A facile solvothermal synthesis of magnetite nanoparticles controlled in size and shape

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Abstract: Inorganic nanoparticles exhibit various functions according to their sizes and shapes. Magnetite (Fe_3O_4) is a representative magnetic particle and it has been expected to show various functions derived from its sizes and shapes. The uniform Fe_3O_4 nanoparticles have been synthesized under highly condensed conditions via a simple solvothermal method. By change in basic conditions, such as the pre-aging period, the concentration of reactants, heating temperatures and aging periods, their effects on the sizes and shapes of Fe_3O_4 particles were also studied.

Keywords: Magnetite, Solvothermal method, Nanoparticle.

1. Introduction

Fe_3O_4 particle has attracted considerable attention as a representative magnetic particle. It has been applied in many aspects, like microwave absorption, catalyst, hyperthermia therapy, and magnetic fluids. The magnetic properties are strongly influenced by the particle sizes and shapes.

To date, most of the Fe_3O_4 particles were prepared under low concentration (0.001~0.1 mol/L) by solvothermal synthesis so that to prevent the particles from random agglomeration during the growth process. From the view point of the practical usage of the Fe_3O_4 particles, liquid phase synthesis tends to obtain pure and homogeneous Fe_3O_4 particles under a highly condensed system. Besides, solvothermal technique can easily control the nucleation and growth, thus synthesizing functional Fe_3O_4 particles with specific shapes. [1]

In this research, the direct synthesis of Fe_3O_4 particles from the liquid phase, controlled in size and shape, was investigated under highly condensed conditions. Ethylene glycol (EG) is a polar solvent with a relatively high boiling point (197 °C) and viscosity and it can be used to dissolve reactants and serve as a reducing agent in order to make the homogeneous solution. [2] Fe_3O_4 particles were synthesized in EG solution with high concentrations of reactants, including 0.40 M of iron(II) perchlorate hexahydrate ($Fe(ClO_4)_2 \cdot 6H_2O$) and 1.0 M of tetramethyl-ammonium hydroxide (TMAH).

2. Experimental

In a typical experiment, 0.08 mol of $Fe(ClO_4)_2 \cdot 6H_2O$ was dissolved into the EG and then the total volume of mixture was fixed to 100 ml. And 2.0 M of TMAH/EG mixture (100 ml) was dropped into the $Fe(ClO_4)_2$/EG mixture at the rate of 20 ml/min in a separable flask. After stirring the mixture solution at the rate of 400 rpm (revolution per minute) for half an hour, the mixtures were transferred into the Teflon-lined autoclaves. Then the autoclaves were maintained at 250 °C for 3 hours and cooled down to room temperature naturally. Finally, the obtained samples were collected centrifugation (18000 rpm, 5 min, 20 °C) and further washed by ethanol and water for several times. The nanoparticles were obtained after drying in the oven at 60 °C for 12 hours.

3. Results and discussion

To study the effect of the concentration on the particle sizes and shapes, the molar ratio of the $Fe(ClO_4)_2$ and the TMAH was set as 2:5 while modulated the amount of EG. The obtained Fe_3O_4 nanoparticles' sizes and shapes changed with different concentrations as exhibited in TEM images (**Fig.1**). Among the four samples, the sample B can present relatively homogeneous sizes and uniform shapes, and its average diameter is about 31 nm. The obtained samples are further characterized by the SEM observation. The SEM image (**Fig.2**) indicates that the obtained Fe_3O_4 particles (Sample B) are in fact polyhedral particles.

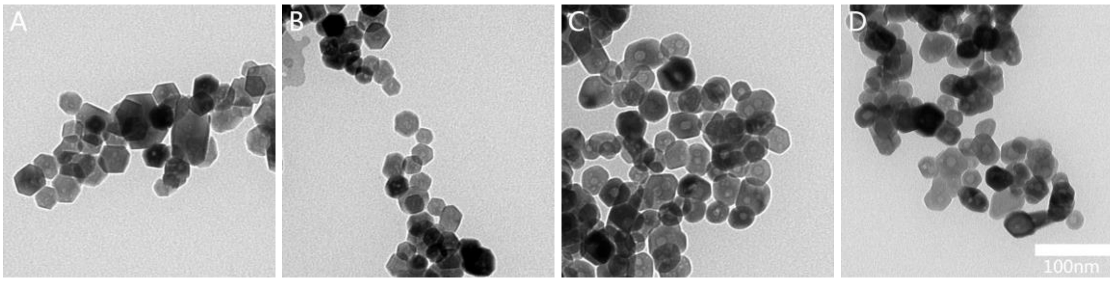

Figure 1. TEM images of Fe_3O_4 particles with different concentrations (A, $Fe(ClO_4)_2$:0.53 M, TMAH:1.3 M; B, $Fe(ClO_4)_2$:0.40 M, TMAH:1.0 M; C, $Fe(ClO_4)_2$:0.27 M, TMAH:0.67 M; D, $Fe(ClO_4)_2$:0.20 M, TMAH:0.50 M). The scale bar shown in D is common for all images.

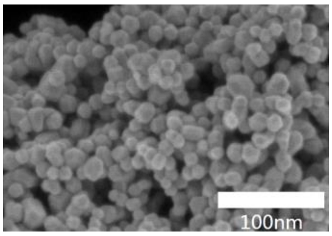

Figure 2. A SEM image of Fe_3O_4 particles (Sample B, $Fe(ClO_4)_2$:0.40 M, TMAH:1.0 M).

The factor of aging period was also considered while other conditions keep constant. The TEM images in Fig.2 demonstrated that most of the Fe_3O_4 nanoparticles show irregular shapes when they had been aged for only 1 hour at 250 °C. However, regular shapes can also be observed when these samples were aged for over 3 hours at 250 °C, and their sizes also became larger if they were heated for longer time. Due to the increase of both average sizes and aging time, Ostwald ripening can be supposed to be a main mechanism for the nanoparticles growth.

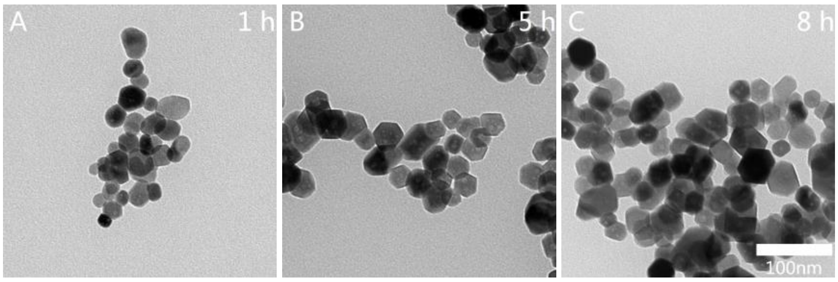

Figure 2. TEM images of Fe_3O_4 particles with different aging periods (A: 1 h; B: 5 h; C: 8h).

4. Conclusions

The Fe_3O_4 particles with a homogeneous size and shape were successfully obtained via a simple solvothermal method. It reveals that mass production of Fe_3O_4 particles with controlled sizes and shapes can be realized under a direct and highly condensed condition. Considering the characteristic of uniform size and internal holes, the resulting Fe_3O_4 particles with a polyhedral shape might be expected to show various functions as functional materials.

References

1. G. Xu, L. Li, Z. Shen, Z. Tao, Y. Zhang, H. Tian , X. Wei, G. Shen, G. Han. *J. Alloy. Comp*. **629**.36 (2015).
2. X. Wang, J. Yu, G. Shi, G. Xu, Z. Zhang. *J. Mater. Sci*. **49**.6029 (2014).