Magnetic Nanocomposite Particles and Hollow Spheres Constructed by a Sequential Layering Approach

Frank Caruso,*,[†] Marina Spasova,[†,||] Andrei Susha,[†,§] Michael Giersig,[‡] and
Rachel A. Caruso[†]

*Max Planck Institute of Colloids and Interfaces, D-14424 Potsdam, Germany, and
Hahn-Meitner-Institute, Glienicker Strasse 100, D-14109 Berlin-Wannsee, Germany*

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The fabrication of magnetic composite core−shell particles and hollow spheres with tailored dimensions and compositions has been accomplished by a multistep (layer-by-layer) strategy. Composite particles were prepared by coating submicrometer-sized anionic polystyrene (PS) latices with magnetite (Fe_3O_4) nanoparticle layers alternately adsorbed with polyelectrolyte from aqueous solution. The thickness of the deposited multilayers could be finely tuned with nanoscale precision, either by selection of the number of adsorption cycles performed or by the number of polyelectrolyte layers deposited between each nanoparticle layer (i.e., interlayer). As demonstrated by transmission electron microscopy, a marked improvement in the growth, uniformity, and regularity of the composite multilayers was achieved when the number of polyelectrolyte interlayers was increased from one [(poly(diallyldimethylammonium chloride) (PDADMAC)] to three [(PDADMAC/poly(styrenesulfonate) (PSS)/PDADMAC)]. Hollow, intact magnetic spheres were obtained by calcination of the core−shell particles at elevated temperature. Furthermore, composite hollow spheres were prepared by calcination of PS latices coated with multilayers of silica and Fe_3O_4 nanoparticles. These nanoengineered colloidal particles may potentially find applications as delivery systems, or in diagnostics, where the particles can be directed by application of an external magnetic field.

Introduction

Advanced materials derived from coating or templating colloidal particles often exhibit unique properties (e.g., electrical, optical, magnetic, catalytic, mechanical), and are therefore of extensive scientific and technological interest.[1−19] For example, inverse opals, obtained by templating colloidal crystals by silica,[1,4] metal oxide precursors,[2−4] gold,[5] or polymers,[6−9] are of particular appeal as photonic band-gap materials. Composite particles (or core−shell materials) produced by controlled coating of core particles with inorganic or organic layers are exploited in the areas of electronics, catalysis, and separations.[10−16] In addition, hollow spheres produced by colloidal templating are of interest in diverse applications, ranging from fillers to coatings to drug delivery.[12,17,18]

Recent efforts to produce uniformly coated colloidal particles in solution have relied on a number of different approaches.[19] Synthetic routes developed to produce polymer-coated particles include polymerization at the particle surface,[15] for example, monomer adsorption onto particles followed by subsequent polymerization,[20−22] heterocoagulation polymerization,[23] and emulsion po-

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[*] To whom correspondence should be addressed. Fax: +49 331 567 9202. E-mail: frank.caruso@mpikg-golm.mpg.de.

[†] Max Planck Institute of Colloids and Interfaces.

[‡] Hahn-Meitner-Institute.

[§] Permanent address: Physico-Chemical Research Institute, Belarusian State University, 220050 Minsk, Belarus.

[||] Current address: Institute of Semiconductors and Optics, Technical University of Braunschweig, 38106 Braunschweig, Germany.

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lymerization.[15,24] Inorganic and hybrid coatings (or shells) on particles have been commonly prepared by precipitation and surface reactions that make use of specific functional groups on the cores to induce coating.[11,13,25−40] Inorganic shells prepared using these procedures comprise silica,[11,13,25−36] yttrium basic carbonate,[27] titania,[37−39] and iron compounds.[29,40] Alternatively, particles can be coated by the direct adsorption of polymer (typically a single layer is adsorbed)[15,41] or by adsorption of preformed inorganic colloids onto larger particles utilizing electrostatic interactions.[31,42−44]

Hollow capsules are an important class of materials that can be obtained from the precursor core−shell particles by direct removal of the core material using a variety of chemical and physical methods.[12,18] Various groups have employed this approach, where the core is used as a sacrificial template to produce a range of hollow capsules (usually spherical in shape).[26,28−30,40,45,46] Removal of the core by thermal or chemical means from colloidal particles coated with a variety of *inorganic* layers has yielded hollow capsules of yttrium compounds,[26] silica,[29] iron oxides,[29,40] and monodisperse hollow silica nanoparticles.[17,28] Hollow polymer nanocapsules have been produced by polymer-coating nanoparticles trapped and aligned in membrane pores by vacuum filtration (rather than coated while in aqueous solution), followed by removal of the core by dissolution.[21,22] Furthermore, semiconductor CdS submicrometer-sized hollow spheres were fabricated by an in situ source−template−interface reaction,[45] which involved using carbon disulfide as the reaction source and template on which CdS nanocrystals were formed and subsequently mineralized, and then removing the core by heating. The advantages of fabricating hollow capsules using the template-based sacrificial-core approach are that the capsule composition and geometry can be predetermined, depending on the core and coating materials used, thereby providing an attractive and highly flexible route to their production.

We recently reported a modified templating approach, based on electrostatic self-assembly and colloidal templating, for the controlled synthesis of novel nanocomposite core−shell materials and hollow capsules.[17,18] This process entails the stepwise adsorption of charged polymers or nanocolloids and oppositely charged polyelectrolytes onto colloidal particles, exploiting primarily electrostatic interactions for layer buildup. Notably, it allows the controlled formation of multilayers of various materials (and combinations thereof) on selected core particles in a straightforward and versatile manner and uniquely permits nanoscale control over the multilayer thickness. Using this strategy, colloidal particles have been coated with alternating layers of polyelectrolytes,[47−50] nanoparticles,[17,51−55] and proteins.[56−58] Furthermore, we have demonstrated that submicrometer-sized hollow silica spheres[17,53] or polymer capsules[48,50] could be obtained after removal of the template from the solid-core multilayered-shell particles either by calcination or by chemical extraction. Other related studies using a similar approach have described the preparation of particles consisting of a solid core covered with either a single layer of nanoparticles (zirconium phosphate,[59] alumina,[60] or metals[10,32]) or a composite multilayer shell.[32,59,60]

Magnetic colloidal supports have become increasingly important because of their widespread use in fields such as biotechnology,[61−63] for example, in bioseparations or immunoassays. Furthermore, magnetic colloidal suspensions have been used as building blocks for the formation of ordered patterns on surfaces via manipulation using magnetic fields.[54,64] This paper demonstrates the extension and applicability of the facile, electrostatic self-assembly/colloidal templating method to magnetite

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(Fe_3O_4) nanoparticles for the production of a new class of polystyrene−core (PS−core) multilayered magnetic shell particles and magnetic hollow capsules. It is illustrated that the number of polymer layers separating each (nearest) nanoparticle layer is a crucial parameter in facilitating regular growth of the multilayers, which in turn controls the final composition and shell/wall thickness of both the core−shell particles and hollow capsule materials. The construction of *heterocomposite* multilayers on PS particles and the resulting composite magnetic hollow spheres is also detailed. The novel materials presented here offer specific advantages over previously synthesized core−shell particles and hollow capsules because of their tailorable composition, dimension, and shell/wall thickness. The ability to control these features is a prime requirement for a number of potential uses of colloids.[12,18] It is therefore anticipated that the magnetic colloidal entities produced will be exploited as delivery vehicles and supports in bioscience applications and as core units in patterned assemblies.

Experimental Section

Materials. Poly(diallyldimethylammonium chloride) (PDADMAC), M_w <200 000, and poly(sodium 4-styrenesulfonate) (PSS), M_w 70 000, were obtained from Aldrich. PSS was dialyzed against Milli-Q water (M_w cutoff 14 000) and lyophilized before use. Negatively charged, sulfate-stabilized PS latices of 640-nm diameter were prepared as described elsewhere.[65] Anionic (sulfonate) PS latices of 270-nm diameter were purchased from Microparticles GmbH, Berlin, Germany. The SiO_2 nanoparticles (40 wt % SiO_2 suspension, Ludox TM40, diameter = 26 ± 4 nm as determined by TEM) were purchased from DuPont. Sodium chloride (AR grade) was obtained from Merck. The water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus 185 purification system and had a resistivity higher than 18.2 MΩ cm. Magnetite (Fe_3O_4) nanoparticles, 8−12 nm in diameter, were tetrabutylammonium hydroxide-stabilized and were prepared as follows: A solution of 50 mL of 1-propanol and 8 mL of tetrabutylammoniumhydroxide (1 M in methanol, Aldrich) was deaerated for 45 min using N_2. Following this, 0.3244 g of $FeCl_3$ was added to the solution and heated to reflux while stirring with a magnetic stirrer. In a similar fashion, 50 mL of 1-propanol and 2 mL of tetrabutylammoniumhydroxide (1 M in methanol) were mixed and deaerated for 45 min, after which 0.1988 g of $FeCl_2 \cdot 4H_2O$ was added to the solution and heated to reflux while stirring. The two solutions (while still hot) were then mixed rapidly and heated to reflux for 30 min. After cooling to room temperature, the black-brown colloidal particles were collected using a permanent magnet and separated from the liquid. The particles were then redispersed in 100 mL of deaerated ethanol, sonicated for 10 min, and separated again from the liquid. Finally, the magnetite nanoparticles (containing ≈10% Fe_2O_3, calculated from the number of particles with the corresponding lattice planes found in TEM measurements) were redispersed in 100 mL of H_2O to give a colloidal solution of $\approx 1 \times 10^{15}$ particles mL^{-1}.

Preparation of Coated Colloids. The first step in the coating of the 640-nm PS particles involved depositing a precursor polyelectrolyte multilayer film (PDADMAC/PSS/PDADMAC) (PE_3) on the PS latices.[49,51] This film provides a uniformly charged surface and facilitates subsequent nanoparticle adsorption.[51,52] The outermost surface layer was in all cases PDADMAC, making the coated particles positively charged (verified by electrophoresis measurements).[49] Electrostatic interactions between the negatively charged nanoparticles and PDADMAC were utilized to build up the nanocomposite multilayers. Fe_3O_4 nanoparticles were adsorbed on the PS latices by adding 0.3 mL of the Fe_3O_4 sol ($\approx 3 \times 10^{14}$ particles) to the precoated 640-nm PS latices ($\approx 5 \times 10^{9}$ particles) dispersed in 0.5 mL of water. The nanoparticles were allowed to adsorb for 20 min, with occasional stirring, and excess Fe_3O_4 nanoparticles were subsequently removed by four repeated centrifugation (7000*g*, 7 min)/dispersion cycles; that is, the supernatant was removed after centrifugation and replaced with water for each cycle. The PS particles were then coated with either one (PDADMAC) or three (PDADMAC/PSS/PDADMAC, PE_3) polyelectrolyte layers. PDADMAC or PSS were deposited by adding 0.5 mL of a 1 mg mL^{-1} aqueous polyelectrolyte solution (containing 0.5 M NaCl) to the coated particles (dispersed in 0.5 mL of H_2O). (The final NaCl concentration in the solution from which polyelectrolyte adsorption occurred was 0.25 M.) After an adsorption time of 20 min, excess polyelectrolyte was removed by four centrifugation (7000*g*, 7 min)/redispersion cycles. Additional Fe_3O_4 nanoparticle/polyelectrolyte layers were deposited using the same procedure and conditions outlined above, resulting in nanocomposite multilayer-coated PS latices. Multicomponent layers were prepared on PS latices by adsorption of SiO_2 and Fe_3O_4 nanoparticle layers, separated by polyelectrolyte layers. The SiO_2 nanoparticles (50 μL of the 40 wt % aqueous suspension) were adsorbed onto coated PS particles dispersed in 0.1 M NaCl with an adsorption time of 20 min[51−53] and cleaned using four centrifugation (7000*g*, 7 min)/redispersion cycles. The coating procedure was also successfully applied to 270-nm PS latices: an Fe_3O_4 nanoparticle PDADMAC multilayer shell was formed around the PS core (shell thickness of ≈22 ± 5 nm) (data not shown). This indicates that the layer-by-layer strategy can be extended to smaller core particles.

Preparation of Hollow Spheres. Magnetic hollow and composite silica/magnetic hollow spheres were produced by drying the coated PS latices on quartz slides at room temperature and then calcining (heating rate, 15 K min^{-1}) at 500 °C under N_2 for 4 h and for an additional 12 h under O_2. The hollow spheres were redispersed by gentle sonication in water for 1 min.

Characterization. Electrophoresis measurements were performed using a Malvern Zetasizer 4 on particles redispersed in air-equilibrated pure water (pH ∼ 5.6).[52] The coated particles and hollow spheres were examined by transmission electron microscopy (TEM) with a Philips CM12 microscope operated at 120 kV and scanning electron microscopy (SEM) with a Zeiss DSM 940 instrument operated at an accelerating voltage of 20 kV. Samples for TEM were sonicated in water for 1 min, deposited onto a carbon-coated copper grid, and the extra solution blotted off. Ultrathin sections of the hollow spheres (30−50 nm in thickness) were obtained by slicing with a Leica ultracut UCT ultramicrotome after setting them in a LR-White resin. The thin sections were placed onto either carbon- or noncoated copper grids. SEM samples (on carbon or quartz surfaces) were sputter-coated with about 5 nm of Pd or Au. A Netzsch TG 209 apparatus was used for thermogravimetric analysis of the coated particles. Single-particle light-scattering measurements were performed on a home-built instrument; details of the experimental system and measurement principle can be found elsewhere.[66,67]

Results and Discussion

Fe_3O_4 nanoparticle/polyelectrolyte multilayer shells were prepared on PS latices precoated with a precursor three-layer polyelectrolyte film (PE_3), with an outermost PDADMAC layer. The Fe_3O_4 nanoparticles were adsorbed onto the modified PS latices in alternation with PDADMAC (or PE_3) under conditions where electrostatic interactions are utilized for layer buildup (pH ∼

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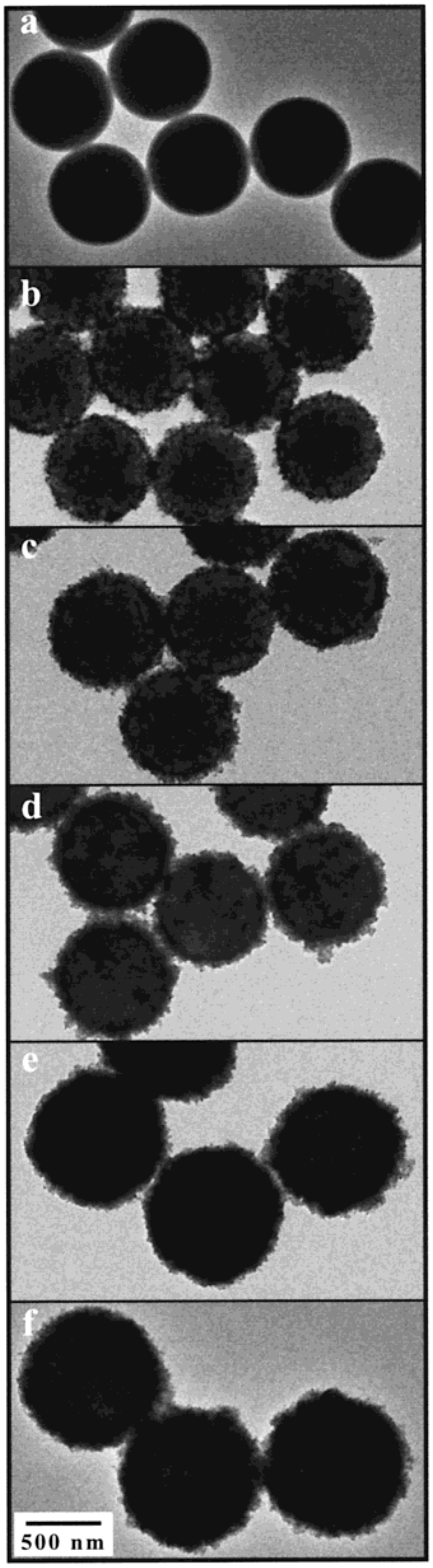

Figure 1. TEM micrographs of (a) uncoated PS latices and PE_3-modified PS latices coated with (b) one, (c) two, (c) three, (d) four, and (e) five Fe_3O_4 nanoparticle/PE_3 layers. The average diameters of the composite particles are (top to bottom) 650, 700, 770, 820, 890, and 960 nm (the error is approximately ±10 nm). The stepwise increase in the diameter of the coated particles indicates the regular deposition of Fe_3O_4 nanoparticles and polyelectrolytes. The polyelectrolyte interlayer spacing between each Fe_3O_4 nanoparticle layer was PDADMAC/PSS/PDADMAC (i.e., PE_3). The scale bar corresponds to all the images shown.

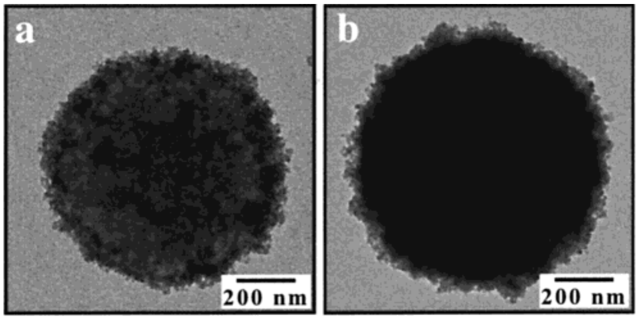

Figure 2. TEM micrographs of PE_3-modified PS latices that were exposed to four alternate depositions of Fe_3O_4 nanoparticles and polyelectrolytes. The effect of the polyelectrolyte interlayer spacing is displayed. (a) A single polyelectrolyte interlayer (PDADMAC) was deposited, and (b) three polyelectrolyte interlayers (PDADMAC/PSS/PDADMAC) were deposited between each Fe_3O_4 nanoparticle layer.

5−6). Electrophoresis measurements revealed a ζ-potential of approximately +50 mV for the PE_3-coated PS latices and −30 mV for the Fe_3O_4 nanoparticles. TEM was employed to follow the assembly of the Fe_3O_4 nanoparticle/polyelectrolyte multilayers on the PS latices and to examine the morphology of the coated particles. TEM micrographs of neat PS latices (a) and those coated with Fe_3O_4 nanoparticle/PE_3 multilayers (b−f) are shown in Figure 1. The spherical, uncoated particles have a smooth surface (a). Deposition of the three precursor polyelectrolyte layers onto the PS latices does not cause a noticeable change in the particle morphology (images not shown). The Fe_3O_4 nanoparticle/polyelectrolyte multilayer coatings produced are rather uniform and more regular than those obtained by seeded polymerization of iron salts on PS microspheres, where large aggregates of Fe_3O_4 nanoparticles were obtained.[29] More recently, the controlled hydrolysis of aqueous solutions of $FeCl_3$ in the presence of PS particles has produced relatively uniform coatings of iron compounds on particles.[40]

The diameter of the particles regularly increases with the number of Fe_3O_4 nanoparticle/PE_3 multilayers deposited, reflecting the increased magnetite nanoparticle content in the shell structure with each deposition cycle (Figure 1). The average diameter increment for each Fe_3O_4 nanoparticle/PE_3 multilayer is between 50 and 80 nm, which corresponds to a layer thickness of between 25 and 40 nm. The layer thickness of PE_3 is typically ≈5 nm,[49] indicating an average thickness of about 20−35 nm for each Fe_3O_4 nanoparticle layer. This coverage is equivalent to ≈2−3 monolayers (on average) of Fe_3O_4 nanoparticles per deposition (particle diameter ≈10 nm). The clustering of Fe_3O_4 nanoparticles on the surface of the PS latices visualized is, in part, attributed to the magnetic interactions between the magnetite nanoparticles.[54] Nonetheless, the above data clearly show that the thickness of the nanocomposite Fe_3O_4 multilayer shell surrounding the colloidal particles can be tailored using the layer-by-layer adsorption process, depending on the number of deposition cycles employed. This finding is in agreement with that observed for Fe_3O_4 nanoparticle/polyelectrolyte multilayer films constructed *on planar substrates* via the layer-by-layer strategy, where regular film growth with layer number

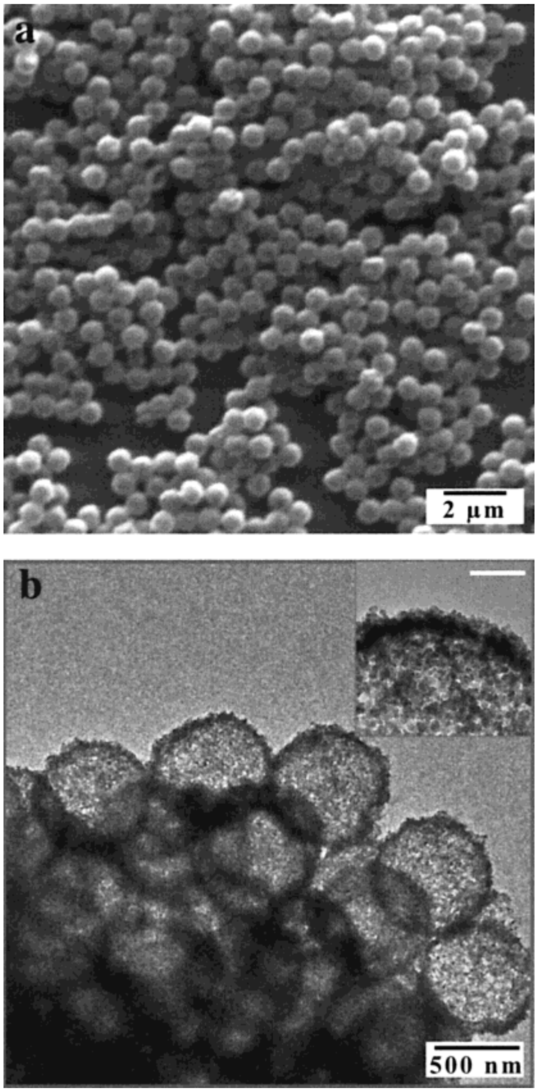

Figure 3. (a) SEM image of magnetic hollow spheres prepared by exposing PE_3-coated PS particles to five adsorption cycles of Fe_3O_4 nanoparticles and PDADMAC, followed by calcination at 500 °C. (b) TEM image of the same sample showing the hollow nature of the particles. The inset shows the regularity of the wall structure. The scale bar in the inset represents 100 nm.

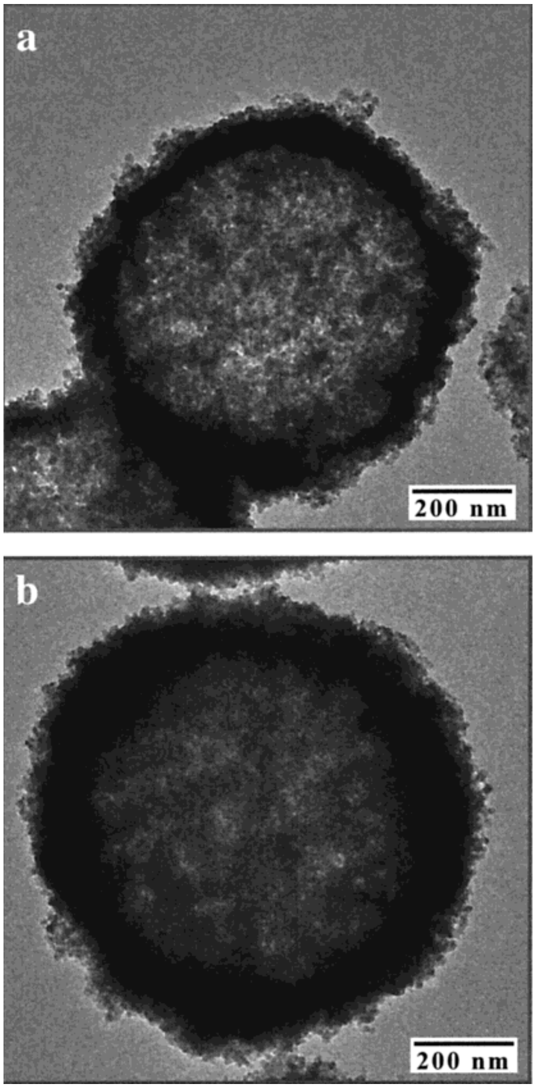

Figure 4. TEM images of magnetic hollow spheres prepared by depositing (a) three and (b) five Fe_3O_4 nanoparticle layers, in alternation with PDADMAC/PSS/PDADMAC, on PE_3-coated PS particles, followed by calcination at 500 °C.

was observed.[68,69]

In the current work, it was found that regular multilayer growth and homogeneous Fe_3O_4 nanoparticle coatings were obtained on PS spheres when the interlayer spacing consisted of three polyelectrolyte (PDADMAC/PSS/PDADMAC) layers instead of PDADMAC alone. This can be ascribed to the creation of a smoother and more uniform surface by the consecutive adsorption of several polyelectrolyte layers for subsequent nanoparticle deposition. This effect is exemplified in Figure 2, which shows PS latices exposed to four depositions of Fe_3O_4 nanoparticles (alternating with polyelectrolyte) under the same conditions, but with a single (a) or three (b) polyelectrolyte interlayers. Regular growth of the multilayer shell was not observed for the coated particles prepared using a single interlayer: the first adsorption of Fe_3O_4 nanoparticles resulted in, on average, the deposition of the equivalent of $\approx 2-3$ monolayers (image a) with little growth observed for subsequent depositions. No improvement in either the degree of Fe_3O_4 nanoparticle coating or uniformity was obtained by using salt (0.1 M NaCl) and/or higher nanoparticle concentrations in the adsorbing solutions.

In addition to the above-mentioned particles being uniformly coated with Fe_3O_4 nanoparticle/polyelectrolyte multilayers, no aggregation of coated particles in solution was detected by means of single-particle light scattering (SPLS). (SPLS is an optical technique that provides information on the state and degree of aggregation of colloids.[49,66,67]) Slow flocculation of the multilayer-coated particles occurred when Fe_3O_4 nanoparticles formed the outermost layer, although the particles could be easily redispersed by gentle agitation. The colloidal stability of the coated particles was found to be higher when PDADMAC was the outer layer. This is most likely because the polyelectrolyte provides enhanced electrostatic and steric stabilization to the

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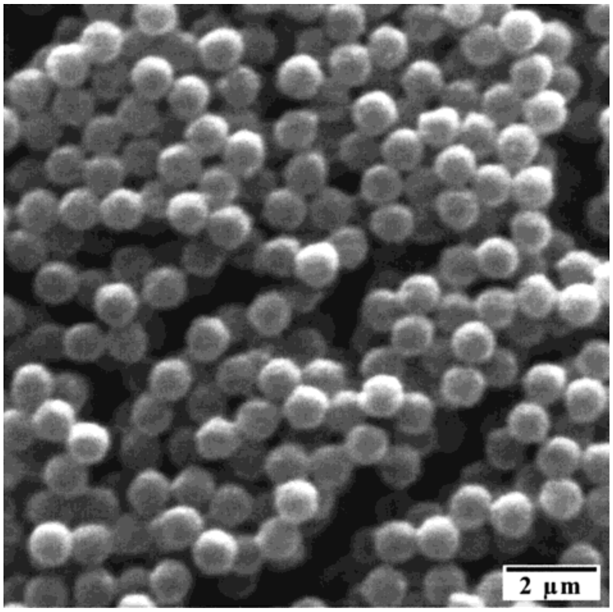

Figure 5. SEM micrograph of magnetic hollow spheres prepared by depositing five Fe_3O_4 nanoparticle layers, in alternation with PDADMAC/PSS/PDADMAC, on PE_3-coated PS particles, followed by calcination at 500 °C.

particles.[49] The coated particles displayed magnetic properties and could be easily drawn out of solution by using a permanent magnet. Preliminary magnetic measurements indicate that the saturation of the magnetic moment of the coated particles increases proportionally with the number of Fe_3O_4 nanoparticle layers deposited (data not shown).

As the thickness of the multilayers enveloping the particles can be readily controlled using the layer-by-layer process, our procedure permits the construction of hollow capsules with defined wall thicknesses by employing appropriate methods of core removal. To produce magnetic hollow capsules, the multilayer-coated PS latices were subjected to elevated temperature (500 °C). This process (calcination) results in the removal of the PS core and (bridging) polymer during heating, which was confirmed by thermogravimetric analysis.[17,53] Total decomposition of PS latices before 500 °C has been previously confirmed by IR[40] and TGA.[26] In addition, the heating process induces sintering of the inorganic particles,[17,70] thus imparting structural stability to the hollow spheres. Figure 3 illustrates the hollow spheres obtained after calcination of PS latices exposed to five Fe_3O_4 nanoparticle/PDADMAC deposition cycles. As mentioned earlier, the use of a single polyelectrolyte interlayer resulted in only a small increase in wall thickness (<20%) after the first Fe_3O_4 nanoparticle deposition step. The hollow spheres were complete and structurally intact after calcination, as confirmed by SEM (Figure 3a). A TEM image of the calcined samples (Figure 3b) reveals a reduced electron density of the spheres after calcination, indicating that hollow spheres were obtained. A higher magnification of the sphere wall is shown in the inset; the wall thickness is ≈20−30 nm. The diameters of the hollow spheres produced are ≈5−10% smaller than those of the corresponding nanocomposite multilayer-coated PS latices. Similarly, complete and intact hollow spheres were also produced by heating samples of PS latices coated with one to four Fe_3O_4 nanoparticle layers, separated by a single PDADMAC interlayer. In some instances broken spheres were also observed. The hollow spheres retained their magnetic properties, which was confirmed by placing a permanent magnet near the side of the tube after redispersing the spheres, resulting in their movement toward the magnet.

Figure 4 shows TEM images of magnetic hollow spheres obtained by calcining PS latices coated with (a) three or (b) five Fe_3O_4 nanoparticle layers, each separated by three polyelectrolyte interlayers. (Again, the hollow spheres were confirmed to be magnetic by using a magnet.) Uniform, well-defined magnetic hollow spheres were produced upon heating. The wall thickness (and outer diameter) of the hollow spheres can also be controlled on the nanoscale level. The thickness of the wall for the three-layer magnetic hollow spheres is about 70 nm (a) and 130 nm for the five-layer hollow spheres (b). A shrinkage of about 5% in the diameter of the spheres was observed after calcination. The uniform wall thickness further demonstrates the high regularity of the coating process. Figure 5 displays an SEM image of magnetic hollow spheres prepared by calcination of PS latices coated with five Fe_3O_4 nanoparticle layers (separated by three polyelectrolyte interlayers), and confirms that structurally intact hollow spheres were

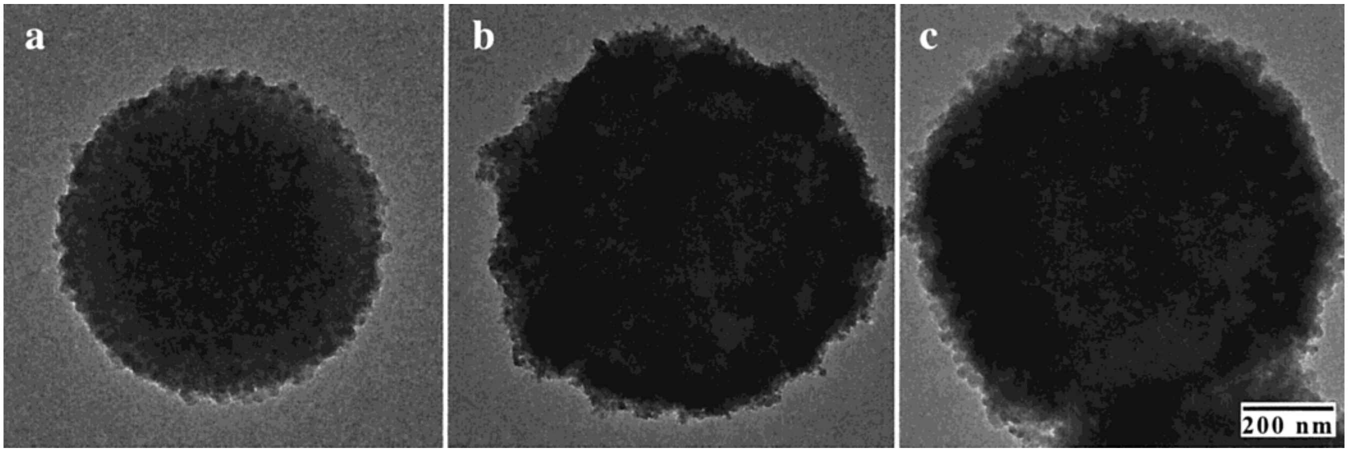

Figure 6. TEM images of PS−core multicomposite-shell particles prepared by the sequential adsorption of (a) SiO_2 nanoparticles/PE_3, (b) three additional layers of Fe_3O_4 nanoparticle/PE_3 layer pairs, and (c) an additional SiO_2 nanoparticle/PDADMAC layer pair onto PE_3-modified PS particles. The scale bar corresponds to all three images.

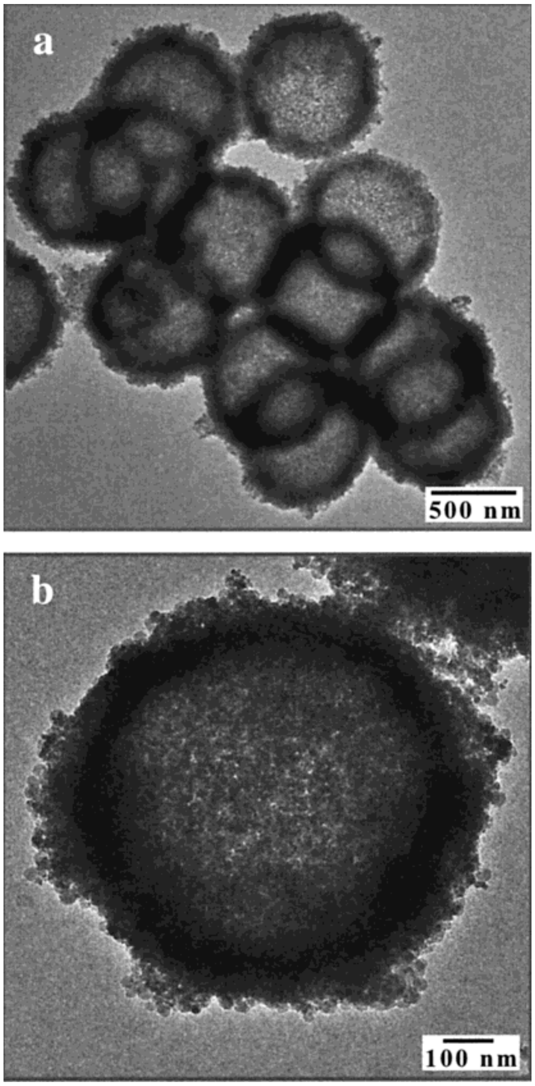

Figure 7. TEM micrographs of magnetic hollow spheres prepared by calcination (500 °C) of PE_3-modified PS particles coated with inner and outermost SiO_2 nanoparticle layers and three intermediate Fe_3O_4 nanoparticle layers (each inorganic nanoparticle layer was separated by PE_3): (a) low-magnification and (b) higher magnification images.

produced. Although hollow spheres were also formed using a single polyelectrolyte interlayer (Figure 3), control over the hollow sphere wall thickness (and hence diameter) was achieved by using three polyelectrolyte interlayers (Figures 4 and 5). The coating on the particles, with regard to thickness and/or nanoparticle content, is dependent on the number of interlayers, which in turn influences the morphology and ultimately the properties of the hollow spheres produced. Control over these parameters is an inherent feature of the layer-by-layer strategy, thereby making it an attractive process for the preparation of hollow materials.

The magnetic hollow spheres produced are comprised of densely packed layers of crystalline maghemite *and* haematite nanoparticles, as determined by high-resolution TEM and electron diffraction measurements (data not shown). It is well established that the composition of iron oxide particles can be altered, depending on the heating conditions.[71] Breulmann et al. found that magnetic copolymer−mineral composites, prepared by immersing copolymer gels in a colloidal dispersion of magnetite nanoparticles, produced an inorganic replica composed of maghemite when heated to 450 °C in air.[70] Shiho and Kawahashi recently reported the formation of hollow spheres of iron compounds by first coating polystyrene particles by the hydrolysis of ferric chloride aqueous solution in the presence of urea, hydrochloric acid, and poly(vinylpyrrolidone) and aging at 100 °C for 2 days, followed by calcining the coated particles in air.[40] It was found that hollow *haematite* spheres were formed by heating the coated PS latices for 3 h in air at 500 °C, while hollow *magnetite* spheres were obtained by further heating the hollow haematite spheres for 1 h at 350 °C in hydrogen.[40]

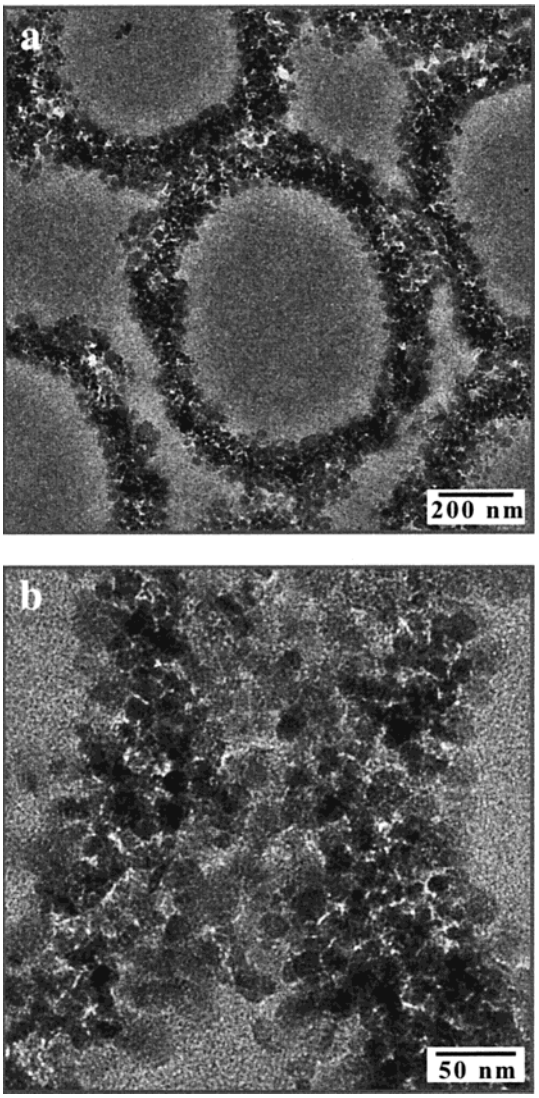

Figure 8. TEM micrographs of cross sections of the same magnetic hollow spheres displayed in Figure 7: (a) low-magnification and (b) higher magnification images.

The layer-by-layer approach allows a rich variety of structures to be assembled, both on planar substrates[72] and on colloidal templates.[18] The technique also permits a large degree of structural complexity and numerous

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components to be introduced into defined layers, thereby allowing the creation of new materials with potential in wide ranging applications. In this context, and to demonstrate the extension of the process to multicomposite inorganic layers on colloidal particles, we fabricated heterocomposite multilayers on PS latices. The multilayers were constructed by first depositing SiO_2 nanoparticles onto PE_3-coated PS latices, followed by PE_3, an additional sequence of three Fe_3O_4 nanoparticle/ PE_3 layer pairs, and finally another layer pair of SiO_2 nanoparticles and PDADMAC. The stepwise growth of the multicomposite particles is shown in Figure 6. A dense packing of SiO_2 nanoparticles was obtained on the PS latices by electrostatic adsorption of the negatively charged SiO_2 nanoparticles onto the positively charged PE_3-coated PS particles (Figure 6a). The additional coating of three Fe_3O_4 nanoparticle/ PE_3 layers resulted in both a roughness and a diameter increase (Figure 6b), and continued growth of the multilayer shell occurred as a result of further deposition of a SiO_2 nanoparticle/PDADMAC layer pair (Figure 6c). Controlled heating at 500 °C removed the organic core and polymer interlayers to give intact, composite hollow inorganic spheres (Figure 7). Some degree of surface roughness can be seen, but overall well-defined silica/ magnetic hollow spheres were obtained. SEM confirmed that unbroken, composite inorganic hollow spheres were produced. TEM of cross sections of the hollow spheres further demonstrated the regularity and uniformity of the shell wall, with a thickness of $\approx$100 nm (Figure 8). Higher magnification (Figure 8b) shows that the iron oxide nanoparticles (darker contrast and smaller) are essentially sandwiched between layers of silica nanoparticles, in accordance with the order of fabrication of the multilayer shell. It is worthy to note that TEM images indicate that the hollow spheres are mesoporous. The fabrication of these hollow spheres highlights the advantages associated with the application of the layer-by-layer technique; namely, multicomposite hollow materials with defined wall thickness, dimension, and composition can be produced. Control over these parameters is essentially unattainable by using traditional methods of hollow capsule production.

Conclusions

This work has demonstrated that colloidal particle templates have general use for the controlled adsorption of preformed inorganic nanoparticles into core−shell particles, which can be subsequently transformed into hollow spheres. Submicrometer-sized magnetic core−shell particles with defined shape, composition, and multilayer shell thickness were produced by the layer-by-layer assembly of magnetite nanoparticles and polyelectrolytes onto PS colloids. Subsequent removal of the core via calcination resulted in structurally intact magnetic hollow spheres. Composite hollow spheres were produced by incorporating different types of inorganic nanoparticles in the multilayer shell wall prior to removal of the colloidal core. It was also found that the polyelectrolyte interlayer separation between each nanoparticle layer played a key role in obtaining regular multilayer growth. The strategy employed provides a viable route to fabricate new classes of colloidal materials with increased structural and compositional complexity. Current work is focusing on the use of these and related core−shell particles and hollow spheres as building blocks in the fabrication of two- and three-dimensional ordered colloidal structures.

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