

Letter

## Tuning Chemical Interface Damping: Interfacial Electronic Effects of Adsorbate Molecules and Sharp Tips of Single Gold Bipyramids

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## **Jargon box**

#### i) Localized surface plasmon resonance (LSPR)



#### iii) Electronic effects

• An electronic effect influences the structure, reactivity, or properties of molecule but is neither a traditional bond nor a steric effect.

## Inductive Effect

Groups

+I (electron

- ii) Plasmonic decay channels: hot-e transfer
- A) Indirect transfer pathway
- B) Direct transfer pathway or CID



 $O^- > CO_2^- > CR_3$ >  $CHR_2 > CH_2R$ >  $CH_3 > D$ 



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## Correlated Rayleigh Scattering Spectroscopy and Scanning Electron Microscopy Studies of Au-Ag Bimetallic Nanoboxes and Nanocages

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# Single-particle correlation study: chemical interface damping induced by biotinylated proteins with sulfur in plasmonic gold nanorods<sup>†</sup>

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## **Motivation**

• Correlation of DFM (optical) and FESEM (electron) studies to understand laser-induced reshaping at single particle level.



• To get insights on vibrational tomography of analytes adsorbed on anisotropic nanostructures.

## Why this paper?

• This is the first report where they have shown the possibility of tuning and optimizing CID for efficient photochemical and sensing processes using correlative SEM-DFM and spectroscopic measurements on single Au nanostructures.

✓ Scanning electron microscopy (SEM) correlated dark-field (DF) microscopy and spectroscopic measurements of gold nanorods (AuNRs) and gold bipyramids (AuBPs) with sharp tips were performed to determine their impact on CID at the single particle (SP) level.

✓ It addresses the effects of electrophilic strength of thiolated aromatic benzene rings with additional functional groups on SP.

✓ It discuss about the isomeric effects of additional functional groups on CID.

✓ It shows the possibility of tuning and mastering the CID for efficient sensing processes.

## **Results and discussion**



**Figure 1.** Characterization of gold bipyramids (AuBPs) and gold nanorods (AuNRs) used in this study. (A) SEM image of AuBPs with sharp tips. (B) SEM image of AuNRs with a similar size. (C) Normalized extinction spectrum of the AuBPs dispersed in water (yellow curve) overlaid with that of the AuNRs (red curve).



**Figure 2.** (A) A photograph to show the experimental setup for single particle microscopy and spectroscopy and (B) schematic diagram to show the working principle of scattering-based DF microscopy and spectroscopy for single Au nanoparticles.







**Figure 3. (A-D)** SEM images of AuNRs in same region and deposited on a slide with gold pattern. The gold pattern allowed to locate same Au nanoparticles (AuBPs, AuNRs) under optical microscopy.



**Figure 4.** Single particle scattering microscopy and spectroscopy of the AuBPs and AuNRs. (A,B) DF scattering images of single AuBPs (A) and single AuNRs (B) fixed on a glass slide in water and excited by white light illumination. (C) Overlaid DF scattering spectra of a single AuBP1 (red curve) and AuNR1 (orange curve). (D) Single particle scattering spectrum of AuBP1 fitted using a Lorentzian function to extract the homogeneous LSPR line width.



**Figure 5.** Effects of the medium RI on the homogeneous LSPR line width (or fwhm), as well as the wavelength. (A) Normalized single scattering spectra of AuBP2 in Figure 2A recorded in air (green curve), water (blue curve), and oil (red curve). The black dotted line indicates the fit to the Lorentzian function. (B) Normalized single scattering spectra of AuNRs in Figure 2B recorded in air (green curve), water (blue curve) and oil (red curve). (C,D) Changes in the homogeneous LSPR line widths of a single AuBP (C) and single AuNR (D). The fwhm remains almost constant for both AuBPs and AuNRs as a function of the medium RI. (E,F) Changes in the LSPR wavelengths for a single AuBP (E) and single AuNR (F) in terms of the change in medium RI from air to oil. The LSPR wavelength increases proportionally with the local RI media for both AuBPs and <sup>1</sup>AuNRs.



**Figure 6.** Chemical interfacial damping of single AuBPs with thiol molecules. (A) Single particle scattering spectra of AuBP recorded in ethanol before adding a drop of 1-decanethiol (grey-curve) and 10 minutes after adding an ethanolic solution of 1-decanethiol through a homebuilt flow cell (red-curve). (B) Single particle scattering spectra normalized to better compare the LSPR wavelength shift as well as the LSPR linewidth broadening.



Figure 7. Scaling from low EDGs to high EWGs for the bare material as a control without CID. (A) Time dependence of thiol adsorption observed via LSPR line width (or fwhm) broadening for single AuBPs for each sample (NH2, OH, CF<sub>3</sub>, and NO<sub>2</sub>). The scattering spectra of 20 single AuBPs were repeatedly obtained from each sample for a period of approximately 60 min and the LSPR line width,  $\Delta\Gamma$ , was extracted with respect to the starting value. The fitted curves are shown in black. (B) The shift in the homogeneous LSPR line width with increasing electronic effects (EDG to strong EWG). The inset depicts the binding of thiol (or sulfur) onto single AuBP. а



**Figure 8.** Effects of ortho-, meta-, and para- isomers on the shift in the fwhm using the bare material (without thiol) as a control. (A) Time dependence of thiol adsorption observed via LSPR line width (or fwhm) broadening for single AuBPs for each sample (NH2, CF3). The scattering spectra of 20 single AuBPs were repeatedly obtained from each sample over a period of approximately 60 min and the LSPR line width,  $\Delta\Gamma$ , was extracted with respect to the starting value. The fitted curves are shown in black. (B) Electronic effects of the LSPR line width shift induced by the ortho-, meta-, and para-isomers of ATP (NH2) and TFMTP (CF3).

The effects of the sharp tips of AuBPs and the EWG and EDG effects of thiolated benzene rings were investigated with respect to AuNRs with a similar size and AR.

Single AuBPs with sharp tips were observed to induce more broadening of the homogeneous LSPR line widths than single AuNRs.

EWGs and EDGs increase the interfacial contact between the nanoparticles and adsorbate molecules by reducing the effective distance between the hot electrons and AuBP particle surfaces, as well as increasing the contribution of CID to the total LSPR damping channel.

> 4-NTP, which features a strong EWG, induced more broadening of the homogeneous LSPR line width than 4-ATP bearing an EWG. This shows that EWGs significantly increased the effectiveness of the interfacial Au-S bonds for inducing plasmon dephasing during the CID process.

The EDG isomers of aminothiophenols and trifluoromethylthiophenols showed that ortho- and para- substitutions increase the fwhm's more significantly than meta-substitutions.

➤ These findings show that the CID in the LSPR total decay channels can be tuned by controlling the EW and ED features of adsorbate molecules with the surface topology of the metal.