Hollow Capsule Processing through Colloidal Templating and Self-Assembly

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Abstract: Hollow capsules of nanometer to micrometer dimensions constitute an important class of materials that are employed in diverse technological applications, ranging from the delivery of encapsulated products for cosmetic and medicinal purposes to their use as light-weight composite materials and as fillers with low dielectric constant in electronic components. Hollow capsules comprising polymer, glass, metal, and ceramic are nowadays routinely produced by using various chemical and physicochemical methods. The current article focuses on a recent novel and versatile technique, based on a combination of colloidal templating and self-assembly processes, developed for synthesizing uniform hollow capsules of a broad range of materials. The strategy outlined readily affords control over the size, shape, composition, and wall thickness of the hollow capsules.

Keywords: colloids · hollow capsules · layered compounds · self-assembly · template synthesis

Introduction

The impetus for the intense research into the production of uniform-sized hollow capsules, typically in spherical geometry, emanates from their scientific and technological interest. Hollow spheres are utilized for the encapsulation and controlled release of various substances (e.g., drugs, cosmetics, dyes, and inks) in catalysis and acoustic insulation, in the development of piezoelectric transducers and low dielectric constant materials, and for the manufacture of advanced materials.[1]

Lipid liposomes and vesicles are a special group of hollow (sphere) structures; they are formed from phospholipids through self-assembly and create closed bilayer aggregate systems. Since the bilayer structures separate an aqueous interior from an aqueous exterior, water-soluble drug species can be encapsulated within them. They are widely used as delivery vehicles for various compounds in the pharmaceutical and cosmetic industries.[2] There are, however, a number of problems associated with their stability and permeability for various applications, prompting the use of different methods to effect their stabilization.[3]

There are a variety of methods currently used to fabricate a wide range of stable, hollow spheres of various compositions. These include nozzle reactor processes, emulsion/phase separation procedures (often combined with sol–gel processing), and sacrificial core techniques.[4] The nozzle and sacrificial core approaches generally produce coarse hollow spheres in the micrometer-to-millimeter size range, whilst emulsion/sol–gel methods afford hollow spheres of nanometer-to-micrometer sizes. Using nozzle-reactor methods (spray drying or pyrolysis), hollow polymer, oxide, metal, and glass composite microspheres have been produced.[1, 5–7] Bruinsma et al.[5] used spray drying to prepare hollow silica spherical particles. More recently, an aerosol-assisted self-assembly approach was employed to produce spherical nanoparticles possessing nanometer-scale pores.[6] Hollow microspheres of titanium dioxide with an extremely thin shell (50 nm) have also been prepared by spray drying of a colloidal suspension of exfoliated titanate sheets, followed by heating.[7]

Various groups have produced hollow and porous polymer spheres of submicrometer and micrometer size using emulsion polymerization or through interfacial polymerization strategies.[8] Micron-sized, hollow monodisperse cross-linked polymer particles were produced by suspension polymerization of emulsion droplets with polystyrene dissolved in an aqueous solution of poly(vinyl alcohol).[8a] Latex particles with a multihollow structure were prepared by seeded emulsion polymerization,[8b] while polymer hollow spheres were obtained by cross-linking polymerization of hydrophobic monomers in the interior of the surfactant bilayer of vesicles.[8c] Single and mixed ceramic oxides as well as ceramic hollow microspheres have also been processed by emulsion/phase separation procedures;[1, 9] for example, hollow silica spheres with diameters of 1–100 μm were prepared by interfacial reactions conducted in oil/water emulsions.[9a]

In the sacrificial core process, a coating is deposited on the core by controlled surface precipitation of inorganic molecular precursors from solution or by direct surface reactions.[10–15] The core is then subsequently removed by thermal

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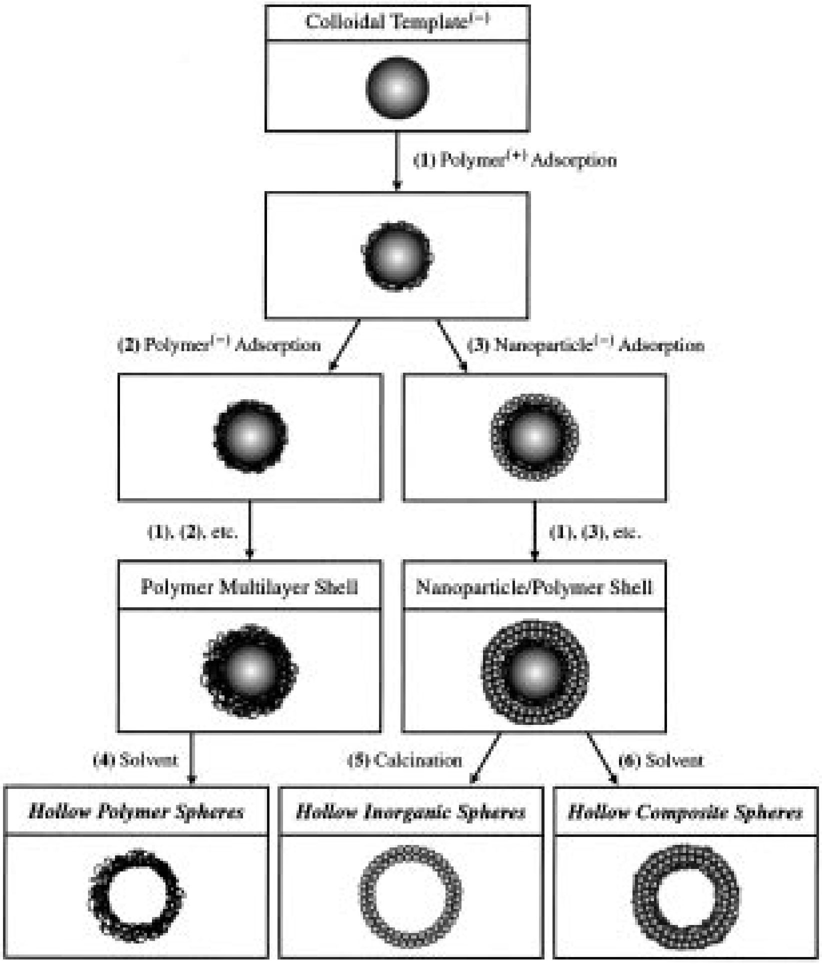
or chemical means, leaving behind hollow spheres.[10a, 11, 12] Submicron- and micron-sized hollow spheres of yttrium compounds[10a] and silica spheres,[12] and monodisperse hollow silica nanoparticles[11] have been generated by using this approach.

The application and commercialization of hollow spherical structures has, however, been limited mainly because of the disadvantages associated with the techniques used for their production. Relatively harsh conditions are employed in some methods, making them unsuitable for the encapsulation of sensitive materials, and encapsulation of materials after their formation is often difficult. Other disadvantages are the lack of control over size, geometry, wall thickness, and wall uniformity of the hollow spheres produced.[1, 16] For example, a key parameter controlling the performance of hollow spheres for various technologies is the diameter-to-wall thickness (d:t) ratio.[16] It is expected that the generation of hollow spheres with thin walls, increased wall thickness uniformity, and higher d:t ratios will extend the potential uses of hollow spherical materials.[1, 7, 16]

An alternative, facile approach for producing hollow spheres that has been pioneered in our research group is that which combines colloidal templating and self-assembly strategies, followed by colloidal core removal.[17–20] The general concept applied is to arrange a broad range of macromolecules into highly ordered (nanostructured) architectures by self-assembly through noncovalent interactions on colloidal templates, followed by removal of the decomposable colloidal core (Scheme 1). By using this process, important parameters such as size, geometry, composition, wall thickness and uniformity, and the diameter-to-wall thickness ratio of the hollow spheres can be readily controlled. The procedure can also be extended to encapsulate biologically significant materials in the form of biocolloids.

Concept

Our approach is based on the principle of depositing oppositely charged macromolecular species by their sequential (layer-by-layer, LbL) electrostatic self-assembly onto colloidal templates. The notion of adsorbing particles onto solid substrates in a LbL manner was introduced by Iler in the mid 1960s.[21] Decher and co-workers extended Iler's work to a combination of linear polycations and polyanions in the early 1990s.[22] Other groups later adapted the LbL technique to include inorganic nanoparticles, biomolecules, clays, and dyes in polyelectrolyte multilayer assemblies.[23] The above studies all focused on employing macroscopically flat (two-dimensional), charged surfaces as the substrates for adsorption. More recently, the LbL method was applied to colloidal particles, thus permitting the formation of composite core-shell particles,[24–26] the precursors to hollow capsules (spheres).



Scheme 1. Schematic diagram for hollow capsule production by exploiting colloidal templating and self-assembly methods. Colloidal templates of different composition, size, and geometry can be employed; these range from spherical polymer particles to nonspherical biocolloids with diameters in the submicrometer to micrometer regime. The first step (1) involves the deposition of a charged polymer layer onto colloidal particles. The charged polymer, which exhibits the opposite charge (depicted as positive) to the particle surface, is added to the colloidal suspension and allowed to adsorb through electrostatic interactions. Subsequent exposure of the polymer-coated colloids to oppositely charged polymer (step 2) or nanoparticles (step 3) results in another polymer or nanoparticle layer being deposited. Additional layers can be deposited by repeated deposition cycles, making use of the surface charge reversal that occurs upon adsorption of each layer, thereby producing colloidal core-multilayer shell particles. Following the deposition of each layer, excess unadsorbed polyelectrolyte or nanoparticles are removed by repeated centrifugation or filtration and wash cycles. Hollow capsules are produced by the subsequent removal of the core from the composite colloids, achieved either by chemical or thermal means. Exposure of the coated colloids to a solvent which decomposes the core results in hollow polymer (step 4) or composite (step 6) spheres, while heat treatment (calcination, step 5) of the coated particles removes both the colloidal core and bridging polymer, thereby producing hollow inorganic spheres.

Formation of colloidal core-multilayer shell particles

In the colloid-directed templating strategy,[17–19,24] a colloidal solution (typically a few wt%) is exposed to a polymer solution of concentration sufficient to cause saturation adsorption. The added polymer bears an opposite charge to that on the colloids, thereby utilizing electrostatics for adsorption. Unadsorbed polymer is then removed by repeated centrifugation (or filtration), with intermittent washings. At this point a reversal in the sign of the zeta (ζ)-potential is observed (compared with the bare particles). This indicates the successful adsorption of polymer (Figure 1). Subsequent consecutive adsorption of oppositely charged polymer or nanoparticles (or other oppositely charged macromolecules[27]) produce particles that exhibit alternating ζ-potentials in sign. Such alternating values qualitatively demonstrate a successful recharging of the particle surface, and are characteristic of stepwise growth of multilayer films on colloids.[24]

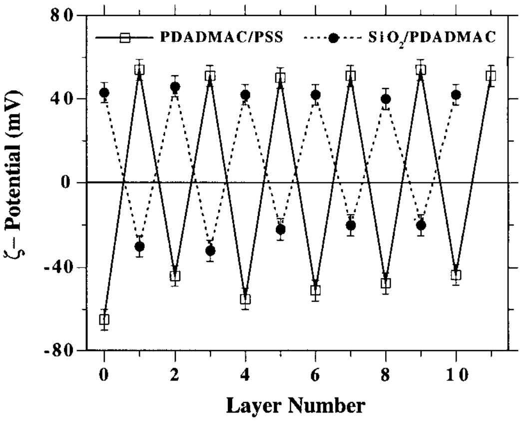


Figure 1. ζ-Potential as a function of layer number for polymer multilayers (squares) and nanoparticle/polymer multilayers (circles) on sulfate-stabilized polystyrene (PS) latices. The polymer multilayers comprise poly(diallyldimethylammonium chloride) (PDADMAC) and poly(styrenesulfonate) (PSS), while the nanoparticle/polymer layers were formed from SiO_2 nanoparticles and PDADMAC. Polymer layers were directly assembled onto the negatively charged PS latices (−65 mV). The negatively charged PS latices were made positively charged (+45 mV) by precoating with a three-layer polymer film to facilitate the electrostatic deposition of the first SiO_2 nanoparticle layer. The alternating values observed for both systems indicate successful recharging of the particle surface with deposition of each layer: Negative values are observed for PSS or SiO_2 depositions, and positive values for PDADMAC adsorption.

Quantification of multilayer deposition on colloids is obtained through single-particle light scattering measurements (SPLS), a technique that enables determination of the thickness of adsorbed layers, as well as the state and degree of the coated colloids with respect to aggregation.[24a,b] Regular, stepwise growth of pure polymer multilayers as well as nanoparticle/polymer multilayers occurs as a result of using the LbL strategy (Figure 2). The average thickness of each polymer layer is about 1.5 nm.[24a] The thickness for each nanoparticle (SiO_2)/polymer layer is 30–40 nm, corresponding to the adsorption of approximately one monolayer of nanoparticles with each deposition step.[24b,c] These data show that the shell thickness can be controlled at the nanometer level: to within 2 nm forthe polymer shells, and the diameter of the nanoparticles for the inorganic/polymer composite shells. Furthermore, SPLS reveals that the colloidal core-multilayer shell particles prepared in this way exist as single, unaggregated particles in solution.

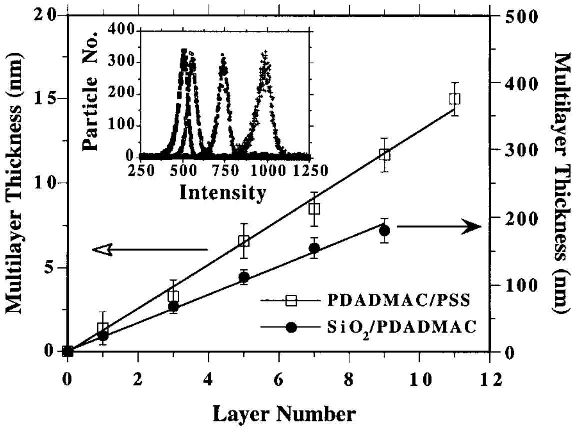


Figure 2. Shell thickness of PDADMAC/PSS (squares) and SiO_2/PDADMAC (circles) multilayers assembled on PS latices as a function of layer number. The layers were assembled by the consecutive adsorption of PDADMAC and PSS or SiO_2 and PDADMAC. The thicknesses were determined from single-particle light scattering (SPLS) measurements. The inset shows representative SPLS intensity distributions from which the thicknesses were derived: from left to right, bare PS latices, and PS latices coated with one, three, and five SiO_2/PDADMAC multilayers. The systematic shift in the intensity of the SPLS distributions with increasing layer number is characteristic of an increase in thickness of the multilayer shell on colloidal particles. No aggregation of the coated particles was observed.

Direct visualization of the morphology of, for example, nanoparticle (SiO_2)/polymer-coated colloids, and confirmation of their regular assembly is provided by electron microscopy. Atomic force, scanning electron, and transmission electron microscopy (AFM, SEM, and TEM, respectively) reveal a homogenous nanoparticle coating and a systematic increase in the diameter of the coated colloids. The TEM data (Figure 3) yields an average diameter increment of about 65 nm, or a layer thickness of approximately 30 nm for each nanoparticle/polymer layer pair.[24b,c] These values are in agreement with the SPLS data.

The above examples highlight the versatility of the strategy employed to fabricate composite multilayers on colloids: pure polymer or nanocomposite inorganic–organic multilayers can be assembled. The general nature of the approach presented is further demonstrated by the recent fabrication of micrometer-sized composite particles with ordered multilayer arrays of proteins,[27] magnetic nanoparticles,[28] luminescent semiconductors,[29] or functional metallo-supramolecular coordination polyelectrolytes.[30] Furthermore, the LbL procedure can be extended to colloidal templates with diameters in the nanometer regime.[30] Spectroscopic investigations have also been undertaken to investigate the nature of the electrostatic interactions in the polyelectrolyte multilayer films assembled on colloids.[24a] In addition to using polymer latex particles as the colloidal template, biocolloids with diameters in the micrometer range can also be successfully templated, thereby effecting their encapsulation.[31,32] The use of colloidal particles as templates for the assembly of

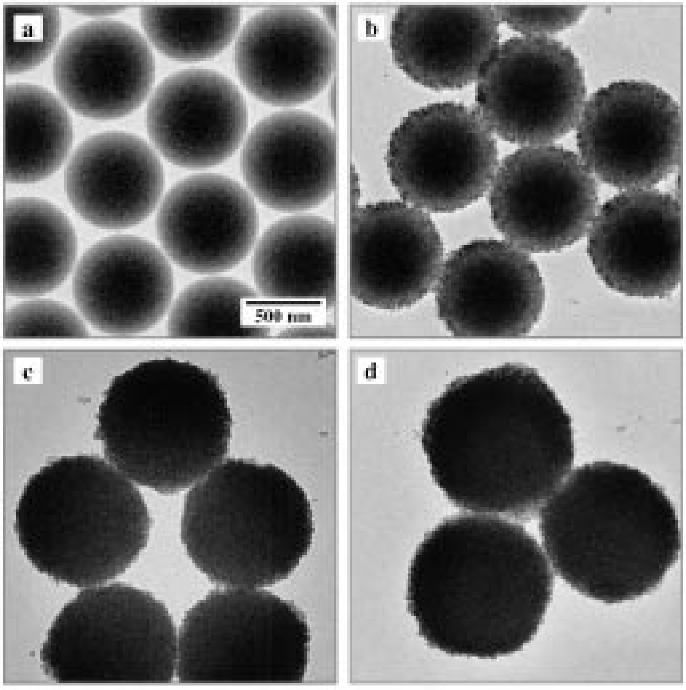


Figure 3. TEM micrographs of a) uncoated PS latices and polyelectrolyte-modified PS latices coated with b) one, c) three and d) five SiO_2/PDADMAC multilayers. The presence of SiO_2 nanoparticles on the surface is evident from the increase in surface roughness. The systematic increase in diameter of the particles with increasing layer number confirms regular, step-wise growth of SiO_2/PDADMAC multilayers on PS latices. The scale bar corresponds to all four TEM images shown.

multilayer shells through solution self-assembly provides a viable route to the production of tailored new materials with unique properties for various applications.

Hollow capsule production

Scheme 1 shows that removal of the templated colloid, either chemically or thermally, permits the formation of hollow spheres of different composition (polymer, inorganic or composites). The procedure makes use of the inherent permeability of the multilayer shell: if the shell has sufficiently high permeability for removal of the decomposed core constituents, then the shell can be preserved and hollow (porous) spheres obtained.

Polymer capsules: Figure 4 demonstrates the versatility of the approach for producing polymer shells with regard to the size, shell composition, colloidal template, and core removal procedure. Figure 4a is a TEM micrograph of an air-dried polymer capsule [Fe^{II} metallo-supramolecular coordination polyelectrolyte/poly(styrenesulfonate), Fe^{II}-MEPE/PSS] that was produced by templating weakly cross-linked melamine-formaldehyde (MF) particles of 1.7 μm diameter, and subsequently decomposing the core by exposure of the coated particles to an acidic solution of $pH < 1.6$.[30] The acid causes decomposition of the MF particle into its constituent oligomers, and the oligomers are then readily expelled from the core by permeating the polyelectrolyte multilayer shell.[18] Remarkably, even the deposition of only three polyelectrolyte layers onto colloids results in the production of polyelectrolyte capsules when the core is removed.[18] This affirms the exceptionally strong electrostatic forces involved in the formation of ultrathin polyelectrolyte layers assembled in a LbL manner. Figure 4b shows a representative AFM image of an air-dried hollow polymer multilayer capsule comprising PSS and poly(allylamine hydrochloride) (PAH). Such capsules were obtained after exposing PSS/PAH multilayer-coated catalase enzyme crystals of approximately 10 μm diameter to an oxidizing solution (e.g. deproteinizer).[31] The enzymes are decomposed by the treatment, allowing the expulsion of their fragment constituents from the interior by permeating the polymer capsule walls. Some residual enzyme can still be seen inside the polymer shell.

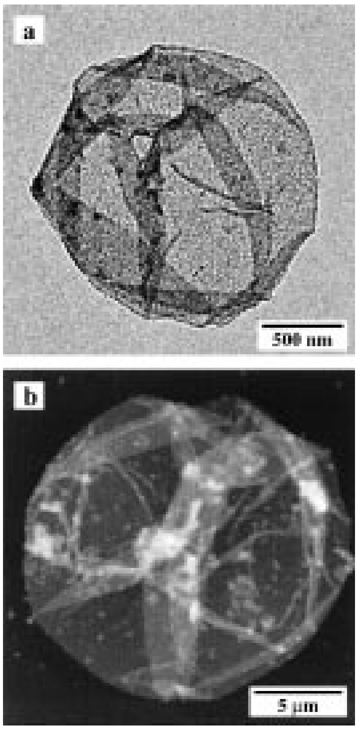


Figure 4. Microscopy images of air-dried hollow polymer multilayer capsules, obtained by coating polymer- and bio-colloids of submicrometer- and micrometer-size, respectively, with polymer multilayers, and then removing the templated core. a) TEM micrograph of a hollow polyelectrolyte shell comprising a total of five layers of an Fe^{II} metallo-supramolecular coordination polyelectrolyte (Fe^{II}-MEPE) and PSS. The layers were formed on melamine-formaldehyde (MF) particles and the core was subsequently decomposed by an acidic solution of $pH < 1.6$. b) AFM image of a hollow polymer multilayer capsule comprising eight PSS and poly(allylamine hydrochloride) (PAH) layers. Note the different sizes of the hollow polymer spheres, which is determined by the size of the colloidal template: the Fe^{II}-MEPE/PSS capsule has a diameter (long-axis) of approximately 2 μm, and the PSS/PAH shell a diameter of 20 μm. The capsules were air-dried which causes them to undergo some spreading, explaining their larger size than the original particle template (diameters of 1.7 μm and about 10 μm for the polymer- and bio-colloid templates, respectively).

The images in Figure 4 show that the drying process (evaporation of the aqueous content by air-drying) induces folds and creases in the polymer capsules, and some spreading is noticed; the diameters of the dried polymer capsules are larger than those of the original templates. However, hydrated polymer capsules or those filled with resin maintain their original (spherical) shape, as shown by confocal microscopy and cross-section TEM, respectively.[18] In contrast, polymer multilayers assembled on essentially rectangular enzyme crystals undergo a morphology change from rectangular to spherical upon solubilization of the enzyme crystal.[31] This is most likely due to the osmotic pressure build-up caused by solubilization of the enzyme.

Inorganic capsules: Calcination of sulfate-stabilized PS latices coated with nanoparticle/polymer multilayers results in the production of hollow silica spheres.[17, 20] The calcination process removes the organic matter (the colloidal core and bridging polymer) during heating to 450 °C, as confirmed by thermogravimetric analysis. Importantly, it also causes condensation of the silica nanoparticles, hence providing structural integrity for the hollow spheres. Figure 5 shows TEM micrographs of hollow silica spheres produced by calcining PS latices coated with (a) a single SiO_2/PDADMAC layer pair, and (b) three SiO_2/PDADMAC layer pairs. Comparison of these images with those of the corresponding coated PS latices prior to calcination (Figures 3b and 3c) reveals that the interior of the calcined samples are less electron dense, as expected for hollow spheres. The diameters of the hollow silica spheres produced are 5–10 % smaller than those of the uncalcined multilayer-coated PS latices. The difference in the thickness of the capsule wall is also noticeable for the hollow spheres shown. Complete, unbroken silica hollow spheres which preserved the original shape of the template were obtained when the wall thickness consisted of two or more silica layers, whereas both broken and unbroken hollow spheres were produced when the wall comprises a single silica layer.

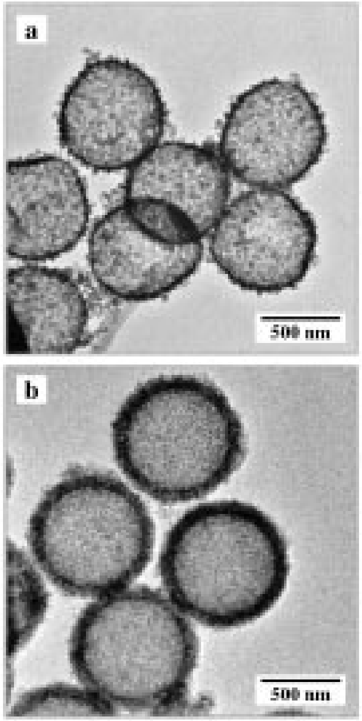


Figure 5. TEM micrographs of hollow silica spheres produced by calcining PS latices coated with a) a single SiO_2/PDADMAC layer pair, and b) three SiO_2/PDADMAC layer pairs. The hollow silica spheres retain the spherical shape of the original PS particle templates. The high uniformity of the capsule walls is evident. The hollow sphere wall thickness is approximately three times greater for the spheres in image (b) compared with that for the spheres in image (a).

TEM micrographs of ultrathin (30–50 nm) cross-sections of the silica spheres confirm that they are hollow (Figure 6). The inset shows an SEM micrograph of the same spheres, one of which was deliberately broken by crushing, and the other which remained intact. The average thickness of the silica shell is 100 ± 10 nm. Simply altering the number of nanoparticle/polymer deposition cycles can control the wall thickness and outer diameter of the hollow silica spheres: the wall thickness and outer diameter increments with each silica nanoparticle/polymer layer deposition are 30 nm and 60 nm, respectively. This opens the way to produce hollow capsules with higher *d*:*t* ratios, as desired for various applications. Although coalescence of individual silica particles occurs as a result of calcination, coalescence between hollow spheres is limited. The hollow silica spheres can be easily re-dispersed in water, and individual hollow silica spheres are readily obtained (for example, see Figures 5 and 6). Larger hollow silica spheres, of several micrometers in diameter, were also produced by using larger templating polymer particles.[20] More recently we have been successful in producing hollow magnetic spheres using this approach. The potential uses of these hollow spheres include separations, affinity chromatography, catalysis and delivery systems.

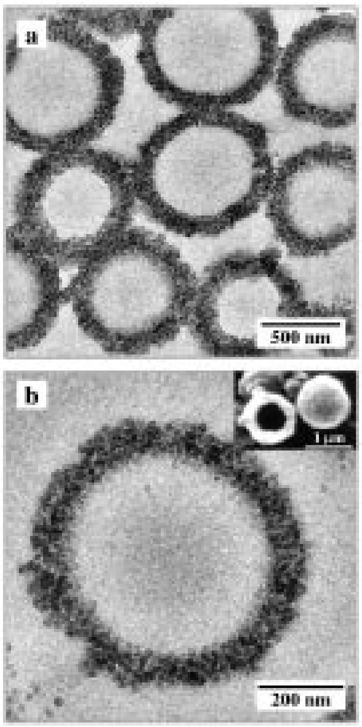


Figure 6. TEM micrographs of cross-sections of hollow silica spheres. The inset shows an SEM micrograph of a deliberately broken silica sphere beside an intact hollow sphere. The hollow spheres were prepared by calcining [$(SiO_2/PDADMAC)_3$]-coated PS latices.

Composite capsules: Hollow inorganic–organic composite spheres can be obtained by selection of a solvent that decomposes the templated core but leaves the polymer bridging the nanoparticles in the shell. The choice of solvent depends on the type of core employed; for example, acidic or dimethyl sulfoxide solutions cause the removal of MF polymer latex core templates, tetrahydrofuran the removal of some polystyrene cores, and highly oxidizing solutions decompose proteinaceous cores. Figures 7 and 8 illustrate two examples of hollow composite shells produced using this approach. In Figure 7 the nanoparticle/polymer multilayer shell assembled onto MF particles (a) obtained upon decomposition of the MF core by acid assumes a rather flat confirmation on the substrate when dried (b),[20] similar to the pure polymer shells. Confocal microscopy images of the hollow composite microspheres again show that the shells often maintain their spherical shape in solution. Interestingly, the oligomers produced as a result of decomposing the MF particles are still readily expelled by permeating the nanoparticle/polymer shell. Higher magnification TEM reveals that the shell is composed of nanoparticles embedded in the polymer matrix.[20]

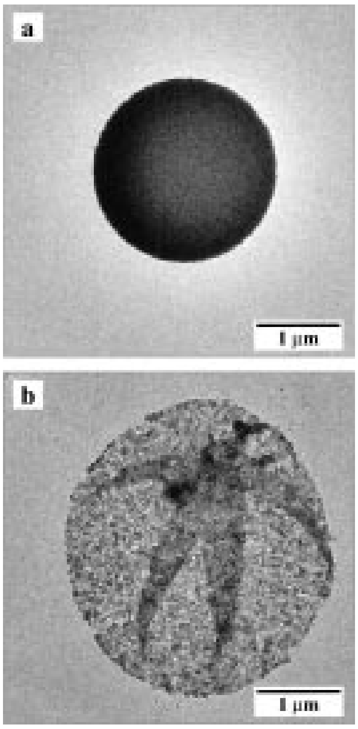


Figure 7. TEM micrographs of a) a SiO_2/PDADMAC-coated MF particle and b) a hollow composite nanoparticle/polymer sphere (or shell) dried on a carbon grid. The hollow composite shell was obtained after removal of the MF core by treatment with hydrochloric acid at pH <1.6. The "shadowing" (more electron dense) feature seen is caused by the collapse and overlapping of the composite hollow sphere. Four additional polymer layers were deposited as outer layers prior to acid treatment to avoid cross-linking between coated spheres by condensation.

Figure 8 shows that nanoparticle/polymer coated biocolloids (gluteraldehyde-fixed echinocytes) can also be utilized for the production of composite hollow structures. The template in this example has a jagged and highly structured surface. After removal of the core by exposure to deproteinizer, hollow composite silica/polymer capsules are obtained (b).[33] Unlike the polymer or nanoparticle/polymer shells produced by removal of MF-templated cores by acid solutions, these hollow structures mimic the original shape, including the secondary structure (spikes) of the templates, and do not significantly spread-out on the surface when dried. This is most probably due to gelation of the silica particles as a result of the decomposing solution (pH 11–12).[34] SEM experiments confirmed that these structures were hollow.

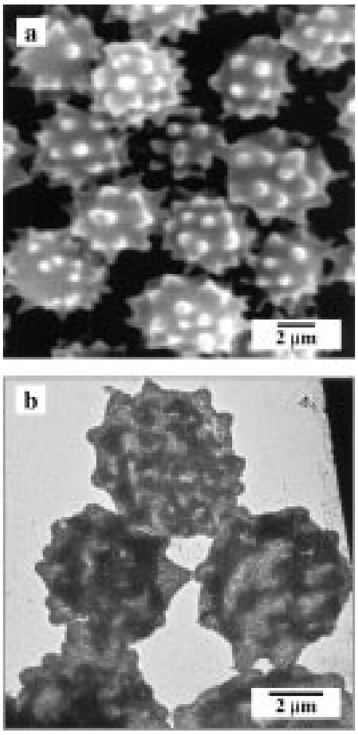


Figure 8. a) SEM micrograph of gluteraldehyde-fixed echinocytes and b) TEM image of hollow composite nanoparticle/polymer structures. The hollow capsules in b) were prepared by depositing three SiO_2/PDADMAC layer pairs on polyelectrolyte-modified echinocytes and then removing the core using an oxidizing solution.

Conclusions and Outlook

The coupling of colloidal-templating with self-assembly allows the fabrication of a broad range of coated colloids and hollow capsules of varying and defined composition in the submicrometer to micrometer-size regime. Their geometry, diameter, and wall thickness can be controlled with nanometer precision by employment of colloids of a given shape and size, and by varying the number of coating cycles. The uniformity in size of the hollow capsules is predetermined by the monodispersity of the colloidal templates.

The successful production of such hollow capsules opens many new and exciting avenues in the areas of chemistry, biotechnology-, and materials science. They are potentially suitable for a variety of applications including the loading of drugs, as confined environment reactor systems, and for targeting by utilization of the surface functionalities on the capsule walls to attach specific receptors. Controlling the thickness and composition of the capsule walls should allow selective and switchable permeation for the encapsulation and release of various substances. The use of cross-linkable, pH- or temperature-sensitive polymers as capsule wall constituents are attractive candidates for controlling and varying the permeability, while the incorporation of specific reactive groups inside the capsule walls would allow specific chemistry to be carried out in these systems (e.g. crystallization, polymerization). Coupling of biospecies to the surfaces of the capsules through functional groups (e.g. utilizing silica capsules) would provide bio-functionalized capsules.

Recent experiments demonstrate that it is possible to coat the outer and inner surfaces of hollow polymer capsules with phospholipid bilayers. The polymer capsules are permeable to small low molecular weight dyes (similar to related supported films[24a,d]), but not to polyelectrolytes with molecular weights greater than 4000 or molecules larger than 5–10 nm in diameter. The phospholipid coating reduces the permeability to small organic dyes. The precipitation of small organic dye molecules inside polymer capsules has been achieved, as has the solubilization of various organic solvents. Functional biomolecules (enzymes) have also been encapsulated at a very high loading capacity in polymer capsules;[31] these systems are expected to be used in enzyme catalysis applications. The coating technique is currently being extended to inorganic templates to create novel hollow capsules of nanometer size and to emulsion-based systems.

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