Supporting Information for

Reversible Shape and Plasmon Tuning in Hollow AgAu Nanorods

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Section 1. Nanoparticle Synthesis

Chemicals and reagents. Sodium citrate trisodium dihydrate (≥99.0%, ACS grade), sodium borohydride (99.99%), silver nitrate (≥99.0%), gold(III) chloride trihydrate (≥99.9%, trace metal grade) and ICP calibration standards (TraceCERT®, 1000 mg/L Au in hydrochloric acid; 1000 mg/L Ag in nitric acid; 1000 mg/L In in nitric acid) were purchased from Sigma Aldrich. Silver nitrate (99.9995%) was obtained from Strem Chemicals. Hydrochloric acid (36.5–38.0%, Reagent, ACS) and nitric acid (68.0–70.0%, Reagent, ACS) were purchased from VWR International. Anhydrous N,N-dimethylformamide (extra dry over molecular sieve, 99.8%, Acros Organics) was purchased from Fisher Scientific. All chemical and reagents were used without further purification. Nanopure water (18 MΩ) was used throughout.

Preparation of AgAu alloy nanoshells. 45-nm Ag precursor nanoparticles were synthesized using a seed-growth method previously described elsewhere. Briefly, silver seeds were obtained by heating 75 mL of nanopure water and 20 mL of 1 wt% aqueous sodium citrate at 70 °C under vigorous stirring in a 250-mL round bottom flask. Once the temperature was stabilized, fresh aqueous solutions of 1 wt% AgNO₃ 99.0% (1.7 mL) followed by 1 wt% aqueous NaBH₄ (0.2 mL) were quickly added to the flask and the mixture was stirred for 30 min. After the solution was allowed to cool to room temperature, the volume was completed to 100 mL and this stock solution of Ag seeds (5–10 nm in diameter) was kept overnight in the dark at 4 °C. Then, 45-nm silver nanoparticles were grown from these seeds in two successive steps. To 75 mL of nanopure water were added 15 mL of seed solution and 2.0 mL of 1 wt% aqueous sodium citrate in a 250-mL round bottom flask and heated to reflux under vigorous stirring. Once the solution reached boiling, 1.7 mL of a fresh 1 wt% AgNO₃ aqueous solution was quickly added and the mixture was left to stir for 60 min to produce nanoparticles with a 20-nm average diameter. To obtain 45-nm
diameter nanoparticles, this procedure was repeated a second time with 12.5 mL of 20-nm silver nanoparticles as starting material in an oil bath kept at 88 °C. Finally, AgAu alloy nanoshells were prepared from the 45-nm Ag nanoparticles using a procedure inspired from various sources[^2-^4]. Briefly, in a 100 mL round bottom flask, 10 mL of 45-nm Ag colloidal solution was diluted with 10 mL of nanopure water and mixed with 7.5 mL of aqueous citrate tribasic solution (6.25 mM) and brought to a boil with a condenser under vigorous stirring. After the temperature was stabilized, an excess of gold(III) chloride trihydrate (7.93 mL of 0.465 mM aqueous solution, 0.3 equiv. Au:Ag molar ratio) was added with a syringe pump at 100 µL/min followed by stirring for 30 min.

**Figure S1.** Normalized extinction spectra of Ag (blue trace) and AgAu (red trace) nanoparticles. (NPs)
Section 2. Nanoparticle Size and Shape Distribution

The average diameter of nanoparticles was determined by transmission electron microscopy (TEM) and dynamic light scattering (DLS). TEM images presented in Figure S2 were obtained on a TECNAI Spirit G2 Biotwin from FEI with an AMT (Orca HR, 11 Megapixels) bottom-mounted camera at 120 kV. Average sizes and size distributions were calculated with ImageJ software. DLS measurements were performed on a Zetasizer Nano ZS from Malvern Instruments with a He-Ne laser source (\(\lambda = 633\ \text{nm}, 4\ \text{mW}\)) in nanopure water at 25 °C.

![TEM images of Ag nanoparticles (average diameter ~45 nm, left) and AgAu alloy nanoparticles (average diameter ~60 nm, right).](image)

**Figure S2.** TEM images of Ag nanoparticles (average diameter ~45 nm, left) and AgAu alloy nanoparticles (average diameter ~60 nm, right).

<table>
<thead>
<tr>
<th>Sample type</th>
<th>TEM (nm)</th>
<th>DLS (nm)</th>
<th>PDI §</th>
</tr>
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<tr>
<td>Ag</td>
<td>47 ± 8</td>
<td>66 ± 2</td>
<td>0.469</td>
</tr>
<tr>
<td>AgAu alloy</td>
<td>59 ± 8</td>
<td>76 ± 1</td>
<td>0.249</td>
</tr>
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§: Polydispersity index

Table S1. Nanoparticle average diameters.
Section 3. Composition Analysis of AgAu Alloy Nanoparticles

Two analytical procedures were used for the elemental analysis of the AgAu nanoparticles by inductively-coupled plasma atomic emission spectrometry, and the results are reported and compared in Table S2. Both methods used separate external calibration curves for Au and Ag, and care was taken to keep the concentration of Ag below 2 mg/L in calibration standards and sample solutions, since we observed that Ag$^+$ ions are not stable in aqua regia at higher concentrations. In the first method, 10, 50, 100, and 200 µL of 1000 mg/L Ag or Au standard solutions were added to 1 mL of concentrate nitric acid and 3 mL of concentrate hydrochloric acid in 100-mL volumetric flasks and completed to volume with nanopure water (i.e., 0.1, 0.5, 1, and 2 mg/L of Ag or Au in 4% aqua regia). To digest the samples, 1 mL of AgAu nanoparticles was mixed with 1 mL of concentrate nitric acid and 3 mL of concentrate hydrochloric acid in a 100 mL volumetric flask and stirred for two hours, then completed to volume with nanopure water. The samples were analyzed immediately after preparation on a Perkin-Elmer Optima 3000 ICP-AES spectrometer. In the second method, separate calibration curves were prepared for Au and Ag in the same concentration range in 6% aqueous nitric acid, with indium added as an internal standard. 1-mL aliquots of colloid solution were mixed with 6 mL of concentrated nitric acid and brought to a boil for 30 min under reflux. The digested samples were allowed to cool to room temperature and transferred to 100-mL volumetric flasks with the indium internal standard and completed to volume with nanopure water. The samples were analyzed immediately after preparation.

Elemental composition of the AgAu alloy nanoparticles was also determined by energy dispersive X-ray spectroscopy (FEI, Model Quanta-3D-FEG). 1 mL of AgAu nanoparticle solution was centrifuged at 7500g for 7 min, the supernatant was removed, and 10 µL of the resulting
concentrated solution was deposited on a chrome-plated coverslip and left to dry. Voltage was set at 10 kV to scan a region of interest of about 50 µm².

Table S2. Elemental composition of AgAu alloy nanoparticles.

<table>
<thead>
<tr>
<th>Element</th>
<th>mg/L ICP(3HCl:HNO₃)</th>
<th>% At ICP(3HCl:HNO₃)</th>
<th>mg/L ICP(HNO₃)</th>
<th>% At ICP(HNO₃)</th>
<th>% At Bulk SEM-EDS</th>
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<tr>
<td>Ag</td>
<td>35±1</td>
<td>71±2</td>
<td>35±1</td>
<td>71±2</td>
<td>78±1</td>
</tr>
<tr>
<td>Au</td>
<td>26±2</td>
<td>29±2</td>
<td>26±1</td>
<td>29±1</td>
<td>22±1</td>
</tr>
</tbody>
</table>
Section 4. Trapped Solution: Thermogravimetric and Core-Loss EELS Analysis

Thermogravimetric Analysis

Figure S3. TGA curves of hollow AgAu nanoparticles (red solid trace), Ag nanoparticles (long dashed trace) and sodium citrate (short dashed trace).

The thermal behavior of prepared hollow AgAu nanoparticles was investigated by thermogravimetric analysis (Model TGA/SDTA 851e, Mettler-Toledo). The nanoparticles were centrifuged against methanol three times in order to eliminate excess sodium citrate tribasic. The concentrated nanoparticles were deposited on a piranha-cleaned watch glass and dried in a laboratory oven at 80 °C for 3 hours. Thermogravimetric analysis measurements (Figure S3) run at 10 °C/min from 50 °C to 750 °C reveal a rapid weight loss of 2 wt% at 250 °C consistent with dehydration and the theoretical percentage by weight of the water-filled void of hollow nanorods.
The same procedure applied to Ag precursor nanoparticles showed no mass loss, an indication that any sodium citrate remaining on the nanoparticle surface after the purification step does not contribute significantly to the mass loss observed for the AgAu hollow nanorods.

**Core-Loss EELS Analysis**

![Core-loss EELS spectrum](image)

**Figure S4.** Core-loss EELS spectrum acquired in TEM mode at 300 kV from the AgAu nanoparticles that were drop-cast on a lacy carbon TEM grid, showing the O K-edge of trapped water in the AgAu nanoparticles (red: raw signal, black: background and blue: background subtracted signal). The 540 eV O K-edge peak matches the near-edge fine structure of water\(^5\).
Section 5. Cross-Sectional TEM Specimen Preparation

Cross-sectional TEM specimens from AgAu nanorods were prepared using the technique of \textit{in situ} lift-out in an FEI Helios 660 dualbeam system. The nanoparticles were drop-cast on a Si substrate. For maintaining the structural integrity of the drop-cast nanoparticles and protecting them from Ga ion damage, a few hundred nanometers thick electron-beam deposited Pt layer followed by a few micrometer thick FIB-deposited Pt layer were added before FIB-milling (Figure 1c). At the final stage of preparation the lamella surfaces were polished with low voltage (2 kV) Ga ion beam to minimize the thickness of the damaged layer caused by 30 kV Ga ion beam during the thinning process.\textsuperscript{6}
Section 6. Restructuring the AgAu Nanorod Interior

**Figure S5.** Restructuring the interior of AgAu nanorods. HAADF-STEM images showing the process of shaping the corner state by step by step moving the Ag towards the electron beam. The small pair of arrows on each image points to the area on which the electron beam was scanned to shape the interior structure in the next subsequent image.
Section 7: Electron Microscopy Approaches to Avoid Reshaping

The nanorods could be imaged in STEM-HAADF without reshaping (Figure 2c(1–4)) by using short pixel dwell times (typically 5 μs). To obtain sufficient X-ray counts in EDS mapping, a significantly longer dwell time was required such that EDS could not be obtained on full nanorods without reshaping them. However, it was possible to scan a filled end, as long as the beam did not cross a liquid-filled area. EDS of cut structures (such as in Figure 1) could also be obtained because of the absence of the liquid medium.
**Section 8. Acquiring and Analyzing STEM-EELS Spectrum Images**

All EELS spectrum images in this study were acquired in STEM mode at 80 kV in an FEI Titan Themis (S)TEM equipped with a monochromator and Gatan Quantum ERS electron spectrometer. Full width at half maximum (FWHM) of the zero-loss peak (ZLP) was measured to be 0.16 eV, and energy dispersion per channel of 0.01 eV and pixel dwell time of 0.005 s were used. The spectrum images were acquired on the window that was drilled using the electron beam in the Si$_3$N$_4$ membrane adjacent to the AgAu nanorod (Figure S6).

The method of non-negative matrix factorization (NMF) was applied in HYPERSPY (open source software, available at hyperspy.org) for analyzing the EELS spectrum images. Using this method, the EELS spectrum image is decomposed into two matrices: 1) spectral components which include LSPR peaks if an appropriate number of spectral components is chosen and 2) loadings which can be considered as the spatial distribution of the spectral components. Since the number of spectral components is defined by the user in this method, we systematically studied the effect of this choice on the LSPR peak position and spatial distribution. Figures S5, S8, and S11 show the loading matrices (spatial distribution of spectral components) for spectrum images acquired at the corner, center, and split states in Figure 4 for the choices of 4, 5, 6, and 7 spectral components. The spectrum at each point in the spectrum image is fit by a linear combination of the components while the loadings are the component coefficients. The raw spectrum as well as the fitted spectrum using different number of spectral components are shown for two points in Figures S6, S7, S9, S10, S12, and S13. These figures show that the user input, *i.e.*, the number of components, does not affect the position and spatial distribution of the LSPR peaks shown in Figure 4.
Figure S6. Opened window. By using a beam current of 200 pA in the STEM mode at the operation voltage of 80 kV, a window was drilled in a 10 nm thick Si$_3$N$_4$ membrane adjacent to the AgAu nanorod. EELS spectrum images were acquired within this window.

Figure S7. NMF analysis for the CORNER state. Systematic study of the effect of the number of components extracted in NMF analysis for the hollow AgAu nanorod in Figures 3a and 4a with the hollow region in a corner. Regardless of the number of components extracted, the spatial distribution of the LSPRs remains constant. By increasing the number of components to 7, the fourth component splits into two components (4 and 7) with almost no LSPR difference. This can be seen in the following figure (Figure S8). The position from where the spectrum image (22×98 pixels) was acquired is marked with a green box on the HAADF image on the left bottom inset.
Figure S8. NMF spectral components for the CORNER state at a corner position. Spectral components obtained from NMF decomposition with different numbers of components, for the hollow region in the corner in Figures 3a and 4a, at the position marked with a white circle in the inset (1×1 pixel, 2.29×2.29 nm; inset white marker size exaggerated for clarity). For 7 components, the fourth and seventh components overlap.
Figure S9. NMF spectral components for the CORNER state at a middle position. Spectral components obtained from NMF decomposition with different numbers of components, for the hollow region in the corner in Figures 3a and 4a, at the position marked with a white circle in the inset (1×1 pixel, 2.29×2.29 nm; inset white marker size exaggerated for clarity).
**Figure S10. NMF analysis for the CENTER state.** Systematic study of the effect of the number of components extracted in NMF analysis for the hollow AgAu nanorod in Figures 3b and 4b with the hollow region at the center. Regardless of the number of components extracted, the spatial distribution of the LSPRs remains constant. The position from where the spectrum image (21×100 pixels) was acquired is marked with a green box on the HAADF image on the left bottom inset.
Figure S11. NMF spectral components for the CENTER state at a corner position. Spectral components obtained from NMF decomposition with different numbers of components, for the hollow region at the center in Figures 3b and 4b, at the position marked with a white circle in the inset (1×1 pixel, 2.44×2.44 nm; inset white marker size exaggerated for clarity).
Figure S12. NMF spectral components for the CENTER state at a middle position. Spectral components obtained from NMF decomposition with different numbers of components, for the hollow region at the center in Figures 3b and 4b, at the position marked with a white circle in the inset (1×1 pixel, 2.44×2.44 nm; inset white marker size exaggerated for clarity).
Figure S13. NMF analysis for the SPLIT state. Systematic study of the effect of the number of components extracted in NMF analysis for the hollow AgAu nanorod in Figures 3c and 4c with the hollow region split into three across the nanorod. Regardless of the number of components extracted, the spatial distribution of the LSPRs remains constant. The position from where the spectrum image (36×138 pixels) was acquired is marked with a green box on the HAADF image on the left bottom inset.
Figure S14. NMF spectral components for the SPLIT state at a corner position. Spectral components obtained from NMF decomposition with different numbers of components, for the hollow region split into three across the nanorod in Figures 3c and 4c, at the position marked with a white circle in the inset (1×1 pixel, 2.24×2.24 nm; inset white marker size exaggerated for clarity).
Figure S15. NMF spectral components for the SPLIT state at a middle position. Spectral components obtained from NMF decomposition with different numbers of components, for the hollow region split into three across the nanorod in Figures 3c and 4c, at the position marked with a white circle in the inset (1×1 pixel, 2.24×2.24 nm; inset white marker size exaggerated for clarity).
Section 9. Theory: FDTD Calculations and Plasmon Hybridization

Method

We used the commercial package Lumerical FDTD Solutions\textsuperscript{7} to solve Maxwell's equations using the finite-difference time-domain (FDTD) method to calculate the far-field and near-field optical properties of the nanorods. The FDTD parameters used here are: (i) a FDTD domain of 1500 nm\textsuperscript{3}, (ii) a simulation time of 100 fs, (iii) a conformal mesh of 2 nm to discretize the structure (mesh accuracy set to 4), and (iv) boundary conditions set to the perfectly matched layers (PMLs). The optical excitation is taken a broadband plane wave polarized either along the longitudinal or transverse to nanorod axis. Similarly to the EELS-FDTD calculations, the dielectric permittivity tabulated by Johnson and Christy was used for gold,\textsuperscript{8} a constant refractive index of 1.33 was used for the water void, and the background dielectric medium was set to vacuum. The geometry and dimensions are the same as the ones used for the EELS-FDTD calculations ($L_{\text{Au}}$=195 nm, $a_{\text{Au}}$=47 nm, $L_{\text{water}}$=80 nm, and $a_{\text{water}}$=35 nm).

Results

We calculated the extinction cross-section as a function of the void position $\Delta$ (Figure S16). The extinction spectra exhibit several LSPRs both for the longitudinal (Figure S16a) and transverse (Figure S16b) polarizations. All of these LSPRs spectrally shift when the void is displaced from its central position ($\Delta$=0 nm) to the end of the nanorod ($\Delta$=49 nm). This energy shift is the result of the plasmon hybridization, as observed in the EELS-FDTD calculations (Figures S17 and S19) and as illustrated in the plasmon hybridization diagram (Figure S18).\textsuperscript{9–11}
Figure S16. Morphology dependence of the plasmonic properties. Calculated extinction cross-section as a function of the void position $\Delta$ for a) longitudinal and b) transverse polarizations.
Figure S17. EELS-FDTD results for a center-state nanorod (Δ=0 nm). a) NMF decomposition of the calculated loss probability (Γ_{EELS}) maps calculated using the EELS-FDTD method. b–d) NMF decomposition of the loss probability spectra calculated using EELS-FDTD for an electron beam impacting at positions P1–P3, respectively. The electron velocity is taken equal to c/2 (i.e., 80 keV).
Figure S18. Plasmon hybridization. Schematics of the plasmon hybridization energy level diagram of a hollow nanorod showing the primitive modes of the cavity ($\omega_C$, right) and of the nanorod ($\omega_R$, left) forming the hybridized bonding ($\omega_-$) and antibonding ($\omega_+$) plasmon modes of the hollow nanorod (center). a, b) Transverse and longitudinal plasmon modes, respectively. Blue lines indicate the hybridized modes of concentric nanorod-cavity nanoparticle. When the symmetry is broken (i.e., the cavity is offset from the nanorod center), a finite interaction between the primitive modes of the nanorod with higher order modes of the cavity (red dashed lines) gives rise to an additional spectral shift of the hybridized modes (red arrows). The quantities $l$ and $m$ are multipolar indices describing the primitive plasmon modes (i.e., $l=1, 2$ refers to the dipole and quadrupole, respectively, while $m=0, 1$ refers to the longitudinal and transverse nature of the charge oscillation).
Section 10. Theory: Symmetry Dependence of the EELS-FDTD Spectra

Figure S19. Symmetry dependence. Loss probability, $\Gamma_{\text{EELS}}$, calculated using the EELS-FDTD method for a gold nanorod with $\Delta=-49$, 0, and 49 nm and for the electron beam impacting at a) the tip (P3) and b) the center (P2) of the nanorod. The electron velocity is taken equal to $c/2$ (i.e., 80 keV). In position P3 the electron beam is positioned at $+74$ nm from the nanorod center.

When exciting close to the end of the nanorod (P3, Figure S19a) the calculated EELS spectra exhibit three distinct LSPRs at about 1.30, 2.05, and 2.38 eV, respectively. Changes in the LSPRs relative intensity together with energy shifts up to 60 meV, observed for different values of $\Delta$ highlight the plasmon hybridization between the LSPRs of the void (i.e., cavity) and of the nanorod. When exciting close to the center of the nanorod (P2, Figure S19b), the spectra now exhibit a strong LSPR at $\sim 2.1$ eV and an additional, weaker, mode at $\sim 2.4$ eV. The latter, while hardly visible for $\Delta>0$ nm, tends to disappear in the tail of the mode at $\sim 2.1$ eV when $\Delta=0$ nm.
Once again, because of the plasmon hybridization, the LSPR exhibits an energy shift of ~50 meV when displacing the void (Figure S18). Spectral differences between theory and experiments are easily explained by (i) the morphological defects, (ii) the presence of the substrate (not accounted for in the calculations), and (iii) the actual position of the void.

References