

Solvothermal Synthesis of Tunable Electroactive Magnetite Nanorods by Controlling the Side Reaction

Haiyan Sun, Bo Chen, Xiuling Jiao, Zhen Jiang, Zhenhua Qin, and Dairong Chen**

*Key Laboratory for Special Functional Aggregate Materials of Education Ministry, School of Chemistry & Chemical
Engineering, Shandong University, Jinan 250100 P. R. China*

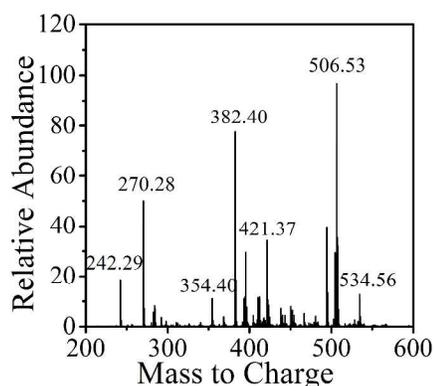
Supporting Information

Table S1. Elemental analyses result of as-prepared Fe₃O₄ nanorods.

Element	C	H
Content (wt%)	11.684	1.843

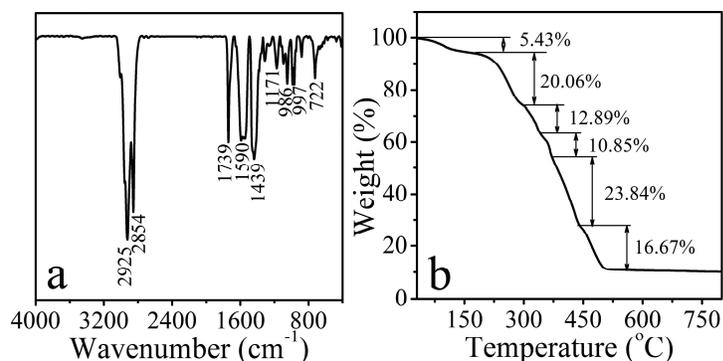
According to the elemental analyses, the molar ratio (C/H) is calculated to 0.528, which is closed to that in oleic acid (0.529).

Figure S1. Mass spectrum of the supernate of typical experiment.



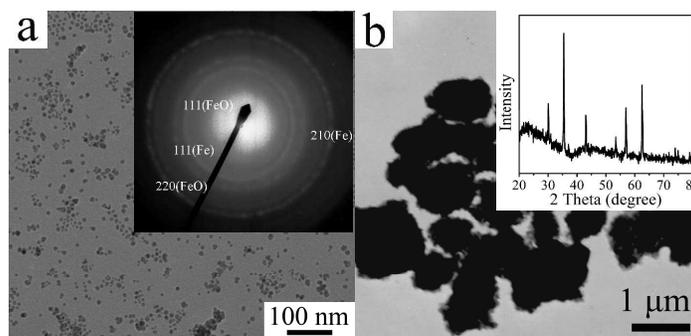
There are several signals in the mass spectrum, indicating a series reactions have been occurred in the system. It is difficult to index all the signals, but the signal at 506.53 can be ascribed to [C₁₇H₃₃CONH⁺C₁₆H₃₃], demonstrating oleic acid condensed with hexadecylamine, and at the same time water was produced.

Figure S2. IR spectrum (a) and TG curve (b) of the product obtained in the presence of oleic acid (41.43 mmol) and Fe(CO)₅ (13.81 mmol) without hexadecylamine. Reaction temperature and time are 200 °C and 6 h.



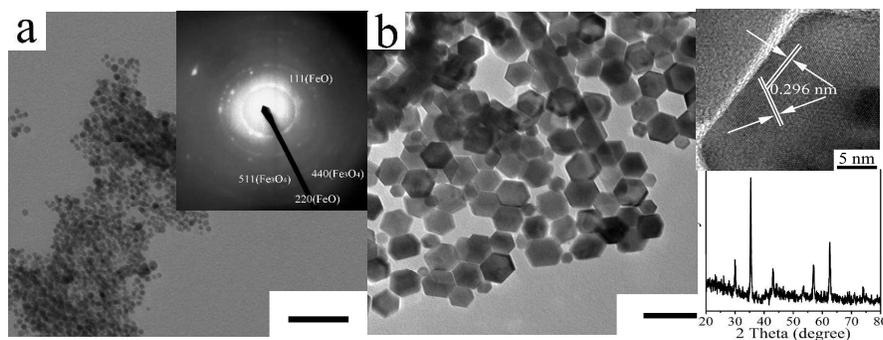
The adsorptions at 1739, 1590, 1439 and 1171 cm⁻¹ are the characteristic IR vibrations of metal carboxylate and the frequency difference (151 cm⁻¹) between 1590 cm⁻¹ and 1439 cm⁻¹ indicates the bridging coordination mode, which is consistent with iron oleate reported in the literature.^{1,2} The TG analysis is performed under N₂ atmosphere with heating rate of 5.0 °C/min. From the TG curve, the weight loss is similar to that reported in the literature.² The rest of the decomposition product is ca.10.52 wt% and it is higher than the theoretical value (ca.8.89 wt%), which is due to the carbonization of the organics in nitrogen atmosphere at a high temperature. This result reveals that Fe(CO)₅ and oleic acid can solvothermally reacted to form iron oleate in the system.

Figure S3. TEM images of the samples obtained without adding hexadecylamine and oleic acid. (a) 60 min, (b) 6 h. The insets in (a) and (b) are the corresponding ED and XRD pattern.



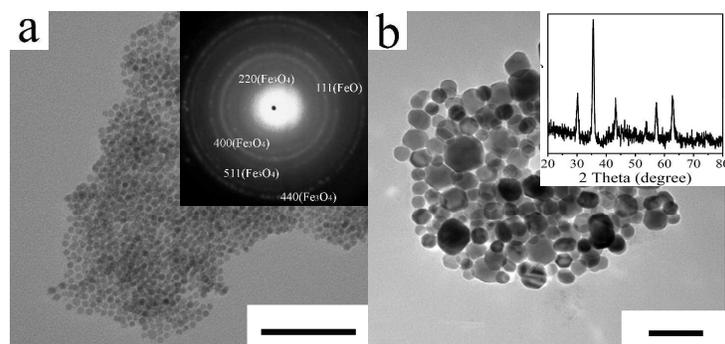
Without oleic acid and hexadecylamine, the 60 min product is the mixture of Fe and FeO from the ED pattern and the size of the nanoparticle is ca. 6 nm as shown in Figure S3a. When reaction time is 6 h, the agglomerated Fe₃O₄ nanoparticles are formed.

Figure S4. TEM images of samples prepared by in absence of hexadecylamine with other conditions constant. (a) 100 min, (b) 6 h. The inset in (a) is the corresponding ED pattern. The right two figures are the corresponding HR-TEM image and XRD pattern of sample 2. The scale bars are 100 nm.



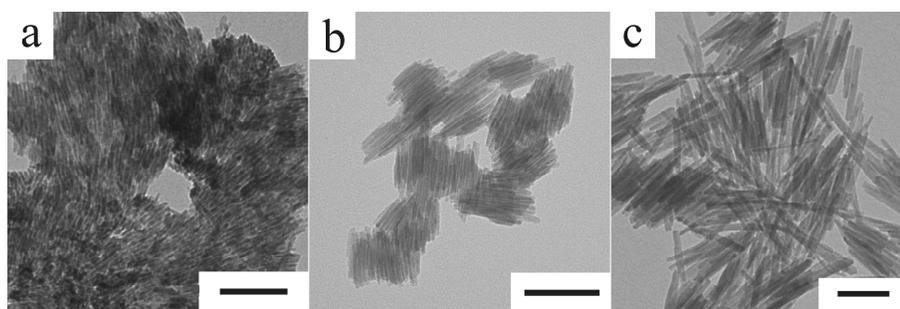
There is no product when reaction time is shorter than 100 min, indicating oleic acid makes the reaction slow. If the reaction is prolonged to 100 min, the product is so little that can only be characterized by TEM. As shown in Figure S4a, the product for 100 min is the mixture of FeO and Fe₃O₄ with size of ca. 8 nm. When reacting for 6 h, the XRD pattern indicates the product is Fe₃O₄. Hexagonal nanoplate is the main product with side length of ca. 30 nm (Figure S4b). From the HR-TEM image, the lattice space (ca. 0.296 nm) matches with {220} facets, demonstrating that the hexagonal plate is surrounded by six {220} facets and two {111} facets.

Figure S5. TEM images of the products obtained in absence of oleic acid with other conditions constant. (a) 60 min, (b) 6 h. The insets in (a) and (b) are the corresponding ED and XRD patterns. The scale bars are 100 nm.



If hexadecylamine was only added to the reaction system, nanoparticles with uniform size of ca. 7 nm are the mixture of FeO and Fe₃O₄ from the ED pattern shown in the inset of Figure S5a. As the reaction pronged to 6 h, the nanoparticles become bigger nonuniform phase-pure Fe₃O₄ from the XRD pattern and TEM in Figure S5b.

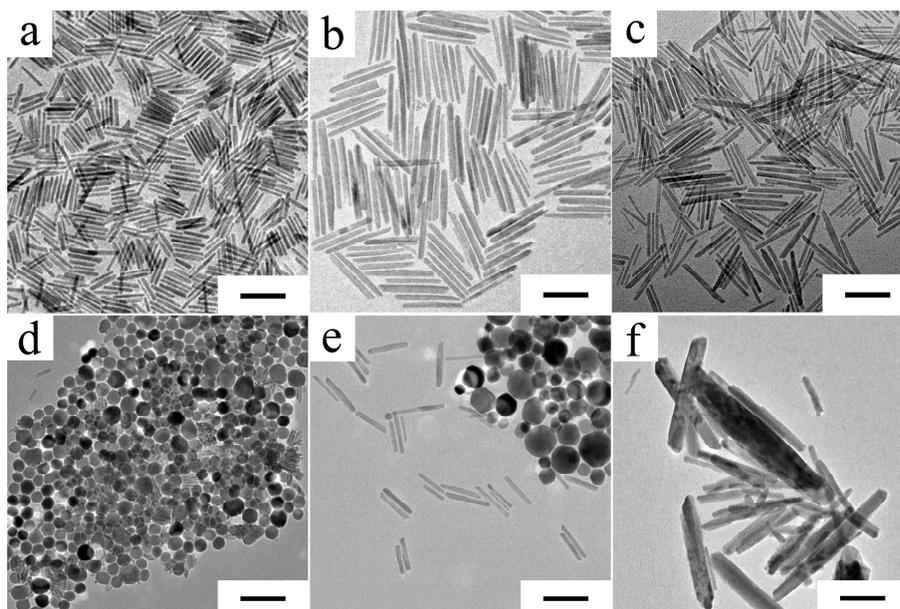
Figure S6. TEM images of the products prepared by replacing hexadecylamine with (a) 15 μ L, (b) 45 μ L or (c) 100 μ L water. The scale bars are 100 nm



The theoretical amount of water according to the condensation between 0.2 g of hexadecylamine and 2 mL of oleic acid is 15 μ L. Therefore, 15, 45, 100 μ L of water were respectively added to the reaction system in the absence of hexadecylamine. From the TEM images shown in Figure S6, with the increase of water from 15 to 45 and 100 μ L, the nanorods gradually lengthen from 28 to 65 and 130 nm.

However, the nanorods tend to agglomerate, which might be due the abundant hydroxyl on the surface of the nanorods. This result indicates that the magnetite nanorods can be formed in presence of water and oleic acid.

Figure S7. TEM images of Fe_3O_4 prepared by adding different amounts of hexadecylamine/oleic acid. (a) 0.2 g/2.0 mL, (b) 0.6 g/2.0 mL, (c) 0.8 g/2.0 mL, (d) 0.2 g/0.6 mL, (e) 0.2 g/1.2 mL and (f) 0.2 g/2.5 mL. The scale bars in (a)-(e) are 100 nm.



Changing the amount of hexadecylamine could tune the size of the nanorods with 2 mL of oleic acid. When 0.2 g hexadecylamine was added, nanorod was the main product with the length of ca. 63 nm and diameter of 6.5 nm (Figure S7a). Increasing hexadecylamine to 0.6 g, the length and diameter of the nanorods turned to 140 nm and 12 nm (Figure S7b). Further increasing it to 0.8 g, the length and the diameter of the nanorods became nonuniform (Figure S7c). The longer nanorods were ca. 145 nm and the shorter ones were only 55 nm. This observation might be reasoned that at higher hexadecylamine concentration, water releasing rate was raised, which results in the fast growth of the nanorods.

When the amount of hexadecylamine was constant (0.2 g), increasing the amount of the oleic acid could tune the morphology of the final product. While 0.6 mL oleic acid was added to the reaction system, nanorods less than 35 nm in length appeared although most were nanoparticles (Figure S7d),

and this can be reasoned that iron oleate was not enough to supply the growth of the nanorods. With oleic acid increasing to 1.2 mL, nonuniform nanoparticles and nanorods with length of 80 nm were obtained (Figure S7e). If oleic acid was continuously increasing to 2.5 mL, the length and diameter of the rods became nonuniform (Figure S7f). Based on above experimental results, it could be concluded that appropriate amount of iron oleate is necessary for the formation of the nanorods.

References

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- (2) Palchoudhury, S.; An, W.; Xu, Y.; Qin, Y.; Zhang, Z.; Chopra, N.; Holler, R. A.; Turner, C. H.; Bao, Y. *Nano Lett.* 2011, *11*, 1141-1146.