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Silica Encapsulation of Ferrimagnetic Zinc Ferrite Nanocubes Enabled by Layer-by-layer Polyelectrolyte Deposition

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Abstract

Stable suspensions of magnetic nanoparticles (MNPs) with large magnetic moment, m , per particle have tremendous utility in a wide range of biological applications. However, due to the strong magnetic coupling interactions often present in these systems, it is challenging to stabilize individual, high moment, ferro- and ferrimagnetic nanoparticles. A novel approach to encapsulate large, *i.e.*, >100 nm, ferrimagnetic zinc ferrite nanocubes (ZFNCs) with silica after an intermediary layer-by-layer polyelectrolyte deposition step is described in this paper. The seed ZFNCs are uniform in shape and size and have high saturation mass magnetic moment ($\sigma_s \sim 100$ emu/g, $m \sim 4 \times 10^{-13}$ emu/particle at 150 Oe). For the MNP system described within, successful silica encapsulation and creation of discrete ZFNCs were realized only after depositing polyelectrolyte multilayers composed of alternating polyallylamine and polystyrene sulfonate. Without the intermediary polyelectrolyte layers, magnetic dipole-dipole interactions led to the formation of linearly chained ZFNCs embedded in a silica matrix. Characterization of particle samples was performed by electron microscopy, energy-dispersive X-ray spectroscopy, infrared spectroscopy, powder X-ray diffraction, dynamic light scattering (hydrodynamic size and ζ -potential), and vibrating sample magnetometry. The results of these characterizations, which were performed after each of the synthetic steps, and synthetic details are presented.

Keywords

magnetic nanoparticle interaction; silica encapsulation; zinc ferrite nanocubes; layer-by-layer deposition; polyelectrolyte

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Supporting Information. Further characterization data is supplied as Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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NOTES

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INTRODUCTION

The synthesis and preparation of magnetic nanoparticles (MNPs) with large magnetic dipole moments, m , have been gaining traction in a variety of technologies, including those focused on magnetic recording media,¹ biological² and environmental separations,³ chemical catalysis,⁴ nanomedicine,⁵ ferrofluid applications,⁶ magnetic resonance imaging (MRI) contrast reagents,⁷ and biosensors.^{8, 9} However, one of the shortcomings of high m MNPs is their tendency to spontaneously aggregate. Approaches to prevent MNP aggregation include creating a shell around the MNPs,¹⁰ fabricating synthetic antiferromagnetic nanoparticles,^{3, 11} or decreasing the MNP size until superparamagnetic behavior is observed.¹² Superparamagnetism (at 298 K) occurs in single-domain ferro- and ferrimagnetic nanoparticles of sufficiently small size that their magnetic dipole undergoes random thermal fluctuations in the absence of an external magnetic field (H); this situation results in the absence of an observable moment.¹³ Despite the advantage of zero residual magnetism afforded by superparamagnetic nanoparticles (SPMNPs), the diminution in MNP size results in a commensurate decrease in m , which can limit utility. For example, the signal-to-noise ratio of a magnetic biosensor is proportional to m , and MNPs with large m are generally required in magnetic drug delivery and cell separation. SPMNPs are also not suitable for permanent magnetic storage media, which require ferro- or ferrimagnetic nanoparticles (FMNPs) with nonzero coercivity (H_C) and remanent magnetization (M_R).

In addition to tailoring MNP size to counteract magnetic interparticle attraction, several particle-coating strategies have been used with similar results. Simple surface-ligand exchange has been used to effectively stabilize SPMNP dispersions.¹⁴⁻¹⁶ However, ligand-exchange does not mitigate the aggregation of FMNPs. In these cases, polymeric coatings have been employed to avoid magnetically induced aggregation during and after synthesis. The charged or polar groups of the polymer stabilize moderate m MNPs via electrostatic repulsion and the physical coating limits particle-particle approach distance.¹⁷⁻¹⁹ In instances of large m FMNPs, extraordinarily strong electrostatic repulsion or an increase in the MNP-MNP closest-approach induced by thicker polymeric coatings is necessary to produce a stable FMNP colloid.¹⁷⁻¹⁹ The effectiveness of these polymeric coatings, however, is generally limited to FMNPs smaller than 50 nm in size.

Another means to overcome magnetic-induced aggregation is to encapsulate MNPs in a shell of gold, graphite, or silica creating a core-shell architecture (core@shell).¹⁵ This form of encapsulation has several advantages over other coating strategies: 1) it can increase the MNP-MNP closest approach distance thereby reducing interparticle interactions; 2) it protects the magnetic core from dissolution; and 3) it can be modified with molecular recognition elements (*e.g.*, antibodies, nucleic acids) by established linking chemistries. Among those coating materials, silica is biocompatible and can further enhance colloidal stability in aqueous media since the terminal hydroxyl groups are ionized at the pH of physiologically relevant matrices.²⁰ Although the application of silica coatings on small FMNPs has been reported,¹ there are few reports detailing the encapsulation of large FMNPs with high m . In these scenarios, silica encapsulation often leads to aggregates of particles embedded in a silica matrix.²¹⁻²³ However, Kolhatkar et al. have reported that FeCo ferromagnetic nanocubes (>150 nm in size) with a high saturation magnetization, M_s ,

could be coated with silica after stabilizing with a layer of polyvinylpyrrolidone (PVP),¹⁰ and Marcelo et al. described the stabilization of hydrophobic Fe₃O₄ ferrimagnetic nanocubes (>70 nm in size) in water by coating the particles with silica under sonication after citric acid ligand-exchange.²⁴ While it appears that these intermediary coating procedures were sufficient to stabilize the particles prior to silica encapsulation, it is not clear that a high yield of single-core, silica-coated MNPs was realized. In our experience, these methods are not effective in stabilizing >100 nm zinc ferrite nanocubes with $M_s \sim 100$ emu/g.

Herein, we report a novel method for the production of discrete, silica-coated ferrimagnetic zinc ferrite nanocubes (ZFNCs). High-moment ($m \sim 10$ -13 emu/particle at $H = 150$ Oe) ZFNC seeds (~ 130 nm) were first prepared via thermal decomposition in benzyl ether and oleic acid. The resulting hydrophobic oleic acid surface-molecules of as-synthesized ZFNCs were replaced with a hydrophilic ligand and transferred to aqueous media. To further increase the suspension stability of the seed ZFNCs, a total of six layers of two alternating polyelectrolytes, polyallylamine (PAAm) and polystyrene sulfonate (PSS), were deposited by a layer-by-layer (LbL) process. The LbL-stabilized ZFNCs were then encapsulated with silica, resulting in primarily discrete silica-coated ZFNC (ZFNC@SiO₂) particles. The ZFNC@SiO₂ particles were characterized by electron microscopy, energy dispersive X-ray spectroscopy, powder X-ray diffraction, dynamic light scattering, infrared spectroscopy, and vibrating sample magnetometry.

EXPERIMENTAL SECTION

Materials

Iron acetylacetonate (Fe(acac)₃, 99%), zinc acetyl-acetonate (Zn(acac)₂, 95%), benzyl ether (99%), tetraethyl orthosilicate (TEOS, 95%), dimercaptosuccinic acid (DMSA, 99%) and poly(sodium-p-styrene sulfonate) (PSS, linear, $M_w \sim 70,000$ g/mol) were purchased from Acros organics (USA). Polyethyleneimine (PEI, branched, $M_w \sim 25,000$ g/mol) and citric acid (CA, 99%) were received from Sigma-Aldrich (USA). Polyallylamine hydrochloride (PAAm, linear, $120,000 < M_w < 200,000$ g/mol), oleic acid (90%) and ammonium hydroxide (NH₄OH, 30%) were purchased from Alfa Aesar (USA). Ethanol (EtOH, 200 proof) was acquired from Decon Lab (USA). Dimethyl sulfoxide (DMSO, 99%) and toluene (99%) were obtained from Fisher Scientific (USA). All chemicals were used as-received without further purification.

Synthesis of Magnetic Nanoparticles

The synthesis of cubic ferrimagnetic nanoparticles was adapted from the procedure of Noh et al.²⁵ Typically, 0.353 g Fe(acac)₃ and 0.395 g Zn(acac)₂ were added to a mixture of 1.2 mL oleic acid and 10.0 mL benzyl ether. This solution was heated under nitrogen at a rate of 15 °C/min to 290 °C and then refluxed for 30 min. After cooling to room temperature, 20 mL of EtOH was added to precipitate cubic zinc ferrite particles. The sample was then centrifuged at 10,190×g for 10 min and the supernatant was discarded. This washing procedure was repeated two more times. The MNPs were finally resuspended in 10 mL of toluene.

Ligand-exchange of Magnetic Nanoparticles

Surface functionalization with a hydrophilic exchange ligand (*i.e.*, CA, DMSA, and PEI) was used to transform the as-prepared hydrophobic ZFNCs to a hydrophilic state for subsequent suspension in water. A 10 mL aliquot of ligand solution (ligand concentration ~70 mg/mL in DMSO) was added to the MNP suspension, followed by a 3-h sonication at 60 °C and agitation on a rocking table for 16 h. The hydrophilic, ligand-coated MNPs were next washed three times with 10 mL EtOH and resuspended in 18.2 MΩ-cm deionized water (DI H₂O). The final concentration of the ligand-exchanged MNPs was ~5 mg/mL.

Layer-by-layer (LbL) Deposition of Polyelectrolytes

Prior to LbL deposition, 1.0 mL of the PEI-coated zinc ferrite particles (~5 mg) was diluted to 10 mL with DI H₂O. This step was followed by the addition of 5.0 mL aqueous PSS (10 mg/mL) and a 1-h sonication. Next, the excess PSS was centrifuged (10,190×g, 10 min) and the supernatant was removed. The MNPs were then resuspended in 10 mL DI H₂O and a 200 µL aliquot was removed for characterization. This process was repeated two more times. A subsequent layer of PAAm was formed using the same procedure with an aqueous solution of PAAm (10 mg/mL). These two deposition steps were repeated until the desired number of polyelectrolyte layers were deposited; typically six polyelectrolyte layers were deposited prior to silica coating. The terminal PAAm layer possessed a net positive surface charge (–NH₃⁺) in DI H₂O (pH = 6.5). The resulting MNPs were resuspended in DI H₂O to a final concentration of ~5 mg/mL.

Silica Coating

Silica was deposited on the polyelectrolyte-coated zinc ferrite seed particles by a modified Stöber method.²⁶ Briefly, 1.0 mL of the LbL-coated MNP suspension (~5 mg in DI H₂O) was added to 10 mL EtOH, followed by the sequential addition of 0.65 mL DI H₂O and 1.0 mL TEOS solution (25 µL/mL in EtOH) at room temperature. The magnetic suspension was sonicated for 90 min after which 0.98 mL NH₄OH was added drop-wise to the suspension with continued sonication. Then, another 1.0 mL of TEOS solution was added drop-wise, which was followed by a 90-min sonication, and then agitation on a rocker plate for 18 h. The silica-coated MNPs were isolated after three centrifugation (10,190×g, 10 min) steps in EtOH and a final resuspension in 10 mL DI H₂O. The overall process is depicted in Scheme 1.

Electron Microscopy

Field-emission scanning electron microscopy (FESEM) was performed with a Hitachi S-4800 equipped with an energy dispersive X-ray (EDX, INCA, Oxford Instruments) spectroscopy module. In general, MNP samples for imaging and EDX analysis were prepared by pipetting 20 µL aqueous particle suspension onto a 1×1 cm silicon chip that was allowed to dry at ambient temperature. Images were obtained at an acceleration voltage of 15 kV.

For transmission electron microscopy (TEM), a JEM-2800 S/TEM instrument (JEOL, Japan) was used at 200 kV with the magnetic samples dropcast on a 3-mm carbon-coated

copper grid. EDX mapping data was collected with a 1 nm probe at a 512×512 pixel density, ~0.5 nm/pixel.

X-ray Diffraction (XRD) Analysis

The crystallinity of the MNPs was determined by powder X-ray diffraction (XRD, Rigaku, D/max-2200V, Japan). XRD was carried out with Cu K α radiation ($\lambda = 0.154059$ nm) and operated at 40 kV and 30 mA. The diffractograms were obtained with a 2θ step of 0.02° at 0.5 s/step from 15° - 100° . Three sample libraries, the International Centre for Diffraction Data (ICDD), the RUFF Project Database,²⁷ and the National Bureau of Standards X-ray diffraction powder pattern monograph,²⁸ were used for identification of samples.

Infrared (IR) Spectroscopy

IR transmission spectra were collected using a Nicolet Magna 850 Fourier transform IR spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride detector. Spectra were collected in a nitrogen atmosphere using 512 scans at a resolution of 0.198 cm^{-1} with p-polarized light. The MNP samples were prepared as 1% particle (w/w) dispersions in KBr.

Dynamic Light Scattering (DLS)

The zeta (ζ)-potential and hydrodynamic sizes of particle samples were measured using a Zetasizer Nano (Malvern Instruments, U.K.) with a disposable folded capillary cell. The particles were diluted to 0.1 wt % in DI H₂O. Nanoparticle suspensions were sonicated for 2 min before being injected into the cell and left to equilibrate for 2 min prior to measurement. The specific conditions for DLS measurement are described in the Supporting Information.

Vibrating Sample Magnetometry (VSM)

Magnetic hysteresis curves, isothermal remanent magnetization (IRM), and dc demagnetization (DCD) remanence measurements were carried out using a vibrating sample magnetometer (VSM EZ7, MicroSense, Lowell, MA) operated at 298 K. For the measurements, MNPs were mounted on a piece of Kapton tape which was folded in half and gently compressed in a pellet press to fix the particles to the tape and remove trapped air. Another piece of the tape without the MNPs served as the blank. The signal of the blank was subtracted from the sample signal. The particular procedures for IRM and DCD measurements are provided in the Supporting Information.

Throughout this work, we have adopted the convention of using the term magnetization, M , interchangeably with mass magnetic moment, σ . However, by definition, M has units of emu/cm^3 and σ has units of emu/g .

RESULTS AND DISCUSSION

Monodispersed ZFNC seed particles were synthesized by thermal decomposition of zinc and iron acetylacetonates.²⁵ Shown in Figure 1 is a representative SEM image of the as-synthesized ZFNCs and their size distribution. These cube-shaped particles have an average edge length of ~130 nm and their faces appear rough, which is usually found with particles

larger than 100 nm and is most likely due to crystalline defects and step edges. The as-synthesized particles are composed of Fe, O, and Zn and have an empirical formula of $[\text{Zn}_{0.41}\text{Fe}_{0.59}]\text{Fe}_2\text{O}_4$ determined by EDX (Figure S1). The X-ray powder diffractogram for the ZFNCs (Figure S2) shows that the particles are crystalline with characteristic diffraction peaks of magnetite (Fe_3O_4 , ICDD No. 01-086-0510 and RRUFF Database No. R080025) and zinc ferrite (ZnFe_2O_4 , NBS Monograph²⁹ and RRUFF Database No. R070137).

The ZFNCs then underwent a ligand-exchange process to replace the hydrophobic surface group, oleic acid,³⁰ with a hydrophilic species. We chose to study CA, DMSA, and branched PEI based on their previously demonstrated effectiveness as ligand-exchange agents.³¹ The ζ -potential values, which are an indication of surface charge and, therefore, colloidal stability, measured for the CA-, DMSA-, and PEI-coated ZFNCs were -6.5 ± 3.6 , -15.9 ± 4.6 , and $+52.7 \pm 4.4$ mV, respectively, in DI H_2O . The negative values for the first two systems are consistent with the deprotonation of the carboxylic acid groups of CA and DMSA, whereas the positive value for the third system follows the expectation for protonation of the PEI amine groups. Of the three ligand-exchanged ZFNCs, only the PEI-coated ZFNCs appear to have an absolute ζ -potential indicative of stable colloids ($|\zeta| > 30$ mV). Indeed, when the CA- and DMSA-coated ZFNCs were suspended in DI H_2O , they precipitated within 10 min. The PEI-coated ZFNCs, however, remained suspended in DI H_2O for a few hours. The colloidal stability due to PEI, compared to CA and DMSA, is believed to arise from: 1) the multivalent adsorption of the polymer, leading to stronger particle-polymer interactions compared to the adsorption of mono- or divalent ligands,^{32, 33} and 2) an increase in MNP-MNP separation due to PEI-induced steric hindrance and electrostatic repulsion of the profuse protonated amine groups. We note that the ligand-exchange procedures appeared to have no effect on the morphology of seed ZFNCs, which was investigated by SEM.

Once the ZFNCs were stabilized with PEI and effectively dispersed in aqueous media, silica encapsulation was attempted to create a potentially more suitable species for bioanalytical applications. Coating nanoparticles that possess a nonzero remanent magnetization with silica or metals can be problematic due to their tendency to aggregate, which is brought on by strong interparticle magnetic dipole-dipole interactions; indeed, there are only a few reports detailing the successful encapsulation of these particles.^{10, 24, 33} Shown in Figure 2 are SEM micrographs of the CA-, DMSA-, and PEI-modified ZFNCs after silica coating. While a one-step ligand-exchange successfully altered the surface properties of our ZFNCs (*i.e.*, from hydrophobic to hydrophilic), the particles tended to aggregate into linear chains during silica encapsulation. Individual ZFNC@ SiO_2 particles were not observed; rather, linear aggregates of ZFNCs embedded in a silica matrix were formed. It is important to note that the high ζ -potential of the PEI-coated ZFNCs, indicating strong electrostatic repulsion between PEI-modified ZFNCs, did not prevent the seed ZFNCs from aggregating during the silica coating procedure.

Linear or face-to-face assemblies of different MNPs are frequently observed in dispersions or silica matrices.³⁴⁻³⁶ The mechanism of MNP aggregation can involve several phenomena including Brownian motion (thermal energy), magnetostatic and electrostatic forces, and van der Waals interactions.³⁷ We believe that the linear arrangement of ZFNCs arises primarily

from interparticle magnetic dipole-dipole interactions. In other words, the magnetic dipole-dipole interaction between the nanocubes leading to the observed anisotropic structures (e.g., linear chains, flux-closure rings, etc.) is stronger than Brownian forces, van der Waals interactions, or electrostatic forces that are typically responsible for isotropic aggregation.³⁸

To prevent linear chain formation of the ZFNC seeds, a series of polyelectrolyte layers were applied to the seed ZFNCs using an LbL technique. The LbL deposition of polyelectrolytes is a versatile method used to create robust, polymeric multilayer structures.³⁹⁻⁴² In principle, fabrication of polyelectrolyte multilayers utilizes electrostatic interactions between oppositely charged polyelectrolytes, which enables cyclic deposition of oppositely charged polyelectrolytes. As a consequence, LbL deposition enables one not only to control the thickness of multilayers in nanometer scale, but also to take advantage of the polyelectrolyte charge. Of the potential polyelectrolytes, we opted to assess the utility of PSS and PAAm, which contain sulfonate and amine groups, respectively. As the PEI-coated seed ZFNCs were positively charged, PSS was deposited as the first polyelectrolyte, followed by the deposition of PAAm. We repeated this cycle until six polyelectrolyte layers were deposited. The deposition of each polyelectrolyte layer was characterized by ζ -potential and IR (Figure 3). The charge reversal between PSS layers (odd numbered) and PAAm terminal layers (even numbered) in Figure 3 (A) indicates that the sequential deposition of polyelectrolytes was successful. The IR spectra shown in Figure 3(B) follow the stepwise formation of ZNFC@SiO₂, starting with the PEI-coated ZFNCs (black line). All three spectra have strong bands around 580 cm⁻¹, which are associated with Fe-O lattice vibrations.⁴³ The features at 1560 and 1630 cm⁻¹ in the PEI-coated ZFNC sample are due to the NH and NH₂ deformation in PEI, and the broad band from 3200 to 3425 cm⁻¹ is assigned to the N-H stretching vibration.⁴⁴ These spectral features confirm the presence of PEI after ligand-exchange. After depositing the six polyelectrolyte layers (red line), sharp bands at 1007 and 1037 cm⁻¹ are observed and attributed to the S=O symmetrical stretching vibration and an aromatic in-plane vibration of PSS, respectively.⁴⁵ There is also a band around 1630 cm⁻¹, which is a bending mode of the primary amine in the PAAm layers.⁴⁶ The progression of spectral features support the successful deposition of PSS and PAAm polyelectrolyte layers on the ZFNC@PEI particles.

Discrete ZFNC@SiO₂ particles were subsequently formed using a modified Stöber procedure. The thickness of the silica layer was ~30 nm and the particles retained their cubic morphology (Figure 4). The discrete nature of the ZFNC@SiO₂ particles is observed by noting the distance between particles is twice the thickness of the silica shell. The IR spectrum of the silica-coated ZFNCs (green line in Figure 3) shows a broad, strong band at 1100 cm⁻¹, which arises from the asymmetric vibration of Si-O bonds. Strong asymmetric and symmetric vibrations of Si-OH and Si-O are observed at 950 and 795 cm⁻¹, respectively.⁴⁷ A broad band at 3500 cm⁻¹ and a slightly weaker band around 1600 cm⁻¹ are attributed to O-H stretching and bending vibrations, respectively; these two bands are likely from surface hydroxyl (-OH) groups of silica and adsorbed water.⁴⁸ The measured ζ -potential of ZFNC@SiO₂ particles in DI H₂O was -63.1 ± 7.0 mV, indicating that the surface (-OH) groups are deprotonated, which is consistent with pI of silica (~pH 2).²⁰ It should be noted that the XRD peaks of the silica-coated ZNFCs closely resemble the Bragg

reflections of the seed ZFNCs (Figure S2), indicating that the silica shell is amorphous and the crystallinity of the magnetic core is not affected by encapsulation.

The particle size progression of the PEI-, polyelectrolyte-, and silica-coated ZFNCs was also followed by DLS (Figure S3) and compared to the SEM micrograph analysis (Table S1). The average size of particle increases with synthesis step. The hydrodynamic size based on intensity distribution ($D_{h,int}$) of the PEI-coated ZFNCs was ~225 nm prior to LbL deposition. After the sequential deposition of six polyelectrolyte layers and silica coating, $D_{h,int}$ increased to 297 nm and 360 nm, respectively. Considering a sphere is the only object whose size can be correctly described by a single dimension in DLS, the $D_{h,int}$ of a cube is roughly interpreted as the maximum corner-to-corner dimension of that cube ($\sqrt{3}$ longer than a cube edge).⁴⁹ Therefore, the hydrodynamic size intensity distributions of the ZFNC@SiO₂ from the DLS measurements are consistent with those determined from SEM (Table S1).

EDX mapping analysis acquired during the course of TEM imaging provided chemical composition and elemental distribution information of discrete ZFNC@SiO₂ particles. Representative results are presented in Figure 5. The images indicate that Fe, Zn, and O are distributed throughout the particle core and the distribution of Si and S is weighted towards the encapsulating shell. It is important to note that polyelectrolyte layers deposited prior to silica encapsulation persist after silica coating. The S signal is presumed to be due to the presence of PSS between the core and the SiO₂ shell, which is clearly observed in Figure 5(A) — the composite of grayscale, Fe, Si, and S. The ability to capture intermediary components between the core and silica shell suggests that much smaller nanoparticles, fluorophores, or other materials could potentially be incorporated within the polyelectrolyte layers, creating multifunctional silica-coated ferrimagnetic nanoparticles. For example, by incorporating quantum dots within the multilayer polyelectrolyte structure, further development of multi-modal imaging and theranostic agents could be realized.⁵⁰

To delineate the effect that the number of polyelectrolyte layers has on the formation of ZFNC@SiO₂ particles, we attempted to silica coat the seed particles with different numbers of polyelectrolyte layers. The number of polyelectrolyte layers is a critical parameter to keep the ferrimagnetic ZFNCs separated during the silica coating process. Shown in Figure 6(A–D) are silica-coated ZFNCs with zero, two, four, and six polyelectrolyte layers respectively. In general, as the number of polyelectrolyte coatings increases, the tendency to form linear chains or aggregates during silica encapsulation decreases. Very few single-core, ZFNC@SiO₂ particles were obtained when the seed ZFNCs were coated with only 0 or 2 polyelectrolyte layers. The seed ZFNCs with four polyelectrolyte layers demonstrated few single-core ZFNC@SiO₂ particles, and large aggregates still dominate. Once the ZFNCs are encapsulated with six or more polyelectrolyte layers, discrete ZFNC@SiO₂ particles are clearly evident. The SEM images in Figure 6(D) and Figure 4 show the gap distance between two seed particles is roughly twice as large as the silica layer thickness, indicative of discrete ZFNC@SiO₂. Furthermore, the DLS size distributions of the different ZFNC@SiO₂ samples are in good agreement with the SEM data in Figure 6. Only the silica-coated ZFNCs with six polyelectrolyte layers showed one prominent $D_{h,int}$ peak (Figure S4). As expected, the average hydrodynamic size of the ZFNC@SiO₂ particles decreases

with increasing polyelectrolyte layer; a testament to aggregation remediation. The colloidal stability of the ZFNC@SiO₂ particles also increases with the number of polyelectrolyte layers applied. The ZFNC@SiO₂ particles with six polyelectrolyte layers remained suspended for over 12 h in DI H₂O. However, the ZFNC@SiO₂ particles with 0 and 2 polyelectrolyte layers sedimented in less than 30 min in DI H₂O.

Together, the DLS and SEM data indicate that at least six polyelectrolyte layers are essential to stabilize the seed particles and ensure successful fabrication of discrete ZFNCs@SiO₂ particles. We believe that the success of LbL stabilization is due to an increase in the closest approach distance between the ZFNCs, and therefore a reduction in magnetic dipole-dipole interaction, and electrostatic repulsion brought on by the charge of the outermost layer of the LbL-coated seed ZFNCs.

To understand the ramifications that the coatings have on the resulting magnetic properties of the ZFNCs, a series of magnetometry experiments were performed. Shown in Figure 7 are representative magnetization curves of PEI- (black), LbL-coated ZFNCs (red), and ZFNC@SiO₂ (green). The measured values of M_r and H_c for the PEI-coated ZFNCs are 16.8 emu/g and 50.5 Oe, respectively, indicating that the ZFNCs are ferrimagnetic at room temperature.

The value for M_s (this is the quotient of the measured sample moment to the total mass of particles in the sample) of the PEI-coated ZFNCs is 98.4 emu/g at 298 K. This value is higher than the reported M_s of magnetite nanoparticles (80-85 emu/g),^{33, 51} which is consistent with the M_s enhancement of Zn-doped Fe₃O₄ nanoparticles.^{52, 53} The magnetic moment of one ZFNCs (Table S2) is estimated at 10⁻¹³ emu/particle ($H = 150$ Oe) and 10⁻¹² emu/particle at fields sufficient to saturate the sample (15,000 Oe). These values are also higher than that reported for Fe₃O₄ and other commercial magnetic particles.^{10, 54} However, M_s decreases with each coating step: 82.4 emu/g after six polyelectrolyte coatings and 46.9 emu/g after silica coating. This decrease is due to the increased mass of the non-magnetic coatings. Despite the decrease of M_s after silica coating, both the ZFNCs and ZFNC@SiO₂ particles are easily collected from a 10-mL suspension using a 1-cm³ neodymium magnet (~4,000 Gauss) in 10 s or 20 s, respectively. Commensurate with the decrease in M_s , H_c increases slightly from 50.5 Oe to 51.8 Oe to 61.6 Oe when coated with PEI, LbL polyelectrolytes, and silica, respectively. We believe that the increase in H_c is a result of decreased magnetic dipole coupling. The polyelectrolyte and silica shells physically separate the core ZFNCs, which causes a reduction of the interaction field (magnetic dipole interactions decay as the cube of interparticle separation),⁵⁵ leading to an increase in H_c . Morales et al. observed a similar coercivity enhancement when γ -Fe₂O₃ MNPs were dispersed in a silica matrix.⁵⁶ This observation is in agreement with the report by Che et al., in which they demonstrated that magnetization reversal is assisted by strong dipole coupling, which results in a decrease in H_c .⁵⁷

Particle-particle interactions can be assessed by remanence techniques (see Supporting Information). The quantitative validity of these approaches depends on several assumptions: the particles are assumed to be single-domain ferromagnetic particles with uniaxial anisotropy. Given the size of our ZFNPs, we anticipate the particles are comprised of

multiple domains. However, remanence techniques, which are based on comparing the IRM curve to the DCD curve, can still provide qualitative interaction information in systems that deviate from the basic assumptions.

Shown in Figure 8(A) are Henkel plots of three particle samples: PEI-coated ZFNCs (open circles), polyelectrolyte-coated ZFNCs (open triangles), and ZFNC@SiO₂ (open squares). All three MNPs demonstrate negative curvature from the Wohlfarth line (gray line in Figure 8(A)), with the magnitude of curvature decreasing from ZFNC@PEI to ZFNC@LbL to ZFNC@SiO₂. The negative deviation from the Wohlfarth line originates from magnetic dipole-dipole interactions.⁵⁸ As the interaction increases, the magnitude of deviation increases. Thus, the magnetic dipole-dipole interaction of the PEI-coated particles is reduced by LbL-polyelectrolyte coating and the interaction is further lessened by silica encapsulation.

A modified form of the Henkel representation, the δm plot, provides particle interaction information as a function of H . Shown in Figure 8(B) are δm plots of the three ZFNC systems. A non-interacting assembly of single-domain ferromagnetic particles with uniaxial anisotropy has a $\delta m = 0$ at all H . However, all three ZFNC systems demonstrate negative deviations from $\delta m = 0$. A field-shift of the minimum of the δm plot to larger values as a function of coating step is also observed. That is, δm for the PEI-coated ZFNCs reaches a more negative value than that of the other two samples and decays faster at lower fields. Since the interparticle distance between the PEI-coated ZFNCs is smaller than those of the multiple polyelectrolyte- and silica-coated ZFNCs, the strong dipole coupling interaction field of the PEI-coated ZFNCs aids the other ZFNCs in close proximity to reverse their magnetization at a lower applied field. Therefore, an ensemble of the PEI-coated ZFNCs demagnetizes faster than that of ZFNCs encapsulated by further coatings. This clearly indicates that the silica encapsulating layer separates ZFNCs and reduces their dipole-dipole interaction. Similar results for ferromagnetic FePt and silica-coated ferrimagnetic CoFe₂O₄ nanoparticle systems have been reported by others.^{1, 18, 58, 59} The reduction of magnetic dipole coupling interactions by silica encapsulation is also consistent with the enhancement of the magnetic hardness (coercivity) of the ZFNCs@SiO₂.⁶⁰

CONCLUSIONS

The drive to create silica-encapsulated MNPs stems not only from the fact that the shell acts to reduce magnetic-induced aggregation, but also that silica provides a surface amenable to *in vivo* use and is conducive to functionalization with molecular recognition moieties (*e.g.*, antibodies, peptides). However, the realization of silica-encapsulated, high m MNPs is challenging due to the strong interparticle attractive forces that exist during the coating procedure.

We have developed a method to deposit a uniform silica coating around high moment ($m \sim 4 \times 10^{-13}$ emu/particle at $H = 150$ Oe) ferrimagnetic zinc ferrite nanocubes (~ 130 nm). By depositing multiple polyelectrolyte layers around ZFNCs using an LbL process, a MNP suspension can be stabilized allowing the preparation of uniformly-coated individual ZFNC@SiO₂ particles. The polyelectrolyte multilayers increase the particle-particle closest

approach distance and provide an increased surface charge, which in turn helps minimize dipole-induced aggregation. Our results indicate that successful creation of discrete core-shell nanocubes is realized only after depositing multiple polyelectrolyte layers. Without the intermediary polyelectrolyte layers, magnetic dipole-dipole interactions lead to the formation of linearly chained ferrimagnetic nanoparticles embedded in a silica matrix.

We foresee this encapsulation method being implemented to easily and routinely prepare discrete silica-coated ferrimagnetic nanoparticles for use in many biomedical applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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ABBREVIATIONS

MNP	magnetic nanoparticle
ZFNC	zinc ferrite nanocube
m	magnetic dipole moment
H	magnetic field
H_{ext}	external magnetic field
M_s	magnetization saturation
M_R	remanent magnetization
H_C	coercive field
IRM	isothermal remanent magnetization
DCD	dc demagnetization
$M_{IRM}(H)$	isothermal remanence magnetization
$M_{IRM}(\infty)$	isothermal saturation remanence magnetization
$M_{DCD}(H)$	DC remanence magnetization
$M_{DCD}(\infty)$	DC saturation remanence magnetization
TEOS	tetraethyl orthosilicate
EtOH	ethanol

DI H₂O	18.2 MΩ-cm water
DMSO	dimethyl sulfoxide
PEI	polyethyleneimine
CA	citric acid
DMSA	dimercaptosuccinic acid
NH₄OH	ammonium hydroxide
PAAm	polyallylamine
PSS	polystyrene sulfonate
M_w	molecular weight
pI	isoelectric point
FESEM	field-emission scanning electron microscopy
EDX	energy dispersive x-ray
TEM	transmission electron microscopy
XRD	X-ray diffraction
U_E	electrophoretic mobility
VSM	vibrating sample magnetometer
LbL	layer-by-layer
DLS	dynamic light scattering
SAF	synthetic antiferromagnetic nanoparticles
SPMNP	superparamagnetic nanoparticle
core@shell	core-shell particle architecture
vdW	van der Waals

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Figure 1.

(A) Representative scanning electron micrograph of as-synthesized ZFNCs. (B) Histogram of the edge length of as-synthesized ZFNCs.

Figure 2. Scanning electron micrographs of the linear arrangement of ZFNCs in silica matrices. The as-synthesized ZFNCs were ligand-exchanged with (A) CA, (B) DMSA, and (C) branched PEI before the silica coating step.

Figure 3.

(A) ζ -potential measurements showing surface charge reversal of the ZFNC seeds in the course of LbL deposition of PSS (odd layer number) and PAAm (even layer number). (B) IR spectra of the particles after PEI ligand-exchange, LbL deposition of PSS and PAAm, and silica encapsulation. Note that the particle sample of ZFNC@LbL used in the IR study had six polyelectrolyte layers.

Figure 4. Electron micrograph of the ZFNC@SiO₂ particles assisted via LbL deposition. The discrete nature of the ZFNC@SiO₂ particles is shown in the representative SEM image and bright field TEM image (inset).

Figure 5. EDX images depicting elemental distribution of (C) Fe, (D) Zn, (E) Si, (F) S, and (G) O. The figure shown in (A) is a composite of the grayscale TEM image (B) and Fe, Si, and S. Scale bar in each image is 50 nm.

Figure 6. SEM images of silica-coated ZFNCs. The seed ZFNCs had different numbers of polyelectrolyte layers prior to silica encapsulation: (A) 0, (B) 2, (C) 4, and (D) 6 layers.

Figure 7. Hysteresis curves of the ZFNCs with different coatings; PEI (black), LbL (red), and silica (green). H_c increases (inset) with coating step: 50.5, 51.8, and 61.6 Oe.

Figure 8.

(A) Henkel and (B) δm plots produced from IRM and DCD measurements. The δm minima occur at 100, 150, and 350 Oe for the PEI-, LbL-, and silica-coated ZFNCs respectively.

Scheme 1.
Synthesis of core-shell ZFNC@SiO₂ particles.