A NH₄Ac-assisted solvothermal fabrication and properties of size-controlled cobalt ferrite nanospheres

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Abstract. Monodisperse cobalt ferrite nanospheres with the mean size 100 nm have been synthesized via a simple solvothermal method by using NH₄Ac as protective agent. The sizes of the particles can be controlled from 20 to 200 nm by changing reaction time or protective agents. Magnetic and microwave absorption properties of Co ferrite nanospheres with the different sizes were investigated in details. Magnetic studies revealed that the saturation magnetization (Ms) and the coercivity (Hc) increased with the increase in particle size, that is, the Ms and Hc are 53.5 A·m²/kg and 14.6×10³ A·m⁻¹ (100 nm), 68.9 A·m²/kg and 49.9×10³ A·m⁻¹ (125 nm) and 72.5 A·m²/kg and 54.5×10³ A·m⁻¹ (200 nm), respectively. Electromagnetic and resulting microwave adsorption properties showed that the maximum magnitudes of the dips are −11.96 dB (at 9.00 GHz for 100 nm), −23.02 dB (at 5.55 GHz for 125 nm), and −32.79 dB (at 10.47 GHz for 200 nm), respectively.

1. Introduction
As an important functional material, cobalt ferrite exhibits excellent properties such as high coercivity, moderate magnetization, high Curie temperature, large magneto-crystalline anisotropy, excellent chemical stability, and mechanical hardness [1-3]. Cobalt ferrite thus is realized as a promising candidate material that used for high density information storage device [4], ferrofluids technology [5], biomedical drug delivery [6], and magneto-optical devices [7], etc. On the other hand, as the physical and chemical properties of nanomaterials are strongly depended on their morphology and size, the relationship between size and property over cobalt ferrite materials are widely investigated. For example, when the size of cobalt ferrite nanoparticle is decreased to 5 nm, cobalt ferrite becomes superparamagnetic at room temperature, which makes it highly useful in cell-separation and drug delivery in biomedicine field [8]. Therefore, synthesis of monodisperse cobalt ferrite nanoparticles with adjustable sizes is great significance.

Up to now, considerable efforts have been done on the shape-controlled synthesis of cobalt ferrite crystals. Among them, one-dimensioned cobalt ferrites nanoparticles such as nanowires [9], nanorods

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[10], and three-dimensioned cobalt ferrites [11], such as nanospheres and nanocubes have been successfully synthesized. Recently, cobalt ferrite nanoparticles with the diameter of particles from 2.7 nm to 17 nm have been synthesized through the “Self-propagating High temperature Synthesis technique (SHS)” [12]. However, the controlled synthesis of cobalt ferrite nanoparticles with monodisperse particle size is still a highly sophisticated challenge. Herein, we demonstrated a one-step, economical and efficient solvothermal method for the large-scale fabrication of monodisperse cobalt ferrite solid nanospheres. In this route, NH4Ac was used as protective agent, and the size and inner-structure of these particles could be readily controlled by simply adjusting reactive time or the nature of the protective agent. The size-dependent properties of magnetic, electromagnetic and microwave adsorption properties were investigated.

2. Experimental section

FeCl3·6H2O (2.0 mmol), CoCl2 (1.0 mmol), and NH4·Ac (15.0 mmol) was dissolved in 30.0 ml ethylene glycol. The mixture was magnetically stirred to form clear solution at room temperature. Then, the mixture was sealed in a teflon-lined stainless-steel autoclave (50 ml capacity) and heated at 180°C for 24 hours (h). After reaction, the autoclave was cooled down to room temperature naturally. At last, the product was centrifuged at 2000 rpm for 10 min, washed (with deionized water and 99.5% ethanol), and dried (at 60°C for 6 h) to obtain cobalt ferrite powder.

The obtained samples were characterized on a Rigaku Dmax-2000 X-ray powder diffractometer (XRD) with Cu Kα radiation (λ=1.5418 Å). The operation voltage and current were kept at 40 kV and 40 mA, respectively. The size and morphology of the as-synthesized products were determined at 20 kV by a XL30 S-FEG scanning electron microscope (SEM) equipped with an Energy-dispersive X-ray spectroscopy (EDS). Magnetic properties of the samples were carried out by using a LDJ-9600 vibrating sample magnetometer (VSM). The complex permittivity and permeability and resulting microwave adsorption property have been studied by HP-8720ET vector network analyzer.

Figure 1. (A) A XRD pattern of Co ferrite nanoparticles synthesized used NH4Ac as protective agents at 180°C for 24 h. (B) A TEM image of the same batch of sample. The inset shows the SAED pattern taken from an individual nanosphere. (C) A SEM images of the same batch of sample. (D) An EDS pattern of the same batch of sample.
3. Result and discussion

Figure 1A shows the XRD pattern of the product prepared at 180°C for 24 h. All the peaks could be readily identified as the pure cubic phase [space group: Fd3m (227)] with cell constants a = 8.394 Å (JCPDS 22-1086), indicating that the as-prepared product shows high purity. So, well-crystallized and pure phase Cobalt ferrite crystalline was successfully synthesized. Then, the morphology and sizes of prepared Cobalt ferrites are characterized by transmission electron microscope analyses. Figure 1B shows a typical TEM image of the Co ferrite nanospheres, which illustrates that the cobalt ferrite nanoparticles prepared by the solvothermal method are monodisperse with monodisperse nanoparticles about 100 nm. The inset is a corresponding selected area electron diffraction pattern, which further confirmed that the nanoparticle has well crystallinity. The labeled diffraction rings could be indexed to the spinel structure of cobalt ferrites, which are consistent with XRD result. Figure 1C shows the SEM image of the product observed in large area. It is shown all the particles are sphere like with monodisperse particle size about 100 nm. Then, the chemical compositions of sample have also been investigated by EDS, which is shown in figure 1D. The as-prepared particles contain Fe, Co and O and there is no other contamination element detected. So, high purity Cobalt ferrets is successfully obtained.

![Figure 1A](image1A.png) ![Figure 1B](image1B.png) ![Figure 1C](image1C.png) ![Figure 1D](image1D.png)

**Figure 2.** TEM or SEM images of Co ferrites prepared under different conditions. (A and B) The same as in figure 1, except that growth time was changed from 24 h to 12 and 48 h, respectively. (C and D) The same as in figure 1, except that the protective agent of NH₄Ac was substituted with NaAc and the mixed protective agents of 15.0 mmol NaAc and of 3.0 mmol SDS, respectively. The inset in (C) shows the higher magnification SEM image obtained from a selected area of the figure 2(C).

The morphology and sizes of the final product were found to strongly depend on reaction conditions and the nature of the protective agent. For example, when the reaction time was reduced from 24 to 12 h, the average sizes of cobalt ferrite decreased from 100 nm to 75 nm and the shape of the as-prepared was not monodisperse nanospheres (as shown in figure 2A). However, if the reaction time was prolonged from 24 to 48 h, the sizes of monodisperse Co ferrite spheres were increased to about 125 nm and the nanospheres self-assembled (figure 2B). Besides that, the sizes of nanoparticles prepared in this condition are also not as monodisperse as the product prepared at reaction time of 24 h.
So, the 24 h is an optimized reaction time for preparing monodisperse Co ferrite nanospheres.

We have also tried to use the different protective reagent to prepare Co ferrite nanoparticles under similar reaction conditions. As shown in figure 2C, when 15.0 mmol of the NH4Ac was substituted with equal NaAc, Co ferrite nanoparticles with average size about 20 nm is obtained with reaction time of 24 h. The inset in figure 2(C) is a higher magnification SEM image obtained from a selected area of the figure 2(C) and reveals that these nanospheres were monodisperse. Furthermore, when some surface agent is added, such as sodium dodecyl sulfates (SDS), only nanoparticles with sizes about 200 nm could be obtained (mixture of 15.0 mmol NaAc and of 3.0 mmol SDS, reaction time 24 h).

In the following study, the relationship between sizes and magnetic properties was studied by using a vibrating sample magnetometer (VSM). Figure 3 shows the typical hysteresis loops of the different sizes Co ferrites nanocrymaterials at 300 K. It can be seen from figure 3 that both of the saturation magnetization (Ms) and the coercivity (Hc) gradually increases with as the particle size increases. The values of Ms and Hc of 100 nm as-synthesized sample are respectively 53.5 A·m⁻¹/kg and 14.6×10³ A·m⁻¹, while the two corresponding values are 68.9 A·m⁻¹/kg and 49.9×10³ A·m⁻¹ (125 nm) and 72.5 A·m⁻²/kg and 54.5×10³ A·m⁻¹ (200 nm).

The relationship between sizes and microwave absorption properties calculated from a computer simulation using the values of electromagnetic parameters (ε′, ε″, μ′ and μ″) and other parameters, such as the speed of light (c) and the thickness of the samples (t) was also investigated. The real and imaginary parts of complex permittivity (ε′, ε″) and permeability (μ′, μ″) of Co ferrite particles were measured using an 8720ET vector network analyzer working at the 2–18 GHz band (the test samples were firstly mixed together as-synthesized cobalt ferrites and paraffine with the mass ratio of 3:1 and then molded into the 3.1 mm-thickness hollow pipe of rectangular cavities). The results are shown in figure S (Supporting Information), in which the letters “a”, “b” and “c” correspond to particle size of about 100, 125 and 200 nm, respectively. The calculation process referred to the work of Yusoff [13]. Figure 4 shows that an enhanced microwave absorption properties as the particle size of Co ferrites increases. Figures 4(a), 4(b) and 4(c) also correspond to the particle sizes of Co ferrites with 100, 125 and 200 nm, respectively. Figure 4(a) shows that there is only one wide and shallow dip around 9.00 GHz and the reflection loss minimum or the dip in plot which is equivalent to the occurrence of minimal reflection of the microwave absorber is −11.96 dB at 9.00 GHz. The number, magnitudes and situations of the dips vary as the sizes of the as-prepared Co ferrites increases. Two dips can be observed in the different frequency ranges for 125 samples (figure 4(b)) and 200 nm one (figure 4(c)). The maximum magnitudes of the dips are −23.02 dB at 5.55 GHz for 125 nm one, and −32.79 dB at...
10.47 GHz for 200 nm one, respectively. Further study is needed to fully probe the mechanism leading to the difference of microwave absorption properties of Co ferrites nanoparticles with the different sizes.

4. Conclusion
In conclusion, monodisperse cobalt ferrite nanospheres have been successfully synthesized via a simple NH₄Ac-assisted solvothermal method. The sizes of these particles can be controlled by changing some experimental parameters, such as reaction time and the nature of protective reagents. Magnetic studies revealed that the saturation magnetization and the coercivity increased with the increase in particle size (the values of Ms and Hc are 53.5 A·m²/kg and 14.6×10³ A·m⁻¹ for 100 nm cobalt ferrite nanospheres, 68.9 A·m²/kg and 49.9×10³ A·m⁻¹ for 125 nm one and 72.5 A·m²/kg and 54.5×10³ A·m⁻¹ for 200 nm one). Microwave absorption properties studies revealed that the maximum magnitudes of the dips are $-11.96$ dB at 9.00 GHz for 100 nm cobalt ferrite spheres, $-23.02$ dB at 5.55 GHz for 125 nm one and $-32.79$ dB at 10.47 GHz for 200 nm one, respectively.

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Appendix

![Graphs showing frequency dependence on (A) real and (B) imaginary parts of permittivity, and (C) real and (D) imaginary parts of permeability for different average sizes of Co ferrite nanospheres. (a) 100 nm, (b) 125 nm, and (c) 200 nm.](image)

Figure S. Frequency dependence on (A) real and (B) imaginary parts of permittivity, and (C) real and (D) imaginary parts of permeability for different average sizes of Co ferrite nanospheres. (a) 100 nm, (b) 125 nm, and (c) 200 nm.
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