Evaluating Nanogaps in Ag and Au Nanoparticle Clusters for SERS Application Using COMSOL Multiphysics®

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Introduction: The hot spots generated in the nanogaps of plasmonic metal nanoparticles are the primary cause for surface enhanced Raman spectra (SERS). But, *matching the SERS laser wavelength and surface plasmon resonance of noble metal nanoparticles is crucial* to achieve higher enhancements. Near-field simulations using COMSOLÈ provide crucial insights into the phenomenon underlying the electromagnetic enhancement of SERS.

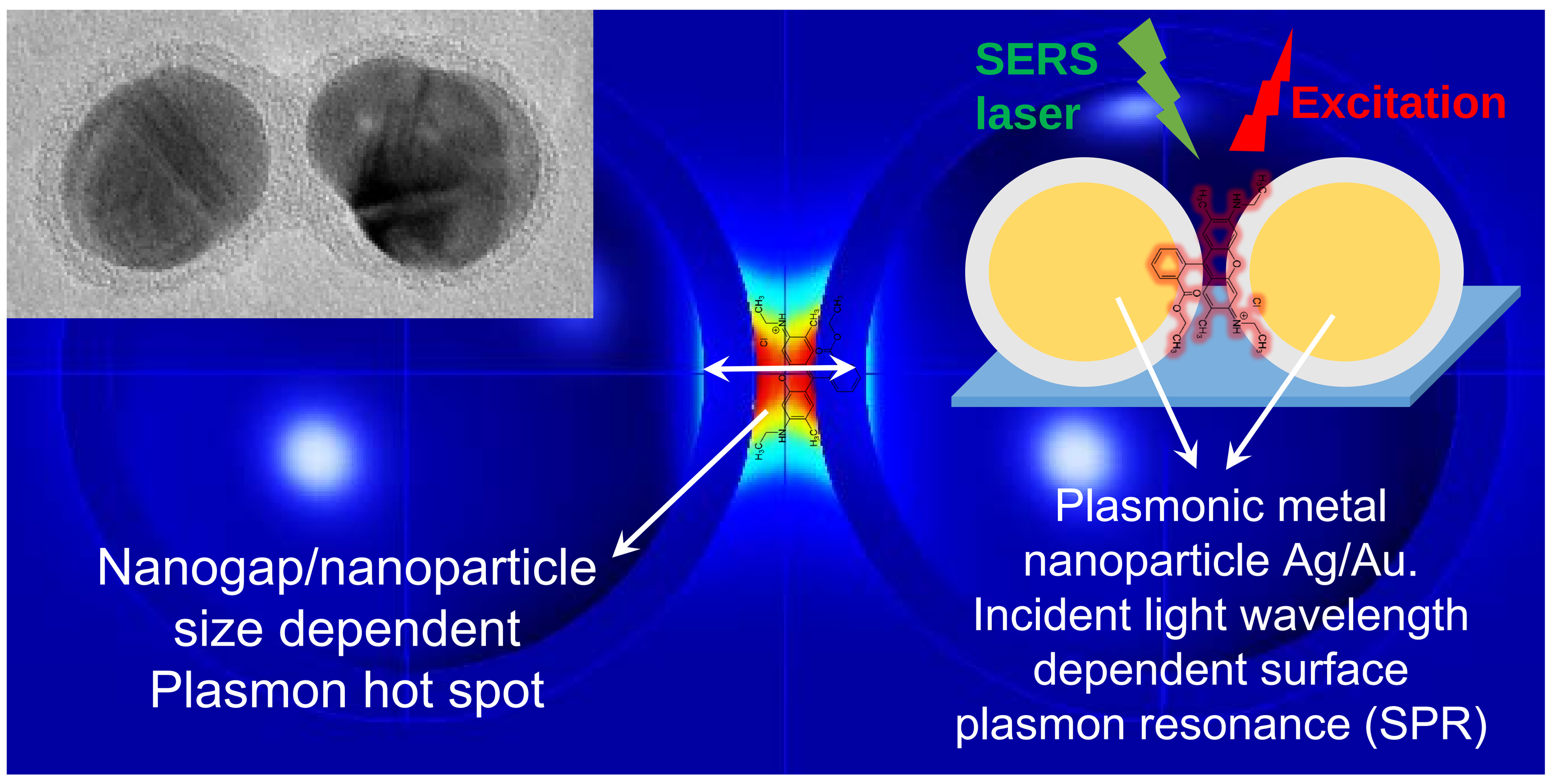

Figure 1. Electromagnetic enhancement in SERS

Computational Methods: In wave optics module, Maxwell's electromagnetic wave equation is solved for scattered electric field, E_{sca}.

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

3D models of nanosphere and core-shell nanoparticles with required diameter were built with air is the surrounding medium enclosed within a PML. A mesh quality of ca. 0.7 was maintained and a plane wave polarized in the Z-direction, and propagating along the X-axis direction was solved in a wavelength domain study.

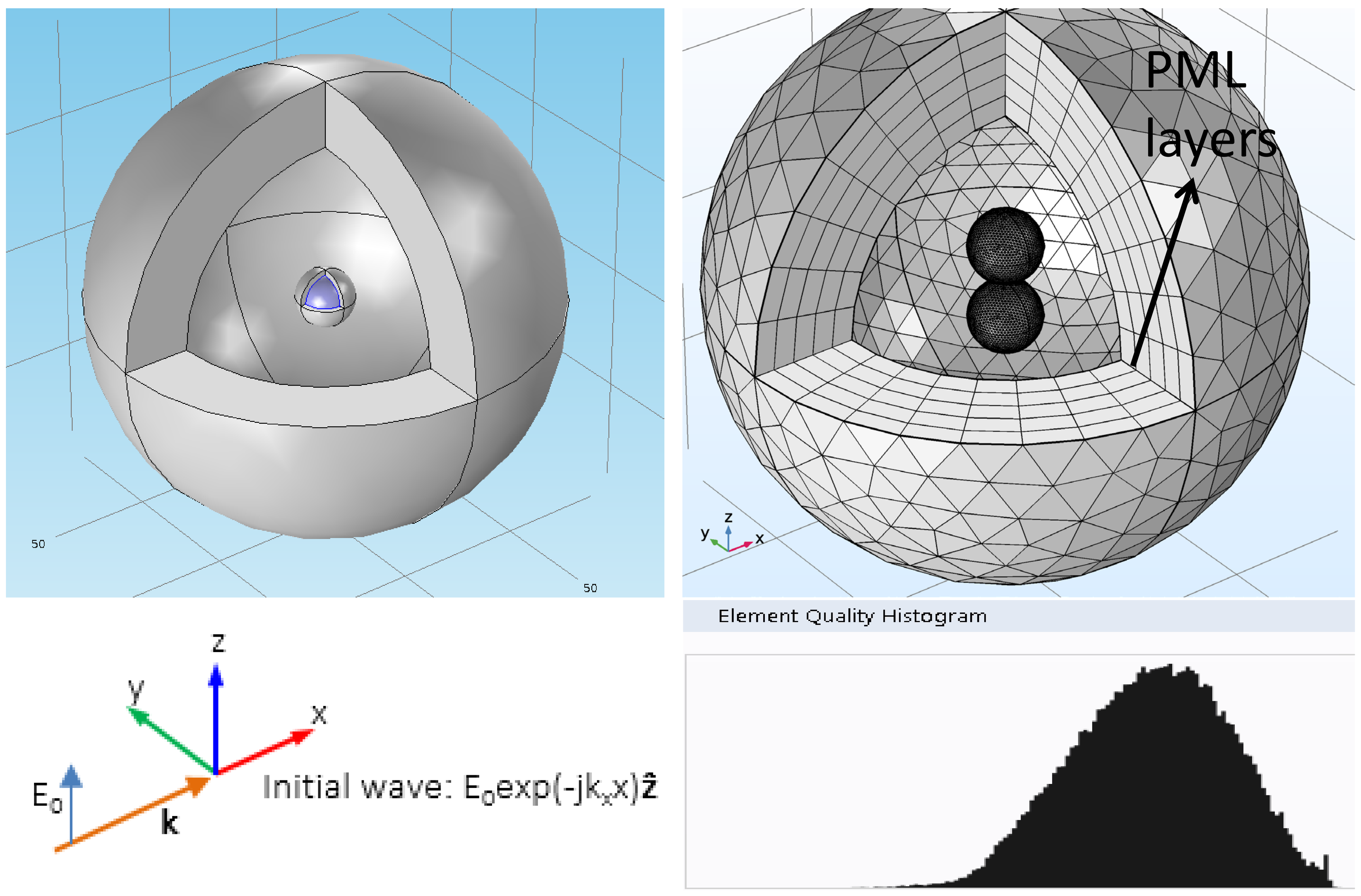

Figure 2. Model details with geometry and meshing

Results: Increase in nanogap results in the intensity loss of the hot spots, but gold nanoclusters perform better than silver nanoclusters as seen from enhancement factors, $EF = |E/E_0|^4$ approx., and near-electric field maps.

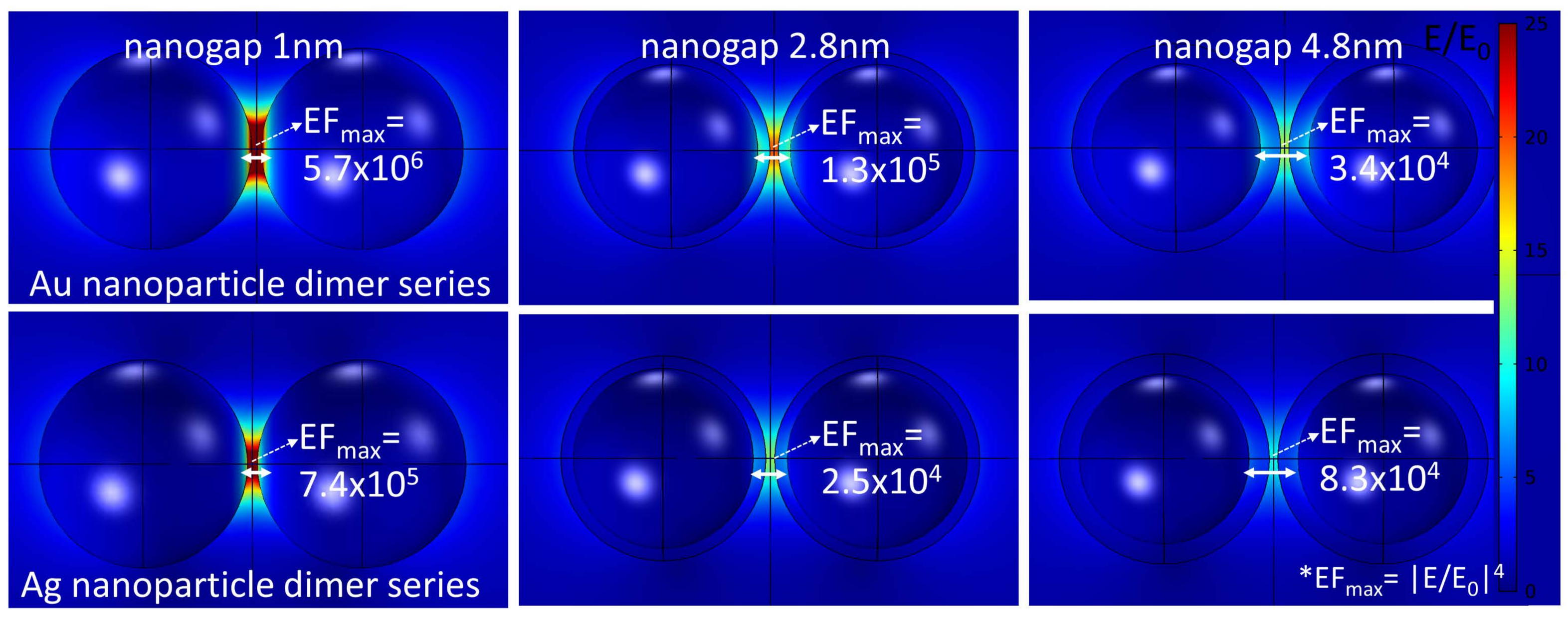

Figure 3. Near-field maps and EF for Au/Ag dimers, Nanoparticle diameter ~ 20 nm

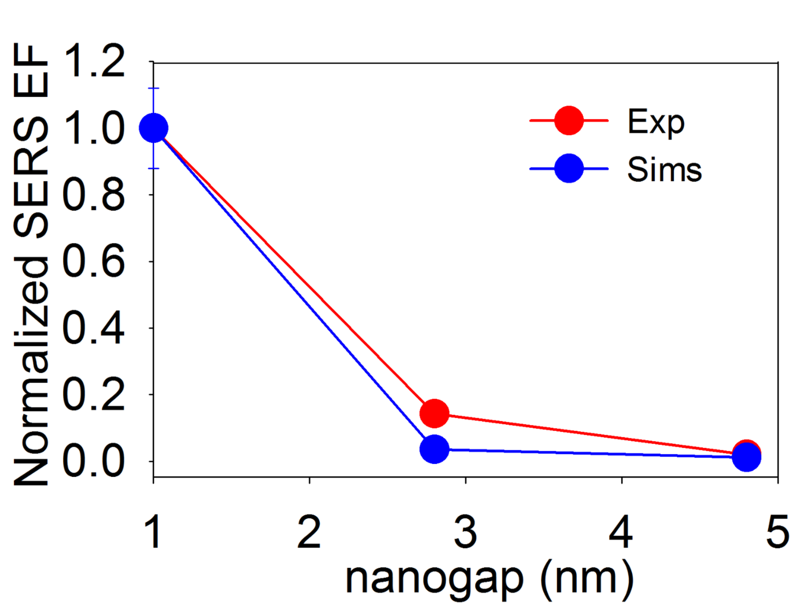

Figure 4.SERS EF for Ag nanoclusters (dia.~20 nm)

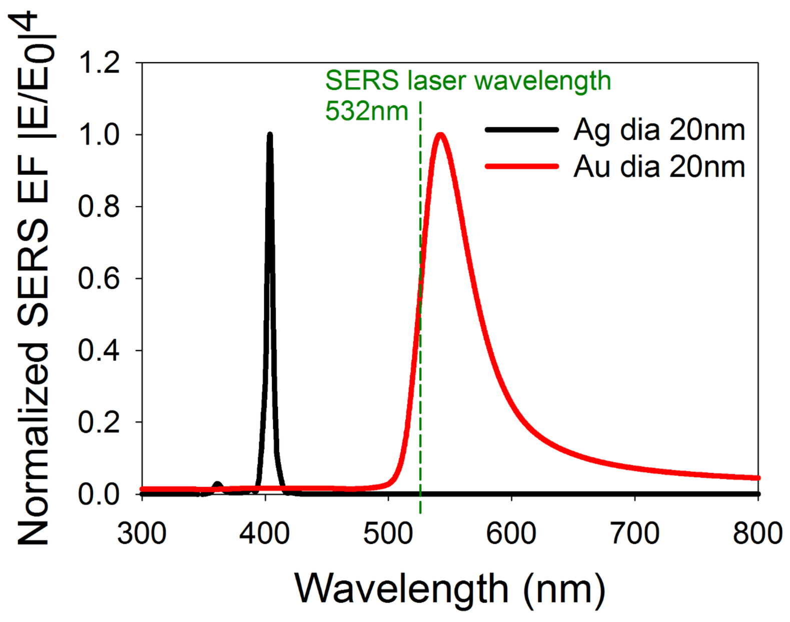

Figure 5. SERS EF for Ag / Au nanoclusters (dia.~ 20 nm)

Nanoparticle size dia.	EF_{532}-Gold (Au)	EF_{532}-Silver (Ag)
10 nm	1.4×10^5	3.0×10^4
20 nm	5.7×10^6	7.4×10^5
30 nm	3.6×10^7	8.1×10^6
40 nm	9.8×10^7	7.2×10^7
50 nm	2.0×10^8	6.1×10^8
60 nm	3.0×10^8	8.3×10^9
80 nm	4.1×10^8	1.1×10^{11}
100 nm	3.3×10^8	2.4×10^{10}

Table 1. Plasmonic metal nanoparticle size dependence on EF at a laser excitation wavelength of 532 nm

Conclusions: Nanogaps are crucial for the enhancement factor in SERS as the intense near-electric fields drop drastically within a few nanometers. Tuning the nanoparticle size and nanogap to match the surface plasmon resonance of the nanocluster system with the SERS laser wavelength will greatly enhance the Raman signal.

References:

1. Stiles, P. L. & Van Duyne, R. P. et al. Surface-Enhanced Raman Spectroscopy. Annual. Rev. Anal. Chem.1, 601–26 (2008).
2. Schlucker, S. Surface-Enhaced Raman Spectroscopy. Angew. Che. Int. Ed. 53, 4756–95 (2014).