Shell-isolated nanoparticle-enhanced Raman spectroscopy: Insight from COMSOL simulations

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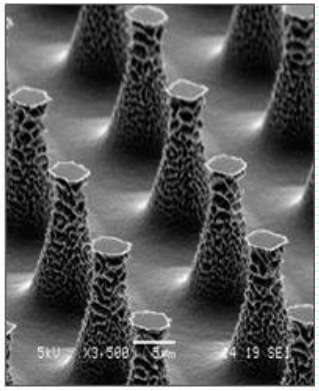
Excerpt from the Proceedings of the 2016 COMSOL Conference in Shanghai

Outline

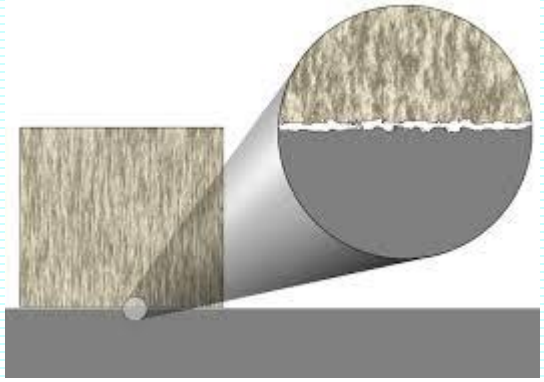
- Principle of surface-enhanced Raman spectroscopy for surface analysis of materials
- Features of hybrid structure with gold nanoparticle aggregates electromagnetically coupled with a flat metal surface
- Some tricks for the COMSOL simulation of nano-optics.

Everything is surface and interface

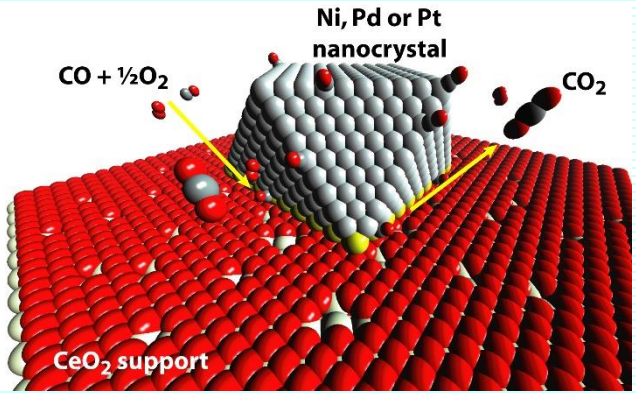
Adhesion



Wear and wetting

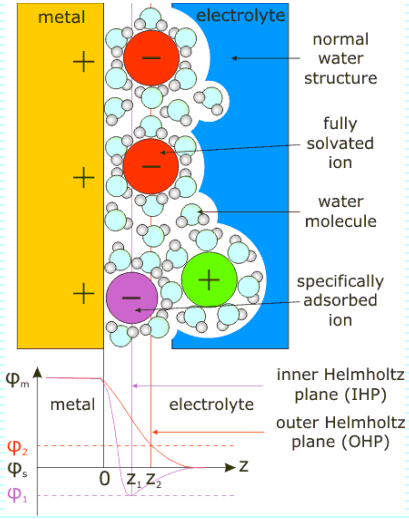


Friction



Catalysis

Corrosion

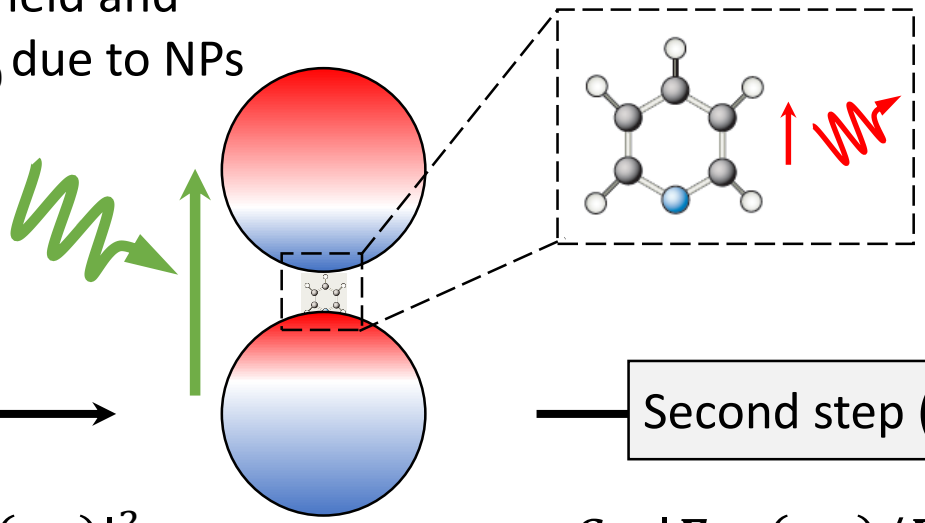


electrochemistry

Handbook of surfaces and interfaces of materials; *J. Surf. Interf. Mater.* **1**, 1-3 (2013).

The enhanced local field and induced dipole at ω_0 due to NPs

If there were no mutual excitation from m-NPs system at ω_R, no enhanced apparent Raman polarizability exist



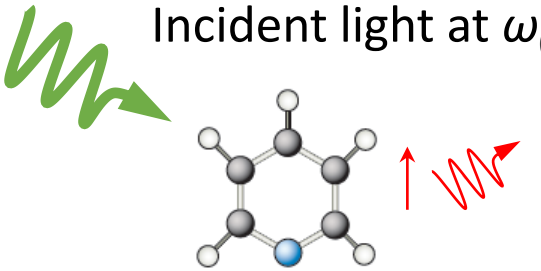
First step (G_1)

Second step (G_2)

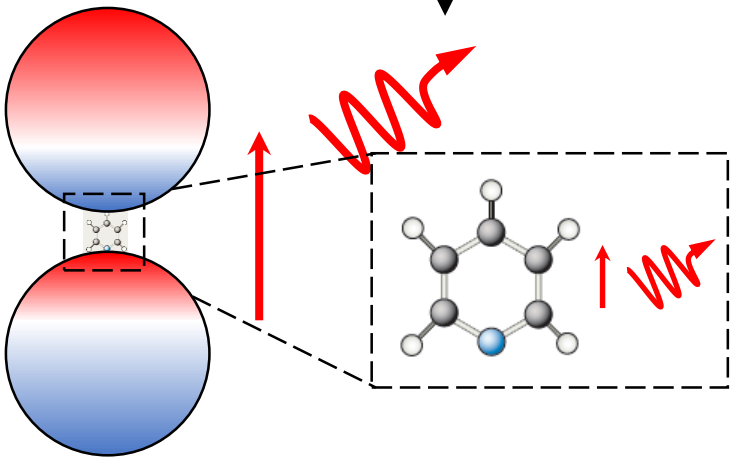
$$G_1 \sim |\boldsymbol{E_{loc}}(\omega_0)/\boldsymbol{E_0}(\omega_0)|^2$$

$$G_2 \sim |\boldsymbol{E_{loc}}(\omega_R)/\boldsymbol{E_0}(\omega_R)|^2$$

Incident light at ω_0

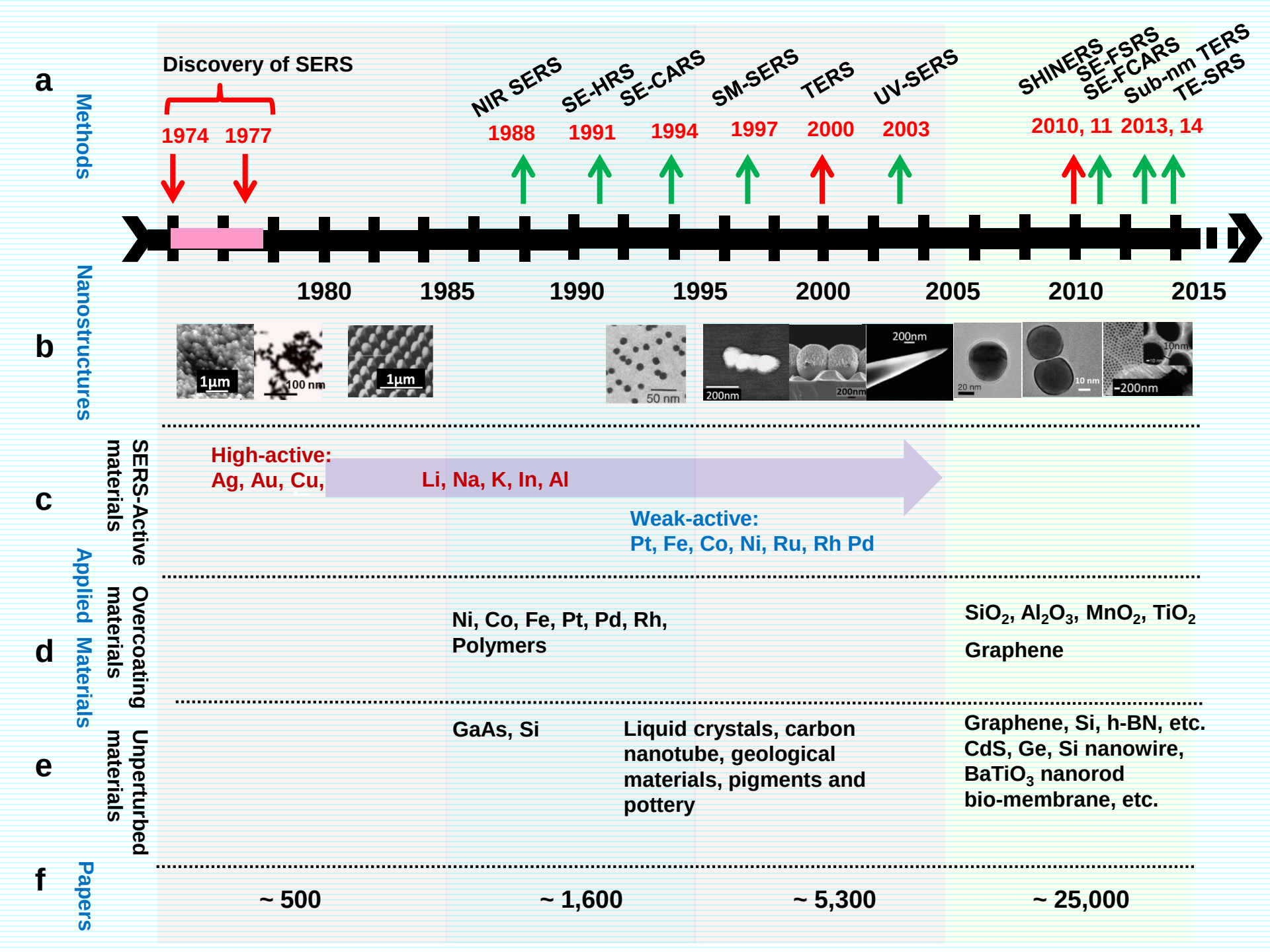


Normal Raman

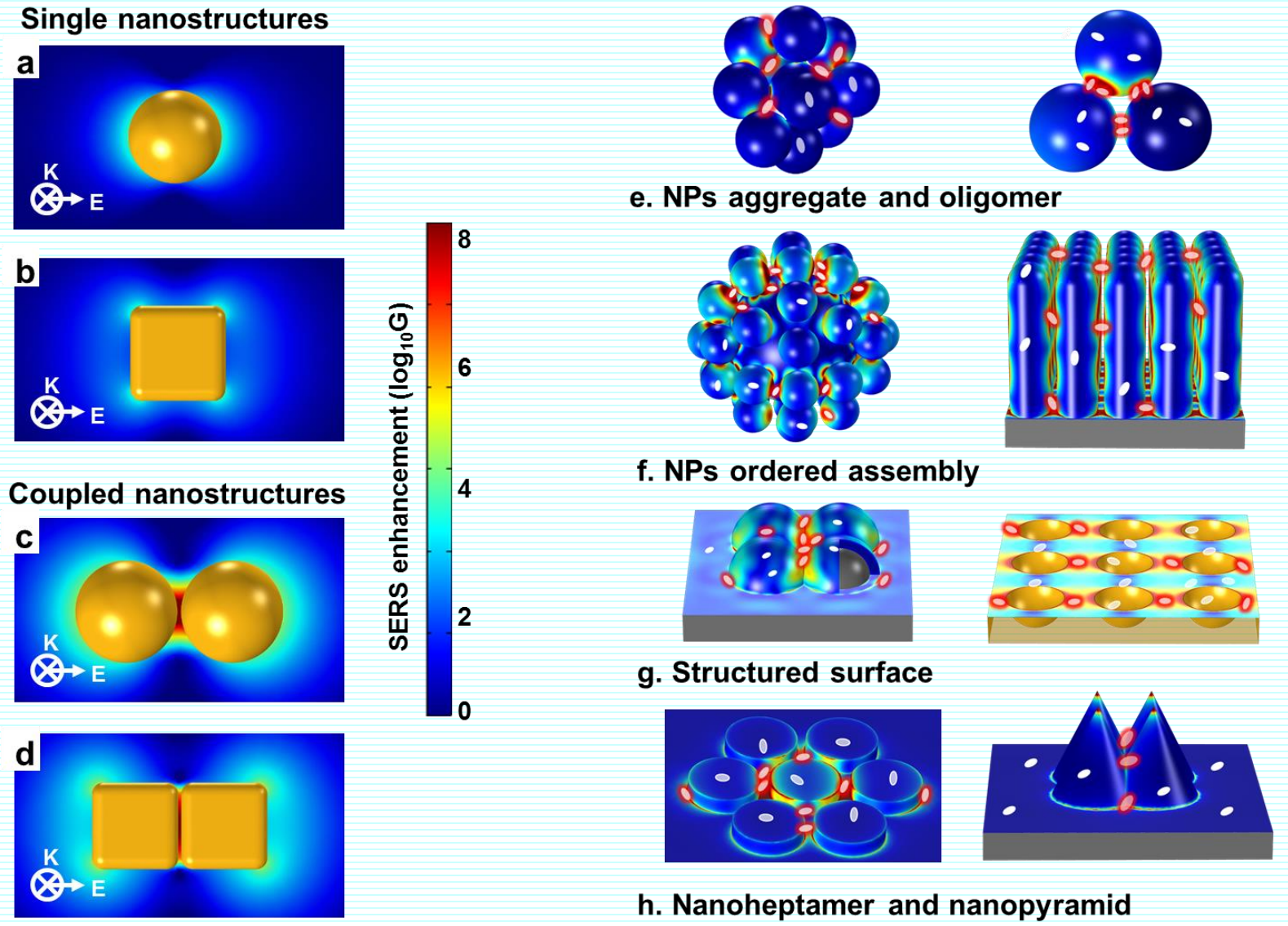


SERS

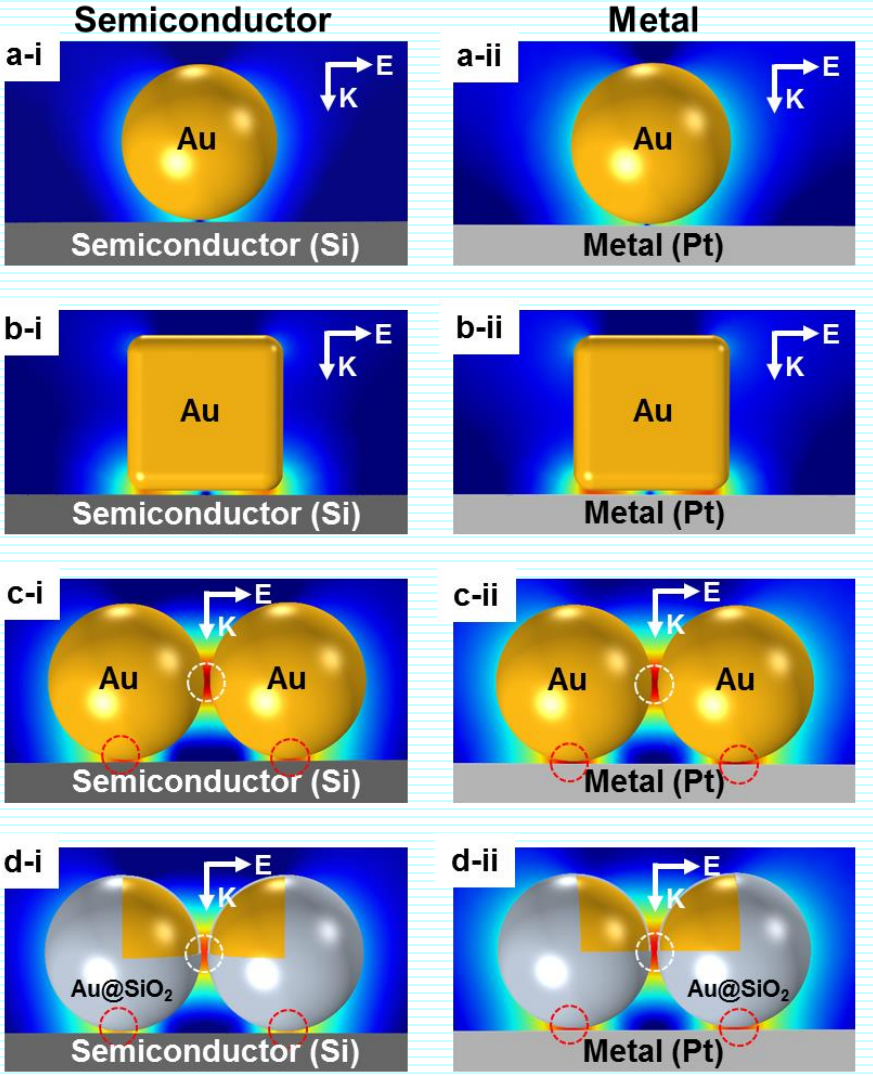
$$I_{SERS}/I_{Raman} = G_1 G_2 \sim |\boldsymbol{E_{loc}}(\omega_0)/\boldsymbol{E_0}(\omega_0)|^4$$

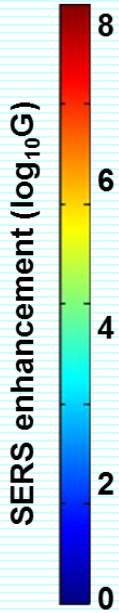

a
Methods
Discovery of SERS
1974
1977
NIR SERS
1988
SE-HRS
1991
SE-CARS
1994
SM-SERS
1997
TERS
2000
UV-SERS
2003
SHINERS
SE-FSRS
SE-FCARS
Sub-nm TERS
TE-SRS
2010, 11
2013, 14
1980
1985
1990
1995
2000
2005
2010
2015
b
Nanostructures
1μm
100 nm
1μm
50 nm
200nm
200nm
200nm
20 nm
10 nm
10nm
200nm
c
Applied Materials
SERS-Active materials
High-active:
Ag, Au, Cu,
Li, Na, K, In, Al
Weak-active:
Pt, Fe, Co, Ni, Ru, Rh Pd
d
Overcoating materials
Ni, Co, Fe, Pt, Pd, Rh,
Polymers
SiO2, Al2O3, MnO2, TiO2
Graphene
e
Unperturbed materials
GaAs, Si
Liquid crystals, carbon nanotube, geological materials, pigments and pottery
Graphene, Si, h-BN, etc.
CdS, Ge, Si nanowire,
BaTiO3 nanorod
bio-membrane, etc.
f
Papers
~ 500
~ 1,600
~ 5,300
~ 25,000

Materials are hard to be squeezed into hotspot in nanogap!
Any new concept of hotspot for surface analysis of materials?



The 3rd generation hotspots generated by hybrid structures with nanostructures and probe materials



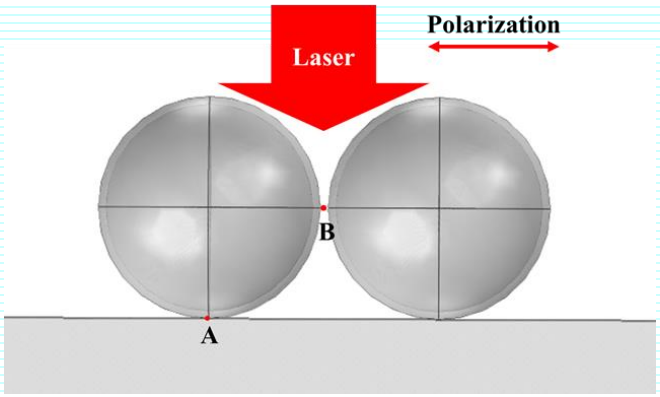


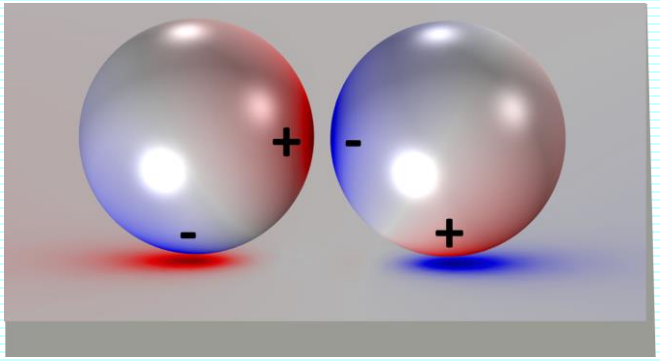
No.	$\langle G_{sub} \rangle$	$G_{max,sub}$	$G_{max,NP}$
a-i	94	$2.0*10^3$	
a-ii	$1.3*10^3$	$4.3*10^4$	
b-i	$1.5*10^6$	$1.4*10^7$	
b-ii	$7.3*10^5$	$5.2*10^6$	
c-i	$1.0*10^5$	$6.9*10^6$	$6.8*10^7$
c-ii	$1.0*10^6$	$9.0*10^7$	$7.2*10^7$
d-i	$1.7*10^4$	$8.4*10^5$	$6.6*10^6$
d-ii	$2.1*10^5$	$1.2*10^7$	$1.4*10^7$

a(NP) = 60 nm, t(SiO_2) = 2 nm
g(NP-NP) = 2 nm, g(NP-Sub) = 1 nm

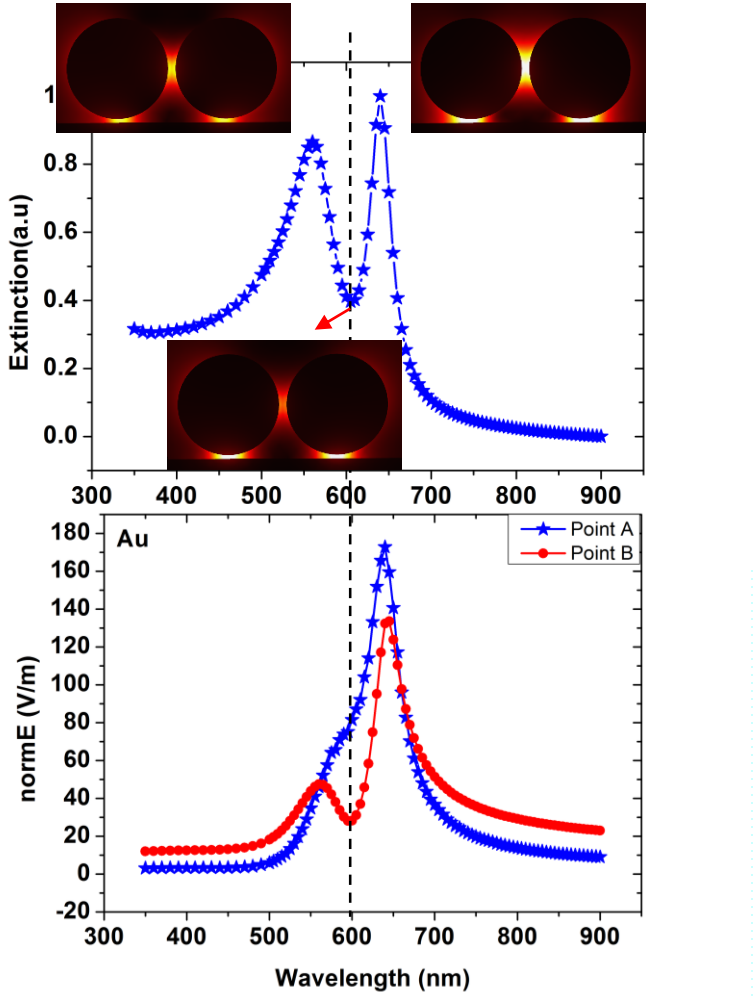
Ding, Yi, Li, et al, *Nat. Rev. Mater.* **2016**, 1, 16021.

Fano-resonance Plasmon-enhanced Raman Scattering of nanospheres-Flat Surface Systems ?



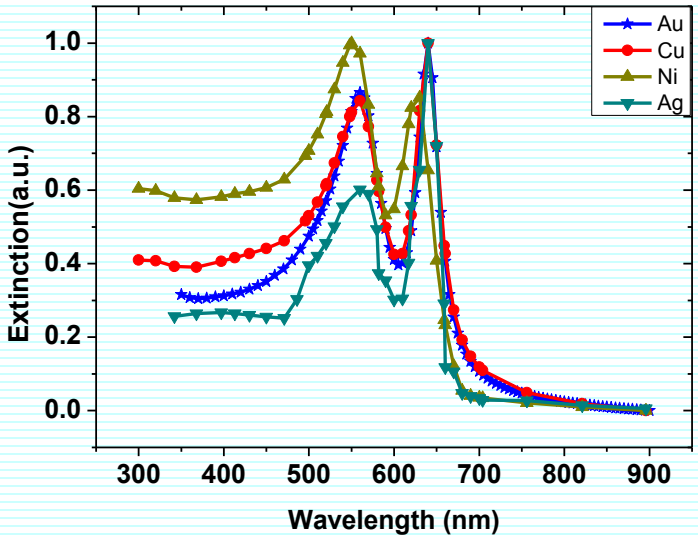


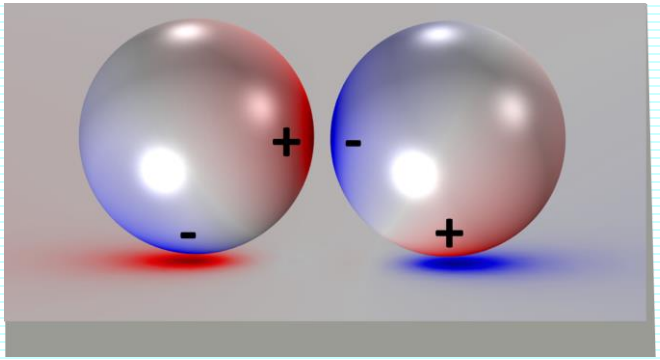
Surface Charge density at 650 nm

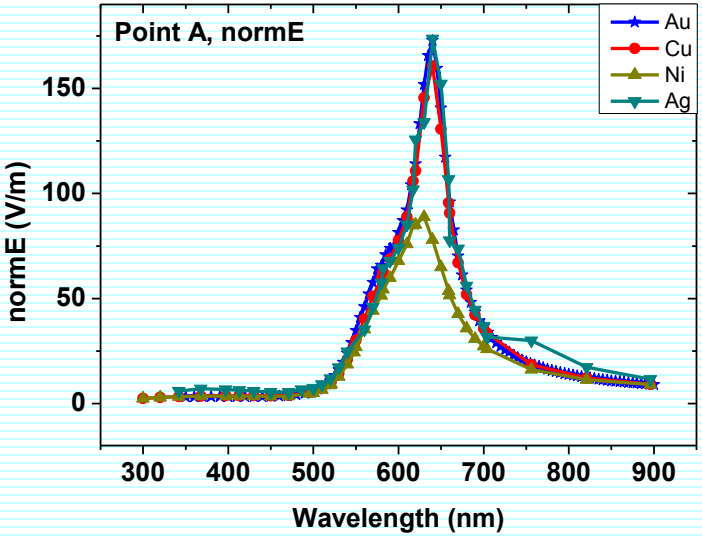


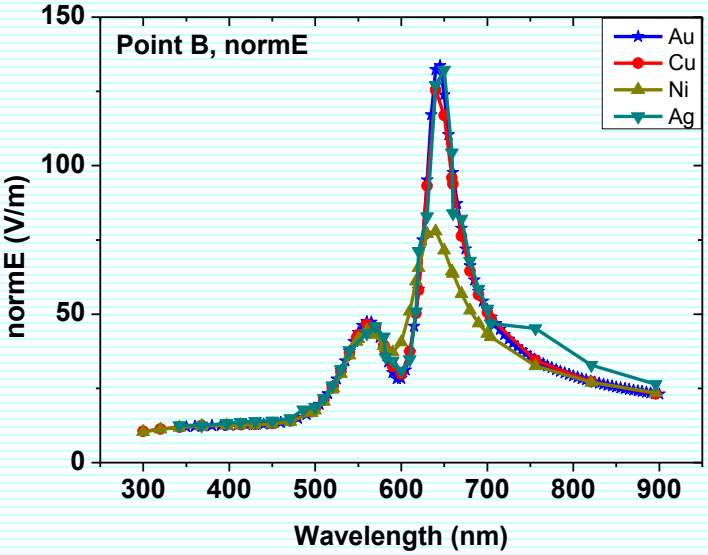
Fano Resonance: Coupled dipole of Nanoparticles induce the imaginary dipole on the metal or dielectric surfaces, to form a magnetic-dipole-like mode. It is the plasmonic dark mode with less irradiative efficiency, but with strong near field.

SHINERS works on single crystal surfaces of different materials beyond Au, Ag, Cu metals



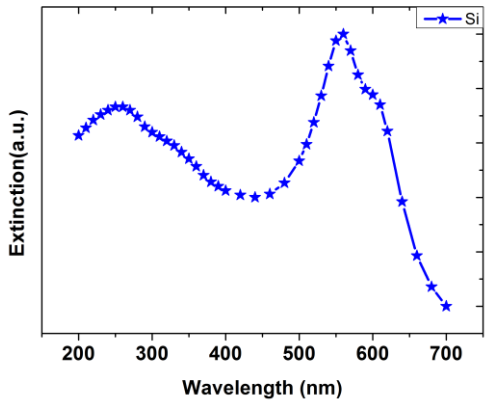


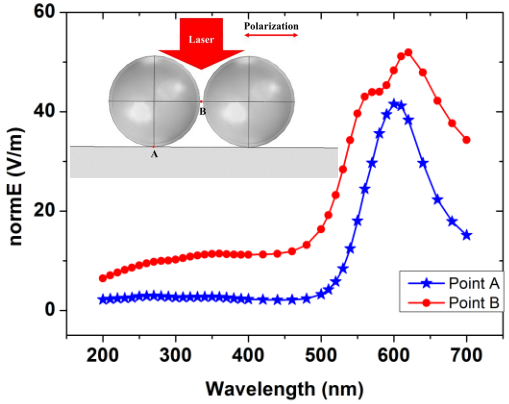


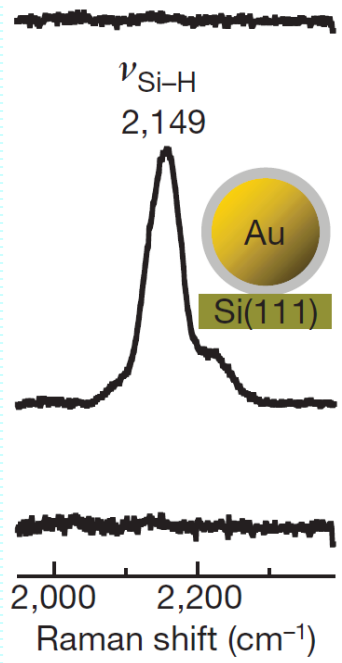


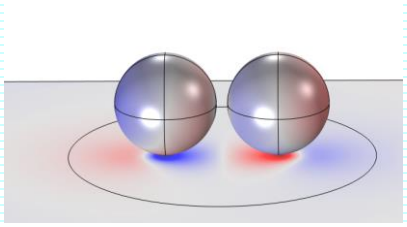
Ding, Yi and Tian, *Surf. Sci.*, 631 (2015) 73-80.

SHINERS of Si-H

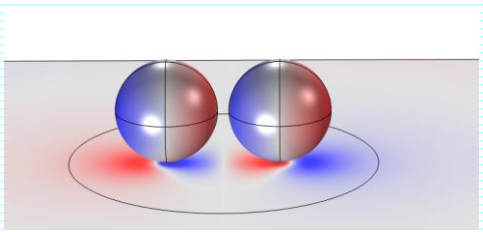




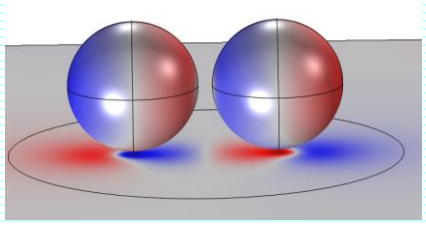




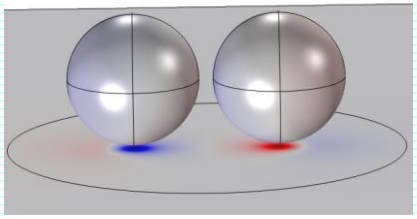
260nm



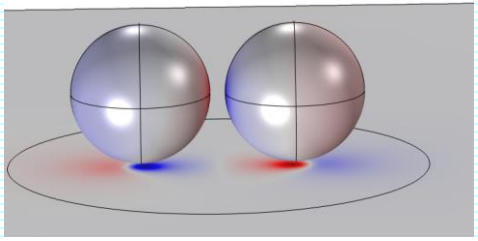
360nm



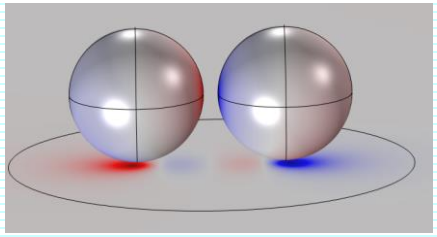
440nm



560nm



600nm

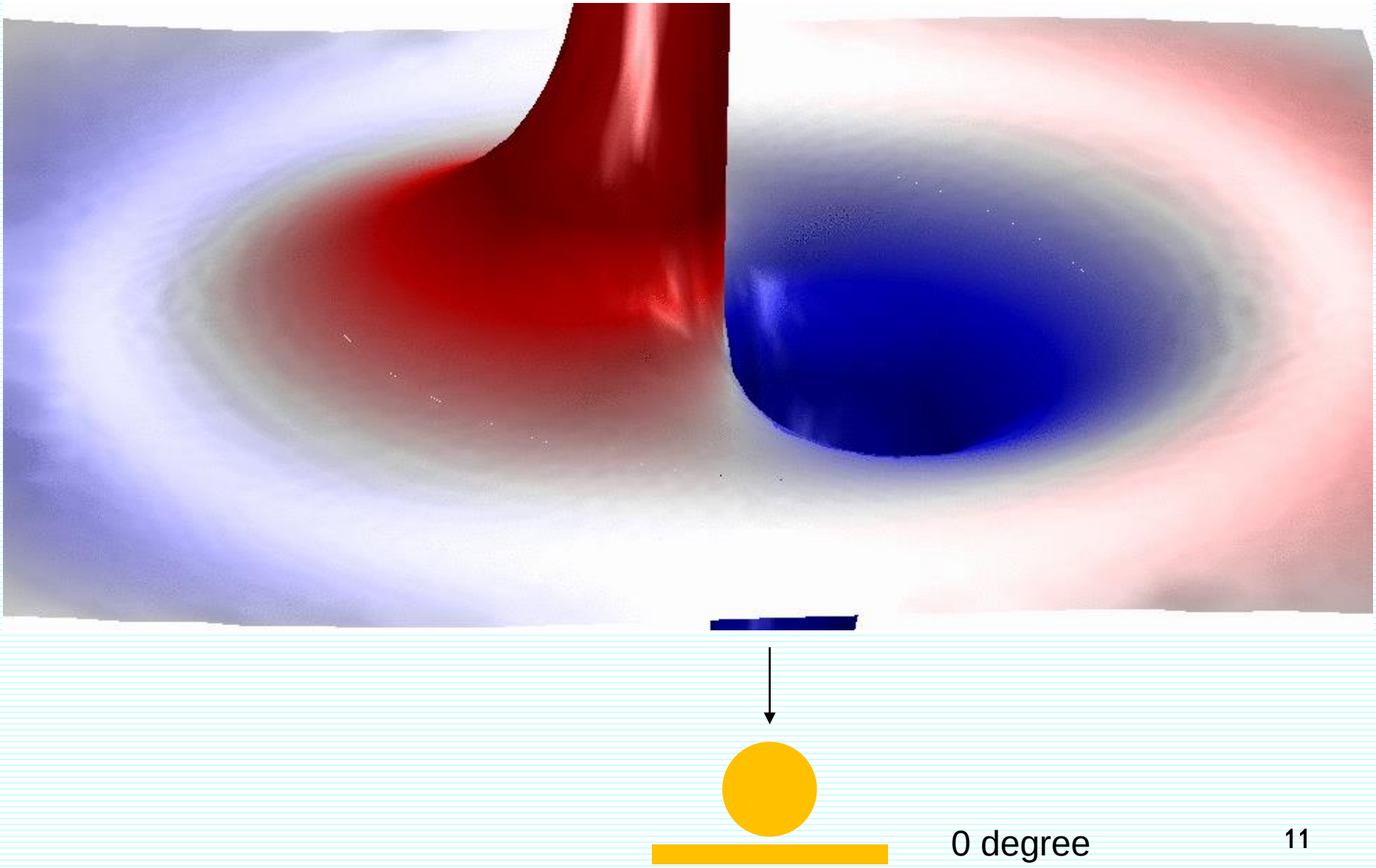


700nm

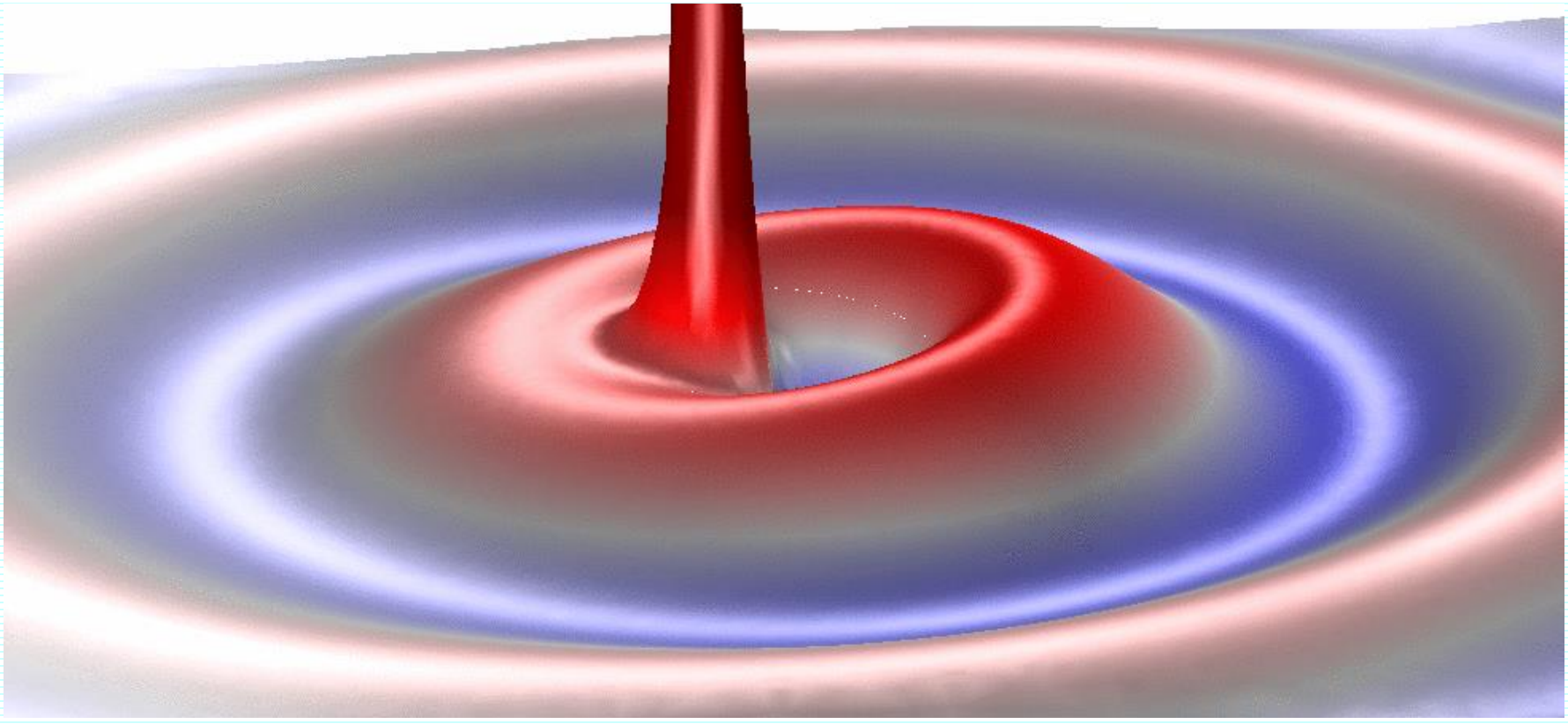
(a) Si(111) treated with 98% H_2SO_4 (b) treated with 30% HF solution, (c) treated with O_2 plasma

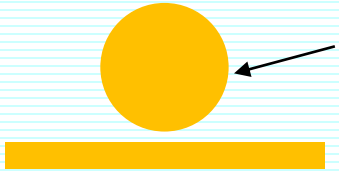
Li et al, *Nature* **464**, 392-395 (2010); Ding, Yi and Tian, Surf. Sci., 631 (2015) 73-80.

There is always a node line underneath a single particle on a flat metal surface



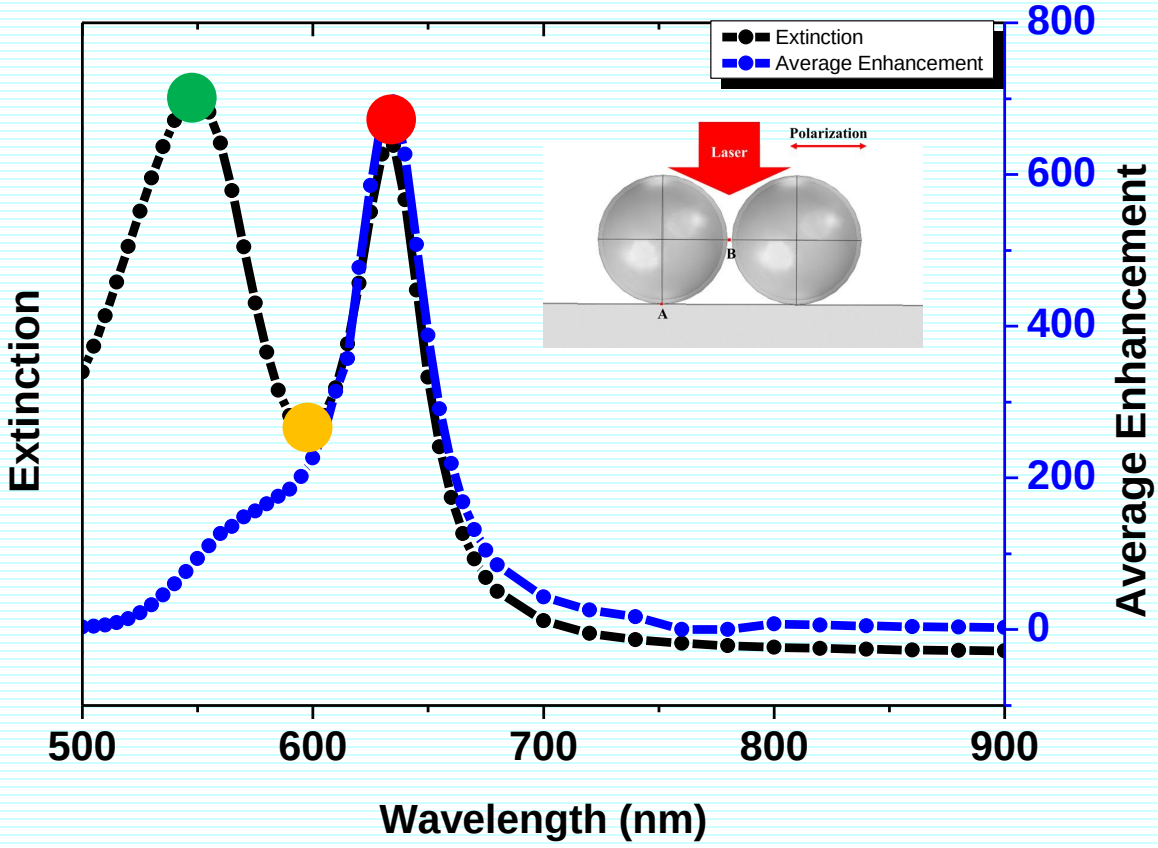
0 degree



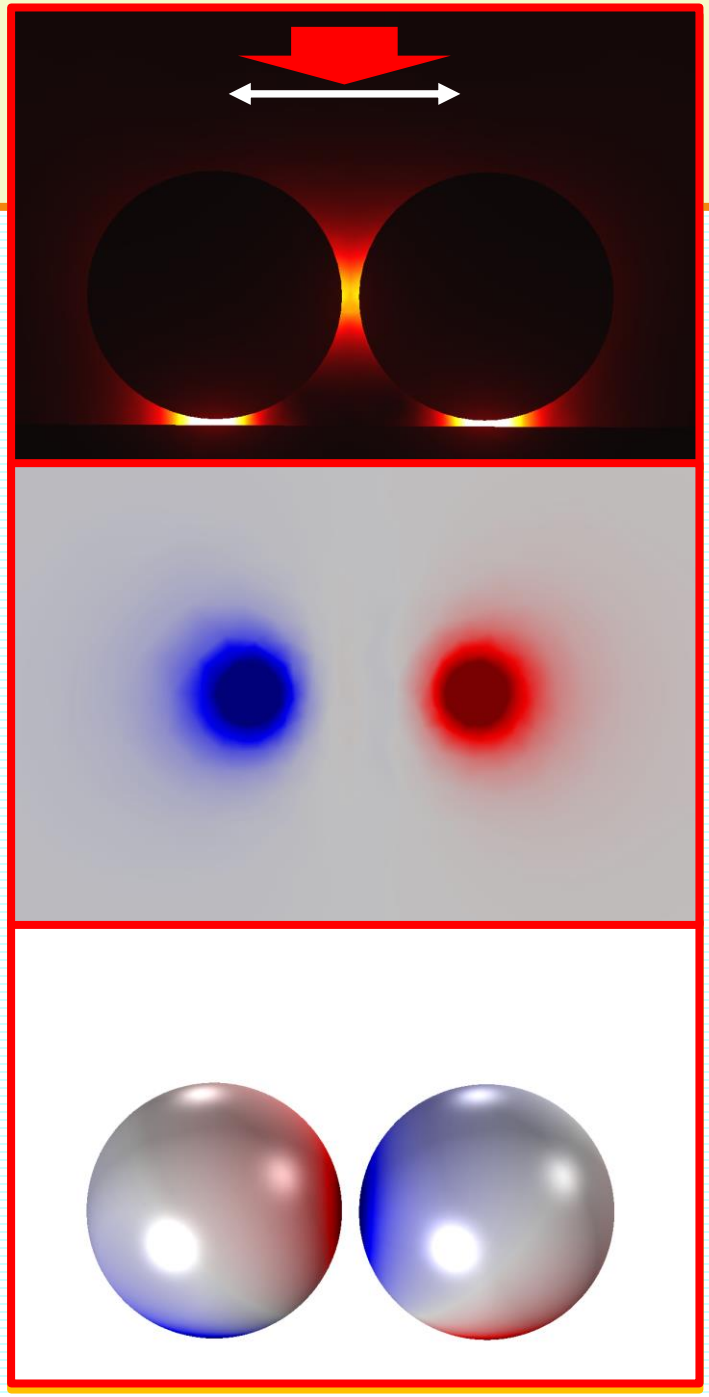


75 degree,

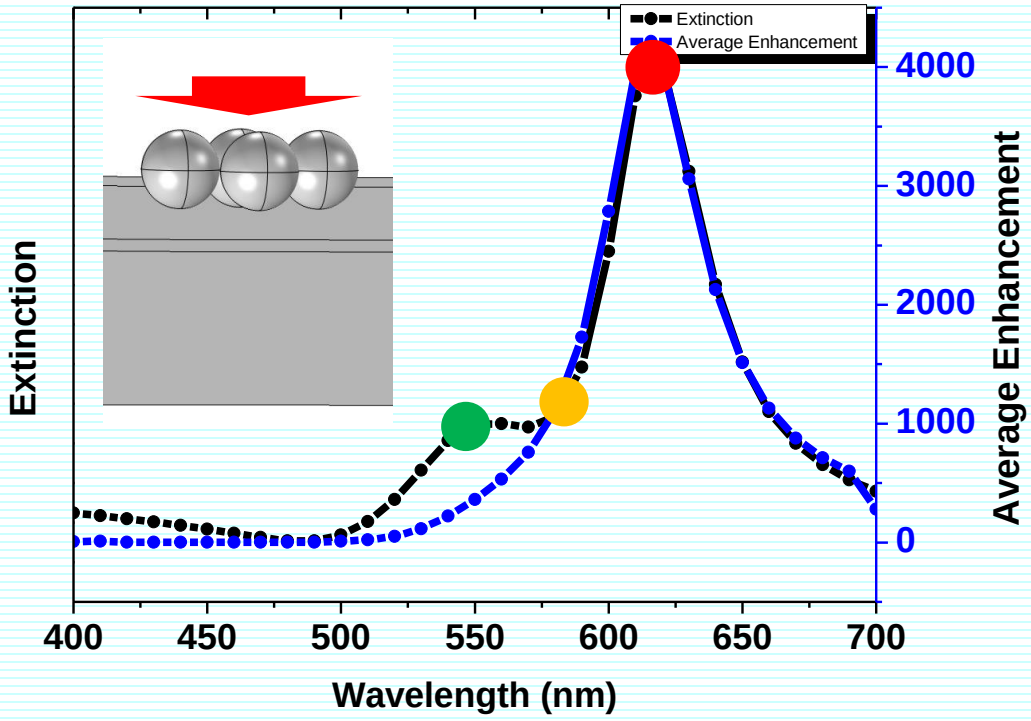
PERS ‘hot domain’?

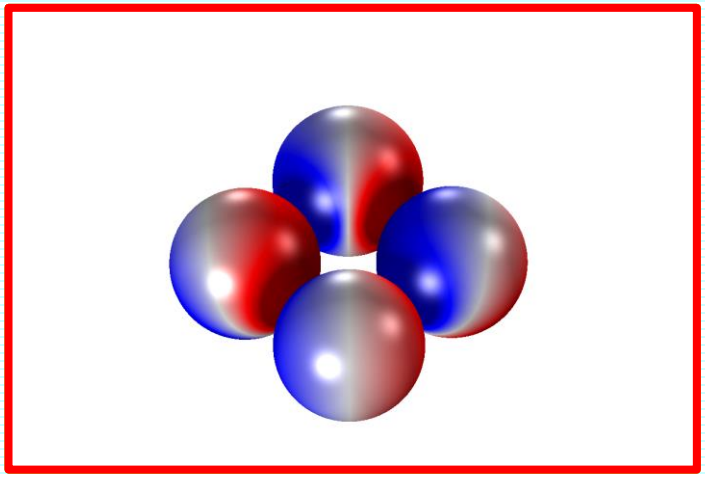


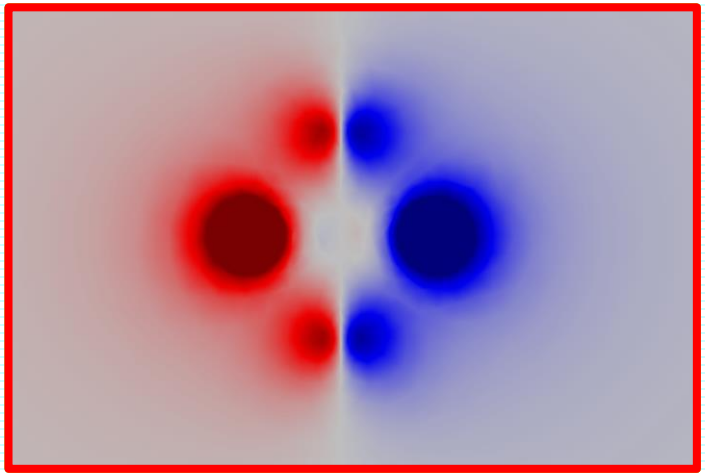
55nm AuNP, d(NP-NP) = 4 nm, d(NP-AuSurf)= 2 nm



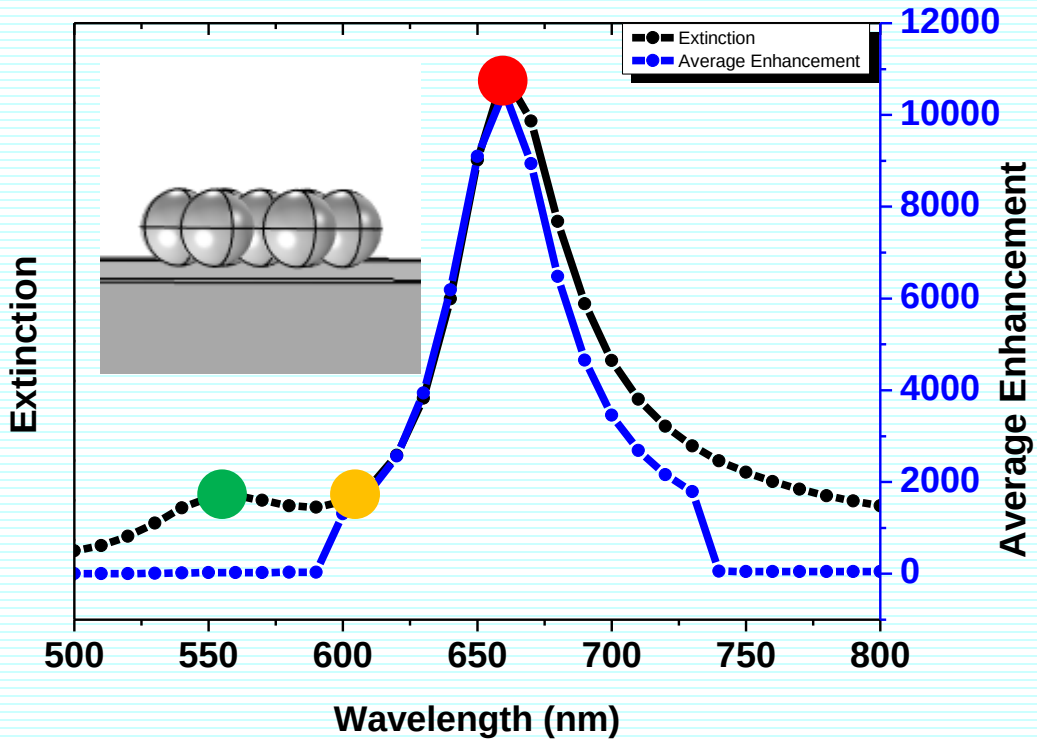
PERS ‘hot domain’?

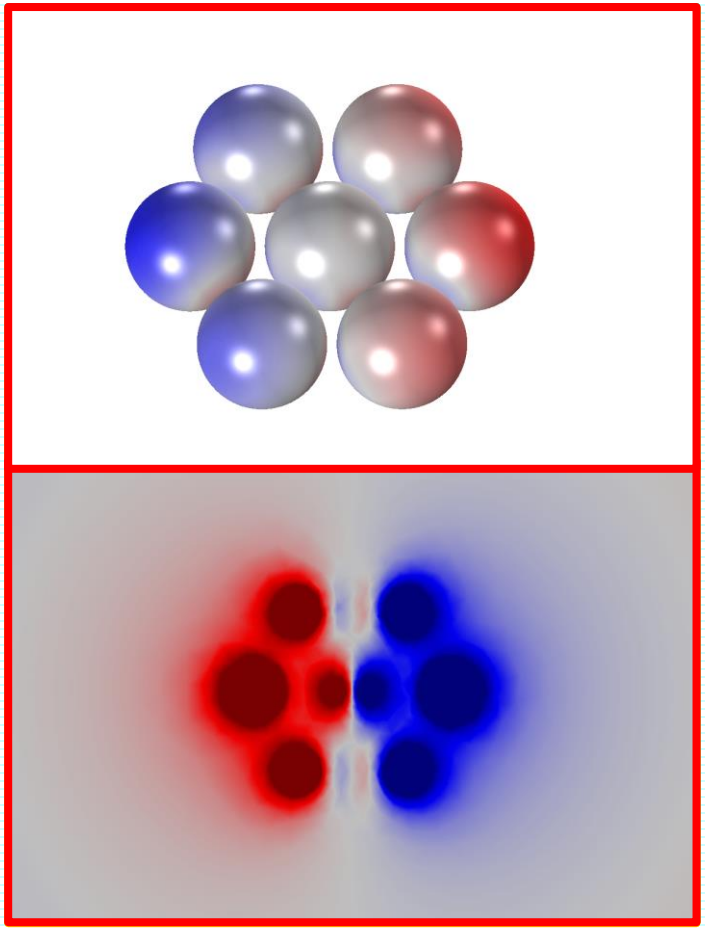


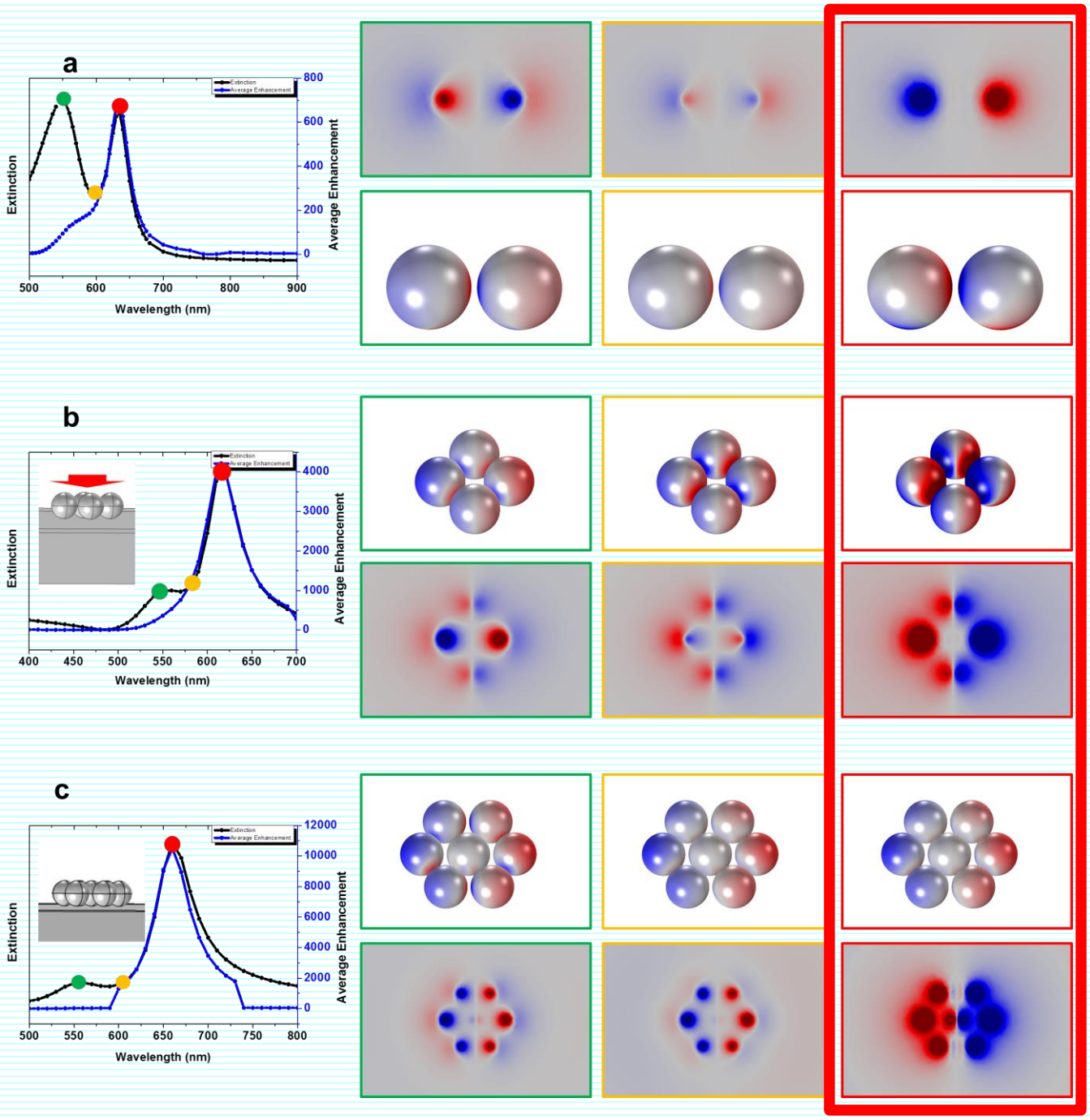




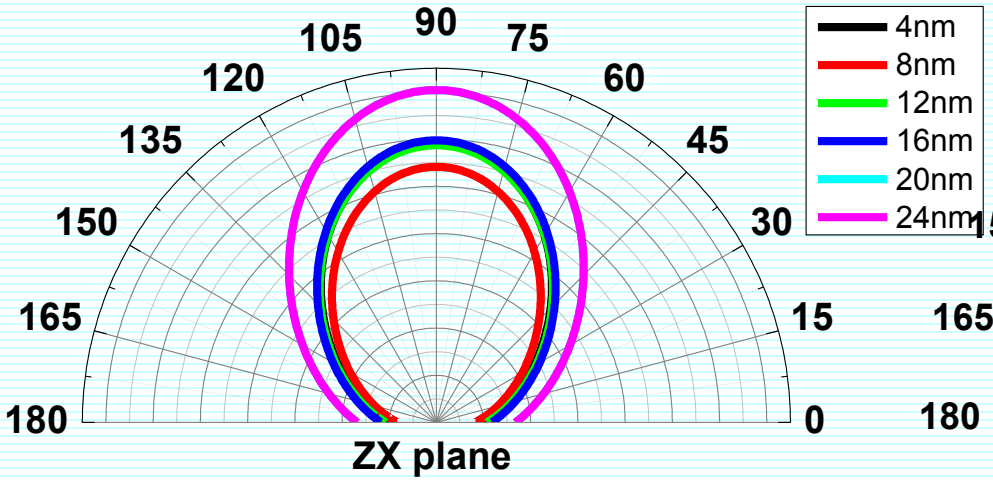
Hot domains created by $AuNS_7$ on a flat Au surface

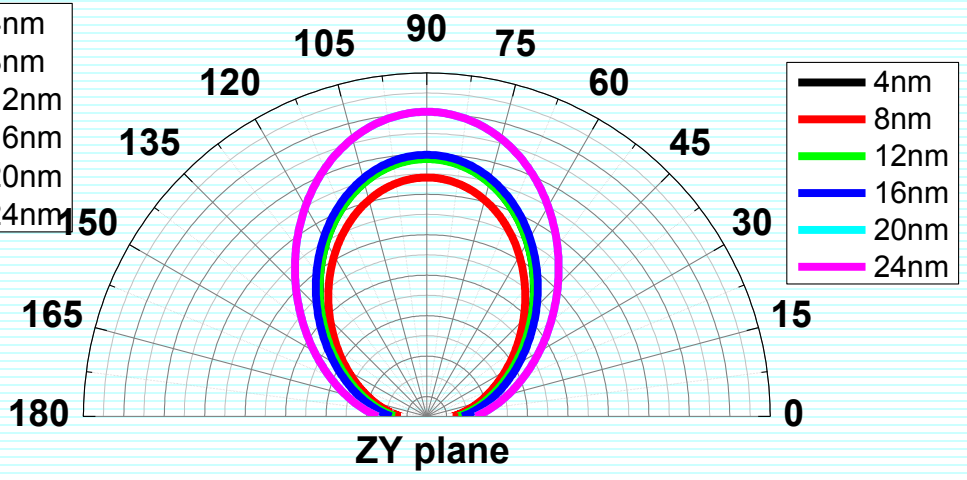


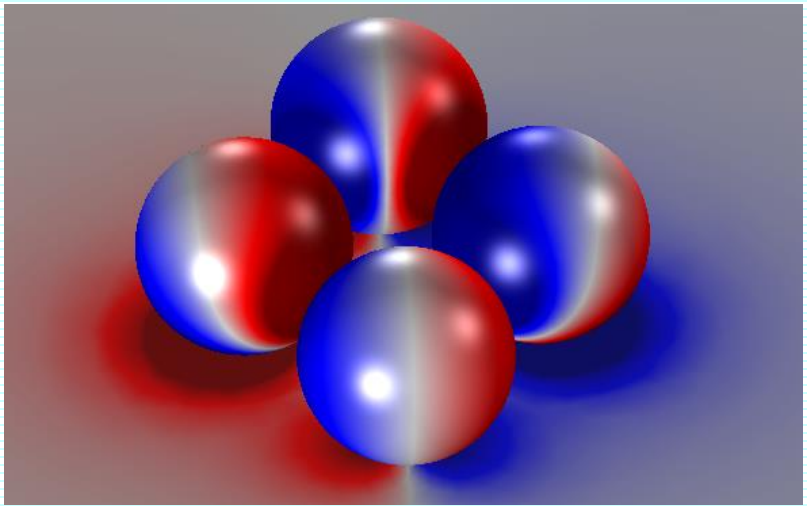


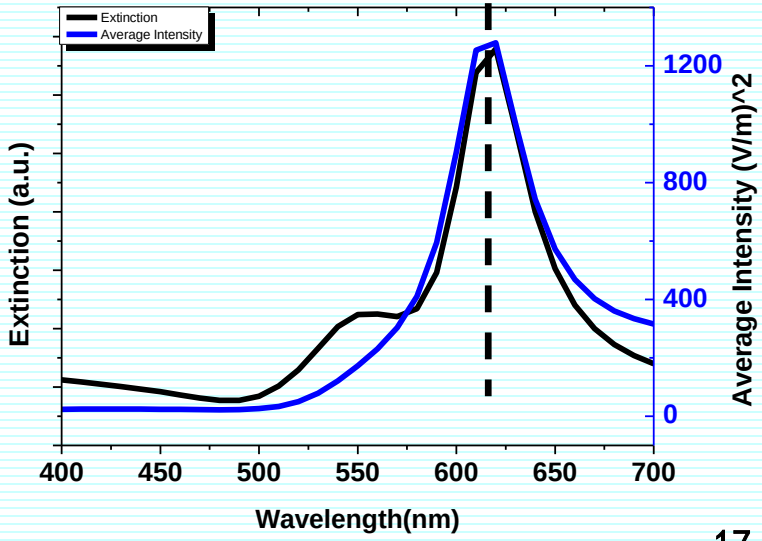

a
Extinction
Average Enhancement
Wavelength (nm)
b
Extinction
Average Enhancement
Wavelength (nm)
c
Extinction
Average Enhancement
Wavelength (nm)

Good directional receiving and emission of AuNPs-Au surfaces









Conclusion

- COMSOL is very useful for the design of novel nanostructures for surface-enhanced Raman spectroscopies
- Care should be taken for evaluation of near-field on the surface of nanostructures
- Tricks on the simulation of a point dipolar source.