Evaluating nanogaps in Ag and Au nanoparticle clusters for SERS applications using COMSOL Multiphysics®

Ramesh Asapu[1], Radu-George Ciocarlan[2], Nathalie Claes[3], Natan Blommaerts[1], Sara Bals[3], Pegie Cool[2], Siegfried Denys[1], Silvia Leanerts[1] and Sammy Verbruggen[1]

[1]Department of Bioscience Engineering, DuEL, University of Antwerp, Belgium
[2]Department of Chemistry, LADCA, University of Antwerp, Belgium
[3]Department of Physics, EMAT, University of Antwerp, Belgium

Sustainable Energy,
Air & Water Technology
University of Antwerp

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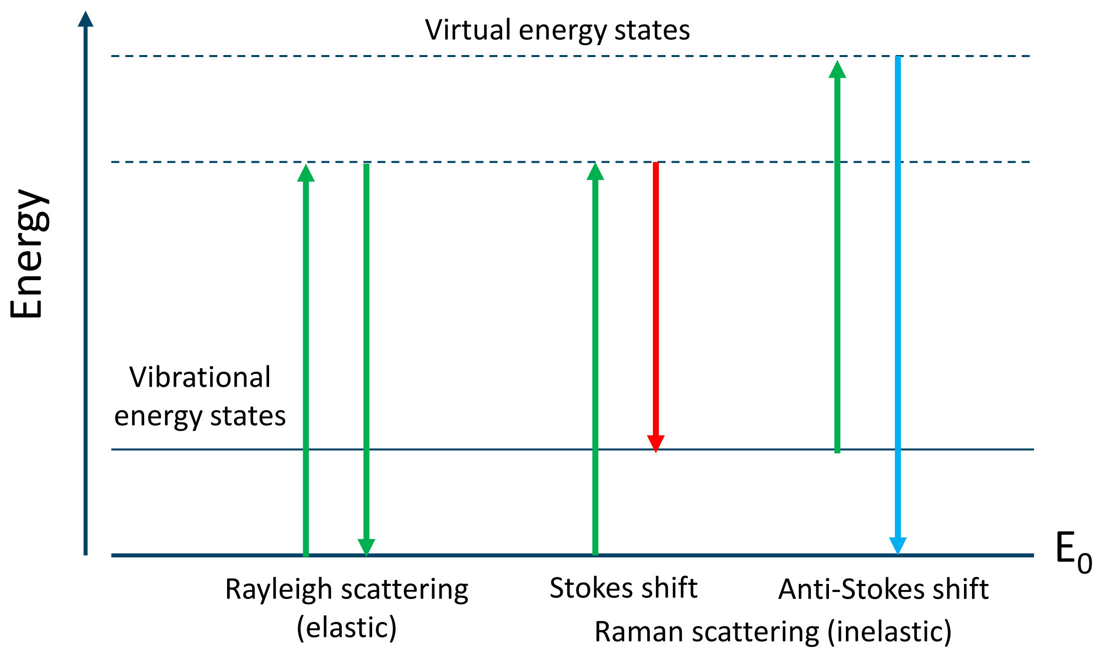
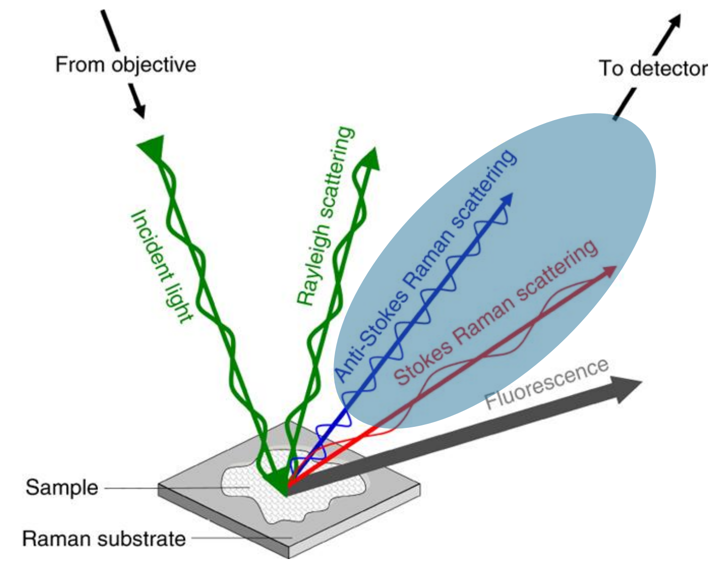
Introduction: Raman Spectroscopy

- Inelastic scattering of incident monochromatic light through interactions of photons with molecular vibrations and excitations. (similar to IR: absorption of light)
- Chemical identification and structural finger printing of molecules.





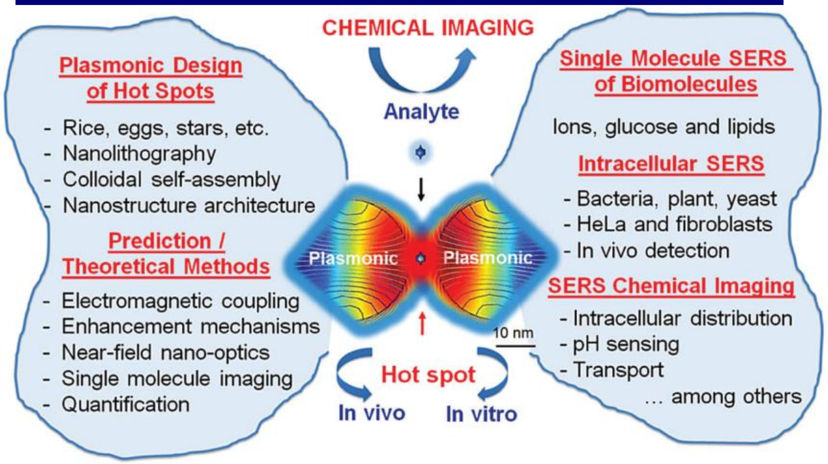
*Nature Protocols 11, 664–687 (2016) doi:10.1038/nprot.2016.036

- Constraints: Raman scattering is *weak phenomenon*, the number of photons which are Raman scattered is quite small.

Introduction: Surface-Enhanced Raman Spectroscopy (SERS)

- Raman effect: based on interaction between electron cloud of sample and external electric field produced by incident monochromatic light.
- Interaction of incident monochromatic light with noble metals (Ag, Au, Pt) and adsorbed probe molecule give rise to enhanced Raman intensity signal*
- EM or near-field enhancement dependent*
  - *Intense near electric fields*
    - *Dielectric environment*
- $EF_{exp} = \frac{\left[{}^{I_{SERS}}/_{N_{SERS}}\right]}{\left[{}^{I_{RS}}/_{N_{RS}}\right]}$ $EF_{calc} = \left|\frac{E}{E_0}\right|^4$

N – number of molecules probed/illuminated by the laser spot, I – RS, SERS : Raman spectra and Surface-Enhanced Raman spectra

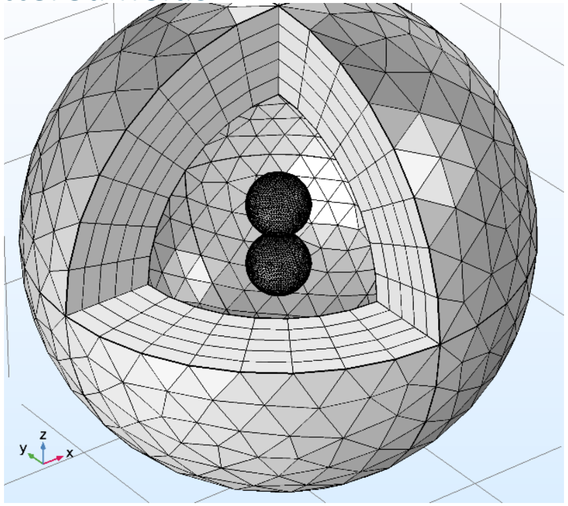


*Darya Radziuk et al. *Phys. Chem. Chem. Phys., 2015, 17, 21072*

*Chemical Physics Letters, 26 , 163-166 (1974), [2]Journal of Electroanal. Chem. and Interface Electrochem., 84, 1-20 (1977),
*J. Am. Chem Soc., 99, 5215-5217 (1977).

COMSOL near-electric field simulations: How and Why?

- Wave Optics physics in wavelength domain study
- Maxwell's Electromagnetic wave equations are solved for scattered fields



$$\nabla \times \left[\frac{1}{\mu_r}(\nabla \times E_{sca})\right] - K_0^{\,2}\left[\left(\varepsilon_r - \frac{j\,\sigma}{\omega\varepsilon_0}\right)\right] E_{sca} = 0$$

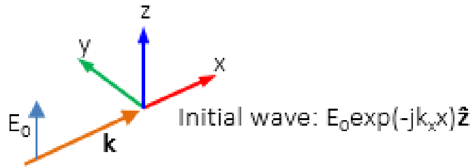
where E_{sca} – scattered electric field

K_0 - wavenumber in free space

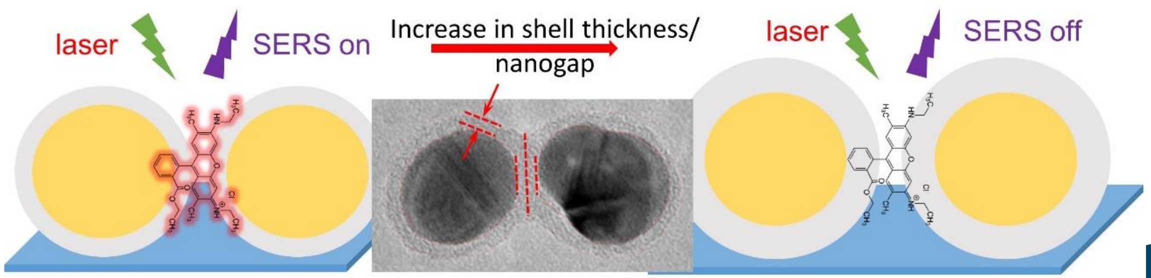
μ_r - relative permeability of medium

ε_r – permittivity of medium

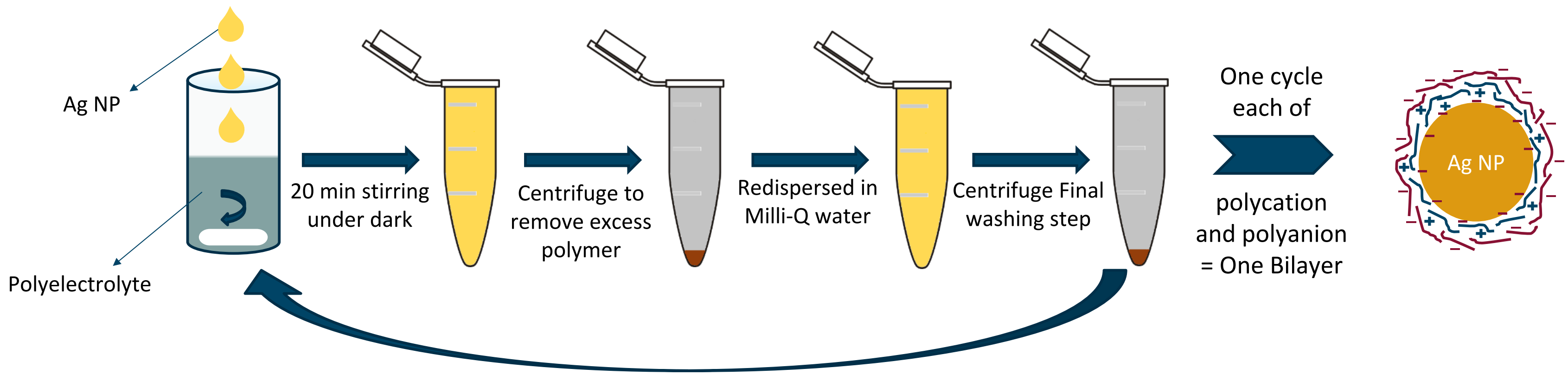
- Enhancement is due to both incident and scattered fields.



- EM or field enhancement $|E/E_0|$ is dependent:
  - Inter-particle distance & probe molecule distance dependence: ***nanogap***
  - laser excitation wavelength
  - NP shape and size

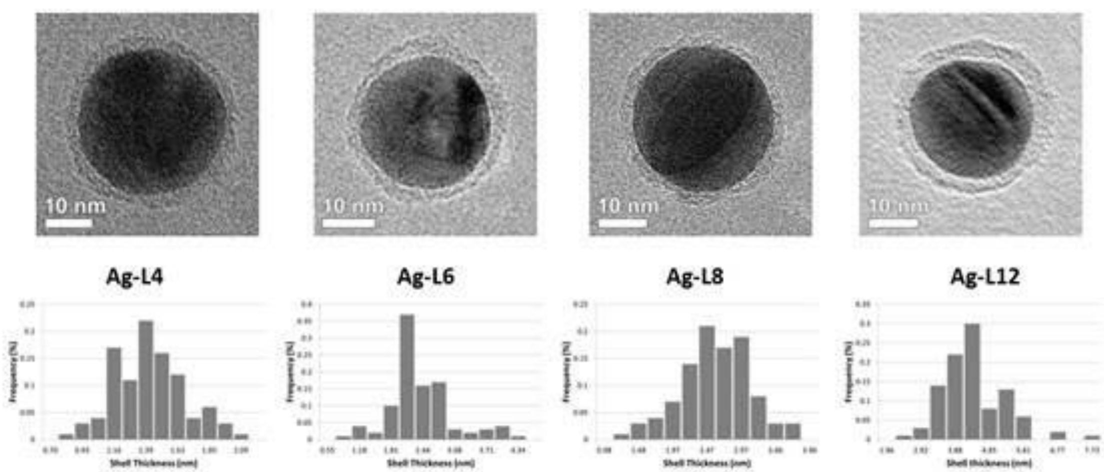


Nanogap control via LBL (Layer-by-Layer) method using charged polyelectrolytes

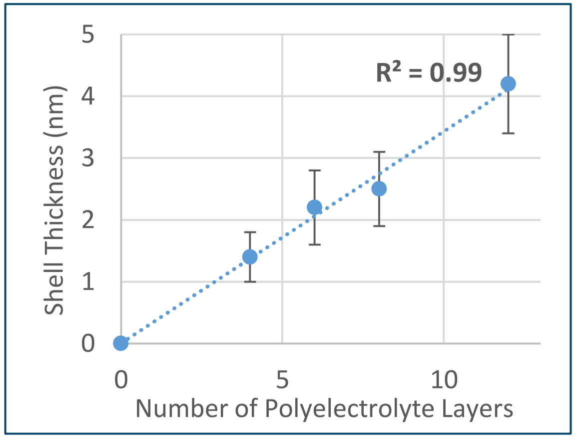


Polymer shell thickness Increase with number of layers

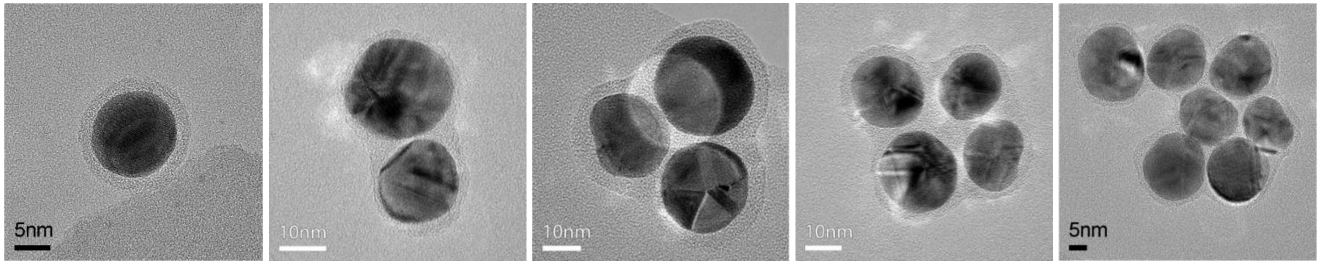
Size distributions of the polymer shell thickness (100 measurements) for the different samples:



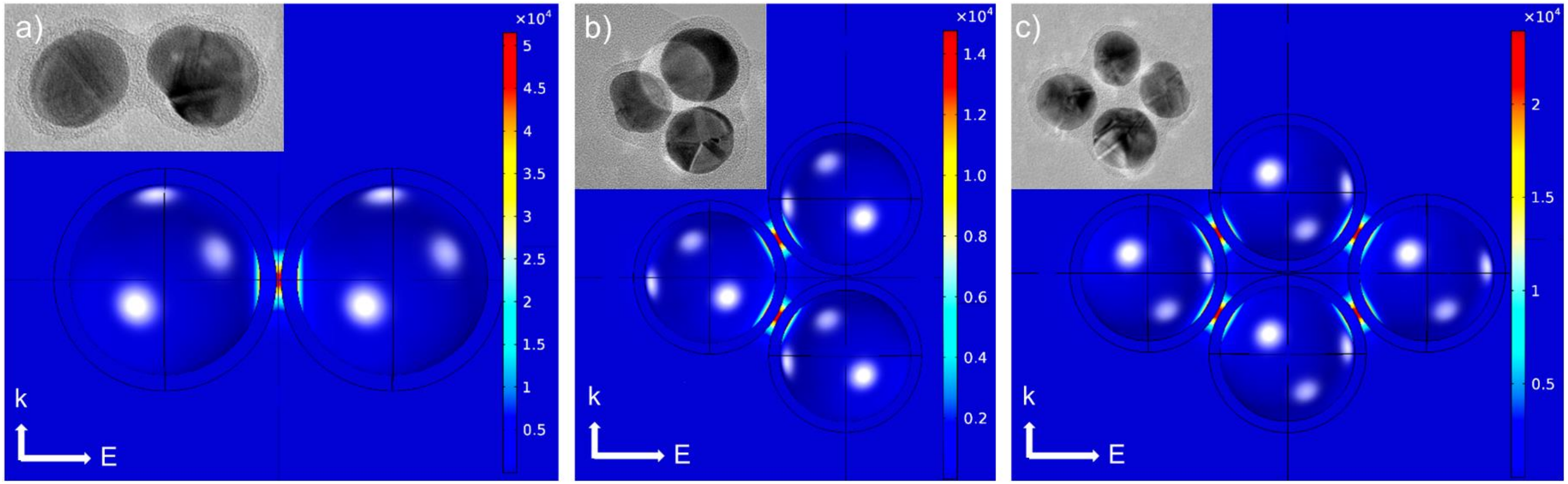
<t> = 1.4 ± 0.4 nm   <t> = 2.2 ± 0.6 nm   <t> = 2.5 ± 0.6 nm   <t> = 4.2 ± 0.8 nm



Hotspots in the nanoparticle clusters: Quantification for SERS



- Wet chemical methods→ no control over alignment of nanoparticles: single, dimer, trimer, tetramer clusters

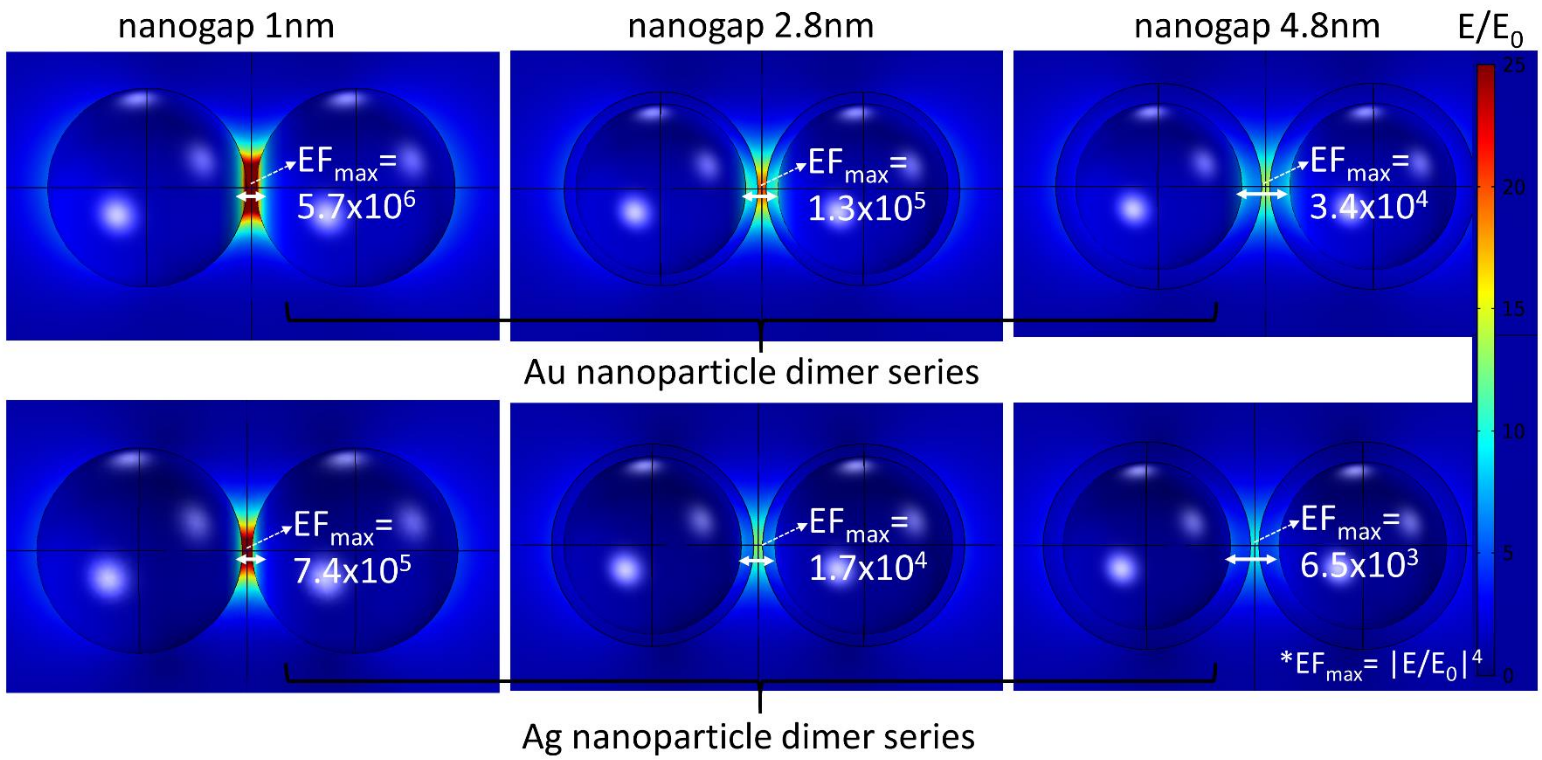


- Simplification of the models and EF calculations by assuming dimers representing nanocluster systems.

SERS hot spots: gap/distance dependence theoretical analysis

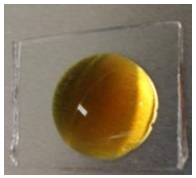
Study with core-shell nanoparticles:

- Using polymer as the spacer layer for increasing the gap/distance of interface between nanoparticles

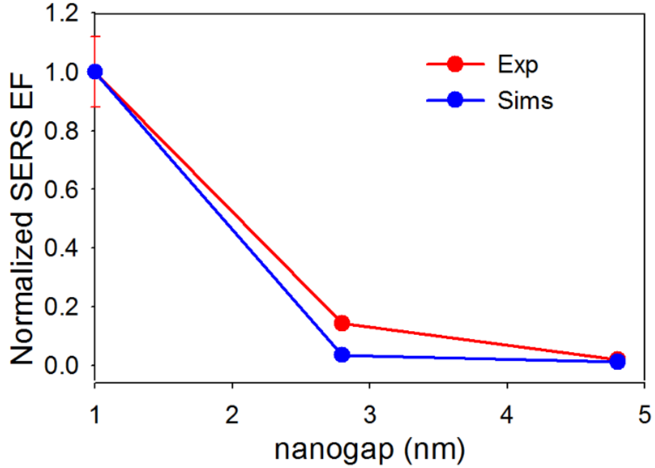


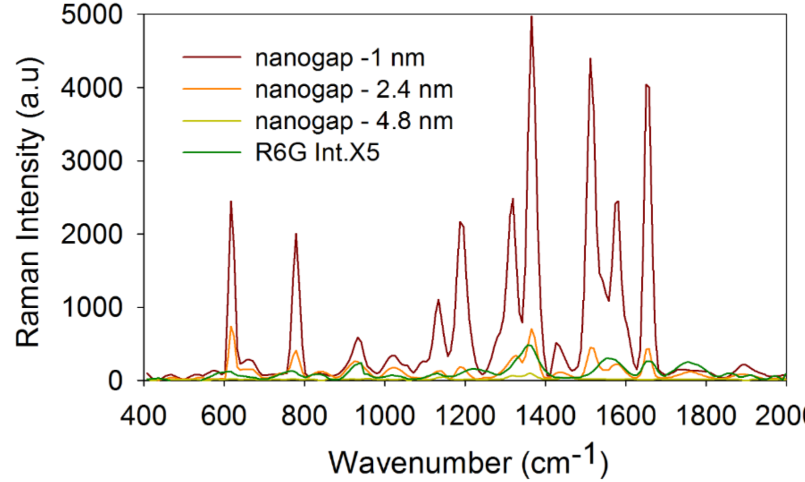
Experimental vs Theoretical (COMSOL) EF comparison

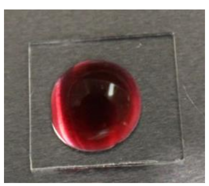
- Validation of COMSOL EF calculations for Au and Ag silver nano-dimers with experimental SERS signal.



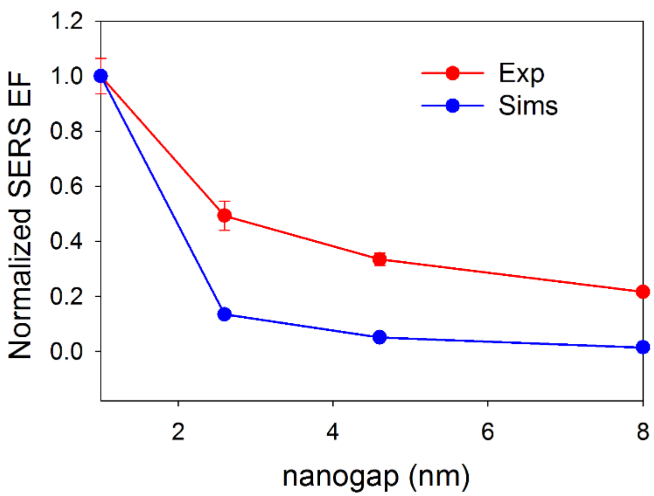
Silver NPs

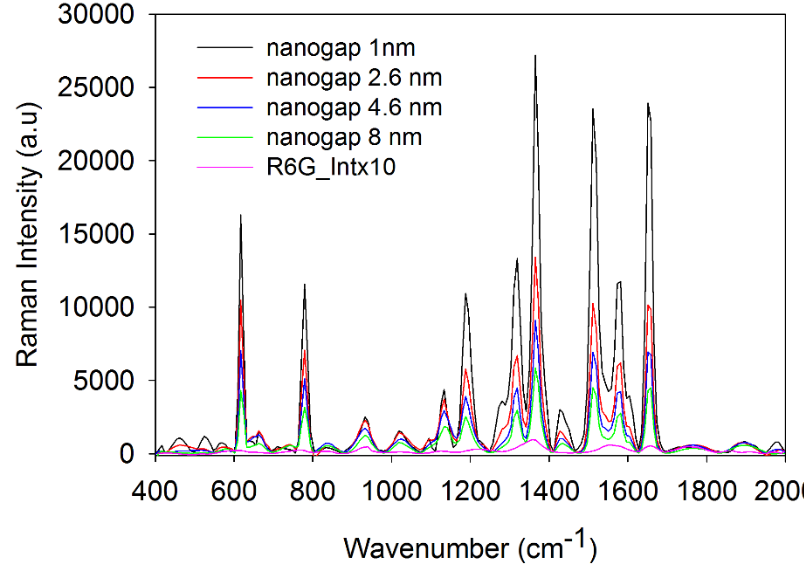




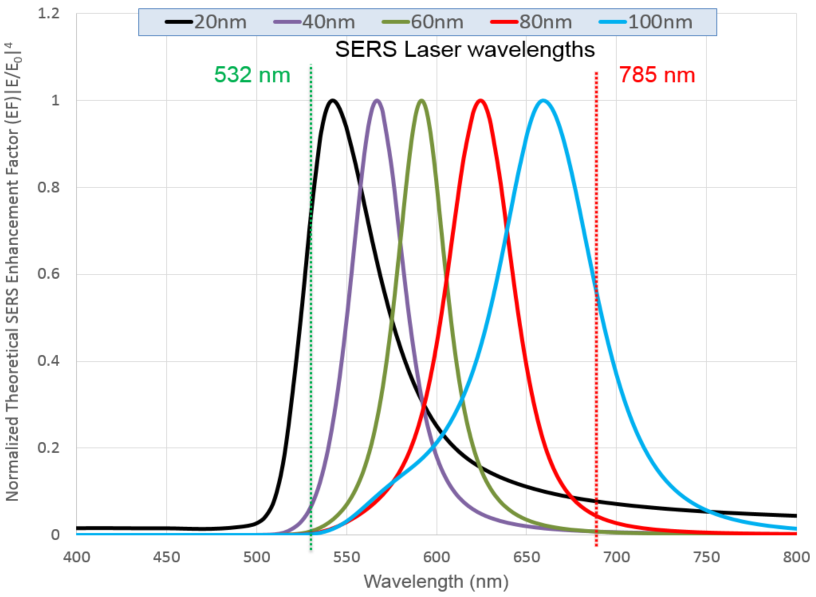


Gold NPs

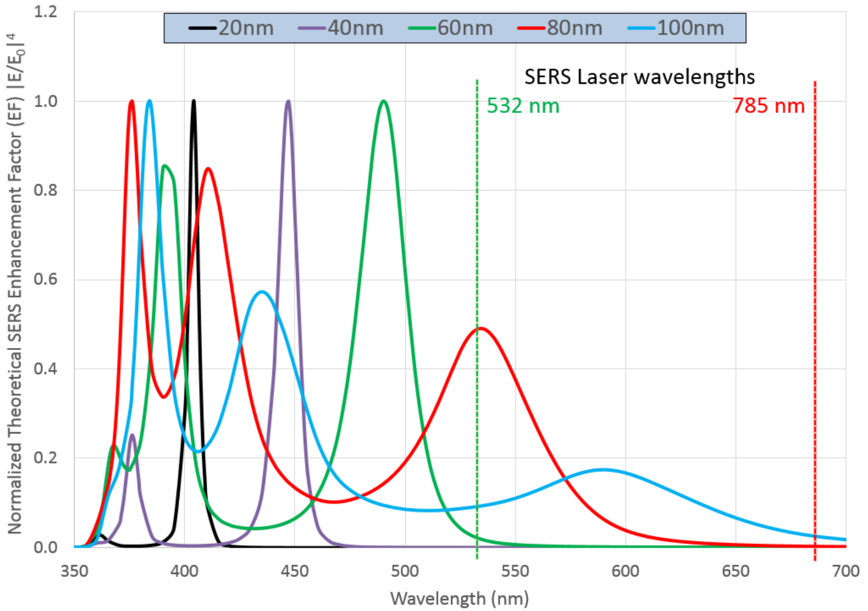




SERS: Plasmonic nanoparticle size dependence

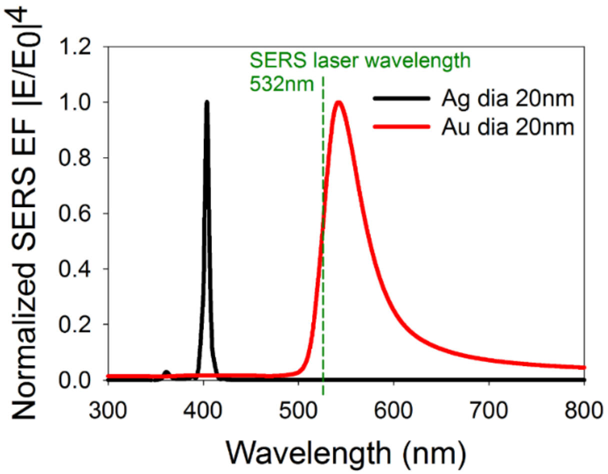


Gold nanoparticles: EF vs particle size dia.



silver nanoparticles: EF vs particle size dia.

- COMSOL EF simulations: crucial information λ_{spr}(max)
- Essential to check the overlapping of plasmon resonance with Raman laser excitation wavelength
- Achieve maximum possible enhancement factor

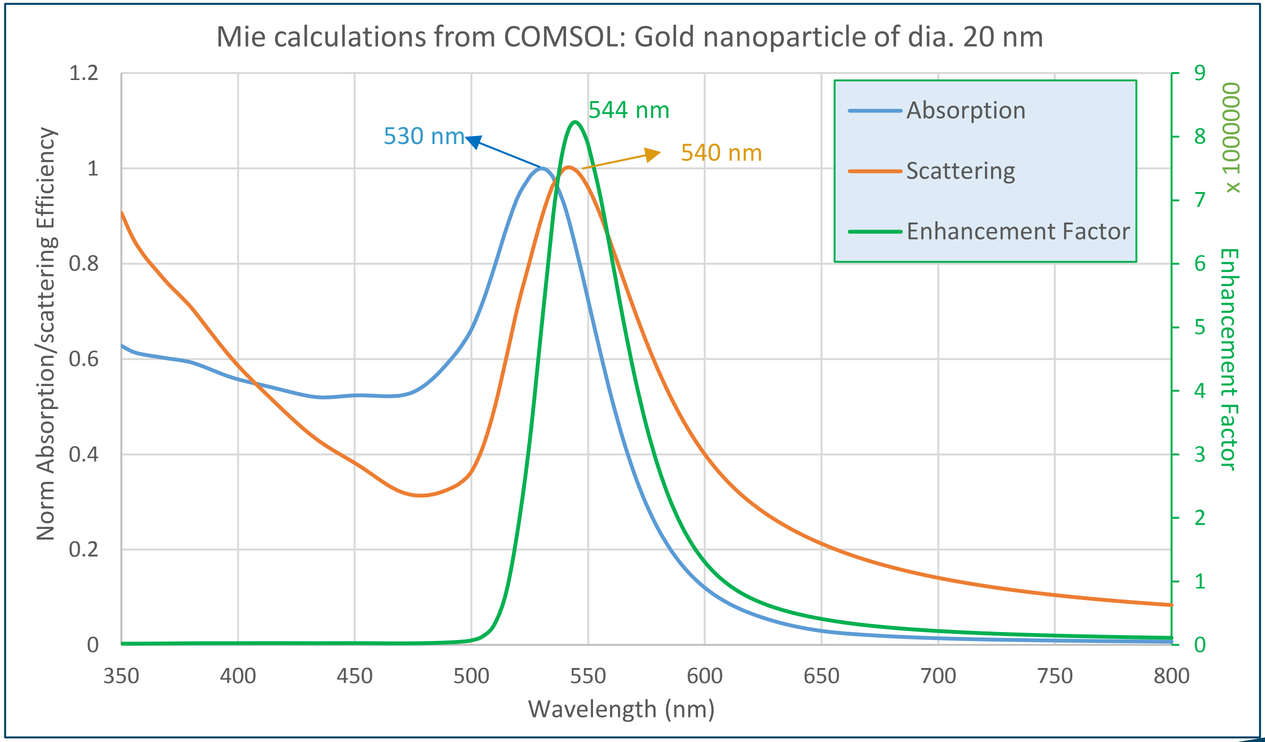


Maximum attainable EF: Absorption vs scattering by plasmonic nanoparticles

- Maximum EF→very high enhanced Raman signal→single molecule detection(parts per trillion levels)
- The plasmon resonance should be slightly red-shifted from Raman laser wavelength to maximize signal*
- Mie calculations in COMSOL by implementing Mie equations to plot absorption and scattering efficiencies:

$$W_{abs} = \oiiint_{NP} Q_{loss} dV, \quad W_{sca} = \oiint_{A} S_{sca} . ndA$$

$$C_{abs} = \oiiint \frac{ewfd.Q_h}{\frac{E^2{}_0}{2 * Z0\_const}} \qquad C_{sca} = \oiint \frac{(n_x * ewfd.relPoav_x + n_y * ewfd.relPoav_y + n_z * ewfd.relPoav_z)}{\frac{E^2{}_0}{2 * Z0\_const}}$$



*McFarland, A.D. et. Al., J Phys Chem B (2005), 109(22), 11279

Conclusion:

- *FEM simulations can provide crucial insights: from synthesis, design and application perspective*
- *Study the effect of medium and design of nanoparticle plasmonic system for SERS applications*
- *COMSOL Multiphysics, a vital mechanistic tool : plasmonic nanoparticles viability for hotspot applications*

Thanks for your attention

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