Discriminating Nanoparticle Dimers from Higher Order Aggregates through Wavelength-Dependent SERS Orientational Imaging

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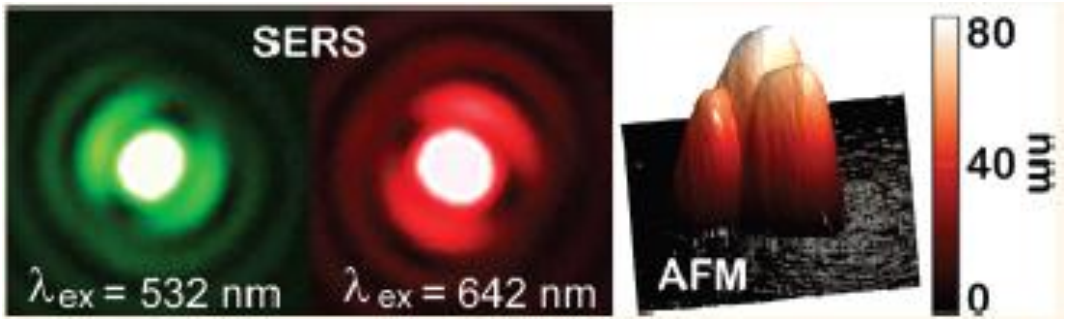


By -
Kamalesh
24-03-2012

Background

1. Optical characterization of dimer structure and orientation is most often accomplished by measuring the polarization dependent localized surface plasmon resonance (LSPR) scattering spectra from assembled or fabricated dimers.

2. Dimer LSPR spectra strongly depend on the orientation, shape, and size of the individual nanoparticles that comprise the dimer, leading to significant differences between individual dimer spectra.

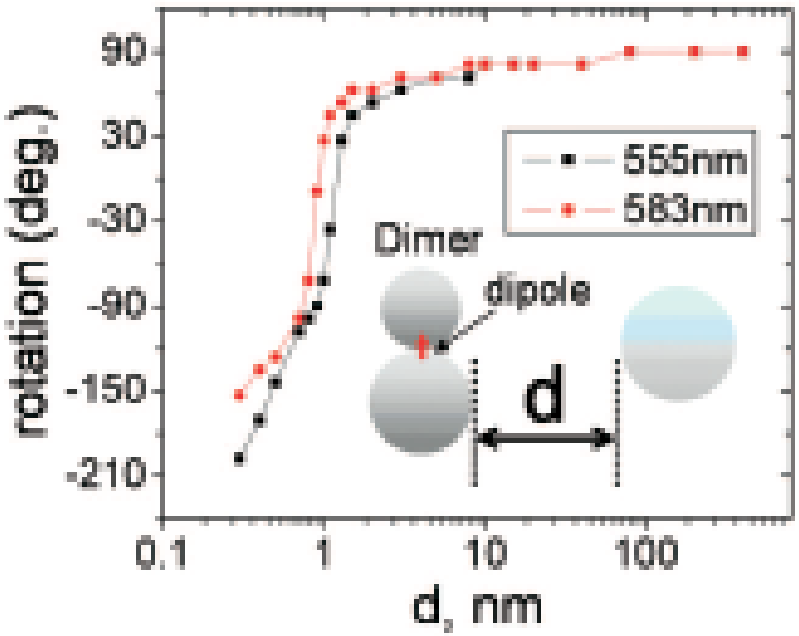
3. Unlike single molecule orientational imaging, SERS images do not need to be defocused to observe emission patterns because the inherent high-signal nature of SERS produces enough high-angle light to form the emission pattern features.

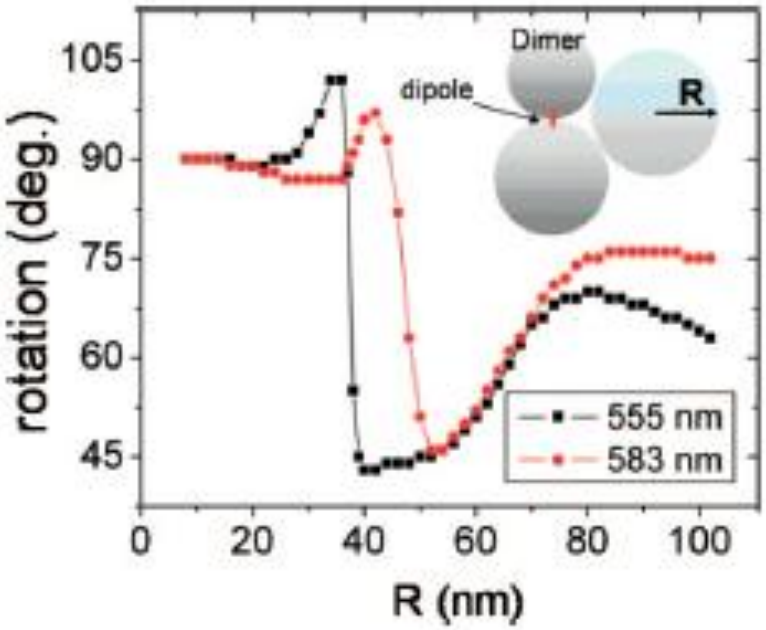
4. Shegai et al. have shown that SERS originating from dye-labeled nanoparticle dimers is linearly polarized along the long axis of the dimer, independent of the excitation wavelength, while the polarization properties of SERS from a nanoparticle trimer changes with excitation wavelength.

Shegai, T.; Li, Z.; Dadosh, T.; Zhang, Z.; Xu, H.; Haran, G. Proc. Natl. Acad. Sci. U.S.A. 2008, 105, 16448–16453.

Background

The third particle breaks the dipolar symmetry of the two-particle junction, generating a wavelength-dependent polarization pattern. The scattered light becomes elliptically polarized and its intensity pattern is rotated in the presence of the third particle.

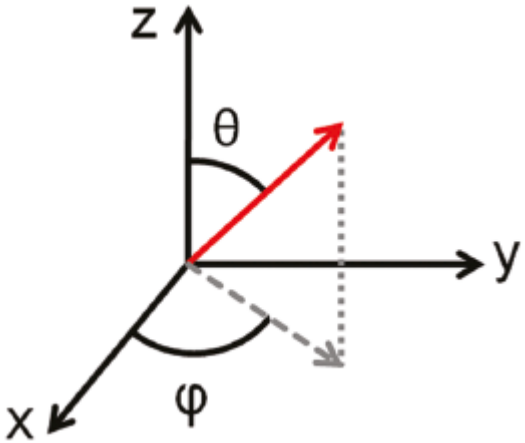


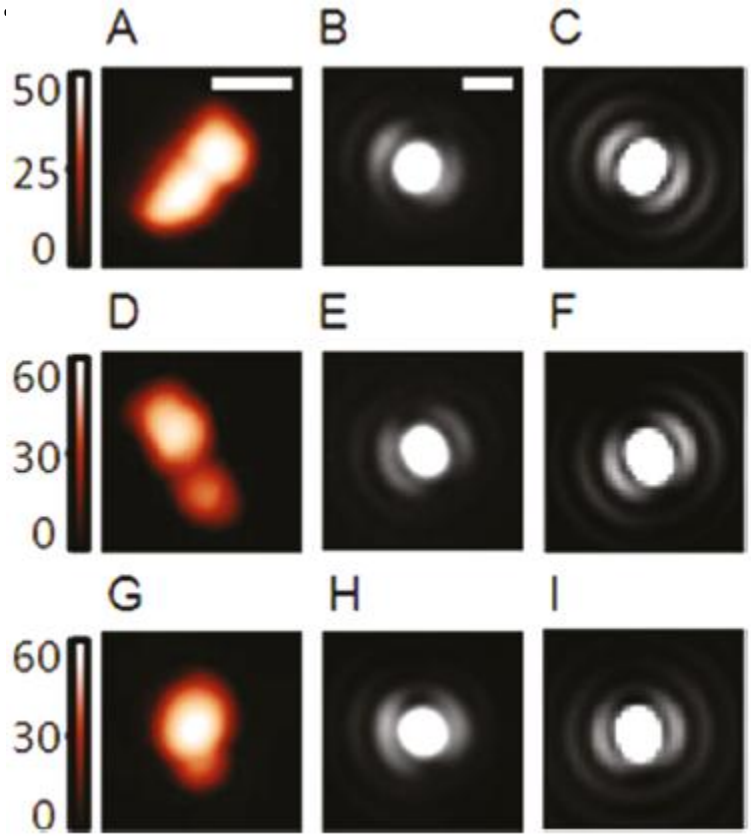


Shegai, T.; Li, Z.; Dadosh, T.; Zhang, Z.; Xu, H.; Haran, G. Proc. Natl. Acad. Sci. U.S.A. 2008, 105, 16448–16453.

SERS Orientation

(A,D,G) AFM topography images of three SERS-active silver nanoparticle dimers with (B,E,H) correlated optical images of R6G SERS emission patterns originating from the respective dimers and (C,F,I) theoretical dipole emission patterns.





The angles for each are as follows:

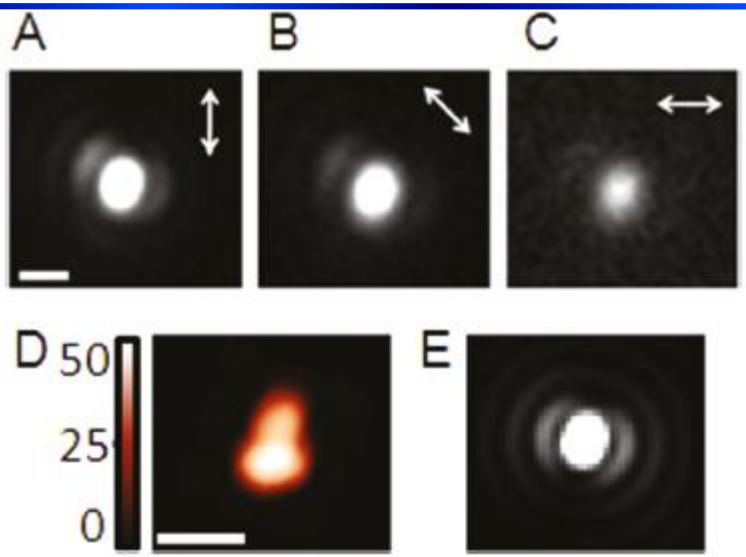
(AC) ϕ = 60, θ = 90;

(DF) ϕ = 115, θ = 84 ;

(GI) ϕ = 100, θ = 78.

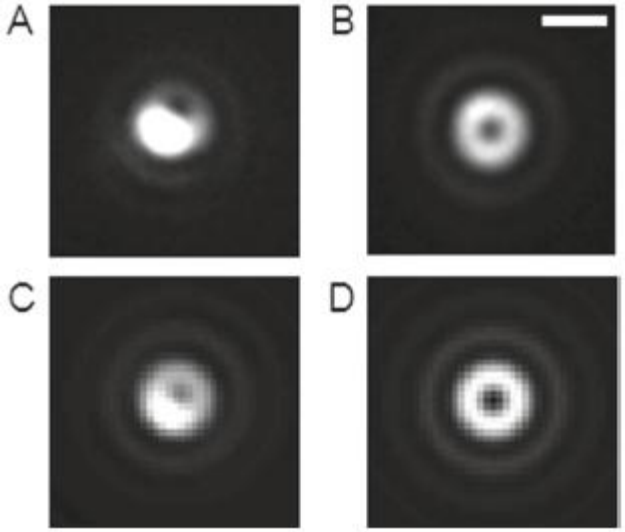
Stranahan, S. M.; Titus, E. J.; Willets, K. A. SERS Orientational Imaging of Silver Nanoparticle Dimers. J. Phys. Chem. Lett. 2011, 2, 2711–2715.

SERS Orientation



R6G SERS emission patterns (A-C) originating from the silver nanoparticle in (D) upon excitation with light polarized at 90, 45, and 0. (E) Theoretical dipole emission pattern using $\phi = 75$ and 96.

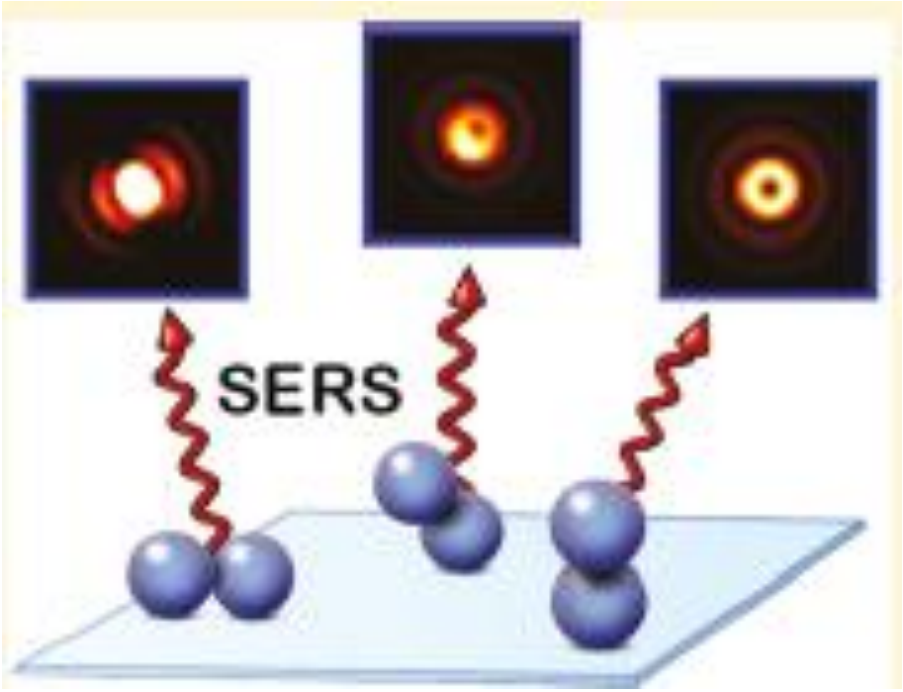
Experimental SERS emission patterns (A,B) and corresponding theoretical dipole emission patterns (C: $\phi = 55$; $\theta = 34$) and (D: $\phi = 0$; $\theta = 0$) arising from silver nanoparticle aggregates with strong out-of-plane plasmon modes.



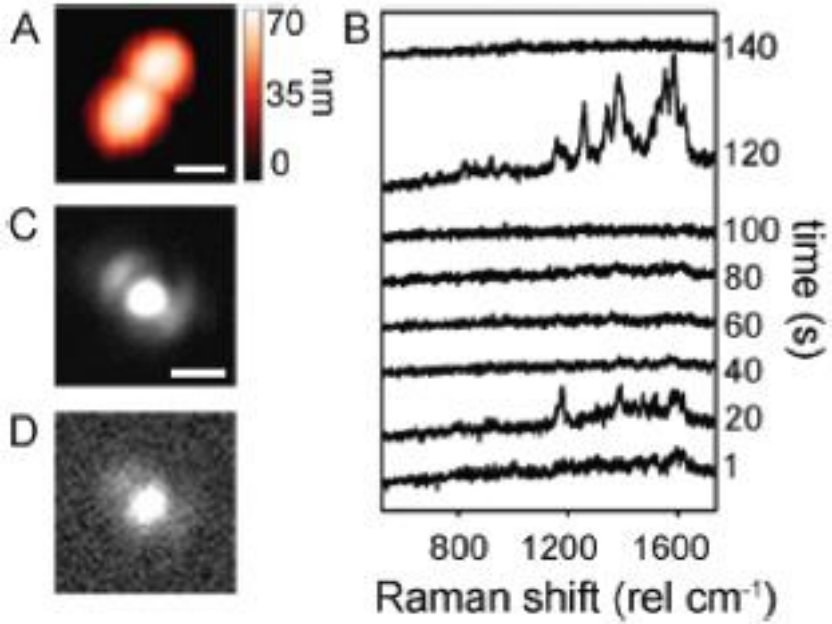
Stranahan, S. M.; Titus, E. J.; Willets, K. A. SERS Orientational Imaging of Silver Nanoparticle Dimers. J. Phys. Chem. Lett. 2011, 2, 2711–2715.

Concept

Surface-enhanced Raman scattering (SERS) orientational imaging has been demonstrated as a powerful far-field optical technique for determining the in-plane and out-of-plane orientations of SERS active nanoparticle dimers and their discrimination from trimers.

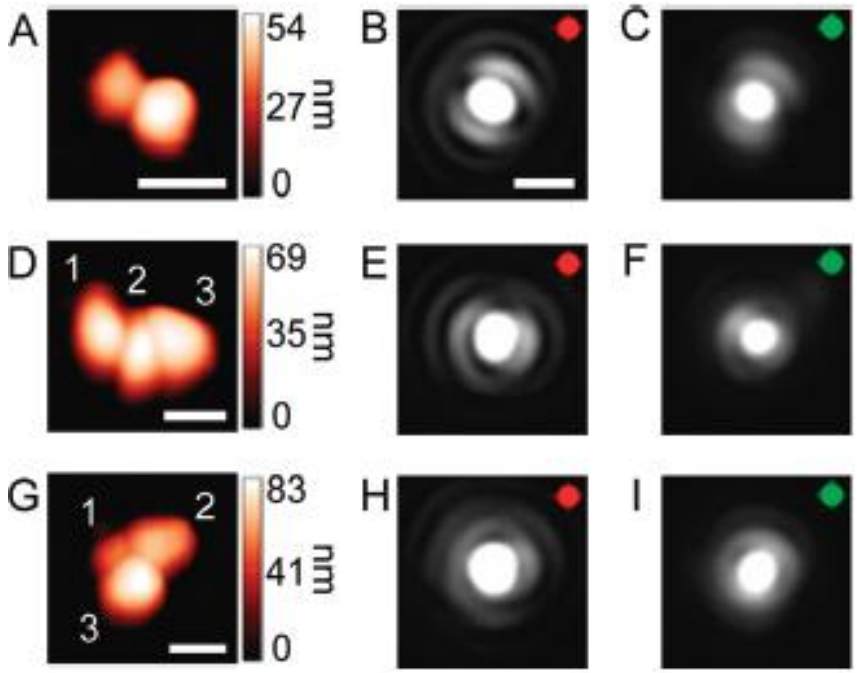


SERS and silver luminescence



(A) AFM topography of a SERS-active Nile Blue labeled (~1 nM) nanoparticle dimer with (B) corresponding selected SERS spectra taken over 140 s with 1 s acquisition times. (C) Nile Blue SERS emission pattern image corresponding to the spectrum taken at 120 s, and (D) background emission image corresponding to the spectrum taken at 100 s. The emission images are acquired with 0.2 s acquisitions. The scale bar in A is 100 nm, and the scale bar in C is 1 µm.

Dimers, aggregates and dye concentration



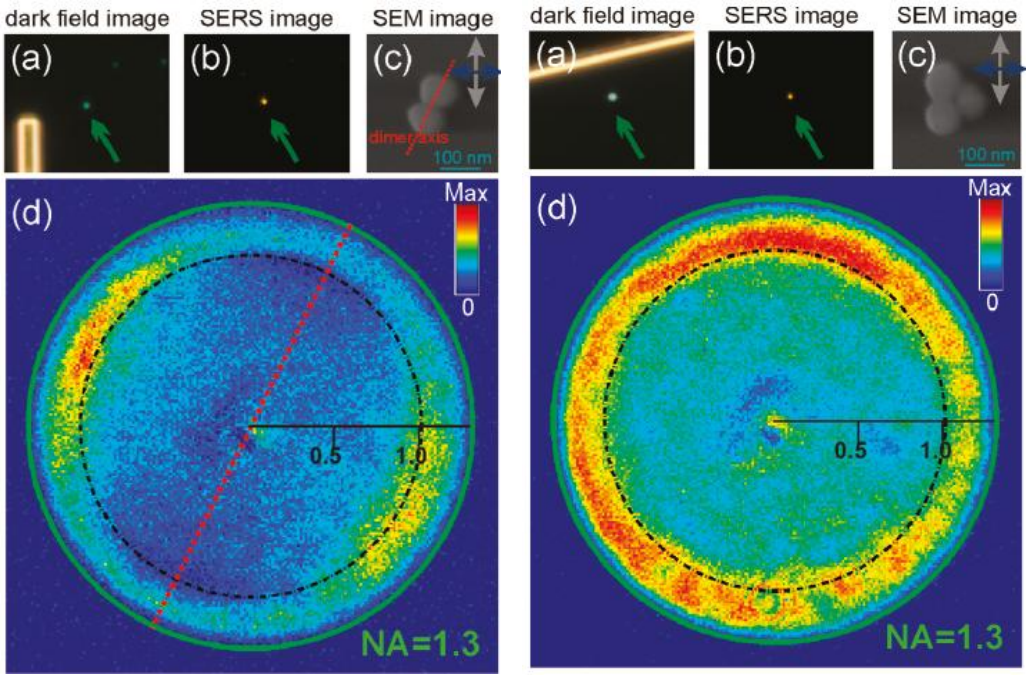
Quasi-circularly polarized excitation light is used to excite all emission images after Figure 1 to access all plasmon modes in the nanoparticle aggregates of interest.

Changing the excitation wavelength will change the measured intensity of the SERS if the plasmon mode is excited more efficiently by one excitation wavelength over the other but will not change the output polarization of the emitted SERS. Hence varying the SERS excitation wavelength can be used to differentiate nanoparticle dimers from larger aggregates.

Dimers, aggregates and dye concentration

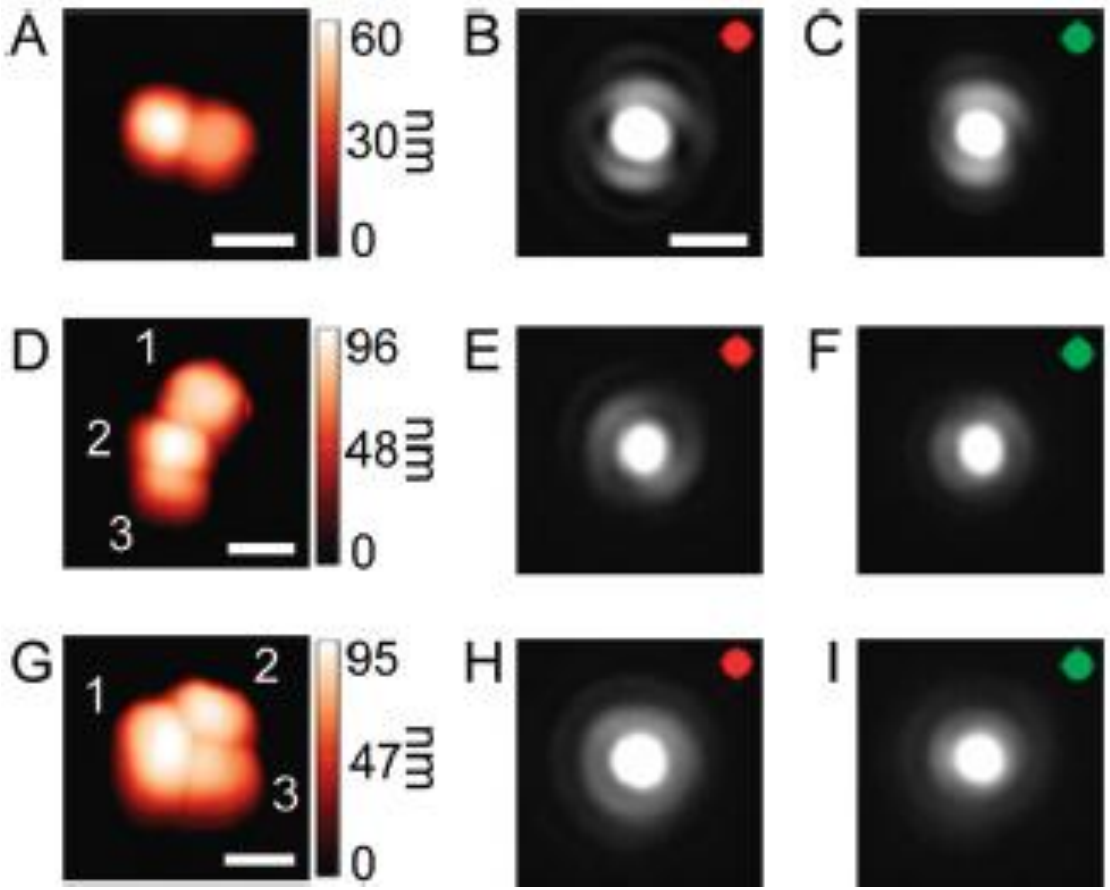
Discrete nature of the SERS emission pattern lobes at high dye concentrations reconfirms that the longitudinal plasmon mode of the dimer dominates the SERS emission polarization.

Trimer structures with a high degree of symmetry show nearly isotropic emission polarization behavior.

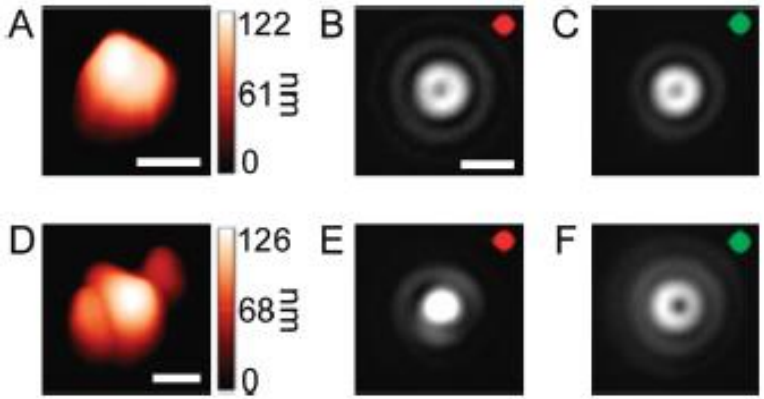


Shegai, T.; Brian, B.; Miljkovic, V. D.; Kall, M. Angular Distribution of Surface-Enhanced Raman Scattering from Individual Au Nanoparticle Aggregates. ACS Nano 2011, 5, 2036–2041.

Dimers, aggregates and dye concentration



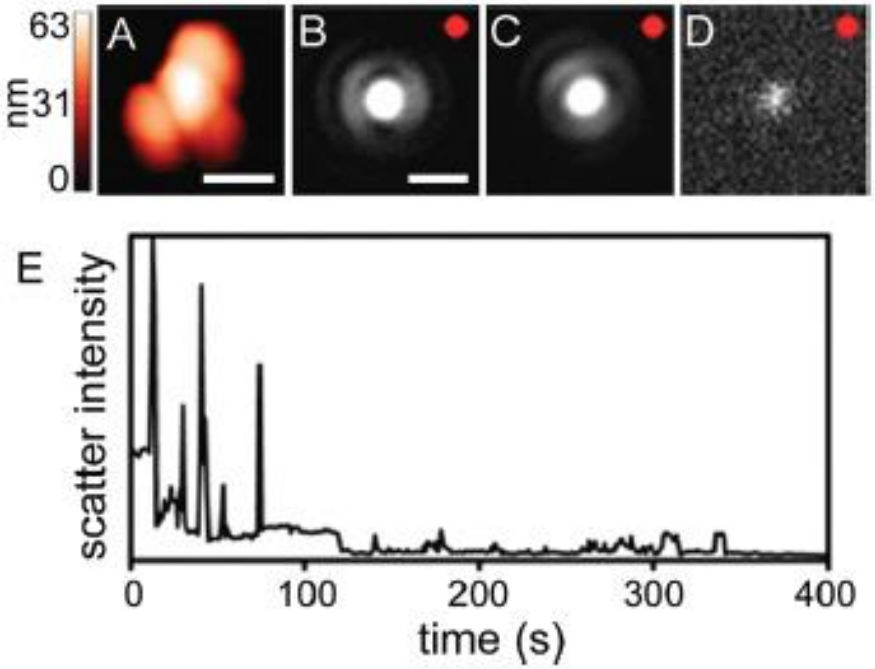
Stacked nanoparticles



(A) AFM topography of a SERS-active silver nanoparticle stacked dimer and (B,C) the corresponding SERS emission pattern images excited with (B) 642 nm and (C) 532 nm light.

The radially symmetric donut shape of the SERS emission patterns in Figure reveals the presence of the vertically oriented plasmon mode.

Tetramers



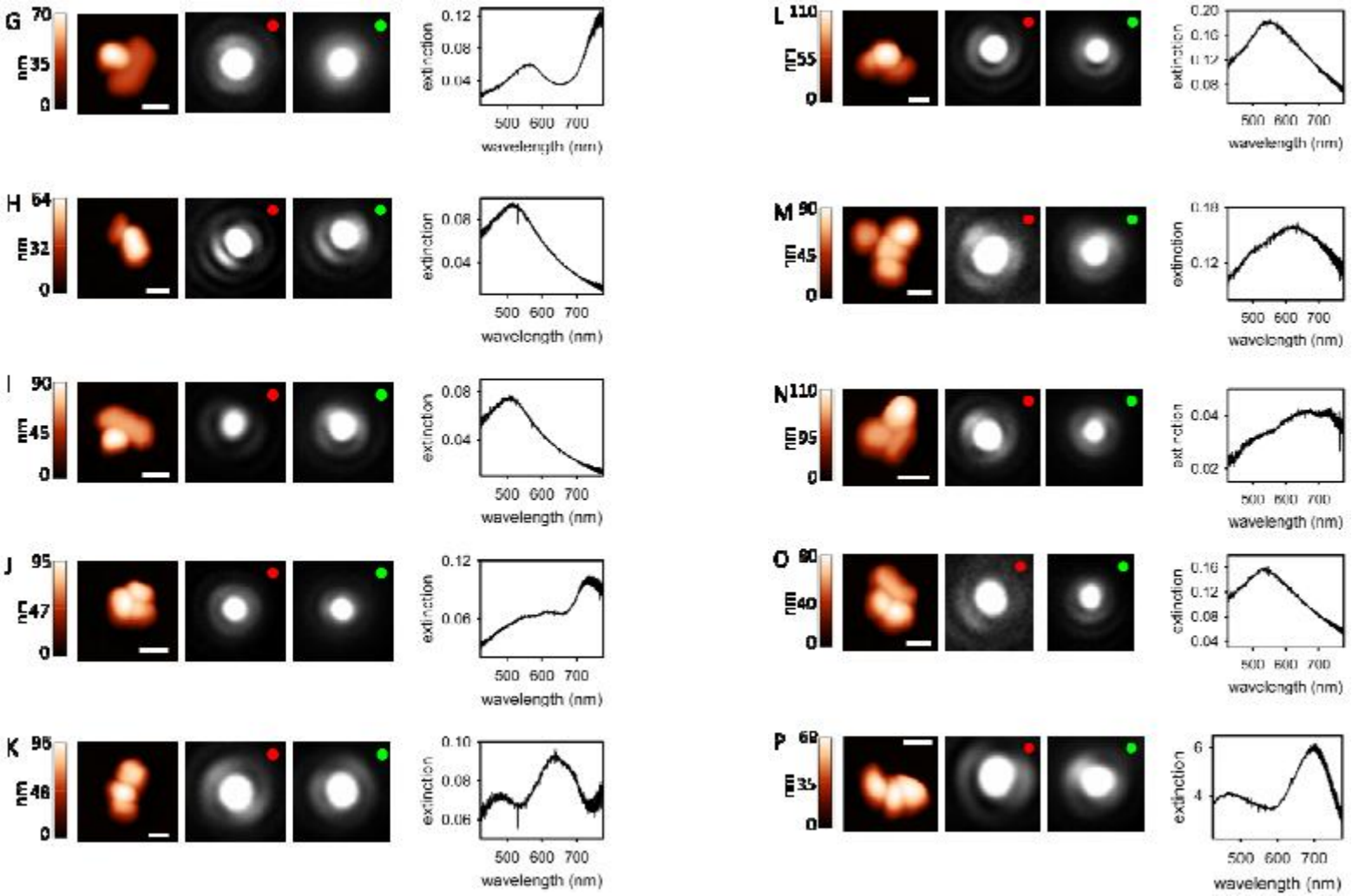
The SERS intensity fluctuates with time, indicative of single- or few-molecule SERS.

The discrete switching behavior of the SERS emission patterns indicates that the SERS emission is originating from a different junction within the tetramer.

Previous calculations from Xu and co-workers have shown that the emission polarization from a molecule located in a fixed nanoparticle junction is stable, regardless of the orientation of the molecule.

Li, Z.; Shegai, T.; Haran, G.; Xu, H. Multiple-Particle Nanoantennas for Enormous Enhancement and Polarization Control of Light Emission. ACS Nano 2009, 3, 637–642.

Extinction spectra



Conclusion and scope

This strategy allows simple discrimination of dimers, asymmetrically assembled trimers, and symmetrically assembled trimers for rapid comparison of SERS signal enhancements as a function of available SERS-active junctions.

Using the SERS emission pattern to determine which junction is occupied by the single emitter and therefore responsible for the SERS emission is complex and will be the focus of a future publication.

Development of a model to describe wavelength-dependent SERS emission patterns in higher order aggregates.

Future plans

1. In view of Raman-HSI coupling.

2. Tracking the behavior and changes in the biological environment (intracellular) of NPs simultaneously.

3. Using only analyzer instead of polarizer-analyzer pair to check orientation.

Thank you