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Rhombic dodecahedral Fe₃O₄: ionic liquid-modulated and microwave-assisted synthesis and their magnetic properties†

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Rhombic dodecahedral (RD) Fe₃O₄ nanocrystals (NCs) were for the first time prepared via a rapid and facile microwave-assisted route in the presence of ionic liquids (ILs). The reaction could be finished within 15 min at temperatures as low as 90 °C. A proper amount of ILs played a key role in the synthesis of pure RD Fe₃O₄ NCs. In addition, the HMT-to-phenol molar ratio was also crucial for the growth of the RD Fe₃O₄ NCs. The phase structures, morphologies, and sizes of as-prepared products were investigated in detail by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM). The magnetic study reveals that the T_B of the RD Fe₃O₄ NCs is found to be at 120 K, and the saturation magnetization is 86 emu g⁻¹ at room temperature.

The design and rational synthesis of inorganic nanocrystals (NCs) with controlled size and morphology have attracted intensive interest due to their strongly determined physical properties for optical, electrical, magnetic, and catalytic applications.^{1–3} Magnetic NCs, especially iron oxide NCs, have been extensively studied owing to their unique magnetic features and important applications.⁴ As a kind of conventional magnetic material, magnetite (Fe₃O₄) has been widely used as data storage media,⁵ a ferrofluid,⁶ a contrast agent for magnetic resonance imaging,⁷ and a drug targeting carrier.⁸ Furthermore, Fe₃O₄ NCs have been reported to possess intrinsic peroxidase-like activity which poses the potential for novel applications.⁹ Recently, a variety of Fe₃O₄ morphologies, including nanospheres,¹⁰ truncated cubes, nanocubes,¹¹ truncated octahedra, nanooctahedra,¹² etc., have been successfully synthesized. However, most of these morphologies are usually bound by {111}, {100} or both {111} and {100} facets. On the basis of the fact that the surface energies of different crystallographic planes are in the order of $\gamma\{111\} < \gamma\{100\} < \gamma\{110\}$,¹³ the formation of these structures can be ascribed to the result of the minimization of surface energy. Until now, magnetite NCs exclusively enclosed by {110} surfaces, like rhombic dodecahedron or regular dodecahedron, have been rarely

exploited, because the {110} facet has the highest surface energy among the low-index facets, thus exhibiting faster growth kinetics than the others, resulting in their disappearance during the crystal growth.¹³ It is widely accepted that fabrication of Fe₃O₄ NCs possessing high-energy facets is significant for their potential applications such as conspicuous catalytic activity.

Diverse solution-based approaches, such as co-precipitation, reverse micelle, thermal decomposition, and hydrothermal methods,^{8,10,14} have been pursued in the literature for the synthesis of Fe₃O₄ nanostructures. However, these methods mostly require long reaction times (5–24 h) and the procedures are always energy consuming. In this regard, microwave-assisted synthesis approaches are extremely appealing as they can shorten the reaction time from several hours to a few minutes with enormous energy savings and cleanliness.¹⁵ Ionic liquids (ILs), as green and efficient recyclable solvents, have gained a great deal of attention in organic and inorganic chemical reactions, separation, and electrochemical processes due to their favorable properties such as negligible vapor pressures, wide liquid ranges, good thermal stability, tunable solubility of both organic and inorganic molecules, and much synthetic flexibility.¹⁶ Though ILs have been widely used as solvents or additives in the preparation of iron oxide NCs,¹⁷ to the best of our knowledge, this is the first time of achieving rhombic dodecahedral (RD) Fe₃O₄ bound by twelve {110} crystal planes under microwave irradiation with the help of hydrophilic ILs of *N*-dodecylpyridinium perchlorate [C₁₂Py]⁺[ClO₄]⁻. The reaction can be finished within 15 min at a low temperature of 90 °C, which is quite fast and simple.

All the chemicals were of analytical grade and used as received without further purification, and [C₁₂Py]⁺[ClO₄]⁻ was synthesized by Lanzhou Greenchem ILS, LICP, CAS, China. In a typical synthesis, 0.2 g of ILs [C₁₂Py]⁺[ClO₄]⁻, 0.6 mmol of phenol and 0.3 mmol of hexamethylenetetramine (HMT) were dissolved in 18 mL of water. Then, 0.1 mol of FeSO₄·(NH₄)₂SO₄·6H₂O was added. After stirring mildly for about 15 min, the solution was transferred into quartz vessels and heated to 90 °C for 15 min under microwave irradiation (StartSYNTH, Milestone). The resultant black sample was purified by washing with ethanol to remove excess reagents. Fig. 1a shows a representative scanning electron microscopy (SEM) image of the as-prepared products. The high-magnification SEM images are also shown in Fig. 1b and c. It is observed from Fig. 1a and b that the main morphology of the prepared products is RD NCs with an average edge length of 50 ± 10 nm, and some irregularly shaped small particles are also observed with particle sizes of about 30 nm. As

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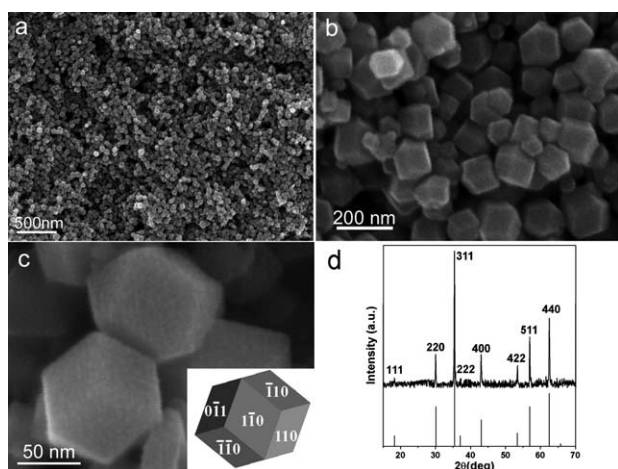


Fig. 1 Low- (a) and high-magnification SEM images (b and c) of the RD Fe_3O_4 NCs. Inset: models of corresponding ideal rhombic dodecahedra enclosed by 12 $\{110\}$ facets; (d) XRD patterns of the RD Fe_3O_4 NCs and standard JCPDS file (76-1849) of magnetite.

shown in Fig. 1c, the ideal RD structures bound by twelve $\{110\}$ crystal planes viewed along different orientations correlate well with the corresponding NCs. Fig. 1d shows the powder X-ray diffraction (XRD) pattern of the samples under microwave irradiation. The position and relative intensity of diffraction peaks of the RD NCs are in accordance with those of pure Fe_3O_4 with face-centered cubic structure (*fcc*, JCPDS No. 76-1849). The columns at the bottom of Fig. 1d represent the characteristic peaks of the standard magnetite sample from a JCPDS file (76-1849). X-Ray photoelectron spectroscopy (XPS, Fig. S1†) data show three main peaks at 710, 724, and 531 eV, which are the characteristic binding energy peaks of $\text{Fe } 2p_{3/2}$, $\text{Fe } 2p_{1/2}$, and $\text{O } 1s$ of Fe_3O_4 , respectively. These data also confirm that the obtained product is Fe_3O_4 .¹⁸

The crystal structure of the prepared NCs was further determined by transmission electron microscopy (TEM) and high-resolution TEM characterizations. Fig. 2a shows a typical TEM image of the RD NCs, and the bottom-right inset shows the selected area electron diffraction (SAED) pattern obtained from a single rhombic dodecahedron with the electron beam perpendicular to one of the rhombic facets. The SAED pattern can be indexed to the $[110]$ zone axis of a single crystal of *fcc* Fe_3O_4 , indicating that the synthesized NCs are single-crystalline and bound by $\{110\}$ basal planes. The lattice spacing of 0.297 nm measured from the high-resolution TEM

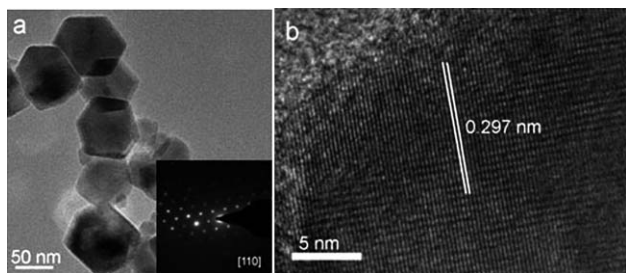


Fig. 2 (a) TEM image of the RD Fe_3O_4 NCs, bottom-right inset shows the corresponding SAED pattern; (b) High-magnification HRTEM image of the RD Fe_3O_4 NCs.

image corresponds to the (220) crystalline plane of *fcc* Fe_3O_4 , which also demonstrates the exposed surface of the $\{110\}$ facets.

In order to get further understanding about the shape control of the NCs in the reaction system, control experiments were conducted to elucidate the growth mechanism of the RD NCs. It is found that the ILs of $[\text{C}_{12}\text{Py}]^+[\text{ClO}_4]^-$ play an important role in the formation of the RD structured Fe_3O_4 , and 0.2 g of ILs is the optimal dosage for the fabrication of the RD structures as shown in Fig. 1 and 2. If in the absence of ILs, the morphology of the as-obtained products is composed of RD structures and some unexpected rods. These RD structures have a wide size distribution in the range of 75–150 nm and the length of rods is about 100 nm (Fig. 3a). When the amount of the ILs is kept at 0.1 g, the size of the RD structure became uniform with the average edge length decreased to 70 ± 10 nm, however, there still exist some rods in the SEM image. XRD analysis of the as-prepared products shows that the products with RD and rod structures are in the impure phase (Fig. S2†). By increasing the amount of the ILs to 0.3 g, it becomes difficult to distinguish the RD structured NCs due to the smaller edge length which has decreased to about 35 nm (Fig. 3c). However, further increasing the amount of ILs to 0.4 g, the RD structured NCs completely disappeared instead of some irregular nanoparticles with a diameter of about 50 nm (Fig. 3d).

In addition to the ILs, the amount of HMT-to-phenol molar ratio (in mmol) is also crucial for the growth of the RD Fe_3O_4 NCs. As reported above, RD structures mixed with rods are obtained in the absence of ILs (Fig. 3a), which indicates that HMT/phenol could be selectively adsorbed on $\{110\}$ crystal planes to tune the structure of the products. Given the unchanged amount of ILs (0.2 g) and other parameters, different structures of the products could be obtained by tuning the molar ratio of HMT/phenol. As shown in Fig. 4a, the NCs are composed of both RD structures and irregular particles without adding phenol in the synthetic system. Changing the molar ratio of HMT-to-phenol to 0.3 : 0.06, polyhedral NCs with not evident faces are observed (Fig. 4b). However, when the molar ratio decreased to 0.3 : 1.5, the size of the regular RD NCs decreased but their size distribution became wider (Fig. 4c).

In general, the size and shape of inorganic NCs can be modulated by controlling the crystal nucleation and relative growth rate on

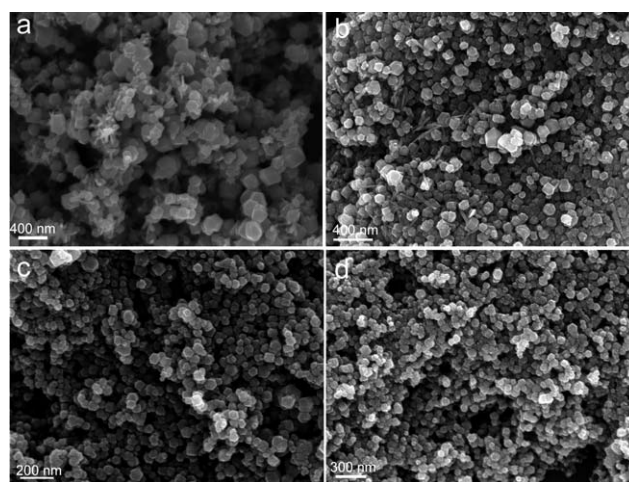


Fig. 3 SEM images of the products prepared with the amount of ILs: (a) 0 g, (b) 0.1 g, (c) 0.3 g, (d) 0.4 g, other reaction conditions were kept constant.

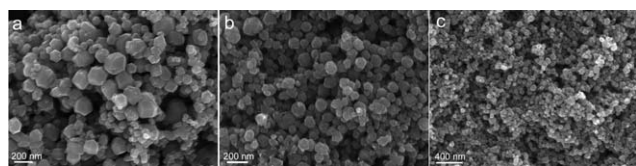


Fig. 4 SEM images of the products prepared with the HMT-to-phenol molar ratio (in mmol): (a) 0.3 : 0, (b) 0.3 : 0.06, (c) 0.3 : 1.5, other reaction conditions were kept constant.

particular crystal surfaces during the crystal growth. On the other hand, the crystal habit of inorganic crystals is generally determined by the relative order of surface energies,¹⁹ and the fastest growth occurs in the direction perpendicular to the faces with the highest surface energy. For a *fcc* structure, the sequence for the surface energies of the magnetite structure is $\gamma\{111\} < \gamma\{100\} < \gamma\{110\}$.¹³ Therefore, a RD polyhedron of *fcc* structured Fe_3O_4 with twelve $\{110\}$ facets is not the thermodynamically most favored shape. However, in the solution-phase synthesis, adsorbates such as surfactants or small molecules can interact selectively with different crystal facets and alter their surface energies, so as to affect the relative growth rates of different facets.¹⁸ As a result, the facet with a slower growth rate will be exposed more on the NC surface. Based on our experiments, it is also found that the ILs with the cations of $[\text{C}_{12}\text{Py}]^+$ may be able to coordinate with Fe^{2+} to form complexes at the beginning.²⁰ Well known, Fe^{2+} ions in water are not stable and will be quickly oxidized by O_2 in air to form ferric hydroxide in the presence of HMT (HMT can hydrolyze slowly to ammonia and formaldehyde during the preparative process).²¹ It is seen that in our reaction system the solution suddenly turned into a yellow floccus without addition of ILs, and the final poor products shown in Fig. 3a and b were obtained. However, the color of the reaction solution began to change slowly from transparent solution to yellow floccus in the presence of ILs. That means the formation of Fe^{2+} /IL complexes may help to retard the oxidation rate that seems to be necessary for preparing the purer RD structured Fe_3O_4 NCs,²² and the ILs as ionic surfactants have altered the surface conditions of the Fe_3O_4 NCs.²³ In addition, HMT/phenol also played a key role in the formation of RD structures, which could be preferentially adsorbed on $\{110\}$ crystal planes (Fig. 3a), confines crystal growth along $\langle 100 \rangle$ directions, therefore resulting in the formation of thermodynamically unstable RD NCs. As a matter of fact, this has been a common approach to the modification of crystal morphology in materials science research.^{22,23}

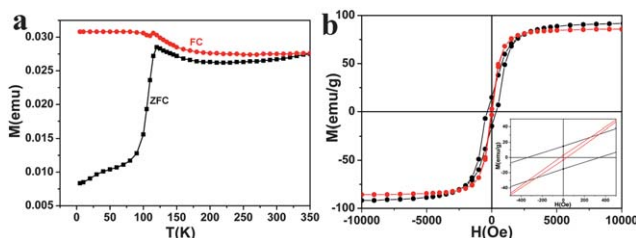


Fig. 5 (a) ZFC-FC curves of the as-prepared RD Fe_3O_4 NCs measured with an applied magnetic field of 100 Oe. (b) The hysteresis loops for the as-prepared RD Fe_3O_4 NCs at 300 (red line) and 5 K (black line). The inset is magnified views of the hysteresis loops at low applied fields.

The magnetic properties of the as-synthesized RD Fe_3O_4 NCs were measured with a Quantum Design superconducting quantum interference device (SQUID). Fig. 5a shows the temperature-dependence of magnetization measured with zero-field cooling (ZFC) and field cooling (FC) procedures in an applied magnetic field of 100 Oe between 5 and 300 K. When the sample is cooled at zero field, the total magnetization of the NCs will be zero, since the magnetization moment of individual NC is randomly oriented. An external magnetic field favors the moments of the individual NC to reorient along the applied field at low temperature. When the temperature increases, the FC curve shows a flat line at a low temperature due to saturation of the magnetic moment until 120 K. The ZFC curve shows a steep increase of the magnetization up to the maximum value at 120 K, which corresponds to the blocking temperature (T_B). It has been reported that the definition of T_B could be given as follows:

$$T_B = (E_a + E_{\text{int}})/K_B \ln(f_0)$$

where K_B is Boltzmann's constant, f_0 is a frequency factor on the order of 10^9 s^{-1} , and E_a is the anisotropy barrier that can be determined by $E_a = KV$, in which K is the anisotropy energy density constant and V is the volume of particles.^{24,25} E_{int} is introduced to indicate the interaction energy.^{26,27} Obviously, the T_B of magnetic nanoparticles is related to their size. Among these parameters, only E_{int} is uncertain even if the size of the magnetic particles keeps unchanged. It seems to be the only variable in this equation, so the weaker interaction between the magnetic particles may directly cause the decrease of E_{int} , and hence lead to the lower T_B .²⁸ As seen the size of the as-prepared Fe_3O_4 NCs is in a range of 30–50 nm, and they show lower T_B compared with that reported in some cases. However the existence of the long-chain ILs on the surface of the nanoparticles might increase steric hinderance between particles so as to reduce the particle couplings of each other, resulting in a smaller blocking temperature. In addition, the ILs are charged species, so they might also severely influence the value of E_{int} .²⁷ The hysteresis loops of the as-prepared RD Fe_3O_4 NCs measured at both 300 and 5 K are shown in Fig. 5b, all of which show a strong magnetic response to a varying magnetic field. The coercive force (H_c) of the as-synthesized RD Fe_3O_4 NCs is 25 and 340 Oe at 300 and 5 K, respectively. The saturation magnetization value is 86 emu g^{-1} at room temperature, which is slightly smaller than that of bulk Fe_3O_4 of 92 emu g^{-1} .²⁹

In summary, we have successfully synthesized RD Fe_3O_4 NCs via a convenient microwave-assisted route with the help of ILs. The reaction can be finished within 15 min at temperatures as low as 90 °C. The shape and structure of the final products could be readily tuned by adjusting the experimental parameters, such as the amount of ILs and HMT-to-phenol molar ratio. The T_B of the RD Fe_3O_4 NCs is found to be at 120 K, and the saturation magnetization is 86 emu g^{-1} at room temperature. This convenient synthetic method is possibly applicable to synthesis of different spinel ferrites that are difficult to prepare by traditional methods. Furthermore, the RD Fe_3O_4 NCs bound with twelve high-energy $\{110\}$ facets probably lead to future prospects toward their potential applications such as conspicuous catalytic activity.

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Notes and references

- 1 G. Schlegel, J. Bohnenberger, I. Potapova and A. Mews, *Phys. Rev. Lett.*, 2002, **88**, 137401.
- 2 L. J. Zhao, H. J. Zhang, Y. Xing, S. Y. Song, S. Y. Yu, W. D. Shi, X. M. Guo, Y. Q. Lei and F. Cao, *Chem. Mater.*, 2008, **20**, 198.
- 3 Y. Sun and Y. N. Xia, *Science*, 2002, **298**, 2176.
- 4 N. A. Frey, S. Peng, K. Cheng and S. H. Sun, *Chem. Soc. Rev.*, 2009, **38**, 2532.
- 5 M. H. Kryder, *MRS Bull.*, 1996, **21**, 17.
- 6 K. Raj, R. Moskowitz and R. Casciari, *J. Magn. Magn. Mater.*, 1995, **149**, 174.
- 7 D. G. Mitchell, *J. Magn. Reson. Imaging*, 1997, **7**, 1.
- 8 S. Guo, D. Li, L. Zhang, J. Li and E. Wang, *Biomaterials*, 2009, **30**, 1881.
- 9 L. Gao, J. Zhuang, L. Nie, J. Zhang, Y. Zhang, N. Gu, T. Wang, J. Feng, D. Yang, S. Perrett and X. Yan, *Nat. Nanotechnol.*, 2007, **2**, 577.
- 10 S. H. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang and G. X. Li, *J. Am. Chem. Soc.*, 2004, **126**, 273.
- 11 D. Kim, N. Lee, M. Park, B. H. Kim, K. An and T. Hyeon, *J. Am. Chem. Soc.*, 2009, **131**, 454.
- 12 L. Zhang, J. Wu, H. Liao, Y. Hou and S. Gao, *Chem. Commun.*, 2009, 4378.
- 13 L. Zhang, R. He and H. C. Gu, *Mater. Res. Bull.*, 2006, **41**, 260.
- 14 (a) T. Hyeon, S. S. Lee, J. Park, Y. Chung and H. B. Na, *J. Am. Chem. Soc.*, 2001, **123**, 12798; (b) E. Tronc, P. Belleville, J. P. Jolivet and J. Livage, *Langmuir*, 1992, **8**, 313.
- 15 I. Bilecka, I. Djerdj and M. Niederberger, *Chem. Commun.*, 2008, 886.
- 16 (a) M. Zhen, J. H. Yu and S. Dai, *Adv. Mater.*, 2010, **22**, 261; (b) R. E. Morris, *Angew. Chem., Int. Ed.*, 2008, **47**, 442; (c) V. I. Pârvulescu and C. Hardacre, *Chem. Rev.*, 2007, **107**, 2615.
- 17 (a) H. S. Park, Y.-C. Lee, B. G. Choi, Y. S. Choi, J.-W. Yang and W. H. Hong, *Chem. Commun.*, 2009, 4058; (b) Z. H. Li, P. Rabu, P. Strauch, A. Manton and A. Taubert, *Chem.-Eur. J.*, 2008, **14**, 8409.
- 18 X. Y. Li, Z. J. Si, Y. Q. Lei, J. K. Tang, S. Wang, S. Q. Su, S. Y. Song, L. J. Zhao and H. J. Zhang, *CrystEngComm*, 2010, **12**, 2060.
- 19 J. W. Mullin, *Crystallization*, Butterworths, London, 1971.
- 20 Y. J. Zhu, W. W. Wang, R. J. Qi and X. L. Hu, *Angew. Chem., Int. Ed.*, 2004, **43**, 1410.
- 21 S. R. Guo, J. Y. Gong, P. Jiang, M. Wu, Y. Lu and S. H. Yu, *Adv. Funct. Mater.*, 2008, **18**, 872.
- 22 X. D. Liang, L. Gao, S. W. Yang and J. Sun, *Adv. Mater.*, 2009, **21**, 2068.
- 23 J. H. Yang and T. Sasaki, *Cryst. Growth Des.*, 2010, **10**, 1233.
- 24 M. El-Hilo, K. O'Grady and R. Chantrell, *J. Magn. Magn. Mater.*, 1992, **114**, 295.
- 25 D. A. Dimitrov and G. M. Wysin, *Phys. Rev. B: Condens. Matter*, 1996, **54**, 9237.
- 26 J. L. Dormann, D. Fiorani and M. El Yamani, *Phys. Lett. A*, 1987, **120**, 95.
- 27 J. L. Dormann, L. Spinu, E. Tronc, J. P. Jolivet, F. Lucari, F. D'Orazio and D. Fiorani, *J. Magn. Magn. Mater.*, 1998, **183**, 255.
- 28 J. B. Dai, J.-Q. Wang, C. Sangregorio, J. Y. Fang, E. Carpenter and J. K. Tang, *J. Appl. Phys.*, 2000, **87**, 7397.
- 29 R. M. Cornell and U. Schwertmann, in *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses*, VCH, Weinheim and New York, 1996, ch. 6, p. 117.