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Preparation and characterization of La- and Ni-doped magnetite nanoparticles

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La- and Ni-doped Fe_3O_4 nanocomposite particles with a high saturation magnetization were prepared by a homogeneous precipitation method in aqueous solutions. The obtained nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), inductively-coupled plasma atomic emission spectroscopy (ICPAES) and vibrating sample magnetometry (VSM). The results showed the diameters of La- or Ni-doped Fe_3O_4 composite particles to be in the range of 10–25 nm. The specific saturation magnetization of La- or Ni-doped Fe_3O_4 was considerably higher than that of pure Fe_3O_4 nanoparticles. The nanocomposite particles exhibited superparamagnetic behaviour.

Key words: magnetic material; nanocomposite; superparamagnetism; doped Fe_3O_4

1. Introduction

The superparamagnetic nanometer scale composites, with its special properties, have been widely applied in the fields of aviation and spaceflight, electronic, chemical and machinery industries, energy production and metallurgy, environmental protection and medical treatment [1–3]. Fe_3O_4 nanoparticles are one of several widely used magnetofluids, its saturation magnetization however, is generally insufficient to meet the requirements of some technical applications. Many research groups have proved that the magnetic performance of ferromagnetic nanoparticles, in particular Fe_3O_4, could be improved by doping them with rare earth or transition metal elements [4–9]. In this paper, superparamagnetic La- or Ni-doped Fe_3O_4 nanoparticles were prepared by a new method of homogeneous precipitation in aqueous solutions. The synthesized composite particles exhibited superparamagnetic behaviour and the specific saturated magnetization was highly improved.

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2. Experimental

Materials. Lanthanum oxide of purity not lower than 99.9 wt. % was used. Other reagents were of analytical grade used without further purification, including ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), iron chloride ($FeCl_2 \cdot 4H_2O$), sodium dodecylbenzene sulfonate (NaDS), ammonium hydroxide ($NH_3 \cdot H_2O$), absolute ethanol, acetone and methanol.

Preparation of La- or Ni-doped Fe_3O_4 nanoparticles. An appropriate NaDS aqueous solution was placed in a 250 cm^3, four-necked round-bottom flask equipped with a condenser, a nitrogen gas inlet, and a mechanical stirrer. Then, a mixture of $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ (molar ratio 2:1) in deionized water and a selected amount of lanthanum oxide in HCl solution (or $NiCl_2$ in deionized water) were added into the flask. The mixture was stirred under nitrogen atmosphere for 30 min, followed by the addition of 1.5 mol/dm^3 $NH_3 \cdot H_2O$ aqueous solution until pH equaled 9. The reaction was allowed to run for 2 h at this pH level. After that, the mixture was aged at 80 °C for 40 min. Finally, the composite nanoparticles were obtained by purification repeatedly using magnetic field separation, and propanone and deionized water washing.

Characterization. The morphologies of the resulting composites were examined with a Hitachi H-800 transmission electron microscope. X-ray diffraction diagrams were recorded on a RD/MAX-RC diffractometer using Cu K_α radiation (λ = 1.5406 Å). The contents of Fe and La were measured with an IRIS Advantage 1000 inductively-coupled plasma atomic emission spectrometer (ICPAES) produced by the Thermo Jarrell Ash. The magnetization measurements were performed at room temperature using a Lakeshore 7400 vibrating sample magnetometer.

3. Results and discussion

3.1. Structure and morphology

In Table 1, the results of elemental analysis are given determined by ICPAES measurements, showing that Fe_3O_4 was successfully doped by La or Ni using the method of homogenous precipitation in aqueous solution.

Table 1. Results of elemental analysis of La- or Ni-doped Fe_3O_4

Fe_3O_4	Element	Contents [wt. %]
La doped	Fe	62.9±0.5
	La	3.5±0.5
Ni doped	Fe	64.5±0.5
	Ni	2.3±0.5

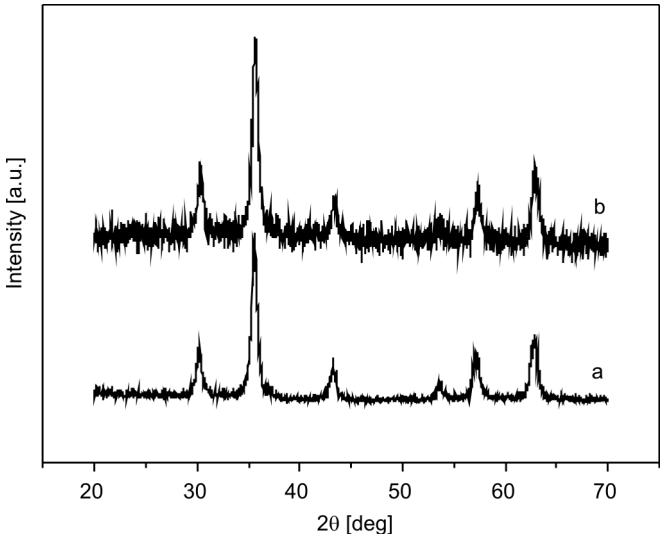

Fig. 1. XRD patterns of Fe_3O_4 (a) and La-doped Fe_3O_4 (b)

Figure 1 shows XRD patterns of Fe_3O_4 and La-doped Fe_3O_4 nanoparticles. The main peaks at 2θ in the pattern of La-doped Fe_3O_4 are 35.54, 43.18, 57.24 and 62.24°, similarly as in the standard Fe_3O_4, indicating that La-doped Fe_3O_4 nanoparticles mainly contain Fe_3O_4 crystal phase. The lattice constants (a) of the standard bulk Fe_3O_4 and the Fe_3O_4 nanocrystals estimated from XRD spectra are given in Table 2. The lattice constant for La-doped Fe_3O_4 nanoparticles is higher compared to that in pure Fe_3O_4 nanoparticles, suggesting that La well incorporated into the magnetite lattice and results in the expansion of the crystal cell. However, the measured La and Fe weight contents (Table 1) in the synthesized products suggest that they are far too nonstoichiometric to sustain the magnetite lattice. Thus, our La doped sample most probably contains La oxide, but is of too small volume to be observed in the XRD pattern.

Table 2. The calculated lattice constants in Fe_3O_4

Sample	Lattice constant a [Å]
Standard bulk Fe_3O_4	8.3960
Undoped Fe_3O_4 nanoparticles	8.3573
La-doped Fe_3O_4 nanoparticles	8.3710
Ni-doped Fe_3O_4 nanoparticles	8.3125

A typical XRD diffraction profile of Ni-doped Fe_3O_4 particles is given in Fig. 2. Compared with JCPDS 19-0629 of standard Fe_3O_4, the main peaks at 2θ = 30.3, 35.8, 43.22, 57.46 and 63.04° are attributed to the diffractions of the (020), (311), (400),

(511) and (440) planes of Fe_3O_4 magnetic particles, indicating the resulting composites contain Fe_3O_4 crystals.

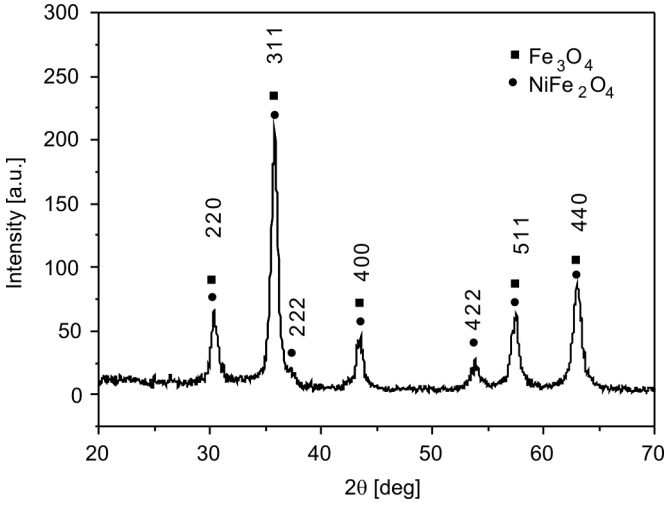

Fig. 2. XRD pattern of Ni-doped Fe_3O_4 particle

Furthermore, the lattice constant *a* for Ni-doped Fe_3O_4 nanoparticles (Table 2) is somewhat smaller in comparison with that for pure Fe_3O_4 nanoparticles, suggesting that Ni is also incorporated into magnetite lattice, resulting in the shrinkage of crystal cell. Similar to La-doped Fe_3O_4, some oxygen is also probably present in Ni oxide. According to the appearance of the diffraction peaks of the (222) and (422) planes and JCPDS10-0325 of $NiFe_2O_4$ crystals, it is concluded that the resulting Ni-doped Fe_3O_4 particles may contain $NiFe_2O_4$ crystals, although characteristic diffraction peaks of $NiFe_2O_4$ may overlap.

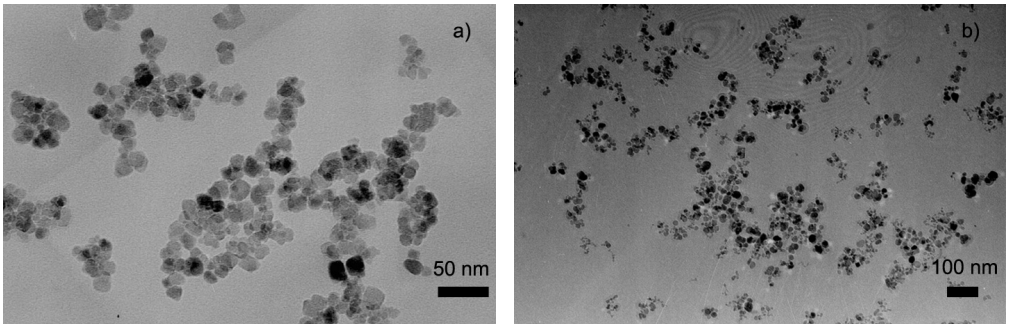

Fig. 3. TEM of La-doped Fe_3O_4 nanoparticle (a) and Ni-doped Fe_3O_4 nanoparticle (b)

The morphologies of the resulting La- or Ni-doped Fe_3O_4 composites are shown in Fig. 3. The size of the nanoparticles is in the range of 10–25 nm. Some of them form multiparticle aggregates, presumably due to the magnetic dipolar interparticle interaction.

3.2. Magnetic properties

Dependences of magnetizations of Fe_3O_4, La-doped Fe_3O_4 and Ni-doped Fe_3O_4 on the applied magnetic field at room temperature are shown in Fig. 4. The specific saturation magnetization of our Fe_3O_4 nanocrystals is 76.12 emu/g, which is somewhat smaller than that of the bulk magnetite (92 emu/g) [10]. The difference in the magnetization value between the bulk examined nanoparticles might be attributed to the small particle size effect [11].

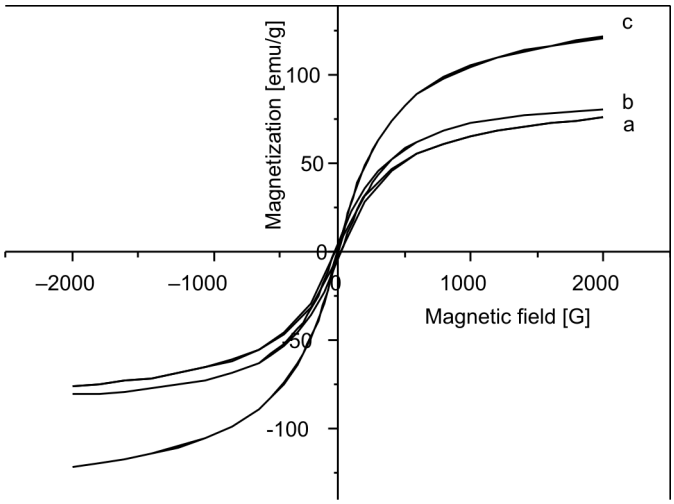

Fig. 4. Hysteresis loops of Fe_3O_4 and La or Ni-doped Fe_3O_4:
a) Fe_3O_4; b) La-doped Fe_3O_4; c) Ni-doped Fe_3O_4

Conversely, the specific saturation magnetization of Ni doped Fe_3O_4 is 121.78 emu/g, being much higher than the standard value (92 emu/g) and that of pure Fe_3O_4 nanoparticles. It can be established from the surface effects that the magnetization would increase as the surface anisotropy decreases [9, 12]. The impurity $NiFe_2O_4$, for which the magnetocrystalline anisotropy constant is lower than that of Fe_3O_4 [8], may preferentially be localized on the surface of Ni doped magnetite nanocrystal, thus, resulting in the increase of saturation magnetization. The saturation magnetization of La-doped Fe_3O_4 is 80.97 emu/g, higher than that of the Fe_3O_4 nanocrystals, but smaller than the standard value. The corresponding coercive forces of the doped composites are nearly 0 Oe and no hysteresis effects occur, which is typical of superparamagnetic materials.

4. Conclusions

Fe_3O_4 and La- or Ni-doped Fe_3O_4 nanocomposites were prepared by the chemical coprecipitation method in aqueous solution. The results show that the particle diame-

ters of La- or Ni-doped Fe_3O_4 are in the range of 10–25 nm. The specific saturation magnetization of Fe_3O_4 is 76.12 emu/g. The specific saturation magnetizations of La- or Ni-doped Fe_3O_4, being 80.97 and 121.78 emu/g, respectively, are considerably higher than that of pure Fe_3O_4 nanoparticles synthesized by the authors and those doped composites exhibit superparamagnetic behaviour.

Acknowledgements

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