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Communication

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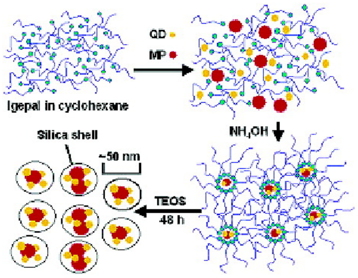

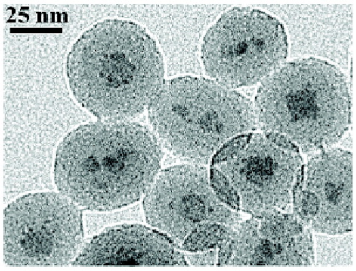

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Silica-Coated Nanocomposites of Magnetic Nanoparticles and Quantum Dots

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In this communication, we report the synthesis of a novel water-soluble hybrid material consisting of quantum dots (QDs) and magnetic nanoparticles (MPs) encapsulated in a silica shell. QDs or semiconductor nanocrystals have been extensively studied for their unique optical and electronic properties,[1,2] sharp emission band with broad excitation, and strong resistance to photobleaching. They are of great interest for their dimensional similarities to bio-macromolecules (e.g., DNA and protein) and for applications in biological imaging[3] and bioconjugation.[4] Superparamagnetic nanoparticles have been studied for biomedical applications,[5] such as MRI contrast enhancement,[6] magnetic immobilization, and drug targeting.[7] For many applications, these nanoparticles would benefit from having a silica shell to impart wettability and biocompatibility. Silica can also be easily surface modified to link bioconjugators, such as avidin, with interesting biofunctionalities. Herein we describe the encapsulation of both MPs and QDs within a silica shell to form a hybrid material denoted as SiO_2/MP−QD. Although MP−QD systems have been examined before,[8] SiO_2/MP−QD nanocomposites have not yet been reported. These materials have potential in bioimaging, drug targeting, biosensing, and biolabeling applications; their core−shell asymmetric refractive property has promise for novel optical communication systems such as photonic crystals. Silica-capped QDs have been achieved using alkoxysilane with a silica shell thickness ranging from 2−5 nm[9a] to 40−80 nm.[9b] QDs have also been coated with silica with a reverse microemulsion approach.[10] MP encapsulation within silica has been attained through modified Stöber method[11] and reverse microemulsion.[12] *In situ* reverse microemulsion synthesis generally led to poorly crystalline magnetic cores. Therefore, magnetic cores were prepared separately, prior to silica capping.[12a]

A two-step synthesis was used to derive SiO_2/MP−QD (see Scheme 1). MPs and QDs were first prepared separately, prior to their introduction to the reverse microemulsion medium for silica coating. Specifically, polyoxyethylene(5)nonylphenyl ether (0.544 mmol, Igepal CO-520, containing 50 mol % hydrophilic group) was dispersed in cyclohexane (4.5 mL) by sonication. Next, 400 μL of γ-Fe_2O_3 solution[13] (0.5 mg/mL of cyclohexane) and 160 μL of CdSe QD solution[14] (1 mg/mL of cyclohexane) were added. The resulting mixture was vortexed, and ammonium hydroxide (29.4%, 40 μL) was added to form a transparent, brown solution of reverse microemulsion. Last, tetraethyl orthosilicate (TEOS, 30 μL, Aldrich) was added, and the reaction was continued for ≤48 h. The resulting SiO_2/MP−QD nanocomposite particles were collected by magnet or centrifuging, washed, and redispersed in ethanol or deionized water.

Transmission electron microscopy (TEM) images showed that the MPs were monodispersed (11.8 ± 1.3 nm in diameter) and single crystalline (Figure 1a and inset). X-ray diffraction (XRD) pattern, as well as X-ray photoelectron Fe($2p_{3/2}$) and Fe($2p_{1/2}$) peaks at 711.4 and 724.7 eV, respectively, confirmed that the MPs were γ-Fe_2O_3 crystallites (see Supporting Information, SI). When only MPs were introduced for silica encapsulation, the resulting particles could include one, two, or three MPs each (Figure 1b). Uniform particles containing a single MP and tailored SiO_2 shell thickness could be derived under controlled experimental conditions.[15]

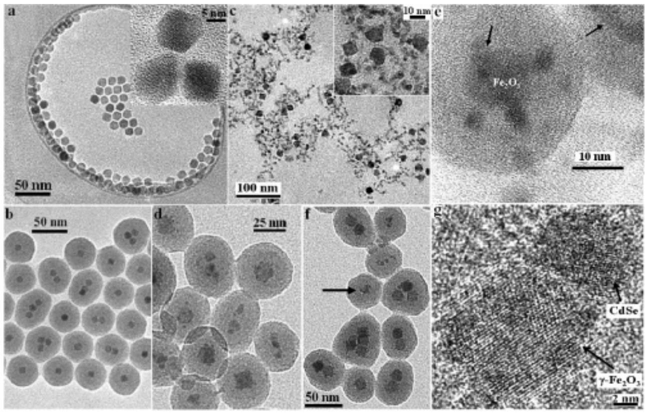
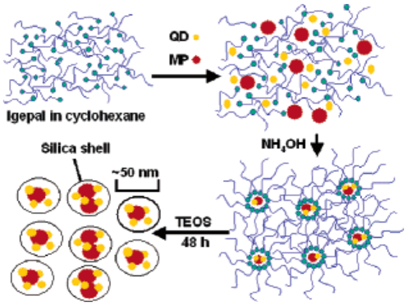


Figure 1. TEM micrographs of (a) γ-Fe_2O_3 MPs, (b) SiO_2/MP, (c) interconnected MPs and CdSe QDs (after 8 h of SiO_2/MP−QD reaction), (d,e) SiO_2/MP−QD nanocomposites (after 48 h of SiO_2/MP−QD reaction; note the presence of both Fe_2O_3 MPs and CdSe QDs (finer crystallites denoted by arrows in panel e), and (f) SiO_2/MP−QD nanocomposites formed at a lower CdSe concentration (0.5 mg/mL of cyclohexane). (g) High-resolution TEM micrograph of the area marked by the arrow in (f), showing the presence of CdSe QDs and γ-Fe_2O_3 MPs.

Scheme 1. Synthesis of SiO_2/MP−QD Nanocomposites



For SiO_2/MP−QD synthesis, MPs (~11.8 nm) and QDs (~3.5 nm) were shown to form silica-mediated conjugation within 8 h of reaction, but spherical shells were not achieved at this initial stage (see Figure 1c and inset). Energy-dispersive X-ray (EDX) analysis indicated the presence of CdSe, Fe_2O_3, and silica (see SI). After 48 h of reaction, silica shells were observed to have developed around the MP−QD cores (Figure 1d). Although spatial discrepancies between QDs and MPs within the silica shell caused the MPs to be out of focus, QDs were clearly seen (marked by arrows

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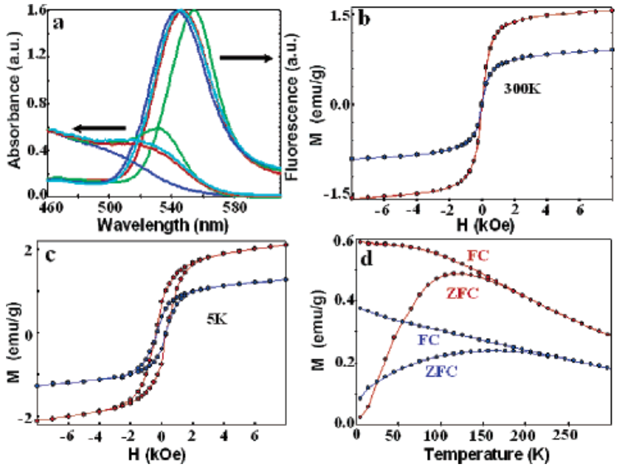

Figure 2. (a) UV−vis and normalized fluorescence spectra ($\lambda_{ex} = 365$ nm) of CdSe QDs (green), SiO_2/MP−CdSe after 8 h (red) and 48 h (blue) of reaction, and SiO_2/MP−ZnS-capped CdSe after 48 h of reaction (cyan). Field-dependent magnetization at (b) 300 K and (c) 5 K, and (d) temperature-dependent magnetization at 100 Oe for SiO_2/MP (red) and SiO_2/MP−CdSe (blue).

in Figure 1e). Even at a lower QD concentration of 0.5 mg/mL of cyclohexane, both QDs and MPs were successfully encapsulated in the silica shells (Figure 1f,g). EDX analysis of the region shown in Figure 1g confirmed the presence of CdSe, Fe_2O_3, and silica (see SI). N_2 sorption isotherm of the SiO_2/MP−QD particles indicated that the silica shells were nonporous (see SI).

Bare CdSe showed an absorption peak at 530 nm and an emission peak at 554 nm. As the silica coating reaction proceeded from 8 to 48 h, the absorption peak shifted to lower wavelength and became less pronounced. This blue shift was also observed in the fluorescence spectra, and the excitonic band became broader (Figure 2a). The quantum yield (QY) of the emission was estimated to be 11.4% for CdSe, and 3.2% and 1.1% for SiO_2/MP−QD 8 and 48 h after the coating reaction, respectively; ethanol-solubilized Rhodamine 6G (QY = 94%) was used as a reference dye.[16] The QY of SiO_2/MP−QD was increased to 4.8% when ZnS-capped CdSe QDs (QY = 14.5%) were used. Magnetic characterization was performed using a superconducting quantum interference device (SQUID). Field-dependent magnetization plots illustrated that both SiO_2/MP and SiO_2/MP−QD particles were superparamagnetic at 300 K (Figure 2b) and hysteretic at 5 K (Figure 2c). SiO_2/MP particles showed higher magnetization compared to SiO_2/MP−QD particles at both 5 and 300 K. These raw data were presented in electromagnetic units per gram of sample. When normalized to the γ-Fe_2O_3 content in each sample, magnetization values in electromagnetic units per gram of γ-Fe_2O_3 were found to be similar for SiO_2/MP and SiO_2/MP−QD within experimental uncertainty (see SI).

The coercivity values of SiO_2/MP and SiO_2/MP−QD were similar at 5 K (Figure 2c). Zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves were obtained under an applied field of 100 Oe between 5 and 300 K (Figure 2d). They exhibited the typical behavior of γ-Fe_2O_3 nanoparticles.[13] The blocking temperatures (T_B) were 125 and 165 K for SiO_2/MP and SiO_2/MP−CdSe particles, respectively, which were comparable to that of γ-Fe_2O_3 nanoparticles.[13] For uniaxial anisotropy, the superparamagnetic relaxation time is given by $\tau_s = \tau_0 \exp(KV/k_BT)$,[17] where τ_0 is a constant on the order of 10^{-9} s, and V is the particle volume. For our γ-Fe_2O_3-containing SiO_2/MP and SiO_2/MP−CdSe particles, the magnetic anisotropy density (K) was 0.39×10^5 J/m^3 and 0.51×10^5 J/m^3, respectively, assuming a SQUID characteristic measuring time of 10 s. The presence of CdSe increased the effective magnetic anisotropy of the γ-Fe_2O_3-containing particles, indicating that the QDs were closely connected to the MPs. In conclusion, the SiO_2/MP−QD nanocomposite particles preserved the unique magnetic property of γ-Fe_2O_3 and optical property of CdSe QDs.

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Supporting Information Available: Enlarged images for Figures 1 and 2, EDX, XRD, X-ray photoelectron spectroscopy (XPS), N_2 sorption isotherm, normalized magnetization data, and detailed experimental procedure for SiO_2/MP−QD preparation. This material is available free of charge via the Internet at http://pubs.acs.org.

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