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Preparation of water-soluble magnetite nanocrystals through hydrothermal approach

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Abstract

Water-soluble Fe₃O₄ nanocrystals have been prepared through hydrothermal approach. These nanocrystals capped with C₆H₆O₆ (the oxidation state of ascorbic acid) could be readily dispersed in hydrated aqueous systems. The final product was characterized with X-ray powder diffraction (XRD), transmission electron microscope (TEM), Fourier Transform Infrared and X-ray photoelectron spectroscopy. From XRD patterns, we confirm the product to be Fe₃O₄. The nanoparticles several nanometers long were well dispersed as shown in TEM image. Magnetic hysteresis loop measurements showed that the Fe₃O₄ nanocrystals display superparamagnetism. A possible formation mechanism of the Fe₃O₄ nanocrystals was suggested.

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1. Introduction

Magnetite nanocrystals have been widely studied because of their potential applications in biomedical fields such as biological labeling, tracking, detection and separations, [1] target–drug delivery, [2] clinical diagnosis and treatment, [3] and magnetic resonance imaging. [4] For these applications, many efforts have been devoted to the synthesis of magnetite nanoparticles, such as microemulsions [5], laser pyrolysis [6], sonochemical synthesis [7], chemical co-precipitation [8], etc. However, the relative poor size uniformity and low crystallinity of magnetite nanoparticles obtained strongly affect their use in many applications. Recently, Rockenberger et al. [9] reported a thermal decomposition approach to synthesize near-monodisperse maghemite nanocrystals. By a similar method, Sun and Zeng [10] succeeded in synthesizing monodisperse magnetite through decomposition of [Fe(acac)₃]

(acac=acetylacetonate) in the presence of 1,2-hexadecanediol, oleic acid and oleylamine. 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, and this limits their application in biomedical fields, especially for in vivo applications. Therefore, it is very important to further develop the synthesis method to fabricate water-soluble magnetite nanoparticles. Very recently, Li and coworkers improve the thermal decomposition method using strong polar 2-pyrrolidone as a coordinating solvent to produce water-soluble magnetite nanocrystals [11]. They also have succeeded in preparing magnetite nanocrystals by using hydrated ferric salts as iron precursors instead of costly [Fe(acac)₃] [12]. Nevertheless, the development of a synthesis strategy for the magnetic particles in one step still is a pressing need not only for the fundamental interest but also for their high efficiency and facility.

In the last few years, a hydrothermal method has been developed to prepare magnetic nanoparticles. Si et al. [13]

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have reported a facile method to produce monodisperse magnetite nanoparticles via the reaction between Fe powder and FeCl_3 in the presence of oleic acid and laurylamine. Though this method has been proved to be effective in increasing the crystallinity, the magnetite nanoparticles obtained exhibit poor water solubility, which limits their application in biomedical fields. Here, we reported the preparation of water-soluble magnetite nanoparticles by a hydrothermal method. In this work, hydrated ferric salt was employed as a single iron precursor and ascorbic acid as a reducing agent to synthesize superparamagnetic Fe_3O_4 nanocrystals, which capped with $\text{C}_6\text{H}_6\text{O}_6$ (the oxidation state of ascorbic acid). In addition, the mechanism leading to magnetite is discussed.

2. Experimental

In a typical experiment, 0.54 g analytically pure $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 25 ml H_2O with continuous stirring. Then, 10 ml 0.6 M Na_2CO_3 was added to the solution drop by drop; 10 min later, 0.12 g ascorbic acid was added into the above-mentioned solution under vigorous stirring. After being stirred for another 15 min, the solution was transferred and sealed in a 40 ml Teflon-sealed autoclave. The autoclave was kept at 160°C for 3 h before being cooled in air naturally. The final products were separated from the reaction medium by centrifugation. A rinsing process including three cycles of centrifugation/washing/centrifugation procedure in deionized water and in alcohol was required before oven drying at 60°C for 12 h.

The phase of the samples was examined by X-ray power diffraction (XRD) with Cu-K α radiation on an MXP18AHF X-ray diffractometer at room temperature. X-ray photoelectron spectra (XPS) were measured on an ESCA Lab MKII instrument with Mg K α radiation as the exciting source. Infrared (IR) spectra were recorded in the wave numbers ranging $4000\text{--}500\text{ cm}^{-1}$, with a Nicolet Model 759 fourier transform infrared (FT-IR) spectrometer using a KBr wafer. The morphology of the samples was examined by transmission electron microscope (TEM). Powder samples for TEM were prepared by ultrasonically dispersing the products into absolute ethanol, then placing a drop of this suspension onto a copper grid with amorphous carbon film and then drying in air. Their magnetic properties ($M\text{--}H$ curve) were measured at room temperature on an MPMS XL magnetometer made by Quantum Design Corporation.

3. Results and discussion

Typical syntheses of Fe_3O_4 nanocrystals were carried out in a hydrothermal system by reduction reactions between FeCl_3 and ascorbic acid. The crystalline structure was characterized by XRD. As shown in Fig. 1c, the patterns can be easily indexed to Fe_3O_4 (JCPDS 85-1436), the broad nature of the peaks results from nanosized magnetite

particles. The average size of the individual magnetite nanoparticles is about 5.2 nm, calculated by the Scherrer equation. [14] In our experiment, an experimental session was conducted by adjusting the content of ascorbic acid while keeping other parameters constant. The XRD patterns in spectra a–e are corresponding to the product produced with the content of ascorbic acid 0.06, 0.09, 0.12, 0.18 and 0.24 g, respectively. It is seen that samples a, b and c exhibit identical face-centered structure of Fe_3O_4 , indicating that a little excess of reducing reagent in our system dose not induce any obvious change in the crystal structure of the finally magnetic nanoparticles. However, the excessive increase in the ascorbic acid leads to the formation of FeCO_3 (samples d and e).

The TEM image of the typical sample is shown in Fig. 2. It can be seen that the Fe_3O_4 nanoparticles consist of spherical particles several nanometers long, which agreed well with the result from XRD. As investigated from the image, part of small particles has aggregated because of

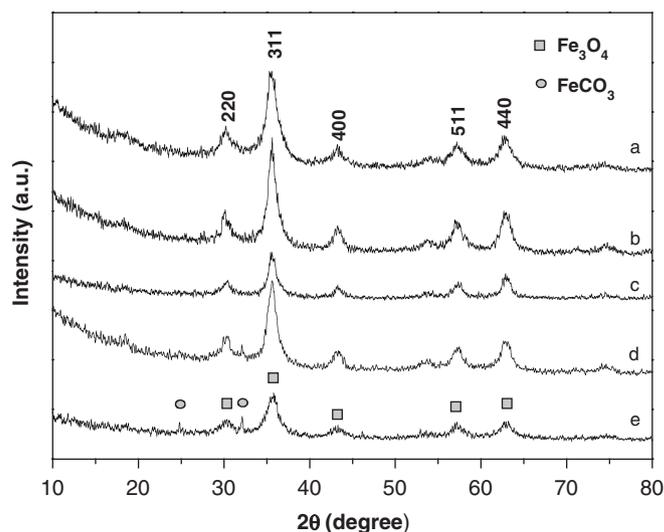


Fig. 1. Influence of the content of ascorbic acid on the XRD pattern of Fe_3O_4 . Spectra a–e are corresponding to the product produced with the content of ascorbic acid 0.06, 0.09, 0.12, 0.18 and 0.24 g, respectively.

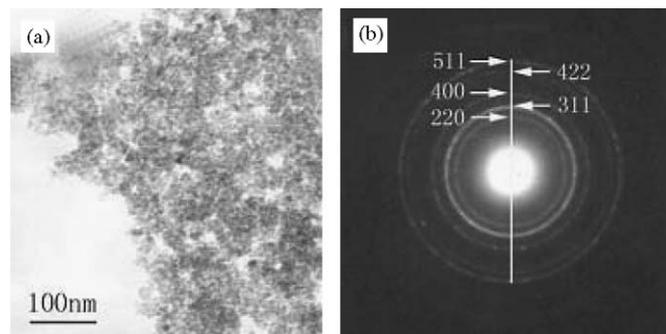


Fig. 2. (a) TEM images of magnetic particles. (b) Selected-area electron diffraction pattern of the sample.

their extremely small sizes and high surface energies [15]. Hence, it was difficult to precisely determine the size and the size distribution of the nanoparticles by simply viewing the TEM image. The electron diffraction pattern of the sample in Fig. 2b also supports the magnetite crystal structure. The face-centered cubic structure of Fe_3O_4 is identified and the reflection planes of 220, 311, 400, 422 and 511 are clearly seen.

FT-IR analysis was performed to characterize the surface nature of the resulting magnetite nanoparticles, as depicted in Fig. 3c. A strong absorption band at 593 cm^{-1} related to the vibrations of the Fe–O functional group. The intense and broad band appeared in the region $3200\text{--}3600\text{ cm}^{-1}$, it can be noted that the iron oxide surfaces are readily covered with hydroxyl groups in an aqueous environment [16]. In our experiment, the Fe_3O_4 nanocrystals were capped with $\text{C}_6\text{H}_6\text{O}_6$ (the oxidation state of ascorbic acid) through carbonyl group. As we know, two binding modes have been suggested for the surface carboxylate bonding [17]. In one mode, the carboxylate is connected to the surface through one oxygen atom, and both the symmetric C=O (1441 cm^{-1}) and the asymmetric (1552 cm^{-1}) stretchings were observed [18]. In the other mode, the carboxylate is bound symmetrically to the surface and only the symmetrical C=O stretching band appears at 1404 cm^{-1} [19]. Therefore, it was suggested here that the carboxylate in the $\text{C}_6\text{H}_6\text{O}_6$ might symmetrically bind to the surface, for there was only one symmetrical C=O stretching band appearing at 1402 cm^{-1} . Moreover, the evident stretching at 1634 cm^{-1} , which was consistent with that of the C=O in the $\text{C}_6\text{H}_6\text{O}_6$, indicated the existence of free carbonyl groups. The observed C–H stretching bands (2921 and 2851 cm^{-1}) and C–O–C stretching (1100 cm^{-1}) further supports the attachment of $\text{C}_6\text{H}_6\text{O}_6$ onto the particle surface.

The surface chemical structure of the magnetite nanocrystals was further characterized by XPS (Fig. 4). The iron band appearing at 710.9 eV was assigned to the Fe2p3

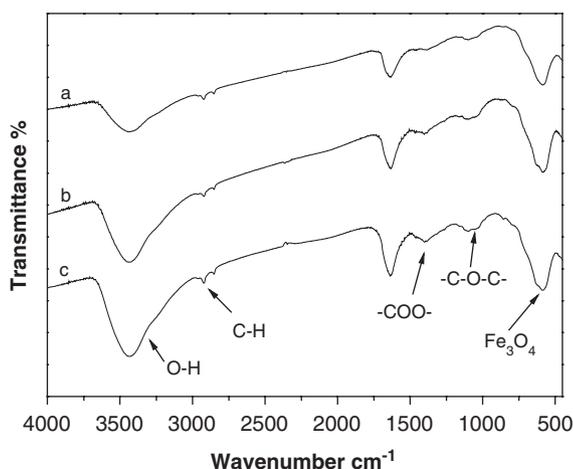


Fig. 3. FTIR spectra of the magnetite nanoparticles prepared under (a) 0.06 g, (b) 0.09 g and (c) 0.12 g of ascorbic acid.

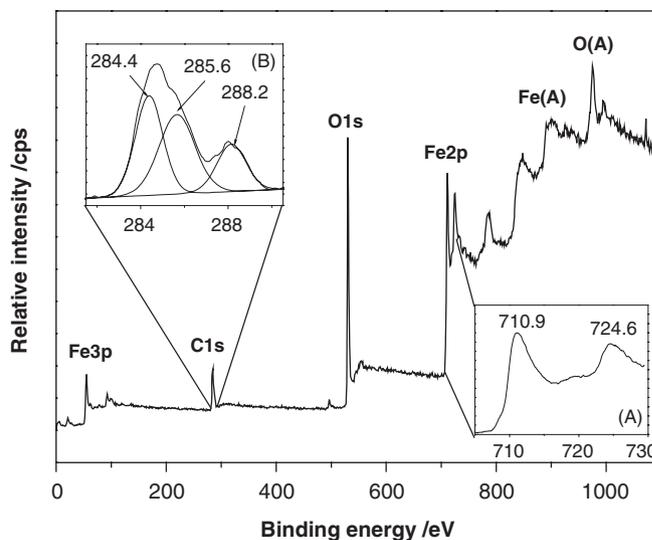


Fig. 4. X-ray photoelectron spectra of magnetite nanoparticles. Insets are expanded spectra of Fe2p (A) and C1s (B).

(Fig. 4a), which is in a good agreement with the literature values [20]. Fig. 4b displays the typical XPS spectrum of the C1s region. The carbon 1s peak was deconvoluted into three spectral bands at 284.4, 285.6 and 288.2 eV. The most intense peak at 284.4 eV attributed to the C–C/C–H. The 285.6 eV of binding energy is due to the C–O and the relatively small peak at 288.2 represents the C=O in the $\text{C}_6\text{H}_6\text{O}_6$ molecule. These assignments for the C1s components agree with those in previous studies [21].

The atomic ratio between Fe and C in the nanocrystals is determined to be 0.972 by XPS. This suggests that there are roughly 213 $\text{C}_6\text{H}_6\text{O}_6$ molecules forming a layer on the surface of a 5 nm magnetite particle. The $\text{C}_6\text{H}_6\text{O}_6$ layer forming on the surface of magnetite nanocrystals renders not only stability but also solubility to the magnetite nanocrystals. These magnetic nanocrystals reported here can be dissolved in water; however, they are difficult to dispersed in ethanol. In the rinsing process, the products were washed by water, but these nanoparticles could not be separated from the solution by centrifugation. Therefore, the same volume of ethanol was introduced to this solution, and these magnetic particles could be separated either by centrifugation or magnetic separation.

Magnetic characterization of the magnetite nanocrystals measured at 300 K is shown in Fig. 5. The saturation magnetization of the product is 5.2 emu/g much smaller than that (68.7 emu/g) of the Fe_3O_4 nanoparticles sized about 70 nm prepared through a hydrothermal method without any surfactants [22]. The small saturation magnetization in our case is most likely attributed to the much smaller size of Fe_3O_4 nanoparticles and the existence of surfactants ($\text{C}_6\text{H}_6\text{O}_6$) on the surface [23]. The coercivity of as-synthesized magnetites approaches to be 0 Oe, indicating that the obtained magnetite nanocrystals are superparamagnetic.

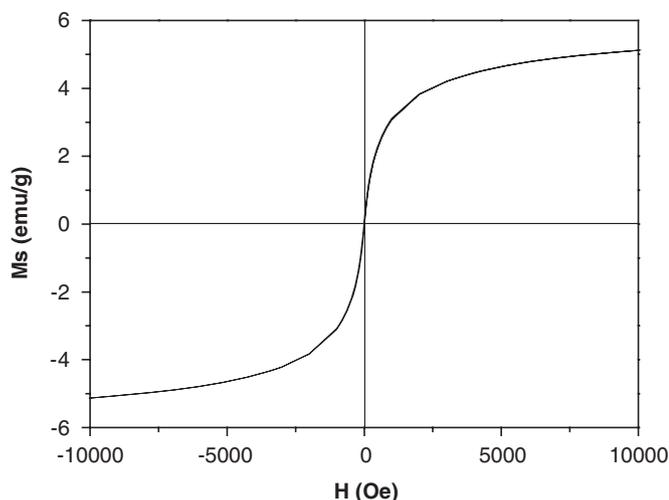
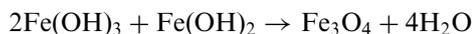


Fig. 5. Hysteresis loop measurements of Fe_3O_4 nanoparticles at 300 K.

A possible formation mechanism of the magnetite nanocrystals was suggested as follows:



In our system, when Na_2CO_3 was added to the red FeCl_3 solution, yellow precipitates were observed, indicating the generation of $\text{Fe}(\text{OH})_3$, which was due to the hydrolysis of Fe^{3+} . As soon as ascorbic acid was introduced to the colloid solution, the color of the reaction system changed from yellow to black. In this hydrothermal method, the as-prepared product was capped with $\text{C}_6\text{H}_6\text{O}_6$. It is easy to know that one-third of 2 mmol Fe^{3+} could be deoxidized by 1/3 mmol ascorbic acid to give 2/3 mmol Fe^{2+} , and this ensures the molar ratios of $\text{Fe}^{2+}/\text{Fe}^{3+}$ to be 1/2. In our system, while the amount of the ascorbic acid is more than 2/3 mmol, too many ferrous ions were obtained. The excess Fe^{2+} will react with the CO_3^{2-} to give FeCO_3 . Therefore, the excessive increase in the ascorbic acid lead to the formation of FeCO_3 . When the amount of the ascorbic acid is more than 0.3 g, pure FeCO_3 will be obtained.

4. Conclusions

In summary, we reported a hydrothermal approach for preparing water-soluble magnetite nanocrystals. The experimental results reveal that ascorbic acid not only serves as a reducing reagent for the reaction, but also the oxidation state of ascorbic acid involves surface coordination which renders the magnetite nanocrystals water

soluble and the colloidal solution stable. These particles are only several nanometers long, as shown by TEM. They show the typical behavior of superparamagnets at room temperature. A possible formation mechanism of magnetite nanocrystals is suggested here according to the experimental results.

Acknowledgements

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References

- [1] J.W.M. Bulte, T. Douglas, B. Witwer, S.C. Zhang, E. Strable, B.M. Moskowitz, L.D. Duncan, J.A. Frank, *Nat. Biotechnol.* 19 (2001) 1141.
- [2] P.K. Gupta, C.T. Hung, F.C. Lam, D.G. Perrier, *Int. J. Pharm.* 43 (1988) 167.
- [3] A. Jordan, R. Scholz, K. Maier-Hauff, M. Johannsen, P. Wust, J. Nadobny, H. Schirra, H. Schmidt, S. Loening, W. Lanksch, R. Felix, *J. Magn. Magn. Mater.* 225 (2001) 118.
- [4] M. Lewin, N. Carlesso, C.H. Tung, X.W. Tang, D.T. Scadden, R. Weissleder, *Nat. Biotechnol.* 18 (2000) 410.
- [5] S. Mann, H.C. Sparks, R.G. Board, *Adv. Microb. Physiol.* 31 (1990) 125.
- [6] S. Veintemillas-Verdaguer, O. Bomati-Miguel, M.P. Morales, *Scr. Mater.* 47 (2002) 589.
- [7] R.V. Kumar, Y. Koltypin, X.N. Xu, Y. Yeshurun, A. Gedanken, I.J. Felner, *Appl. Phys.* 89 (2001) 6324.
- [8] W.Q. Jiang, H.C. Yang, S.Y. Yang, H.E. Horng, J.C. Hung, Y.C. Chen, C.Y. Hong, *J. Magn. Magn. Mater.* 283 (2004) 210.
- [9] J. Rockenberger, E.C. Scher, P.A. Alivisatos, *J. Am. Chem. Soc.* 121 (1999) 11595.
- [10] S.H. Sun, H. Zeng, *J. Am. Chem. Soc.* 124 (2002) 8204.
- [11] Z. Li, H. Chen, H.B. Bao, M.Y. Gao, *Chem. Mater.* 16 (2004) 1391.
- [12] Z. Li, Q. Sun, M.Y. Gao, *Angew. Chem. Int. Ed.* 44 (2005) 123.
- [13] S.F. Si, C.H. Li, X. Wang, D. Yu, Q. Peng, Y.D. Li, *Crys. Growth Desi.* 5 (2005) 391.
- [14] H.P. Klug, L.E. Alexander, *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, Wiley, New York, 1962, pp.491–538.
- [15] J.H. Du, H.R. Liu, *J. Magn. Magn. Mater.* 302 (2006) 263.
- [16] F.Y. Cheng, C.H. Su, Y.S. Yang, C.S. Yeh, C.Y. Tsai, C.L. Wu, M.T. Wu, D.B. Shieh, *Biomaterials* 26 (2005) 729.
- [17] Y.T. Tao, *J. Am. Chem. Soc.* 115 (1993) 4350.
- [18] K.V.P.M. Shafi, A. Ulman, X.Z. Yan, N. Yang, C. Estournes, H. White, M. Rafailovich, *Langmuir* 17 (2001) 5093.
- [19] L.A. Harris, J.D. Goff, A.Y. Carmichael, J.S. Riffle, J.J. Harburn, T.G. St. Pierre, M. Saunders, *Chem. Mater.* 19 (2003) 1367.
- [20] *Hand book of X-ray Photoelectron Spectroscopy*, Perkin Elmer Corporation Physical Electronics Division, USA, 1979.
- [21] C. Moreno-Castillaa, M.V. Lopez-Ramonb, F. Carrasco-Marina, *Carbon* 38 (2000) 1995.
- [22] Wang, Q.W. Chen, C. Zeng, B.Y. Hou, *Adv. Mater.* 16 (2004) 137.
- [23] R.H. Kodama, A.E. Berkowitz, E.J. McNiff, S. Foner, *Phys. Rev. Lett.* 77 (1996) 394.