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Nanoshells made easy: improving Au layer growth on nanoparticle surfaces

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Abstract

The growth of a continuous, uniform Au layer on a dielectric nanoparticle is the critical step in the synthesis of nanoparticles such as nanoshells or nanorice, giving rise to their unique geometry-dependent plasmon resonant properties. Here we report a novel, streamlined method for Au layer metallization on prepared nanoparticle surfaces using carbon monoxide as the reducing agent. This approach consistently yields plasmonic nanoparticles with highly regular shell layers and is immune to variations in precursor or reagent preparation. Single particle spectroscopy combined with scanning electron microscopy reveal that thinner, more uniform shell layers with correspondingly redshifted optical resonances are achievable with this approach.

Graphical abstract

Introduction

Nanoparticles consisting of a dielectric core surrounded by a thin metallic shell form a class of nanostructures with remarkable optical properties.¹⁻³ Au nanoshells, consisting of spherical silica nanoparticle cores surrounded by a uniform nanoscale gold shell layer, and Au nanorice, prolate hematite nanoparticles surrounded by a gold shell layer, are two examples of this general nanoparticle morphology. The unique optical properties of these nanoparticles are due to their geometry dependent, plasmon-derived optical resonances whose frequencies depend sensitively on the inner and outer dimensions of their metallic

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shell layers. The intense optical absorption and scattering properties of this class of nanoparticles can be made to span a remarkably large region of the electromagnetic spectrum, from visible frequencies to the far infrared.^{1,4} This property has led to the use of these types of nanoparticles in numerous applications, from fluorescence enhancement of weak molecular emitters,⁵ substrates for surface plasmon resonance sensing,⁶ biosensing,⁷ surface enhanced Raman and surface enhanced infrared absorption spectroscopies,⁸⁻¹⁰ to contrast enhancement in bioimaging and photothermal cancer therapy.^{11, 12}

The plasmon-derived optical properties of metallic shell particles have been explicitly verified using fully quantum mechanical calculations¹³⁻¹⁵ but can be understood in simple physical terms using the plasmon hybridization concept.¹⁶⁻¹⁸ In plasmon hybridization, the tunability of the plasmon resonances of dielectric-core metal-shell nanoparticles arises from the interaction of cavity plasmons associated with the inner shell surface with sphere plasmons associated with the outer shell surface. The plasmons associated with the inner and outer surface of the shell mix and hybridize, resulting in a lower energy, “bright” or “bonding” plasmon that couples strongly to incident light, and a higher energy “dark” or “anti-bonding” plasmon that couples weakly to incident light. The hybridization interaction is stronger for thinner shell layers, leading to a strongly redshifted resonance for the “bright” plasmon at a wavelength determined by the thickness of the shell and the overall particle radius. Therefore to position the plasmon resonance at a wavelength of interest it is crucial to be able to synthesize metallic shell particles with thin, uniform shells.

Synthesis of dielectric core-Au shell nanostructures is a multistep process. It is initiated by functionalizing oxide nanoparticles with aminopropyltriethoxy- or -methoxysilane, followed by the binding of very small (1-2 nm diameter) Au nanoparticles onto the nanoparticle surface to a saturation coverage of nominally 25-30%.^{2,19} This is subsequently followed by the chemical reduction of $\text{Au}^{3+}_{(\text{aq})} \rightarrow \text{Au}^0_{(\text{s})}$ onto the nanoparticle precursor surface. In this last reduction step, the tiny Au islands grow larger and ultimately merge, resulting in the formation of a continuous, multicrystalline metallic shell layer. Once formation of the shell layer is complete, the optical properties of the plasmonic nanoparticles correspond quantitatively to classical electromagnetic theory.²⁰ Although the plasmon resonance of a nanoshell is robust with respect to small defects or variations in surface roughness,^{21, 22} for the electromagnetic response of plasmonic nanoparticles to agree quantitatively with theory, it is critically important that the shell layer formation on the nanoparticle surface have a continuous and uniform morphology. A striking example of a “nanoshell defect” that can give rise to drastic changes of the optical properties is the nanoegg, a metallic nanoshell with a homogeneous metallic shell of nonuniform thickness. This particle can be fabricated in a controlled manner²³ and is described as a nanoshell with a displaced (nonconcentric) dielectric core. The symmetry breaking of core displacement modifies the optical properties quite dramatically, giving rise to additional hybridized plasmon resonances in the extinction spectrum of the nanoparticle.^{23, 24}

The aqueous phase synthesis of gold nanoparticles depends on the reduction of tetrachloroauric acid in the presence of a reducing agent. Several reducing agents have been reported for the synthesis of metallic nanoparticles, and typically have a significant influence on the morphology of the final nanoparticle product. For the growth of gold or silver shell

layers on silica nanospheres, the shell layer morphology depends on the reducing agent used in the metallization process.^{19, 25} For example, in the case of Au nanoshells, the reducing agents formaldehyde (H_2CO), hydroxylamine-hydrochloride, and sodium borohydride do not produce equivalent results in otherwise comparable synthesis protocols.¹⁹ Also associated with the use of certain reductants have been variations in shell layer morphology due to specifics of reagent preparation. Both colloidal solutions and reductant solutions are known to change slowly over time, resulting in the growth of nanostructures with morphologies deviating from those achieved with freshly prepared solutions. These slow variations are most likely due to changes in equilibrium concentrations of the various ionic constituents or of dissolved gases, and are quite challenging to monitor, as is their precise influence on shell layer growth. A reducing agent method immune to such variations would provide consistent reproducibility in shell formation and improve the reliability of plasmonic nanoparticle fabrication.

In this paper we report a robust and reliable method for the growth of an Au layer on a prepared dielectric nanoparticle surface based on the use of carbon monoxide gas (CO) as the reducing agent.^{26, 27} The shell growth is demonstrated on silica core-Au shell nanoshells and hematite core-Au shell nanorice structures. We compare nanoparticles prepared with this new method to nanoparticles prepared using the conventional liquid phase reductant, formaldehyde (H_2CO). For both nanoparticles, the growth of a continuous Au shell layer is achievable at smaller thicknesses with CO as the reducing agent. Ensemble extinction spectra, single particle scattering spectra and SEM images of specific single nanoshells and nanorice grown by both methods provide clear evidence that thinner, more uniform shell layer morphologies on nanoshells and nanorice can be fabricated with this approach. When precursor chemicals are prepared within a few days of nanoparticle synthesis both CO and H_2CO reduction methods produce comparable high quality nanoparticles. However, the reduction of Au^{3+} by CO results in the growth of high quality shell layers independent of the age of precursor reagents.

Experimental Section

A multistep procedure was performed to prepare the various precursors,¹ followed by reduction of aqueous Au^{3+} to Au^0 , resulting in nanoshell or nanorice formation. With the exception of core functionalization by APTES or APTMS in ethanol, all components of the nanoparticle precursor solutions and suspensions were prepared using Milli-QTM water.

Chemicals and Materials

Chemical compounds, components of the precursor particles

Unless otherwise specified, all chemicals were supplied by Sigma-Aldrich or Fisher Scientific and used without further modification. Deionized water (18 M Ω) was provided by a Milli-QTM system. 1) Chloroauric acid: gold (III) chloride ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99%), 2) THPC colloidal gold suspension: Tetrakis(hydroxymethyl)phosphonium chloride (THPC, 80% solution in H_2O), sodium hydroxide (1 M), and chloroauric acid, 3) Plating Solution: potassium carbonate (certified A.C.S., Fisher Sci.) and chloroauric acid, 4) SiO_2 core functionalization: condensed silica core particles (Ammonia stabilized, 30% colloid silica,

Precision Colloids, Cartersville, Georgia) and 3-aminopropyltriethoxysilane (APTES, minimum 98% Sigma), 5) Hematite cores: ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and potassium phosphate (KH_2PO_4), 6) Precursor nanoparticle synthesis: functionalized silica or hematite cores, THPC gold solution, sodium chloride, 200 proof ethanol (Plarmco-Aaper), 7) Reducing agents: carbon monoxide (CO , 99.0%) (Matheson-Trigas) or formaldehyde (H_2CO , 37%). 7) electron microscopy sample preparation: silicon substrates (Addison Engineering, Inc.), glass microscope slide cover slips, poly(4-vinylpyridine) (PVP, MW 160,000).

Caution: *ethanol, H_2CO , CO , chloroauric acid, THPC, APTMS, APTES and piranha present potential health and or fire hazards. Appropriate precautions should be observed at all times.*

Synthesis of Precursor Components

Chloroauric acid—A 1% by weight (2.54 mM) aqueous chloroauric acid solution was prepared and stored in an amber glass container for a minimum of three days before use.

Ferric Chloride solution—An aqueous solution containing 20 mM FeCl_3 – 400 μM KH_2PO_4 was prepared prior to the precipitation of hematite particles.

Synthesis of THPC Gold Suspension—A THPC gold solution composed of 1-2 nm Au colloid was prepared according to Duff et al.²⁸ Under rapid stirring, 1.2 mL of 1 M NaOH was added to 180 mL of H_2O , followed by the addition of 4 mL of a 1.2 mM aqueous THPC solution to yield a final THPC concentration of 2.6 μM . After five minutes of continuous stirring, 6.75 mL of 1 wt % aqueous chloroauric acid was added in one quick motion, after which the solution immediately turns to a medium brown color. The final solution was refrigerated for at least 2 weeks before use. The product has a shelf life of ~ 6 months when stored at -4°C . The suspension quality, which degrades with increasing Au colloid size, can be monitored by watching for a pronounced Au colloid peak in the optical absorption spectrum, which appears upon nanoparticle restructuring or aggregation.^{28, 29}

Synthesis of Au Plating Solution—A 44 μM aqueous HAuCl_4 plating solution was produced by the addition of 3 mL of 1 wt % chloroauric acid to 200 mLs of a 1.8 mM aqueous K_2CO_3 . The solution is then stored for a minimum of 24 hours. Typically, when the plating solution is reduced by H_2CO , the highest quality nanoshells, as assessed by SEM imaging and optical properties, were obtained when used between 24 and 72 hours after preparation. In the case of reduction by $\text{CO}_{(\text{g})}$ the shelf-life time is extended beyond 6 weeks.

Synthesis of Hematite Core Particles—Spindle-shaped hematite particles with an aspect ratio of 6.3 ($340 \pm 20 \text{ nm} \times 55 \pm 5 \text{ nm}$)² were prepared by forced hydrolysis of ferric chloride salts in an alkaline media. Briefly, 100 mL of reaction mixture containing 20 mM of FeCl_3 and 400 μM of KH_2PO_4 solution were sealed in a round bottom flask and heated at 100°C for 72 h. The resulting dark orange precipitate consisting of $\alpha\text{-Fe}_2\text{O}_3$ particles were washed several times in water and ethanol at 3900 RCF for 25 minutes per centrifugation cycle. The final precipitate was redispersed in 25 mL ethanol and used as stock solution.^{2, 30}

APTES Functionalization of Silica Cores—Here the protocol used for 126 nm diameter cores is presented. This general procedure is applicable for various silica core sizes, however, the volume of APTES will scale with the available silica core surface area and the relative centrifugal force is inversely related to particle size. For example, silica core particles with a 36, 95, and 190 nm radii were centrifuged at 6000, 1000, and 400 RCF, respectively. As-purchased SiO₂ particles were diluted from 30 wt % to 1 wt % in water. Amine stabilization of the particles was removed by: washing the functionalized cores three times via centrifugation at 4000 RCF for 30 minutes; removal of the supernatant, followed by redispersion in 40 mL of water using an ultrasonic probe. After the final removal of the supernatant, the particles were redispersed in ethanol. This process (in ethanol) was repeated an additional three times. The final suspension was redispersed in 40 mL of ethanol, placed in a polypropylene flask, and stirred rapidly. Fresh APTES (300 μ L) was added to the suspension with continuous stirring for 10 minutes. The solution was sealed and slowly stirred overnight under ambient conditions.

Next, the mixture was boiled in a borosilicate container for two hrs. Total evaporation of the solvent during the synthesis of the functionalized cores was prevented by the continuous addition of ethanol. Again, the functionalized core particles were washed three times in ethanol by centrifugation at 3500 RCF for 30 minutes as described in the previous section. After the last centrifuge cycle and removal of supernatant, the functionalized particles were redispersed in 20 mL of ethanol. This process resulted in amine-terminated nanoparticles that may be stored and reliably used to fabricate high quality nanoshell precursor particles for at least a year. However, the actual shelf life has not been characterized beyond this period of time. An ultrasonic probe was used to redisperse the cores immediately before the synthesis of the nanoshell precursor particles in the next step.

APTMS-Functionalized Hematite Particles—5 ml of as-prepared hematite nanoparticles were stirred to a rapid vortex, after which 600 μ L APTMS was added. The stirring velocity was reduced to a weak vortex and continued for 12 hours. Excess APTMS was removed by several centrifugation / ethanol cycles after which the core particles were redispersed in ethanol.

Synthesis of Nanoshell Precursor Particles—First, 40 mL of a THPC gold solution (see above) was sonicated for 1 minute. During sonication, 4 mL of 1 M NaCl was added, followed immediately by the addition of 300 μ L of the APTES functionalized silica or APTMS functionalized hematite nanoparticle suspension. After continuous sonication for an additional 1-2 minutes, the solution was allowed to reach equilibrium over a 12 hr period. This step was followed by centrifugation at 1400 RCF for 20 minutes to remove excess THPC. The precursor nanoparticles formed a pellet at the bottom of the centrifuge tube. After removal of the supernatant, the particles were resuspended in 30 mL of H₂O with a sonicating probe; centrifuged a second time and redispersed in 5 mL of H₂O. The nanoparticle precursor suspension was refrigerated when not in use. The highest quality and thinnest complete shells are produced within a few days of synthesis, yet complete nanoshells may still be obtained after 1-2 months.

Synthesis of Nanoshells and Nanorice—The synthesis of nanoshells and nanorice follow a common protocol. Under ambient conditions, two $\text{Au}^{3+}_{(\text{aq})}$ reducing agents: $\text{CO}_{(\text{g})}$ and $\text{H}_2\text{CO}_{(\text{aq})}$ were compared in nanoshell and nanorice synthesis. For nanoshells, the plating solution (aged 5 and 6 days, used with H_2CO and CO reduction methods, respectively) and nanoparticle precursor suspension (aged 9 and 49 days, H_2CO and CO , respectively) measured by volume, were combined to produce a sequence of 6 mL suspensions with Au ion to particle ratios between 2.5×10^7 and 2×10^8 . Pairs of 3 mL aliquots of each nanoshell or nanorice precursor solution were prepared in glass vials. (Nanoshells were successfully synthesized using plating solutions as old as 37 days with the same batch of precursor nanoparticles used in the experiments reported in this paper.) Nanoparticle concentrations can vary significantly batch-to-batch between nanoshell precursor solutions.

The Au^{3+} reduction technique by H_2CO (Eq. 1-3) includes the rapid discharge of 15 μL of H_2CO from a 100 μL pipette into 3 mL of the precursor suspension, after which the sample vial is gently vortexed by hand for about 10 seconds. (When the process is scaled to produce larger quantities of nanoshells, typically 200 mL of plating solution would be used. In this case, the nanoshell precursor material is stirred rapidly, to produce a strong vortex before the addition of H_2CO .) The nanoshell and nanorice suspensions produced by H_2CO reduction were subsequently aged for a minimum of 10 minutes, allowing for complete consumption of the Au^{3+} stock solution before the collection of optical spectra. SEM samples were prepared within the hour. H_2CO -reductant nanoshells must be promptly washed by centrifugation at 300 RCF for 10-15 minutes and redispersed in H_2O or an aqueous 1.8mM K_2CO_3 solution to remove residual H_2CO . Failure to wash the H_2CO -nanoshells will result in particle aggregation within a few hours.

Reduction of Au^{3+} by CO (Eq. 4-6) was performed either by aeration or by exposure of solution to a CO atmosphere. For the aerated samples, CO was delivered through a glass diffusion tube (Chemglass) immersed in the bottom of the vial at a flow rate (Cole Parmer) of 25 sccm for periods of 10 to 15 seconds. In the atmospheric CO technique, the volume in the sample vial above the suspension was filled with CO , after which the vial was capped and gently rocked for five to ten seconds. CO -reductant nanoshell and nanorice optical absorption spectra were collected immediately. SEM samples were prepared within the hour. CO -nanoshells do not require post reduction washing.

Instrumentation

Optical absorption spectra of aqueous samples in 1 cm path length polystyrene cuvettes (Fisher Scientific) were collected using a Varian Cary 5000 UV-VIS-NIR scanning spectrophotometer.

Optical scattering spectra were collected for individual nanoshells deposited over SiO_2 using an inverted microscope (Zeiss Axiovert 200 MAT) in the dark-field configuration. A reflection dark-field objective (100 $\times$, NA 0.9) was used to focus the image of each single nanoparticle at the entrance slit of the spectrograph (SP-2156; Acton Research, Acton, MA). Data were collected with a charge-coupled device array (PhotonMax 512; Princeton Instruments, Trenton, NJ).²⁰ Scanning electron micrographs were obtained with an FEI

Quanta 400 Scanning Electron Microscope (SEM) operated at 30 kV in the environmental (ESEM™) mode with an H₂O vapor pressure of ~2 Torr.

To facilitate the analysis of the same particle by both ESEM and optical scattering experiments, acetone-cleaned glass substrates were patterned by the deposition of an Au film through an alphanumerically indexed transmission electron microscope grid (e.g., a mask; Ted Pella, Inc.) in contact with the SiO₂ surface. An adhesion layer was added to the substrate by immersion in a 1 wt. % PVP-ethanol solution for 8-12 hours after which they were rinsed with ethanol and dried with filtered N₂. Nanoshells were allowed to deposit on the surface for 20 seconds, which resulted in an interparticle spacing of nominally 5 μm.

For the single particle optical scattering spectra collection, ESEM images and the optical microscope dark field of view were correlated to locate a specific nanoshell. By designing samples with an appropriate particle-to-particle separation, an adjustable slit can be used to optically isolate an individual nanostructure. Spectral data were acquired using the previously described spectroscopic system and processed by our own analysis software (MatLab).

Sample Preparation for Electron Microscopy—For high-resolution SEM imaging Si substrates were cleaned by immersion in a 3:1 H₂SO₄: H₂O₂ (piranha) for 20 minutes, thoroughly rinsed with Milli-Q water and dried with filtered N₂. *Piranha and the components of piranha are highly corrosive chemicals that present numerous health hazards. When H₂O₂ and H₂SO₄ are combined, an endothermic, potentially explosive reaction will result. Prior to working with piranha solutions, the reader is encouraged to review OSHA form 174, Sept. 1985, and to take all necessary precautions.* The substrates were then coated with a PVP adhesion layer as described above. They were subsequently rinsed with ethanol, dried with filtered N₂, and allowed to cure under ambient conditions for 12 hours.

Nanoparticles were immobilized on the substrate surface by the sedimentary deposition for a period of 1-2 hours after which they were gently rinsed with water and dried with filtered N₂.

Characterization of Nanoshells—Theoretical spectra which agree well with the empirical optical absorption spectra were calculated using generalized Mie theory.³¹ Both experimental and theoretical spectra were normalized at the maximum absorption values. An r_1 value of 63 nm was determined by combined scanning electron microscopy (SEM) and Mie scattering theory. Using this value of r_1 (63 nm) and the dielectric constant of the medium, (H₂O, 1.77), the Au shell³² and the dielectric core (SiO₂, 2.04), the value of r_2 (85 nm) and the theoretical absorption efficiency ($A_{\text{theoretical}}$, 4.98) was determined using Mie theory.^{31, 33, 34} To determine the concentration of the nanoparticle precursor suspension, the Beer-Lambert law was used:

$$NS/mL = \frac{2.303 \times A_{Dp}}{A_{\text{theoretical}} \times L \times 2\pi \times r_2^2} \quad (1)$$

where L is the optical cell path length ($L = 1$ cm), r_2 is the overall nanoshell radius in nm, $A_{\text{theoretical}}$ is the peak absorption value extracted from the theoretical extinction spectra for $[r_1, r_2]$ nanoshells, and A_{DP} is the experimentally measure peak absorption efficiency value. The $\text{CO}_{(\text{g})}$ -reductant [63,85] nm nanoshells (Figure 2A vi) were chosen as the point of reference for the precursor Au^{3+} to nanoparticle ratio, based on SEM, optical absorption, and Mie theory. The nanoshell density was determined to be $2.86 \times 10^9/\text{ml}$ thus the precursor Au^{3+} / nanoparticle ratio was 3.05×10^7 . The sample set was scaled relative to this value.

Results and Discussion

A schematic of a nanoshell precursor nanoparticle consisting of ultrasmall Au nanoparticles bound to a silica nanoparticle surface, two reductant methods used for shell layer growth, and the morphological differences in the final metalized nanoparticle are shown in Figure 1. This schematic represents the final reduction step where the silica nanoparticle-bound Au nanoparticles coalesce into a continuous, multicrystalline metallic layer on the nanoparticle surface. In particular, this schematic illustrates the thin shell layer limit, where just enough $\text{Au}^0_{(\text{s})}$ is deposited on the nanostructure to result in the formation of a continuous shell layer. In general, different reductants may require different concentrations in Au^{3+} to achieve continuous coverage of the nanoparticle: a complete shell layer that forms at lower Au^{3+} concentrations would be thinner, and the resulting nanoparticle would have a longer wavelength plasmon resonance.

The evolution of the optical extinction of the nanoshell precursor nanoparticles during shell layer growth as a function of Au^{3+} concentration, for the $\text{CO}_{(\text{g})}$ and H_2CO reductants, is shown in Figure 2. At low Au^{3+} concentrations, metal deposition onto the precursor nanoparticle enlarges the discrete Au nanoparticles on the nanostructure surface. In this concentration regime, the absorption peak shifts to longer wavelengths due to the increased size of the nanoscale Au islands on the nanoparticle surface and decreased distance between these islands, resulting in increased interparticle plasmon coupling and a redshifted plasmon resonance. This redshifting continues with increasing Au^{3+} until a concentration resulting in the formation of a complete shell layer. Once a complete shell layer is formed higher Au^{3+} concentrations, result in increased thickness of the metal shell layer and a shift of the nanoshell plasmon to shorter wavelengths. The long wavelength limit therefore corresponds to the minimum Au^{3+} concentration required to form a continuous shell layer. The longer the wavelength, the thinner the shell layer of the nanoparticle formed. In Figure 2A we see this transition of the extinction peak to longer wavelengths, then shorter wavelengths, with increasing Au^{3+} concentration. The maximum wavelength depends significantly on the type of reductant. In this case, the CO reductant yields nanoparticles with a peak extinction wavelength shifted to a measurably longer wavelength (780 nm) than the formaldehyde reductant (745 nm) for the thinnest shells. The large wavelength difference seen here, between nanoshells grown using the CO and H_2CO reducing agents, corresponds to the use of older nanoshell precursor and H_2CO reductant solutions, and is generally a function of the age of these solutions. The longer peak wavelength achieved for nanoshells formed using the CO reductant occurs at a ~40% lower Au^{3+} concentration per nanoparticle than for shell layers grown using the formaldehyde reductant, consistent with the formation of thinner continuous shell layers. These two characteristics indicate that less Au^{3+} is required to form

a complete shell layer for the CO reductant than for the formaldehyde reductant in this case. Absorption spectra representative of various stages in the growth of the shell layer (Fig. 2A(i)-(vi)) are shown in Figure 2(B,C). Spectra corresponding to the regime of incomplete shell layer growth, (i) and (iv), show a broad and relatively featureless curve, while the other curves show evidence of both dipole and quadrupole resonances in the spectral lineshape, corresponding to the extinction spectrum of a nanoshell with a continuous shell layer. Comparison with Mie scattering theory indicates that the difference in shell thickness for the two reductant methods in the thin shell limit is approximately 3-5 nm. However, a closer examination of the nanoparticles in the thin shell limit reveals significant reductant-dependent differences in morphology for nanoshells fabricated with these two reducing agents.

An examination of nanoshells grown with Au^{3+} concentration corresponding to the maximum wavelength shift reveals the largest differences in nanoshell morphologies obtainable with these two reductants (Fig. 3). In the case where nanoshells are synthesized from reductant and nanoparticle precursor solutions aged 5 and 9 days respectively, comparable nanoshell morphologies result, with continuous uniform layers (Fig. 3(A-C)). Occasional pinhole defects can be detected on the nanoshells grown using the H_2CO reducing agent solution (Fig. 3(C)) but are generally not visible for the nanoshells grown with the CO reductant (Fig. 3(B)). For the case where the reducing agent and precursor solutions have been aged for 6 and 49 days respectively, a greater variation in nanoshell morphology between the two reducing agents results. The extinction spectra and representative SEM images are shown in Figures 3(D-F). Nanoshells grown with the CO reductant are observed to have continuous and uniform shell layers (Fig. 3(E)). Nanoshells obtained using the H_2CO reductant show incomplete shell layer growth with extended, interconnecting fissures in the shell layer. The extinction spectrum of the nanoshells prepared with the CO reducing agent agreed quantitatively with Mie scattering theory. An extension of the thin shell limit by CO reduction was also observed for nanoshells synthesized with silica core radii of 36, 95, and 190 nm (data not shown). This variation in shell quality also extends to the synthesis of nanorice, which incorporates spindle shaped hematite core nanoparticles. In the synthesis of nanorice, similar changes in morphology that depend upon the type of reducing agent used are obtained. For a thin shell layer, nanorice grown using CO as the reducing agent have significantly more continuous shell layers with fewer defects than is typical of nanorice synthesized using H_2CO as the reducing agent (Fig. 3(G-I)).

Single particle scattering spectra of the specific individual nanoshells, correlated with the ESEM images of each nanoparticle, provide the most detailed picture of how the nanoparticle morphology affects the plasmon response of the nanoparticle.^{20, 35} Typical scattering spectra obtained for individual nanoshells in the thin-shell limit, prepared with the same Au^{3+} concentration but using the two different reductants, are shown in Figure 4. The nanoshell grown using CO as the reductant (Fig. 4(A)) has both a highly uniform shell morphology and a high quality nanoshell plasmon lineshape. A representative nanoshell grown at the same Au^{3+} concentration but with H_2CO as the reducing agent has an incomplete shell layer, and a correspondingly poorly defined plasmon lineshape and peak wavelength in its scattering spectrum (Fig. 4(B)). The particle-to-particle spectral variation

for the nanoshells grown using the H₂CO reductant was far greater than for the nanoshells grown using CO as the reductant, which is directly a result of a greater particle-to-particle variation in shell morphology. In addition, the higher energy “dark” plasmon mode at 450 nm, only weakly allowed for a spherically symmetric nanoshell, appears much more prominently in the scattering spectrum of the incomplete H₂CO-reductant nanoshells, in some cases having an amplitude approaching the “bright” plasmon at ~700 nm. The H₂CO reductant does, however, yield high quality nanoshells when thicker shell layers are grown, as seen in spectra and image of a representative nanoshell in Figure 4(C).

Conclusion

A improved method for the growth of continuous Au shell layers on dielectric oxide nanoparticles is reported. The reduction of Au³⁺ by CO results in the formation of thin, uniform shell layers on these nanoparticles at lower Au³⁺ concentrations, where continuous shell layers are not achievable with current liquid phase reduction methods. This approach relies only on the introduction of CO(g) into the solution of prepared precursor nanoparticles and Au³⁺, and is not susceptible to variations in shell layer morphology influenced by preparation of reductant or precursor solutions, a limitation of current shell layer growth methods. The use of CO as a reductant also has the potential to transform the manufacturing of nanoshells from a batch to a continuous flow process.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Schematic of shell layer deposition for nanoshell synthesis in the thin shell limit. A SiO_2 core decorated with Au nanoparticles, in a HAuCl_4 solution, serves as the deposition substrate, upon which a shell layer is grown using either carbon monoxide or formaldehyde reductants. Variations in shell morphology observed using H_2CO reductant solutions can be avoided using CO as the reducing agent.

Figure 2.

(A) Surface plasmon resonance wavelength as a function of available Au ions per particle for nanoshells grown with CO (red) and H₂CO (blue) reducing agents. (B,C) Selected extinction spectra corresponding to the data points (i-vi) in (A) for nanoshells grown with (B) H₂CO and (C) CO reducing agents. (i) and (iv) are extinction spectra corresponding to incomplete shell layer growth, (ii) and (v) correspond to nanoshells near the thin shell limit, and (iii) and (vi) correspond to nanoshells with thicker shell layers.

Figure 3.

(A) Optical extinction spectra of nanoshells synthesized under optimal conditions (reductant solution aged 5 days and precursor nanoparticle suspension aged 9 days) (i) $[\text{63},\text{83}] \text{H}_2\text{CO}$ -nanoshells, (ii) $[\text{63},\text{83}] \text{CO}$ -nanoshells. Scanning electron micrograph (SEM) images of (B) CO and (C) H_2CO -nanoshells corresponding to the spectra are shown in (A). (D) Optical extinction spectra of nanoshells synthesized using aged precursor solutions (reductant solution aged 6 days and precursor nanoparticle suspension aged 49 days) (iii) H_2CO -nanoshells, (iv) $[\text{63},\text{75}] \text{CO}$ -nanoshells and the Mie theory fit corresponding to (iv). (E,F) SEM images of nanoshells grown using (E) CO and (F) H_2CO reductant solutions corresponding to the spectra shown in (D). G) Optical extinction spectra of nanorice grown using (v) H_2CO and (vi) CO reductant solutions. SEM images of nanorice grown using (H) CO and (I) H_2CO reductant solutions whose spectra are shown in (G).

Figure 4.

Normalized scattering spectra and corresponding SEM images of individual nanoshells grown using (A) CO and (B) H₂CO reducing agents in the thin Au layer limit, using the same Au³⁺ ion concentration. (C) nanoshell grown with H₂CO reductant (not in the thin Au layer limit).