

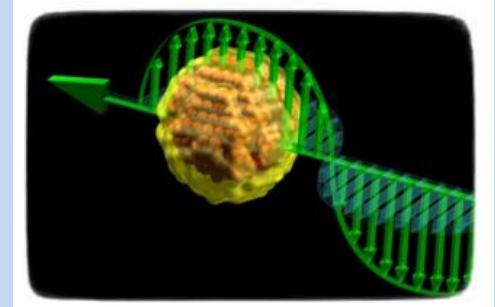
Magneto-optics and Magnetoplasmonics

César de Julián Fernández



IMEM-CNR Parma

Magnetic Materials Group



Advanced magnetic materials and devices for biomedical applications

Italian School of Magnetism

Turin , 21-25 May 2018

1. Magneto-optics

- a General phenomenology and materials
- b Applications of plasmonics in bio

2. Plasmonics

- a General phenomenology and materials
- b Applications of plasmonics in bio

3. Magnetoplasmonics

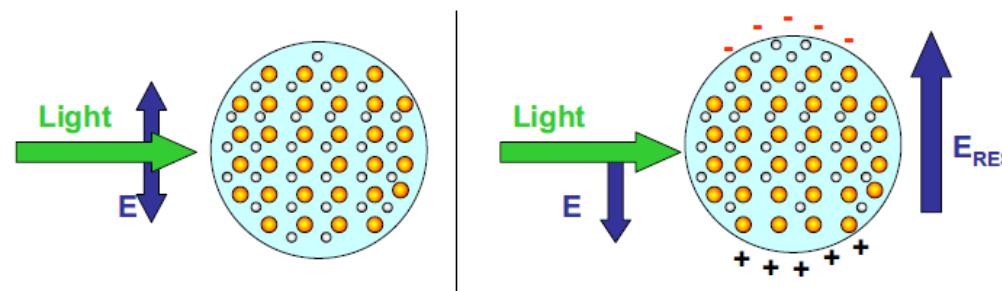
- a Plasmonics and magnetism?
- b Magnetoplasmonics materials and phenomena
- c Applications in bio

Plasmons are resonant modes that involve the interaction between free charges and electro(magnetic) field

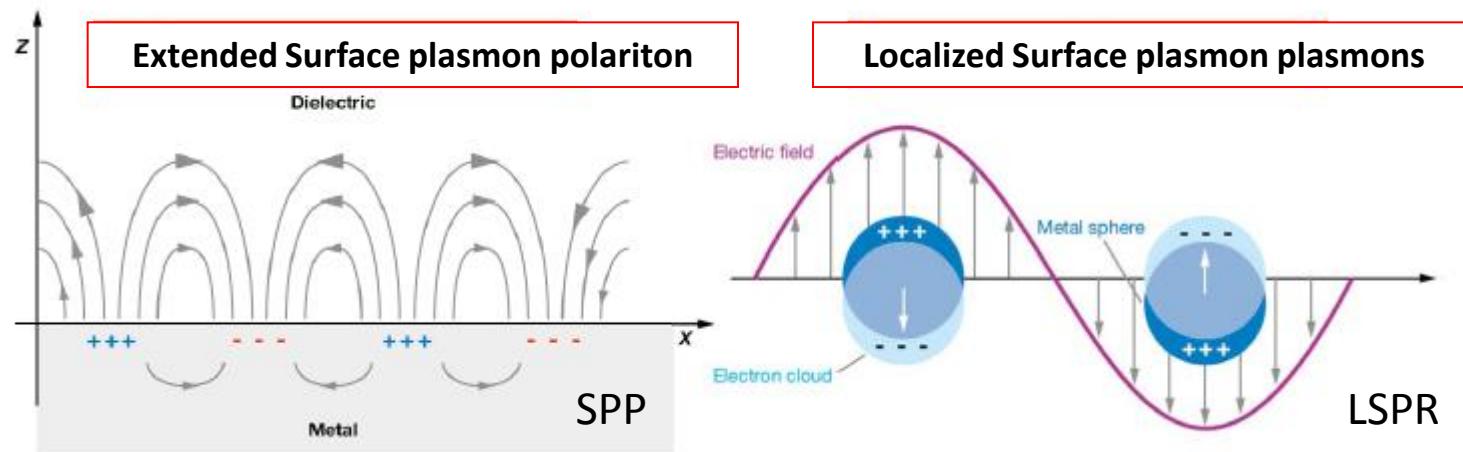


What are surface plasmons?

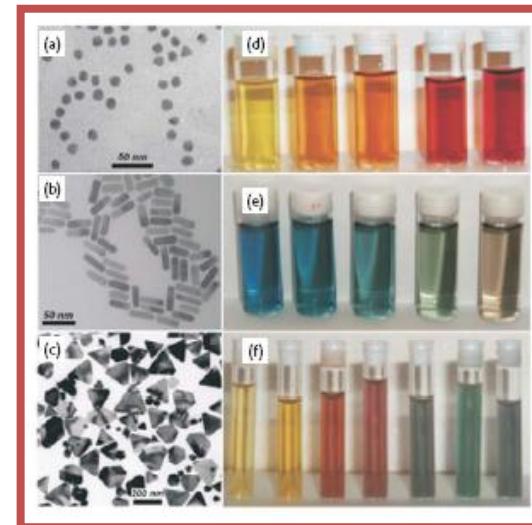
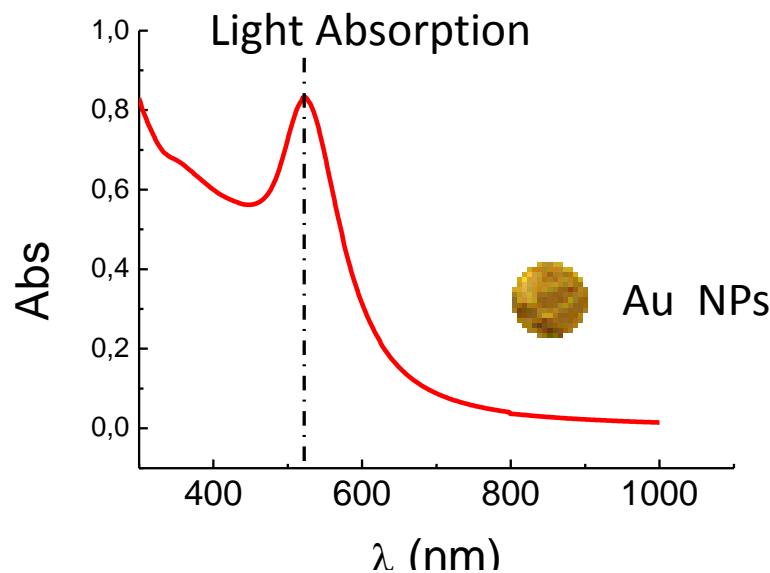
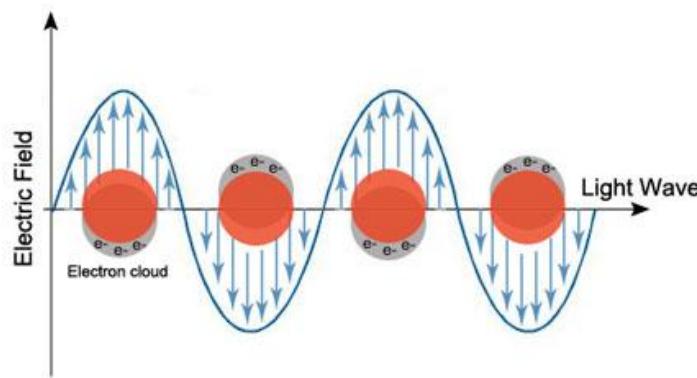
Surface Plasmons are collective oscillations of the surface free charges in an interface between two media with permittivities (dielectric constants) with opposite sign,
e.g. a dielectric and a metal



Surface Plasmon Resonance

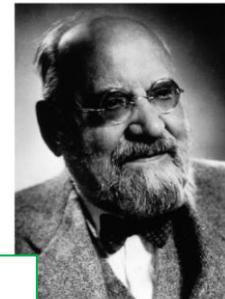


Localized Surface Plasmon Resonance (LSPR)



Mie Model

G. Mie, Annalen der Physik 330 (1908) 377

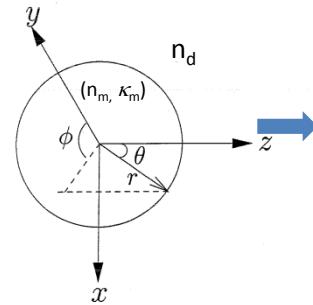


GUSTAV MIE
(1868 – 1957)

Maxwell equations

$$\begin{aligned}\nabla \cdot \mathbf{D} &= \rho \\ \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \\ \nabla \times \mathbf{H} &= \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}\end{aligned}$$

Incident radiation



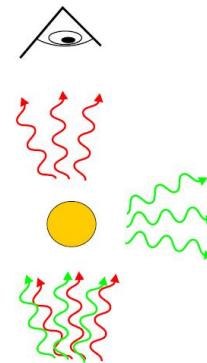
$$\sigma_{\text{ex}} = \frac{2\pi}{|k^2|} \sum_{L=1}^{\infty} (2L+1) \cdot \text{Re}[a_L + b_L]$$

σ_{ex} Extinction cross section

$k = n_d/\lambda$ Cross section of the dielectric
 $a_L, b_L (D, n_d, n_m, \kappa_m)$

Colour

$$\sigma_{\text{ex}} = \sigma_{\text{sc}} + \sigma_{\text{abs}}$$



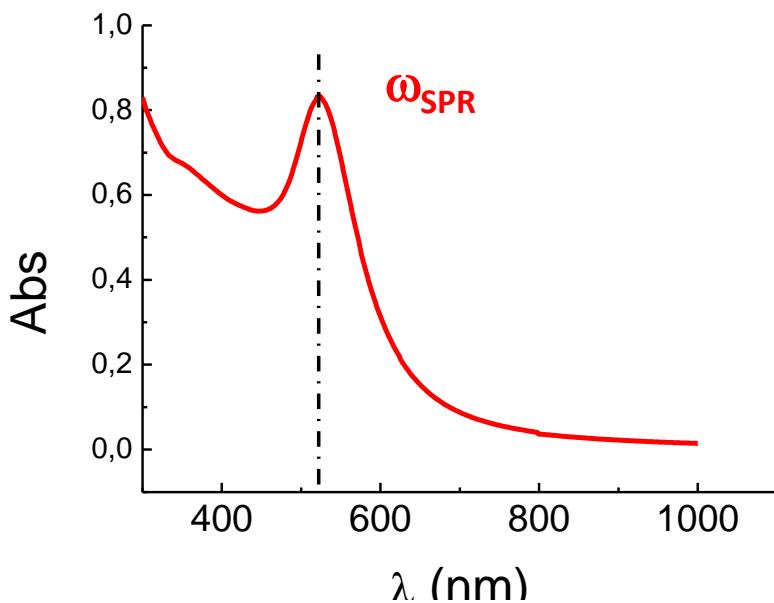
$$\text{Nano} \quad \sigma_{\text{ex}} = \sigma_{\text{sc}}$$



Mie Model: The dipolar approximation

- ϵ_m real
- Size $<< \lambda$
 - No scattering
 - Dipolar mode ($L=1$)
- Non interacting (diluted)
- Spherical Particles

$$\sigma_{\text{ext}} = \frac{24\pi^2 R^3 \epsilon_m^{3/2}}{\lambda} \frac{\epsilon_2}{(\epsilon_1 + 2\epsilon_m)^2 + \epsilon_2^2}$$

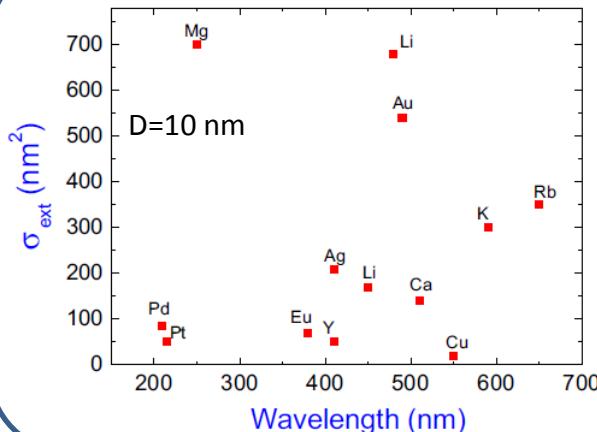


Frequency resonance

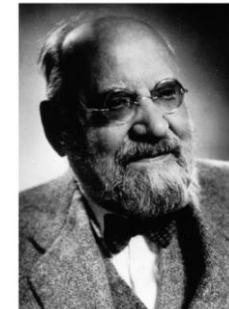
$$\begin{aligned} & (\epsilon_1(\omega_{\text{SPR}}) + 2\epsilon_m(\omega_{\text{SPR}}))^2 + \epsilon_2^2(\omega_{\text{SPR}}) = 0 \\ & \epsilon_1 = -2\epsilon_m \end{aligned}$$

Mie Model

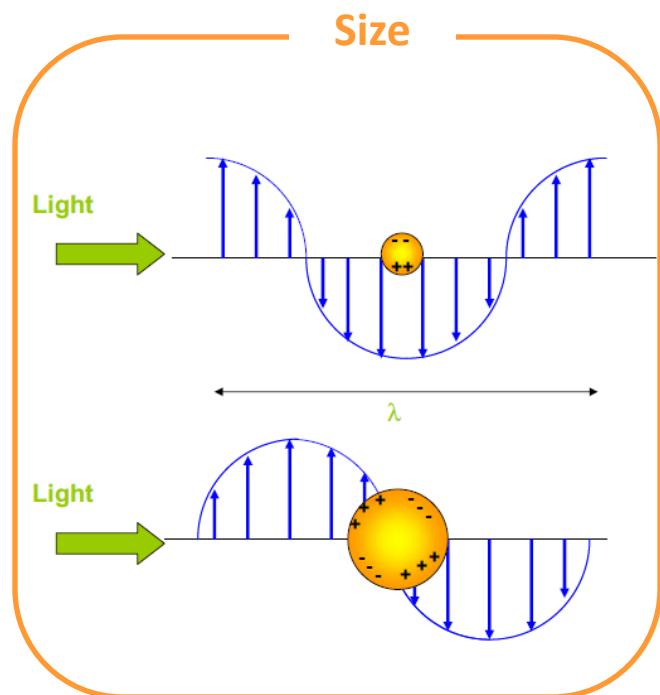
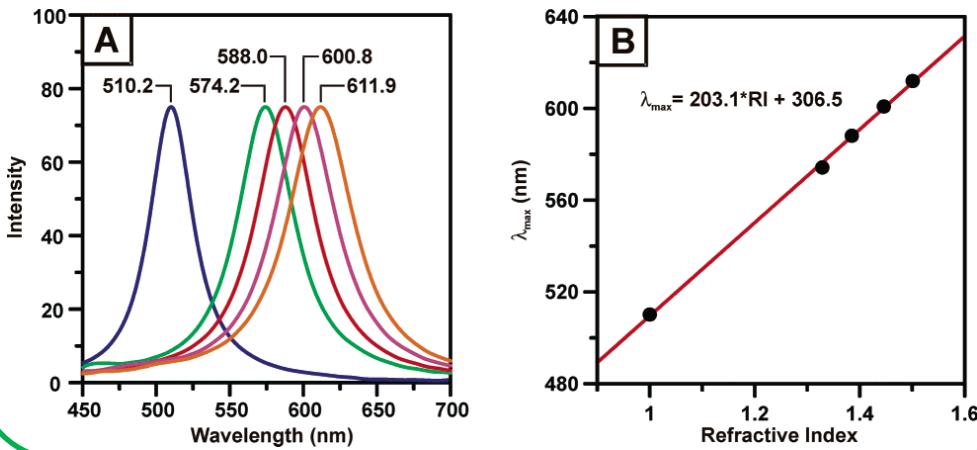
Composition



$$\sigma_{\text{ex}} = \frac{2\pi}{|k^2|} \sum_{L=1}^{\infty} (2L+1) \cdot \text{Re}[a_L + b_L]$$



Matrix



Mie Model The dipolar approximation is a painting of the SPR

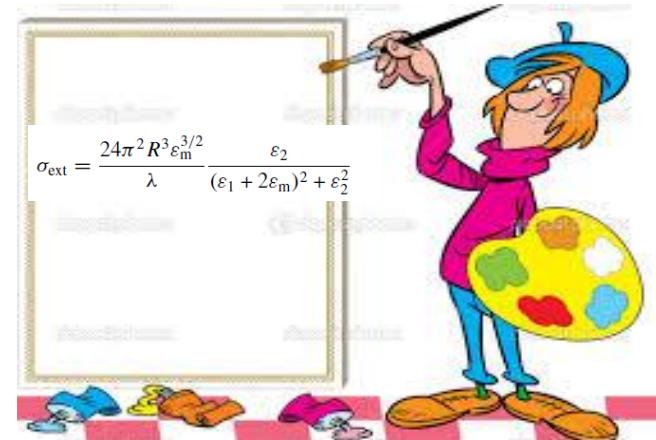


Physicist



Be a spherical cow with
No friction

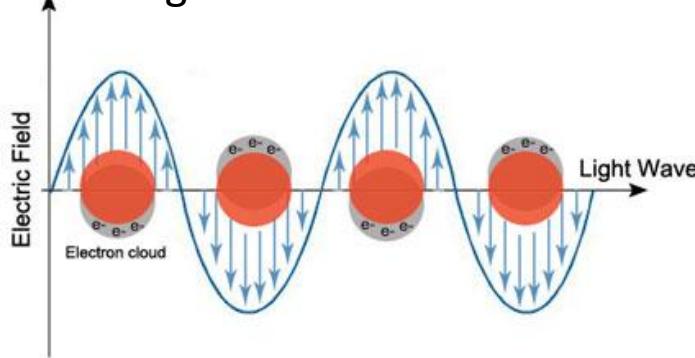
Plasmonist



Be a spherical non-interacting
dipolar cow

Localized Surface Plasmon Resonance (LSPR)

Interaction of the light with a confined metallic nanostructure



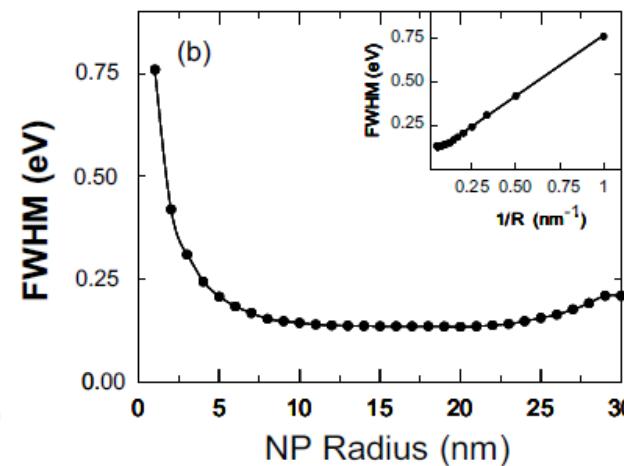
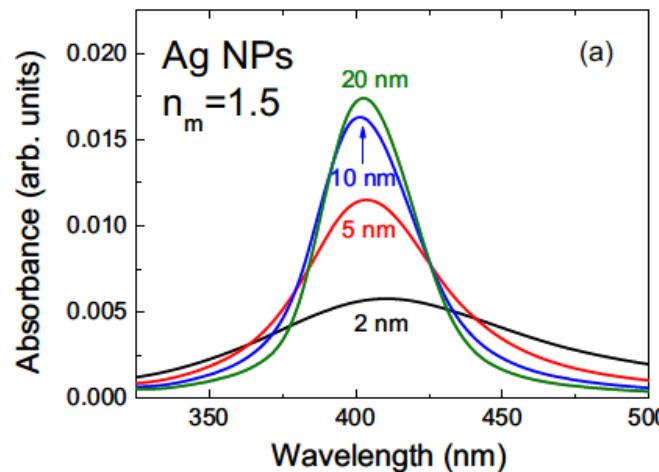
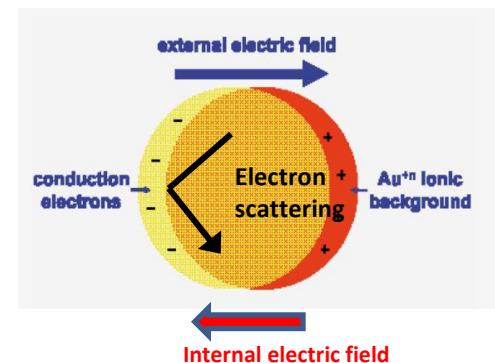
Radiation	Interaction	Materials	Sizes
Visible	Electric (Dipolar)	Al, Au, Ag, Cu Ni, Co, Fe, NiFe	Nanometric
Infrared	Electric	Doped-ZnO, ITO, Semiconductors	Nanometric
Microwaves	Magnetic	Magnetic Garnets	mm-cm

Plasmonic resonance and size effects

Chemical dumping

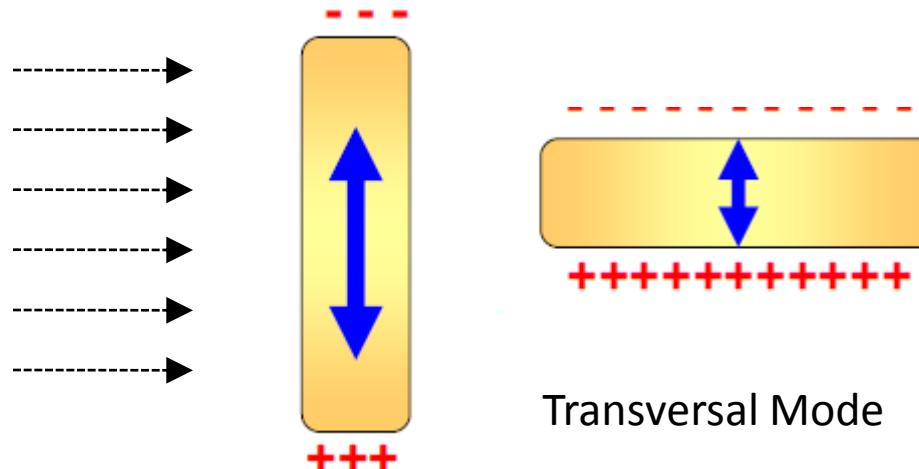
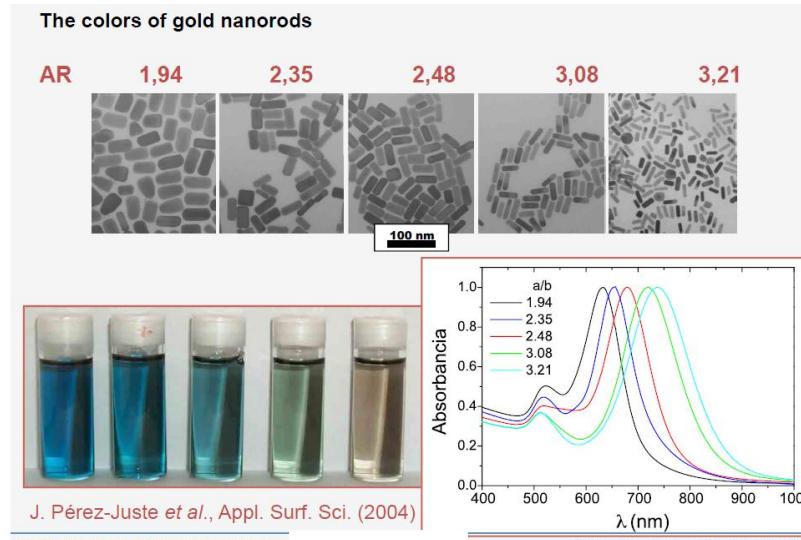
$$\varepsilon_{ef}(\omega) = \varepsilon_{int} - \frac{\omega_p^2}{\omega^2 + \gamma_{ef}^2} + i \frac{\omega_p^2 \gamma_{ef}}{\omega(\omega^2 + \gamma_{ef}^2)}$$

$$\gamma_{ef} = \gamma_b + A \frac{v_F}{D} \quad \gamma_b = \frac{v_F}{\lambda_{mfp}} \quad \sigma_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2}$$



Size influences both SPR frequency and width of the peak

SPR and Shape

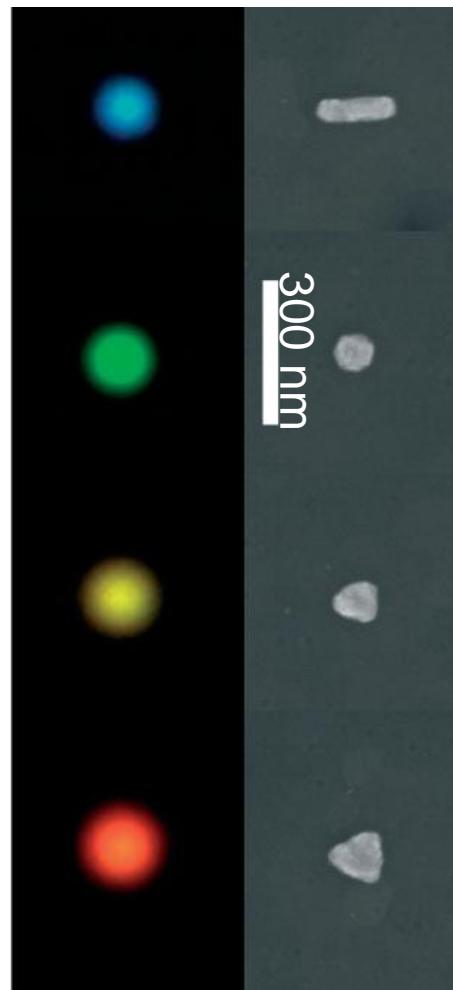
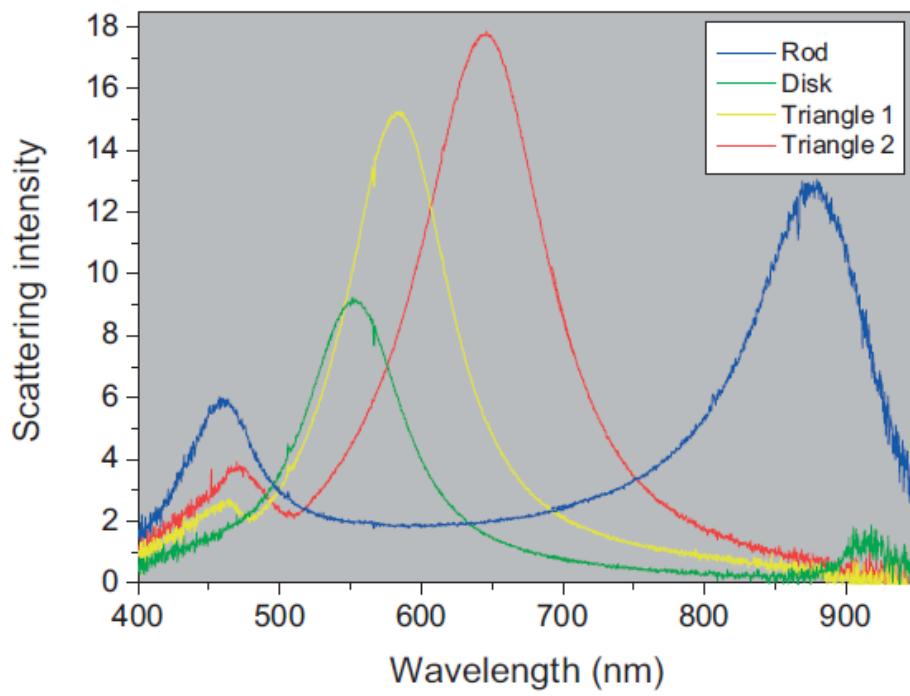


Longitudinal Mode

Transversal Mode

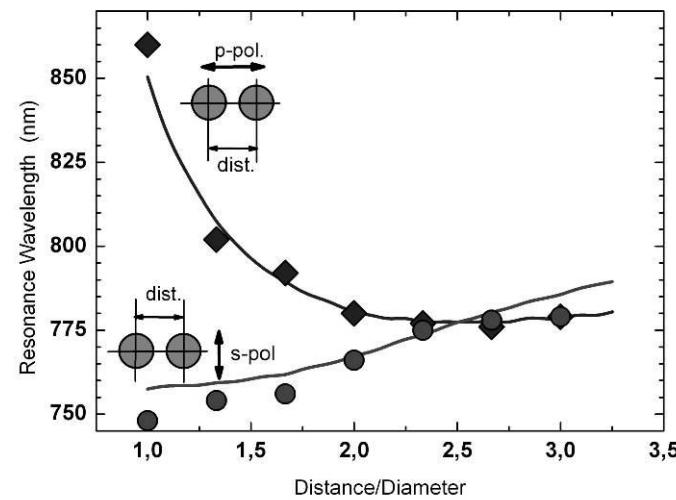
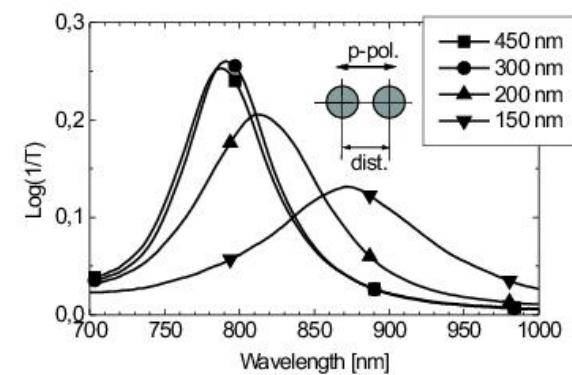
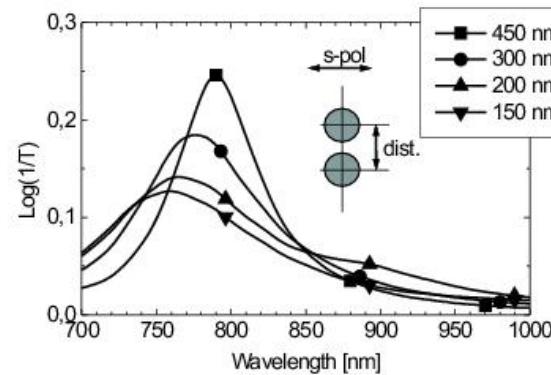
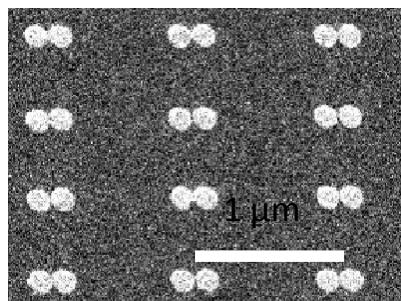
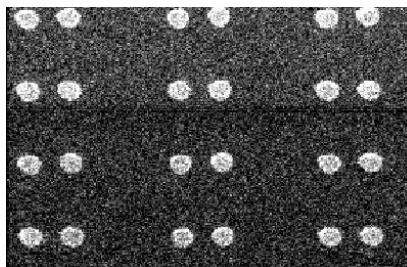
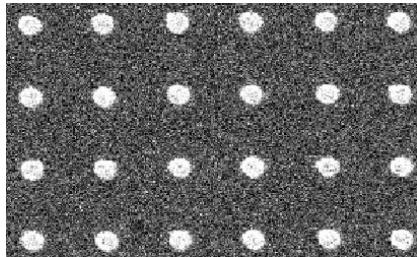
SPR and shape

DF spectra



SPR, local effects and interactions

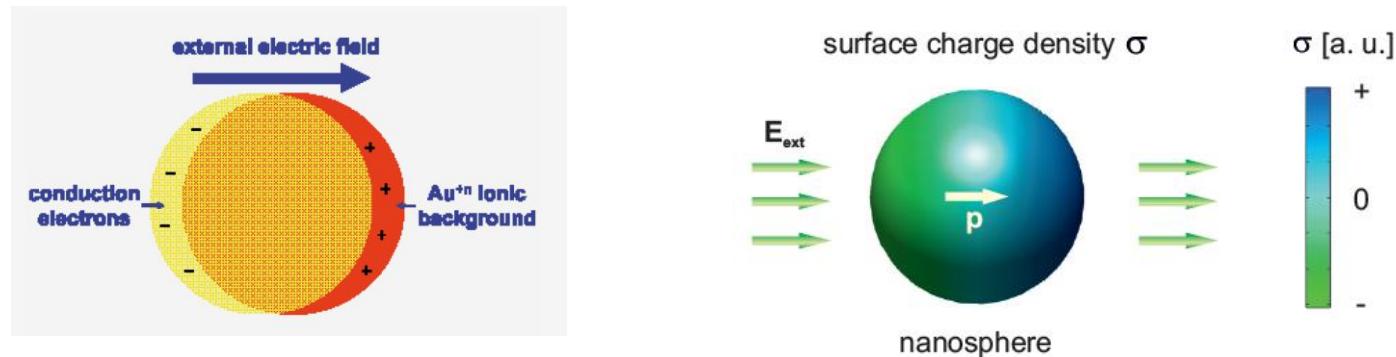
Near-field coupling of particle plasmons



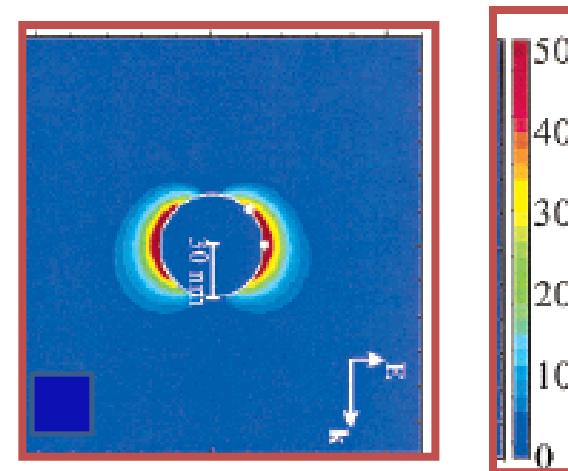
Aggregates ≠ Isolated NPs

SPR, local effects and interactions

Strong localization of charge density



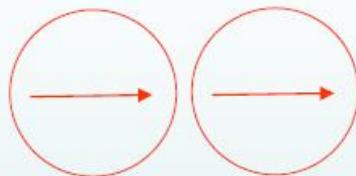
Huge Electromagnetic field localization



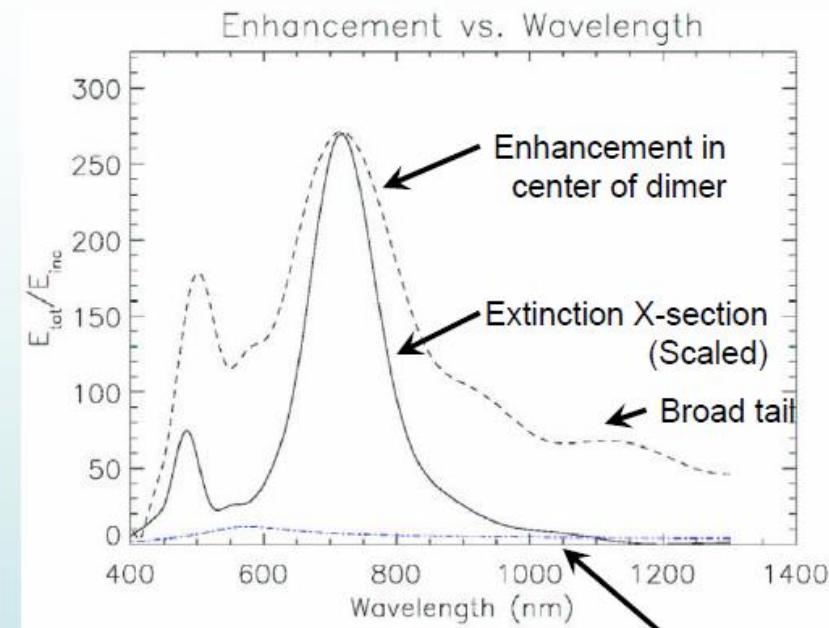
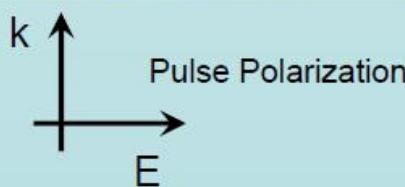
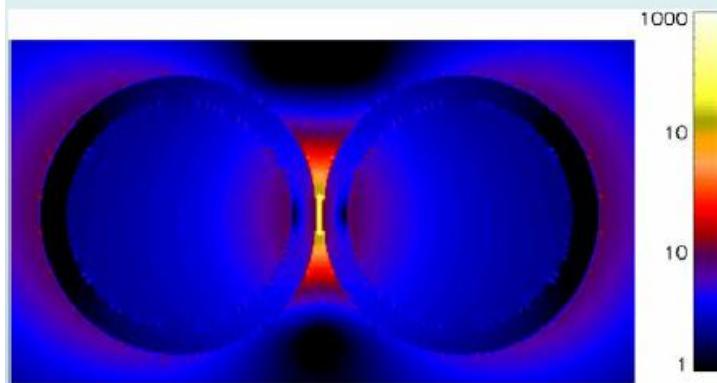
Modifies
dumping and
resonance

SPR, local effects and interactions

Symmetric dimer plasmon



Electric field enhancements
Ag(39,48) dimer, DD=1.5nm at 718nm

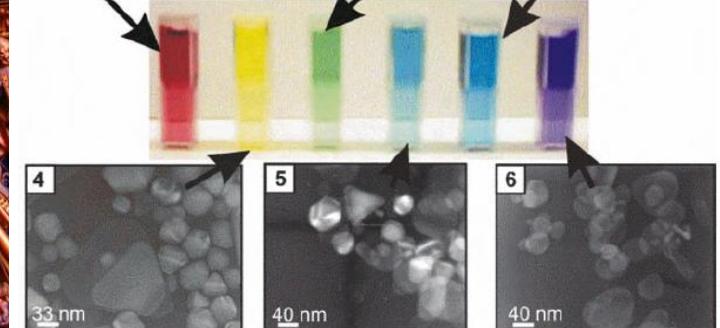
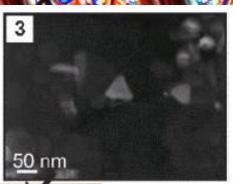
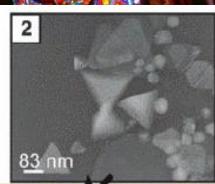
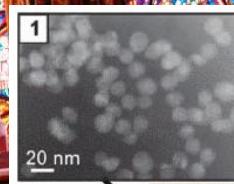
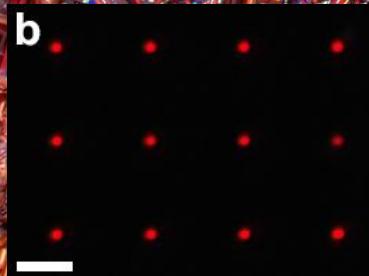
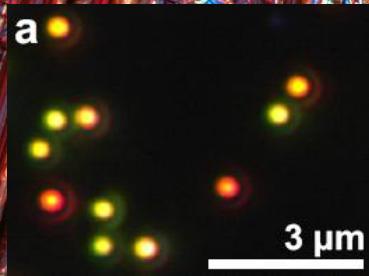
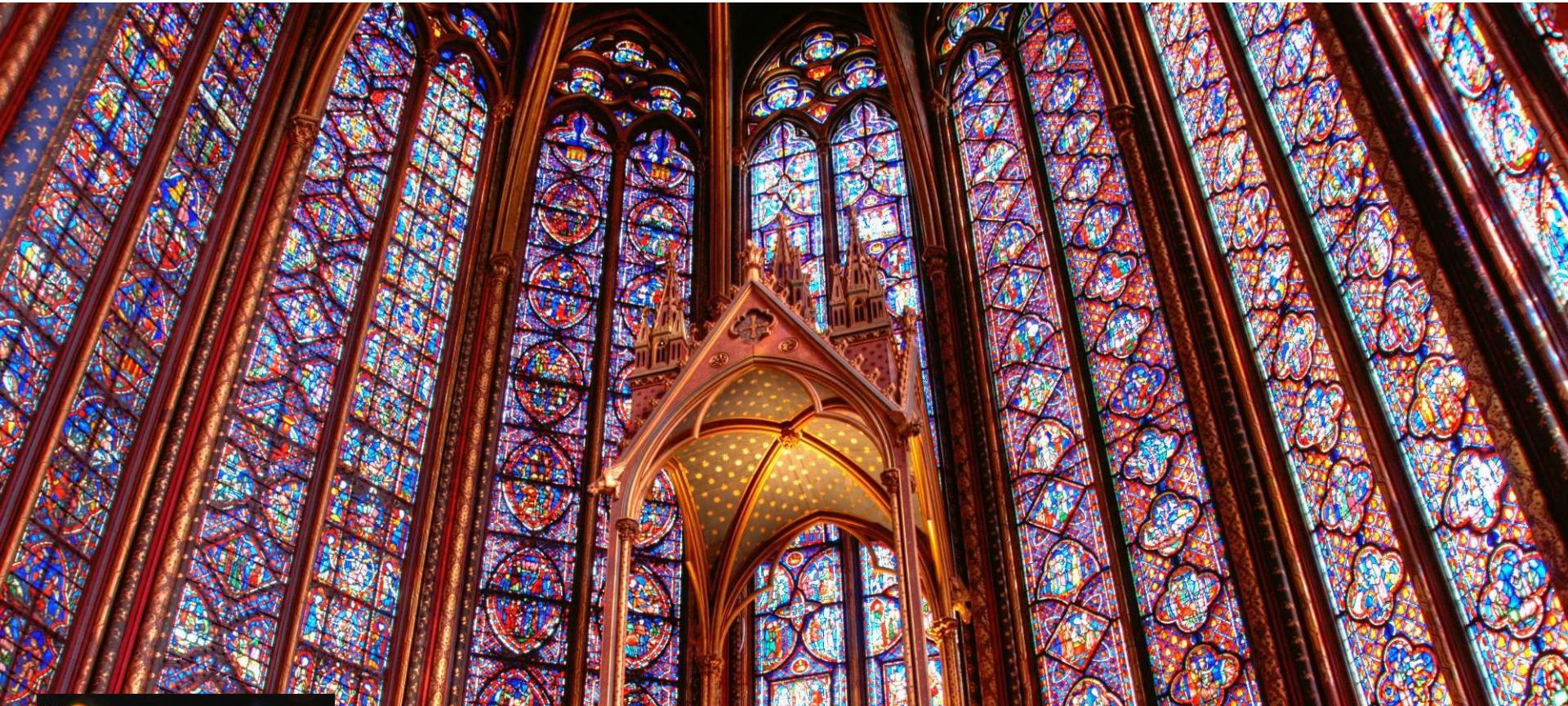


Average enhancement of ~ 250 over a 34 nm^3 region between the shells!

Large enhancement over wide range of wavelengths!

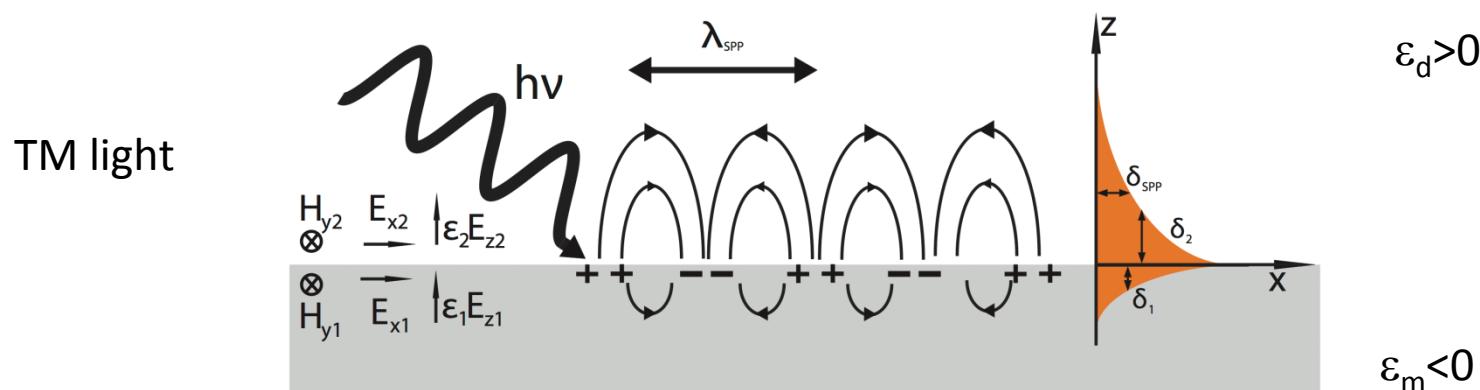
Single Shell Enhancement

“Hot spots”



Propagating Surface Plasmon Resonance

Surface Plasmon Polaritons (SPP)



Conditions of resonance

Frequency and wavevector of light have to match with those of the SPP

$$k_{EMF} = \omega/c\sqrt{\epsilon_d}$$

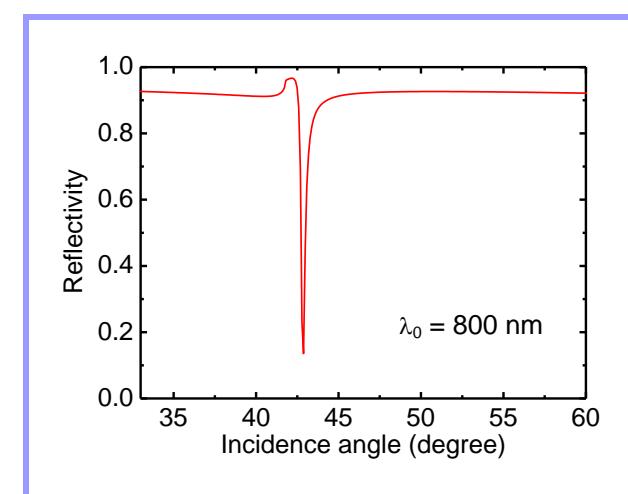
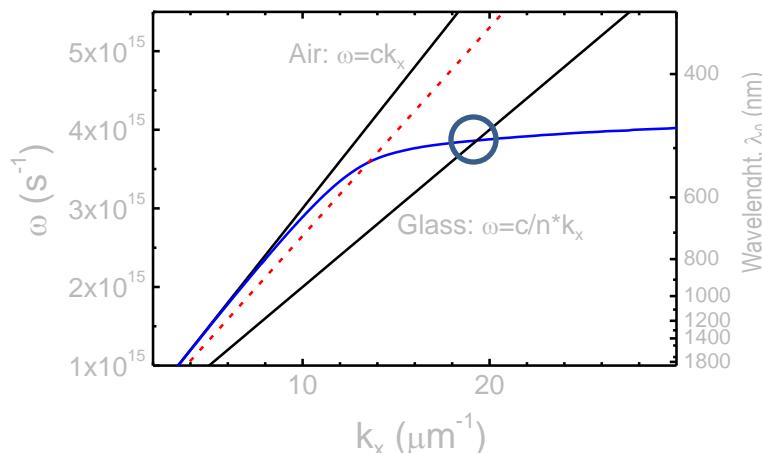
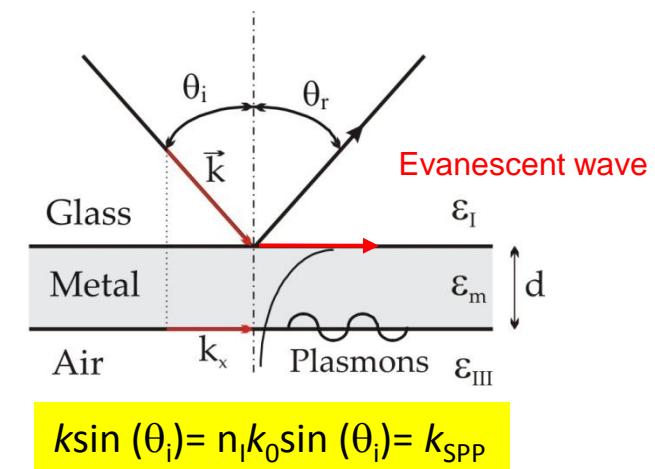
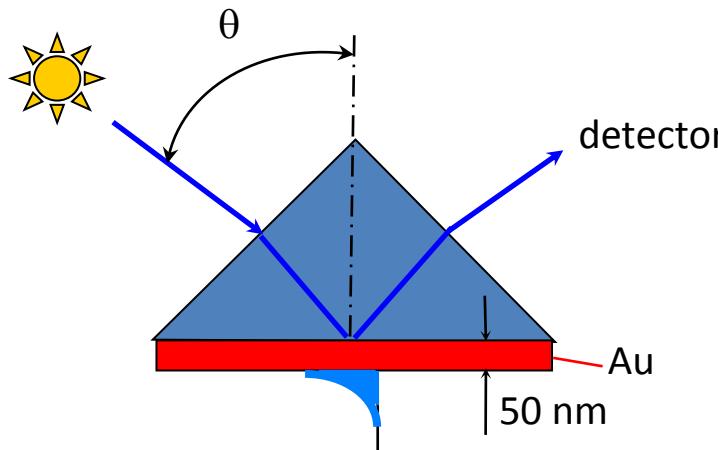
$$k_{SP} = \frac{\omega}{c} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}}$$

SPP and Localized electromagnetic fields

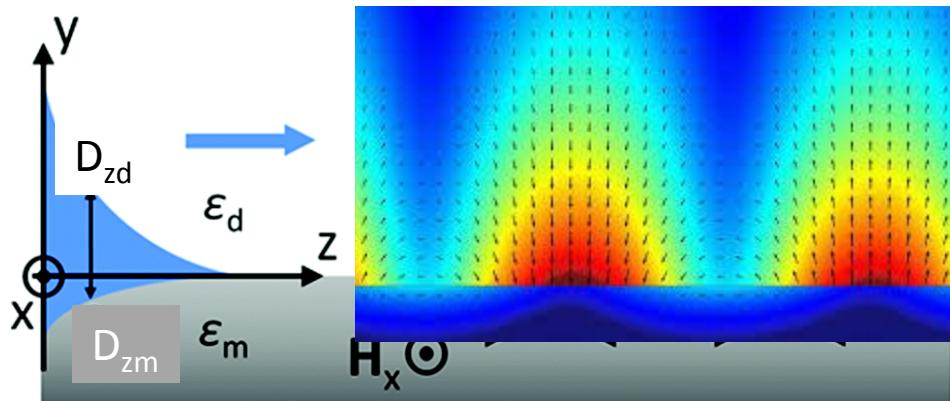
Surface Plasmon Polaritons (SPP)

Kretschmann Configuration

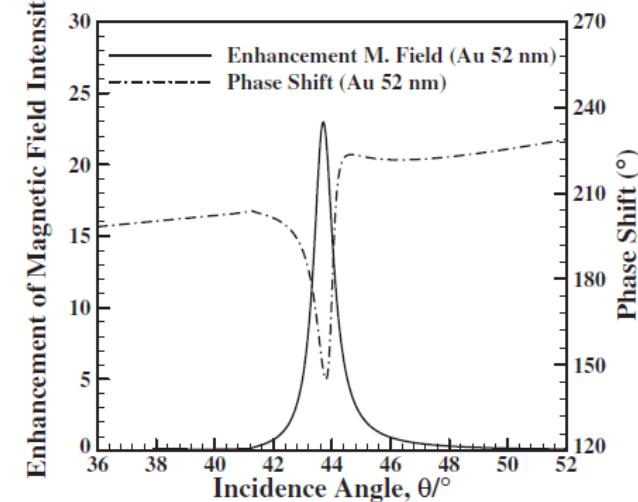
Excitation in Attenuation Total reflection (ATR) conditions



Surface Plasmon Polaritons (SPP)



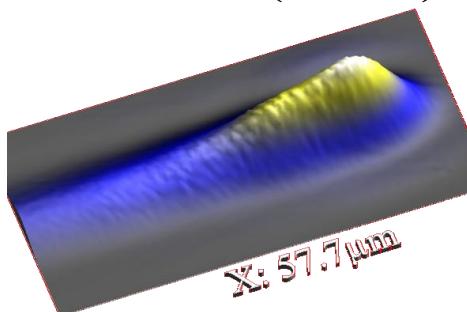
Enhancement of the EMF



Characteristic lengths

SPP Propagation length

$$\delta_{SPP} = \lambda_0 \frac{(\epsilon_m^r)^2}{2\pi\epsilon_m^i} \left(\frac{\epsilon_m^r + \epsilon_d}{\epsilon_m^r \epsilon_d} \right)^{3/2}$$



Evanescence field length

$$D_{zd} \approx 1/3 \lambda_0$$

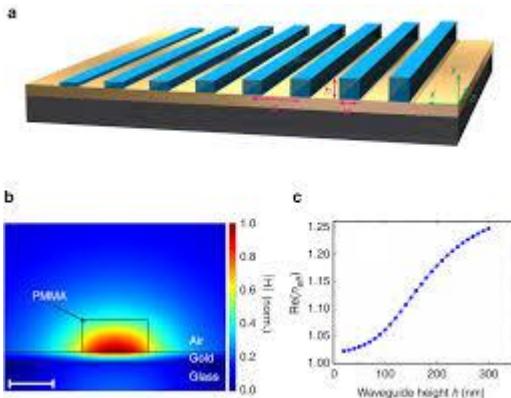
$$D_{zd} \approx \lambda_m$$

For Au at 800 nm: $\rightarrow D_z \approx 300 \text{ nm}$
 $\rightarrow \delta_{SPP} = 40 \mu\text{m}$

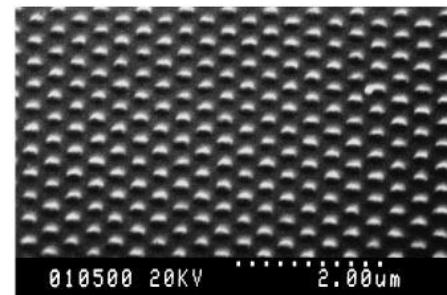
Confinement of the EMF

SPPs in other structures

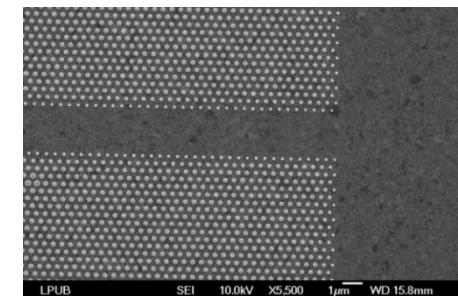
Gratings



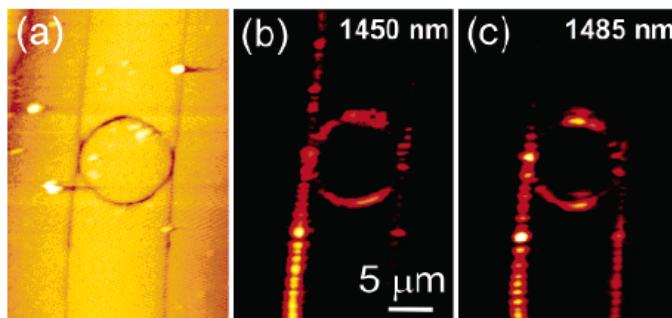
2-D systems



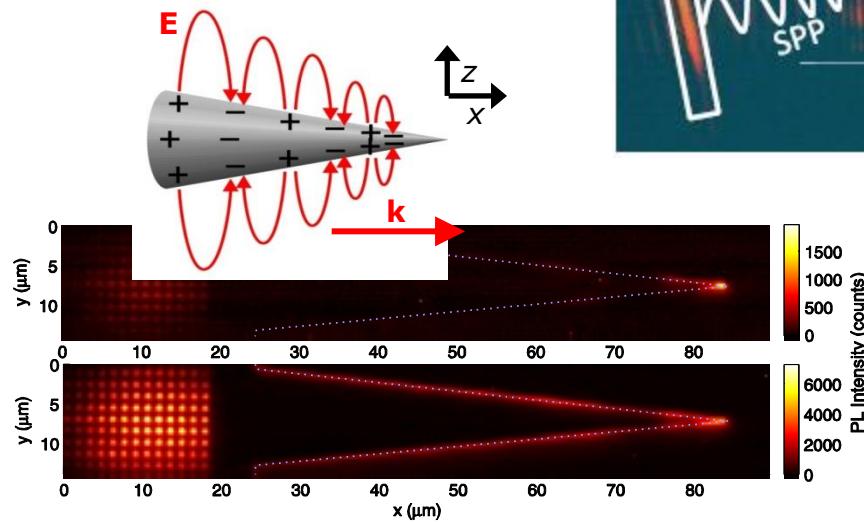
2 D - Waveguides



Channel plasmon polaritons

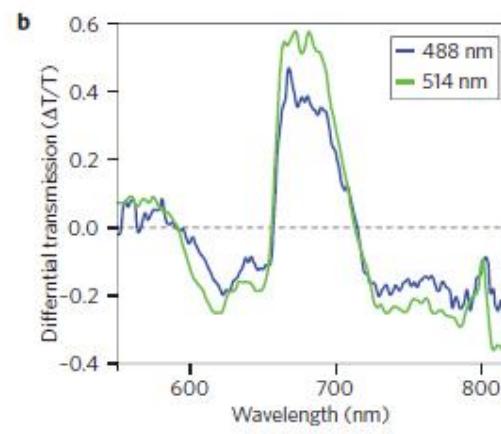
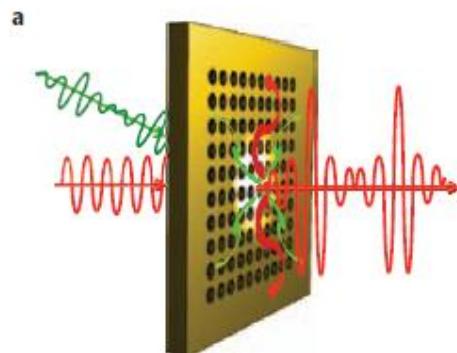


Plasmon tip



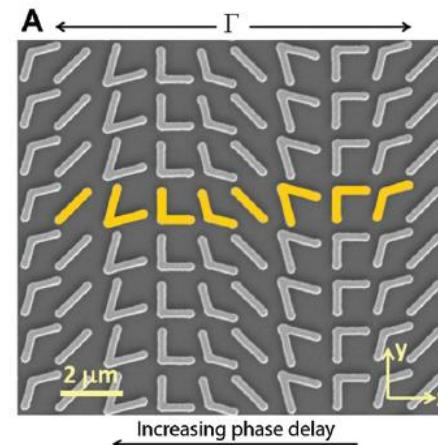
SPPs in other structures

Supertransmission



Kauranen Nat. Phot. 6 (2012)

Plasmonics metamaterials



Applications of Plasmonics materials

1. Inks

2. Photonics

Optoelectronics and Telecomm

3. Photovoltaic

4. Biomedicine

5. Catalysis

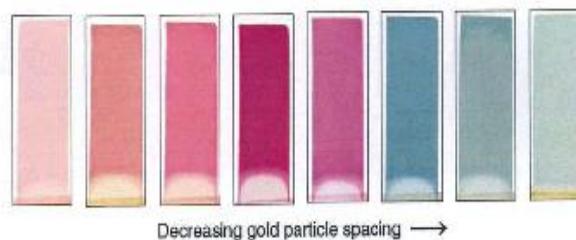
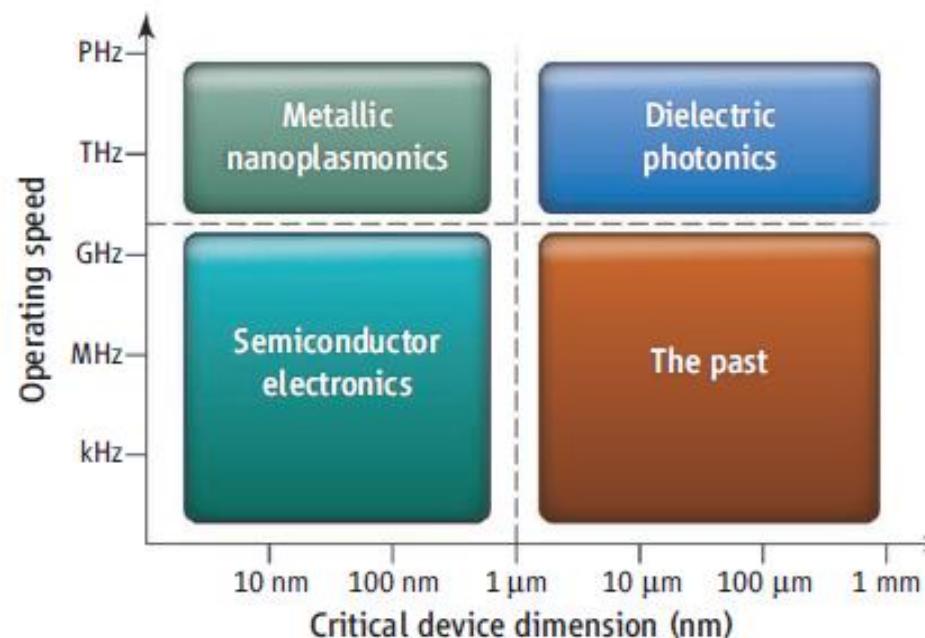


Figure 5. The transmitted colors of a series of gold particle films with decreasing particle spacing. The gold core particles are 15 nm in diameter; the shell thicknesses are, from left to right, 17.5 nm, 12.5 nm, 4.6 nm, 2.8 nm, 1.5 nm, 1.0 nm, 0.5 nm and 0 nm. Films are each 1 cm × 3 cm. The spectra shift smoothly between the two curves shown in Figure 3 as the spacing is varied.¹⁰

Mulvaney MRS Bull (2001)

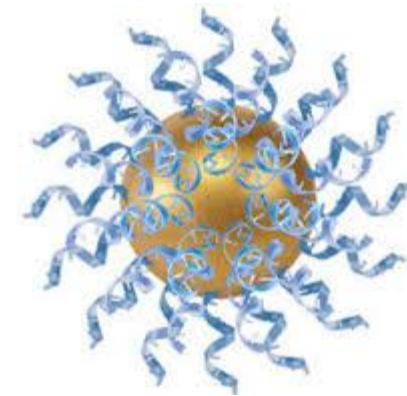
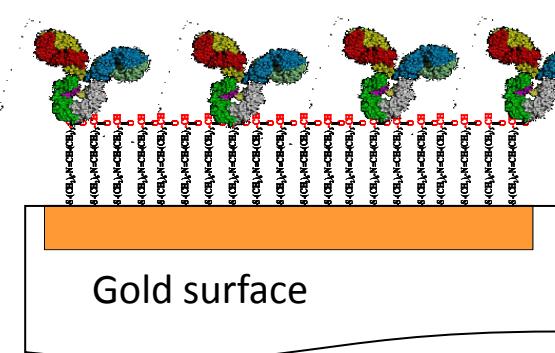


Source : Brongersma et al., Science 328, 440 (2010)

Noble metal **NANO**structures

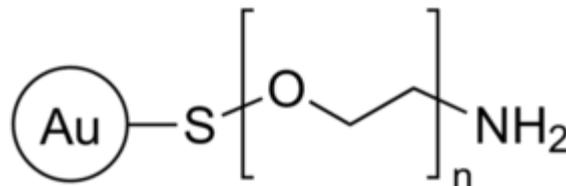
Inertness

Biocompatibility

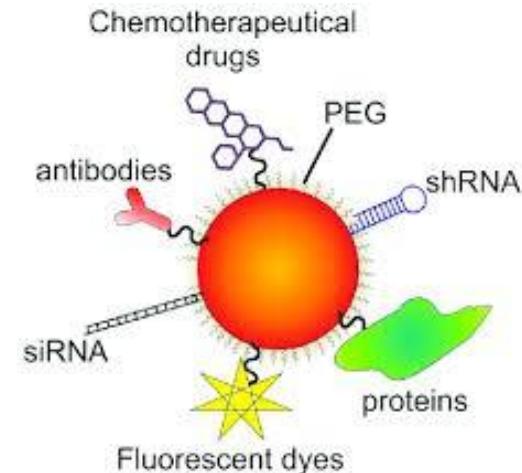
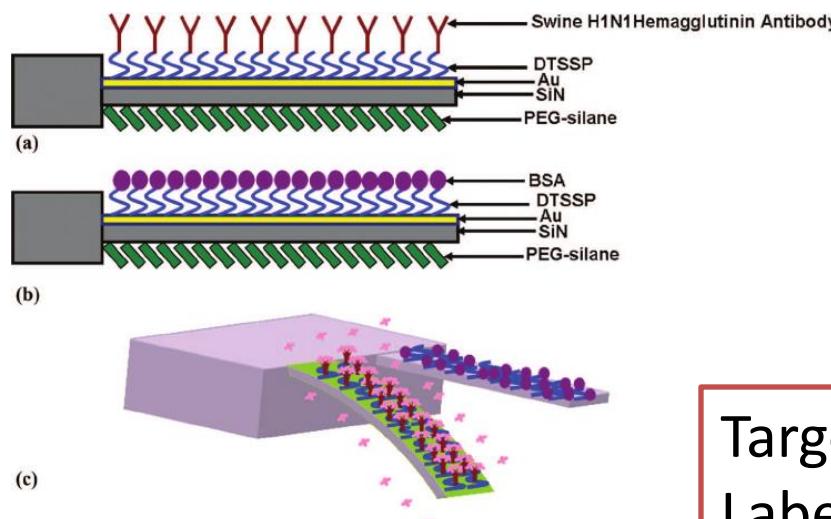


Functionalization of surfaces

Thiol capping of Au NPs or surface
Further capping for functionalization or biocompatibility



Strong Covalent bonding between Au and S



Targeting
Labeling

Targeting
Labeling

+

Imaging



Diagnostics

Cells labelling

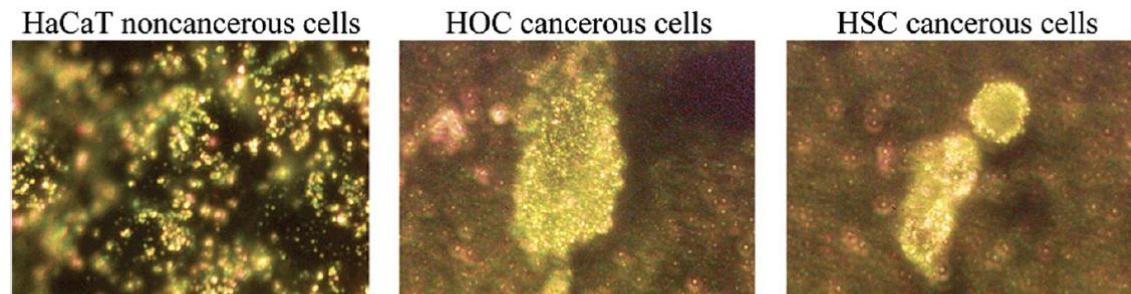


Figure 16. Light scattering images of HaCaT non-cancerous cells (left), HOC cancerous cells (middle), and HSC cancerous cells (right) after incubation with anti-EGFR antibody conjugated gold NPs. The conjugated NPs bind specifically to the surface of the cancer cells (right). Reproduced with permission from [77].

El-Sayed, I. H., et al., *Nano Lett.* (2005) 5, 829

Imaging

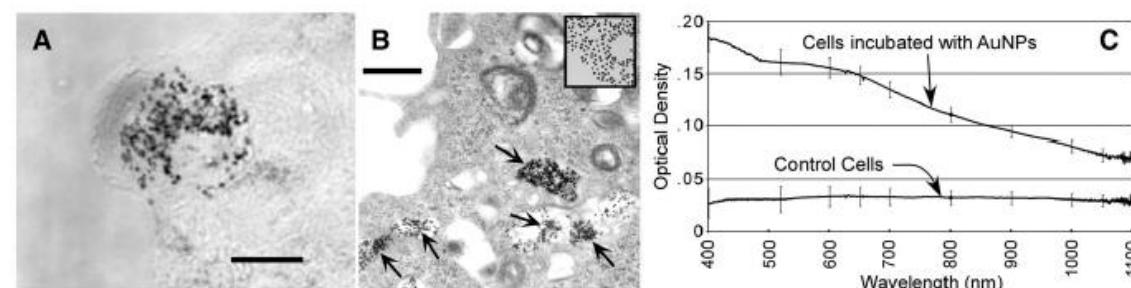
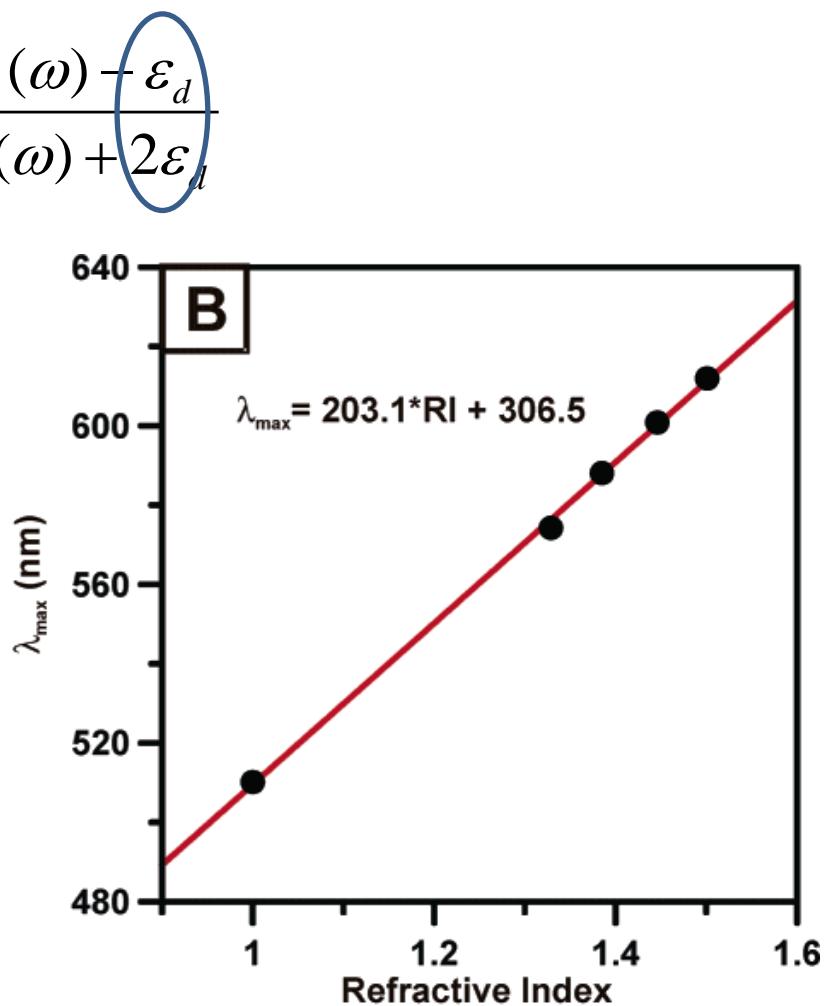
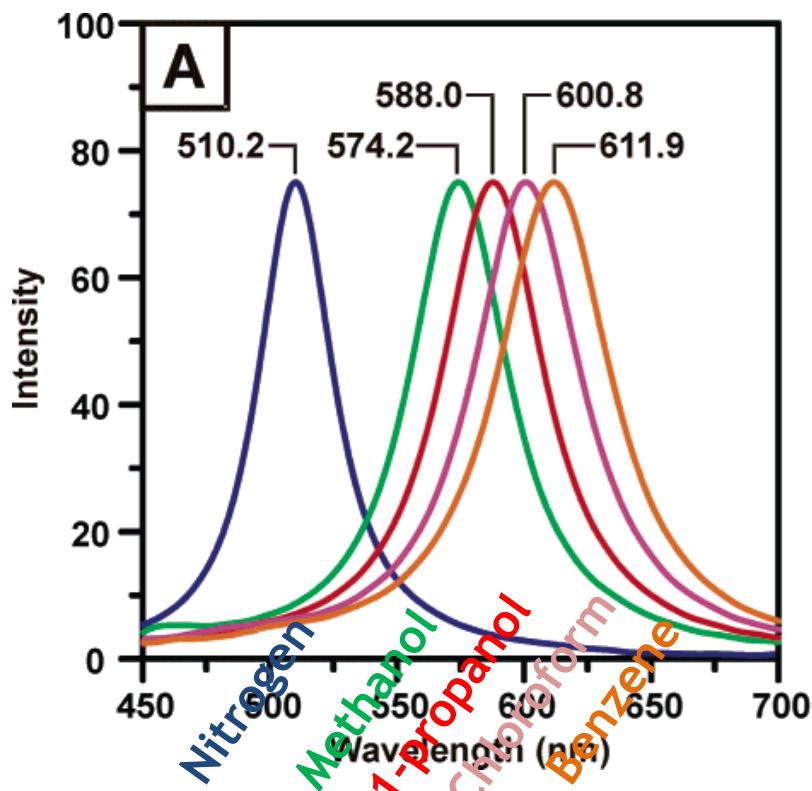


Figure 2. (A) Light micrograph of the in vitro uptake and aggregation of lipoic acid AuNPs in the cytoplasm of one tumor cell. Bar = 10 μ m. (B) Higher magnification electron micrograph of a cell after incubation with AuNPs. Aggregation of AuNPs can be seen in the endosomes/lysosomes. Inset at the same magnification shows unaggregated 15 nm AuNPs that exhibit the unaggregated spectrum shown in Figure 1, A. Bar = 500 nm. (C) Spectra of cells incubated with or without AuNPs. Cells incubated with AuNPs showed absorption in the NIR region. Error bars are from 6 separate measurements.

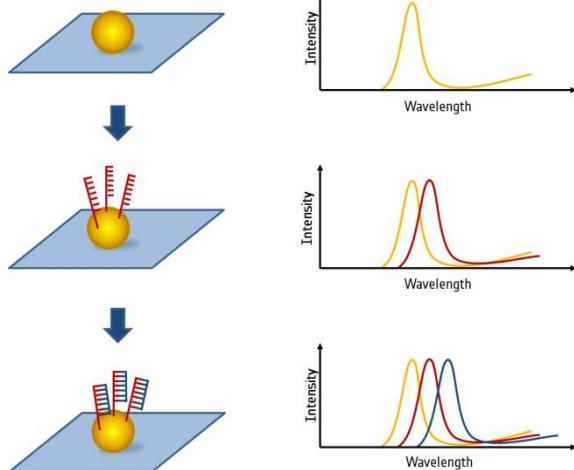
Hainfeld et al., *Nanomed. Nanotech Biol. Med.* 10 (2014) 1607

Direct sensing LSPR

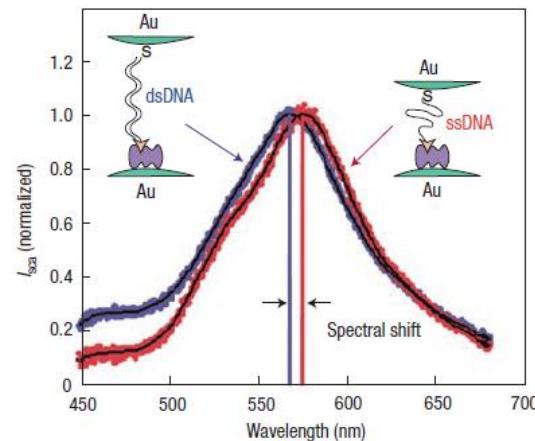
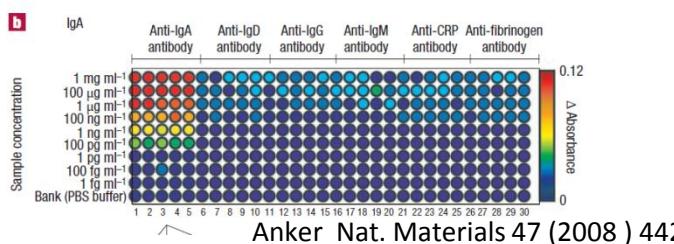
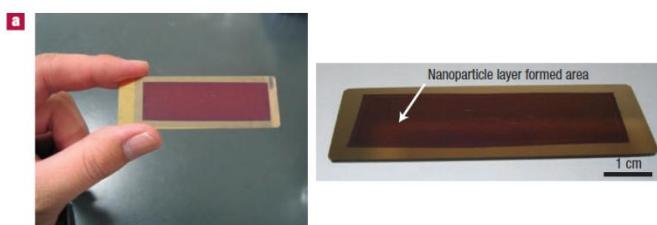
$$\alpha(\omega) = 4\pi\epsilon_d a^3 \frac{\epsilon_m(\omega) - \epsilon_d}{\epsilon_m(\omega) + 2\epsilon_d}$$



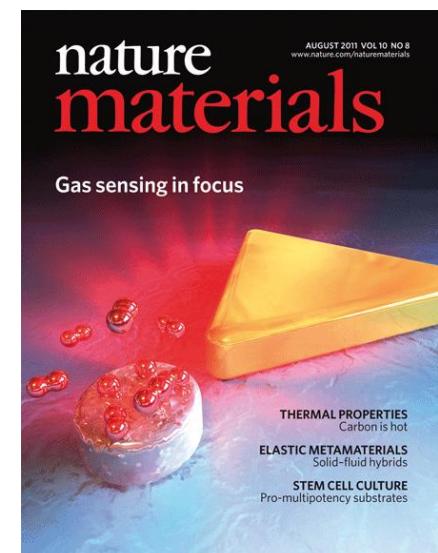
Direct sensing LSPR



Hutter. Advanced Materials 16 1685-1706

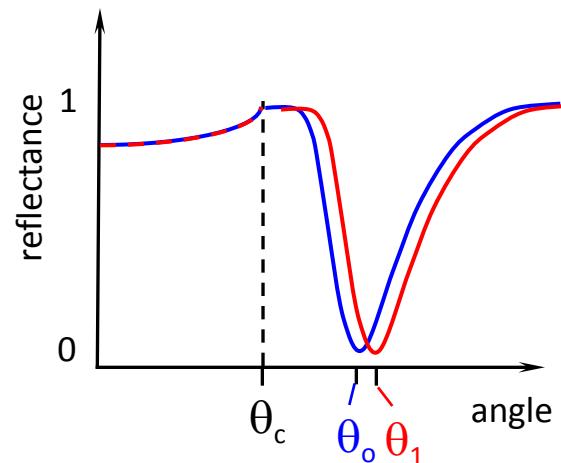
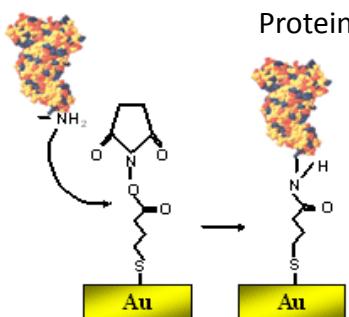
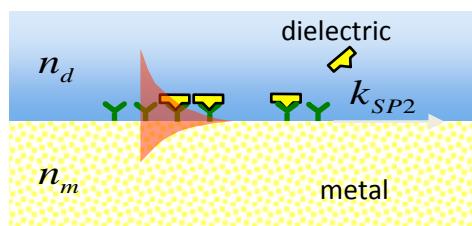


C. Sönnichsen et al., Nature Biotechnol. 23, 741 (2005)



Single molecule detection

Direct sensing: SPP



- High sensitivity**, especially at the surface
- Direct measurement (no labels) and in real time** (kinetic analysis)



- Time resolved
- Imaging
- Spectroscopy

Indirect optical Imaging /sensing

→ SPR

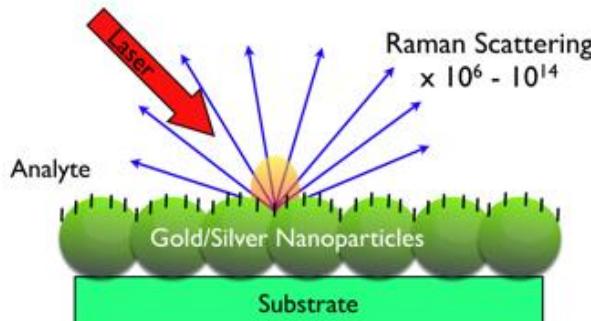
Amplification effect

- Due to the EMF localization
- Plasmon transfer energy

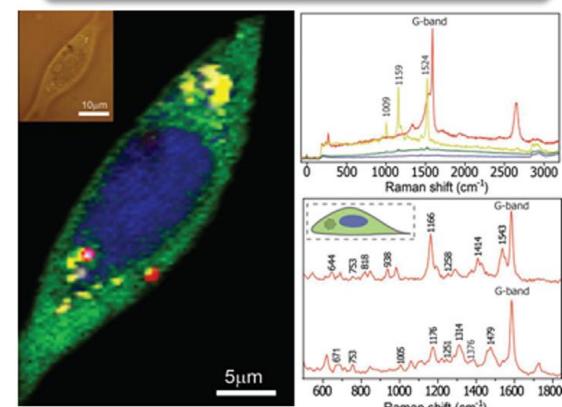
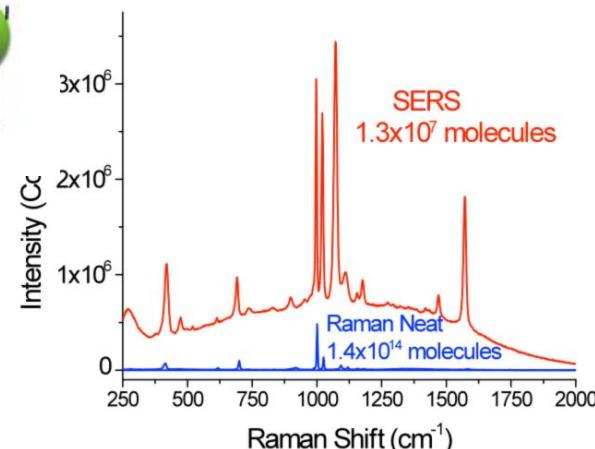
SERS Surface enhanced Raman Spectroscopy

SERS Imaging

Nanoparticles = nano amplifier



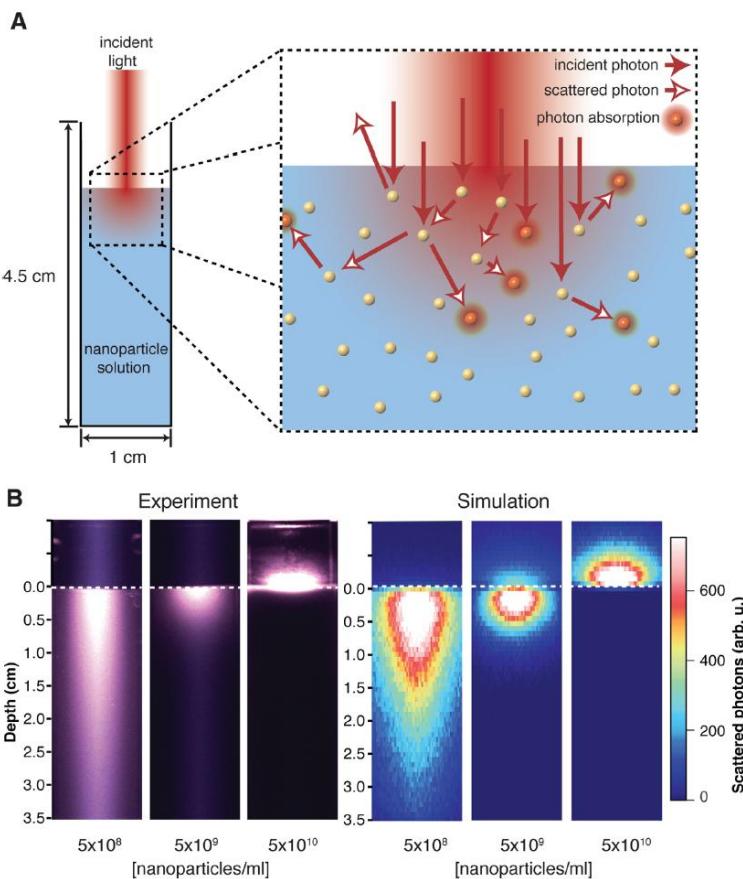
Caldwell and Glemboki, U.S. Naval Research Laboratory



A. Yashchenok, et al. Small 9 (2013) 351.

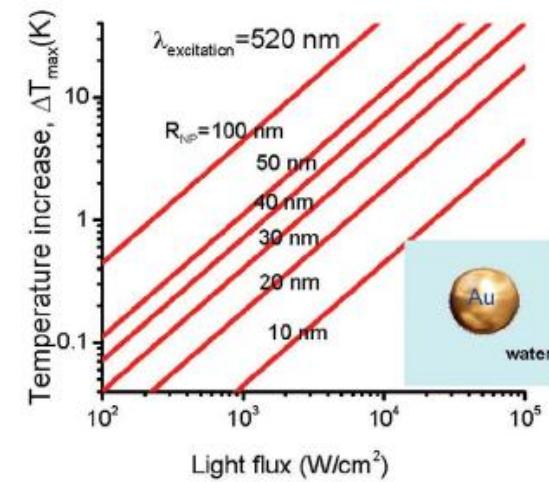
Plasmon assisted heating

Heat release at the SPR



$$\Delta T_{\max}(I_0) = \frac{R^2}{3\kappa_0} \frac{\omega}{8\pi} \left| \frac{3\epsilon_0}{2\epsilon_0 + \epsilon} \right| \text{Im}\epsilon \frac{8\pi I_0}{c\sqrt{\epsilon_0}}$$

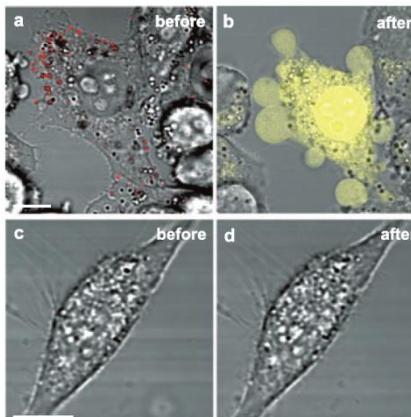
A. O. Govorov and H.H., Richardson Nano Today, 2 (2007) 30-38.



Huang Lasers Med Sci 23 (2008) 217–228
Giner Casares Materials Today 19 (2016) 19

Hogan Nano Lett. 14 (2014) 4640

Photothermal therapy



With NRods

Without NRods

Figure 9. Photothermal lysis mediated by folate-conjugated nanorods (F-NRs) (34). (a, b) KB cells with membrane-bound F-NRs (red) exposed to fs-pulsed near-infrared laser irradiation (0.75 mW, 81.4 s) experienced membrane damage and blebbing. The loss of membrane integrity was indicated by ethidium bromide nuclear staining (yellow). (c, d) NIH-3T3 cells were unresponsive to F-NRs and did not suffer photoinduced damage at the same condition. Bar = 10 μ m.

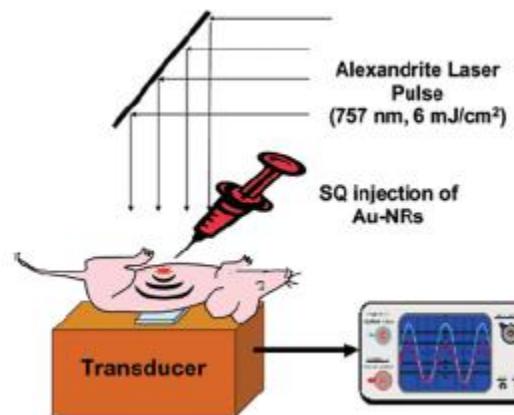
Tong et al Photochem Photobiol 85 (2009) 21

Photo-ablation
NIR fs pulses

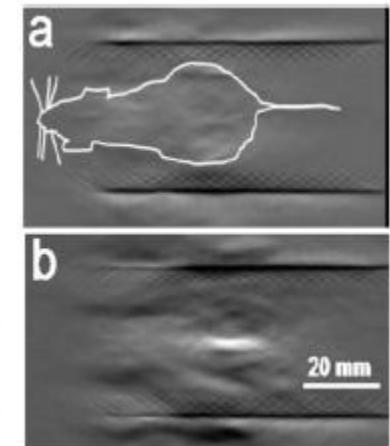
HyperThermia

$T_{\text{local}} < 48^\circ\text{C}$

Synergy with other therapy methods



Optoacoustic imaging



Eghtedari, Nano Lett. 7 (2007) 1914

Imaging thanks to the thermal- driven local heating
Combined with ultrasound imaging

Limits:

- **Passive**

No modification of the SPR

Hard to mechanically manipulate

- **In vivo – Optical absorption of the skin**

NIR- window

