Investigation of the dissipative properties of Au-Ag nanostructures through Electron Energy Loss Spectroscopy

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Abstract:

We describe the unusual dielectric properties of Au-Ag nanostructures at a single particle level using electron energy loss spectroscopy. It has been shown previously that these nanostructures deviate from their usual metallic characteristics of metallic Ag and Au. In particular certain variants of these materials appear to undergo a transition to an immeasurably low resistive state as well as a strong diamagnetic state that is not usually associated with Au and Ag themselves. More significantly these nanostructures exhibit absence of Mie like resonances associated with Au and Ag. Instead, these exhibit negligible optical absorption in the UV-VIS-NIR range. Here this unconventional electromagnetic response was probed at a single particle level. We find that the absence of dissipation is also reflected in the electron loss spectra. The lack of distinct electron energy loss features in particles with a known composition enables us to unambiguously assign these observations to actual particle properties. We tentatively interpret our observations as arising due to a reduction of free electron density in Au and Ag nanostructures. Further it was also shown that the conventional plasmonic modes can be recovered by altering material composition.

Introduction:

Confining metals to nanoscale dimension induce intriguing optical responses unobserved in bulk. The simplest of these is the possibility of a localized surface plasmon resonance (LSPR) that is a dipole active plasmon mode. This is feasible in particles where the dimensions of the nanoparticle are comparable or smaller than the radiation wavelength. This mode concentrates electromagnetic fields in the vicinity of a metal nanoparticle; nanoparticles of noble metals such as gold (Au) and silver (Ag) have hence been widely used in various
applications in optical sensing and photonics.\textsuperscript{1,2,3,4} The requirement of tailoring the surface plasmon resonance has led to the exploration of various schemes to vary nanoparticle morphology, core/shell nanostructuring of particles and also alloying.\textsuperscript{5,6,7} Other, more counterintuitive effects are observed in systems with more extreme confinement. These include stronger electron damping as well as activation of quantum tunnel effects.\textsuperscript{8,9} A sharper deviation from usual metallic character was reported by Thapa \textit{et al.}\textsuperscript{10} who noted the emergence of vanishing resistance and diamagnetism in engineered Au-Ag nanostructures. Other electrical anomalies were also noted.\textsuperscript{11,12}

Optically, these nanostructures did not seem to obey Mie theory, since they lack usual Au and Ag like plasmon resonances and exhibit a single broad scattering resonance that covers the ultraviolet-visible spectrum. In a subset of samples, this resonance exhibits an indistinct maximum at \textasciitilde 4 eV. This indicates a significant restructuring of electron configuration inside the material and thus an anomalous change in the dielectric constant. It was further shown that sequential growth of Au on Au-Ag nanostructures can restore the LSPR modes in these nanoparticles.

Here we further probe the dielectric properties of these materials at a single particle level using Electron Energy Loss Spectroscopy (EELS). EELS is a convenient tool that can be utilized to probe as well as excite various plasmonic modes of a nanoparticle.\textsuperscript{13,14,15} Furthermore, the simultaneous determination of structural and spectroscopic properties at a high spatial resolution can give valuable information about the material that is difficult to get otherwise.\textsuperscript{16,17} A strong added benefit that is of great relevance to the Au-Ag system is the ability to determine the structure and dielectric properties of a single particle within the same instrument. This enables unambiguous assignment of structure-property correlations with a greater level of confidence than is feasible in other experiments.

In the following, we will refer to systems that contain a dispersion of Ag particles in Au as an Au-Ag nanostructure (NS) (Figure 1a, inset). These NS may be formed into nanoparticles with varying exterior morphology, while essentially retaining their internal nanostructuring. Figures 1a and 1b show Transmission Electron Microscope (TEM) images of Au/Ag nanostructures. From fig. 1a it is evident that these samples are composed of nanoparticles of Au-Ag NS that are of 20-30 nm in diameter. The High-Resolution Transmission Electron Microscope (HRTEM) image (fig. 1b) shows the crystalline nature of individual nanoparticles. The [111] and [200] planes of Au are observed in this image. Sample crystallinity is also reflected in the Selected Area Electron Diffraction (SAED) image fig. 1c. It can be seen here that [111], [200], [220], and [311] crystalline planes are present in the system that is in agreement with the reports of conventional Au and Ag crystalline nanoparticles.\textsuperscript{18,19} Figure 1d shows the typical optical extinction spectra of the Au-Ag NS as well as Au nanospheres. The nanoparticles were dissolved in water and taken in a quartz cuvette. Samples were illuminated by a Deuterium-Halogen UV-VIS-NIR light source and extinction spectra were recorded with an Ocean Optics USB2000 spectrometer. As mentioned earlier, these NS do not show any plasmon resonance associated with Au (2.35 eV) or Ag (3.1 eV). A broad extinction ("R1") is observed instead.\textsuperscript{20} Structural information for members of this ensemble was obtained using Scanning Transmission Electron Microscopy (STEM) in High-Angle Annular
Dark Field (HAADF) imaging mode in a TITAN Themis electron microscope operating at 300 kV. These images along with elemental mapping are presented in fig. 1e-1g. These images confirm that the NS comprises of Ag particles embedded in Au. A line mapping analysis of the position of Ag clusters on the Au matrix was done in the supplementary information fig. S1. Overall, it suggests the discrete position of Ag clusters on Au nanoparticles. We observed that this structuring is essential for unconventional properties witnessed so far.

In the Mie theoretic framework, nanoparticles exhibit optical resonances depending upon the real component of the dielectric constant, the particle shape, and the medium refractive index.\(^{21}\) For spheroidal particles smaller than the wavelength of light, the resonance criterion is satisfied for photon energies for which \(\epsilon' = -2\chi n^2\). Here, \(\epsilon'\) is the real part of the dielectric constant of metal, \(\chi\) is a shape dependent geometric parameter greater than or equal to unity\(^{22}\) and \(n\) is the medium refractive index. In general, \(\epsilon'\) is treated as a function of photon energy, while in most cases, \(n\) is treated as a constant over the range of interest. The real dielectric constants of bulk Au and Ag are -2 at 2.55 and 3.5 eV respectively.\(^{23}\) Au and Ag nanospheres consequently exhibit medium index dependent Mie resonances at photon energies below these two energies. These resonances are usually referred to as localized surface plasmon resonances or LSPR due the presence of free electrons in these materials. The absence of regular Mie-type resonances in Au-Ag NS nanoparticles is consistent with a departure of the material dielectric from the usual Au and Ag dielectric constants. In a past study, nanoparticles of the Au-Ag NS were probed by optical means. Very briefly, the study observed that in solution, these materials exhibited immeasurable optical losses as well as no optical nonlinearities in the visible region of the spectrum. Clearly, optical methods alone are insufficient to infer the material dielectric constant, and additional tools are required to precisely determine structure-dielectric correlations.

Figure 1 a. TEM image of Au-Ag NS. b. HRTEM image of Au-Ag NS. c. SAED pattern. d. Extinction spectra of both Au-Ag Nanostructures (red curve) and Au Nanospheres (blue curve).
curve). The arrow at 2.35 eV denotes the plasmon resonance peak of Au Nanospheres. e. HAADF image of Au-Ag NS. Elemental mapping of f. Au and g. Ag respectively.

The present study is based on Au/Ag nanostructures prepared via chemical routes as well as through physical methods that will be described elsewhere. Samples were deposited onto a 300-mesh carbon-coated TEM grid and were subjected to STEM EELS study. The TEM was equipped with a monochromator and was operated at an accelerating voltage of 80kV or 300kV. It is known that the threshold energy of the incident electron beam required for Au atom displacement is 1320 keV. Our accelerating voltage ranges thus probe only the dielectric constant and are not expected to induce structural degradation such as Au atom displacement in the nanostructures. 80kV/300kV monochromated STEM-EELS was performed on a Titan Themis (60-300kV) fitted with a monochromator and post column Gatan 965 imaging filter (GIF). The column parameters for 80kV and 300kV operation are available in the following table. In both cases, the monochromator was excited to an excitation of 0.6 and a portion of the dispersion utilized by insertion of a circular slit of 0.5um diameter resulting in an energy resolution of 0.25 eV (at 300kV) and 0.16eV (at 80kV). The high-resolution aperture (2.5mm) of the GIF was chosen so that the ratio of GIF entrance aperture diameter (converted to mrad) to the semi-convergence angle of the probe (in mrad) is ~ 1.5 to maximize signal to noise ratio of the EELS signal.

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<tr>
<td>Zero-loss peak FWHM (eV)</td>
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Figure 2a shows the STEM image of a sample of Au-Ag nanoparticles. An EELS spectrum image was obtained by scanning the particles in a raster fashion. The red box in fig. 2a indicates the region selected for the EELS spectrum in fig. 2b. Standard methodologies were employed to process and analyse the data. In this figure, the as-collected spectrum is indicated by the red curve, the zero-loss peak (ZLP) is green, while the corrected data are shown by the blue curve. The zero-loss peak was extracted by fitting it with Gaussian and Lorentzian model as depicted by the green spectrum. The ZLP-corrected blue curve still contains background electron losses arising from the graphitic substrate. It is known that π-plasmon or the first plasmon peak of amorphous carbon is located at the 3.5-4.5 eV energy range. This background was corrected by measuring the EELS spectrum associated with the substrate at a region away from the particles. The spectrum is shown in fig. 2c. Here the background corrected spectrum is yellow, while the uncorrected spectrum is blue and the background is black. It is evident that the background corrected electron loss of the Au-Ag particle lacks well-defined Au or Ag plasmon peaks in the 1.5-3.5 eV energy range. It is further clear that this absence is not due to artefacts arising from improper background subtraction.
since distinct features are not observed either in the raw data or in the background. To confirm the generality of this observation, we repeated the same procedure on other particles. The corresponding spectra are shown in fig. 2d-f. Here a different set of physically deposited Au-Ag NS nanoparticles were excited by a monochromated electron beam with an accelerating voltage of 80kV. At 300kV there is a possibility that the tail of the zero loss peak may obscure the plasmonic peak. Considering this possibility, we shifted to 80 kV which minimizes this tail due to a reduced point spread function of the camera, minimizing background contribution (due to ZLP tail) to any plasmonic peak in 1.5-2 eV range. This enabled us to verify the robustness of our observation of zero electron loss against the measurement conditions as well as sample preparation. Again, as shown in fig. 2f, we observe that the particle does not exhibit losses associated with LSPRs.

**Figure 2** a. is the ADF image of Au-Ag nanostructures taken at 300 kV accelerating voltage. The marked area (red box) has been analysed for EELS. b. is the obtained EELS spectrum from the marked area. c. compares the particle spectra with the background. It represents the background. d. is similarly taken ADF image like a. but with an accelerating voltage of 80kV. Accordingly, e. is similar to b.; f. is similar to c.

Even more significant than the lack of measurable Au and Ag resonances is the observation that the electron energy loss background can be almost entirely attributed to the substrate.
In other words, the samples lack distinct features associated with electron energy losses in an energy range extending to 8 eV (Fig. 2d, black line). It is also interesting to note that the carbon π-plasmon resonance is prominent here, rising from 3.25 eV. The presence of carbon π-plasmon in these images is expected from the substrate. A contribution may also arise from carbon generated due to degradation of surface ligands employed in the synthesis (cetyltrimethylammonium bromide or CTAB). We note that it is highly improbable for a thin layer of organic ligand on nanoparticles to obscure electromagnetic interactions. As a matter of fact, the use of insulating material on small nanoparticles as an encapsulate had been demonstrated in earlier studies to resolve higher-order surface plasmon modes from dipolar modes. Thus, the spectra are expected to arise due to the nature of the particles themselves, rather than a measurement anomaly. We note that in Fig. 2f the corrected spectrum (yellow) is negative. This is consistent with fewer electrons being transmitted through the NS than are transmitted through the substrate.

We further analyzed our observations in the context of conventional plasmonics. As is well known, LSPR resonance energies are particle shape dependent. In particular, anisotropic particles show more than one resonance mode. For example, nanorods are associated with a transverse mode as well as a lower energy longitudinal mode. The availability of different morphologies of Au-Ag nanoparticles in these samples enabled us to further probe the deviations of these materials from conventional Mie-like LSPRs. Data from various shapes of Au-Ag nanostructures are shown in Fig. 3. Figure 3a shows nanoparticles with miscellaneous shapes including oblate-shaped (top), triangle-shaped (centre), and rod-shaped (bottom). Each particle was scrutinized under the electron beam and the obtained inelastically scattered spectra were analysed. As performed earlier in this study, a specific area, denoted by rectangular boxes, over the nanoparticle was selected for the same. Special care was taken in determining the area of interest that contains the edges of nanoparticles since it is known that surface plasmonic modes are much prominent along the edges rather than the centre of a nanoparticle. Figure 3b shows the background-subtracted inelastically scattered spectra of the concerned areas. It can be seen from the red and green curve, corresponding to red and green squares from Fig. 3a, both the oblate-shaped and triangular-shaped particles lack any well-defined plasmon resonance. In the red spectrum, we do observe a gradual rise in the lower range of electron energy loss. However, its linewidth and shape suggest an artefact of background subtraction rather than a plasmon resonance. Indeed, some particles exhibit a similarly structured dip at these energies (see for example Fig. 2c, yellow curve and Fig. 3d, green curve). For an oblate-shaped or triangle-shaped Au nanoparticle, the optical spectrum, and the position of plasmon peaks depend on the aspect ratio, which is the ratio between longer and shorter radii. Based on different aspect ratio values, for particles < 100 nm, it has been shown both experimentally as well as through numerical simulations that the dipolar and quadrupolar plasmon mode typically lie in the range of 1eV-2.25eV. Similar to the previous framework, the spatial asymmetry of a nanorod does promote the longitudinal and the transverse plasmonic mode; thus, it is expected for a Au nanorod of 87 nm in length and 17 nm in width to have extinction peak maxima at 1.3-1.45 eV. Contrary to this conventional behaviour, we again encountered a featureless spectrum as represented by in blue and black curves in Fig. 3b. As evident these effects, though typical of plasmonic systems, are not
observed in the Au-Ag system. The absence of any LSPR features as noted above suggests the emergence of a new non-lossy dielectric constant, possibly indicative of a state of insulating/bound electrons that are unresponsive towards external perturbation.

**Figure 3** a. STEM images of Au-Ag nanoparticles with various shapes. Each images have a marked area shown by rectangular boxes. b. is the background corrected inelastic scattering spectra of each marked boxes from a; c. is the ADF image with particle junctions marked as various boxes. d. is the background corrected inelastic scattering spectra of each marked boxes from c.

Next, we investigate the coupling between two nanoparticles to further confirm deviations from traditional Mie-like LSPRs. As detailed in fig. 3c, we had selected four junctions of interest that include various shapes of nanoparticles. The red square box indicates an overlapping area of two almost spherically shaped particles whereas, the green box represents a junction between an almost spherical and an almost oblate-shaped particle. Likewise, the blue and the black box denotes distinctive junctions between an almost oblate-shaped, triangle-shaped, and rod-shaped nanoparticle. The coupling between two localized plasmon modes of different nanoparticles results in the shift of SPR peak in the energy scale.\(^{30,31}\) Traditionally dipolar SPR modes relocate towards a higher energy value with an increase in the interparticle distance.\(^{32}\) Nevertheless, as seen in fig. 3d we do not observe any supplemental energy loss features due to the coupling. Interparticle separation also does not appear to influence electron loss in this system.

From these observations it is evident that the response of Au-Ag is not explained by the bulk dielectric constants of Au and Ag. We note that the experimentally accessible window in these experiments is restricted to above 0.5 eV due to uncertainties introduced by the ZLP. A significant possibility in this class of materials is the reduction of the material LSPR to a value below the sensitivity threshold of our experiment or alternately a net decrease in LSPR cross section to a value below our detection threshold. We further note that the plasma frequencies of Au and Ag are at 9.096 eV and 8.9 eV.\(^{33}\) The existence of an LSPR at energies greater than our measurement window is thus not expected. Thus, the former two possibilities appear to be the only way of interpreting these data.
In light of the above arguments, we tentatively interpret our observations by considering Lindhard-like behavior. Although both Au and Ag do not follow these properties due to interband absorption, we argue below that the Au-Ag NS may be associated with reduced free electron densities. Under these circumstances, the Lindhard dielectric function is expected to be obeyed since the new LSPR in Au-Ag is anticipated at energies lower than the interband absorption.

In particular, considering Lindhard-like behaviour, we derived the real and imaginary dielectric constants for Au-Ag materials. According to the Lindhard model the real part of dielectric function ($\varepsilon'$) of a material can be expressed as $\varepsilon' = \varepsilon_{\infty} - \frac{\omega_p^2 (\omega^2 - \gamma_L^2)}{(\omega^2 + \gamma_L^2)^2}$

and the imaginary part ($\varepsilon^*$) can be written as $\varepsilon^* = \frac{2\omega_p^2 \gamma_L \omega}{(\omega^2 + \gamma_L^2)^2}$

Here $\varepsilon_{\infty}$ is the contribution to the dielectric from the bound electrons. For Au $\varepsilon_{\infty}$ is 9.84 and for Ag it is 3.7. $\omega_p$ is the plasma frequency obtained from the formula $\omega_p^2 = \frac{ne^2}{m}$, $\gamma_L$ is the average damping constant of bulk material; 0.072 eV for Au and 0.021 eV for Ag, $n$ is the number density of electrons, $m$ is the electron effective mass. While comparing with Au we have taken the same damping constant value for Au-Ag as of Au and while comparing with Ag we have used the same value as of Ag. Generally, $\omega_p$ for Au is 9.096 eV and for Ag is 8.9 eV. For different values of $\omega_p$ we can obtain different values of free electron density inside the system. By considering two possible plasma frequencies for Au-Ag materials such as 0.5 eV and 0.05 eV, the exemplary electron densities come out to be $4.8 \times 10^{18}$ electrons/cm$^3$ and $4.8 \times 10^{16}$ electrons/cm$^3$. These are shown in fig. 4. An alternative but significant possibility is the decrease in LSPR cross section in Au-Ag materials.

We can achieve an estimate of free electron density of Au-Ag materials with respect to Au by considering the signal to noise (S/N) of our measurements. We find that for ordinary Au particles, an S/N ratio of 40:1 is observed. Considering this signal to arise from the imaginary component of the dielectric, we expect Au-Ag material to be associated with an imaginary dielectric at least 40-fold lower than Au. This indicates the reduction of free electron density by at least in the order of $10^2$. For the limiting threshold electron density, the LSPR peak is then anticipated to lie at energies below 0.23 eV or below for Drude like behavior. We thus see that a reduced free electron density could account for our observations. Our measurements appear to be limited by the measurement window of energies accessible to us, rather than an S/N effect. In particular, at least a 10 fold reduction in free electron density is required to explain the lack of a measurable LSPR in the energy window > 0.5 eV.

This interpretation of the Au-Ag system thus fundamentally relies on the presumption of a reduced electron density. Such an interpretation also suggests the recovery of the usual Mie
like resonances if the material deviates from its ideal structure and contains excess of any one constituent.

Figure 4.a-b. Comparison between the dielectric function of Au/Ag material and Au ($\omega_p=9.096$ eV) for 2 different $\omega_p$ 0.5 eV and 0.005 eV, a. Real part and b. Imaginary part of dielectric function. c-d. Comparison with Ag ($\omega_p=8.9$ eV), c. Real part and d. Imaginary part of dielectric function.

We therefore examined particles with higher Au content (89%, 95% and 100%). These percentages were obtained from Energy-dispersive X-ray Spectroscopy (EDS) data considering the Au-L and Ag-L shells. The results are presented in fig. 5. Images of particles are shown in fig. 5a while the corresponding EELS spectra are presented in fig. 5b. Each inelastic spectrum has been background corrected to suppress the substrate contribution. With increasing Au mole fraction, the nanoparticles exhibit a resonance mode in the 1.7-2.3 eV range. These modes' nature and peak position now resemble the Au SPR modes. For comparison, the extinction spectra of the nanoparticle ensemble have also been presented in fig. 5c. Extinction spectra have been collected by dispersing nanoparticles in water. Particle-to-particle deviations in stoichiometry morphology do exist, enabling the study of effects of these
parameters on particle properties. Each spectrum in fig. 5b represents the single-particle analogue concerning their corresponding ensemble level extinction spectra in fig. 5c. Furthermore, the availability of extended energy range in the inelastic spectra allowed us to study the bulk plasma modes of these materials. As evident from fig. 5b the green, and black curves that contain surface plasmon modes also manifest a broad peak at far UV range with maxima around 8.5 eV and 8.7 eV respectively. Here, the electron counts are arbitrary. It is evident that the peak intensity, as well as the linewidth (e.g. full width half maximum of $\sim 4.46$ eV and $\sim 4.57$ eV for the green and black curves respectively in fig. 5b) and the peak maxima associated with the nanoparticles vary from particle to particle essentially as a function of particle morphology. These observations are consistent with the restoration of free electron density and associated plasmonic modes upon presence of excess Au in Au-Ag materials.

**Figure 5 a.** STEM image of Au-Ag nanoparticles (scale bar 20 nm) with increasing Au mole fraction (from top to bottom). **b.** Background corrected inelastic scattering spectra of the corresponding nanoparticles from a.; **c.** Optical extinction spectra of the same nanoparticles in an ensemble level.

**Conclusion:**

In conclusion we have studied the unique optical properties of engineered Au-Ag nanostructures on single particle level via Electron Energy Loss Spectroscopy. The suppression of any well-defined localised surface plasmon mode firmly corroborate the previously obtained optical responses at ensemble level. These observations are tentatively explained by invoking a $>10$-fold reduction of electron density in Au-Ag NS. Studies of nanoparticles with higher Au content reveals that the LSPR modes can be regenerated corresponding to Mie like behaviour.
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References:


Supplementary Information

Investigating the suppression of conventional plasmonic modes of Au-Ag nanostructures via Electron Energy Loss Spectroscopy (EELS)

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Figure S1 a. HAADF-STEM image of Au/Ag nanoparticles. Red lines have been drawn on each particle. Along the lines elemental distribution of Ag was taken. b. Plot 1-4 represents the line mapping data of Ag on each particle along the red lines in a.