Mechanistic Study of Plasmonic Photocatalysts through Near-electric Field Simulations

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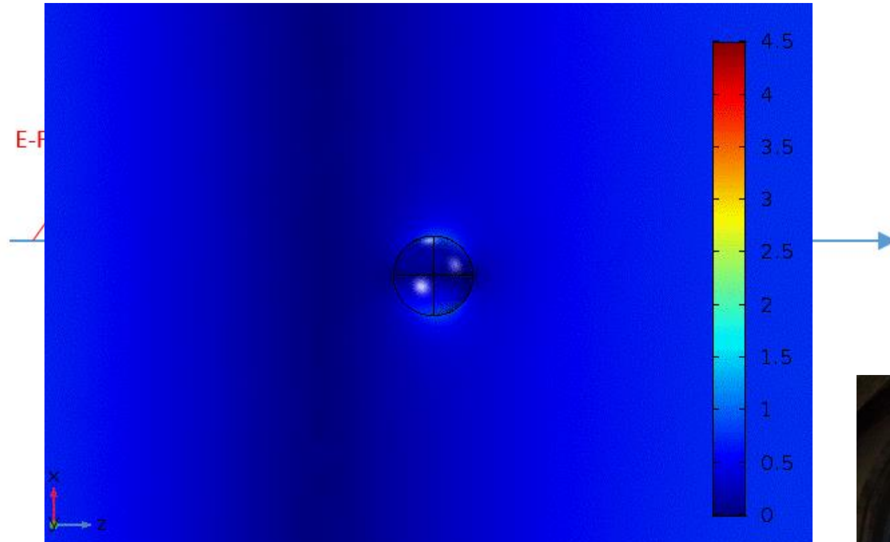
Introduction: Plasmons

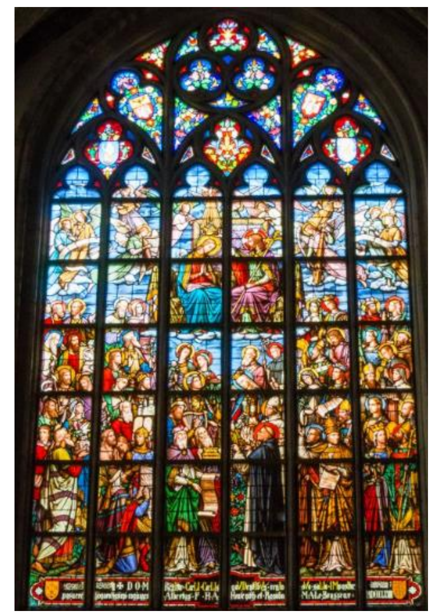
- ***Plasmonic nanoparticles:*** Plasmons → oscillating cloud of electrons in resonance with $\vec{E}$ of incident light wave



Gold >>>>>>> nanoscale

Nanoparticle size → color *Sigma Aldrich

*iStockphoto/Thinkstock

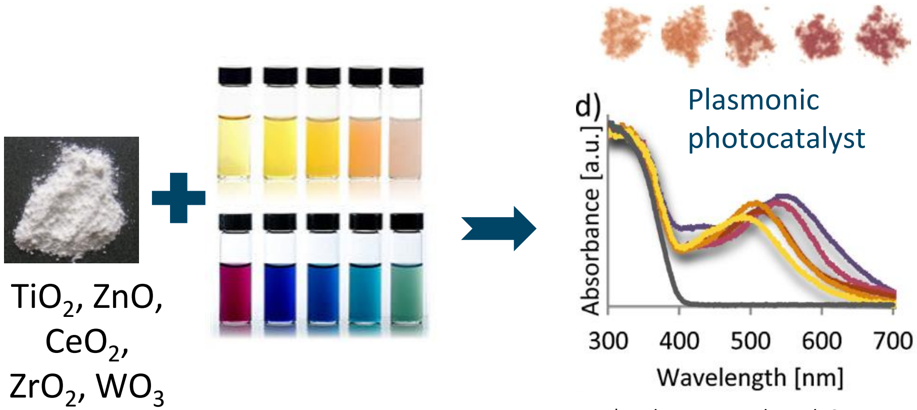


* Church of our Lady, Antwerp Cathedral

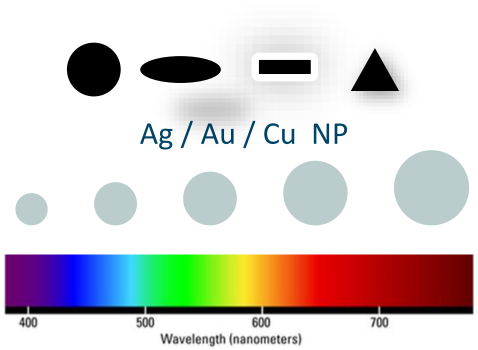
- Medieval artisans: mixing gold and silver salts to create stained glass → SPR of nanoparticles

Plasmon-enhanced Photocatalysis

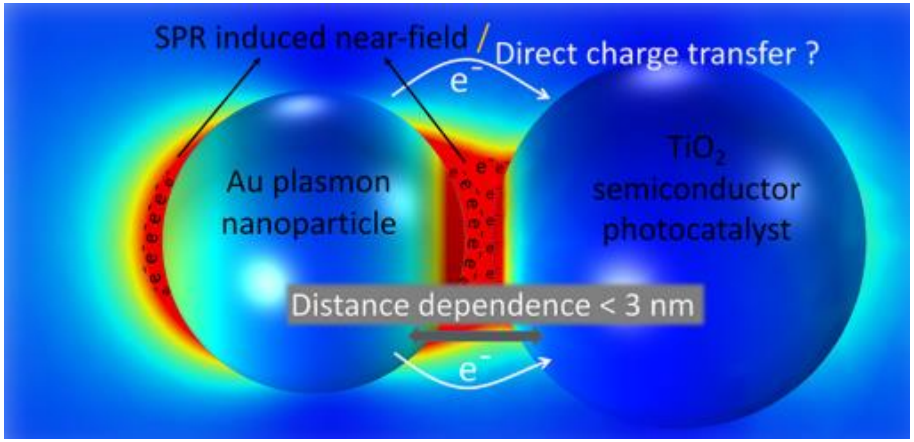
- Coupling plasmonic nanoparticles i.e., Ag/Au/Cu with photocatalysts
- Induces broad visible light response using SPR properties
- Mechanism – How! Parameters!



**Verbruggen et al. Appl. Cat. B: Environmental 188 (2016) 147–153*



Surface Plasmon Resonance (SPR) properties



Hot spots and the resulting near-field and charge transfer effects at the interface of metal-semiconductor photocatalyst.

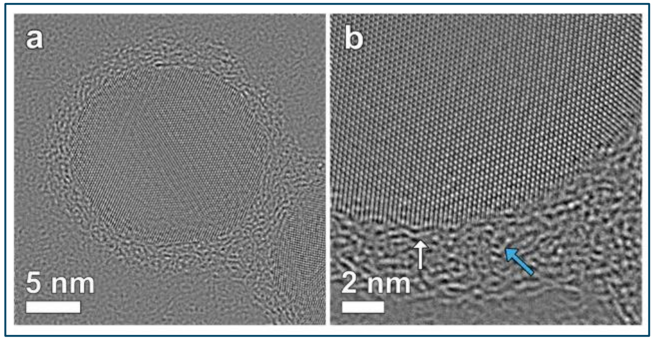
**R. Asapu et al. ACS Appl. Nano Mater. 2, 4067–4074 (2019)*

Plasmonic Photocatalysis: Mechanistic Study

Understanding the role of near-field and charge transfer

Mechanistic approach: Different Photocatalytic Systems

- Insulating shell/spacer layer: Layer-by-Layer (LbL) method
  - 4 layers: 1.7 ± 0.5 nm separation
  - 12 layers: 3.2 ± 0.8 nm separation
- Conductive shell/spacer layer: In-situ polymerization method (PANI)
  - 30 min: 1.4 ± 0.5 nm separation
  - 180 layers: 7.5 ± 1.6 nm separation



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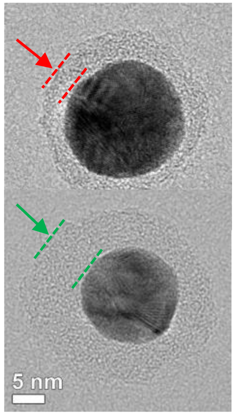
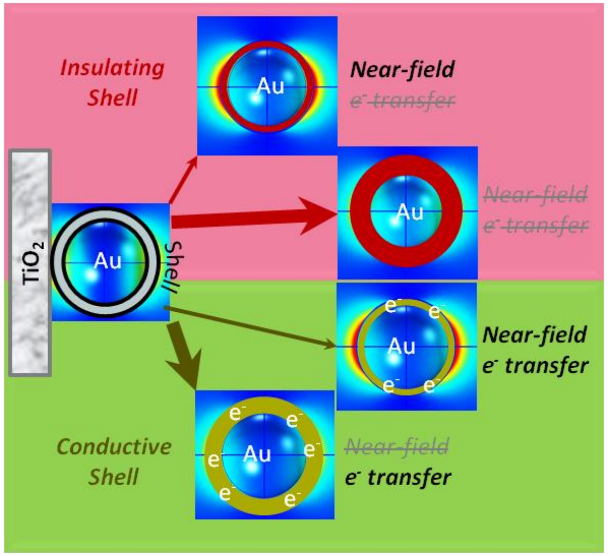
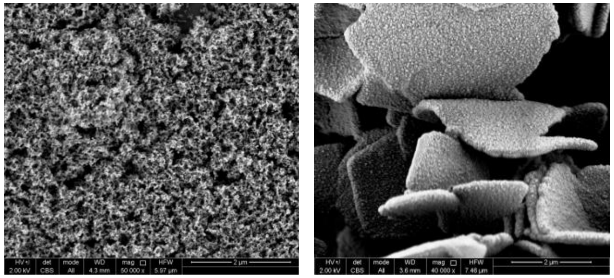


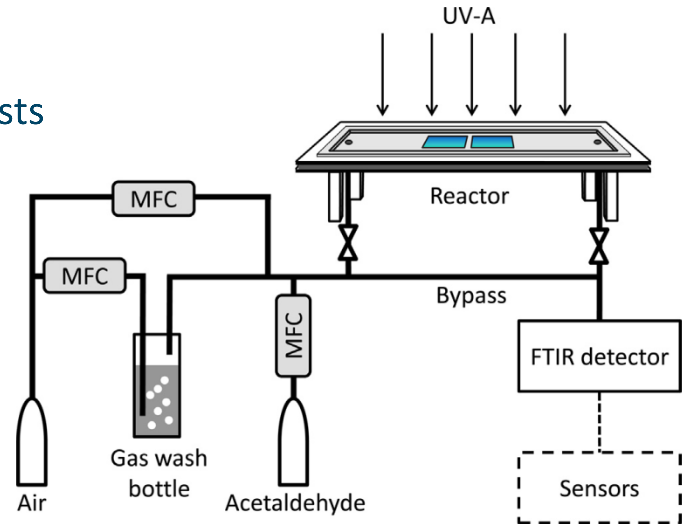


*R. Asapu et. al. ACS applied materials & interfaces 9 (47), 41577-41585

Photocatalytic Activity Tests

Scale: 2 μm



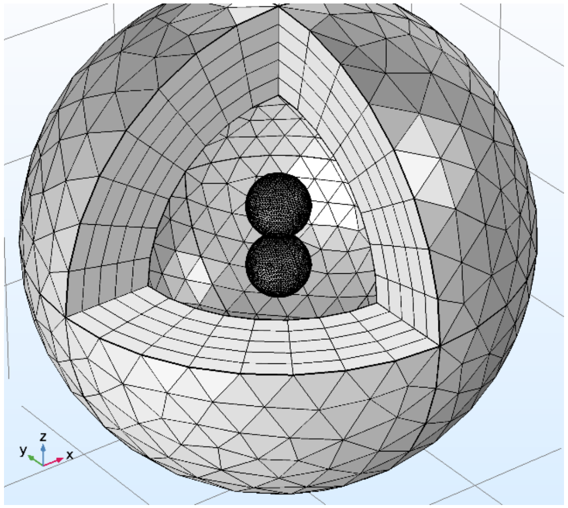


- Spin coating on glass and ALD (atomic layer deposition) on COK Si substrates
- Acetaldehyde and stearic acid as model pollutants

R. Asapu et. al. Applied Catalysis B: Environmental 200, 31-38

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



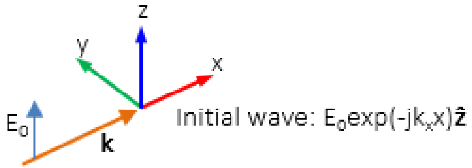
$$\nabla \times \left[\frac{1}{\mu_r}(\nabla \times E_{sca})\right] - K_0{}^2\left[(\varepsilon_r - \frac{j\,\sigma}{\omega \varepsilon_0})\right] E_{sca} = 0$$

where E_{sca} – scattered electric field

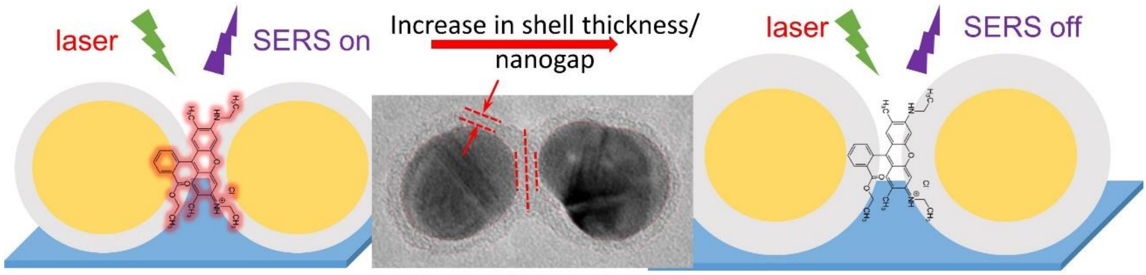
K_0 - wavenumber in free space

μ_r - relative permeability of medium

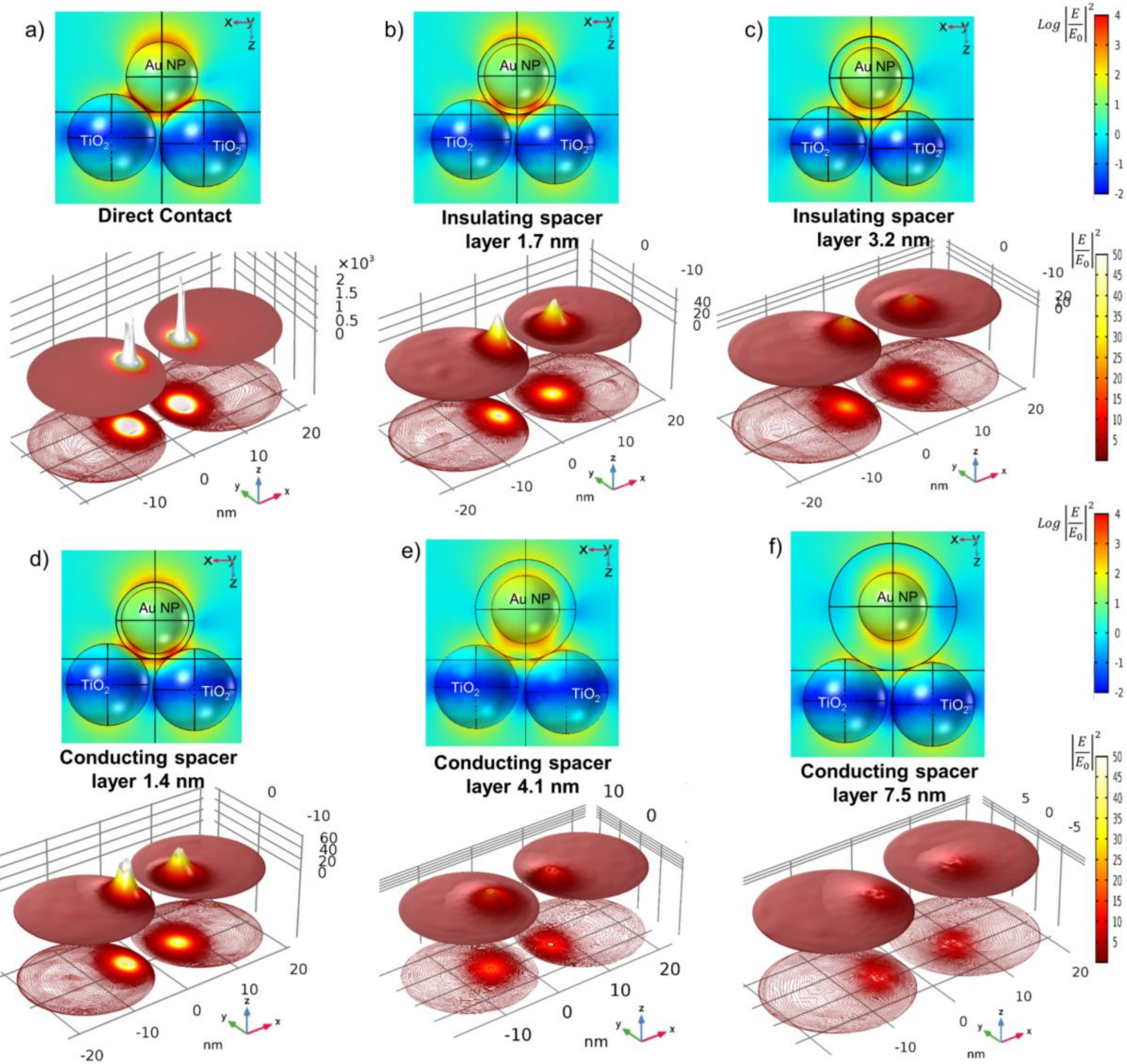
ε_r – permittivity of medium



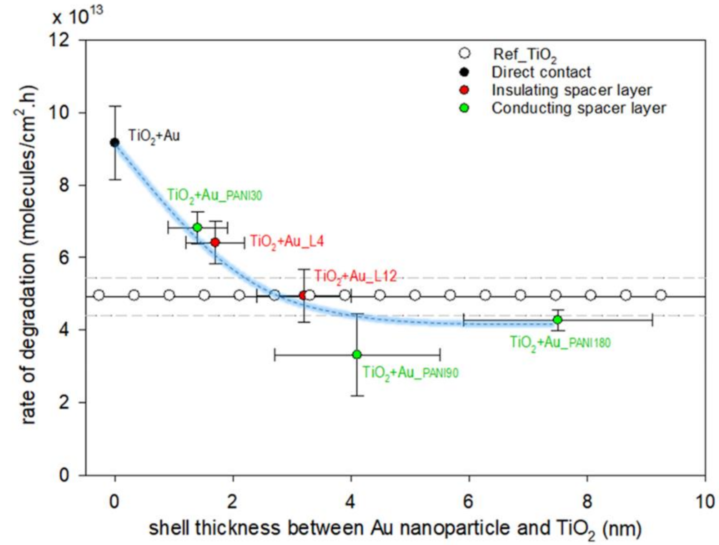
- Enhancement is due to both incident and scattered fields.
- EM or field enhancement $|E/E_0|$ is dependent:
  - Inter-particle distance & probe molecule distance dependence: *nanogap*
  - laser excitation wavelength
  - NP shape and size



Plasmonic Photocatalysis: Insights via Mechanistic Study



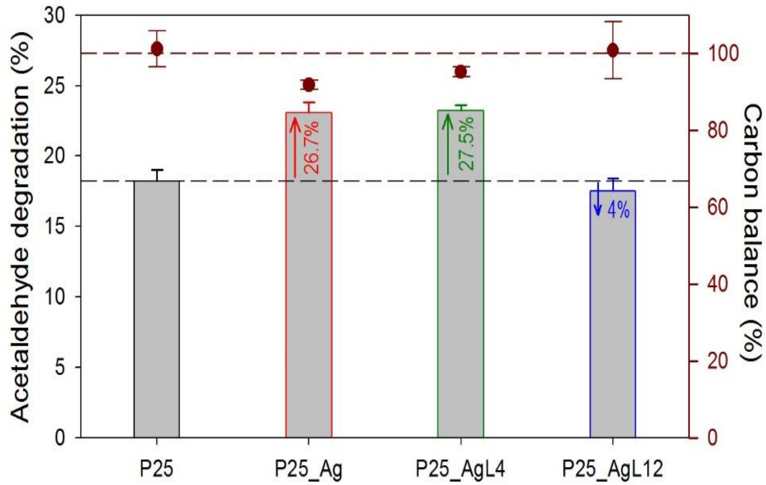
Field enhancement distribution maps of Au-TiO_2 systems with the projection of TiO_2 surface contours with a height intensity scale the bottom for different systems.



Experimental results of photocatalytic activity tests

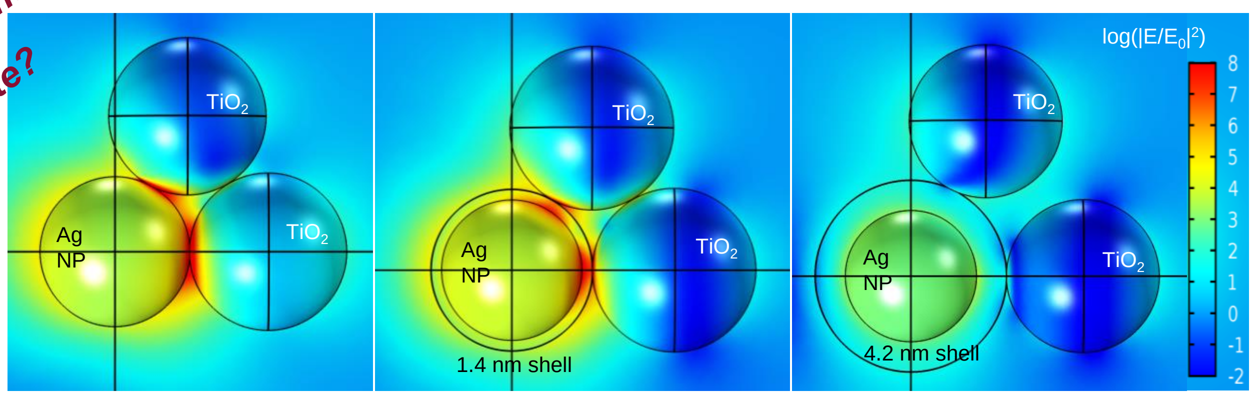
**R. Asapu et al. ACS Appl. Nano Mater. 2, 4067–4074 (2019)*

Ag plasmon enhanced TiO_2 gas phase photocatalysis



I don't trust you pal!

Simulations accurate?

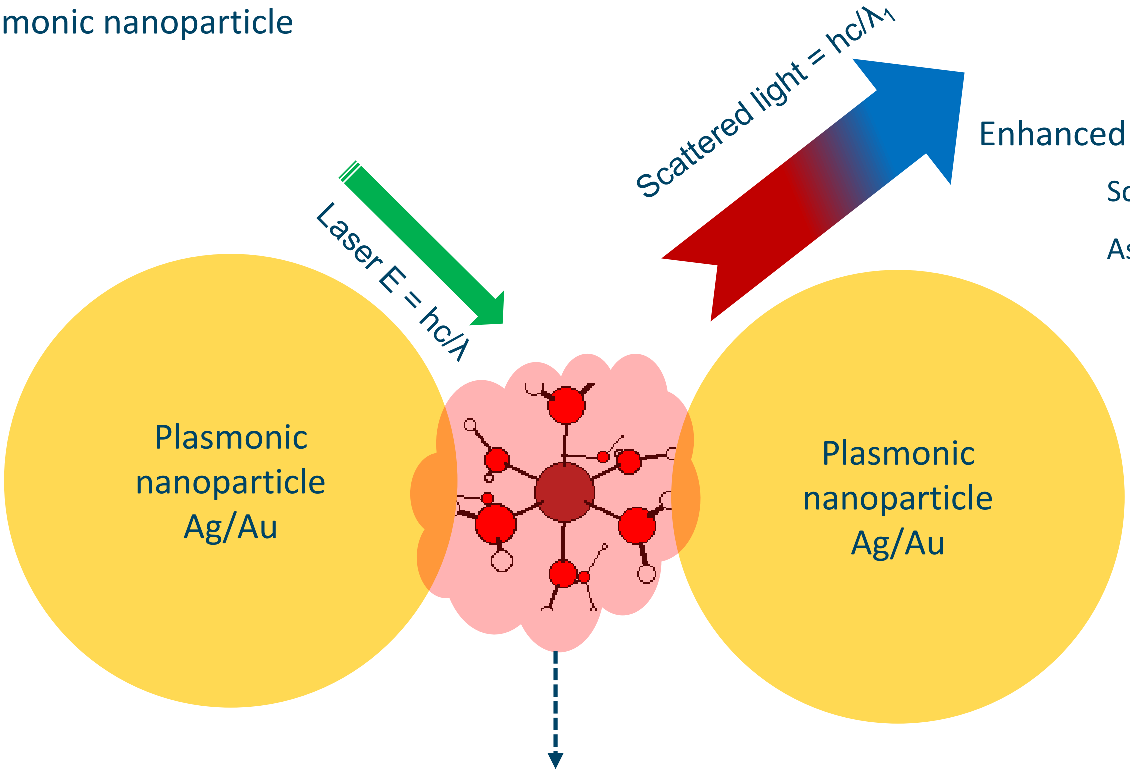


P25_Ag P25_AgL4 P25_AgL12

- Significance of Near-field enhancement → a more important role!

Experiments to support simulation trends
SERS (Surface enhanced Raman spectroscopy)

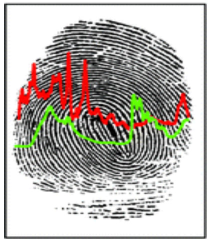
- Surface enhanced Raman spectroscopy → Scattering of light / photons by molecule located near plasmonic nanoparticle



Enhanced signal

Scattering light wavelength shift →

Assigned to particular molecules



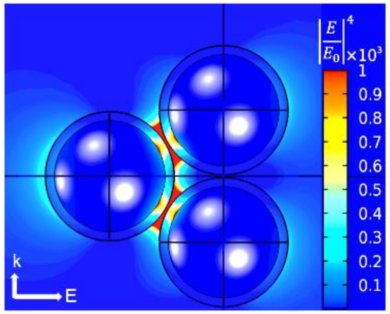
Molecule fingerprinting

Hot spots → Electromagnetic enhancement or near-field enhancement

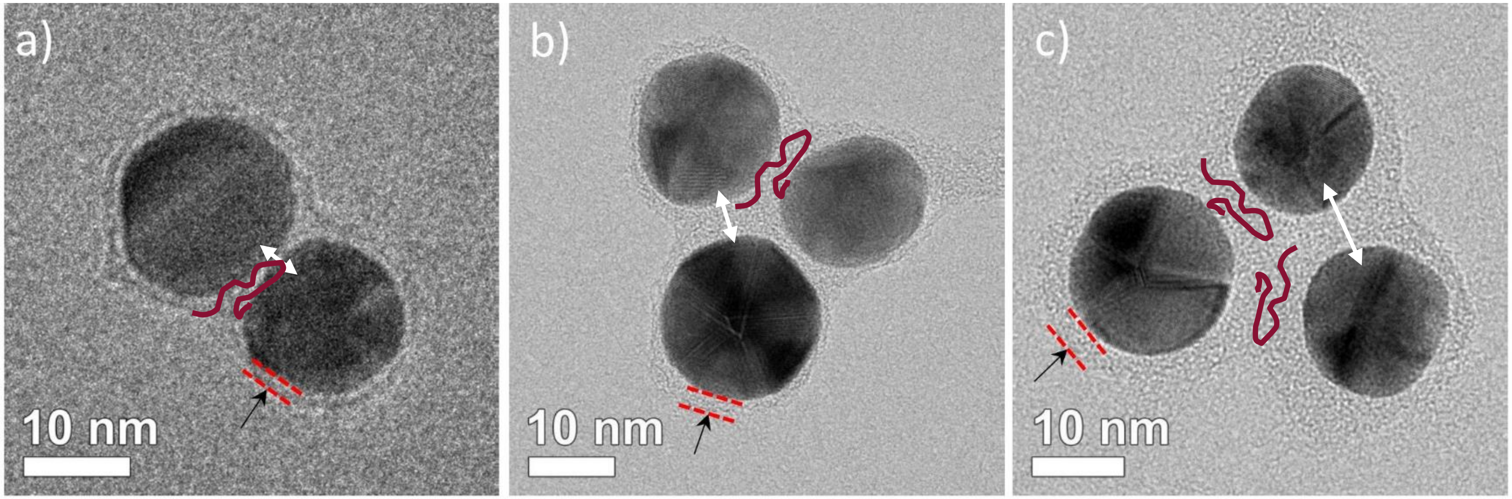
- SERS applications: Identifying of substances → detection of drugs up to ppb i.e., 0.000001 g

SERS: An experimental support for theoretical near-field simulations

- SERS – Enhancement Factor (EF) depends on:
  - Electromagnetic enhancement in hot spots

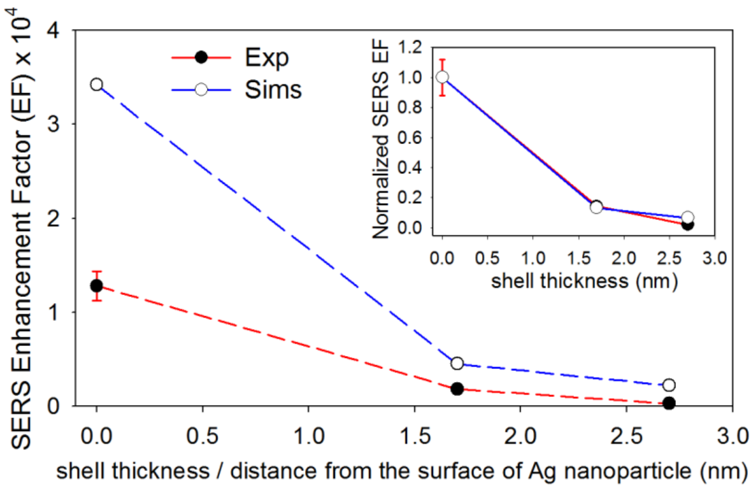


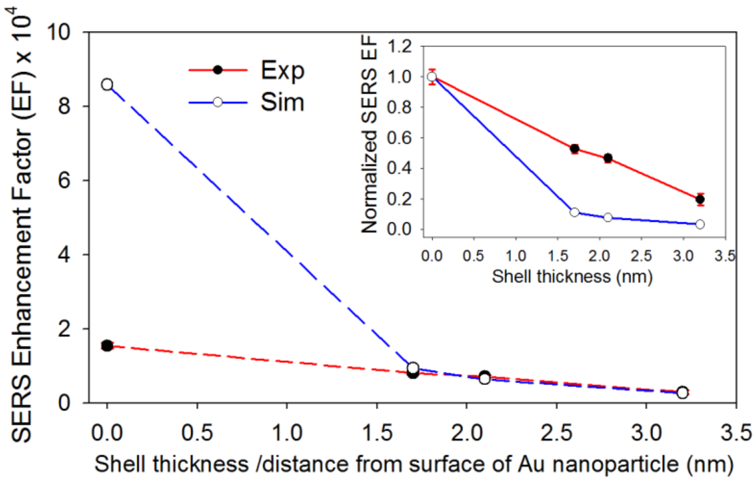
- Nanogap between nanoparticles is controlled by shell thickness
  - Charge transfer / chemical enhancement can be ruled out due to *Insulating property* of the polyelectrolyte shell
  - Shell thickness increase → increase in Nanogap → Decay of SERS EF (experimental vs theoretical)



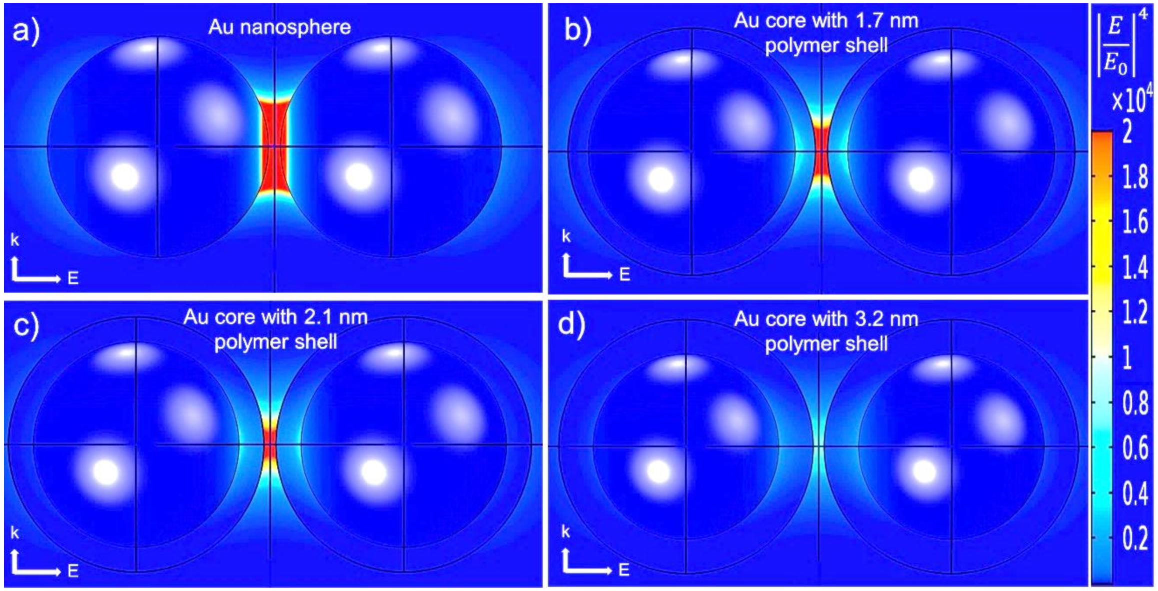
Au NPs encapsulated with a) four (Au_L4), b) eight (Au_L8) and c) twelve (Au_L12) layers of polyelectrolyte

SERS EF: Experimental vs Theoretical Near-field decay





- $EF_{exp} = \frac{\left[{}^{I_{SERS}}/_{N_{SERS}}\right]}{\left[{}^{I_{RS}}/_{N_{RS}}\right]}$
- $EF_{calc} = \left|\frac{E}{E_0}\right|^4$
- Distance decay of SERS EF
  - Ag plasmonic systems < 2 nm
  - Au plasmonic systems < 3 nm
- SERS experiments and near-field simulations complement each other.



Conclusions & Future work

- The near-electric field simulation results corroborate the experiments
  - ➢ crucial insight that near-field enhancements are vital for the photocatalytic reaction rate enhancement
- Near-field effect becomes insignificant for shell thicknesses exceeding 3 nm.
  - ➢ hints at a dominant role of the near-field enhancement mechanism.

❑ **Future Work: Quantification of near-electric field simulations**

  - Near-Field Scanning Optical Microscopy (NSOM)
  - Mapping the nanoscale electromagnetic near-field using optical forces

Thanks
Q&A!

References:

- *R. Asapu et al. ACS Appl. Nano Mater. 2, 4067–4074 (2019)*
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