

Lanthanide(III)-Doped Magnetite Nanoparticles

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Magnetic nanoparticles are a class of nanostructured materials of current interest, due largely to their advanced technological and medical applications, envisioned or realized.¹ Among the various magnetic nanoparticles under investigation, magnetite (Fe₃O₄) nanoparticles are arguably the most extensively studied.^{1a,c,2} Procedures for the controlled synthesis of magnetite nanoparticles of specific size and narrow size distribution have been established.³ Furthermore, with an eye on possibly altering the structure and properties of the parent nanoparticles and creating multifunctional materials, doping of magnetite nanoparticles with other metal ions has been explored.^{3d,4}

Lanthanide ions (Ln) are an interesting class of dopants that possess unique optical and magnetic properties associated with their *f*-electronic configurations.^{4d,5} Coprecipitation of Fe(II/III) and a desired lanthanide ion in an alkaline aqueous solution or a reverse micelle has been utilized for preparing lanthanide-doped magnetite (Ln:Fe₃O₄) nanoparticles.^{4a,b,d,6} However, a number of issues have been identified with this approach, most notably the difficulty in controlling the particle size and achieving a monodisperse size distribution.⁷ In addition, the doped particles so prepared have been found to possess physical and chemical characteristics not significantly different from the parent, undoped magnetite nanoparticles.^{6a,c}

Stimulated by the foregoing preparative issues and aiming at creating novel, property-modified magnetic materials, we have recently initiated the effort to synthesize Ln:Fe₃O₄ nanoparticles by thermally decomposing a mixture containing suitable precursors of iron and a chosen lanthanide ion in the presence of passivating surfactant molecules. The lack of reports of such efforts is rather surprising, as thermal decomposition of inorganic or organometallic precursors has been a time-honored approach to nanoparticle synthesis.^{4c,8} For example, monodisperse magnetite nanoparticles have been obtained by thermally decomposing Fe(CO)₅, Fe(CH₃CO₂)₂, or Fe(acac)₃ (acac = acetylacetonate) in a high-boiling point solvent such as diphenyl or dioctyl ether.^{2a,7,9} This route has been utilized to obtain magnetite nanoparticles doped with various transition metal ions.^{4c,7a} A similar procedure has also been applied to the synthesis of lanthanide oxide nanoparticles using hydrated lanthanide acetates or diketonates as precursors and oleic acid and oleyl amine as surface-protecting ligands.¹⁰

Herein the synthesis of highly monodisperse Ln:Fe₃O₄ nanoparticles by thermally decomposing a mixture of Fe(acac)₃ and hydrated lanthanide acetylacetonates, Ln(acac)₃·2H₂O (Ln = Sm, Eu, Gd), is reported. Interestingly, these nanoparticles display distinct, albeit weak, ferromagnetic behaviors at room temperature. This is in sharp contrast to their undoped parent obtained using an otherwise identical procedure or lanthanide-doped particles prepared by the

aforementioned coprecipitation method; both exhibit superparamagnetism under ambient conditions.^{3b,7b}

The synthesis of Sm:Fe₃O₄ nanoparticles is described below as a representative. Briefly, a mixture of Fe(acac)₃ (0.47 mmol), Sm(acac)₃·2H₂O (0.093 mmol), and 1,2-hexadecanediol (1.12 mmol) in 10 mL of diphenyl ether was heated to 100 °C to afford a clear solution. Oleyl amine (1.0 mmol) and oleic acid (1.0 mmol) were then injected into the reaction flask. The resulting mixture was refluxed at 260 °C for 22 h, producing a black dispersion. Addition of ethanol caused the precipitation of a black solid. Further purification was carried out by redispersing this solid in toluene, followed by ethanol-induced precipitation (Supporting Information). Solutions of the particles in low-polarity solvents such as toluene, hexane, or dichloromethane can be stored at 4 °C for months without noticeable change. Doping of other lanthanide ions was achieved by using desired Ln(acac)₃·2H₂O (Ln = Eu, Gd) under otherwise identical conditions.

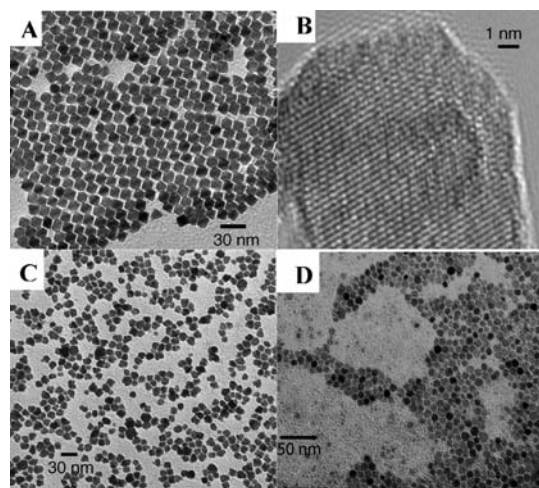


Figure 1. TEM micrographs of nanoparticles of (A) Sm:Fe₃O₄; (B) Sm:Fe₃O₄ (high resolution); (C) Eu:Fe₃O₄; (D) Gd:Fe₃O₄.

Transmission electron micrographs (TEM) of three different Ln:Fe₃O₄ (Ln = Sm, Eu, and Gd) nanoparticles are shown in Figure 1. A narrow distribution of particle size is clearly seen in all three cases. Particularly noteworthy are the almost perfect, diamond-shaped Sm:Fe₃O₄ particles with an average size of 12 nm, for which a high-resolution TEM micrograph is also provided (Figure 1B). The crystallinity of these nanoparticles is manifested by the lattice fringes which correspond to a series of atomic planes present in a single crystalline phase.

X-ray powder diffraction (XRD) patterns of as-prepared doped nanoparticles confirm that the particles maintain the cubic spinel

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structure of Fe_3O_4 (Figure S1).^{3b,6a,11} Thus, no fundamental structural changes occur upon lanthanide doping of the parent magnetite particles. Energy dispersive X-ray (EDX) and X-ray photoelectron spectroscopic (XPS) analyses were used to verify the presence of Fe, O, C, and Ln (Figures S2) and to determine the oxidation states of the metal ions. For example, the peaks at 710 eV ($\text{Fe}2p_{1/2}$) and 724 eV ($\text{Fe}2p_{3/2}$) in the XPS spectrum of the Sm: Fe_3O_4 nanoparticles confirm the presence of Fe(III), while the broadening of the $\text{Fe}2p_{1/2}$ and $\text{Fe}2p_{3/2}$ peaks with shoulders at 708 and 722 eV, respectively, indicates the presence of Fe(II) (Supporting Information).^{1d,3b} The presence of Sm is confirmed by elemental analysis (Supporting Information), and its trivalent oxidation state is established by the peaks at 1081 eV ($\text{Sm}3d_{3/2}$) and 1108 eV ($\text{Sm}3d_{5/2}$).¹²

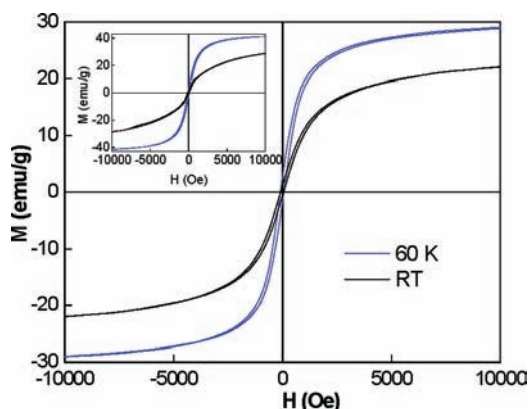


Figure 2. Magnetic hysteresis loops of $\text{Eu:Fe}_3\text{O}_4$ and $\text{Sm:Fe}_3\text{O}_4$ (inset) nanoparticles.

In contrast to the undoped, superparamagnetic magnetite nanoparticles prepared under otherwise identical conditions, these doped particles are unquestionably ferromagnetic at room temperature. This transition in magnetic behavior is ascribed to the introduction of lanthanide ions and possibly due to an increase in magnetic anisotropy of the doped particles. The coercivity (H_c) values are small, however, at 85.7 and 74.3 Oe for $\text{Sm:Fe}_3\text{O}_4$ and $\text{Eu:Fe}_3\text{O}_4$ nanoparticles, respectively. The magnetization (hysteresis) curves are shown in Figure 2. The room-temperature saturation magnetizations (m_s) are 31.3 and 23.6 emu/g for $\text{Sm:Fe}_3\text{O}_4$ and $\text{Eu:Fe}_3\text{O}_4$ nanoparticles, respectively. These values are in the same range as those reported for $\text{Ln:Fe}_3\text{O}_4$ nanoparticles synthesized by the coprecipitation route^{6a} but smaller than those reported for the undoped magnetite nanoparticles.^{2a,4c}

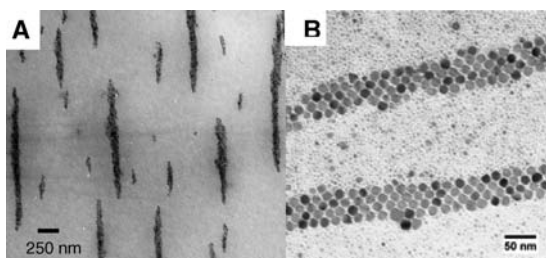


Figure 3. TEM image of self-assembled stripes (A) and a magnified view (B) of $\text{Sm:Fe}_3\text{O}_4$ nanoparticles upon casting a toluene solution of the particles in a 1-T magnetic field.

Casting a toluene solution of $\text{Sm:Fe}_3\text{O}_4$ nanoparticles under a magnetic field resulted in “islands” of stripe-like nanoparticles, as shown in Figure 3A. A magnified TEM micrograph of the ordered structure self-assembled due to interparticle dipolar interactions is shown in Figure 3B.

In summary, nearly monodisperse lanthanide-doped magnetite nanoparticles have been successfully prepared by thermally decomposing a mixture of acetylacetonates of iron and that of a chosen lanthanide. Magnetic studies indicate ferromagnetic behavior of the doped nanoparticles at room temperature.

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Supporting Information Available: Synthetic and characterization details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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