Synthesis and magnetic properties of gold coated iron oxide nanoparticles

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We report on synthesis, structural, and magnetic properties of chemically synthesized iron oxide (Fe$_3$O$_4$) and Fe$_3$O$_4$@Au core-shell nanoparticles. Structural characterization was done using x-ray diffraction and transmission electron microscopy, and the magnetite phase of the core ($\sim$6 nm) and fcc Au shell (thickness of $\sim$1 nm) were confirmed. Magnetization ($M$) versus temperature ($T$) data at $H=200$ Oe for zero-field-cooled and field-cooled modes exhibited a superparamagnetic blocking temperature $T_b\sim$35 K (40 K) for parent (core-shell) system. Enhanced coercivity ($H_c\sim200$ Oe) at 5 K along with nonsaturating $M$-$H$ loops observed for Fe$_3$O$_4$@Au nanoparticles indicate the possible role of spin disorder at the Au–Fe$_3$O$_4$ interface and weak exchange coupling between surface and core spins. Analysis of ac susceptibility ($\chi'$ and $\chi''$) data shows that the interparticle interaction is reduced upon Au coating and the relaxation mechanism follows the Vogel–Fulcher law. © 2009 American Institute of Physics. [DOI: 10.1063/1.3059607]

Layered assembly of different materials in core-shell nanoparticle (NP) form is an attractive way to fabricate systems possessing diverse physical and chemical properties. Multicomponent NPs exhibit distinct optical, catalytic, and magnetic properties. Recently, incorporation of optically active components into magnetic NPs has attracted considerable attention. Gold (Au) coated superparamagnetic NPs are very attractive composite systems. Dumbbell-like Au–Fe$_3$O$_4$ (Refs. 3 and 11) and CdS–FePt (Ref. 12) NPs have been synthesized and exhibit interesting optical properties (due to Au or CdS) and magnetic properties (due to Fe$_3$O$_4$ or FePt). One of the drawbacks in these composite systems is that the magnetic moment decreases considerably, which is a major constraint for biomedical applications. This can originate from several sources such as interface coupling, nonmagnetic surface layer, reduction in interparticle interactions, etc. In this study, we report on the synthesis, structure, and magnetic characterization of nearly spherical iron oxide NPs ($D\sim6$ nm) and its gold-coated counterpart, with shell thickness of Au of about 1 nm.

The Fe$_3$O$_4$ NPs capped with oleylamine and oleic acid were synthesized using a chemical procedure reported elsewhere. In a typical synthesis process, 10 mmol 1,2-hexadecanediol, 6 mmol oleic acid, 6 mmol oleylamine, and 20 ml benzyl ether were added to 2 mmol iron (III) acetylacetone. The mixture was heated to 200 °C for 2 h with constant stirring and then refluxed at $\sim300$ °C for another 1 h in the presence of argon. Then 40 ml ethanol was added to the cooled mixture and a black precipitate was separated by centrifugation. The black product was dissolved in hexane in the presence of oleic acid ($\sim0.05$ ml) and oleylamine ($\sim0.05$ ml) and centrifuged to remove the undispersed residue. The product of 6 nm Fe$_3$O$_4$ particles was then precipitated with ethanol, centrifuged to remove the solvent, and redispersed into hexane. The synthesis of Au-coated Fe$_3$O$_4$ NPs was followed by an initial synthesis of Fe$_3$O$_4$ NPs as seeds and a subsequent reduction in gold acetate [Au(OOCCH$_3$)$_3$] in the presence of the seeds.

Figure 1 shows a representative set of transmission electron microscopy (TEM) micrographs of Fe$_3$O$_4$ nanoparticles before and after the formation of the gold shell. Histograms (not shown) of the particle size distribution from the TEM images with a sampling of 50 particles were analyzed, and this yielded mean particle sizes of 6 nm for particles before coating [Fig. 1(a)] and 7 nm for the particles after coating [Fig. 1(b)] with Au.

The x-ray diffraction (XRD) patterns of parent and Au-coated Fe$_3$O$_4$ NPs exhibit the diffraction peaks for inverse spinel ferrite structure and fcc phase of gold, respectively.

FIG. 1. XRD pattern of as-synthesized Fe$_3$O$_4$ and Fe$_3$O$_4$@Au NPs. Shown in the inset are TEM pictures of (a) Fe$_3$O$_4$ and (b) Fe$_3$O$_4$@Au NPs.
shown in Fig. 1. The absence of the diffraction peaks for Fe₃O₄ phase in Fe₃O₄@Au NPs is a strong evidence for complete coverage of the iron oxide core by the gold shell. This is most likely due to the heavy atom effect of gold compared to iron oxide.¹⁴

Temperature and field dependent DC and AC magnetization along with radio frequency (RF) transverse susceptibility were done in a commercial physical properties measurement system from Quantum Design. The M vs T data measured at H=200 Oe in ZFC-FC modes for the Fe₃O₄ and Fe₃O₄@Au NPs exhibit a characteristic superparamagnetic response at high T with blocking temperature (T_B) around 35 and 40 K, respectively, as shown in Fig. 2. The slight increase in blocking temperature for Au-coated particles can be due to the overall increase in particle size as observed from TEM. M vs H was measured at applied fields of ±50 kOe at 5 K under ZFC-FC modes. The saturation magnetization Mₛ of Fe₃O₄ NPs and Fe₃O₄@Au are estimated to be 33 and 1.8 emu/g, respectively, which are significantly lower than that of bulk Fe₃O₄ (Mₛ=84 emu/g). This reduction is expected in NPs as the surface magnetic order can be affected by structural distortions that cause spin canting.¹⁵ The drastically reduced moment in Fe₃O₄@Au NPs indicates that the contribution of surface effects should be significantly higher when compared with uncoated Fe₃O₄. M-H loops did not exhibit hysteresis in the superparamagnetic state for both the parent Fe₃O₄ and Fe₃O₄@Au NPs as expected, and at T =5 K within the blocked state, the measured coercivities were Hₑ=160 and 200 Oe, respectively (insets of Fig. 2). We also measured the M-H loops after field cooling to 5 K to look for any possible exchange bias that could result in coercivity enhancement. However, the loops were symmetric and no exchange bias was found for both particle systems.

The temperature-dependent (5–150 K) ac susceptibility [both in phase χ'(T) and out of phase χ''(T)] was measured over the frequency window from 10 Hz to 10 kHz for both uncoated and Au-coated samples (Figs. 3 and 4). The magnetic relaxation of noninteracting NPs is expected to follow the thermally activated Néel–Arhenius law given by the expression \( f = f₀ \exp(-E_a/k_B T_B) \), where \( f₀ \) (attempt frequency) is of the order of \( 10^8–10^{13} \) Hz, \( k_B \) is Boltzmann’s constant, and \( E_a \) is the anisotropy energy. In the case of weakly interacting NPs, the system is expected to conform to the framework of the Vogel–Fulcher relaxation: \( f = f₀ \exp[-E_a/k_B T_B] \) with \( T_B \) as the effective strength of interparticle interactions. As expected from these expressions, the blocking temperature increases with increasing frequency. It is clearly seen that the \( T_B \) shifts to a slightly higher value in Fe₃O₄@Au compared to the uncoated Fe₃O₄ NPs, which also supports the dc magnetization (M vs T) results. Fits to the Néel–Arrhenius model yields unphysical values for \( f₀ \) and \( E_a \) for the uncoated (coated) particles are \( 5.0 \times 10^{13} \) (\( 5.0 \times 10^{12} \)) Hz, 1003 (1042) K, and 32 (28) K, respectively, and the plots are shown in the inset of Fig. 3. These parameters extracted from the fits suggest that the interparticle interaction is reduced a bit in gold-coated NPs. We have also analyzed the χ''(T) vs T data using a phenomenological relation:

\[ \Phi = \Delta T_P/T_p \Delta \log_{10} f, \]

where \( \Delta T_P \) is the shift in peak temperature \( T_p \) observed in the frequency interval \( \Delta \log_{10} f \). It has been shown from a number of experimental observations that the numerical value of \( \Phi > 0.1 \) for noninteracting NPs, \( \Phi = 0.03–0.1 \) for interacting...
NPs, and $\Phi<0.03$ for spin-glass system.\textsuperscript{18} Our experimental result gives the $\Phi$ values of 0.07 (0.1) for the uncoated (coated) samples. These results again confirm that the gold shells on iron oxide cores encapsulate and shield the magnetic particles and cause a reduction in the overall interparticle magnetic interaction.

Over the years, we have pioneered the method of rf TS as a powerful method for directly probing the effective magnetic anisotropy in nanoparticle systems.\textsuperscript{19,20} Field-dependent TS data for field scans of $\pm 10 \text{ kOe}$ were collected over a temperature range $10 \text{ K} < T < 300 \text{ K}$ for both the uncoated and Au-coated NP systems (Fig. 5). The two peaks corresponding to the anisotropy field ($\pm H_k$) were observed below blocking temperature and the peaks merge into a single peak at $H=0$ above blocking temperature, consistent with earlier studies on NP samples.\textsuperscript{19,20} At $T=10 \text{ K}$, the anisotropy field is around 450 Oe, which is in the range of values (250–500 Oe) typically observed in $\text{Fe}_3\text{O}_4$ NPs. The effective anisotropy is determined by various factors such as particle size, shape, interparticle interactions, and surface/core spin ordering. The inset of Fig. 5 shows the temperature dependence of $\pm H_k$ values for both $\text{Fe}_3\text{O}_4$ and $\text{Fe}_3\text{O}_4@\text{Au}$. The values are similar, indicating that the thin Au shell in these NPs with nearly spherical symmetry do not significantly change the effective anisotropy. However, we note that the relative magnitude of TS decreases an order of magnitude in the gold-coated sample, consistent with the large reduction in magnetic moment.

FIG. 4. Temperature dependence of ac susceptibility $\chi''$ (out of phase) of (a) $\text{Fe}_3\text{O}_4$ and (b) $\text{Fe}_3\text{O}_4@\text{Au}$ NPs for several frequencies.

FIG. 5. TS measurement of the $\text{Fe}_3\text{O}_4@\text{Au}$ NPs. Inset figure shows temperature dependence of $H_k$ for both the coated and uncoated NPs.

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