

# Polyelectrolyte-Coated Colloid Spheres as Templates for Sol–Gel Reactions

Dayang Wang and Frank Caruso\*

Max Planck Institute of Colloids and Interfaces,  
D-14424 Potsdam, Germany

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The preparation and study of core–shell colloids are of burgeoning interest, principally because such particles can display novel and enhanced properties (e.g., electrical, magnetic, catalytic, mechanical, chemical, and optical) when compared with those of the core particles.<sup>1–5</sup> This has led to their recent exploitation in optical applications such as photonic crystals<sup>6</sup> and microcavities<sup>7</sup> and in catalysis<sup>8,9</sup> and immunosensing.<sup>10</sup> The properties of core–shell particles are often associated with the coating or encapsulating material forming the shell.<sup>5</sup> Strategies for the preparation of coated colloids include polymerization, sol–gel, and self-assembly processes.<sup>1–5,11–14</sup> Recently, we introduced a versatile self-assembly approach to colloid coating,<sup>5,15</sup> which entails the layer-by-layer (LbL)<sup>16</sup> deposition of oppositely charged species from solution onto colloid templates. Coatings have comprised polyelectrolytes,<sup>15b–d</sup> inorganic nanoparticles,<sup>15a</sup> and proteins,<sup>8a–c</sup> and the

coating thickness can be tuned with nanometer precision. Among the inorganic species, *preformed* nanoparticles (e.g., SiO<sub>2</sub>, TiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, CdTe, and Au) have been extensively used.<sup>15a,17</sup>

Metal oxide precursors are widely used to form thin inorganic coatings on surfaces, including colloids, via sol–gel processes. However, many such precursors are extremely sensitive to water, readily hydrolyzing and condensing upon direct contact with water.<sup>18</sup> This necessitates the use of optimized conditions (colloid concentration, reactant quantities, pH, etc.) as well as compatibility between the particle surface and the inorganic precursors to generate uniformly coated particles with thin inorganic layers.<sup>5,11,13,14</sup> Often it is difficult to control the precipitation of the inorganic species in solution, leading to nonuniform coatings and hence aggregation of the particles.<sup>5,19</sup> The water sensitivity of the precursors also limits their direct application in the LbL coating of colloids, as typically charged species are deposited from aqueous-based solutions.

In this communication, we report the preparation of core–shell colloids and hollow spheres by a new route that combines LbL colloid templating and in situ sol–gel processes. The method exploits polyelectrolyte (PE) multilayer-coated particles as the templates for the sol–gel reactions (Scheme 1) because colloids coated with PE multilayer films possess some key characteristics. First, the PE coating thickness can be tuned at the nanometer level, depending on the number of layers deposited: each PE layer has an average thickness of ~1–2 nm.<sup>15d</sup> This provides a means to control the thickness of the coatings. Second, PE multilayers can be exploited as nanoreactors. It has already been shown that PE layers formed on macroscopic, planar supports are suitable hosts for the preparation of metals, metal oxides, and semiconductors.<sup>20–23</sup> By combining these two features of PE films, here, we demonstrate the use of PE-coated spheres as templates for sol–gel reactions to prepare inorganic-based coatings of controllable thickness on colloids dispersed in nonaqueous solution. The common problem of particle aggregation upon coating with sol–gel precursors is overcome by localizing the reactions within the thin polyelectrolyte coatings on the colloids. Once the sol–gel reaction is completed and

\* To whom correspondence should be addressed. Fax: (+49) 331 567 9202. E-mail: frank.caruso@mpikg-golm.mpg.de.

(1) *Hollow and Solid Spheres and Microspheres: Science and Technology Associated with Their Fabrication and Application*, Wilcox, D. L., Berg, M., Bernat, T., Kellerman, D., Cochran, J. K., Eds.; Materials Research Society Proceedings 372; MRS: Pittsburgh, PA, 1995.

(2) Matijevic, E. In *Fine Particle Science and Technology*; Pelizzetti, E., Ed.; Kluwer: Dordrecht, The Netherlands, 1996; pp 1–16.

(3) Hofman-Caris, C. H. M. *New J. Chem.* **1994**, *18*, 1087, and references therein.

(4) Partch, R. In *Materials Synthesis and Characterization*; Perry, D., Ed.; Plenum: New York, 1983.

(5) For a review, see: Caruso, F. *Adv. Mater.* **2001**, *13*, 11.

(6) (a) van Blaaderen, A. *MRS Bull.* **1998**, *10*, 39. (b) Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. *Adv. Mater.* **2000**, *12*, 693. (c) Ozin, G. A.; Yang, S. M. *Adv. Funct. Mater.* **2001**, *11*, 95.

(7) (a) Artemyev, M. V.; Woggon, U. *Appl. Phys. Lett.* **2000**, *76*, 1353. (b) Artemyev, M. V.; Woggon, U.; Wannemacher, R.; Jaschinski, H.; Langbein, W. *Nano Lett.* **2001**, *1*, 309. (c) Artemyev, M. V.; Woggon, U.; Wannemacher, R.; *Appl. Phys. Lett.* **2001**, *78*, 1032.

(8) (a) Schüler, C.; Caruso, F. *Macromol. Rapid Commun.* **2000**, *21*, 750. (b) Caruso, F.; Schüler, C. *Langmuir* **2000**, *16*, 9595. (c) Lvov, Y.; Caruso, F. *Anal. Chem.* **2001**, *73*, 4212. (d) Jin, W.; Shi, X.; Caruso, F. *J. Am. Chem. Soc.* **2001**, *123*, 8121.

(9) Mecking, S.; Thomann, R. *Adv. Mater.* **2000**, *12*, 953.

(10) Yang, W.; Trau, D.; Renneberg, R.; Yu, N. T.; Caruso, F. *J. Colloid Interface Sci.* **2001**, *234*, 356.

(11) (a) Garg, A.; Matijevic, E. *J. Colloid Interface Sci.* **1988**, *126*, 243. (b) Oyama, H. T.; Spryca, R.; Xie, Y.; Partch, R. E.; Matijevic, E. *J. Colloid Interface Sci.* **1993**, *160*, 298.

(12) Marinakos, S. M.; Novak, J. P.; Brousseau, L. C.; House, A. B.; Edeki, E. M.; Feldhaus, J. C.; Feldheim, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 8518.

(13) (a) Liz-Marzán, L. M.; Giersig, M.; Mulvaney, P. *Langmuir* **1996**, *12*, 4329. (b) Giersig, M.; Ung, T.; Liz-Marzán, L. M.; Mulvaney, P. *Adv. Mater.* **1997**, *9*, 570.

(14) Imhof, A. *Langmuir* **2001**, *17*, 3579.

(15) (a) Caruso, F.; Caruso, R. A.; Möhwald, H. *Science* **1998**, *282*, 1111. (b) Donath, E.; Sukhorukov, G. B.; Caruso, F.; Davis, S. A.; Möhwald, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2201. (c) Caruso, F.; Donath, E.; Möhwald, H. *J. Phys. Chem. B* **1998**, *102*, 2011. (d) Caruso, F.; Lichtenfeld, H.; Donath, E.; Möhwald, H. *Macromolecules* **1999**, *32*, 2317.

(16) (a) Decher, G.; Hong, J.-D. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1430. (b) For a review, see: Decher, G. *Science* **1997**, *277*, 1232.

(17) (a) Caruso, F.; Susa, A. S.; Giersig, M.; Möhwald, H. *Adv. Mater.* **1999**, *11*, 950. (b) Caruso, F.; Spasova, M.; Susa, A.; Giersig, M.; Caruso, R. A. *Chem. Mater.* **2001**, *13*, 109. (c) Caruso, F.; Spasova, M.; Salgueirino-Maceira, V.; Liz-Marzán, L. M. *Adv. Mater.* **2001**, *13*, 1090. (d) Rogach, A.; Susa, A.; Caruso, F.; Sukhorukov, G.; Kornowski, A.; Kershaw, S.; Möhwald, H.; Eychmüller, A.; Weller, H. *Adv. Mater.* **2000**, *12*, 333.

(18) Brinker, C. J.; Scherer, G. W. *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing*; Academic Press: San Diego, 1990.

(19) (a) Hsu, W. P.; Yu, R.; Matijevic, E. J. *J. Colloid Interface Sci.* **1993**, *156*, 56. (b) Castillo, R.; Koch, B.; Ruiz, P.; Delmon, B. *J. Mater. Chem.* **1994**, *4*, 903.

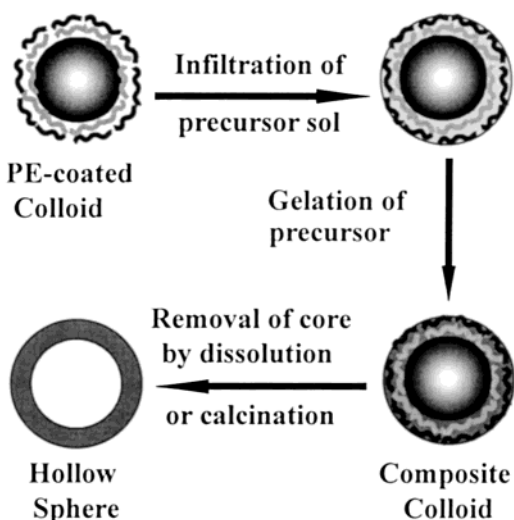
(20) Joly, S.; Kane, R.; Radzilowski, L.; Wang, T.; Wu, A.; Cohen, R. E.; Thomas, E. L.; Rubner, M. F. *Langmuir* **2000**, *16*, 1354.

(21) Dante, S.; Hou, Z.; Risbud, S.; Stroeve, P. *Langmuir* **1999**, *15*, 2176.

(22) Wang, D.; Caruso, R. A.; Caruso, F. *Chem. Mater.* **2001**, *13*, 364.

(23) (a) Mayya, K. S.; Gittins, D. I.; Caruso, F. *Chem. Mater.* **2001**, *13*, 3853. (b) Shi, X.; Cassagneau, T.; Caruso, F. *Langmuir* **2002**, *18*, 904.

**Scheme 1. Schematic Diagram of the Procedure Used To Form the Core–Shell Composite Colloids and Hollow Spheres by Using PE-Coated Colloids as Templates<sup>a</sup>**



<sup>a</sup> Before the coated colloids were exposed to precursor solutions, they were centrifuged and re-dispersed with absolute alcohol: ethanol and IPA were used for the  $\text{LiNbO}_3$  and  $\text{TiO}_2$  precursor solutions, respectively. Following gelation of the precursor within the PE layers, which contain water, the particles were repeatedly washed with anhydrous alcohol.

after several washing cycles with ethanol, the particles can be readily dispersed in an aqueous solution without aggregation.

The PE coatings were formed by the LbL deposition of poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS) onto negatively charged polystyrene or silica colloids.<sup>24</sup> Prior to addition of the PE-coated colloids to the precursor solutions, the particles were centrifuged and re-dispersed in anhydrous alcohol (either ethanol or 2-propanol) 10 times to replace water in the colloidal dispersion with alcohol. This process may also cause extraction of some water that is entrapped in the PE multilayer film, although it is possible that a water gradient could be formed in the PE shell. The precursor ( $\text{LiNb}(\text{OC}_2\text{H}_5)_6$  for lithium niobate or titanium (IV) isopropoxide, TIP, for  $\text{TiO}_2$ ) was then added to the PE-coated colloids in alcohol,<sup>25</sup> causing it to infiltrate the PE shell. Hydrolysis and condensation of the precursor occurred upon interaction with water adsorbed in the PE layers (i.e., in situ sol–gel), causing its gelation<sup>25</sup> and the formation of thin, inorganic/PE hybrid coatings of defined thickness. Hollow spheres were subsequently obtained by removing the colloid cores by either chemical or thermal pathways.<sup>25</sup> Such hollow spheres are of potential interest in drug delivery, photonics, and catalysis applications.<sup>26</sup>

Figure 1a shows a representative transmission electron microscopy (TEM)<sup>27</sup> image of a 640-nm-diameter polystyrene (PS) particle coated with a total of nine alternating layers of PAH and PSS, PS–PE<sub>9</sub> (outermost

layer is positively charged, PAH). A slight increase in surface roughness occurred as a result of the coating (compared with the PS particles), although the PE multilayer film cannot be clearly distinguished because of the similar contrast between the PE and PS core in the electron beam. The particle diameter increased (from about 640 nm) to 675 nm as a result of coating, yielding a thickness of about 18 nm for the PE<sub>9</sub> film. This corresponds to an average thickness of  $\approx 2$  nm for each PE layer, a value in good agreement with previous data.<sup>15d</sup> The lithium niobate sol–gel precursor in absolute ethanol was added to ethanol dispersions of the PS–PE<sub>9</sub> colloids, and following hydrolysis and condensation, composite colloids comprising a PS core and a lithium niobate<sup>25</sup> ( $\text{LiNbO}_3$ )/PE hybrid shell were constructed. The shell can be visualized by TEM because  $\text{LiNbO}_3$  has a higher electron contrast than the PS core and PE (Figure 1b). There is also an increase in the surface roughness due to the presence of  $\text{LiNbO}_3$ . The diameter of the resulting PS–PE<sub>9</sub>/ $\text{LiNbO}_3$  colloids is, within experimental error, the same as that of the initial PS–PE<sub>9</sub> colloids ( $\approx 675$  nm). Energy-dispersive X-ray (EDX) spectra identified the presence of Nb in the shell (data not shown), suggesting the formation of  $\text{LiNbO}_3$ .<sup>25</sup>

PE<sub>9</sub>/ $\text{LiNbO}_3$  hybrid capsules were obtained after the PS core was dissolved with tetrahydrofuran (THF), leaving behind “porous” shells (Figure 1c). The diameters of the shell (or capsules) are about 750–850 nm. This spreading as well as the folds and creases seen are due to the influence of drying them on a substrate.<sup>15b</sup> The above observations (porosity, spreading, etc.) are consistent with those made for inorganic/PE composite shells prepared from PE and preformed nanoparticles,<sup>26</sup> further showing that the sol–gel reaction has occurred within the PE coating. In an alternative route to hollow sphere preparation, the organic materials, including the PS core and the PE multilayer, were removed by calcining the coated particles at 500 °C, resulting in  $\text{LiNbO}_3$  hollow spheres (Figure 1d). During calcination, the  $\text{LiNbO}_3$  nanoparticles formed are expected to coalesce, but a porous structure is observed for the resulting

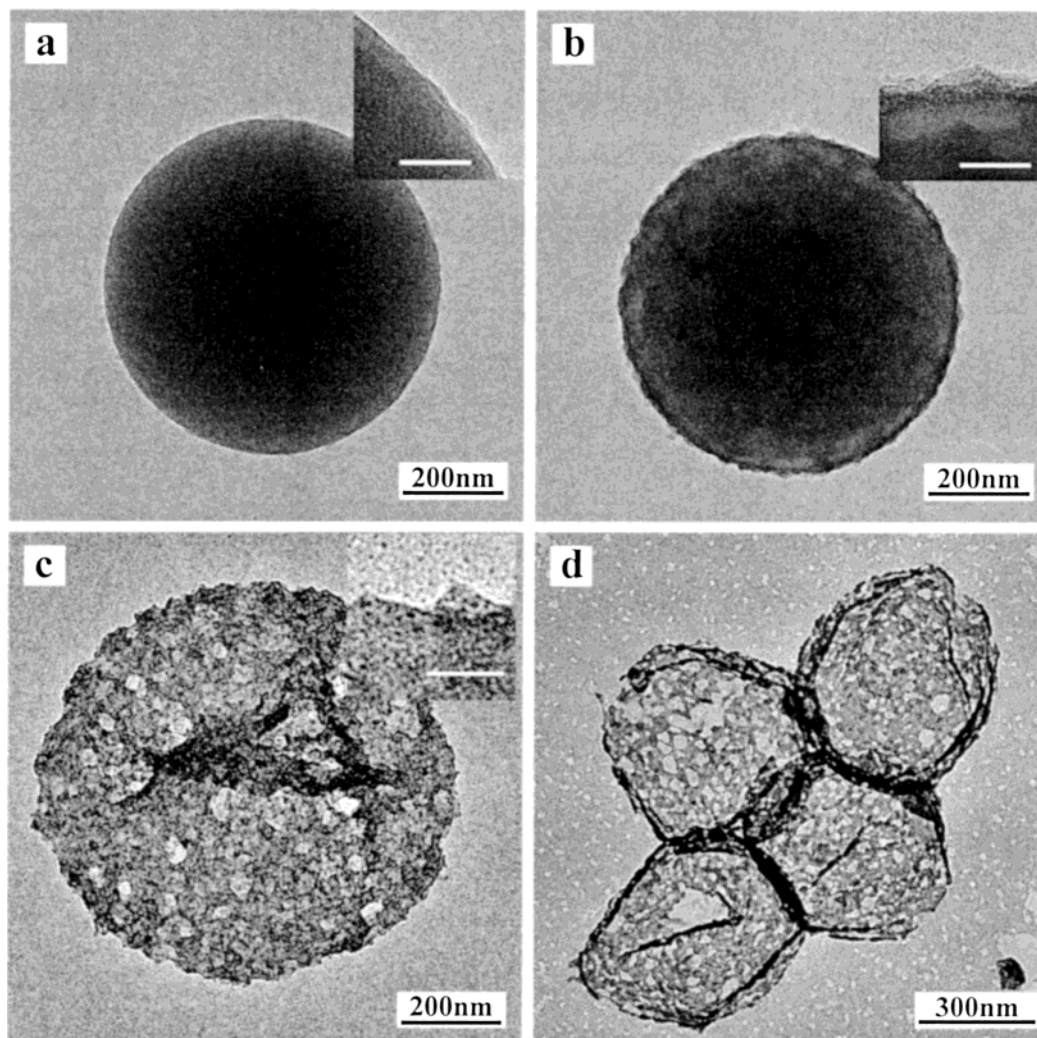
(25) Lithium ethoxide,  $\text{LiOC}_2\text{H}_5$ , and niobium ethoxide,  $\text{Nb}(\text{OC}_2\text{H}_5)_6$ , were used as sources for forming  $\text{LiNbO}_3$ . Both ethoxides were dissolved in absolute ethanol at a mole ratio of 1:1. After stirring and refluxing under  $\text{N}_2$  at 78.5 °C for 24 h, a 1.5 M solution of the  $\text{LiNbO}_3$  precursor,  $\text{LiNb}(\text{OC}_2\text{H}_5)_6$ , was obtained. It has been reported that the stoichiometry of lithium niobate is dependent on the Li:Nb ratio of the precursors used. Using  $\text{LiNb}(\text{OC}_2\text{H}_5)_6$  with a Li:Nb ratio of 1:1 as a precursor leads dominantly to  $\text{LiNbO}_3$  (Hirano, S.; Kato, K. *J. Non-Cryst. Solids* **1988**, 100, 538). A 2-propanol (IPA) solution of titanium(IV) isopropoxide (TIP, Aldrich) was used as the precursor solution of  $\text{TiO}_2$  with a ratio of TIP to IPA of 1:10 (v/v). The PE-coated colloids were centrifuged and re-dispersed with alcohol (absolute ethanol was used in the case of  $\text{LiNbO}_3$  and IPA for  $\text{TiO}_2$ ). One milliliter of the precursor solution was added to 0.1 mL of the “anhydrous” PE-coated colloids dispersed in alcohol and the mixture was gently shaken for 30 min. A centrifugation (10000g)/re-dispersion/re-exposure cycle was repeated five times to achieve thorough infiltration of the PE films with the precursors. After three further centrifugation (10000g)/re-dispersion/washing cycles (washing with the anhydrous alcohol) to remove the excess precursor from solution, the resulting dispersions were left at room temperature for 24 h. Finally, core–shell colloids were produced. These particles could be readily dispersed in water. Hollow spheres were obtained by removing the PS cores by dissolving with tetrahydrofuran (THF) or by calcination. The samples were slowly heated to 500 °C (5 °C min<sup>−1</sup>) under nitrogen and then kept at 500 °C for 1–2 h under oxygen.

(26) For a review, see: Caruso, F. *Chem. Eur. J.* **2000**, 6, 413.

(27) Transmission electron microscopy (TEM) measurements and energy-dispersive X-ray (EDX) spectra were obtained with a Philips CM12 microscope operating at 120 kV equipped with an EDX attachment.

(24) PE multilayers were formed by the alternate adsorption of PAH ( $M_w$  8000–11000, Aldrich) and PSS ( $M_w$  70000, Aldrich) from 1 mg mL<sup>−1</sup> aqueous solutions (containing 0.5 M NaCl) onto negatively charged PS or  $\text{SiO}_2$  colloids as described elsewhere.<sup>15d</sup> The PS spheres were kindly donated by H. Zastrow (MPI) and the  $\text{SiO}_2$  spheres were purchased from Polysciences (USA).





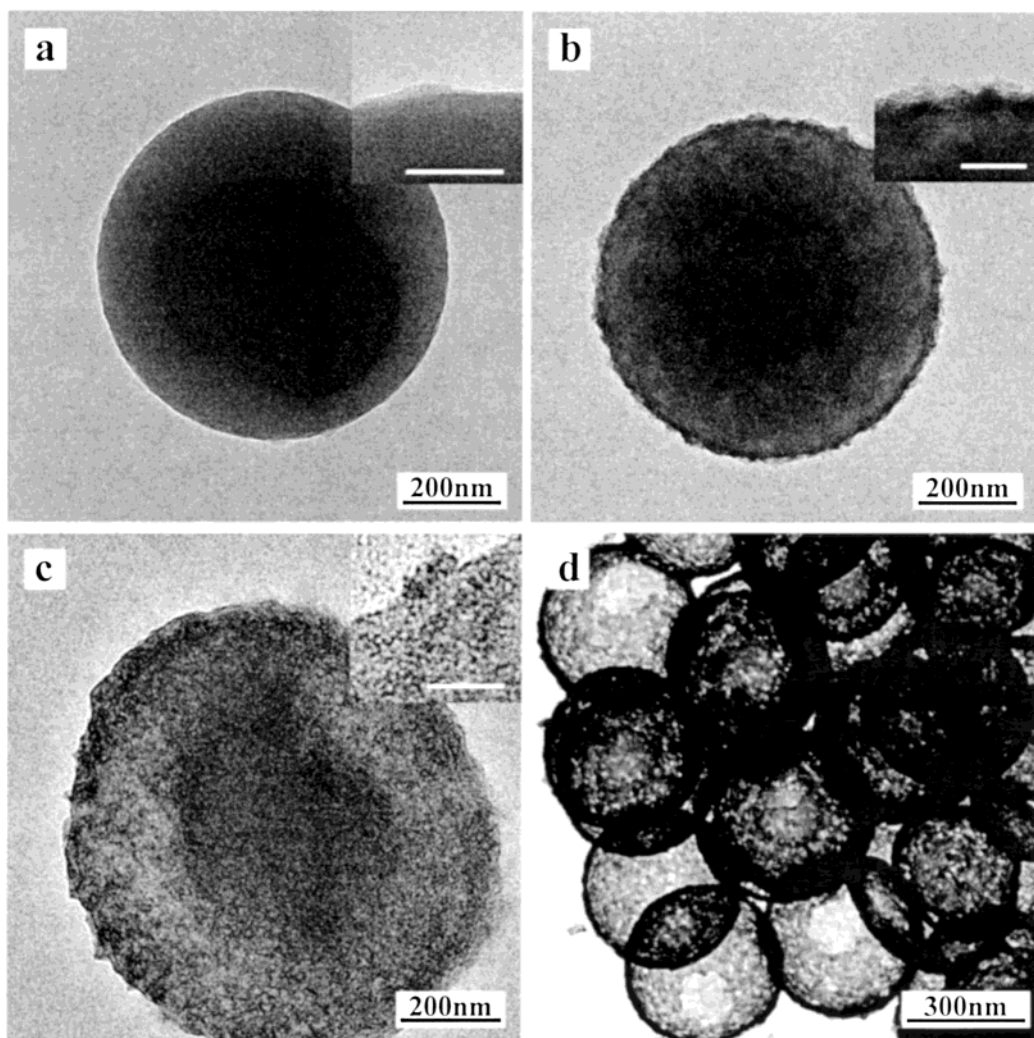
**Figure 1.** TEM micrographs of (a) PS-PE<sub>9</sub> colloids, (b) PS-PE<sub>9</sub>/LiNbO<sub>3</sub> core-shell colloids, (c) PE<sub>9</sub>/LiNbO<sub>3</sub> hybrid capsules formed by dissolving the PS cores with THF, and (d) LiNbO<sub>3</sub> hollow spheres prepared by calcining the coated spheres at 500 °C (the bright, small spots seen around the spheres are due to the quality of the carbon film covering the TEM grids). The PS colloids used were 640 nm in diameter. The scale bars in the insets correspond to 50 nm.

shell. This indicates that there is an insufficient quantity of inorganic material in the shell coating or that the inorganic wall thickness is too thin to form complete capsules upon calcination, which causes them to deform.<sup>15a</sup>

To examine the influence of both the thickness of the PE multilayer film and the nature of the outermost surface charge on the precursor infiltration process, PS colloids coated with 18 PAH/PSS layers, PS-PE<sub>18</sub>, were employed as templates. The outermost layer in this case was negatively charged (PSS). The PS-PE<sub>18</sub> colloids are about 705 nm in diameter, as shown in Figure 2a, giving a thickness of  $\approx 33$  nm for the PE<sub>18</sub> film or an average thickness of about 1.8 nm for each PE layer. Figure 2b shows the TEM micrograph of a PS-PE<sub>18</sub>/LiNbO<sub>3</sub> composite colloid. The presence of LiNbO<sub>3</sub> in the PE shell is indicated by the increase in surface roughness (compare Figure 2b with 2a). There is no significant change in diameter of the colloids after infiltration of the precursor (diameter  $\approx 700$  nm). EDX spectra again confirmed the presence of Nb in the shell. In a comparison of the PE<sub>18</sub> and PE<sub>9</sub> layer systems, it is evident that solid, composite colloids with tuned PE/LiNbO<sub>3</sub> shell thickness (and hence overall diameter) can be

prepared by controlling the number of the PE layers precoated on the colloids. Notably, the coated particles formed were unaggregated.

After the PS core was dissolved with THF, PE<sub>18</sub>/LiNbO<sub>3</sub> hybrid capsules of about 800–1000 nm in diameter were obtained when dried on a TEM grid, as shown in Figure 2c. The resulting morphology of these capsules, however, is rather different from that of the PE<sub>9</sub>/LiNbO<sub>3</sub> spheres (Figure 1c): there are no apparent large pores nor are there folds or creases in the shell. This points to a higher loading of precursor in the PE<sub>18</sub> film, which then gels, forming a less porous shell network structure. This may prevent complete removal of the PS chains of the core particles dissolved with THF; the dark contrast seen in the middle of the PE<sub>18</sub>/LiNbO<sub>3</sub> hybrid capsule shown is in accord with this reasoning. As was observed for a titania-based inorganic species that infiltrated PE films in aqueous solution,<sup>23b</sup> the amount of LiNbO<sub>3</sub> precursor in the PE films would also be expected to increase with increasing PE film thickness. This would account for the more highly LiNbO<sub>3</sub> precursor-loaded shell observed for the PS-PE<sub>18</sub> colloids, compared with those coated with only nine layers. Further evidence for a higher precursor loading



**Figure 2.** TEM micrographs of (a) PS-PE<sub>18</sub> colloids, (b) PS-PE<sub>18</sub>/LiNbO<sub>3</sub> core-shell colloids, (c) PE<sub>18</sub>-LiNbO<sub>3</sub> hybrid capsules prepared after removal of the PS cores with THF, and (d) LiNbO<sub>3</sub> hollow spheres formed by calcining the PS-PE<sub>18</sub>/LiNbO<sub>3</sub> core-shell colloids at 500 °C. PS core colloids of 640-nm diameter were used. In (d), a large number of hollow spheres are seen as a result of drying a concentrated dispersion on a TEM grid. Calcination introduced some sintering between the spheres. The scale bars in the insets are 50 nm.

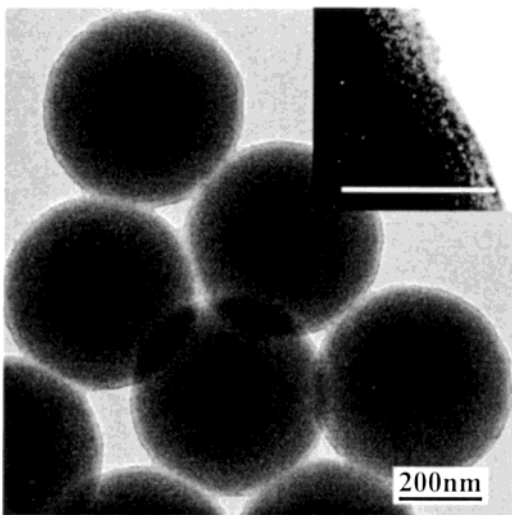
with increasing film thickness was provided by calcining the PE<sub>18</sub>/LiNbO<sub>3</sub>-coated PS spheres, which resulted in the formation of LiNbO<sub>3</sub> hollow spheres (Figure 2d). Although some broken spheres are observed, the spherical shape of the original template is retained, indicating a higher precursor loading in the PE<sub>18</sub> films versus the PE<sub>9</sub> films. The resulting hollow spheres are about 400 nm in diameter, corresponding to a shrinkage of 44% in size compared with the original size of the core-shell particles. This degree of shrinkage is considerably larger than that observed in our previous work using pre-formed nanoparticles or a layered inorganic compound (10–15%).<sup>15a,28</sup> The thickness of the shell, estimated by TEM from the dark ring around the perimeter of the hollow spheres, is about 15–20 nm. This indicates that each PE layer contributes an average thickness of  $\approx 1$  nm to that of the LiNbO<sub>3</sub> shell. The data for the PS-PE<sub>9</sub> and PS-PE<sub>18</sub> systems, which have a different outermost surface charge, show that infiltration occurs regardless of the nature of the charge.

Despite the fact that titania-coated silica supports are widely utilized in catalysis applications,<sup>29</sup> colloids with uniform titania coatings are generally difficult to synthesize.<sup>14</sup> Hence, we extended the current approach to silica colloids. The silica particles, 450 nm in diameter, were coated with 10 PAH/PSS layers, SiO<sub>2</sub>-PE<sub>10</sub>.<sup>30</sup> The aqueous SiO<sub>2</sub>-PE<sub>10</sub> colloidal dispersions had the water replaced by IPA and were then exposed to an IPA solution of the titania precursor, TIP.<sup>25</sup> After hydrolysis and condensation of TIP within the PE layers, composite colloids comprising a silica core and a PE<sub>10</sub>/TiO<sub>2</sub> hybrid shell were produced, SiO<sub>2</sub>-PE<sub>10</sub>/TiO<sub>2</sub>. The TEM micrograph in Figure 3 clearly indicates the core-shell structure of the resulting SiO<sub>2</sub>-PE<sub>10</sub>/TiO<sub>2</sub> colloids. EDX spectra demonstrated that the shells surrounding the silica cores comprise Ti, indicating the formation of TiO<sub>2</sub>.

(29) (a) Kamat P. V. *Nanoparticles and Nanostructured Films*; Fendler, J. H., Ed.; Wiley-VCH: Weinheim, 1998; Chapter 9, and references therein. (b) Stafford, U.; Gray, K. A.; Kamat, P. V. *J. Phys. Chem.* **1994**, *98*, 6343.

(30) Prior to coating of the PSS/PAH multilayers, a poly(ethyleneimine) (PEI) layer was deposited on the silica colloids to prime the silica surface, as is routinely performed on macroscopic silica supports.<sup>16</sup>

(28) Caruso, F.; Shi, X.; Caruso, R.; A. Susha, A. *Adv. Mater.* **2001**, *13*, 740.



**Figure 3.** TEM micrographs of  $\text{SiO}_2\text{-PE}_{10}/\text{TiO}_2$  core-shell colloids prepared by infiltrating  $\text{SiO}_2\text{-PE}_{10}$  colloids with TIP. The silica colloids used were 450 nm in diameter. The scale bar in the inset is 50 nm.

These core-shell colloids are  $\approx 490$  nm in diameter, similar in size to the  $\text{SiO}_2\text{-PE}_{10}$  colloid templates (TEM image not shown). Accumulation of  $\text{TiO}_2$  at the surface of the spheres is identified as dark spots because of the higher electron contrast of  $\text{TiO}_2$  compared with that of the PE (inset in Figure 3).

In summary, we have demonstrated the applicability of a new approach, based on the in situ sol-gel synthesis

of metal oxides in PE shell coatings formed on colloids, to construct core-shell particles with metal oxide composite shells of defined thickness. The coating process is independent of the nature of the PE charge forming the outermost layer, and the coating thickness can be tuned by the number of PE layers deposited. Subsequent removal of the colloid templates by calcination yields hollow, porous metal oxide spheres. The inherent flexibility of the LbL technique with respect to the choice of colloid cores and PE shell coatings, when coupled with the array of sol-gel precursors available, provides a versatile and powerful route for the preparation of tailored, composite colloids. We are currently furthering our studies using PE multilayers as templates for preparing colloids coated with a variety of inorganic materials, with the aim of introducing different properties and functions, thereby making them suitable for various technological applications.

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