Università di Pisa
LM Materials and Nanotechnology - a.a. 2016/17

Spectroscopy of Nanomaterials II sem – part 7

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Plasmonics and nanoparticles: from fine art to sensor applications

OUTLOOK

We have seen how surface charge oscillations at a metal/dielectric interface can lead to specific properties when interaction with light is concerned

So far, we have analyzed plane interfaces, leading to SPP, but metal/dielectric interfaces exist also at the “border” of metal nanoparticles

Plasmonics plays a relevant and appealing (from the applicative point of view) role here, too. The relevant topic is often denoted as **local plasmon resonance** (or with a similar name)

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Today's menu:
- Colourful starters of metal nanospheres
- First dish: localized plasmon resonances and related
  effects
- Main course of potential or existing applications (a
  small selection of)
- No dessert
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ALREADY SEEN IN OUR INTRODUCTION

Lycurgus Cup in Roman times

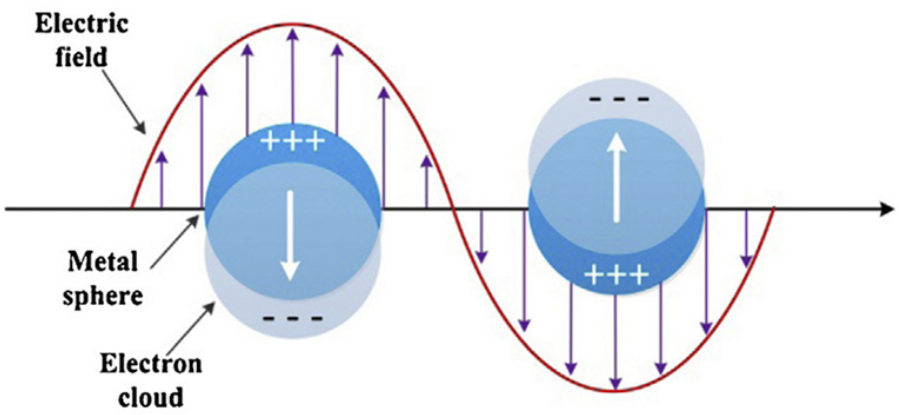
Dr. Juen-Kai Wang

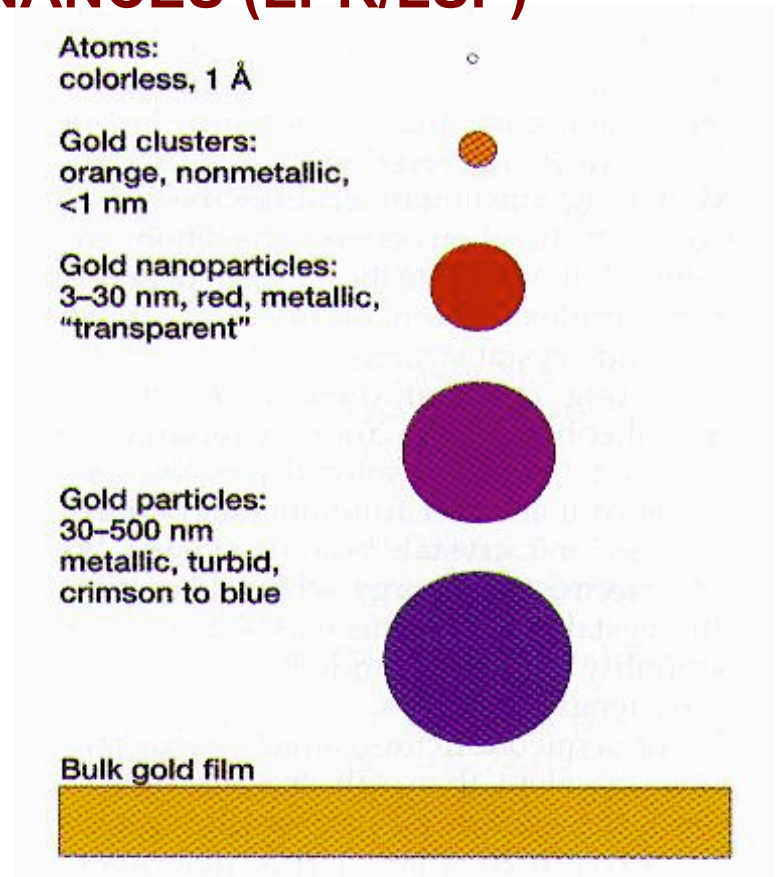
The glass appears green in daylight (reflected light), but red when the light is transmitted from the inside of the vessel.

Interpretation:
"nanostructured" glass
(i.e., containing gold and silver nanoparticles,
i.e., a "nanomaterial")

The Lycurgus Cup, Roman (4th century AD), British Museum *(www.thebritishmuseum.ac.uk)*
F. E. Wagner et al., Nature ***407****, 691 (2000).*

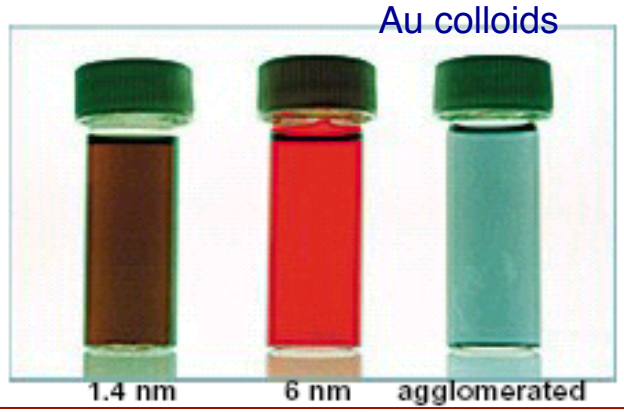
LOCALIZED PLASMON RESONANCES (LPR/LSP)





Color changes ascribed to Rayleigh's (or Mie's, depending on size) scattering with a specific wavelength-depending cross-section

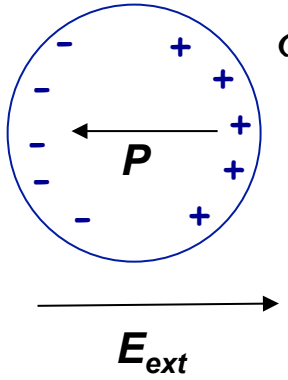
LPRs, entailing in-phase oscillations of the charge at the surface of a (noble) metal nanoparticle (a sphere, for ease of description) are responsible for the specific wavelength-depending behavior, i.e., for the occurrence of a **resonance**



STATIC POLARIZABILITY OF A DIELECTRIC SPHERE

Let's consider a dielectric, rather than metal, sphere: we will see that the result can be exported to the metal case with no major change

The problem considere here is thus the calculation of polarizability according to Clausius-Mossotti (aka Lorentz-lorenz) formula



$$\sigma_{pol} = -P\cos\theta$$

$$\vec{P} = \varepsilon_0 \chi \vec{E}_{ext} = \frac{N}{\frac{4}{3}\pi a^3}\vec{p}$$

$$\vec{p} = \alpha \vec{E}$$

$$E_{loc,z} = -\frac{1}{4\pi\varepsilon_0}\int_S \frac{\sigma_{pol}\cos\theta}{a^2} dS \qquad E_{loc,z} = \frac{P}{2\varepsilon_0}\int_0^{2\pi} \cos^2\theta \sin\theta \, d\theta = \frac{P}{3\varepsilon_0} \rightarrow \vec{E}_{loc} = \frac{\vec{P}}{3\varepsilon_0}$$

with $dS = 2\pi a^2 \sin\theta d\theta$

$$\vec{E} = \vec{E}_{ext} + \frac{\vec{P}}{3\varepsilon_0}$$

$$\vec{P} = \frac{N}{\frac{4}{3}\pi a^3}\alpha\left(\vec{E}_{ext} + \frac{\vec{P}}{3\varepsilon_0}\right) = \varepsilon_0(\varepsilon - 1)\vec{E}_{ext} \rightarrow \alpha \propto \frac{\varepsilon - 1}{\varepsilon + 2}$$

DETAILED TREATMENT FOR A METAL NANOSPHERE

Here we discuss in some more detail a LSP model in case of a small spherical particle. We assume a sphere of radius a in a uniform static electric field $\mathbf{E}_{in} = E_0\mathbf{e}_z$ The surrounding medium is isotropic and non-absorbing with dielectric constant ϵ_d, the metal sphere is described by a complex dielectric constat ϵ_s. We are interested in a solution of the Laplace equation $\Delta\Phi = 0$ from which we can obtain the electric field $\mathbf{E} = -\text{grad}\Phi$. In spherical coordinates, the Laplace equation is of the form

$$\frac{1}{r^2\sin\theta}\left[\sin\theta\,\partial_r(r^2\partial_r) + \partial_\theta(\sin\theta\,\partial_\theta) + \frac{1}{\sin\theta}\partial_\phi^2\right]\Phi(r,\theta,\phi) = 0$$

Due to the azimuthal symmetry, the general solution is independent of ϕ and has the form

$$\Phi_s(r,\theta) = \sum_{l=0}^{\infty} A_l r^l P_l(\cos\theta) \quad (336)$$

$$\Phi_d(r,\theta) = \sum_{l=0}^{\infty} (B_l r^l + C_l r^{-l-1}) P_l(\cos\theta) \quad (337)$$

where Φ_s is the potential inside the sphere and $\Phi_d = \Phi_{\text{scatter}} + \Phi_0$ the potential outside the sphere, consisting of an incoming and a scattered part.

When applying boundary conditions at the interface $r = a$ for tangential part of the electric field ($\partial_\theta\Phi_i = \text{const.}$, for $i = s, d$) and for the longitudinal part of the displacement field ($\epsilon_i\partial_r\Phi_i = \text{const.}$), the potentials evaluate to

$$\Phi_s(r,\theta) = -\frac{3\epsilon_d}{\epsilon_s + 2\epsilon_d} E_0 r\cos\theta \quad (338)$$

$$\Phi_d(r,\theta) = -E_0 r\cos\theta + \frac{\epsilon_s - \epsilon_d}{\epsilon_s + 2\epsilon_d} E_0 \frac{a^3}{r^2}\cos\theta \quad (339)$$

$$= -E_0 r\cos\theta + \frac{\mathbf{p}\cdot\mathbf{r}}{4\pi\epsilon_0\epsilon_d r^3} \quad (340)$$

$$\text{with} \quad \mathbf{p} = 4\pi\epsilon_0\epsilon_d a^3 \frac{\epsilon_s - \epsilon_d}{\epsilon_s + 2\epsilon_d}\mathbf{E}_0 \quad (341)$$

Here we have introduced the dipole moment $\mathbf{p}$ that is induced in the sphere by the external field. The electric field can then be expressed as

$$\mathbf{E}_s = \frac{3\epsilon_d}{\epsilon_s + 2\epsilon_d}\mathbf{E}_0 \quad (342)$$

$$\mathbf{E}_d = \mathbf{E}_0 + \frac{1}{4\pi\epsilon_0\epsilon_d}\frac{3\mathbf{n}(\mathbf{n}\cdot\mathbf{p}) - \mathbf{p}}{r^3} \quad (343)$$

$\mathbf{n} = \mathbf{r}/r$ is the unit vector in direction of the point of interest.

The polarizability, defined by the relation $\mathbf{p} = \epsilon_0\epsilon_d\alpha\mathbf{E}_0$ then becomes

$$\alpha = 4\pi\epsilon_0 a^3 \frac{\epsilon_s - \epsilon_d}{\epsilon_s + 2\epsilon_d}$$

$$\alpha = 4\pi\varepsilon_0 a^3 \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d}$$

https://www.physik.hu-berlin.de/de/nano/lehre/Gastvorlesung%20Wien/plasmonics

The expression of the metal sphere polarizability is very much similar to the Clausius-Mossotti one but for the presence of the dielectric constant of the metal, complex and frequency dependent

SCATTERING FROM A METAL NANOSPHERE

Total radiated power by the oscillating dipole (Rayleigh scattering)

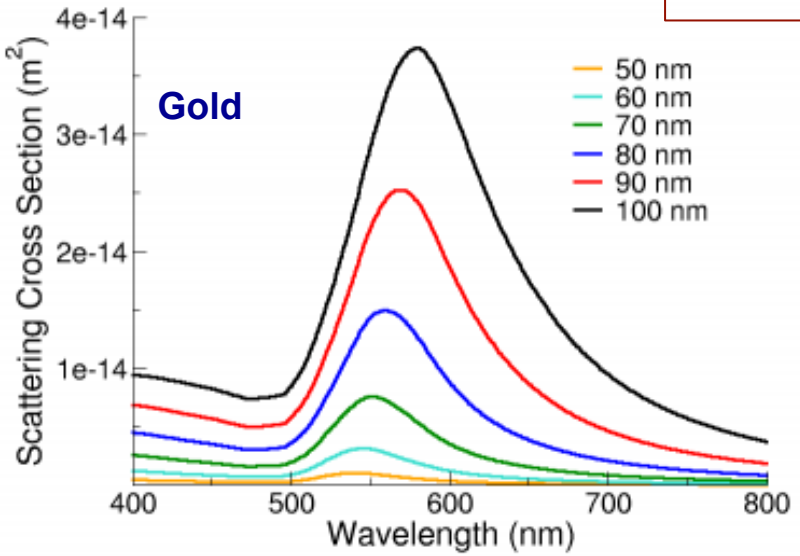
$$P = \frac{\omega^4}{12\pi\varepsilon_0\varepsilon_d c^3}\left|\vec{p}\right|^2$$

Intensity of the incident radiation

$$I = \frac{c\varepsilon_0\varepsilon_d}{2}E_0^2$$

Scattering cross-section

$$\sigma_{scatt} = \frac{P}{I} = \frac{k^4}{6\pi\varepsilon_0^2}\left|\alpha\right|^2 = \frac{8\pi}{3}k^4a^6\left|\frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d}\right|^2$$



Resonance at a specific wavelength

Absorption cross-section

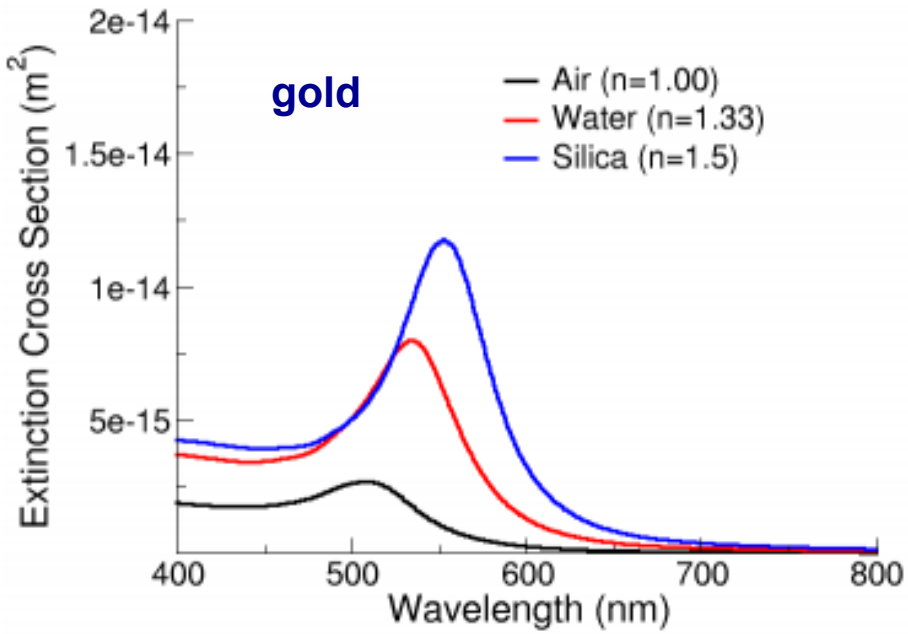
$$\sigma_{abs} = \frac{k}{\varepsilon_0}\mathrm{Im}\{\alpha\} = 4\pi k a^3 \mathrm{Im}\left\{\frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d}\right\}$$

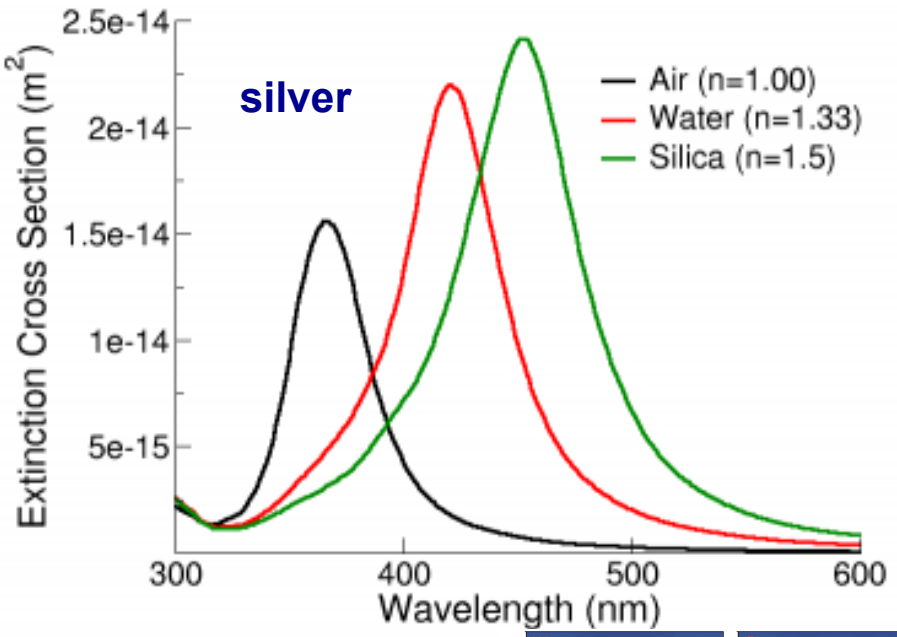
Extinction is the combination of absorption and scattering

$\sim a^3$ $\sim a^6$

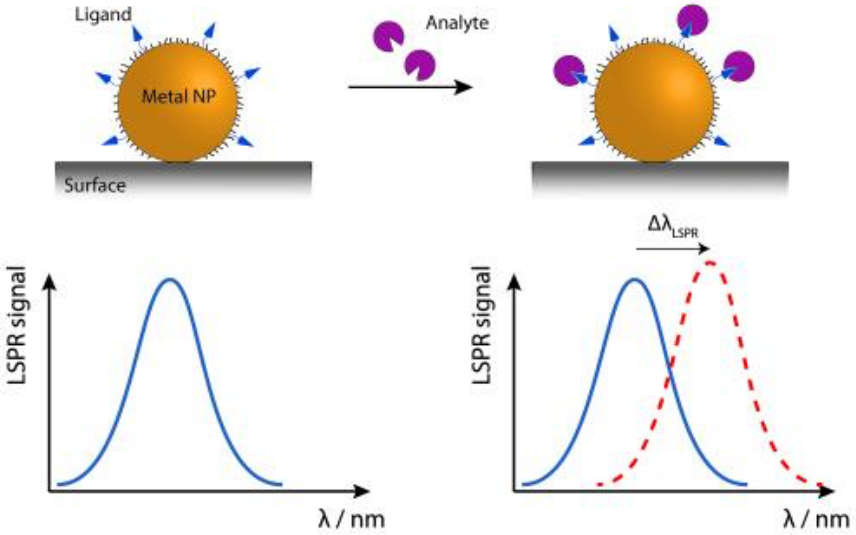
Scattering prevails for small particles

EXAMPLES I

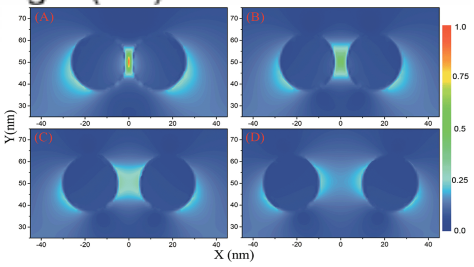


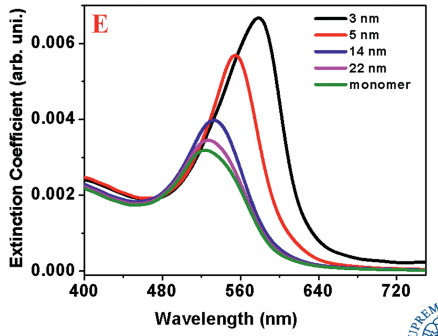


Sensitivity to the “environment”

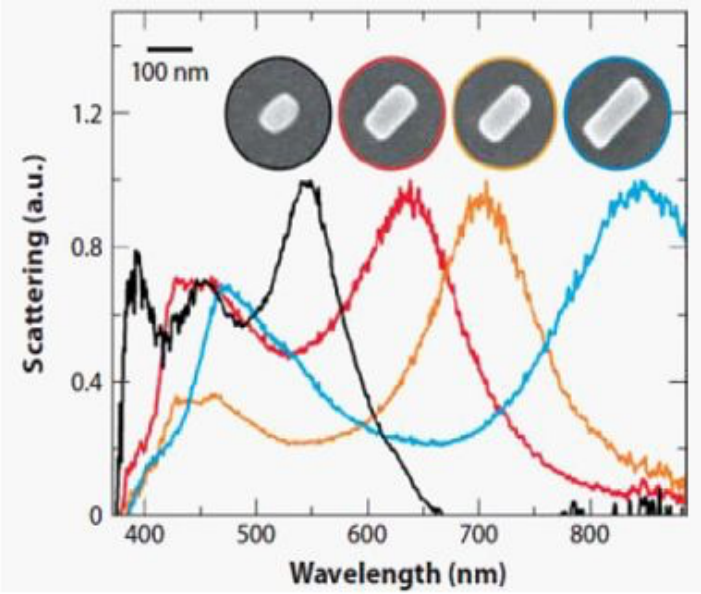


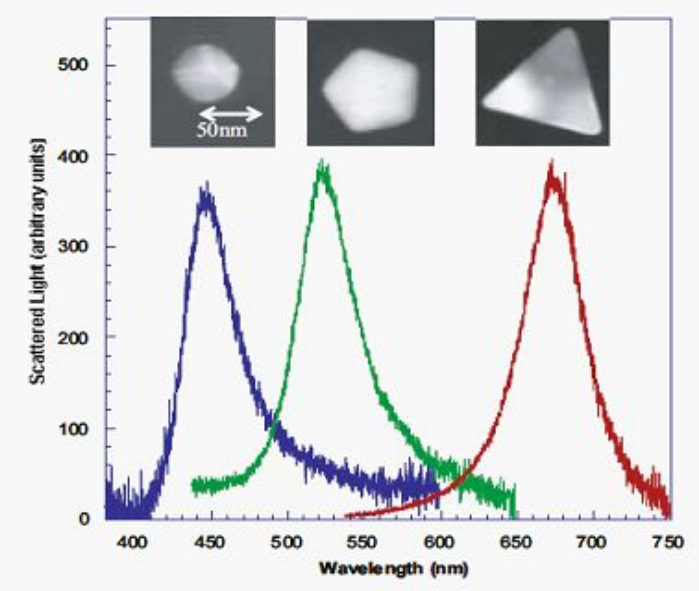
Coupling (collective LPR) possibilities





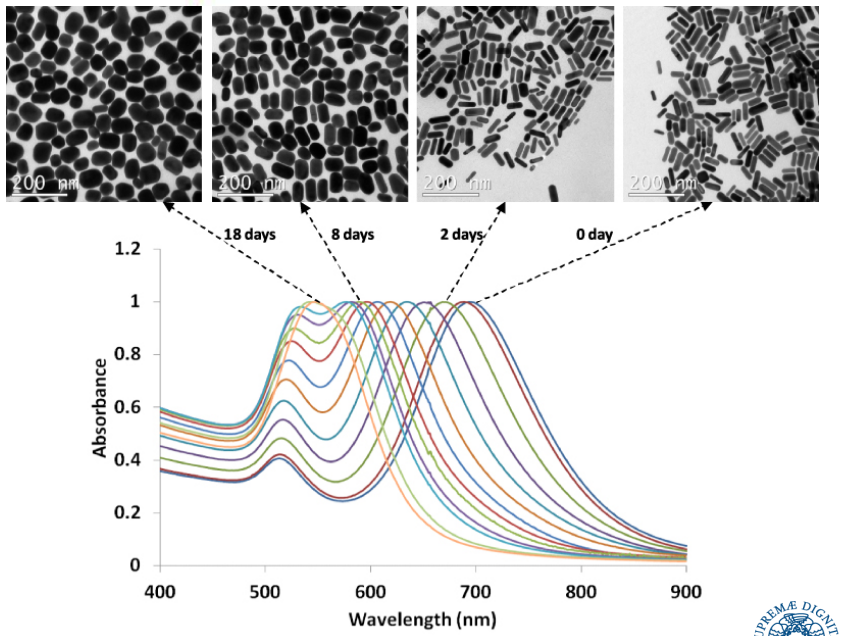
EXAMPLES II





When non-spherical shapes are considered, the plasmon oscillation contains also terms at a higher order with respect to dipole (multipolar expansions are needed)

Spectral properties are usually red-shifted (and often broadened)



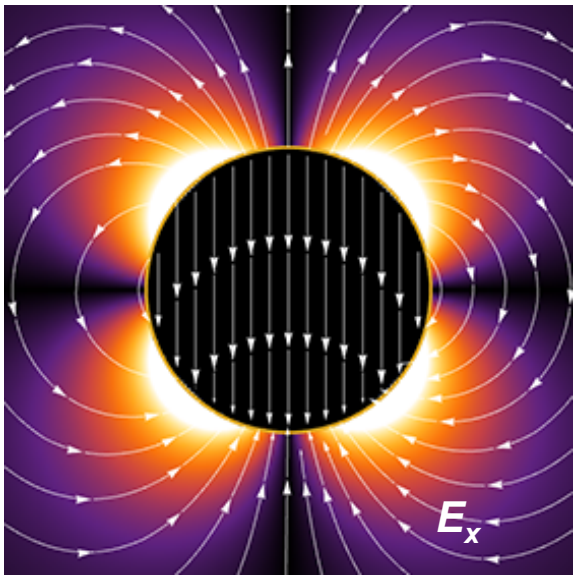
FIELD ENHANCEMENT

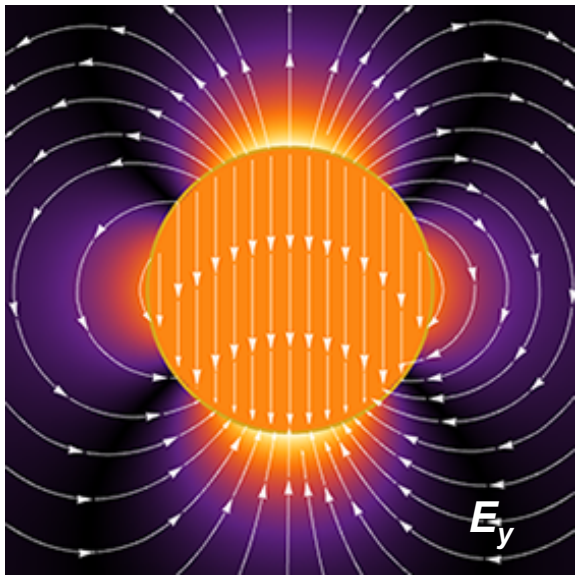
At the LPR resonance polarizability explodes (in the reality, it is not a divergence because of damping, interband transitions, etc.)

The polarization explodes and gives rise to a strong electric field

Joined with the lightning rod effect, this leads to a local enhancement of the electric field

$$\alpha = 4\pi\varepsilon_0 a^3 \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d}$$





At resonance, electric field is strongly enhanced close to the nanoparticle surface

$$E_{nanoparticle} \simeq E_{driving} \left| 1 + \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \right|$$

Simulation of the electric field intensity (and lines of field) for a metal nanoparticle resonant with an e.m. field ($E_{driving}$) polarized along *y*

http://people.ee.duke.edu/~drsmith/plasmonics/enhancement.htm

COUPLED RESONANCES

A metal nanoparticle at the LPR resonance is one of the most efficient scatterer one can envision
but
damping, including interband transitions, set a limit to the field enhancement

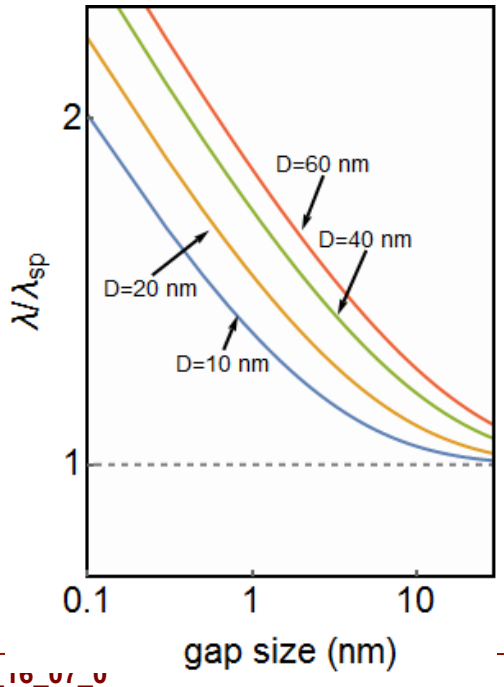
Moreover, excitation of higher order modes (e.g., quadrupolar) is unavoidable in real nanoparticles due do their finite size (and to the actual geometry): higher order modes do not emit, they just absorb through Joule effect

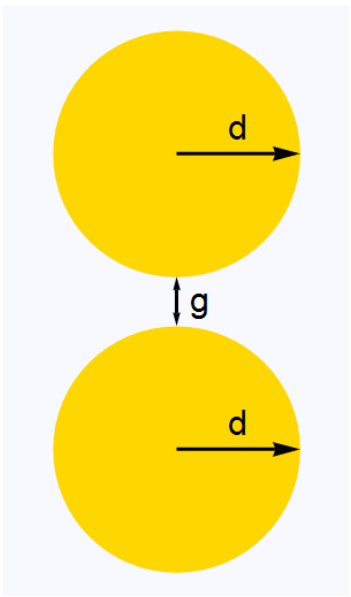
→ *engineering geometries able to give a radiative character also to higher order modes*
→ *"breaking the spherical simmetry"*
→ *creating "collective resonances" involving two, or more, nanoparticles*

Example: two discs (or cylinders) with small diameters (few tens of nm) placed in close proximity (a few nm) one another

$$\left(\sqrt{\frac{g}{2d}}+\sqrt{1+\frac{g}{2d}}\right)^4=\frac{\varepsilon_m-\varepsilon_d}{\varepsilon_m+\varepsilon_d}$$

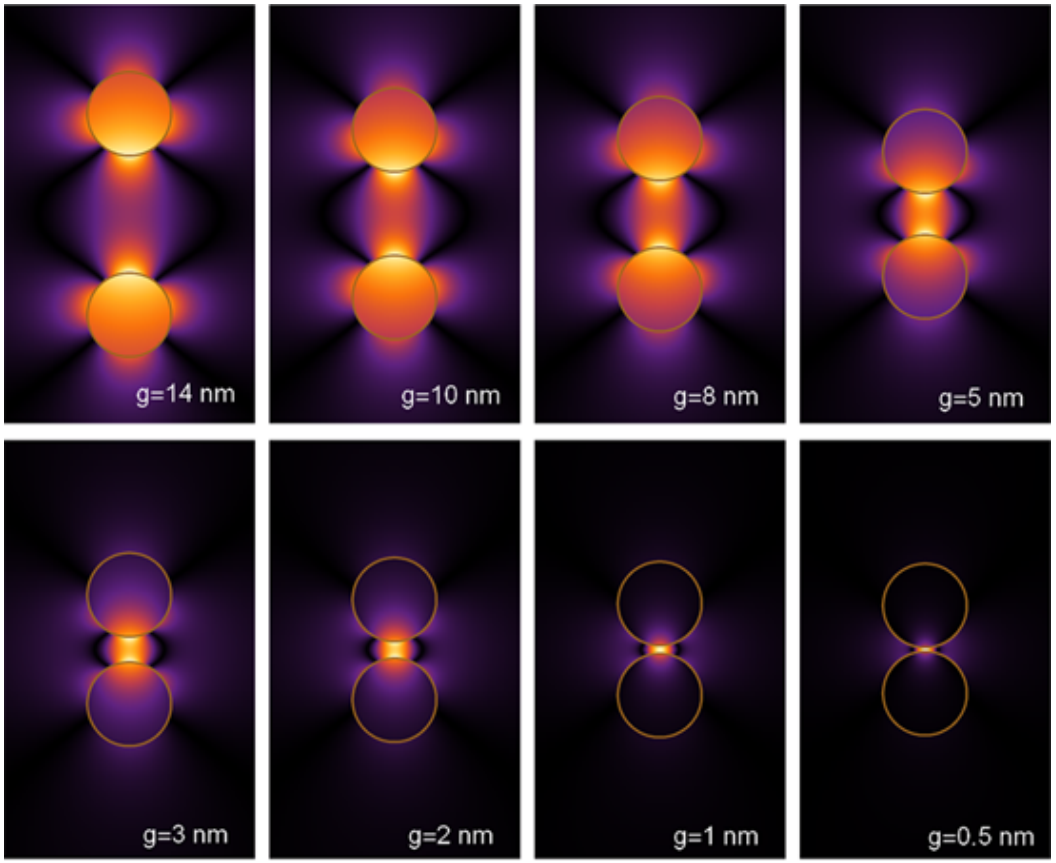
New resonance wavelength (red-shifted and tunable with the gap size *g*)

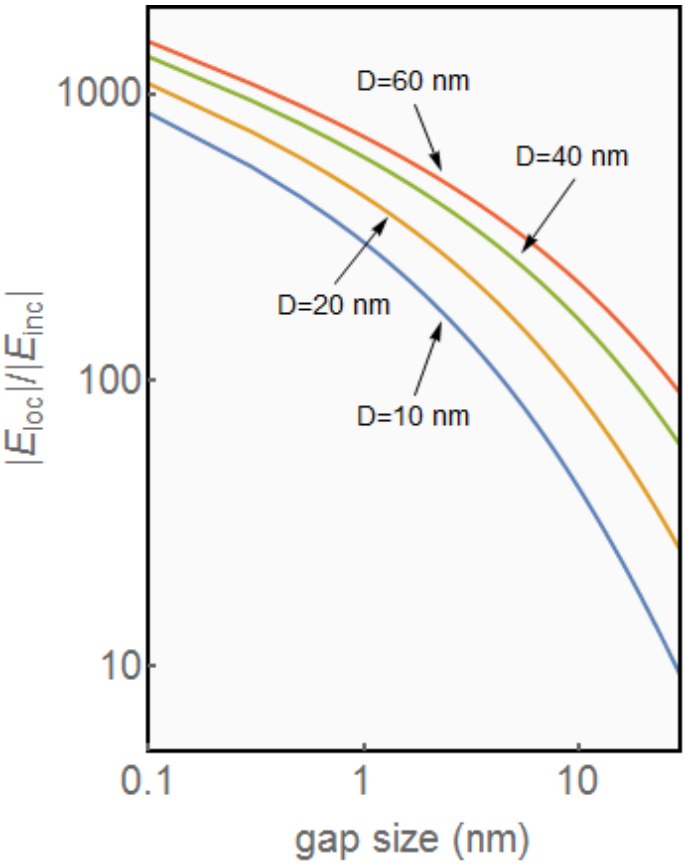




Physical Review Letters **105**, 233901 (2010)

FIELD ENHANCEMENT IN THE GAP



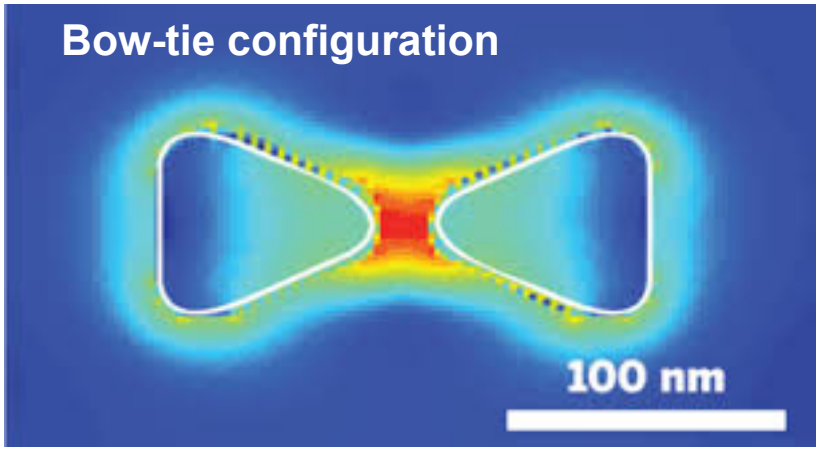


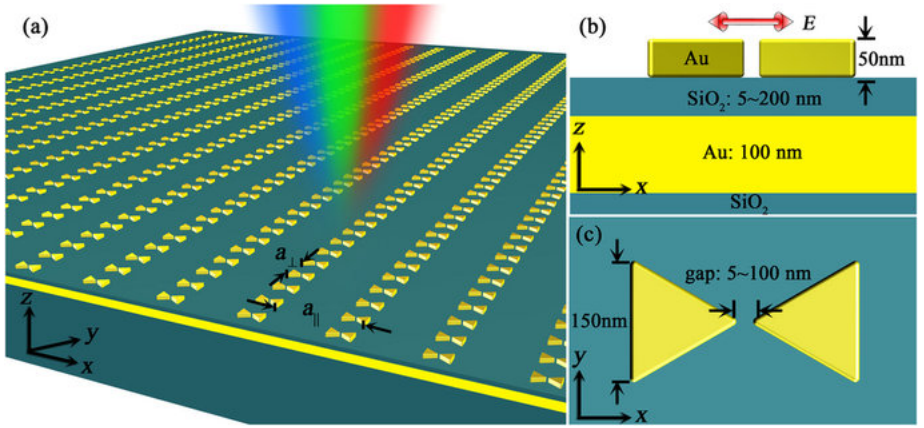
An extraordinary field enhancement is found (in the gap between metal nanoparticles

THE CONCEPT OF NANOANTENNA

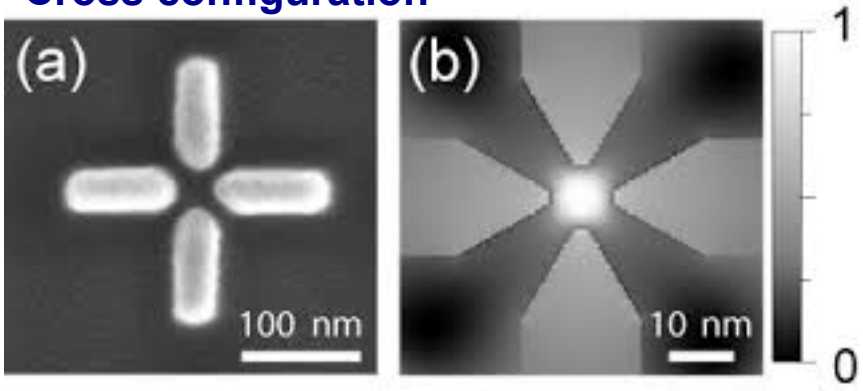
An antenna is a device able to catch the e.m. radiation (at some specific frequency) and convert it into oscillating electric fields, or viceversa

A nanoantenna performs the same in a **strongly subwavelength size scale**





Cross configuration



Huge efforts are presently carried out in order to:

- **optimize geometries**
- **further increase the enhancement at desired wavelengths**
- **exploit additional control possibilities (e.g., polarization)**

FABRICATION OF (NOBLE) METAL NPs I

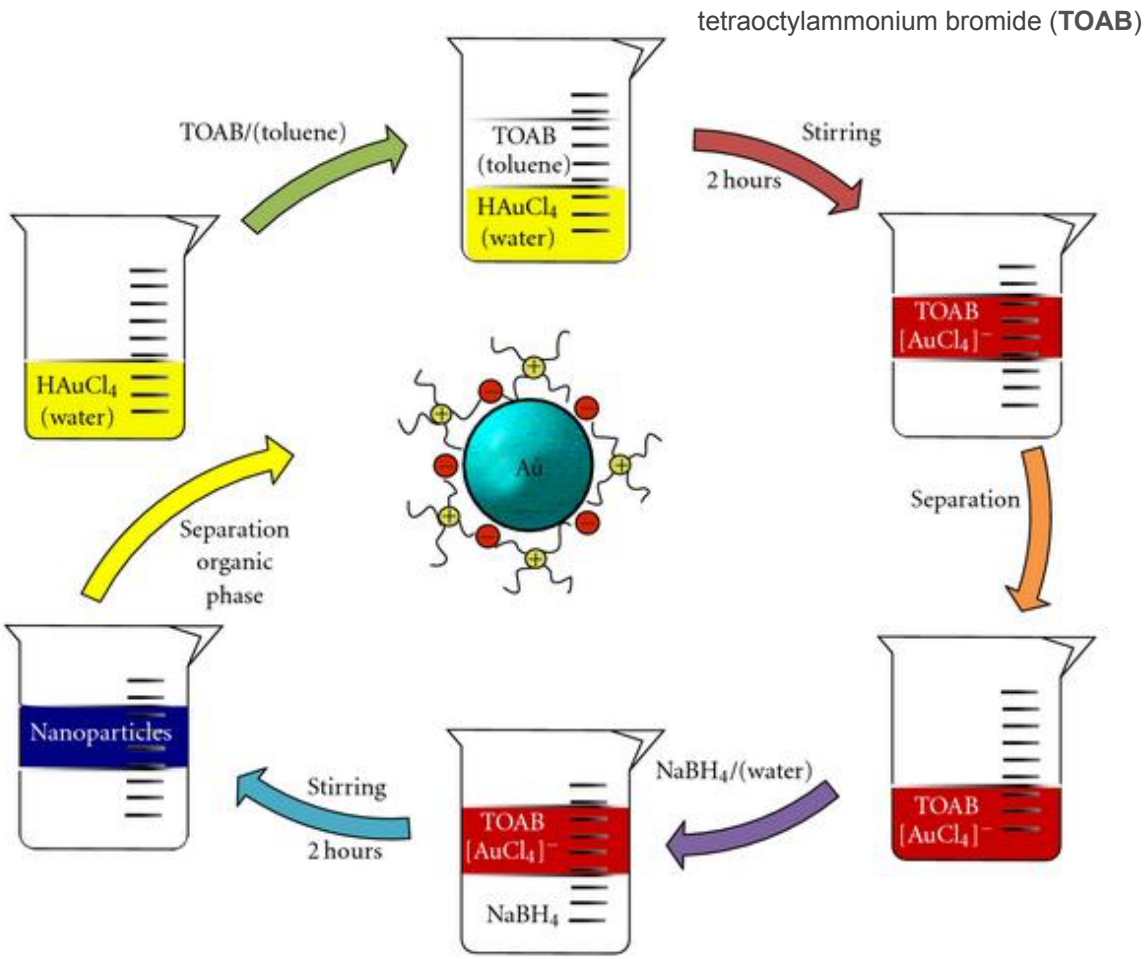
Simple and straightforward chemical methods are available for synthesis of metal NPs in the form of colloids

They typically use controlled **reduction of a (noble) metal salt** (e.g., $HAuCl_4$) followed by self-aggregation of (noble) metal atoms in stable NPs

A surfactant is used in order to avoid precipitation, leading to NP sizes relatively well defined

Photoreduction can be used as well to initiate salt decomposition

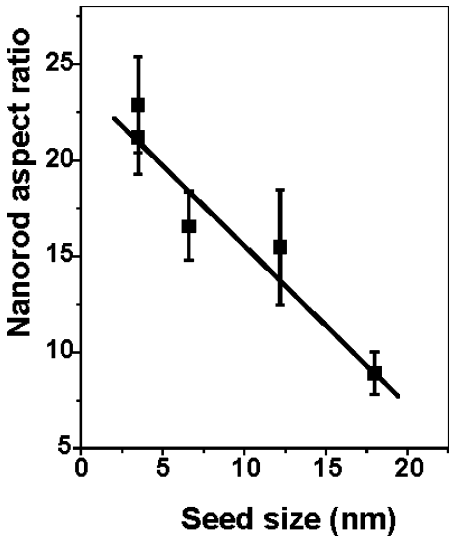
A huge variety of processes has been developed, including “green” ones



FABRICATION OF (NOBLE) METAL NPs II

Shapes different with respect to the spherical one can be obtained by using a controlled **seed growth** method

Gold nanorods are now commercially available with excellent size and aspect ratio control



I. Synthesis of seed

2.5×10^{-4} M $HAuCl_4$ +
2.5×10^{-4} M Na-citrate

Gold nanoparticle seeds
(~ 4nm diameter)

+ 0.6 mL 0.1 M Ice-cold aq $NaBH_4$

II. Stock solution

Stock solution
2.5×10^{-4} M $HAuCl_4$
+ 0.1 M CTAB

=

Addition of Ascorbic acid

Reduction of Au^{3+} to Au^{1+} results in disappearance of color

II. Three step protocol for nanorod synthesis

Step A

1 mL seed +
9 mL of stock solution

Add 1mL of A

Step B

1 mL A +
9 mL of stock solution

Step C

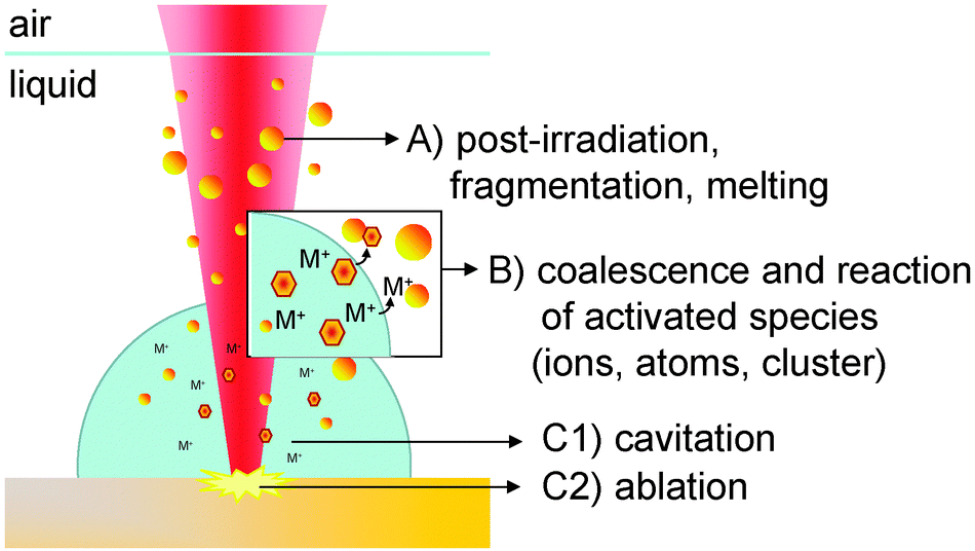
10 mL B +
90 mL stock

=

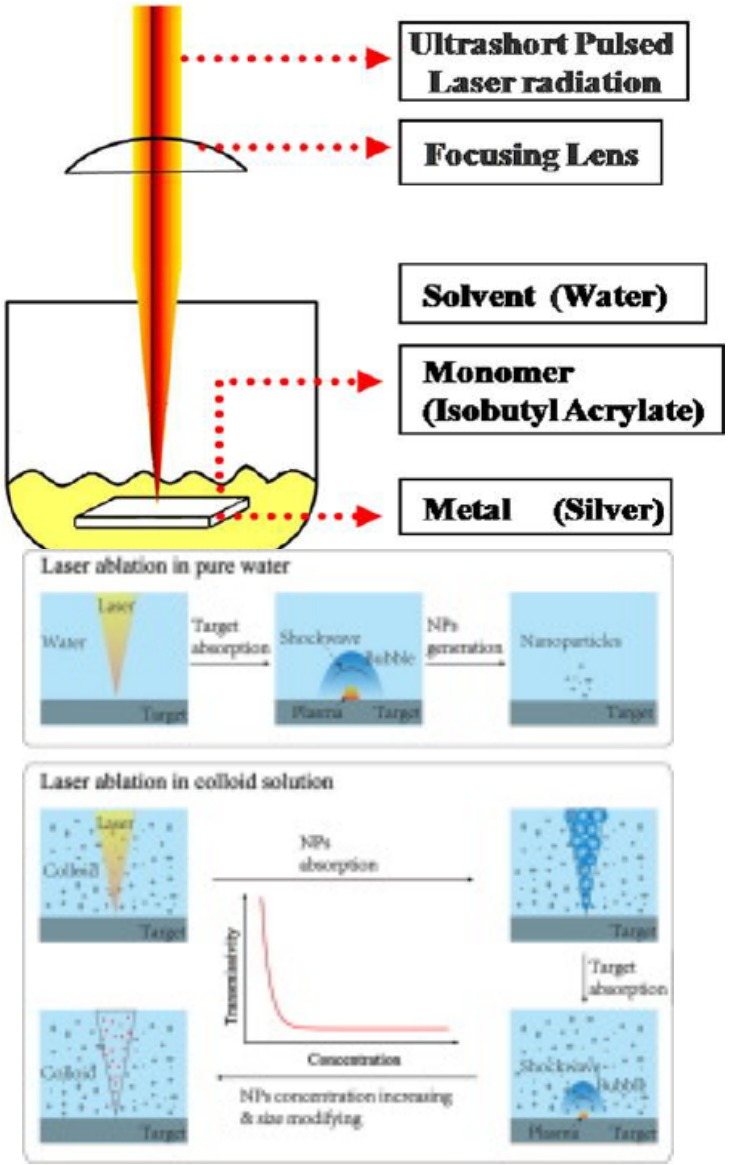
J. Phys. Chem. B, Vol. 109, No. 29, 2005

FABRICATION OF (NOBLE) METAL NPs III

A few (typically less efficient and more expensive/ cumbersome) **physical methods** have been developed as well, such as **laser ablation in liquid**



Complicated dynamical processes occur during the ablated material evolution in the liquid, including cavitation and non-linear processes: when duly tuned, they can enable sharp size distribution of the NP size (and even formation of non-spherical shapes)



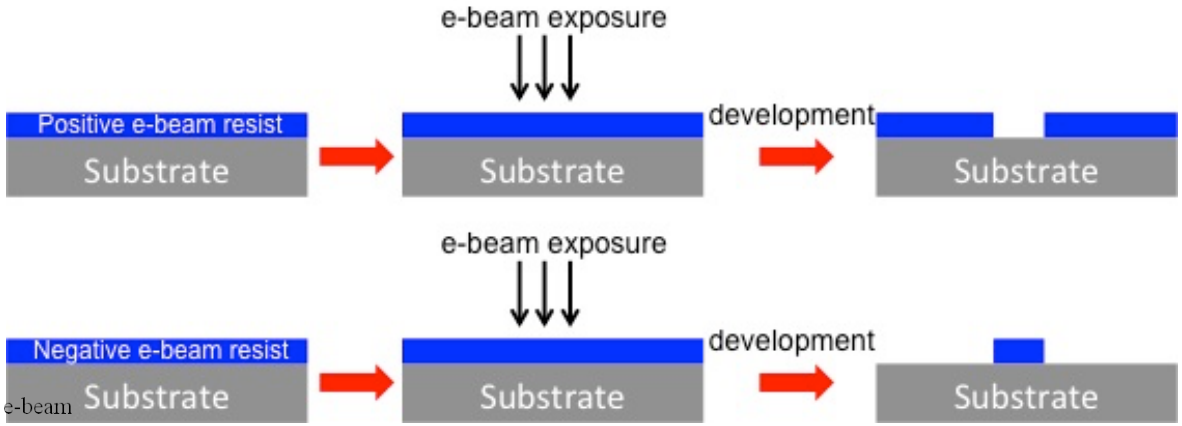
METAL NPs SUPPORTED ON A SUBSTRATE

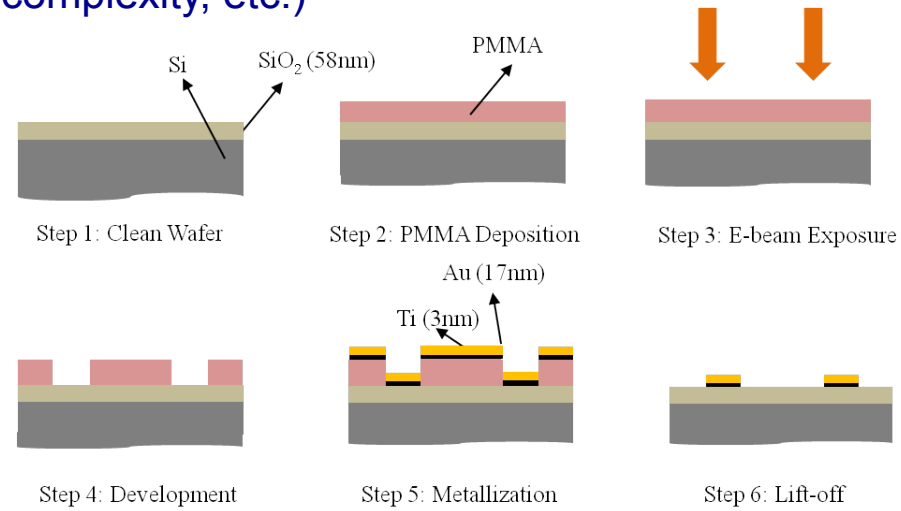
In many applications (noble) metal NPs have to be anchored to a substrate, possibily, forming a predefined pattern

Many (mostly physical) methods exist to attain the goal, generally indicated as **lithographies**

The very high spatial resolution requested makes optical lithography typically unsuited for producing NP arrays, dimers, nanoantennas

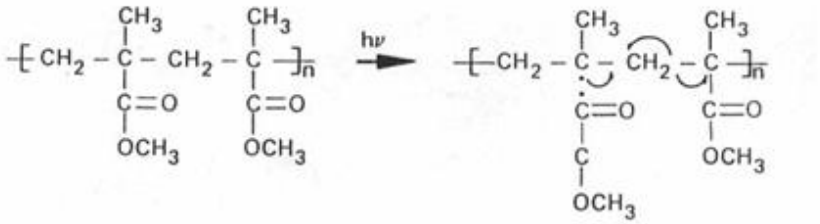
Electron lithography is used (at the expenses of low yield, cost, complexity, etc.)



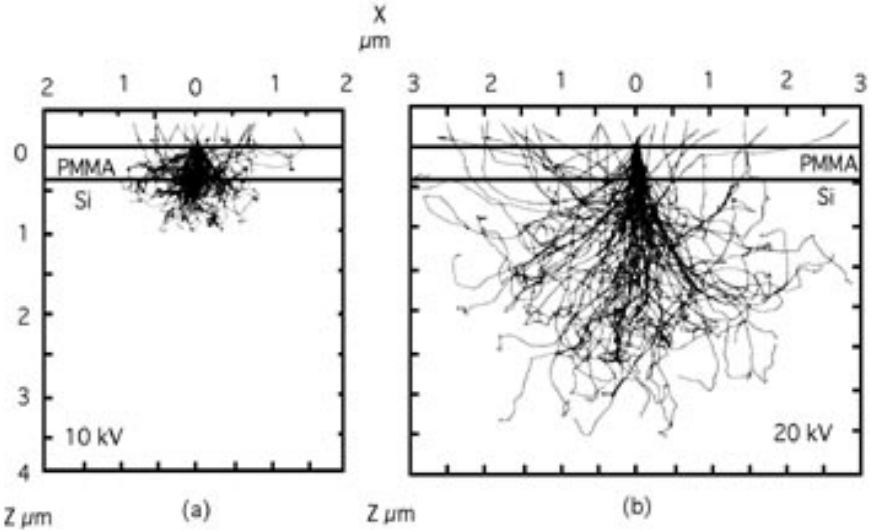


Mutuated from well established semiconductor microtechnologies, **lift off** is often used to obtain metal patterns on a substrate

RESIST AND SPIN COATING

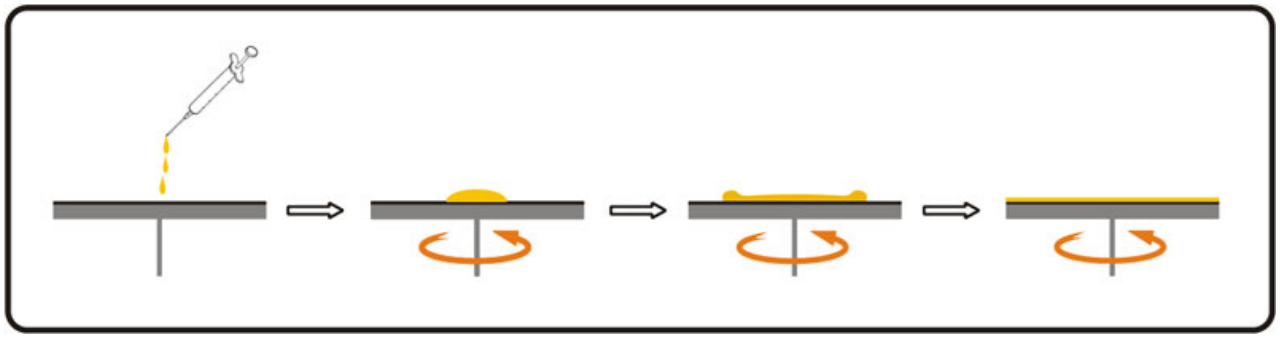


Resist (e.g., PMMA) plays the role of an electron-impact activated (or photo-activated) medium modifying its physical/ chemical properties (e.g., solubility, idrofobicity, etc.)

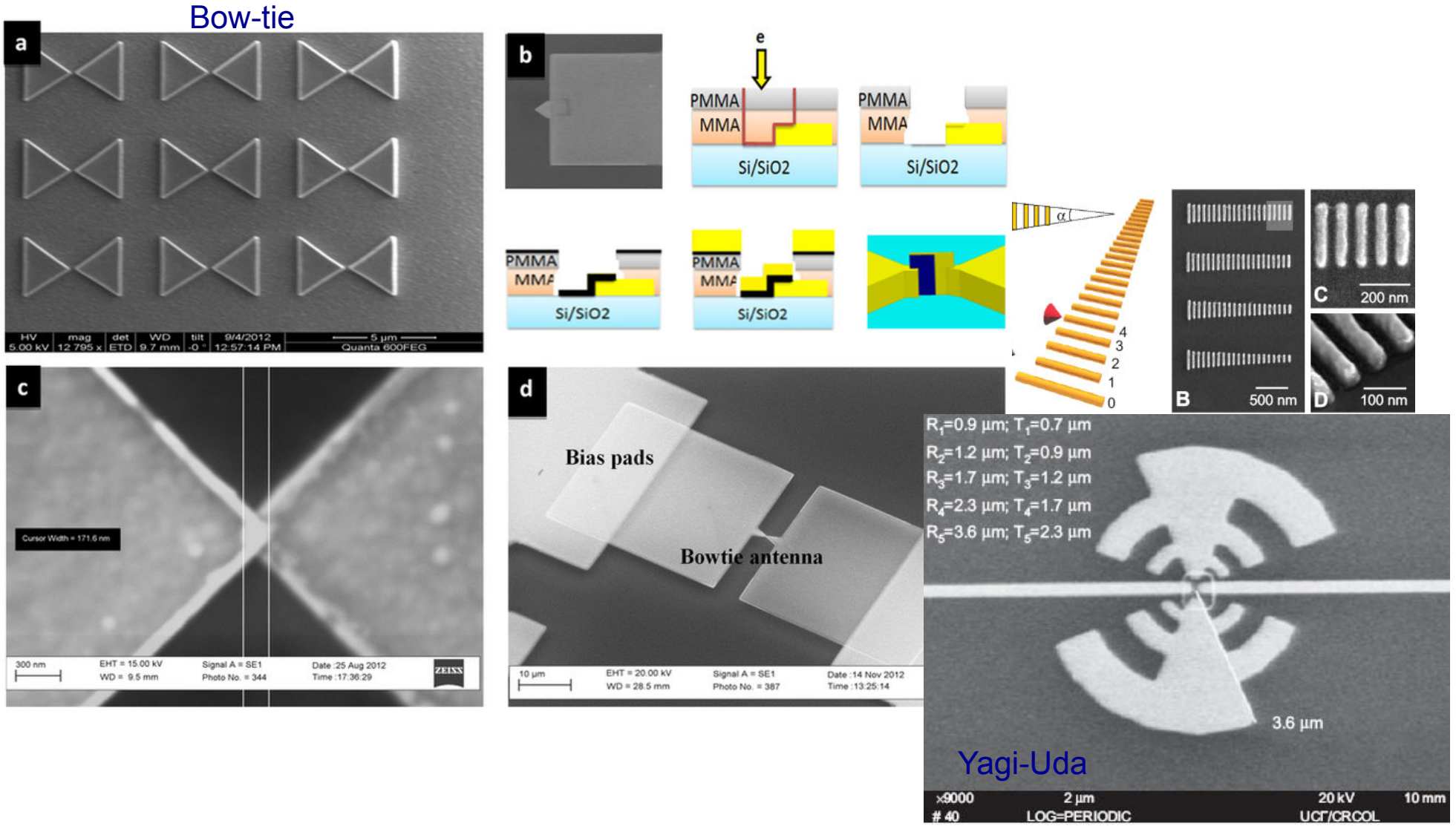


Care must be used to limit material damage due to unwanted e-beam penetration into the substrate (exposure times have to carefully chosen to avoid under or overexposure)

Spin-coating typically used to obtain relatively thin and **homoegeneous** resist layer onto the substrate

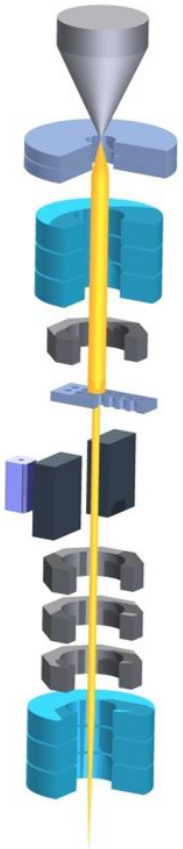


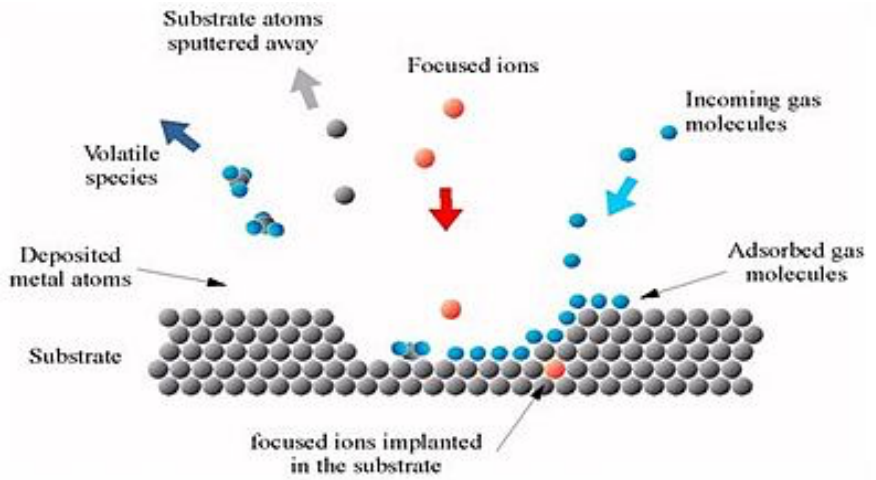
EXAMPLES OF EBL-MADE NANOANTENNAS



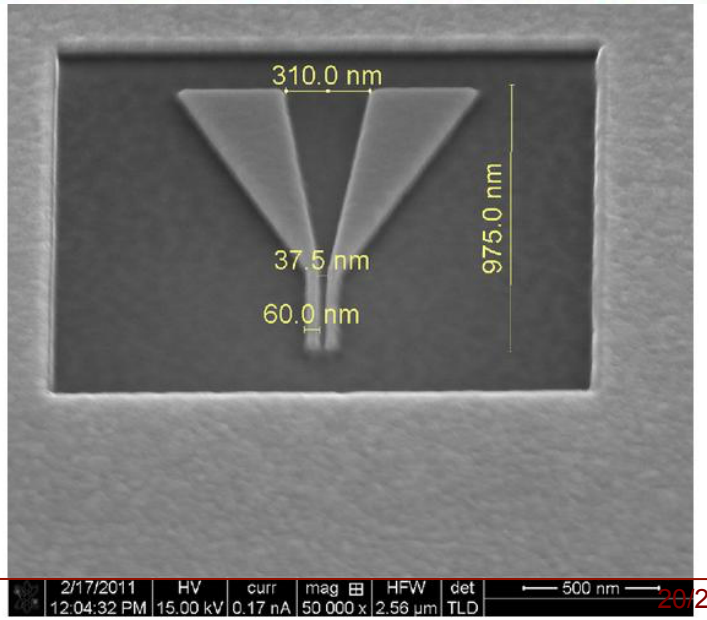
Sci Rep 4, 4270 (2014)

FOCUSED ION BEAMS (FIB)





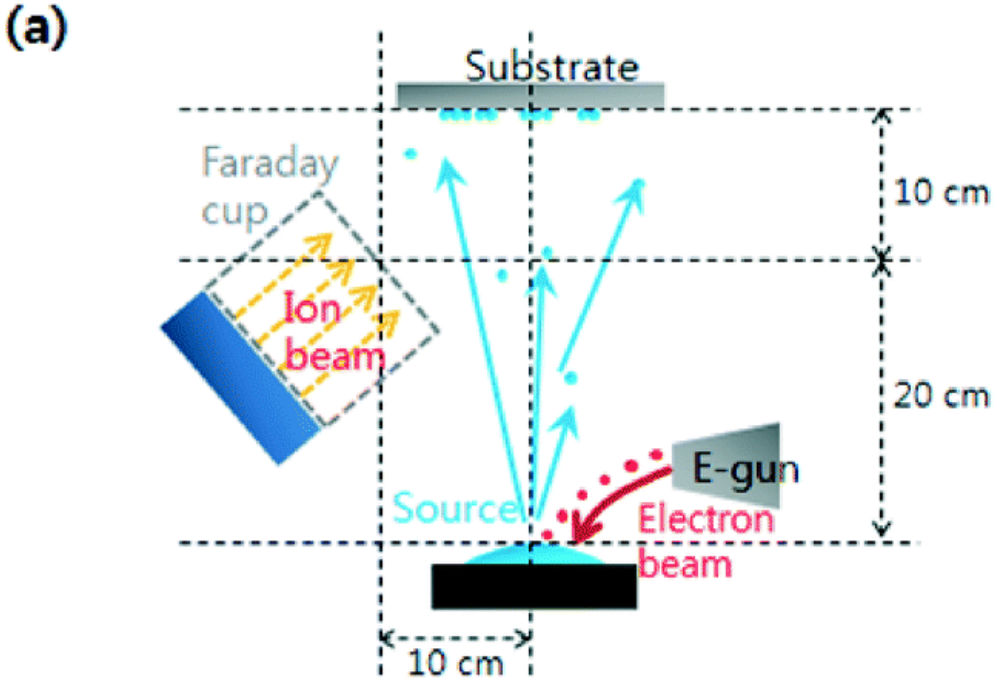
1. Adsorption of the gas molecules on the substrate
2. Interaction of the gas molecules with the substrate
   Formation of volatile and non volatile species
3. Evaporation of volatile species and sputtering of non volatile species

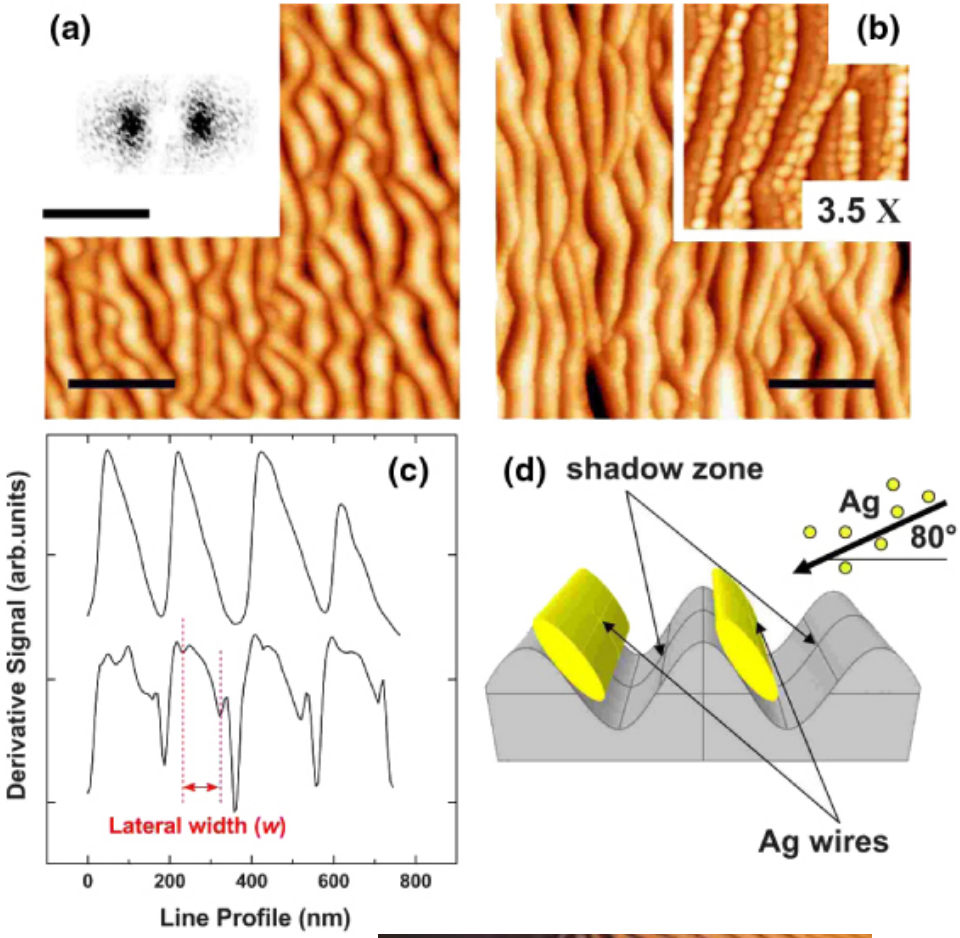


Another technique used for creating a nanosized pattern out of a continuous metal film (deposited onto a substrate) is **Focused Ion Beam (FIB)**

(Heavy) ions are focused and scanned onto the surface leading to localized material milling
→ ***No need for resist!***

SELF-ORGANIZED METHODS





Combining evaporation (either thermal or electron-beam induced) with (heavy) collimated ion beams sent at same angle to cross the atomic vapor, self-induced organization of metal patterns can be **efficiently** deposited onto solid substrates

Similar to wind-induced sand distribution in the desert

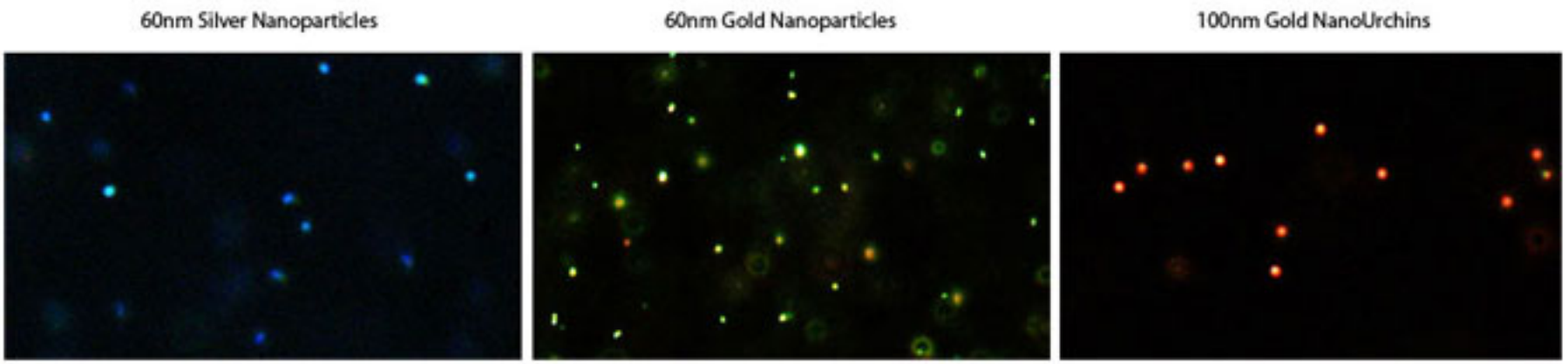
J. Phys.: Condens. Matter 21 (2009) 224022

(A FEW) EXAMPLES OF APPLICATIONS

Plasmonics (in general) is one of the most active fields of nanophotonics research in the last few years

A great variety of applications is envisioned: here a very small selection is considered!

Dark-field optical microscopy (conventional)

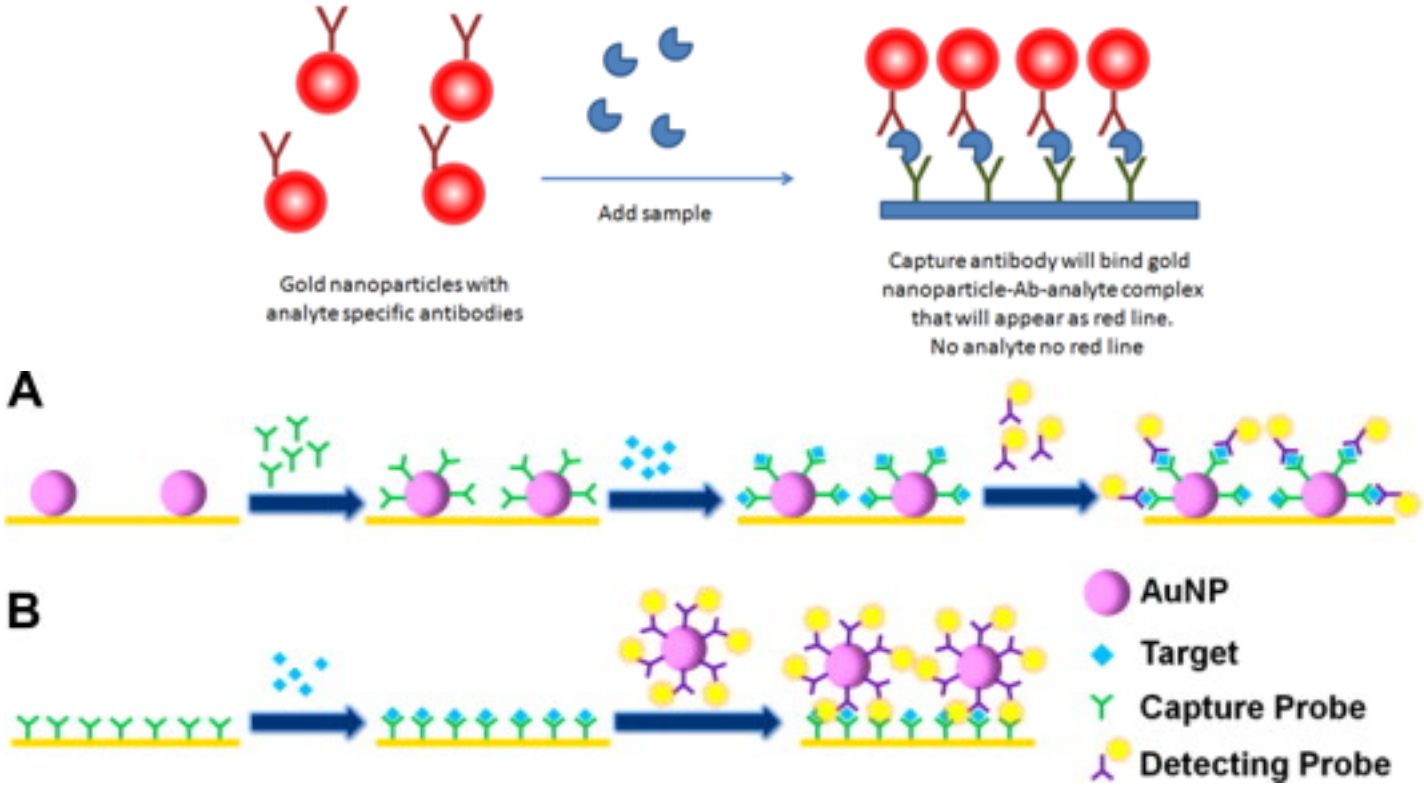


Colloidal (gold) metal NPs can be used as a bio-compatible substitute for fluorescent markers (molecular dyes, Q-dots)

Although they do not emit spontaneously, metal NP can be discriminated thanks to the enhanced scattering cross-section, e.g., by **dark-field** optical microscopy

Optical bio-sensors can be engineered and tailored to specific sensitivies thanks to the ease of functionalization for gold surfaces

OPTICAL NANOBIOSENSORS

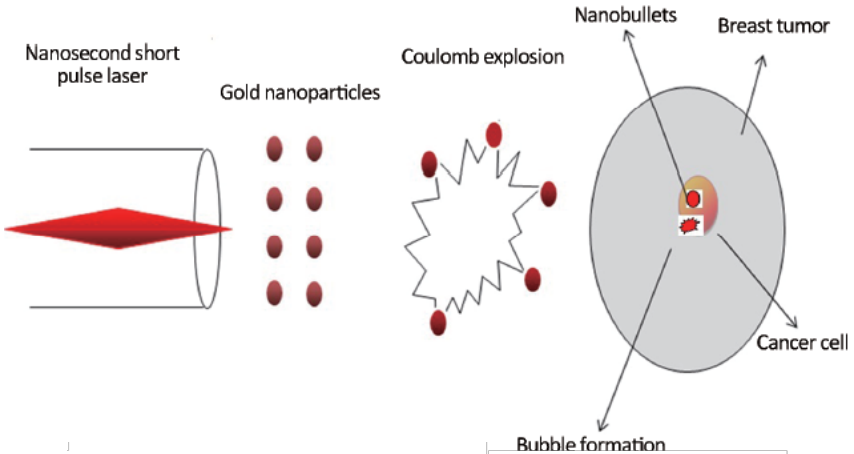


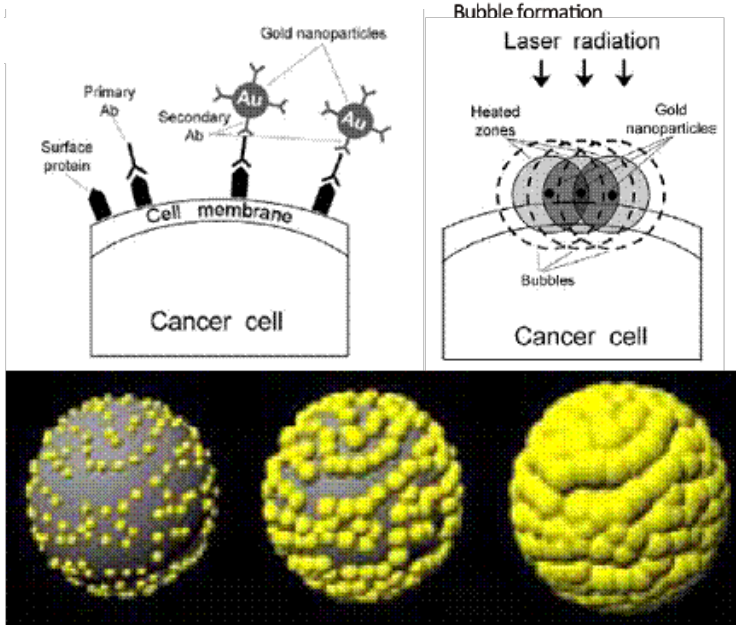
In general terms, gold NPs can be selectively attached to specific functional groups

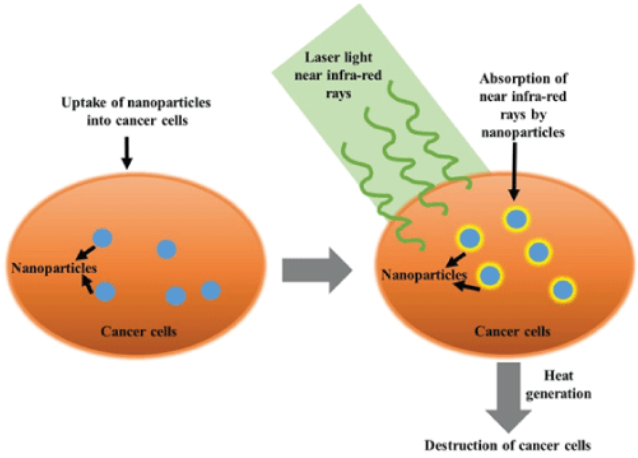
Similar to Surface Plasmon Spectroscopy, the optical properties of the gold NP are modified due to the presence of even a single molecule located in proximity with the NP

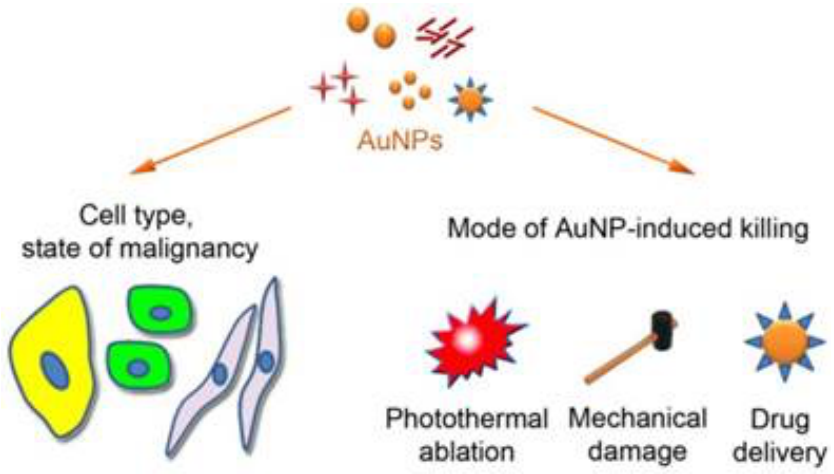
Strong species selectivity and sensitivity can be achieved

OPTICAL THERAPIES

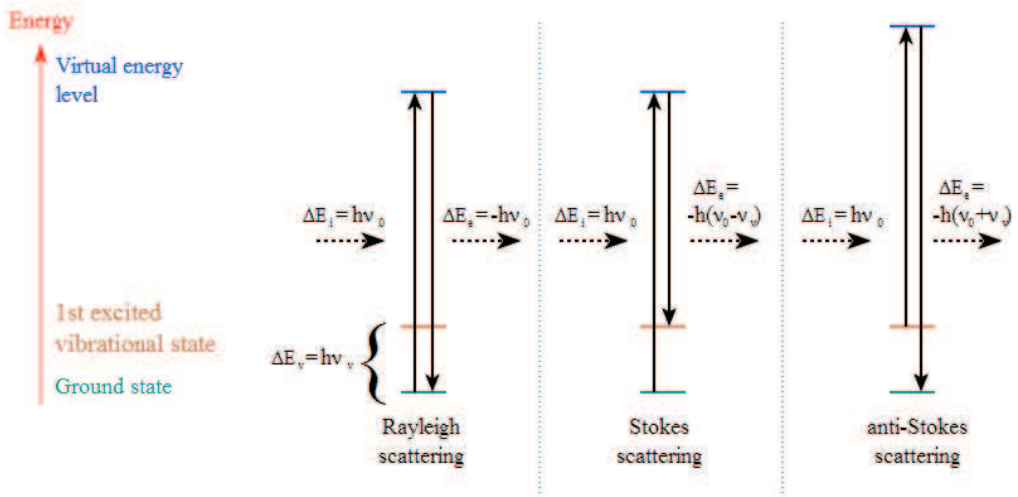








SURFACE-ENHANCED RAMAN SPECTROSCOPY (SERS)



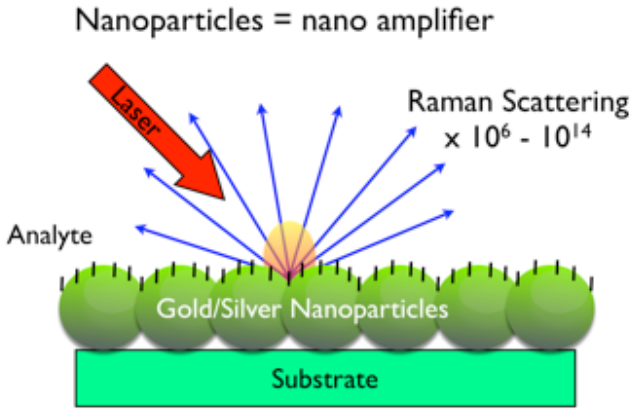
As you know, Raman spectroscopy is an extremely powerful analyitical technique thanks to the ability of identifying narrow lines corresponding to molecular (or even solid-state) transitions

Traditionally, Raman spectroscopy suffer from sensitivity issues limitng the ability to probe small clusters or even single molecules

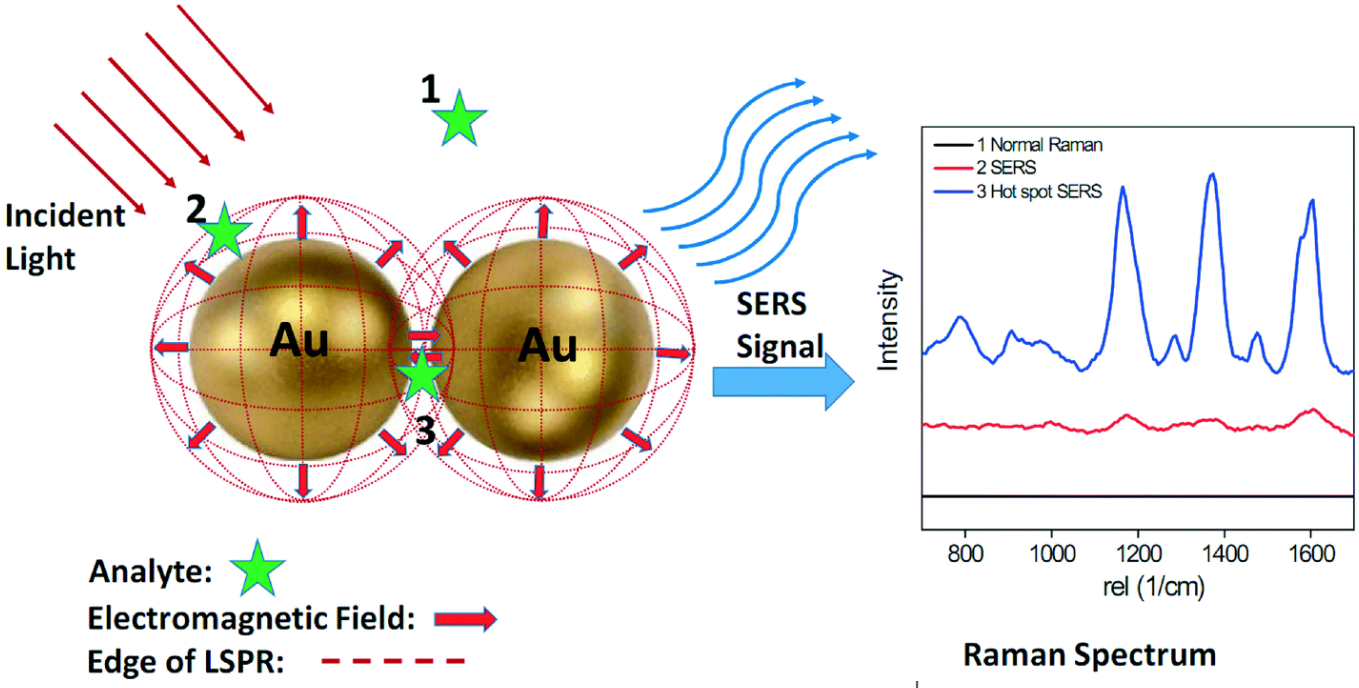
In fact, Raman cross-section is typically around 10 orders of magnitude smaller than fluorescence cross-section ($\sigma_{Raman} \sim 10^{-31}$–$10^{-29}$ cm^2/molecule)

Field-enahncement enabled by LSP resonances can increase the local e.m. field felt by the molecule

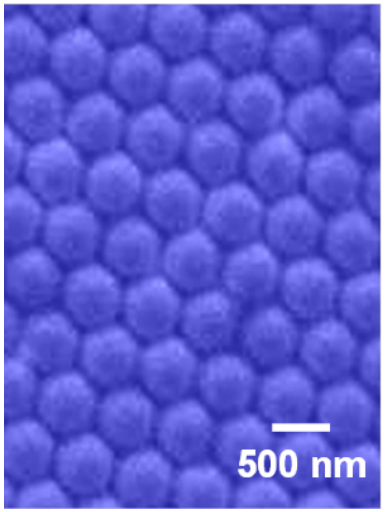
→ *Surface Enhanced Raman Spectroscopy*

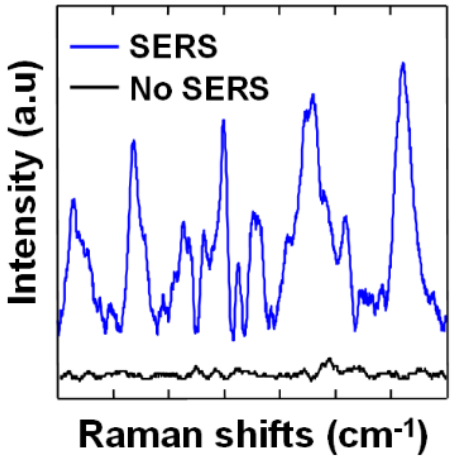


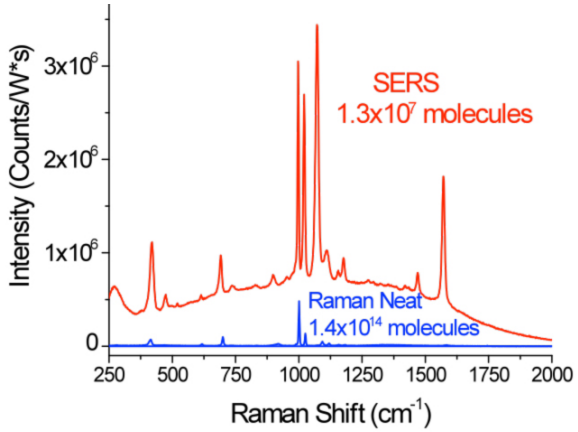
SERS EXAMPLES



Raman Spectrum

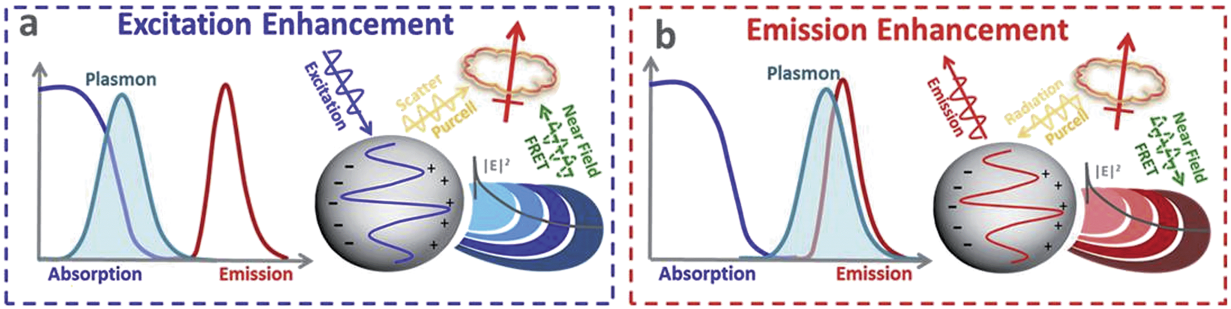


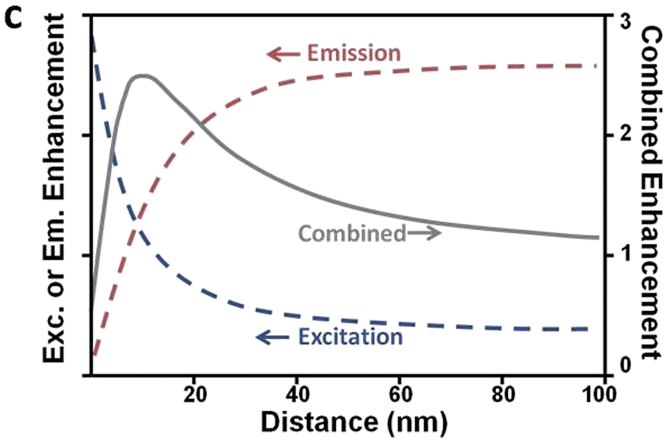


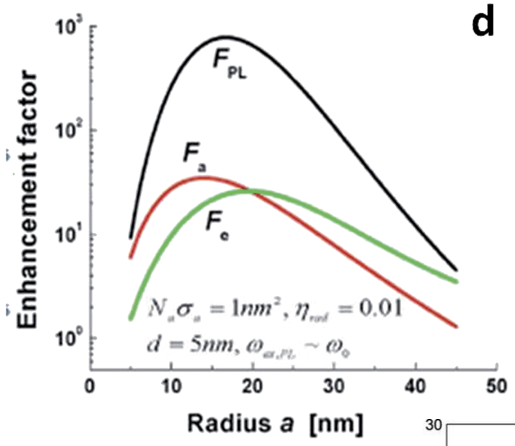


Sensitivity increase by orders of magnitude

FLUORESCENCE ENHANCEMENT



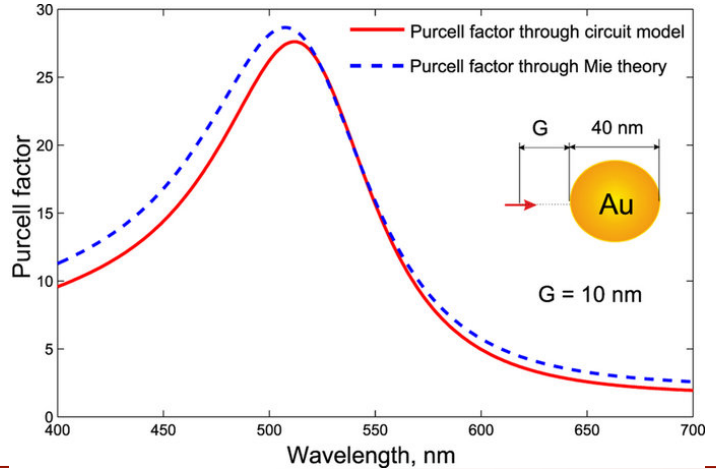




A metal NP placed in proximity to a nanosized emitter (a molecule, a Q-dot, etc.) can effectively modify the fluorescence (spontaneous emission) properties, through, e.g.:

- Quenching (i.e., opening of non-radiative pathways);
- Excitation enhancement (due to e.m. field enhancement)
- Emission enhancement (in particular when in resonance with the LSP)

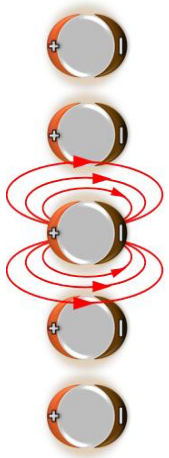
Wavelength-depending Purcell effect (well known in atomic physics, occurs when an atom is placed inside a resonant cavity, leading to an increase of the spontaneous emission rate) can be obtained with LSPs: this might be used to increase lasing efficiency in nanosized laser sources

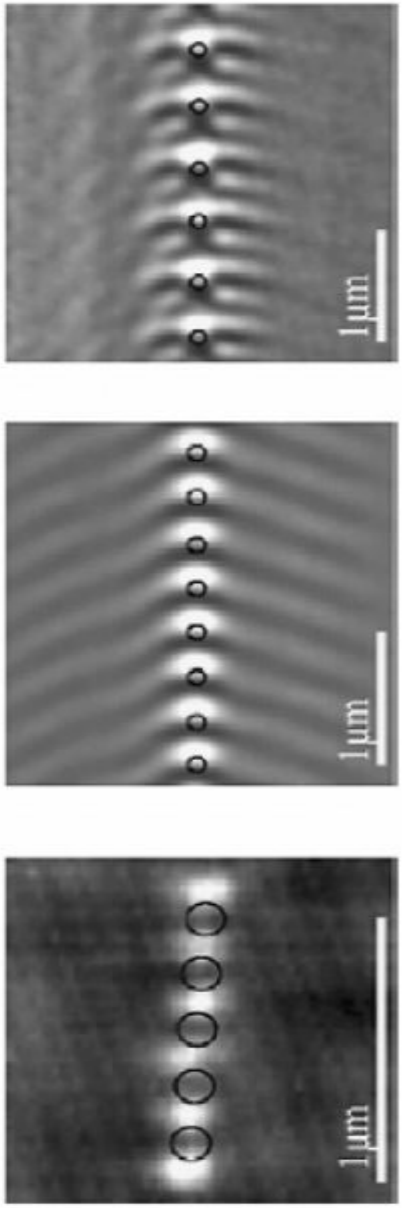


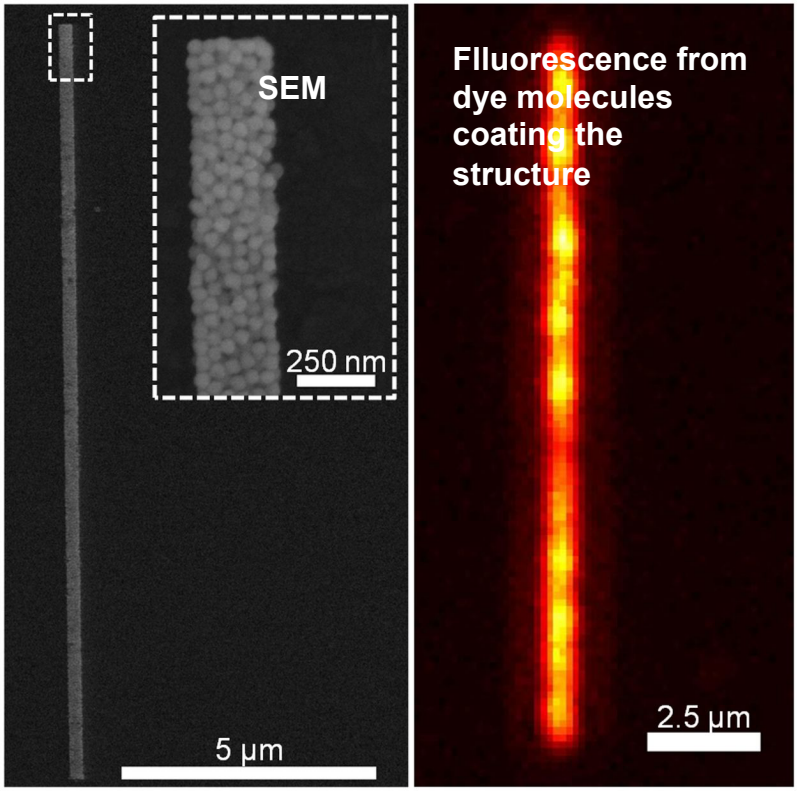
COUPLED LSP WAVEGUIDING

Arrays of metal (gold) nanoparticles can transfer e.m. energy in multiple, collective, LPR excitation

Waveguiding and spatial confinement of the e.m. energy is accomplished, similar to SPP waveguides, but with (potential) advantages in terms of wavelength selectivity, ease of excitation, losses, desing flexibility







http://pubs.acs.org/doi/abs/10.1021/nl2039327

Hohenau, et al. (2007)

CONCLUSIONS

- ✓ Plasmon oscillations and their interaction with the light can be realized and exploited also with nanoparticles
- ✓ The magnificent scattering properties of metal nanoparticles are known since from thousands years and used for fine arts applications
- ✓ There is a wealth of potential modern applications for localized plasmon resonances, where the wavelength depending behavior is joined with field enhancement (in the proximity of the nanoparticles) leading to, e.g., improved optical sensors interfacing with nanoemitters, waveguiding in sub-wavelength size, photonics, photovoltaics (not considered here), optoelectronics and lasers (not considered here)

We will see how several concepts and methods considered for the plasmonics can be shared with devices and systems using dielectrics and/or other "strange" artificial materials (next lecture)!

FURTHER READING

For a complete textbook on plasmonics:

S.A. Maier, Plasmonics: Fundamentals and Applications, Springer, New York (2007).

For a solid and well-established textbook on the same topic (without much applications!):

H. Raether, Surface Plasmons, Springer-Verlag, Berlin Heidelberg (1988).
Brandon, W.D. Kaplan, Microstructural Characterization of Materials, Wiley, New York (1999).

For a useful and comprhensive analysis, Maier's inspired:

O. Benson, Uni Berlin, Chapter 7 of his Nanophotonics lectures [freely available at https://www.physik.hu-berlin.de/de/nano/lehre/Gastvorlesung%20Wien/plasmonics]

For a review on LSP:

S. Link and M.A. El-Sayed, J. Phys. Chem. B 103, 8410-8426 (1999).

For a comprehensive review on plasmonic nanoantennas:

L. Novotny and N. van Hulst, Nature Photonics 5, 83–90 (2011) doi:10.1038/nphoton.2010.237