

Atom Transfer Radical Polymerization Synthesis and Magnetic Characterization of MnFe_2O_4 /Polystyrene Core/Shell Nanoparticles

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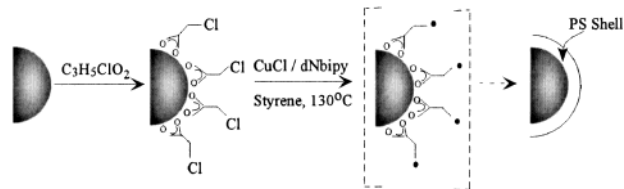
In recent years there has been increased interest in coating surfaces of nanoparticles with a thin shell material for various electronic and biomedical applications.^{1,2} Recently, polymeric shells have been formed on gold and silica nanoparticles for organized assembly.^{3,4} Methods to coat a polymer shell with a controllable thickness on magnetic nanoparticles may aid in the development of ordered arrays of magnetic nanoparticles. The formation of polymeric shells is essential for biomedical applications of magnetic nanoparticles such as magnetic targeting drug delivery and magnetic resonance imaging (MRI) contrast enhancement. Current methods usually create micrometer-sized magnetic polymer particles, which are too large for *in vivo* applications.^{5,6} For instance, a less than 20-nm size has been suggested for the efficient diffusion of nanoparticles through tissue in MRI applications.⁷ An emulsion polymerization of poly(methyl methacrylate) (PMMA) on ~10 nm core of mixed-phase iron oxides has made improvement, but the particle size is still >130 nm.^{8,9} Polystyrene is easy to synthesize for testing various strategies of coating nanoparticles with polymer shells. We herein report the formation of magnetic MnFe_2O_4 polystyrene nanoparticles using atom transfer radical polymerization (ATRP) yielding a core-shell nanoparticle with size <15 nm.

ATRP is a versatile technique which offers several advantages over other polymerization routes including control over molecular weight and molecular weight distribution.^{10,11} Also, the polymers can be end-functionalized or block copolymerized upon the addition of other monomers.¹¹ Not only does this feature offer tailorability of the polymer coating with a variety of compositions and functionalities, but this feature may be important in biomedical applications to modify the polymer shell with biological moieties for specific cellular interactions. ATRP has been able to form PMMA and polystyrene shells on silica nanoparticles.^{4,10}

Most polymer coating studies on magnetic nanoparticles form the nanoparticle core (typically Fe, Fe_2O_3 , or Fe_3O_4) at the same time as that of polymerization.^{12–14} Here, the MnFe_2O_4 nanoparticles as the magnetic core were separately prepared by a reverse micelle microemulsion procedure.¹⁵ Polymerization initiators are chemically attached onto the surface of nanoparticles. The modified nanoparticles are then used as macro-initiators in the subsequent polymerization reaction (Scheme 1). This approach provides great flexibility in the selection of magnetic core. Consequently, magnetic tunability is able to be introduced into these core/shell nanoparticulate systems to achieve the desired superparamagnetic response.¹⁶

MnFe_2O_4 nanoparticles with a mean size of ~9 nm were stirred overnight in 1.0 M aqueous initiator solution, 3-chloropropionic

Scheme 1



acid (Aldrich, 98%). The pH of the solution was kept at 4 by adding HCl. The particles were collected with a magnet and washed several times to remove excess initiator. Air-dried nanoparticles (0.22 g) were added into 8 mL of nitrogen-purged styrene solution (J. T. Baker, 99%). CuCl (0.3 mmol, J. T. Baker, 96%) and 4,4'-dinonyl-2,2'-dipyridyl (1.1 mmol, Aldrich, 97%) were dissolved in 4 mL of xylene (Aldrich, AR), and then the solution was added to the styrene/nanoparticle mixture. The final solution was stirred and kept at 130 °C for 24 h. The particles were collected with a magnet and repeatedly washed with toluene.

Surface photoacoustic infrared spectroscopy of the dried product indicates the presence of polystyrene on the surface of the nanoparticles. Characteristic peaks of polystyrene at 2700–3500, 1000–1400, and 700 cm^{-1} are observed, which are not present in the spectra of the MnFe_2O_4 nanoparticle precursors.

For transmission electron microscopy (TEM) studies, samples were suspended in toluene and dispersed onto a holey carbon grid. Figure 1 displays MnFe_2O_4 particles coated with a thin polystyrene shell. The individual particle shows as the dark center that is surrounded by a light polymer shell (Inset, Figure 1). Particle sizes and shell thickness were determined by manually counting over 100 particles. The core/shell nanoparticles shows a core of 9.3 ± 1.5 nm with a 3.4 ± 0.8 nm polystyrene shell. The few aggregates are likely due to polymer chain entanglement during solvent evaporation.⁴ Polymer particles without magnetic core have not been observed. In contrast, a free radical polymerization using $\text{K}_2\text{S}_2\text{O}_8$ as the catalyst has created a majority of polystyrene particles without magnetic core.

Although thermal polymerization of styrene will occur at the experimental temperature, control experiments using MnFe_2O_4 nanoparticles that had not been modified with 3-chloropropionic acid have shown no observable polystyrene shell under the TEM. Furthermore, no characteristic polystyrene peaks were discernible in the surface photoacoustic IR spectra.

Magnetic studies with a Quantum Design MPMS-5S SQUID magnetometer have shown some changes in field-dependent magnetization after the addition of a polystyrene shell (Figure 2). However, the blocking temperature remains the same after the formation of polymer shell. There was a slight decrease in the saturation magnetization (M_S) and in the remnant magnetization (M_R), while the coercivity (H_C) underwent a larger decrease.

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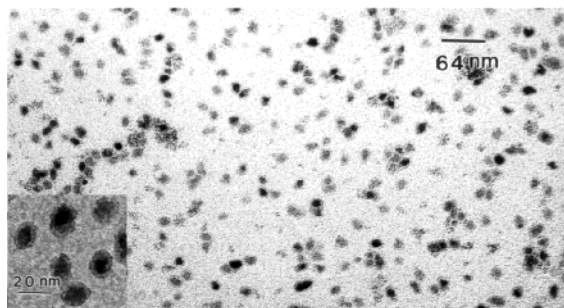


Figure 1. TEM micrographs of ~ 9 nm MnFe_2O_4 /polystyrene core/shell nanoparticles from a JEOL 100C instrument operating at 100 kV.

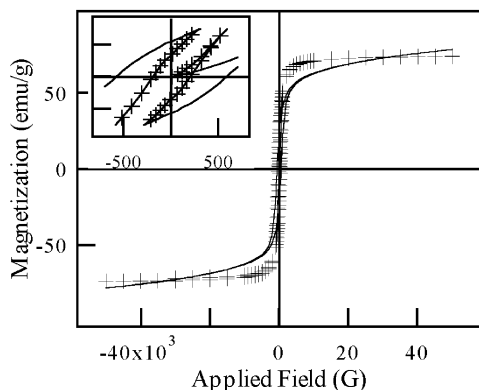


Figure 2. Hysteresis curves of core/shell (+) and pure core (solid line) MnFe_2O_4 nanoparticles at 5 K. Inset shows the coercivity and remnant magnetization in an expanded scale.

Studies on magnetic core/shell systems (e.g., Co-core/CoO-shell) usually show an increase in H_C and M_R ,¹⁷ which has been attributed to an increase in the magnetocrystalline anisotropy (K) resulting from exchange anisotropy that occurs between the ferromagnetic core and the antiferromagnetic shell.¹⁸ Other coating studies in which magnetic nanoparticles were coated with or embedded in a nonmagnetic matrix such as polymers or silica have reported field-dependent magnetization results at room temperature.^{5,12,19} Since the particles in those systems were superparamagnetic at room temperature, no hysteresis was displayed. Consequently, a comparison of M_R and H_C changes cannot be made. A reduction of M_S has been observed upon coating with the nonmagnetic material. Because units for the magnetization are reported per gram of material, this decrease could reflect a smaller percentage of net magnetic material in per gram of overall sample. The slight decrease in M_S and M_R in our samples is likely a result of the small contribution of the polystyrene shell to the overall mass. Our observed decrease in H_C is considered as a result of a decrease in magnetic surface anisotropy (K_S) due to the polystyrene shell formation. K_S results from low coordination symmetry for spin-orbit couplings at the surface of nanoparticles and contributes to the effective magnetocrystalline anisotropy (K_{eff}):

$$K_{\text{eff}} = K_b + (6/d)K_S \quad (1)$$

where K_b is the bulk anisotropy and d is the particle diameter.²⁰ K_S is usually maximum for free surfaces and is reduced by solid coverage.²¹ According to Stoner–Wohlfarth theory, the coercivity of a single domain particle is proportionally related to the anisotropy:

$$H_C = 2K/(\mu_0 M_S) \quad (2)$$

where μ_0 is the permeability of vacuum.²² In our systems, which display little change in M_S between nanoparticulate core and the core/shell nanoparticle, the decrease in H_C can be correlated with a decrease in K by eq 2. K_b is very unlikely changed by the addition of a polymer shell. The decrease in K_S resulting from the particle coverage by the polystyrene shell reduces the K , and therefore decreases the coercivity.

In summary, an atom transfer radical polymerization route works very well to form polystyrene shell on nanoparticulate MnFe_2O_4 and provides magnetic core/shell nanoparticles with size < 15 nm. Magnetic studies show a decrease in coercivity, which is consistent with the reduction of magnetic surface anisotropy upon polymer coating. Certainly the magnetic core of these core/shell nanoparticles can be selected, depending upon the desired superparamagnetic properties for specific applications such as in data storage and MRI contrast enhancement.^{23,24} Moreover, the resulting core/shell nanoparticles are within the biological size restrictions and may potentially be modified for a particular biospecificity.

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Supporting Information Available: Photoacoustic infrared spectra of bare MnFe_2O_4 nanoparticles, 3-chloropropionic acid-modified nanoparticles, and polystyrene coated nanoparticles (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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