Gold Plating of Silver Nanoparticles for Superior Stability and Preserved Plasmonic and Sensing Properties

Nimer Murshid, a Ilya Gourevich, b Neil Coombs b and Vladimir Kitaev a *

a Chemistry Department, Wilfrid Laurier University, 75 University Ave. W, Waterloo, Ontario, Canada, N2L 3C5. E-mail: vkitaev@wlu.ca

b Centre for Nanostructure Imaging, Chemistry Department, University of Toronto, 80 St George Street, Toronto, Ontario, Canada M5S 3H6.

Experimental section:

Reagents

Silver nitrate (99.9%), tetrachloroauric acid (99.5%), hydrogen peroxide (30-32 wt.% solution in water (ca. 10.4 M), semiconductor grade, 99.99%, L-arginine (TLC, 98%), sodium citrate tribasic dihydrate (99+%), and sodium borohydride (99%), were supplied by Aldrich and used as received, polyvinylpyrrolidone (PVP, M_w = 40K) was supplied by Caledon. High-purity deionized water (> 18.3 MΩcm) was produced using Millipore A10 Milli-Q.

Synthesis of silver decahedral nanoparticles (AgDeNPs)

AgDeNPs were synthesized using a new-generation photochemical synthetic protocol developed by our group. 1,2 To a 20-mL vial containing 14.00 mL of high-purity deionized water, the following solutions were added in the listed order: 0.520 mL of 0.050 M sodium citrate, 0.0150 mL of 0.050 M PVP (total concentration of monomer units), 0.050 mL of 0.005 M L-arginine, 0.400 mL of 0.0050 M silver, and freshly prepared 0.200 mL of 0.100 M sodium borohydride. A
pale yellow solution is first formed, which then turned to bright yellow upon continuing stirring (600 rpm). Subsequently, 0.300 mL of ca. 10.4 M hydrogen peroxide was added. The solution then has been kept stirring for further ca. 20 min. Subsequently, the produced solution was exposed to royal blue 449 nm LED for 14 hrs.

**Synthesis of silver pentagonal rod nanoparticles (AgPRNPs)**

Silver pentagonal rods nanoparticles with average length of ca. 120 nm are typically produced thermally using an adapted synthetic protocol that reported by our group.\textsuperscript{1,3} An aqueous preparation containing 6.00 mL of high-purity deionized water, 0.720 mL of 0.05 M citrate and 0.135 mL of 0.05 M PVP was heated at controlled temperature near boiling (ca. 98 °C) for 10 minutes. Subsequently, 1.00 ml of five-time concentrated AgDeNP dispersion followed by a 0.800 mL of 0.005 M silver nitrate were added. Finally, the reaction mixture was heated for additional 15 minutes.

**Gold coating of AgDeNPs**

In a typical synthetic procedure to produce gold coated silver decahedral nanoparticles (Au@AgDeNPs), (shell@core), a 3.00 mL of freshly prepared aqueous solution (in a 5.0 ml plastic syringe) containing 0.077 mL of 0.0005 M tetrachloroauric acid (10% molar relative to silver present in plated AgDeNPs) and 2.92 ml of high-purity deionized water was dispensed at a constant rate of 3.21 nmol/hr during 12 hours into a 20-mL vial containing 3.00 mL of as prepared AgDeNP solution upon uniform stirring at 200 rpm using 8 by 1.5 mm stir bar.
Sample preparation for Raman spectroscopy measurements

AgNPs and Au@AgNPs were centrifuged and concentrated to ca. 1.64 mM of silver, then dispensed onto a quartz slide and dried in an oven at 65 °C for ca. 4-5 minutes. After multiple cycles of deposition and drying, the typical surface coverage of NP substrate was ca. 2-3 µmol of silver per cm² with propping area of ca. 0.25-0.5 cm². Thiosalicylic acid has been used as a probing molecule in a range from 25 pmol (5 µL of 5.0 µM) to 2.5 nmol (5 µL of 0.5 mM) that was directly dispensed onto the prepared NP substrate, dried, and then measured. Comparison peak intensity data given in Fig. 3b are averages for 1034 cm⁻¹. Error bars represent standard deviations from average peak intensities.

Characterization

AgNPs and Au@AgNPs were cleaned and concentrated using a Clinical 100 Centrifuge (VWR). For slow controlled addition, a KDS100 syringe pump (KDS Scientific) has been used. UV-vis spectra were acquired with either Ocean Optics QE65000 fibre-optic UV-Vis spectrometer or Cary 50Bio UV-vis spectrophotometer and measured in a 0.5-cm path length cell. EM imaging was performed with a Hitachi S-5200 using a copper grid with a formvar/carbon film (FCF-200, Electron Microscopy Science). EDX was carried out using an Oxford Inca system for quantitation, line scans and mapping. Zeta potentials of AgNPs were measured using Zetasizer S (Malvern Instruments). Raman spectra were scanned using R-3000QE fiber optic Raman spectrometer equipped with 290 mW laser at 785 nm (RSI). The typical laser power used was 200 mW with the integration time of 5 seconds.
**Figures**

![UV-vis spectra](image)

**Fig. S1** UV-vis spectra of the 10% Au@AgDeNPs (10 mol. Au% relative to Ag present in gold coated AgDeNPs) produced using different addition times of gold precursor solution (volume of the gold precursor solution is 3.00 mL).
**Fig. S2** Transmission electron microscopy (TEM) images of (a) silver decahedral nanoparticles (AgDeNPs) before gold coating with the largest dimension across the pentagonal rim \((d_{av})\) of 41 \(\pm\) 2 nm and (b) Au@AgDeNPs (shell@core) with the largest dimension across the pentagonal rim of 42.5 \(\pm\) 2 nm. Preservation of the decahedral shape uniformity and sharp edges after coating is indicative of the uniformity of the gold coating layer. The scale bars are 100 nm for all TEM images.

The largest dimension across the pentagonal rim of AgDeNPs is increased by ca. 1.5 nm after the deposition of 10 mol. % Au which is close to the calculated value (1.3 nm) as seen below.

**Size increase calculation:** since gold and silver metallic radii are the same (0.144 nm), then

\[
V \text{ (Au@AgDeNP)} = V \text{ (AgDeNP)} + 10 \% V \text{ (AgDeNP)}
\]

\[
d_{av}^3 \text{(Au@AgDeNP)} = 1.1 \times d_{av}^3 \text{ (AgDeNP)}
\]

\[
d_{av} \text{ (Au@AgDeNP)} = \sqrt[3]{1.1} \times d_{av} \text{ (AgDeNP)}
\]

\[
d_{av} \text{ (Au@AgDeNP)} = \sqrt[3]{1.1} \times 41 \text{ nm} = 42.3 \text{ nm}
\]
Fig. S3 (a) Energy-dispersive X-ray (EDX) spectra and (b) EDX analysis of the gold coated decahedra nanoparticles prepared by deposition of 5 mol. % of gold relative to silver present in precursor AgDeNPs. The EDX analysis is performed for the Au@AgDeNPs plated with 5 Au%. The deposited Au% (4.64 at%) illustrates that almost all of gold (calculated 5 at.%) were delivered onto the AgDeNPs by using the optimized plating procedure.
Fig. S4 Stability of the uncoated silver decahedral nanoparticles (AgDeNPs) in aqueous solution of (a) 0.5 M hydrogen peroxide and (b) 0.5 M NH₃ monitored by UV-vis spectroscopy.
**Fig. S5** Transmission electron microscopy (TEM) images of Au@AgDeNPs (shell@core) after treatment for five days in (a) 1.5 M NH$_3$ and (b) 0.30 M of NaCl (with 1.5 mM PVP) solutions. The scale bars are 100 nm for all TEM images.
Fig. S6 UV-vis spectra (a) and TEM image (b) of Au@AgDeNPs (shell@core) after treatment in L-arginine solution (1.5 M total concentration) for 2 days. The intensity of SPR peak is decreased over time with the formation of a new red-shifted peak at 650-750 nm that is indicative of the aggregation of the particles, which is also confirmed by TEM. At the same time, the stability of the gold coated particles is fully preserved, as can be seen in the TEM image. The scale bar is 100 nm for TEM image.
Fig. S7 UV-vis spectra of gold coated silver pentagonal rod nanoparticles (Au@AgPRNPs) before (blue) and after (red) the treatment for five days with 0.5 M (total concentration) hydrogen peroxide solution.
**Fig. S8** (a) The effect of the amount of gold in the coating (expressed as Au% relative to silver in AgDeNPs) on the $\lambda_{\text{max}}$ of the SPR peak of the produced Au@AgDeNPs. (b) Optical photographs of the AgDeNPs and Au@AgDeNP (shell@core) dispersions prepared using various percentages of gold.
**Fig. S9** TEM images of the Au@AgDeNPs prepared using different Au%. The scale bars are 100 nm for all TEM images.
**Fig. S10** Surface enhanced Raman scattering (SERS) spectra illustrating detection of 2.5 nmol of thiosalicylic acid using AgDeNPs and 10% Au@AgDeNPs as substrates. The integration time was 15 seconds, the probed area ca. 0.5 cm², and the laser power ca. 200 mW.
Fig. S11 TEM images of Au@AgNPs prepared by slow addition of [AuCl₄]⁻ to AgDeNPs in the presence of (a) KOH, (b) ascorbate, (c) formate and (d) KI. Produced Au@AgNPs were subsequently treated with 0.2 M (total concentration) hydrogen peroxide solution. The scale bars are 100 nm for all TEM images.
Fig. S12 Transmission electron microscopy (TEM) images of Au@AgDeNPs (shell@core) prepared using 80 Au% (gold relative to silver) (a) without using additional citrate and (b) with addition of Au-citrate solution. The scale bars are 100 nm for all TEM images.
Fig. S13 TEM image of silica encapsulation of Au@AgDeNPs using 1.0 M NH₃ solution as the hydrolysis medium of a silica precursor. Stability of the prepared 10% Au@AgDeNPs has been preserved during encapsulation process. The scale bar is 100 nm.
Fig. S14 UV-vis spectra (a,b) and TEM images (c,d) of Au@AgDeNPs illustrating their stability and dampening of SPR upon exposure to hydrosulphide solution and hydrogen sulphide gas. (a) UV-vis spectra of Au@AgDeNPs after 5-days exposure to different concentrations of NaHS solution. (b) Stability of Au@AgDeNPs in aqueous solution of 0.001 mM NaHS monitored by UV-vis spectra. (c and d) TEM images of Au@AgDeNPs exposed to saturated hydrogen sulfide atmosphere in closed container for 2 hrs. Despite the significant dampening in SPR, the coating integrity remains largely preserved, as can be seen in TEM images. The dampening in the plasmon resonance likely occurs due to strong absorption of the surface layer of silver sulphide.