Synthesis of Fe₃O₄ nanoparticles and their magnetic properties

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Abstract

Fe₃O₄ magnetic nanoparticles (MNPs) were synthesized by a co-precipitation method using sodium citrate and oleic acid as modifiers. Phase composition and microstructure analysis indicate that the sodium citrate and oleic acid have been successfully grafted onto the surface of Fe₃O₄ MNPs. The magnetic behaviors reveal that the modification can decrease the saturation magnetization of Fe₃O₄ MNPs due to the surface effect. Fe₃O₄ MNPs modified by sodium citrate and oleic acid show excellent dispersion capability, which should be ascribed to the great reduction of high surface energy and dipolar attraction of the nanoparticles.

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Keywords: Fe₃O₄; magnetic nanoparticles; modification.

1. Introduction

Compared to atomic or bulky counterparts, nano-sized materials owe superior physical and chemical properties due to their mesoscopic effect, small object effect, quantum size effect and surface effect. Recently, Fe₃O₄ MNPs have been intensively investigated because of their superparamagnetity, high coercivity and low Curie temperature[1–4]. In addition to these characters, Fe₃O₄ MNPs are also non-toxic and biocompatible. Therefore, Fe₃O₄ MNPs have brought out some new kinds of biomedical applications.

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such as dynamic sealing [5], biosensors [6], contrasting agent in magnetic resonance (MR) imaging [7],
localizer in therapeutic hyperthermia [8] and magnetic targeted-drug delivery system [9], etc.

It is well known that it is very important to ensure the narrow size distribution, good dispersion and
high magnetic response of Fe₃O₄ MNPs in tissue fluid for applications. However, magnetic attractive
forces combined with inherently large surface energies (>100 dyn/cm) make them easy for the
aggregation Fe₃O₄ MNPs in fluids. Therefore, lots of synthesized polymers [10-14] (e.g., poly (vinyl alcohol)
phosphate, polyethylene glycol, polyamides, polyglycidyl methacrylate, poly(acrylic acid), chitosan (CS)
and o-carboxymethylchitosan) were employed as coating agent in order to modify the surface of iron
oxide particles. Although the polymeric coatings can reduce the aggregation of MNPs, they also increase
the overall size of the particles and thus limit the expression of magnetic property, tissue distribution,
metabolic clearance and penetration ability into interstitial spaces. So it is very important to develop an
efficient surface-modification method for preparing Fe₃O₄ MNPs with narrow size distribution and
excellent dispersion in aqueous or inaqueous solution using small molecular compounds.

In this work, we developed an efficient modification method using sodiumcitrate and oleic acid for the
synthesis of Fe₃O₄ MNPs with narrow size distribution and excellent dispersion in fluids. Fe₃O₄ MNPs
were synthesized by a co-precipitation method at different temperatures, and modified with sodiumcitrate
and oleic acid respectively. The effect of temperature and modifiers on the crystal structure, morphology,
dispersion and size distribution, and magnetic properties of Fe₃O₄ MNPs were investigated in detail.

2. Experimental

The reagents of analytic grade (FeCl₃·6H₂O, FeCl₂·4H₂O, NaOH and C₂H₆O) were used as raw
materials. Chemical grade sodiumcitrate (Na₃C₆H₅O₇·2H₂O) and oleic acid (C₁₇H₃₃COOH) were used as
modifiers. Four samples were prepared depending on their synthesis conditions (shown in Table 1).
Firstly, FeCl₃·6H₂O and FeCl₂·4H₂O with molar proportion of 1:2 were dissolved in ethanol or deionized
water maintained at different temperatures (Table 1), and then NaOH solution (3 mol·L⁻¹) was added into
the above solution using a peristaltic pump under constant magnetic stirring for 30 min, and the final pH
was 10. Afterwards, the sodiumcitrate and oleic acid were respectively added into the suspensions to
modify the obtained Fe₃O₄ MNPs for 12h. The substance obtained were aged and digested at maintained
temperature for 30 min and cooled at room temperature. The resulted particles were magnetically
separated and washed repeatedly with deionized water and ethanol until pH was 7. The products were
then dried at 60 °C in vacuum for 6 h for further characterizations.

| Table 1. Preparation conditions for the Fe₃O₄ MNPs |
|-----------------------------------------------|
| Samples | Temperature (°C) | Sodiumcitrate Concentration (mol L⁻¹) | Oleic Acid Concentration (ml L⁻¹) | Total Fe Concentration (mol L⁻¹) |
|---------|-----------------|--------------------------------------|----------------------------------|--------------------------------|
| (a)     | 40              | /                                    | /                                | 0.15                            |
| (b)     | 80              | /                                    | /                                | 0.15                            |
| (c)     | 80              | 0.43                                 | /                                | 0.86                            |
| (d)     | 80              | /                                    | 0.86                             | 0.86                            |

The crystal structure of as-prepared samples was analyzed by X-ray diffraction (XRD) with a Rigaku
D/Max-C model diffractometer using Fe target. The molecular structure of Fe₃O₄ MNPs was
characterized by a Perkin-Elmer Paragon 1000 Fourier transform spectrometer (FT-IR) at room
temperature (25 °C). The magnetic property of Fe₃O₄ MNPs was measured using a vibrating sample magnetometer (VSM, LakeShore 7307). The morphology of the magnetite nanoparticles were determined using transmission electron microscopy (TEM, Hitachi H-600-II, Japan).

3. Results and discussion

XRD measurement was used to identify the crystalline structure of the products. As shown in Fig. 1, the XRD peaks can match well with the characteristic peaks of inverse cubic spinel structure (JCPDS 19-0629), which indicate that the crystalline structure of Fe₃O₄ MNPs can be remained after the surface modification with sodium citrate and the oleic acid. The average crystallite size d calculated using the Debye–Scherrer equation \( d = K\lambda/(\beta\cos\theta) \) are about 12.6 nm (a), 13.4 nm (b), 14.2 nm (c) and 13.8 nm (d), respectively.

![Fig. 1. XRD patterns of as-prepared Fe₃O₄ MNPs.](image_url)

Figure 2 shows the FT-IR spectra of Fe₃O₄ MNPs of all samples. It can be seen that the characteristic absorption of Fe-O bond is at 580 cm⁻¹ and 634 cm⁻¹, while that of -OH bond is at 3398 cm⁻¹. The similar characteristic peaks can be found in Fig. 2b. Compared with Fig. 2b, we can see some new absorption peaks in Fig. 2c. The absorptions at 1393 cm⁻¹ and 1587 cm⁻¹ are characteristic peaks of the COO-Fe bond, which may be due to the reaction of hydroxide radical groups on the surface of Fe₃O₄ with carboxylate anion of sodium citrate. The peaks at 2855 cm⁻¹ and 2924 cm⁻¹ are from the vibration of in long alkyl chain -CH₂ and -CH₃. Furthermore, the characteristic peak of -OH bond at 3378 cm⁻¹ is obviously enhanced. These peaks reveal that sodium citrate has been successfully grafted onto the surface of Fe₃O₄ MNPs as well. As compared with Fig. 2b, we also find some new absorption peaks in Fig. 2d. These peaks at 1384 cm⁻¹ and 1412 cm⁻¹ are attributed to the vibration of the double covalent bond in -CH=CH₂ and the peaks at 2853 cm⁻¹ and 2924 cm⁻¹ correspond to -CH₂ and -CH₃ bond. Obviously, the characteristic absorption peaks of -OH bond at 3387 cm⁻¹ decreased, which indicates that oleic acid has been successfully grafted onto the surface of Fe₃O₄ MNPs through the chemical reaction of hydroxide radical groups on the surface of Fe₃O₄ with carboxylic acid groups of oleic acid. Both the peak at 598 cm⁻¹ in Fig. 2c and the peaks at 581 cm⁻¹ and 628 cm⁻¹ in Fig. 2d confirm the existence of Fe-O bond.
M-H hysteresis curves of all samples are shown in Fig. 3. Symmetric hysteresis and saturation magnetization can be observed, and all as-prepared Fe₃O₄ MNPs show ferrimagnetic behaviors. This is because that the diameter of MNPs is smaller with that of critical threshold of Fe₃O₄ (25 nm). It can be seen that the saturation magnetization of sample a, b, c and d are 50.61, 61.36, 56.05 and 55.43 emu·g⁻¹, respectively, which are obviously lower than that of the bulk Fe₃O₄ (90 emu·g⁻¹)[11]. This phenomenon may attribute to the small particle size effect since a noncollinear spin arrangement occurs primarily at or near the surface, which results in the reduction of magnetic moment in Fe₃O₄ NPs [12, 13]. The saturation magnetization of sample b is larger than that of sample a, which may be ascribed to the increase of particle size of Fe₃O₄ MNPs. The saturation magnetization decreases evidently when the Fe₃O₄ MNPs were modified with sodiumcitrate and oleic acid. This result could be attributed to the surface spin effect on Fe₃O₄ MNPs caused by modification, which subsequently decrease the saturation magnetization value. Nevertheless, compared to the decrease of saturation magnetization value in polymer-modification[10-14], the reduction by sodiumcitrate or oleic acid modification is significantly lower, showing the obvious advantage using small molecular compounds as modifiers.
The morphology and distribution of these samples were further characterized using TEM as shown in Fig. 4. All the Fe₃O₄ MNPs show homogeneously spherical shape with diameter about 12-15 nm, which is in agreement with the results of the XRD analysis. The Fe₃O₄ MNPs prepared without modification aggregate in deionized water (Fig. 4a). The sodiumcitrate and oleic acid -modified Fe₃O₄ MNPs show good dispersion capability in deionized water and oleic acid solution, which should be due to the fact that the high surface energy and dipolar attraction of the MNPs greatly reduced after modified by sodiumcitrate and oleic acid.

**Figure 4.** TEM images showing the Fe₃O₄ MNPs synthesized by a co-precipitation method at 80 °C. (a) Fe₃O₄ MNPs without any modifier, (b) Fe₃O₄ MNPs modified by sodiumcitrate, (c) Fe₃O₄ MNPs modified by oleic acid.
4. Conclusions

In summary, we have presented a simple and effective technique to prepare and modify Fe₃O₄ MNPs. The results indicate that the sodium citrate and oleic acid modification has little effect on the crystallization of Fe₃O₄ MNPs. FT-IR spectra reveals that sodium citrate and oleic acid have been successfully grafted onto the surface of Fe₃O₄ MNPs by chemical bond. Sodiumcitrate and oleic acid modified Fe₃O₄ MNPs show excellent dispersion capability in aqueous or inaqueous solution, which make Fe₃O₄ MNPs as a promising biomedical material.

Acknowledgments

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Erratum to “Synthesis of Fe$_3$O$_4$ Nanoparticles and their Magnetic Properties” [Procedia Engineering. 2012, doi: 10.1016/j.proeng.2011.12.498]

In the abovementioned article, we are very sorry that the Fig.1c and Fig.4b were given incorrectly. We have tried to contact Procedia Engineering, but the journal has been discontinued. The last issue we could found online was published in 2018. Since this journal was affiliated to Elsevier publishing group, we are still trying to get contact with the Elsevier editorial office. Anyhow, we would like to firstly make erratum here in arXiv. We are sincerely sorry for the inconvenience for those interested in our research.
Fig. 1c should be corrected as follows.

Fig. 4b should be corrected as follows.