Synthesis and characterization of core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ fluorescent magnetic nanoparticles

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We report on the successful preparation and characterization of fluorescent magnetic core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ nanoparticles (NPs) with a spherical shape by organometallic synthesis. The 7 nm core/3 nm shell NPs show good magnetic and photoluminescence (PL) responses. The observed PL emission/excitation spectra are shifted to shorter wavelengths, compared to a reference ZnSe NP sample. A dramatic reduction of PL quantum yield is also observed. The temperature dependence of the magnetization for the core/shell NPs shows the characteristic features of two coexisting and interacting magnetic (Fe_3O_4) and nonmagnetic (ZnSe) phases. Compared to a reference Fe_3O_4 NP sample, the room-temperature Néel relaxation time in core/shell NPs is three times longer.

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Engineered multifunctional nanoparticles (NPs) with highly integrated imaging modalities are a key focus area in bionanotechnology that will have a profound impact on molecular diagnosis, imaging, and therapeutics.^{1–3} However, combining multiple components on a nanometer scale to create new imaging modalities not available from the individual components has proven to be challenging.⁴ An example of such multifunctional NPs are fluorescent magnetic NPs that bear two attractive features, fluorescence and superparamagnetism, allowing their intracellular movements to be controlled using magnetic force and monitored using a fluorescent microscope. These features could lead to effective multifunctional drug-loaded magnetic NPs that would facilitate increased drug transport rates, mucus penetration, and antibiotic efficiency in biofilms.¹ In this paper, we have used a two-step solution phase route to prepare cadmium-free core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ colloidal NPs with a spherical shape. Both individual components show good characteristics in terms of good chemical stability, biocompatibility, and low toxicity.

Bulk magnetite Fe_3O_4 is a mixed-valence $3d$ transition metal compound. It has an inverted cubic spinel structure, in which tetrahedral A sites contain one-third of the Fe ions as Fe^{3+} , whereas octahedral B sites contain the remaining Fe ions, with equal numbers of Fe^{2+} and Fe^{3+} at $B1$ and $B2$ sites, respectively. Below 860 K, bulk magnetite is ferromagnetic, with the A -site magnetic moments aligned antiparallel to the B -site moments. Photoemission measurements clearly showed a gap of ~ 0.14 eV in the spectra.⁵

ZnSe has a room temperature bulk bandgap of 2.7 eV (460 nm). ZnSe shells have long been used as a capping material for CdSe-core quantum dots (QDs) for surface passivation and biological labeling reagents. The organometallic synthesis of pure band-edge fluorescent ZnSe size-tunable QDs has been reported to result in highly luminescent UV-blue NP materials with bandgaps tunable between 2.8 and 3.4 eV and a quantum yield (QY) between 20% and 50%.⁶ More recently, Cozzoli *et al.* studied the shape and phase control of colloidal ZnSe NPs, where the as-prepared NPs exhibited distinguishable, shape-dependent optical properties in the UV-blue region.⁷ They observed that a red-shift of the bandgap in longer nanorods, or in general branched nanostructures with long rod sections, was generally accompanied by a significant decrease in the photoluminescence (PL) QY, which could be much lower than 1% for the branched structures.

Considering the characteristics of both individual materials described above, we note that in the simple approach of dimer particles, i.e., magnetite NPs attached to semiconductor QDs, such as ZnSe, PL emission from these multifunctional NPs should be expected to be strongly reduced due to the fact that magnetite is a semimetal with a much smaller bandgap than ZnSe, providing a leakage path to electrons excited in ZnSe. Similar problem should be expected with multifunctional NPs involving other semiconductor materials, such as CdSe with a bulk bandgap of ~ 1.75 eV. However, it has been shown that multicomponent CdSe/iron oxide core/shell and dimer NPs can have good PL efficiency.⁴

All NPs described in this paper were synthesized using standard air-free procedures and commercially available reagents. The main reaction involves the nucleation and growth of nominally Fe_3O_4 NPs with a mean size of 7 nm

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FIG. 1. (Color online) TEM image of (a) reference Fe_3O_4 NPs and (b) core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NPs. The white circles indicate the Fe_3O_4 core (lighter) and ZnSe shell (darker). Inset: HR-TEM image of the core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NPs. (c) EDS spectrum measured for the core/shell NPs. The Cu and C peaks originate from the holding grid.

and a size deviation of ~ 1.2 nm. Briefly, following a modified procedure of Sun and Zeng,⁸ a solution of iron (III) acetylacetonate [$\text{Fe}(\text{acac})_3$, 2 mmol] in the presence of 1,2-hexadecanediol (10 mmol) and the surfactants oleic acid (6 mmol) and oleylamine (OLA, 6 mmol) in octyl ether (30 mL) was heated to reflux for 1 h. The obtained black-brown reference sample was labeled as Fe_3O_4 NPs and was used thereafter as a seed for the core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NP growth. In a typical procedure, modified after Zhong *et al.*,⁹ 2 mL of the reference Fe_3O_4 NP sample in 1-octadecene (ODE, 0.05 g/mL) was transferred into a reaction flask and mixed with 8.4 mmol of OLA and ODE (3 mL) at 120°C in an inert Ar atmosphere under vigorous stirring. Subsequently, zinc oleate/OLA/ODE precursor (6.3 mL) was injected into the flask at 120°C , and the solution was purged with Ar for 30 min. The solution was then heated up to 300°C , and a selenium powder/trioctyl phosphine/ODE mixture (6 mL) was quickly injected. After 10 min at 300°C , the final black-brown solution was cooled to room temperature. The obtained NPs were easily dispersed in nonpolar solvents such as hexane or chloroform. This sample was labeled as $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NPs. Alternatively, the light-yellow reference sample of ZnSe NPs with a mean size of 3.5 nm and a narrow size distribution ($\sigma=0.15$) was synthesized following the modified procedure of Zhong *et al.*⁹ This reference sample was labeled as ZnSe NPs.

Figure 1 shows TEM images of Fe_3O_4 NPs [Fig. 1(a)] and core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NPs [Fig. 1(b)]. For the core/shell NPs [Fig. 1(b)], the TEM images confirm the presence of regions of two different contrasts in the morphology of the majority of the particles. Roughly, the TEM signal at every projected point of a particle with a constant density is inversely proportional to Z^2 , with the thickness of the material being much less important.¹⁰ Therefore, the ZnSe particles, which have a higher Z (mean value of 32) compared with the Fe_3O_4 particles (mean value of $Z \approx 15.7$), are imaged as darker objects. From the shape of the particles, we can infer that Fe_3O_4 NPs play the role of seeding sites for ZnSe growth, leading to the appearance of core/shell spherical NPs. The size of the core/shell NPs is estimated as a diameter of 6.8 ± 1.5 nm for Fe_3O_4 cores and a thickness of 3.8 ± 1.2 nm for ZnSe shells, which is in a good agreement with the diameter of 7 nm for the reference Fe_3O_4 sample. The elemental presence of Zn, Se, and Fe in the composition of the synthesized core/shell NPs was verified by energy dispersive x-ray spectroscopy (EDS), as shown in Fig. 1(c).

Figure 2 shows the XRD patterns ($\text{CuK}\alpha$, $\lambda_{\text{ave}} = 0.15418$ nm) for the ZnSe and Fe_3O_4 reference samples and for the core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ sample. The pattern for the ZnSe NPs [Fig. 2(a)] indicates that the NPs have a noncentrosymmetric cubic $F43m$ symmetry, as expected from the bulk crystal structure. The peaks are broader for the smaller nanocrystals, but the pattern is centered on the bulk crystal lines, with no other features. For the Fe_3O_4 NPs [Fig. 2(b)], the broad and relatively low signal-to-noise ratio peaks corresponding to magnetite Fe_3O_4 (cubic phase, $Fd3m$) suggest a short crystalline order and an internal polycrystalline structure in the particles. Taking the full width at half-maximum of the most intense peak and using the Scherrer equation, we determined the lower bound on the average crystalline size to be 4.0 ± 0.9 nm for the ZnSe NPs and 4.7 ± 1.5 nm for the Fe_3O_4 NPs. While these values are in good agreement with the morphological information obtained from the TEM images for the

FIG. 2. Powder XRD patterns for the reference (a) ZnSe NPs, (b) Fe_3O_4 NPs, and (c) core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NPs. The positions of the ZnSe and Fe_3O_4 (coinciding with Fe_2O_3) lines taken from the International Centre for Diffraction Data database are indicated at the top of the figure.

FIG. 3. (Color online) (a) Magnetization against T under ZFC and FC conditions for the reference Fe_3O_4 and core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NP samples. (b) PLE and PL spectra measured at room temperature for the reference ZnSe and core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NP samples.

ZnSe NPs, the agreement is not so good for the Fe_3O_4 NPs. The discrepancy in particle sizes obtained from TEM and XRD analyses has been frequently observed in this type of iron oxide compound synthesized by chemical methods, which is explained by polycrystalline structure of the compound.

It should be noted that the lattice parameters of the spinel structures, magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), are quite similar. Because the XRD lines of the NP samples are broadened, it is difficult to distinguish between magnetite and maghemite NPs by XRD.^{8,11} However, the decomposition of $\text{Fe}(\text{acac})_3$ at high temperature has been claimed to lead to magnetite as the final product⁸; hence we ascribe a magnetite structure to our iron oxide NPs.

The $\text{Fe}_3\text{O}_4/\text{ZnSe}$ XRD pattern [Fig. 2(c)] shows a strong contribution from the peaks originating from ZnSe and a much weaker contribution from the broad peaks of magnetite. The detailed analysis of the peak positions and their relative intensities confirms a lattice expansion for the magnetite that has been estimated to be $d_{511} = 1.64(3)$ Å, which is 2% larger than the corresponding value for the reference Fe_3O_4 sample [$d_{511} = 1.60(5)$ Å], a tendency also observed in dimer $\text{Ag-Fe}_3\text{O}_4$ NPs.¹⁰ At the same time, no sign of lattice distortion is observed in the ZnSe -related peaks in the core/shell NPs.

Figure 3(a) shows the T dependence of the magnetization for the reference Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NP samples under zero-field-cooling (ZFC) and field-cooling (FC) conditions ($H = 20$ Oe). The samples were prepared in a powder form and encased in a gelatin capsule. The shape of the $M_{\text{ZFC-FC}}$ magnetization curves for the reference magnetite sample is that typically observed for monodispersed weakly dipole-dipole interacting systems of randomly oriented NPs, where the M_{ZFC} curve shows a maximum at $T_M = 32$ K and the M_{FC} curve monotonically rises as T decreases. For the core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NPs, the M_{ZFC} curve clearly shows a shift to higher temperatures, with a maximum at $T_M = 45$ K. Furthermore, the M_{FC} monotonically rises as T decreases, and eventually saturates at temperatures below 41 K. The increase in T_M from 32 K to 45 K corresponds to a slight enhancement of the magnetic anisotropy in the $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NPs. Moreover, the shift in the energy barrier E_B to higher values for the core/shell NPs should be critical in the super-

paramagnetic response at room temperature. According to the Néel relaxation model, $\tau_N = \tau_0 \exp(\sigma)$, where $\tau_0 \sim 10^{-10}$ s, σ is the ratio of anisotropy energy to thermal energy ($E_B/k_B T$), and k_B is the Boltzmann constant. Therefore, the increase of $\Delta E_B/k_B = 28 \cdot (45 \text{ K} - 32 \text{ K}) = 364 \text{ K}$ corresponds to a three-fold increase in the Néel relaxation time τ_N at room temperature. In good agreement with the M versus T experiments, the increase in the coercive field from 250 Oe to 390 Oe is obtained at $T = 2$ K (figure not shown), and both samples are superparamagnetic at room temperature, i.e., without coercivity or memory effects.

The photoluminescence excitation (PLE) and PL spectra measured at room temperature for the reference ZnSe and core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NP samples are compared in Fig. 3(b). The core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NPs demonstrate a significant blue-shift in PL excitation/emission spectra as compared to the reference ZnSe NPs. In particular, the PL excitation/emission peaks are shifted from 377 nm to 325 nm and from 433 nm to 390 nm, respectively. The observed effect is primarily due to a change of shape between spherical ZnSe NPs and nanoshell ZnSe emitters in core/shell NPs. Most dramatically, the QY dropped from 10% for the reference ZnSe NPs to 1% for the core/shell NPs. We ascribe this effect to carrier leakage at the interface between Fe_3O_4 and ZnSe in the core/shell NPs. Alternatively, the reduction of the QY in the ZnSe component of the core/shell NPs may be explained by the change in its geometry from spherical to a nanoshell.

In summary, we report a new colloidal synthesis method to obtain core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NPs. By comparing the magnetic properties of the reference Fe_3O_4 NPs and the core/shell $\text{Fe}_3\text{O}_4/\text{ZnSe}$ NPs, we have shown the enhancement of the energy barrier in the core/shell composite NPs. This effect directly modifies the relaxation time, which is of fundamental interest to biomedical applications. The synthesized magnetic core/shell NPs demonstrated PL activity. However, the multi-component NPs showed a considerable reduction in QY from 10% to 1%, which could be attributed to the interface effects between the Fe_3O_4 and ZnSe components.

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