Gold−Titania Core−Shell Nanoparticles by Polyelectrolyte Complexation with a Titania Precursor

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Received May 17, 2001

The nanoscale coating of colloid particles with materials of different composition is currently an active area of research.[1−3] Such coatings not only stabilize colloidal dispersions but also allow modification and tailoring of the particle properties (e.g., optical, magnetic, catalytic) depending on the coating composition.[1−4] Two approaches widely used for the surface modification of particles are the direct precipitation of (inorganic) shell materials from solution and the layer-by-layer deposition of charged species.[1] Among the inorganic coatings, metal oxides have been of significant interest. Silica has been used extensively to coat different colloid particles, including noble metal colloids. Liz-Marzan and coworkers have shown that a vitreophilic metal nanoparticle surface facilitates the formation of uniform silica coatings.[5] Gold nanoparticles were made vitreophilic by using the coupling agent (3-aminopropyl)trimethoxysilane, and silica coatings were obtained by subsequent exposure of the particles to a sodium silicate solution followed by the Stöber process.[6] In a recent study, Hardikar and Matijevic demonstrated that under well-defined conditions the Stöber process can be directly used to coat (vitreophobic) silver nanoparticles.[7]

Titania is another metal oxide that is of interest for coating applications as it is widely known to be a useful catalyst.[8,9] Catalytic applications demand titania with a high surface area-to-volume ratio. However, unsupported high surface area forms of titania are thermally unstable. Hence, significant efforts have focused on coating titania on high surface area supports such as colloid particles. Previous reports have mostly concentrated on titania coating of silica or alumina particles with diameters ranging from a few hundred nanometers to several micrometers.[10−19] With the exception of a recent investigation reporting the formation of a thin shell of titanium dioxide on silver nanoparticles via silver reduction and condensation of titanium butoxide,[20] few studies have dealt with titania coating of particles less than 50 nm in diameter. The advantage of using smaller particles as supports is that they have inherently higher surface areas.

In this communication we report the nanoscale coating of gold nanoparticles with titania by using a facile approach based on complexation of a negatively charged titanium precursor, titanium(IV) bis(ammonium lactato) dihydroxide (TALH), with poly(dimethyldiallylammonium chloride) (PDADMAC). Compared to other metal oxides (including those of titania), which hydrolyze rapidly in the presence of water, TALH is stable in aqueous solution at room temperature.[21−23] TALH has already been used for producing titania coatings on silica gels[21] and polymeric substrates.[23] The primary advantage of using TALH for the preparation of core−shell particles is that nanoparticles can be coated with titania by controlling the hydrolysis and condensation reactions. The controlled temperature and pH-dependent hydrolysis of TALH is well-documented.[21−23] In addition, because TALH is a water-soluble precursor, the coating process does not require the use of organic solvents. In the method employed, the templates (or core particles) primarily determine the size distribution of the coated colloid. Gold was chosen as the core particle as the growth of a titania shell can be monitored spectrophotometrically by following changes in the plasmon band absorption.[5]

Gold−titania core−shell particles were synthesized by first coating surface-modified gold particles with three layers of polyelectrolytes, followed by complexation with the water-soluble TALH and hydrolysis.[24] The gold particles were derivatized by the self-assembly of sodium 10-mercaptodecanesulfonate (MDS) to obtain negatively charged particles. Sulfonate derivatization of gold nanoparticles via a thiolate linkage to the gold surface facilitates the uniform growth of polyelectrolyte multilayers.[25,26] The sulfonated particles were coated with two layers of polyelectrolyte by the electrostatic layer-by-layer self-assembly of PDADMAC and poly(sodium-4-styrenesulfonate) (PSS).[25,26] The choice of polymer molecular weight and salt concentration em-

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10.1021/cm011128y CCC: $20.00

ployed was based on our previous studies.[25,26] The particles were then further coated with an additional layer of PDADMAC, followed by complexation with TALH.[27] The growth of the polyelectrolyte multilayers and subsequent complexation of TALH were investigated by using UV−visible spectrophotometry (Figure 1A).[28] A red shift in the peak plasmon absorption band was observed on adsorption of each polyelectrolyte layer. The peak plasmon absorption shifted from 528 nm for sulfonated particles (dashed line in Figure 1A) to 535 nm on adsorption of three polyelectrolyte layers (spectrum a). The absorption peak further shifted to 546 nm on adsorption of one TALH layer (spectrum b). This red shift in the peak absorption maximum is due to an increase in the local dielectric constant[29] ($n_{\text{polymer}} = 1.47$, $n_{\text{TALH}} = 1.52$). In the case of TALH adsorption, particle aggregation also contributes to the red shift (see later). The particle solution was heated under reflux for 24 h (in the presence of excess PDADMAC[30]) to convert the titania precursor into crystalline titanium dioxide nanoparticles. At temperatures above 70 °C, TALH is known to undergo fast hydrolysis, resulting in precipitation of bulk titania from solution.[23] To avoid such precipitation, which could result in cross-linking of the TALH-rich core−shell particles, the temperature was maintained at 65 °C for 3 h. The temperature of the refluxing mixture was then slowly increased to 95 °C over a period of 1 h and maintained at this temperature for a further 24 h. This heating procedure resulted in a slower, more controlled hydrolysis of TALH surrounding the gold nanoparticles. Purification of the refluxed mixture to obtain dispersed core−shell gold−titania nanoparticles was followed using UV−visible spectrophotometry (Figure 1B). Spectrum 1 (Figure 1B) corresponds to the UV−visible spectrum of the core−shell gold−titania nanoparticle dispersion obtained immediately after hydrolysis. The peak plasmon absorption was found to be at 546 nm. The solution was centrifuged for 5 min at 1700*g* and the supernatant was removed. Spectrum 2 corresponds to the UV−visible spectrum of the residual solid dispersed in pure water. The peak plasmon absorption was found to be red-shifted at 549 nm (with respect to spectrum 1), corresponding to the aggregated nanoparticles. The peak plasmon absorption of the isolated particles in the supernatant was found to be at 536 nm (spectrum 3**,** Figure 1B). This represents a slight (1 nm) red shift compared with the MDS-capped gold nanoparticles coated with three polyelectrolyte layers (dashed spectrum, Figure 1A). Anatase−titania has a refractive index of ≈2.5.[31] In the present case, the refractive index of the titania shell lies between that of the shell and the dispersing medium, depending on the porosity of the shell.

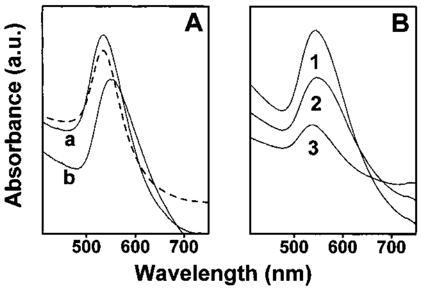

Figure 1. (A) UV−visible spectra of gold particles at different stages of coating. MDS-capped gold nanoparticles (dashed spectra). (a) After deposition of three polyelectrolyte layers (PDADMAC/PSS/PDADMAC). (b) After complexation with TALH. (B) UV−visible spectra of core−shell gold−titania nanoparticles at different stages of separation. (1) Titania-coated gold particles immediately after hydrolysis. (2) Residue (dispersed in pure water) obtained on centrifugation of (1**)** at 1700*g*. (3) Supernatant containing isolated core−shell particles obtained after centrifugation of (1) at 1700*g*. See text for further details.

The core−shell nanoparticles prepared were also characterized by energy-dispersive X-ray (EDAX) analysis and transmission electron microscopy (TEM).[32] EDAX examination of the coated gold nanoparticles

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[24] Poly(sodium-4-styrenesulfonate) (PSS), M_w 15200 (Fluka), and poly(diallyldimethylammonium chloride) (PDADMAC), M_w 20000 (Aldrich), both with a concentration of 10 mg mL^{-1} in 1 mM NaCl solution, and an aqueous 5% (v/v) titanium (IV) bis(ammonium lactato) dihydroxide (TALH) (Aldrich) solution were used as stock solutions. All the materials were used as received without further purification. TALH was prefiltered through a 0.2-μm filter prior to use (the presence of preformed nanometer-sized titania particles cannot be ruled out). Gold nanoparticles capped with MDS were synthesized using the procedure described in one of our earlier reports (described in ref 25). The peak plasmon band absorption of the as-prepared surface-modified gold colloid solution was at 542 nm. One milliliter of this sulfonated gold nanoparticle solution was transferred to a 2-mL Eppendorf tube and centrifuged at 8500*g*. The supernatant was then removed and the residue was dispersed in 1 mL of deionized water. This washing cycle was repeated twice. At the end of each washing cycle, a loss of particles in the form of small dark pellets (aggregated particles) occurred. This washing cycle not only removes unbound thiol but also helps to decrease the polydispersity, with particles smaller than ≈30 nm in diameter remaining in the supernatant and larger particles sedimenting to form a dark pellet. The plasmon band absorption peak of the surface-modified gold particle solution was now at 528 nm (Figure 1A dashed line). The surface-modified gold nanoparticle solution with a peak plasmon absorption maximum at 528 nm (Figure 1A, dashed line) was used as the stock solution. To this solution, 0.1 mL of PDADMAC was added and mixed vigorously. The solution was allowed to stand for 20 min, after which the excess polymer was removed in the supernatant fraction after centrifugation (8500*g*, 7 min). This washing cycle was repeated two more times. The same solution concentrations and conditions described for the deposition of PDADMAC were used for coating the nanoparticles with further layers of polyelectrolyte. However, salt-free solutions were used during the TALH complexation step. The particles coated with TALH were then diluted by the addition of 9 mL of water and placed in a round-bottomed flask with inner walls hydrophobized using standard silane coupling chemistry (see Gun, J.; Sagiv, J. *J. Colloid Interface Sci.* **1986**, *112*, 457.) to avoid particle attachment to the flask; 0.1 mL of PDADMAC from the stock solution was then added to the flask. The particle solution was maintained at 65 °C for 3 h, after which time the temperature was increased to 95 °C over 1 h and then maintained at this temperature for 24 h. The mixture was allowed to cool and then sonicated for 15 min. The refluxed mixture was then washed using three centrifugation cycles (8500*g*). After the final centrifugation step the sedimented particles were collected and resuspended in 1 mL of water. The particles were further centrifuged at 1800*g* and both the supernatant and residue were analyzed by UV−visible spectrophotometry and transmission electron microscopy.

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[27] Only one TALH adsorption step was performed, as gold particles coated with one TALH layer showed high titania surface coverages.

[28] UV−vis samples were placed in quartz crystal cuvettes (Hellma SUPRASIL, path length 1 cm) and analyzed using a double-beam spectrophotometer (CARY 4E, Varian). A solvent spectrum was subtracted from all the measured spectra. Samples requiring sedimentation were centrifuged (3K30, Sigma Laboratory Centrifuges) in 2 mL disposable Eppendorf tubes.

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[30] PDADMAC was employed to provide steric/electrostatic stabilization to the particles during hydrolysis. The particles were found to aggregate significantly in the absence of PDADMAC.

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[32] TEM measurements were performed on a Philips CM12 microscope equipped with an EDAX attachment, using 120 kV of accelerating voltage. Samples for TEM were prepared by drying a 5-μL drop of the sample on carbon-coated copper grids (Plano).

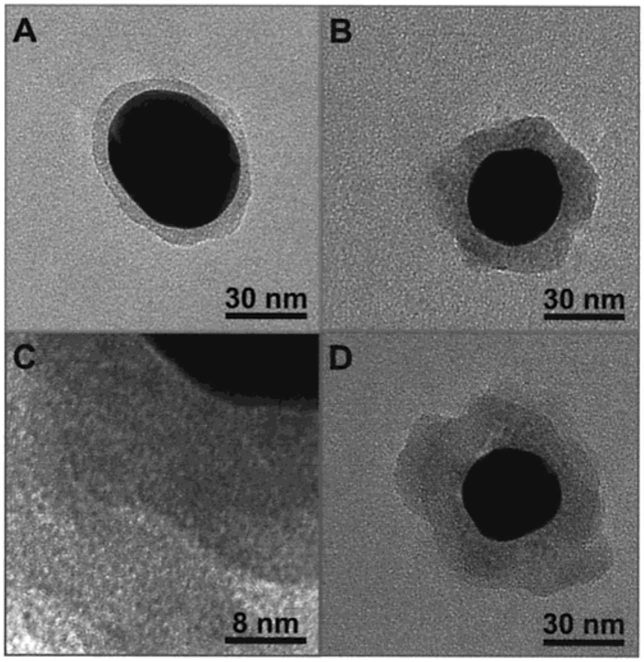

Figure 2. Transmission electron micrographs of core–shell nanoparticles. (A) MDS-capped gold nanoparticles coated with a polyelectrolyte bilayer, PDADMAC/PSS. (B) Gold–titania core–shell particles prepared by complexation of TALH with PDADMAC/PSS/PDADMAC. (C) Higher magnification of the shell of the particle shown in (B). (D) Core–shell gold–titania nanoparticle prepared by the complexation of TALH with PDADMAC-coated MDS-capped gold particles. For (B), (C), and (D), TEM analysis was carried out after TALH hydrolysis.

revealed the presence of atomic titanium, confirming the deposition of TALH. TEM images of the core–shell particles are shown in Figure 2. As can be seen from Figure 2A, the polyelectrolyte deposits uniformly around the gold nanoparticles. This coating serves as a primer for further coating of these particles with polyelectrolytes and/or TALH. The shell thickness of the (PDADMAC/PSS)-coated MDS-capped gold particles (*in vacuum*) from the TEM images, as shown in Figure 2A, was found to be ca. 4 ± 1 nm. Figure 2B shows a representative TEM image of the core–shell gold–titania nanoparticles obtained by exposing PDADMAC/PSS/PDADMAC-coated MDS-capped gold nanoparticles to TALH, followed by hydrolysis. A shell thickness of $\approx$10 nm was measured. High-resolution TEM analysis of the shell (Figure 2C), obtained after hydrolysis of TALH, showed the presence of connected, crystalline titania nanoparticles with a measured lattice spacing of 0.350 nm, assigned to the (110) plane of the anatase phase (expected 0.352 nm).

One of the important prerequisites for employing layer-by-layer self-assembly of oppositely charged polyelectrolytes for the formation of polymer multilayers is that charge reversal is obtained with each adsorption step.[33] The ζ-potential for gold nanoparticles coated with three layers of polyelectrolytes (PDADMAC/PSS/PDADMAC) was found to reverse from +20 to −30 mV on complexation with TALH.[34] Studies show that TALH complexes electrostatically with PDADMAC, allowing the formation of TALH/PDADMAC multilayers.[35] The addition of TALH (0.1 mL of 5 wt %) solution to PDADMAC (0.1 mg mL^{-1} in 1 mL of water) was found to sediment PDADMAC, further verifying that TALH binds to PDADMAC. The large increase in thickness (5 nm) on adsorption of TALH can, in part, be attributed to the deposition of oligomers from solution.[35] TALH was also deposited onto sulfonated gold particles coated with a *single layer* of PDADMAC. The shell thickness, as measured by TEM (Figure 2D), is larger (16 vs 10 nm) compared with the particles coated with TALH in the presence of the PDADMAC/PSS/PDADMAC trilayer. This difference in thickness obtained could be due to the fact that a greater number of positively charged (amino) groups of PDADMAC are available for complexation by TALH for gold particles coated with a single PDADMAC layer (compared with the three-layer-coated particles). PDADMAC in the three-layer-coated particles will have many of its charged groups electrostatically compensated by the negatively charged groups of PSS.[36] It is important to note that although the thickness of the shell is higher in the case where PDADMAC-coated particles were used, the three-layer-coated particles provided a better surface for obtaining a more uniform TALH coating, as can be seen from the TEM images (Figures 2B and 2D). Previous studies on the deposition of thin films of titanium dioxide on flat substrates using TALH show that the presence of sulfonic acid end groups on the substrate promote heterogeneous nucleation of titanium dioxide.[23] Control experiments, however, showed that TALH does not bind to MDS-capped gold particles or to polyelectrolyte-coated gold particles with PSS as the outer layer. No shift in the peak plasmon absorption was found for bare gold nanoparticles exposed to TALH solution, suggesting no coating was obtained.

In summary, it has been shown that core–shell gold–titania nanoparticles can be obtained by an approach based on complexation of a titania precursor TALH with a positive polyelectrolyte, followed by hydrolysis. Nanoparticle surface charge reversal (from positive to negative) was observed on complexation of TALH with PDADMAC. This could facilitate further loading of TALH onto gold particles via the additional adsorption of PDADMAC followed by complexation with TALH. The shell was found to be comprised of connected titania nanoparticles with the thickness and uniformity of the coating determined mainly by the precoated polymer layers deposited. With control of the hydrolysis of the titanium precursor, this method can be used to increase the thickness of titania surrounding the particles with nanometer-level control. This demonstration is the first of its kind for titania coatings on gold nanoparticles. Future work will concentrate on tailoring the shell thickness as well as coating these particles with other metal oxides, followed by dissolution of the core to pro-

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(34) Electrophoretic mobilities of the coated gold nanoparticles were measured with a Malvern Zetasizer 4 by taking the average of five measurements at the stationary level, as described in ref 36. All measurements were performed in air-equilibrated pure water (pH ~ 5.6) without added electrolyte.

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duce hollow nanospheres with a reactive inner surface. Such hollow spheres could have potential applications in the fields of catalysis[37] and photonic materials.[38]

Acknowledgment. The German Federal Ministry of Education, Science, Research and Technology (BMBF) supported this work as part of its BioFuture research program. We thank Uli Bloeck of the Hahn-Meitner Institute, Berlin, for the high-resolution TEM analysis, Christine Pilz (MPI) for the electrophoresis measurements, and Thierry Cassagneau (MPI) for helpful discussions.

CM011128Y