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## Synthesis of Size and Shape Controlled Silver Nanoparticles Coated by a Thin Layer of Gold and Their Use as Ultrasensitive Biomolecular Probes.

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### ABSTRACT

Silver nanoparticles coated by a layer of gold (Ag@Au) have received much attention because of their potential application as ultra sensitive probes for the detection of biologically important molecules such as DNA, proteins, amino acids and many others. However, the ability to control the size, shape, and monodispersity of the Ag@Au structure has met with limited success. In our own research we have addressed this challenge by creating an aqueous wet chemical synthesis technique towards size and shape controllable Ag@Au nanoparticles. These materials are highly interesting because of the tunable silver core size, and the tunable gold shell thickness, opening many avenues to the modification of the particle properties in terms of bio-molecular sensing. The resulting nanoparticle probes were functionalized with two complementary stranded DNA oligonucleotides. When combined, the complementary strands hybridized, causing the Ag@Au nanoparticles to assemble into large nano-structures. The presence of the oligonucleotide was confirmed through a series of techniques including UV-Vis and RAMAN spectroscopy, as well as HR-TEM, XPS, DLS, and many others. The results reflect the role that the nanoparticle physical properties play in the detection of the bio-molecules, as well as elucidate the characteristics of the bio-molecule/nanoparticle interaction.

### INTRODUCTION

Both silver and gold nanoparticles (NPs) have received wide attention for their enhanced properties in a multitude of potential applications such as sensing, microelectronics, and catalysis, [1,2] because of the many desirable chemical and physical properties of the materials. In terms of bio-diagnostics and sensing, it is the optical properties that make Ag NPs exceptional, while for Au NPs it is the resistance to oxidation and enhanced thiol chemistry that is attractive [3,4]. The current trend in this area of research is the coupling of these two materials as a core@shell structure that takes advantage of the optical properties of silver and the stability/thiol chemistry of gold. These Ag@Au nanoparticles are expected to have use as bio-probes with unprecedented sensitivity and selectivity. Despite the excitement surrounding these materials though, there are still many challenges to address, including the ability to synthesize Ag NPs in aqueous phase with a desired size, shape, or monodispersity [5], and the ability to coat the silver particle with a uniform and controllable layer of gold [6]. The approach we have taken to these challenges is a modification to the synthesis of Ag NPs in terms of synthetic conditions and reagents towards particles of controllable size and monodispersity. In terms of coating Ag particles with Au, we use a technique where additional reducing agent is added in tandem with Au precursor to minimize the etching of the Ag particles during the coating process. While it is possible that some degree of etching or alloying of Ag and Au take place, we show that it can be controlled by the amount of Au precursor added, the amount of additional reducing agent added, and the control of the remaining experimental conditions.

## EXPERIMENT

*Chemicals.* Silver nitrate, sodium acrylate, gold tetrachloroaurate trihydrate and common solvents were obtained from Aldrich. Water was purified with a Millipore Direct-Q system (18.2 M $\Omega$ ). Dialysis membranes with molecular weight pore size of 10,000 daltons were obtained from Spectra/Por and were rinsed in pure water before use.

*Synthesis of Ag NP Cores:* Ag NPs were synthesized by first mixing 50ml of water with  $1.25 \times 10^{-5}$  moles of silver nitrate, and then adding  $6.75 \times 10^{-6}$  moles of sodium hydroxide, which results in a dilute yellow colored solution of silver hydroxide. This solution is purged with argon and is then brought to reflux. At reflux,  $2.55 \times 10^{-4}$  moles of sodium acrylate are added causing the solution to turn completely clear. The solution is refluxed for 1 hour, over this time the solution color changes from clear to green-yellow to yellow-orange.

*Purification of as-synthesized Ag NPs:* Prior to deposition of Au on the Ag NP seeds, the as-synthesized particles are purified to remove excess acrylate, silver, sodium, and other ions from the solution. Purification is performed by enveloping the particle solution inside of a cellulose dialysis membrane with pore size of 10,000 daltons and soaking in a distilled water bath. The water was changed every 12 hours for 48 hours.

*Deposition of Au on the Ag Cores to form Ag@Au NPs:* 50ml of the dialyzed Ag particles are brought to reflux and 10ml of a gold tetrachloroaurate trihydrate solution (ranging from  $6.25 \times 10^{-7}$  to  $3.13 \times 10^{-6}$  moles according to the thickness of the Au shell desired) and 10ml of a sodium acrylate solution (from  $5.10 \times 10^{-5}$  to  $2.55 \times 10^{-4}$  moles) are added dropwise simultaneously. The solution color changes depending on the amount of Au added. In general, as Au and sodium acrylate is added to the Ag particles, the color changes from yellow-amber to dark amber to grey to grey-purple and finally to purple.

*Instrumentation and Measurements:* An array of techniques including Transmission Electron Microscopy (TEM), High Resolution TEM and Energy Dispersive Spectroscopy (HR-TEM, EDS), X-Ray Photoelectron Spectroscopy (XPS) and Ultra-Violet Visible Spectroscopy (UV-Vis) were used to characterize the size, shape, composition and other properties of the materials. TEM analysis was performed on an Hitachi H-7100 transmission electron microscope operated at 100kV. HR-TEM and EDS analysis was performed on an Hitachi H-9000NAR transmission electron microscope operated at 300kV. TEM samples were prepared by dropping the suspended particles onto a carbon coated copper grid and drying in air overnight.

## DISCUSSION

In general, our synthetic route towards Ag@Au NPs consists of 2 main steps. First we synthesize the Ag cores in aqueous phase with an acrylate capping agent. In the first part of the results and discussion section we show our synthetic approach to monodispersed Ag particles. The second step of this research is the coating of Au on the Ag particle surface. In the second part of the results and discussion section we illustrate the coating of the Ag particles by Au and discuss the ability to control the thickness of the Au layer and the resulting morphology of the nanostructures. The overall technique of our synthetic approach is shown in Scheme 1. In this approach, first we used silver nitrate and sodium hydroxide to create a dilute solution of silver hydroxide. This solution was brought to reflux, whereupon sodium acrylate was added, initiating the formation of Ag NPs. The Ag particles formed over the course of one hour as evidenced by the appearance of a yellow-amber solution. Figure 1A shows the TEM image of the as-

synthesized Ag NPs capped by the acrylate molecule. The particle size distribution is  $20.5 \pm 3.3$  nm (16% deviation). Given the size of the particles and their total mass, we calculated the Ag NP concentration to be  $7.28 \times 10^{-11}$  M and their extinction coefficient to be  $2.11 \times 10^{10}$  M<sup>-1</sup>cm<sup>-1</sup>.

After synthesis, the particles were purified by using dialysis to remove excess acrylate, silver ions, and other species. The coating of the silver NPs by gold is achieved in what is essentially a seeded growth reaction. Briefly, first the Ag NPs are brought to reflux, then dilute aqueous gold and sodium acrylate solutions are added simultaneously, dropwise, causing the Au to reduce at the Ag NP surface, causing a coating of Au to be formed. The primary challenge in this reaction is the propensity of Ag to be oxidized as Au is reduced during the coating. Such an occurrence can lead to either hollow Au particles or alloyed Au and Ag NPs. In our own reaction, the alloying or etching of the Ag NPs can be minimized through control of the concentration of gold being added, the rate that it is added, and by addition of the sodium acrylate capping and reducing agent. Here, the role of sodium acrylate is to cause the Au to become reduced before the Ag can be oxidized.

**Scheme 1:** Reaction Rout for the Synthesis of Ag NPs and their Coating with Au.

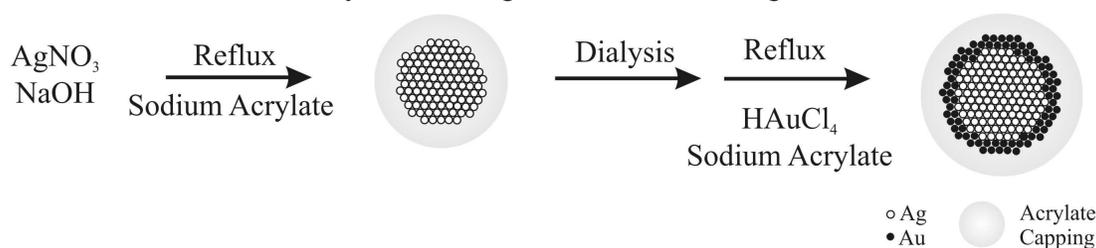
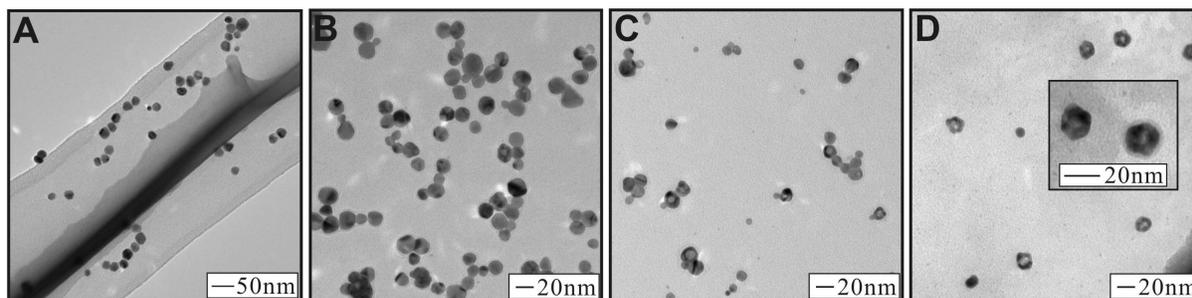


Figure 1 shows a series of TEM images of Ag@Au NPs synthesized using the method described above. For each sample, the amount of gold and sodium acrylate added was incrementally increased. Figure 1B shows a sample of Ag@Au NPs synthesized by adding  $6.25 \times 10^{-7}$  moles of Au and  $1.38 \times 10^{-4}$  moles of sodium acrylate (corresponding to 5% Au in terms of atomic composition). Inspection of the TEM image reveals particles with a uniform spherical morphology. The direct observation of a deposition of a layer of gold on the surface of the silver nanoparticles is difficult to ascertain in this image. The size distribution of these particles is  $17.5 \pm 3.7$ nm. Figure 1C shows a sample of Ag@Au NPs synthesized by adding  $1.88 \times 10^{-6}$  moles of Au and  $1.38 \times 10^{-4}$  moles of sodium acrylate (corresponding to 15% Au in terms of atomic composition). The TEM image shows several particles with a spherical morphology, but now several particles are observed that have a lighter spherical center and darker outside ring. The observation of this dark outside and light center is inconsistent among different particles in the sample, some particles display no darker ring and light center at all, or some particles display simply a light spot near the periphery of the NP. We attribute this observation to the formation of an incomplete Au shell on the Ag particle surface. In effect, the round holes that are observed on the particles in the TEM image are a gap or hole in the Au shell, allowing us to see the Ag core inside the particle [6]. The size distribution of these NPs is  $16.3 \pm 2.7$  nm. In addition, a few NPs are observed in the TEM image with much smaller size than the parent Ag NPs (~9nm), which could be attributed to the non-specific formation of Au NPs without coating on the Ag surface. The presence of these small particles was not observed in techniques such as UV-Vis, probably because of their low concentration as compared to the coated particles. Finally, Figure 1D shows a sample of Ag@Au NPs synthesized by adding

$3.13 \times 10^{-6}$  moles of Au and  $1.38 \times 10^{-4}$  moles of sodium acrylate (corresponding to 25% Au in terms of atomic composition). The TEM image reveals many particles with a light center and thick dark outside. Now the particles seem to have adopted roughly hexagonal or pentagonal shapes, likely reflecting the tendency of Ag nanocrystals to be oriented in the twinned structure, templating the growth of Au at their surface. The size distribution of these particles is  $17.5 \pm 5.1$  nm. Among these three samples the particle sizes are generally smaller than the precursor Ag NP seeds (size of  $20.5 \pm 3.3$  nm). We attribute this size decrease to a small degree of etching of the silver surface at the initial reaction stage as the gold layer is deposited [6]. As the reaction progresses, the acrylate reducing agent plays a more significant role in reducing the gold as it is deposited on the particle surface, thereby preventing the entire silver core from being etched away.



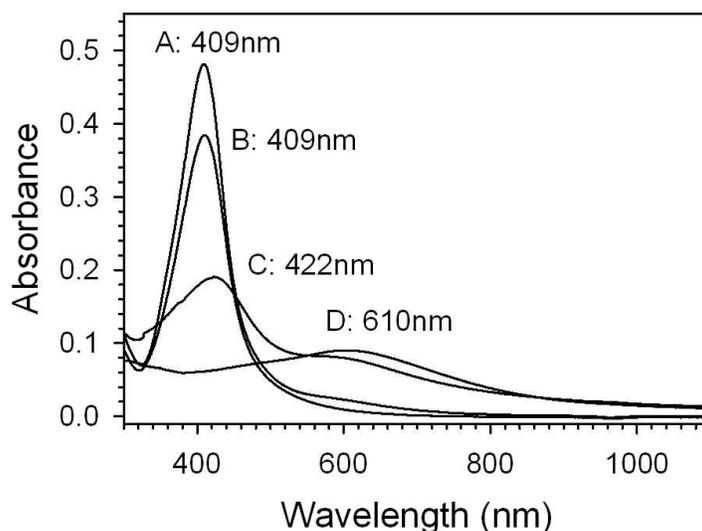
**Figure 1.** TEM images for as-synthesized Ag NPs (A), and Ag@Au NPs with atomic feeding ratio of: 5% Au (B), 15% Au (C), and 25% Au (D).

The composition of these NPs was analyzed using both EDS and XPS techniques. Table 1 shows the atomic feeding ratio for each sample as well as the composition as determined by EDS and XPS. The primary difference between the EDS and XPS techniques is that EDS could be used to determine the composition of several different particles individually, and then an average was taken of the composition, while for XPS a relatively large analysis area resulted in simultaneous analysis of several particles. For the NPs synthesized with 5% feeding ratio of Au, the composition is consistent among the metallic feeding ratio and both EDS and XPS techniques. However, for the sample prepared with atomic feeding ratio of 15% Au, both EDS and XPS show a heightened amount of Au in the final sample (both  $\sim 40\%$  Au), this is likely an effect of attenuation of the beam for EDS and XPS techniques, which have finite penetration depths of the sample, resulting in higher sensitivity to surface species, in this case Au at the surface of the core@shell structure. Finally the sample prepared with atomic feeding ratio of 25% Au also shows a heightened amount of Au in the determined composition for both EDS and XPS techniques, however there is a slight discrepancy between the compositions determined by XPS and EDS. This could arise from inhomogeneity in the prepared samples, or because of a difference in the relative penetration depths of each instrumental technique. The observation of the general decrease in the amount of Ag and the increase in the amount of Au is consistent with a core@shell structure with Ag on the inside of the particle and Au on the outside. It is important to note that for the case of addition of 25% Au by atomic feeding ratio, this amount of Au is sufficient to completely etch away all of the Ag metal in the sample, however we still detect the presence of Ag in our NP system. This observation reinforces our assertion that acrylate works to suppress the oxidation of Ag by Au and is key in forming Ag@Au structures instead of hollow Au shells.

**Table 1.** Comparison of Metallic Feeding Ratio and EDS/XPS Determined Composition of Ag@Au NPs

<b>Metallic Feeding Ratio</b>	<b>EDS</b>	<b>XPS</b>
Ag <sub>100</sub>	Ag <sub>100</sub>	Ag <sub>100</sub>
Ag <sub>95</sub> Au <sub>5</sub>	Ag <sub>93.0</sub> Au <sub>7.0</sub>	Ag <sub>94.8</sub> Au <sub>5.2</sub>
Ag <sub>85</sub> Au <sub>15</sub>	Ag <sub>60.6</sub> Au <sub>39.4</sub>	Ag <sub>57.7</sub> Au <sub>42.3</sub>
Ag <sub>75</sub> Au <sub>25</sub>	Ag <sub>50.8</sub> Au <sub>49.2</sub>	Ag <sub>60.6</sub> Au <sub>39.4</sub>

Figure 2 shows the UV-Vis spectra collected for each sample of Ag and Ag@Au NPs. Spectrum A is that for the as-synthesized Ag NPs with SPR peak maximum of 409nm. Spectrum B is that for the Ag@Au NPs with 5% addition of Au. This spectrum also has a peak maximum of 409nm, illustrating the retention of the NP size after coating with a small amount of Au. However, now the SPR band intensity has decreased, illustrating the suppression of the SPR band by the coating with Au. Spectrum C is for the Ag@Au NPs with 15% addition of Au. This spectrum now has two main bands. The primary band at 422nm has shifted to higher wavelength than that for Ag particles, which could indicate the formation of an alloy at the interface of Au and Ag in the NP. In addition, this bands intensity is drastically decreased from that of the earlier samples, which has been supported by previous calculation studies [7]. A new band has also formed around 600nm, which is indicative of the increasing amount of Au in the sample being coated on the surface of the Ag particles. Spectrum D is for the Ag@Au NPs with 25% Au added. The original Ag peak is now completely suppressed, and a long wavelength band has formed around 610nm. This long wavelength band for Au is significantly shifted to higher wavelength in the UV-Vis spectrum than is typically observed for solid Au NPs (~525nm). This red-shift of the SPR band for Au is a result of the Au shell formation over the Ag core, in this case the SPR band from the Au shell becomes red-shifted from the solid Au particle peak [7].



**Figure 2.** UV-Vis spectra for Ag and Ag@Au NPs prepared with increasing Au content, as-synthesized Ag NPs (A), 5% Au atomic feeding ratio (B), 15% Au atomic feeding ratio (C), 25% Au atomic feeding ratio (D).

## CONCLUSIONS

We have demonstrated a straightforward technique for the synthesis of monodispersed silver nanoparticles and their coating by a shell of gold of variable thickness that can be controlled by the amount of gold precursor used in the coating process. The use of acrylate as a dual reducing and encapsulating agent minimized the etching of metallic silver particles by the aqueous gold precursor. The characterization of the materials show that silver is present in each coated sample as well as increasing amount of gold indicative of a core@shell structure. The optical characterization using UV-Visible spectroscopy also supports the core@shell structure. In this study, we did not utilize XRD to address the core@shell structure because the lattice spacing of gold and silver are nearly identical, making the gold and silver XRD patterns indistinguishable. These materials have potential applications as sensors or bio-diagnostics. The sensitive detection of DNA and other biomolecules using these probes is part of our ongoing work.

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