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Synthesis and Stabilization of Monodisperse Fe Nanoparticles

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Synthesis of iron (Fe) nanoparticles and their dispersion in various liquid media has been one of the most attractive goals in magnetic nanomaterial research. Iron is a class of ferromagnetic material with high magnetic moment density (218 emu/g, or 1713 emu/cc) and is magnetically soft. Iron nanoparticles in the size range below 20 nm are in the superparamagnetic regime, and their stable dispersions with high magnetic moment are predicted to have important applications in bioseparation, biosensing, drug delivery, and MRI contrast enhancement.[1] Procedures leading to monodisperse Fe nanoparticles have been well documented.[2] The common chemical methods used for the preparations include thermal decomposition of iron pentacarbonyl ($Fe(CO)_5$),[3] reductive decomposition of iron(II) bis(trimethylsilyl)amide ($Fe[NSi(CH_3)_3]_2]_2$),[4] and reduction of iron(III) acetylacetonate ($Fe(acac)_3$) or other iron salts.[5] Although the size of the particles is well controlled, the syntheses do reveal that the particles so prepared are extremely reactive and subject to facile oxidation, giving various iron oxide nanoparticles. As a result, the syntheses have difficulty in producing stable Fe nanoparticle dispersions, especially aqueous dispersions, for potential biomedical applications.

Here we report an improved, yet very simple, one-pot reaction that gives monodisperse Fe nanoparticles. The nanoparticles are more efficiently stabilized by the crystalline Fe_3O_4 shell and are readily functionalized and dispersed in phosphate-buffered saline (PBS). In searching for an efficient approach to produce stable Fe nanoparticle dispersion, we found that decomposition of $Fe(CO)_5$ in octadecene (ODE) at 180 °C gave monodisperse Fe nanoparticles. These Fe nanoparticles in hexane dispersion were quickly oxidized and/or agglomerated within 2 h when the dispersion was exposed to air. Structural characterization of the nanoparticles showed that both metallic core and oxide shell in the as-synthesized nanoparticles were amorphous, indicating that the amorphous iron oxide shell could not protect the metallic Fe core from deep oxidation. Our further experiments indicated that the crystalline Fe_3O_4 shell offered more robust protection to the metallic core and the core/shell-structured Fe/Fe_3O_4 nanoparticles were stable in hexane or water dispersion. These results indicate that it is possible to produce small Fe nanoparticles (<10 nm in radius) with desired stability for highly efficient bioseparation and drug delivery and highly sensitive biodetection applications.

The synthesis is based on a recent publication[3g] and is further modified, as outlined in Scheme 1. The reaction uses the decomposition of $Fe(CO)_5$ in ODE solvent in the presence of oleylamine.[6] Figure 1 shows the transmission electron microscopic (TEM) image of the 4-nm/2.5-nm Fe/Fe_3O_4 nanoparticles. Analysis on the TEM images of the nanoparticles indicates that the nanoparticles are monodisperse with very narrow size distribution (<7%). Dynamic light scattering (DLS) shows that the hydrodynamic size of the particles is ∼15.2 nm (Figure S1), matching with the sum of the inorganic core size (6.5 nm in radius) and the organic coating (∼2 nm). The core/shell structure with 4-nm Fe core (in radius) and 2.5-nm shell is shown in the inset of Figure 1A. The Fe_3O_4 layer is formed due to the sample exposure to air. Deposition of the hexane dispersion of the nanoparticles on an amorphous carbon-coated copper grid and slow evaporation of the hexane solvent under N_2 lead to a self-assembled superlattice array with nanoparticles forming hexagonal close packing (Figure 1B).

Scheme 1

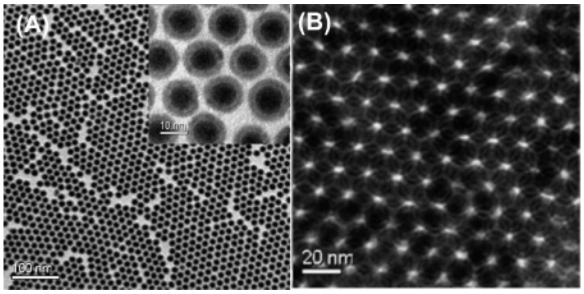

Figure 1. TEM images of (A) 4-nm/2.5-nm Fe/Fe_3O_4 nanoparticles. (Inset) HRTEM image of the Fe/Fe_3O_4 nanoparticles. (B) Self-assembled Fe/Fe_3O_4 nanoparticle superlattice.

X-ray diffraction (XRD) pattern of the as-synthesized Fe/Fe_3O_4 nanoparticles shows no obvious diffraction peaks (Figure S2A), indicating that both iron and iron oxide in the nanoparticles are amorphous. This further reveals that in current reaction conditions, oxidation of the amorphous Fe by air does not yield crystalline Fe_3O_4. The Fe and Fe_3O_4 structures are characterized by detailed XRD studies of the assemblies that have been annealed at 400 °C and 500 °C under Ar (Figure S2C and D). Magnetic measurements were carried out on nanoparticle powders precipitated from the hexane dispersion that had been exposed to air. The nanoparticles are superparamagnetic with saturation moment reaching 66.7 emu/g particles (Figure 2A), corresponding to 102.6 emu/g [Fe] ([Fe] = Fe + Fe_3O_4)).[7] The calculated average moment density based on the relative weight percentage of Fe (7.86 g/cm^3, 218 emu/g) and Fe_3O_4 (5.18 g/cm^3, 80 emu/g) in the core/shell structure for the 4-nm (radius) Fe core and 2.5-nm Fe_3O_4 shell is 123.5 emu/g [Fe]. The reduced value (102.6 emu/g [Fe]) from the as-synthesized nanoparticles is close to the calculated average moment from 3-nm/3.5-nm Fe/Fe_3O_4 nanoparticles (99.4 emu/g [Fe]), revealing further oxidation of the 4-nm/2.5-nm Fe/Fe_3O_4 nanoparticles during the measurement. Figure 2B shows the magnetic moment drop of the nanoparticles in the hexane dispersion that has been exposed to air. It can be seen that the magnetic moment of the particles declines quickly within 4 h but reaches a plateau between 4 and 14 h before

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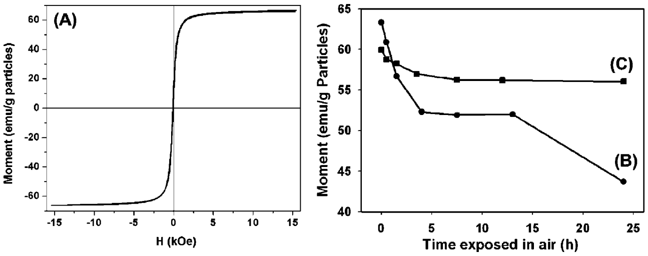

Figure 2. (A) Room-temperature hysteresis loop of the as-synthesized Fe/Fe_3O_4 nanoparticles; and magnetic moment drop of (B) as-synthesized 4-nm/2.5-nm Fe/Fe_3O_4 nanoparticle and (C) the 2.5-nm/5-nm Fe/Fe_3O_4 nanoparticle dispersions versus time exposed to air at room temperature.

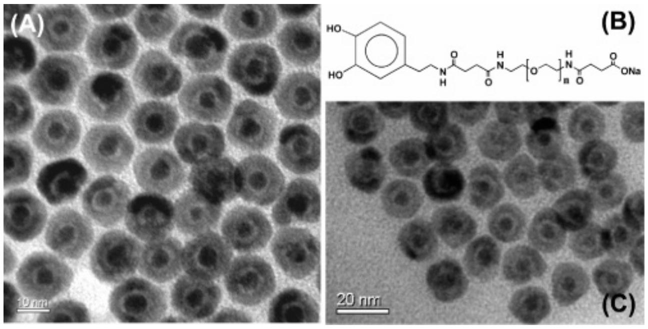

Figure 3. (A) TEM image of the 2.5-nm/5-nm Fe/Fe_3O_4 nanoparticles from hexane dispersion. (B) Dopamine-based molecule. (C) TEM image of the particles coated with new surfactant from the molecule (B). The assembly was obtained by evaporating the PBS dispersion of the particles.

droping to the value close to that for the Fe_3O_4 nanoparticles (43 emu/g particles). The plateau is likely caused by agglomeration—thus the reduction in oxidation rate—of the particles in the dispersion during the experiment. The dispersion was cloudy only after 2 h of its exposure to air, and the particles were precipitated out completely from the dispersion after 8 h of exposure to air. Clearly, the amorphous Fe_3O_4-coated Fe nanoparticles are not stable in the dispersion state.

To make Fe/Fe_3O_4 nanoparticles more stable, a crystalline Fe_3O_4 shell was produced by controlled oxidation of the as-synthesized nanoparticles using an oxygen transferring agent $(CH_3)_3NO$.[6] This controlled oxidation gives core/shell-structured Fe/Fe_3O_4 in which Fe_3O_4 has inverse spinel structure, while Fe is still amorphous and can be converted to bcc-Fe, as shown in the XRD studies of the nanoparticle assemblies (Figure S3, B and D). The thickness of the shell is tuned by controlling the amount of $(CH_3)_3NO$ added into the reaction mixture. For example, the core/shell 2.5-nm/5-nm Fe/Fe_3O_4 nanoparticles (shown in Figure 3A) were prepared by oxidizing 80 mg of the as synthesized Fe nanoparticles with 6 mg of $(CH_3)_3NO$. (Note that there exists a void gap between the core and the shell, which will be addressed in a separate publication.) Magnetic measurements of the 2.5-nm/5-nm Fe/Fe_3O_4 nanoparticles show that they are superparamagnetic with magnetic moment reaching 61.6 emu/g particles (90.6 emu/g [Fe]).[7] Figure 2C shows a magnetic moment drop for the 2.5-nm/5-nm Fe/Fe_3O_4 nanoparticles dispersed in hexane under the ambient conditions. Compared to the as-synthesized 4-nm/2.5-nm Fe/Fe_3O_4 nanoparticle dispersion, the controlled oxidized 2.5-nm/5-nm Fe/Fe_3O_4 nanoparticle dispersion shows a much slower drop in moment density. After its exposure to air for 8 h, the moment is stabilized at 56.2 emu/g particles. This moment is larger than that from the as-synthesized nanoparticles in Figure 2B, indicating that the metallic Fe core exists in the 2.5-nm/5-nm Fe/Fe_3O_4 nanoparticle dispersion even though the dispersion has been exposed to air for over 8 h. The 2.5-nm/5-nm Fe/Fe_3O_4 nanoparticle dispersion is also much more stable than the as-synthesized nanoparticle one: no agglomeration was detected after the dispersion's exposure to air for over 14 h as evidenced by the DLS analyses. These indicate that the crystalline Fe_3O_4 shell does offer the required protection to the metallic Fe core and nanoparticle dispersion.

Replacing the oleylamine from the 2.5-nm/5-nm Fe/Fe_3O_4 nanoparticles with dopamine-based surfactant (Figure 3B), as in the surface modification of Fe_3O_4 nanoparticles,[8] renders the nanoparticles water soluble. Figure 3C is the TEM image of the particles from the PBS (pH = 7.4) dispersion after the ligand exchange.[6] Two TEM images in Figure 3 (A and C) show negligible change in the nanoparticles, indicating that the structure of the core/shell nanoparticles is stable during the ligand-exchange process. Detailed studies in surface chemistry of the Fe/Fe_3O_4 nanoparticles and their link with various biomolecules are underway.

In conclusion, monodisperse Fe nanoparticles are synthesized via a simple one-pot thermal decomposition of $Fe(CO)_5$ in the presence of oleylamine. Controlled oxidation of the iron surface leads to a crystalline Fe_3O_4 shell and results in a dramatic increase in the chemical and dispersion stability of the nanoparticles. Surface ligand exchange is readily applied to transfer the core/shell nanoparticles from hydrophobic to hydrophilic, forming stable aqueous dispersion of the nanoparticles in PBS. Once linked with biomolecules, such nanoparticles should serve as promising magnetic labels for highly efficient bioseparation/drug delivery, and highly sensitive biodetection.

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Supporting Information Available: Experimental procedures and characterization data of the Fe/Fe_3O_4 nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) See Supporting Information.
(7) Thermal annealing of the nanoparticle powder at 800 °C under Ar for 1 h was used to measure the wt % of the inorganic core. The as-synthesized 6.5 nm (radius) nanoparticles have 65%, while the 2.5-nm/5-nm Fe/Fe_3O_4 ones have 68%, of Fe and Fe_3O_4.
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