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A General Method to Coat Colloidal Particles with Titania

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We describe a general one-pot method for coating colloidal particles with amorphous titania. Various colloidal particles such as silica particles, large silver colloids, gibbsite platelets, and polystyrene spheres were successfully coated with a titania shell. Although there are several ways of coating different particles with titania in the literature, each of these methods is applicable to only one type of material. The present method is especially useful for giving the opportunity to cover many types of colloidal particles with titania and forgoes the use of a coupling agent or a precoating step. We can produce particles with a smooth titania layer of tunable thickness. The monodispersity, which improves during particle growth, and the high refractive index of titania make these particles potential candidates for photonic crystal applications. We also describe various ways of fabricating hollow titania shells, which have been intensively studied in the literature for their applications in electronics, catalysis, separations, and diagnostics. Note that our method initially produces amorphous shells on the particles, but these can be easily turned into crystalline titania by a calcination step. We also find that the growth of titania is a surface-reaction-limited process.

1. Introduction

Colloidal titania, in its crystalline form, is a widely studied material for its unique optical, electrical, and chemical properties. It is well-known in photovoltaic[1−3] and photocatalytic[4,5] applications, and it is used as a pigment,[6] filler,[7] and whitener in the paint, paper, cosmetic, and food industries.[8] It is also studied in applications of colloids in photonic crystals by virtue of its high refractive index.[9,10]

Titania colloids with a core−shell structure also constitute a class of materials widely used in many fields of colloid and materials science. One particular goal in the fabrication of core−shell particles is the production of hollow titania shells[11−13] by removal of a sacrificial core. This has found applications from photonics to microencapsulation. Titania-coated colloids are also useful in reducing the cost of pigment and filler materials, because a titania shell alone has nearly the scattering properties of titania, while the core may be made of a cheaper material.[14] Other applications of titania-coated colloids include changing the surface properties to obtain different particle interactions and tuning the optical properties of the cores, especially when these are metal nanoparticles.[15,16] One notable application of core−shell particles with a titania shell was the fabrication of dielectric shell structures obtained by converting the titania shell into perovskites, which have useful dielectric properties.[17]

Coating of metal colloids with titania was demonstrated by Caruso et al. and Sakai et al. for gold and silver particles, respectively.[18,19] The method of coating gold particles with titania reported by Caruso and co-workers is relatively laborious, including several steps to couple titania precursors to surfactants and finally to the surface.[18] Sakai et al. have reported an interesting way of coating silver particles in the presence of cetyltrimethylammonium bromide (CTAB), which also initiated the condensation of the titania precursor.[19] In their work, the authors also reported a red shift of the absorbance peak of the silver particles with a 5−10 nm titania shell, caused by an increase in the local refractive index.

In principle, many surfaces have a suitable chemical affinity to make direct titania coating possible, such as clay minerals, hematite, zirconia, zinc oxide, and silica. The main difficulty appears to be maintaining colloidal stability during the coating to prevent aggregation. Thus, few articles report a facile method for coating even these colloids with titania, including the silica−titania couple. Although (amorphous) silica and titania are similar to each other in structure and it is easy to coat titania particles with silica with or without use of any surfactant,[20] methods to coat silica particles with a titania shell are scarce. Matijevic and co-workers reported a simple way of coating silica particles with titania, but synthesis conditions still involved several steps, including heating and aging, and resulted in a thin,

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rough shell of titania.[14] Matijevic and co-workers also reported methods for coating zinc oxide and copper compounds, while Shiho and Kawahashi succeeded in coating polystyrene.[21] These methods again included prolonged heating steps and yielded only rather thin titania layers.[22,23] Indeed, literature methods almost always result in a thin titania layer that is not very smooth. This well-known difficulty is probably due to the formation of smaller titania particulates, which aggregate onto a particle to form the shell.[24−26] Large-scale aggregation usually ensues when a thicker coating is applied.[27]

Smooth titania coatings up to 130 nm thickness have been applied on polystyrene colloids, but they are rather specific in that they require functionalization of the polystyrene surfaces.[11,28] The difficulties in titania coating, compared to, for example, silica, are mostly caused by the fast and aggressive reaction kinetics of the titania precursors, making the coating process hard to control. This problem already makes it difficult to make monodisperse, homogeneous titania colloids. However, these challenges can be overcome by using a surfactant, a salt, or a different solvent to slow down the reaction rate, as was shown in a number of recent reports.[20,29,30]

The procedure we present here to coat particles with titania is similar to that of Eiden-Assman et al.[20] for making homogeneous titania particles in that it uses surfactant assisted precipitation of titania formed by the hydrolysis of a titanium alkoxide. We modified it such that it now allows one to coat ethanol-dispersible seed particles of many different types in one step. We demonstrate this for the examples of silica, silver, gibbsite, and polystyrene. Our method is versatile in its availability of the titania shell for postsynthesis modification, such as the incorporation of a fluorescent dye to label the particles for fluorescent microscopy or the inclusion of different types of precursors for converting the shell to perovskites.[31] The method also provides the flexibility to control the shell thickness from 10 to 250 nm at room temperature.

2. Experimental Section

Synthesis of Particles. A typical coating of submicrometer particles proceeded as follows. Two solutions were prepared. First, 80 μL of a 0.1 M aqueous solution of the nonionic surfactant Lutensol ON50 (BASF) was dissolved in a 10 mL dispersion of core particles in ethanol. Then, another 10 mL of ethanol was mixed with 0.1−0.2 mL of $Ti(OC_4H_9)_4$ (TBT, Sigma-Aldrich). The diluted titania precursor solution was then added to the core particles dispersion, followed by vigorous shaking. The mixture was sonicated for at least 20 min in a sonication bath during the reaction. It was then left for 2 h to allow the reaction to go to completion. The titania-coated particles were collected by centrifugation and dispersed in fresh ethanol without drying the particles. The absolute ethanol used in this work was kept in the refrigerator at around 7 °C prior to use. This slows down the condensation of the titania precursor. When needed for confocal microscopy measurements, the fluorescent dye rhodamine isothiocyanate (RITC) or fluorescein isothiocyanate (FITC) was added to the dispersion of as-synthesized particles. The particles were then centrifuged and redispersed. Because the dye was only physisorbed to the particles, the particles were not washed more then twice. Note that the drying mentioned throughout the Article was done at 50 °C.

Table 1. Coating Particles with Titania

particle	conc of particle (g/L)	Lutensol ON50 (μL)[a]	conc TBT (mL/L)	shell thickness dry (nm)	shell thickness nondried (nm)[b]
silica	1.86	80	10	55	110
polystyrene	0.19	80	10	250	460
polystyrene	0.38	80	7	15	42
silver	0.23	80	7	140	
silver	0.14	80	7.5	220	
gibbsite	0.76	80	10	35	

[a] Amount of 0.1 M Lutensol ON50 solution added for 20 mL of synthesis solution. [b] Size of particles prior to drying was found from SLS measurements.

We now describe the coating of the various particles in more detail. Details are also shown in Table 1. SiO_2@TiO_2 particles were synthesized by coating 600 nm RITC labeled silica particles, which had been prepared according to the procedure of van Blaaderen and Vrij.[32] An amount of 80 μL of 0.1 M aqueous Lutensol ON50 solution was added to 10 mL of an ethanolic dispersion of silica particles. In another 10 mL of ethanol, 0.2 mL of TBT was dissolved. The diluted titania precursor was mixed with the core particles dispersion under vigorous shaking. Part of the product was calcined to obtain a crystalline titania shell. The silica core of these particles was etched with a 8% (v/v) HF solution.

Ag@TiO_2 particles were prepared by using 250 nm Ag particles synthesized according to the procedure of Tao et al.[33] These particles were initially dispersed in water but could be readily dispersed in ethanol without any treatment. An amount of 80 μL of 0.1 M aqueous Lutensol ON50 solution was added to a 10 mL ethanolic dispersion of silver particles. In another 10 mL of ethanol, 0.2 mL of TBT was dissolved. Subsequently, this solution was mixed with the seed particles dispersion. The relative amounts of titania precursor and the silver seeds were varied in order to vary the titania shell thickness.

Cationic polystyrene (PS) spheres were prepared by surfactant free emulsion polymerization as described by Goodwin et al.[34] These particles could be readily dispersed in ethanol. Particles dispersed in 10 mL of ethanol were mixed with 80 μL of 0.1 M aqueous Lutensol ON50 (BASF) solution. In another 10 mL of ethanol, 0.2 mL of TBT was dissolved. These solutions were mixed and sonicated.

Gibbsite platelets were prepared from aqueous aluminum oxide solutions by hydrothermal treatment at 85 °C and purified by dialysis against demineralized water as described by Wierenga et al.[35] They were transferred to ethanol by centrifugation. Titania coating was made similarly; for details, see Table 1.

For the titania coating to occur in a typical synthesis, an amount of 80 μL of Lutensol ON50 solution was dissolved in a total of 20 mL of ethanol. For this synthesis, at least 0.1 mL of TBT was added. TBT concentrations lower than this did not result in condensation of titania within a reasonable time. On the other hand, an amount of TBT larger than 0.2 mL gave rise to aggregation and formation of secondary nucleates. Thus, the coating thickness was tuned not through the TBT concentration

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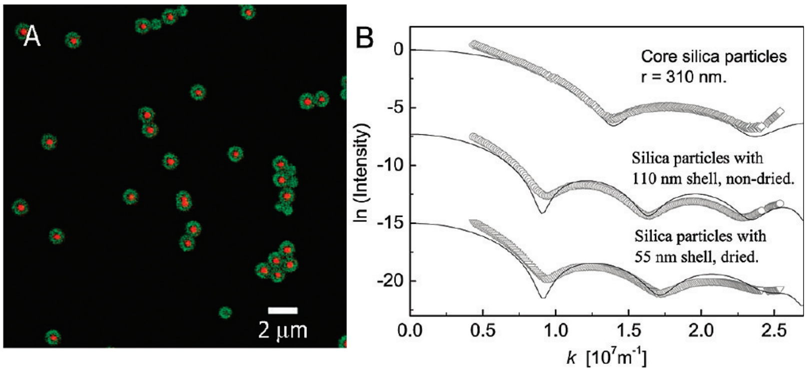

Figure 1. (A) Confocal microscopy image of RITC labeled silica particles coated with an FITC labeled titania layer. (The particles that look completely green are either second nucleations or particles that are not exactly in the same plane with the others, so that only the shell is imaged.) (B) SLS graphs of, from top to bottom, bare silica particles with 5% polydispersity, nondried 110 nm titania-coated silica particles, and the same particles after drying, leaving a 55 nm titania shell. [Image size of (a) = 26.9 μm × 26.9 μm.]

but through the concentration of seed particles. With this method, slight changes in the concentration of Lutensol ON50 amount are also possible. For example, increasing the amount of Lutensol ON50 to 90 μL increased the reaction rate and also decreased the lower limit of TBT for condensation from 0.1 mL to ~0.07 mL TBT.

Characterization of Particles. Energy dispersive X-ray (EDX) analysis and transmission electron microscopy (TEM) images with a high-angle annular dark-field (HAADF) detector were obtained with a Philips Tecnai 20 electron microscope. Cryo-TEM was conducted by vitrification of a water dispersion of particles on a TEM grid free of any coatings.

Static light scattering (SLS) was performed with home-built equipment using a He–Ne laser as the light source (632.8 nm, 10 mW). The logarithm of scattering intensity was plotted against the scattering vector $k = 4\pi n \sin(\theta/2)/\lambda$, where n is the solvent refractive index, θ is the scattering angle, and λ is the wavelength in vacuum. The data were compared to numerical Mie solutions for core–shell particles assuming the shell as monodisperse while the core included a polydispersity measured on the uncoated particles.

The powder X-ray diffraction (XRD) measurement was performed on a Philips PW 1820 diffractometer with a Philips PW 1729 X-ray generator (Cu Kα radiation). We used a glass substrate for the XRD measurement.

3. Results and Discussion

Coating Silica with Titania. In our previous work, we found that amorphous titania particles synthesized with Lutensol ON50 are very sensitive to and modified by drying; particles dried in oven at 50 °C for 2 h could be coated with silica under Stöber conditions yielding core–shell particles.[36] However, particles treated with silica prior to drying formed homogenously mixed composite TiO_2–SiO_2 particles.[31] The formation of homogeneously mixed composite particles shows that particles as-synthesized are porous and open to access for species added after the synthesis. The porosity difference between dried and nondried particles was also demonstrated by the addition of a fluorescent dye to the dispersions of both types of particles.[17] As-synthesized particles yielded fully dyed particles, whereas dried particles fluoresced only from a surface layer. We used this knowledge to image the core–shell particles with a confocal microscope by labeling the amorphous titania shell. Dye could only penetrate as deep as the shell; the silica core is denser and does not let the dye go further in. This would lead to a thick visible shell labeled with fluorescent dye as a sign of the core–shell structure.

Red fluorescent RITC labeled silica particles with a 620 nm diameter were coated with titania. The titania coating of these particles was also labeled, but with green fluorescent FITC, to obtain contrast between the core and the shell. Figure 1A shows a confocal microscopy image of these silica–titania core–shell particles. The particles that look completely green are either second nucleations or particles that are not exactly in the same plane with the others, so that only the shell is imaged. The coating thickness can be measured with SLS. The SLS graphs for these particles with and without the titania coating are given in Figure 1B. The symbols in the graphs are the experimental data, and the lines are the full Mie calculations for the core–shell form factor. From the scattering data, the polydispersity for the silica core was estimated to be 5%. The thickness of the titania shell is sensitive to drying, and it decreased from 110 to 55 nm after drying with an accompanying increase in the refractive index of the shell from 1.55 to 1.8.

Silica@Titania particles were also used to produce titania shells by selective etching of the silica core with HF. TEM images of as-synthesized Silica@Titania particles and of calcined and etched particles are given in Figure 2A and B, respectively. The result is clear evidence that a titania coating was deposited on the particles.

Coating Polystyrene with Titania. We could also coat polystyrene (PS) particles successfully with titania. To show that we can tune the thickness of the titania shell, we show two extreme examples of thin and thick coating of cationic PS particles by changing the amount of titania precursor solution used per particle. Figure 3A shows a typical confocal microscopy image of titania-coated PS particles where the thick titania layer is fluorescently labeled. Figure 3B is a TEM image of the titania-coated PS particles found to be 1210 nm in diameter with 3% polydispersity. The original PS particles had a size of 770 nm. In our previous work, we have found that amorphous titania particles that were as large as 1.8 μm prior to drying shrank to 1.3 μm when dried, as determined by the static light scattering technique.[31] Here, we observe a similarly large shrinkage of the amorphous titania-coated particles. When PS particles with a titania shell were calcined in an oven at 500 °C for 1 h, the core burned away and the shells became crystalline. A TEM image of crystalline titania shells is shown in Figure 3C, and the corresponding XRD graph is given in Figure 3D. The XRD graph has the typical peaks of the anatase form of titania. An SLS graph of these anatase shells is also given in Figure S1 in the Supporting Information, where the refractive index is estimated as 2.3 for a shell thickness of 100 nm. This SLS graph proves that with this technique it is possible to make very monodisperse thick titania

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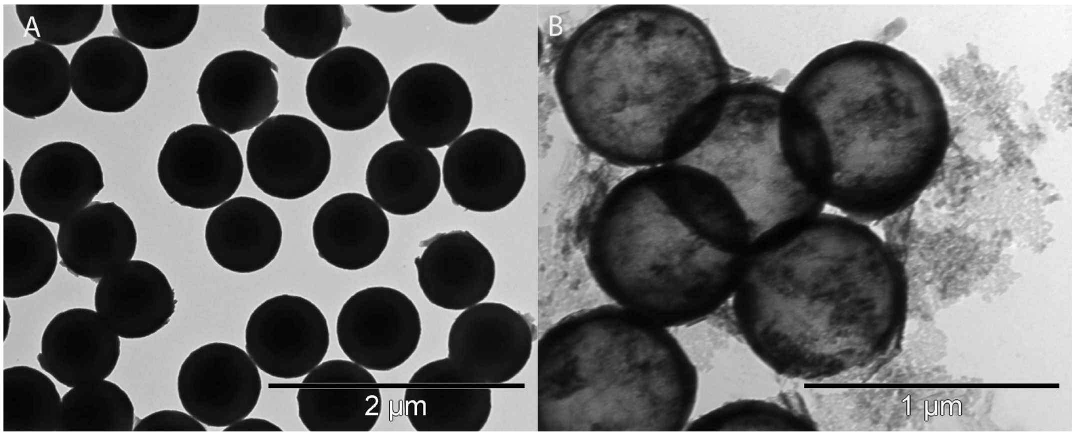

Figure 2. (A) TEM image of silica particles coated with titania. (B) TEM image of anatase titania shells, obtained after HF etching of Silica@Titania particles calcined at 500 °C for 0.5 h.

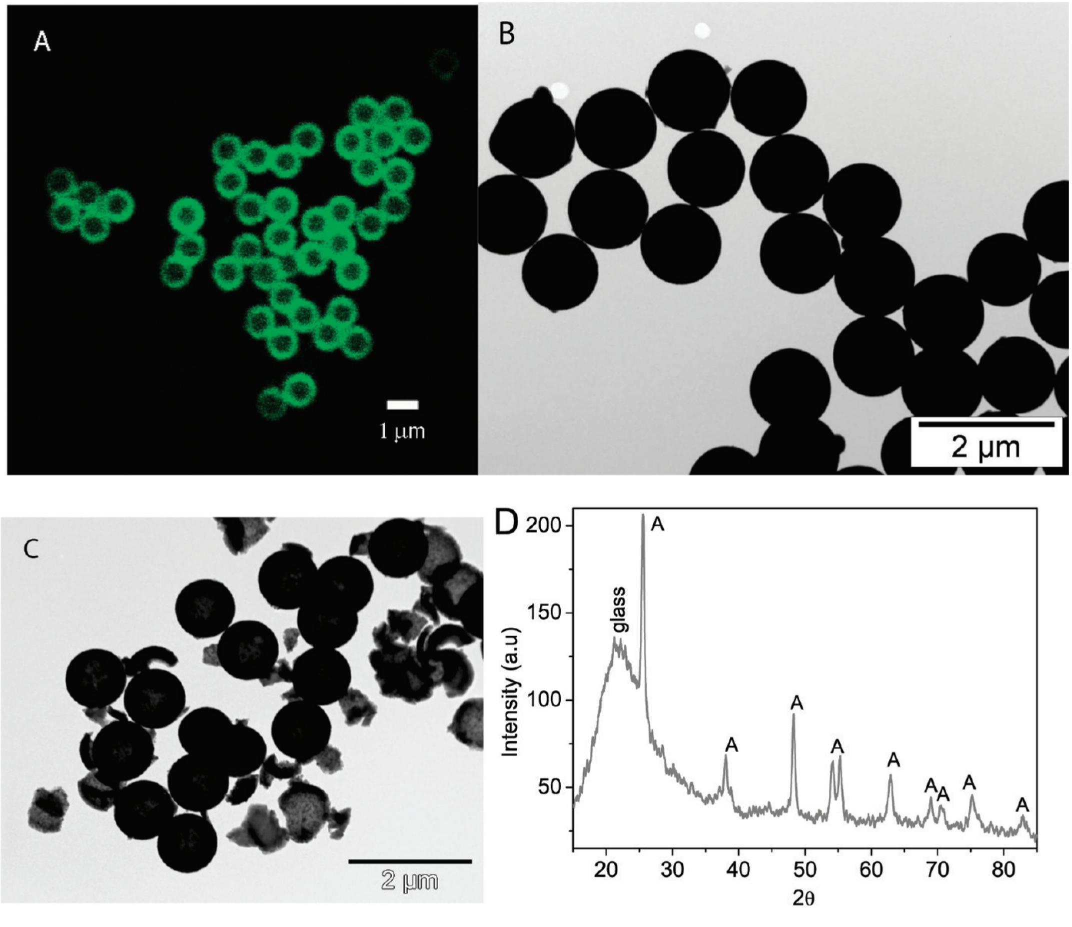

Figure 3. (A) Confocal microscopy image of as-synthesized polystyrene core, titania shell particles labeled with fluorescent dye that can only penetrate the shell. (B) TEM image of the particles shown in (A). (C) TEM image of crystalline titania shells after calcination of PS particles at 500 °C. (D) XRD of the titania shells showing that the shell is anatase; peaks are labeled “A” for anatase. The broad peak at around 20 is due to the glass substrate. [Image size of (a) = 15.0 μm × 15.0 μm.]

shells. It should be noted that the thick titania layer hinders the burning process of the PS core and this can be the reason for the bursting of some particles seen the TEM image of an uncleaned batch (Figure 3C). However, it is also possible that a thicker shell is simply less flexible under heat stress, causing it to break.

The scattering features, specific to size and refractive index of both the material of the core and shell, give a possibility of estimating a refractive index for (the core and) the shell. From SLS measurements, where we used the known PS refractive index of 1.59, we estimated the refractive index of the titania shell to be 1.55 prior to drying and 1.8 after drying. As shown in the SLS graphs in Figure 4, it was possible to coat the PS particles with a thick and a thin layer of titania. In Figure 4A(1), (2), and (3), an SLS graph of the original PS particles is given together with the SLS graphs of the PS@Titania particles with a thick shell before and after drying, respectively. The SLS graphs for the same PS particles coated with a thin titania layer are given in Figure 4B(1) and (2). The shell thicknesses were 42 and 15 nm before and after

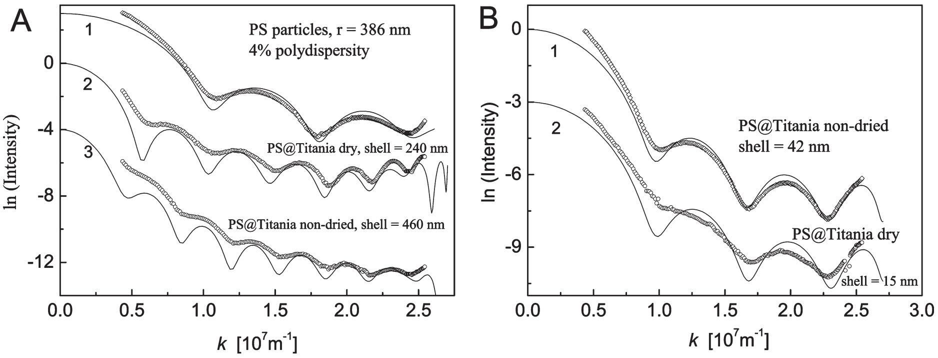

Figure 4. SLS graphs of PS particles coated with titania. Experimental curves of the particles (symbols) in ethanol fitted to theoretical calculations of the full Mie solutions to the form factor (lines, offset for clarity). (A) PS particles coated with a thick layer of titania: (1) belongs to the original PS particles with a radius of 386 nm, (2) the PS particles coated with a 250 nm thick titania shell after drying, and (3) the same particles as (2) but prior to drying so that the shell thickness amounts to 460 nm. (B) SLS graphs of PS particles coated with a thin layer of titania, which amounts to 42 nm (1) for particles prior to drying and 15 nm (2) for the dried particles.

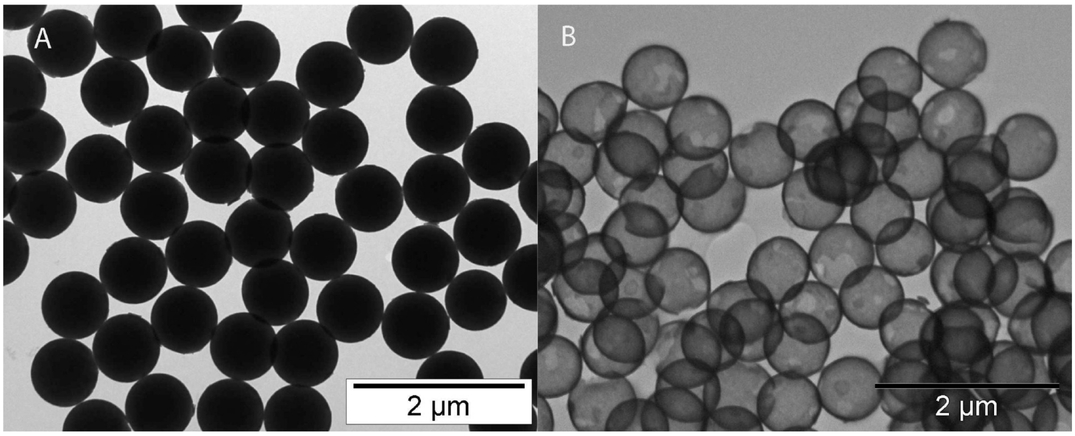

Figure 5. TEM images of (A) PS particles with a 15 nm thin shell of titania and (B) titania shells after dissolving the PS core with THF.

drying, respectively. In the thick titania coating case, we found a titania shell of 240 nm from SLS and 230 nm from TEM analysis. This thick titania shell blocks the dissolution of the inner PS by good solvents: We tried to dissolve the core in tetrahydrofuran (THF), but it was still not dissolved after several days (see Supporting Information Figure S2). This experiment shows that, although porous, the shell's thickness prevents the dissolution of the core by slowing down the process to an impractical rate. However, when the same particles were coated with a 15 nm thin titania layer (Figure 5A), core dissolution was straightforward, resulting in nice and monodisperse amorphous titania shells (Figure 5B).

Because of the difficulties that are often encountered in the coating of colloids with a smooth titania layer, and the success of the present method, it is of some interest to deduce the titania growth mechanism. This can be established by analyzing the competitive growth in a dispersion of spheres with a bimodal size distribution.[37] We investigated this with a 1:1 mixture of PS spheres with sizes of 340 and 670 nm, that is, an initial size ratio of $\beta_0 = 1.97$. The final size ratio R_a/R_b after growth was plotted against the relative increase in the radius of the smallest spheres $\gamma = R_b/R_{0b}$. This plot, shown in Figure 6A, is consistent with a surface-reaction-limited growth, rather than with a diffusion-limited growth. Here, α describes the power-law dependence of the rate of incorporation of hydrolyzed monomers on a particle with radius R. Different growth mechanisms are characterized by a different value of α. In a reaction-limited process, the growth rate is limited by the condensation of hydrolyzed monomers on the particle surface. Thus, the rate of change in particle mass or volume is then proportional to the particle surface, and for smooth surfaces $\alpha = 2$. If, on the other hand, diffusion of monomers to the particle surface is rate-limiting, particle growth is proportional to the radius of the particles: $\alpha = 1$. It is clear that the data show that the titania coating follows a reaction-limited growth with $\alpha = 2$.

After growth, the sizes of the particles were analyzed by TEM. However, as our particles shrink when dried, a correction for the (known) degree of shrinkage had to be applied. To check that this did not introduce unwanted errors, we also measured the sizes by using cryo-TEM, where shrinkage is avoided. These data are included in Figure 6A. Figure 6B shows an example of cryo-TEM images made on a bidisperse sample of PS@Titania particles.

Coating Metal Oxides with Titania. Next, we describe an example of the titania coating of a metal oxide colloid, namely, gibbsite platelets of 450 nm diameter and 25 nm thickness. The titania coating on the platelets was 30 nm on the edges. The titania shell can be distinguished from the gibbsite core due to the density contrast of the core and shell in the TEM image given in Figure 7. Although the titania coating is visible in Figure 7B, the contrast with the gibbsite is a bit low. Therefore, we analyzed the particles with EDX as well. On a single spot near the center of the particle, the EDX graph shows peaks both of titanium and aluminum,

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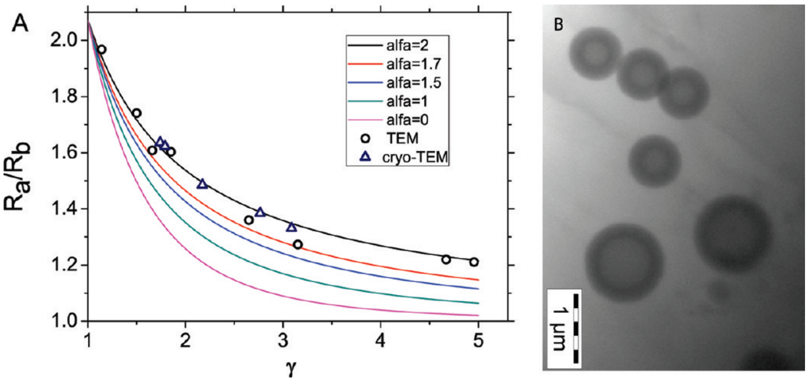

Figure 6. R_a/R_b plotted against the relative increase in the radius of the smallest spheres $\gamma = R_b/R_{0b}$, where R_a and R_b are the size of large and small spheres, respectively. Circles are TEM data, which were corrected for shrinkage using a dried to nondried density ratio of 2.63, as found from SLS measurements of five different samples. Triangles are cryo-TEM data, which did not require such a correction. The lines compare the data to growth models with different growth exponents α.

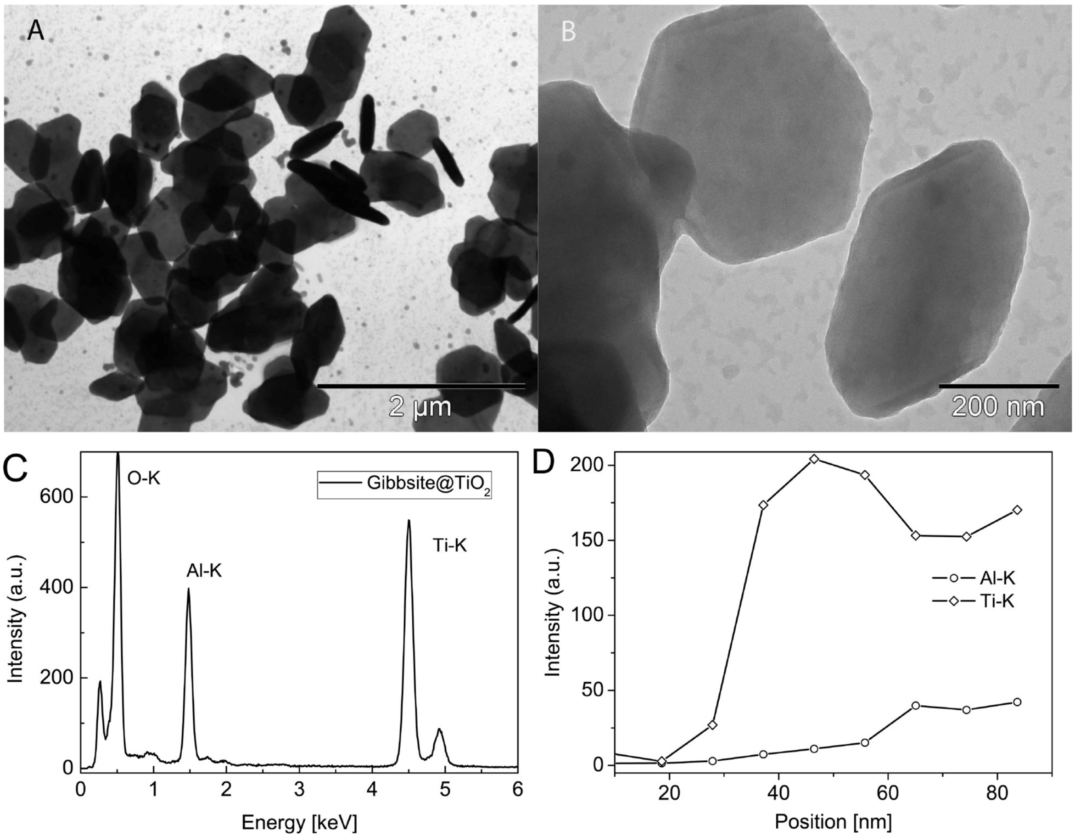

Figure 7. (A) Gibbsite platelets 450 nm in size coated with a 30 nm titania shell. (B) Zoomed image of a single gibbsite particle for better visibility of the titania shell. (C) EDX analysis on a spot on the particles in (B), showing the presence of Al from gibbsite and Ti from titania. (D) EDX line scan through the edge of the particle in (B) clearly showing the core−shell structure.

which are clear signs for the presence of titania and gibbsite, respectively (see Figure 7C). To show the fact that titania forms a coating on the gibbsite platelet, we did a line scan across the edge of a particle seen in Figure 7B. From the EDX line scan (Figure 7D), it is seen that the titanium peak starts before the appearance of the aluminum peak and then decreases as the aluminum peak shows up. The aluminum peak appears approximately 30 nm after the titanium peak, which agrees with the titania shell thickness measurements. These features of the EDX line clearly show the core−shell structure of particles.

Coating a Noble Metal with Titania. As an example of the coating of metal particles with titania, we used well-defined silver particles. These particles of 250 nm have an octahedral shape and are stabilized by poly(vinylpyrrolidone) (PVP). They were successfully coated with a 220 nm thick titania layer in one step. A TEM image of the coated particles is given in Figure 8A. Note that the facets of the silver cores are clearly visible. To show that the coating thickness can be tuned by changing the silver colloid concentration, we also performed the synthesis with a lower TBT/seed ratio. We indeed obtained thicker shells when we used half the amount of seed particles compared to the above example (see Table 1 for details). An EDX spectrum taken at the Ag core is given in Figure 8C (taken at point 1 in Figure 8B) and shows Ag and Ti peaks, whereas an EDX spectrum taken in the shell

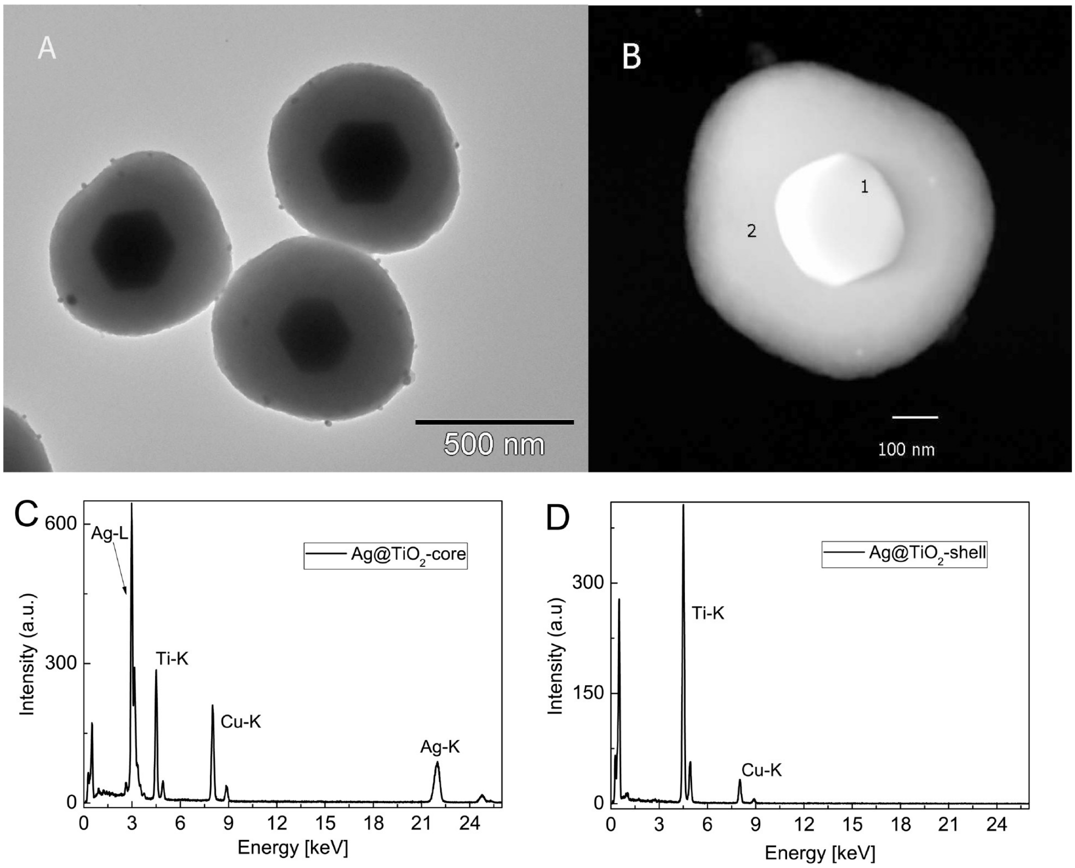

Figure 8. (A) TEM image of Ag@TiO$_2$ particles. (B) Transmission image of a single Ag@TiO$_2$ particle in HAADF mode. (C) EDX on a single spot in the core of the particle (point 1 in (B)), detecting the elements of both silver in the core and titania in the shell. (D) EDX on a single spot on the edge of the particle (point 2 in (B)), showing only the titanium in the shell. The copper signal is due to the substrate.

(Figure 8D, taken at point 2 in Figure 8B) shows only Ti. These EDX analyses clearly prove the core–shell structure. Since it is known that concentrated HNO$_3$ can etch silver by oxidizing it, we have tried to etch the core of Ag@TiO$_2$ particles with HNO$_3$. Although the etching works within a few seconds for nondried particles (by completely leaving the dispersion transparent, meaning that the titania is also etched away.), it took 1 day to partially etch the silver core of dried Ag@TiO$_2$ particles. This observation agrees with the results found when dissolving the PS core from coated particles. Additionally, the surprising results in our previous work[17] that the silver core of Ag@BaTiO$_3$ particles could not be oxidized upon heating at 900 °C for 1 h can be understood better with these results.

4. Conclusion

We developed an easy method for coating colloidal particles with an amorphous titania layer of controllable thickness. This new method can be applied to a broad range of submicrometer sized colloids, especially those that are directly dispersible in ethanol. The amphiphilic and nonionic character of the surfactant, which defines the character of the synthesis, makes the method available for a broad range of colloid surfaces as demonstrated here for silica, silver, gibbsite, and polystyrene. The coated particles are monodisperse in size and have a smooth surface. This method offers the flexibility of tuning the thickness of the titania shell by changing the number of seeds in relation to the amount of precursor added. Based on the methods we have described before, it is also possible to make silica–titania composite shells on the particles shown here.[31] Heat treatment of the amorphous titania shells turns the shells to crystalline titania: depending on the temperature, this is either anatase at 400–600 °C or rutile at 800–900 °C. Metal core, titania shell particles have importance in photonics and may find use in production of percolative capacitors by converting the titania shell to perovskites.[17]

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Supporting Information Available: SLS of the crystalline titania shells and TEM image of PS@Titania particles without dissolution of the core in THF (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.