

Synthesis of monodisperse iron oxide nanocrystals by thermal decomposition of iron carboxylate salts†

William W. Yu, Joshua C. Falkner, Cafer T. Yavuz and Vicki L. Colvin*

Department of Chemistry, Rice University, 6100 Main Street, Houston TX 77005, USA.

E-mail: colvin@rice.edu

Received (in Cambridge, UK) 24th June 2004, Accepted 3rd August 2004

First published as an Advance Article on the web 2nd September 2004

Iron oxide (Fe₃O₄, magnetite) nanocrystals of 6 to 30 nm with narrow size distributions ($\sigma = 5\text{--}10\%$) were prepared by the pyrolysis of iron carboxylate salts.

Magnetic nanocrystals, including magnetite (Fe₃O₄) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), have been intensively studied because of their unique and tunable magnetic properties.¹ Their magnetic features have found widespread use in applications as diverse as environmental remediation, magnetic recording and magnetic resonance imaging.^{2–7} For all applications, synthetic techniques which provide precise control over nanocrystal grain size are crucial in that they permit engineering of the magnetic properties (*e.g.* superparamagnetic *versus* paramagnetic). Additionally, in many cases large quantities of highly monodisperse materials are ultimately required in order to enable large scale testing and development. Our interest here is in the development of particles for magnetic separations. In this instance, the production of nanocrystals with large and permanent magnetic dipole moments requires particles with diameters from 10 to 25 nm.⁸

There has been much interest in the development of synthetic methods to produce high quality iron oxide systems. The traditional approach to iron oxide colloids has relied on the aqueous precipitation or hydrolysis of Fe²⁺ and/or Fe³⁺ salt(s); these materials can be poorly crystalline and polydisperse in many cases.^{1,9} Recently, high quality iron oxide nanomaterials have been generated using high temperature solution phase methods similar to those used for semiconductor quantum dots. Alivisatos and coworkers¹⁰ demonstrated that near-monodisperse $\gamma\text{-Fe}_2\text{O}_3$ could be obtained by thermal decomposition of an iron cupferron complex in octylamine. Hyeon *et al.*¹¹ reported $\gamma\text{-Fe}_2\text{O}_3$ nanocrystal synthesis using Fe(CO)₅, oleic acid and trimethylamine oxide in octyl ether. Cheon's group¹² recently published a study of $\gamma\text{-Fe}_2\text{O}_3$ nanocrystals with different shapes. Iron acetylacetonate was also used as a starting material to form Fe₃O₄ in a mixed solution of oleic acid, 1,2-hexadecanediol, oleylamine and phenyl ether.^{13,14} Yin and O'Brien¹⁵ reported that narrow dispersed cubic-shaped Wuestite structure FeO nanocrystals were prepared by applying iron acetate as a precursor in oleic acid and trioctylamine. Other approaches to this problem using ultrasound and laser heating have also been reported.^{16,17}

Though the iron sources in those reports were quite diverse, we hypothesized that at the high temperatures where pyrolysis occurred iron carboxylate salts were the actual precursors. In this sense, these strategies could be seen as direct analogs of cadmium chalcogenide quantum dot preparations. For these reactions, a variety of cadmium sources are initially treated to form cadmium carboxylate precursors before pyrolysis to produce nanocrystals.^{18–20} We thus pursued the use of simple and easy to find iron sources, and relied on oleic acid at high temperatures to generate the iron carboxylate precursors. If iron dissolution from the source material is optimized, we find that this method makes a stable precursor; its pyrolysis produces magnetite nanocrystals in high yields without the use of passivating solvents. This paper

outlines this strategy for making monodisperse magnetite nanocrystals with continuously tunable sizes from 6 to 30 nm in octadecene.

Similar to the cadmium chalcogenide preparations, this synthetic system relies on only an iron carboxylate salt (iron(III) oleate), and a solvent (1-octadecene or docosane).^{18–20} The generation of iron carboxylate salts is straightforward though we note that there may be both mononuclear and polynuclear iron carboxylate salts.^{21–23} In one approach, we made this precursor through dissolution of iron oxides in oleic acid. Many commercially available iron-containing oxides were tested as iron sources for this approach. Dissolution of the starting material was often challenging, and subsequent pyrolysis reactions failed because of the lack of available and soluble iron. However, several candidate materials, including FeO(OH) from Aldrich (iron(III) oxide, hydrated; catalyst grade, 30–50 mesh; cat. # 371254), did successfully dissolve in carboxylic acids such as oleic acid to form iron carboxylate salts. FeO(OH) from Aldrich was ground to 100–150 mesh before its introduction into the reaction flask. Other iron sources, including Fe(OH)₃ made by the reaction of FeCl₃ with NaOH gave similar results to the above described FeO(OH). Currently we are evaluating this reaction using carboxylate salt generated from the neutralization reaction of FeCl₃ and carboxylic acids in alcohols.^{22,24}

Magnetite nanocrystals were synthesized in a three-neck flask equipped with condenser, magnetic stirrer, thermocouple and heating mantle. Typically, a mixture of 0.178 g FeO(OH) fine powder (2.00 mmol), 2.26 g oleic acid (8.00 mmol) and 5.00 g 1-octadecene was heated under stirring to 320°C and kept at this temperature for the desired time. During this time the solution turned from turbid black to clear brown as the iron source material dissolved and formed an iron carboxylate salt; FTIR of this intermediate material confirms the presence of carboxylate moieties in the iron containing compound. Ultimately, the pyrolysis of the material resulted in the formation of a clear black solution consisting of iron oxide nanocrystals. The reaction was protected under argon in order to avoid any undesired side-reactions (*e.g.* oxidation of oleic acid). However, the presence of air had little effect on the resulting nanocrystals' size or quality.

The magnetite nanocrystals were easily purified using standard methods developed for quantum dots.¹⁸ Magnetite materials were completely recovered during the purification process, and no size selective precipitation was applied to these samples.

The TEM micrographs (Fig. 1) of these nanocrystals demonstrate the high quality of the as-synthesized nanocrystals. The

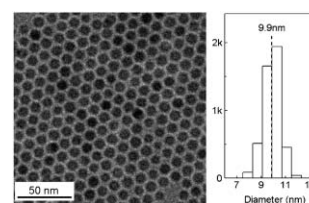


Fig. 1 TEM micrograph (left) and histogram (right) of the as-prepared magnetite nanocrystals. The y-axis of the histogram represents the number of particles (1k = 1000).

† Electronic supplementary information (ESI) available: FTIR of oleic acid and iron oleate complex and TEM photographs of magnetite nanocrystals. See <http://www.rsc.org/suppdata/cc/b4/b409601k/>

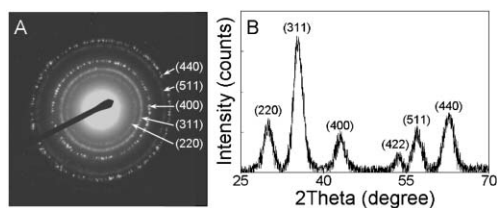


Fig. 2 Electron diffraction pattern (A) and X-ray diffraction pattern (B) of 12.5 nm magnetite nanocrystals.

magnetite nanocrystals appear as spherical dots with very narrow size distributions, typically 5–10%. The spontaneously formed ordered assembly pattern is an additional confirmation of the monodispersity of the nanocrystals.

Fig. 2A shows an electron diffraction pattern of magnetite nanocrystals and five distinct diffraction rings are apparent; their calculated d -spacings match well to the major d -spacings of magnetite (Fe_3O_4).^{1,25} X-Ray diffraction patterns (Fig. 2B) of these samples further confirm the magnetite crystal structure of the as-prepared nanocrystals.^{1,25} The crystal domain size of this particular sample is 11.7 nm calculated from line broadening by the Scherrer equation, which is in good agreement with the average diameter measured from TEM (12.5 nm).

The nanocrystal average diameter increased with the reaction time. For example, 6.4, 7.7 and 9.0 nm diameter magnetite nanocrystals could be obtained when the reaction time was 35, 45 and 60 minutes, respectively (Fig. 3A). However, the nanocrystal diameter remained unchanged for a long period of time (60–120 min, Fig. 3A) though the size distribution broadened slightly, possibly due to Ostwald ripening.²⁶ It was found in the synthesis of CdS semiconductor nanocrystals that the higher the ligand concentration, the lower the monomer reactivity; therefore, there would be less nuclei formed resulting in larger nanocrystals because of the increased availability of precursor in the solution phase.¹⁸ A similar phenomenon was also observed here in the synthesis of magnetite nanocrystals. Fig. 3B shows the ligand (oleic acid) concentration effect in the nanocrystal nucleation and growth of magnetite nanocrystals (the diameter data shown here are the equilibrium sizes as shown in Fig. 3A after 60 min). Magnetite nanocrystals with average diameters of 7, 20 and 28 nm were obtained when the molar ratios of oleic acid to $\text{FeO}(\text{OH})$ were 3.2, 6.0 and 8.0, respectively. We did not find any nanocrystals after 3 hours when the molar ratio of oleic acid to $\text{FeO}(\text{OH})$ was greater than 10, and we believe this is because the excess acid inhibited the formation of iron oxide nuclei.

Magnetite nanocrystals with larger sizes, 20–30 nm, could also be formed when the reaction temperature was increased to 340 °C (using docosane instead of 1-octadecene as solvent); however, at these temperatures particle size distributions ($\sigma = 10$ –15%) were not as good as those at lower temperatures. At higher temperatures, nucleation and growth may not be easily separated and size focusing methodologies may be required to achieve quality equivalent to the lower temperature reactions.²⁶

The general yield of iron oxide nanocrystals by this method could be as high as 95%. Gram scale iron oxide nanocrystals were obtained by simply scaling up the material quantities. The magnetite nanocrystal solution (in chloroform or hexane) was very stable; there was no obvious aggregation or precipitation over two months. We hypothesize that the particles are capped with oleate species, analogous to the quantum dot materials. After being stored in air for two months, the solid-state magnetite nanocrystals were still easily dispersed in chloroform or hexane to form homogeneous solutions. The magnetic properties of the 7 nm diameter magnetite nanocrystals were measured at room temperature. As expected, the material was superparamagnetic and further study of these properties is under way.

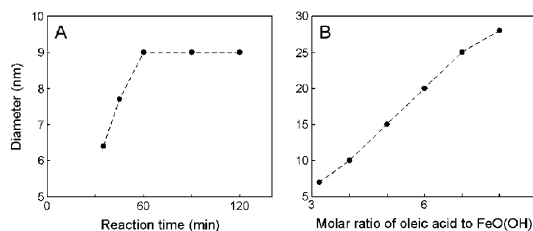


Fig. 3 Size evolution of magnetite nanocrystals with reaction time (A) and molar ratio of oleic acid to $\text{FeO}(\text{OH})$ (B).

In summary, this paper presents a simple, reliable and environmentally friendly method to produce magnetic iron oxide nanocrystals. This method may be extended to other metal oxide nanocrystals, although preliminary results with titania, for example, did not result in materials with such monodispersity.

This work was supported by the National Science Foundation through the Center for Biological and Environmental Nanotechnology at Rice University [EEC-0118007], and the Robert A. Welch Foundation [C-1349].

Notes and references

- R. M. Cornell and U. Schwertmann, *The Iron Oxides*, VCH Publishers, Weinheim, 2nd edn., 2003.
- D. S. Tang, S. S. Xie, Z. W. Pan, L. F. Sun, Z. Q. Liu, X. P. Zou, Y. B. Li, L. J. Ci, W. Liu, B. S. Zou and W. Y. Zhou, *Chem. Phys. Lett.*, 2002, **356**, 563.
- M. C. K. Wiltshire, J. B. Pendry, I. R. Young, D. J. Larkman, D. J. Gilderdale and J. V. Hajnal, *Science*, 2001, **291**, 849.
- P. Trivedi and L. Axe, *Environ. Sci. Technol.*, 2000, **34**, 2215.
- S. Bucak, D. A. Jones, P. E. Laibinis and T. A. Hatton, *Biotechnol. Prog.*, 2003, **19**, 477.
- A. Moser, K. Takano, D. T. Margulies, M. Albrecht, Y. Sonobe, Y. Ikeda, S. Sun and E. E. Fullerton, *J. Phys. D: Appl. Phys.*, 2002, **35**, R157.
- P. Tartaj, M. D. P. Morales, S. Veintemillas-Verdaguer, T. Gonzalez-Carreño and C. J. Serna, *J. Phys. D: Appl. Phys.*, 2003, **36**, R182.
- M. Kryszewski and J. K. Jeszka, *Synth. Met.*, 1998, **94**, 99.
- R. F. Ziolo, E. P. Ginnelis, B. A. Weinstein, M. P. O'Horo, B. N. Ganguly, V. Mehrotra, M. W. Russell and D. R. Huffman, *Science*, 1992, **257**, 219.
- J. Rockenberger, E. C. Scher and A. P. Alivisatos, *J. Am. Chem. Soc.*, 1999, **121**, 11595.
- T. Hyeon, S. S. Lee, J. Park, Y. Chung and H. B. Na, *J. Am. Chem. Soc.*, 2001, **123**, 12798.
- J. Cheon, N.-J. Kang, S.-M. Lee, J.-H. Lee, J.-H. Yoon and S. J. Oh, *J. Am. Chem. Soc.*, 2004, **126**, 1950.
- S. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang and G. Li, *J. Am. Chem. Soc.*, 2004, **126**, 273.
- S. Sun and H. Zeng, *J. Am. Chem. Soc.*, 2002, **124**, 8204.
- M. Yin and S. O'Brien, *J. Am. Chem. Soc.*, 2003, **125**, 10180.
- R. V. Kumar, Y. Kolytyn, X. N. Xu, Y. Yeshurun, A. Gedanken and I. Felner, *J. Appl. Phys.*, 2001, **89**, 6324.
- M. P. Morales, S. Veintemillas-Verdaguer and C. J. Serna, *J. Mater. Res.*, 1999, **14**, 3066.
- W. W. Yu and X. Peng, *Angew. Chem., Int. Ed.*, 2002, **41**, 2368.
- W. W. Yu, L. Qu, W. Guo and X. Peng, *Chem. Mater.*, 2003, **15**, 2854.
- W. W. Yu, Y. A. Wang and X. Peng, *Chem. Mater.*, 2003, **15**, 4300.
- T. Nakamoto, M. Katada and H. Sano, *Inorg. Chim. Acta*, 1999, **291**, 127.
- K. Miki and T. Furuya, *Chem. Commun.*, 1998, 97.
- Y. Konishi, T. Kawamura and S. Asai, *Ind. Eng. Chem. Res.*, 1996, **35**, 320.
- A. B. Bourlinos, A. Simopoulos and D. Petridis, *Chem. Mater.*, 2002, **14**, 899.
- W. F. McClune, *Powder Diffraction File Alphabetical Index Inorganic Phase*, JCPDS, Swarthmore, 1980.
- X. Peng, J. Wickham and A. P. Alivisatos, *J. Am. Chem. Soc.*, 1998, **120**, 5343.