

# A General Method To Coat Colloidal Particles with Silica

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A general method to coat colloids with silica is described. The amphiphilic, nonionic polymer poly(vinylpyrrolidone) (PVP) was adsorbed to various colloidal particles such as small gold colloids, gold-shell silica-core particles, small and large silver colloids, boehmite rods, gibbsite platelets, and positively or negatively charged polystyrene. After this functionalization the stabilized particles could be transferred to a solution of ammonia in ethanol and directly coated with smooth and homogeneous silica shells of variable thickness by addition of tetraethoxysilane in a seeded growth process. The length of the polymer used strongly influences the stability of the colloids and the homogeneity and smoothness of the initial silica coating. This method is especially useful for colloidal particles that cannot be covered directly with SiO<sub>2</sub> by a Stöber-like growth process. Compared to methods known from the literature for the coating of such particles, this new method is faster and requires neither the use of silane coupling agents nor a pre-coating step with sodium silicate, which is poorly reproducible.

## Introduction

Silica-coated colloidal particles are a class of materials widely used in many fields of colloid and materials science. A wide variety of coating procedures has been developed for these samples. These surface coatings allow manipulation of the interaction potential and make it possible to disperse colloids in a wide range of solvents from very polar to apolar. The so-called Stöber growth<sup>1</sup> of silica shells by addition of tetraethoxysilane to solutions of seed particles in an ethanol/ammonia mixture yields smooth surfaces since the growth takes place on a molecular scale.<sup>2–4</sup> If silica-coated particles are grown further by this procedure, the polydispersity of the particles decreases with  $R^{-1}$ , where  $R$  is the particle radius.<sup>4</sup> This makes it possible to grow crystals of core shell particles even when the cores are polydisperse.

Silica colloids and silica-coated particles are often used as model particles to study phase behavior, rheology, and diffusion. Surface modifications of silica spheres have yielded systems with hard-core potentials,<sup>5</sup> short-range attractive potentials,<sup>6</sup> and Yukawa potentials.<sup>7</sup>

In addition, the silica layer allows for controlled placement of various dyes.<sup>8</sup> Such dye-labeled particles can be used in quantitative real-space studies with confocal

fluorescence microscopy<sup>9</sup> or as tracer particles in, for example, fluorescence recovery after photobleaching (FRAP)<sup>10</sup> or time-resolved phosphorescence anisotropy<sup>11</sup> measurements. Moreover, the possibility of the placement of dye molecules with nanometer precision allows the study of the local density of states in photonic applications.<sup>12</sup>

Interest in the use of silica-coated particles as building blocks for photonic crystals is increasing.<sup>13–16</sup> Here the outer silica shell allows tuning of not only the interaction potential of the particles but also the optical properties of the crystal.

An outer silica coating also offers new possibilities for the shape control of a particle. Silica particles can be anisotropically deformed in a controlled way by ion beam irradiation.<sup>17</sup> This method was successfully applied to silica-coated gold particles.<sup>17</sup> Due to deformation of the silica shell it was possible to deform spherical gold particles into prolate colloids in a controlled way, while normally gold particles remain unchanged under these conditions.

There are many surfaces that can be directly coated with silica because of the significant chemical affinity of these materials, like clay minerals,<sup>18</sup> hematite,<sup>19</sup> zirconia, and titania.<sup>20</sup> However, many other surfaces can only be coated with the help of stabilizers, surfactants, silane coupling agents, or a fast precipitation from a water glass

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solution, and most of these coating methods are multistep processes. For instance, in procedures using mercapto- or aminosilanes as coupling agent gold colloids,<sup>21</sup> silver colloids,<sup>22</sup> and semiconductor nanocrystals<sup>23,24</sup> could be coated with silica.

A critical step in many silica-coating procedures is the transfer of colloids that are only stable in aqueous solution to ethanol where the classical Stöber process is performed. A widely used technique to achieve this transfer is the water glass process.<sup>18,21,25</sup> First, colloidal particles are covered with a thin layer of sodium silicate in aqueous solution. If the particles are then sufficiently stabilized, they can be transferred into ethanol and be further coated with a thicker silica layer using seeded growth. In this way boehmite rods could be coated with silica via a three-step coating procedure.<sup>25</sup> Such a step was also necessary for the coating of gold and silver colloids via the use of silane coupling agents. A disadvantage of this method is that the growth of the initial shell with sodium silicate is strongly pH dependent and not very well controllable. The formation of such an initial silica coating on gold colloids requires reaction times between 24 h and several weeks<sup>14,21,26,27</sup> before a sufficiently thick shell for transfer of the particles into ethanol is achieved.

In this paper we present a general, simple and fast method to coat colloids with silica. This method is based on the use of poly(vinylpyrrolidone) (PVP) as a coupling agent. This amphiphilic, nonionic polymer is widely used in science and technology and adsorbs onto a broad range of different materials such as metals (e.g., gold, silver, iron), metal oxides (kaolinite, TiO<sub>2</sub>, iron oxide, alumina),<sup>28</sup> polystyrene,<sup>29</sup> silica,<sup>30</sup> graphite,<sup>31</sup> and cellulose.<sup>32</sup> It stabilizes colloidal particles in water and many nonaqueous solvents. In this article we show how PVP can be adsorbed onto various colloids which can then be directly transferred into an ammonia/ethanol mixture where smooth and homogeneous silica coatings of variable thickness can be grown by addition of tetraethoxysilane (TES). Further, we show that the length of the PVP used plays an important role in the stability of the particles during the growth process and the smoothness and homogeneity of the silica shells obtained.

## Experimental Section

**Materials.** Tetraethoxysilane (TES,  $\geq 98.0\%$ ) was obtained from Fluka. Poly(vinylpyrrolidone) with average molar masses of 360 kg/mol (PVP-360), of 40 kg/mol (PVP-40), and of 10 kg/mol (PVP-10) was purchased from Sigma-Aldrich. Poly(vinylpyrrolidone) with an average molar mass of 3.5 kg/mol (PVP-3.5) was obtained from Acros Organics. Ethanol (p.a.), acetone (p.a.), ammonia (29.3 wt % NH<sub>3</sub> in water), and hydrofluoric acid (38–40%) were purchased from Merck. All chemicals were used as received. Water used in the described reactions and for cleaning

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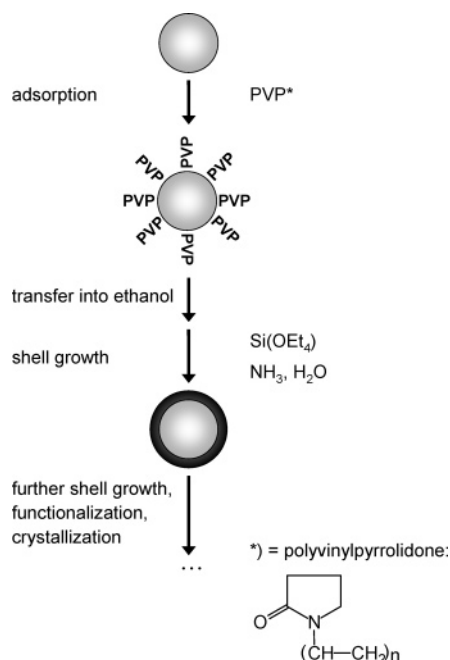
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**Figure 1.** Diagram of the general procedure for the coating of colloids with silica. In the first step poly(vinylpyrrolidone) is adsorbed onto the colloidal particles. Then these stabilized particles are transferred into a solution of ammonia in ethanol. A silica shell is grown by consecutive additions of tetraethoxysilane.

of the glassware was obtained from a water purification system, WATER PRO PS from Labcono, and had a measured resistivity of 2 M $\Omega$ .

**Syntheses.** The general procedure to coat colloids with silica consist of two steps: adsorption of PVP and growth of the silica shell after transfer of the particles to ethanol. An outline of the synthesis is shown in Figure 1. *Synthesis of the Colloids.* Small gold colloids of 7 and 19 nm radius were synthesized according to the standard sodium citrate reduction method<sup>33,34</sup> and were not further purified. Silica particles (228 nm radius) with a 38 nm thick gold shell were prepared as described in ref 14 and purified by repeated sedimentation and redispersion in water. Small silver particles of 13 nm radius were synthesized by a modified polyol process:<sup>35</sup> Silver nitrate was reduced in ethylene glycol in the presence of PVP-10. After the synthesis, the particles were separated from ethylene glycol by addition of acetone (500 mL of acetone/75 mL of reaction mixture) and subsequent centrifugation at 600g as described in ref 35. Next, the supernatant was removed and the particles were redispersed in ethanol, again centrifuged at 600g, and redispersed in a solution of ammonia in ethanol (4.2 vol % ammonia (29.3 wt % NH<sub>3</sub> in water) in ethanol). This solution ( $c = 0.31$  g/L) could be directly used in the silica-coating step (see below). Large silver colloids of 320 nm radius were synthesized by reducing silver nitrate with ascorbic acid in the presence of the polymeric stabilizer gum arabic<sup>36</sup> and purified by repeated sedimentation and redispersion in water. Boehmite rods and gibbsite platelets were prepared from aqueous aluminum oxide solutions by hydrothermal treatment at 85 °C (gibbsite) and at 150 °C (boehmite) and purified by dialysis against demineralized water as described in refs 37 and 38.

Cationic polystyrene spheres were prepared by surfactant-free emulsion polymerization as described in ref 39 and anionic sulfate stabilized polystyrene spheres as described in ref 40.

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Table 1. Coating with Silica

sample	radius [nm]	colloid solution		PVP solution			centrifugation $s^f$ [g]	(EtOH)/NH <sub>3</sub> <sup>a</sup> V [mL]	TES <sup>b</sup> V [ $\mu$ L]
		c <sup>c</sup> [g/L]	V <sup>d</sup> [mL]	M <sub>w</sub> <sup>e</sup> [kg/mol]	c [g/L]	V [mL]			
gold colloids	7	0.098	40.00	10	25.6	3.45	600	6.57	66.3
gold colloids	19	0.058	34.70	10	25.6	0.65	60	1.97	19.9
gold-shell silica-core particles	266	1.43	30.00	40	110.0	2.11	1	58.50	261.0
small silver colloids	13			10				9.90	100.0
large silver colloids	320	4.72	5.00	40	9.5	8.7	1	8.63	87.2
boehmite rods	5 <sup>g</sup>	9.08	0.55	10	10	99.45	500	40.59	410.0 <sup>h</sup>
gibbsite platelets	167 <sup>i</sup>	8.00	2.00	40	34	198.00	200	138.60	1400.0
cationic polystyrene colloids	186	0.41	4.75	360	7.0	4.75		0.25	500
	386	18.97	4		7.6	4		0.33	1500
anionic polystyrene colloids	170	5.40	4	360	6.5	4		0.33	500

<sup>a</sup> Ammonia (29.3 wt % NH<sub>3</sub> in water; polystyrene spheres) or solution of 4.2 vol % ammonia (29.3 wt % NH<sub>3</sub> in water) in ethanol. <sup>b</sup> TES solution (10 vol % in ethanol). <sup>c</sup> Concentration. <sup>d</sup> Total volume. <sup>e</sup> Molecular mass of poly(vinylpyrrolidone). <sup>f</sup> Acceleration. <sup>g</sup> Length 121 nm. <sup>h</sup> Stepwise addition over 6 h (see Experimental Section). <sup>i</sup> Height 10 nm.

**Coating with Silica.** The reaction vessels used in the silica-coating step were cleaned with hydrofluoric acid (8 vol %) and after that rinsed several times with water. All reaction steps with gold or silver colloids were carried out under exclusion of light.

**Functionalization with PVP.** The molar mass of the PVP used in this step depends on the size of the particles used and is given in Table 1. The concentration and amounts of the colloidal solution are also given in Table 1.

The amount of PVP was calculated to provide the colloids with about 60 PVP molecules per nm<sup>2</sup> surface, independent of the molar mass of the PVP (Table 1). The PVP was dissolved in water by ultrasonication of the solution for 15 min. Subsequently, the PVP and the colloidal solutions were mixed under stirring (600 rpm in the case of the gold and silver colloids and 100 rpm in the case of the boehmite rods and the gibbsite platelets.). To guarantee that adsorption was complete, the reaction mixture was stirred for 24 h at room temperature.

The polystyrene particles were already in an ethanol solution. These particles were sedimented, the supernatant was removed, and a solution of PVP in ethanol was added. Because of the large size of the PVP (PVP-360) used for these particles, the chosen PVP concentrations were lower in relation to the total surface area. These solutions were directly used for the silica-coating step.

**Transfer into Ethanol.** To transfer the PVP-stabilized particles into ethanol, the solutions were centrifuged or sedimented (see Table 1) and the supernatant was removed.

**Synthesis of the Silica Shell.** The sediments were redispersed in a solution of ammonia in ethanol (4.2 vol % ammonia (29.3 wt % NH<sub>3</sub> in water) in ethanol). In the case of the polystyrene spheres, ammonia (29.3 wt % NH<sub>3</sub> in water) was added to the PVP polystyrene solutions. Immediately after this a TES solution (10 vol % in ethanol) was added under stirring (600 rpm in the case of the gold and silver colloids and 100 rpm in the case of the boehmite rods and the gibbsite platelets). In the case of the boehmite rods the TES solution was added in four steps over 6 h (first 51.25  $\mu$ L of TES was added, after 2 h again 51.25  $\mu$ L, after 4 h 102.5  $\mu$ L, and after 6 h 205  $\mu$ L). The total amount of TES added was chosen depending on the desired thickness of the silica shell. The reaction mixtures were then stirred for another 12 h.

**Characterization.** TEM. Samples for transmission electron microscopy (TEM) were prepared by dipping copper 400-mesh carrier grids covered with carbon-coated Formvar films in the dispersions ( $c \approx 0.5$ – $5$  g/L). The boehmite, gibbsite, and polystyrene particles were imaged with a Philips Tecnai 20 FEG high-resolution transmission electron microscope (HRTEM) operated at 200 keV. All other colloids were imaged with a Philips Tecnai 12 transmission electron microscope operated at 120 keV.

The size of the colloids was determined with the measurement tools of the Analysis software provided with the Philips Tecnai microscopes by binarization of the images, separation of the particles by standard image analysis techniques, and estimation of the mean particle radius from the measured surface area. A diffraction grating was used to calibrate the magnification.

SEM. Scanning electron microscopy (SEM) was used to study the positively and negatively charged polystyrene spheres and the silica-coated gold shell silica core particles. Samples were prepared by dropping a dilute dispersion ( $c \approx 0.05$ – $0.005$  g/L) on a silicon substrate (used as received). Colloidal crystals of silica-coated gold-shell silica-core particles were obtained by putting an ethanolic solution of these particles ( $c = 1.43$  g/L) on a silicon wafer and drying in air. The measurements were carried out with a Philips XL30SFEG scanning electron microscope.

EDX. To determine the elemental composition of the particles studied during electron microscopy measurements, an energy-dispersive X-ray (EDX) detector from EDAX was used together with the HRTEM or SEM. For the measurements in combination with the HRTEM, the same samples were used as for the TEM imaging. For the measurements in combination with the SEM, diluted colloidal dispersions ( $c \approx 5$  mg/L) were dropped onto an aluminum substrate (cleaned with acetone) to give well-separated particles on the surface.

## Results and Discussion

**Coating of Small Gold Colloids and Influence of the Polymer Length.** A detailed discussion of our method is presented for the coating of small gold particles, because under many conditions silica cannot be grown directly on such particles.

We began by trying a number of alternative methods described in the literature. The growth of silica shells on colloidal particles based on the method of Stöber et al.<sup>1</sup> is usually performed in an ethanol/ammonia mixture. If the total surface area of the seed particles per volume is large enough compared to the added amount of TES, the formation of new silica particles can be completely suppressed and therefore the thickness of the silica shell can be precisely controlled by the added amount of TES.<sup>2,4,41,42</sup> For gold particles made by the standard sodium citrate reduction method,<sup>33,34</sup> we found it not possible to coat them directly in this way with silica. In this case large aggregates of uncoated gold particles and silica are formed. However, recently a method was reported to grow a silica shell directly onto gold particles by addition of TES to a diluted 2-propanol solution.<sup>43</sup> We found that this procedure was not applicable to citrate-stabilized particles.

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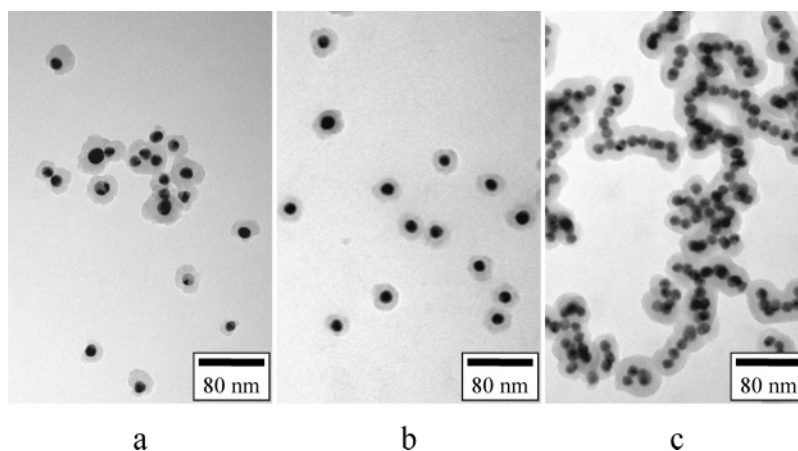
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**Figure 2.** TEM pictures of gold particles (7 nm radius) coated with silica after functionalization with PVP-40 (a), PVP-10 (b), or PVP-3.5 (c).

With the procedure of ref 43, only some of the gold colloids and most of these particles were coated. Also, a lot of new silica particles were formed. It is possible that on the surface of the particles used in ref 43 a polymeric stabilizer was present on the particles, but the supplier of the colloids (Ted Pella, Inc.) did not provide this information. Liz-Marzan et al.<sup>21</sup> developed a method to coat citrate-stabilized gold particles with silica using the silane coupling agent (3-aminopropyl)trimethoxysilane as a primer to reach a higher affinity of the gold surface to silica. After the formation of a thin silica layer in aqueous solution from sodium silicate, the particles were transferred into ethanol for further growth using the Stöber method. In this way, homogeneously coated gold particles could be obtained. However, in this synthesis the gold particles easily aggregate during the transfer to ethanol if the initial silica shell grown in water is not thick enough.

To achieve both a stabilization of the gold colloids during the shell growth and a higher affinity of the gold surface to silica, poly(vinylpyrrolidone) of different molar masses (3.5, 10, and 40 kg/mol) was adsorbed onto the particles. Poly(vinylpyrrolidone) (PVP) (see Figure 1) is an amphiphilic polymer that is soluble in water and many nonaqueous solvents.<sup>44,45</sup> This behavior arises from the presence of a highly polar amide group within the pyrrolidone ring and apolar methylene and methine groups in the ring and along its backbone.<sup>29</sup> Due to its amphiphilic character it can be adsorbed onto many different surfaces.

After 24 h of stirring in the presence of PVP, the particles remained not visibly changed after sedimentation by centrifugation. This could be shown by electron microscopy and UV-vis spectroscopy. To achieve complete dissolution of the PVP in the aqueous solution and a homogeneous coating of the gold colloids, it is important to homogenize the polymer solution by ultrasonication before it is added to the colloid solution. Otherwise the silica coatings were observed to be less homogeneous as shown by TEM measurements. Redispersion of the gold colloids in a mixture of ammonia and ethanol (gold particle concentration 0.59 g/L) also gave no loss of particle stability, contrary to the citrate-stabilized spheres. To these solutions a diluted TES solution was added, and in all three cases after that the gold particles were covered with silica (see Figure 2).

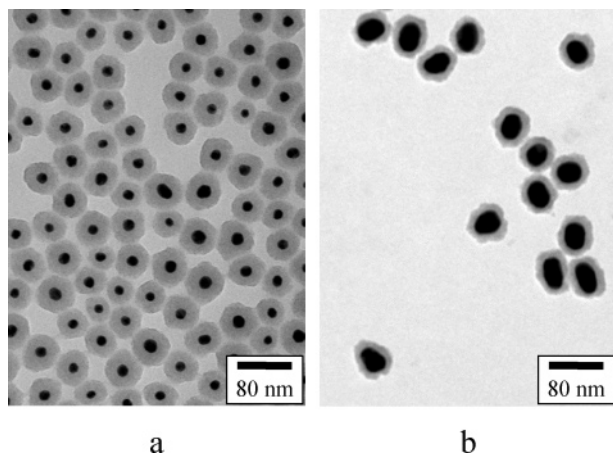
The PVP makes the affinity of the gold surface to silica sufficiently high, so that no coupling agent is necessary.

For all three chain lengths practically no secondary nucleation of small silica colloids was observed, because the total particle surface per volume was sufficiently high (see ref 42). In the case of the particles stabilized with the longer polymer, mostly single gold colloids covered with a silica shell were found (see Figure 2a for PVP-40 and Figure 2b for PVP-10). However, the particles stabilized with PVP-3.5 form silica-covered aggregates of several gold particles (see Figure 2c). Apparently, the shorter polymer cannot sufficiently stabilize the particles during the growth of the silica shell, possibly because it does not sufficiently shield the large van der Waals forces between these particles. The comparison of Figure 2a and Figure 2b shows a second important influence of the length of the polymer used: while the particles coated with PVP-10 have a relatively smooth and homogeneous coating thickness of the silica layer (see Figure 2b), the particles coated with PVP-40 have a much more inhomogeneous coating thickness and some particles with multiple gold cores are observed (see Figure 2a). The sizes of the larger two adsorbed polymers are comparable to the size of the gold colloids ( $r = 7$  nm) and the thickness of the silica shell (about 10 nm); e.g., in water the hydrodynamic radius of PVP-10 is 4 nm and that of PVP 40 is 8 nm (from ref 29). The silica coating of the PVP-3.5 coated gold colloids is also smooth and everywhere is of the same size. The results obtained for the different PVP lengths show that the silica is growing directly onto the adsorbed polymer. If a polymer is used that is very large compared to the colloid radius (such as PVP-40), sometimes particles appear to be only partially coated with silica (see Figure 2c), so in this case the particles are not sufficiently stabilized by an outer silica layer during the conditions of the Stöber growth and grow together with other particles. This explains why some aggregation is observed despite the fact that a large polymer was used. The use of PVP with an average molar mass of 10 kg/mol appears to be an optimum for this size of particles, because it provides sufficient steric stabilization of the colloids to avoid aggregation during the silica shell growth, but it is on the other hand small enough to form a relatively homogeneous layer onto colloids of this size to obtain a smooth silica coating.

It should be noted that the PVP functionalized colloids should not be stored too long in water (less than 2 days) before the silica shell is grown. If the particles are stored for a longer time, the silica coatings become less complete and some particles remain uncoated. Three weeks after the initial polymer coating it is not possible to grow any

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**Figure 3.** TEM pictures of gold particles coated with silica. (a) Gold particles (7 nm radius, polydispersity 15%) with an 18 nm shell (total polydispersity 9%) grown by two additions of TES. (b) Gold particles (20 nm radius, polydispersity 12%) with 12 nm shell (total polydispersity 9%).

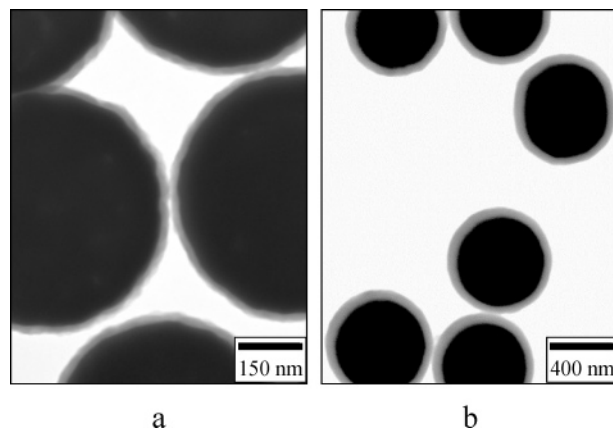
silica shell on the gold colloids. The reason for this is probably a slow decomposition of PVP.

Thicker silica shells could be grown by repeated addition of TES to the solution of the silica-covered gold colloids (with PVP-10 adsorbed onto the gold colloids before the shell growth) (see Figure 3a). With increasing silica shell thickness the polydispersity decreases. (For a 9 nm thick shell (Figure 2b) the polydispersity is 13% and for a 18 nm thick shell (Figure 3a) the polydispersity is 9%. The polydispersity of the gold cores is 15%.) This has been reported before for the seeded growth of pure silica particles.<sup>4</sup> This effect is important if metal particles are to be used as building blocks for photonic crystals.

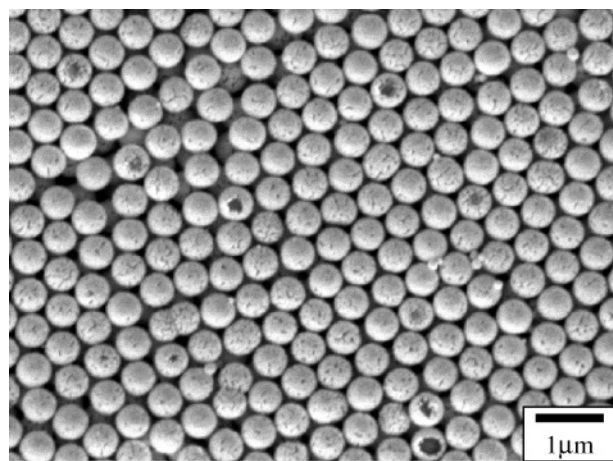
Figure 3b shows particles with a 20 nm radius gold core coated with a smooth silica shell using the same procedure.

**Other Noble Metal Particles.** To grow photonic crystals of gold-shell silica-core particles with a high volume fraction, an outer silica shell is indispensable to reduce strong attractive interparticle forces.<sup>14</sup> A method to coat such particles consisting of a water glass coating step in water and a further silica shell growth in ethanol similar to the method of Liz-Marzan et al.<sup>21</sup> to coat small gold colloids was already described in ref 14. The gold shell of these particles was made not by the citrate method but by reduction of HAuCl<sub>4</sub> with hydroxylamine onto small gold clusters (made by reduction of HAuCl<sub>4</sub> with tetrakis(hydroxymethyl)phosphonium chloride) attached onto the silica spheres. Due to the different stabilization of these particles, no initial coating with 3-aminopropyltrimethoxysilane (APS) is necessary for a water glass coating. As mentioned above, the growth of sodium silicate is not well controlled. Despite the fact that these particles are also stable in ethanol, no shell growth was observed by direct Stöber coating experiments with TES.

To coat these particles with silica, a longer PVP (PVP-40 or PVP-360) was adsorbed onto the particles because of their much larger size (266 nm radius). This step was carried out at a lower TES concentration (1.99 mM instead of 4.48 mM) to prevent aggregation of the particles during the growth of the initial silica shell. At higher TES concentrations some of the particles grew together during the formation of the silica shells regardless of the length of the polymer used. Because of the less favorable TES to surface area ratio as compared to the smaller gold particles, secondary nucleation of small silica particles (less than 20 nm radius) was observed. However, due to the much larger radius and much higher density of the



**Figure 4.** TEM pictures of silica particles (228 nm radius) with a 38 nm thick gold shell (total polydispersity 4.4%), which have been coated with an outer silica shell of  $21 \pm 2$  (a) or  $60 \pm 6$  nm (b) thickness. Due to the gold shell the silica core cannot be observed.

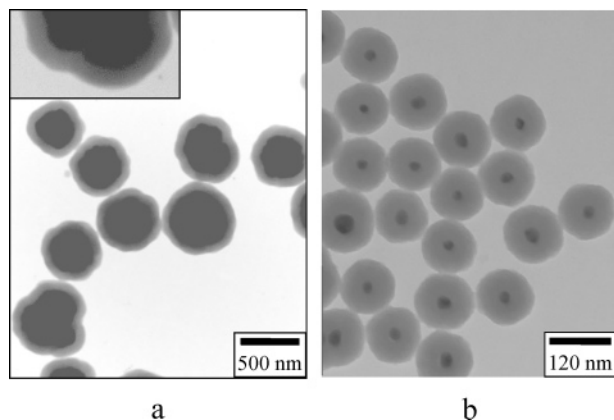


**Figure 5.** SEM picture of silica particles (228 nm radius) with a 38 nm gold shell and an outer silica shell of 10 nm thickness (total polydispersity 4.4%) dried from ethanolic solution on a silicon wafer.

gold-shell silica-core particles ( $8.3 \text{ g/cm}^3$  respectively  $2 \text{ g/cm}^3$ ), these newly formed particles could be easily removed by repeated sedimentation and redispersion. The initially relatively thin silica shell (about 10 nm) could be grown further by repeated addition of TES (see Figure 4). These further growth steps were carried out at a higher particle and TES concentration to prevent further secondary nucleation. Aggregation of the particles during these further growth steps was not observed due to shielding of the gold-gold van der Waals forces by the silica layer.

The silica layer stabilizes the particles. Because of their low polydispersity (4.4%), the silica-coated gold-shell silica-core particles form large crystals in solution or when they are dried from ethanol onto a silicon wafer (see Figure 5). Uncoated gold shell particles form crystals in solution but aggregate during the drying process before they can form an ordered structure.

Because of their low bulk absorption, silver colloids are the most suitable metal particles for the creation for photonic crystals with a band gap in the visible.<sup>16</sup> For the synthesis of crystals with a high volume fraction of metal particles, it is necessary to tune the particle surface potential, which can easily be achieved by coating them with an outer silica layer. Under certain conditions silver particles can be directly coated with silica if they are

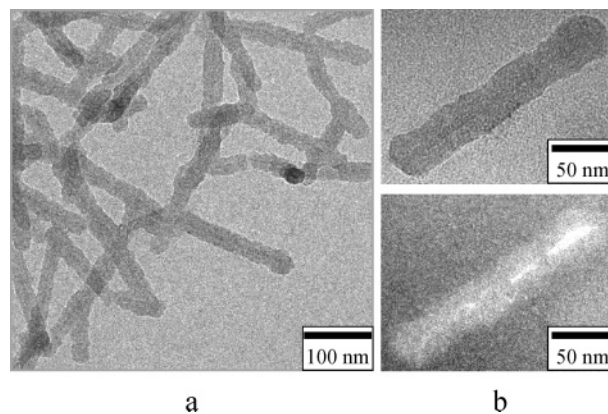


**Figure 6.** TEM pictures of large silver particles (320 nm radius, polydispersity 15%) with  $80 \pm 12$  nm silica shell (a; the inset shows an enlarged part of one of the silica coated particles) and of small silver particles (13 nm radius, polydispersity 23%) with a 47 nm silica shell (total polydispersity 5.9%) (b).

stabilized by organic surfactants.<sup>46</sup> However, as for gold particles this is not possible. Procedures for coating silver particles with silica based on the use of a silane coupling agent and a pre-coating with sodium silicate similar to those mentioned above for small gold colloids have been described.<sup>22</sup>

Large silver colloids prepared by the reduction of silver nitrate with ascorbic acid in the presence of the polymeric stabilizer gum arabic can be coated directly with silica in ethanol; however, the reaction is not very well controllable and most of the particles aggregate during shell formation.<sup>19</sup> Furthermore, it turned out that if the particles were cleaned once by centrifugation or sedimentation in water, more than 95% of the particles remained uncoated during a Stöber growth process, very probably because most of the gum arabic was removed from the colloidal surface. If PVP-40 was adsorbed onto these particles, all of them were coated with a smooth silica layer (see Figure 6a). In contrast to the unpurified particles with gum arabic adsorbed onto their surface, nearly no aggregates were formed during this reaction. Because the large silver colloids are formed through the aggregation of smaller ( $\leq 20$  nm) subunits, the surface roughness is on the order of about 10 nm. As shown in Figure 6a, the surface became smoother due to the outer silica layer.

The polyol process<sup>47,48</sup> is a widely used synthesis method for various metal colloids<sup>49</sup> in high concentration in organic solution. In a variant of this method PVP is already used during the synthesis of metal colloids such as nickel,<sup>50</sup> copper,<sup>51</sup> gold,<sup>52</sup> silver,<sup>35</sup> platinum, palladium, and ruthenium<sup>53</sup> as a reductor and stabilizer. The PVP added in this synthesis can be also used for coating with silica: For the coating of silver colloids of 13 nm radius prepared by such a polyol process,<sup>35</sup> the PVP present has a suitable molar mass (PVP-10) for the direct growth of a smooth



**Figure 7.** (a) HRTEM pictures of boehmite rods (thickness 9 nm, length 120 nm, length polydispersity 38%) coated with a 10 nm thick silica layer. (b) Bright field image (top) and dark field image (bottom) of the same rod.

silica shell onto these particles (see Figure 6b). The combination of the polyol process with the silica-coating method presented here opens a simple and quick way to obtain well-defined silica-coated metal colloids.

**Coating Metal Oxide Colloids with Silica.** Here we describe two examples of anisotropic metal oxide particle systems that cannot be directly coated with silica. A laborious method to coat boehmite rods with silica was already developed by van Bruggen.<sup>25</sup> This procedure comprises one sodium silicate step in water, because untreated boehmite rods are not stable in ethanol, and then two further coating steps in ethanol, because also the pre-coated particles aggregate very easily.

After stirring for 24 h in an aqueous PVP-10 solution, boehmite rods (thickness 9 nm, length 120 nm, length polydispersity 38%) are already stable in ethanol. Centrifugation and the transfer into the ethanol/ammonia solution also did not influence the stability of the particles. To coat the rods with silica, a TES solution was added in four portions to the particles under mild stirring. In this way boehmite rods were directly coated with a smooth  $10 \pm 2$  nm thick silica layer (see Figure 7). Practically no secondary nucleation was observed under the conditions chosen. To show more clearly the core shell structure of the coated rods, a single rod was imaged with HRTEM in bright field mode (Figure 7b, top) and in dark field mode (Figure 7b, bottom). In dark field mode a beam diffracted by a correctly oriented crystal is used to form the image. Therefore, the amorphous silica shell and all parts of the boehmite core, which do not have the correct crystal orientation, stay dark while the oriented crystalline core appears bright.

A method to coat hexagonal gibbsite platelets with silica has not been published. Like boehmite rods gibbsite platelets flocculate in ethanol, so a direct coating with silica is not possible. With a PVP-10 coating the platelets (10 nm thickness, 167 nm radius, radius polydispersity 53%) could be redispersed in an ethanol/ammonia mixture. However, after the growth of a smooth silica shell of about 8 nm thickness, some of the platelets were grown together. As was the case for the small gold particles (see above), it turned out that when a longer PVP was chosen (PVP-40) aggregation could be prevented under the same reaction conditions, while a smooth and homogeneous silica coating was still obtained (see Figure 8). Because of the larger size of the gibbsite platelets (167 nm radius) compared to the gold colloids (7 nm radius), a longer poly(vinylpyrrolidone) (PVP-40 instead of PVP-10) was re-

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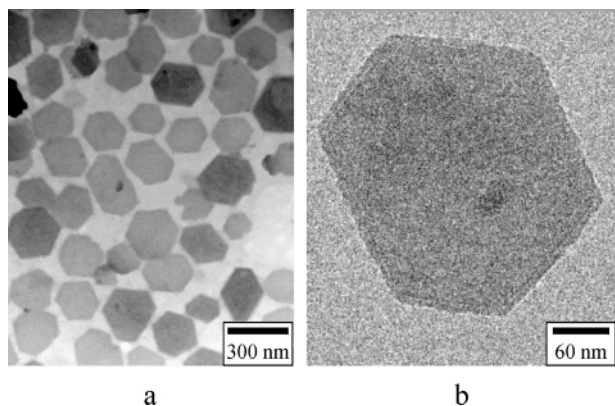
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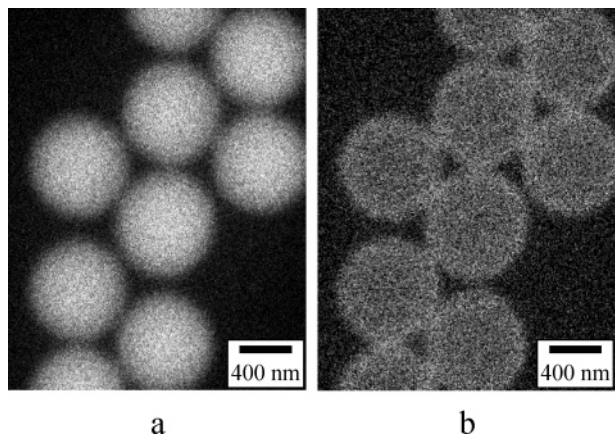
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**Figure 8.** TEM picture of gibbsite platelets (167 nm radius, polydispersity 53%) with  $10 \pm 2$  nm thick silica shells (a) and HRTEM-picture of a single silica coated gibbsite platelet (b).

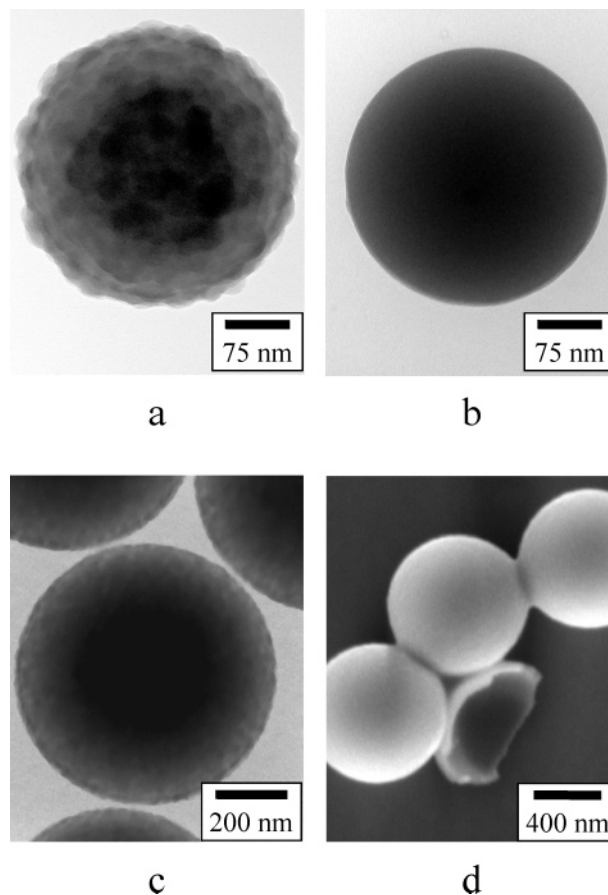


**Figure 9.** EDX image (elementary composition as a function of position) of cationic polystyrene spheres (386 nm radius, polydispersity 2.6%) with a 32 nm silica shell (total polydispersity 2.4%). In (a) the carbon content ( $K\alpha$  line) and in (b) the silicon content ( $K\alpha$  line) per pixel is imaged. A lighter color corresponds to a higher number of counts.

quired in this case to obtain sufficient stability during the shell growth process.

**Coating of Positively and Negatively Charged Polystyrene Spheres with Silica.** To test the generality of our method, we also coated a surface that is in part hydrophobic. For this we chose polystyrene particles. Such particles can be prepared by various methods. Here we used two different emulsifier-free emulsion polymerization synthesis procedures resulting in colloidal particles with positively<sup>39</sup> or negatively charged groups on the surface<sup>40</sup> resulting from the initiator. Here the PVP adsorption steps and the silica-coating steps were carried out in ethanol. The coverage of the particles with a silica layer could be proven for both systems by analyzing the elementary composition of the colloids with EDX. The results for large positively charged polystyrene spheres (386 nm radius) are shown in Figure 9. Similar results were obtained with small positively (186 nm radius) and negatively charged polystyrene spheres (170 nm radius). While the carbon content is maximal in the center of the particles (see Figure 9a), the silicon content is maximal at the edge (see Figure 9b), demonstrating the presence of the coating.

For three different systems of polystyrene (168 nm radius and large 386 nm radius for positively charged polystyrene spheres and 170 nm radius for negatively charged), a PVP polymer relatively large compared to the particle size (PVP-360, hydrodynamic diameter (in water<sup>29</sup>) = 46 nm) was used to functionalize the surface. For



**Figure 10.** TEM pictures of a cationic polystyrene sphere (186 nm radius) with 22 nm silica shell (a), an anionic polystyrene sphere (170 nm radius) with 10 nm silica shell (b), and cationic polystyrene spheres (386 nm radius) with 32 nm silica shell (c). (d) SEM picture of particles with the same core size as in (c) with a piece of a silica shell broken off a particle.

the smaller positively charged polystyrene particles this results, as already observed for the small gold colloids, in a relatively rough silica coating (see Figure 10a). In contrast with this result, the negatively charged polystyrene particles of nearly the same size have a smooth silica coating (see Figure 10b). These findings are in good agreement with the results of Smith et al.<sup>29</sup> for the adsorption on negatively charged polystyrene in water. According to the photon correlation spectroscopy measurements presented in ref 29, the adsorbed layer thickness was only 1–3 nm for molar masses of PVP between 10 and 2500 kg/mol, indicating that the molecules were lying flat on the surface in the form of trains. For other types of colloids (gold colloids, positively charged polystyrene) it is more likely that the polymer is not adsorbed flat onto the gold colloids but is adsorbed more in the form of coils, so that here the shorter the polymer the more homogeneous is the obtained silica layer. For the larger positively charged polystyrene, the size of the polymer used is relatively small compared to the total particle size. Thus, here the silica coverage appears to be relatively smooth (see TEM image (Figure 10c) and SEM image of a part of a silica shell broken off during strong ultrasonification (Figure 10d)).

## Conclusions

We have developed a new and general method to coat colloids with silica. By adsorbing poly(vinylpyrrolidone) (PVP) onto the colloidal surface, particles that are stable in both water and ethanol were obtained. These particles

could be directly coated with a silica layer of variable thickness by addition of tetraethoxysilane (TES) to an ammonia–ethanol solution containing the particles in a seeded growth process. When longer PVP chains were used, the particles were stabilized better. However, the coatings obtained with longer polymers were also less smooth in most cases. An exception was the negatively charged polystyrene particles, probably because in this case even large molecular weights of PVP form only a thin layer.<sup>29</sup>

For colloidal particles between 7 and 320 nm radius optimal PVP lengths were found, which depended on the size of the colloids. At the optimal PVP length stable colloidal particles coated with a smooth and homogeneous silica layer were achieved. Due to the amphiphilic and nonionic character of the polymer used, this new process can be applied to a broad range of colloids and was demonstrated for gold, silver, gibbsite, boehmite, and positively and negatively charged polystyrene. This method is especially useful for particles that cannot be coated directly by a Stöber-like<sup>1</sup> growth process, for instance when the particles are not stable in ethanol or the affinity of the particle surface to silica is too low. Compared to published methods for specific particles,<sup>21,22,25</sup>

our method is faster and requires neither the use of silane coupling agents nor of a poorly reproducible precoating step with sodium silicate.

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