Multilayered Titania, Silica, and Laponite Nanoparticle Coatings on Polystyrene Colloidal Templates and Resulting Inorganic Hollow Spheres

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Received September 15, 2000. Revised Manuscript Received November 8, 2000

The applicability of the layer-by-layer (LbL) technique for the formation of a range of polymer-core inorganic-shell particles and inorganic hollow spheres is demonstrated. Titanium dioxide, silica, and Laponite nanoparticles were used as the inorganic building blocks for multilayer formation on polystyrene (PS) sphere templates. Composite organic−inorganic particles were formed by the controlled assembly of the preformed nanoparticles in alternation with oppositely charged polyelectrolytes onto PS microspheres. The influence of nanoparticle type, shape (spherical to sheetlike), and size (3−100 nm), and the diameter of the PS sphere templates (210−640 nm) on the formation of multilayer shells was examined by transmission and scanning electron microscopy. In addition, the LbL technique for coating polymer spheres has been shown to be adaptable with small variations in the coating steps used to optimize the nanoparticle coatings of the different materials. For example, the number of polyelectrolyte multilayers separating the nanoparticle layers, and the number of nanoparticle/polyelectrolyte deposition cycles were varied to generate uniformly coated nanocomposite spheres. These hybrid core−shell particles were subsequently calcined to create well-defined hollow spheres with predetermined diameters. Such hollow spheres may find application in diverse areas, ranging from photonics to fillers and pigments to microencapsulation.

Introduction

The fabrication of colloidal materials with desired structural, optical, and surface properties has recently been the subject of intense investigations.[1−8] Facile and flexible strategies that afford fine control over the synthesis and modification of particles are of paramount importance in building new classes of colloids.[9] Composite particles, often comprised of a solid core surrounded by a well-defined shell layer, are known to exhibit unique and enhanced characteristics over single-component colloids, making them attractive for use in a wide range of applications.[5,8,9] A commonly employed route to creating composite colloids is the postsynthesis modification of core particles, for example, by coating and/or encapsulating them with thin polymer or inorganic shells. Procedures to achieve this have predominantly relied on the in situ synthesis of polymer layers[2,7] or surface reactions (e.g., precipitation and sol−gel condensation) to deposit a range of inorganic layers onto preformed cores.[1,3−6,8]

Recently, an alternative and remarkably adaptable approach, termed the layer-by-layer (LbL) self-assembly technique,[10,11] has been applied to the coating of colloids.[9,12] The basis of this method is the electrostatic association between alternately deposited, oppositely charged species.[11] Multilayered shells of polyelectrolytes,[13−15] inorganic nanoparticles,[16−20] or proteins[21−24]

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10.1021/cm001175a CCC: $20.00

have been deposited onto particle templates, giving rise to novel colloidal entities. Organic−inorganic composite particles, comprising latex cores and silica nanoparticles,[16,17] luminescent semiconductors (CdTe),[18,19] or iron oxide nanoparticle multilayer coatings[20] have been fabricated. An interesting extension of these tailor-made core−shell particles has been the subsequent removal of the templated cores, resulting in hollow capsules.[12,25−30] Whereas a variety of hollow capsules of polymers have been produced already,[25−28] to date only silica,[29] zeolite,[30] and magnetic[31] hollow spheres have been fabricated using this strategy. The primary motivation behind the current work was to explore the possibility of creating novel and desirable core−shell particles as well as hollow materials from a range of inorganic nanoparticles, with particular emphasis on TiO_2, using the LbL assembly technique.

Titanium dioxide, because of its unique optical, electrical, and chemical attributes is a widely studied material.[32] It is well-known for its photovoltaic[33] and photocatalytic[34] properties, along with its applications in the paint, paper, and food industries as a pigment,[35] filler,[36] and whitener.[37] Surface area is an especially important characteristic of TiO_2, as the catalytic activity or sensor sensitivity, for example, is greatly enhanced with increasing TiO_2 surface area. The production of core−shell or hollow materials comprising TiO_2 nanoparticles is expected to be of benefit to such applications.

Titanium dioxide has been coated on various inorganic and organic particles using titania precursors and by carrying out subsequent reactions on the particle surface.[38−45] Typically, titania precursors are hydrolyzed in the presence of various particles to effect coating. However, there are a number of disadvantages associated with such strategies for producing TiO_2 coatings on particles. These include the formation of irregular coatings, aggregation of the coated particles, and little control over the coating thickness. This can in part be attributed to the precise control needed over the reaction conditions (e.g., concentration of reagents, pH, temperature, and mixing methods) to produce uniform coatings. Therefore, despite the intense interest in TiO_2-modified particles and hollow materials, it has been difficult to produce uniform and controlled TiO_2 coatings on colloidal particles. A main feature that distinguishes these above-mentioned approaches from the technique described herein is that metal oxide precursors were used and hydrolysis and polycondensation reactions exploited in the presence of the templates to form TiO_2 coatings, as opposed to the use of preformed nanoparticles.

The production of hollow spheres of inorganic materials can be achieved using a number of methods, including nozzle-reactor systems, sacrificial cores, or emulsion/water extraction techniques.[12,46] Large (millimeter-size range) hollow ceramic spheres are commonly obtained using nozzle-reactor techniques where slurries of micron-sized particles in acetone are passed through a nozzle within which another outlet passes an inert gas.[46] The resulting spheres generally have wall thicknesses ranging between 40 and 200 μm. Hollow microspheres of titanium dioxide with a wall thickness of 50 nm were prepared by spray drying a colloidal suspension of exfoliated titanate sheets, followed by heating.[47] Using an elegant approach, smaller hollow spheres of *amorphous* titania, with diameters in the hundreds of nanometers, have recently been formed using ordered polystyrene (PS) beads as sacrificial cores.[44] The PS spheres were packed to form a crystalline array around which the subsequent hydrolysis and condensation reactions of the titanium alkoxide occurred.[44] Control of the wall thickness using this method is dependent on the sol−gel solution concentration, with wall thicknesses of about 30, 60, and 100 nm being achieved. Tin dioxide hollow spheres were also formed using this strategy; however, hollow silica spheres could not be produced[44] as the rates of the hydrolysis and condensation reactions are slower than those for the titania and tin precursors.

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Here, we describe the coating of PS spheres with preformed colloidal nanoparticles and the subsequent formation of hollow spheres, using the LbL deposition technique. The use of templates, such as PS particles, on which layers of nanoparticles were deposited by the alternate adsorption of oppositely charged polyelectrolytes and nanoparticles results in nanoparticle multilayer shells surrounding the template core. The advantages of this process are that it allows nanometer control of both the final diameter and the multilayer wall thickness of the composite particles by choice of the initial template diameter and the number of layers deposited, respectively. The colloidal core can be removed by various methods, including heating of the sample, inducing pyrolysis of the organic material, and leaving behind hollow inorganic spheres.

To demonstrate the adaptability of the LbL deposition approach for producing core−shell materials and consequently hollow spheres of different composition, the technique has also been extended to examine the role of (i) different inorganic nanoparticles (TiO_2, SiO_2, Laponite), (ii) microsphere template diameter, and (iii) size (SiO_2) and shape (Laponite) of the inorganic nanoparticles used in the formation of the multilayer shells. Particles of ≈100-nm-diameter and smaller particles (≈5 nm) were used as the coating materials to determine whether they would be suitable as the building blocks for hollow sphere fabrication. The smaller particles are expected to lead to higher surface areas in the final materials. In addition, because in most cases the nanoparticles used to coat the colloidal templates have been close to spherical,[12] the ability to use sheetlike nanoparticles (or nanoplatelets) in combination with the LbL method was investigated. A clay, Laponite, which is a synthetic layered silicate [$Na_{0.7}(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4$], was chosen. The dimensions of these nanoplatelet disks are ≈1 nm (thickness) × 30 nm (diameter).[48] In addition, it is negatively charged on the flat large surfaces and has localized positive charge where the crystal structure terminates at the edge of the disk.[48c] Exfoliated anionic zirconium phosphate sheets (dimensions 0.8 × 10−20 nm) were previously deposited in alternation with charged redox polymers onto high surface area silica particles.[49] In the current work, not only was the concept to coat PS spheres with Laponite nanoparticle multilayers of interest but it was also desired to examine whether hollow Laponite spheres could be produced upon removal of the core. Both TEM and SEM were used to characterize the formation of the core−shell particles and hollow spheres.

It is expected that the core−shell and hollow TiO_2 colloids produced may find application in the rapidly emerging area of photonic band gap crystals, while the hollow clay colloidal entities may be attractive as fillers or pigments.

Experimental Section

Materials. Anionic polystyrene particles with diameters of 640, 350, 270, and 210 nm, purchased from Microparticles GmbH, were used as templates. Poly(diallyldimethylammonium chloride) (PDADMAC), M_w < 200 000, poly(sodium 4-styrenesulfonate) (PSS), M_w 70 000, and poly(allylamine hydrochloride) (PAH), M_w 8 000−11 000, were obtained from Aldrich. All polyelectrolytes (PE) were used as received, except for PSS, which was dialyzed against Milli-Q water (M_w cutoff 14 000) and lyophilized before use. Sodium chloride (AR grade) was obtained from Merck. 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. A number of different titanium dioxide colloids were employed in this work. These included a milky white solution formed by the hydrothermal treatment of a titanium(IV) bis(ammonium lactato)dihydroxide solution.[50] The resulting negatively charged crystalline (anatase) TiO_2 nanoparticles, stabilized by lactate (ζ potential ca. −40 mV), were around 5 nm in diameter. A positively charged TiO_2 colloid (ζ potential +42 mV) was produced by ammonia hydrolysis of $TiCl_4$, followed by washing and redispersion upon the addition of nitric acid by ultrasonic treatment. These particles show crystallinity (anatase) and have a diameter of about 6 nm. A sol of a 1 wt % aqueous suspension of Degussa P25 (10−50-nm-diameter range, surface area of 50 $m^2\,g^{-1}$, crystal phase mainly anatase) was also used. SiO_2 particles (ζ potential ca. −35 mV) were obtained from Snowtex with quoted diameters in three ranges: 10−20 nm (40 wt % solution), 40−50 nm (20 wt %), and 70−100 nm (40 wt %). Laponite RD clay nanoplatelets

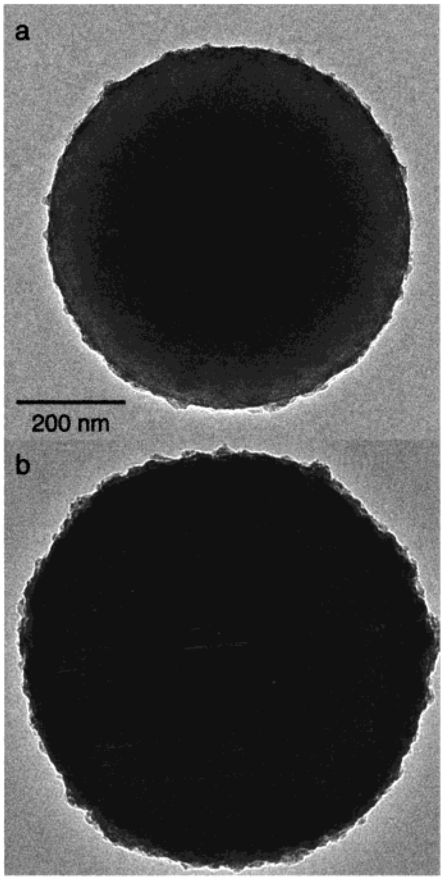

Figure 1. TEM images showing the increase in overall particle diameter and surface roughness after the deposition of (a) one and (b) four layers of hydrothermally produced TiO_2 nanoparticles (negatively charged) with three PE interlayers onto 640-nm PS spheres. (Bare PS spheres exhibit a smooth surface with no apparent surface roughness by TEM at the resolution of the images shown.) The scale bar corresponds to both images.

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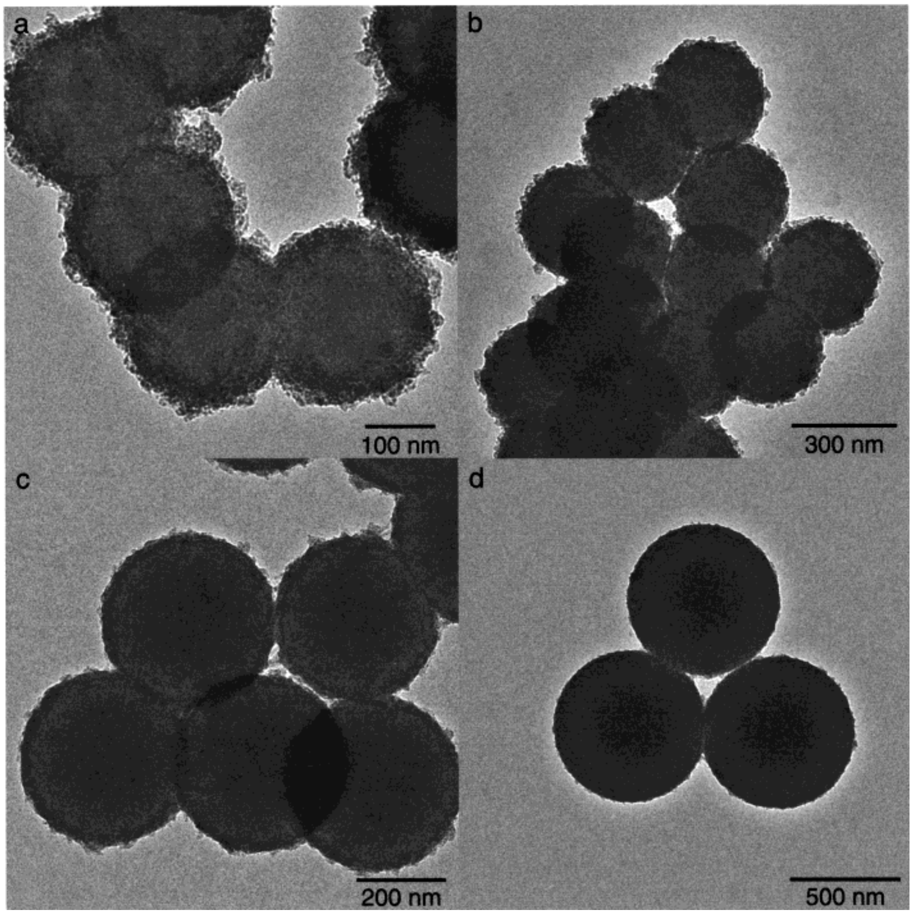

Figure 2. TEM images of core−shell particles consisting of (a) 210-, (b) 270-, (c) 350-, and (d) 640-nm-diameter core PS spheres coated with three TiO_2 nanoparticle (positively charged)/PE_3 multilayers.

were from Laporte Industries Limited, UK, and were used as received.

Core−Shell Particle Fabrication. *PS Particle Priming.* Before adsorption of the inorganic particles, the surface of the PS particles was modified by the adsorption of polyelectrolytes. The PS spheres were negatively charged, as were most of the nanoparticles under the conditions at which the experiments were conducted. Hence, a positively charged polymer (PDADMAC or PAH) was first deposited, followed by a negative polymer (PSS), and then PDADMAC (or PAH), a total of three PE layers, PE_3, yielding a positive particle surface.[13−15] Prior to deposition of positively charged nanoparticles, the polymer spheres were modified by adsorption of PDADMAC/PSS/PDADMAC/PSS, viz. PE_4, resulting in a negative surface charge for the template particles.[13−15] These initial polyelectrolyte layers have been found to produce a rather uniform and homogeneous surface for subsequent nanoparticle adsorption.[16,17] The procedure employed for the deposition of PE multilayers on the particles is as follows: 0.5 mL of PE solution (1 mg mL^{-1} in aqueous 0.5 M NaCl) was added to a solution of 0.2 mL of a 2.5 wt % latex solution dispersed in 0.3 mL of water. An adsorption time of 20 min was used before subjecting the particles to the cleaning procedure where a centrifugation (8000*g* for 10 min)/wash/redispersion (in water or 0.5 M NaCl) cycle was repeated three times after each layer was deposited. Following the final washing step, the particles were redispersed in 0.5 mL of water. This process was repeated until the desired number of polyelectrolyte layers was deposited.

Nanoparticle/PE Multilayer Formation. (a) TiO_2. TiO_2 sol (0.5 mL) was added to 0.5 mL of PE_3- or PE_4-precoated PS particles. After an adsorption time of 20 min for the nanoparticles, four centrifugation (8000*g*, 5 min)/wash/redispersion cycles were performed. (The washing procedure was sufficiently effective to remove the TiO_2 nanoparticles residing in solution.) Three PE layers were subsequently deposited to recharge the surface after nanoparticle deposition as this resulted in more uniform nanoparticle coverage. (For the positively charged TiO_2 nanoparticles, PSS/PDADMAC/PSS interlayers were used, while PDADMAC/PSS/PDADMAC layers were employed for the negatively charged TiO_2 nanoparticles.) Both the hydrothermally produced TiO_2 colloid and the positive TiO_2 nanoparticles were used for the formation of multilayers on the smaller PS diameter spheres (350, 270, and 210 nm). Higher centrifugation speeds, 10 000*g* for 10 min, were used for the separation cycles for the smaller particles.

(b) SiO_2. In all depositions a 2 wt % silica solution was used. Here, the larger SiO_2 particles (70−100 nm) were first adsorbed, followed by the 40−50-nm particles, and then the smaller particles (10−20 nm). An adsorption time of 15 min was used for the nanoparticle deposition.[16,17] A centrifugation speed of 4000*g* was required for 5 min to pellet the coated latex particles prior to the wash/redispersion cycles. A single PDADMAC interlayer was used with an adsorption time of 20 min, followed by washing and redispersion prior to adsorbing the next layer of smaller SiO_2 nanoparticles.

(c) Laponite. Mineral clay sols of 1 wt % were prepared by dispersing 10 mg of the sheetlike clay particles in 1 mL of water. PDADMAC was used as the polyelectrolyte interlayer during the coating. Adsorption times of 20 min were used, along with centrifugation (4000*g*, 10 min) wash/redispersion/cycles.

In all cases (i.e., for TiO_2, SiO_2, and Laponite nanoparticle/polyelectrolyte multilayers), polyelectrolyte formed the outermost layer of the coated particles.

Hollow Sphere Fabrication. Once the core−shell particles were analyzed and satisfactory coverage of the template was achieved, the samples were prepared for calcination at 500 °C. The samples were dried on glass slides and then heated under a ramp of 15 K min^{-1} to the maximum temperature under N_2. After 4 h under N_2 the gas was changed to O_2 and

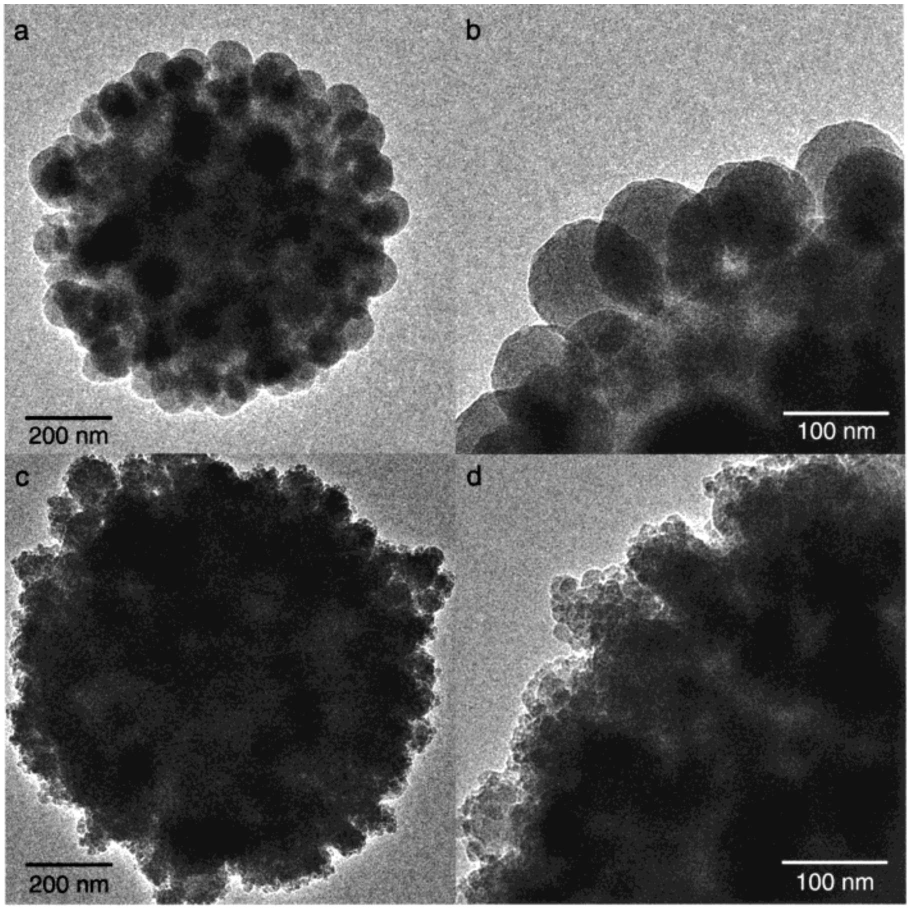

Figure 3. TEM micrographs of PS spheres (640 nm) with (a, b) a single layer of 70−100-nm SiO_2 nanoparticles and (c, d) after deposition of 40−50-nm SiO_2 nanoparticles and 10−20-nm SiO_2 nanoparticles. PDADMAC was the interlayer in all cases.

the sample heated for an additional 8 h at 500 °C. The sample was then cooled under a flow of O_2.

Characterization of Core−Shell Particles and Hollow Spheres. A Phillips CM12 transmission electron microscope (TEM) fitted with an energy-dispersive X-ray analyzer (EDAX) and a JEOL 6330F scanning electron microscope (SEM) allowed observation of the particles at the various stages of nanoparticle multilayer formation. For TEM measurements, the samples were prepared by deposition onto carbon-coated copper grids. Calcined samples were scraped from the glass surface with a sharp blade and dispersed in water before deposition onto the grids. Thin sections of the calcined samples were also prepared using a Leica ultracut UCT ultramicrotome after setting the samples in a LR-white resin. For SEM analysis the samples were dried on a glass slide, which was placed on a carbon-coated stub and then sputter-coated with Pd. Gas sorption measurements were conducted by using either a Micromeritics Gemini II 2375 surface area analyzer or a TriStar 3000 instrument.

Results and Discussion

This section has been separated into two parts. The first deals with the coating of PS spheres using the LbL method to produce core−shell particles comprising TiO_2, SiO_2, or Laponite nanoparticle/polyelectrolyte multilayers on PS spheres of various diameters. The second part centers on the hollow spheres produced after removal of the organic core and polyelectrolyte interlayers from the core−shell particles.

1. Core−Shell Particles. *TiO_2 Nanoparticle/PE_3 Multilayers.* Several TiO_2 nanoparticles (see Experimental Section) were examined for their suitability to coat PS spheres. Both negatively and positively charged TiO_2 particles were successfully deposited onto the colloidal cores. Figure 1 shows TEM images of the core−shell particles prepared after the deposition of one (a) and four (b) layers of the negatively charged hydrothermally produced 5-nm TiO_2 nanoparticles separated by PE_3 interlayers. (PE_3 interlayers have been previously shown to be more effective than a single polyelectrolyte interlayer in facilitating regular (iron oxide) nanoparticle deposition on particle surfaces.[31]) An increase in the overall diameter of the particles was observed as the number of multilayers deposited increased. An average diameter increment of 30 nm per TiO_2 nanoparticle/PE_3 multilayer was calculated, indicating that the equivalent of about 2−3 monolayers (on average) of TiO_2 nanoparticles is adsorbed with each deposition cycle. This may be a result of the formation of TiO_2 nanoparticle aggregates in solution that are subsequently adsorbed and/or due to nanoparticle aggregation on the surface of the spheres once adsorbed. There is also a roughening of the particle surface as a result of growth of the TiO_2 multilayers. Similar coatings were obtained with the positively charged TiO_2 nanoparticles, although a diameter increase of 10 nm per TiO_2/PE_3 multilayer was observed. (Examples of positive TiO_2 nanoparticle coatings on smaller PS particles are discussed below.) The overall diameter increase of the core−shell particles is dependent on the initial diameter of the nanoparticles used for coating, the type of nanoparticle (including their surface functionality), and any nanoparticle aggregation effects either prior to adsorption or on the surface of the template particles.

The larger TiO_2 sample, Degussa P25, did not result in uniform coatings because the TiO_2 suspension did not remain stable during the coating procedure. These TiO_2 nanoparticles severely aggregated in solution and therefore aggregates were deposited onto the surface of the PS spheres, which generally led to agglomeration of the coated particles. The addition of salt to the suspension from which adsorption proceeded did not reduce the degree of aggregation. (In our previous work, it was found that the presence of salt in the (SiO_2) nanoparticle solution was essential for the uniform coating of larger particle templates.[16]) Hence, the use of Degussa P25 for coating latex particles was not pursued further.

The ability to coat smaller template particles with TiO_2 nanoparticles by using the LbL technique was also investigated. Figure 2 shows (a) 210-, (b) 270-, (c) 350-, and (d) 640-nm-diameter PS templates coated with three TiO_2 nanoparticle (positively charged) layers interspersed with PE_3 multilayers. The TiO_2 nanoparticles can be seen around the PS spheres, causing a roughening of the surface. The layer thickness for the TiO_2 (25 ± 5 nm for three nanoparticle coatings) was the same, within experimental error, regardless of the diameter of the PS core template. This thickness corresponds to an average of about a monolayer of TiO_2 nanoparticles per deposition cycle. The smaller PS templates were also uniformly covered; however, some aggregation of the resulting core–shell entities was observed. This is most probably due to the experimental parameters used for separation of the unadsorbed TiO_2 nanoparticles in the centrifugation process; higher spin speeds were used for the smaller particles, leading to difficulties in redispersing at times. Optimization of the experimental parameters, for example, centrifugation speed and/or time, or use of filtration methods[27] to separate unadsorbed TiO_2 nanoparticles from the coated spheres, is expected to prevent aggregation and thereby produce well-dispersed smaller PS/TiO_2 core–shell particles. Nonetheless, the results obtained illustrate that smaller PS particles can be uniformly coated with TiO_2 nanoparticle multilayers.

The above data demonstrate that the LbL procedure is highly effective in producing multilayered TiO_2 nanoparticle coatings of defined thickness on particles of various diameters. A number of previous studies have also examined the coating of particles with titania, but mainly by hydrolysis of titania precursors rather than by the use of preformed nanoparticles.[38–45] For example, silica spheres have been coated with titania by the hydrolysis of a titanium alkoxide on silica spheres of 550-nm diameter, yielding a 46-nm-thick titania coating.[38] This titania thickness is substantially higher than that obtained in an earlier study by Hanprasopwattana (7-nm thick) by hydrolysis of a titania precursor in the presence of 270-nm silica spheres.[39] Large spherical alumina and zirconia particles (diameter 300–400 μm) have also been coated with 1–25-μm-thick amorphous titania or zirconia layers, which upon calcination produce highly crystalline phases of the oxides.[43] In that study, the hydrolysis step, including the water-to-alkoxide ratio and the addition of acid, led to some control of the coating thickness and the resulting coated particle morphology. In addition, titanium butoxide has been hydrolyzed onto copper(II) basic carbonate particles (average radius 780 nm) and zinc oxide (diameter 400 nm), resulting in titania-coated copper oxide composite particles[41] and zinc titanates[42] after calcination. In these studies, reaction conditions have to be carefully monitored to prevent aggregation of the coated particles and the production of second-phase TiO_2 particles that precipitate during the reaction. It has also been difficult to achieve control over the thickness of the TiO_2 coating by hydrolysis of the alkoxide precursors.

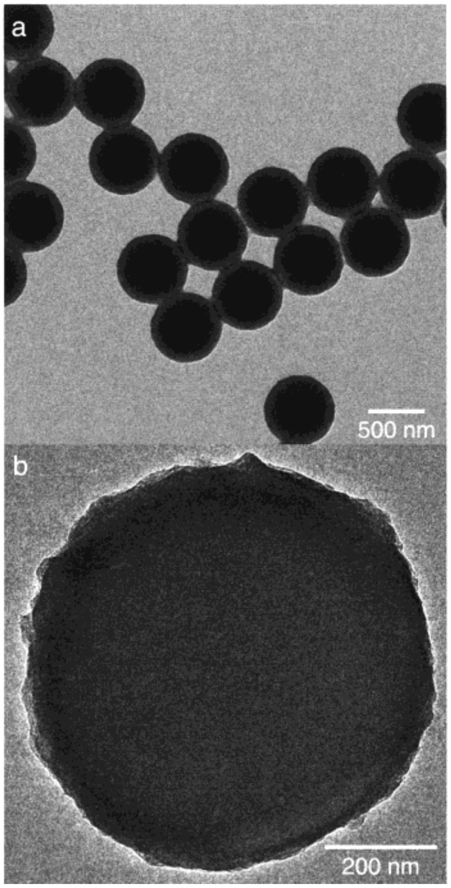

Figure 4. TEM images of (a) three Laponite nanoparticle/PDADMAC multilayers and (b) seven Laponite nanoparticle/PDADMAC multilayers deposited onto 640-nm-diameter PS spheres.

SiO_2 Nanoparticle/PE Multilayers. The ability to coat core particles with differently sized nanoparticles was examined as it was of interest to determine whether the larger particles would uniformly coat template cores of submicron-size dimensions, particularly when the coating particles are about one-fifth the diameter of the template. Previous work has focused on depositing nanoparticles of sizes <30 nm onto 640-nm-diameter cores (i.e., coating nanoparticle:core particle size of <1:20).[29] In addition, the deposition of smaller particles onto preadsorbed larger particles would potentially enhance both the surface area and overall density of the final material. For the example shown here, the larger diameter SiO_2 (70–100 nm) sample was deposited first onto 640-nm-diameter PS spheres, followed by 40–50-nm-diameter nanoparticles, and then the smallest SiO_2 nanoparticles (10–20 nm). The coating uniformity of the first SiO_2 nanoparticle layer on the 640-nm PS spheres is shown in Figure 3 (parts a and b). The large SiO_2 particles are well packed and from the higher magnification image (b) it is obvious that these particles are

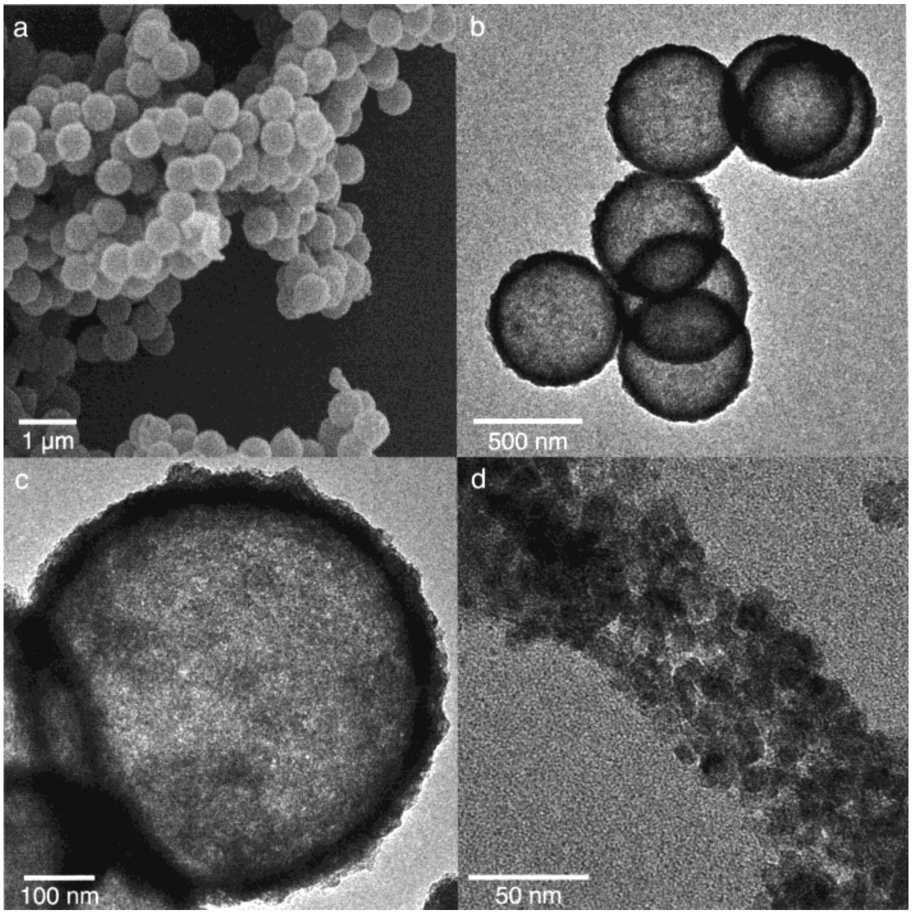

Figure 5. SEM (a) and TEM (b−d) micrographs of hollow TiO_2 spheres (composed of anatase crystals) produced after heating 640-nm-diameter PS spheres coated with four multilayers of the hydrothermally produced TiO_2 nanoparticles. Each TiO_2 nanoparticle layer is separated by three PE layers. Part (d) is a TEM image of a cross section of the walls of two contacting hollow spheres.

not of uniform size. The increase in diameter with the additional layers of medium and smaller sized SiO_2 particles can be seen in Figure 3c, where the smallest SiO_2 nanoparticles have coated the medium-sized SiO_2 nanoparticles. This can be seen more clearly in the higher magnification image (Figure 3d). It is interesting to observe how, in each case, the smaller SiO_2 nanoparticles have deposited in such a way to coat the larger SiO_2 particles. The use of more monodisperse nanoparticles could give interesting information on the particle packing and pore-filling capacity within these multilayers of differently sized nanoparticles. Furthermore, this procedure presents an attractive means to tailor the porosity of the shell layers, which is an important aspect of the hollow materials (see later).

Laponite Nanoparticle/PE Multilayers. Laponite, with its elongated disklike shape (1 × 30 nm), is an interesting nanoparticle for coating PS microspheres to study the influence of particle shape on coating uniformity. TEM images of the PS particles coated with Laponite nanoparticle/PDADMAC multilayers are shown in Figure 4; the surface of the coated PS particles with three and seven deposited layer pairs are shown in parts a and b, respectively. The coating thickness for the seven-layer sample is ≈50 nm, with the shell thickness of the Laponite sheets an intermediate of its dimensions. The clay nanoplatelet coating on the particle surface can be described as “a tiling of colloids” on the nanometer level. Drying effects appear to have resulted in “necking” between the surface of the core−shell particles (Figure 4a); “necking” was also seen between these coated particles and other surfaces on the TEM grids.

2. Hollow Spheres. After the production of the core−shell particles, the core template and the polymer interlayers were removed to produce hollow spheres of the inorganic material. In all cases discussed here the organic material was removed by heating[29,51,52] at elevated temperature (500 °C).

Hollow TiO_2 Spheres. Hollow TiO_2 spheres were obtained after a certain number of TiO_2 nanoparticle/PE_3 layers had been deposited on PS sphere templates and the core subsequently removed by calcination. With only one or two deposited TiO_2 nanoparticle layers, the spherical shape of the initial template particle was not retained upon removal of the core: SEM (images not shown) revealed that collapse of the TiO_2 shell occurred after heating PS particles coated with a single TiO_2 nanoparticle layer, while some distortion and collapse resulted for particles coated with two TiO_2 nanoparticle layers. With a coating comprising three layers of TiO_2 nanoparticles on PS spheres, hollow spheres were obtained upon heating, along with some distorted (elongated) hollow entities; collapse was no longer

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observed. Similar results were previously obtained during the production of hollow SiO_2 spheres, using SiO_2 particles with a diameter of 30 nm deposited onto 640-nm particle templates.[29] In that work, two or more layers of SiO_2 nanoparticles were required for the resulting inorganic hollow material to retain the spherical shape of the template.

Figure 5 shows electron microscopy images of the hollow TiO_2 spheres obtained after heating PS particles coated with four TiO_2 nanoparticle (negatively charged) layers. From the images, it can be seen that complete, hollow spheres are obtained. The SEM micrograph (Figure 5a) shows that the spheres remain spherical and intact after calcination. The cross-sectional image (Figure 5d) verifies the hollow nature of the TiO_2 spheres. In addition, SEM images of deliberately broken spheres also proved that they were hollow (data not shown). The individual particles making up the wall structure can be seen in the ultramicrotomed sample (Figure 5d, which shows an area of contact between two sphere walls). HRTEM revealed the crystal phase of the final hollow TiO_2 material to be anatase. There is an overall shrinkage of about 20% in size for the hollow spheres, compared with the initial core−shell particles. The successful production of these hollow spheres confirms the high uniformity of the TiO_2 coating on the particle templates afforded by the LbL procedure. It is emphasized that a prime requirement for the formation of such inorganic hollow spheres using this strategy is that a relatively close and uniform packing of the inorganic nanoparticles is obtained on the core template. Upon removal of the core by calcination, the neighboring nanoparticles sinter, thereby conferring structural stability to the hollow spheres.

N_2 sorption experiments on hollow TiO_2 spheres resulting from calcination of PS particles coated with four layers of the positively charged, 6-nm, TiO_2 nanoparticles (alternating with PE_3 multilayers) were conducted. The specific surface area (SA) from BET analysis of these hollow spheres is 87 $m^2\ g^{-1}$, compared to 12.5 $m^2\ g^{-1}$ for the core−shell particles (i.e., before calcination). Assuming the initial TiO_2 particle diameter to be 6 nm and monolayer coverage with each deposition, a calculated surface area of around 250 $m^2\ g^{-1}$ would be expected for the calcined particles. The measured SA of the calcined sample is significantly lower than that calculated. Bridging (as a result of sintering) between neighboring nanoparticles forming the hollow spheres and the possibility of crystal growth would decrease the surface area; neither of these factors was taken into account in the calculations.

Hollow TiO_2 spheres resulting from calcination of PS particles coated with three TiO_2 nanoparticle (positively charged)/PE_3 multilayers can be seen in Figure 6. The first two parts of the figure show the spheres obtained after heating 350-nm PS particles. Similar to the larger templates, a shrinkage of 15% was observed. In Figure 6c, smaller hollow TiO_2 spheres can be seen; these are the final products after heating of 210-nm PS spheres coated with three positively charged TiO_2 nanoparticle/PE_3 multilayers. The average final diameter of these spheres is 195 nm, which again represents about 15% shrinkage as a result of the template removal process. In summary, TiO_2 hollow spheres of different diameters have been readily produced by using the LbL approach applied to colloidal particles coupled with subsequent removal of the templated core.

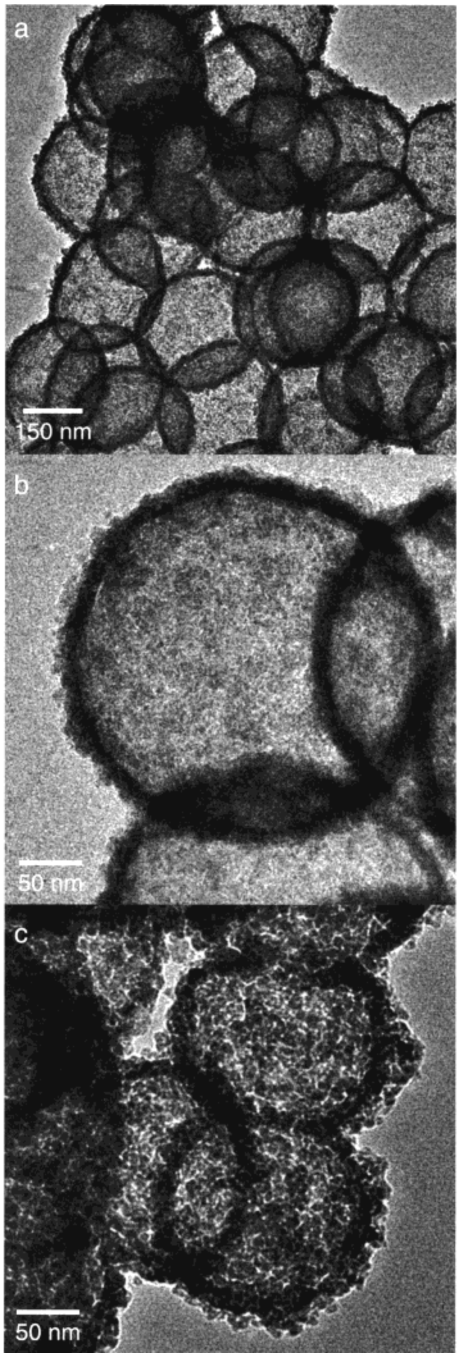

Figure 6. TEM images of hollow TiO_2 spheres (composed of anatase crystals) formed after heating PS spheres coated with three TiO_2 nanoparticle (positively charged)/PE_3 multilayers. (a, b) 350-nm-diameter PS spheres; (c) 210-nm-diameter PS spheres.

Hollow SiO_2 Spheres. In our earlier work,[29] we showed that hollow silica spheres could be produced by coating PS microspheres with uniformly sized SiO_2 nanoparticles and then removing the core by heating. The high temperatures induced sintering of the SiO_2 nanoparticles comprising the hollow spheres. Here, we explored the possibility to fabricate hollow silica spheres formed from differently sized SiO_2 nanoparticles. The images in Figure 7 display the hollow SiO_2 spheres resulting after calcination of the PS-core/SiO_2 nanopar-

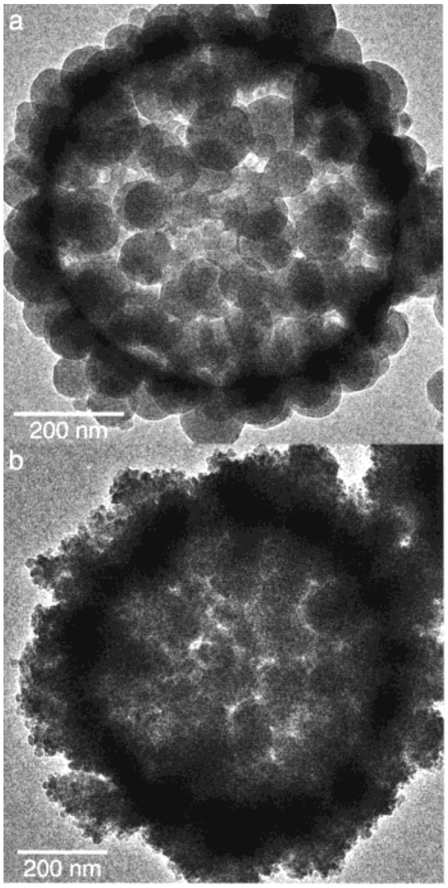

Figure 7. TEM micrographs of hollow SiO_2 spheres formed by calcination of 640-nm PS spheres coated with SiO_2 nanoparticles of various sizes (as shown in Figure 3): (a) a single layer of large SiO_2 nanoparticles and (b) three layers containing large, medium, and then small SiO_2 nanoparticles. The interlayer used was PDADMAC.

ticle–shell spheres. Figure 7a shows that the template sphericity is retained even when the core is removed from PS spheres coated with a single layer of 70–100-nm-diameter coating particles. Large pores between the SiO_2 nanoparticles making up the hollow spheres can also be seen. For hollow silica spheres comprised of layers of three differently sized nanoparticles (large, medium, and small), it is seen that the smaller particles fill the pores (to some degree) created by the packing of the larger particles as well as coat the larger SiO_2 particles (Figure 7b). This strategy provides a straightforward means to create inorganic spheres with controlled porosity.

From these results and those obtained earlier the relationship between the nanoparticle diameter and the number of particle multilayers required to produce hollow spheres can be established. For larger particles (≈100 nm), coating PS spheres of about 600 nm in diameter with a single layer is sufficient. For nanoparticles of silica with a diameter of 30 nm, two or more layers were required,[29] and for TiO_2 nanoparticles of diameter <5 nm, more than three TiO_2 nanoparticle layers were required to obtain spherically intact hollow inorganic spheres upon removal of the template. Hence, it can be deduced that decreasing the size of the nanoparticles used for coating, while keeping the template diameter uniform, requires the deposition of a greater number of nanoparticle layers for the inorganic hollow entity to retain the template shape after calcination.

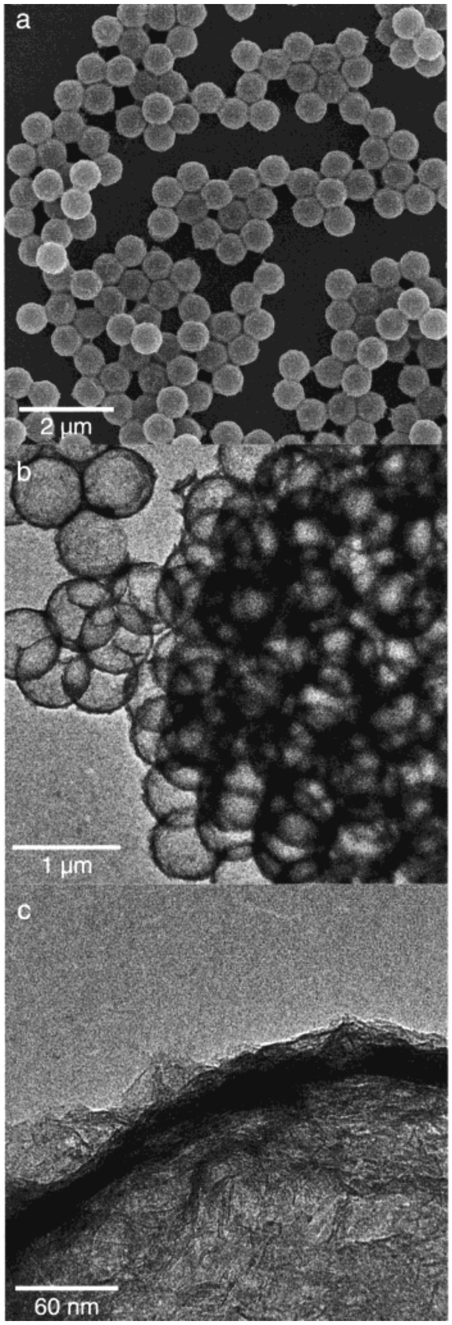

Figure 8. SEM (a) and TEM (b, c) images of hollow Laponite spheres obtained after calcination of PS spheres (640 nm) coated with five Laponite nanoparticle/PDADMAC multilayers.

Hollow Laponite Spheres. After removal of the template from Laponite multilayer-coated PS spheres, hollow Laponite spheres were obtained. Such hollow spheres resulting from PS cores coated with five Laponite multilayers are displayed in Figure 8. The SEM image (Figure 8a) shows that the hollow spheres remain intact and preserve the three-dimensional spherical nature of the template particles. TEM suggests that the spheres are hollow (compare Figure 8b,c with Figure 4); this was confirmed by SEM measurements of purposely broken spheres. Figure 8c shows a higher magnification of Laponite nanoparticles comprising the hollow spheres. The reason for preservation of the template shape and structural integrity can be attributed to the cross-linking of adjacent Laponite nanoparticles as a result of calcination because the surface of the Laponite has silica-type properties. The above result demonstrates the ability to use differently shaped nanoparticles in the LbL self-assembly process on colloidal templates to produce hollow spherical entities of clay. Such hollow clay spheres may find applications as new fillers with unique chemical and mechanical properties. Furthermore, the use of clay platelets in the process may provide a simple means to produce inorganic hollow spheres with highly reduced permeability characteristics. Related work involves the formation of hollow, thin-walled (1.5-nm) clay/silica shells of about 300-nm diameter, which were produced by coating poly(methyl methacrylate) (PMMA) latex with a layered magnesia-silicate clay, subsequently sealing the clay platelets by condensation of tetramethylorthosilane, and finally removing the core of PMMA by depolymerization using electron degradation.[53] The advantage of the LbL strategy is the ability to tailor the wall thickness and composition simply by the electrostatic self-assembly of charged species.[9]

Conclusions

Composite particles comprising a PS core and well-defined TiO_2, SiO_2, or Laponite nanoparticle/PE multilayers have been successfully fabricated by using the LbL approach. Nanoparticles of different diameters have been shown to work effectively in the coating process, as have sheetlike clay particles. TiO_2 hollow spheres with diameters ranging from about 200 to 600 nm have been produced by calcination of the PS−TiO_2 core−shell entities. In a similar way, SiO_2 hollow spheres comprised of differently sized nanoparticles as well as Laponite hollow spheres were also prepared (from their respective core−shell particles), further demonstrating the versatility and general nature of the strategy employed. By adapting the procedure to other inorganic materials,[54] it should be possible to create an even larger range of composite colloidal entities with enhanced and tailored properties. Experiments with other metal oxides as well as metal nanoparticles are currently underway, as are studies on the packing of the core−shell and hollow materials to form colloidal crystals. Furthermore, the use of a titanium dioxide precursor deposited between polyelectrolytes has also been studied, providing a novel approach from which hollow TiO_2 spheres could be fabricated. This will be reported in a separate publication.

Acknowledgment. Rona Pitschke (MPI) is thanked for ultramicrotoming of samples, Michael Giersig (Hahn-Meitner-Institute, Berlin) for access to HRTEM, and Manfred Pinnow (Fraunhofer Institute for Applied Polymer Research, Golm) for assistance with SEM. The authors thank Hermann Möckel (Hahn-Meitner-Institute, Berlin) for the hydrothermally produced TiO_2 sol, Natasha Shkorik (Institute of General and Inorganic Chemistry of the National Academy of Science, Belarus) for preparing the positively charged TiO_2 sol, Degussa for supplying the P25 sample, and Bernd Struth (ESRF, Grenoble) for the Laponite. This work was supported by The German Federal Ministry of Education, Science, Research and Technology and the Volkswagen Foundation.

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