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Green magnetite (Fe_3O_4): Unusual optical Mie scattering and magnetic isotropy of submicron-size hollow spheres

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Magnetite hollow spheres with a diameter of 650 nm and shell thickness of 40 nm exhibit an unexpected green color, in contrast with usual magnetite solids appearing black. This unusual green color is interpreted in terms of the Mie scattering on the inhomogeneous and low-density structure of the hollow spheres with a characteristic diameter that is comparable to the wavelength of the visible light. Further, thin films of the hollow spheres exhibit no two-dimensional shape anisotropy, reflecting the isotropic structure of individual particles. These results indicate the potential advantages in achieving unique physical properties through constructing hollow structures. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3079407]

Magnetite (Fe_3O_4) is the oldest magnet for humankind, discovered as loadstone in the 6th century B.C. Since then, mysterious powers of this black solid greatly fascinated people and has been utilized in various tools and instruments, such as the compass,[1] ferrofluid,[2] etc. Besides these applications, magnetite attracted academic interest due to the Verwey transition: a metal-insulator transition caused by electron-electron correlation,[3] and the half-metallic behavior that is applicable in spintronics.[4] Recently there were extensive studies on nanostructuring of magnetite[5,6] toward modern applications in magnetic separation, spintronics, and biological fields because of its biocompatibility.

Since the physical properties of magnetic materials depend strongly on the size and shape, the preparation of submicron magnetic hollow spheres is a promising approach toward the development of advanced magnetic materials.[7–9] Their comparatively large size means that the critical temperatures of magnetic ordering or magnetization blocking would be sufficiently high for practical applications. Their isotropic shape weakens the magnetic anisotropy, but brings about the controllable magnetization. Their hollow structure brings another dimension to tune physical properties, which may lead to potential applications in biomedical fields (drug delivery agents, bioencapsulation) and engineering (low density materials). In our previous works, we reported the preparation and the magnetic properties of powder samples of magnetite hollow spheres.[8,9] Here we report that the magnetite hollow spheres exhibit an unusual green color and no shape anisotropy. We discuss the green color, based on the Mie scattering due to the characteristic size and structure of the present particles, and the magnetic properties based on their isotropic structures.

The magnetite hollow spheres were fabricated by a homogeneous precipitation of iron hydroxides on the surface of polystyrene (PS)-bead (600 nm) template, followed by the calcination at 500 °C under N_2 for 3 h. The detailed procedure was described in our previous papers.[8,9] The obtained particles exhibit an extremely uniform size, with a diameter 650 nm and a shell thickness 40 nm [Fig. 1(a)]. To prepare thin films of the magnetite hollow spheres, the precursor particles, namely PS-beads coated with iron hydroxides, were accumulated on a glass slide by the fluidic-cell method;[10] the capillary force caused by slow evaporation of the water solvent brought about self-assembling of the particles and uniform thin films with a thickness of $\sim 3-5$ μm. These thin films were transformed into those of magnetite by the calcinations without breaking the hollow structure. For comparison, magnetite dense particles with a diameter of ca. 820 nm were prepared by the method reported in Ref. 11. Thin films of the dense particles were also prepared by the fluidic-cell method from aqueous solution of the magnetite dense particles exhibiting good dispersibility.[11] The obtained magnetite materials were identified through their x-ray diffraction patterns and x-ray photoemission spectra (see supplemental material).[12]

Figures 1(a) and 1(b) show the transmission electron microscope (TEM) images for the hollow and dense particles of magnetite, respectively. The hollow spheres exhibit a clear contrast between the dark outer rim and the transparent core, while there is no such a contrast on the dense particles. Figures 1(c) and 1(d) show the photographs for the powder samples of the two magnetite particles, indicating an obvious color difference. The hollow spheres look green; this color is thoroughly different from the black color of the dense particles with similar spherical shape and size to those of the hollow spheres. Note that magnetite materials always appear black in the bulk solids,[11] and even as nanoparticles.[5]

To confirm this unusual green color of the hollow spheres, we measured the diffuse reflectance spectra on a UV-visible spectrometer (JASCO, UV/vis/near infrared spectrometer V-670) with an integrating sphere (JASCO, ISN-723). The green curve in Fig. 2 shows the results for the powder sample of the hollow spheres. This curve indicates an obvious peak at around 510 nm, which corresponds to the wavelength of the green light. The black curve in this figure depicts the results for the powder sample of the dense particles; it is featureless and there is no peak around 510 nm.

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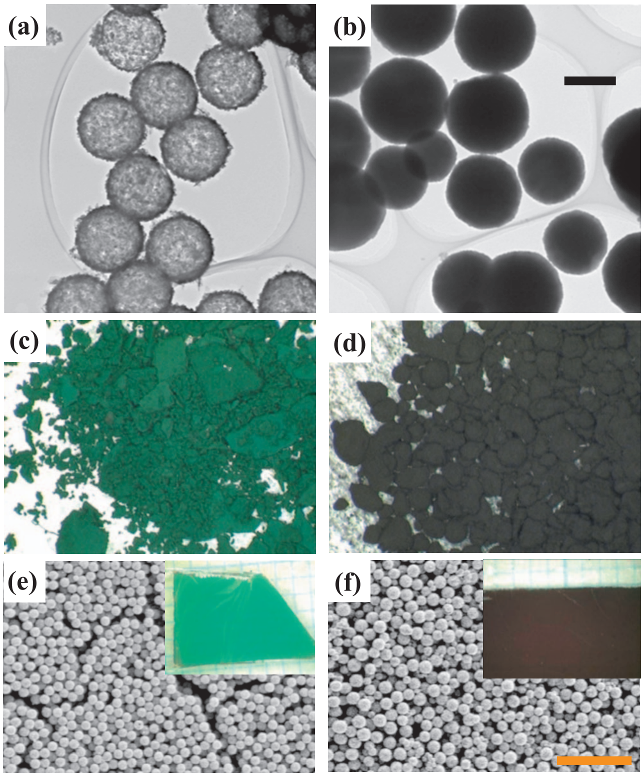

FIG. 1. (Color) Representative TEM images of the magnetite (a) hollow and (b) dense spheres. Photographs of powder samples of the (c) hollow and (d) dense spheres. SEM images of thin films of the (e) hollow and (f) dense spheres. The insets in (e) and (f) are photographs of the corresponding films of the hollow and dense particles, respectively. The scale bars are 500 nm in (a) and (b), and 5 μm in (e) and (f).

These results are consistent with the appearances of the two materials.

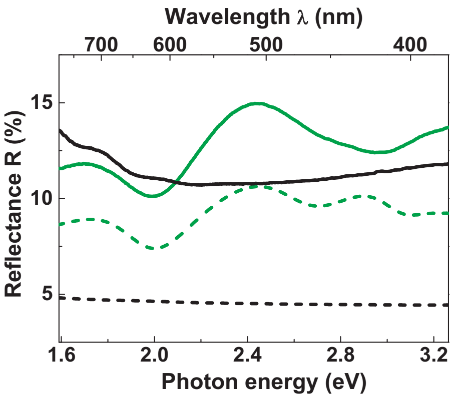

FIG. 2. (Color) Diffuse reflectance spectra for the powder samples of the magnetite hollow spheres (green solid curve) and the dense particles (black solid curve). Calculated reflectance spectra based on the theory of Mie scattering for the hollow spheres (green dashed curve) and the dense particles (black dashed curve) reproduce the peak positions of the experimental data. Note that the absolute experimental values are typically not reproduced by the calculations due to the approximation of the Kubelka–Munk approach.

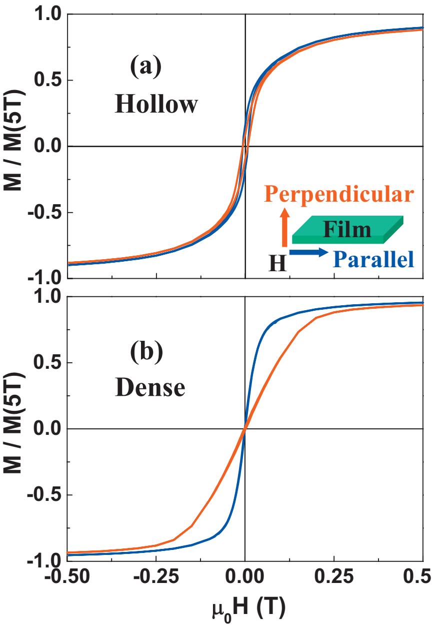

FIG. 3. (Color) Field dependence of magnetizations (*M-H* curves) at 300 K for the thin films of (a) the hollow spheres and (b) the dense particles, with magnetic field *H* parallel and perpendicular to the film plane [see the inset of (a)]. Magnetizations are normalized by the value at 5 T.

In general, color results from the interactions between light and matter, namely, absorption, scattering, and reflection.[13] These are strongly dependent on the shape and size of the substance. When the size of the substance is comparable to the wavelength of incident light, the Mie scattering occurs.[13] Since the size of the present particles (650 nm) is comparable to the wavelength of green light, we will interpret the green color in terms of Mie scattering. When the model of coated spheres is adopted for the hollow spheres,[13] the Mie coefficients a_n and b_n are written as

$$a_n=\frac{\psi_n(y)[\psi_n'(m_2y)-A_n\chi_n'(m_2y)]-m_2\psi_n'(y)[\psi_n(m_2y)-A_n\chi_n(m_2y)]}{\xi_n(y)[\psi_n'(m_2y)-A_n\chi_n'(m_2y)]-m_2\xi_n'(y)[\psi_n(m_2y)-A_n\chi_n(m_2y)]},$$

$$b_n=\frac{m_2\psi_n(y)[\psi_n'(m_2y)-B_n\chi_n'(m_2y)]-\psi_n'(y)[\psi_n(m_2y)-B_n\chi_n(m_2y)]}{m_2\xi_n(y)[\psi_n'(m_2y)-B_n\chi_n'(m_2y)]-\xi_n'(y)[\psi_n(m_2y)-B_n\chi_n(m_2y)]},$$

with

$$A_n=\frac{m_2\psi_n(m_2x)\psi_n'(m_1x)-m_1\psi_n'(m_2x)\psi_n(m_1x)}{m_2\chi_n(m_2x)\psi_n'(m_1x)-m_1\chi_n'(m_2x)\psi_n(m_1x)},$$

$$B_n=\frac{m_2\psi_n(m_1x)\psi_n'(m_2x)-m_1\psi_n(m_2x)\psi_n'(m_1x)}{m_2\chi_n'(m_2x)\psi_n(m_1x)-m_1\psi_n'(m_1x)\chi_n(m_2x)}, \tag{1}$$

where ψ (ψ'), ξ (ξ'), and χ (χ') are the Bessel–Riccatti functions (their derivatives) and m_1 and m_2 are the refractive indices for the ambient inner core and the outer shell magnetite, respectively. The variables x and y are defined as $x=2\pi r_1/\lambda$ and $y=2\pi r_2/\lambda$, where r_1 and r_2 are the inner and outer radii of the hollow sphere, respectively, and λ is the wavelength of light. The integral index n runs from 1 to the integer closest to $N=y+4y^{1/3}+2$.[13] Using the Mie coefficients in Eq. (1), the scattering efficiency Q_{sca}, the extinction efficiency Q_{ext}, the absorption efficiency Q_{abs}, and the asymmetric factor $\cos\theta$ for a single particle are obtained (see supplemental material).[12]

The reflectance R for highly aggregated particles can be calculated through the Kubelka–Munk approach,[14]

$$R=1+\frac{K}{S}-\left(\frac{K^2}{S^2}+\frac{2K}{S}\right)^{1/2},$$

with

$$K=\frac{3C_{\mathrm{abs}}}{2\pi r_2^3}=\frac{3Q_{\mathrm{abs}}}{2r_2},$$

$$S=\frac{9C_{\mathrm{sca}}(1-\overline{\cos\,\theta})}{16\pi r_2^3}=\frac{9Q_{\mathrm{sca}}(1-\overline{\cos\,\theta})}{16r_2}, \tag{2}$$

where C_{abs} and C_{sca} are the cross sections of the absorption and scattering, respectively. The green dashed curve in Fig. 2 is the theoretical best fit to the experimental curve for the hollow spheres, computed with MATLAB program[15] with the following parameters: $m_1=1.0$ (fixed), $m_2=2.55+0.70i$, $r_1=285$ nm (fixed), and $r_2=325$ nm (fixed). The obtained m_2 values are consistent with the reported values for bulk magnetite.[16] The theoretical curve can explain the weak reflectance peak at around 725 nm and the higher one at 510 nm, though it displays an extra peak at 425 nm. This disagreement is presumably caused by the size distribution and/or the presence of partially broken particles in the present sample.

For the dense particles, which can be regarded as a homogeneous medium, we carried out the simulation of the reflectance spectra using Eqs. (1) and (2), only by setting $m_1=m_2=m$ and then $A_n=B_n=0$. The coefficients a_n and b_n become those for a homogeneous sphere.[13,15] The black dashed curve in Fig. 2 shows the results of this simulation with the refractive index $m=2.55+0.70i$, which is the value optimized above, and the particle radius $r_2=410$ nm. The theoretical one well reproduces the weak wavelength dependence of the dense particles. Although the dense particles had a noticeable size distribution, the calculated reflectance spectra did not show large differences by setting the radius r_2 from 250 to 450 nm. It is notable that this feature is caused mainly by the light absorption in the visible range due to the dense structure; the absorption of the hollow spheres is much weaker than that of the dense particle due to its low-density structure. It is concluded that the green color of the hollow spheres can be explained in terms of the Mie scattering, as an inevitable property of the particle size of 650 nm and the peculiar hollow structure.

Magnetite is a low magnetocrystalline-anisotropy material, but usually its thin films exhibit a two-dimensional (2D) shape anisotropy; with magnetizations lying in film plane.[17] However, the shape and size of the hollow spheres suggest magnetic isotropy in thin films as an intriguing property of the present particles. We carried out magnetic measurements on thin films of the magnetite hollow spheres and dense particles. Figures 1(e) and 1(f) show their scanning electron microscope (SEM) images and photographs (inset); the particles are rather densely packed and there is no essential difference in packing and surface morphology between the two samples. Field dependence of the magnetizations of the films was measured at 300 K under magnetic fields parallel and perpendicular to the 2D film on a Quantum Design MPMS XL susceptometer with a horizontal sample rotator. The results for the hollow and dense particles are shown in Figs. 3(a) and 3(b), respectively. The blue and red curves indicate the magnetizations parallel and perpendicular to the 2D layer, respectively. While the multilayer thin films of the dense particles clearly exhibit the magnetic anisotropy especially below 0.5 T [Fig. 3(b)], as expected from the usual magnetite thin films, the parallel and perpendicular magnetization curves for the hollow spheres are superimposed [Fig. 3(a)], indicating no magnetic anisotropy in this thin film.

Regarding the one-particle magnetization, there should be no magnetic anisotropy in both the hollow and dense spheres. Therefore, the anisotropy of the dense spheres is considered to be caused by the interparticle magnetic dipole-dipole interactions. Since the hollow spheres are low spin-density magnets, such magnetic interactions between the hollow magnets would be very much weaker than those in the dense particles.

It is noteworthy that the *M-H* curves for the hollow-sphere film exhibit a higher coercivity (7 mT) than that of the dense-particle film (<2 mT) (Fig. 3). It is considered that the interparticle contacts would operate as pins for the magnetization changes and such a pinning would be more effective for the surface magnetizations of the hollow spheres than the magnetizations in the core part of the dense particles.[9,18]

In conclusion, the unusual green color and magnetic isotropy of magnetite caused by the effects of the submicron size and the hollow structure are demonstrated. The green color opens a promising way to design novel magneto-optical function of magnetite materials; we are exploring wavelength specific Kerr and/or Faraday effects. The completely isotropic magnetization of the hollow spheres indicates an advanced methodology for the suppression of magnetic anisotropy. More importantly, the results presented here imply a facilitated route to tune physical properties (such as color change) through the construction of hollow structures.

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