Preparation and Characterization of Titania-Coated Polystyrene Spheres and Hollow Titania Shells

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A procedure has been developed to coat colloidal polystyrene spheres with a smooth and well-defined layer of amorphous titanium dioxide. The thickness of the coating can be easily varied from a few nanometers upward and can be increased further by seeded growth. The resulting composite particles are very monodisperse. The core–shell particles can be turned into spherical hollow titania shells by dissolution of the polystyrene cores in suspension or by calcination of the dried particles in a furnace. Calcination also crystallizes the titania into its anatase form. The coated particles were characterized with electrophoresis, thermogravimetric analysis, X-ray diffraction, electron microscopy, and light scattering. We find that the coating strongly densifies when the particles are dried but that it is not dense and about twice as thick when the particles are still in suspension. Calcination results in spherical shells composed of a dense arrangement of TiO_2 (anatase) nanocrystals. This way, we obtained colloidal crystals consisting of hollow shells.

1. Introduction

Coating of colloidal particles with a layer of a different material is used as a means to modify their surface chemical,[1] reactive,[2] catalytic,[3] optical,[4–6] or magnetic properties.[7,8] Such core–shell particles can often be prepared by controlled precipitation of inorganic precursors onto the core particles, in some cases assisted by a coupling agent as with the combination silica and gold or silver.[2,4,5] A second approach is to deposit small particles of the coating material on the cores by heterocoagulation, such as in the case of yttrium basic carbonate or zirconia on polystyrene.[9,10] An especially versatile example of the second approach is the layer-by-layer technique, in which successive layers of anionic particles are deposited, alternated by layers of a cationic polymer.[8,11] The layer-by-layer technique has the great advantage that it is not very specific for the coating material, where other methods usually depend on the particular combination of core and shell material. Disadvantages are that the layers are added in discrete steps of about 30 nm and that a lot of redundant polymer is also incorporated in the shell.

Hollow particles form a special kind of core–shell particle in which the core consists of air or solvent. Hollow inorganic particles are made by removal of the core with a solvent or by heating (calcination). Removal of polystyrene cores by calcination has been used to make hollow spheres of yttrium compounds,[9] zirconia,[10] and silica.[12,13] Holow silica particles have been made by dissolution of silver and gold[2] or zinc sulfide.[14] Colloidal crystals of particles with a low-index core and a high-index shell such as titania are suitable building blocks for photonic crystals, provided that they can be made monodisperse with a smooth coating.[15–17]

Particles coated with titania are generally exceptionally difficult to synthesize because the titania precursors are highly reactive, making it difficult to control their precipitation. This easily causes the core particles to aggregate or the titania to form separate particles. Titania-coated particles are very useful as catalysts[3,18–21] and as white pigments.[6,22,23] Titanyl sulfate in sulfuric acid was used to deposit titania on silica spheres.[22] Rather irregular coatings were obtained. The slightly low isoelectric point indicated that the coverage was incomplete. This was also found to be the case by using $TiCl_4$ to coat silica.[19] Other methods use the hydrolysis of titanium alkoxides in nonaqueous solvents as the precursor. Only a monolayer of titania was deposited on silica spheres in tetrahydrofuran.[18] Using a similar approach, thicker coatings can be deposited on copper compounds,[23] zinc oxide,[6] silica,[3,20] and gold nanoparticles.[21] These methods lead to particles

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with a complete coating but with a lot of surface roughness. They also take place at a rather low concentration of the alkoxide, typically around 0.01 M. This concentration needs to be well controlled because too high concentrations easily lead to particle aggregation or formation of secondary titania particles.[20] This is why multiple steps are often used to obtain thicker coatings.

In this work we present a one-step method to coat cationic polystyrene spheres with titania precipitated during the hydrolysis of a titanium alkoxide. Although this is an example of coating by heterocoagulation, it leads to unusually smooth and uniform titania shells that can be made as thin as a few nanometers. This is attributed to a very rapid collection of the negatively charged titania oligomers by the positively charged surfaces. These particles can further be turned into hollow shells both by calcination and by dissolution of the core. Apart from the usual characterization techniques, such as electron microscopy, electrophoresis, and thermogravimetric analysis, we also investigated the coated particles with angle-resolved light scattering. This provides information about the coating while the particles are still in suspension. It is thus demonstrated that the coating is much less dense while the particles remain in suspension than after they have been dried.

2. Experimental Section

Cationic Polystyrene Spheres. The preparation of cationic polystyrene cores was accomplished by surfactant-free emulsion polymerization using the cationic initiator azodiisobutyramidine dihydrochloride (AIBA, Aldrich), as described by Goodwin et al.[24] Monodisperse spheres of 378 nm diameter were obtained using 475 mL of deionized water, 25 mL of styrene (Aldrich), and 0.359 g of AIBA at 70 °C. After 24 h a conversion of 88% was found by drying of a sample. After this the suspension was dialyzed against deionized water in cellulose membrane tubing (Spectrapore), which was placed in a polypropylene bottle. The latex became iridescent within the hour. The solvent was changed to ethanol by repeated centrifugation and redispersal. This should limit the suspected slow hydrolysis of the surface amidine groups.[24] The suspension was stored in a polypropylene bottle and kept in a refrigerator.

Polystyrene Spheres Coated with Titania. The coating reaction is done in ethanol at room temperature by hydrolyzing titanium tetraisopropoxide (TTIP, Aldrich) in the presence of cationic polystyrene spheres. The hydrolysis is very fast. To ensure the formation of a smooth coating and to prevent the formation of secondary titania particles, the hydrolyzed titania species must be captured rapidly by the polystyrene particles. At the neutral pH used these titania species have a slight negative charge (the isoelectric point of titania is ~5). The positive charge on the spheres thus ensures a rapid capture of the titania species. During the reaction the charge on the particles reverses from positive to negative. Preliminary experiments showed that although the reaction is completed very quickly (1 or 2 min), there is still significant aggregation of the cores. It was found, however, that the particles can be stabilized during charge reversal by the addition of about 1% of poly(vinylpyrrolidone) (PVP, molecular weight 360 000, Aldrich), which adsorbs on both polystyrene[25] and titania.[26] Preliminary experiments also showed that addition of ~0.1 mM NaCl widens the concentration ranges in which unaggregated particles are obtained without formation of secondary titania particles.

Several series of coating reactions in which one of the reactant concentrations was varied were done on a scale of 5 mL in glass vials in order to establish the concentration ranges in which

unaggregated coated particles are formed without the formation of any secondary titania particles.

A typical coating reaction on a larger scale was as follows: 400 mL of absolute ethanol was placed in a plastic bottle. 4.0 g of PVP and 10 mL of an aqueous 5 mM NaCl solution were added. Then 31 mL of the latex containing 96 mg/mL of cationic polystyrene in ethanol was added. Finally, a solution of 4.5 mL of TTIP in 60 mL of ethanol was rapidly mixed in under vigorous stirring. After a minute the magnetic stir bar was stopped, and the suspension was allowed to stand for 15 min. If a thicker coating was desired, subsequent additions of TTIP were made (seeded growth). The particles were then centrifuged and redispersed in ethanol several times to remove PVP, which is no longer necessary for stabilization. Transmission electron microscopy showed unaggregated spheres with a titania coating of 13 nm.

Hollow Titania Spheres by Dissolution of the Polystyrene Cores. The polystyrene cores were removed by adding an amount of titania-coated spheres in ethanol to an excess of toluene. After a few hours the particles were centrifuged at 1500 rpm for 15 min and resuspended in toluene. This step was repeated once more. Somewhat surprisingly, the particles formed a stable suspension in this apolar solvent. Finally, the particles were transferred to ethanol again by two more centrifugation/redispersal steps.

Hollow Titania Spheres by Calcination. The polystyrene cores could also be removed by calcination in a furnace. First, a drop of suspension in ethanol was placed on a glass slide and dried, first at room temperature and then for 1 h at 60 °C. It was then placed in furnace heated to 600 °C in air at a heating rate of 5 °C/min. After 3 h it was cooled to room temperature at a rate of 10 °C/min.

Characterization. The morphology of the particles was examined with a JEOL 2000FX transmission electron microscope (TEM) with an accelerating voltage of 200 kV. Samples were prepared on carbon-coated grids. A JEOL 6300F scanning electron microscope (SEM) was used at a voltage of 5 kV on samples coated with about 5 nm of Au.

The processes taking place during calcination were studied by thermogravimetric analysis (TGA) on a Mettler TA3000 on samples dried at 60 °C. The heating rate was 20 °C/min. Infrared spectra were taken on a Perkin-Elmer RX1 FTIR spectrophotometer of samples dried at 125 °C and pressed into KBr pellets. X-ray powder diffraction (Philips X′pert-MPD) was used to determine the crystalline phase of the titania. Electrophoretic mobility measurements were done on a Zeta-Meter 3.0 with dilute suspensions in water with a background electrolyte of 0.001 M NaCl. The pH was adjusted to about 3 by adding some hydrochloric acid and then increased in steps by additions of NaOH.

Static light scattering was used to measure particle sizes and coating thicknesses. A very dilute suspension of test particles in ethanol thermostated at 25.0 °C was illuminated by a He−Ne laser beam (632.8 nm). The angular distribution of scattered light was measured at scattering angles from 20° to 150° relative to the transmitted beam with a photomultiplier tube mounted on a goniometer turntable. Scattered intensities were plotted vs the scattering wave vector K

$$K = \frac{4\pi n}{\lambda} \sin(\theta/2) \qquad (1)$$

where n is the refractive index of the suspending liquid, λ the wavelength of the light in a vacuum, and θ the scattering angle. The background scattering due to the solvent was subtracted. These data were then compared to theoretical curves calculated for coated spheres[27] to obtain the thickness and refractive index of the coating.
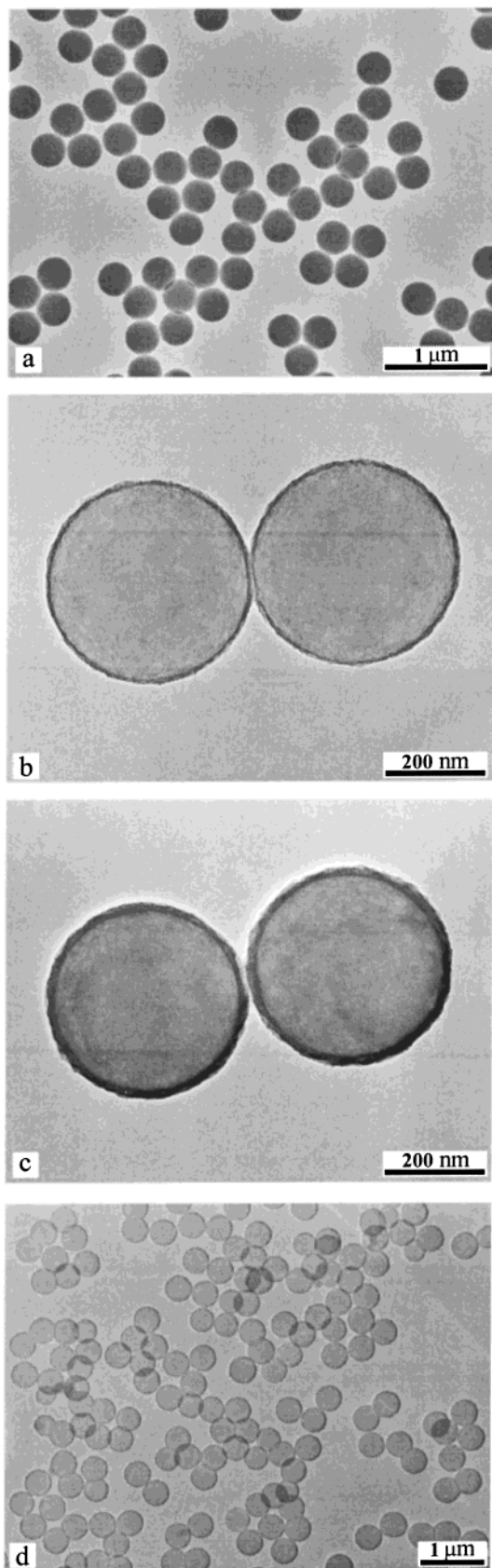
3. Results and Discussion

Polystyrene Spheres Coated with Titania. Transmission electron micrographs (TEM) of the polystyrene

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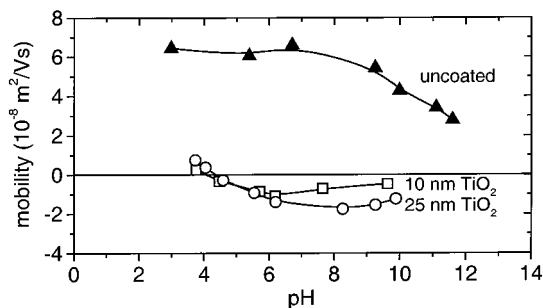(25) Smith, S. N.; Meadows, J.; Williams, P. A. *Langmuir* **1996**, *12*, 3773.

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Figure 2. Electrophoretic mobilities of (a) the polystyrene cores, (b) polystyrene coated with 10 nm of titania, and (c) polystyrene coated with 25 nm of titania (as measured with TEM).

Table 1. Variation of the Titania Shell Thickness by Changing the Concentration of Polystyrene Spheres[a]
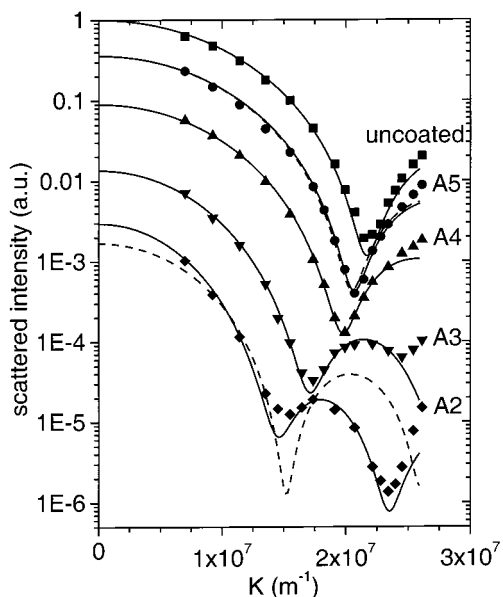
sample	[polystyrene] (mg/mL)	d_{shell} (dry) (nm)	d_{shell} (wet) (nm)	remarks
A1	0.84	55	120	many TiO_2 particles
A2	1.68	53	120	some TiO_2 particles
A3	3.36	32	72	stable
A4	6.72	18	30	stable
A5	13.4	7	16	stable

[a] Other concentrations used in these preparations were [TTIP] = 0.033 M, [H_2O] = 1.1 M, [NaCl] = 1.0×10^{-4} M, and [PVP] = 0.76 wt %. Shell thicknesses were determined in their dried state by TEM and in suspension by SLS.

due to the cationic initiator. The electrophoretic mobility measurements in Figure 2 gave a ζ-potential of +82 mV at a neutral pH and below. The isoelectric point is above 12. These results are very similar to those found by Goodwin et al.[24] They also noted that measurements at higher pH are complicated by contamination of the particle surfaces by silicate species dissolved from the glass surface of the electrophoresis cell.

From several series of coating reactions on a small scale the concentration ranges were found in which unaggregated coated particles are formed without the formation of any secondary titania particles. The concentrations used in one such series are shown in Table 1. The PVP concentration did not appear to be very critical. The water concentration had to be between 0.5 and 1.5 M; aggregation will occur both above and below this range. The useful concentration ranges of TTIP and polystyrene core particles were related to each other such that the maximum coating thickness that could be achieved in one step was ~50 nm (measured by electron microscopy). When thicker coatings were tried, nucleation of secondary titania particles would always occur, although the polystyrene spheres would still carry a smooth coating. Apparently, the particles then become unable to collect the rapidly forming titania quickly enough. Raising the TTIP and PS concentrations in constant proportion led to aggregation when the TTIP concentration was raised above 0.1 M.

Figure 1 shows TEM pictures of some titania-coated polystyrene spheres. The coated spheres are as monodisperse as the original polystyrene particles. It is immediately evident that the titania coating on the polystyrene spheres is very smooth and uniform. This suggests that deposition of titania onto the particle surfaces occurs in the form of oligomers or very small particles. Very thin coatings of a few nanometers are possible, which are still smooth and cover the whole sphere surface (see Figure 1b). The thickness of the coating is easily varied by changing the ratio of TTIP to polystyrene.

Figure 1. Transmission electron micrographs of (a) the polystyrene spheres used as the core and (b) the same particles coated with 7, (c) 25, and (d) 32 nm of titania.

core particles are shown in Figure 1a. The particles have a diameter of 378 nm and a polydispersity of 2.5% (standard deviation of the size distribution divided by the mean). They carry a positive surface charge that is entirely

Figure 3. Scattered intensity as a function of scattering wave vector measured on titania-coated polystyrene spheres. Curves have been offset for clarity. Uncoated polystyrene is shown by the squares; other data sets are labeled as in Table 1. The full curves are calculated with Mie theory taking a single refractive index for the coating in all curves simultaneously, giving a best fit of 1.53. The fitted coating thicknesses are then much larger than is observed with TEM. The two dashed curves are calculated by taking the coating thickness from TEM and then fitting the refractive index. This procedure gives an index of 1.75 but completely fails to describe the data sets with two minima.

Since there appears to be a maximum coating thickness of 50 nm that can be made in one step without a secondary nucleation, thicker coatings should be made through several additions of TTIP. Such seeded growth is indeed possible, but we have not yet systematically explored this for larger thicknesses.

The electrophoretic mobility of the coated particles is negative at the neutral pH at which they are synthesized (Figure 2), showing that a layer of titania is indeed present. Particles coated with 10 nm of titania had a ζ-potential of -14 mV, and particles with a 25 nm coating had a ζ-potential of -20 mV. The isoelectric point is 4.5, in agreement with previous determinations of amorphous titania colloids,[22,28] showing that the particles have been completely coated. At high pH the mobility tends to decrease somewhat, perhaps due to dissolution of the titania coating.

Static light scattering (SLS) measurements were performed to characterize the coating of the particles while in solution (see Figure 3). The coated spheres in this figure were all prepared at the same concentrations of water and TTIP. Only the concentration of polystyrene cores was increased, resulting in a decreasing coating thicknesses. Details of the synthesis and the coating thicknesses found with TEM are shown in Table 1. Because of the monodispersity of the spheres, their scattering curves exhibited one or two pronounced minima. The locations of these minima make possible a detailed comparison with theory, which allows us to obtain the thickness (d_{shell}) and the refractive index (n_{shell}) of the coating, as follows.

The upper curve in Figure 3 is that of the uncoated polystyrene. The data can be fitted very well with Mie theory,[27] taking the well-known value of $n_{core} = 1.59$ for

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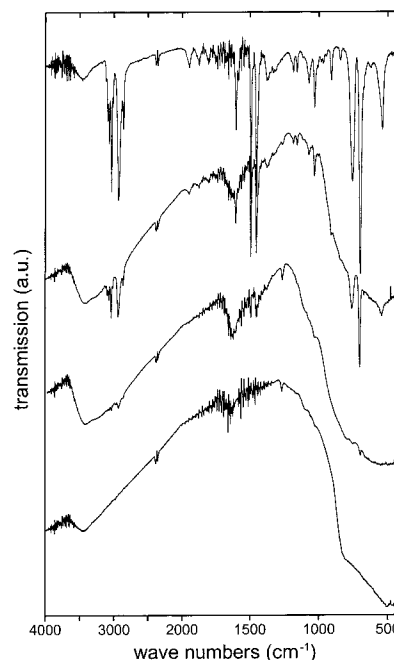
Figure 4. Infrared spectra (FTIR). The characteristic bands of the polystyrene latex (upper spectrum) are clearly seen in the titania-coated spheres (second spectrum from top). After dissolution of the cores in toluene only the strongest bands remain barely visible (third spectrum from top), indicating that only a trace of polystyrene is left. Calcination at 600 °C leaves no trace of polystyrene at all (lower spectrum). Above 2000 cm^{-1} the spectra have been compressed by a factor of 2.

the index of refraction of polystyrene and a polydispersity of 2.5%. A core diameter of $d_{core} = 378$ nm is found from the fit. Only at very large scattering angles (large K) are the measurements slightly too high due to stray light close to the backward direction. Placing a coating on the spheres causes the minimum to shift inward and a secondary minimum to appear for thick coatings. These measurements were fitted to the theory using the same parameters for the core. For curves with a single minimum it was possible to find a good fit for almost any n_{shell}, each leading to a different d_{shell}. Adopting the d_{shell} from TEM, a value $n_{shell} = 1.75$ was found (upper dashed curve in Figure 3). However, this refractive index will not at all fit the two lower data sets in Figure 3 (lower dashed curve), which have two minima. The latter curves can only be fitted with a surprisingly low $n_{shell} = 1.53 \pm 0.03$, giving for d_{shell} about double the value measured with TEM.

We are thus led to the conclusion that the titania coating is far from compact when the particles are still in suspension. If the particles are dried, however, the coating dries up against the polystyrene and densifies, producing the much smaller thicknesses seen in the TEM photos. More evidence for this picture will come later from samples from which the cores have been dissolved.

Hollow Titania Shells by Dissolution of the Polystyrene Cores. It was found that the polystyrene core could be removed by suspending the coated particles in toluene and going through two centrifugation/redispersion cycles. Toluene is a good solvent for polystyrene, so most of the polystyrene is expected to go into solution. Somewhat surprisingly, the titania-coated spheres formed a stable suspension in toluene; no aggregation of particles was ever observed. Titania is hydrophilic and does not by itself form a stable colloid in an apolar solvent like toluene. It is therefore likely that some of the dissolving polystyrene adsorbs onto the outer surfaces of the particles, sterically
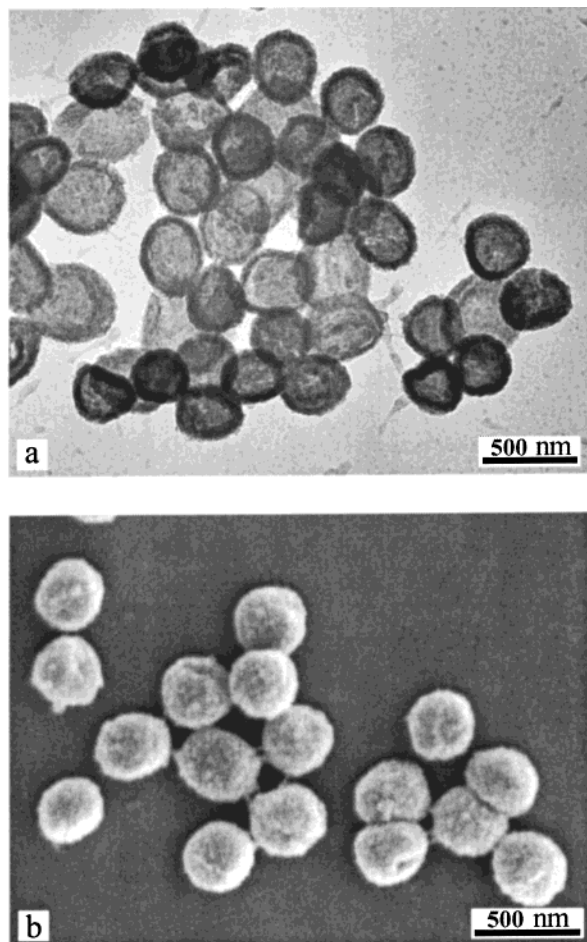
Figure 5. (a) TEM and (b) SEM of titania shells obtained after removal of the polystyrene cores with toluene. The original core−shell particles of this sample are shown in Figure 1c.

stabilizing them. After dissolution of the cores the particles were transferred back to ethanol for characterization.

To verify the removal of the polystyrene, FTIR spectra of the titania-coated spheres and the toluene-treated spheres were measured (see Figure 4). The characteristic bands of polystyrene are clearly observed in the titania-coated sphere sample: C−H stretch around 3000 cm^{-1}, aromatic C−C stretch around 1470 cm^{-1}, C−H out-of-plane bend at 765 cm^{-1}, and aromatic C−C out-of-plane bend at 700 cm^{-1}. Aromatic overtones are visible in the range 1700−2000 cm^{-1}. These bands have almost disappeared in the toluene-treated sample, showing that most of the polystyrene was removed in the process. The small remaining trace of polystyrene may be the cause of the stability of the shells in toluene.

Figure 5 shows TEM and SEM pictures of the shells. Figure 1c is a TEM picture of these same particles before dissolution of their core. It is clear that the loss of their core causes the particles to deform, and they appear much more polydisperse. Also, the inside diameter of the shells has shrunk to 270 nm, and the shell is thicker (about 50 nm) and much less smooth. From light scattering we obtain evidence that this shrinkage, and deformation has not yet occurred when the shells are in suspension. The SLS data are shown in Figure 6. It is evident that the shells have two deep scattering minima in the measurable range. Deep minima only occur when particles are not only monodisperse but also spherical: for nonspherical particles the average over all orientations, each with a minimum at a different scattering vector, will average the minima away. The two data sets can be brought into
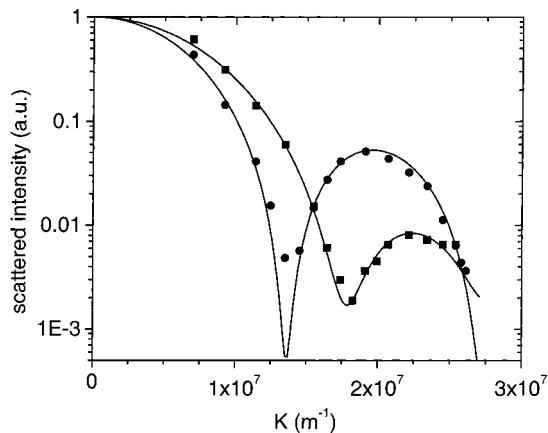

Figure 6. Scattered intensity as a function of scattering wave vector measured on titania-coated polystyrene spheres (squares, sample of Figure 1c) and on the same particles after removal of the polystyrene with toluene (circles, sample of Figure 5). The full curves are theoretical calculations using a 60 nm thick coating with a refractive index of 1.53 sitting on a 378 nm diameter core consisting of polystyrene or ethanol (the solvent), respectively. The agreement with the data shows that the hollow shells are spherical when in suspension and only deform and shrink when dried.

excellent agreement with scattering theory using only a single set of parameters: $d_{core} = 378$ nm, $d_{shell} = 60$ nm, $n_{shell} = 1.53$. For the cores we took $n_{core} = 1.59$ for coated polystyrene and 1.36 for hollow, ethanol-filled particles. Note that the low value of n_{shell} is the same as for the data in Figure 3, producing more evidence that the titania shells in suspension are relatively thick and not very dense.

From this we conclude that the hollow titania shells are spherical when in suspension and that they shrink and deform when dried (to make electron microscopy samples). The dried empty shells, however, still appear much thicker than dried shells sitting around polystyrene spheres. Apparently, to densify the titania needs a solid substrate such as polystyrene to dry up against.

Hollow Titania Spheres by Calcination. The polystyrene cores can also be removed by calcination of the coated particles in air at elevated temperatures. After this treatment no trace of polystyrene can be seen in the infrared spectrum (Figure 4). Figure 7a shows an SEM picture of a crystal of titania shells. It was prepared by drying a drop of coated-sphere suspension on a glass slide before calcination. The evolution of gases during calcination has caused some damage to the shells, though not excessive. We have not yet optimized the heating conditions that could prevent this damage. A close-up of the shells with TEM (Figure 7b) shows that the shells actually consist of small crystallites, roughly 30 nm in size. X-ray powder diffraction (Figure 8) showed that the crystallites are mostly anatase but that ∼10% of rutile was present. Before calcination X-ray diffraction showed that the titania was amorphous. Calcination has also caused some shrinkage; the shells in Figure 7 have an inside diameter of 260 nm and a shell thickness of on average 27 nm (about one crystallite). Before calcination the diameter was 378 nm with a shell thickness of 25 nm in the dried state, implying that calcination has nearly halved the shell volume. These results are summarized in Table 2. Calcination at 1000 °C produced pure rutile, but the shell structure had completely disappeared.

Figure 9 shows the results of thermogravimetric analysis of this sample. By comparison with a sample of uncoated spheres the large loss of weight at around 400 °C was found to be due to the removal of polystyrene. The initial
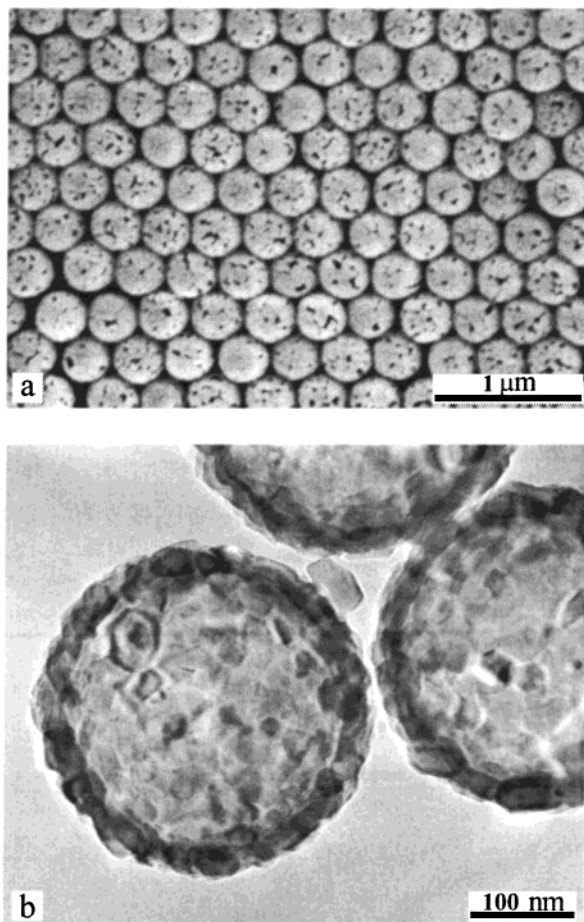
Figure 7. (a) SEM picture of a crystal of titania shells obtained after calcination of the titania-coated polystyrene spheres of Figure 1c at 600 °C in air. (b) TEM picture of some titania shells, showing that they are built up of small (anatase) crystallites.
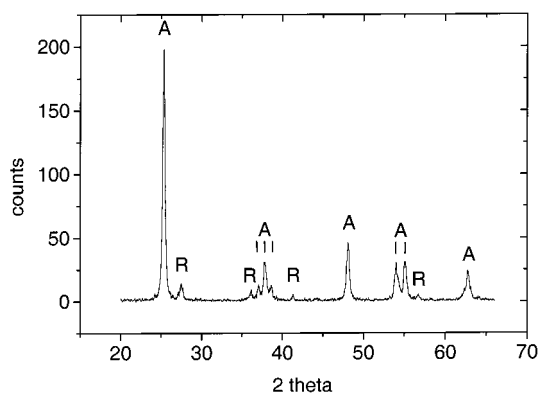

Figure 8. X-ray powder diffraction spectrum of titania shells calcined at 600 °C. This sample consisted of anatase and ~10% rutile. The reflections are labeled A for anatase and R for rutile.

weight loss is due to desorption of physically adsorbed water. The smaller loss at 250 °C is probably due to dehydroxylation and the removal of residual organics from the titania. The final weight loss is 61%, and the weight ratio of TiO_2 to polystyrene is 0.84. Assuming densities of 3.84 g/cm^3 for TiO_2 (anatase) and 1.05 g/cm^3 for polystyrene, their volume ratio is 0.23. From this and the sizes of the polystyrene core and the shrunk hollow shell we calculate an anatase shell thickness in the calcined sample of 25 nm. This agrees quite well with the thickness seen in TEM pictures, implying that the shells are highly dense.

Table 2. Results of the Characterization of a Sample of Titania-Coated Polystyrene Spheres[a]

state of particles	d_{core} (nm)	d_{shell} (nm)	densification of shell (%)	Figure
in suspension	378	60	21	
dried	378	25	55	1c
core dissolved/in suspension	378	60	21	
core dissolved/dried	270	50	43	5
core burnt by calcination	260	27	100	7

[a] Core and shell sizes were determined with static light scattering for samples in suspension (ethanol) and from TEM pictures for the dried samples. The percentage densification of the shells was found from a mass balance assuming that the calcined shells are fully dense.
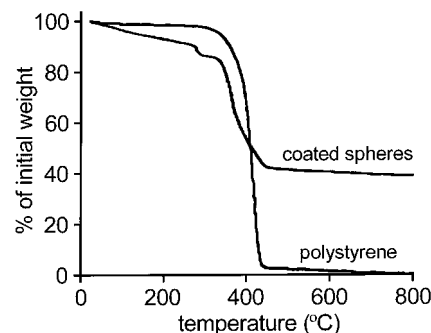
Figure 9. Thermogravimetric trace of the titania-coated polystyrene spheres of Figure 1c. At 500 °C weight loss is complete, the final loss being 61%. For comparison, a trace of the uncoated polystyrene spheres is shown.

Knowing that the calcined shells are fully dense titania, it becomes possible to estimate the titania volume fraction in the shells when they are in suspension or in the dried state, the rest being solvent, residual organics or air, by taking into account the amounts of shrinkage of core and shell (see Table 2). We thus find that the shell consists of 21% titania when in suspension and 55% titania when dried (by volume). The volume average refractive index of a mixture of 21% titania (index 2.5) and 79% ethanol (index 1.36) should be around 1.60. This certainly explains why such a low value (1.53) was found in the light scattering experiments.

4. Conclusions

Stable colloidal core−shell particles consisting of a polystyrene core and a titania coating were prepared in one step by the hydrolysis of a titanium alkoxide in the presence of a cationic polystyrene latex. Although this study used polystyrene as a core, it should be possible to replace it with other polymer colloids that can be given cationic surface groups or with negatively charged particles that can be made positive by coating with a polyelectrolyte.[11] The coatings are very smooth and uniform and can be varied in thickness from just a few nanometers to at least 50 nm. Thicker coatings should also be possible but only through a multistep seeded growth process. The coated spheres have the same monodispersity as the starting latex, allowing them to form colloidal crystals.

Measurement of the coating thickness with light scattering and electron microscopy showed that the titania coating is not dense when the particles are in suspension in ethanol but that it densifies when the particles are dried. From the ratio of titania to polystyrene, measured by thermogravimetric analysis, it was found that the coating consists of 21 vol % titania and that drying

increases this to 55 vol %. In the process, the shells become much thinner.

Hollow titania particles can be made by removal of the polystyrene cores either by dissolution in toluene or by firing in a furnace. The dissolution route leaves stable colloidal titania shells that are spherical and monodisperse. Drying of these shells causes them to deform because of their softness. The firing route produces dense, unde-formed shells, consisting of a mosaic of small anatase crystallites.