# Size-Controlled Synthesis of Nanoparticles. 1. "Silver-Only" Aqueous Suspensions via Hydrogen Reduction

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A method for size-controlled synthesis of chemically clean silver nanoparticles is proposed and described. The synthesis is based on the reduction of silver(I) oxide by hydrogen gas in water and offers the advantages of being easily scalable and able to produce essentially naked particles still exhibiting long-term stability with the metal surface readily accessible to various chemical modifications. The method allows synthesis of particles of any diameter between 15 and 200 nm simply by varying the reaction time. The addition of filtration and centrifugation techniques produces suspensions of narrow size distribution and relatively high,  $10^{12}$ – $10^{14}$  particles/mL, concentration. The addition of various complexating agents potentially allows control of nanoparticle shape. The nanoparticles were characterized by UV–vis spectroscopy, electron microscopy, and electron and X-ray diffraction techniques.

## Introduction

In the past twenty years, the use of noble metal nanoparticles in various fields of research has increased dramatically. This is undoubtedly due to not only the bulk properties of noble metals such as chemical stability, electrical conductivity, and in some cases high catalytic activity, but also due to the unique optical, electrical, catalytic, and magnetic properties that are a consequence of nanometer dimensions. Silver nanoparticles, in particular, are of great interest because of their ability to efficiently interact with light by virtue of plasmon resonances, which are the collective oscillations of the conduction electrons in the metal. Silver nanoparticles certainly have the potential to be the building blocks of future photonic and plasmonic devices as the field of nanotechnology matures.

A requirement for this progress is the development of a method that can reliably produce large quantities of silver nanoparticles of narrow and controlled size distribution. Undoubtedly, different applications will require particles of various dimensions and the ability to tailor surface chemistry. The ideal method of synthesis should yield essentially naked particles so that different surface functionalities can be readily introduced for template-assisted or self-assembly based fabrication methods for nanoscale devices.

Over the years, many methods for the synthesis of silver nanoparticles have been implemented. These methods can be divided into several categories. The first is various modifications to either the Creighton method, which employs the reduction of silver nitrate by sodium borohydride,<sup>1</sup> or the Lee–Meisel method, which is generally considered to be the reduction of silver nitrate with sodium citrate, although several methods were originally suggested in their paper.<sup>2</sup> AgNO<sub>3</sub> <sup>1-15</sup> is the most common source of silver ions although Ag<sub>2</sub>SO<sub>4</sub>,<sup>2</sup> silver 2-ethylhexonate,<sup>16</sup> and silver perchlorate<sup>17</sup> have also been used. NaBH<sub>4</sub>,<sup>1,2,5–8,17</sup> sodium citrate,<sup>1,2,15</sup> ascorbic acid,<sup>4,10</sup> DMSO,<sup>16</sup> hydrazine dihydrochloride,<sup>9,11</sup> potassium bitartate,<sup>12</sup> ethanol, pyridine, DMF,<sup>13</sup> and poly(ethylene glycol)<sup>14</sup> have all been used

as reducing agents, to name a few. The monovalent silver ion has a large reduction potential, 0.7996 V,<sup>18</sup> and can be easily reduced by many different organic and inorganic compounds. While many methods do not suggest the use of additional protecting agent, those touting long-term stability often employ surfactants, such as NaAOT,<sup>5,19</sup> CTAB,<sup>20</sup> and Daxad 19,<sup>4</sup> sodium citrate,16 various thiols,6,8 gum Arabic,10 PEG,14 and poly(Nvinyl-2-pyrrolidone)<sup>12,13</sup> to protect the particles from aggregation. Stabilizers such as NaAOT,<sup>19,22</sup> CTAB,<sup>20</sup> and PVP<sup>21</sup> have also been effectively used to direct the aspect ratio of the particles producing plates and rods and other shapes, although a recent report indicates that such stabilizers are not necessary to produce rod particles with very high aspect ratios.<sup>15</sup> In general, all of the above methods produce mainly small particles, although very careful control of the reducing environment and stabilizer concentration makes it possible to synthesize larger particles as well.

Another category entails impinging high-intensity electromagnetic radiation on a system to either ablate particles from a metal target surface<sup>23</sup> or to stimulate the photoreduction of a silver salt.<sup>24,25</sup> A recent report suggests that irradiation with light allows further manipulation of particle size and shape through the selective plasmon excitation after the initial reduction step.<sup>26</sup> Silver particles can also be prepared by vacuum deposition of the metal. Particle size and shape can be controlled by varying the geometry between the source and substrate<sup>27</sup> or by surface treatment of the substrate, either through chemical modifications<sup>28</sup> or by patterning with polymeric spheres,<sup>29</sup> followed by thermal or solvent annealing. The latter method, known as nanosphere lithography, has proven to be a versatile approach to the fabrication of monodispersed periodic arrays of metallic nanoparticles but seems impractical for large-scale production. The electrolysis of silver ion solutions at an electrode surface followed by monolayer capping<sup>30</sup> or stripping with ultrasonic cavitation<sup>31</sup> also results in the suspension of silver nanoparticles. Other methods include the reduction of silver ion solutions by a pulsed electron beam,32 solutions trapped in supercritical fluidinduced, reverse micelles,33 or by the rapid expansion of a supercritical fluid containing Ag<sup>+</sup> solution into a reducing

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environment.<sup>34</sup> Silver particles can even be grown by the uptake of silver ions by living alfalfa plants.<sup>35</sup>

None of the above methods appear suitable for general utility. While most of the methods offer an acceptably narrow size distribution, they do not offer much variability in the size that can be produced. In the methods that can control particle size over a wide range, scalability and "chemical cleanness" of both the nanoparticle surface and the suspension can be a problem. In this paper, we propose a general synthetic method that produces silver nanoparticles in water without any extraneous chemical species. The methods offer the advantages of being easily scalable and able to produce essentially naked particles still exhibiting long-term stability with the metal surface readily accessible to various chemical modifications. Importantly, the method allows synthesis of particles of any diameter between 15 and 200 nm simply by varying the reaction time. The addition of filtration and centrifugation techniques produces suspensions of narrow size distribution and relatively high, 1012-1014 particles/mL, concentration.

The proposed synthetic method is based on the reduction of silver(I) oxide by hydrogen gas in water. Hydrogen gas is a common reducing agent. It was suggested by Lee and Meisel to use hydrogen gas to reduce silver ions in a boiling solution<sup>2</sup> and is a very common reducing agent for the preparation of silver nanoparticle composites.<sup>36–39</sup> Hydrogen is an excellent choice as a reducing agent because it imparts no residual chemical impact on a system. Ag<sub>2</sub>O has been known since the 1960s to undergo a slow decomposition to metallic silver in a basic solution.<sup>40,41</sup> Although generally considered insoluble in water, Ag<sub>2</sub>O has a low solubility of 0.053 g/L at 80 °C,<sup>18</sup> which is sufficient for nanoparticle synthesis.

#### **Experimental Section**

**Chemicals.** Ag<sub>2</sub>O (99.99%) was purchased from Alfa Aesar. Hydrogen gas (99.9999%) was purchased from National Welders. **Hazard**: hydrogen gas mixed with air in concentrations larger than 4% is explosive and must be handled in wellventilated areas. A 40 000 MW poly(4-vinylpyridine) and AgNO<sub>3</sub> were purchased from Aldrich. Ag<sub>2</sub>SO<sub>4</sub> was purchased from Fluka. NaBH<sub>4</sub>, HF (49%), and Reagent alcohol (HPLC Grade) were purchased from Fisher Scientific. **Hazard**: HF solutions and their fumes are highly toxic and corrosive and must be handled in fume hoods with proper personal protection equipment. (Tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane was purchased from Gelest, Inc. All chemicals were used without further purification. Water with a resistivity greater than 18 MQ•cm was acquired from a four-bowl Millipure Milli-Q system.

Methods. The vessel used for particle synthesis was a 5000mL Pyrex round-bottomed flask purchased from Ace Glass, Inc. Filtration employed 90-cm Osmonics nylon filter membranes purchased from Fisher Scientific. Centrifugation was done using a Beckman J2-HS centrifuge with a JA-10 centrifuge head. Extinction spectra were collected using a Shimadzu UV-2501PC spectrometer. All spectra were processed and figures prepared using Spectra-Solve for Windows (LasTek Pty. Ltd.). Particle diameters were measured using a Hitachi S-4700 FE-SEM operating between 8 and 12 keV. The substrates for SEM were ITO glass slides ( $R = 15 \Omega$ ) purchased from Delta Technologies. Electron diffraction patterns and corresponding images were collected on a Hitachi HD-2000 STEM operating at 200 keV, with ED patterns being collected in a mode that uses a quasi-parallel beam. Formvar-coated gold and copper grids with type B carbon were purchased from Ted Pella, Inc. Powder



Figure 1. Apparatus for silver nanoparticle synthesis.

X-ray diffraction patterns were collected using a Scintag 3100 PXRD with a Cu K $\alpha$  source.

## **Results and Discussion**

Synthetic Method. Silver nanoparticles can be synthesized by the reduction of silver(I) oxide by  $H_2(g)$  in ultrapure water. Simple bubbling of the gas through the saturated silver oxide solution at elevated temperature results in the formation of a colloidal suspension. This procedure, however, is not very efficient and does not provide required experimental control for the synthesis of well-defined nanoparticles. A slow-growth approach was developed, in which silver nanoparticles are synthesized in saturated silver oxide solution at elevated temperature in equilibrium with hydrogen gas at elevated pressure. This method is quite efficient as hydrogen is consumed only as needed for the metal reduction. Varying the temperature controls the rate of the reaction and the overall time required to grow particles to specific dimensions. Because hydrogen, water, and silver oxide are the only components used in the reaction, no other chemicals are present in the final colloidal suspension. The method can be used for large-scale production as the amount of nanoparticles produced is limited only by the size of the reaction vessel.

A special reactor was constructed that consists of a 5000mL Pyrex round-bottomed flask with an attached reverse condenser, thermometer, and spout (Figure 1). A hydrogen line with two backflow preventers to ensure that no water vapor can enter the gas cylinder and to limit a maximum allowable gas pressure in the vessel is attached to the condenser. The gas vent allows the vessel to be flushed prior to pressurization to remove any residual air from the space above the liquid. The vessel is filled with 3 L of ultrapure water and 2-3 g of Ag<sub>2</sub>O is added. The mixture is shaken well before connecting to the condenser and hydrogen line. A heating mantle is placed under the vessel and its contents heated and maintained at 70 °C without further agitation. Once the temperature has equilibrated, the vessel is flushed with H<sub>2</sub> and pressurized to 10 psi. Hazard: overpressurizing or using a defective vessel may result in explosion and cause severe injuries. Within 10-15 s of the initial pressurization, the contents of the vessel become faint yellow in color indicating the formation of metallic silver particles 10-15 nm in diameter. As the reaction progresses, aliquots can be taken through the spout. Removing the aliquots from the reducing environment stops further growth of the



**Figure 2.** Extinction spectra of silver nanoparticle suspensions taken as aliquots from a single reaction in timed intervals.

particles. Likewise, the reaction can be stopped at any time simply by releasing the gas from the vessel. In this way, control of the particle diameter is purely a function of total reaction time.

Variations in the overall amount of silver oxide, hydrogen pressure, volume of water, and temperature have little effect on the final product but can significantly alter the rate of the reaction. The reaction proceeds in a more consistent way if a significant gas volume is left above the liquid in the vessel and a large excess of silver oxide is used to maintain saturation. An elevated temperature was selected to increase Ag<sub>2</sub>O solubility allowing rapid seed formation at the initial stage of the reaction leading to high particle concentration in the final suspension and relatively fast particle growth. Consistency in temperature, H<sub>2</sub> pressure, and the Ag<sub>2</sub>O/water ratio allows a fairly accurate predication of the time required to grow particles to a selected diameter.

UV-Vis Spectroscopy. Extinction spectra of aliquots collected in the course of a single reaction are shown in Figure 2. Each curve corresponds to an aliquot taken in 1-10-min intervals so that the total reaction time covered in the figure is approximately 3 h representing 25 different particle sizes. The spectra have not been normalized and the apparent consistent evolution of the extinction maximum indicates the gradual increase of particle size in a suspension of constant particle concentration. In other words, as the reaction proceeds, no new particles are formed-only further growth of already existing particles. The evolution of the maximum in the extinction spectra starts from the initial peak position around 400 nm representing the dipole component of the plasmon resonance of small silver particles. As the particle size increases, the intensity of the resonance increases and its position shifts to longer wavelengths. Suspensions of small particles appear yellow and totally transparent as the absorption contribution of the dipole resonance dominates the extinction spectrum. For larger particles, increased opalescence can be observed, as the resonant scattering contribution of the dipole resonance becomes a dominating spectral component.44

The dependence of optical density on the spectral position of the dipole component of the plasmon resonance for a typical reaction is given in Figure 3A. Optical density depends on two



**Figure 3.** (A) Optical density of the silver nanoparticle suspension as a function of the spectral position of the dipole component of the plasmon resonance as observed in a typical reaction. (B) Dependence of the spectral position of the dipole component of the plasmon resonance on particle diameter.

factors: particle concentration and the extinction cross sections of individual particles. Experimental determination of extinction, scattering, and absorption cross sections for different size silver nanoparticles synthesized by this method is presented in the subsequent article. The measured extinction cross sections support the statement that the concentration of particles in suspension remains constant as the reaction progresses. Consequently, Figure 2 clearly indicates that large particles interact with light to a much greater extent than small ones by virtue of a larger number of electrons participating in the plasmon resonance. As long as the particles are not large enough to exhibit strong retardation effects, the ability of particles to interact with light scales as the particle volume (total number of electrons). This trend can be observed in Figure 3A, in which the optical density changes rapidly while peak position changes slowly. The position of the kink on the curve (ca. 450 nm) indicates the particle size at which phase retardation of incident radiation becomes important resulting in a slower increase in extinction during further particle growth. The effect of phase retardation is also evident in Figure 3B at a particle diameter of ca. 60 nm as the position of the dipole component of the plasmon resonance begins to shift to longer wavelengths with increasing particle size. The slower increase of extinction after the plasmon resonance maximum begins to shift indicates that, when retardation becomes significant, not all electrons in a particle contribute equally to the resonance.

In addition to the dipole component of the plasmon resonance, the extinction spectrum of small particles reveals two features: a minimum around 320 nm caused by an interband transition in the metal<sup>42</sup> that causes damping of plasmon oscillations in this spectral region and a shoulder at 350 nm. This shoulder, although its exact nature is not fully understood, is a part of plasmon resonance and its appearance is predicted by theoretical calculations based on Mie formalism.<sup>43</sup>



**Figure 4.** SEM images of different sizes of silver nanoparticles synthesized by hydrogen reduction. The corresponding extinction, scattering, and absorption spectra can be found in Figure 2 of the subsequent article. Mean particle diameters are (A) 29 nm, (B) 34 nm, (C) 37 nm, (D) 44 nm, (E) 48 nm, (F) 52 nm, (G) 58 nm, (H) 61 nm, (I) 75 nm, (J) 78 nm, (K) 92 nm, (L) 97 nm, (M) 105 nm, (N) 113 nm, (O) 120 nm, (P) 136 nm. The scale bar on each micrograph is 1  $\mu$ m.

As the particles continue to grow and phase retardation begins to play a significant role, the dipole maximum shifts to the red revealing a new peak at ca. 420 nm. This peak represents the quadrupole component of the plasmon resonance of large particles.<sup>43</sup> Another feature at ca. 380 nm in the spectra of large particles is likely the result of two phenomena. A higher-order multipole of the resonance such as the hexapole<sup>43</sup> that is no longer hidden under the envelope of the dipole resonance as well as the transverse resonance of high aspect ratio particles.

present in the suspension<sup>21</sup> contribute to this shoulder. This shoulder can be reduced but never completely eliminated by centrifugation and filtration procedures, as described in subsequent discussion.

**Electron Microscopy.** SEM images of nanoparticles from 16 different suspensions are shown in Figure 4. The corresponding extinction, scattering, and absorption spectra can be found in Figure 2 of the subsequent article. Whereas the smallest size (29 nm) shown in the figure is from a suspension that

resulted after ca. 10 min reaction time, the largest size (136 nm) corresponds to a reaction time of ca. 4 h. Neither of these sizes represents the limits to which silver particles can be synthesized using this reaction: particles as small as 10 nm and as large as 180 nm with a dipole plasmon resonance position of 670 nm can readily be produced. Larger sizes can also be synthesized although this requires that the reaction mixture be stirred to keep the particles suspended.

An immobilization technique was developed to determine true size and shape distributions, as well as aggregation state of nanoparticles in suspension via electron microscopy (SEM). Samples were prepared by first exposing a freshly plasmacleaned ITO glass slide to a 2 wt % poly(4-vinylpyridine) (PVP) solution in ethanol for 3 h with gentle agitation. Afterward, the slides were rinsed with copious amounts of ethanol and water to remove any nonadsorbed PVP, dried with a stream of N<sub>2</sub>, and treated in an oven at 110 °C for 1 h. This heat treatment serves to relax the monolayer of polymer facilitating even distribution across the surface. The lone pair of electrons on the nitrogen of the pyridine ring binds strongly to silver. Exposing the modified ITO slide to a silver suspension for ca. 24 h will produce an evenly distributed, nonaggregated monolayer of silver particles on the slide.<sup>45</sup> We believe that this method of sample preparation for electron microscopy has a distinct advantage over the conventional method of drying a suspension of nanoparticles onto a carbon-coated grid for TEM. Simple drying of the samples on a grid does not accurately represent the true particle size and shape distribution of a suspension. As the solvent evaporates, capillary forces tend to segregate particles of different size and shape. We consistently observe concentrating and stacking of high aspect ratio nanoparticles in selected areas of the grid which could, if taken out of context, lead to the incorrect determination of particle distribution. In addition, drying of suspensions induces aggregation of nanoparticles and does not allow the evaluation of the suspension's true aggregation state. In the immobilization technique, the pyridine ring has the same affinity for silver metal regardless of particle size, shape, or aggregation state, as long as the substrates are exposed to the suspension for the amount of time required to establish equilibrium between the surface and the suspension. A single SEM image in this case provides an accurate representation of the shape and size distribution of a suspension as well as aggregation state. With proper experimental conditions, this general approach can also be used for imaging of other nanoparticles.

Filtration and Centrifugation. An SEM image of an asprepared suspension of silver nanoparticles synthesized via hydrogen reduction is shown Figure 5A. As can be seen, the reaction produces a fairly monodispersed suspension that contains, in addition to the major fraction, a small percentage of very small particles and particles with high aspect ratio. The latter is typically present as 10-15% of the total number of particles whereas the contribution from the former does not exceed a few percent and, in some preparations, was completely absent. The high aspect ratio particles have a short axis of ca. 30 nm and a long axis between 0.1 and 10 microns.

To remove the high aspect ratio particles, any aggregated clusters, and any silver oxide particulates that may remain in the suspension, the mixture is gravity-filtered through hydrophilic nylon membranes with mean pore sizes of 0.45, 0.22, and 0.1 microns. The 0.1 micron membrane is omitted for suspensions with mean particle diameters greater than 130 nm. The method of filtration can also be used to collect the high



**Figure 5.** SEM images of (A) silver nanoparticles as prepared and (B) after filtration.



Figure 6. SEM image of a resuspended precipitate. Inset shows the extinction spectrum of the suspension.

aspect ratio particles and, as long as the membrane is not dried, the particles can be resuspended in water by gentle sonication. An SEM image of such a suspension and the corresponding extinction spectrum (inset) are shown in Figure 6. The extinction spectrum exhibits a maximum around 380 nm typical of the transverse resonance of such high aspect ratio particles.<sup>21</sup>

As can be seen from Figure 7, the extinction spectrum of a silver suspension synthesized via hydrogen reduction does not change substantially after the filtration procedure indicating an overall small percentage of high aspect ratio particles and aggregates in the preparation. A noticeable reduction on the blue side of the resonance indicates a decrease in the percentage of high aspect ratio particles because the transverse resonance of these particles is no longer contributing to the extinction. Typically, filtration reduces the fraction of high aspect particles to 3%.

Centrifugation was employed to remove the fraction of smaller particles, if present, and to concentrate the nanoparticle suspension. The required time and speed depend on the diameter of the major fraction but as a general rule, several hours at 150g gently precipitates the main fraction without aggregation, leaving the smaller particles in the supernatant. Once the supernatant is removed the precipitate can be resuspended to a desired particle concentration. The optical density, that is, concentration of the silver suspension, can be readily increased 250 times without affecting particle stability or aggregation state.



**Figure 7.** Normalized extinction spectra of suspensions after filtration through membranes with decreasing pore size. The inset depicts the spectra prior to normalization. The spectra were normalized using two points, the maximum of the dipole resonance and the minimum at 320 nm.



**Figure 8.** (A) Powder X-ray diffraction pattern of a silver nanoparticle suspension. (B-D) Typical electron diffraction patterns of silver nanoparticles showing the [111] (B) and [011] (C) planes and a corresponding STEM image (D). The scale bar is 150 nm.

**Electron and X-ray Diffraction.** The nanoparticles synthesized by hydrogen reduction appear to be crystalline as crystal faces are evident in SEM images. A PXRD pattern of an aqueous suspension of silver nanoparticles with a diameter of 130 nm and concentration of ca.  $1 \times 10^{12}$  mL<sup>-1</sup> is shown in Figure 8A. The pattern exhibits peaks at  $2\theta$  angles of 37.9, 44.0, 63.9, 76.7, and 80.9 that correspond to the [111], [200], [220],

[311], and [222] crystal planes of silver, respectively. The background is most likely caused by Brownian motion of the particles during the scan, solvent scattering, or the short-range order of the solvation cage around the particles. Previous PXRD studies of similarly prepared, dry silver nanoparticles coated with titania did not exhibit any background further supporting the crystalline nature of the particles synthesized by this method.<sup>46</sup>

Crystallinity of the nanoparticles was further studied with electron diffraction. Diffraction patterns were captured using a convergent beam TEM operating in a mode that approximates a parallel beam. As can be seen in Figure 8B and 8C, the ED patterns demonstrate the highly crystalline nature of the particles although some patterns exhibit weaker, secondary spots that may indicate twinned crystals or a submonolayer of an adsorbed species, most likely silver oxide.

**Particle Nucleation, Growth, and Stability.** The reaction of silver(I) oxide and hydrogen gas is represented by eq 1.

$$Ag_2O(aq) + H_2(g) \rightarrow 2Ag^0(s) + H_2O(l)$$
 (1)

While this equation highlights the simplicity of the reaction and the "chemical cleanness" of the resulting nanoparticle suspension, it sheds little light on the mechanism by which the particles are formed and stabilized. The solubility of silver(I) oxide in water  $(2.2 \times 10^{-4} \text{ mol Ag kg}^{-1})^{47}$  is described by the following reactions and solubility constants.<sup>48</sup>

$${}^{1}/_{2}Ag_{2}O(s) + {}^{1}/_{2}H_{2}O \leftrightarrow Ag^{+} + OH^{-} \qquad K_{s0} = 1.9 \times 10^{-8}$$
(2)

$${}^{1}/_{2}Ag_{2}O(s) + {}^{1}/_{2}H_{2}O \leftrightarrow AgOH \qquad K_{s1} = 2 \times 10^{-6}$$
 (3)

$${}^{1}/{}_{2}Ag_{2}O(s) + {}^{1}/{}_{2}H_{2}O + OH^{-} \leftrightarrow Ag(OH)_{2}^{-}$$
  
 $K_{s2} = 1.9 \times 10^{-4} (4)$ 

The pH of a 70 °C silver(I) oxide/water mixture in the Pyrex reaction vessel has been measured to be ca. 10. Using the above  $K_{\rm sp}$  values, the major contributor of silver oxide solubility is the monovalent silver ion, which roughly has a concentration of  $1 \times 10^{-4}$  M. The concentration of the Ag(OH)<sub>2</sub><sup>-</sup> would be around  $3 \times 10^{-8}$  M. Because of the low solubility product, these values are only estimates as the composition of the saturated solution can vary greatly depending on the presence of CO<sub>2</sub>-(g).<sup>48</sup> Because of the basic nature of the saturated solution, the composition may also be affected by the dissolution of the glass, increasing the concentration of the silver cation.

The interior glass surface of the reaction vessel plays a major role not only in silver(I) oxide solubility but also in the synthesis mechanism. To study this effect, nanoparticle suspensions synthesized in a Pyrex vessel were compared to those synthesized in a quartz vessel and in a Pyrex vessel treated with a fluorinated silane. The silanation of the vessel is similar to a previously reported procedure.<sup>28</sup> Briefly, a Pyrex vessel was etched with a 3% hydrofluoric acid solution for 10 min and then rinsed with copious amounts of water. The vessel was dried for several hours in an oven at 110 °C. An aliquot of (Tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane was placed in a small Teflon boat on a warm hot plate and the hot, dry vessel was placed over the boat and allowed to sit for about 15 min. The vessel was then rinsed well with water to facilitate hydrolysis of the precursor and to remove any unattached fluorosilanes and was heated in an oven at 250 °C for an hour



**Figure 9.** Extinction spectra from the synthesis of silver nanoparticles using a fluorocarbon-coated Pyrex vessel. Inset: an STEM image of the final suspension. The scale bar is 600 nm.



Figure 10. Comparison of silver nanoparticle suspensions with the same plasmon resonance maximum grown in a Pyrex vessel (solid line) and a quartz vessel (dashed line).

to allow cross-linking of the silanes, making the interior of the vessel hydrophobic. The extinction spectra from aliquots taken during a 3-h synthesis are shown in Figure 9. The inset shows an STEM image of the nanoparticles produced in the synthesis. The particles are almost exclusively square plates that are not stable under the 200 keV electron beam, "melting" into clusters of small particles as was captured in the inset. The overall concentration of particles in the suspension is quite low.

When silver suspensions are synthesized in a high-purity quartz vessel, size and shape distributions were generally similar to that of a suspension grown in Pyrex but the resulting concentration of the particles was typically 10 times lower (Figure 10). This result indicates that the chemical properties of the surface play a crucial role in the formation of the initial seeds.

Silver(I) oxide, specifically when it dissociates to yield  $Ag^+$ , has different solubility constants in glass and passivated glass



Figure 11. Extinction spectra of aliquots taken during the reduction of  $AgNO_3$  by  $H_2$  in a Pyrex vessel.

vessels.<sup>48</sup> To determine whether there is a direct relationship between the concentration of Ag<sup>+</sup> and the resulting nanoparticle concentration, hydrogen reduction was performed on a  $3 \times 10^{-4}$ M AgNO<sub>3</sub> solution at 85 °C for 2 h. The extinction spectra of aliquots taken during the reaction are shown in Figure 11 indicating a very low concentration of formed nanoparticles. The result suggests that, although the monovalent silver cation is a major component in the saturated silver(I) oxide solution, Ag<sup>+</sup> alone is not readily reduced to form silver nanoparticles.

It appears that the surface of the Pyrex glass plays a key role in the formation of silver nanoparticles by catalytically inducing nucleation through the interaction of the positive ions in Pyrex and the negatively charged silver hydroxide complexes. These negative hydroxide complexes anchor to the walls of the vessel and are reduced by hydrogen molecules forming nucleation centers that are weakly attached to the surface. The nucleation centers undergo further growth and eventually leave the surface as small silver particles. As the concentration of the particles in the suspension increases, the reduction of silver shifts from the surface of the vessel to the surface of small particles. Consequently, the growth of the existing seeds becomes more favorable than the formation of new ones. The surface of the Pyrex vessel becomes coated with a silver mirror during the nanoparticle synthesis indicating that not all seeds that are formed on the walls of the vessel leave the surface. Some seeds remain attached and grow into a continuous mirror film. The same is not true for quartz and fluorocarbon-modified vessels; however, the addition of Pyrex shot to these vessels greatly increases the final concentration of nanoparticles and the shot becomes coated with a mirror film. This observation additionally supports the catalytic role that the surface of the vessel plays in this reaction. The finite time required for the reaction to switch from seed formation to particle growth determines the initial size distribution of nanoparticles. During the remainder of the reaction, all particles grow quite uniformly preserving the initial size distribution and, as the particle become larger, they appear more monodispersed.

Particle stability is more than likely achieved by strong coordination of water to the silver surface. The solvation cage of the particles can be considered sufficiently "thick" to prevent coalescence of the metal particles resulting in stable suspensions. Comparing the extinction spectra of suspensions freshly prepared



**Figure 12.** Extinction spectra of a "seeded" hydrogen reduced silver suspension. Inset A: SEM image of the resultant suspension (scale bar = 1  $\mu$ m). Inset B: Extinction spectrum of the seed suspension.

to those stored for more than a year revealed no change in the position of the resonance and only a minimal change in optical density. SEM imaging showed no change to the larger particles and only a slight change to the smaller ones most likely caused by photodegradation.

Effect of Extraneous Species. The purity of the reactants is an absolute essential for the synthesis of the monodispersed, nonaggregated silver nanoparticles by this reaction. Any inorganic or organic contaminants in water or Ag<sub>2</sub>O can passivate the surfaces of the growing particles leading possibly to preferential growth along specific crystallographic axes. Using this strategy, the growth of high aspect ratio particles was achieved by using small, passivated silver particles to "seed" the synthesis reaction. The small silver seeds were synthesized by the reduction of a 5  $\times$  10<sup>-5</sup> M Ag<sub>2</sub>SO<sub>4</sub> solution with 2  $\times$ 10<sup>-4</sup> M NaBH<sub>4</sub> under rapid stirring and sonication in an ice cold bath. The suspension was then heated to near boiling for 5 h to decompose any residual borohydride, break up the aggregates, and concentrate the suspension. Following two-step centrifugation to narrow size distribution (Figure 12, inset B), the seeds were added to the reactor containing silver(I) oxide and the mixture was adjusted to an optical density of 0.3 at the plasmon resonance maximum of the seeds.

The mixture was then placed in a hydrogen environment and the reaction proceeded as before. Figure 12 shows the extinction spectra of aliquots taken at 30-min intervals and a typical SEM image of the resultant suspension (inset A). The suspension appears to be a very complex mixture of rods, prisms, and plates with only a few spherical particles.

Because of the 10-fold excess of NaBH<sub>4</sub> used in the synthesis of the seeds, the surface of the particles is passivated by borates, which hinder silver deposition at certain crystal faces more than at others leading to preferential growth along certain crystal-lographic axes. It seems possible that with proper control of the seed particles' surface chemistry, this reaction could yield particles of many different shapes. Conceivably, high aspect ratio particles that grow in the unseeded reaction result from

surface passivation by uncontrolled contaminants, which may come from the reactants or from the glass itself when exposed to a pH 10 silver oxide solution.

Organic contaminants in the water supply are also of great concern as they can act as a reducing agent for silver oxide. Silver oxide/water mixture with trace organics will turn yellow even at room temperature indicating the formation of small silver nanoparticles that are passivated by reaction products. These products are present in excess and are capable of passivating more seeds as they form at the beginning of hydrogen reduction that follows. As a result, the concentration of nanoparticles increases as more particles must form since the reaction products hinder the growth of the initial seeds. Large concentrations of small particles lead to the collapse of the suspension before the particles can grow to diameters greater than ca. 40 nm.

## Conclusions

A method for size-controlled synthesis of chemically clean silver nanoparticles is developed. The method is highly efficient and easily scalable to large production. By conducting the synthesis in the presence of various complexating species, control is potentially achieved for synthesis of nanoparticles with variety of shapes.

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## **References and Notes**

(1) Creighton, J. A.; Blatchford, C. G.; Albrecht, M. G. J. Chem. Soc., Faraday Trans. 2 1979, 75, 790.

(2) Lee, P. C.; Meisel, D. J. Phys. Chem. 1982, 86, 3391.

(3) Nie, S.; Emory, S. R. Science 1997, 275, 1102.

(4) Sondi, I.; Goia, D. V.; Matijević, E. J. Colloid Interface Sci. 2003, 260, 75.

(5) Cason, J. P.; Khambaswadkar, K.; Roberts, C. B. Ind. Eng. Chem. Res. 2000, 39, 4749.

(6) Li, X.; Zhang, J.; Xu, W.; Jia, H.; Wang, X.; Yang, B.; Zhao, B.; Li, B.; Ozaki, Y. *Langmuir* **2003**, *19*, 4285.

(7) Shirtcliffe, N.; Nickel, U.; Schneider, S. J. Colloid Interface Sci. 1999, 211, 122.

(8) He, S.; Yao, J.; Jiang, P.; Shi, D.; Zhang, H.; Xie, S.; Pang, S.; Gao, H. *Langmuir* **2001**, *17*, 1571.

(9) Leopold, N.; Lendl, B. J. Phys. Chem. B 2003, 107, 5723.

(10) Velikov, K. P.; Zegeres, G. E.; van Blaaderen, A. Langmuir 2003,

19, 1384.
(11) Nickel, U.; Castell, A.; Pöppl, K.; Shirtcliffe, N. Langmuir 2000, 16, 9087.

(12) Tan, Y.; Dai, X.; Li, Y.; Zhu, D. J. Mater. Chem. 2003, 13, 1069.

(13) He, R.; Qian, X.; Yin, J.; Zhu, Z. J. Mater. Chem. 2002, 12, 3783.

(14) Chen, D.-H.; Huang, Y.-W. J. Colloid Interface Sci. 2002, 255, 299

(15) Caswell, K. K.; Bender, C. M.; Murphy, C. J. Nano Lett. 2003, 3, 667.

(16) Rodríguez-Gattorno, G.; Díaz, D.; Rendón, L.; Hernández-Segura,
 G. O. J. Phys. Chem. B 2002, 106, 2482.

(17) Van Hyning, D. L.; Zukoski, C. F. Langmuir 1998, 14, 7034.

(18) *CRC Handbook of Chemistry and Physics*, 60th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1979.

(19) Maillard, M.; Giorgio, S.; Pileni, M.-P. J. Phys. Chem. B 2003, 107, 2466.

(20) Chen, S.; Carroll, D. L. Nano Lett. 2002, 2, 1003.

(21) Sun, Y.; Yin, Y.; Mayers, B. T.; Herricks, T.; Xia, Y. Chem. Mater. 2002, 14, 4736.

(22) Zhang, J.; Han, B.; Liu, M.; Liu, D.; Dong, Z.; Liu, J.; Li, D.; Wang, J.; Dong, B.; Zhao, H.; Rong, L. J. Phys. Chem. B 2003, 107, 3679.

(23) Mafuné, F.; Kohno, J.-Y.; Takeda, Y.; Kondow, T.; Sawabe, H. J. Phys. Chem. B 2000, 104, 8333.

(24) Abid, J. P.; Wark, A. W.; Brevet, P. F.; Girault, H. H. Chem. Commun. 2002, 7, 792.

(25) Huang, H. H.; Ni, X. P.; Loy, G. L.; Chew, C. H.; Tan, K. L.; Loh, F. C.; Deng, J. F.; Xu, G. Q. *Langmuir* **1996**, *12*, 909.

(26) Jin, R.; Čao, Y. C.; Hao, E.; Mötraux, G. S.; Schatz, G. C.; Mirkin, C. A. *Nature* **2003**, *425*, 487.

(27) Zhao, Y.-P.; Ye, D.-X.; Wang, G.-C.; Lu, T.-M. Nano Lett. 2002, 2, 351.

- (28) Malynych, S. Z.; Chumanov, G. J. Vac. Sci. Technol., A 2003, 21, 723.
- (29) Jensen, T. R.; Malinsky, M. D.; Haynes, C. L.; Van Duyne, R. P. J. Phys. Chem. B 2000, 104, 10549.
- (30) Kotov, N. A.; Zaniquelli, M. E. D.; Meldrum, F. C.; Fendler, J. H. Langmuir **1993**, *9*, 3710.
- (31) Zhu, J.; Liu, S.; Palchik, O.; Koltypin, Y.; Gedanken, A. *Langmuir* **2000**, *16*, 6396.
- (32) Rele, M.; Kapoor, S.; Mukherjee, T. Mater. Res. Bull. 2002, 37, 2275.
- (33) McLeod, M. C.; McHenry, R. S.; Beckman, E. J.; Roberts, C. B. J. Phys. Chem. B 2003, 107, 2693.
- (34) Meziani, M. J.; Rollins, H. W.; Allard, L. F.; Sun, Y.-P. J. Phys. Chem. B 2002, 106, 11178.
- (35) Gardea-Torresdey, J. L.; Gomez, E.; Peralta-Videa, J. R.; Parsons, J. G.; Troiani, H.; Jose-Yacaman, M. *Langmuir* **2003**, *19*, 1357.
- (36) Mitrikas, G.; Trapalis, C. C.; Kordas, G. J. Non-Cryst. Solids 2001, 286, 41.
- (37) Pol, V. G.; Srivastava, D. N.; Palchik, O.; Palchik, V.; Slifkin, M. A.; Weiss, A. M.; Gedanken, A. *Langmuir* **2002**, *18*, 3352.

- (38) Plyuto, Y.; Berquier, J.-M.; Jacquiod, C.; Ricolleau, C. Chem. Commun. 1999, 17, 1653.
- (39) Wang, T. C.; Rubner, M. F.; Cohen, R. E. Langmuir 2002, 18, 3370.
- (40) Dirkse, T. P.; Vander Lugt, L. A.; Schyders, H. J. Inorg. Nucl. Chem. 1963, 25, 859.
- (41) Dirkse, T. P.; Vander Hart, D.; Vriesenga, J. J. Inorg. Nucl. Chem. 1965, 27, 1779.
- (42) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer Series in Materials Science 25; Springer-Verlag: New York, 1995; p 18.
  - (43) Kreibig, U.; Zacharias, P. Z. Phys. 1970, 231, 128.
- (44) Kawata, S. Near-Field Optics and Surface Plasmon Polaritons; Topics in Applied Physics; Springer-Verlag: New York, 2001; pp 107-8.
- (45) Malynych, S.; Luzinov, I.; Chumanov, G. J. Phys. Chem. B 2002, 106, 1280.
- (46) Kumbhar, A.; Chumanov, G. J. Nanosci. Nanotech. 2004, 4, 299.
- (47) Dirkse, T. P. Solubility Data. Silver (1) Oxide in Water and Aqueous Solvents; Solubility Data Series 23; Pergamon Press: New York, 1986; p 95.
  - (48) Biedermann, G.; Sillén, L. G. Acta Chem. Scand. 1960, 14, 717.