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Gas-phase production of gold-decorated silica nanoparticles

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Abstract
Gold-decorated silica nanoparticles were synthesized in a two-step process in which silica nanoparticles were produced by chemical vapor synthesis using tetraethylorthosilicate (TEOS) and subsequently decorated using two different gas-phase evaporative techniques. Both evaporative processes resulted in gold decoration of the silica particles. This study compares the mechanisms of particle decoration for a production method in which the gas and particles remain cool to a method in which the entire aerosol is heated. Results of transmission electron microscopy and visible spectroscopy studies indicate that both methods produce particles with similar morphologies and nearly identical absorption spectra, with peak absorption at 500–550 nm. A study of the thermal stability of the particles using heated-TEM indicates that the gold decoration on the particle surface remains stable at temperatures below 900°C, above which the gold decoration begins to both evaporate and coalesce.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Gold-decorated nanoparticles are of interest due to their unique plasmon resonance [1] and catalytic effects [2]. The catalytic effects have applications in various industrial products such as fuel cell production [3, 4] and chemical synthesis by hydrocarbon oxidation [5, 6]. Researchers are considering gold-decorated nanoparticles because of their plasmon resonance effects for biological applications including drug delivery [7], thermal therapies [8] and cancer diagnostics [9]. A recent study by Gaiduk et al highlights the use of gold nanoparticles in imaging single molecules for biological applications [10].

Currently most gold nanoparticles and nanoparticle coatings are synthesized using wet-chemistry techniques that require the use of solvents with inherent impurities that can affect the surface of the nanoparticles. A review by Daniel and Astruc [11] discusses methods of synthesizing and controlling solution-phase nanoparticles with gold surfaces and demonstrates the complexities of controlling gold growth in a solution. The preeminent gold coating process used currently is one developed by the Halas group [12, 13] whereby silica particles are prepared by a wet-chemistry technique and then gold nanoparticles are attached to the surface. To facilitate the attachment of gold onto the nanoparticle surface, organosilane molecules are attached to the silica nanoparticle which make available amine sites for subsequent gold attachment. This process results in a gold surface coverage of 30% on ~100 nm diameter silica particles. The attached gold islands act as nucleation sites for successive attachment of gold until a gold shell is completed. As the gold islands on the particle surface grow and begin to form a continuous film, the absorption spectrum of the particles shifts from the visible to the infrared region due to changes in surface plasmon resonance in accordance with Mie theory [13]. Wet-chemistry synthesis processes of this sort typically require multiple solution steps, take hours or days to complete, and are batch processes.

An alternative to wet-chemistry batch synthesis is the continuous production of gold-decorated silica nanoparticles by a gas-phase method. The synthesis can be conducted in an inert or non-reacting gaseous environment with low impurities, thus avoiding the inherent impurities of synthesis when
using liquid solvents. Also, because the gas-phase synthesis is a continuous process in which gas-phase precursors are reacted within a flow stream, the overall production of nanoparticles occurs within seconds rather than hours. Several methods exist for the production of nanoparticles within the gas phase including flame synthesis [14], inert-gas condensation [15, 16], plasma synthesis. [17], hot-wire generation [18], spark discharge [19], sputtering [20] and chemical vapor synthesis [21]. Chemical vapor synthesis is an attractive method for producing nanoparticles from precursors that have sufficiently high vapor pressures to allow the precursors to be delivered to a hot-wall reactor and thermally decomposed in the presence of an inert or non-reacting gas such as nitrogen. Hot-wire generators are an effective, low-cost way of producing gas-phase nanoparticles from solid, electrically conductive materials such as metals.

In the current work, we demonstrate the first known creation of gold-decorated silica nanoparticles by a gas-phase production method. The gas-phase production method allows for particles to be produced that are smaller (~5–80 nm) than typical of wet-chemistry processes, allowing for enhanced use in biological applications, where it has been shown that particles <100 nm have better permeation and accumulation within tumors [22]. The silica nanoparticles are produced by chemical vapor synthesis, in which tetraethylorthosilicate (TEOS, Si(OC2H5)4) is decomposed in a tube furnace within a nitrogen environment. The silica nanoparticles are subsequently decorated with gold produced from two different evaporation methods, hot-wire and tube-furnace evaporation, downstream of the silica nanoparticle synthesis. We experimentally investigate the particle morphologies available from this gas-phase production method by varying critical system parameters and we discuss the fundamental mechanisms behind the two different methods.

2. Experimental procedure

The gold-decorated silica synthesis method is shown schematically in figure 1. TEOS is evaporated into a flow stream by bubbling nitrogen (~26 sccm) through a liquid TEOS bubbler (results in ~0.06 sccm) which is then mixed with oxygen (1 slm) and additional nitrogen (2 slm) before it enters the decomposition furnace (900 °C). The furnace dissociates the TEOS, which then homogeneously nucleates to form silica nanoparticles in the gas phase. The high concentration of silica nanoparticles quickly begin to agglomerate. The high concentration of silica nanoparticles quickly begins to agglomerate. The agglomeration is suppressed by additional nitrogen dilution flow (~2 slm). The agglomerated particles are sent to a form fully coalesced, spherical particles by passing them through a second tube furnace (800–1400 °C). The typical residence time of the process is approximately 6 s. All tubing has an inner diameter of 3.75 mm except for the tubes within the furnaces which have an inner diameter of 10.4 mm in the decomposition furnace and 20 mm in the sintering furnace.

Gold decoration occurs by passing the silica particles through one of two different gold evaporation chambers. In path A, the aerosol passes through a tube furnace (1200–1500 °C) whereby the entire aerosol is heated before it passes over a gold slug which evaporates, introducing gold vapor into the aerosol. Upon cooling, the vapor heterogeneously nucleates on the surface of the nanoparticles, thus creating gold decoration. The particles are then either directly collected or characterized in situ.

In path B the aerosol passes over a hot-wire evaporator where a gold-coated platinum wire is heated by electrical resistance to introduce gold into the aerosol. The diameter of the tube decreases in the region surrounding the gold-coated wire to 3 mm, as discussed in a previous study [23]. In the hot-wire evaporator the gold is heated directly and the aerosol remains cooler than the surface temperature of the wire, resulting in a different delivery method of the gold to the particle surface. Once the gold is introduced into the aerosol, the particles are then either passed through an agglomeration chamber, which increases the residence time (~30 s) to allow for further agglomeration, or collected and/or characterized in situ.

The in situ characterization techniques used for the aerosol synthesis process are particle mobility measurement by differential mobility analyzers (DMAs) and on-line infrared spectroscopy. The DMA (TSI model 3085) coupled with an ultrafine condensation particle counter (CPC, TSI model

![Figure 1. Schematic of gold-decorated silica particle production with hot-wire (path A) and tube-furnace (path B) evaporative techniques.](image-url)
with and without oxygen.

3025A) are configured as a discrete mobility particle sizer (DMPS) by adding a single DMA and the CPC in series at the end of the process to measure the mobility diameter of the synthesized particles. Additionally, a tandem differential mobility analysis (TDMA) set-up is used to study coating mechanisms by adding another DMA after the silica synthesis to select a monodisperse stream of silica particles for subsequent gold decoration. In situ infrared spectroscopy is performed by collecting the nanoparticles in flight on a stainless steel mesh within the analysis cell of a Fourier transform infrared (FTIR) spectrometer (Magna-IR Model 550, Nicolet Instrument Corp. Madison, WI). The particles are collected for ex situ characterization by electrostatic precipitation at +3 kV onto lacey carbon microscopy grids. An FEI Tecnai G² F30 transmission electron microscope (TEM) is used to image particles and perform dispersive x-ray (EDX) analysis.

3. Results and discussion

Silica nanoparticles were synthesized using 0.06 sccm of TEOS, 2 slm of nitrogen and 1 slm of oxygen in a tube furnace at 900 °C. The particles were diluted with an additional 2 slm of nitrogen and sintered at varying temperatures. As seen in figure 2(a) the particle concentration increased with increasing sintering temperature up to 1200 °C, indicating that in addition to sintering the furnace caused unreacted TEOS to nucleate, producing more particles. Above 1200 °C the increase in temperature did not increase the total concentration of particles, indicating that all of the TEOS had been decomposed and only sintering was occurring. For particles sintered at 1500 °C, there was actually a slight loss in particle concentration when compared to sintering at 1400 °C, indicating that losses to the tube walls increased with increasing temperature. Therefore, the optimal particle production was found to occur from 1200 to 1400 °C where all of the TEOS was decomposed but losses to the wall were not substantial. As seen in figure 2(b), the TEM image of particles produced at a sintering temperature of 1400 °C shows that the particles were spherical and largely unagglomerated. Figure 2(c) shows the effect of adding oxygen when producing silica nanoparticles by comparing the infrared spectra of particles produced with oxygen to those produced without. In each case, the particles were produced with the aforementioned conditions and collected on a stainless steel mesh in the FTIR cell for 45 min. As shown, the particles produced with oxygen exhibit a much more intense peak at the Si–O–Si stretching region, 800 cm⁻¹, and at the Si–OH stretching region ∼940 cm⁻¹. Additionally, the presence of oxygen shifts the peak from the Si–O–Si asymmetric stretch, 1000–1200 cm⁻¹, towards higher wavenumbers, an indication of more structurally ideal silica [24]. As these results indicate, the silica particles are best produced with a sintering temperature from 1200 to 1400 °C and with 1 slm of oxygen. All of the following results in this study use this production method unless otherwise noted.

Gold decoration of the silica nanoparticles was investigated by passing the silica aerosol through path A, whereby the entire aerosol was heated and then passed over a gold evaporation slug. By heating the entire aerosol gold-decorated particles were produced, figure 3. For lower temperatures, as shown in figure 3(a), almost all of the gold decorated the silica surface and little gold appeared independently on the lacey carbon grid. As the furnace temperature increased, so too did the amount of gold vapor entering the aerosol stream, resulting in an increase in the number of gold nanoparticles that are independent of the silica particles observed on the lacey carbon shown in figures 3(a) and (b). A likely explanation for this behavior is that, at lower vapor concentrations, the gold preferentially nucleated on the silica particle surface. However, as the vapor pressure of the gold increased so too did the propensity for gold to homogeneously nucleate. The homogeneous nucleation of gold results in increasing numbers of independent gold particles. In all cases the gold appeared to ‘ball up’ on the surface of the silica nanoparticles, which was likely due to the difference in surface energies between silica and gold. At temperatures near the melting point of gold, ∼1063 °C, the contact angle of gold on a pure silica surface is 140° [25]. Because the silica particles are hot when the gold condenses on their surfaces, the gold atoms possess enough energy that they are able to arrange in a manner that lowers the collective surface energy of the gold, resulting in gold decoration rather than a thin film.
To investigate the effect of heating just the gold rather than the entire aerosol, silica particles were passed through the hot-wire evaporator along path B as indicated in figure 1. As shown in figure 4, the amount of gold decoration on the silica particle surface increased when the power applied to the gold-coated wire was increased. The increased gold evaporation from the hot wire, due to the increase in wire surface temperature at higher powers, also resulted in more gold being collected independent of the silica particles, a similar result as found in path A. In all cases, gold decorated the particle surface rather than forming a continuous film. Unlike when the aerosol was purposely heated to evaporate gold, along path A, the aerosol was only heated indirectly as it came into contact with the gold-coated hot wire. Therefore, as gold vapor left the surface of the wire, gold homogeneously nucleated. Upon nucleation, the gold particles were then scavenged by the larger silica nanoparticles.

In addition to experimental studies, a computational fluid dynamics (CFD) model was developed to give a better understanding of the temperature and velocity profiles within the hot-wire nanoparticle generator. A discretized CFD model was developed within Fluent (a commercially available computational fluid dynamics platform by ANSYS, Inc.). The model solves both the conservation of energy and momentum equations for a compressible fluid. A standard $k-\varepsilon$ two-equation model was used to solve for the turbulent conditions [26]. A standard laminar flow model was also solved for comparison. No viscous heating or radiant heat transfer was included. The model was single phase with only gas-phase nitrogen present in the flow. Nitrogen was modeled as an ideal gas with density varying accordingly. The specific heat of nitrogen varied with temperature according to a piecewise linear function. The thermal conductivity and viscosity were held constant at 0.0242 W m$^{-1}$ K$^{-1}$ and 1.663 $\times$ 10$^{-5}$ kg m$^{-1}$ s$^{-1}$, respectively. The boundary conditions of the system included a constant face velocity at the inlet corresponding to a flow rate of 2 slm, a no-slip boundary condition at the walls, an axisymmetric condition at the center of the tube and a constant pressure outlet that was maintained at atmospheric pressure. The incoming gas had a temperature
Figure 5. Computational fluid dynamics simulation of the temperature profile within a hot-wire generator with 2 slm of nitrogen flow and a wire temperature of 1065°C within a 3 mm converging–diverging nozzle.

Figure 6. (a) TDMA particle size distribution of bare and gold-decorated silica nanoparticles produced using a hot-wire generator with and without being passed through an agglomeration chamber. (The plot is normalized to the bare silica particle peak.) Corresponding TEM images of gold-decorated silica nanoparticles produced by a hot-wire generator (b) without and (c) with an agglomeration chamber.

of 20°C and all other surfaces acted as insulating walls. The model uses a body-force-weighted pressure solution method where the effect of gravity was included in the direction perpendicular to the flow. The momentum, turbulent kinetic energy, turbulent dissipation rate and energy equations were all solved with the first-order upwind method.

As shown in figure 5, the hot-wire generator with the 3 mm nozzle was modeled with the wire surface at a constant temperature of 1065°C (the melting temperature of gold, which is the minimum required temperature to produce particles [18]). Models with a constant power boundary condition that corresponds to the experimental powers discussed previously resulted in unrealistically high wire temperatures that were the result of the single-phase model in which the latent heat of evaporation was not accounted for when gold vapor leaves the solid surface (an endothermic process), nor was it accounted for downstream where the particles nucleate (an exothermic process). As a result, the model cannot be used to determine absolute values, but rather was useful to indicate temperature and velocity trends. The temperature profile with the constant wire temperature indicates that a strong temperature gradient exists near the wire surface and that 0.5 mm away from the wire surface the gas temperature is less than 200°C. These results suggest that, as the gold vapor leaves the wire surface, it is quickly entrained by the nitrogen cross-flow. The gold then likely nucleates as it is supersaturated in the much lower gas temperatures before encountering the silica particles. The gold particles are then likely scavenged by the larger silica particles, resulting in decoration.

In order to confirm that the gold particles nucleate homogeneously and are then scavenged by the silica particles in the hot-wire method, a series of TDMA studies were conducted where silica was size-selected at 30 nm prior to entering the hot-wire evaporator. Upon size selection with the first DMA, the concentration of the aerosol was reduced. The resulting aerosol passed through the hot-wire evaporator at a flow rate of 1 slm. On-line analysis and subsequent TEM study confirmed that particle decoration only occurred in the hot-wire evaporator when a smaller particle mode developed as shown in figure 6(a). When the aerosol was analyzed immediately after leaving the hot-wire evaporator the silica particle mode shifted to a larger size but there remained a significant difference between the smaller gold particle mode and the larger silica particle mode. The TDMA measurements of the directly collected nanoparticles are confirmed in figure 6(b) where it is apparent that, while some gold lies on the silica particle surface, a large number of gold particles remained unattached to the silica particles. When the silica particles and nucleated gold were instead passed through the agglomeration chamber the TDMA analysis, figure 6(a), shows that the shift in the silica particle mode was greater when using the agglomeration chamber. Additionally, with the increased residence time, the gold particles agglomerate, resulting in an increase in the diameter of the lower mode of the size distribution. The
gold and silica particles have a greater collision frequency function ($\beta_{30\,nm,\,30\,nm} \approx 10^{-8} \text{ cm}^3 \text{ s}^{-1}$) due to their difference in size than do silica–silica or gold–gold particle collisions ($\beta_{3\,nm,\,3\,nm} \approx \beta_{30\,nm,\,30\,nm} \approx 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) [27]. As a result more gold was found on the silica particle surface and fewer individual gold particles were present when the particles were allowed to agglomerate, as shown in the TEM image seen in figure 6(c).

Further densification of gold on the silica nanoparticle surface was found to be possible by increasing the number of gold particles produced by the hot-wire evaporator. Increased gold particle production can be accomplished by increasing the power of the hot-wire evaporator or by increasing the gas velocity across the wire surface, which serves to produce a higher concentration of smaller particles [23]. By increasing the aerosol flow rate from 1 slm (figure 6) to 5 slm and increasing the hot-wire power to 27 W, more gold particles were produced. The gold-decorated silica particles were then passed through the agglomeration chamber and size-selected at 15 nm before being collected on a lacey carbon TEM grid. As shown in figure 7, the TEM image of the gold-decorated silica nanoparticle shows that it has a high density of gold on its surface. The gold on the nanoparticle surface was found to be crystalline as shown by the lattice fringes present in figure 7. Analysis of the fringes from several images found gold spacings of 2.0 and 2.3 Å, which correspond to the [111] and [002] faces of gold, respectively [28]. These results are in agreement with previous analyses of lattice spacings conducted for independent gold nanoparticle generation by the hot-wire evaporator [23]. Previous XPS results also indicate that the gold production is free of contamination. Despite the high surface density of gold, the surface remains decorated rather than coated by a thin continuous film. While size-selecting the particles after their production eliminates gold particles other than those attached to the surface of silica particles, it also reduces the overall particle yield.

In order to confirm that higher contrast areas seen in the TEM images represent gold on the silica particle surface, EDX analysis was conducted on a gold-decorated silica particle. The composite particles were produced by the hot-wire evaporator at a power of 12 W with the flow rates and temperatures as used to produce figure 6(b), but with a polydisperse aerosol, rather than a size-selected monodisperse aerosol. The resulting particles were not passed through the agglomeration chamber. As seen in figure 8(a), a silica particle was imaged using scanning transmission electron microscopy (STEM) and shows a silica particle with gold decoration (high-contrast regions). When EDX was performed on the same particle, the elemental analysis, figure 8(b), showed that the core particle consists...
primarily of oxygen and silicon in roughly a 2 to 1 ratio as is expected in silica. The elemental analysis shows that the gold signal peaked in two spots which correspond to the locations of high contrast seen in the STEM image. It should be noted that no traces of platinum were detected with the elemental analysis, indicating that only the gold coating on the wire was evaporating and not the inner platinum core.

Many studies have investigated the radiation absorption properties of gold nanoparticles due to the unique plasmon resonance that occurs in nanosized gold particles and films [11, 13]. The absorption characteristics of the gold-decorated silica nanoparticles produced in this study were measured by collecting the particles on glass-fiber filters for 15 min from both production methods. The collected particles were then analyzed directly without dispersion by placing the filter within an integration cell, and the absorption spectra were collected using a UV–NIR spectrometer (Ocean Optics Model USB4000). The results, as shown in figure 9, appear similar for the particles produced in both evaporation methods. Both methods resulted in particles that absorb in the 500–550 nm wavelength region, which is typical of gold nanoparticles [29]. As the tube furnace temperature or hot-wire power was increased, the amount of absorption increased while the peak absorption location did not shift. These results confirm that the nanoparticles were decorated with gold rather than coated with a thin film, which would tend to shift the peak in the absorbance toward the infrared region [29]. It should be noted that there was no difference seen in the particles that were synthesized using the agglomeration chamber to those synthesized without the chamber.

Many of the potential applications for gold-decorated silica particles require the particles to be stable at high temperatures. Therefore, the particles were examined using a heated-TEM stage to determine whether the gold becomes mobile or leaves the silica particle surface. Gold-decorated silica particles were prepared using the tube-furnace evaporator at 1350°C. The particles were collected on lacey carbon TEM grids and imaged while being heated. As shown in figure 10, the original grids contained mostly gold-decorated silica particles with few standalone gold nanoparticles. As the particles were heated, the gold remained stable on the particle surface at temperatures below 900°C. As the temperature increased above 957°C, the gold began to reorient on the silica particle surface forming gold agglomerates on the silica particle as seen in the enlarged images of figure 10(c). Also, while the grid temperatures remain below the melting point of bulk gold, it is apparent that the vapor pressure is

![Figure 9](image-url) UV–NIR spectrum of gold-decorated silica nanoparticles produced at varying hot-wire powers and tube-furnace temperatures.

![Figure 10](image-url) The evolution of gold-decorated silica nanoparticles at increasing temperatures. The figure includes (a) low resolution images, (b) example of gold evaporation and (c) example of gold coalescence.
high enough that gold begins to evaporate. As shown in figure 10(b), the gold decoration is reduced on several of the particles, but no increase in size is seen on the remaining gold islands. The migration of gold on the surface of particles and wires has been noted by several researches and is particularly important in silicon nanowire growth with gold catalysts [30]. Several studies have examined the effect of size on thermodynamic properties, such as vapor pressure and melting temperature [31, 32], and demonstrate that, as the particle size decreases the atoms on the surface are more loosely bound, leading to a decrease in melting point and an increase in vapor pressure at a given temperature.

4. Summary and conclusions

The present study demonstrates the gold decoration of silica nanoparticles by gas-phase methods. The nanoparticle production is carried out in a nitrogen environment and is a throughput process that, in contrast to wet-chemistry techniques, does not require the use of solvents, leaves the nanoparticle surface free of contamination and is scalable to obtain high flow rates. The gold decoration is achieved by evaporating solid gold by two different processes and it was shown that gold can be delivered to the particle surface by two distinct mechanisms. When the entire aerosol (silica nanoparticles and surrounding gas) was heated in the presence of gold, gold vapor entered the aerosol stream and condensed on the particle surface upon cooling. Due to the surface energies of gold and silica, the gold atoms rearranged themselves to minimize their surface energy and ‘balled up’ on the particle surface. Using a second method, hot-wire evaporation, the aerosol remained cool which caused the nucleation of the gold particles upon leaving the hot-wire surface. Then when the gold particles reached the silica surface particle by agglomeration they again formed a decoration of the surface, but through a different mechanism. The resulting nanoparticles had a core diameter of 10–50 nm with islands of gold surface decoration with diameters of 1–3 nm. Monodisperse distributions of particles were achieved by size-selecting particles according to the electric mobility. The small sizes of the synthesized particles make them advantageous for use in biological applications. Increased gold density was achieved by adding additional residence time to the system to allow the gold particles produced from the hot-wire evaporator to be scavenged by the silica particles. In both cases the particles had similar absorbance spectra with peak intensities at wavelengths from 500 to 550 nm. It was shown that the gold decoration remained stable at temperatures below 900 °C, above which the gold decoration evaporated and formed larger islands on the silica surface. The thermal stability of the gold nanoparticles on the surface of silica at elevated temperature is an important result for catalytic applications where elevated temperatures are required.

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