doi:10.1246/cl.2012.686

Published on the web June 23, 2012

Surfactant-free Synthesis and Formation Mechanism of Fe_3O_4 Nanospheres in Mixed Solvent Ethylene Glycol–Water System

Yanyan Xu,* Yanyan Cao, Yaqiu Sun, Guoying Zhang, and Dongzhao Gao
Tianjin Key Laboratory of Structure and Performance for Functional Molecules, School of Chemistry, Tianjin Normal University, Tianjin 300387, P. R. China

(Received February 4, 2012; CL-120091; E-mail: hxxyxyy@mail.tjnu.edu.cn)

Uniform Fe_3O_4 nanospheres have been synthesized by a simple ethylene glycol–H_2O system without adding any additives. The average diameter of the Fe_3O_4 nanospheres was 120–190 nm, and the nanospheres are formed by nanoparticles of several tens of nanometers. The presence of a certain amount of deionized water and the controlled reaction temperature plays an important role in the formation of the Fe_3O_4 nanospheres. The formation mechanism of the nanospheres is discussed on the basis of the experimental results.

Magnetite (Fe_3O_4) nanoparticles have attracted considerable attentions due to excellent magnetic properties, low cost, good biocompatible properties, and potential applications in many fields including high-density information storage, gas sensors, drug-targeting, and magnetic resonance imaging (MRI).[1,2] As is well known, size, morphology, and microstructure of nanomaterials affect their chemical and physical properties significantly and, hence, determine their applications. Therefore, a range of techniques have been developed for the controlled synthesis of magnetic nanomaterials. Among these methods, hydrothermal/solvothermal method is of particular interest owing to its advantage in generating highly crystalline products with high purity, narrow size distribution, and low aggregation.[3] Various well-defined Fe_3O_4 nanostructures including nanoparticles, nanospheres, nanocubes, octahedra, nanorods, nanowires, and nanosheets have been obtained.[4–12] Among these nanostructures, uniform nanospheres and nanoparticles exhibit abundant size- and shape-dependent physical and chemical properties. Thus, the controlled synthesis of uniform Fe_3O_4 nanospheres/nanoparticles has attracted considerable attention. Especially, ethylene glycol (EG) process has been widely used in preparation of Fe_3O_4 nanospheres/particles. Different polymers or surfactants, such as poly(vinylpyrrolidone) (PVP),[13] poly(acrylic acid) (PAA),[5] poly(ethylene glycol) (PEG),[14] dodecylamine (DDA),[15,16] oleic acid,[17] and L-serine,[18] have been usually used as additives. Although these additives improve the morphology, size, or dispersibility of the products, they are usually difficult to eliminate, which may affect their properties. On the other hand, the polymer and surfactant are usually expensive and difficult to decompose, which will increase the cost and bring environmental problems. Therefore, the exploration of simple, surfactant-free, low-cost, and environmentally benign methods for the preparation of uniform Fe_3O_4 nanospheres/nanoparticles with high purity is necessary. Until now, only a few results have been reported. For example, different morphological single-crystal magnetites (Fe_3O_4) have been synthesized by a polyol process under the assistance of KOH at 200 °C for 24 h.[7] Zhou's group has prepared monodisperse magnetite Fe_3O_4 crystals in a EG/NaOH system at 200 °C.[19] In addition, in these reports the reaction temperature was usually 200 °C or above, and the reaction time was usually longer that 10 h,[2,5,7,8,14–19] which is relatively of high energy-cost and time-cost. In this report, we present a very simple solvothermal approach for the synthesis of Fe_3O_4 nanoparticles in an EG–H_2O–urea system at 180 °C for 6 h without using any additive. This relatively low temperature, short reaction time, and additive-free synthetic method can be considered a low-cost and green synthesis route.

All the reagents are of analytical grade and are used as received. Fe_3O_4 nanospheres were prepared by a solvothermal process using $FeCl_3 \cdot 6H_2O$ and urea as reagents and the mixture of ethylene glycol and distilled water as solvent. In a typical synthesis, 0.140 g of $FeCl_3 \cdot 6H_2O$ and 0.150 g of urea were dissolved into a mixture of 13.5 mL of EG and 1.0 mL of distilled water to form a bright yellow solution. Then, the solution was sealed into a Teflon-lined autoclave, heated at 180 °C for 6 h. The product was collected by centrifugation, washed with distilled water and ethanol several times, and dried at ambient temperature. The phase composition and purity of the samples were characterized by X-ray diffraction (XRD) on a Bruker D8 ADVANCE diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm). Thermogravimetric and differential thermal analyses (TG/DTA) were carried out on a Rigaku PTC-10A differential thermal analyzer at a heating rate of 10 °C min^{-1} from 20 to 700 °C under air atmosphere. The morphology and microstructure of the products were characterized by transmission electron microscopy (TEM, JEM100-CXII), high-resolution transmission electron microscopy (HR-TEM, GEOL-2010), and field-emission scanning electron microscopy (FE-SEM, NOVA Nano SEM 230). Hysteresis loops were collected on a Quantum Design PPMS-9 instrument at 300 K.

The XRD pattern of typical Fe_3O_4 nanoparticles is shown in Figure 1a, and all the diffraction peaks can be indexed to a face-centered cubic phase Fe_3O_4 (JCPDS No. 65-3107) without the presence of any impurities. The phase structure was further confirmed by TG and DTA results showing a weight gain of 2.8% in the temperature range of 170–500 °C (Figure 1b). The weight gain was lower than the theoretical value of Fe_3O_4 due to the decomposition of the surface hydroxy and adsorbed solvent molecules. The morphology and size of the product were examined by TEM and SEM techniques. From the SEM image in Figure 1c and TEM image in Figure 1d, it can be seen that the products are uniform nanospheres of 120–190 nm in diameters with good dispersibility. A representative higher magnification TEM image of several nanospheres (Figure 1e) shows that the nanospheres are composed of nanoparticles of several tens of nanometers. Figure 1f is a representative HRTEM image of a single nanoparticle. The 0.25- and 0.29-nm spacing between two adjacent lattice planes corresponds to the interplanar distance of

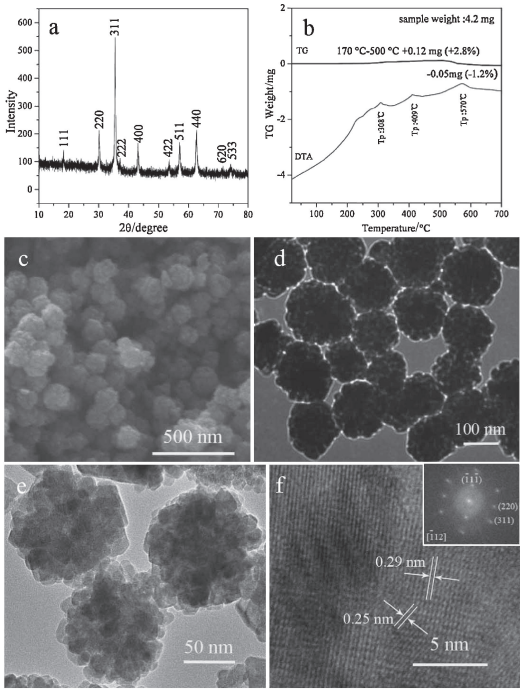

Figure 1. XRD pattern (a), TG/DTA curve (b), SEM image (c), TEM images (d, e), and HR-TEM image (f) of the typical Fe_3O_4 nanospheres prepared at 180 °C for 6 h.

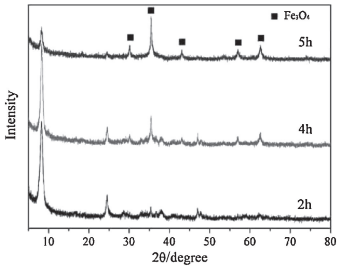

Figure 2. XRD patterns of the products obtained at 180 °C with different reaction time.

the (311) and (220) lattice planes of Fe_3O_4, respectively, which is consistent with the XRD result. The corresponding fast Fourier transform (FFT) pattern (Figure 1f inset) shows a typical diffraction pattern of the cubic structure.

To investigate the formation mechanism of the products, detailed time course experiments of 2, 3, 4, and 5 h were conducted, while other reaction conditions were kept the same as the typical experiment. Figure 2 shows the XRD patterns of the time series samples. It can be seen that $Fe_2O_3 \cdot H_2O$ (Green Rust II, JCPDS No. 13-0092) was formed after hydrothermal treatment for 2 h and then was gradually converted to cubic Fe_3O_4 as the time was prolonged. At 6 h, pure Fe_3O_4 phase was formed (Figure 1a). The corresponding SEM image shows that the samples obtained at 2 h are nanoplatelets with sizes of ca. 100–200 nm (Figure 3a). A few nanospheres of 60–100 nm in diameter were observed as denoted by the white arrows in addition to the nanosheets in the 3 h products (Figure 3b). Then, the amount of nanospheres increased and the nanosheets

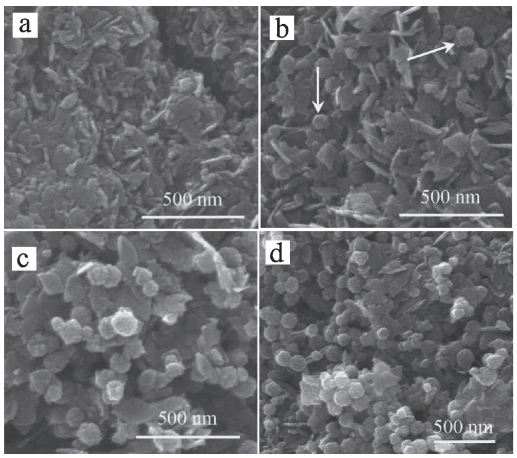

Figure 3. SEM images of the products obtained at 180 °C with different reaction time: (a) 2, (b) 3, (c) 4, and (d) 5 h.

decreased as the reaction time was prolonged to 4 h (Figure 3c). After a reaction time of 5 h, the products were mainly nanospheres and only few nanoplatelets can be observed (Figure 3d). Meanwhile, further experiments showed that when pure ethylene glycol was used as solvent, the products were microflowers composed of nanosheets, and their XRD pattern is similar to those of Mn–EG, Co–EG, and Fe–EG reported previously.[20] This result indicated that the addition of water was necessary for the formation of the Fe_3O_4 phase. In the formation of Fe_3O_4 nanospheres, EG act as both a solvent and reductant, and urea is introduced as a homogeneous precipitator which will decompose and hydrate to form hydroxide groups at elevated temperature.[21] The presence of water can promote the decomposition of urea and accordingly increase the hydrolysis of Fe(III) cations and the following reduction process. Thus, Fe_3O_4 nanospheres were formed when the reaction systems were heated at a relatively low temperature of 180 °C for only 6 h. From these experimental results and analysis, the possible formation process of the Fe_3O_4 nanospheres can be described as follows: First, Fe^{3+} cations hydrolyzed at high temperature under the assistance of urea and water, crystallized in the form of $Fe_2O_3 \cdot H_2O$ nanoplatelets. Then, the $Fe_2O_3 \cdot H_2O$ nanosheets were partially reduced and recrystallized to form Fe_3O_4 nanoparticles. The nanoparticles were unstable because of high surface energy, and thus they tend to aggregate rapidly to form spherical nanospheres.

Further experiments showed that the reaction temperature has important effects on the phase structure and morphology of the final products. When reacted at 140 °C for 6 h, the products were $Fe_2O_3 \cdot H_2O$ nanoplatelets of ca. 100–200 nm in size (Figures 4a and 4b). When the temperature was raised to 160 °C, a mixture of nanoplatelets and nanospheres can be obtained (Figure 4c). However, the phase structures were still $Fe_2O_3 \cdot H_2O$ (Figure 4a). When the reaction time was prolonged to 12 h at 160 °C, the final products were still the mixture of nanoplatelets and nanospheres, indicating that at lower reaction temperature $Fe_2O_3 \cdot H_2O$ could not be converted to Fe_3O_4 completely. When the temperature was further raised to 220 °C, single-crystal nanoparticles of Fe_3O_4 of ca. 35–70 nm in diameter were obtained (Figures 4a and 4d). Thus, 180 °C was an adequate temperature for the formation of the Fe_3O_4 phase and the nanospheres.

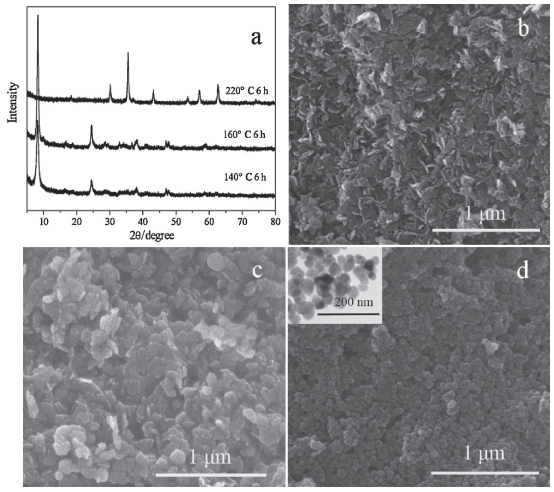

Figure 4. XRD patterns (a) and SEM/TEM images of the products prepared at different temperature for 6 h: (b) 140, (c) 160, and (d) 220 °C.

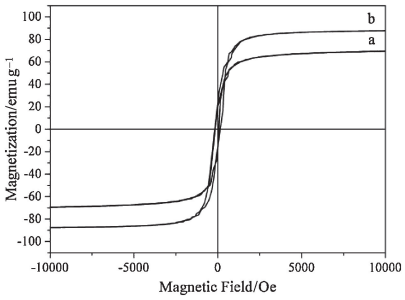

Figure 5. The magnetization curves measured at 300 K of the products obtained at 180 (a) and 220 °C (b).

Figure 5 shows the magnetization curve of the nanospheres obtained at 180 °C and the nanoparticles obtained at 220 °C. The hysteresis loops show ferromagnetic behavior for both the products with high saturation magnetization (M_s) of about 69.4 and 87.3 emu g^{-1} for the nanospheres and nanoparticles, respectively. As previously reported, Fe_3O_4 nanoparticles exhibit superparamagnetic behavior when the particle size decreases to around 20 nm,[22] and their M_s values are usually low due to the small size effect.[23] Therefore, the lower M_s values of the nanospheres than the nanoparticles can be attributed to both the small primary particle size of several tens nanometers and the attachment structure among primary particles within the spherical aggregates.

In summary, we have successfully synthesized uniform Fe_3O_4 nanospheres in the EG–H_2O system at a relatively low temperature without the addition of any additives. Experimental results showed that the control of the reaction temperature and the presence of a certain amount of water were necessary in the formation of Fe_3O_4 nanospheres. The formation of the Fe_3O_4 nanospheres experienced hydrolysis, reduction, recrystallization, and aggregation processes successively. The developed method represents an economical and facile green process for the synthesis of Fe_3O_4 nanospheres.

This work was supported by the National Natural Science Foundation of China (Nos. 21001081, and 21043004), the Education Commission of Tianjin (No. 20110510), and the Excellent Introduced Talents of Tianjin Normal University (No. 5RL071).

References

1 R. Hao, R. Xing, Z. Xu, Y. Hou, S. Gao, S. Sun, *Adv. Mater.* **2010**, *22*, 2729.
2 S. Xuan, Y.-X. J. Wang, J. C. Yu, K. C.-F. Leung, *Chem. Mater.* **2009**, *21*, 5079.
3 S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L. V. Elst, R. N. Muller, *Chem. Rev.* **2008**, *108*, 2064.
4 W. W. Yu, J. C. Falkner, C. T. Yavuz, V. L. Colvin, *Chem. Commun.* **2004**, 2306.
5 J. Ge, Y. Hu, M. Biasini, W. P. Beyermann, Y. Yin, *Angew. Chem., Int. Ed.* **2007**, *46*, 4342.
6 M. V. Kovalenko, M. I. Bodnarchuk, R. T. Lechner, G. Hesser, F. Schäffler, W. Heiss, *J. Am. Chem. Soc.* **2007**, *129*, 6352.
7 L. Zhao, H. Zhang, Y. Xing, S. Song, S. Yu, W. Shi, X. Guo, J. Yang, Y. Lei, F. Cao, *Chem. Mater.* **2008**, *20*, 198.
8 L. Zhao, L. Duan, *Eur. J. Inorg. Chem.* **2010**, 5635.
9 T. Zhu, J. S. Chen, X. W. Lou, *J. Phys. Chem. C* **2011**, *115*, 9814.
10 J. R. Morber, Y. Ding, M. S. Haluska, Y. Li, J. P. Liu, Z. L. Wang, R. L. Snyder, *J. Phys. Chem. B* **2006**, *110*, 21672.
11 K. C. Chin, G. L. Chong, C. K. Poh, L. H. Van, C. H. Sow, J. Lin, A. T. S. Wee, *J. Phys. Chem. C* **2007**, *111*, 9136.
12 L. Chen, C. Zhao, Y. Zhou, H. Peng, Y. Zheng, *J. Alloys Compd.* **2010**, *504*, L46.
13 Y. Zhu, W. Zhao, H. Chen, J. Shi, *J. Phys. Chem. C* **2007**, *111*, 5281.
14 H. Deng, X. Li, Q. Peng, X. Wang, J. Chen, Y. Li, *Angew. Chem., Int. Ed.* **2005**, *44*, 2782.
15 D. Yu, X. Sun, J. Zou, Z. Wang, F. Wang, K. Tang, *J. Phys. Chem. B* **2006**, *110*, 21667.
16 S.-W. Cao, Y.-J. Zhu, J. Chang, *New J. Chem.* **2008**, *32*, 1526.
17 G. Xi, C. Wang, X. Wang, *Eur. J. Inorg. Chem.* **2008**, 425.
18 H. Cao, R. Liang, D. Qian, J. Shao, M. Qu, *J. Phys. Chem. C* **2011**, *115*, 24688.
19 R. Liu, Y. Zhao, R. Huang, Y. Zhao, H. Zhou, *Eur. J. Inorg. Chem.* **2010**, 4499.
20 L.-S. Zhong, J.-S. Hu, H.-P. Liang, A.-M. Cao, W.-G. Song, L.-J. Wan, *Adv. Mater.* **2006**, *18*, 2426.
21 C. Cheng, Y. Wen, X. Xu, H. Gu, *J. Mater. Chem.* **2009**, *19*, 8782.
22 Y. P. He, S. Q. Wang, C. R. Li, Y. M. Miao, Z. Y. Wu, B. S. Zou, *J. Phys. D: Appl. Phys.* **2005**, *38*, 1342.
23 X. Jia, D. Chen, X. Jiao, S. Zhai, *Chem. Commun.* **2009**, 968.

