Core−Shell Particles and Hollow Shells Containing Metallo-Supramolecular Components

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Core−shell particles consisting of a polystyrene (PS) latex colloidal core and Fe(II) metallo-supramolecular polyelectrolyte (Fe(II)−MEPE)/poly(styrenesulfonate) (PSS) multilayer shells were fabricated by the consecutive assembly of Fe(II)−MEPE and PSS on PS particles. The layers were deposited under conditions where the Fe(II)−MEPE and PSS are oppositely charged, thereby utilizing electrostatic attractions for multilayer buildup. Formation of Fe(II)−MEPE/PSS multilayers on weakly cross-linked melamine−formaldehyde (MF) particles, followed by MF particle decomposition and removal, resulted in hollow Fe(II)−MEPE/PSS shells. The Fe(II)−MEPE/PSS multilayer shell on the colloidal particles and the Fe(II)−MEPE/PSS hollow shells were found to be stable, resisting decomposition upon exposure to acidic solutions or chelating agents. PS latices as small as 70 nm in diameter were also employed as templates for the successful fabrication of Fe(II)−MEPE/PSS and poly(allylamine hydrochloride)/PSS multilayer shells. These results demonstrate that our approach can be extended to colloidal templates with diameters less than 100 nm. This work represents a first study of structurally well-defined metallo-supramolecular polyelectrolyte−colloid assembles combining the functional units from supramolecular chemistry with the restricted dimensionality of colloids.

Introduction

The engineering of particle surfaces is currently an active area of research and of great technological interest.[1] The particle characteristics can be modified through tailoring of their surface properties. This is often accomplished by coating the particles or encapsulating them within a shell. Core−shell particles, which typically consist of solid or liquid cores surrounded by shells of either organic or inorganic material, are frequently prepared by a variety of approaches. Methods for their preparation include heteroaggregation (aggregation of oppositely charged particles),[2] polymerization processes (e.g., interfacial polymerization in emulsions, photopolymerization of monomers in two-phase aerosol droplets, dispersion/precipitation polymerization),[3] controlled phase separation of polymers within droplets of oil-in-water emulsions,[4] and direct surface reactions or controlled surface precipitation in the case of inorganic coating of the core.[5−10]

An alternative approach, which allows the fabrication of a novel class of core−shell particles, is that which combines colloid science and self-assembly strategies. This method uses colloidal particles as templates to assemble nanocomposite multilayer shells.[11−15] The primary driving force for the multilayer shell formation on the particles is the electrostatic attraction between the oppositely charged species that are deposited. The assembly proceeds via the successive deposition of the

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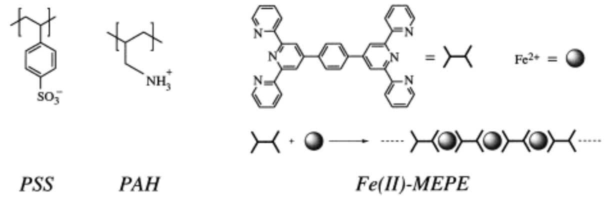
Scheme 1. Schematic of the Polyelectrolytes used for Forming Multilayer Shells on Colloidal Particles[a]



[a] PSS = Poly(styrenesulfonate); PAH = poly(allylamine hydrochloride); Fe(II)−MEPE = Fe(II) metallo-supramolecular coordination polyelectrolyte. The counterions are omitted for clarity.

macromolecules of opposite charge. The thickness of the nanocomposite multilayer shells produced by this layer-by-layer (L-b-L) approach can be controlled with nanometer precision. By use of this strategy, multilayer shells of polyelectrolyte[14] and nanocomposite shells of polyelectrolytes containing zirconium phosphate sheets,[11] inorganic nanoparticles,[12,13] or biomolecules[15] have been assembled on colloidal core particles.

Recently, Kurth et al. reported the L-b-L assembly of a new class of metallo-supramolecular polyelectrolytes into layered two-dimensional films.[16] Supramolecular components as operative units in structurally well-defined assemblies open exciting avenues toward new functional materials.[17] The realization of such materials will rely on improving existing preparative methods and on finding new strategies to integrate active components into structurally coherent macroscopic supramolecular architectures. This has prompted us to investigate a strategy to combine metallo-supramolecular components with the restricted dimensionality of colloidal surfaces. In contrast to the extended two-dimensional analogues,[16] metallo-supramolecular polyelectrolyte−colloid assemblies constitute self-contained, yet macroscopic assemblies that remain in solution.[18]

In this paper, we provide a detailed investigation on the construction of a novel class of core−shell particles by the L-b-L method: The core−shell particles comprise polystyrene (PS) latices or weakly cross-linked melamine formaldehyde (MF) particles as the core, and a novel coordination polyelectrolyte which contains metallo-supramolecular functional subunits (Fe(II)−MEPE, Scheme 1),[16] assembled in alternation with poly(styrenesulfonate), as the encapsulating multilayer shell. The colloidal core templates employed vary in diameter from 1.7 μm down to 70 nm. In addition, it is shown that stable hollow Fe(II)−MEPE/PSS shells can be produced from the core−shell particles by decomposition and removal of the core. The present work demonstrates that it is possible to assemble functional supramolecular polyelectrolytes on colloidal particles of micro- and nanometer size, thereby creating particles with molecularly engineered properties. The particles produced are expected to have potential applications in electronics, photonics, and catalysis. The functional and stable hollow shells constructed are potentially useful as microreactor systems and for the incorporation of various species.

Experimental Section

Materials. Poly(allylamine hydrochloride) (PAH), M_w 8000−11 000, and poly(sodium 4-styrenesulfonate), M_w 70 000, were obtained from Aldrich. Low M_w PSS (1100) was obtained from Polymer Standards Service, Mainz, Germany. All polyelectrolytes were used as received, except for the 70 000 M_w PSS, which was dialyzed against Milli-Q water and lyophilized before use. The coordination polyelectrolyte (M_w > 14 900) was prepared as described earlier.[16] The sulfate-stabilized polystyrene latices (diameter 640 nm) were prepared as described elsewhere.[19] Cetyltrimethylammonium-stabilized PS latices of 70 nm diameter were obtained from Katharina Landfester, Max Planck Institute of Colloids and Interfaces. Details of the synthesis of the 70 nm PS latices can be found in the literature.[20] The positively charged, weakly cross-linked melamine formaldehyde particles (diameter of ca. 1.7 μm) were purchased from Microparticles GmbH, Berlin. 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.

Fe(II)−MEPE/PSS Multilayer Formation on Colloids. Typically, 10^{10} particles were dispersed in approximately 0.5 mL of water, and 1 mL of a 1 mg mL^{-1} aqueous polyelectrolyte solution was added. (This polyelectrolyte concentration is much larger than that needed for saturation coverage of the particles. The polyelectrolyte added was in all cases oppositely charged to the particles, and no additional salt was added to the polyelectrolyte solutions from which adsorption proceeded.) The polyelectrolyte was allowed to absorb on the colloids for 15 min, during which time the dispersion was occasionally stirred. The dispersions were then centrifuged for 15 min at 13 500*g* for the 640 nm diameter PS latices, 15 min at 5 000*g* for the MF particles, and 15 min at 40 000*g* for the 70 nm diameter PS latices. After centrifugation, the supernatant was removed, approximately 1 mL of water was added, and the particles were redispersed by agitation with a vortex. The centrifugation, washing, and redispersion cycles were repeated three times to ensure that all free polyelectrolyte in solution was removed. Additional polyelectrolyte layers were deposited following the method described above for adsorption of the first layer, resulting in polyelectrolyte multilayers on colloids. In some cases the coordination polyelectrolyte was adsorbed from methanol; no differences in the adsorbed amount were observed when compared to its adsorption from water.

Decomposition of the MF Particles. For the production of hollow shells from the polyelectrolyte-templated MF particles, 0.2 mL of the coated MF particles were exposed to 1 mL of HCl at pH = 1 for 10 min. This time was sufficient for decomposition of the MF particles.[14b] The shells were then centrifuged at 10 000*g* for 15 min and redispersed in water, and the supernatant was exchanged for pure water. The acid treatment and water washing steps were repeated a further two times.

Electrophoretic Mobility (EPM) Measurements. Electrophoretic mobilities were measured using a Malvern Zetasizer 4. The ζ-potential was calculated from the electrophoretic mobility u by using the Smoluchowski relation $\zeta = u\eta/\epsilon$, where η and ϵ are the viscosity and permittivity of the solution, respectively. All ζ-potential measurements were performed without added electrolyte.

UV−vis Measurements. UV−vis absorption spectra were recorded using a Cary model 4E UV−visible spectrophotometer.

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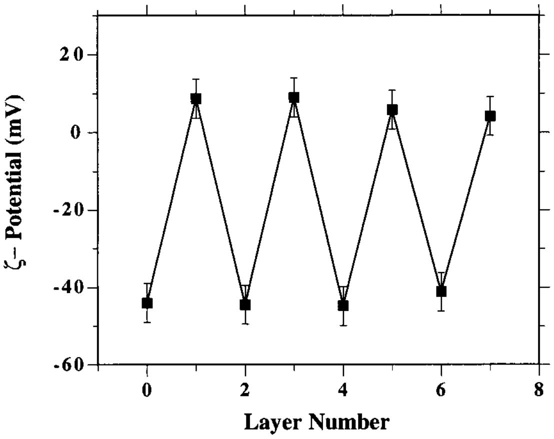

Figure 1. ζ-potential as a function of polyelectrolyte layer number for (PSS/Fe(II)−MEPE)-coated 640 nm PS latices. The PS latices were precoated with a PAH layer prior to the first PSS deposition. The even layer numbers correspond to PSS adsorption and the odd layer numbers to Fe(II)−MEPE deposition. High M_w PSS (70 000) was used for coating these particles. The coated particles were redispersed in air-equilibrated pure water (pH ~ 5.6) prior to measurement of the ζ-potential.

Transmission Electron Microscopy (TEM). TEM measurements were performed on a Philips CM12 microscope operating at 120 kV, equipped with an energy-dispersive X-ray analysis (EDAX) 9800 analyzer. Samples for TEM were prepared by depositing aqueous solutions of the coated particles upon a carbon-coated copper grid. The mixtures were allowed to air-dry for 1 min, and the extra solution was then blotted off.

Atomic Force Microscopy (AFM). AFM images were taken using a Digital Instruments Nanoscope IIIa AFM in tapping mode (TM). Samples were prepared by applying a drop of the shell solution onto cleaned glass slides. After the shells were allowed to settle, the slides were extensively rinsed in Millipore water and then air-dried.

Single-Particle Light Scattering (SPLS). The SPLS equipment and measurement principles are described in detail elsewhere.[21] Briefly, the dispersion of uncoated or polyelectrolyte-coated particles was passed through a capillary with a 0.1 mm diameter orifice at the end and directed through an argon laser (Innova 305) beam, which was focused to allow only a single particle in focus at a particular time. Forward-scattered light pulses recorded from particles flowing through the scattered volume were detected in the angular region of 5−10°. The intensity distributions were collected by a multichannel analyzer and then stored on a PC. Further details can be found in earlier publications.[14,21]

Results and Discussion

Assembly of Fe(II)−MEPE/PSS Multilayers on 640 nm and 1.7 μm Colloids. The ζ-potential as a function of polyelectrolyte layer number for the 640 nm diameter PS latices coated with Fe(II)−MEPE/PSS multilayers is shown in Figure 1. Adsorption of PSS onto the PS latices precoated with PAH polyelectrolyte produces particles that have a ζ-potential of ca. −45 mV. Subsequent deposition of Fe(II)−MEPE results in a reversal in sign of the ζ-potential, ca. +10 mV. Further polyelectrolyte depositions cause the ζ-potential to alternate in sign from positive to negative, depending on whether the outermost layer is the polyanion (PSS) or polycation (Fe(II)−MEPE). The ζ-potential observed for the PSS/Fe(II)−MEPE multilayers with Fe(II)−MEPE as the outer layer (+10 mV) is considerably less than that for PSS/PAH multilayers assembled on the same particles with PAH forming the outermost layer (+50 mV).[22] This difference in magnitude of the ζ-potential can be ascribed to variations in the conformation of the polyelectrolytes at the surface,[23] which may arise from the differences in the underlying surface morphology of the particles. Because the magnitude of the ζ-potential is not proportional to the charge density,[23] no quantitative conclusions are drawn from the magnitude of the ζ-potential values. The alternating values do, however, qualitatively demonstrate a successful recharging of the particle surface with each polyelectrolyte deposition.[14,15]

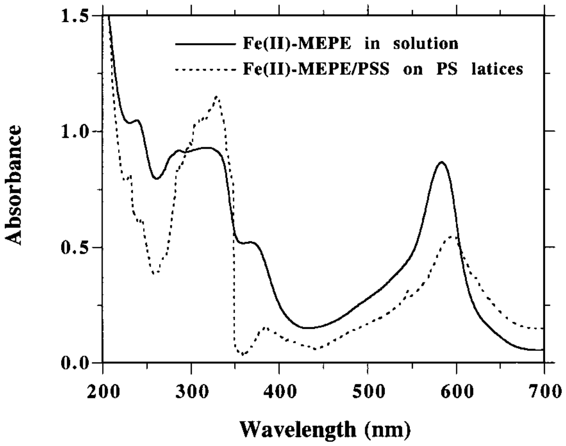

Figure 2. Absorption spectra of the metallo-supramolecular polyelectrolyte (Fe(II)−MEPE) in aqueous solution (0.01 mg mL^{-1}) (solid spectrum) and of Fe(II)−MEPE/PSS multilayers on PS latices of 640 nm diameter (dashed spectrum). The multilayer shell comprises [PAH(PSS/Fe(II)−MEPE)$_3$]. The background spectrum of the PS latices was subtracted from the spectrum of the Fe(II)−MEPE/PSS multilayers on the colloids and multiplied by 5.

Evidence for adsorption of the Fe(II)−MEPE/PSS multilayers on the colloids is provided by UV−vis measurements. The absorbance spectra of Fe(II)−MEPE in aqueous solution and Fe(II)−MEPE/PSS multilayers on 640 nm PS latices are shown in Figure 2. In aqueous solution, the metallo-supramolecular polyelectrolyte has absorption maxima at 300 (broad), 366, and 583 nm. The peak at 583 nm is due to the metal-to-ligand charge transfer (MLCT) transition in Fe(II)−MEPE.[16] A typical absorption spectrum for the Fe(II)−MEPE/PSS multilayers on 640 nm PS latices (Figure 2) shows the distinct MLCT absorption band at 595 nm. This peak arises due to the presence of Fe(II)−MEPE on the particle surface, as it is not present in the spectrum of pure PS latices. The redshift (about 10 nm) of the MLCT transition most probably results from a change in polarity/environment of the surface-confined Fe(II)−MEPE.[24] Quantitative

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evaluation of the UV−vis data in order to follow Fe(II)−MEPE/PSS multilayer growth is not possible due to the complicated scattering from the particles and the different particle concentrations in the samples as a result of particle loss during preparation. Nevertheless, the characteristic MLCT transition clearly observed for MF and PS particles coated with 1−10 Fe(II)−MEPE layers in Fe(II)−MEPE/PSS multilayer films confirms the presence of the coordination polyelectrolyte on the particle surface. Further qualitative proof of the layer buildup is directly obtained by visual inspection: the particles turn blue with deposition of Fe(II)−MEPE layers. In addition, EDAXS measurements reveal the presence of Fe on particles that were coated with Fe(II)−MEPE/PSS multilayers.

SPLS is a sensitive optical technique, which enables the determination of the thickness of layers assembled onto colloids, as well as the state and degree of the coated colloids with respect to aggregation.[15,21,22] SPLS measurements show that no aggregation of the PS colloids occurs as a result of coating them with Fe(II)−MEPE/PSS multilayers. Optical absorption due to the Fe(II)−MEPE layers at the wavelength of the SPLS laser light does not allow determination of the particle size and hence layer thickness. Atomic force and transmission electron microscopy reveal a change in surface morphology of the coated PS latices, compared with the uncoated particles (data not shown). The presence of polyelectrolyte multilayers causes an increase in surface roughness. Accurate evaluation of the thickness from microscopy is difficult due to the small (nanometer) layer thickness changes on the micrometer-sized particles.

To further support that Fe(II)−MEPE/PSS multilayers can be successfully deposited onto colloidal particles, we employed a decomposable colloidal template particle, namely weakly cross-linked MF particles. The creation of hollow polymer shells after removal of the MF template would provide unequivocal evidence for Fe(II)−MEPE/PSS multilayer growth. Therefore, Fe(II)−MEPE/PSS multilayers were assembled on 1.7 μm diameter MF particles. (Alternating ζ-potentials are observed with each PSS or Fe(II)−MEPE deposition on the MF particles, again indicating stepwise multilayer growth.) A typical TEM image of an Fe(II)−MEPE/PSS multilayer-coated MF particle is displayed in Figure 3a. The [(PSS/Fe(II)−MEPE)$_2$/PSS] (five-layer) coated particles were then repeatedly exposed (three times) to hydrochloric acid at pH = 1.0 for 10 min. As a result of acid decomposition of the MF particles into its constituent oligomers,[14b] the solution rapidly becomes transparent with a tinge of blue (due to Fe(II)−MEPE). The oligomers have a cross section of approximately 1 nm and are readily expelled from the core by permeating the polyelectrolyte layers forming the shells.

The polyelectrolyte shells fabricated were characterized using transmission and atomic force microscopy techniques. TEM and tapping mode AFM images of five-layer [(PSS/Fe(II)−MEPE)$_2$/PSS] shells are shown in parts b and c of Figure 3. Both images show folds and creases in the polyelectrolyte walls, which are present as a result of drying the shells. Flattening of the shells is also observed. The long-axis diameter of the dried shells, approximately 2 μm, is slightly larger than that of the original MF template, indicating that some spreading occurs upon drying. The minimum height of the five-layer shell in the AFM image, corresponding to twice the wall thickness, is approximately 10 nm. Thicknesses of up to 40 nm are observed for the folded sections. Similar observations were reported earlier for hollow polymer shells comprising PAH and PSS.[14b,c] The formation of these shells demonstrates that the electrostatic layer-by-layer assembling of polyelectrolytes

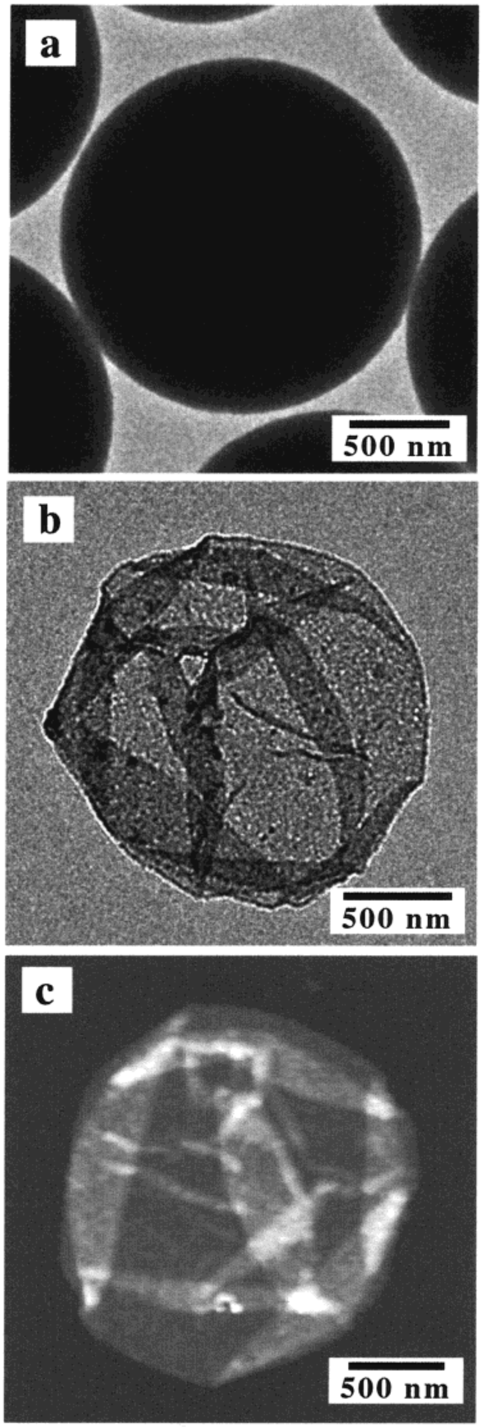

Figure 3. (a) TEM image of [(PSS/Fe(II)−MEPE)$_2$/PSS]-coated MF particles. The template MF particles used have a diameter of 1.7 μm. (b) TEM and (c) AFM images of five-layer [(PSS/Fe(II)−MEPE)$_2$/PSS] polyelectrolyte shells, obtained after decomposition of the MF template. The outer layer is PSS. High M_w PSS (70 000) was used for coating these particles.

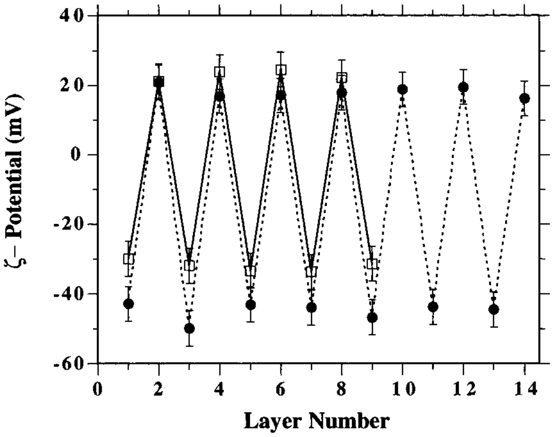

Figure 4. ζ-potential as a function of polyelectrolyte layer number for PSS/PAH (open squares) and PSS/Fe(II)−MEPE (filled circles) multilayers on 70 nm diameter PS latices. The odd layer numbers correspond to PSS adsorption, and the even layer numbers to PAH or Fe(II)−MEPE deposition. Low M_w PSS (1100) was used for coating these particles. The coated PS latices were redispersed in air-equilibrated pure water (pH ∼ 5.6) prior to measurement of the ζ-potential.

with metallo-supramolecular subunits, in alteration with PSS, can successfully be accomplished on colloidal particles.

Assembly of Fe(II)−MEPE/PSS Multilayers on Nanometer-Sized PS Latices. Our previous investigations focused on the assembly of polyelectrolyte multilayers on colloidal particles with diameters greater than 200 nm. It was of particular interest to ascertain whether polyelectrolyte multilayers on particles of smaller dimension could be fabricated. Such a task represents a number of challenges, one of which is the successful separation of polyelectrolyte-coated particles and free/unadsorbed polyelectrolyte in solution. To achieve this goal, we selected cetyltrimethylammonium-stabilized PS latices with an average diameter of 73 ± 14 nm (determined from light scattering). Although it was difficult to successfully centrifuge these particles even under high speeds (e.g., 40 000*g*), it was possible to pellet them using centrifugation after deposition of one polyelectrolyte layer on their surface. To investigate the assembly process, we chose two polyelectrolyte systems: the commonly employed PSS/PAH system and the PSS/Fe(II)−MEPE system described above for the larger particles. To avoid bridging flocculation of the PS latices by the polyelectrolyte, low-molecular-weight (M_w 1100) PSS was used. If the polyelectrolyte chains are much longer than the diameter of the particles, one polyelectrolyte molecule can bind on the surface of two or more particles and aggregates can form, thereby preventing homogeneous coating of the particle surface and the formation of regular polyelectrolyte multilayer shells around each particle.

As was observed for the larger PS latices, alternating ζ-potentials (in sign) are obtained for the positively charged (ζ-potential = +60 mV) ∼70 nm diameter PS latices coated with PSS/PAH or PSS/Fe(II)−MEPE multilayers (Figure 4); the negative ζ-potentials correspond to PSS deposition, and the positive ζ-potentials to PAH or Fe(II)−MEPE. These data indicate that the layer buildup is also successful with smaller diameter particles. Values of ca. +20 mV are obtained for coated particles with either PAH or Fe(II)−MEPE as the outermost layer. It is noted that when PAH is adsorbed on larger (640 nm) PS latices and forms the outer layer, values of +50 mV are recorded,[22] whereas +10 mV is observed for Fe(II)−MEPE on the same latices when it is the outer layer (Figure 1).

TEM examination of the polyelectrolyte-coated 70 nm diameter PS latices was undertaken to confirm multilayer shell growth and to investigate differences in particle surface morphology as a result of polyelectrolyte deposition. Figure 5 shows TEM micrographs of the uncoated 70 nm PS latices (Figure 5a,b) and those coated with 15 [(PSS/Fe(II)−MEPE)$_7$/PSS]-layer polyelectrolyte shells. The sphericity and polydispersity of the uncoated PS latices can be seen in Figure 5a,b. At higher magnification (part b), the particles are seen to have a rather smooth surface. The presence of either PAH/PSS or Fe(II)−MEPE/PSS multilayers on the PS latices is immediately hinted at by the packing of the particles on the carbon-coated TEM grid: the particles are closely packed and stacked on top of one another, as depicted in Figure 5c for the Fe(II)−MEPE/PSS-coated PS latices. SPLS measurements show that the coated particles exist as single particles in solution; that is, they are not aggregated. Hence, any aggregation (as observed in Figure 5c) is due to the drying process as a result of sample preparation for TEM analysis. The thickness of the polyelectrolyte multilayers cannot be determined by either TEM or SPLS due to the polydispersity of the uncoated PS latices.

Closer observation of the surface of the coated particles reveals a different surface texture (compared to the uncoated particles), suggesting the presence of polyelectrolyte multilayers on the surface (Figure 5c,d). The surface morphology of the PAH/PSS-coated particles is marginally rougher than that observed for the uncoated particles (data not shown). More noticeably, the (Fe(II)−MEPE/PSS)-coated PS latices display an uneven contour (Figure 5c,d). The reason for this may be the linear conformation of the Fe(II)−MEPE polymer. Such differences in surface morphology are likely to impact on the multilayer structure of the films. Permeability and probe binding studies are currently underway to examine differences in the layer structures of multilayer films comprising PAH/PSS and Fe(II)−MEPE/PSS.

As outlined above for the larger PS latices, the Fe(II)−MEPE-coated 70 nm latices display a blue color upon deposition of Fe(II)−MEPE layers, indicating the assembly of Fe(II)−MEPE/PSS multilayers. This is also supported by UV−vis measurements: the absorption spectrum of Fe(II)−MEPE/PSS multilayer PS latices show the characteristic MLCT transition band at 595 nm. The EPM, TEM, and UV−vis data all demonstrate that it is possible to assemble polyelectrolyte multilayers on particles with an average diameter of less than 100 nm. The coating of nanosized particles is a first step toward the production of nanometer-sized hollow shells. Such hollow capsules are envisioned to have applications in drug delivery, i.e., by incorporating active species within the polymer shell or as chemical reactors.[25,26]

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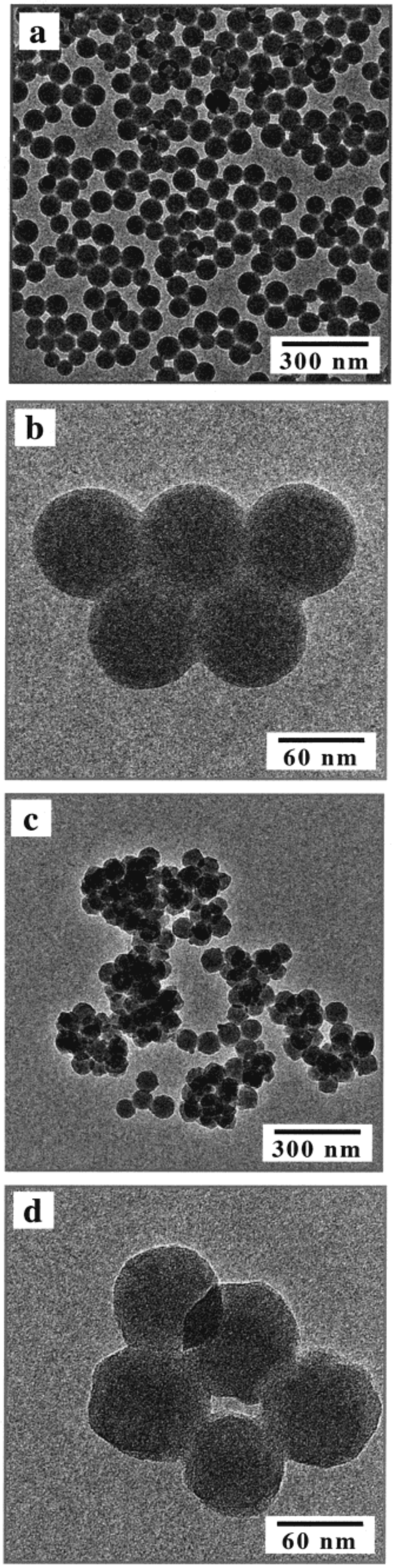

Figure 5. (a) and (b) TEM images of uncoated 70 nm diameter PS latices and (c) and (d) the same PS latices coated with [(PSS/Fe(II)−MEPE)$_7$/PSS] (15 layers). Low M_w PSS (1100) was used for coating these particles. Differences in the surface morphology can be observed between the uncoated and polyelectrolyte-coated particles.

It is well-known that the metal−ion coordination complex can be disassembled by exposure to strong chelating agents.[27] This is also the case for the Fe(II)−MEPE polyelectrolyte: *o*-phenanthroline and salicylic acid disassemble the iron(II) coordination polyelectrolyte. (The *o*-phenanthroline is added to alcohol, whereas the salicylic acid is added to water solutions.) Exposure of the Fe(II)−MEPE assembled in alternation with PSS in a multilayer shell on colloidal particles to strong chelating agents (or acid, pH = 1) does not cause its breakup. This is also the case for a single layer of Fe(II)−MEPE adsorbed on the PS latices or on weakly charged carboxyl-stabilized PS particles. Similarly, the Fe(II)−MEPE/PSS hollow shells could not be disassembled. It was found that complexation of the Fe(II)−MEPE polyelectrolyte with PSS in solution prevents its disassembly upon exposure to a chelating agent. These experiments show that the Fe(II)−MEPE/PSS polyelectrolyte complexes are stable and resistant to decomposition in various media, which is important from a stability viewpoint. Experiments are also currently underway to examine the stability of complexes that are formed from polyelectrolytes that contain less strongly binding ions.

Conclusions

A new class of a functional metallo-supramolecular polyelectrolyte was assembled in a multilayer shell configuration (in alternation with PSS) on colloidal particles. It has been demonstrated that hollow shells comprising Fe(II)−MEPE/PSS multilayers can be produced by decomposition of the core from Fe(II)−MEPE/PSS-templated MF particles. The Fe(II)−MEPE/PSS multilayers were found to be stable and resistant to decomposition by acid (pH 1.0) or chelating agents. The enhanced stability is attributed to complexation between the coordination polyelectrolyte and PSS, both when bound at the surface and as hollow shells in solution. Polyelectrolyte multilayers were also assembled onto colloids of diameter less than 100 nm, demonstrating that the method employed can be used to produce colloidal-core multilayer shell particles with diameters in both the micro- and nanometer size ranges. The surface morphology of the resulting Fe(II)−MEPE/PSS-coated particles was found to be considerably rougher than uncoated particles and those coated with other polyelectrolyte (PAH/PSS) multilayers. This may result from the Fe(II)−MEPE being more linear than the other polyelectrolytes commonly used.

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(26) A manuscript concerning the assembly of polyelectrolyte multilayers on nanometer-sized particles and the subsequent decomposition of the nanoparticles to produce hollow polymer spheres of nanometer dimensions will be reported elsewhere.

(27) Constable, E. C. *Metals and Ligand Reactivity*; VCH: Weinheim, Germany, 1996.