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# Solvothermal synthesis and characterization of monodisperse superparamagnetic iron oxide nanoparticles



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## ABSTRACT

A series of magnetic iron oxide nanoparticle clusters with different structure guide agents were synthesized by a modified solvothermal method and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), thermogravimetric analyses (TG), a vibrating sample magnetometer (VSM) and Fourier transform infrared spectroscopy (FTIR). It is found that the superparamagnetic nanoparticles guided by NaCit (sodium citrate) have high saturation magnetization ( $M_s$ ) of 69.641 emu/g and low retentivity ( $M_r$ ) of 0.8 emu/g. Guiding to form superparamagnetic clusters with size range of 80–110 nm, the adherent small-molecule citrate groups on the surface prevent the prefabricated ferrite crystals growing further. In contrast, the primary small crystal guided and stabilized by the PVP long-chain molecules assemble freely to larger ones and stop growing in size range of 100–150 nm, which has saturation magnetization ( $M_s$ ) of 97.979 emu/g and retentivity ( $M_r$ ) of 46.323 emu/g. The relevant formation mechanisms of the two types of samples are proposed at the end. The superparamagnetic ferrite clusters guided by sodium citrate are expected to be used for movement controlling of passive interference particles to avoid aggregation and the sample guided by PVP will be a candidate of nanometer wave absorbing material.

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## 1. Introduction

The design and synthesis of functional magnetic nanoparticles with controlled shapes, sizes and morphology have initiated a wide range of research interests due to their unique properties [1–3]. Currently, the iron oxide magnetic nanomaterials with uniform size are mainly used in biomedical applications [4] as the carrier of the proteins [5], drugs [6] and enzymes [7] because its toxicity is lower than those of other magnetic materials. However, the iron oxide magnetic nanoparticles tend to aggregate due to their attractive magnetic forces and this aggregation effect can decrease the stability of the magnetic colloidal dispersion so as to limit their biomedical applications. To minimize the attractive magnetic forces between nanoparticles, different capping materials such as precious metals [8–11], organic polymer [12,13] and CNT (carbon nanotube) [14,15] have been employed to coat the surface of the magnetic colloids to increase their electrostatic repulsion and steric hindrance. Unfortunately, the coating methods still have some shortages where their capping structures significantly reduce their magnetization intensity. Besides, it is also found that the magnetization direction of the small-size nanoparticles can

randomly flip as the variation of their surrounding temperature and the thermal flippings of the small-size nanoparticles can change their magnetic properties from ferromagnetism to superparamagnetism.

The superparamagnetic nanoparticles should have characters of remarkable saturation magnetization ( $M_s$ ), negligible coercive force ( $H_{ci}$ ) and retentivity ( $M_r$ ). The prepared superparamagnetic  $Fe_3O_4$  particles are stable in solution and demonstrate rapid magnetic response to an externally applied magnetic field. Since their magnetic responses are much stronger and faster than those of normal paramagnetic materials and their dipole–dipole interactions can be fully initiated and controlled by external fields, the motion of the nanoparticles with superparamagnetism can be easily controlled in certain magnetically responsive biomedical applications, photonic crystals and shielding materials [16–18].

In recent years, including self-assembly [19], cooperative assembly [20], microemulsion templating [21] and solvophobic interactions [22], a number of approaches have been explored to synthesize superparamagnetic  $Fe_3O_4$  materials. Compared to these two-step processes, the direct one-step solvothermal route [23] to form the particles with cluster structure seems to be more convenient, reliable and simpler for mass production.

In this study, we prepared two kinds of monodisperse iron oxide nanoparticles with size range of 100–150 nm by a one-step

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solvothermal method using different surfactants as structure guide agents. These two kinds of iron oxide nanoparticles have different structures, surface features, magnetic properties and crystalline states. The reaction mechanism of solvothermal system is speculated and the relationship between the magnetic performance and the structure state is discussed.

## 2. Materials and methods

### 2.1. Materials

Iron (III) chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ammonium hydrogen carbonate ( $\text{NH}_4\text{HCO}_3$ ), ammonium acetate ( $\text{NH}_4\text{Ac}$ ), K30 polyvinyl pyrrolidone (PVP), sodium citrate (NaCit), and monoethylene glycol were purchased from Aladdin, Shanghai. All reagents are of analytical purity and used without further purification.

### 2.2. Synthesis of nanoparticles

The monodisperse superparamagnetic iron oxide nanoparticles were synthesized by solvothermal method in ethylene glycol. In a typical experiment, 1.5 mmol  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 18 ml of ethylene glycol; after that 7.5 mmol  $\text{NH}_4\text{Ac}$ , 7.5 mmol  $\text{NH}_4\text{HCO}_3$  and 0.2 g polyvinyl pyrrolidone (or 0.75 mmol sodium citrate) were added into the solution under ultrasonic processing. Before the solution turned clear, a lot of gas bubbles were generated from the system. After half an hour, the solution was sealed into a 25 ml Teflon-lined stainless-steel autoclave. The autoclave was heated to 220 °C for 10 h (or 20 h), then cooled to room temperature naturally. The black particles were subjected to magnetic decantation and centrifugation, followed by repeated washing with deionized water and ethanol. The final products were dried in a vacuum oven at 50 °C for 12 h.

### 2.3. Characterization

A transmission electron microscope (TEM, Hitachi H9500) was used to examine the structure of the samples. Phase and composition analyses of the products were performed by X-ray diffraction (XRD, Bruker-AXSD 8 Advance) with Cu target radiation and Fourier Transform Infrared Spectroscopy (FTIR Bruker, Equinox 55). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a ESCALAB 250Xi (Thermo Scientific) spectrometer operating at  $10^{-7}$  Pa. Thermogravimetric analyses (TG) were conducted on a Mettler-Toledo TG/SDTA 851e thermo-analyzer in flowing nitrogen gas at a heating rate of 10 °C/min. The magnetic properties of the particles were measured at room temperature (298 K) using a vibrating sample magnetometer (VSM, MicroSense EV9).

## 3. Results and discussion

### 3.1. Structure and configuration analyses

Fig. 1 shows the powder XRD patterns of the samples prepared with the two kinds of structure guide agents. According to the patterns, all peaks of the four samples match well with those of standard  $\text{Fe}_3\text{O}_4$  XRD diffraction (JCPDS Card No. 19-0629). It is clear that the intensity and full width at half maximum (FWHM) of the strongest characteristic peak for PVP- $\text{Fe}_3\text{O}_4$  sample are stronger and narrower than those for NaCit- $\text{Fe}_3\text{O}_4$  sample, indicating that the crystal size of PVP- $\text{Fe}_3\text{O}_4$  sample is larger than that of NaCit- $\text{Fe}_3\text{O}_4$  sample. Table 1 summarizes calculated grain sizes using the Scherrer equation based on the strongest (311) peak of

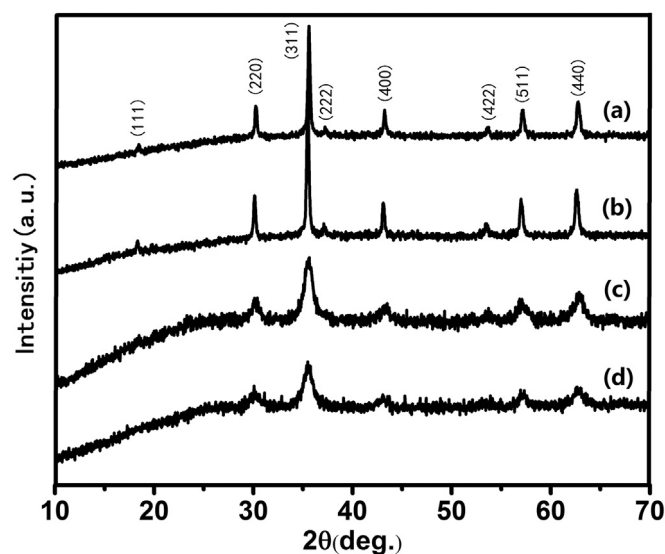


Fig. 1. X-ray diffraction patterns for (a, b) the  $\text{Fe}_3\text{O}_4$  particles synthetic reaction with PVP for 20 h and 10 h; (c, d) the reaction with NaCit for 20 h and 10 h.

Table 1

Grain size of the samples calculated for the strongest peak (311).

Sample	PVP- $\text{Fe}_3\text{O}_4$ sample		NaCit- $\text{Fe}_3\text{O}_4$ sample	
Reaction time /h	20	10	20	10
Grain size /nm	50.13	41.79	11.40	10.45

XRD patterns. It is known that the superparamagnetic limit for magnetite is approximate 20 nm [24–26]. The broadenings of the diffraction peaks shown in Fig. 1(c) and (d) demonstrated that the NaCit- $\text{Fe}_3\text{O}_4$  samples are composed of small-sized grains, which indicates that the NaCit- $\text{Fe}_3\text{O}_4$  samples might have superparamagnetism. Besides, from Table 1, it is found that the grain size of the NaCit- $\text{Fe}_3\text{O}_4$  particles increases slightly from 10.45 to 11.40 nm and the grain size of the PVP- $\text{Fe}_3\text{O}_4$  particles increases slightly from 41.79 to 50.13 nm when the reaction time is extended from 10 to 20 h. The increase of the NaCit- $\text{Fe}_3\text{O}_4$  particle size as a function of the reaction time suggests that NaCit can significantly suppress the crystal growth of the grains, while the increase of the PVP- $\text{Fe}_3\text{O}_4$  particle size as a function of the reaction time indicates that the prefabricated nanocrystals gradually grow larger over the reaction period.

To confirm the suggestion from X-ray measurements, we recorded the TEM images of the prepared  $\text{Fe}_3\text{O}_4$  monodisperse nanoparticles, as shown in Fig. 2. The results shown in Fig. 2 revealed that the prepared PVP- $\text{Fe}_3\text{O}_4$  monodisperse spherical nanoparticles have a diameter range of 100–150 nm in (a, c) and NaCit- $\text{Fe}_3\text{O}_4$  sample of 80–110 nm in (b, d). From Fig. 2(b, d), it is found that the NaCit- $\text{Fe}_3\text{O}_4$  nanoparticles are clusters of vast superfine particles and the diameters of the superfine particles are less than 10 nm, and from Fig. 2(c), it is found that the nanoparticles guided by PVP are composed of some micro-balls with diameter range of 20–40 nm. The TEM measurement gave consistent results with the XRD measurements.

### 3.2. Component analysis

To study the components of the two  $\text{Fe}_3\text{O}_4$  monodisperse nanoparticles and the roles of two different structure guide agents played in the solvothermal processes, we made further analysis. X-ray photoelectron spectroscopy (XPS) was first tested. The X-ray

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