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Oxidation Kinetics and Magnetic Properties of Elemental Iron Nanoparticles

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Magnetic nanoparticles (MNPs) are increasingly utilized in various biological, medical and engineering applications.^[1] MNPs, for instance, play a key role as catalysts in chemical reactions,^[2] sensing agents in biomedical diagnosis/imaging,^[3–5] recording media for data storage,^[6] and delivery vehicles for therapeutics.^[7,8] The utility of MNPs is generally commensurate with their magnetic moment. Synthetic efforts have thus focused on preparing particles from highly magnetic materials.^[5,9–11]

While most MNPs are comprised of metal oxide, elemental iron (Fe) has been identified as a superior constituent material for MNPs.^[12,13] Among ferromagnetic crystals, Fe exhibits the highest saturation magnetization and relatively low magnetocrystalline anisotropy at room temperature. It is therefore possible to create large Fe MNPs that possess high magnetic moments but still remain superparamagnetic. Conversely, Fe MNPs are highly reactive and undergo rapid oxidation, which can significantly change the particle magnetization over time. Compared with bulk material,^[14–16] however, characterizing the magnetic properties and oxidation mechanism of Fe MNPs remains challenging. Although there have been intensive investigation on Fe-MNPs,^[17–21] most of these studies employed particles with wide size distribution. The measured physical properties were effectively volume-weighted averages, which tend to be biased by large particles.

We herein report on the systematic characterization of elemental Fe MNPs. Using highly monodisperse particles with different diameter, we could precisely determine 1) the size-

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Supporting

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dependent effect on magnetic properties (e.g., magnetization, coercivity), 2) the critical diameter for superparamagnetism in Fe-MNPs, and 3) the oxidation kinetics of Fe-cores. Under ambient conditions, Fe MNPs were found to be passivated with a native oxide to form a core-shell structure. Magnetic measurements showed that Fe-cores assume magnetization values close to those of bulk iron, whereas the coercivity of the overall particles was highly dependent on the Fe-core size. The magnetic moments of the particles gradually reduced over time due to progressive oxidation of the Fe cores. The oxidation kinetics of Fe-MNPs was independent of the initial particle size and followed a universal, logarithmic time-dependence. These observations evidenced electron tunneling as the dominant oxidation mechanism of Fe MNPs at ambient condition. Importantly, the oxide growth in Fe MNPs should be considered as a volumetric process, due to their large surface-to-volume ratio. This explained the observed faster thickening of the oxide layer than would be expected in bulk material. The oxide formation thus had significant impact on the magnetic properties of Fe MNPs, necessitating additional protection mechanisms for robust magnetic applications.

Fe MNPs were synthesized by thermally decomposing metal complexes $[\text{Fe}(\text{CO})_5]$ in the presence of surfactant (oleylamine; OY), following the procedures previously reported.^[10,13] We maintained a fixed molar ratio ($[\text{Fe}]:[\text{OY}] = 15:1$) of the metal source (Fe) and the surfactant (OY) for all particle synthesis, which was found to yield monodisperse particles with uniform OY coating. The particle size was fine-tuned by controlling the reaction temperature; higher decomposition temperature led to larger particles, presumably owing to the higher mobility and reactivity of decomposed iron atoms. Prepared Fe MNPs were highly monodisperse, with relative size variations of $< 5\%$ (Figure 1a and Figure S1a). When exposed to air, the particle surface was rapidly oxidized to form a natural oxide shell with an average thickness of 2.2 nm. Particles with a starting diameter of < 5 nm were found to be completely oxidized in < 2 hrs and formed hollow spheres. The phenomena could be attributed to the nanoscale Kirkendall effect. The outward diffusion of iron cations is faster than the inward diffusion of oxygen anions, and iron atoms are oxidized on the outer surface of the particle.^[21] The resulting vacancies left by migrating Fe atoms will coalesce to form a void in the particle center.^[22,23] X-ray diffraction on oxidized Fe-MNPs showed a peak pattern pertaining to iron oxide. The peaks, however, were broad, indicating a weakly-crystalline nature of the oxide shell (Figure 1b). The iron composition was further analyzed by X-ray photoelectron spectroscopy. Along with peaks from Fe^0 , distinct photoelectron signature from Fe^{2+} and Fe^{3+} oxidation states were observed (Figure 1c); the shell thus could be considered as in the mixed phase of ferrous (FeO) and ferric (Fe_2O_3) oxides.^[24]

We also investigated the morphology and phase of Fe-cores. Under high resolution transmission electron microscopy (TEM), we observed no grain boundaries inside Fe-cores (Figure S2a). X-ray diffraction patterns of as-synthesized Fe-MNPs (Figure S2b) showed a peak ($2\theta \approx 44^\circ$) corresponding to $\alpha\text{-Fe}$. The size of Fe-crystal domain, estimated using Scherrer equation, was ~ 10 nm, which was in good agreement with TEM data (~ 11.6 nm). These results indicated that the synthesized Fe-cores were in a single-domain state.

The prepared Fe-MNPs were next subjected to comprehensive magnetic characterization. All measurements were performed with particles in a powder form and 2 hours after synthesis. The number of MNPs in a sample was quantified by measuring Fe amounts through an inductively-coupled plasma atomic emission spectroscope (ICP-AES). Figure 2 shows the temperature-dependent magnetization (M) of Fe MNPs (see Experimental Section for details). For particles with 13.6 nm Fe-core, zero-field cooled (ZFC) and field cooled (FC) curves showed the presence of two blocking temperatures ($T_{B1} > T_{B2}$), which can be associated with the separate onset of superparamagnetism in the Fe core (T_{B1}) and the oxide shell (T_{B2}).^[25] Such association was further validated by similar measurements with smaller

Fe MNPs. When the core size was reduced to 11.6 nm, T_{B1} decreased considerably; the change in T_{B1} (58%) agreed well with the expected reduction (62%) of anisotropy energy due to the smaller Fe-core volume. T_{B2} , on the other hand, remained relatively constant for all Fe MNPs, and its value was close to a single blocking temperature (T_B) of shell-only, hollow particles. The anisotropy constant (K_{Fe}) of Fe-core, estimated from the observed T_{B1} , was $\sim 8 \times 10^5$ erg/cm³, slightly larger than the magnetocrystalline anisotropy constant of bulk material ($\sim 5 \times 10^5$ erg/cm³). As previously reported,^[26] the increase in K_{Fe} could be attributed to both stress-induced anisotropy and high surface energy.

We next characterized the field-dependent magnetization of Fe MNPs at $T = 300$ K (Figure 3a and Table S1). The saturation magnetization M_s of the overall particle increased in proportion to the Fe-core portions (Figure 3b). Directly measuring the saturation magnetization of Fe-cores (M_{Fe}) was difficult due to the presence of native oxide shells. We instead measured the magnetization of shell-only hollow particles, and used the value to compensate for the shell contribution in the total M_s . The oxide shell had a relatively small magnetization M_{oxide} (~ 48 emu/cm³). The magnetization M_{Fe} of the Fe-core was then obtained by fitting the measured data to

$$M_s = (V_{Fe} \cdot M_{Fe} + V_{oxide} \cdot M_{oxide}) / (V_{Fe} + V_{oxide}), \quad (1)$$

where V_{Fe} and V_{oxide} are the volume of the Fe-core and the oxide shell, respectively. The estimated M_{Fe} of the Fe-core was ~ 1416 emu/cm³, a value close to that of the bulk material (~ 1600 emu/cm³). Hysteresis curves further revealed that Fe MNPs were superparamagnetic with the Fe-core diameter (D_c) ~ 11.6 nm. Past this critical diameter ($D_p = 11.6$ nm), Fe MNPs assumed permanent magnetic moments and the coercivity (H_c) increased with the core size (D_c). The observed H_c behavior was analyzed by applying the Bean-Livingston model.^[27,28] For single-domain, ferromagnetic MNPs, the model predicts the size-dependent changes of coercivity, $H_c = H_{c0} \cdot [1 - (D_p/D_c)^{1.5}]$, where H_{c0} is the intrinsic coercivity. When used to fit the observed data with H_{c0} as the only fitting parameter, the model showed excellent agreement (dotted line in Figure 3c). From the fitting, H_{c0} was found to be 464 ± 21 Oe, which was in good agreement with an estimated H_{c0} ($= 0.96 \cdot K_{Fe} / M_{Fe} = 515$ Oe) from the Stoner-Wohlfarth model.^[29]

To study the oxidation kinetics of Fe MNPs, we exposed the particles to air under ambient condition, and monitored changes in particle morphology and magnetic properties. As confirmed by electron microscopy, Fe MNPs underwent gradual oxidation of the metallic cores (Figure 4a). Correspondingly, the total magnetization of the particles (M_s) decreased, as the portion of weakly-magnetic oxide increased. By monitoring M_s values over time and using Equation 1, we estimated the oxide volume (V_{oxide}). The observed temporal changes of V_{oxide} revealed important aspects of the oxidation process of Fe MNPs. First, the oxidation kinetics were nearly identical regardless of the particle size. The relative changes of the oxide volume, when normalized against that of the initial 2.2-nm thick oxide layer, followed a single curve (Figure 4b), indicating that differently-sized Fe MNPs underwent the same oxidation mechanism. Note that we used the oxide-volume, not the oxide thickness, as a relevant metric, in order to account for the geometrical constraint (i.e., the spherical shape) on oxide growth. Second, the oxidation process showed logarithmic time-dependence, progressively becoming slower over time. The observed kinetics could be explained in the framework of Mott-Cabrera model.^[14,30] To form oxide layers, free electrons from metal should enter the conduction band of oxide, either through tunneling or thermionic emission. At room temperature, the dominant transport mechanism is through tunneling across the oxide barrier; the tunneling barrier potential for metal/oxide is about 1.25 eV,^[15] which is much larger than thermal energy (0.025 eV). Because the tunneling

efficiency decreases exponentially with the barrier thickness, the oxide growth correspondingly slows down. Indeed, as shown in Figure 4c, the measured growth rate from all Fe MNPs displayed an exponential damping, confirming that electron tunneling is the rate-limiting process.

Although oxidation becomes progressively slower, it still has profound impact on the magnetic properties of Fe-MNPs. Since the oxide growth is a volumetric process, the effect is much more pronounced in MNPs with a spherical geometry. For example, it is estimated to take > 600 years to form a 4-nm thick oxide film in bulk Fe material. Fe-MNPs (initial diameter 16 nm), in contrast, would develop a 4-nm thick layer in much shorter time (< 1 year), losing > 85% of their starting magnetic moments. For robust magnetic applications of Fe MNPs, it is thus necessary to stabilize the particles against oxidation. One potential approach is to enlarge the particle size, which would reduce the relative effect of oxidation on the particle magnetization. The method, however, would be limited by technical challenges involved in synthesizing large and uniform MNPs. A more promising strategy would be to encase Fe-particles with gas-impermeable matrices (e.g., ferrite, noble metals). A hybrid core-shell particle, consisting of a Fe-core and a protective shell, could be an ideal format, as the shell can prevent not only the oxidation of individual particles but also inter-particle aggregation.^[31–33]

In summary, we have characterized magnetic and oxidation properties of elemental Fe MNPs. Overall, Fe MNPs assumed magnetic properties (e.g., saturation magnetization, magnetic anisotropy, intrinsic coercivity) similar to those of bulk material, and the coercivity of differently-sized particles could be estimated by the classical Bean-Livingston model.

Oxide layers on Fe MNPs followed a logarithmic growth pattern, which confirmed electron-tunneling as the main oxidation mechanism. These observations would allow accurate prediction of the magnetic behavior of Fe MNPs, and thereby facilitate optimizing the particles for robust magnetic applications.

Experimental Section

Iron pentacarbonyl (99.999%, Fe(CO)₅), oleylamine (70%, OY), 1-octadecene (95%, ODE), and chloroform (99%) were purchased (Sigma-Aldrich) and used without further modification. Isopropanol (99.5%), hexane (98.5%), ethanol (99.5%) and NaHCO₃ were purchased (Fisher Scientific) and used without further purification.

Synthesis of Fe MNPs

To synthesize Fe MNPs, 20 mL ODE and 0.3 mL oleylamine (0.64 mmol) were added into a 250 mL 3-neck glass round-bottom flask. A condenser and a thermocouple were connected to separate necks of the flask. The mixture was heated up to 60 °C under vacuum for 1 hour and recharged with N₂ gas to completely remove O₂. To form differently-sized particles, the mixture was heated to the following temperature: 140 °C, 5 nm Fe MNPs; 160 °C, 9 nm; 220 °C, 12 nm; 240 °C 14 nm; 260 °C, 16 nm. When the temperature became stable, Fe(CO)₅ (1.4 mL, 10 mmol) was injected into the reactor under vigorously stirring. The solution quickly turned black as the carbonyl decomposed and nanoparticles began forming. The solution was kept at the elevated temperature and under N₂ flow for 1 hour. Following the completion of the reaction, the solution was cooled to room temperature, and 150 mL isopropanol solution (ODE/isopropanol = 0.2 v/v) was added. MNPs were collected via centrifugation (3,000 rpm, 15 minutes) and dispersed in 10 mL hexane. To wash the particles, 50 mL ethanol was added to the particle solution, the mixture was centrifuged, and

the precipitate was redispersed in 10 mL hexane. These washing steps were repeated three times to ensure removal of excess chemicals.

Characterization of Fe MNPs

Excess ethanol was added to Fe MNP in hexane, and precipitates were collected through centrifugation (3,000 rpm, 15 min). The precipitates were dried in vacuum to obtain particles in a powder form. Purified particles were highly stable over time, and could be resuspended in hexane without aggregation. The shape, structure, and composition of particles were characterized using a transmission electron microscope (TEM; JEOL 2100, JOEL USA), an X-ray powder diffractometer (XRD; RU300, Rigaku), and an inductively-coupled plasma atomic emission spectrometer (ICP-AES; Aativa-S, HORIBA Jobin Yvon), respectively. Oxidation states of Fe MNPs were measured by an X-ray photoelectron spectrometer (XPS; PHI VersaProbe II Scanning XPS, Physical Electronics), and the data was analyzed by CasaXPS (Ver. 2.3.15, Casa software). The magnetic properties of Fe MNPs were analyzed using a vibrating sample magnetometer (EV-5, ADE Magnetics) and a superconducting quantum interference device (SQUID) magnetometer (MPMS-5, Quantum Design). For ZFC and FC measurements, samples were subject to the magnetizing field of 100 Oe. The maximum magnetization values (from FC measurements) were 0.76 emu/g (13.6 nm Fe core), 0.56 emu/g (11.6 nm Fe core), and 0.11 emu/g (hollow particles). After the magnetic measurements, samples were dissolved in acid (HCl 10%), and the amounts of metals were quantified by ICP-AES.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Synthesis and characterization of Fe MNPs

(a) Particle size was varied by controlling the reaction temperature during synthesis. When exposed to air, all particles developed an oxide shell with an initial thickness of 2.2 nm. Particles with diameter < 5 nm were completely oxidized to form hollow spheres (left). (b) The oxide shells had a weakly crystalline structure as revealed by X-ray diffraction. The peak positions corresponded with those of iron oxide. (c) The composition of Fe MNPs was probed by X-ray photoelectron spectroscopy. The raw data (black solid line) was fitted (dotted line), and multiple peaks were resolved. Besides having a pure iron (Fe^0 , solid pattern) at the core, the particles had a mixture of irons in different oxidation states, Fe^{3+} (clear) and Fe^{2+} (hatched).

Figure 2. Temperature-dependent magnetization

Fe MNPs with a core diameter of 13.6 nm showed two blocking temperatures ($T_{B1} > T_{B2}$). When the core size was reduced to 11.6 nm, only T_{B1} was lowered. The result indicated that T_{B1} represented the blocking temperature for the Fe-cores. Similar measurements on the oxide-shell hollow particles showed a single peak at low temperature (T_B) comparable to T_{B2} . We thus associated T_{B2} to the blocking temperature of the shell in Fe MNPs. Applied field strength was 100 Oe. ZFC, zero-field cooling; FC, field cooling.

Figure 3. Magnetic characterization of Fe MNPs

(a) Field-dependent magnetization was measured at 300 K. All Fe MNPs with a core diameter (D_c) ≤ 11.6 nm were superparamagnetic. (b) The saturation magnetization (M_s) linearly increased in proportion to the Fe-core volume fraction. The measured data was fitted (dotted line) to estimate the saturation magnetization (M_{Fe}) of the Fe-core. The obtained value ($M_{Fe} = 1416$ emu/cm³) was close to that of bulk iron (1600 emu/cm³). (c) Past the superparamagnetic limit ($D_c > 11.6$ nm), the coercivity (H_c) increased with the Fe-core size. The observed H_c behavior could be described by the coercivity model (dotted line) for single-domain particles, developed by Bean and Livingston.

Figure 4. Oxidation kinetics of Fe MNPs

(a) Under ambient conditions, the oxide shell grew over time at the expense of the Fe core. The shell thickness nearly doubled in 5 months post particle synthesis. (b) When normalized against its initial value, the oxide volume followed a universal, logarithmic growth pattern, confirming that Fe MNPs were under the same oxidation mechanism. (c) The oxide growth rate decreased exponentially as the oxide volume increased. This result indicates that electron tunneling from the Fe-core to the oxide shell is the rate-limiting process.