2O_3 magnetic fluid; Saturation magnetization

1 Introduction

Magnetic fluid is a colloidal solution or suspension with ferromagnetic and superparamagnetic fine particles that were dispersed in the solvent with the help of surfactant which is appropriate for the particles and solvent [1–3]. After decades of research and development, magnetic fluid has been used in a large variety of biomedical and engineering applications [4–8], such as aerospace, electronics, chemical industry, machinery, energy, metallurgy, environmental protection, and medical instrument. However, the application fields have gradually been enlarged for further study of the magnetic fluid.

The γ-Fe_2O_3 magnetic powder, one of the qualified magnetic materials, is widely applied in various storage medium and magnetic recordings for its lower price and great oxidation resistance. Compared with the usual structure, the γ-Fe_2O_3 gets more excellent magnetic properties while its grain comes into nanosize. And its coercive force improved so greatly that the magnetic recording materials made by the γ-Fe_2O_3 powder can achieve high-density information recording while getting better signal-to-noise ratio and image quality. The traditional method for preparing γ-Fe_2O_3 is heating Fe_3O_4 or γ-FeOOH in appropriate temperature, and the particle size is in micrometer. With the development of nanomaterials, preparation of γ-Fe_2O_3 has also been improved, and kinds of high-performance γ-Fe_2O_3 nanoparticles have been prepared. However, most of them are complicated and expensive. In order to realize industrial production, the most important thing is to cut the cost and make the large-scale preparation of uniform γ-Fe_2O_3 nanoparticles that have controllable size happen [9–12].

In this paper, the γ-Fe_2O_3 magnetic nanoparticles were prepared by thermal oxidation of Fe_3O_4 nanoparticles directly, and silicone oil was used as carrier liquid and oleic acid was as surfactant for preparing γ-Fe_2O_3 magnetic fluid. The prepared silicone-oil-based γ-Fe_2O_3 magnetic fluid could be widely used in sealing device.

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2 Experimental

2.1 Preparation of γ-Fe_2O_3 magnetic fluid

The reaction process of chemical co-precipitation for Fe_3O_4 was: $Fe^{2+} + Fe^{3+} + OH^- \rightarrow Fe_3O_4 + H_2O$. According to Fe^{3+} to Fe^{2+} mole ratio of 3:2, $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ were mixed into deionized water and placed into a 75 °C thermostatic beaker for 10–15 min [13, 14]. Then, enough 25 vol%–28 vol% $NH_3 \cdot H_2O$ was fast poured into the mixed solution. After 10–15 min, the sodium oleate powder was put into the solution and isothermally stirred for 40 min to ensure that the Fe_3O_4 particles were fully covered by oleate ligands [15–17]. Under the external magnetic field, the supernate was removed and the deposition was washed by deionized water until the pH of supernate was about 7. Finally, the products were dried at low temperature. Then, the Fe_3O_4 magnetic nanoparticles were obtained, as shown in Fig. 1a. The γ-Fe_2O_3 was prepared by fully thermal oxidizing of Fe_3O_4 in a poor vacuum drying oven, as shown in Fig. 1b. The γ-Fe_2O_3 magnetic fluid was proceeded as follows: 3.5 ml organic silicone oil (VPO-705) was used as the solvent, 1.0 ml oleic acid and 0.5 ml emulsifier OP-7 as surfactant, and 5 g γ-Fe_2O_3 ultrasonic dispersion in it for 0.5 h. All reagents were analytically pure.

2.2 Characterization method

The magnetic particles were identified by X-ray diffraction (XRD, DMAX-RB12 KW), Fourier transform infrared spectroscopy (FTIR, Vanquish Flex UHPLC), transmission electron microscopy (TEM, JEM-2010), and vibrating sample magnetometer (VSM, BKT-4500).

3 Results and discussion

3.1 XRD pattern of magnetic powder

Figure 2 shows XRD pattern of γ-Fe_2O_3 nanoparticles prepared. The characteristic peaks at $2\theta = 18.43°$, 30.35°, 35.61°, 43.15°, 53.66°, 57.22°, 62.77°, 74.02°, 87.46°, 90.47° corresponding to (111), (220), (311), (400), (422), (511), (440), (532), (444), (800), respectively, which matches well with the standard JCPDS card of γ-Fe_2O_3, indicating that the products of thermal oxidizing of Fe_3O_4 are γ-Fe_2O_3 [18–23], and it is inverse cubic spinel phase. In addition, no characteristic peaks of impurities such as Na^+, $SO_4{}^{2-}$, and Cl^- and other precursor compounds are found. It explains that the prepared product is pure phase. The particle size (D) is estimated by Scherrer formula.

$$D = K\lambda / \beta \cos\theta \tag{1}$$

where $K = 0.89$ is Scherrer constant, $\lambda = 0.154$ nm is the wavelength of X-ray, β is the diffraction peak width of (311) crystal surface, and θ is Prague diffraction angle. The grain size of both magnetic nanoparticles is about 10 nm.

3.2 FTIR analysis of magnetic particles

Figure 3 shows FTIR spectra of nanoparticles prepared. Figure 3(1) shows FTIR spectrum of Fe_3O_4 magnetic nanoparticles that are surrounded by oleate ligands. It can be seen that the possessed absorption band in 1634 and 1425 cm^{-1} is due to the symmetric and asymmetric carboxylate (COO–Fe) stretch. In Fig. 3(1), the peak at 575 cm^{-1} can be assigned as the characteristic absorption of Fe–O bond [24–26]. In Fig. 3(2), the thermal oxidation leads to the appearance of the bifurcated peak at 633 cm^{-1}. In addition, the peak at 1042 cm^{-1} in Fig. 3(1) represents

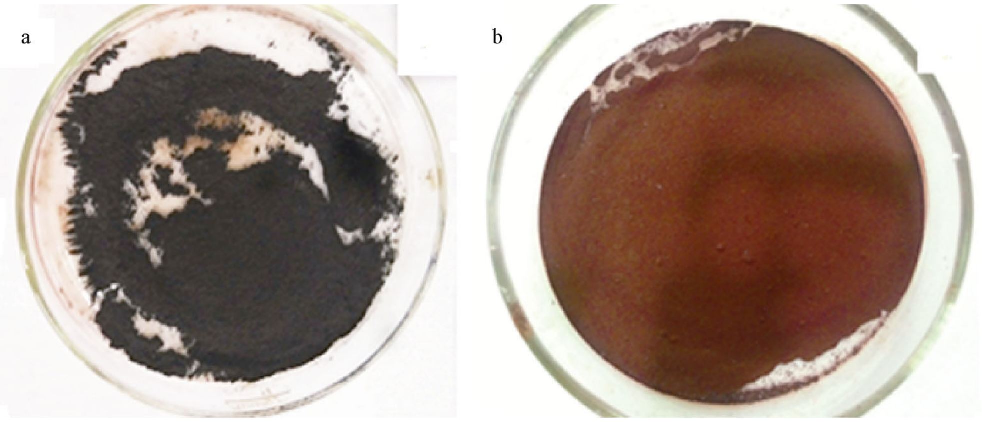

Fig. 1 Microphotographs of magnetic particles: **a** Fe_3O_4 and **b** γ-Fe_2O_3 (1:1 measured scale)

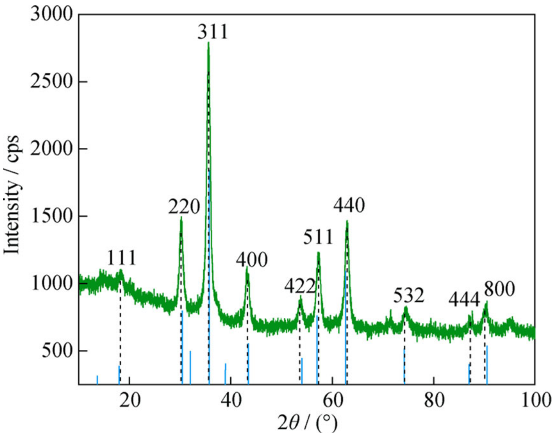

Fig. 2 XRD pattern of γ-Fe_2O_3 magnetic particles

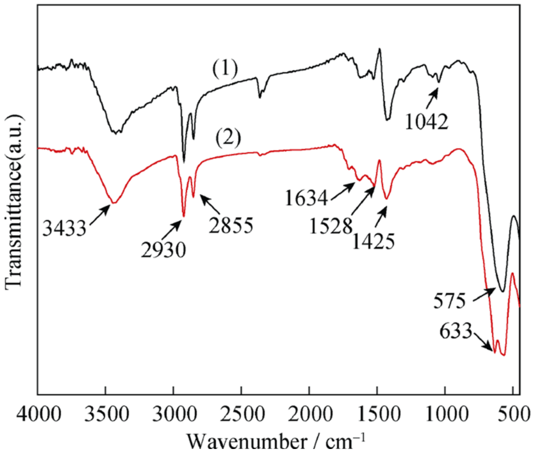

Fig. 3 FTIR spectra of magnetic particles: (1) Fe_3O_4 coated with sodium oleate and (2) γ-Fe_2O_3 coated with oleate ligands

stretching vibration of (–C=C–) bond. However, the peak disappears in Fig. 3(2) after thermal oxidation. And the peaks in Fig. 3(2) have no obvious changes compared with those in Fig. 3(1). So the γ-Fe_2O_3 nanoparticles prepared are also covered with oleate ligands. It can be concluded that the thermal oxidation of Fe_3O_4 nanoparticles does not destroy the surface coating of oleic acid. The surface coating layer also prevents the growth and aggregation of the magnetic nanoparticles during the thermal oxidation.

3.3 Hysteresis loop of magnetic particles and magnetic fluid

Figure 4 shows the hysteresis loops of magnetic nanoparticles and magnetic fluid prepared. The hysteresis loop shows that the γ-Fe_2O_3 magnetic nanoparticles prepared have no remanence and coercivity, indicating that the obtained γ-Fe_2O_3 magnetic nanoparticles are superparamagnetic. After thermal oxidation, the saturation magnetization of magnetic nanoparticles decreases to 57.56 $A \cdot m^2 \cdot kg^{-1}$ while that of Fe_3O_4 is 64.25 $A \cdot m^2 \cdot kg^{-1}$. However, the saturation magnetization of γ-Fe_2O_3 magnetic fluid is 14.25 $A \cdot m^2 \cdot kg^{-1}$, higher than that of Fe_3O_4 magnetic fluid (12.45 $A \cdot m^2 \cdot kg^{-1}$). It is possible that the γ-Fe_2O_3 has higher solid content of 61 wt% (Table 1) than Fe_3O_4 of 50 wt% for the same carrier of magnetic fluid, while the amount of surfactant is also the same. It is the main factor that the saturation magnetization of γ-Fe_2O_3 magnetic fluid is higher than that of Fe_3O_4 magnetic fluid. Table 1 shows the component of different magnetic fluids that share the same viscosity.

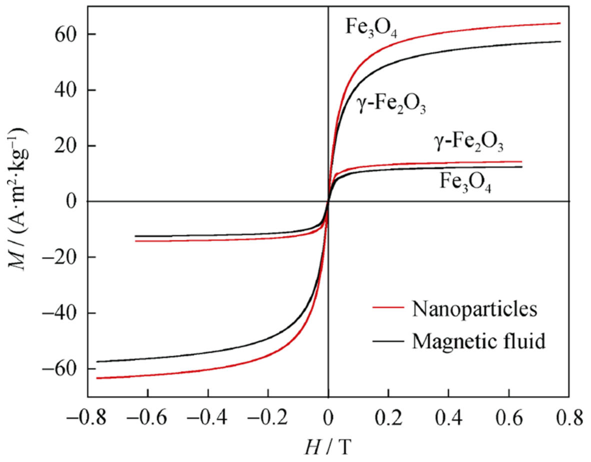

Fig. 4 Hysteresis loop of magnetic particles and magnetic fluid (*H*, magnetic field intensity; *M*, magnetization)

3.4 TEM results of magnetic particles

Figure 5 shows TEM images of γ-Fe_2O_3 and Fe_3O_4 nanoparticles prepared. It can be seen that the nanoparticles show similar spherical. The diameter of the nanoparticle is within a range of 10–20 nm that matches well with XRD results. From the analysis above, it can be concluded that the γ-Fe_2O_3 magnetic nanoparticles have no obvious changes during the thermal oxidation. It is also found that the magnetic nanoparticles could be uniformly dispersed in the carrier liquid–silicone oil, and there is no obvious aggregation.

3.5 Appearance of magnetic fluid

Figure 6 shows the appearances of prepared magnetic fluid in different strength magnetic fields. The field strength was adjusted for these photographs by changing the distance between the magnet and glass dish. The magnetic

Table 1 Components of magnetic fluid

Samples	Powder/g	Solvent/ml	Surfactant/ml	OP-7/ml	Solid content/wt%
Fe_3O_4	5	3.5	1.0	0.5	50
γ-Fe_2O_3	5	2.0	0.6	0.5	61

nanoparticles are uniformly distributed along the magnetic field lines, and the magnetic needle appears. The conventional looking like puddle (Fig. 6a_1, b_1) becomes significantly distorted upon application of a weak field (Fig. 6a_2, b_2). The size of the needle (Fig. 6a_3, b_3) increases with the field increasing. Both of them have significant and uniform distribution magnetic needle, which shows excellent anisotropy. The needle of Fig. 6b is much bigger than that of Fe_3O_4 magnetic fluid, and it gets better magnetic properties.

4 Conclusion

The γ-Fe_2O_3 magnetic particles were successfully prepared by thermal oxidizing of Fe_3O_4 nanoparticles. The structure of Fe_3O_4 surrounded by oleic acid is not damaged during the thermal oxidizing. The coated oleic acid layer prevents the aggregation of magnetic nanoparticles, and the prepared γ-Fe_2O_3 nanoparticles have also been coated with oleate ligands. The γ-Fe_2O_3 magnetic nanoparticles prepared have lower saturation magnetization than that of Fe_3O_4, while the saturation magnetization of γ-Fe_2O_3 magnetic fluid prepared is improved because of its high solid content of 61 wt%, and the saturation magnetization of γ-Fe_2O_3 magnetic fluid is 14.25 $A \cdot m^2 \cdot kg^{-1}$. Furthermore, it gets more obvious magnetic phenomenon in the same magnetic field. The needle of γ-Fe_2O_3 magnetic fluid is more clear and obvious than that of Fe_3O_4 magnetic fluid under magnetic field, and it shows better magnetic

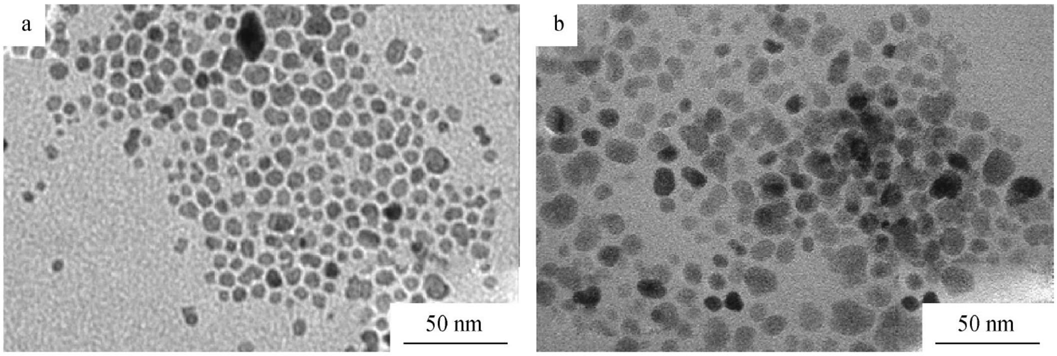

Fig. 5 TEM images of magnetic nanoparticles: **a** Fe_3O_4 and **b** γ-Fe_2O_3

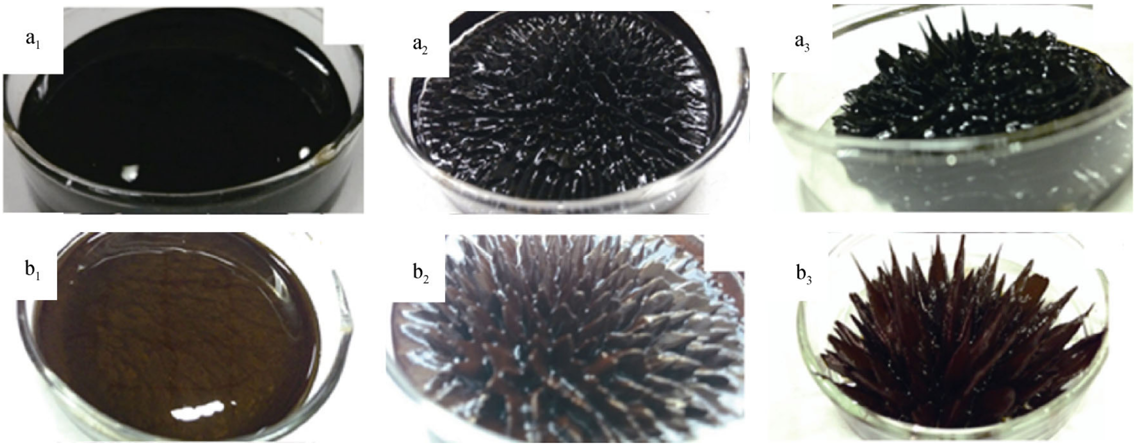

Fig. 6 Appearances of magnetic fluid with strength magnetic field increasing (1 conventional; 2 weak; 3 stronger): **a** Fe_3O_4 magnetic fluid and **b** γ-Fe_2O_3 magnetic fluid (1:1.2 measured scale)

properties. The γ-Fe_2O_3 magnetic nanoparticles prepared remain similar spherical, and their mean size is about 10 nm.

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