Magnetic Nanoparticles

Preparation of Water-Soluble Magnetite Nanocrystals from Hydrated Ferric Salts in 2-Pyrrolidone: Mechanism Leading to Fe_3O_4**

*Zhen Li, Qiao Sun, and Mingyuan Gao**

Magnetic nanoparticles of iron oxides (γ-Fe_2O_3 and Fe_3O_4) and their suspensions have extensive applications in magnetic sealing, oscillation damping, and position sensing,[1] ultrahigh-density magnetic storage media,[2] clinical diagnosis and

---

[*] Z. Li, Q. Sun, Prof. M. Y. Gao
Key Laboratory of Colloid, Interface Science and Chemical Thermodynamics
Institute of Chemistry, Chinese Academy of Sciences
Zhong Guan Cun, Bei Yi Jie 2, Beijing 100080 (P.R. China)
Fax: (+86) 10-8261-3214
E-mail: gaomy@iccas.ac.cn

[**] The authors thank Prof. D.-X. Wang for his assistance with PES measurements. Funding was provided by an 863 project (2002AA302201) and NSFC projects (20225313, 90206024, 90201006).

DOI: 10.1002/anie.200460715

treatment,[3] and biological labeling, tracking, imaging, detection, and separations.[4] For these applications, major efforts have recently been devoted to the synthesis of magnetic iron oxide nanoparticles.[5] Generally, magnetic iron oxide nanoparticles can be prepared by co-precipitating ferrous and ferric ions in aqueous solution. However, variations in the molar ratio of Fe^{3+} and Fe^{2+} often lead to rather complicated changes in the crystalline structures of the iron oxides obtained.[6] Both pH and the ionic strength, which play critical roles in the preparations, also affect the surface chemical composition of the magnetite nanoparticles.[5] Furthermore, the relatively poor size uniformity and low crystallinity of magnetic iron oxide nanoparticles obtained to some extent limit their use in many applications. Although sol–gel and hydrothermal methods were proven to be effective in increasing the crystallinity, the magnetic nanoparticles obtained exhibit poor solubility or dispersibility.[7] Recently, Alivisatos et al. reported a thermal decomposition approach to synthesize nearly monodisperse maghemite nanocrystals.[8] Sun et al. succeeded in preparing monodisperse magnetite nanocrystals by decomposition of $[Fe(acac)_3]$(acac = acetylacetonate) in the presence of 1,2-hexadecanediol, oleic acid, and oleylamine.[9] Hyeon et al. obtained high-quality maghemite nanocrystals by thermal decomposition of $[Fe(CO)_5]$ followed by oxidation with $(CH_3)_3NO$.[10] However, the direct products of the thermal decomposition method are generally soluble in organic solvents. Sophisticated post-preparative approaches are required to make those magnetic nanocrystals water-soluble,[11] and this limits their applications in biomedical fields. Furthermore, the mechanisms for the formation of magnetic nanocrystals by thermal decomposition are far from clear.[8–10]

Recently, we demonstrated the possibility of producing water-soluble magnetite nanocrystals by the thermal decomposition method using strong polar 2-pyrrolidone as a coordinating solvent.[12] Here we report the preparation of magnetite nanocrystals by using hydrated ferric salts as iron precursors instead of costly $[Fe(acac)_3]$. In addition, the mechanism leading to Fe_3O_4 in 2-pyrrolidone is discussed.

$FeCl_3{\cdot}6H_2O$ was used as a single iron source in the preparation of magnetic nanocrystals. Figure 1 shows TEM images of three typical samples of iron oxide nanoparticles obtained after refluxing a certain amount of $FeCl_3{\cdot}6H_2O$ in 2-pyrrolidone for 1, 10, and 24 h. Their average particle sizes are 4, 12, and 60 nm, respectively. In addition to the difference in size, the nanoparticles also change their shape with increasing reflux time. During the early stages, spherical nanoparticles appear and then grow larger and larger, and finally they lose the original shape and form cubic particles after 24 h. The crystalline structure of the samples shown in Figure 1 was determined by powder XRD. The diffraction patterns and relative intensities of all diffraction peaks match well with those of JCPDS card 19-0629 for magnetite. The electron diffraction pattern inserted in Figure 1c also supports the magnetite crystal structure. In addition, FT-IR spectra of the particles exhibit characteristic peaks of magnetite at around $\tilde{\nu} = 589\ \text{cm}^{-1}$.[13]

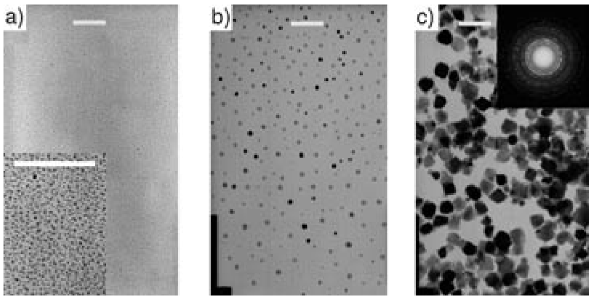


Figure 1. TEM images of nanoparticles obtained after $FeCl_3{\cdot}6H_2O$ was refluxed in 2-pyrrolidone for 1, 10, and 24 h, respectively. The inset in a) is an enlarged part. The scale bar corresponds to 100 nm.

The magnetic properties of the as-prepared magnetite nanoparticles were investigated with a vibrating sample magnetometer (VSM). Figure 2 presents the magnetic hysteresis curves of the nanocrystals shown in Figure 1. The saturation magnetization increases from 3 to 59 to 84 $\text{emu}\,\text{g}^{-1}$ with increasing reflux time, which can be attributed to the growth of particle size and enhancement in crystallinity. Samples a and b in Figure 1 are superparamagnetic at room temperature, while the cubic particles exhibit a magnetic coercivity of 85 Oe. This is because their size already exceeds the critical size of single magnetic domains.[14]

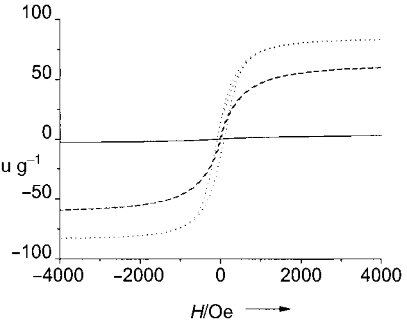


Figure 2. Room-temperature magnetization curves of the magnetic nanocrystals shown in Figure 1: 4 nm (solid line), 12 nm (dashed line), and 60 nm (dotted line) magnetite nanocrystals.

Similar to our previous report, the as-synthesized magnetite nanocrystals reported here can also be dissolved in water under both acidic and alkaline conditions, especially when the particles are smaller than 10 nm. This makes our investigation significant since $FeCl_3{\cdot}6H_2O$ is a very inexpensive iron source. To the best of our knowledge, the current synthetic approach is the first example using $FeCl_3{\cdot}6H_2O$ as a single iron source to prepare water-soluble Fe_3O_4 nanocrystals by the high-temperature wet-chemical approach. Therefore, nearly nothing is known about the mechanism leading to Fe_3O_4 nanocrystals in this reaction system. To investigate the formation of Fe_3O_4 nanocrystals in 2-pyrrolidone, photoelectron spectroscopy (PES) was used to analyze the small molecules released during the reaction. A stream of nitrogen carried these small molecules through a glass U-tube whose bottom was immersed in liquid nitrogen in a Dewar flask. Then the U-tube was connected to a double-chamber UPS machine-II for PES measurements.

He I photoelectron spectroscopy is a powerful tool for characterizing unstable, metastable, and transient species.[15] The gaseous species entrapped in the glass U-tube were released on slow addition of alcohol to the Dewar flask. Gases with different boiling points were released successively. The photoelectron spectrum of the early released gas is shown in Figure 3a. The peaks centered at 13.78, 17.59, 18.08, and 19.41 eV are characteristic for carbon dioxide.[16] The generation of carbon dioxide during reflux indicates that 2-pyrrolidone is not stable at its boiling point even in an oxygen-free environment. The photoelectron spectrum of the gaseous species released at higher temperature is shown in Figure 3b. The PES peaks at 12.66 and 13.01 eV can be attributed to water,[16] and those at 9.08 and 11.51 eV can be assigned to the first and second bands of azetidine according to a previous report.[17] In addition, hydrogen chloride was also detected when the initial concentration of $FeCl_3{\cdot}6H_2O$ was relatively high.

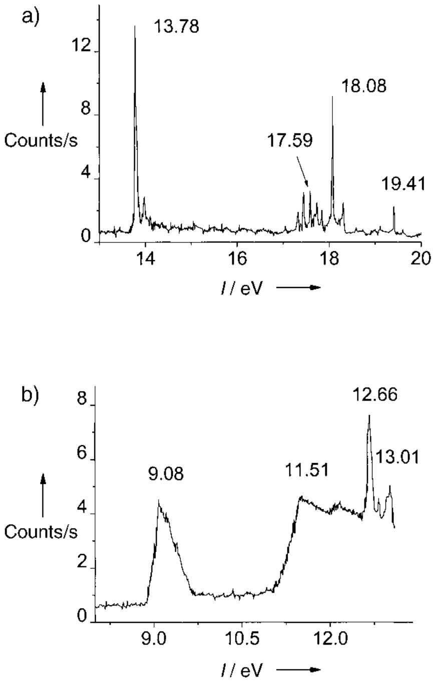
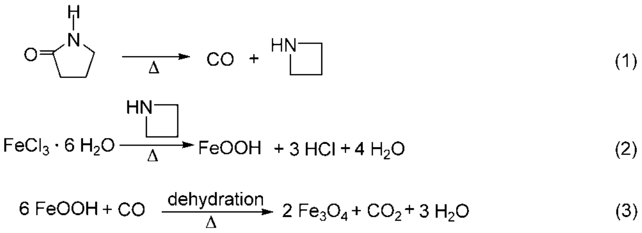


Figure 3. Photoelectron spectra of gaseous species released during the preparation of magnetite nanocrystals. Spectra a) and b) were recorded in sequence with increasing temperature.



Scheme 1. Chemical reactions involved in the formation of magnetite nanoparticles. Equation (2) is a process involving dissolution of $FeCl_3{\cdot}6H_2O$ in 2-pyrrolidone and azetidine-catalyzed hydrolysis of $FeCl_3$.

In accordance with these results, a possible mechanism leading to magnetite nanocrystals is proposed in Scheme 1. In fact, the thermal decomposition of 2-pyrrolidone is rather complex. We observed that prolonged reflux of 2-pyrrolidone also generated fluorescent species in solution. Therefore, Scheme 1 does not depict all decomposition reactions that take place. Only those related to the formation of magnetite nanocrystals are shown. Since carbon dioxide and azetidine were released during reflux, it can be deduced that thermal decomposition of 2-pyrrolidone produces carbon monoxide and azetidine by cleavage of the acylamide bond. Azetidine catalyzes the hydrolysis of $FeCl_3{\cdot}6H_2O$ to form ferric oxide hydroxide (FeOOH) which is then partially reduced by CO. Upon dehydration it forms magnetite and carbon dioxide is released as a by-product. The thermal decomposition of 2-pyrrolidone and the formation of intermediate CO also explains why only magnetite was produced even when [Fe(cup)$_3$] (cup = *N*-nitrosophenylhydroxylamine) or [Fe(acac)$_3$] was used instead of $FeCl_3{\cdot}6H_2O$ in the preparation.

To provide direct proof for the generation of carbon monoxide, a typical identification reaction was used to determine CO. At room temperature CO can reduce Pd^{2+} to give black precipitates of Pd metal. We purged the reaction system with nitrogen during reflux and allowed the N_2 flow to pass successively through a glass tube filled with KOH powder and a flask with H_2SO_4 solution. At the end of this gas line, a fine glass tube was used to introduce the N_2 flow into an aqueous solution of $PdCl_2$. Black precipitates were observed after long enough time and shown to be Pd metal by TEM measurements. The *d* spacings of 0.2244, 0.1945, 0.1391, 0.1190, and 0.0894 nm calculated from selected-area electron diffraction on the black precipitates match well with the *d* values for (111), (200), (220), (311), and (331) lattice planes of Pd metal, respectively.

In summary, we have presented a simple route to synthesize water-soluble magnetite nanocrystals by refluxing inexpensive $FeCl_3{\cdot}6H_2O$ in 2-pyrrolidone. Differently sized and shaped magnetite nanocrystals can be obtained simply by varying the reaction time. Carbon monoxide generated during the reaction plays a critical role in the formation of magnetite nanocrystals, since it partly reduces Fe^{3+} to Fe^{2+}. We believe this novel synthetic approach will not only pave a new way for the preparation of water-soluble magnetite nanocrystals but also provide a new route for mass production of high-quality magnetic nanocrystals, since much more concentrated colloidal solutions can be directly obtained by the current method.

Experimental Section

In a typical synthesis of magnetite nanocrystals, a solution of 10 mmol $FeCl_3{\cdot}6H_2O$ in 100 mL 2-pyrrolidone was first purged with nitrogen to remove oxygen and then heated to the boiling point of 2-pyrrolidone. Samples were taken after the mixture was refluxed for 1, 10, and 24 h, and then cooled to room temperature. A threefold volume of methanol/diethyl ether (1:3) was added to precipitate the nanoparticles. The resultant black precipitate was washed with acetone several times and then dried for characterization.

The magnetite nanocrystals were characterized by TEM, XRD, FTIR, and VSM. TEM images were obtained on a JEM-2010 microscope. XRD patterns were obtained with a Rigaku D/Max-2500 diffractometer equipped with a rotating anode and a $Cu_{K\alpha 1}$ radiation source ($\lambda = 1.54056$ Å). FT-IR spectra were recorded on a Bruker EQUINOX55 FT-IR spectrometer. VSM spectra were collected on a homemade magnetometer.

PES measurements were performed on a double-chamber UPS machine-II. Argon and methyl iodide were used as internal standards for measurements.

Received: May 19, 2004
Revised: September 9, 2004

Keywords: iron · magnetic properties · magnetite · nanostructures · photoelectron spectroscopy

---

[1] K. Raj, R. Moskowitz, *J. Magn. Magn. Mater.* **1990**, *85*, 233–245.
[2] H. Zeng, J. Li, J. P. Liu, Z. L. Wang, S. H. Sun, *Nature* **2002**, *420*, 395–398.
[3] A. Jordan, R. Scholz, K. Maier-Hauff, M. Johannsen, P. Wust, J. Nadobny, H. Schirra, H. Schmidt, S. Deger, S. Loening, W. Lanksch, R. Felix, *J. Magn. Magn. Mater.* **2001**, *225*, 118–126.
[4] a) J. W. M. Bulte, T. Douglas, B. Witwer, S. C. Zhang, E. Strable, B. K. Lewis, H. Zywicke, B. Miller, P. V. Gelderen, B. M. Moskowitz, L. D. Duncan, J. A. Frank, *Nat. Biotechnol.* **2001**, *19*, 1141–1147; b) J. M. Nam, C. S. Thaxton, C. A. Mirkin, *Science* **2003**, *301*, 1884–1886.
[5] P. Tartaj, M. P. Morales, S. Veintemillas-Verdaguer, T. González-Carreño, C. J. Serna, *J. Phys. D* **2003**, *36*, R182–R197.
[6] E. Tronc, P. Belleville, J. P. Jolivet, J. Livage, *Langmuir* **1992**, *8*, 313–319.
[7] a) K. Woo, H. J. Lee, J. P. Ahn, *Adv. Mater.* **2003**, *15*, 1761–1763; b) J. Wang, J. J. Sun, Q. Sun, Q. W. Chen, *Mater. Res. Bull.* **2003**, *38*, 1113–1118.
[8] J. Rockenberger, E. C. Scher, P. A. Alivisatos, *J. Am. Chem. Soc.* **1999**, *121*, 11595–11596.
[9] a) S. H. Sun, H. Zeng, *J. Am. Chem. Soc.* **2002**, *124*, 8204–8205; b) S. H. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang, G. X. Li, *J. Am. Chem. Soc.* **2004**, *126*, 273–279.
[10] T. Hyeon, S. S. Lee, J. Park, Y. Chung, H. B. Na, *J. Am. Chem. Soc.* **2001**, *123*, 12798–12801.
[11] a) Y. Wang, J. F. Wong, X. W. Teng, X. Z. Lin, H. Yang, *Nano Lett.* **2003**, *3*, 1555–1559; b) L. E. Euliss, S. G. Grancharov, S. O. Brien, T. J. Deming, G. D. Stucky, C. B. Murry, G. A. Held, *Nano Lett.* **2003**, *3*, 1489–1493.
[12] Z. Li, H. Chen, H. B. Bao, M. Y. Gao, *Chem. Mater.* **2004**, *16*, 1391–1393.
[13] U. Schwertmann, R. M. Cornell, *Iron Oxides in the Laboratory: Preparation and Characterization*, 2nd ed., Wiley, New York, **2000**.
[14] R. E. Dunin-Borkowski, M. R. McCartney, R. B. Frankel, D. A. Bazylinski, M. Pósfai, P. R. Buseck, *Science* **1998**, *282*, 1868–1870.
[15] J. Wang, Z. Sun, X. J. Zhu, X. J. Yang, M. F. Ge, D. X. Wang, *Angew. Chem.* **2001**, *113*, 3145–3147; *Angew. Chem. Int. Ed.* **2001**, *40*, 3055–3057.
[16] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, S. Iwata, *Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules*, Japan Scientific Societies, Tokyo, **1981**.
[17] K. Yoshikawa, M. Hashimoto, I. Morshima, *J. Am. Chem. Soc.* **1974**, *96*, 288–289.