Synthesis and Magnetic Studies of Uniform Iron Nanorods and Nanospheres

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The fabrication and magnetic properties of rod-shaped magnetic iron nanoparticles will be presented in the contribution. Recently, the development of uniform magnetic nanoparticles of ∼10 nm became a very important issue in their application to ultrahigh-density magnetic storage devices.[1] Several synthetic approaches including thermal[2] and sonochemical decomposition of organometallic precursors,[3] high-temperature reduction of metal salts,[4] and reduction inside reverse micelles[5] have been applied to fabricate magnetic metal (Fe and Co) nanoparticles. Many studies on nanoparticles have focused on the synthesis of uniform spherical forms and the control of their particle sizes.[6−8] Recently, the shape control of nanoparticles was recognized as a very important issue in the nanoparticle synthesis, which turned out to be a challenging problem.[9−12] In particular, anisotropic magnetic nanoparticles are expected to exhibit interesting magnetic properties because of shape anisotropy. Only a few anisotropic magnetic nanoparticles have been developed so far;[9,13,14] nonetheless, the particle dimensions are too big to exhibit any nanosize (quantum) effect, and they are often extensively agglomerated. In this report, we would like to present the fabrication of nearly uniform rod-shaped iron nanoparticles produced from the controlled growth of monodisperse spherical nanoparticles. We also compared the magnetic properties of the spherical and the rod-shaped iron nanoparticles.

The spherical iron nanoparticles were prepared by the thermal decomposition of organometallic precursor ($Fe(CO)_5$) in the presence of a stabilizing surfactant, which is the modified procedure of the previously reported method.[6,15] A 0.2 mL portion of $Fe(CO)_5$ was added to 5.0 g of trioctylphosphine oxide (TOPO) at 340 °C under argon atmosphere, and the resulting solution was aged for 30 min at 320 °C. The preparation temperature was set to over 320 °C so that a complete thermal decomposition of $Fe(CO)_5$ could be achieved to generate metallic iron atoms. The reaction mixture was added into excess acetone to produce black precipitate. The precipitate was retrieved by filtration and washed several times with acetone. The synthesized powder form of spherical nanoparticles can be easily re-dispersed in pyridine to yield a clear homogeneous solution. The transmission electron micrograph (TEM) revealed that uniform 2 nm particles were well dispersed in the solution, and for many parts of the image close-packing of the particles were clearly observed (Figure 1a). Electron diffraction pattern showed that these iron nanoparticles are amorphous.

The following procedure was applied to synthesize rod-shaped nanoparticles. At first, spherical 2 nm-sized nanoparticles were prepared by the previously described procedure. To the resulting spherical nanoparticles in TOPO, 5 mL of 2.6 mM $Fe(CO)_5$ in trioctylphosphine (TOP) was added at 320 °C, and the resulting black solution was aged for 30 min at 320 °C. This step was repeated once more, and the resulting reaction mixture was cooled to room temperature to get a black solid. Butanol was added to solubilize the reaction mixture, and the resulting butanol solution was added into excess acetone, resulting in a black precipitate. The precipitate was collected by centrifugation and was washed several times with acetone to remove excess surfactant. The precipitate was dissolved in 19 mL of pyridine containing 0.5 g of didodecyldimethylammonium bromide (DDAB), and the resulting solution was refluxed for 12 h. The precipitate formed during the reflux was removed by centrifugation, and the supernatant was vacuum-dried to yield a black powder. The dry powder was soluble in pyridine, and the solution was kept stable for a week without precipitation under an ambient condition. The TEM image of the sample (Figure 1b) revealed nearly monodisperse rod-shaped particles with dimensions of 2 nm (width) × 11 nm (length) with a standard deviation of 5.7% (length). Electron diffraction pattern of the material (Figure 1c) exhibited a body center cubic (*bcc*) structure of α-Fe. When the DDAB concentration in pyridine was varied, rod-shaped particles with higher aspect ratios were obtained. The width of these nanorods (2 nm) was kept nearly unchanged, only the length was increased to 22 nm (standard deviation of 5.9%) and 27 nm (standard deviation of 5.5%). The transformation of nanospheres to nanorods seems to be caused by the irreversible binding of strongly binding DDAB surfactant on the central region of the growing nanoparticles.[16] After the fusion of two nanospheres, the third nanospheres will be bound on the edge (instead of the central region where DDAB was strongly bound), generating a catenated structure. The continued growth of nanospheres on the edge of the growing nanoparticles would generate unidirectional nanorods.

Magnetic studies were conducted on the spherical 2 nm iron nanoparticles and 2 nm × 11 nm nanorods using a superconducting quantum interference device (SQUID). The temperature dependence of magnetization was measured in an applied magnetic field of 100 Oe between 5 and 300 K using zero-field-cooling (ZFC) and field-cooling (FC) procedures. The results shown in Figure 2 are typical for magnetic nanoparticles.[4,17] The blocking temperature of 2 nm × 11 nm rod-shaped nanoparticles (110 K) was found out to be much higher than that of 2 nm spherical nanoparticles (12 K). These results are consistent with the classical micromagnetic theory that predicts the anisotropy energy to be proportional to the volume of single particle and the anisotropy constant. The magnetic anisotropy constant (K) was deduced from the blocking temperature using the equation $K = 25k_bT_B/V$, where k_b is the Boltzman constant and V is the volume of single nanoparticle.[17] The magnetic anisotropy constant of 2 nm-sized nanospheres was calculated to be 9.1×10^6 ergs/

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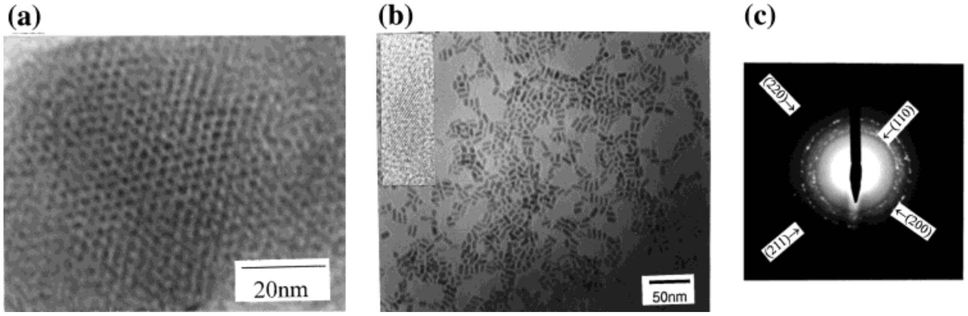

Figure 1. Transmission electron micrographs (TEM) of spherical iron nanoparticles with diameters of 2 nm (a), rod-shaped iron nanoparticles with dimensions of 2 nm × 11 nm, (Inset: High-resolution electron micrograph of a single nanorod) (b), and the electron microdiffraction pattern of these nanorods (c). The images were obtained with a JEOL JEM-2000EX II instrument.

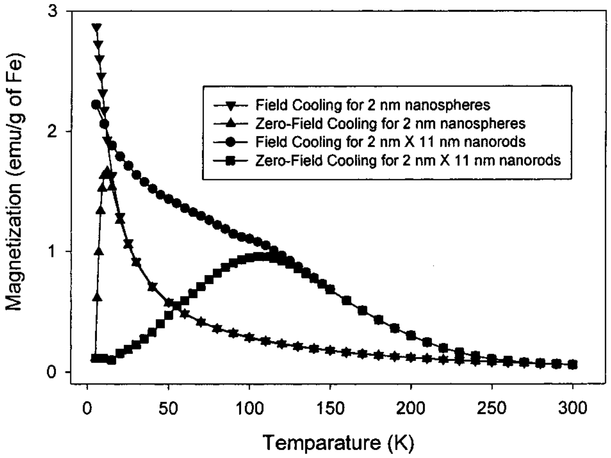

Figure 2. Magnetization normalized by mass versus temperature for the 2 nm spherical iron nanoparticles and the 2 nm × 11 nm iron nanorods at the applied magnetic field of 100 Oe. The magnetic studies were conducted with a Quantum Design MPMS SQUID magnetometer.

cm^3. The magnetic properties of the rod-shaped nanoparticles would be very interesting because they would demonstrate the effect of shape anisotropy. The magnetic anisotropy constant (K) of the rod-shaped particles was calculated to be 1.6×10^7 ergs/cm^3. By treating the rod-shaped particles as prolate spheroids, we could calculate the shape anisotropy constant using the equation $K = (1/2)(N_a - N_c)M^2$, where N_a and N_c are demagnetization factors along the minor and major axes, respectively, of a prolate spheroid and $M = 1714$ emu/cm^3 is the saturation magnetization of bulk iron, and the number came out to be 7.9×10^6 ergs/cm^3.[17] When this shape anisotropy constant is added to the magnetocrystalline anisotropy constant from the spheres, the value agrees well with the experimentally found anisotropy constant of the rod-shaped particles.[18]

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Supporting Information Available: TEM images of 3 nm Fe nanospheres, 2 nm × 22 nm Fe nanorods and 2 nm × 27 nm Fe nanorods (PDF). This material is available free of charge via the Internet at http://pubs.acs/org.

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