

Spindly cobalt ferrite nanocrystals: preparation, characterization and magnetic properties

Xuebo Cao^{1,3} and Li Gu²

¹ College of Chemistry and Chemical Engineering, Soochow University, Suzhou, Jiangsu 215006, People's Republic of China

² Department of Biology and Chemical Engineering, Jiaying University, Jiaying, Zhejiang 314001, People's Republic of China

E-mail: xbciao@suda.edu.cn

Received 8 October 2004, in final form 22 November 2004

Published 23 December 2004

Online at stacks.iop.org/Nano/16/180

Abstract

In this paper we describe the preparation of homogeneously needle-shaped cobalt ferrite (CoFe_2O_4) nanocrystals on a large scale through the smooth decomposition of urea and the resulting co-precipitation of Co^{2+} and Fe^{3+} in oleic acid micelles. Furthermore, we found that other ferrite nanocrystals with a needle-like shape, such as zinc ferrite (ZnFe_2O_4) and nickel ferrite (NiFe_2O_4), can be prepared by the same process. Needle-shaped CoFe_2O_4 nanocrystals dispersed in an aqueous solution containing oleic acid exhibit excellent stability and the formed colloid does not produce any precipitations after two months, which is of prime importance if these materials are applied in magnetic fluids. X-ray diffraction (XRD) measurements were used to characterize the phase and component of the co-precipitation products, and demonstrate that they are spinel ferrite with a cubic symmetry. Transmission electron microscopy (TEM) observation showed that all the nanocrystals present a needle-like shape with a 22 nm short axis and an aspect ratio of around 6. Varying the concentration of oleic acid did not bring about any obvious influence on the size distribution and shapes of CoFe_2O_4 . The magnetic properties of the needle-shaped CoFe_2O_4 nanocrystals were evaluated by using a vibrating sample magnetometer (VSM), electron paramagnetic resonance (EPR), and a Mössbauer spectrometer, and the results all demonstrated that CoFe_2O_4 nanocrystals were superparamagnetic at room temperature.

1. Introduction

Ferrite (MFe_2O_4 , $\text{M} = \text{Co}^{2+}$, Ni^{2+} , Fe^{2+} , Zn^{2+} , Cu^{2+} etc) nanocrystals attract great research interests due to their potential application in ferrofluids [1–3], magnetic fluids [4], magnetic recording media [5], and magnetic resonance imaging [6]. Take CoFe_2O_4 , for example: it has a high coercivity (5400 Oe) and moderate saturation magnetization ($\sim 80 \text{ emu g}^{-1}$), a remarkable chemical stability and a mechanical hardness, which make it a possible material for high-density recording media [7, 8]. An additional advantage

for ferrites is that, through the choice of various divalent cations in them, the magnetic properties can be finely tuned and tailored according to practical demands [9].

At present, a variety of methods has been developed to prepare ferrite nanocrystals, such as the sol–gel method [10], hydrothermal method [11], co-precipitation in normal or reverse micelles [12], sonochemical reactions [13], and ball milling [14]. However, in most reports, the nanocrystals obtained were severely aggregated particles without uniform shapes, which is disadvantageous for their application, especially in ferrofluids and magnetic fluids [1, 13, 15–17]. Usually, in order to obtain magnetic nanocrystals with a

³ Author to whom any correspondence should be addressed.

uniform size, a repeated size-selection process is required [18–20]. More importantly, it has been shown that their shape strongly influences the magnetic properties, and the coercive force of needle-shaped particles is generally higher than that of their isometric counterparts [21, 22]. Consequently, for magnetic nanomaterials, one of the most critical issues is the controlled synthesis of mono-dispersed and regular particles without laborious size-selection processes.

To solve the problems, we improved the co-precipitation route by choosing an appropriate precipitant and stabilizer in the preparation of ferrite nanocrystals. On the one hand, we use a reagent smoothly liberating hydroxide ions to replace the strong alkali. Strong alkaline solutions, such as potassium hydroxide and sodium hydroxide, are prone to result in the conversion of Fe^{3+} and M^{2+} into MFe_2O_4 immediately, usually leading to the formation of severely agglomerated nanoparticles with irregular shapes [15–17]. However, the smooth liberation of hydroxide ions by reagents such as urea would retard the nucleation and growth rate of nanocrystals, which is advantageous for obtaining discrete products with a regular shape. An additional advantage of the urea process is that it is economically attractive and environmentally friendly. On the other hand, the selected stabilizer among a variety of surfactants and polymers with metal ion affinities should function well both in the control of the stability and the morphology of the final products. It is well known that oleic acid is a good candidate in the preparation of superlattice structures because it can bind to the surface of the nanocrystals and allows a ‘force-balance’ among van der Waals forces, dipolar interactions and steric repulsion provided by the tails of oleic acid [20, 23–25]. Consequently, it is rational to expect that oleic acid is a better stabilizer for the synthesis of uniform-sized magnetic nanocrystals than others.

In this study, we describe the large-scale preparation of needle-shaped CoFe_2O_4 nanocrystals with a narrow size distribution through the co-precipitation of stoichiometric Co^{2+} and Fe^{3+} in an aqueous solution containing urea under the stabilization of oleic acid molecules. This route was also found to be general to the preparation of other needle-shaped ferrite nanocrystals, such as NiFe_2O_4 and ZnFe_2O_4 . The obtained CoFe_2O_4 nanocrystals dispersed in the aqueous solution containing oleic acid is quite stable, and no obvious precipitation is found in two months. It is worth noting that magnetic nanocrystals dispersed stably in solution for a long time is significant for application in magnetic fluids. Especially, by means of the Langmuir–Blodgett technique, these nanocrystals with regular 1D structures could be arrayed along their long axis or short axis and thus be organized into novel superstructures, as reported by Yang [26]. There is no doubt that the assembled architectures will provide an ideal system for studying the collective magnetic properties, which is interesting both in theoretical research and in practical applications [26, 27].

X-ray diffraction (XRD) measurements were performed to investigate the crystalline structure and components of the products. The morphology and size distribution of CoFe_2O_4 nanocrystals were measured by transmission electron microscopy (TEM). Their magnetic properties were investigated using a vibrating sample magnetometer (VSM), variable temperature electron paramagnetic resonance (EPR), and a Mössbauer spectrometer.

2. Experiment

2.1. Reagents

All reagents (Received from Shanghai Chemical Corporation) were of analytical grade and used without further purification.

2.2. Experiments

In a typical experiment, 0.5 ml oleic acid was ultrasonically dispersed in 100 ml water to form homogeneous micelles. Then excess urea (10 mmol), and stoichiometric iron trichloride (2.5 mmol) and cobalt chloride (1.25 mmol) were dissolved in the above solution. They were refluxed at a temperature of 90 °C heated by a water bath for 8 h. The thermal decomposition of urea led to the increase of the pH value of the reacting solution and the formation of a black colloid. To investigate the influence of oleic acid concentrations on the nanocrystal morphologies, the volumes of oleic acid were changed to 1 and 0.10 ml, respectively, while keeping other experimental conditions unchanged.

Fresh CoFe_2O_4 nanocrystals existed in the form of a stable colloid in the reaction solution and no precipitation phenomenon was observed for at least two months. To separate pure CoFe_2O_4 nanocrystals for subsequent measurements, 20 ml absolute alcohol and 20 ml acetone were simultaneously added into the colloid system for the purpose of de-emulsification. Then the precipitation of CoFe_2O_4 nanocrystals was obtained through centrifugal settling at a speed of 6000 rpm. The final products were washed several times with acetone to remove the residual oleic acid.

2.3. Characterization

The samples were characterized by powder x-ray diffraction (XRD) to investigate the crystalline structures. The XRD analysis was carried out with a Rigaku D/max – γ rotation anode X-ray diffractometer, using graphite-monochromatized $\text{Cu K}\alpha$ radiation sources ($\lambda = 1.54178 \text{ \AA}$). A scanning rate of $0.05^\circ \text{ s}^{-1}$ was applied in the 2θ range of 20° – 70° .

The morphologies were observed with a Hitachi Model H-800 transmission electron microscope (TEM), using an accelerating voltage of 200 kV. Specimens were prepared by spreading a drop of their ethanol suspensions onto copper grids coated with a thin amorphous carbon film and allowed to dry in air.

The magnetization curve of CoFe_2O_4 nanocrystals was recorded on a BHV-55 vibrating sample magnetometer (VSM) at room temperature (296 K).

Variable-temperature ESR spectra were recorded on a Bruker ER200D-SRC electron paramagnetic resonance (EPR) spectrometer operating at 9.64 GHz. The temperature was controlled by an Oxford Instruments cryostat within the temperature range 100–360 K.

^{57}Fe Mössbauer spectra were measured at room temperature (296 K) by an Oxford Instruments MS-500 constant acceleration spectrometer with ^{57}Co :Pd radiation source.

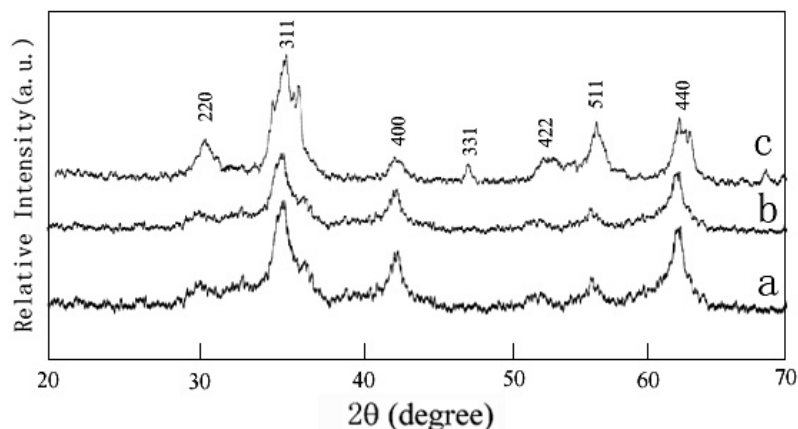
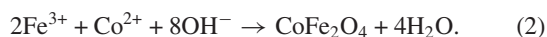


Figure 1. XRD patterns of the as-prepared (a) CoFe_2O_4 , (b) NiFe_2O_4 , and (c) ZnFe_2O_4 . All the reflection peaks can be exactly indexed, demonstrating that they are spinel ferrites.

3. Results and discussions

3.1. Synthesis of CoFe_2O_4 nanocrystals and their stability in solution

When heated in aqueous solution, urea liberates hydroxide ions slowly at 90°C to promote the precipitation of Fe^{3+} and Co^{2+} , as described by the following formulations:



In keeping with the decomposition of urea, the transparent solution turned into black colloid gradually. To prepare pure ferrites, it is important to age the reaction solution at the reflux temperature for at least 8 h. Otherwise, as Lee pointed out, the obtained precipitations are akaganeite ($\beta\text{-FeOOH}$) rather than ferrites [28]. This is because the pH value of the solution is initially low and shows a sharp rise after 8 h. The low pH value (1.2–1.9) is advantageous to the generation of akaganeite, which is not obtained at a pH value above 5.

The colloidal solution was found to be quite stable; this can be learned from the following facts.

- (i) If it was stocked undisturbed at room temperature, we can observe that there are no precipitations in the bottom of the flask over a period of two months.
- (ii) We have tried to separate nanocrystals from the fresh colloidal solution by centrifugal sedimentation, but failed to obtain them even at a centrifugal speed of 12 000 rpm.

These phenomena suggest that the as-prepared nanocrystals have a regular shape and small size, and that oleic acid molecules were bound tightly onto the nanocrystals. Consequently, in order to obtain powders for the characterization of their structure, morphology, and magnetic property, we have to use organic solvents (e.g., alcohol and acetone) to remove the oleic acid from the colloidal solution. Without the protection and stability of oleic acid, precipitations can be easily obtained at a centrifugal speed of 6000 rpm. If the precipitations were re-dispersed in an aqueous solution containing oleic acid, the stability of the formed colloid is still comparable to the fresh colloidal solution.

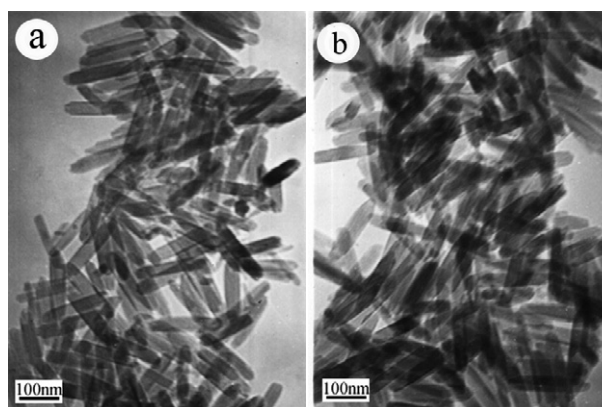


Figure 2. Representative TEM images of CoFe_2O_4 nanocrystals with a needle-like shape prepared under the control of 0.5 ml oleic acid in 100 ml water. The images reveal that needle-shaped nanocrystals were formed with an extremely high yield.

4. Structural analysis of CoFe_2O_4 nanocrystals

The phase and component of the as-prepared product were characterized by powder x-ray diffraction (XRD), and a typical XRD pattern is shown in figure 1(a). The reflection peaks can be readily indexed to the (220), (311), (400), (331), (442), (511), and (440) planes of spinel CoFe_2O_4 with a cubic symmetry (JCPDS file, No. 22-1086), respectively. The broadened diffraction peaks can be attributed to the reduced particle size of the as-prepared product.

5. Morphology and size determination of CoFe_2O_4 nanocrystals

TEM observation was used to investigate the morphology and size of the as-prepared CoFe_2O_4 nanocrystals, and some typical images are shown in figure 2. They reveal that the obtained ferrites are needle-shaped nanocrystals with an aspect ratio of about 6 and a short axis of 22 nm. The conversion to needle-like ferrites is so homogenous that no other shapes, such as particles and prolonged structures (e.g., rods or wires), are found to be present in the final product. The obvious contrast

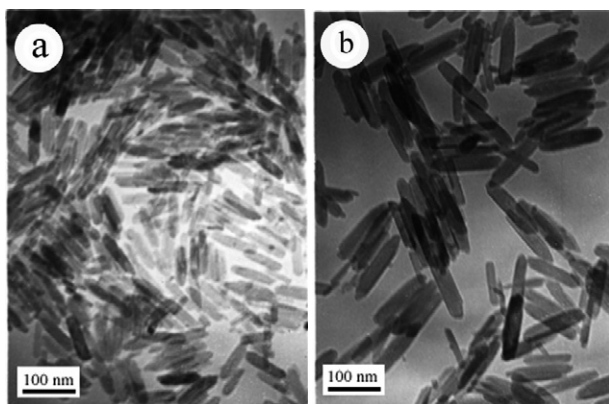


Figure 3. TEM images of needle-shaped (a) NiFe_2O_4 and (b) ZnFe_2O_4 nanocrystals both synthesized via the same route as the preparation of CoFe_2O_4 nanocrystals.

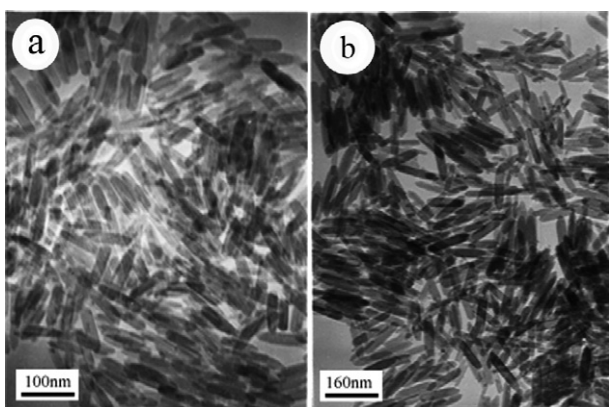


Figure 4. TEM images of CoFe_2O_4 nanocrystals formed at various concentrations of oleic acid. (a) 0.1 ml oleic acid in 100 ml water; (b) 1 ml oleic acid in 100 ml water.

in the nanocrystals may imply that these nanocrystals should be very thin plates [29].

Incidentally, in the experiments we found that this route is also effective in the preparation of other needle-shaped ferrite nanocrystals, such as NiFe_2O_4 and ZnFe_2O_4 . Figures 3(a) and (b) exhibit their representative TEM images, while their corresponding XRD patterns are shown in figures 1(b) and (c), respectively. The results of XRD measurements confirm that these products are spinel NiFe_2O_4 and ZnFe_2O_4 (JCPDS file No. 22-1012 for ZnFe_2O_4 , and No. 3-846 for NiFe_2O_4).

For the purpose of investigating the influence of the concentration of oleic acid on the morphologies of CoFe_2O_4 nanocrystals, we prepared them at a higher concentration of oleic acid (1 ml oleic acid in 100 ml H_2O) and a lower concentration (0.1 ml oleic acid in 100 ml H_2O), respectively. From TEM images (figure 4) of the obtained products we can learn that varying the concentration of oleic acid does not lead to a significant change of the shape and size of the nanocrystals. With the control of 1 ml oleic acid in 100 ml water, the aspect ratio and short axis of the nanocrystals (see figure 4(a)) are almost the same as those controlled by 0.5 ml oleic acid in 100 ml H_2O . But a slight decrease in the short axis (15 nm) and a slight increase of the aspect ratio are observed if 0.1 ml oleic acid in 100 ml water is used (see figure 4(b)).

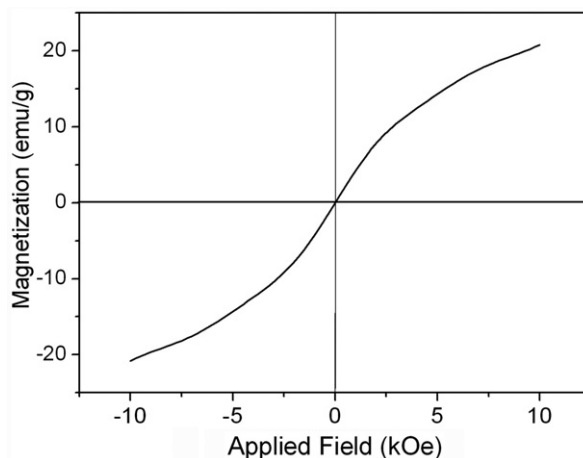


Figure 5. Magnetization curve of CoFe_2O_4 nanocrystals measured at room temperature (296 K).

6. Forming mechanism of needle-shaped nanocrystals

Forming such ultra-thin needle-like plates should be mainly attributed to the ability of a selective attachment of oleic acid molecules to the crystal planes [30]. It is well known that materials with a cubic crystal structure are prone to grow into a spherical shape to minimize the surface tension. However, since oleic acid could bind to crystal planes selectively, the surface tension of the growing crystals is altered and the growth rate of the nanocrystal along the bound crystal planes is slowed down or stopped [31, 32], resulting in the formation of needle-like nanocrystals. Another factor responsible for the formation of such a shape is attributed to the kinetic contribution. The smooth decomposition of urea retards the nucleation and growth rate of the nanocrystals, which is advantageous for the growth of one-dimensional (1D) structures. Since CoFe_2O_4 , NiFe_2O_4 , and ZnFe_2O_4 are all spinel structures, under the same experimental conditions they present the same nucleation and growth mechanism and hence the shapes of the nanocrystals are very similar.

7. Evaluation of magnetic properties of needle-shaped CoFe_2O_4 nanocrystals

The magnetic properties of the as-prepared needle-shaped CoFe_2O_4 nanocrystals were first evaluated by a vibrating sample magnetometer. The magnetization curve (figure 5) measured at room temperature (296 K) demonstrates a typical superparamagnetic behaviour of the as-prepared needle-shaped CoFe_2O_4 nanocrystals with zero coercivity and remanence as the field is cycled between -10 and 10 kOe. Why superparamagnetism is observed in these spindly CoFe_2O_4 nanocrystals should be attributed to their extremely fine crystallite sizes and regular shape of the material [33], which makes it easier for them to be thermally activated to overcome the magnetic anisotropy. Generally, when the size of magnetic materials is smaller than the superparamagnetic critical dimension, above the blocking temperature its thermal fluctuation can overcome the

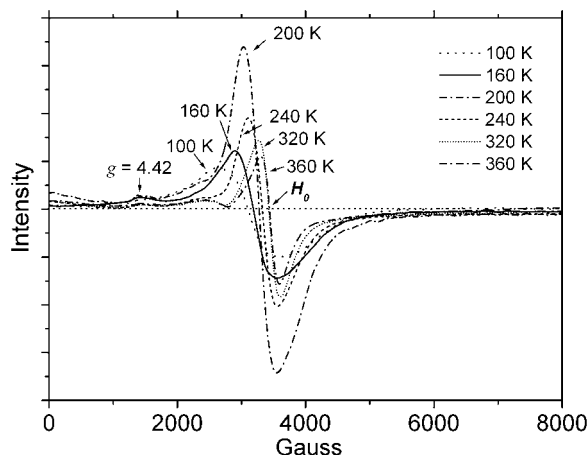


Figure 6. Variable temperature EPR spectra of CoFe_2O_4 nanocrystals measured with temperature ranging from 100 to 360 K.

anisotropy, so the moments can rotate among the different easy directions and superparamagnetism is exhibited [34, 35].

The superparamagnetic behaviour of the as-prepared needle-shaped CoFe_2O_4 nanocrystals is also supported by the subsequent characterization by variable temperature electron paramagnetic resonance (EPR) and room temperature Mössbauer spectrometry. The ESR of ferrites is important for investigating the magnetic properties of magnetic materials at high frequency because the resonance originates from the interaction between spin and electromagnetic waves [36]. Figure 6 shows the variable temperature EPR spectra of CoFe_2O_4 ranging from 100 to 360 K. The resonance line width (ΔH_{pp}), the position corresponding to the zero signal (H_0) and the effective g -factor are the three parameters that characterize the magnetic properties [13, 37, 38]. The effective g -factor is determined from the following equation:

$$g = h\nu/\beta H \quad (3)$$

where h is Planck's constant, ν is the microwave frequency, H is the magnetic field occurring at the maximum resonance and β is the Bohr magneton.

As the temperature increases, the signals gradually get sharper and more symmetrical, with a shift to high field ($H_0 \uparrow$; see figure 6). Furthermore, above 200 K a sharp decrease in the line width and intensity is observed. This is because the thermal fluctuation of magnetic moments can reduce the extent of the anisotropic contributions to the free energy density and the effective magnetic field (the superparamagnetic effect). In this event, at elevated temperatures very narrow resonance spectra are observed, while at low temperatures the thermal fluctuations are gradually frozen out and the magnetization direction is blocked, resulting in the broadening of the resonance line. The broadening and shift to lower magnetic fields of the magnetic resonance spectra with the decrease of temperature is typically observed for superparamagnetic nanoparticles [36, 39, 40], and analogous cases can be found in a number of systems [41–43]. The calculated g -factor for the superexchange coupled pair between the two sites, Fe^{3+} and Co^{2+} ($\text{Fe}^{3+}\text{--O--Co}^{2+}$) is in the range 2.12–2.27, in good agreement with that reported by Gedanken [13]. In addition to the intense signal, weak signals around $g = 4.42$ in EPR

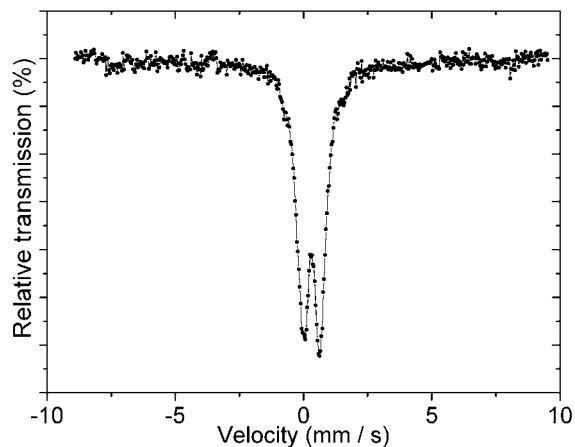


Figure 7. Mössbauer spectrum of CoFe_2O_4 nanocrystals measured at room temperature (296 K).

spectra are observed, implying that there is an impurity of Fe_2O_3 at an EPR detectable level in the as-prepared CoFe_2O_4 sample [13, 44–46].

The room-temperature (296 K) Mössbauer spectrum of needle-shaped CoFe_2O_4 nanocrystals also confirms the superparamagnetic behaviour, as mentioned in the measurement of its magnetization curve and variable temperature EPR spectra. The experimental data show the typical doublet and no traces of the characteristic six lines are observed (figure 7), revealing the fully paramagnetic state of needle-shaped CoFe_2O_4 nanocrystals. The quadrupole splitting (Q) and the isomer shift (IS) are 0.87 and 0.32 mm s^{-1} , which are close to those reported by Gedanken [15].

8. Conclusion

In summary, through the decomposition of urea and the coprecipitation reactions of M^{2+} and Fe^{3+} with oleic acid as the stabilizer, ferrite (MFe_2O_4 , $\text{M} = \text{Co}^{2+}$, Zn^{2+} , and Ni^{2+}) nanocrystals were prepared, all of which have a needle-like shape and narrow size distribution. This is due to the smooth nucleation and the selective attachment of oleic acid to the growing planes of nanocrystals. The measurements of magnetization curves, variable temperature EPR spectra, and Mössbauer spectrum all demonstrate that needle-shaped CoFe_2O_4 nanocrystals are superparamagnetic at room temperature. Furthermore, the homogenous nanocrystals have excellent stability in aqueous solution under the protection of oleic acid molecules, which makes them a good candidate in magnetic fluids.

References

- [1] Sousa M H, Atourinho F, Depeyrot J, da Silva G J and Lara M C 2001 *J. Phys. Chem. B* **105** 1168
- [2] Raj K, Moskowitz R and Casciari R 1995 *J. Magn. Magn. Mater.* **149** 174
- [3] Hyeon T, Chung Y, Park J, Lee S S, Kim Y W and Park B H 2002 *J. Phys. Chem. B* **6** 6831
- [4] Mehtha R V, Upadhyay R V, Dasanacharya B A, Goyal P S and Rao K S 1994 *J. Magn. Magn. Mater.* **132** 153
- [5] Kryder M H 1996 *Mater. Res. Soc. Bull.* **21** 17

- [6] Mitchell D G 1997 *J. Magn. Reson. Imaging* **7** 1
- [7] Dorsey P C, Lubitz P, Chrisey D B and Horowitz J S 1996 *J. Appl. Phys.* **79** 6338
- [8] Lee J G, Park J Y, Oh Y J and Kim C S 1998 *J. Appl. Phys.* **84** 2801
- [9] Hochepeid J F, Bonville P and Pileni M P 2000 *J. Phys. Chem. B* **104** 905
- [10] Sugimoto T, Shimotsuma Y and Itoh H 1998 *Powder Technol.* **96** 85
- [11] Pannaparayil T, Marande R and Komarneni S 1991 *J. Appl. Phys.* **69** 5349
- [12] Lopez Perez J A, Lopez Quintela M A, Mira J, Rivas J and Charles S W 1997 *J. Phys. Chem. B* **101** 8045
- [13] Shafi K V P M, Gedanken A, Prozorov R and Balogh J 1998 *Chem. Mater.* **10** 3445
- [14] Fatemi D J, Harris V G, Browning V M and Kirkland J P 1998 *J. Appl. Phys.* **83** 6867
- [15] Prozorov T, Prozorov R, Koltypin Y, Felner I and Gedanken A 1998 *J. Phys. Chem. B* **102** 10165
- [16] Ahmed S R and Kofinas P 2002 *Macromolecules* **35** 3338
- [17] Rondinone A J, Anna S C S and Zhang Z J 1999 *J. Phys. Chem. B* **103** 6876
- [18] Rockenberger J, Scher E C and Alivisatos A P 1999 *J. Am. Chem. Soc.* **121** 11595
- [19] Fried T, Schemer G and Markovich G 2001 *Adv. Mater.* **13** 258
- [20] Sun S H, Murray C B, Weller D, Folks L and Moser A 2000 *Science* **287** 1989
- [21] Ozaki M, Suzuki H, Takahashi K and Matijevec E 1986 *J. Colloid Interface Sci.* **113** 76
- [22] Ozaki M, Egami T, Sugiyama N and Matijevec E 1988 *J. Colloid Interface Sci.* **126** 212
- [23] O'Brien S, Brus L and Murray C B 2001 *J. Am. Chem. Soc.* **123** 12085
- [24] Wang W, Efrima S and Regev O 1998 *Langmuir* **14** 602
- [25] Fang J Y, Stokes K L, Zhou W L, Wang W D and Lin J 2001 *Chem. Commun.* **18** 1872
- [26] Kim F, Kwan S, Akana J and Yang P D 2001 *J. Am. Chem. Soc.* **123** 4360
- [27] Thurn-Albrecht T, Schotter J, Kastle C A, Emley N, Shibauchi T, Krusin-Elbaum L, Guarini K, Black C T, Tuominen M T and Russell T P 2000 *Science* **290** 2126
- [28] Song H J, Oh J H, Choi S C and Lee J C 2002 *Phys. Status Solidi a* **189** 3849
- [29] Hirsch P, Howre A, Nicholson R B, Dashley D W and Whelan M J 1977 *Electron Microscopy of Thin Crystals* (New York: Huntington)
- [30] Puentes V F, Krishnan K and Alivisatos A P 2002 *Top. Catal.* **19** 145
- [31] Petrovski J M, Green T C and El-Sayed M A 2001 *J. Phys. Chem. A* **105** 5542
- [32] Wang Z L 2000 *J. Phys. Chem. B* **104** 1153
- [33] Chen Q and Zhang Z J 1998 *Appl. Phys. Lett.* **73** 3156
- [34] Bean C P and Livingston J D 1959 *J. Appl. Phys.* **30** 120s
- [35] Wang Z L, Liu Y and Zhang Z (ed) 2003 *Handbook of Nanophase and Nanostructured Material* (New York: Kluwer-Academic)
- [36] Gazeau F, Bacri J C, Gendron F, Perzynski R, Raikher Y L, Stepanov V I and Dubois E 1998 *J. Magn. Magn. Mater.* **186** 175
- [37] Sidorov S N, Bronstein L M, Davankov V A, Tsyurupa M P, Solodovnikov S P, Valetsky P M, Wilder E A and Spontak R J 1999 *Chem. Mater.* **11** 3210
- [38] Diehl M R, Yu J Y, Heath J R, Held G A, Doyle H, Sun S H and Murray C B 2001 *J. Phys. Chem. B* **105** 7913
- [39] de Biasi C, Ramos C A and Zysler R D 2003 *J. Magn. Magn. Mater.* **262** 235
- [40] Bergera R, Bisseya J-C, Kliava J, Daubric H and Estournes C 2001 *J. Magn. Magn. Mater.* **234** 535
- [41] Lachowicz H K, Sienkiewicz A, Gierlowski P and Slawska-Waniewska A 2000 *J. Appl. Phys.* **88** 368
- [42] Parekh K, Upadhyay R V, Mehta R V and Srinivas D 2000 *J. Appl. Phys.* **88** 2799
- [43] Ibrahim M M, Edwards G, Seehra M S, Ganguly B and Huffman G P 1994 *J. Appl. Phys.* **75** 5873
- [44] Shafi K V P M, Koltypin Y, Gedanken A, Prozorov R, Balogh J, Lendvai J and Felner I 1997 *J. Phys. Chem. B* **101** 6409
- [45] Tanaka K, Kamiya K, Yoko T, Tanabe S, Hirao K and Soga N 1989 *J. Non-Cryst. Solids* **109** 289
- [46] She L G, Ping L L, Smith R L and Inomata H 2001 *J. Mol. Struct.* **560** 87