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Characterization and magnetic properties of core/shell structured Fe/Au nanoparticles

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Au-coated Fe nanoparticles have been prepared by using a reverse micelle method through reduction of an aqueous solution. Characterizations have been carried out over time to probe the oxidation of Fe. Immediately after synthesis, the samples exhibit metallic conduction and a negative magnetoresistance, consistent with the presence of α -Fe. The temperature dependence of magnetization displays a maximum at a blocking temperature of around 150 K. After a period of 1 month, the samples exhibit insulating behavior, indicating the oxidation of the Fe core. Mössbauer spectroscopy indicates the presence of an α -Fe component and a broad distribution of local environments. © 2004 American Institute of Physics. [DOI: 10.1063/1.1676033]

Magnetic nanoparticles exhibit a rich variety of interesting phenomena, such as single-domain state, coercivity enhancement, and quantization of spin waves, due to their small dimensions.¹ They have exciting potential applications in magnetic recording, sensing, and biological diagnosis.^{2,3} A more sophisticated structure is a core/shell configuration where the magnetic core is coated by a shell layer. For example, there has been a lot of recent interest in Fe₃O₄/polymer, Fe/Au, and Fe/Fe-oxide core/shell structures.^{4–6} Such structures are not only ideal for studying proximity effects, but are also suitable for structure stabilization, as the shell layer protects the core from oxidation and corrosion. Additionally, the shell layer provides a platform for functionalization, such as coupling the magnetic core through the shell onto organic surfaces or other surfaces.

The combination of Fe core/Au shell is particularly appealing because Au is not ferromagnetic, but is noble and relatively easy to functionalize. Initial studies on Fe/Au core/shell nanoparticles have been reported by Carpenter, Sangregorio, and O'Connor.⁷ However, some recent x-ray absorption spectroscopy studies have shown that such particles often consist of oxidized Fe cores.^{8,9} A key question is whether the oxide forms during or after the synthesis process. Independent evaluation suggests that the Fe/Au nanoparticles may not be prepared via the reduction route in the reversed micelle circumstances.¹⁰ Thus, direct verifications of the Fe/Au core/shell structure over time, particularly the Fe core size and chemical states, are crucial.

In this study, we report the synthesis of Au-coated Fe nanoparticles using a reverse micelle technique, and charac-

terizations of their properties immediately after synthesis as well as after an extended period of time. The core/shell structure has been illustrated by transmission electron microscopy (TEM). The existence of Fe cores is manifested in the blocking behavior and electrical transport properties. The chemical states of the Fe have been probed by Mössbauer spectroscopy.

The Fe/Au nanoparticles were synthesized by modifying previously reported techniques.^{4,7,8,11–13} It was carried out in a reverse micelle reaction under Ar, utilizing Schlenk line techniques. Cetyltrimethylammonium bromide, 1-butanol, and octane were used as the surfactant, the co-surfactant, and the oil phase, respectively. The nanoparticles were prepared in aqueous solutions of micelles by reduction of Fe(II) with NaBH₄, and then of Au(III) with NaBH₄. The NaBH₄ concentration, timing of various steps, and prevention of air contact appeared to affect the resulting particle size. After precipitation, the nanoparticles were collected with a magnet, rinsed to remove the surfactant, and dried under vacuum.

Initial characterizations on the as-made samples were performed within a few days after synthesis. Structural characterizations have been carried out by x-ray diffraction. Topological and chemical analyses have been performed by a Philips CM-12 TEM at 100 keV. Magnetic properties have been measured on a Quantum Design superconducting quantum interference device (SQUID) magnetometer. Temperature dependence of the magnetization has been measured after zero-field cooling (ZFC) and field cooling (FC) in a 100 Oe field. For electrical transport studies, the nanoparticles were cold pressed into a 6 mm die under a 2×10^7 Pa pressure for 10 min to form pellets. Electrical leads were attached by silver paint. Magnetoresistance was measured at 5 K on pressed pellets.

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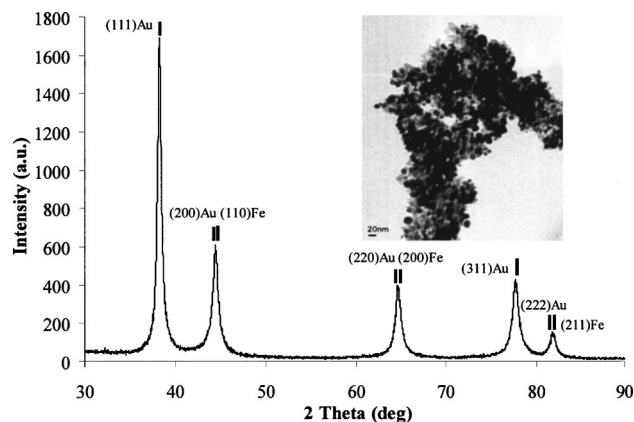


FIG. 1. X-ray diffraction pattern and transmission electron micrograph (TEM) of Fe/Au nanoparticles.

The chemical states of the Fe were probed by Mössbauer spectroscopy at 90 and 295 K on a constant-acceleration spectrometer, approximately 1 month after synthesis. The spectrometer utilizes ^{57}Co in a rhodium matrix and has been calibrated at room temperature with an α -iron foil.

On the as-made samples, x-ray diffraction confirms the presence of the Fe and Au phases (Fig. 1), consistent with previous reports.^{4,7-9} A TEM image of the Fe/Au nanoparticles is shown in the inset of Fig. 1. The typical size of the nanoparticles is about 20 nm. The existence of Fe and Au is again confirmed by energy dispersive x-ray microanalysis.

The temperature dependence of the magnetization was taken within 24 h of sample preparation and is shown in Fig. 2. The ZFC curve displays a broad maximum corresponding to blocking behavior at ~ 150 K; above this temperature the particles are superparamagnetic. This blocking temperature is much higher and indicates a larger Fe core size than that previously reported.^{4,7,9,11} The magnetic hysteresis loop at 5 K is shown in the inset, with a coercivity of 240 Oe. The magnetization value is obtained by dividing the magnetic moment by the total mass of the Fe/Au nanoparticles. By extrapolating the linear M - H slope at high fields to $H=0$,

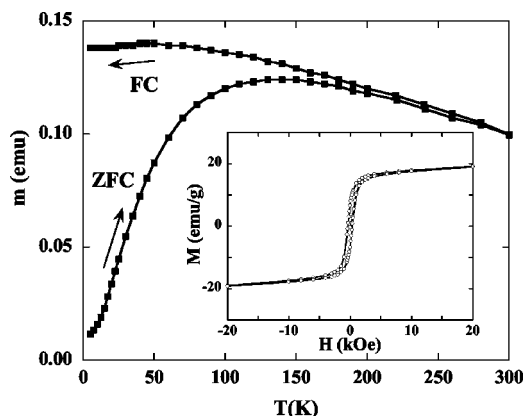


FIG. 2. Temperature dependence of magnetization of the Fe/Au nanoparticles measured in a 100 Oe field, after ZFC and FC. The inset shows the magnetic hysteresis loop at 5 K, normalized to the mass of the Fe/Au nanoparticles.

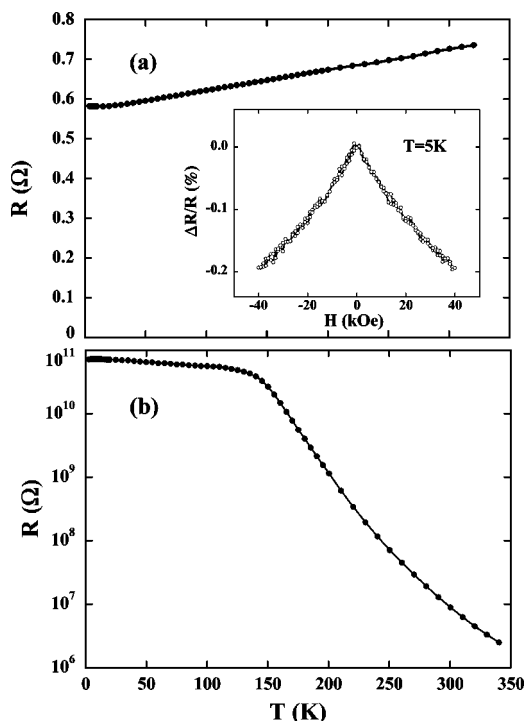


FIG. 3. Temperature dependence of resistance of pressed pellets of Fe/Au nanoparticles in zero magnetic field measured (a) immediately after synthesis and (b) 1 month after synthesis. The inset shows the corresponding magnetoresistance of the pellet at 5 K.

we have obtained a saturation magnetization of approximately 17 emu/g. The remanent magnetization is 2.84 emu/g.

Due to the small size of the magnetic particles, the thermally assisted magnetization reversal process can be described by $1/\tau = f_0 e^{-KV/k_B T}$,¹⁴ where K is the anisotropy constant, V is the magnetic particle volume, f_0 is the frequency factor of $10^9/\text{s}$, and τ is the relaxation time (30 s in the SQUID measurement). If the magnetic contribution is all from bulklike Fe, for a 150 K blocking temperature, we can estimate a Fe core size to be about 12 nm. Thus, the corresponding volume percent of the Fe core in the total 20 nm Fe/Au assembly is 21.6 vol %. The saturation magnetization of the Fe core, corrected for the Fe volume fraction, would be ~ 152 emu/g.

Electrical transport properties have been measured in compact pellets of these nanoparticles. The resistance decreases slightly with decreasing temperature [e.g., from 0.73 Ω at 300 K to 0.60 Ω at 5 K, as shown in Fig. 3(a)]. This positive temperature coefficient of resistance is a signature of metallic conduction, in contrast to the negative temperature coefficient and thermally activated behavior seen in pellets of iron oxide nanoparticles.^{15,16} Thus, the core-shell samples are still metallic right after synthesis.

At 5 K, the resistance decreases in a magnetic field, resulting in a negative magnetoresistance (MR). The MR, defined as $[R(H) - R(0)]/R(0) = \Delta R/R(0)$, is about -0.17% in a field of 40 kOe [Fig. 3(a) inset]. The negative MR is the giant magnetoresistance effect caused by spin-dependent scattering, similar to those seen in magnetic granular solids.¹⁷ In the pellet of Fe/Au nanoparticles, the Fe cores serve as magnetic scattering centers. In zero magnetic field

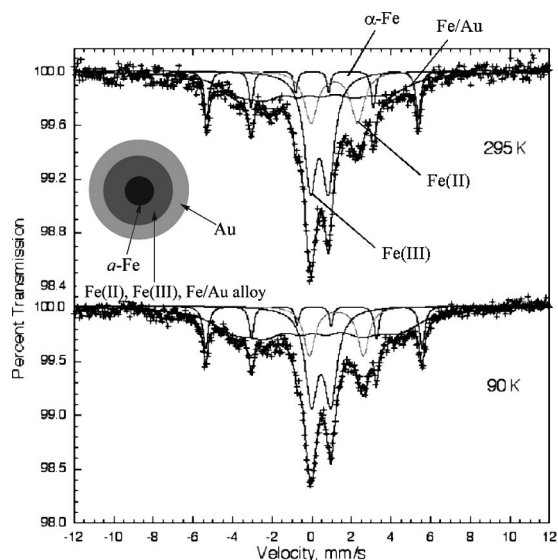


FIG. 4. Mössbauer spectra of Fe/Au nanoparticles obtained at 295 and 90 K. The inset shows the proposed model. The spectral components are α -Fe, Fe/Au alloy, paramagnetic Fe(II), and paramagnetic Fe(III), as marked in the graph.

the orientation of the magnetization of each Fe core is random, resulting in a spin-disordered state. The application of a magnetic field helps to align all the Fe core moments and reduces the spin disorder. This, in turn, reduces the spin-dependent scattering and leads to a reduction in resistance, hence the negative MR.

The sample oxidation status was measured again 1 month after synthesis by Mössbauer spectroscopy to probe the chemical states of the Fe core. The spectra for the sample at 295 and 90 K are shown in Fig. 4. The presence of a metallic Fe component with a reduced hyperfine field and a broad distribution of local environments is apparent. The spectra indicate the presence of $\sim 11\%$ of magnetic Fe with hyperfine parameters that correspond to those of α -Fe, and $\sim 41\%$ of a broad component that presumably corresponds to an alloy of Au and Fe with a broad distribution of Fe sites, i.e., Fe sites with a large variation in the number of Fe and Au nearest neighbors.¹⁸ There is also $\sim 16\%$ of high-spin Fe(II) and $\sim 32\%$ of high-spin Fe(III) present. No appreciable Fe-oxide phases were seen in x-ray diffraction patterns of these samples, measured within 24 h as well as 1 month after synthesis. However, the oxidation is manifested in the electrical transport properties. For a similarly prepared pellet of such oxidized nanoparticles (after a month-long exposure to air), the resistance values are much larger, accompanied by a negative temperature coefficient (from 10 M Ω at 300 K to 26 G Ω at 150 K, measured by a Keithley 617 electrometer with a 200 G Ω impedance) and a thermally activated behavior at high temperatures [Fig. 3(b)].

Therefore, our experiments demonstrate that metallic Fe cores are indeed formed after the chemical reduction processes [also confirmed by a comparison where chemical re-

ductions of only Fe(II), without the Au(III) reduction, produce bare α -Fe particles]. In the core/shell systems, an additional Fe/Au alloy, and finally an Au layer, are formed. Over time the Fe core oxidizes and the Mössbauer measurement confirms this. The Au shell does not protect the Fe core completely from oxidation. The Mössbauer measurement is the first direct evidence of Fe core in samples prepared by this method.^{8–10}

In summary, we have synthesized and characterized Au-coated Fe nanoparticles. The temperature dependence of magnetization displays a broad maximum at a blocking temperature of about 150 K, above which the sample becomes superparamagnetic. Metallic conduction has been observed in a pressed pellet of the Fe/Au nanoparticles. A negative giant magnetoresistance effect has been observed as the Fe cores serve as scattering centers for the electrical transport. These results, which were obtained right after the syntheses, are consistent with a metallic α -Fe core. However, the Mössbauer studies performed 1 month later confirm that oxidation occurs over time, indicating that the Au shell does not coat the entire Fe core outer surface or that the Au shell is permeable to oxygen. They suggest the initial presence of an Fe core and the Fe/Au structure, and subsequently the oxidation of the structure to Fe/Fe(II)/Fe(III) and Au.

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