

Research on the Preparation and Characterization of Magnetic Nanoparticles (MNPs) By Chemical Co-precipitation

Guizhong Zhou^{1,a*}, Shuo XU^{1,b}, Wenqian Li^{1,c}, QianYao^{1,d}, Dayi Zhang^{2,e}

¹ College of Environment and Safety Engineering, Qingdao University of Science and Technology, Qingdao, 266042, China

² Lancaster Environment Centre, Lancaster University, Lancaster LA12YQ, UK

*Corresponding author.

^aemail: zhougz@lqust.edu.cn. ^eemail: d.zhang@lancaster.ac.uk.

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Abstract. The synthesis and characterization of magnetic nanoparticles (MNPs) are attracting more and more attention in recent years. By chemical co-precipitation, $\text{NH}_3 \cdot \text{H}_2\text{O}$ as precipitant, reaction with the mixed solution of Fe^{2+} and Fe^{3+} , then obtain the nanometer magnetite. The sizes of the products are affected by temperature, stirring speed, the concentration of ferric salt, precipitant concentration, the amount of reactants, and the addition with PAAH which makes its good dispersion. The results showed that the best reaction conditions as follows: reactant ratio is $\text{Fe}^{2+}:\text{Fe}^{3+}:\text{NH}_3 \cdot \text{H}_2\text{O}=1:1:10$; precipitant concentration of ammonia is 0.25mol/L; iron concentration (the same solution concentration of Fe^{2+} and Fe^{3+}) is 0.5mol/L; the temperature control at 25°C; the stirring speed of 1000r/min. The XRD and SEM had carried on the preliminary characterization to MNPs analysis which showed the particle size of MNPs is about 20nm. The magnetic properties of MNPs had also tested by VSM.

Introduction

In recent years, with the rapid development of nanotechnology, the ferromagnetic oxide nanoparticles as functional materials are widely used in industrial production and in medical apparatus and instruments. Magnetic nanoparticles (MNPs) are not only widely used in the field of magnetic recording, such as audio tape, high density digital records, data storage, magnetic disk, etc. [1-5], and in special catalytic materials, magnetic pigment, but also has a great purpose in drug synthesis, what is more important in medical equipment, biological medicine uses more and more intensively. The high temperature radio frequency (RF), magnetic resonance imaging, medical diagnosis, cancer therapy and so on is involved in its application [6-9].

At present, the MNPs also more and more applied to the environmental pollution, especially soil restoration and groundwater management. Compared with the conventional iron powder, the size smaller and stronger reactivity of MNPs particle can be suspended in the water pump directly to the location of the polluted. It is helpful to the toxicity of organic pollutants into smaller simple carbohydrates. Heavy metals can also be converted into insoluble form and fixed in the soil [10]. MNPs can improve the structure of activated sludge and conducive to purify water quality[11], its application in the environment will be more and more widely.

Due to the application of magnetic nanoparticles is very broad, and its synthesis and surface modification has become a hot research direction. The preparation methods of magnetic nanoparticles can be roughly classified into physical methods and chemical methods. Physical methods mainly refer to mechanical polishing method; Chemical methods are including hydrothermal method, co-precipitation method, microemulsion method, sol-gel method, nonaqueous solvent synthesis method, high temperature pyrolysis method, etc. [8]. The chemical precipitation method was adopted in this paper, the characterization and the various factors on the properties of nano magnetic ferrous oxides were explored.

Experiments

Reagent and Instruments

FeCl₃ • 6H₂O (A.R); FeSO₄ • 7H₂O (A.R); NH₃ • H₂O (A.R); PAAH (Polyallylamine hydrochloride, 10mg/mL) Precision power electric mixer JJ-1 (guohua co., LTD.); Electrothermal blowing GZX-9076 Boxun industrial co., LTD. (Shanghai medical equipment factory); Constant temperature water-bath HH-4 Ziquan instrument co., LTD (Qingdao); Vortex mixing apparatus Scilogex MX-S; Bench centrifuge TGL-16G (Shanghai anting scientific instrument factory); Field emission scanning electron microscope JSM-6700F (Japanese electronics company); X-ray diffraction D/Max-2500/PC (master company in Japan); Vibrating Sample Magnetometer (VSM 7407, Shanghai University)

Experiment Principle

Chemical coprecipitation method is the process of preparation of ultrafine particles in the solution to form colloid particle coagulation. It can be divided into two stages: the first stage is the formation of crystal nucleus. The second stage is the growth of the crystal (nucleus). And the formation of crystal nucleus speed v_1 and crystal growth speed v_2 can be expressed by the following two type:

$$v_1 = \frac{dn}{dt} = k_1 \left(\frac{c-s}{s} \right) \quad (1)$$

$$v_2 = k_2 D(c-s) \quad (2)$$

Among them, the dn/dt is the number of generated crystal nucleus in per time; c is the concentration of the substance (which is the supersaturated concentration); s is its solubility; so $(c-s)$ is supersaturation; k_1 and k_2 are the proportional constant; D is the diffusion coefficient of solute molecules. When the $v_1 > v_2$, generating a large number of crystal nucleus in the solution, and the grain size is small; When $v_1 < v_2$, generating a small amount of crystal nucleus in the solution, the grain size becomes larger [12].

Using chemical coprecipitation method, mixing the bivalent iron salts solution with trivalent iron salts solution according to certain proportion, then quickly adding a certain percentage of the alkaline precipitant, mixing and reaction immediately after a period of time, centrifugal separation or be powerful magnet separation, after washing, drying, grinding, can get the ferromagnetic oxide nanoparticles. The reaction equation is as follows:



Fe₃O₄ is composite oxide, which can be expressed as FeO • Fe₂O₃. It is transformed by the corresponding hydroxyl. The equation shows that the reaction theory of mole ratio is Fe²⁺:Fe³⁺:OH⁻ = 1:2:8. Considering the bivalent iron easy to oxidation, the response of bivalent iron salts can be appropriately excess, recommended in reaction under nitrogen atmosphere. The ratio of iron salt and precipitating agent added, influence precipitation concentration, iron concentration, temperature, stirring speed and other factors on the performance of MNPs had been examined in this study.

Preparation of Ferroferric Oxide MNPs

The moderate alkaline--NH₃ • H₂O was adopted as precipitant in this experiment. The bivalent iron salts (FeSO₄ • 7H₂O) and trivalent iron salts (FeCl₃ • 6H₂O) were added to the three flask to make mixed solution at a certain ratio, then more than 25% (mass fraction) of ammonia added to the flask, in which the flask pumped in nitrogen starvation, with the blender at a certain speed and in constant temperature water bath. The reaction continued until the solution color change from green to black, and then stirred for 15 minutes ended the reaction. The reaction solution was put in a beaker, under which had a powerful magnets to separate the ferroferric oxide particles. The particles were repeated washing with distilled water several times, put them into the oven to dry for 6 hours under the condition of 60°C. Then after grinding, Ferroferric Oxide MNPs were obtained at last.

Results and discussion

Characterization of MNPs

XRD Analyses

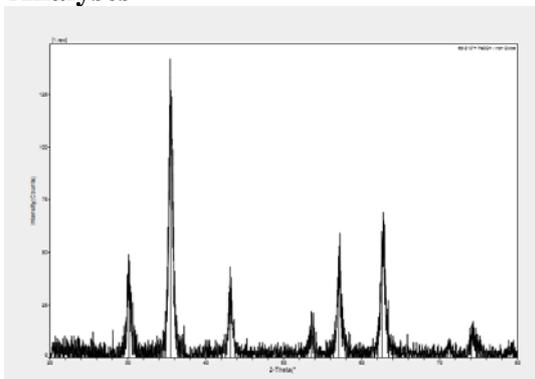


Fig1. XRD of Fe₃O₄ nanoparticles at 25 °C

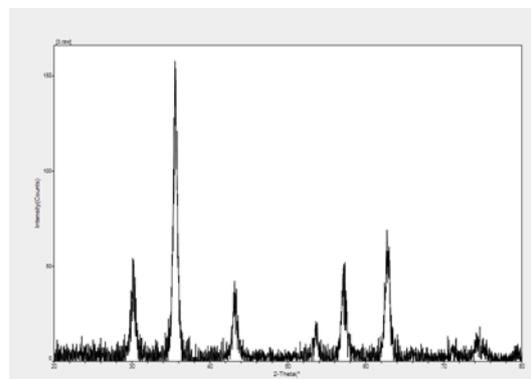


Fig.2. XRD of Fe₃O₄ nanoparticles at 35 °C

From Fig. 1, the particle diameter could be calculated with Scherer's equation, which $D=17.2\text{nm}$. The average particle size was 15.1nm after the peak fitting. The average particle size in the Fig.2 was 18.9nm obtained in the same way.

SEM Analyses

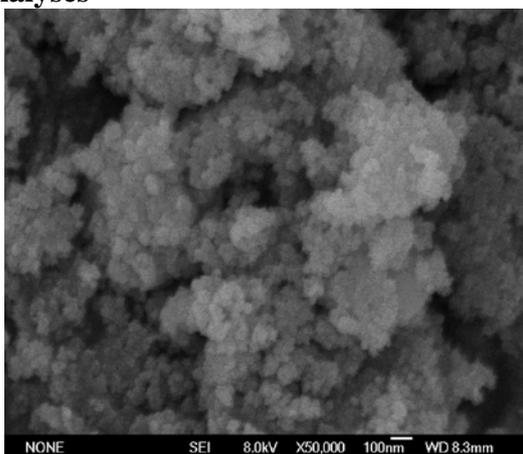


Fig.3. SEM images of the Fe₃O₄ nanoparticles

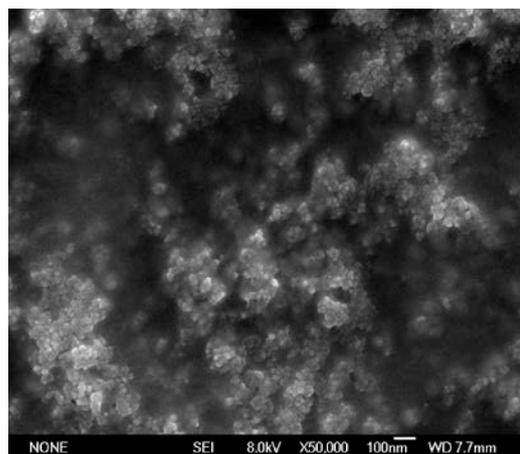


Fig.4. SEM images of the Fe₃O₄ nanoparticles obtained with PAAH

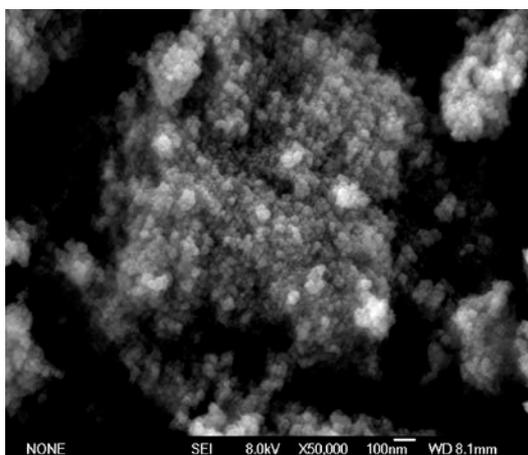
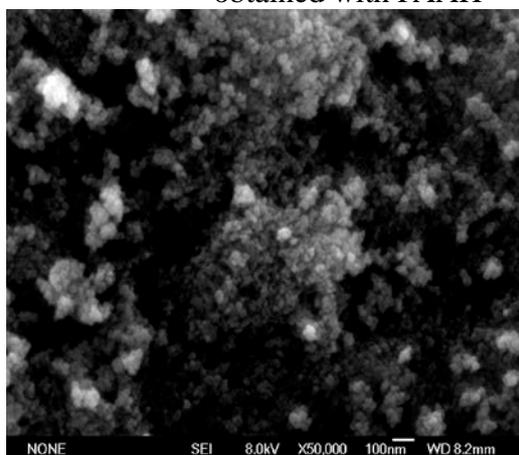


Fig.5. SEM images of the Fe₃O₄ nanoparticles obtained with 0.1mol/L and 0.25mol/L NH₃



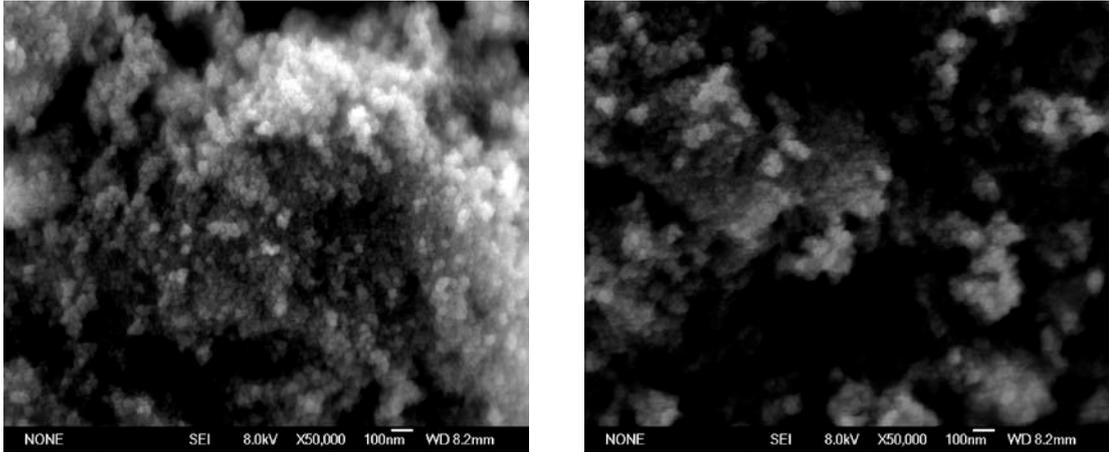
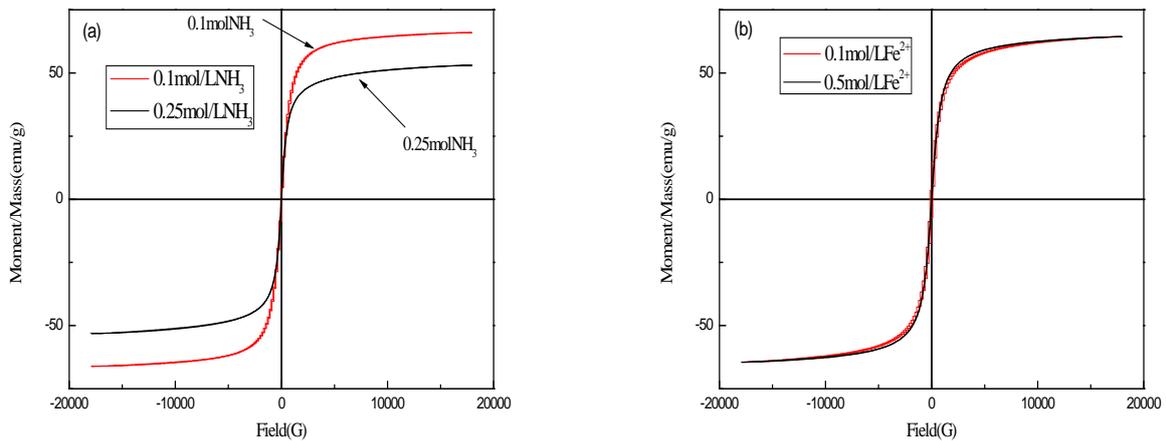


Fig.6. SEM images of the Fe_3O_4 nanoparticles obtained with 0.1 mol/L and 0.5 mol/L Fe^{2+}

From above pictures, ferroferric oxide nanoparticles had mainly spherical structure, within 20nm even size could be found, and XRD calculation tallies the particle size was better. MNPs electron microscope images in Fig. 3 had no dispersing agent and coating agent. MNPs agglomeration was quite serious and difficult to form a good dispersion of the suspension in that situation. Particle dispersion was better, and little change in particle size (remain at around 20nm), when PAAH(10mg/mL) as the dispersant in Fig.4. Fig.5 showed that ammonia concentration changes of MNPs had little effect on particle size; Fig.6 told that the impact of salt concentration change of MNPs particle size was not significantly; as temperature increase, the stirring speed increase MNPs were reunited occur as show.

VSM Analyses

The hysteresis loops of magnetic Fe_3O_4 nanoparticles measured at different factors(0.1mol/L and 0.25 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$, 0.1 mol/L and 0.5 mol/L Fe^{2+} , 25°C and 45 °C, 1000rpm and 2500rpm). The results were shown in figure 7.



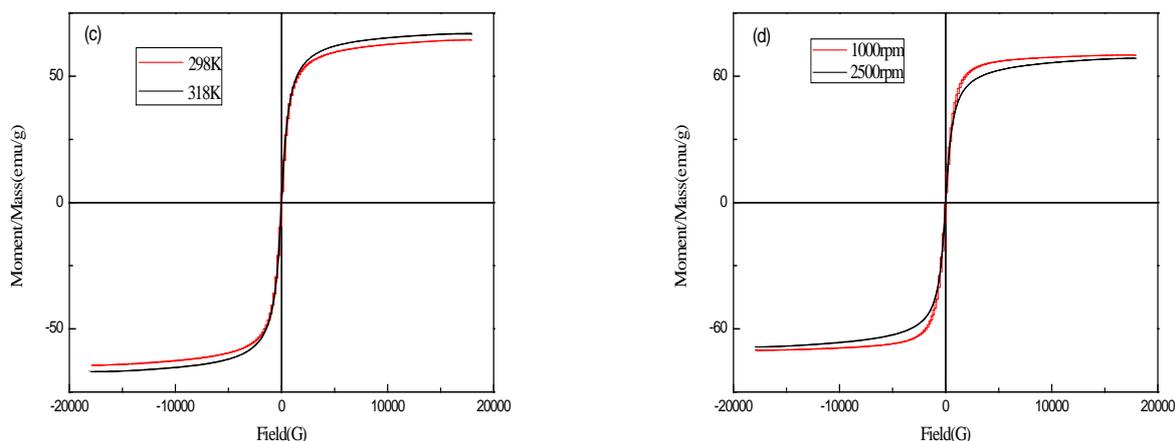


Fig.7. Hysteresis loops of magnetic Fe₃O₄ nanoparticles

Saturation magnetization were 65.8881emu/g and 52.9444emu/g, 64.2985 emu/g and 64.3126 emu/g, 64.2396 emu/g and 66.6094 emu/g, 69.8824 emu/g and 68.4394 emu/g.(a), (b), (c), (d) respectively represent the influence of different factors on the magnetic properties, which had been characterized by paramagnetic, as the magnetic hysteresis curve showed. The concentration of ammonia was the most significant effect on magnetization properties of MNPs from these curves.

The saturation magnetization intensity was dropped down as the increase of ammonia concentration, which was due to the saturation magnetization decreases with the decrease of the crystallinity. Particle size decreases with increased ammonia concentration was consistent; Iron concentration almost had no effect on magnetization properties of MNPs; Temperature and stirring speed had little influence on the magnetization properties of MNPs.

Conclusion

Magnetic ferroferric oxide MNPs were prepared with chemical coprecipitation preparation method in this paper. The best preparation conditions considering in the study were: additive amount of reactant ratio of Fe²⁺:Fe³⁺:NH₃ • H₂O=1:1:10, precipitant concentration of ammonia was 0.25 mol/L, iron concentration (the same solution concentration of Fe²⁺ and Fe³⁺) was 0.5 mol/L, the temperature control was at 25°C or so, the stirring speed of was 1000r/min. In such conditions, particle size of MNPs was stability within 20nm. At the same time, it could be seen that the particle size increased with the increase of temperature. And precipitant concentration of ammonia had little effects on the size and color of the product. Iron concentration should not be less than 0.2mol/L; otherwise easily lead to the final product was not pure oxidation. The mixing speed remain above 1000 r/min was necessary to maintain the small particle size of MNPs.

In addition, the nanoscale magnetic ferroferric oxide easy to reunite, the use of PAAH as the MNPs' dispersant in solution was a good way, and had a little MNPs size change.

The VSM Analyses told that all the MNPs had good magnetic properties. The saturation magnetization intensity was dropped down most significantly as the increase of ammonia concentration in the all concern conditions.

Acknowledgements

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