DOI 10.1007/s11595-015-1285-4

Magnetic Properties for the Single-domain $CoFe_2O_4$ Nano-particles Synthesized by the Hydrothermal Method

YANG Zhi[1], ZHANG Yue[2], SONG Yu[2], WANG Jiawei[2], CHEN Yuang[2], ZHANG Zhe[2], DUAN Nian[2], RUAN Xuefeng[3*]

(1. City College, Wuhan University of Science and Technology, Wuhan 430083, China; 2. School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, China; 3. Center of Nanoscience and Nanotechnology and School of Physics and Technology, Wuhan University, Wuhan 430072, China)

Abstract: The aim of this work was to investigate the size-related magnetism for the single-domain $CoFe_2O_4$ nano-particles synthesized using the hydrothermal method. The effects of the reaction temperature and the reaction time on the lattice constants, particle morphologies, and the room-temperature magnetic properties were studied from the X-ray diffraction, the transmission electron microscope, and the vibrating-sample magnetometer. The experimental results show that the samples are composed of $CoFe_2O_4$ nano-particles with an average crystallite size (D) smaller than 40 nm, and the magnetic properties of the samples can be manipulated in a wide range: the M_S values vary from smaller than 50 emu/g to close to 80 emu/g, and the H_C values are between about 200 Oe and 2000 Oe. Additionally, the relationship between H_C and $1/D^{3/2}$ satisfies linearship, showing the characteristic of single-domain structure. These results indicate that the single-domain $CoFe_2O_4$ nano-particles with size controlled between the superparamagnetic critical size and single-domain critical size can be easily prepared using this hydrothermal method.

Key words: hydrothermal; $CoFe_2O_4$; single-domain nano-particles; magnetic properties

1 Introduction

In recent years, the magnetic nano-material has attracted considerable attention due to its wide application foreground[1,2]. When the size of the magnetic particle is smaller than a critical value (L_d), the single-domain structure can form. Such single-domain magnetic nano-particles may be used in the field of information recording to increase the storage density in hard disk drives, such as the well-known bit-pattern media (BPM)[2]. In addition, when the size is further reduced to be smaller than the other critical value, the superparamagnetic critical size (L_s), the single-domain nano-particles with superparamagnetism will be formed. Such superparamagnetic nano-particles are also widely used.

Among the magnetic materials, the ferrimagnetic ferrites with spinel structure have drawn long interest. As compared with the magnetocrystalline anisotropy constant (K_A) of other soft-magnetic spinel ferrites, the K_A of cobalt ferrite ($CoFe_2O_4$) is larger. The large K_A is not good for some conventional applications of soft-magnetic spinel ferrites, such as micro-wave communication devices, while it may be an advantage to the information storage since a large K_A may lead to a small superparamagnetic critical size (L_s). Additionally, unlike metals or alloys, $CoFe_2O_4$ also has a very good chemical stability[3,4], which is also a key point for the materials used for the information recording.

In the information storage media, storage units are generally formed by single-domain magnetic particles on the nano-meter scale. In recent years, considering the potential application of $CoFe_2O_4$ in the field of information recording, many groups have paid attention to the researches concerning the magnetic properties and

(Received: Sep. 5, 2014; Accepted: Nov. 8, 2014)

YANG Zhi(杨芝): Lecturer; Ph D; E-mail:zhiywh@163.com

*Corresponding author: RUAN Xuefeng(阮学峰): Senior Engineer; E-mail: ruanxuefengwhu@163.com

Funded by the National Natural Science Foundation of China (51172166) and the Ph D Programs Foundation of City College, Wuhan University of Science and Technology (2014CYBSKY003)

the synthesis methods of single-domain $CoFe_2O_4$ nano-particles. For example, based on some studies about the size-dependent magnetic properties, a 30-40 nm single-domain critical size (L_d) for $CoFe_2O_4$ nano-particles has been found, and the coercivity reaches maximum when the particle size is at this critical value[4-7]. Additionally, the single-domain $CoFe_2O_4$ nano-particles have been synthesized using many chemical methods, such as sol-gel[8,9], co-precipitation[4-6,10-13], combustion[7, 4-16], hydrothermal[17-25], and thermal-decomposition[26,27]. Among these synthesis methods, the hydrothermal method has advantages in preparing the single-domain $CoFe_2O_4$ nano-particles with good crystalline, small sizes and regular shapes, which is important for the information storage media. However, the works concerning the magnetic parameters of the single-domain $CoFe_2O_4$ nano-particles synthesized via the hydrothermal method, specially for the size dependence of their magnetic properties which is important for the property of the storage media, are still far from enough.

In our previous work[23], using the hydrothermal method with the addition of $Na_3CA{\cdot}2H_2O$, we have successfully prepared the single-domain $CoFe_2O_4$ nano-particles with an average size of 7.6 nm, approaching the L_s of $CoFe_2O_4$. The addition of a large content of $Na_3CA{\cdot}2H_2O$ can lead to the increase in the viscosity of the starting solutions, resulting in the lower crystal-growth rate and smaller particle sizes, but it seems that the size can only be manipulated in a very small range by changing the masses of $Na_3CA{\cdot}2H_2O$[25].

Besides by adding $Na_3CA{\cdot}2H_2O$, it is widely believed that the size of nano-particles can be manipulated by changing the reaction conditions (the reaction temperature and the reaction time) more effectively. Therefore, in the present work, using the former synthesis procedure under different reaction conditions, single-domain $CoFe_2O_4$ nano-particles with a wide range of sizes were prepared, and the size dependence of their magnetism was studied in detail. The results show that the size of the $CoFe_2O_4$ nano-particles can be well controlled between L_s and L_d. In this size range, the typical size-dependence behaviors for single-domain magnetic nano-particles were observed, and the magnetic properties can also be tuned in a wide range.

2 Experimental

The raw materials for the hydrothermal synthesis were $CoCl_2{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, $Na_3CA{\cdot}2H_2O$ and NaOH. All of the reagents were of analytical grade and used without further purification.

Firstly, 80 mL aqueous solutions were prepared by dissolving 0.555 g $CoCl_2{\cdot}6H_2O$, 1.261 g $FeCl_3{\cdot}6H_2O$, and 8.288 g $Na_3CA{\cdot}2H_2O$ in distilled water. Under vigorous stirring, these solutions were poured into 20 mL 1.625 M NaOH aqueous solutions, respectively. After continuous stirring for 0.5 h, the brown suspensions were transferred into 150 mL autoclaves, which were put into an oven and heated at 200 ℃ for 0.5, 2, 5, 10, 20, 40, 80 h and at 120, 160, 200, 240, 280 ℃ for 10 h, respectively. After these heating treatments, the autoclaves were cooled naturally to room temperature. Finally, the obtained black powders were washed with distilled water and ethanol several times and dried in the oven at 100 ℃ for 2 h.

X-ray diffraction (XRD) phase analysis was performed on a D8-advanced X-ray diffractometer using the CuKα radiation at 2θ scanning from 15 to 65° (1° per minute) at a rate of 0.02°. The lattice constant and average crystallite size were determined by the positions and full-width at half maximum (FWHM) of the (311) peaks using Bragg equation and Scherrer formula, respectively. The morphologies of the particles were observed from a transmission electron microscope (TEM) (JEM2010). The lattice structure of particle was observed via a high-resolution transmission electron microscope(HRTEM) (JEM2010 FEF). The room-temperature magnetic measurements were performed via a vibrating sample magnetometer (VSM) on a physical property measurement system (Quantum Design PPMS-9).

3 Results and discussion

Figs.1(a) and 1(b) depict the XRD patterns of the samples that were synthesized via the hydrothermal method. It is clearly shown that the intensities of the XRD peaks are enhanced by prolonging heating time or by raising heating temperatures, especially by raising temperature.

Figs.1(c) and 1(d) show the lattice constants and the average crystallite sizes for the samples synthesized under different heating conditions. It can be seen that the lattice constants are a little larger than the data in the JCPDS card of $CoFe_2O_4$ (No. 22-1086). This larger lattice constant with the addition of $Na_3CA{\cdot}2H_2O$ can be attributed to the bonding between the carboxylic group in $Na_3CA{\cdot}2H_2O$ and the metallic ions in the solutions of the raw materials[25]. In addition, as shown

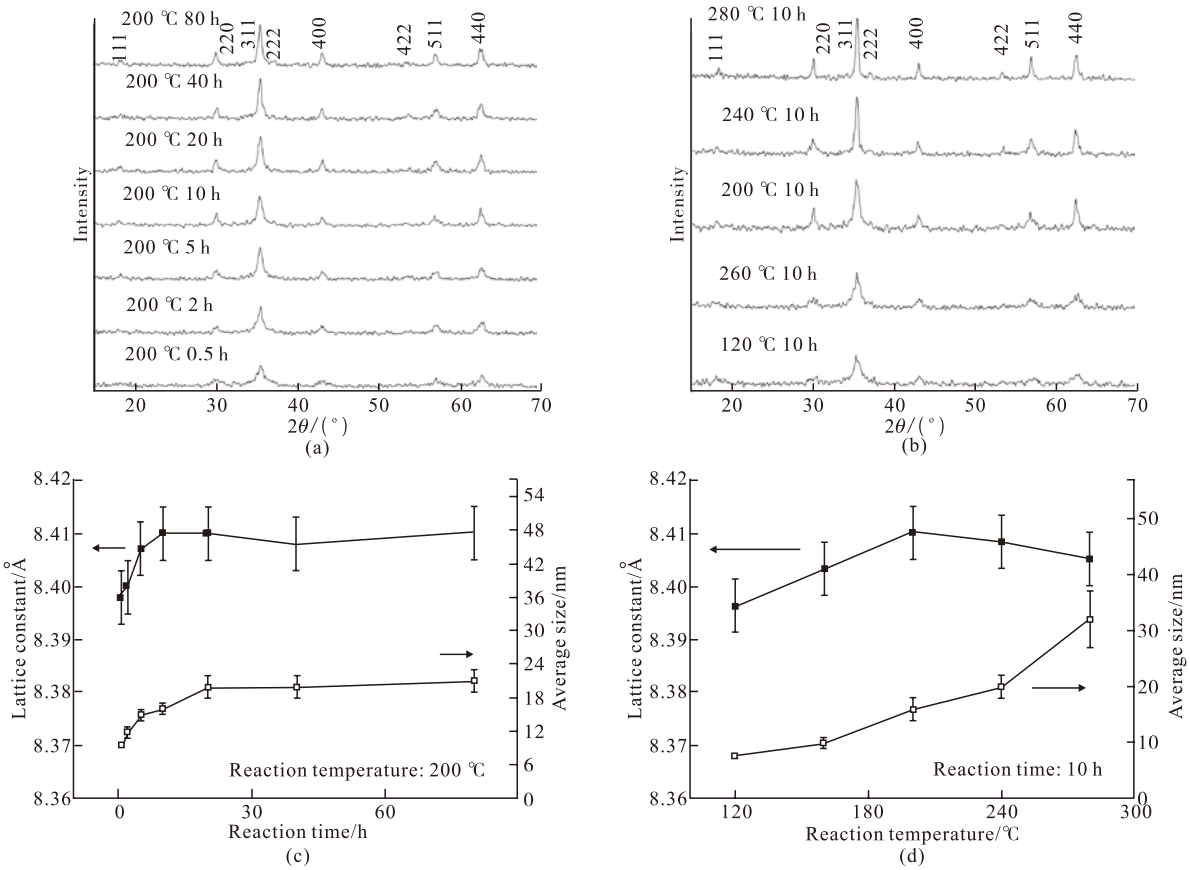

Fig.1 XRD patterns for the $CoFe_2O_4$ nano-particles synthesized by the hydrothermal method at different reaction conditions: (a) at 200 ℃ for different time and (b) at different temperatures for 10 h; The lattice constants and the average crystallite size for the $CoFe_2O_4$ nano-particles synthesized by the hydrothermal method under different reaction conditions: (c) at 200 ℃ for different time and (d) at different temperatures for 10 h

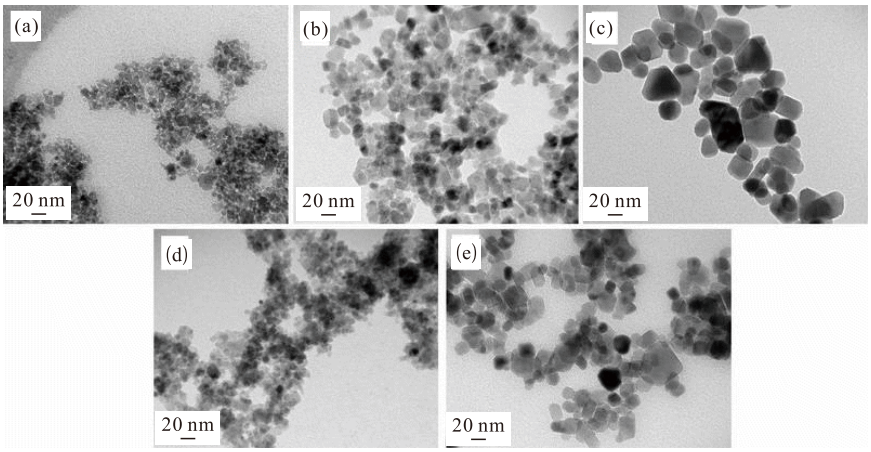

Fig.2 TEM images for the $CoFe_2O_4$ nano-particles synthesized by the hydrothermal method under different reaction conditions: (a) at 120 ℃ for 10 h, (b) at 200 ℃ for 10 h, (c) at 280 ℃ for 10 h, (d) at 200 ℃ for 0.5 h, and (e) at 200 ℃ for 80 h

in Fig.1(c), when the heating temperature is 200 ℃, prolonging heating process from 0.5 h to 10 h causes a small increase of the lattice constants from 8.398 Å to 8.410 Å and an increase in the average crystallite size from 9.5 nm to 20 nm, but when the heating becomes longer, the further change on lattice constants and size is much smaller. This indicates that the crystal growth mainly occurs in the initial 20 h when the heating temperature is 200 ℃. In Fig.1(d), one can see that when the heating time is 10 h, the raising of heating temperature from 120 ℃ to 280 ℃ can make a clear increase of crystallite size from 7.6 nm to 32 nm, but the increase of lattice constant mainly occurs when the heating temperature increases from 120 ℃ to 200 ℃. For the samples prepared under a low temperature or short time, the smaller lattice constants may be ascribed to a small amount of lattice vacancies, which widely exist in the nano-particles prepared by the chemical

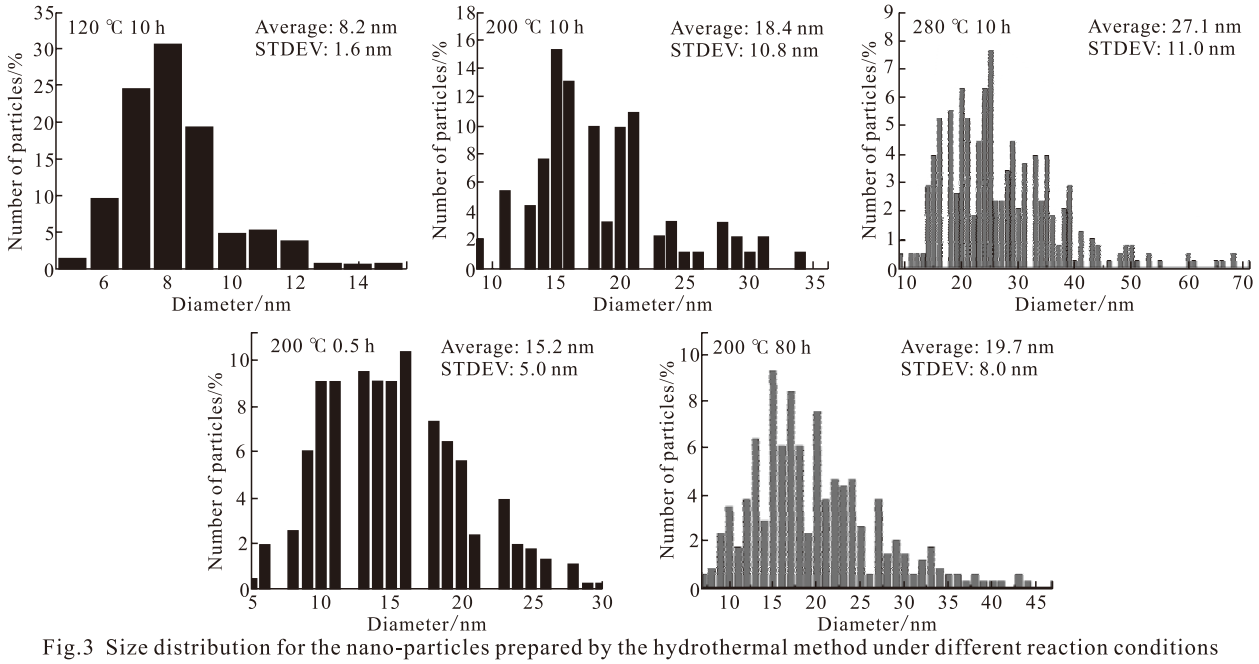

Fig.3 Size distribution for the nano-particles prepared by the hydrothermal method under different reaction conditions

method, and it is reasonable to think that raising heating temperature or prolonging heating time can reduce the amount of such vacancies.

Figs.2(a)-2(e) show the TEM images of the $CoFe_2O_4$ nano-particles that are synthesized under different conditions. From these images one can see that the products are composed of nano-particles with similar sizes and regular shape, indicating good crystallization. From Figs.2(a)-2(c), one can see that when the heating time is 10 h, raising heating temperature from 120 ℃ to 280 ℃ clearly increases the particle sizes. While from Figs.2(d) and 2(e), it can be seen that prolonging sintering time from 0.5 h to 80 h at 200 ℃ can also increase the particle sizes, but the variation range of the size is not very large.

Based on the TEM images, the size distribution has been further characterized by measuring the diameters (the longest length in a particle) of hundreds of particles for every sample. The particle-size histograms of the nano-particles are shown in Fig. 3. The data of the average particle sizes and the standard deviation (STDEV) are also listed in these figures. It can be seen that the average particle sizes of all the samples are close to the values of the average crystallite sizes determined via XRD, and the STDEV are close to the results for the $CoFe_2O_4$ nano-particles prepared using the similar methods[28,29].

The crystallinity and lattice structure of a $CoFe_2O_4$ nano-particle in the sample prepared at 200 ℃ for 10 h are observed via HRTEM. The image is shown in Fig.4. From this image one can see the edge-cutting shape of the nano-particle, and the lattice structure can be clearly seen throughout the whole particle, showing the good crystallinity. Additionally, a 0.26 nm spacing is determined, which is attributed to the (311) crystal faces, corresponding to the main peak in the XRD pattern.

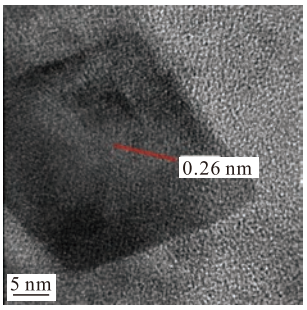

Fig.4 HRTEM image for a nano-particle in the sample prepared at 200 ℃ for 10 h

In Figs.5(a) and 5(b), the room-temperature magnetic hysteresis loops, characteristic hysteresis behavior is shown, and the change of reaction conditions makes a great impact on the magnetic properties such as the coercivity (H_C) and the magnetization under a higher field.

The magnetic parameters were quantitatively determined from the loops. The saturation magnetization (M_S), the effective magnetic anisotropy constant (K_{eff}) and the high-field susceptibility (χ_p) are determined by fitting the curves near the largest field using the law of approach to saturation[13, 25]:

$$M = M_S - \frac{0.076\ 19K_{eff}^2}{M_S H^2} + \chi_p H \qquad (1)$$

where, M is magnetization, H is the strength of the

applied magnetic field, and a coefficient of 0.07619 is used due to the cubic anisotropy of $CoFe_2O_4$[30]. The H_C values were determined by fitting the curves near M=0 emu/g.

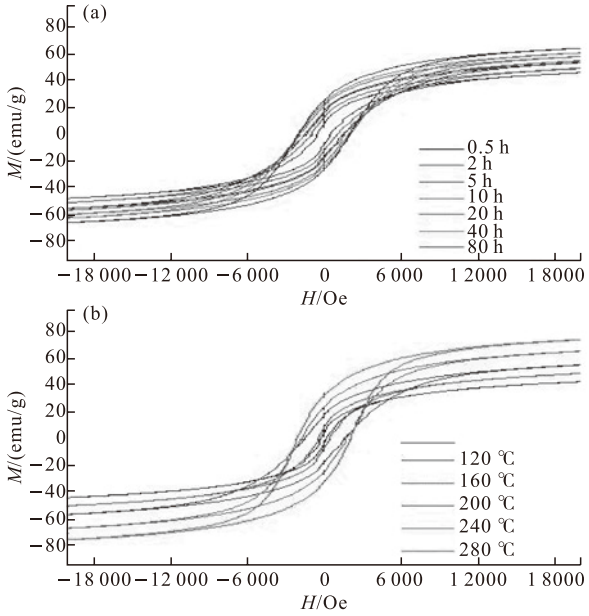

Fig.5 Room-temperature magnetic hysteresis loops for the $CoFe_2O_4$ nano-particles synthesized by the hydrothermal method under different reaction conditions: (a) at 200 ℃ for different time and (b) at different temperatures for 10 h

These magnetic parameters are all depicted in Fig.6. It can be seen that for the product of the heat treatment at 200 ℃ for 0.5 h, the M_S is only 50 emu/g, and the H_C is about 495 Oe; for the product of the heat treatment at 120 ℃ for 10 h, the M_S and H_C are even smaller, only about 46 emu/g and 212 Oe, respectively. These parameters are clearly smaller than those of the bulk $CoFe_2O_4$ (The M_S is about 80 emu/g, and the H_C is near 800 Oe[4, 22]). Prolonging heating time or raising heating temperature enhances M_S and H_C. When the heating time is longer than 20 h, a plateau in the H_C *vs*. time curve is shown; when the heating temperature reaches 280 ℃, the M_S becomes 78.7 emu/g, which is close to the M_S of the bulk $CoFe_2O_4$, and the H_C becomes 2041 Oe, which is about ten times larger than that of the product of the heat treatment at 120 ℃.

As shown in Fig.6, the K_{eff} and χ_p are clearly affected by the conditions of heat treatment: Prolonging heating time enhances K_{eff} and reduces χ_p, and the K_{eff} does not have big change when the heating time is longer than 10 h; raising heating temperature also increases K_{eff} and reduce χ_p, and when the heating temperature is 240 ℃, the K_{eff} reaches its maximum. In addition, it is noticed that the K_{eff} values are larger than 7×10^5 J/m^3, which is larger than the intrinsic magneto-crystalline anisotropy coefficient (K_A) (1.8×10^5-3.0×10^5

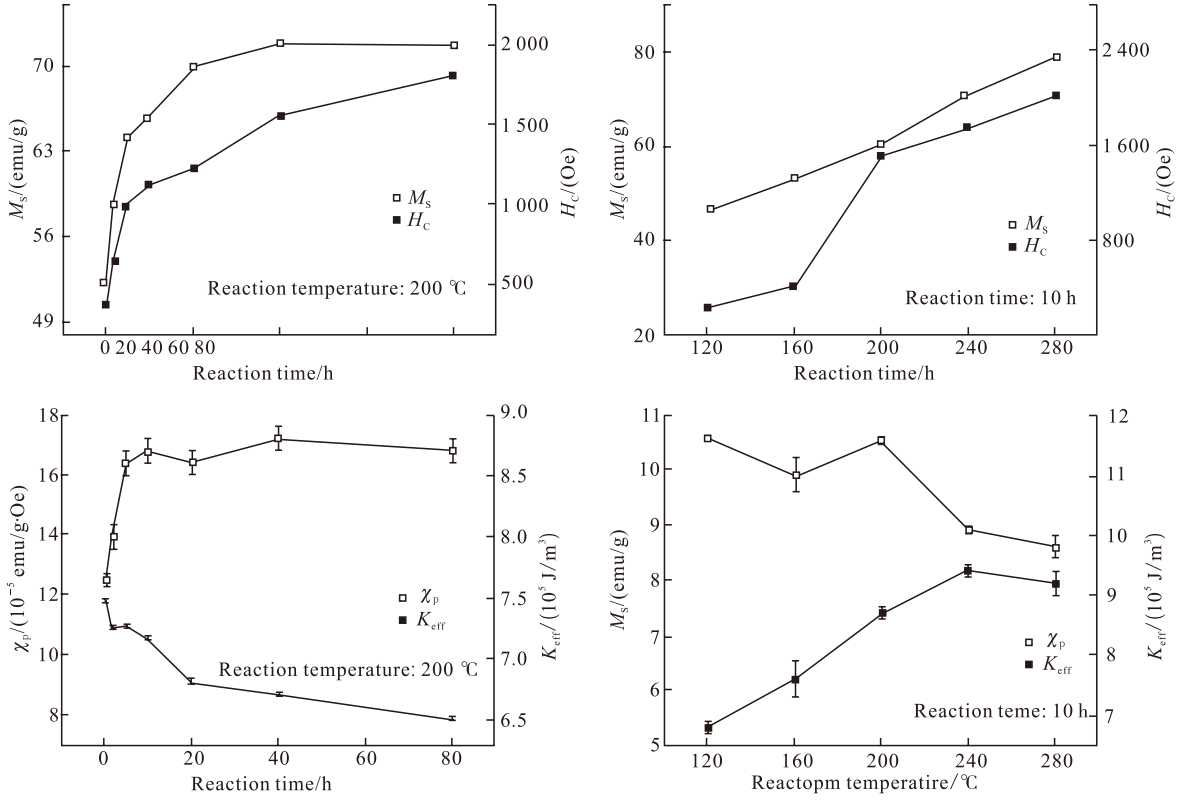

Fig.6 Magnetic parameters for the $CoFe_2O_4$ nano-particles synthesized by the hydrothermal method under different reaction conditions

J/m^3[31]) of the bulk $CoFe_2O_4$.

In the magnetic nano-particles synthesized by chemical methods, lattice vacancies usually exist, and the atomic ratio for surface ions is also large. Near lattice vacancies and surfaces, the exchange interaction is destroyed due to the imperfect coordination number, resulting in weaker ferro-/ferri-magnetic response due to the dead-magnetization effect[4] and the strengthened paramagnetic response under a higher field, which causes the smaller M_S and the larger χ_p.

In magnetic nano-particles, a large magnetic anisotropy constant is usually observed. This is because the factors that impact the magnetic anisotropy of nano-sized magnetic materials are very complicated: Besides the intrinsic magnetocrystalline anisotropy, other extrinsic factors, such as surface anisotropy[4] and stress anisotropy[30], should also be taken into account. Since the magnetic anisotropy energy equals the product of the magnetic anisotropy constant and volume, it is reasonable to think that if the magnetic anisotropy constant is large, the magnetic anisotropy energy cannot be very small unless the particle size is greatly reduced, as a result, superparamagnetism is hindered. Therefore, for the product of the heat treatment at 120 ℃ for 10 h, even though the particle size is as small as 7.6 nm, a coercivity as large as about 212 Oe can still be observed.

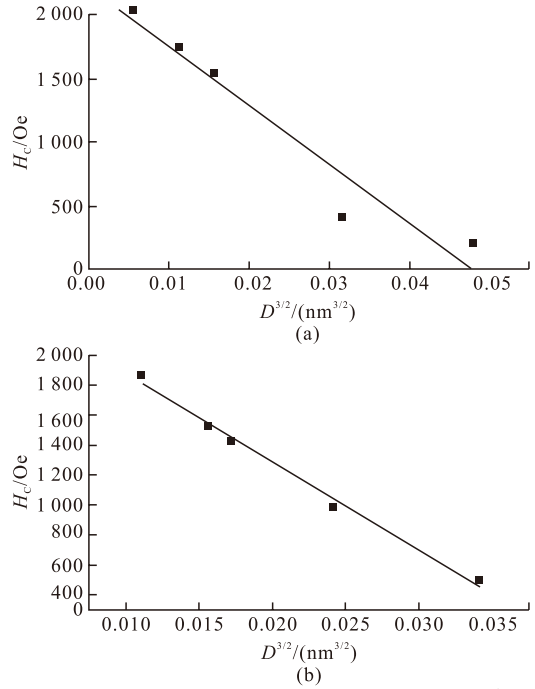

Fig.7 Curves for the relationship between H_C and $D^{3/2}$ (D is the average crystallite size of the $CoFe_2O_4$ nano-particles) under different reaction conditions: (a) at different temperatures (from 120 ℃ to 280 ℃) for 10 h, and (b) for different time (from 0.5 h to 20 h) at 200 ℃

After being heated at the higher temperatures or for longer time, the increase of K_{eff} may reflect the increased magnetocrystalline anisotropy constant due to the reduced lattice vacancies, which may also strengthen the exchange interaction and thus reduce χ_p. After being heated at 280 ℃ for 10 h, when the particle size greatly increases, the surface effect becomes negligible, leading to the smaller K_{eff} due to the reduced surface anisotropy.

In addition, as to the product of the heat treatment at 280 ℃, the particle size has become 32 nm, and the coercivity reaches 2041 Oe, which is very similar to the reported data for the $CoFe_2O_4$ nano-particles with size close to L_d[4-6]. On this critical state, the magnetization and demagnetization are mainly attributed to the rotation of magnetic moment, which will overcome the strong magnetocrystalline anisotropy energy and result in a large coercivity.

To further reveal the single-domain characteristic of the nano-particles, the relationship between H_C and the average crystallite size (named as D) is studied. It is known that in the single-domain magnetic nano-particles, the relationship between H_C and D satisfies the equation[32]:

$$H_C = H_a - \frac{C}{D^{3/2}} \tag{2}$$

where, H_a is the anisotropy field, and C is a constant. If the size is larger than L_d and the multi-domain structure is formed, the relationship between H_C and $1/D^{3/2}$ will deviate from the relationship. Figs.7 (a) and 7(b) depict the relationship between H_C and $1/D^{3/2}$ for the $CoFe_2O_4$ nano-particles synthesized at different temperatures and for different time (from 0.5 h to 20 h), respectively. From this figure an approximate linear relationship between H_C and $1/D^{3/2}$ can be seen, showing the single-domain characteristic for the samples, and the fitting result shows that the Ha is around 2400 Oe, about 400 Oe larger than the maximum H_C values for the sample with the largest size (32 nm). Considering the non-zero H_C for the samples with the smallest size (7.6 nm), we can conclude that under our reaction conditions, we can successfully prepare the single-domain $CoFe_2O_4$ nano-particles with a size between L_s and L_d.

4 Conclusions

In summary, $CoFe_2O_4$ nano-particles were synthesized by the hydrothermal method. By changing

the reaction temperature and reaction time, the magnetic properties are manipulated in a wide range: The M_S values are varied from smaller than 50 emu/g to close to 80 emu/g, and the H_C values are between about 200 Oe and 2000 Oe. The single-domain structure for these samples is further confirmed by the approximate linear relationship between H_C and $1/D^{3/2}$.

References

[1] Bader SD. Opportunities in Nanomagnetism[J]. *Rev. Mod. Phys*., 2006, 78: 1 1-15

[2] Lau JW, Shaw JM. Magnetic Nanostructures for Advanced Technologies: Fabrication, Metrology and Challenges[J]. *J. Phys. D: Appl. Phys*., 2011, 44: 30 303001

[3] Ramos AV, Guittet MJ, Moussy JB, *et al*. Room Temperature Spin Filtering in Epitaxial Cobalt-ferrite Tunnel Barriers[J]. *Appl. Phys. Lett.*, 2007, 91: 30 122107

[4] Maaz K, Mumtaz A, Hasanain SK, *et al*. Synthesis and Magnetic Properties of Cobalt Ferrite ($CoFe_2O_4$) Nanoparticles Prepared by Wet Chemical Route[J]. *J. Magn. Magn. Mater.*, 2007, 308: 2 289-2 295

[5] Chinnasamy CN, Jeyadevan B, Shinoda K, *et al*. Unusually High Coercivity and Critical Single-domain Size of Nearly Monodispersed $CoFe_2O_4$ Nanoparticles[J]. *Appl. Phys. Lett.*, 2003, 83: 14 2862-2864

[6] Qu Y Q, Yang HB, Yang N, *et al.* The Effect of Reaction Temperature on the Particle Size, Structure and Magnetic Properties of Coprecipitated $CoFe_2O_4$ Nanoparticles[J]. *Mater. Lett*., 2006, 60: 29-30 3 548-3 552

[7] Xiao SH, Jiang WF, Li LY, *et al.* Low-temperature Auto-combustion Synthesis and Magnetic Properties of Cobalt Ferrite Nanopowder[J]. *Mater. Chem. Phys*., 2007, 106: 1 82-1 87

[8] Lee JG, Lee HM, Kim CS, *et al*. Magnetic Properties of $CoFe_2O_4$ Powders and Thin Films Grown by a Sol-gel Method[J]. *J. Magn. Magn. Mater.*, 1998, 177: 900-902

[9] Bilecka I, Kubli M, Amstad E, *et al*. Simultaneous Formation of Ferrite Nanocrystals and Deposition of Thin Films Via a Microwave-assisted Nonaqueous Sol-gel Process[J]. *J. Sol-Gel Sci. Technol.*, 2011, 57: 3 313-3 322

[10] Ayyappan S, Philip J, Raj B. Effect of Digestion Time on Size and Magnetic Properties of Spinel $CoFe_2O_4$ Nanoparticles[J]. *J. Phys. Chem. C*, 2009, 113: 2 590-2 596

[11] Limaye MV, Singh SB, Date SK. High Coercivity of Oleic Acid Capped $CoFe_2O_4$ Nanoparticles at Room Temperature[J]. *J. Phys. Chem. B*, 2009, 113: 27 9070-27 9076

[12] Chinnasamy CN, Jeyadevan B, Perales-Perez O. Growth Dominant Co-precipitation Process to Achieve High Coercivity at Room Temperature in CoFe2O4 Nanoparticles[J]. *IEEE Trans. Magn*., 2002, 38: 5 2640-5 2642

[13] Zhang Y, Yang Z, Yin D, *et al.* Composition and Magnetic Properties of Cobalt Ferrite Nano-particles Prepared by the Co-precipitation Method[J]. *J. Magn. Magn. Mater.*, 2010, 322: 21 3470-21 3475

[14] Cannas C, Falqui A, Musinu A, *et al*. $CoFe_2O_4$ Nanocrystalline Powders Prepared by Citrate-gel Methods: Synthesis, Structure and Magnetic Properties[J]. *J. Nanoparticle Res.*, 2006, 8: 2 255-2 267

[15] Júniora AF, de Oliveira Limab EC, Novakc MA, *et al*. Synthesis of Nanoparticles of $Co_xFe_{(3-x)}O_4$ by Combustion Reaction Method[J]. *J. Magn. Magn. Mater.*, 2007, 308: 2 198-2 202

[16] Liu Y, Zhang Y, Feng JD, *et al.* Dependence of Magnetic Properties on Crystallite Size of $CoFe_2O_4$ Nnanoparticles Synthesised by Auto-combustion Method[J]. *J. Exp. Nanosci*., 2009, 4: 2 159-2 168

[17] Zhao D, Wu X, Guan H, *et al*. Study on Supercritical Hydrothermal Synthesis of $CoFe_2O_4$ Nanoparticles[J]. *J. of Supercritical Fluids*, 2007, 42: 2 226-2 233

[18] Ji GB, Tang SL, Ren SK, *et al*. Simplified Synthesis of Single-crystalline Magnetic $CoFe_2O_4$ Nanorods by a Surfactant-assisted Hydrothermal Process[J]. *J. Cryst. Growth*, 2004, 270: 1-2 156-2 161

[19] Liu XM, Fu SY, Zhu LP. High-yield Synthesis and Characterization of Monodisperse Sub-microsized $CoFe_2O_4$ Octahedra[J]. *J. Solid State Chem*., 2007, 180: 2 461-2 466

[20] Chen ZT, Gao L. Synthesis and Magnetic Properties of $CoFe_2O_4$ Nanoparticles by Using PEG as Surfactant Additive[J]. *Mater. Sci. Eng. B*, 2007, 141: 1-2, 82-86

[21] Liu Q, Sun JH, Long HR, *et al.* Hydrothermal Synthesis of $CoFe_2O_4$ Nanoplatelets and Nanoparticles[J]. *Mater. Chem. Phys*., 2008, 108: 2-3, 269-273

[22] Zhao LJ, Zhang HJ, Xing Y, *et al*. Studies on the Magnetism of Cobalt Ferrite Nanocrystals Synthesized by Hydrothermal Method[J]. *J. Solid State Chem*., 2008, 181: 2 245-2 252

[23] Zhang Y, Liu Y, Fei CL, *et al.* The Temperature Dependence of Magnetic Properties for Cobalt Ferrite Nanoparticles by the Hydrothermal Method[J]. *J. Appl. Phys*., 2010, 108: 8 084312

[24] Zhang Y, Fei CL, Liu Y, *et al*. The Effect of Surface Modification on the Magnetic Properties of $CoFe_2O_4$ Nano-Particles Synthesized by the Hydrothermal Method[J]. *J. Nanosci. Nanotech*., 2010, 10: 10 6395-10 6399

[25] Zhang Y, Liu Y, Yang Z, *et al.* Synthesis of $CoFe_2O_4$ Nanoparticles with Tunable Magnetism by the Modified Hydrothermal Method[J]. *J. Nanoparticle Res.*, 2011, 13: 10 4557-10 4563

[26] Sun SH, Zeng H, Robinson DB, *et al.* Monodisperse MFe_2O_4 (M = Fe, Co, Mn Nanoparticles[J]. *J. Am. Chem. Soc*., 2004, 126: 1 273-1 279

[27] Dai Q, Berman D, Virwani K, *et al.* Self-Assembled Ferrimagnet Polymer-Composites for Magnetic Recording Media[J]. *Nano Lett*., 2010, 10: 2 3216-2 3221

[28] Naseri MG, Saion EB, Ahangar HA, *et al.* Simple Synthesis and Characterization of Cobalt Ferrite Nanoparticles by a Thermal Treatment Method[J]. *J. Nanomater*., 2010, 2010: 75 907686

[29] Chiu WS, Radiman S, Abd-Shutor R, *et al.* Tunable Coercivity of $CoFe_2O_4$ Nanoparticles via Thermal Annealing Treatment[J]. *J. Alloy. Compd*., 2008, 459: 1-2 291-297

[30] Liu BH, Ding J, Dong ZL, *et al.* Microstructural Evolution and Its Influence on the Magnetic Properties of $CoFe_2O_4$ Powders during Mechanical Milling[J]. *Phys. Rev. B*, 2006, 74: 18 184427

[31] Tung LD, Kolesnichenko V, Caruntu D, *et al.* Magnetic Properties of Ultrafine Cobalt Ferrite Particles[J]. *J. Appl. Phys*., 2003, 93: 10 7486-10 7488

[32] Kneller EF, Luborsky FE. Particle Size Dependence of Coercivity and Remanence of Single Domain Particles[J]. *J. Appl. Phys*., 1963, 34: 3 656-3 658