J. Am. Chem. Soc. **1998,** *120,* 8523−8524 8523

Electrostatic Self-Assembly of Silica Nanoparticle−Polyelectrolyte Multilayers on Polystyrene Latex Particles

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Received May 1, 1998

The area of thin film fabrication, in which ordered, functional supramolecular structures are the chief goal, has been greatly impacted by the recent introduction of the layer-by-layer (LbL) self-assembly technique.[1] The LbL method permits the fabrication of multilayer thin film assemblies on solid supports by the spontaneous sequential adsorption of oppositely charged species from dilute aqueous solutions onto charged substrates. The driving force for the multilayer film buildup is primarily due to the electrostatic attraction and complex formation between the charged species deposited. The LbL approach was initially employed to construct multilayer films of polyelectrolytes,[1] and subsequently extended to include proteins,[2] nucleic acids,[3] dyes,[4] dendrimers,[5] and various inorganic nanoparticles[6] in polyelectrolyte multilayer assemblies by replacing one of the polyions by a similarly charged species.

The vast majority of studies concerning the LbL technique have employed macroscopically flat charged surfaces as substrates for multilayer film formation. Recently, Keller et al. reported the preparation of alternating composite multilayers of exfoliated zirconium phosphate sheets and charged redox polymers on (3-aminopropyl)triethoxysilane-modified silica particles.[7] In more recent studies,[8] the LbL approach was successfully applied to utilize submicrometer- and micrometer-sized, charged colloidal particles as the adsorbing substrates to produce colloid-supported polyelectrolyte multilayer films: regular stepwise polyelectrolyte multilayer growth was observed on the colloids. In a subsequent investigation,[9] it was shown that the use of soluble colloidal cores as templates for the sequential deposition of polyelectrolytes allow the fabrication of novel three-dimensional hollow polymer shells. The production of multilayer films on colloids is of particular interest in areas where a high surface area is sought: for example, in catalysis, sensing, and separation applications. In addition, the increased surface area provided by colloids (compared to planar substrates) makes them amenable to experimental studies such as nuclear magnetic resonance (NMR) or other methods requiring large amounts of substances, permitting the study of multilayer structures by methods not applicable to films on planar surfaces.

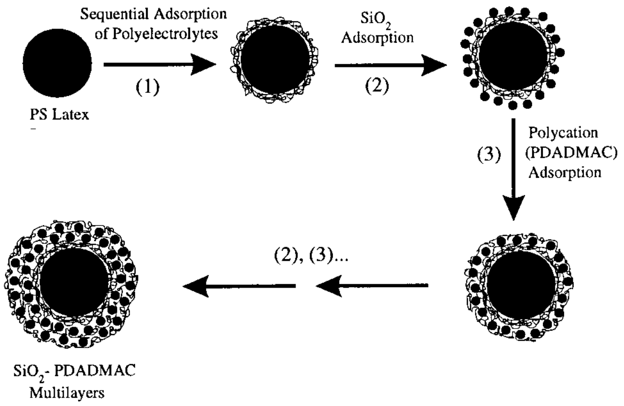

Figure 1. Schematic illustration of the assembly of composite multilayers on PS latices. The first stage involves the sequential adsorption of oppositely charged polyelectrolytes (PDADMAC/PSS/PDADMAC) (Pr$_3$) (step 1) in order to produce a smooth and uniformly positively charged outer surface to facilitate the adsorption of negatively charged SiO$_2$. Subsequent alternate adsorption of SiO$_2$ (step 2) and PDADMAC (step 3) results in SiO$_2$−PDADMAC multilayers being formed on the PS latices.

Herein we report on the construction of composite multilayers of 25 nm diameter silica particles (SiO$_2$) and poly(diallyldimethylammonium chloride) (PDADMAC) on submicrometer-sized polystyrene (PS) latex particles via the sequential electrostatic adsorption of SiO$_2$ and PDADMAC from dilute solution. Alternating SiO$_2$−PDADMAC multilayers with thicknesses ranging from tens to hundreds of nanometers have been fabricated.

The SiO$_2$−PDADMAC multilayers were prepared by the alternate adsorption of SiO$_2$ and PDADMAC on a precursor three-layer film (PDADMAC/poly(styrenesulfonate, sodium salt) (PSS)/PDADMAC, Pr$_3$)[10] assembled onto negatively charged PS latices of 640 nm diameter (Figure 1).[11] Electrophoretic mobility (EPM) measurements reveal that the surface charge of the multilayer-

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(10) The Pr$_3$ film (PDADMAC/PSS/PDADMAC) was formed by the alternate adsorption of PDADMAC (Aldrich, M_w < 200 000) and PSS (Aldrich, M_w 70 000) from aqueous solutions: 0.5 mL of 1 mg mL^{-1} aqueous polyelectrolyte solution (containing 0.5 M NaCl) was added to the PS latices (10^{10} particles in 0.5 mL of H$_2$O), 20 min allowed for adsorption, and excess polyelectrolyte removed by four repeated centrifugation (13500*g*)/wash/redispersion cycles. (SPLS measurements reveal that ca. 0.5% of the PS particles are lost at each wash/centrifugation/redispersion step.) The Pr$_3$-coated PS latices exhibit a positive surface charge, as determined from EPM measurements. Negatively charged sulfate-stabilized PS latices were prepared as described in Furusawa, K.; Norde, W.; Lyklema, J. *Kolloid Z. Z. Polym.* **1972**, *250,* 908.

(11) SiO$_2$−PDADMAC multilayers on the PS latices were prepared by adding 50 μL of an aqueous 40 wt % SiO$_2$ suspension (Ludox TM40, DuPont) to the Pr$_3$-coated PS latices dispersed in 1 mL of 0.1 M NaCl (larger amounts of SiO$_2$ adsorb when the adsorbing solution contains NaCl[6g]), allowing 15 min for SiO$_2$ adsorption, removing excess SiO$_2$ by four repeated centrifugation (13500*g*)/wash/redispersion cycles, and subsequently depositing PDADMAC as described in ref 10. The isoelectric point of the SiO$_2$ particles is 3; therefore, SiO$_2$ is negatively charged under the conditions of adsorption (pH ∼5−6).

S0002-7863(98)01502-9 CCC: $15.00

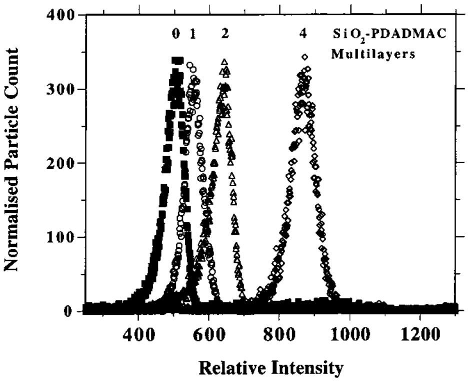

Figure 2. Normalized light scattering intensity distributions of Pr_3-coated PS latices (squares) and PS latices coated with $[Pr_3/(SiO_2/PDADMAC)_N]$ ($N = 1$ (circles), $N = 2$ (triangles), and $N = 4$ (diamonds)).

coated particles alternates from negative to positive with each adsorption of SiO_2 and PDADMAC, respectively.[12] This qualitatively demonstrates that the composite SiO_2−PDADMAC multilayers are formed by the stepwise adsorption of SiO_2 and PDADMAC.[8]

The growth of the SiO_2−PDADMAC multilayers on the PS latices was first followed by the method of single particle light scattering (SPLS).[13] Normalized SPLS intensity distributions for the Pr_3-coated PS latices and those coated with one, two, and four SiO_2−PDADMAC multilayers are shown in Figure 2. Deposition of the SiO_2−PDADMAC multilayers onto the PS latices is manifested as a shift (in the *x*-axis direction) in the SPLS intensity distributions, confirming multilayer growth. Using the SPLS technique, it is also possible to distinguish between singlets, doublets, and triplets:[13] no aggregation of the multilayer-coated particles is observed, as no intensity peaks are observed at higher intensities.

Using the Raleigh−Debye−Gans theory[14] and an estimated refractive index (n) of 1.40[15] for the adsorbed layer(s), the average thickness calculated for each SiO_2−PDADMAC layer pair for $(SiO_2/PDADMAC)_N$ multilayers with $N = 1-5$ is 30 ± 6 nm.[16] This value closely corresponds to the mean diameter of SiO_2 particles (25 ± 4 nm, determined from TEM), and suggests that on average approximately a monolayer of SiO_2 is deposited with each SiO_2 adsorption. The layer thickness increases linearly with the number of SiO_2 or SiO_2−PDADMAC layers deposited onto the PS latices.

Direct observation of the multilayer growth process is provided by transmission electron microscopy (TEM):[17] representative TEM images of uncoated PS latices and Pr_3-modified PS latices coated with SiO_2−PDADMAC multilayers are displayed in Figure 3.

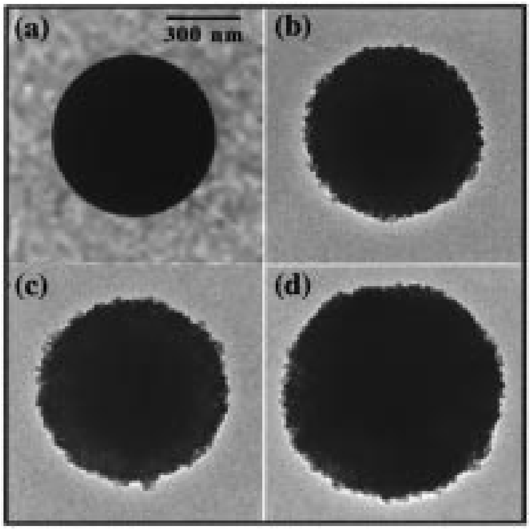

Figure 3. TEM micrographs of uncoated PS latices (a) and PS latices coated with $[Pr_3/(SiO_2/PDADMAC)_N]$ ($N = 1$ (b), $N = 2$ (c), and $N = 4$ (d)). Increased surface roughness is due to SiO_2 deposition. Regular growth of the SiO_2−PDADMAC multilayers is seen, evidenced by an increase in diameter of the coated PS latices. The scale bar corresponds to all four TEM images shown.

The uncoated PS latices feature sharp, smooth edges (a), characteristic of a smooth surface. TEM images obtained for PS latices coated with Pr_3 are essentially identical to those of the uncoated PS latices: the thickness increase (ca. 4 nm, determined from SPLS experiments) is not discernible. The presence of SiO_2−PDADMAC multilayers on the PS latices results in both an increase in surface roughness and an increase in the diameter of the PS latices (b−d). The increase in surface roughness is due to adsorbed SiO_2. It was found that adsorption of PDADMAC onto an outermost layer of SiO_2 reduces the surface roughness of the multilayer.[18] This finding is corroborated by scanning electron microscopy (SEM) measurements.[18]

The increase in diameter with increasing SiO_2−PDADMAC multilayer number of the coated PS latices (relative to uncoated PS latices (a)) is approximately 60 nm (b), 120 nm (c), and 240 nm (d), for one, two, and four SiO_2−PDADMAC multilayers, respectively. Evaluation of the TEM data for $(SiO_2/PDADMAC)_N$ multilayers with $N = 1-5$ yields an average diameter increment of 60 ± 5 nm, corresponding to a layer thickness of ca. 30 nm, for the SiO_2−PDADMAC layer pair.

We are currently preparing composite alternating multilayers of polyelectrolytes and various other nanoparticles, as well as biomolecules (proteins, enzymes, etc.) and other functional charged species, in the hope of utilizing these systems in sensing, catalytic, and separation applications.

Acknowledgment. F.C. acknowledges the Alexander von Humboldt Foundation for support in the form of a Research Fellowship. We thank Heidi Zastrow for assistance with the EPM measurements, and Dr. Edwin Donath for helpful discussions.

JA9815024

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(12) Electrophoretic mobilities of the PS latices were measured using a Malvern Zetasizer 4 (see ref 8 for details on the experimental procedure).

(13) For details on the SPLS experimental system and measurement principle, see: Lichtenfeld, H.; Knapschinsky, L.; Dürr, C.; Zastrow, H. *Prog. Colloid Polym. Sci.* **1997**, *104*, 148.

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(15) The value of n for pure SiO_2 is 1.46, and 1.47[8a] for polyelectrolyte layers. Significantly more SiO_2 is adsorbed than PDADMAC; hence, we take the average n for the SiO_2−PDADMAC multilayers to be 1.46. Since SiO_2 is randomly adsorbed, $n < 1.41$ (i.e., 1.46×0.63 (coefficient for hexagonal packing of spheres) $+ 1.33$ (n_{water}) $\times 0.37$ (assuming the amount of PDADMAC surrounding SiO_2 is small)). n therefore is estimated as ∼1.40; this value yields thickness values in agreement with those from TEM and SEM.

(16) The thicknesses of individual PDADMAC layers could not be calculated due to the simultaneous removal of small amounts of adsorbed SiO_2 and deposition of PDADMAC. Full details of the analysis procedure will be given in a subsequent publication.

(17) TEM measurements were performed on a Phillips CM12 microscope operating at 120 kV.

(18) Loosely adsorbed SiO_2 may be removed by subsequent PDADMAC deposition, thus reducing the surface roughness. Details on the effect of PDADMAC adsorption on surface roughness, along with diameter increases obtained from SEM for the SiO_2−PDADMAC multilayer coated PS latices, will be published elsewhere.