Camden Research Group

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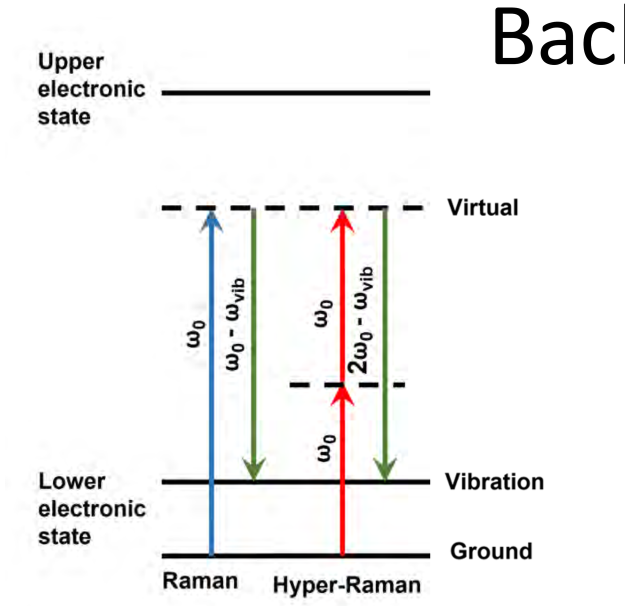
Background

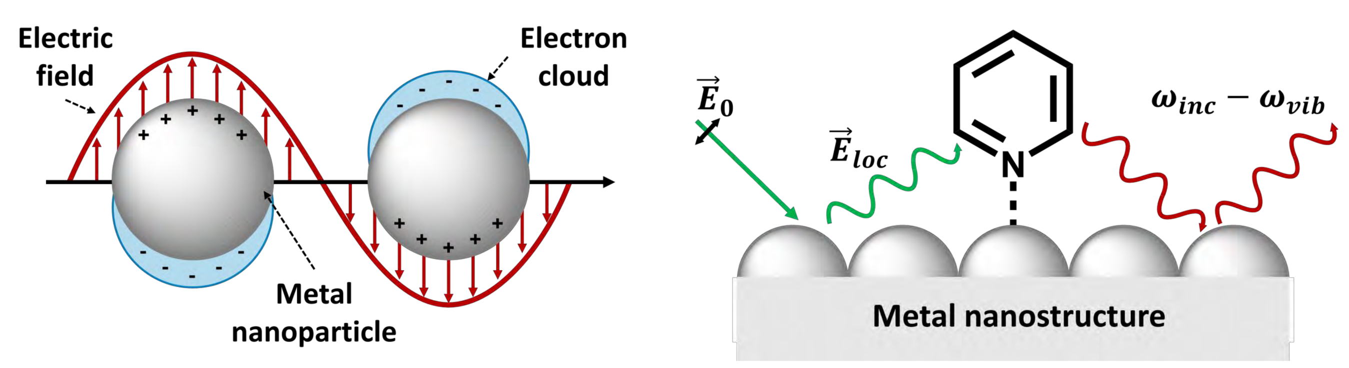


Chandran, Camden. *ACS Nano.* **2024**, 18, 20827-20834.

Raman Scattering: The inelastic scattering of light, most often attributed to molecular vibrations. It is however a very weak effect in that only roughly 1 in every 10^6 scattered photons is inelastically scattered.

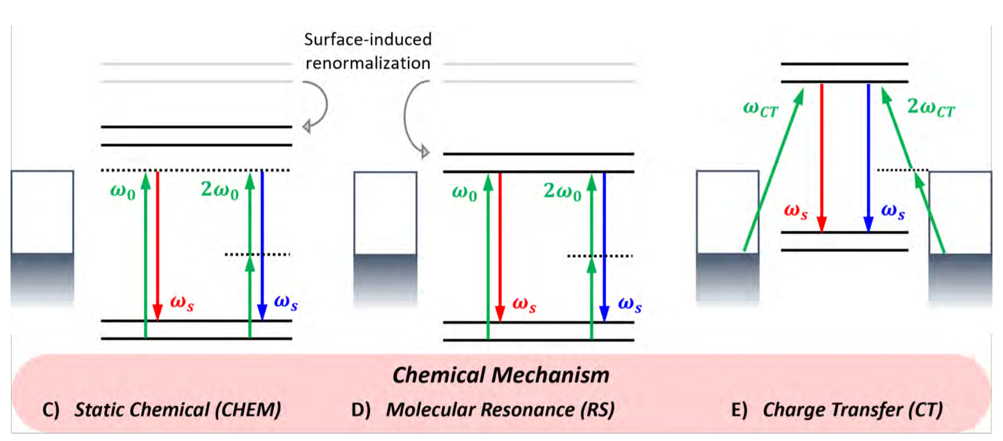
Hyper-Raman Scattering: The non-linear analog of Raman scattering where two photons of incident frequency ω_0 give way to a scattered photon of frequency ω_{HR} that is shifted relative to the second harmonic frequency ($\omega_{HR} = 2\omega_0 \pm \omega_{vib}$). This effect is even weaker than normal Raman scattering.

Localized Surface Plasmon Resonance (LSPR): Surface electromagnetic waves that propagate along a metal/dielectric interface, can be viewed as oscillations of the conduction electrons (left). Excitation of the plasmon provides the local field enhancement required for SERS (right).



Surface Enhanced Raman Scattering (SERS): Adsorption of a molecule on a metal surface increases the Raman effect by $10^6 - 10^8$. The two-photon analog of SERS is **surface-enhanced hyper-Raman scattering (SEHRS)**.
The primary contributor to the overall enhancement is the electromagnetic mechanism, which accounts for 10^4 (SERS) and 10^6 (SEHRS).

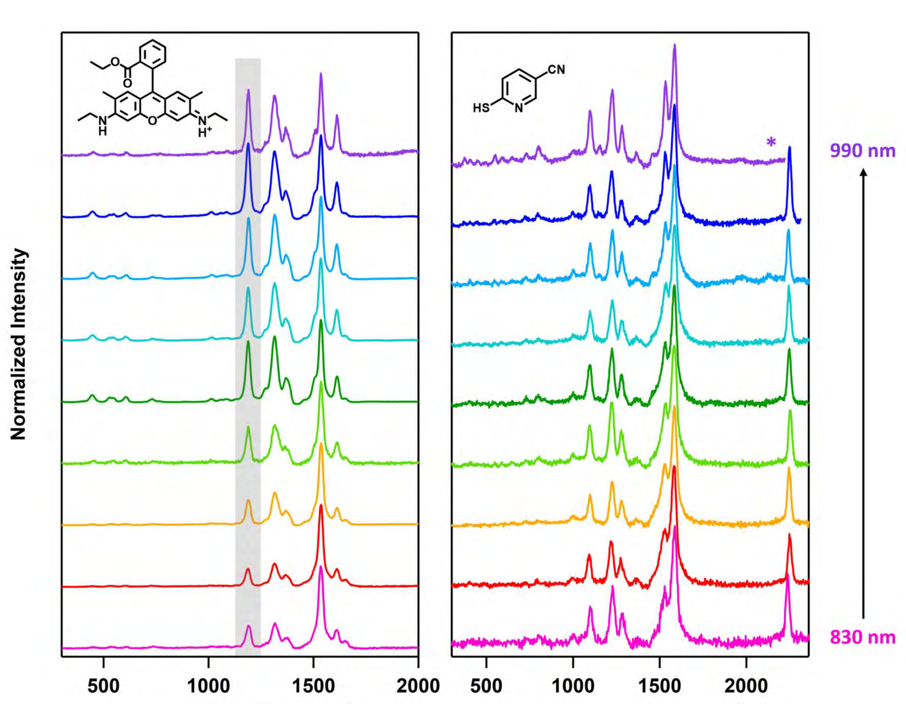
SEHRS and the Chemical Effect



- The other contributor is the chemical mechanism (left), which has been ***approximated*** to be around the order of 10^1-10^2 (SERS) and 10^2-10^4 (SEHRS).

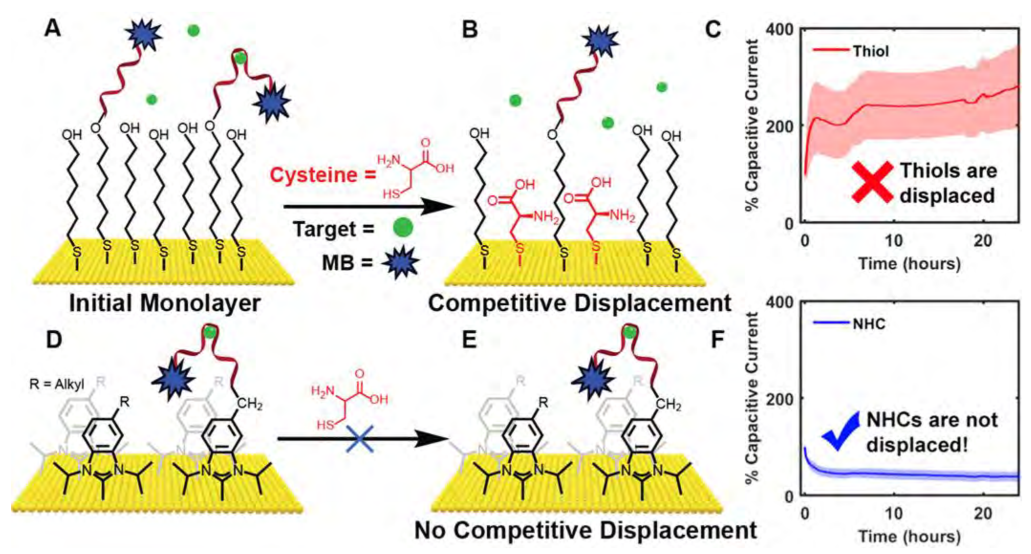
- However, determining SEHRS enhancement factors remains a challenging problem due to the extremely low intensity HR signal of non-surface-enhanced molecules and the difficulty of disentangling the chemical mechanism contributions (CHEM, RS, CT).

- By scanning through a series of wavelengths, we can see if a change in the SEHRS spectrum is observed that can arise from:
  - Molecular resonance-hyper-Raman (RS)
  - The creation of new metal charge transfer states (CT).
- For R6G (right-1st panel), the laser is scanned through its first excited state ($S_1 \leftarrow S_0$, 2ω = 515 nm).
  - Dramatic changes in the relative intensities of modes coupled with the S_1 excited state are observed (gray shaded box), suggesting the presence of resonance effects.

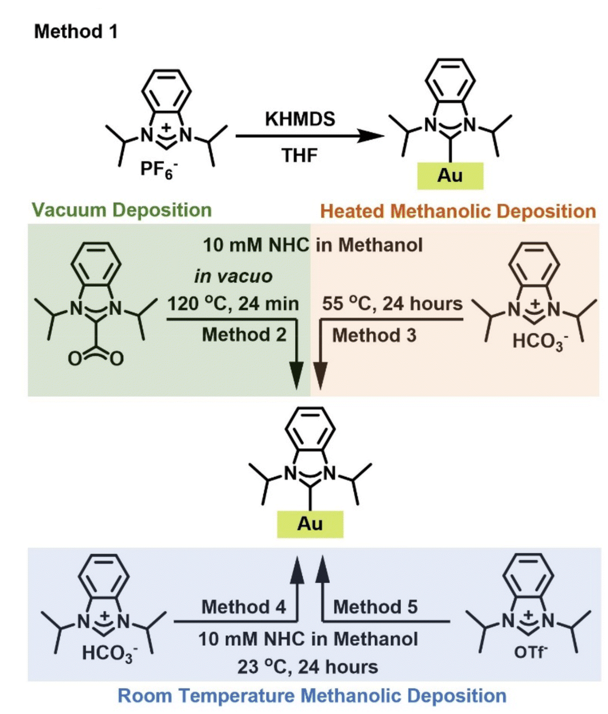


- The wavelength-scanned spectra of p-MPN (above right) are also presented, which remain consistent across all wavelengths.
  - This suggests that there are no molecular resonance-hyper-Raman effects, at least in this wavelength range.

Next-Gen Surface Ligands for Next-Gen Technologies

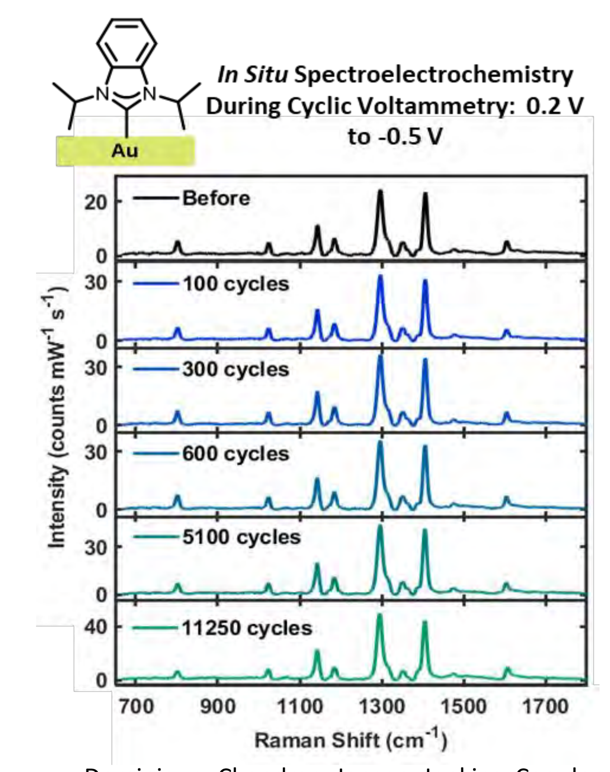


- Electrochemical aptamer-based sensors (E-ABs) utilizes aptamer as the recognition element, enables, continuous, real time, and *in vivo* monitoring of target.
- Target binds to aptamer, changes its shape and causes shift in the electrochemical signal (figure, left) that can be measured.
- E-AB technology utilizes gold–thiol (Au-S) bond and the stability of the monolayer is limited under biological and electrochemical conditions. Figure (left) shows NHCs are not displaced by cysteine *via* competitive displacement



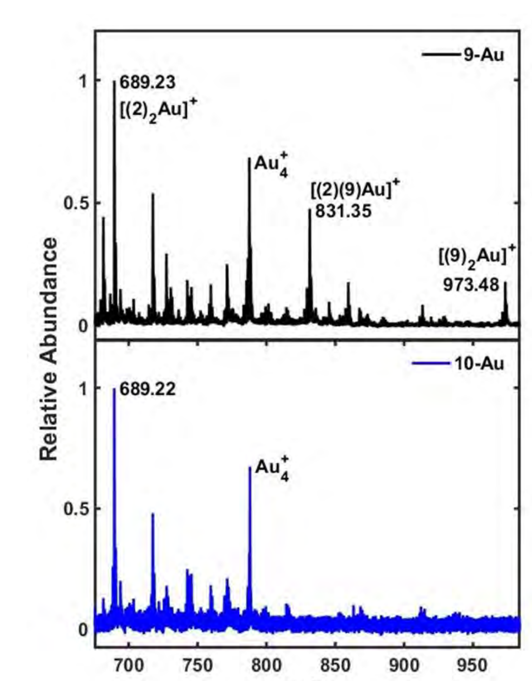
- Deposition protocol (left) matters for the quality of monolayer is crucial for EAB stability and performance
- A systematic comparison of various widely used deposition protocols show that the fundamental characteristics of the Au-NHC monolayer is heavily dependent on the deposition protocol
- As Method 2 produced high quality monolayer, the same has been employed to study the stability of monolayer upon continuous voltametric cycling (figure, right).

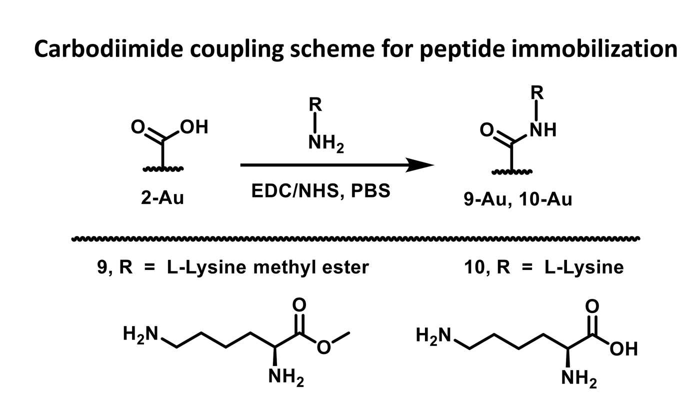
Chandran, Dominique, Kaur, Clark, Nalaoh, Ekowo, Jensen, Aloisio, Crudden, Arroyo-Curras, Jenkins, Camden. *Nanoscale.* **2025.**



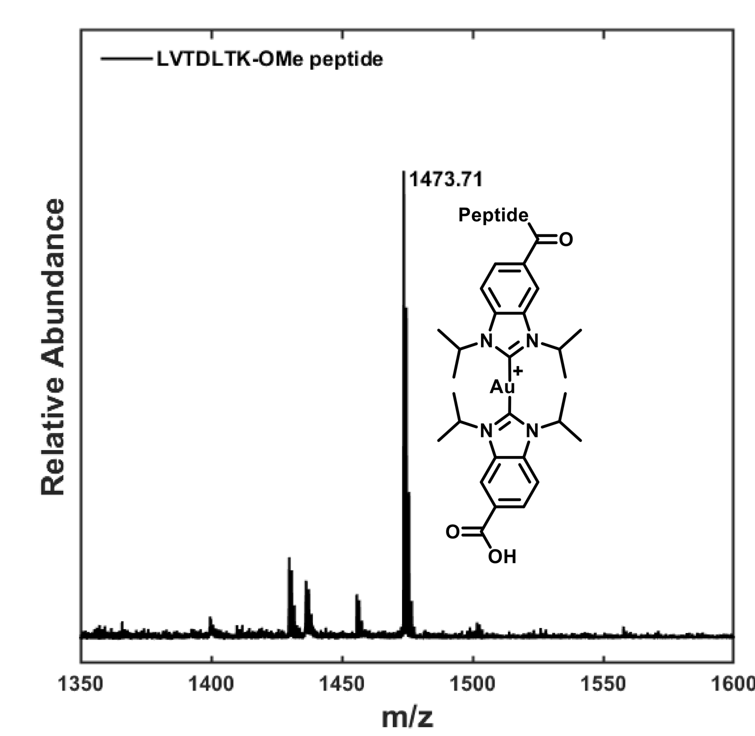
Dominique, Chandran, Jensen, Jenkins, Camden. *Chem. A European Journal.* **2023.** 15, e202303681

NHC ligands as a Mass Ionization Tag for Biomolecules in LDI-MS



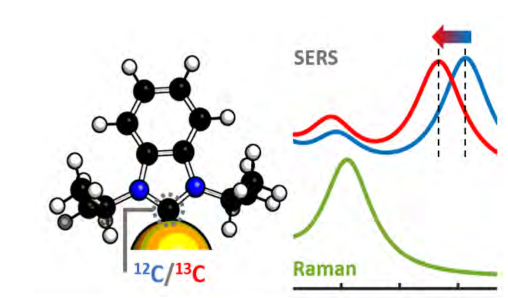


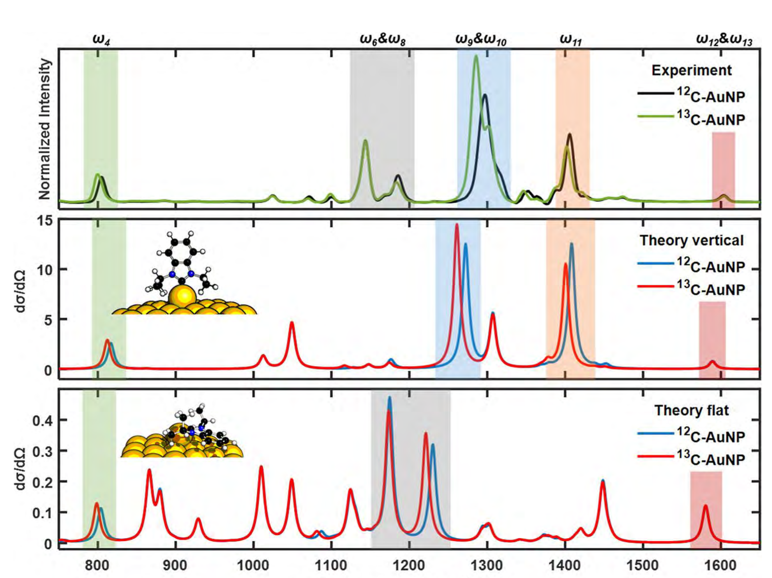
- Conventional thiol ligands fragment extensively in LDI-MS.
- NHC ligands enable the desorption/ionization of biomolecules without fragmentation.
- Carboxylic acid NHC was used to capture L-lysine methyl ester (Figure, left) and LVTDLTK-OMe peptide (Figure, right)

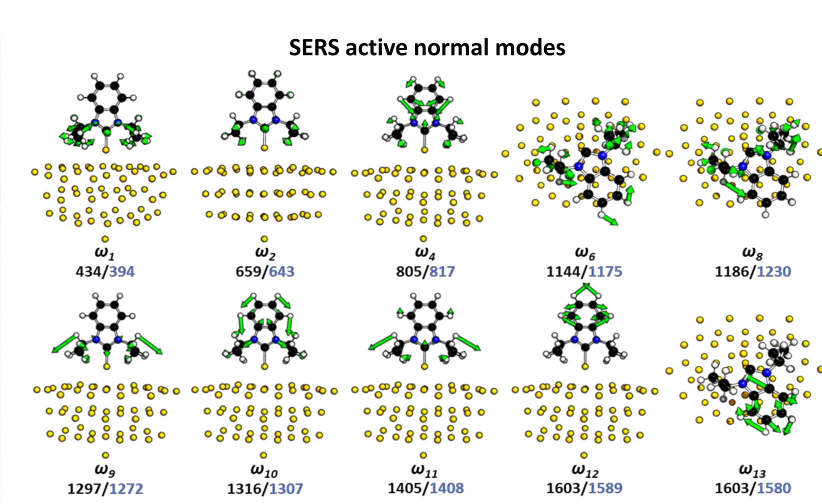


Fundamental Vibrational Spectroscopy Studies of NHC on Gold Nanoparticles

We compared the experimental Raman, SERS and IR spectra of the diisopropyl benzimidazolium NHC and its ^{13}C-labeled isotopologue to first principles theory to definitively assign previously unreported vibrational modes and verify and compile normal modes from prior literature.



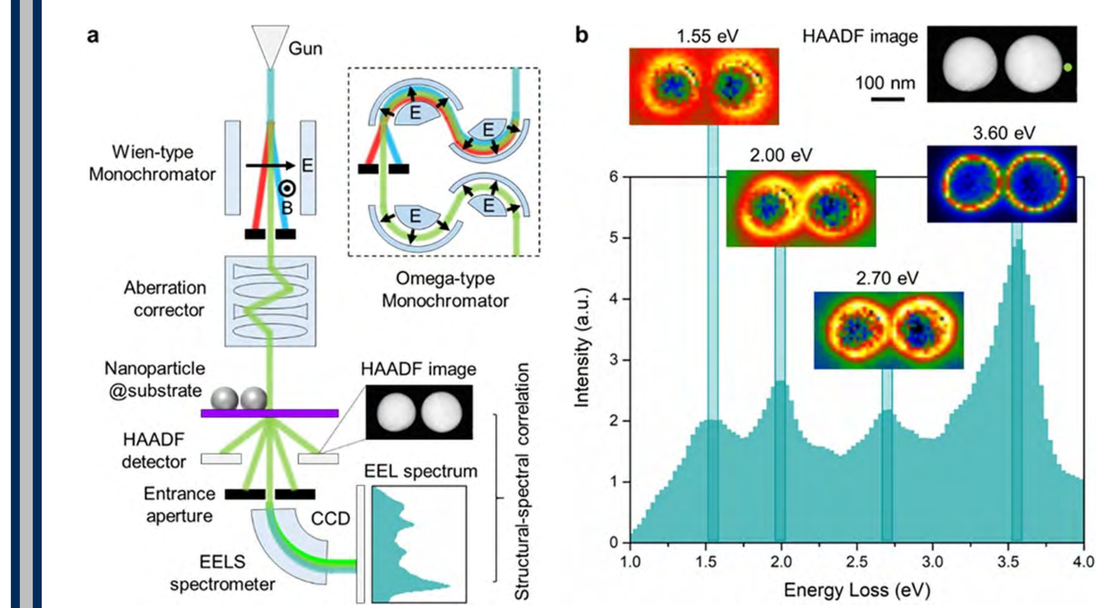




With isotope labeling, we could also isolate the normal modes with Au-C vibration, which allows us to determine chemisorption of the NHC on gold using a few peaks in the SERS spectra.

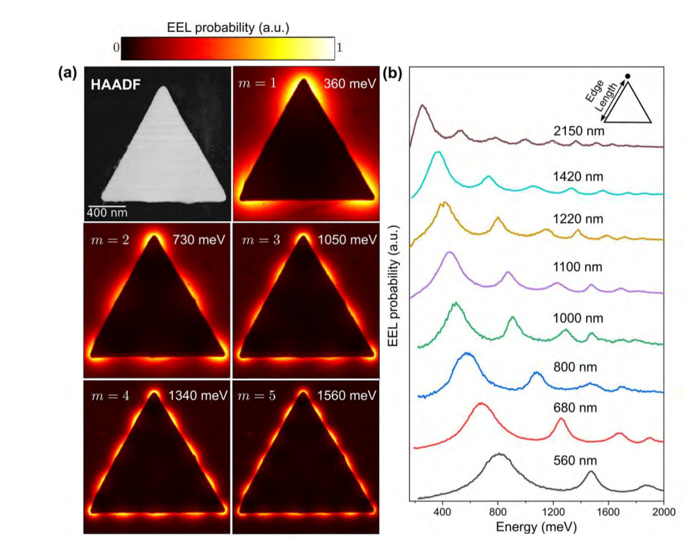
Chowdhury, Hu, Jenkins, Jensen, Camden, et al. *J. Phys. Chem. C.* **2024**, 128, 32, 13550
Jensen, Chowdhury, Jenkins et al. *Chem. Commun.* **2023**, 59, 13524

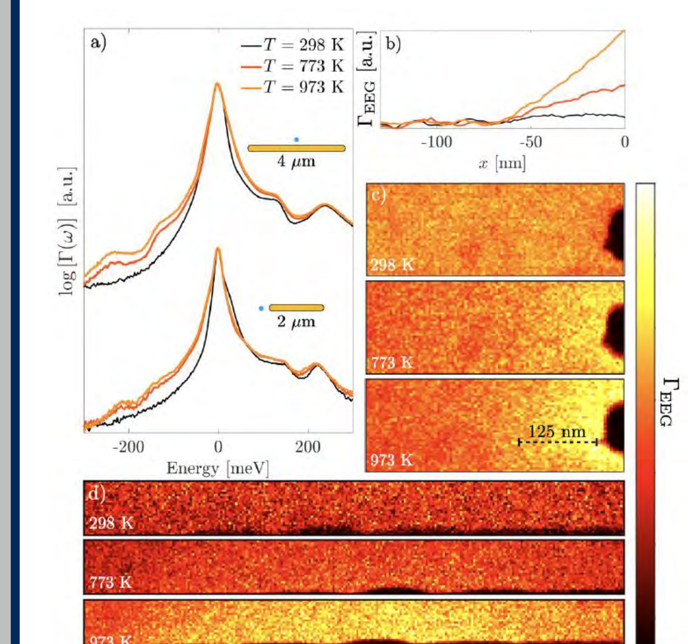
STEM-EELS



A scanning transmission electron microscope (STEM) can probe localized surface plasmons with nanometer spatial resolution and ultra-high energy resolution using electron energy loss spectroscopy (EELS).

Using the world class electron microscope available to us at Oak Ridge National Laboratory, we have recently characterized the near-field response of individual gold nanotriangles (NT) over a broad, visible-to-infrared spectral region. EEL spectrum images for a 1420 nm gold NT displaying the spatial profiles of its *m=1-7* Fabry-Pérot modes (a), and the EEL spectra of a set of gold NTs vs edge length (b) is shown on the right.





In our latest work, we studied the localization of low-grade heat using Au nanowires on a SiN substrate supporting thermally active Fabry-Pérot (FP) resonances. Temperature dependent and spatially resolved EEG spectrum images obtained at *l=1* FP mode energy at the end of the wire (c), and spectrum images obtained at *l=2* FP mode energy near the center of the wire (d) are shown on the right, along with the EEL and EEG point spectra of two wires at different temperatures.

Oak Ridge National Laboratory — Center for Nanophase Materials Sciences

Wu, Li, Camden. *Chem. Rev.* **2018**, 118, 2994-3031.
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Beutler, Kumar, Duddy, Bourgeois, Srijanto, Hachtel, Masiello, Camden. *ACS Energy Lett.* **2024**, accepted.

Acknowledgments

ORISE
Berthiaume Institute for Precision Health
ND Energy – Center for Sustainable Energy at Notre Dame
CBM Center for Bioanalytic Metrology
AFRL Air Force Research Laboratory
ALS
NSF

Collaborators
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The Smith Lab
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