A Facile Chemical Reduction Route to the Preparation of Single-crystalline Iron Nanocubes

Banghua Qi,[1,2] Dongguo Li,[1] Xiaomin Ni,*[3] and Huagui Zheng*[1]
[1]*Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China*
[2]*Anhui Science and Technology University, Fengyang, Anhui 233100, P. R. China*
[3]*State Key Lab of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China*

(Received March 5, 2007; CL-070234; E-mail: nxmin@ustc.edu.cn, hgzheng@ustc.edu.cn)

Iron nanocubes with a diameter of about 200–400 nm were fabricated by reduction of ferrous sulfate with hydrazine in the solvent of ethylenediamine. During the reaction process, ethylenediamine acted as the solvent, complexant, and structure-directing agent, which was crucial for the formation of the cubes. Thus-prepared iron nanocubes exhibited a high saturation magnetism (Ms) of 690 emu/g, much superior to that of bulk or nanoparticulate counterpart.

Iron nanoparticles have been paid great attention for their wide applications in the fields of catalysis, magnetic recording, and electronics.[1–6] In the past decades, diverse methods had been successfully exploited for the fabrication of iron nanoparticles, such as thermal decomposition of iron-containing metal–organic complexes, ball milling, hydrogen arc plasma, borohydride reduction of metallic salts, hydrogen reduction of iron oxides or hydroxides, etc.[7–15] These techniques differed in the degree of effectivity, complexity, cost, and environmental hazard. For example, the method of ball milling always produced a broad particle size distribution. Precursors of thermal and sonochemical decomposition were usually toxic and expensive. Hydrogen reduction involved high temperatures and complicated instruments. In the method of borohydride reduction, the impurity of iron boride was sometimes produced. Currently, it is still challenging to explore simple and efficient approach for the preparation of pure iron nanoparticles. Previously, we developed a one-step hydrazine reduction method for the preparation of iron nanoparticles in the solvent of ethanol or water, which proved to be simple, high yield, and low cost.[16] However, the obtained crystallites were all particulate. The present work, as a continuous part of our research endeavor in this area, reported the formation of iron nanocubes through hydrazine reduction of ferric salts in the solvent of ethylenediamine. Contrast experiments revealed that ethylenediamine was crucial for the formation of the cubic crystallites. To be noted that, as-prepared iron nanocubes exhibited a high saturation magnetism of 690 emu/g, much superior to that of bulk or particulate particles.

All the chemicals were analytic purity. In a typical experiment, 4 mmol of $FeSO_4 \cdot 7H_2O$ were dissolved in 20 mL of ethylenediamine. Then, 6 mL of $N_2H_4 \cdot H_2O$ (85 wt %) and 3.0 g of NaOH was added under magnetic stirring. The mixture was sealed in a 40-mL autoclave and heated at 120 °C for 6 h. The resulted black powder was collected, rinsed with distilled water and ethanol, and finally vacuum dried at 50 °C for 4 h.

X-ray diffraction was carried out on a Philiphs X'Pert Super diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). The morphology of the products was examined by a field emission scanning electron microscope (FE-SEM, JEOL JSM-6300F) and a transmission electron microscope (TEM, Hitachi 800) with the accelerating voltage of 200 kV. The hysteresis loop was recorded by a model vibrating sample magnetometer (BHV-55).

Figure 1 showed the XRD pattern of the resulted product, which could be well indexed as the body-centered cubic (bcc) phase iron (JCPDS: 06-0696). No peaks due to iron oxides or hydroxides were detected, indicating that pure α-Fe was obtained by the present procedures.

Figure 2 showed the morphology of the sample. SEM image of Figure 2a revealed that the iron particles exhibited cubic shape with the diameter in the range of 200–400 nm. The ratio of cubes in the product was above 70%, coexisting with some irregular particles. Figure 2b presented a typical cubic crystallite, with each facet close to a square. The representative TEM image of the sample was shown in Figure 2c, consistent with the morphological characteristics observed by FE-SEM. The corresponding selected-area electron diffraction (SAED) pattern taken from a single cube revealed the single-crystalline nature of the cube, which was governed by the stable (110) and (100) crystalline planes, as arrowed in Figure 2b.

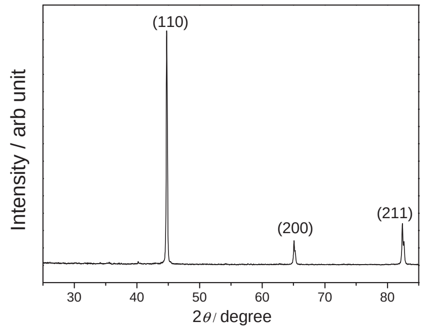

Figure 1. XRD pattern of the iron sample.

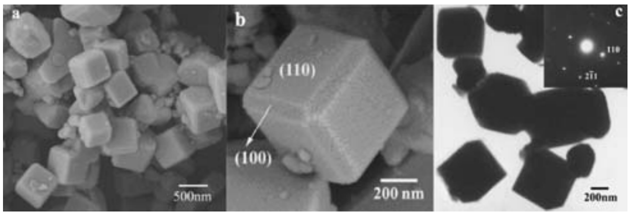

Figure 2. (a) FESEM image of the sample, (b) FESEM image of a typical cubic crystallite, (c) TEM image of the sample, inset is a SAED pattern recorded on one cube.

It was known that ethylenediamine was a strong coordinating solvent. In the current system, it acted an important role for

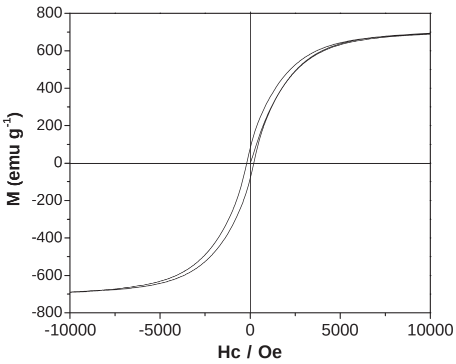

Figure 3. *M–H* loops of the iron sample.

the formation of the iron nanocubes. Generally, Fe^{III} ions were hard to be reduced to Fe^0 because they easily transformed into stable $Fe(OH)_x$ colloids in a basic medium.[16] In our previous systems with water or ethanol as solvent, a great amount of ferric hydroxide colloids were produced when NaOH was added. In the present reaction system, ferrous ions were coordinated by ethylenediamine, which sharply reduced the amount of $Fe(OH)_x$ colloids and made redox reaction easier to be processed. On the other hand, ethylenediamine was believed to also play a role of structure-directing agent. When we changed the complexant of ethylenediamine with other complexant of citrate or phenanthroline, no any cubes could be fabricated and only particulate particles were obtained. It was assumed that during the growth of iron particles ethylenediamine molecules may selectively absorb on the (110) crystalline planes of bcc iron. Thus, the growth rates of different crystal planes were kinetically controlled, in which the (100) planes were passivated, while the (110) planes were possibly unaffected, which eventually led to cubic crystallites. As a result, ethylenediamine was considered to play three important roles of complexant, solvent and structure-directing agent in the formation of iron cubes. Such formation mechanism was similar to that of the solvent coordination molecular template effect in the fabrication of CdE (E: S, Se, Te) nanorods.[17]

Magnetization hysteresis (*M–H*) loops of the obtained iron nanocubes were measured at room temperature in a field of 10000 Oe (Figure 3). The specific saturation magnetization (*M*s) and coercivity (*H*c) of the sample were 690 emu/g and 198 Oe. The *H*c value was close to that of the particles prepared in an aqueous solution, possibly for their similar size.[16] However, the *M*s value was much higher than that of bulk iron (220 emu/g) or iron nanoparticles (212 emu/g).[18,19] To the best of our knowledge, this value was the highest one of α-Fe in the data reported up to date. It was known that the magnetic properties were influenced by various factors such as size, shape, crystallinity, and preparation method.[20] Such an enhanced *M*s could be attributed to the specific shape of the sample.[21] When subjected to an external magnetic filed, these isolated single crystalline nanocubes easily arranged with their magnetic easy axis along the direction of external magnetic field, thus a much high *M*s value was exhibited. More research on the deep reasons is in progress.

In summary, body-centered cubic structured iron nanocubes were successfully obtained by reduction of ferric salts with hydrazine in the solvent of ethylenediamine. Formation of the iron nanocubes could be ascribed to the coordinating solvent templating effect of ethylenediamine, which played three roles of solvent, complexant and structure-directing agent. Thus-prepared cubic iron nanocrystallites exhibited a saturation magnetization of 690 emu/g, much higher than that of bulk iron or iron naoparticles. Such iron nanocubes are expected to find applications in the fields of magnetic recording and catalysis, considering their unique cubic shape and high *M*s value.

References

1 S. G. Marchetti, M. V. Cagnoli, Z. M. Alvarez, J. F. Bengoa, N. G. Gallegos, A. A. Yeramian, R. C. Mercader, *Hyperfine Interact.* **2002**, *33*, 139.
2 E. I. Grigor'ev, S. A. Zav'yalov, S. N. Chvalun, *Polym. Sci., Ser. A* **2003**, *45*, 780.
3 J. L. Menéndez, B. Bescós, G. Armelles, R. Serna, J. Gonzalo, R. Doole, A. K. Petford-Long, M. I. Alonso, *Phys. Rev. B* **2002**, *65*, 205413.
4 B. C. Liu, S. H. Tang, Z. L. Yu, B. L. Zhang, T. Chen, S. Y. Zhang, *Chem. Phys. Lett.* **2002**, *357*, 297.
5 S. M. Ponder, J. G. Darab, J. Bucher, D. Caulder, I. Craig, L. Davis, N. Edelstein, W. Lukens, H. Nitsche, L. F. Rao, D. K. Shuh, T. E. Mallouk, *Chem. Mater.* **2001**, *13*, 479.
6 F. Bødker, S. Morup, S. Linderoth, *Phys. Rev. Lett.* **1994**, *72*, 282.
7 T. R. Malow, C. C. Koch, P. O. Miraglia, *Mater. Sci. Eng., A* **1998**, *252*, 36.
8 Z. L. Cui, L. F. Dong, C. C. Hao, *Mater. Sci. Eng., A* **2000**, *286*, 205.
9 S. J. Park, S. Kim, S. Lee, Z. G. Khim, K. Char, T. Hyeon, *J. Am. Chem. Soc.* **2000**, *122*, 8581.
10 K. S. Suslick, M. Fang, T. Hyeon, *J. Am. Chem. Soc.* **1996**, *118*, 11960.
11 D. J. Cain, D. E. Nikles, *IEEE Trans. Magn.* **1996**, *32*, 4490.
12 Y. P. Sun, H. W. Rollins, R. Gufuru, *Chem. Mater.* **1999**, *11*, 7.
13 K. J. Takeuchi, A. C. Marschilok, C. A. Besel, N. R. Dollahon, *J. Catal.* **2002**, *208*, 150.
14 M. Chen, B. Tang, D. E. Nikles, *IEEE Trans. Magn.* **1998**, *34*, 1141.
15 L. Vayssieres, L. Rabenberg, A. Manthiram, *Nano Lett.* **2002**, *2*, 1393.
16 N. Xiaomin, S. Xiaobo, Z. Huagui, Z. Dongen, Y. Dandan, Z. Qingbiao, *J. Cryst. Growth* **2005**, *275*, 548.
17 Y. D. Li, H. W. Liao, Y. Ding, Y. Fan, Y. Y. Zhang, Y. T. Qian, *Inorg. Chem.* **1999**, *38*, 1382.
18 S. I. Nikitenko, Y. Koltypin, O. Palchik, I. Felner, X. N. Xu, A. Gedanken, *Angew. Chem., Int. Ed.* **2001**, *40*, 4447.
19 B. D. Cullity, *Introduction to Magnetic Materials*, Addison-Eiley, New York, **1972**, p. 171.
20 D. de Caro, T. O. Ely, A. Mari, B. Chaudret, E. Snoeck, M. Respaud, J. M. Broto, A. Fert, *Chem. Mater.* **1996**, *8*, 1987.
21 S. K. Suslick, M. M. Fang, T. Hyeon, *J. Am. Chem. Soc.* **1996**, *118*, 11960.

Published on the web (Advance View) April 28, 2007; doi:10.1246/cl.2007.722