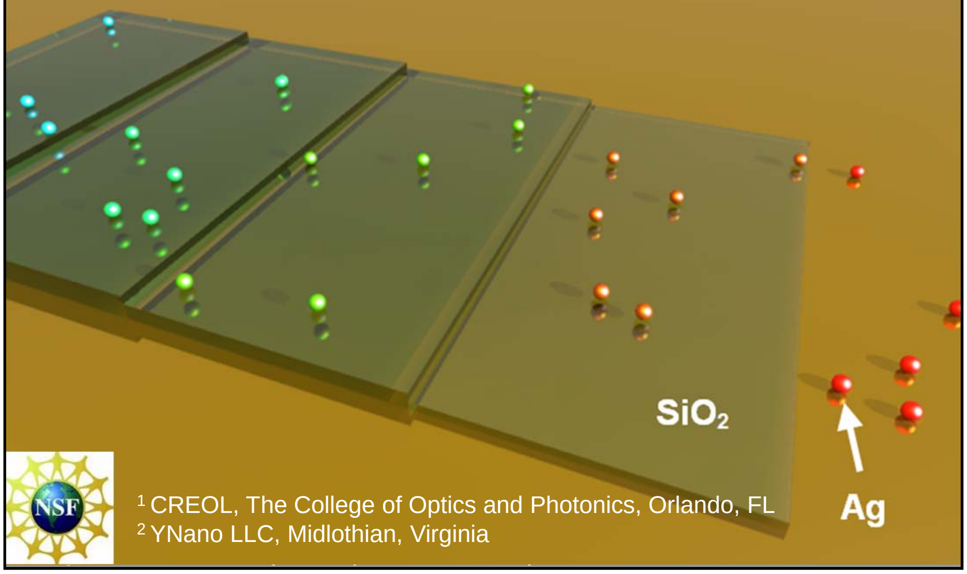
Metal Substrate Induced Control of Ag Nanoparticle Plasmon Resonances for Tunable SERS Substrates

Pieter G. Kik[1], Amitabh Ghoshal[1], Manuel Marquez[2] and Min Hu[1]



[1] CREOL, The College of Optics and Photonics, Orlando, FL
[2] YNano LLC, Midlothian, Virginia

Nanoparticle resonance for SERS

Raman scattering: detection of vib & rot frequencies through optical frequency shift

Weak optical interaction due to configuration dependent polarizability: 'insensitive'

Incident optical fields enhanced ⇒ Raman signal from species near surface increases:

Surface **E**nhanced **R**aman **S**cattering enhancement $$G_{SERS}(r_m,\nu) = \left| \frac{E(r_m,\nu)}{E_{inc}(\nu)} \right|^4$$

Plasmon resonances can enhance local electric field

Achievable field enhancement factors:

- Single noble metal particle: 10-100x — Predicted G_{SERS} 10^4 - 10^8
- Particle clusters, fractals: >100x — Single molecule Raman signals detected

Nanoparticle plasmons provide signal enhancement at specific frequencies

Enhancing local fields using surface plasmon resonance

Spherical metal particles support **localized surface plasmons**

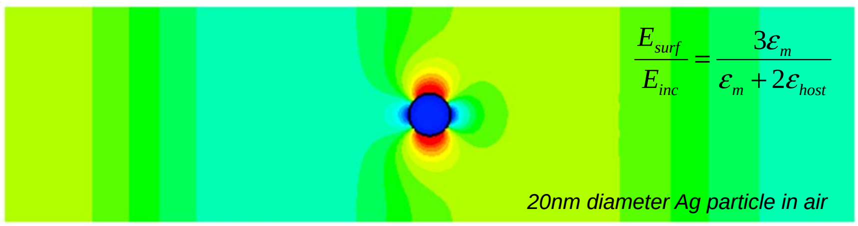
Collective electron oscillations

Strong near-fields at **plasmon resonance frequency**

Typically in UV-visible region of the spectrum

Resonance frequency depends on :

- Metal / Dielectric / **Local environment** / Size / Shape



$$\frac{E_{surf}}{E_{inc}} = \frac{3\varepsilon_m}{\varepsilon_m + 2\varepsilon_{host}}$$

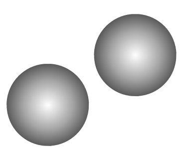
Nanophotonics and Near-field Optics Group http://kik.creol.ucf.edu slide 3

Plasmon resonance tuning

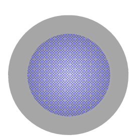
Why do we need control over resonance wavelength?

- wavelength must lie in transparency window of sample
- find optimum balance between Raman cross-section and fluorescence background
- resonance Raman: matching of specific molecular transition wavelengths

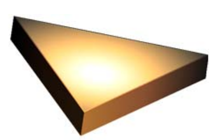
Tuning by : inter-particle interactions / core-shell particles / particle shape



Precise placement needed



Thin shell: electron scattering



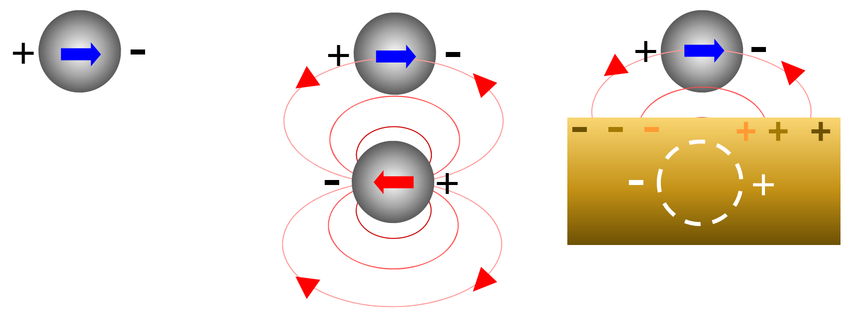
Stability?

Here: control resonance of Ag nanoparticles throughout visible region by placing them near a conductive solid substrate

Nanophotonics and Near-field Optics Group http://kik.creol.ucf.edu slide 4

Tuning particle resonances through dipole-dipole interaction

Isolated dipole | anti-parallel dipoles | dipole + antiparallel image



ω_{LSP} given by charge density, shape

ω_{LSP} reduced by field from neighboring NP

ω_{LSP} reduced by field from image charges

⇒ Expect to achieve tuning by placing silver NP near conductive substrate

Sample preparation

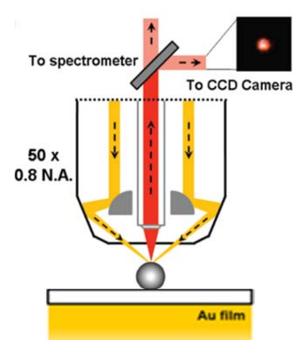
- **Tuning layer:** Sputter deposition **of** 50nm Au film
- **Spacer layer:** Deposition of 10-40nm SiO_2 layer (PECVD)
- **Nanoparticles:** Ag colloid solution (60nm diameter) + PVP (adhesion)
- Droplet placed on sample, removed by air flow

⇒ Typical NP densities **~10 Ag np / 30 × 30 μm²**

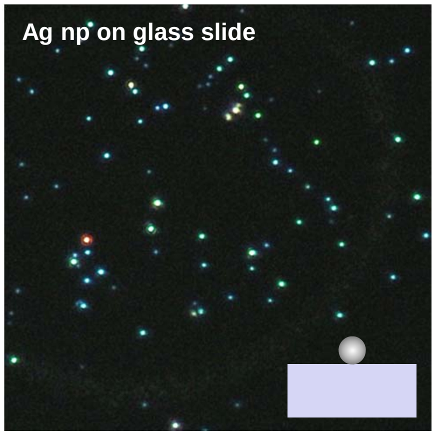
Measurements:

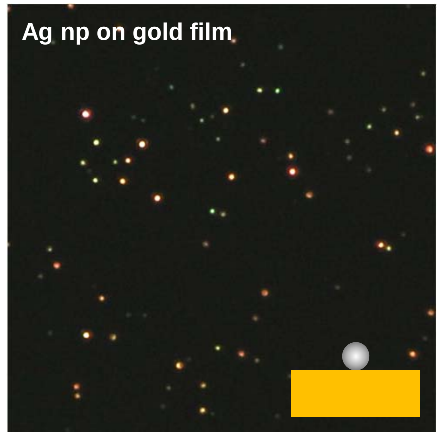
- Dark-field microscopy (50x objective)
- Dark-field spectroscopy using MM optical fiber (core size 200 μm)

⇒ **Scattering spectra of isolated Ag nanoparticles**



Darkfield microscopy – limiting cases



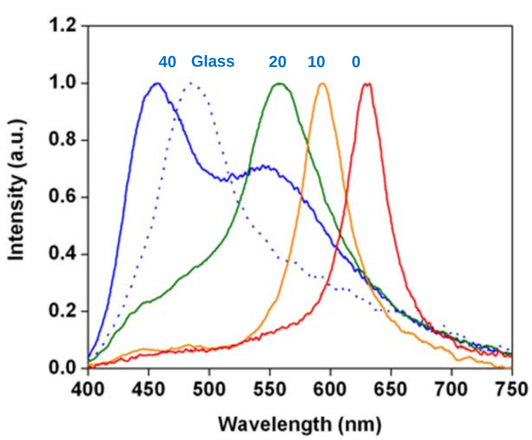


Ag nanoparticles on glass: scattering in blue region of spectrum

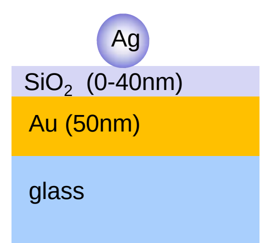
Ag nanoparticles on gold: strongly red-shifted resonance

Quantitative analysis of maximum shift: need **single-particle spectroscopy**

Nanoparticle resonance vs. distance to surface



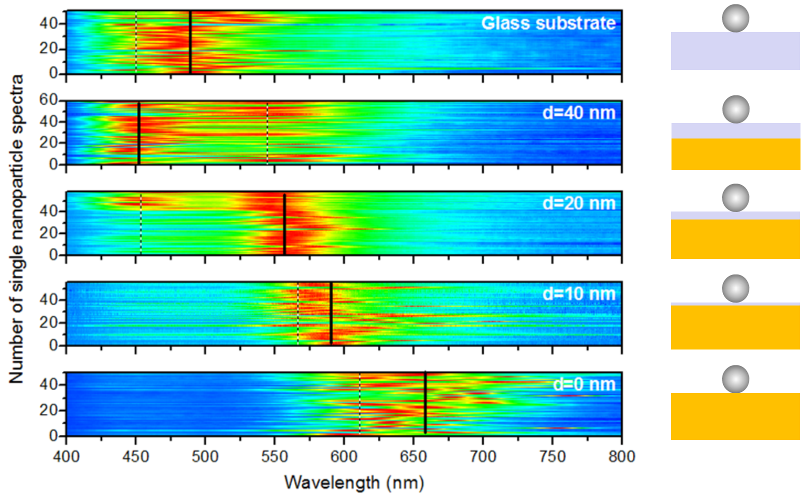
Signal = (np-dark)/(ref-dark)



Large tuning range observed with <50nm SiO_2 ($\Delta\lambda_{res}$ ~ 200nm)

Note: to obtain similar tuning range by shape tuning, need AR = 1:1:5

Reproducibility of substrate-based resonance tuning



Reproducible tuning throughout visible spectrum with single Ag NP

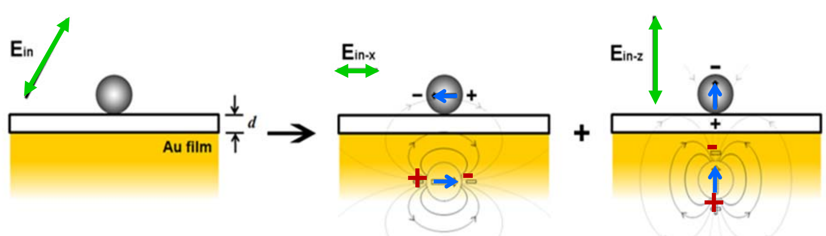
Multiple peaks; multipolar modes? roughness? polarization dependence?

Possible origin of double peak resonances

Convergent illumination: incident light contains normal polarization

Polarization dependence (assuming perfect conducting substrate)

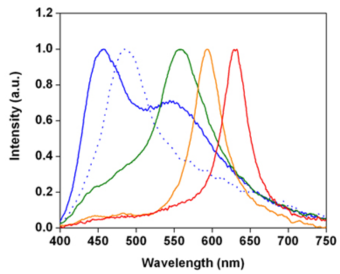
- Lateral dipole : anti-aligned image dipole ⇒ reduced ω_{SP}
- Vertical dipole : aligned dipole ⇒ reduced ω_{SP}

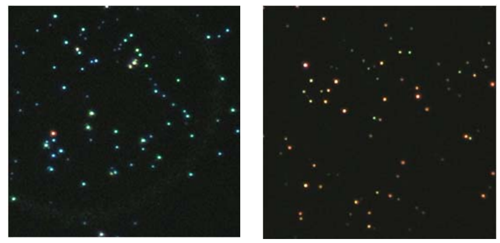


Dipole field distribution: vertical dipole ⇒ stronger coupling

Conclusions

Nanoparticle plasmon resonance frequency of single spherical Ag particles can be tuned throughout entire visible spectrum





J. Phys. Chem. C 144, 7509 (2010)

Substrate tuning combines:

- Thermodynamic stability (compared to nanorods, bow-tie antennas, ..)
- Thermally stable substrate (compared to organic spacer layers)
- Precise control of particle-image dipole spacing

Nanophotonics and Near-field Optics Group http://kik.creol.ucf.edu slide 11

CREOL, The College of Optics and Photonics - Dean: Bahaa Saleh