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Facile Synthesis, Phase Transfer, and Magnetic Properties of Monodisperse Magnetite Nanocubes

Haitao Yang¹, Daiji Hasegawa², Migaku Takahashi¹, and Tomoyuki Ogawa^{2,3}

¹New Industry Creation Hatchery Center, Tohoku University, Sendai 980-8579, Japan

²Department of Electronic Engineering, Tohoku University Sendai 980-8579, Japan

³Center for Research Strategy and Support, Tohoku University, Sendai 980-8579, Japan

The monodisperse Fe₃O₄ nanocubes with controllable sizes from 6.5 to 30.0 nm have been synthesized in organic phase. By the formation of surfactant bilayers with charged hydrophilic ions of α -cyclodextrin, Fe₃O₄ nanocubes were successfully “pulled” into water from hexane for a possible biomedical application. The Fe₃O₄ nanocubes with the surfactant bilayers show a good stability in aqueous solution compared with those in aqueous solution which were transferred from organic phase by ligand exchange using PVP with strong binding group. The hysteresis loop at 300 K of Fe₃O₄ nanocubes with different sizes reveals that a size-dependent behavior of saturation magnetization and the nanocubes with a size less than 25 nm show a typical superparamagnetic behavior at room temperature. The comparison of magnetization of the hydrophilic Fe₃O₄ nanocubes in CD and PVP aqueous solution reveals that the surfactant bilayers can provide a good stability of magnetization.

Index Terms—Magnetite, nanocubes, phase transfer, synthesis.

I. INTRODUCTION

MAGNETIC nanoparticles have inspired broad interests in various areas for both their size- and shape-dependent properties and for a variety of technological applications [1], [2]. The synthesis of magnetite (Fe₃O₄) nanoparticles has long been of keen interest in magnetic data storage, biological application, ferrofluids, and electronics since Fe₃O₄ are a common magnetic iron oxide and an important class of halfmetallic materials [3]. Most of organic-phase synthesis studies on magnetite nanoparticles have mainly focused on size control such as seed-mediated growth of 4 to 20 nm magnetite nanoparticles from iron acetylacetonate and large-scale synthesis from iron oleate [4], [5]. Also different methods have been explored to transfer such organic-soluble nanoparticles to aqueous phase for biomedical applications [6], [7]. While the size control of magnetic spherical nanoparticles has been achieved, controlling the shape is still a real synthetic challenge. Recently, various wet chemical approaches including hydrothermal synthesis and organic-phase synthesis have widely been used to prepare nonspherical nanoparticles since they provide great benefits in control of size, component, and dispersion [8], [9]. However, there are several reports on the organic-phase synthesis of magnetic nonspherical nanoparticles, especially focused on Co [9], MnFe₂O₄ [10], and FePt [11], even though such monodisperse materials with different shapes such as nanocubes and nanorods are of great importance not only in introducing novel electronic and magnetic properties that are different from those observed in their spherical counterparts but also in serving as building blocks to prepare self-assembled arrays for the application in the electronics, data storage, and biological sensors.

In this paper, we present the facile one-pot synthesis of monodisperse Fe₃O₄ nanocubes with controllable size from 6.0 to 30.0 nm by a modified polyol process in organic phase. Using different hydrophilic molecular, polyvinylpyrrolidone (PVP) and α -cyclodextrin (CD), Fe₃O₄ nanocubes were both successfully “pulled” into water from hexane for possible biomedical application. The magnetizations at 300 K of Fe₃O₄ nanocubes with different sizes, as well as that of 10 nm Fe₃O₄ nanocubes before and after phase transfer, have been investigated.

II. EXPERIMENT

All commercially available reagents were purchased from Aldrich without further purification. In a typical synthesis of 15.0 nm Fe₃O₄ nanocubes, a mixture of 0.5 mmol of Fe(acac)₃, 4 mmol of 1,2-hexadecandiol, 8 mmol of oleic acid (OA), 2 mmol of oleyl amine, and 10 ml of benzyl ether was heated at 110°C for 1 h with Ar flow. The temperature was then raised to 200°C and kept at that temperature for 30 min. Under Ar blanketing, the mixture was heated to a reflux temperature of about 290°C at a heating rate of 15°C/min and kept refluxing for 1 h. The solution mixture was quickly cooled down to room temperature by an ice water, and the nanocubes were precipitated out by adding ethanol. The product was washed with ethanol and redissolved in the mixture of toluene and hexane to form a stable dispersion.

The phase transfer was conducted by sonication and rigorously stirring and the mixtures of hexane suspensions of Fe₃O₄ nanocubes and equal volume of CD (Aldrich) or PVP (Aldrich, wt \approx 10000) aqueous solution under room temperature. The typical concentration of nanocubes in hexanes was \sim 0.5 mg particle/mL. The concentration of CD or PVP aqueous solution was 5 mM. It should be noted that a suitable amount of ethanol were added in the PVP aqueous solution to form a buffer layer. After sonicating for 30 min and then stirring for 20 h, the top hexane layer became colorless and was discarded; while the bottom aqueous layer was collected and centrifuged twice to obtain a black suspension.

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Transmission electron microscopy (TEM, JEOL-3010 at 300 kV) was employed to determine the morphology, size, and size distribution of Fe nanoparticles. Samples were formed by depositing toluene/hexane dispersion of particles on amorphous-carbon-coated copper grids in a convective assembly apparatus [12]. The UV-Vis-IR spectra were measured with a Shimadzu UV3600 spectrophotometer in the wavelength range of 400–3300 nm. The total amount of Fe₃O₄ in particles with surfactants was determined by x-ray fluorescence using a Rigaku instrument. The Fe mass was firstly measured by our reported method [13] and the Fe₃O₄ mass was then calculated via the stoichiometric ratio. Magnetic measurements were conducted using a Quantum Design superconducting quantum interference device (MPMS-5) with fields up to 5 T and temperatures from 5 to 300 K.

III. RESULTS AND DISCUSSION

The shape-controlled synthesis of Fe₃O₄ nanocubes have been achieved by increasing the molar ratio of OA to Fe(acac)₃ since OA with a carboxylic group, -COOH, has a selective binding onto the differing energy crystal facets together with a nonpolar tail group for steric hindering [14]. Such an approach enables the control of the reactivity of the carboxylic group and as a result the nucleation and growth dynamics of the particles. The detail discussion of synthesis parameters and mechanism were published elsewhere [15]. Fig. 1 shows the TEM images of monodisperse Fe₃O₄ nanocubes with different sizes of 6.5 nm and 15.0 nm. With a size less than 15.0 nm, the nanocubes usually have a very narrow size distribution of less than 7% and the aspect ratios close to one. Moreover, the nanocubes with small sizes well disperse in most of organic solvent such as toluene or hexane which enable them as building blocks to form the self-assemble Fe₃O₄ nanocubes superlattice. The corresponding SAED pattern of 15.0 nm Fe₃O₄ nanocubes superlattice is displayed in Fig. 1(e), which clearly indicates the orientation ordering among the nanocubes in the self-assembly superlattice. The electron beam of the SAED pattern is parallel to the [001] direction. However, the size distribution of nanocubes with a size more than 25 nm prepared by a long time reflux (usually more than 2h), increases greatly and the aspect ratios located between 1 and 1.5 together with a poor disperse in hexane or toluene. Typically, the 30 nm nanocubes have a size distribution of about 20%.

Such a nonaqueous method offers control over the particle size and shape that affect the chemical and physical properties of the particle. The long hydrocarbon chains of the surfactants are responsible for the hydrophobicity. These long aliphatic chains also cause the nanocubes to be immiscible in the aqueous solution, and the biological applications of these nanocubes are greatly restricted because of their poor solubility in aqueous solution. It is feasible to increase the aqueous phase dispersity of particles by modification of their surface-bound surfactant layers. One strategy is to use ligand exchange with stabilizing agents with strong binding group to increase the dispersity of particles in water [16]. Alternatively, the surface can also be altered via the formation of surfactant bilayers with charged hydrophilic ions exposed to the liquid phase [17]. To realize their potentials in biological applications, CD and PVP were

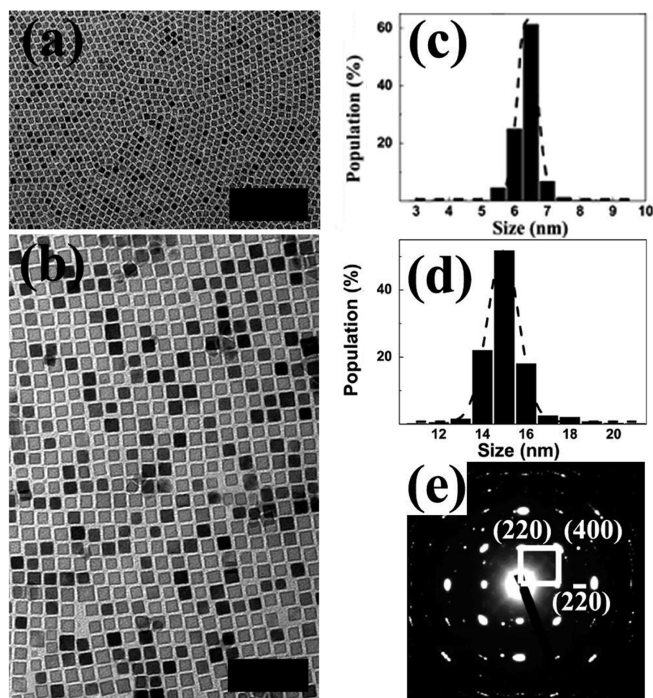


Fig. 1. TEM images of Fe₃O₄ nanocubes with different size (a) 6.5 nm, (b) 15.0 nm and the corresponding size distribution histograms (c) and (d), in which scale bar = 100 nm; (e) SAED pattern of the self-assembly superlattice in (b).

used to transfer the Fe₃O₄ nanocubes from organic phase to aqueous phase since CD and PVP are both biological compatible molecular. CD is composed of hydrophobic cavities that can form complexes with various organic molecules, and the hydrophilic rims of hydroxyl groups. So the complex could form between CD and OA which produces a surfactant bilayer on the nanocubes [18]. However, PVP is a polymeric surfactant including the repeated amide (-N-CO-) group within its polymeric chain and has been known for its protection of transition metal nanoparticles [19]. It could chemically adsorb onto the surfaces of Fe₃O₄ nanocubes and exchange the OA through a stronger bonding ability. During the mixing of Fe₃O₄ nanocubes hexane solution and CD aqueous solution, the black color gradually disappeared from the top hexane phase, while at the same time the aqueous layer became black [as shown in Fig. 2(a), (b)]. Similar phenomenon was observed during the mixing of Fe₃O₄ nanocubes hexane solution and PVP aqueous solution. In a comparison experiment, the same hexane solution of Fe₃O₄ nanocubes was stirred together with only deionized water for 20 h, and no obvious color change was observed in either hexane or aqueous phases, indicating that CD is required for the phase transfer of oleic acid stabilized Fe₃O₄ nanocubes in this process. The Fe₃O₄ nanocubes after transfer to the CD aqueous solution were inspected using TEM. Fig. 2(c) and (d) shows the TEM images of the nanocubes prepared from the hexane suspension before phase transfer and those from CD aqueous suspension after phase transfer, respectively. It should be noted that the TEM images of Fe₃O₄ nanocubes from PVP aqueous suspension after phase transfer is similar to Fig. 2(b). No obvious shape or size change was found between the

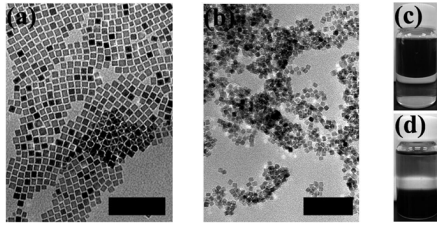


Fig. 2. TEM images and photographs of 10.0 nm Fe_3O_4 nanocubes (a), (c) before and (b), (d) after phase transfer by using CD aqueous phase, in which scale bar = 100 nm.

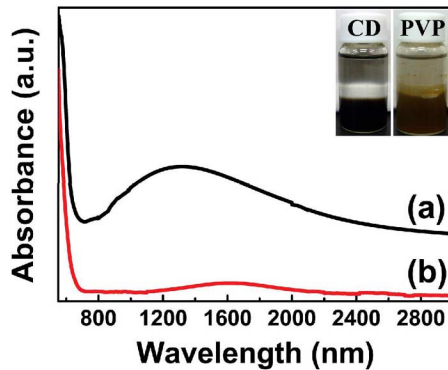


Fig. 3. Optical absorption spectra and photographs of 10.0 nm Fe_3O_4 nanocubes kept in CD aqueous phase and PVP aqueous phase for one month after phase transfer.

samples before and after the phase transfer. This observation suggests that there are negligible effects on the hard surface of iron oxide nanoparticles by using CD or PVP. The particle agglomeration of nanocubes [as shown in Fig. 2(b)] instead of the ordered self-assembly of them from aqueous phase could be due to the modified surfaces and/or the slow evaporation of the solvent.

To compare the stability of Fe_3O_4 nanocubes in aqueous phase with CD-OA and PVP, the as-prepared crude two-phase mixtures were kept for one month. Fig. 3(a) shows the UV-Vis-IR spectrum and the corresponding photograph of Fe_3O_4 nanocubes in aqueous solution after phase transfer with CD and PVP, respectively. After keeping for one month, the aqueous Fe_3O_4 nanocubes solution with PVP became dark yellow while the nanocubes solution with CD was still black. Correspondingly, the aqueous Fe_3O_4 nanocubes solution with PVP shows its optical absorption onset at ~ 650 nm and the aqueous Fe_3O_4 nanocubes solution with CD absorb throughout the UV-Vis-IR spectrum. The strong IR absorption is due to the broad Fe^{2+} - Fe^{3+} charge-transfer absorption band with maximum located at about 1300 nm [20]. Based on these results, the CD-OA surfactant bilayer shows an improved stability of Fe_3O_4 nanocubes in aqueous phase, which are most likely that the long aliphatic chains of OA on the surface of nanocubes prevent water from the surface of the Fe_3O_4 nanocubes. However, the hydrophilic Fe_3O_4 nanocubes only with PVP molecular completely exposed to water and were oxidized because almost all of OA molecular are replaced by PVP ones.

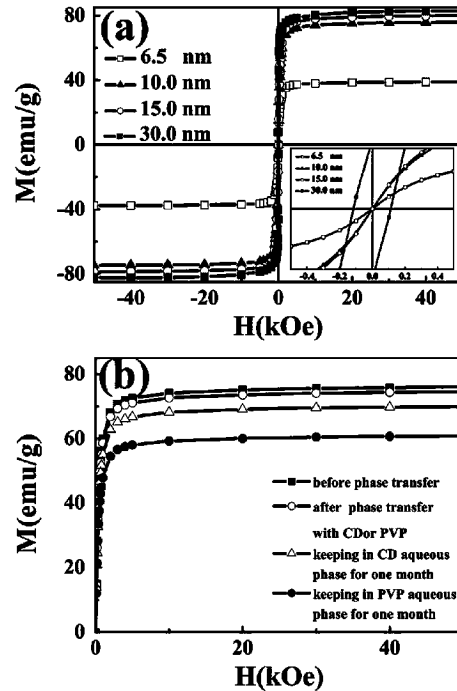


Fig. 4. Hysteresis loops at 300 K (a) for Fe_3O_4 nanocubes with different size of 6.5 nm, 10.0, 15.0, and 30.0 nm and (b) for 10.0 nm nanocubes before phase transfer, after phase transfer, and keeping in CD and PVP aqueous phase for one month, respectively.

Samples for the magnetic measurements were prepared by adding the magnetite nanocubes solution in solution (typically 0.1 vol%) into a quartz tube (ϕ 5 mm \times 15 mm). The tube was then sealed with Araldite and the diamagnetic background from the quartz tube was subtracted. The hysteresis loops of the Fe_3O_4 nanocubes with different sizes at 300 K are shown in Fig. 4(a). The saturation magnetization (M_s) at 300 K of Fe_3O_4 nanocubes with a size of 6.5, 10.0, 15.0, and 30.0 nm were 39.5, 76.0, 80.5, and 83.0 emu/g, respectively. The insert displays partial hysteresis curves for Fe_3O_4 nanocubes with different sizes at an enlarged scale of field strength for clearer viewing. The Fe_3O_4 nanocubes with a size less than 25.0 nm size possess typical superparamagnetic features at room temperature. However, the 30.0 nm Fe_3O_4 nanocubes shows a ferromagnetic behavior with a small coercivity (H_C) of 100 Oe and a high M_s value close to that of the commercial magnetite powder (Aldrich catalog No. 31 006-9). For the nanocubes with small sizes, the loss of magnetization is possibly due to the contribution from small-size effect or spin canting at the outer surfactant layer of the particles. The magnetizations at 300 K of 10.0 nm nanocubes before phase transfer, after phase transfer, and keeping in CD and PVP aqueous phase for one month are presented in Fig. 4(b). After stirring for 12 h in the mixture hexane and CD or PVP aqueous solution, the M_s of 10.0 nm Fe_3O_4 nanocubes transferred in aqueous phase decreases from 76.0 emu/g of the as-synthesized nanocubes to 74.0 emu/g, only a decrement of 2.6%. After keeping in CD aqueous solution, the M_s decreases to 69.5 emu/g. However, after keeping in PVP aqueous solution for one month, the M_s decreases to 60.8 emu/g, namely, a decrement of 20%. Since the

M_s at 300 K of bulk Fe_3O_4 is 89 emu/g and that of bulk Fe_2O_3 is only 78 emu/g, such a dramatic decrease in PVP aqueous solution shows that the Fe_3O_4 nanocubes have been oxidized to Fe_2O_3 nanocubes, which has been confirmed by the UV-Vis-IR spectrum.

IV. CONCLUSION

In summary, we have developed a facile one-pot synthesis method of monodisperse Fe_3O_4 nanocubes in organic phase. By the formation of surfactant bilayers with α -cyclodextrin, Fe_3O_4 nanocubes were successfully transferred into water from hexane for a possible biomedical application. The Fe_3O_4 nanocubes with the surfactant bilayers show a good stability in aqueous solution. It has been confirmed by optic absorption spectra and magnetization measurement. The nanocubes with a size less than 25 nm show a typical superparamagnetic behavior at room temperature. It is of great fundament in magnetic properties and practical interest in biomedical field and nanodevices to prepare the hydrophobic or hydrophilic Fe_3O_4 nanocubes with controlled size and narrow size distribution in future.

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Manuscript received January 01, 2008. Current version published December 17, 2008. Corresponding author: H. Yang (e-mail: htyang@ecei.tohoku.ac.jp).