Colloid Surface Engineering via Deposition of Multilayered Thin Films from Polyelectrolyte Blend Solutions

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Multilayer thin films were constructed on polystyrene colloidal particles by depositing alternating layers of poly(allylamine hydrochloride) (PAH) at pH 7.5 and varying composition blends of poly(acrylic acid) (PAA) and poly(styrenesulfonate) (PSS) at pH 3.5. Following the deposition of each layer, microelectrophoresis experiments showed alternating ζ-potentials, suggesting the formation of multilayered films on the particles. Scanning and transmission electron microscopy were used to examine the surface morphology of the colloidal particles, with homogeneous surface coatings apparent for films deposited from PAA/PSS blend solutions containing up to 90 wt % PAA. The colloidal stability of these particles is greater than those coated with individual PAH and PAA layers. In the case of the blend PAA/PSS = 25:75 wt %, up to 20 layers were assembled without compromising the colloidal stability of the dispersion. The results demonstrate that the deposition of layers from PE blend solutions containing a strong and weak PE can be used as a facile method for controlling the surface properties and hence the colloidal stability of core–shell particles, as well as the thickness and morphology of the coatings. Control of these parameters is important for subsequent processing and application of these particles in controlled delivery, photonics, catalytic, and separation applications.

Introduction

The layer-by-layer (LbL) method has been widely used for the fabrication of core–shell particles with defined shell thickness and functionality.[1–3] It exploits the surface charge of colloidal particles as a basis for surface modification via adsorption. Alternating layers of positively and negatively charged species can be adsorbed, thereby yielding particle-supported multilayered thin films with the thickness tailorable by varying the number of layers adsorbed. To date, a wide range of components have been employed as layer materials in the preparation of these colloidal particles, ranging from polyelectrolytes (PEs)[4–13] to nanoparticles[14–17] and biomolecules.[18] The core–shell

particles prepared have been utilized in catalytic[19–21] and photonic[22–25] studies, as confined environments for chemical reactions within the shell coatings[26,27] and as building blocks to create nanostructured functional thin films for biosensing.[28–30]

One of the most interesting categories of materials used to date in LbL assembly is weak PEs.[21,27,31–44] These are charged polymers in which the extent of ionization (and

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therefore charge density) is dependent on the pH of the surrounding solution. Since pioneering the use of these materials in LbL thin film assembly a number of years ago, Rubner and co-workers have shown that poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) can be used in the preparation of microporous thin films,[31] as nanoreactors for nanoparticle synthesis,[32] as substrates for cell[33] and protein[34] adhesion, and in surface patterning applications.[35] Weak PEs have also been shown to give rise to considerably thicker films than strong PEs (such as poly(styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC)),[36] with bulk and surface properties dependent on the assembly and post-treatment conditions.[37,38] We recently reported the formation of nanoporous films by exposure of preassembled PAA/PAH multilayers to solutions of varying ionic strength.[39]

While there has been considerable use of weak PEs for forming thin films on planar substrates, there have been only limited studies on the application of the LbL method to weak PEs on three-dimensional substrates such as colloidal particles. Burke and Barrett demonstrated that the K_a values of weak PEs (e.g., PAA/PAH) are significantly altered by incorporating them into multilayer thin films (e.g., from 6.7 to as low as 2.7).[40,41] They demonstrated this through ζ-potential studies of multilayers assembled on colloidal silica. However, the issue of colloidal stability or aggregation of the silica particles was not examined in these studies. Further work demonstrated that adsorption of weak PEs under conditions of low ionization (in this case PAH at pH 10) onto colloidal particles can also lead to multilayer separation from the surface and the formation of bulk PE complexes.[42]

Recently, we reported the coating of colloids with weak PEs and showed that there was considerable difficulty in coating colloidal particles (diameter 925 nm) with weak PEs under conditions where the PEs are not highly charged, that is, at low pH (<5.0) for PAA and high pH (>7.5) for PAH.[43] At these extremes, high levels of particle aggregation were observed, and there was difficulty in coating the colloidal particles beyond four layers. Nevertheless, it was demonstrated that weak PEs could be used in successful particle coating when they were adsorbed under conditions of relatively high ionization. The resulting core−shell particles were thus coated with layers comparable in thickness to PE coatings made of strong PEs. We also demonstrated that multilayers of weak PEs can be formed on particles by adsorbing preformed complexes of PAA with copper ions in alternation with PAH.[44] In this case, the copper ions were used to protect some of the carboxylate groups from complexing with the protonated amine groups, thereby leaving a portion of free carboxylate groups in the final multilayer structure. Both adsorption steps in that study were performed at pH 5.5, and smooth, homogeneous coatings were obtained. The coatings achieved were relatively thin, with a PAA/PAH bilayer thickness of ∼3 nm obtained.

An alternative strategy that may be applicable in overcoming colloidal stability difficulties associated with coating particles with weak PEs, as well as permitting control over the film surface functionality, thickness, and morphology, is to deposit layers from PE blend solutions.[45−51] These are systems in which two, rather than one, adsorbing materials are present in the deposition solutions. So far, blending has been used to induce structural,[45,46] compositional,[47,48] and stability[49,50] changes to LbL assembled thin films. In particular, we recently showed that films constructed from PAH at pH 7.5 and a blend solution of PAA and PSS at pH 3.5 were considerably thicker than films prepared solely from PAH/PSS.[51] These films also showed a decreased capacity to rearrange upon exposure to hydrochloric acid. It should be noted that the simultaneous adsorption of two chemically different polymers onto surfaces has been studied for some time,[52−57] though extending this approach to multilayer formation is a more recent development.[45−51]

In the current article, we demonstrate that PE blending can be used as a method for imparting colloidal stability to particles coated with weak PE multilayers. Further, we show that the coating thickness can be increased by using this methodology, relative to particles coated with strong PEs, and that smooth and uniform coatings are formed. Film formation is followed by several techniques, including microelectrophoresis, transmission electron microscopy (TEM), and scanning electron microscopy (SEM). As the coating of colloids is typically performed with intermediate drying steps and in the presence of salt, we also examine the influence of drying between adsorption steps and the presence of salt in the PE adsorption solutions on the thickness of films formed on planar substrates by using surface plasmon resonance (SPR) spectroscopy and quartz crystal microgravimetry (QCM).

Experimental Section

Materials. Polystyrene particles (with diameters of 600 and 980 nm) were obtained from Microparticles GmbH (Germany). Poly(acrylic acid, sodium salt) (PAA) ($M_w = 30\ 000$ g mol^{-1}), poly(styrenesulfonate, sodium salt) (PSS) ($M_w = 70\ 000$ g mol^{-1}), polyethyleneimine (PEI) ($M_w = 25\ 000$ g mol^{-1}), and poly(allylamine hydrochloride) (PAH) ($M_w = 70\ 000$ g mol^{-1}) were purchased from Sigma-Aldrich and used as received. Sodium chloride was obtained from Merck and hydrochloric acid from BDH. High purity water was obtained from a two stage Millipore RiOs/Synergy water purification system and had a resistivity greater than 18.2 MΩ cm.

Solutions were prepared with a total polymer concentration of 1 mg mL^{-1}. Six mass percentage (wt %) compositions of PAA and PSS were studied: PAA/PSS = 97:3, 90:10, 75:25, 50:50, 25:75, and 10:90. Experiments were conducted using blend solutions with either 0 or 0.5 M NaCl, and the pH was adjusted to 3.5 using HCl. The PAH solutions used contained 0.5 M NaCl, and the pH was adjusted to 7.5 using NaOH.

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Surface plasmon resonance (SPR) substrates were prepared on glass microscope slides. The slides were initially cleaned using Piranha solution (70/30 v/v% sulfuric acid/hydrogen peroxide) and further treated with 5:1:1 water/ammonia/hydrogen peroxide at 70 °C for 60 min. The substrates were subsequently coated with a thin layer of chromium (to improve gold adhesion) and a layer of gold (~45 nm). An initial layer of PEI was adsorbed to impart a positive charge to the gold surface, prior to construction of the (PAA/PSS)/PAH multilayers.

Gold-coated quartz crystal microbalance electrodes were obtained from Kyushu Dentsu Co. Ltd (Nagasaki, Japan). PEI was adsorbed to render the surface positively charged.

Film Assembly on Planar Substrates. Films were assembled on QCM electrodes or SPR slides using the following method. After adsorbing the precursor layer of PEI, the substrate was exposed to a solution containing both PAA and PSS for 15 min. The substrate was then rinsed three times with water and dried under a gentle stream of high purity nitrogen. Adsorption of PAH was then performed under the same conditions. Alternation between PAA/PSS and PAH adsorption then continued until the desired number of layers was reached. Aside from the composition of the blend solution, the NaCl concentration and drying protocol were also varied. All adsorptions were performed at room temperature.

Surface Plasmon Resonance (SPR). An Optrel Multiskop SPR spectrometer was used for collecting SPR spectra. The experimental setup has been previously described.[58] SPR spectra were obtained as reflectivity versus angle of incidence curves, and the optical thickness of the dielectric film was extracted by fitting Fresnel theory to these curves. Only film thickness was used as a fitting parameter, assuming a uniform film thickness with a refractive index of 1.47.[59] It is noted that fits to Fresnel theory are relatively insensitive to minor variations in the refractive index of the dielectric material. In our experiments, it is estimated that these variations account for deviations of up to 10% in the calculated thickness of the adsorbed films.

Quartz Crystal Microgravimetry (QCM). The resonance frequency of the QCM electrodes was ~9 MHz. Assuming the film density is 1.2×10^6 g m^{-3}, the average PE layer thickness, d, can be calculated from the change in QCM frequency, ΔF, according to the equation d (nm) $= -0.017 \times \Delta F$ (Hz).[60,61]

Particle Coating. Polystyrene (PS) particles were dispersed in 500 μL of water using ultrasound and vortex mixing. The deposition solution was then added (1.5 mL of PAH or PAA/PSS blend), and the mixture was agitated for 20 min during adsorption. The particle concentration during adsorption was 0.1 wt %. To remove excess PE, the dispersion was centrifuged at either 2000g for 10 min (for 980 nm particles) or 6900g for 10 min (for 600 nm particles), after which the supernatant was removed and replaced by water. The particles were redispersed after washing using a combination of vortex mixing and ultrasonication. This process was repeated twice in order to ensure complete removal of the PE, after which the next adsorption solution was added. The PS spheres used have a negative charge; thus, the first layer adsorbed was PAH, followed by the PAA/PSS blend layer. Up to 10 layers were constructed in most instances. To show the significant thickness increments, 18 and 20 layers were constructed from the PAA/PSS = 50:50 and 25:75 wt % blends, respectively.

Microelectrophoresis. ζ-Potentials were measured using a Malvern Zetasizer 2000 instrument. Measurements were taken on 0.0001 wt % samples. The quoted values were calculated by taking the average of five successive measurements. The pH dependence of the ζ-potential was measured by adding 5 μL of the particle dispersion to dilute aqueous NaOH or HCl with a predetermined pH, no more than 3 min before measurement.

Scanning Electron Microscopy (SEM). SEM images were taken with a Phillips XL30 FEG scanning electron microscope

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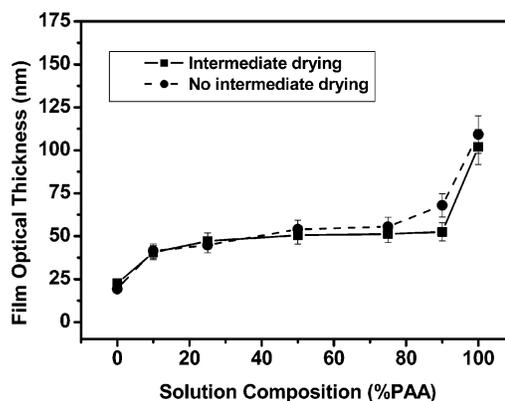
Figure 1. SPR film thickness for ((PAA/PSS)/PAH)$_4$ films prepared from blend adsorption solutions of varying PAA/PSS composition. Films prepared with (squares) and without (circles) nitrogen drying between deposition of each layer.

Table 1. Average Bilayer Thicknesses for (PAA/PSS)/ PAH Films Deposited from PAA/PSS Blend (pH 3.5) and PAH (pH 7.5) Solutions with Different NaCl Concentrations onto Planar Supports

blend solution composition (PAA/PSS wt %)	average bilayer thickness^a (nm)		
	SPR (0 M NaCl)	QCM^b (0 M NaCl)	QCM^b (0.5 M NaCl)
100:0	25.5	27.5^c	31.0^c
90:10	13.3	15.0	20.8
75:25	12.8	11.3	15.3
50:50	12.8	10.5	14.8
25:75	11.8	9.3	11.9
10:90	10.0	9.0	10.5
0:100	0.9^d	2.3	3.5

^{a} Bilayer thicknesses were derived for films made of eight layers total, ((PAA/PSS)/PAH)$_4$. The films were dried with nitrogen between adsorption steps. ^{b} Thicknesses, d, were determined using d (nm) $= -0.017 \times \Delta F$ (Hz). ^{c} Significant nonlinear film growth occurs over eight layers. ^{d} Taken from ref 51.

with an accelerating voltage of 2 kV and a spot size of 2 mm. The working distance was 10 mm. All samples were coated with a thin layer of gold (Edwards S150 B Sputter Coater) prior to imaging to improve the electrical conductivity of the sample.

Transmission Electron Microscopy (TEM). TEM images were taken using a Philips CM 120 BioTWIN microscope operated at 120 kV. TEM samples were prepared by evaporating a droplet of the dispersion on a copper grid coated with Pioloform film.

Results and Discussion

Since the adsorption of PEs onto colloidal particles occurs without drying after each adsorption step,[1–3] we conducted SPR experiments on planar substrates to examine whether drying between the deposition of each layer (i.e., intermediate drying) had a significant effect on the film thickness. Figure 1 shows the SPR film thickness as a function of solution PAA/PSS blend composition for ((PAA/PSS)/PAH)$_4$ (eight-layer) films. Comparison of the data reveals no significant difference in thickness for films prepared with or without intermediate drying. As such, any discrepancy between the thickness of ((PAA/PSS)/ PAH) layers on colloidal particles and planar substrates cannot be attributed to intermediate drying and is therefore likely to arise from other differences in the assembly conditions (see later).

The average SPR bilayer thicknesses for the different blend compositions, derived from the data in Figure 1, are shown in Table 1. The bilayer thickness increases slightly from ~10 nm for a 10:90 wt % PAA/PSS blend to ~13 nm for a PAA/PSS blend of 90:10 wt %. These values are in good agreement with those calculated from QCM

Table 2. Number of Layers Coated for the Formation of (PAA/PSS)/PAH Multilayers onto 980 nm PS Spheres[a]

NaCl in PAA/PSS blend (M)	PAA/PSS blend solution composition (wt %)					
	10:90	25:75	50:50	75:25	90:10	97:3
0	12[b]	12[b]	12[b]	12[b]	9[c]	7[c]
0.5	12[b]	20[b]	18[b]	12[b]	9[c]	7[c]

[a] Blend (PAA/PSS) and PAH adsorption solutions of pH 3.5 and 7.5, respectively, were used. The PAH solutions contained 0.5 M NaCl. [b] The minimum number of layers successfully coated without aggregation. [c] The number of layers at which irreversible aggregation occurs.

for ((PAA/PSS)/PAH)$_4$ films (also shown in Table 1). Salt is typically added to the adsorption solutions to deposit PEs for LbL film formation; therefore, QCM experiments were also performed to examine the influence of added salt on the thickness of the layers. Table 1 shows that bilayers formed from solutions containing 0.5 M NaCl are thicker than those adsorbed from solutions with no added salt (other than that present due to pH modification). We note that, due to the nonlinear growth behavior of some of the (PAA/PSS)/PAH films, the increase in bilayer thickness as a result of added salt becomes more pronounced at higher layer numbers.[51] Similarly, in strong PE systems, the addition of salt usually leads to an increase in the layer thickness.[62] The magnitude of this increase is dependent on the particular PE combination employed.

The formation of (PAA/PSS)/PAH multilayers on colloidal particles was observed using microelectrophoresis (Figure 2). As oppositely charged species are adsorbed onto the surface of the particles, it is expected that there will be a reversal in the measured ζ-potentials of the particles. Adsorption was performed from variable composition PAA/PSS blend solutions assembled in alternation with PAH. In the case of the polyanion blend, studies were undertaken with both 0 M (Figure 2a) and 0.5 M (Figure 2b) added NaCl, while adsorption of PAH was performed from solutions containing 0.5 M NaCl. We found that the absence of added salt in the PAH adsorption solution promoted aggregation of the particles. Charge reversal was seen in each compositional situation, from 10% PAA to 97% PAA, and in both cases of no added electrolyte and 0.5 M NaCl. The reversal of the surface charge is indicative of PE being adsorbed onto the surface of the colloidal particles. The magnitudes of the ζ-potentials observed are similar to those reported for other polyelectrolyte multilayer systems, such as PAH/PSS and PDADMAC/PSS.[4-6] Importantly, the number of layers that could be adsorbed was markedly increased by the addition of only a small amount of secondary PE (i.e., PSS) (see Table 2). In the case of films comprised solely of alternating layers of PAA and PAH, irreversible aggregation occurred after only four layers were adsorbed.[43] With 3 wt % PSS added to the PAA solution, this increased to seven layers, and with 10 wt % added PSS, nine layers were successfully coated. At PSS compositions of 25 wt % and above, it was possible to coat at least 12 layers, and in the case of PAA/PSS = 25:75 wt %, 20 layers were coated without aggregation (see below). Clearly, including a secondary strong PE (such as PSS) in the adsorption solution can be used to augment the adsorption of weak PEs at low pH. We rationalize this improved pH stability as being due to the presence of some sulfonate groups at the interface maintaining sufficient charge at low pH (sulfonate groups will not become protonated at pH 3.5, whereas protonation of some of the carboxylic

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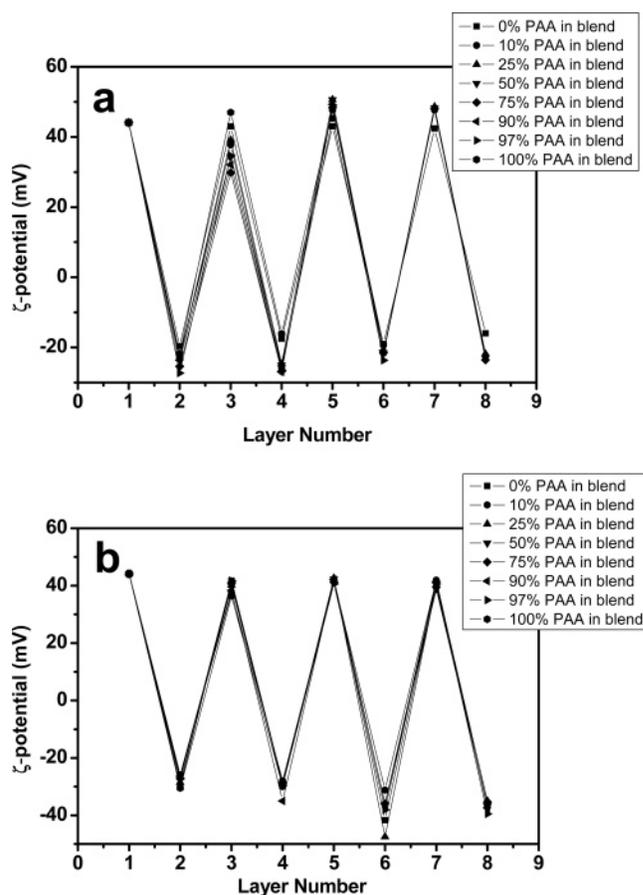
Figure 2. ζ-Potential of (PAH/(PAA/PSS))-coated PS particles (600 nm diameter) as a function of layer number. The (PAA/PSS)/PAH layers were deposited on the particles from solutions of pH 3.5/7.5. Measurements were taken in water at a pH of ~6. The blend solutions contained (a) 0 M NaCl and (b) 0.5 M NaCl. The PAH solutions contained 0.5 M NaCl. Odd layers correspond to PAH, even layers to PAA/PSS blend.

acid groups of PAA will occur), thus preventing aggregation. This is a significant improvement on previous attempts where aggregation was a significant limitation during the assembly of weak PEs on colloidal particles under low ionization conditions.[43]

The ζ-potential of particles coated with multilayers deposited from various PAA/PSS blend compositions (and alternating with PAH) as a function of pH was also measured. Adsorption of the blend occurred at either 0 M NaCl or 0.5 M NaCl. The transition of ζ-potential from positive to negative for (PAH/(PAA/PSS))$_3$-coated particles was observed to be intermediate between the observed behavior for (PAH/PAA)$_2$- and (PAH/PSS)$_3$-coated particles (Figure 3). From pH 2.5-4.0, the ζ-potential of particles coated with (PAH/(PAA/PSS)) multilayers was more negative than that for particles coated with only PAH/PAA. This led to a decreased propensity of the particles to aggregate. The isoelectric point of the particles was shifted to lower pH with the inclusion of PSS in the adsorption solution, leading to improved colloidal stability under the specific adsorption conditions used in this study (pH 3.5). Notably, there was little difference between the profiles obtained for particles prepared from 10 to 90 wt % PAA blends, indicating that the composition of the adsorption blend solution over this range does not significantly influence the isoelectric point of the particles.

The morphology of core—shell particles prepared from blended layers was examined using electron microscopy (Figure 4). TEM indicated that the coating on the particles
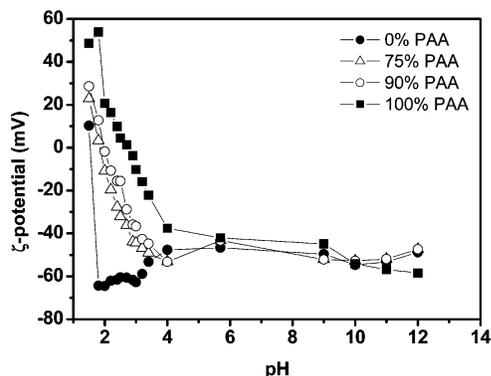
Figure 3. ζ-Potential of (PAH/(PAA/PSS))$_3$-coated PS particles (600 nm diameter) as a function of pH. The (PAA/PSS)/PAH layers were deposited on the particles from solutions of varying blend compositions (wt %) of pH 3.5/7.5. The blend and PAH solutions contained 0.5 M NaCl. For PAA = 100 wt %, the particles were coated with (PAH/PAA)$_2$.
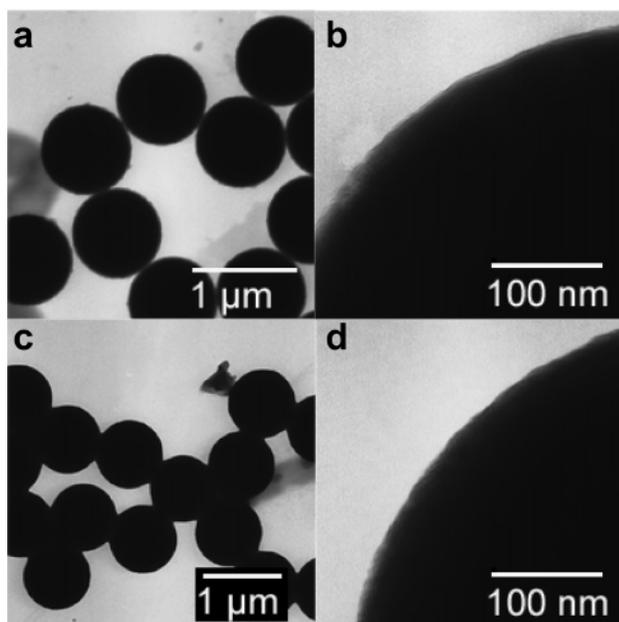
Figure 4. TEM images of 980 nm diameter PS particles coated with six layers using blend (PAA/PSS) and PAH adsorption solutions of pH 3.5 and 7.5, respectively. PAA/PSS blend compositions: (a and b) 10:90 wt % and (c and d) 50:50 wt %. All blend and PAH solutions contained 0.5 M NaCl.

is relatively smooth. This is in stark contrast with particles assembled using solely PAA and PAH. As shown in our previous work, in the case where PAA solutions at pH 3.5 and PAH solutions at pH 7.5 were used, it was not possible to coat beyond four layers, as irreversible aggregation was observed.[43] The coating obtained in that case (100% PAA) was thick and rough and exhibited raspberry morphology. The lowest pH at which successful adsorption of PAA occurred was 5.0. (This was only successful when the pH of the PAH solution was 4.5.) Importantly, the inclusion of PSS in the adsorption solution results not only in more stable colloidal dispersions (see Figure 3) but also in a much smoother coating (Figure 4). There is no apparent increase in the roughness of the particle surface with increasing PAA wt % in the adsorption solution. Further, there is only a weak increase in the coating thickness with increasing PAA wt % in the adsorption solution, as determined from the TEM images (data not shown), which is consistent with measurements on planar substrates.[51]
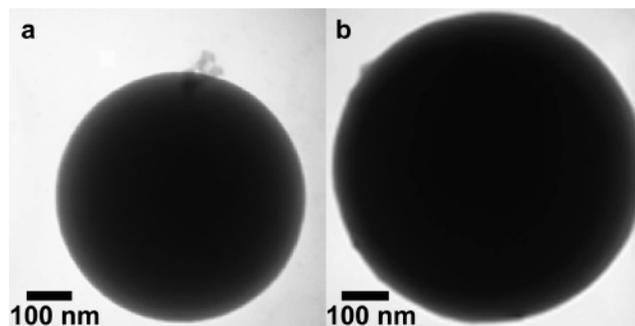
Figure 5. TEM images of (a) a 600 nm diameter PS particle and (b) a 600 nm diameter PS particle coated with 20 layers from blend (PAA/PSS) and PAH adsorption solutions of pH 3.5 and 7.5, respectively. The PAA/PSS blend composition used was 25:75 wt % containing 0.5 M NaCl. The PAH solutions contained 0.5 M NaCl.

A clear depiction of the increase in particle size obtained using blended layers is given in Figure 5. Figure 5a shows a bare PS particle (600 nm diameter), while Figure 5b shows a PS particle with 10 (PAH/(PAA/PSS)) bilayers deposited from 25:75 wt % PAA/PSS solutions. A 25% increase in the radius of the particle was observed, and the coating was significantly thicker than that achieved when using only strong PEs. ((PAH/PSS)$_{10}$ films assembled at 0.5 M NaCl have a thickness of ~35−40 nm.[51,62]) The film thickness for the 10-bilayer blend coating of ~80 nm is, however, considerably less than the 215 nm determined from the QCM studies on planar surfaces. There are a number of possible reasons for this discrepancy. First, the film constructed on the planar substrate was formed on a precursor layer of PEI, whereas, in the case of colloidal particles, the first layer adsorbed onto the particle surface was PAH. This may lead to some variation in the film thickness, particularly in the early stages of multilayer construction where the underlying PEI layer may influence those subsequently deposited. Further, as the particles are redispersed in pure water prior to adsorption, there is a slight increase in the actual pH of the adsorption solution (up to 3.8). This will lead to an increase in the charge density on the PAA chains, the net result of which is the adsorption of thinner layers.[36] To probe this effect, we conducted QCM experiments using PAA/PSS blend adsorption solutions at 3.8, with and without washing. The results indicated a thickness decrease of 15% when adsorption was performed at pH 3.8 (187 nm) compared to 3.5 (215 nm). Third, the use of ultrasound in the redispersion of particles between each adsorption may lead to the removal of some loosely bound material. Fourth, as TEM measurements are performed under high vacuum conditions, there may be some dehydration of the film and subsequent thinning of the coating. Finally, it should be noted that there is a difference in the ratio of adsorbing polymer to surface area between the studies on planar surfaces and those on colloidal particles. In the planar studies, both polymers are in large excess, whereas, in the colloid coating experiments, the excess is considerably less. This may lead to differences in the thickness and composition of the colloid coatings. We attribute the variation in thickness observed between planar and colloidal particles to the combined effect of these differences between multilayer assembly on planar and colloidal substrates. A similar discrepancy between the thickness on planar and colloidal substrates has also been reported by other workers investigating the assembly of H-bonded multilayers on particles.[63]

SEM was also used to examine the multilayer-coated particles. Particles with up to 50 wt % PAA in the
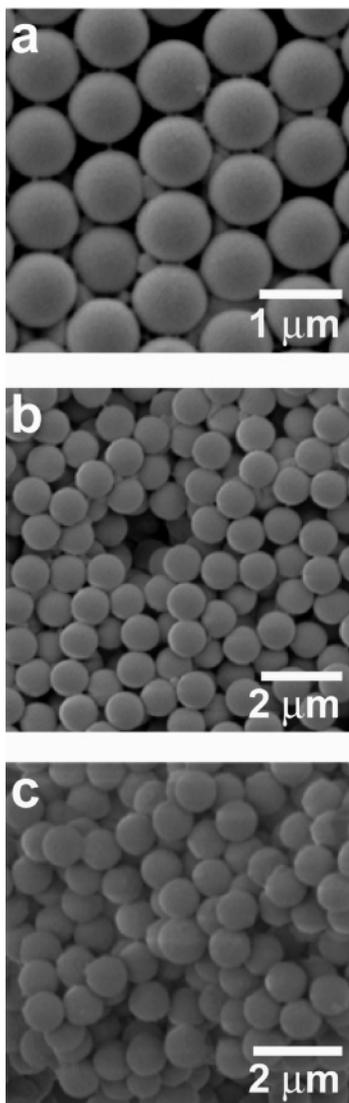
Figure 6. SEM images of 980 nm diameter PS particles coated with six layers using blend (PAA/PSS) and PAH adsorption solutions of pH 3.5 and 7.5, respectively. PAA/PSS blend compositions: (a) 50:50 wt %, (b) 75:25 wt %, and (c) 97:3 wt %. All blend and PAH solutions contained 0.5 M NaCl.

adsorption solution were able to form highly ordered arrays upon drying, which is indicative of well-dispersed, un-aggregated dispersions (e.g., Figure 6a).[22–25] However, as a higher percentage of PAA was incorporated into the adsorption solution, there was no evidence of such highly ordered assemblies, which may indicate decreased colloidal stability (Figure 6b and c). Nevertheless, the particles maintain their spherical shape, and there is little evidence of raspberry morphology. These results confirm that the use of blended layers leads to a smooth, homogeneous coating of PS particles as well as control over colloidal stability.

Conclusions

Colloidally stable core–shell particles were obtained by assembling multilayered thin films on polystyrene particles from PE blend solutions, thereby limiting particle aggregation. As the percentage of PSS in the adsorption solution increased, the number of layers that could be successfully coated also increased. TEM showed that the particle coating was relatively smooth, with no evidence of raspberry morphology, even though PE adsorption occurs under conditions where the PAA has a low charge density, suggesting that PSS contributes to colloidal stabilization. Further, it was demonstrated that thicker coatings could be prepared than those obtained using a strong PE or by adsorbing weak PEs under conditions of high ionization. We have thus demonstrated that the adsorption of weak PEs can be facilitated by incorporating strong PEs in the adsorption solution. These particles may have important applications in fields such as controlled release, catalysis, and photonics. Ongoing work in our laboratories will investigate the shell composition as a function of adsorption conditions and blend ratio and the utilization of these particles as precursors to hollow capsules with responsive surface properties.

(63) Kozlovskaya, V.; Ok, S.; Sousa, A.; Libera, M.; Sukhishvili, S. A. *Macromolecules* **2003**, *36*, 8590.