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Production of Hollow Microspheres from Nanostructured Composite Particles

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Uniform inorganic and hybrid inorganic−organic hollow microspheres have been produced by coating colloidal core templates with alternating layers of oppositely charged nanoparticles and polymer, and thereafter removing the core either by heating or chemical treatment. The multilayers were constructed by consecutively depositing the nanoparticles and polymer onto the colloidal templates, utilizing the electrostatic attraction between the particles and polymer for layer build-up. Hollow silica spheres were obtained by calcining polymer latex spheres coated with multilayers of silica nanoparticles (SiO_2) bridged by polymer [poly(diallyldimethylammonium chloride) (PDADMAC)]. Exposure of SiO_2/PDADMAC multilayer-coated polymer latex colloids to acidic solutions, dimethyl sulfoxide, or tetrahydrofuran yielded hollow composite silica−polymer spheres. The fabricated hollow spheres have been characterized using scanning and transmission electron microscopy. The approach employed is well suited to generating hollow spheres of controlled diameter, wall thickness, and composition.

Introduction

The synthesis of uniform-sized hollow microspheres (size range of tens of nanometers to several millimeters),[1] in liquid or solid form, has gained increasing attention in recent years. Hollow spheres represent a special class of materials which are of interest in the fields of medicine, pharmaceutics, materials science, and the paint industry; they find diverse applications, including encapsulation of products (for the controlled-release of drugs, cosmetics, inks, and dyes), the protection of light-sensitive components, catalysis, coatings, composites, and fillers.[1]

There exist a number of fabrication methods that are capable of producing a broad range of hollow microspheres. These include nozzle−reactor systems (spray drying or pyrolysis), and emulsion/phase separation techniques coupled with sol−gel processing.[1] Various hollow polymer, oxide, metal, and glass composite microspheres have been produced using nozzle−reactor methods.[1−6] The size of the microspheres, generally in the micrometer size range, is limited by the nozzle technology. Emulsion/phase separation procedures, however, offer the opportunity to create microspheres in the nanometer size range: single and mixed ceramic oxides have been processed.[1,7−10] Ceramic hollow microspheres, with micrometer diameters, have also been fabricated.[1,8,11] Yet, another method to produce hollow microspheres is to employ sacrificial cores: in this approach a coating is deposited on the core as a result of controlled surface precipitation of inorganic molecular precursors from solution or direct surface reactions,[12−19] and the core can be subsequently removed by heating (calcination) or by dissolution in a solvent.[12a,13a,b,14] Hollow, submicrometer-sized spheres of yttrium compounds have been produced by coating cationic polystyrene latex particles with yttrium basic carbonate and subsequently calcining.[12a] More recently, hollow silica spheres were generated by seeded polymerization of

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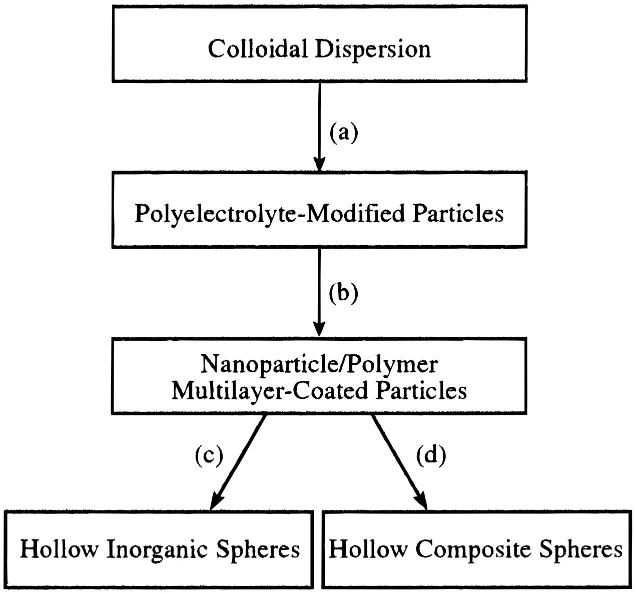
Scheme 1. Schematic of the Process Used to Fabricate Hollow Inorganic and Hollow Composite Microspheres



[a,b] Preparation of colloidal core-nanocomposite multilayer shell particles. First, precursor polyelectrolyte layers (denoted PE_n) are sequentially adsorbed onto the particles to provide a uniformly charged surface and to facilitate subsequent multilayer build-up. Nanoparticle/polyelectrolyte layers are then deposited step-wise onto the polyelectrolyte-modified colloidal templates by making use of the surface charge reversal that occurs upon adsorption of each layer. Unadsorbed polyelectrolyte and nanoparticles are removed by repeated centrifugation/wash cycles. [c] Removal of organic material (colloidal core and bridging polymer) by calcination (heat treatment) to give hollow inorganic (silica) microspheres. [d] Decomposition of the core by chemical means (exposure to acid, dimethyl sulfoxide or tetrahydrofuran), leaving behind hollow nanoparticle/polymer microspheres.

tetraethoxysilane on the surface of polystyrene particles, followed by calcination.[14] By using a similar method, monodisperse, hollow silica nanoparticles have been produced by silica-coating gold nanoparticles and by chemically dissolving the cores.[13a,b] In some cases the formation of uniform and regular shell structures surrounding the particles, as well as control over the shell thickness, are difficult to achieve using these colloid-coating methods.

Herein we report an alternative procedure for fabricating hollow microspheres from colloidal core–nanocomposite multilayer shell particles. Using the colloid as a sacrificial core, hollow microspheres are produced following core removal. Unlike previous studies where the particle coating is achieved via surface precipitation or reaction with organic precursors, in the current work the multilayers are assembled by the sequential adsorption of layers of preformed silica nanoparticles (SiO_2), of $\sim$30 nm diameter, and positively charged polymer [poly(diallyldimethylammonium chloride) (PDADMAC)] (Scheme 1). Building on our previous work,[20] we provide a detailed investigation of hollow microsphere production from nanocomposite multilayer-templated colloids. We also demonstrate that depending on the method of core removal, hollow silica microspheres or hollow inorganic–organic microspheres, each exhibiting different structural properties, can be obtained. Further, it is shown that the colloid-templated multilayer assembly process, which proceeds primarily as a result of electrostatic interactions between the charged species deposited, is relatively straightforward and versatile, allowing a high degree of control to be exerted over the wall (i.e., shell) thickness (in the nanometer range) and composition of the resulting microspheres. The size and shape of the hollow spheres produced are also predetermined by the morphology of the sacrificial core employed: either 640 nm diameter polystyrene (PS) or micrometer-sized melamine formaldehyde (MF) latices. Scanning (SEM) and transmission (TEM) electron microscopy provide information on the morphology and wall thickness of the hollow microspheres.

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. Fluorescein isothiocyanate (FITC-PAH) was provided by M. Auch (Max Planck Institute of Colloids and Interfaces). The SiO_2 nanoparticles (40 wt % SiO_2 suspension, Ludox TM40, diameter = 26 ± 4 nm as determined by TEM) were purchased from DuPont. Negatively charged, sulfate-stabilized polystyrene (PS) latices of diameter 640 nm were prepared as described elsewhere.[21] Positively charged, weakly cross-linked melamine formaldehyde (MF) particles (diameter of either $\sim$2 or 3 μm) were purchased from Microparticles GmbH, Berlin, Germany. Hydrochloric acid (HCl), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), and sodium chloride were 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.

Hollow Microsphere Fabrication. The first step in the fabrication of the hollow spheres was to prepare colloidal core–nanocomposite multilayer shell particles. Prior to deposition of SiO_2/PDADMAC multilayers, a precursor polyelectrolyte multilayer film was assembled on the latex particles: a three-layer polyelectrolyte film [PDADMAC/PSS/PDADMAC] (PE_3) was deposited on the PS latices, and a six-layer [$(PSS/PDADMAC)_3$] (PE_6) film on the MF particles, as described elsewhere.[20,22] The outermost surface layer was in all cases PDADMAC, making the coated particles positively charged. SiO_2/PDADMAC multilayers were fabricated by adding 50 μL of the aqueous SiO_2 suspension to the polyelectrolyte-coated particles ($\sim 10^{10}$ particles dispersed in 1 mL of 0.1 M NaCl), allowing 15 min for SiO_2 adsorption, removing excess SiO_2 by four repeated centrifugation (13 500 g, 15 min for PS latices; 5000 g, 5 min for MF particles)/water wash/redispersion cycles, and subsequently depositing PDADMAC (1 mg mL^{-1} solution containing 0.5 M NaCl, adsorption time of 20 min) in identical fashion. The desired number of SiO_2/PDADMAC multilayers was assembled by the repeated consecutive assembly of SiO_2 and PDADMAC. The build-up of the multilayers is facilitated by the electrostatic interactions between the negatively charged nanoparticles and the positively charged groups ($-NH_3^+$) of PDADMAC.

Hollow silica spheres were produced by drying the PS latices coated with SiO_2/PDADMAC multilayers on quartz slides at room temperature, and then calcining (heating rate 5 K min^{-1}) at 500 °C under N_2 for 4 h and a further 8 h under O_2. Hollow hybrid inorganic–organic spheres were obtained by exposing 0.1 mL of the SiO_2/PDADMAC multilayer-coated MF particles

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to 0.5 mL of 0.1 M HCl for 20 min, centrifuging (10 000 g, 5 min), removing the supernatant, and redispersing in 0.1 mL of H_2O. To ensure complete core removal, this process was repeated a further two times. Following this, the supernatant was exchanged for pure water twice. Hollow composite spheres were also obtained by exposure of PS latices coated with SiO_2/PDADMAC multilayers to dimethyl sulfoxide (DMSO) (i.e., substituting DMSO for HCl in the above procedure), or by exposure to a tetrahydrofuran solution for 24 h.

Characterization. Scanning electron microscopy (SEM) measurements were performed with a Zeiss DSM 940 instrument operated at an accelerating voltage of 20 kV. SEM samples (on carbon or quartz surfaces) were sputter-coated with about 5 nm of Pd or Au. Transmission electron microscopy (TEM) measurements were obtained with a Philips CM12 microscope operating at 120 kV. Samples for TEM were sonicated in water for 1 min (to redisperse the hollow spheres), and then deposited onto a carbon grid and allowed to air-dry. Ultrathin sections of the hollow microspheres (30−50 nm in thickness) were sliced with a Leica ultracut UCT ultramicrotome after sonicating the samples to re-disperse the hollow spheres, drying and setting them in a LR-White resin. The thin sections were placed onto either carbon or noncoated copper grids. A Netzsch TG 209 apparatus was used for thermogravimetric analysis. The specific surface area was obtained from Brunauer−Emmett−Teller (BET) analysis after N_2 sorption with a Micromeritics Gemini II 2375 Surface Area Analyzer. Confocal microscopy (CFM) images were obtained with a Leica confocal scanning system mounted to a Leica Aristoplan.

Results and Discussion

Hollow Silica Microspheres. Using the electrostatic sequential adsorption technique, the thickness of the nanocomposite multilayer shell surrounding the colloidal particles can be tailored depending on the number of SiO_2/PDADMAC layers deposited: the SiO_2/PDADMAC layer pair thickness, ~30−40 nm, increases linearly with layer number.[20,22] This opens the way to fabricate hollow microspheres with controlled wall thicknesses. Figure 1 shows SEM micrographs of PS latices coated with three SiO_2/PDADMAC multilayers (a) before and (b) after calcination. Homogeneous multilayer shell coatings are produced on the PS latices, and the coated particles maintain the spherical shape of the neat PS latices. An increase in their size is also observed. The [$(SiO_2$/PDADMAC$)_3$]-coated PS latices have an average diameter of ~850 nm, giving a shell thickness of ~100 nm, since the average diameter of the coated particles prior to SiO_2 deposition is 650 nm.[20,22] The shell thickness corresponds to approximately three times the diameter (~30 nm) of the silica nanoparticles. Calcination (heating to 500 °C) of the PS latices coated with three SiO_2/PDADMAC layer pairs (as shown in Figure 1a) results in the production of hollow silica microspheres (Figure 1b). (Thermogravimetric analysis on samples confirms that the organic matter, i.e., colloidal core and bridging polymer, are removed during heating to 450 °C.) Both intact and broken hollow silica microspheres are shown in Figure 1b. Only complete, intact hollow microspheres are obtained by calcining the coated PS latices. The broken spheres seen were obtained by deliberately crushing them (i.e., by applying a pressure to them) to confirm that the microspheres are hollow. The diameters of the hollow microspheres produced are about 5−10% smaller than those of the uncalcined nanocomposite multilayer-coated PS latices. Similarly, complete hollow spheres are obtained when PS latices coated with two or more SiO_2/PDADMAC layer pairs are calcined. This, however, is not the case when PS latices coated with a single SiO_2/PDADMAC layer pair are calcined. In these samples both broken and intact hollow silica microspheres are produced. This shows that the silica wall thickness and/or the content of the silica nanoparticle coating with deposition of a single SiO_2 layer are not sufficient to maintain the initial spherical structure of the PS latices upon removal of the colloidal core.

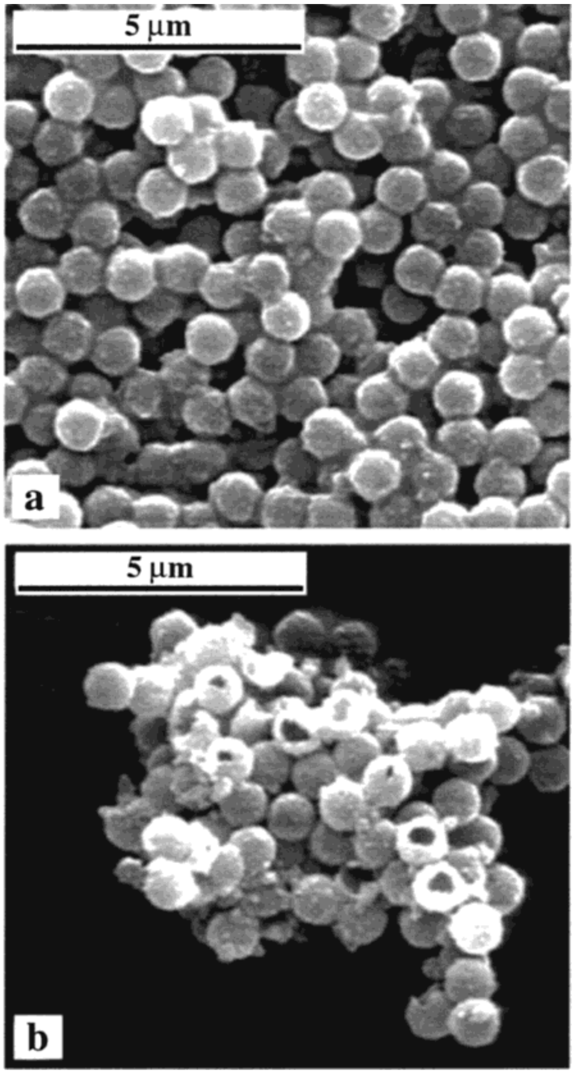

Figure 1. SEM micrographs of [$(SiO_2$/PDADMAC$)_3$]-coated PS latices (a) before and (b) after calcination. Uniform and smooth multilayer coatings are apparent in part a. The calcination process results in the PS latex colloidal core (and bridging polymer) being removed. Both intact and broken hollow silica microspheres are seen in part b. Some of the spheres were deliberately broken to demonstrate that they were hollow.

Figure 2 shows TEM micrographs of a PS latex particle coated with two SiO_2/PDADMAC layer pairs before calcination (a) and hollow silica microspheres obtained after calcination of SiO_2/PDADMAC-coated PS latices (b−d). In agreement with the SEM data, a uniform covering of the PS latices by the silica nanoparticles is observed, as is an increase in diameter of the coated particles (a). The diameter increase is ~120 nm, corresponding to a shell thickness equal to approximately twice the nanoparticle diameter. Calcina-

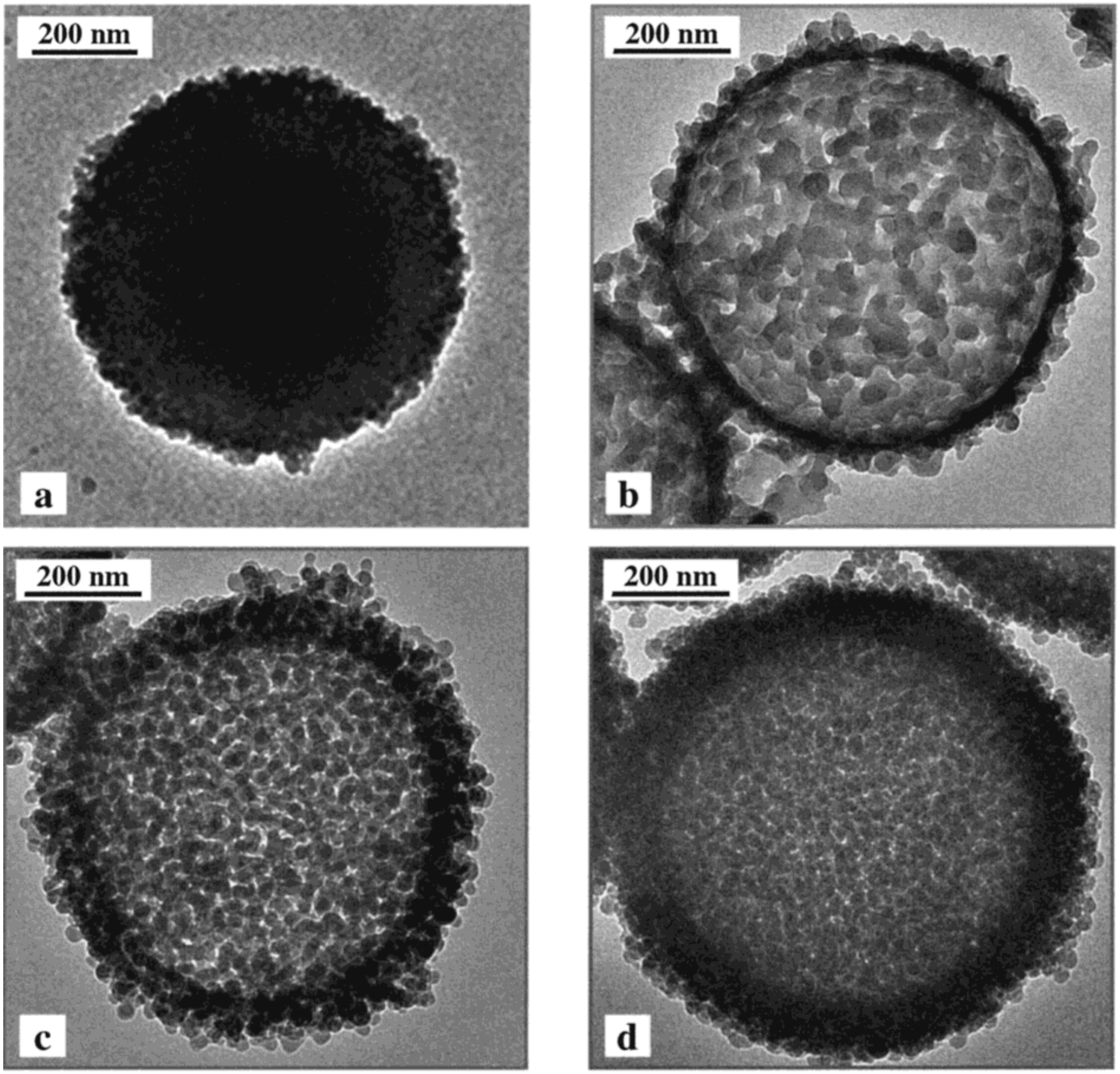

Figure 2. TEM micrographs of (a) a [(SiO_2/PDADMAC)$_2$]-coated PS latex particle and hollow silica microspheres obtained after calcining PS latices coated with (b) one, (c) two, or (d) three SiO_2/PDADMAC layer pairs. Individual SiO_2 nanoparticles can be seen on the surface of the PS latex particle in part a. Calcination results in removal of the core (seen as a reduction in the electron density in the interior of the spheres) and fusing of the nanoparticles (b−d). The micrographs of the hollow silica spheres display the wall uniformity and the nanoscale control of the wall thickness and outer diameter.

tion of the samples results in a noticeable difference in contrast in the image (due to a change in the electron density, i.e., less dense to the electrons) (b−d). This confirms that hollow silica microspheres are produced. Close inspection of the TEM images of the hollow silica microspheres shows that individual silica nanoparticles forming the multilayer shell fuse together after calcination; the high-temperature treatment results in condensation of the silica nanoparticles (i.e., sintering), causing their fusion and hence providing structural integrity for the microspheres. However, cross-linking between the spheres is limited. TEM images of the calcined coated particles that were redispersed by sonication in water show that individual hollow silica spheres can be produced, indicating that coalescence of individual SiO_2 nanoparticles occurs predominantly within individual spheres, rather than between the spheres.

Control over the wall thickness and outer diameter of the hollow silica spheres is also demonstrated in the TEM images shown in Figure 2. Both the wall thickness (increment ~30 nm) and sphere diameter (increment ~60 nm) increase regularly with the number of silica nanoparticle layers deposited. The uniform wall thickness is a reflection of the high regularity of the coating process.

TEM micrographs of cross-sections of hollow silica microspheres (three SiO_2/PDADMAC layer pairs) are shown in Figure 3. These images show the sphericity of the hollow spheres and the regular wall thickness. The average thickness of the silica shell, estimated by TEM from the ring around the perimeter of the hollow spheres, is between 100 and 120 nm.[23] It should be noted that the resin used to set the hollow spheres prior to ultramicrotoming is able to permeate the sphere walls, indicating that the hollow spheres are porous. This is evidenced by the similar electron density contrast in the interior and exterior of the hollow capsules.

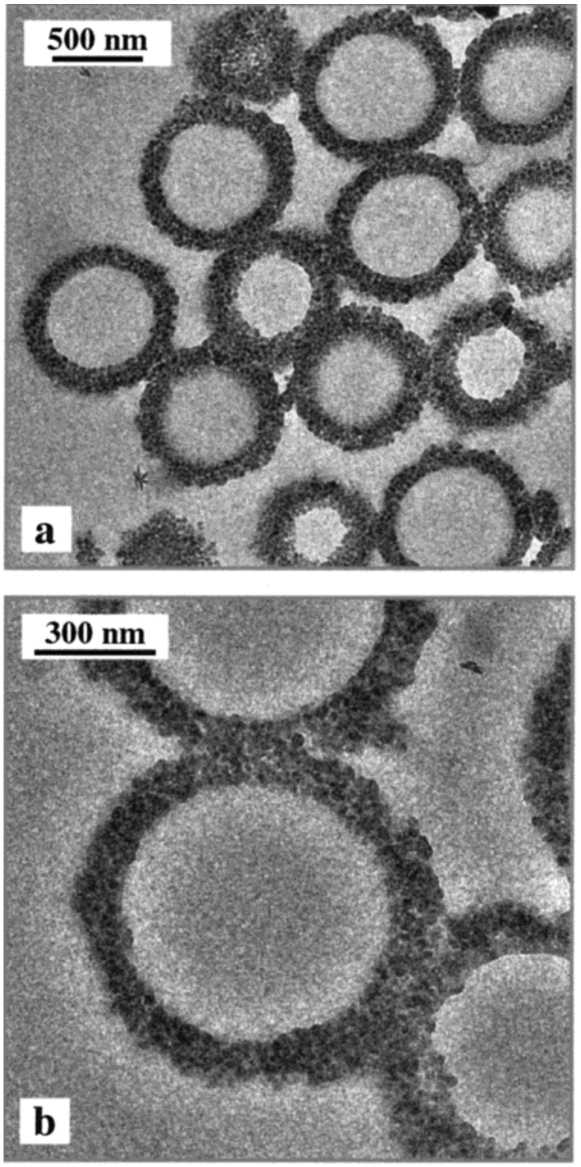

Figure 3. TEM micrographs of cross-sections of hollow silica microspheres. The hollow spheres were prepared by calcining [(SiO_2/PDADMAC)$_3$]-coated PS latices.

BET measurements yielded a surface area of 35 m^2 g^{-1} for composite solid (i.e., coated, nonhollow) microspheres comprising a PS latex core and three SiO_2/PDADMAC layer pairs. This value is considerably larger than the 10 m^2 g^{-1} measured for the uncoated PS latices but is close to that calculated for PS latices coated with a single SiO_2 layer (33 m^2 g^{-1}). This value is less than that calculated for PS latices coated with three SiO_2 layers (56 m^2 g^{-1}) (assuming deposition of a nanoparticle monolayer in each step). This suggests that for the composite microspheres, on average the equivalent of a single layer of the nanoparticles is accessible for N_2 sorption. BET measurements on hollow, pure silica microspheres composed of three SiO_2 layers (i.e., calcined [(SiO_2/PDADMAC)$_3$]-coated PS particles) gave a surface area of 147 m^2 g^{-1}, a value which is in excellent agreement with the 140 m^2 g^{-1} known for the silica nanoparticles used.[24]

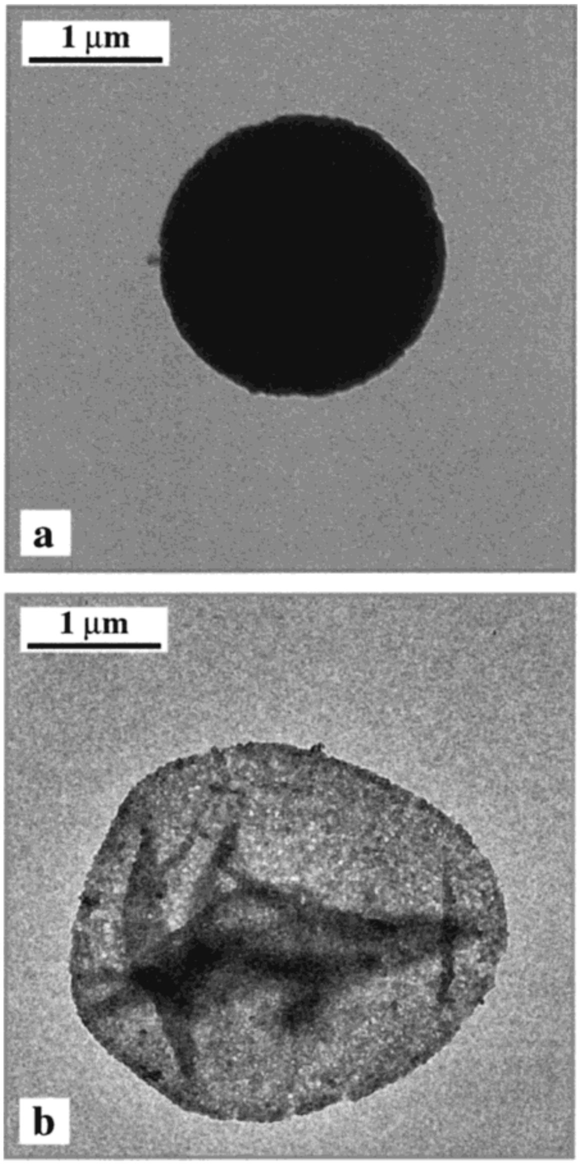

Figure 4. TEM micrographs of (a) a PE$_6$-modified MF particle coated with a [(SiO_2/PDADMAC)$_3$+(PSS/PDADMAC)$_2$] shell, and (b) the corresponding hollow composite shell obtained after removal of the MF core by treatment with HCl, and dried on a carbon surface. The darker feature seen across the center of the shell in part b is caused by collapse and overlap of the composite microsphere. The additional layers, (PSS/PDADMAC)$_2$, were deposited to avoid cross-linking (via silica condensation) between coated microspheres as a result of exposure to HCl.

Thermogravimetric analysis (TGA) showed that the surface coverage of the polystyrene microspheres by the silica nanoparticles was 52 wt % for PS spheres coated with [(SiO_2/PDADMAC)$_3$]. This value is in good agreement with that theoretically calculated for the same size microspheres coated with three silica nanoparticle monolayers (59 wt %). This confirms that our approach produces on average the deposition of a monolayer of nanoparticles. The TGA value is significantly higher than the 18.5 wt % reported for polystyrene micro-

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(23) Since the microspheres can be sliced at different sections, the shell thickness of the ultrathin cross-sections was determined from the TEM images where the sliced microspheres exhibit a diameter equal to that of the coated particles obtained from SEM. This ensures that the value determined is accurate.

(24) DuPont Specialty Chemicals, Product Information Booklet on Ludox Colloidal Silica, 1995.

spheres coated with silica nanoparticles of size 30−40 nm by seeded polymerization of tetraethoxysilane (three coating cycles) on the colloids.[14]

Larger colloids (spherical MF particles of 3 μm diameter) were also employed as templates for SiO_2/PDADMAC multilayer buildup. Calcination of MF particles coated with two or more silica nanoparticle layers also produced hollow silica spheres (data not shown). No significant difference in morphology was observed between the coated (solid) particles and the hollow silica spheres.

Hollow Hybrid Inorganic−Organic Microspheres. Hollow composite microspheres were obtained by removing the core of (SiO_2/PDADMAC)-coated latices by chemical means. (An additional four polyelectrolyte layers were deposited on top of the SiO_2/PDADMAC-coated latices to avoid any condensation, i.e., cross-linking, between coated microspheres as a result of exposure to acid.) SiO_2/polymer-coated MF particles of ~2 μm diameter were exposed to an acidic solution of $pH < 1.5$. The solution became transparent within a few minutes due to decomposition of the MF particles into its constituent oligomers.[25] The oligomers are readily expelled by permeating the nanoparticle/polymer multilayers forming the shells. Figure 4 shows TEM micrographs of the nanocomposite nanoparticle/polymer-coated MF particles (a) and of the corresponding shells obtained after drying on a TEM grid (b). The drying process (evaporation of the aqueous content by air-drying) induces creases and folds in the shells, as the shells have collapsed; the diameters of the dried composite shells are approximately 3.1 ± 0.2 μm, compared with ~2.2 μm for the composite solid particles. The shells are composed of nanoparticles embedded in a polymer matrix. Similar composite shells to that shown in Figure 4b were obtained by using dimethyl sulfoxide as the solvent to decompose MF colloidal cores, or tetrahydrofuran (THF) to decompose PS cores on which SiO_2/PDADMAC multilayers were assembled. However, in systems where the multilayer coating comprised of only one or two nanoparticle/polymer layers and THF was used to remove the PS core, broken composite hollow spheres were often obtained. This is most probably due to the swelling of the PS colloid prior to decomposition by THF, thereby rupturing the SiO_2/polymer coating.

Confocal microscopy measurements on hollow SiO_2/polymer microspheres containing one layer of a fluorescently labeled polyelectrolyte (fluorescein isothiocyanate (FITC)-labeled poly(allylamine hydrochloride) in the multilayer shell show that the shells maintain a close to spherical shape in solution.[26] This is in agreement with our previous finding that pure polyelectrolyte multilayers are also essentially spherical in solution, but collapse and spread when dried out on a solid support.[25]

The above shows that it is possible to produce hollow composite microspheres from colloids coated with nanoparticle/polymer multilayer shells. The incorporation of, for example, magnetic nanoparticles in the shell in a similar fashion yields magnetic composite particles[27] (and shells), thereby making their manipulation relatively straightforward by application of a magnetic field. Furthermore, the spherical shape of the composite shells could be altered through magnetic manipulation, creating asymmetric structures.

Conclusions

The present work demonstrates that it is possible to produce hollow microspheres using a colloid-templated assembly process followed by core removal by either thermal or chemical means. This approach allows the fabrication of hollow microspheres: (i) of tailored composition (inorganic or composites), (ii) with predetermined diameters and size distribution (dependent on the colloidal template), and (iii) of controllable wall thicknesses (ranging from tens to hundreds of nanometers). Currently, the preparation and characterization of other inorganic and composite hollow microspheres, produced from a variety of templates, are underway in our laboratories.

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(26) The hollow composite sphere comprised $[PE_6/(SiO_2/PDADMAC)_3+PSS/FITC\text{-}PAH]$. It was found that prolonged storage of the template MF particles resulted in their hardening (i.e., increased cross-linking), and hence breakage of the SiO_2/polymer shell wall occurred upon solvent decomposition of such multilayer-coated MF particles. This is explained by the larger constituents (as a result of cross-linking) not being readily able to permeate through the multilayer shell.

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