FEM And Near-field Simulations: A Vital Mechanistic Tool for Studying Silver-based Plasmonic Systems

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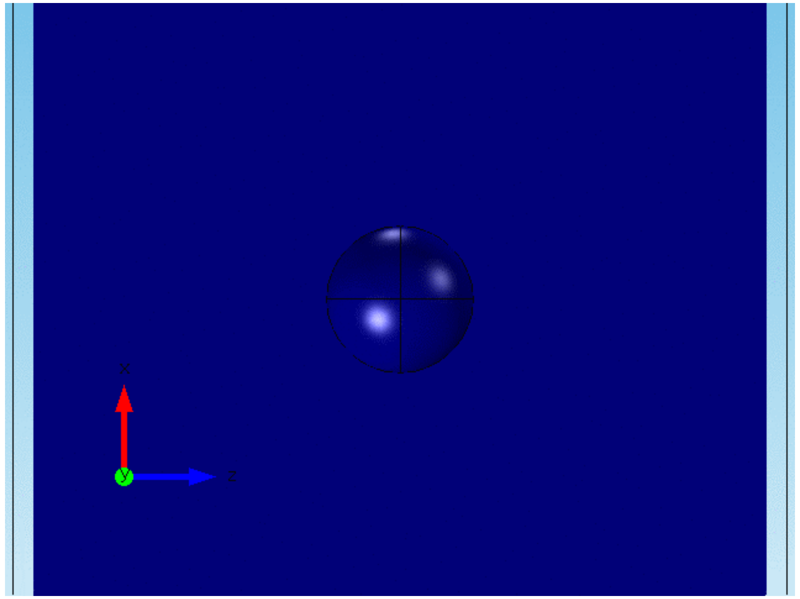
COMSOL CONFERENCE
2016 MUNICH

Silver Plasmonic Systems: What and Where?

Surface Plasmon Resonance:

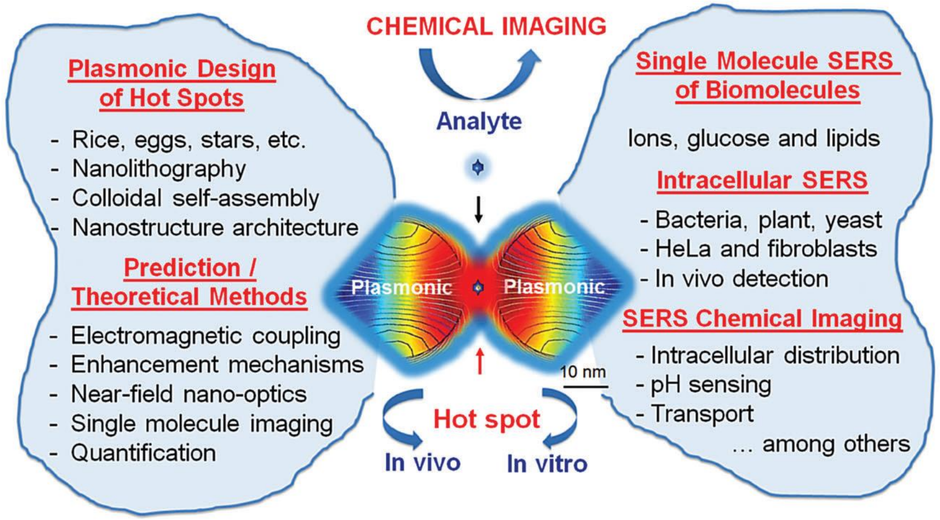
- Collective oscillation of conduction electrons at the dielectric-metal interface of a nanoparticle stimulated by incident light of matching wavelength.
- Highest near field enhancement by silver among the plasmonic noble metals like Au, Ag, Pt, Cu etc.
- Size tuneable plasmonic properties – FEM vital tool for analysis



Time domain simulation of Ag NP (~20 nm) in air, λ_{inc} = 355 nm

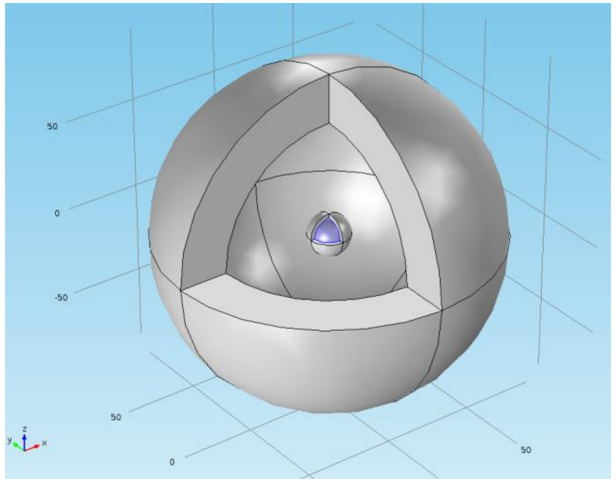
Applications:

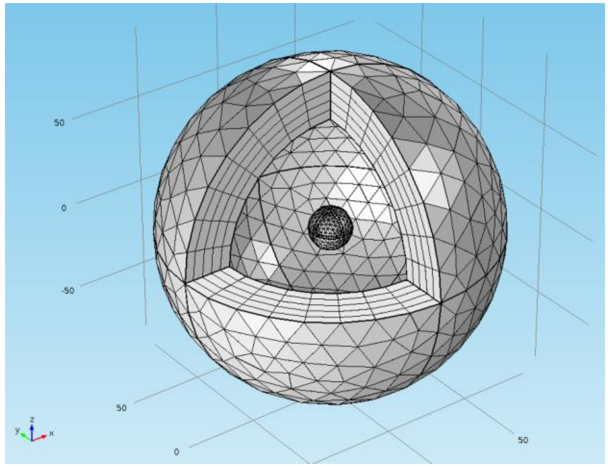
- Biophotonics
  - Sensing, Imaging and Therapeutics
- SERS
  - Identification of chemical species
- Plasmon enhanced semiconductor photocatalysis – TiO_2 systems.



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

Modeling of plasmonic nanoparticles in COMSOL





- COMSOL Wave Optics physics in wavelength domain study.

- Solution to Maxwell's electromagnetic wave equation:

$$\nabla \times \frac{1}{\mu_r}(\nabla \times \mathrm{E}) - \mathrm{K}_0{}^2(\mathcal{E}_r - \frac{j\,\sigma}{\omega \mathcal{E}_0})\mathrm{E} = 0$$

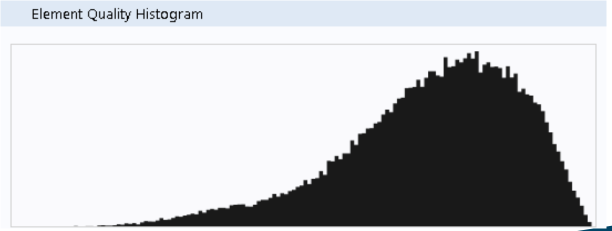
where E – scattered electric field

K_0 - wavenumber in free space

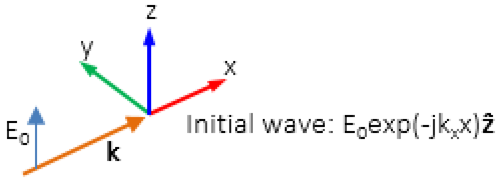
μ_r - relative permeability of medium

$\mathcal{E}_r$ – permittivity of medium

- PML layers to truncate the domain and avoid internal reflections



- Linear polarized plane wave



Mie solution to Maxwells's equations: Implementation in COMSOL

- Mie Solution to Maxwell's wave equation to calculate the extinction efficiency. (for particles d<< λ)

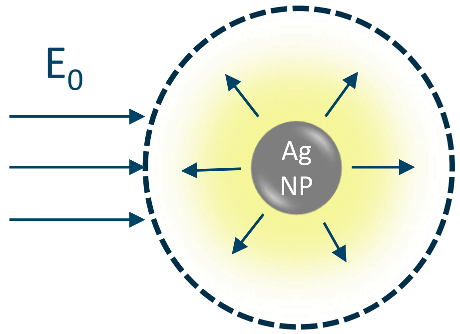
  - Absorption cross section $C_{abs} = \frac{W_{abs}}{I_i}$ 1*
  - Scattering cross section $C_{sca} = \frac{W_{sca}}{I_i}$ 2*

  W_{abs}, W_{sca} are energy rates absorbed and scattered by particle and I_i is energy flux of the incident wave.

  $C_{ext} = C_{abs} + C_{abs}$

  $Q_{ext} = \frac{C_{ext}}{geometric\ crss\ section\ of\ particle}$ 3*

  *Bohren and Huffman, Absorption and scattering of light by small particles, 1983 Wiley
  DOI: 10.1002/9783527618156



$$C_{abs} = \oiiint \frac{ewfd.Q_h}{\frac{E^2{}_0}{2 * Z0\_const}}$$ (volume integral over the nanoparticle)

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

(Surface integral over the nanoparticle)

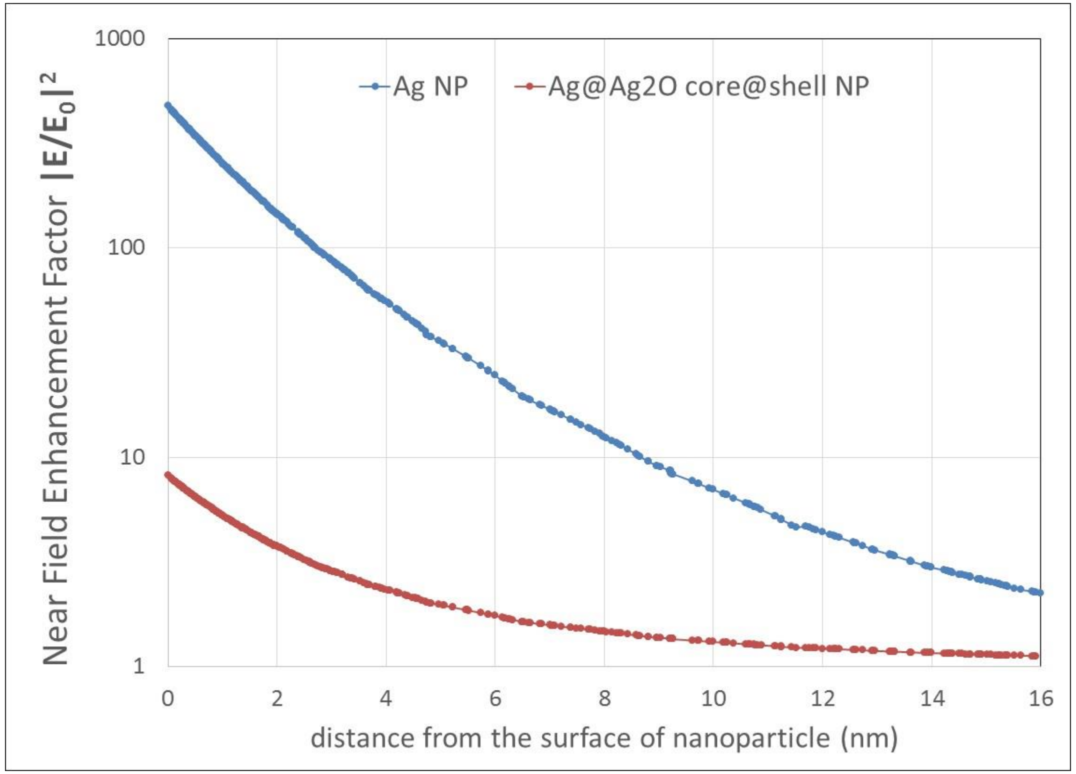
Where Q_h is total power dissipation density

$relPoav_{x,y,z}$ are the time average power flow of relative fields

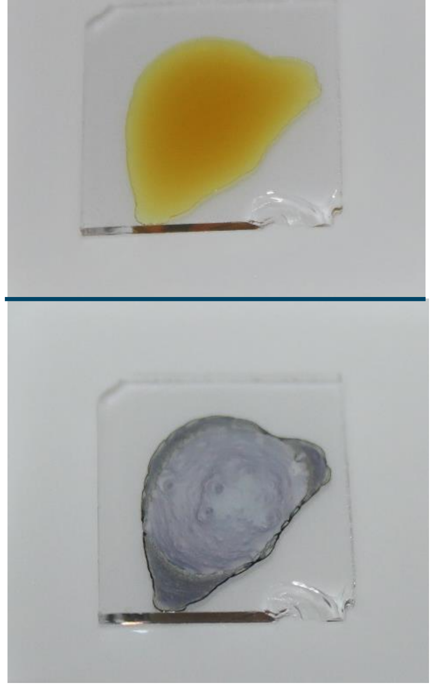
Z0_const is the scaling factor

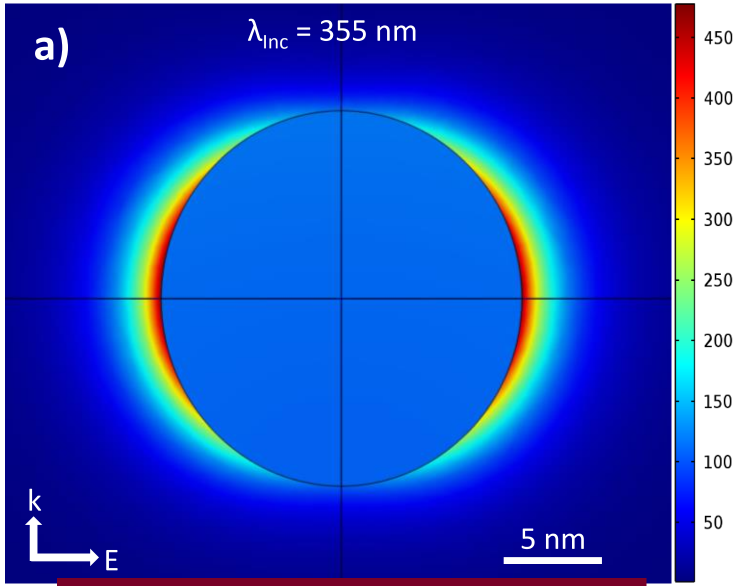
Modeling of Ag nanoparticle

- Ag silver nanoparticles exhibit high near field enhancement
- Prone to oxidation forming a diffuse Ag_2O layer effecting the near field enhancement significantly.
- Not suitable for applications over long period of time or oxidative conditions.

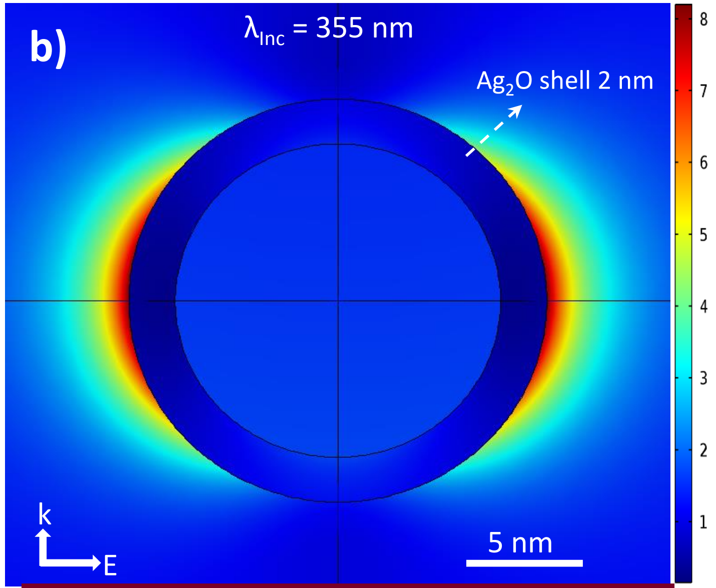


Silver colloidal nanoparticles stability test in air





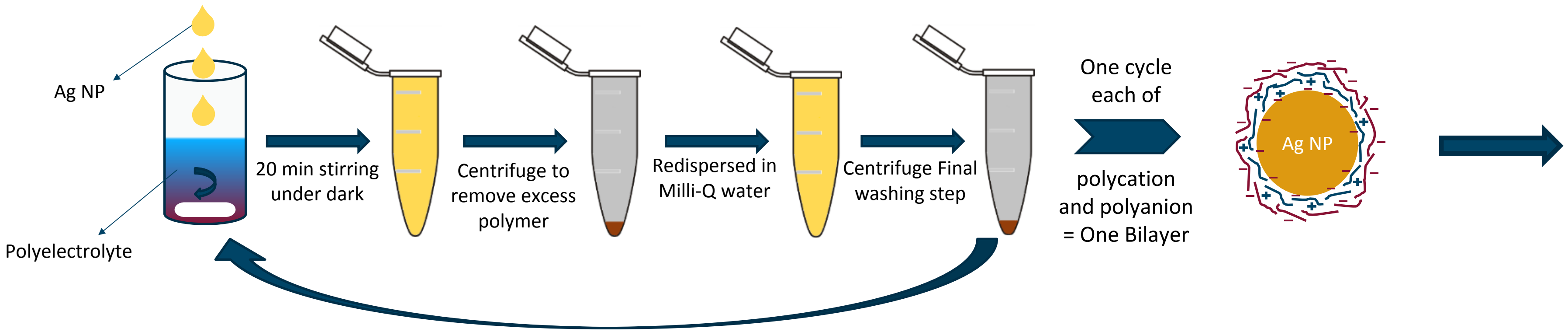
E-Field enhancement contour of Ag nanoparticle



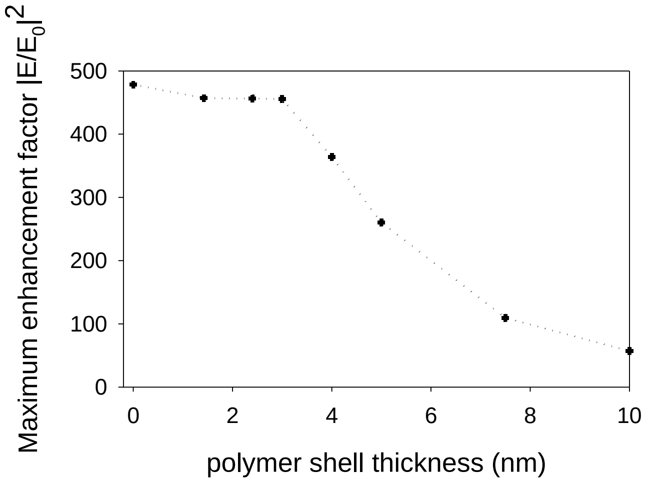
E-Field enhancement contour of $Ag@Ag_2O$ nanoparticle

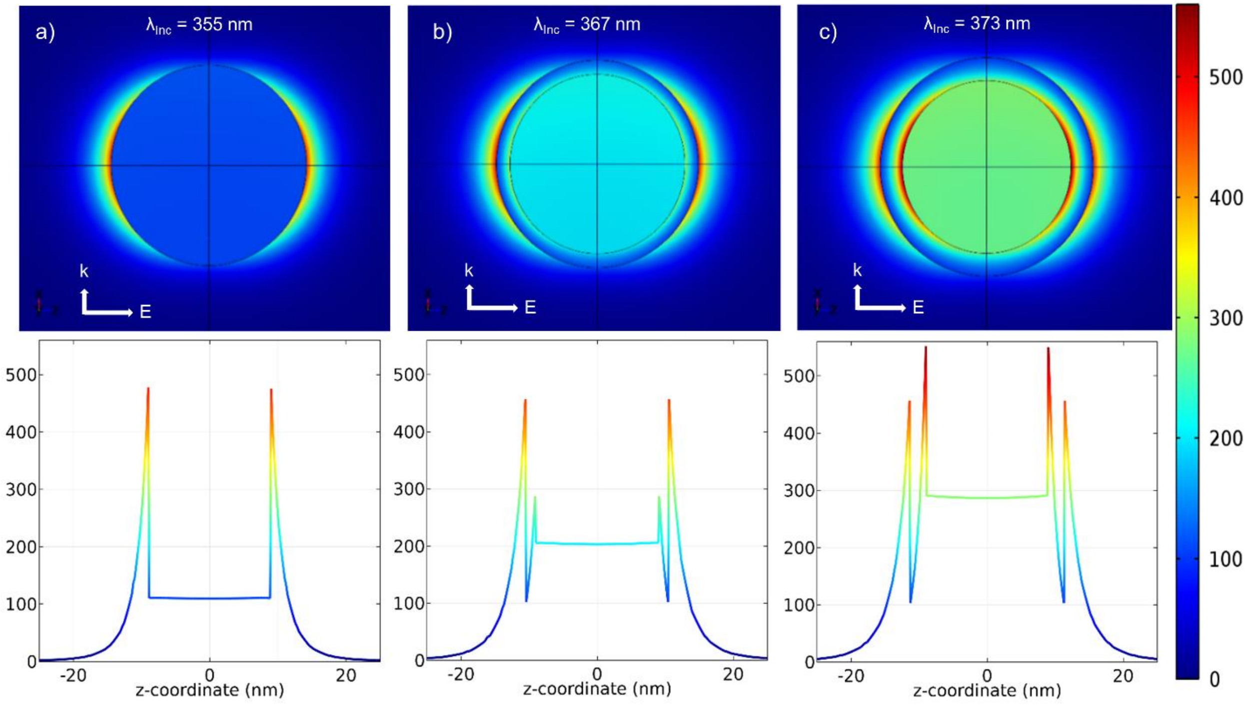
Ultrastable Ag nanoparticles:

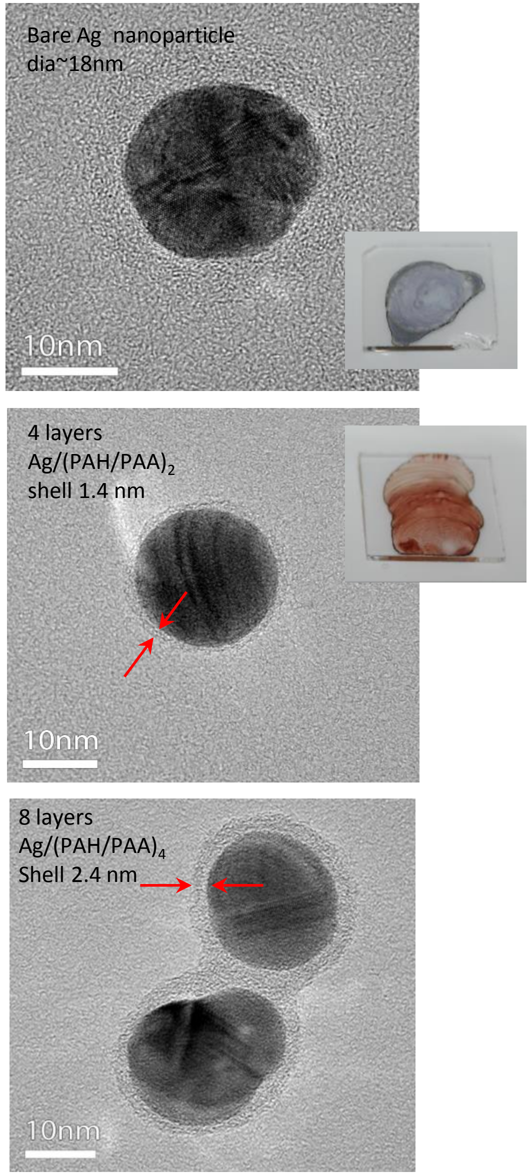
- Encapsulation of Ag NPs with ultrathin protective polymer shell using LbL method.



- Effect of polymer shell on the field enhancement of core-shell nanoparticles.



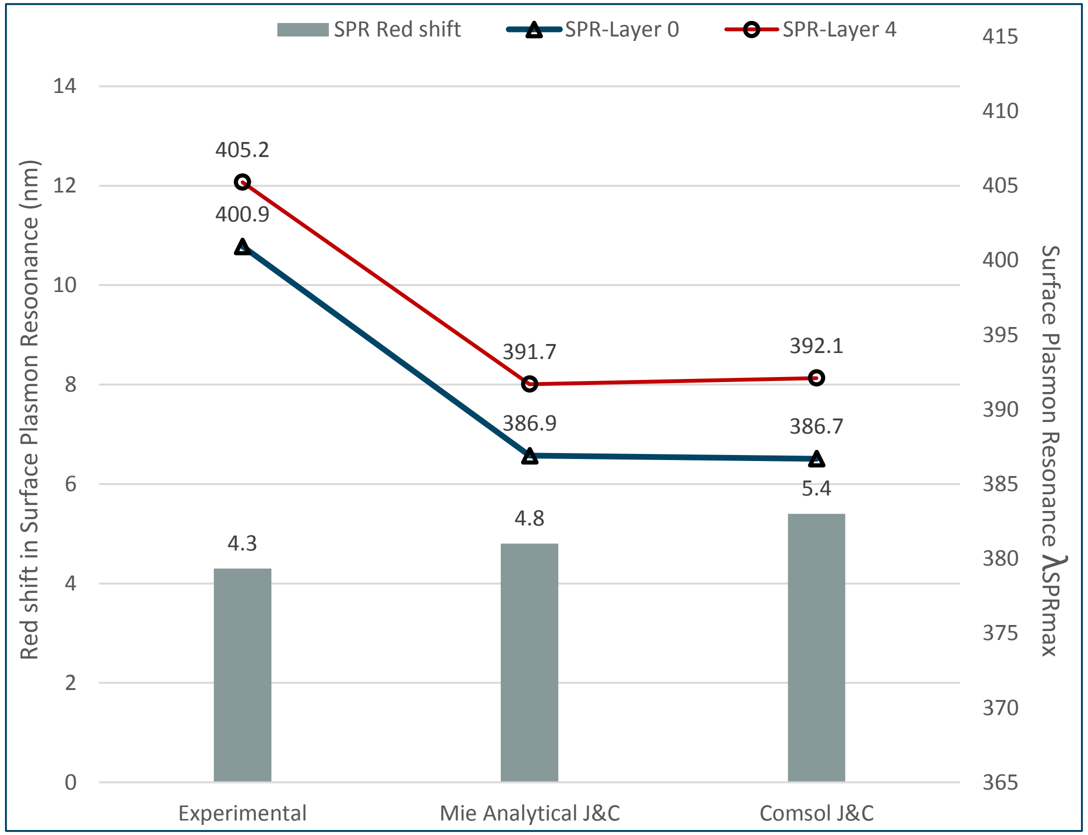


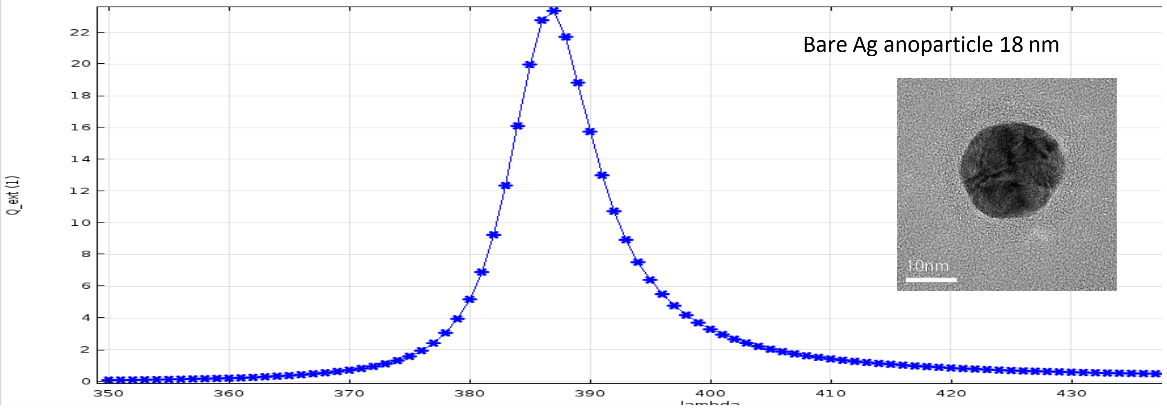


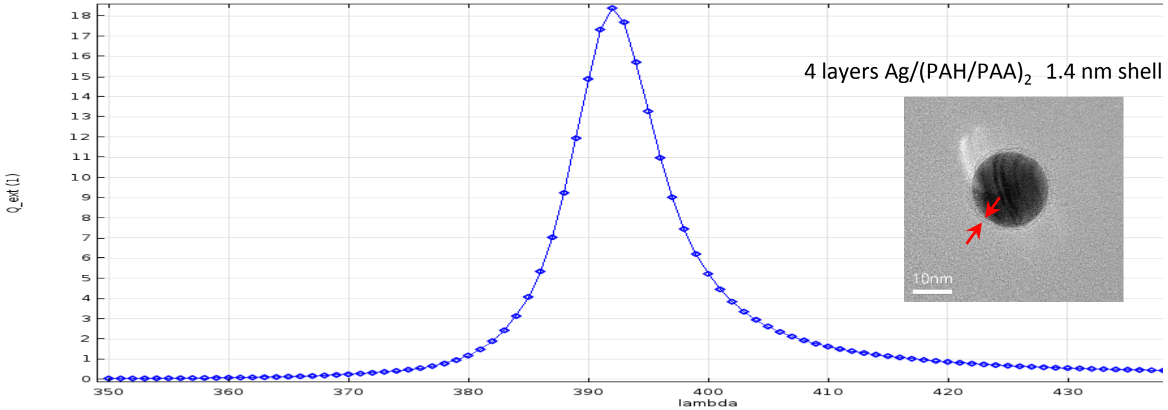
TEM Characterization

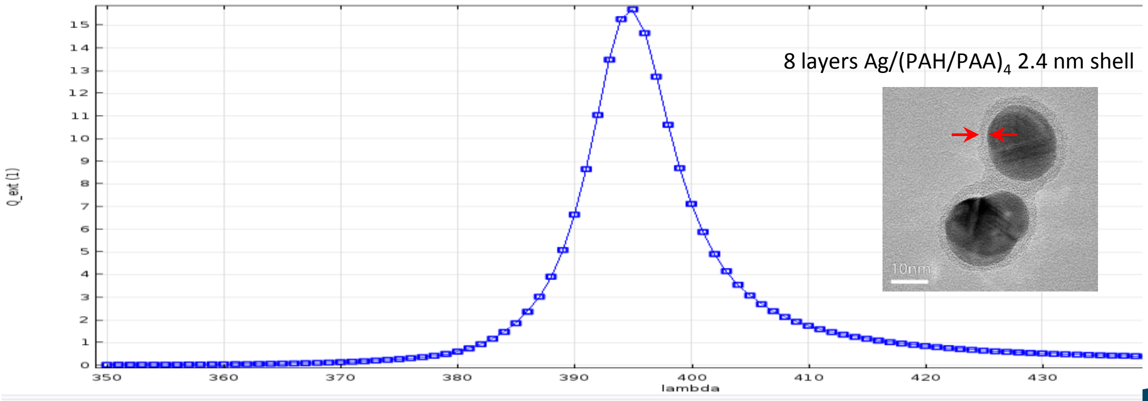
Validation of models:

- Parametric sweep of incident wavelength to generate extincion plots (Mie solution implementation in COMSOL in water and $n_{polymershell}$ = 1.48
- Experimental absorption spectra compared with COMSOL model and Mie analytical solution using Bohren and Huffman's BHCOAT (implemented in MATLAB) for coated nanoparticles. Data from J&C – Jhonson and Christy



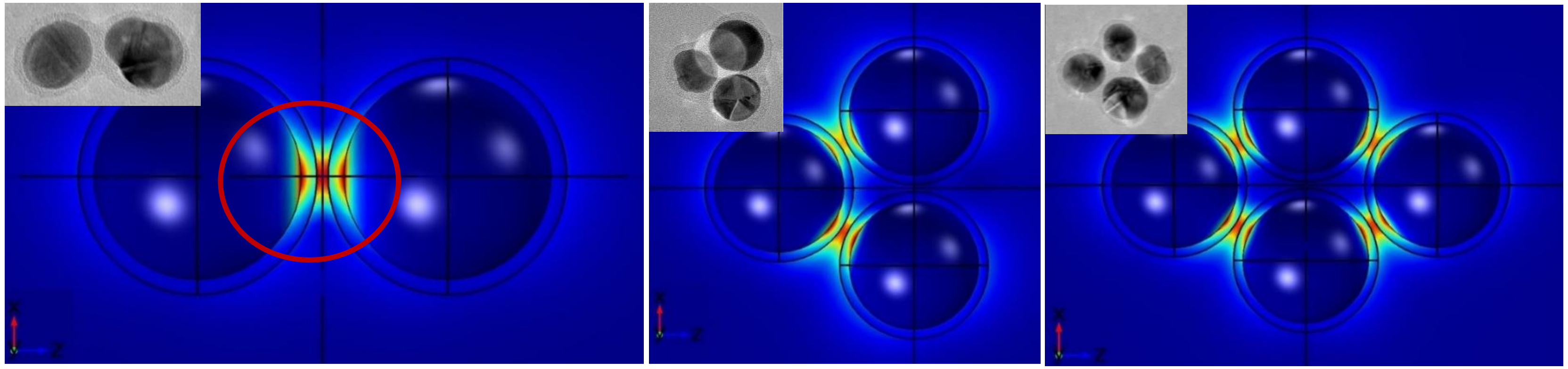






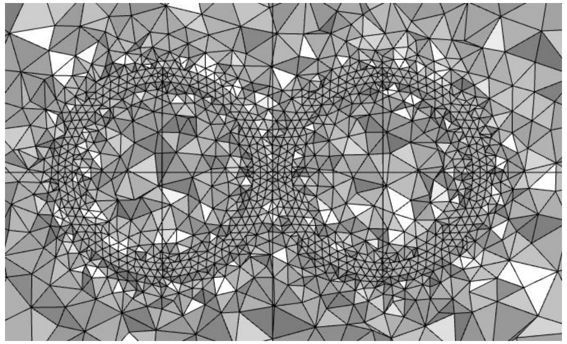
Ultrastable Ag plasmonic nanoarrays for multi-domain applications:

- Ag nanoparticle arrays generate hot spots
  - SERS : $EF^4 \sim 10^8$-10^{11}



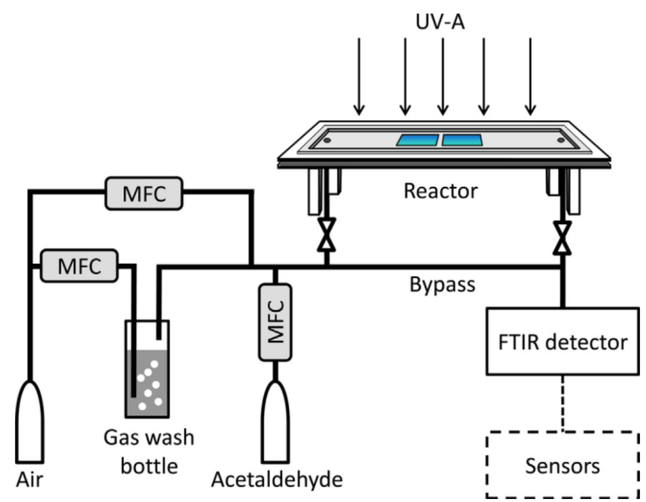
- Engineering of Nano arrays based on the feedback from E-field simulations.
  - Mesh convergence study for core-shell nanoparticle dimers

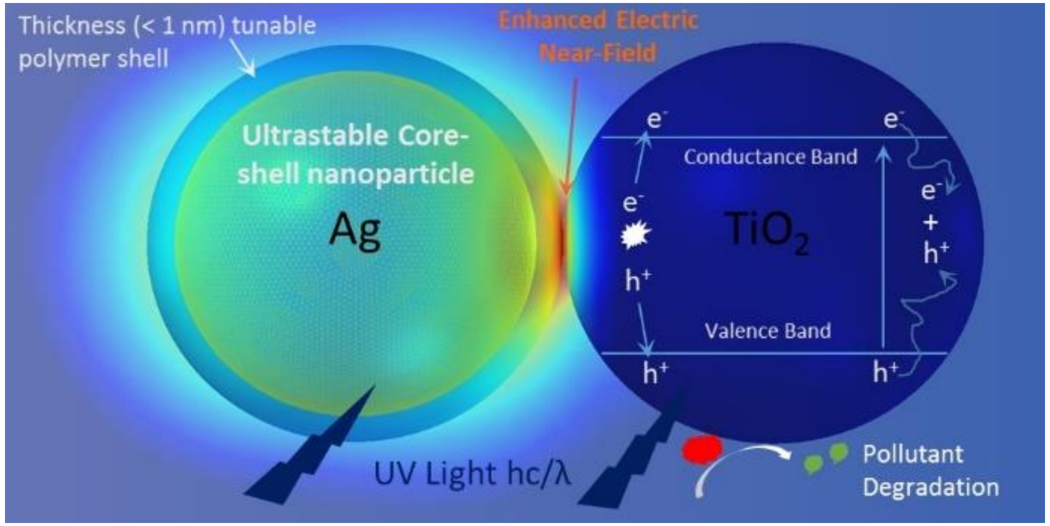
Mesh Density	Number of Elements	Computation time [s]	Max point of (Norm. E-field)^2
Normal	10374	9	3.13E+05
Fine	16588	11	4.64E+05
Finer	42048	24	4.21E+05
Extra fine	135833	85	3.50E+05
Extremely fine	647861	609	3.45E+05



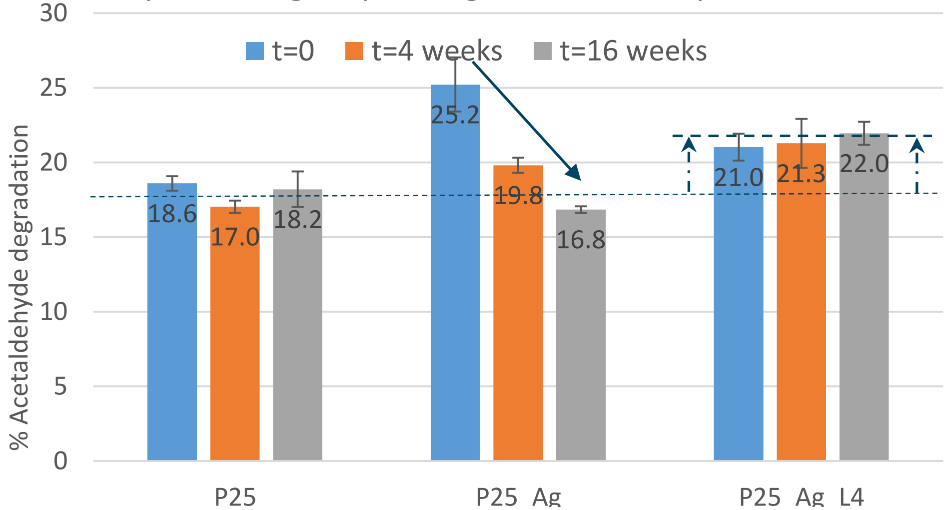
Ag plasmon enhanced TiO_2 gas phase photocatalysis

- Application of silver nanoparticles for long-term stable plasmon enhanced gas phase photocatalysis.
- Acetaldehyde as a model pollutant in gas phase photocatalysis
- FEM numerical simulations to corroborate experimental evidence to identify the major mechanism responsible for plasmonic enhancement.





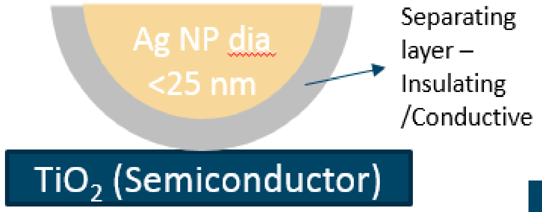
Long term stability study of Ag-TiO_2 photocatalytic system using 4 layered Ag core-shell nanoparticles

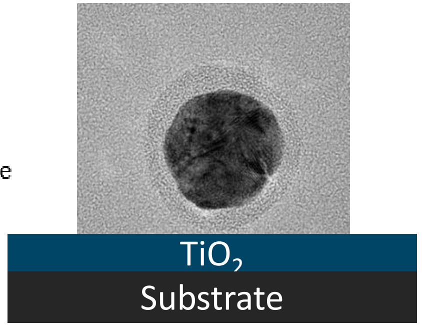


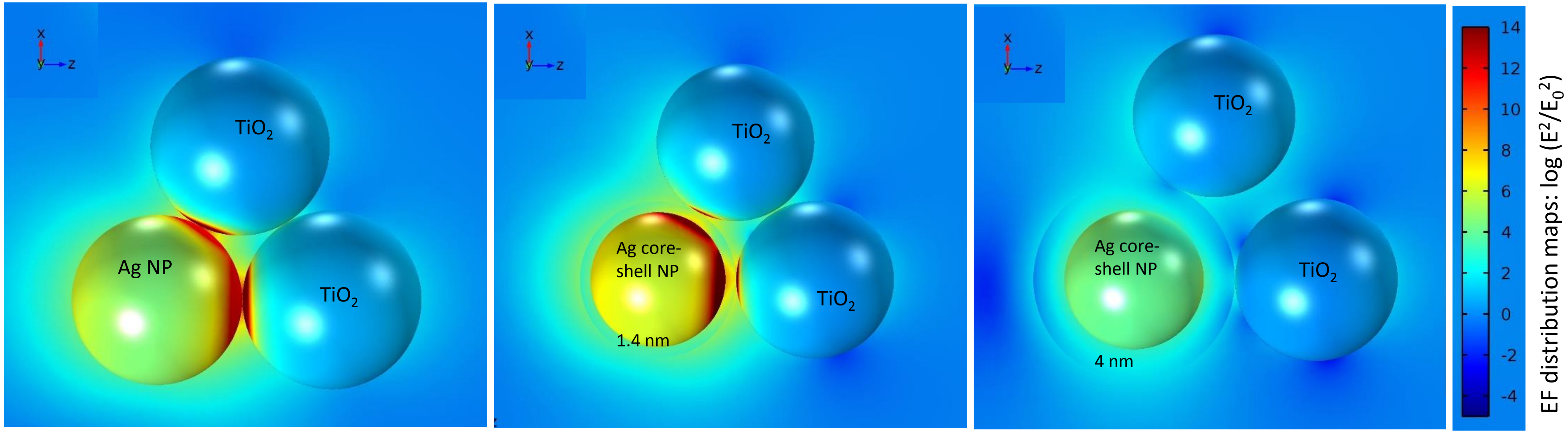
*Ramesh Asapu et al. Applied Catalysis B: Environmental, 200 (2017), 31-38

Ag plasmon enhanced TiO_2 photocatalysis

- Ag@polymer core@shell nanoparticles to study near-field / charge transfer
- Insulating polymer spacer layer rules out charge transfer
- So how distant the near field enhancement is helpful!
  - *FEM simulations provide an estimation* → feedback for experimental synthesis







Influence of spacer layer between Ag plasmon and TiO_2 nanoparticles on the enhancement

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 wide domain of applications*
- *Vital mechanistic tool : plasmon enhanced photocatalysis and hotspot applications*

Thanks for your attention