

Room Temperature Solvent-Free Synthesis of Monodisperse Magnetite Nanocrystals

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We have successfully demonstrated a facile, solvent-free synthesis of highly crystalline and monodisperse Fe₃O₄ nanocrystallites at ambient temperature avoiding any heating. Solid state reaction of inorganic Fe(II) and Fe(III) salts with NaOH was found to produce highly crystalline Fe₃O₄ nanoparticles. The reaction, if carried out in the presence of surfactant such as oleic acid-oleylamine adduct, generated monodisperse Fe₃O₄ nanocrystals extractable directly from the reaction mixture. The extracted nanoparticles were capable of forming self-assembled, two-dimensional and uniform periodic array. The new process utilizes inexpensive and nontoxic starting materials, and does not require a use of high boiling point and toxic solvents, thus is amenable to an environmentally desirable, large-scale synthesis of nanocrystals.

Keywords: Room Temperature, Solvent-Free Synthesis, Monodispersed, Magnetite Nanocrystals.

1. INTRODUCTION

Magnetic nanoparticles are useful for a variety of scientific and technological applications such as magnetic storage media, ferrofluids, magnetic refrigeration, magnetic resonance imaging, hyperthermic cancer treatment, cell sorting, and targeted drug delivery.^{1–3} Iron oxides constitute one of the most fascinating classes of magnetic materials and have been extensively investigated. Based on chemical reactions in liquid or aerosol/vapor phases,^{4,5} different approaches such as coprecipitation,⁶ sol-gel,⁷ aging,⁸ ultrasound irradiation,⁹ and laser pyrolysis,¹⁰ have been established for preparing superparamagnetic iron oxide nanoparticles typically smaller than 20 nm in order to be adaptable to variable applications. However, the relatively poor size uniformity and crystallinity of the nanoparticles obtained strongly affect their magnetic properties.

Using water-in-oil microemulsions (reverse micelles) as nanoscale reactors,¹¹ it is possible to synthesize iron oxide nanoparticles with a narrowed size distribution. However, this method utilizes a large amount of organic solvent for the oil phase and also a surfactant as the reverse micelle stabilizer. Since the total number of micelles is rather limited, the scaled-up production of uniform nanoparticles remains problematic. Organic solution-phase

decomposition of iron precursors at high temperature has also been developed for iron oxide nanoparticle synthesis. Direct decomposition of iron precursors or decomposition of iron precursors followed by oxidation in organic solvents in the presence of surfactants, such as oleic acid and oleylamine, can produce high-quality monodisperse iron oxide nanocrystals.^{12–14} Surfactants bind to the surface of the synthesized nanoparticles, thus acting as particle stabilizer and tuning the nucleation/growth of particles to achieve a higher degree of uniformity. However, this process usually requires relatively high temperature, high boiling point solvents (such as phenyl ether or dioctyl ether) and expensive organic iron precursors (e.g., Fe(CO)₅), some of which may be also toxic, and a complicated procedure. Applying the same type of surfactant stabilizers to the co-precipitation method using aqueous solutions of low-cost inorganic ferrous and ferric salts has some difficulties since these surfactants are only slightly miscible with aqueous solutions under the synthetic conditions. Although synthesis of monodispersed Fe₃O₄ nanoparticles has recently been achieved through thermal decomposition of metal-oleate precursors formed by the reaction of metal chlorides and sodium oleate,¹⁵ a high boiling point solvent such as 1-octadecene (which is still somewhat toxic) and a high refluxing reaction temperature (as high as 320 °C) are still required.

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In this communication we report, for the first time, a novel, facile, and solvent-free synthetic method, which allows us to use inorganic ferrous and ferric solids directly instead of organic iron compounds dissolved in organic solvents, along with surfactants to produce monodisperse magnetite nanocrystals. The reaction is advantageous as it is induced at room temperature instead of refluxing temperatures of $\sim 265\text{--}350\text{ }^{\circ}\text{C}$ utilized in the organic-solution phase decomposition method. Highly-crystalline and monodispersed Fe_3O_4 nanocrystalline particles are obtained by the new process despite the fact that the reaction occurred at room temperature. Such a solvent-free reaction provides a substantial environmental advantage in terms of avoiding disposal or recycling of toxic chemicals. A solvent-free approach based on solid-state reactions was previously utilized for simple synthesis of unassembled nanoparticles, however, no surfactant was utilized for particle size control.^{16,17} The solvent-free synthesis of magnetite nanocrystals described here can be considered as a hybrid of solid-state reaction, co-precipitation and organic solution-phase decomposition processes, but taking advantage of only the beneficial parts of these procedures. In this approach, several modifications were made: (1) inorganic ferrous, ferric and base solids instead of aqueous or organic solutions were used directly for the synthesis; (2) oleic acid-oleylamine adduct solid instead of oleic acid and oleylamine liquids was used as surfactant stabilizers; (3) after the reaction, the Fe_3O_4 nanoparticles were extracted directly into hexane, and the unreacted materials and the byproducts were separated conveniently since they are insoluble in hexane; (4) monodispersed, uniform Fe_3O_4 nanoparticles were obtained and can be assembled into ordered arrays. In addition, this method requires no complex apparatus and techniques, and enables one to synthesize Fe_3O_4 nanocrystals with almost uniform size in high yields and at a large scale. The process is carried out at room temperature, and the synthesis time is very short, on the order of several minutes. Compared to most of the liquid-phase reactions for producing Fe_3O_4 nanocrystals, no solvent is used during the synthesis, therefore less liquid waste is generated. This solvent-free and environmentally desirable synthetic approach may be extended to the synthesis of a wide variety of monodispersed nanoparticles.

2. EXPERIMENTAL DETAILS

Iron(III) chloride hexahydrate (97%), iron(II) chloride tetrahydrate (99%), sodium hydroxide, oleic acid (90%), and oleylamine (75%) were obtained from Aldrich. Hexane and ethanol was purchased from Fisher Scientific. All chemicals were used as received. Prior to solvent-free synthesis, an oleic acid-oleylamine adduct was prepared by mixing oleic acid and oleylamine according to 1:1 molar ratio and shaking at room temperature for 30 min; the mixture changed from a clear liquid to a yellow-brown slurry, which was then dried at $80\text{ }^{\circ}\text{C}$ in vacuum overnight.

The synthesis of magnetic nanoparticles was carried out at room temperature in a glove box filled with flowing N_2 gas. For the solvent-free reaction, 1.35 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.50 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and 1.5 g of oleic acid-oleylamine adduct were thoroughly ground and mixed for 5 minutes using a mortar and a pestle. Occasionally more than 30 gram quantity synthesis was also carried out. During the grinding process, the mixture became a thick liquid, and the initially yellow color gradually changed to light brown, translucent liquid. Ground NaOH powder 0.89 g was then added to the mixture which was then ground for another 5 min. The color of the mixture then turned from brown to black, and the mixture solidified gradually. The mixture was then taken out of the glove box and transferred into a centrifuge tube. 20 mL of hexane was added into the tube and agitated for 1 min followed by 5 min of centrifuge at 4000 rpm. The magnetic nanoparticles were extracted into the hexane phase and the byproducts, mostly sodium chloride, were precipitated on the bottom of centrifuge tube. 50 ml of ethanol was then added to the isolated hexane extract to precipitate the nanoparticles. After centrifugation, the nanoparticles were separated from the supernatant; the excess surfactant mixed with the nanoparticles was removed by several cycles of washing with ethanol, and the final magnetic particles capped with surfactant were dried at room temperature in a high vacuum. The nanoparticles so fabricated are re-dispersible in hexane. For comparison, the solvent-free synthesis in the absence of surfactant stabilizer was also performed. The product was washed with DI water and filtered, which was repeated several times, and the obtained powder was dried in vacuum at room temperature.

X-ray diffraction (XRD) patterns of the produced nanoparticles were recorded on a Rigaku Rotaflex X-ray diffractometer using $\text{Cu K}\alpha$ radiation. The X-ray tube current was 100 mA with a tube voltage of 40 kV. The 2θ angular regions between 20 and 70° were examined at a scan rate of $0.5^{\circ}/\text{min}$. For all XRD tests, the resolution in the 2θ scans was $\sim 0.02^{\circ}$ and the XRD signals for four runs were summed up for improved signals. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) analyses were carried out on a Jeol JEM 2010 microscope with a routine point-to-point resolution of 0.194 nm. The operating voltage of the microscope was 200 keV. All images were digitally recorded with a slow scan CCD camera (image size 1024×1024 pixels) and image processing was carried out using a Digital Micrograph (Gatan). For analysis of nanoparticle structure, a drop of dilute magnetic nanoparticle solution in hexane was allowed to slowly evaporate on a carbon-coated copper TEM grid at room temperature. The amount of the drop was selected in such a way that a monolayer of self-assembled nanoparticles are obtained. During the evaporation, the particles rearrange themselves in the surfactant producing a well-organized monolayer of

particles.¹⁸ For the nanoparticles synthesized by solvent-free reaction without any surfactant stabilizer, suspension in ethanol was used for TEM analysis.

3. RESULTS AND DISCUSSION

XRD patterns of the nanoparticles synthesized by the solvent-free reactions with and without the addition of oleic acid–oleylamine adduct are compared in Figure 1. Both patterns indicate the crystalline nature of the products, and the positions and relative intensities of all diffraction peaks coincide with those of the JCPDS card (19-0629) for Fe_3O_4 . No characteristic peaks of reactants and byproducts (mostly NaCl) were observed. This implies that when the surfactant was applied, the byproducts were removed essentially completely by the extraction method. It is noticeable that with the addition of surfactant during synthesis, the XRD peaks of the product with an identical weight of the Fe_3O_4 nanoparticles become weaker, indicating that the particle size is smaller, which is confirmed by TEM analysis.

Figure 2a shows a low magnification TEM image of the Fe_3O_4 particles produced by room-temperature, solvent-free processing without the addition of surfactant. Obviously all particles are nanometer in size. However, they tend to agglomerate on the TEM grid after the base liquid (ethanol) was dried. Selected area electron diffraction pattern of the particles is shown as an inset in Figure 2a. The white spots as well as the bright diffraction rings indicate that the nanoparticles produced by the solvent-free reaction are highly crystalline. The high-resolution TEM indicates that most nanoparticles are around 8 nm. The lattice fringes of the image correspond to a group of atomic planes within particles, demonstrating that the nanoparticles are structurally uniform. However, the particles exhibit different shapes including either spherical or nearly cubic geometry. With the addition of surfactant

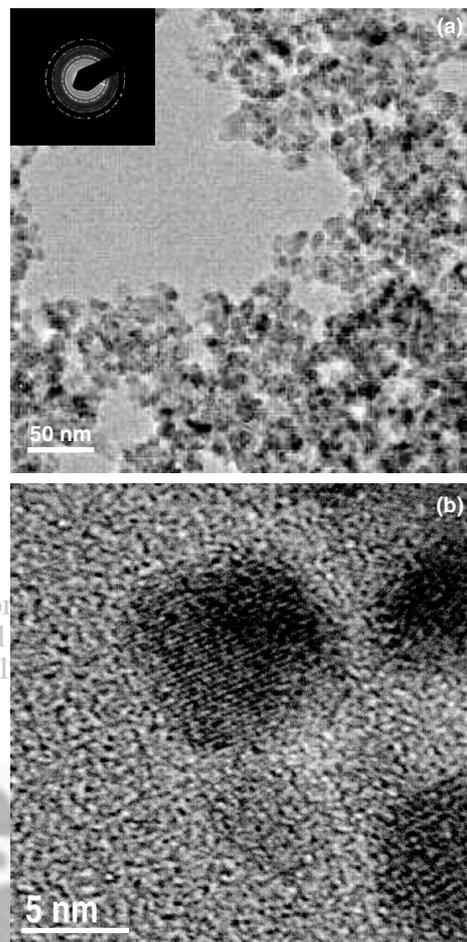


Fig. 2. TEM micrograph for Fe_3O_4 nanoparticles synthesized by solvent-free reaction without the addition of surfactant: (a) Low magnification and (b) high-resolution image showing lattice fringes within the particles.

in the reaction system, the uniformity of the shape for the Fe_3O_4 nanocrystals was significantly improved. The general TEM micrograph of the nanoparticles synthesized by the solvent-free reaction in the presence of surfactant is shown in Figure 3a. The nanoparticles appear almost spherical and monodispersed with an average diameter of 5 nm, and self assemble into a two-dimensional array. A HRTEM image of the patterned nanoparticles is shown in Figure 3b. The lattice spacing seen in the lattice fringe of the particles revealed the satisfactory crystallinity and structural uniformity of the sample.

Solvent-free syntheses of Fe_3O_4 nanocrystals using inorganic ferrous and ferric salts other than $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ has also been performed, and similar results were achieved. For example, a combination of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ salts gave identical results as in the case of iron chlorides. Evidently, this room-temperature and solvent-free synthetic method provides a simple, convenient way for producing surfactant-capped, monodisperse Fe_3O_4 nanocrystals from inexpensive and nontoxic metal salts without using any high boiling point

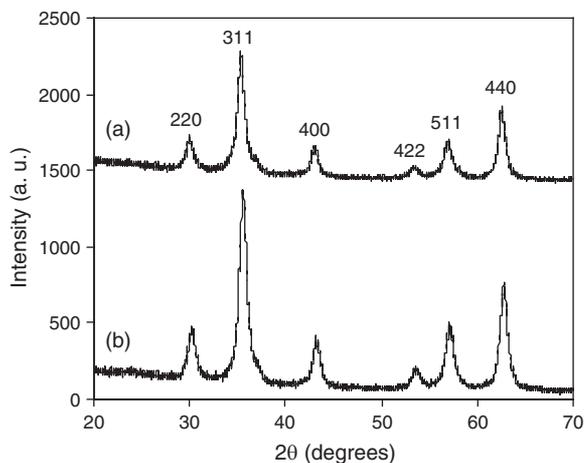


Fig. 1. XRD patterns of the nanoparticles synthesized solvent-free reactions (a) with and (b) without the addition of oleic acid–oleylamine adduct.

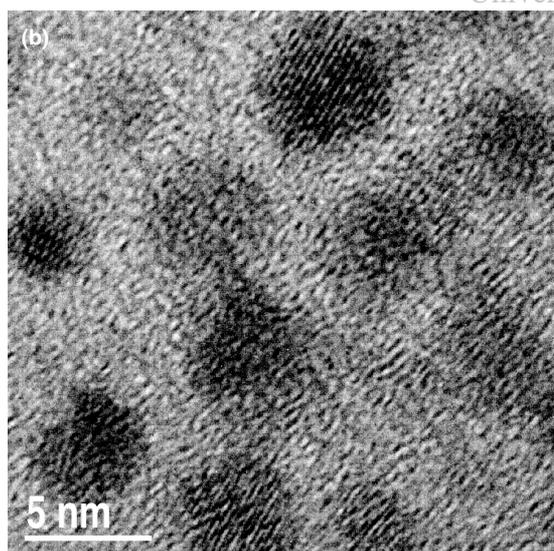
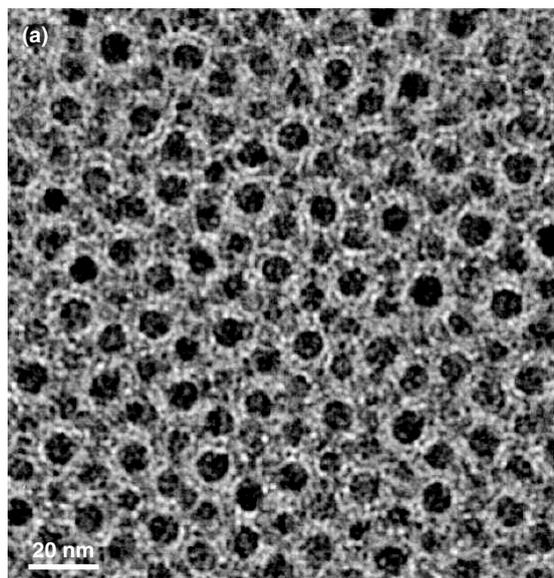
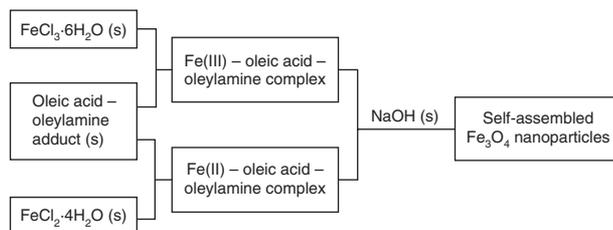


Fig. 3. TEM micrograph for Fe_3O_4 nanoparticles synthesized by solvent-free reaction with the addition of surfactant: (a) Self assembled two-dimensional array and (b) high-resolution microstructure.

solvents. As has been well documented, the fabrication of patterned media arrays of discrete single domain magnetic nanoparticles is important for potential magnetic recording media applications, and the surfactant-coated, self-assembled nanoparticles with superlattice arrangement are known to be suitable for such applications. The new, room temperature and solvent-free process can also be used for synthesis of other magnetic nanoparticles of interest to magnetic recording, for example, high coercivity materials based on cobalt or Fe–Pt.

In the organic solution-phase decomposition process, surfactants like oleic acid and oleylamine, attach to the surface of magnetic nanoparticles *in-situ*, controlling the nucleation and growth of nanoparticles to achieve particle size uniformity and prohibiting nanoparticle

agglomeration. These surfactants stabilize nanoparticles against flocculation by adsorbing onto the particle surfaces and perform the task of assembling nanoparticles into regular arrays through the interaction of their long chain molecules. The performance of oleic acid–oleylamine adduct in the present solvent-free synthesis is similar. Furthermore, it has been demonstrated that surfactants like oleic acid can react with metal chloride to form intermediate surfactant–metal complexes such as metal–oleates, which then undergo thermal decomposition and oxidation in high boiling point solvents to form monodisperse nanocrystals.¹⁵ Alkylamine surfactant can also coordinate with metal ions through $-\text{NH}_2$ group.¹⁹ The reaction of the current solvent-free synthesis in the presence of surfactant is believed to precede a similar intermediate process via the formation of Fe(III)- and Fe(II)-surfactant complexes. However, instead of thermally induced decomposition, the decomposition of metal–surfactant complexes is induced by simple addition of NaOH, which enables the reactions to occur at room temperature instead of a high reflux temperature of 300–350 °C. The co-decomposition of the Fe(III)- and Fe(II)-surfactant complexes causes the formation of Fe_3O_4 nanoparticles capped with oleic acid and oleylamine stabilizer. The hydrocarbon chains of the adsorbed surfactants produced a surface that allowed a quick separation of Fe_3O_4 nanoparticles from byproducts by extraction with hexane or other nonpolar solvent, and the redispersion of these particles in various nonpolar solvents becomes possible. In addition, the formation of thick liquid during the mixing stage of Fe chloride precursors and the oleic acid–oleylamine adduct ensures their uniform mixing before the addition of NaOH, thus providing more uniformity to the synthesis. A detailed study of the growth mechanism of Fe_3O_4 is still in progress, a suggested mechanism is outlined as Scheme 1. In addition, this room temperature, solvent-free synthetic approach can also be modified to prepare water-soluble (biocompatible) Fe_3O_4 nanoparticles. Chelating agents such as dimer-captosccinic acid (DMSA) can be utilized directly as a replacement of oleic acid–oleylamine adduct to form intermediate Fe(III) and Fe(II) chelates. The co-decomposition of Fe(III) and Fe(II) chelates induced by NaOH could then produce Fe_3O_4 nanoparticles tethered by chelating agents with extra multifunctional groups, which make Fe_3O_4 nanoparticles water-soluble and biocompatible.²⁰



Scheme 1. Possible mechanism.

4. CONCLUSIONS

We have successfully demonstrated the synthesis of monodisperse Fe₃O₄ nanocrystals in a novel and easy one-step solvent-free reaction. The reaction can conveniently be carried out at room temperature, avoiding the use of high boiling point and often toxic solvents. With the use of inexpensive and nontoxic inorganic ferrous and ferric salts and an ambient temperature process, the technique is amenable for convenient, large-scale synthesis. With a proper choice of inorganic metal salts and surfactants, this method may be extended to environmentally desirable preparation of a wide variety of monodisperse nanocrystals.

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