

Fast Inducing Synthesis of Spherical Superparamagnetic β -FeOOH Nanoparticles without Aggregation

Honglei Fan,* Baozhen Song, Zhenqiu Yang, and Qiaoxia Li
Institute of Process Engineering, Chinese Academy of Sciences, Beijing, P. R. China 100080

(Received February 23, 2004; CL-040201)

Spherical nanoparticles of superparamagnetic akaganeite (β -FeOOH) without aggregation are prepared by the inducing role of ethyl acetate under 373 K during 10 min. The X-ray diffraction and IR spectra displayed the crystalline nature of β -FeOOH structures. Transmission electron micrograph of the samples revealed that the average diameter of nanoparticles with good dispersity is 14.7 nm. The measurements by superconducting quantum interference device (SQUID) magnetometry showed that the samples is the superparamagnetic above the blocking temperature of 18 K under field cooling.

The synthesis of nanoparticles is of fundamental importance for the development of novel technologies based on nanomaterials.¹ As a kind of iron oxides, akaganeite (β -FeOOH) nanoparticles have been prepared with different morphology, such as rodlike, x-shaped, y-shaped, and needle-shaped.² Beside as pigment industry, akaganeite can be used as magnetic resonance imaging contrast agents³ because of its good biological compatibility, superparamagnetic properties, and low cost. All these applications require that nanoparticles have been narrow size distribution, special morphology and good dispersity.^{4,5} However, the fast preparation of nanoparticles with definite morphologies and good dispersity under mild conditions has still been a problem.^{6,7}

Usually, akaganeite nanoparticles are produced by forced hydrolysis,⁸ gel-sol method,⁹ microwave-irradiation hydrolysis,¹⁰ or sonochemical decomposition.¹¹ The disadvantages of these syntheses are long reaction period and complex production processing. In addition, it is difficult to keep the desired size distribution by thermal hydrolysis. Herein, we report a fast inducing synthesis for β -FeOOH nanoparticles.

Spherical superparamagnetic akaganeite nanoparticles were prepared as follows: FeCl₃·6H₂O (10 mmol) was mixed with oleic acid (3 mmol) in ammonium bicarbonate (50 mmol) solution under vigorous stirring at room temperature for 5 min. Ethyl acetate (0.2 mmol) was added into the suspension obtained, and the suspension was transferred into a three-necked round-bottom flask. And then the as-prepared suspension in the flask was heated quickly and kept 10 min at ca. 373 K with vigorous stirring. The brown precipitate was washed by distilled water to remove remaining Cl⁻ ion. The final products were dried in the air at the temperature of 303 K. XRD measurement were carried out with a Japan RIGAKUD/Max-2500 instrument at a voltage of 45 kV and current of 300 mA with Cu K α radiation. TEM photos were recorded on a Japan H-700 transmission electron microscope at an accelerating voltage of 20 kV. IR spectra were recorded on a England SpectrumGX II FT-IR spectrometer from 400 to 4000 cm⁻¹ at room temperature on KBr mulls. Magnetization measurements were conducted using a SQUID magnetometer

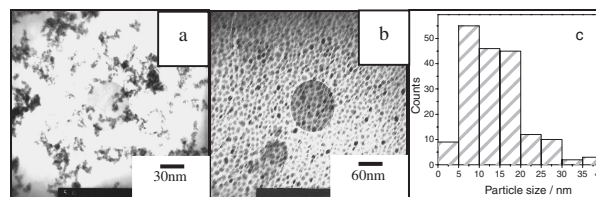


Figure 1. Morphological changes (TEM photos) of spherical akaganeite nanoparticles with elevated temperatures ((a) $T = 353$ K; (b) $T = 373$ K kept 10 min); (c) Particle size distribution diagram based on TEM photo (b).

(MPMS 5, Quantum Design) in a temperature range from 5 to 300 K.

The TEM photos in Figures 1a and 1b show the morphological change of the solid phase with rising temperatures. The products at 353 K (Figure 1a) are obtained as fine flocculent gel at first, and then become nearly spherical after keeping for 10 min at 373 K. The TEM photo in Figure 1b shows that the as-prepared akaganeite nanocrystals are spherical with average diameter of 14.7 nm. From the particle size distribute diagram (Figure 1c) based on Figure 1b, the standard deviation of particle size is 7.0025, indicating that spherical akaganeite nanocrystals are with relative narrow size distribution. In contrast to the above, keeping other conditions the same, no addition of ethyl acetate makes the final product amorphous.¹²

The IR spectra of samples prepared without and with ethyl acetate are presented in Figures 2a and 2b, respectively. IR bands at about 847, 696, and 420 cm⁻¹ are generally considered as the characteristic bands of chloride-containing akaganeite.² The bands at 843 and 694 cm⁻¹ are due to the deformation vibration of the two O-H...Cl hydrogen bands. Another band at 471 cm⁻¹ is attributed to the symmetric Fe-O-Fe stretching vibration. The IR spectra prove that the as-prepared sample is akaganeite, agreeing with its XRD patterns.¹³ In Figure 2a, the bands at 1516 [$\nu_{as}(\text{CO}_2^-)$] and 1411 [$\nu_s(\text{CO}_2^-)$] show the chelation of oleic acid to akaganeite.¹⁴ Other two bands at 2850 and 2921 cm⁻¹ correspond to the symmetric and asymmetric stretching vibrations of CH₂. That the H₂O-bending band in akaganeite is single at about 1628 cm⁻¹ is confirmed.¹⁵ Compared with the Figure 2a, the characteristic bands of oleic acid in Figure 2b are weaker, which shows that the amount of oleic ion adsorbed on the particle surface is reduced. At the same time, we find three new bands located at 1475, 1406, and 1074 cm⁻¹ in Figure 2b. The band at 1475 cm⁻¹ can be ascribed to the in-plane C-H bending vibration of CH₂, the band at 1406 cm⁻¹ to the in-plane C-H bending vibration of CH₃ and the band at 1074 cm⁻¹ to the stretching vibration of C-O in ethanol.¹⁶ In addition, the band at 3351 cm⁻¹ can be ascribed to the OH stretching of ethanol. So, we can infer that there is a little of ethanol adsorbed on the par-

title surface, which comes from the hydrolysis of ethyl acetate. Further, the intensity of the band at 1628 cm^{-1} became stronger in Figure 2b than in Figure 2a, which is due to increasing amount of adsorbed H_2O resulting from increase of ethanol adsorbed and decrease of oleic ion on the particle surface.

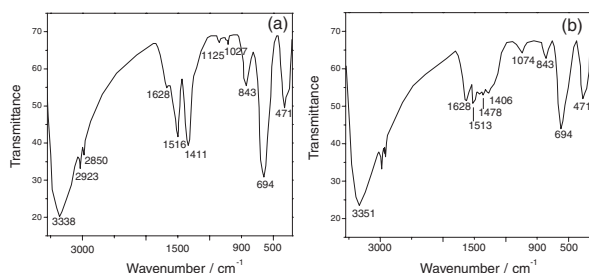


Figure 2. (a) IR spectra of the spherical akaganeite nanoparticles prepared without ethyl acetate; (b) Infrared spectra of spherical akaganeite nanoparticles.

From the TEM photos and IR spectra, we can probably infer the formation of spherical akaganeite. Hydrolysis of ethyl acetate and ferric salt consumes a part of water from the solution under acid conditions, which induces the formation of akaganeite crystal seeds in local areas of the solution.¹⁷ Moreover, ethanol, the hydrolysis products of ethyl acetate, as well as oleic ion is strongly absorbed on the surface of akaganeite nanoparticles hindering the further growth of preliminary particles, which leads to the occurrence of spherical nanoparticles with good dispersity.

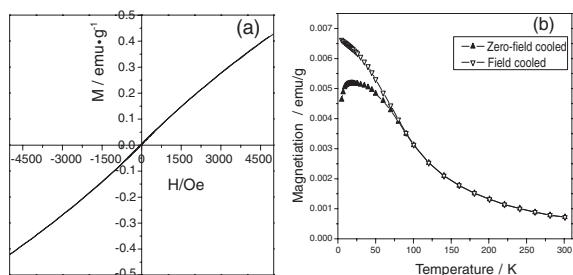


Figure 3. (a) Hysteresis loops of spherical akaganeite nanoparticles under $T = 298\text{ K}$; (b) Magnetization versus temperature at 10 Oe in the zero-field-cooled and field-cooled states for spherical akaganeite nanoparticles.

The magnetization curves (Figure 3a) recorded in 298 K show zero remanence and zero coercivity. These data reveal the superparamagnetic behavior of akaganeite nanoparticles, because thermal fluctuations can prevent the existence of a stable magnetization.¹⁸

The ZFC magnetization measurements (Figure 3b) show a peak at $T_{\text{max}} = 18\text{ K}$ indicative of a characteristic blocking temperature for superparamagnetic particles. Below the blocking

temperature, the spins are blocked by magnetic anisotropy.¹⁹ Above the blocking temperature, all the nanoparticles are in the superparamagnetic state.

We have reported that fast inducing synthesis method can be used to produce spherical akaganeite nanoparticles without aggregation under mild conditions. Experimental results suggested that the fast inducing synthesis not only can modify the morphology of iron oxide nanoparticles but also induce the formation of new phase in a short time.

The project was supported by National Natural Science Foundation of China, Grants No. 50071057. We thank the Institute of Physics, Chinese Academy of Sciences for magnetic measurements.

References and Notes

- 1 F. Dumestre, B. Chaudret, and C. Amiens, *Angew. Chem., Int. Ed.*, **41**, 4286 (2002).
- 2 S. Musić, A. Šarić, and S. Popović, *J. Mol. Struct.*, **410–411**, 153 (1997).
- 3 F. Funk, G. J. Long, D. Hautot, R. Büchi, I. Christl, and P. G. Weidler, *Hyperfine Interact.*, **136**, 73 (2001).
- 4 B. Lindlar, M. Boldt, S. Eiden-Assmann, and G. Maret, *Adv. Mater.*, **14**, 1656 (2003).
- 5 S. Stoeva, K. J. Klabunde, C. M. Sorensen, and L. Dragieva, *J. Am. Chem. Soc.*, **124**, 2305 (2002).
- 6 X. G. Peng, *Chem.—Eur. J.*, **8**, 335 (2002).
- 7 S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, *Science*, **287**, 1989 (2000).
- 8 E. Matijević and P. Scheiner, *J. Colloid Interface Sci.*, **63**, 509 (1978).
- 9 T. Sugimoto, S. Waki, H. Itoh, and A. Muramatsu, *Colloids Surf., A*, **109**, 155 (1996).
- 10 D. C. Dong, P. J. Hong, and S. S. Dai, *Mater. Res. Bull.*, **30**, 537 (1995).
- 11 R. Vijayakumar, Yu. Koltypin, I. Felner, and Gedanken, *Mater. Sci. Eng., A*, **286**, 101 (2000).
- 12 TEM photo of the final amorphous sample prepared without ethyl acetate is shown in Figure S1 of supplemental information.
- 13 XRD patterns of akaganeite nanoparticles are revealed in Figure S2 of supplemental information.
- 14 C. Rocchiccioli-Deltcheff, R. Franck, V. Cabuil, and R. Massart, *J. Chem. Res., Synop.*, **1987**, 126.
- 15 E. Murad and J. L. Bishop, *Am. Mineral.*, **85**, 716 (2000).
- 16 A. Yee, S. J. Morrison, and H. Idriss, *J. Catal.*, **186**, 279 (1999).
- 17 J. Cai, J. Liu, Z. Gao, A. Navrotsky, and S. L. Suib, *Chem. Mater.*, **13**, 4595 (2001).
- 18 I. Zhitomirsky, M. Niewczas, and A. Petric, *Mater. Lett.*, **57**, 1045 (2003).
- 19 M. S. Rao, I. S. Duubenko, S. Roy, N. Ali, and B. C. Dave, *J. Am. Chem. Soc.*, **123**, 1511 (2001).