TÉCNICO LISBOA

Nanostructured Materials and Nanotechnology 2022-2023

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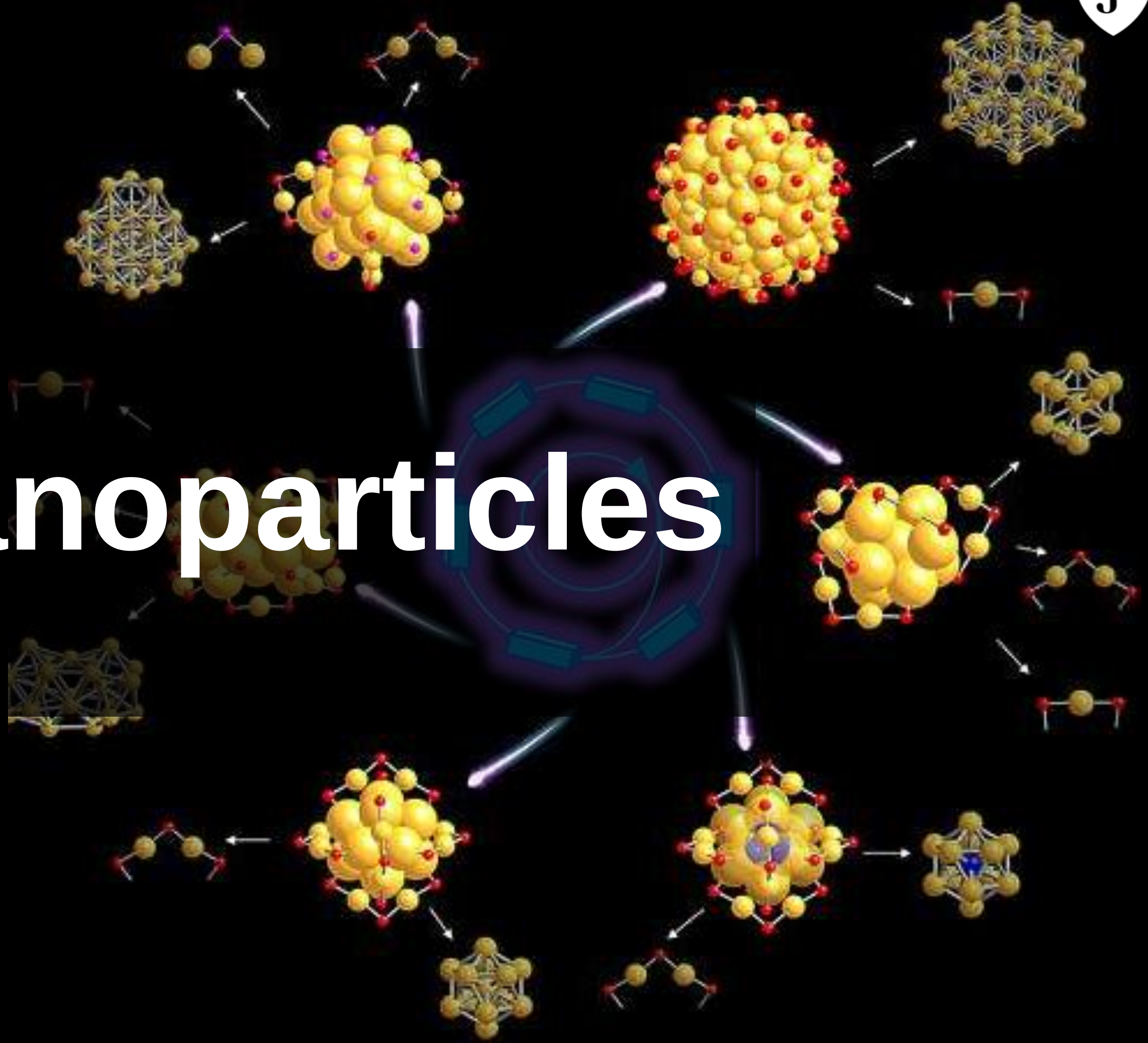
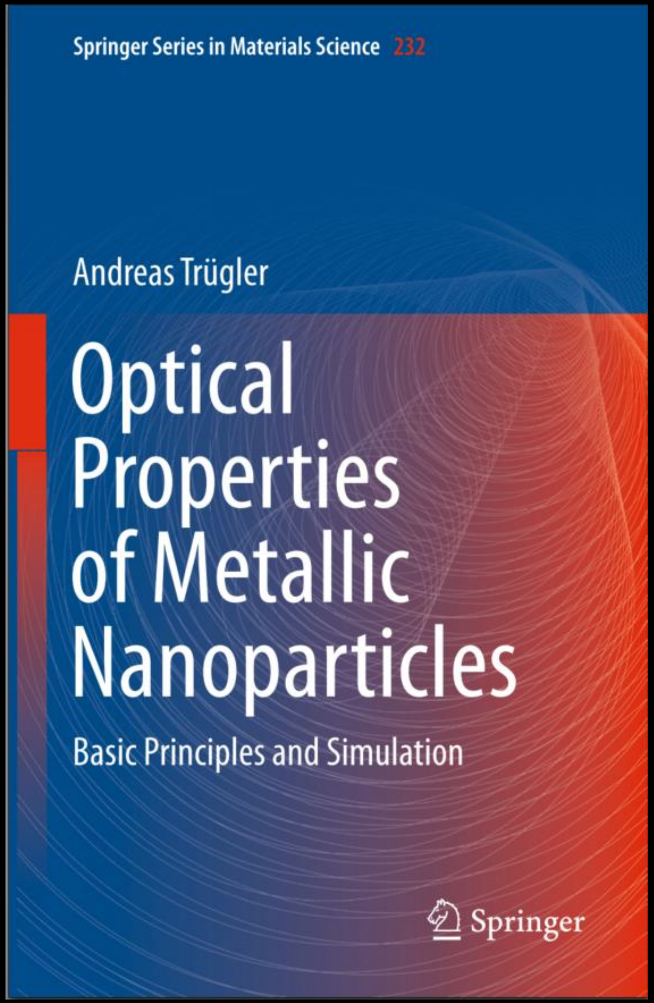


Metal Nanoparticles

Img credit: https://phys.org/news/2015-01-nanogold-potential-biomedicine.html

Bibliography

Extra reading

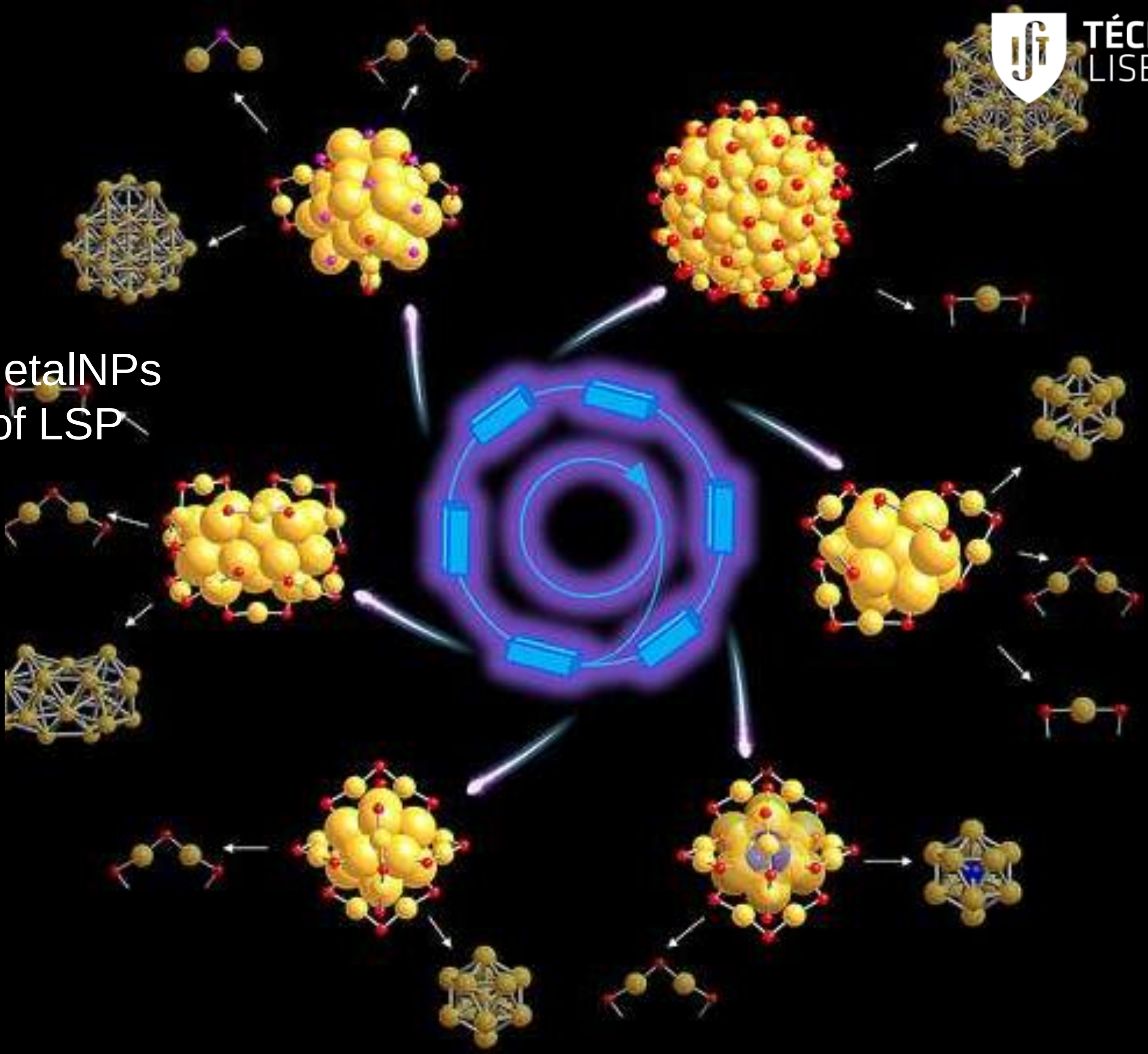


1. “Surface plasmon resonance in gold nanoparticles: a review” Vincenzo Amendola et al 2017 J. Phys.: Condens. Matter 29 203002, https://doi.org/10.1088/1361-648X/aa60f3

2. Gold nanorods: Synthesis, characterization and applications Pérez-Juste et al, Coordination Chemistry Reviews 249 (2005) 1870–1901 doi:10.1016/j.ccr.2005.01.030

Content

- Localized surface plasmon
- Extinction cross-section for spherical MetalNPs
- Resonance conditions for observation of LSP
- Composition Effect on LSPR
- Size Effect on LSPR
- Medium Effect on LSPR
- Shape Effect
- Field enhancement
- Preparation of MetalNPs
- Applications of MetalNPs



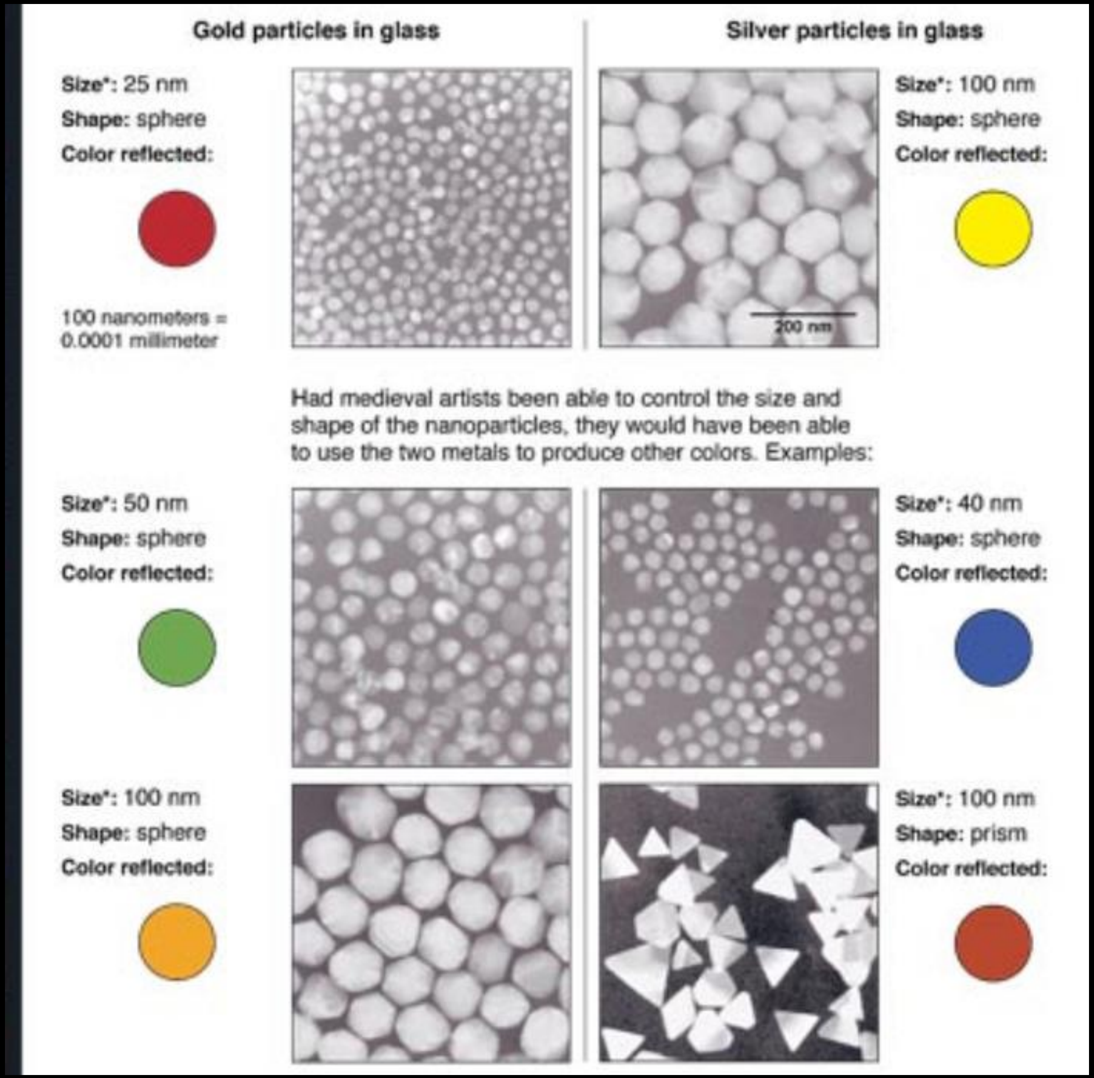
Lateral Flow Immunoassay

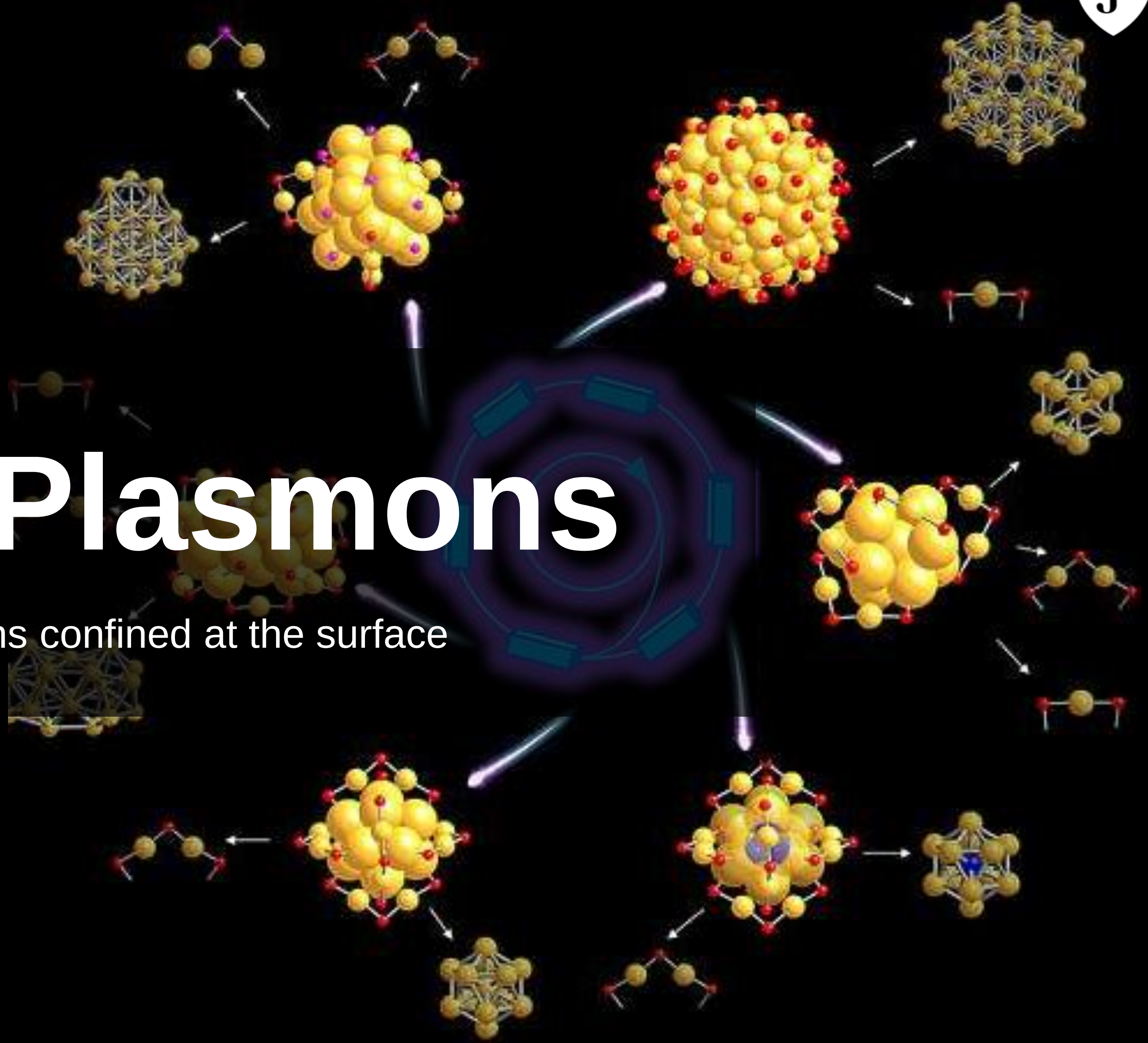
Lycurgus Cup, Roman glass, 4th c.AD. Nanoparticles (70 nm) of gold and silver are responsible for the dichroic effect (red/green)

Img credit|Science direct, picture provided by The British Museum

The First Nanotechnologists

Ancient stained-glass makers knew that by putting varying, tiny amounts of gold and silver in the glass, they could produce the red and yellow found in stained-glass windows. Similarly, today’s scientists and engineers have found that it takes only a small amounts of nanoparticles, precisely placed, to change a material’s physical properties





Surface Plasmons

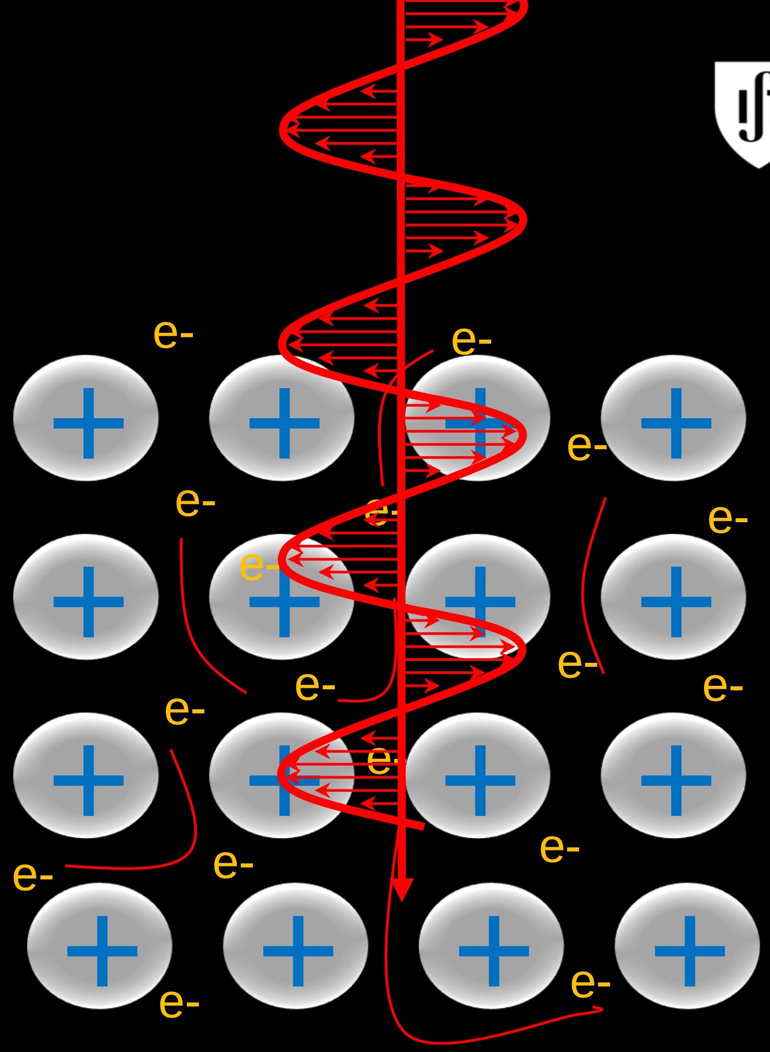
collective electron oscillations confined at the surface

Img credit: https://phys.org/news/2015-01-nanogold-potential-biomedicine.html

Electron gas

A conductor (metal) can be modeled by a regular array of atoms where each atom gives up electrons that are shared amongst the atoms in the material forming a free e- gas (e- sea).

Quantitized system with conduction e- moving in the periodic potential of the nuclei



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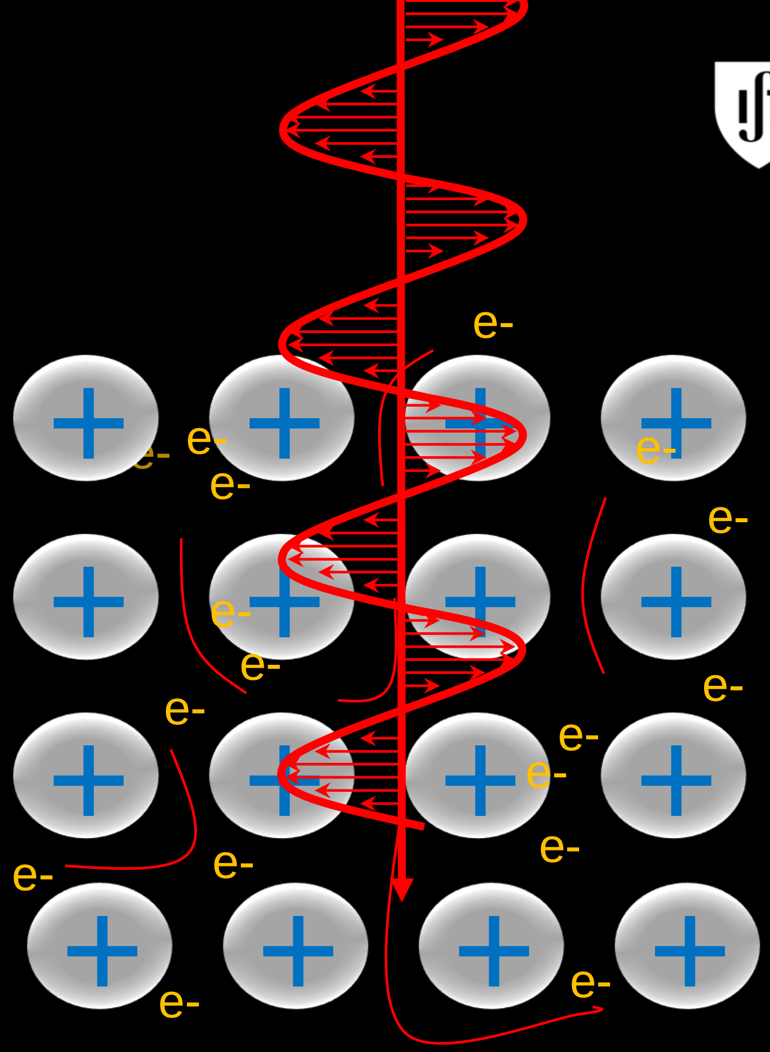
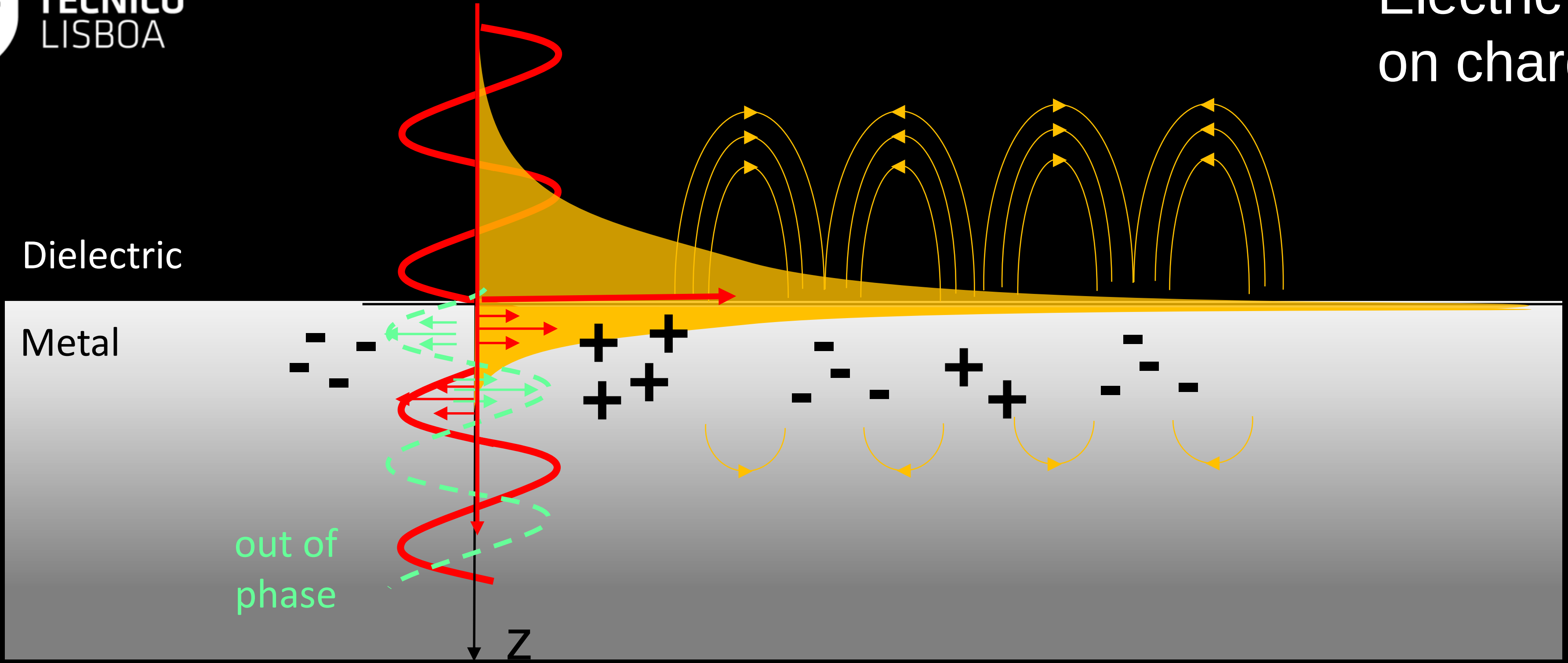
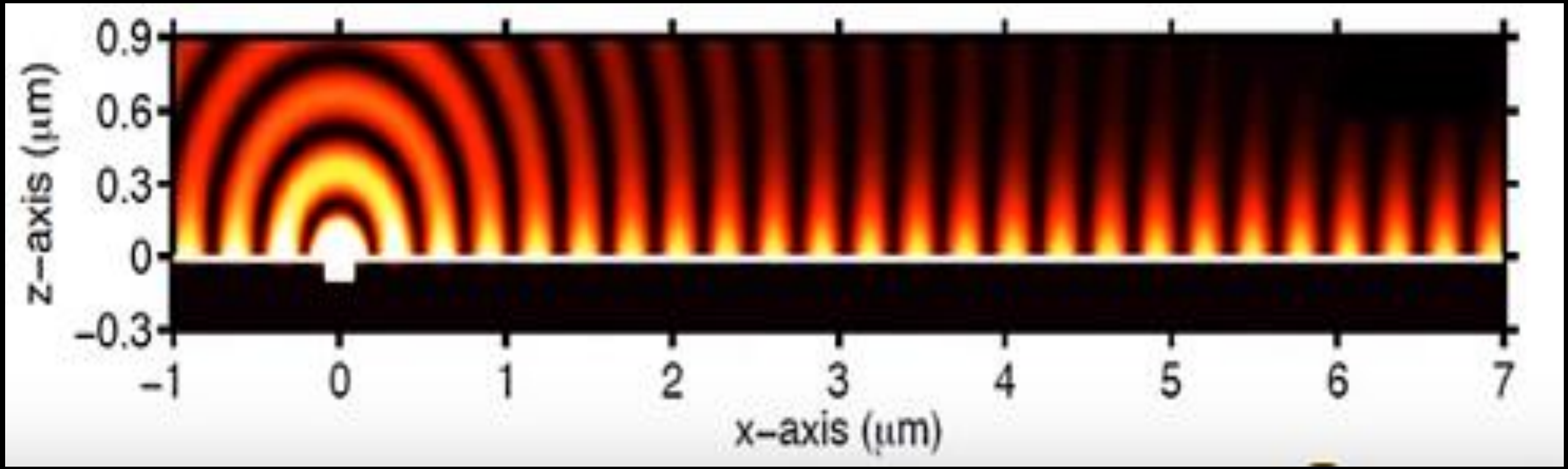


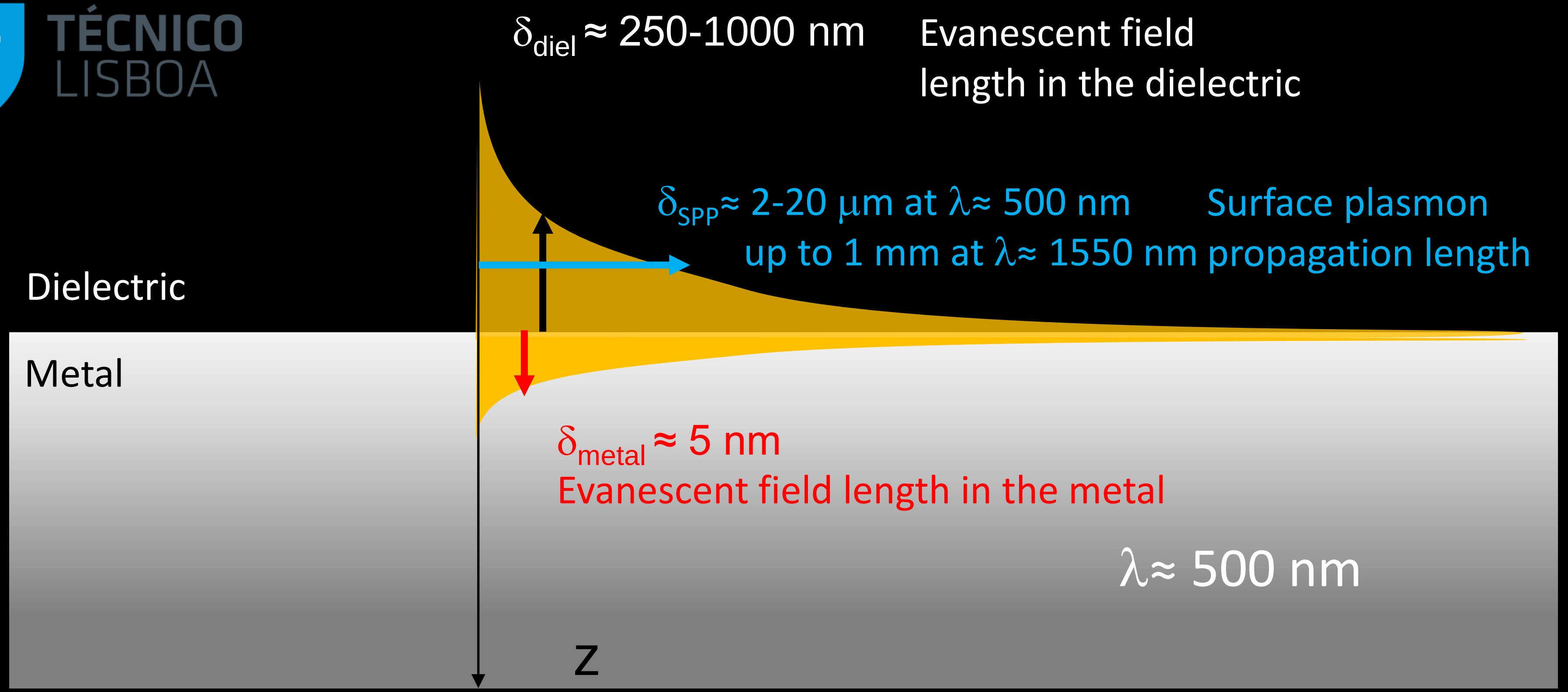
Electric filed exerts forces on charged particles

F=q.E



SPP Intensity is maximal at the interface and it decays exponentially into both the metal and the dielectric





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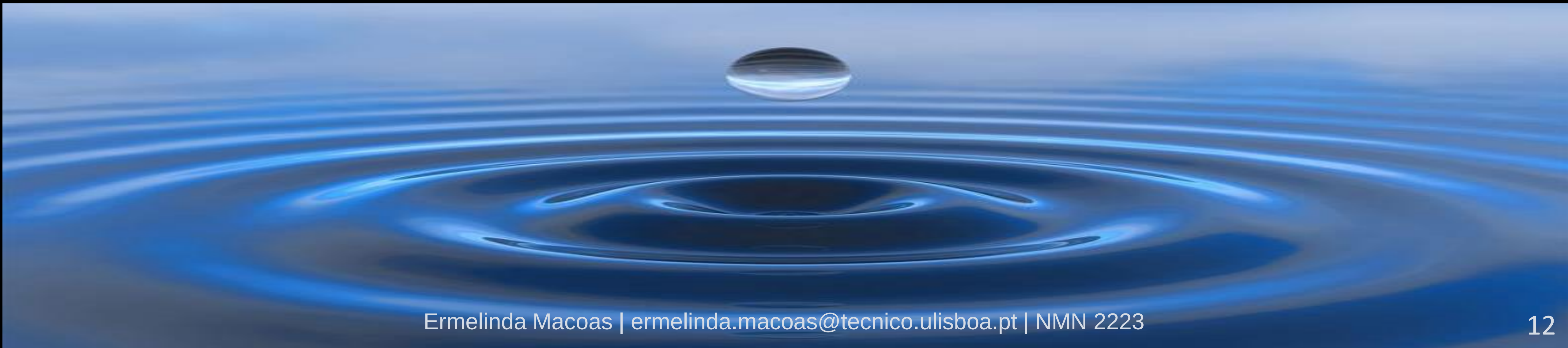
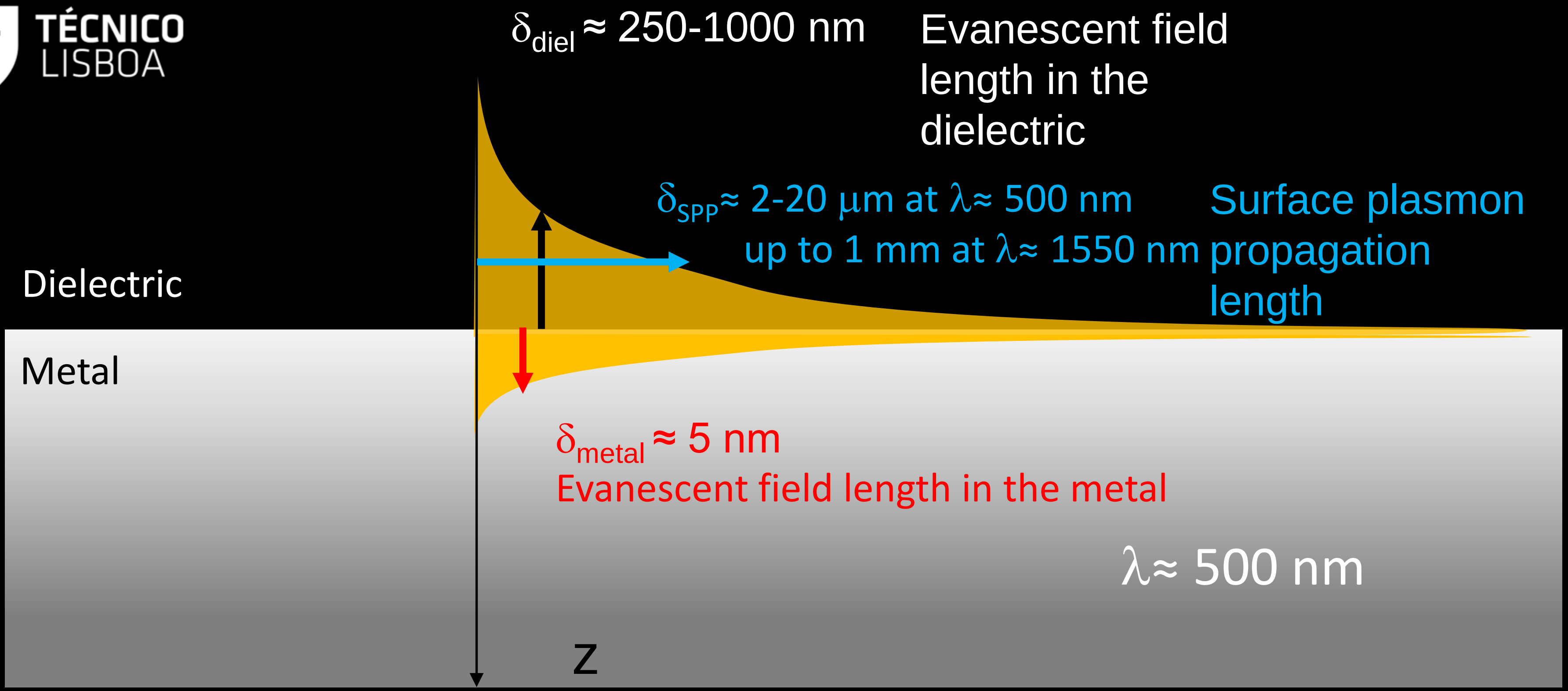
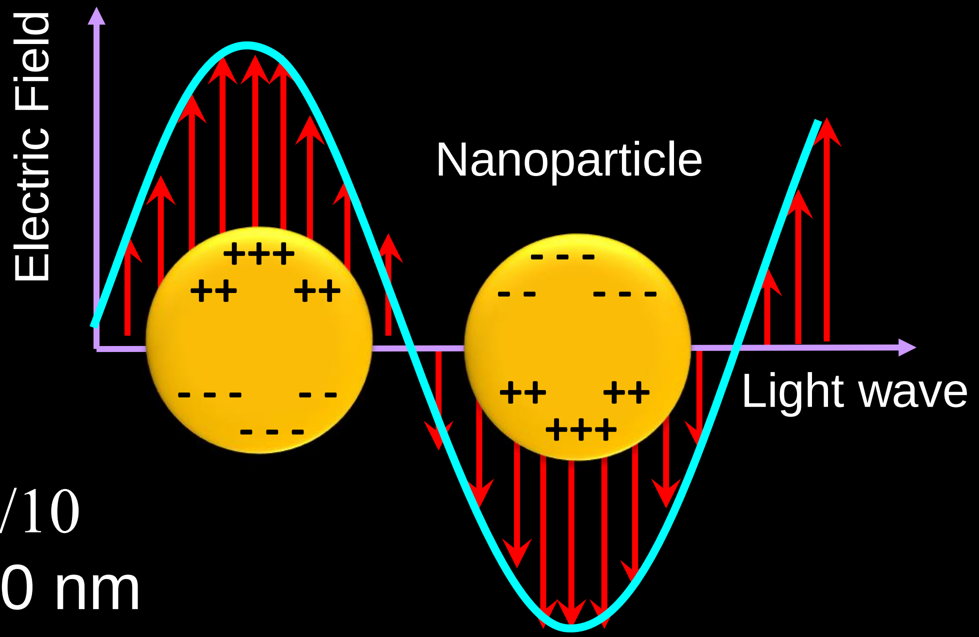




SPP Intensity is maximal at the interface and it decays exponentially into both the metal and the dielectric

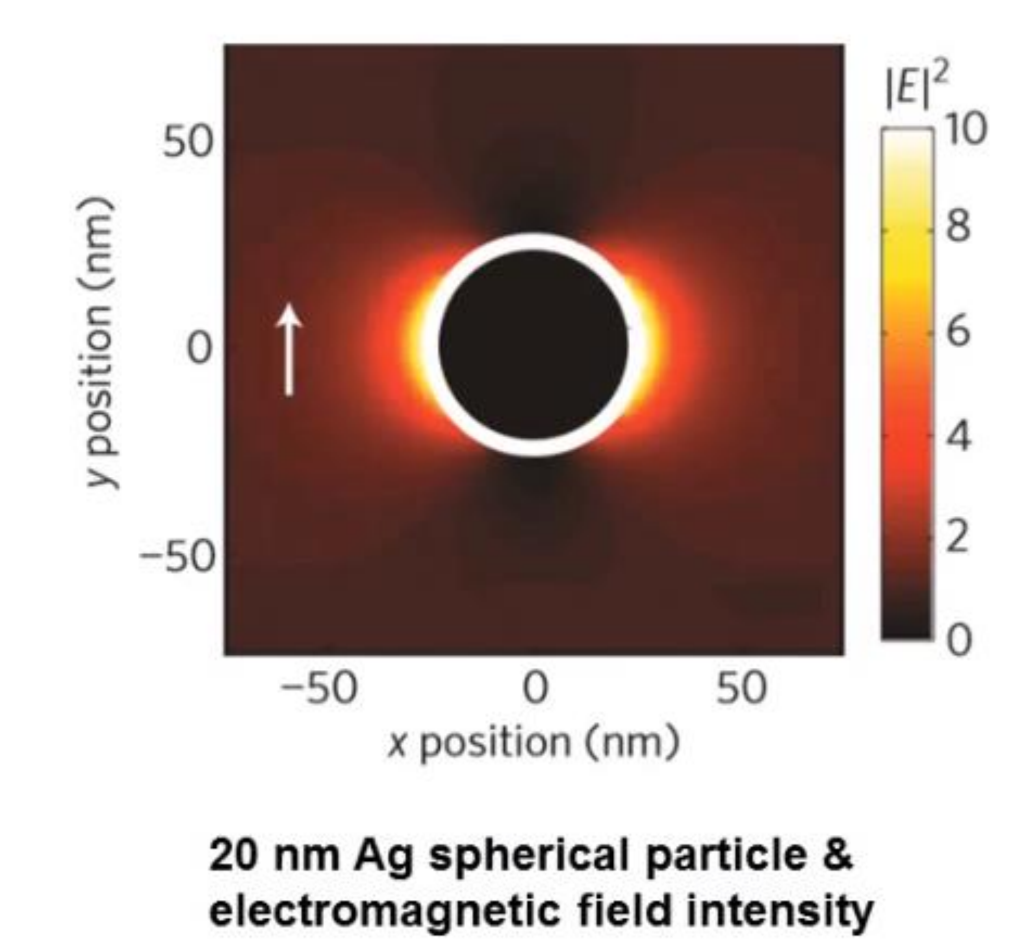
If the lateral dimensions of the interface become much smaller than the surface plasmon propagation length the surface plasmon is said to be localizes
LSPP= localized surface plasmon polariton

In NPs the plasmon field can couple with the incident electric field resulting in field enhancement



$2R<\lambda/10$

$2R<50$ nm



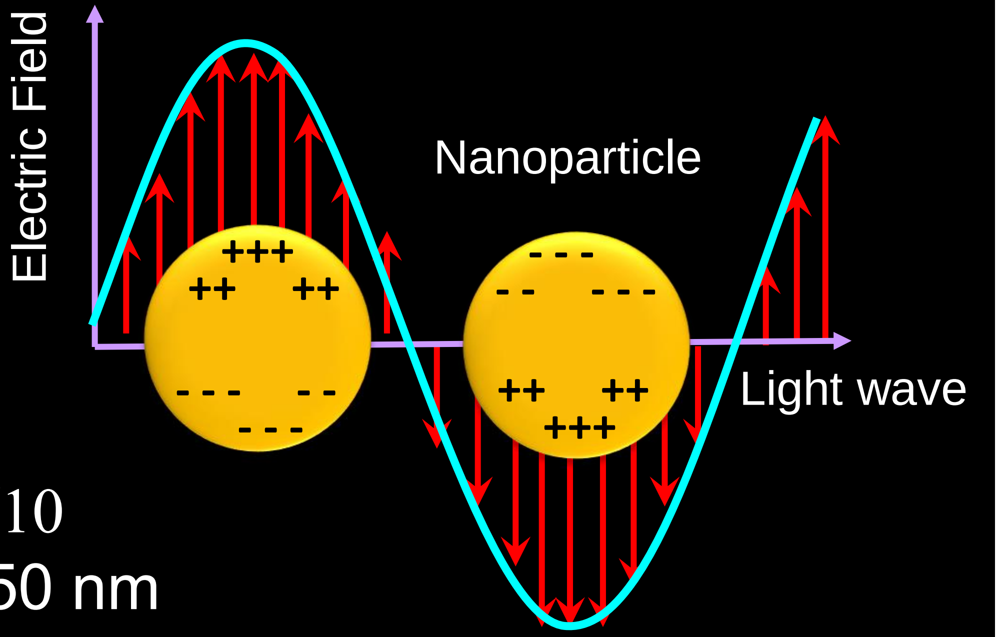
Filed is uniform inside the NPs

NPs are macroscopic dipole

The charge displacement inside the NP generates a field that opposes the incident field.

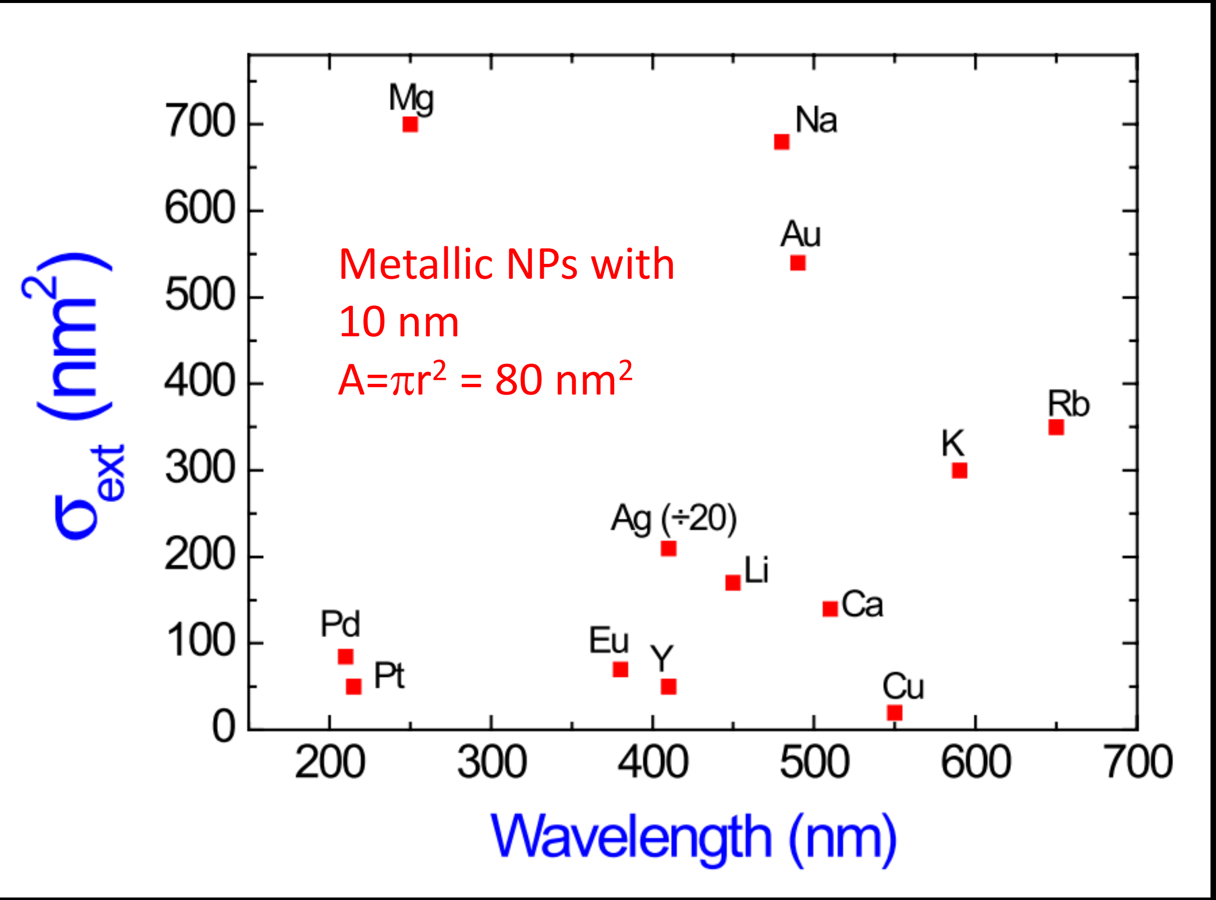
δ_{diel} 20-40 nm for LSPP

LSPP vs SPP in sensing



$2R \leq \lambda/10$
$2R \leq 50$ nm

$$\sigma_{ext} = \sigma_{abs} + \sigma_{sca}$$



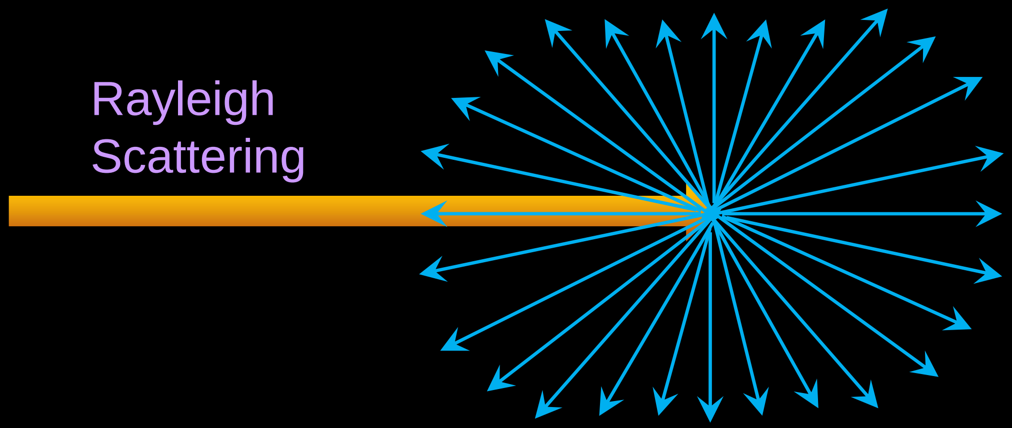
According to Mie's scattering theory (dipolar approximation), particles with radius much smaller than the wavelength of radiation have extinction cross section (σ_{ext}) that can be bigger than the particle

Garcia, J. Phys. D: Appl. Phys. 44 (2011) 283001

For a given particle, the extinction coefficient is a complex function of particle size, wavelength of light, and complex refractive index of the particle.

Different approximations can be employed for certain particle size ranges.

$2R << \lambda/10$ R <10 nm Rayleigh scattering (λ^{-4})



The sky is blue due to Rayleigh scattering (λ^{-4}) by small particle

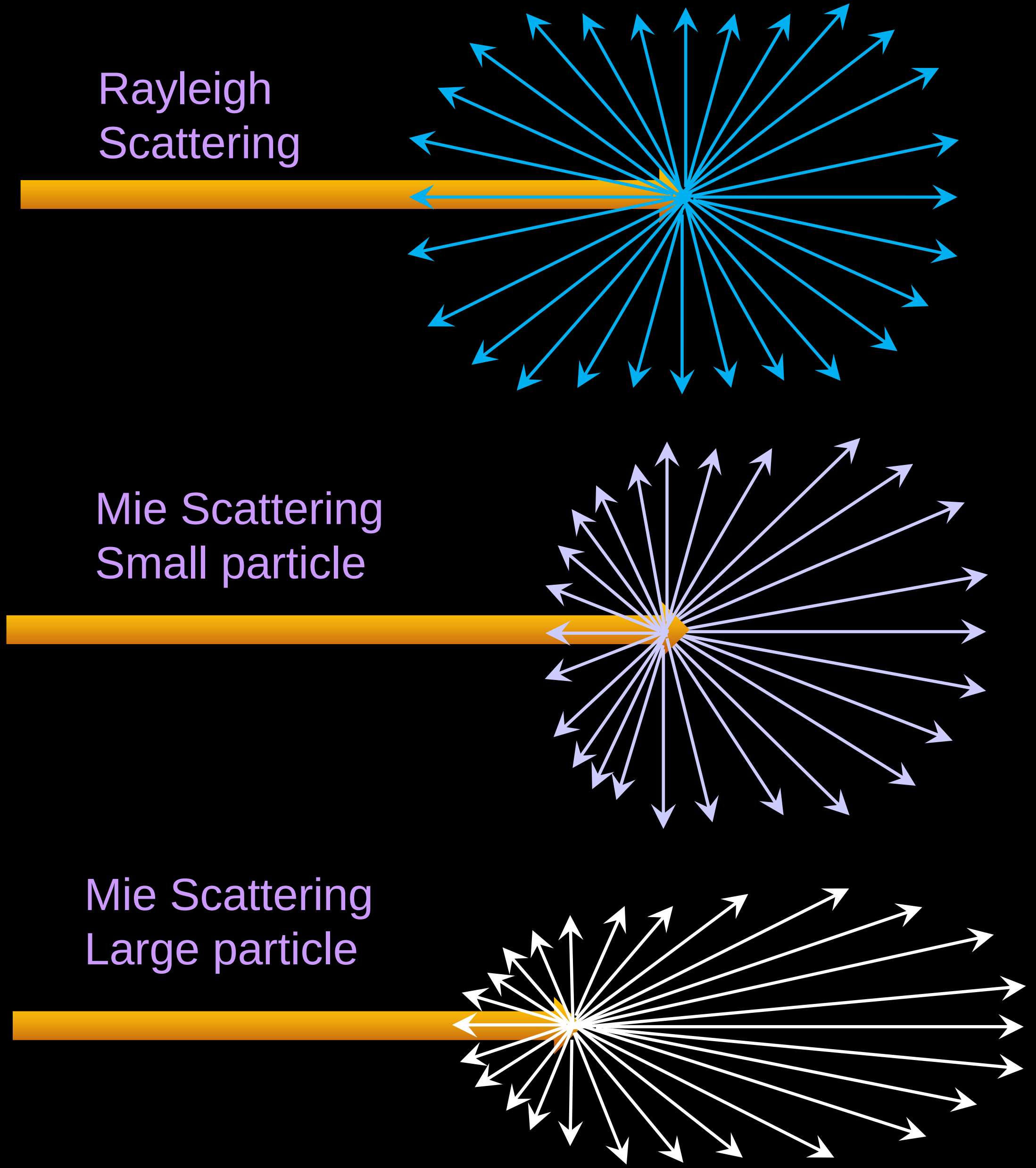
For a given particle, the extinction coefficient is a complex function of particle size, wavelength of light, and complex refractive index of the particle.

Different approximations can be employed for certain particle size ranges.

$2R \ll \lambda/10$ R <10 nm Rayleigh scattering (λ^{-4})

$2R \approx \lambda/10$ 10 < R < 50 nm Mie scattering

$2R > \lambda$ R > 800 nm geometric domain, classical optics apply, non λ selective scattering



Clouds are white because they contain bigger drops of water that have a non wavelength selective scattering

Mie's scattering theory (dipolar approximation)

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$$\sigma_{ext} = \sigma_{abs} + \sigma_{sca}$$

$$\sigma_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \times \frac{\varepsilon_2(\lambda)}{(\varepsilon_1(\lambda) + 2\varepsilon_m)^2 + \varepsilon_2(\lambda)^2}$$

$\varepsilon_1, \varepsilon_2$ are the real (ε_1) and imaginary (ε_2) parts of the wavelength dependent permittivity function of the material that determine the scattering and absorption, respectively

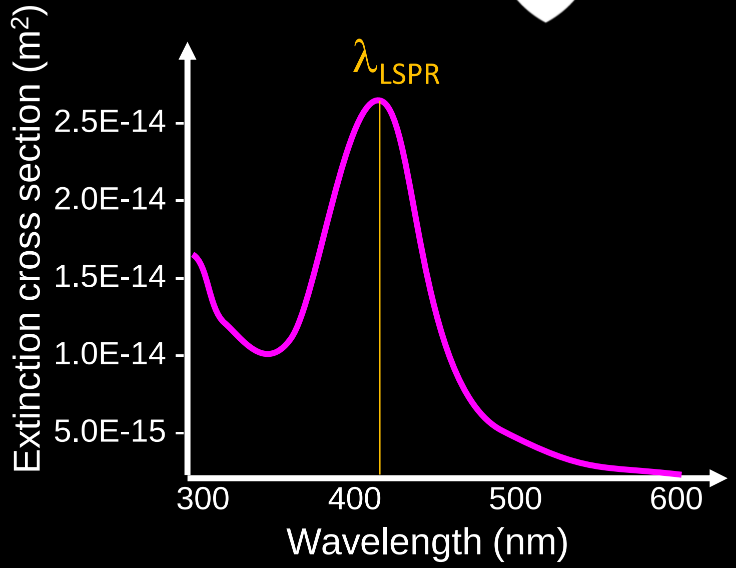
ε_m is the permittivity of the medium (or dielectric function)

$$\varepsilon_m = n^2$$

R radius of the NP

Mie's scattering theory (dipolar approximation)

$$\sigma_{ext} = \sigma_{abs} + \sigma_{sca}$$



$$\sigma_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \times \frac{\varepsilon_2(\lambda)}{(\varepsilon_1(\lambda) + 2\varepsilon_m)^2 + \varepsilon_2(\lambda)^2}$$

Linear with $1/\lambda$

Non-linear λ

$$\varepsilon_1(\lambda_{LSPR}) = -2\varepsilon_m$$

Resonance condition = maximize σ_{ext}

This is verified in some metals depending on the λ

$$\varepsilon_m > 1$$

$$\varepsilon_1(\lambda_{LSPR}) < 0$$

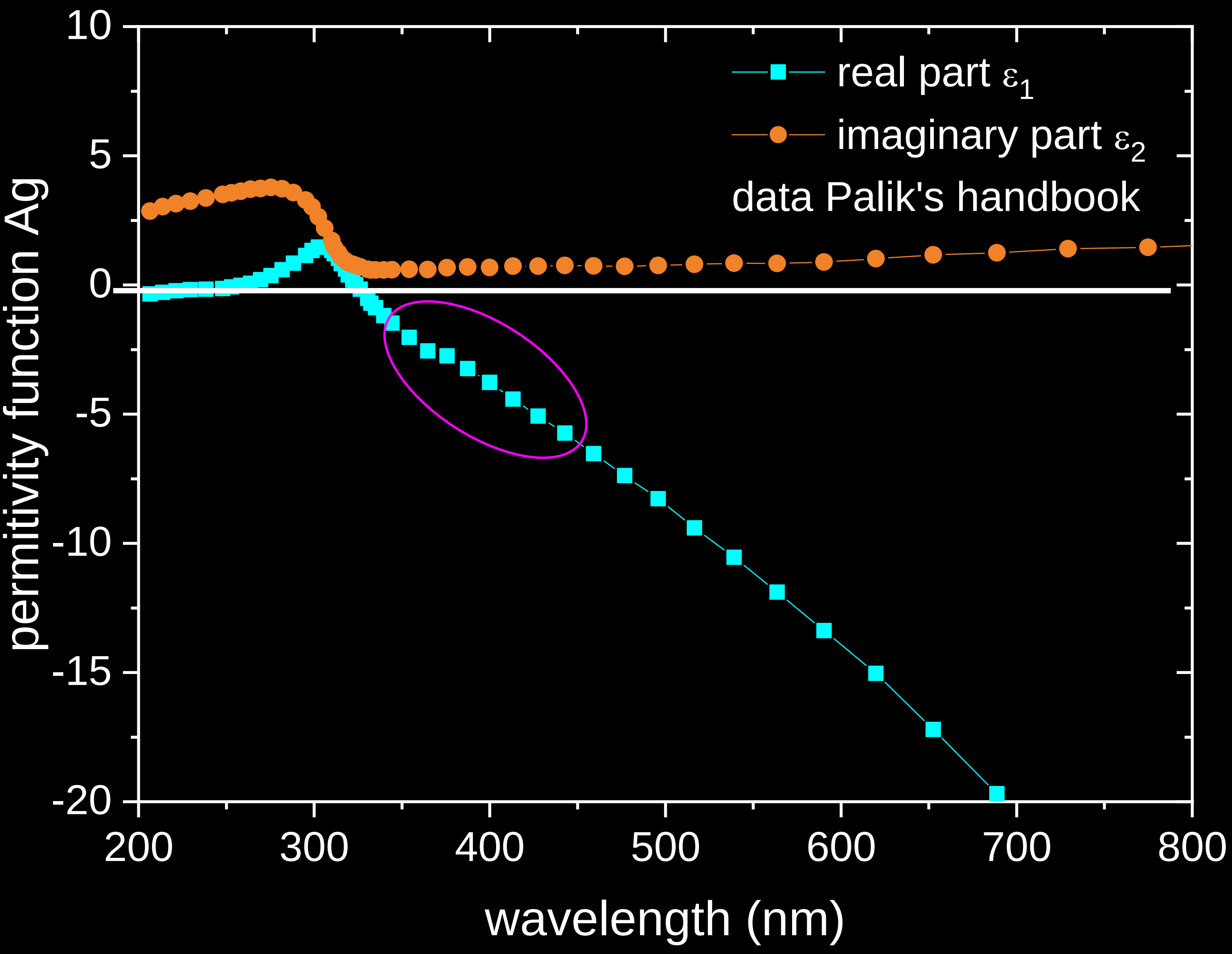
Resonance conditions at optical frequencies for metal

Due to the high electron density of metals the resonance conditions for LSP are met at optical frequencies (> 400 nm)

$$\varepsilon_1 = -2\varepsilon_m$$

$$\varepsilon_m => 1\text{-}3$$

$$\varepsilon_1(\lambda_{LSPR}) < 0$$



Resonance conditions depend on ω_p (electron density)

$$\varepsilon_1\ (\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \gamma_d^2}$$

ε_1
Real
(scattering)

$\gamma_d = {}^{V_F}/_{l}$ dumping frequency (v_F fermi velocity and l is electron mean free path in the metal (~30 nm, Au)

ω_p is the frequency of the bulk plasmon

$$\varepsilon_1(\omega_{LSPR}) = -2\varepsilon_m$$

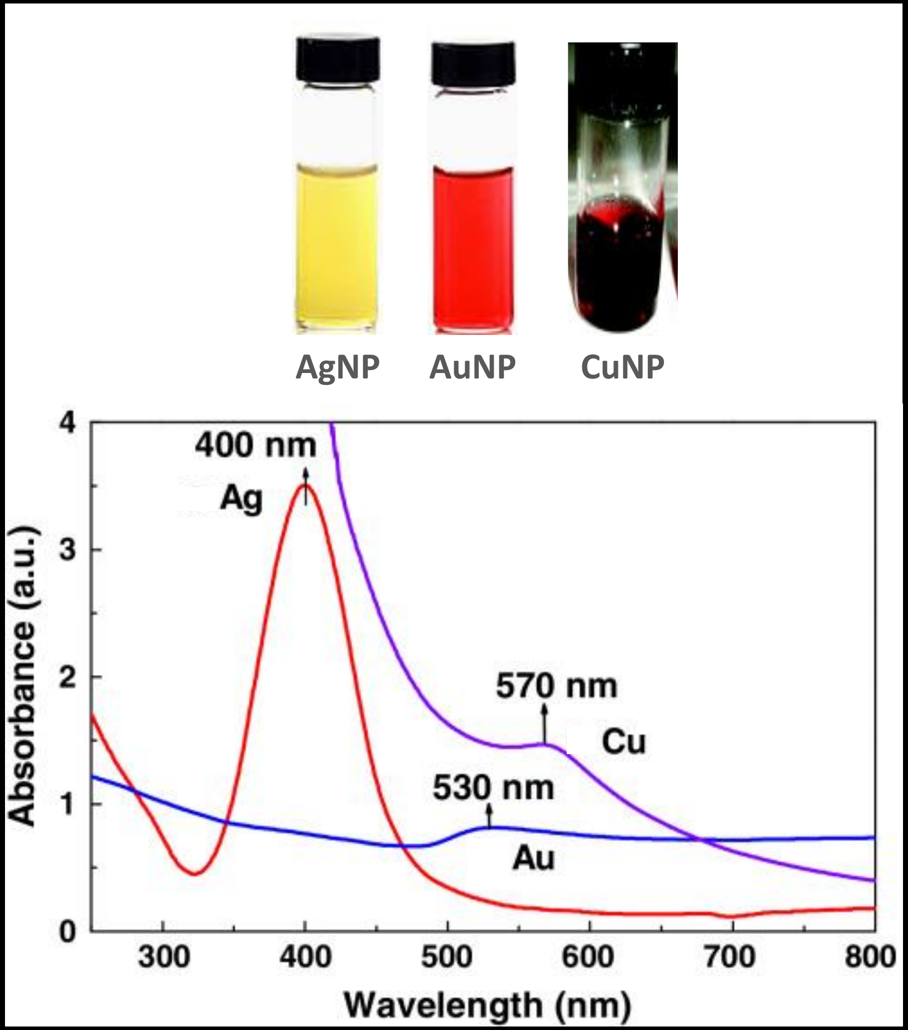
$$\omega_{LSPR} = \sqrt{\frac{\omega_p^2}{1 + 2\varepsilon_m} - \gamma^2}$$

Not an exact answer for LSPR because $\varepsilon_{Drude}(\omega)$ is valid for the bulk

$$\omega_p = \sqrt{\frac{N_e e^2}{\varepsilon_0 m_{eff}}}$$

N_e electron density
e electron charge
ε_0 vacuum permittivity
m_{eff} electron mass

Composition Effect on LSP



LSPR of metal nanostructures appear in the visible

LSPR are easier to observe for coinage metals because they do not oxidize so easily

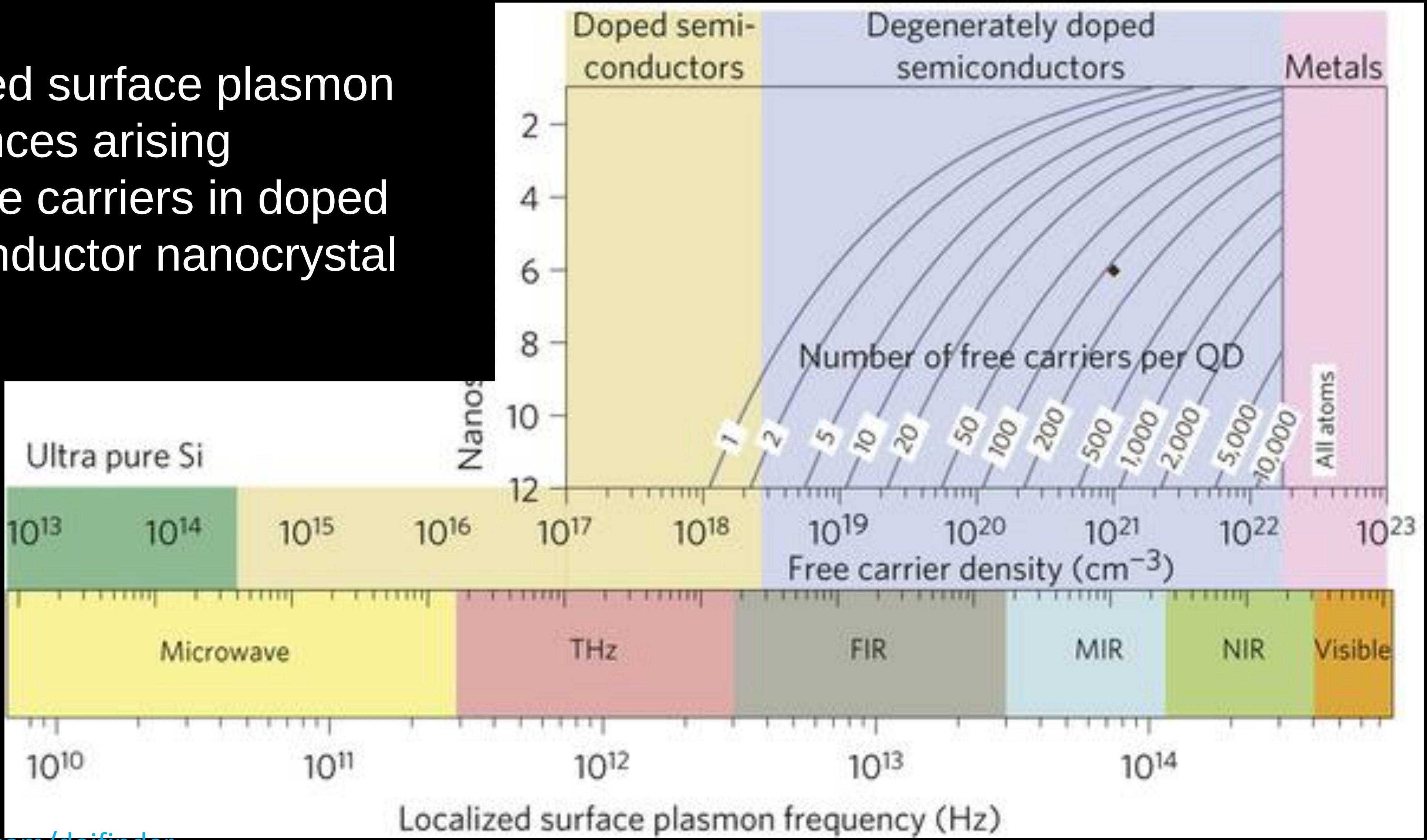
Element	Z	Valence configuration	Ne density 10^{28} e^{-}/m^3
Cu	29	$4s^1 3d^{10}$	8.5×10^{28}
Ag	47	$5s^1 4d^{10}$	5.8×10^{28}
Au	79	$6s^1 5d^{10} 4f^{14}$	5.9×10^{28}

$$\omega_p = \sqrt{\frac{N_e e^2}{\varepsilon_0 m_{eff}}}$$

N_e electron density
e electron charge
ε_0 vacuum permittivity
m_{eff} electron mass

Composition Effect on LSP

Localized surface plasmon resonances arising from free carriers in doped semiconductor nanocrystal



http://www.nature.com/doifinder/10.1038/nmat3004

Size effect (R)

$$\sigma_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \times \frac{\varepsilon_2(\lambda)}{(\varepsilon_1(\lambda) + 2\varepsilon_m)^2 + \varepsilon_2(\lambda)^2}$$

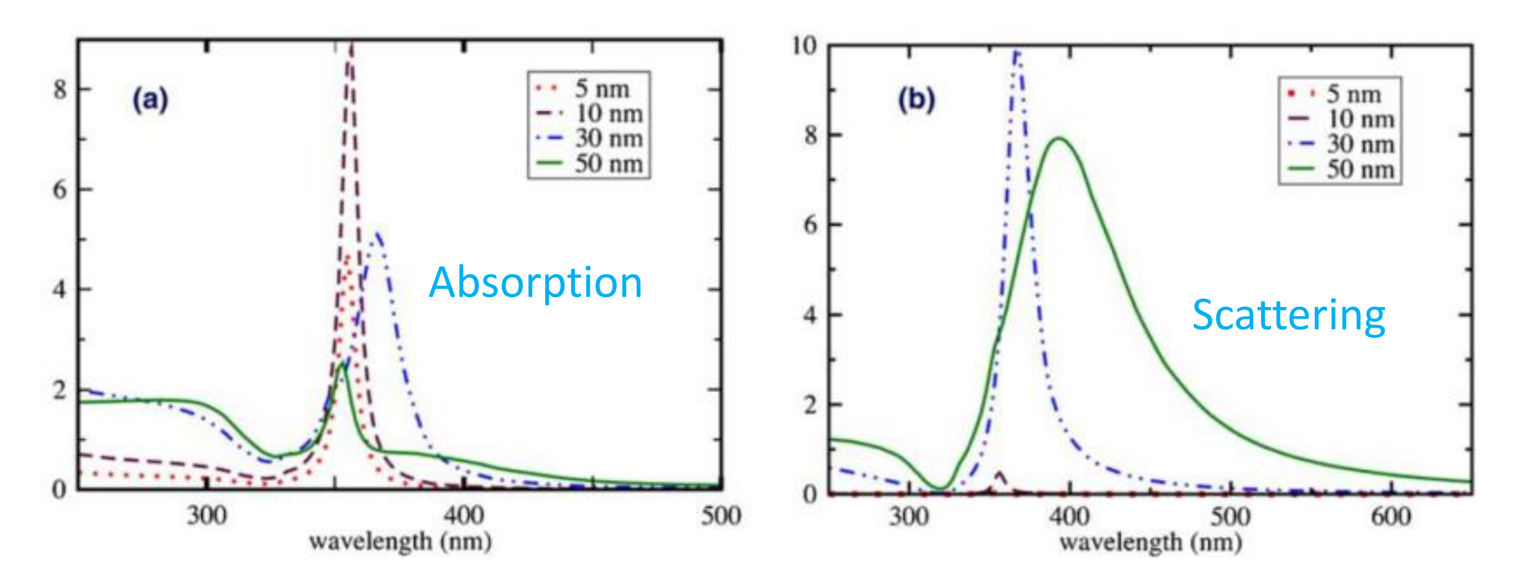


Fig. 1. (a) Absorption and (b) scattering efficiencies for spherical nanoparticles of different radii.

C. Noguez, Optical Materials 27 (2005) 1204–1211

For particle R<10 nm the λ_{SPR} is size independent

R<10 nm Abs dominates with a single peak at 355 nm, intensity increases with R

R > 10 Scattering increases and band broadening occurs due to higher multipoles

Larger particle no longer behave like simple dipole such that high-multipolar distributions can be induced. The spectrum broadens and band shape becomes asymmetric

Size effect

For spherical particles, the effect of particle size on the extinction spectra is small (almost no color change is noticed for AuNPs or AgNPs)

5-100 nm AgNP

5-100 nm AuNP

Effect of the medium (ε_m)

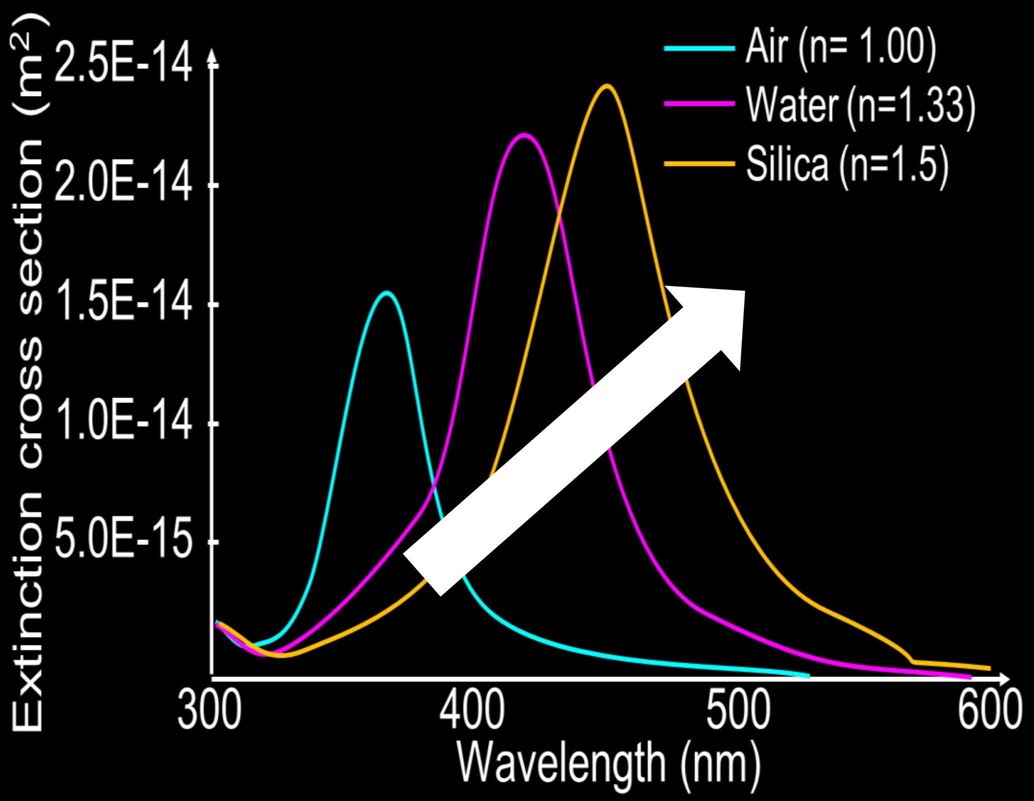
$$\sigma_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \times \frac{\varepsilon_2(\lambda)}{(\varepsilon_1(\lambda) + 2\varepsilon_m)^2 + \varepsilon_2(\lambda)^2}$$

$$\varepsilon_m = n^2$$

$$\omega_{LSPR} = \frac{\omega_p}{\sqrt{1 + 2n^2}}$$

Approximated linear relationship between λ_{SPR} and environment refractive index (n_m)

$$\lambda_{SPR} = \frac{2\pi c}{\omega_p}\sqrt{2n_m^2 + 1}$$



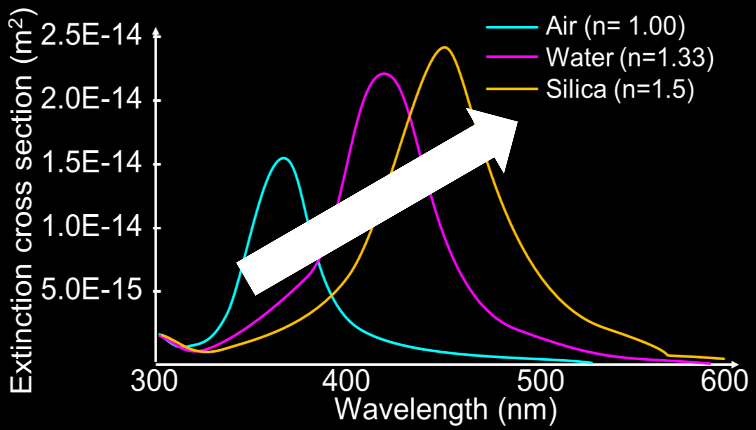
As the refractive index of the medium increases ($\varepsilon_m = n^2$), the nanoparticle spectrum shifts to longer wavelengths.

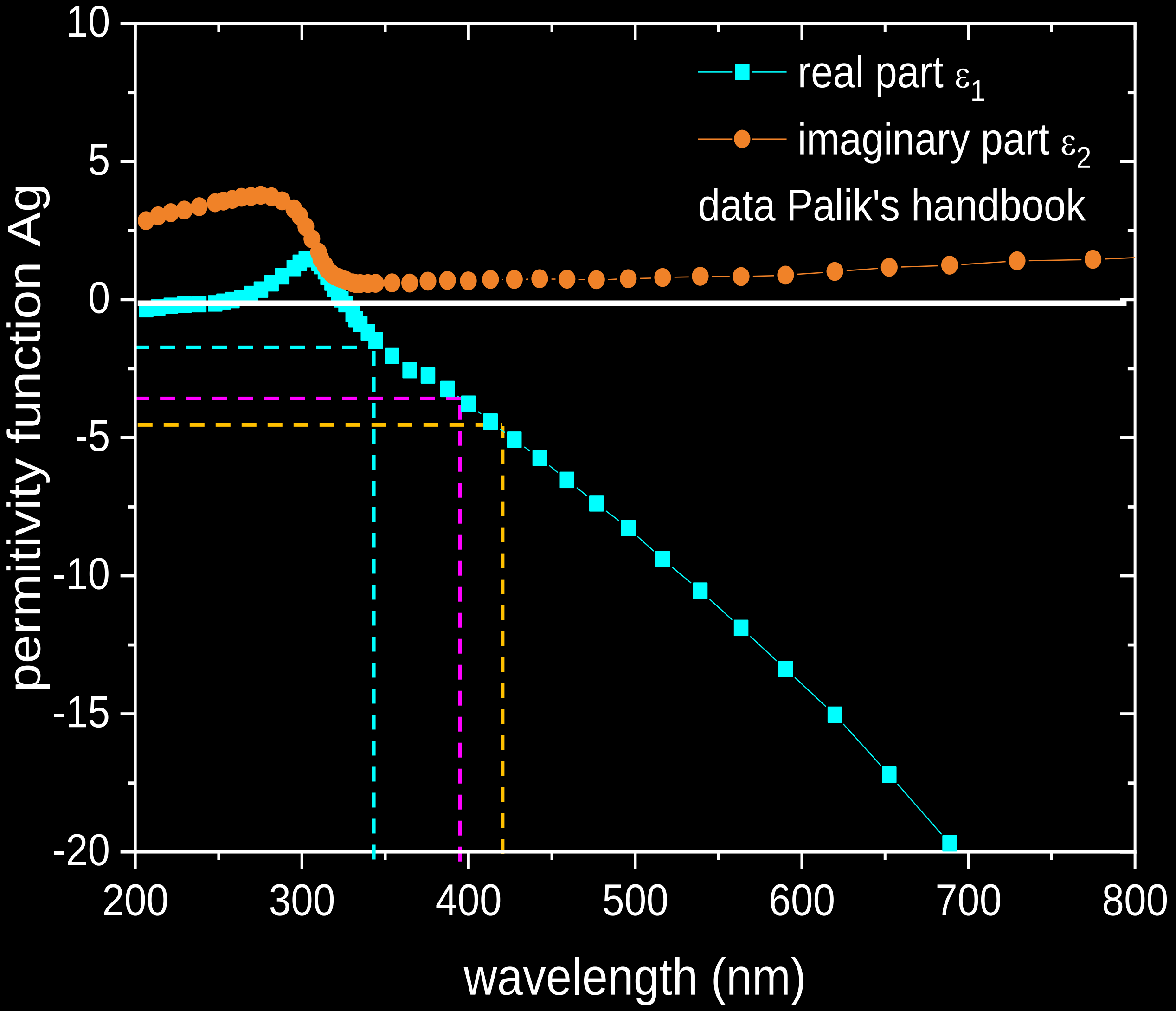
Effect of the medium (ε_m)

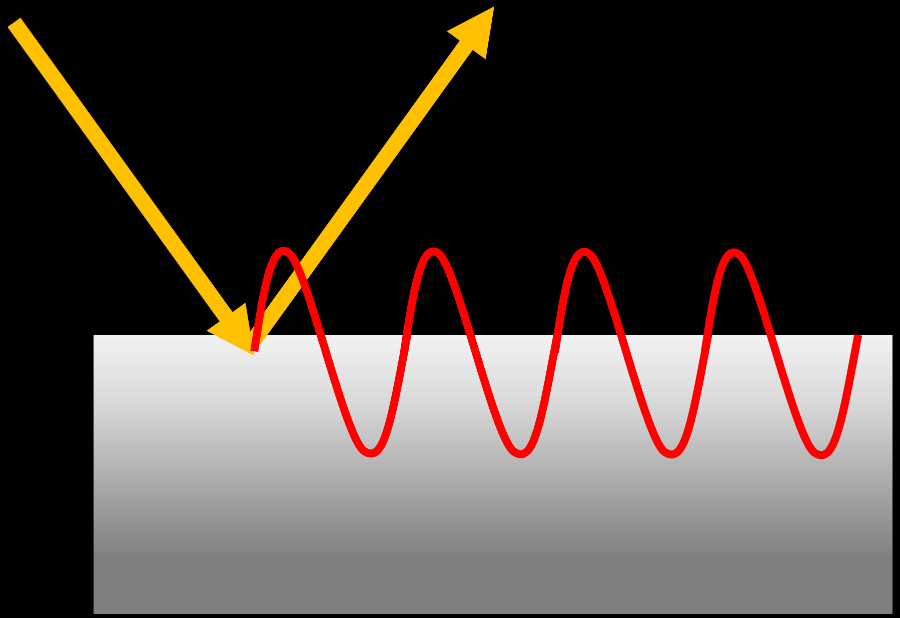
$$\lambda_{SPR} = ???$$

$$n_m^2 = \varepsilon_m$$

$$\varepsilon_1 = -2\varepsilon_m$$







Plasmon polariton are collective oscillation of electrons at the interface of conductor materials and a dielectric

The evanescent wave propagates only very short distances in the dielectric for LSPR (20-40 nm)

Strong coupling of light with SPP require a change in permittivity sign between the NP material and the medium

$$\varepsilon_1 = -2\varepsilon_m$$

Resonance at optical frequencies only occurs for noble metals and some semiconductors with a given electron density

Optical properties of Metal NPs depend on:

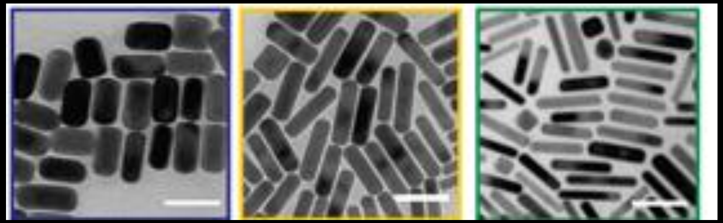
Permittivity of media ε_m
Composition ($\varepsilon(\lambda)$, $\varepsilon(\omega)$)
Size (R or V)
Shape ???

$$C_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \times \frac{\varepsilon_2(\lambda)}{(\varepsilon_1(\lambda) + 2\varepsilon_m)^2 + \varepsilon_2(\lambda)^2}$$

$$\varepsilon_{Drude}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \gamma_d^2} + i\,\frac{\gamma_d \omega_p^2}{\omega(\omega^2 + \gamma_d^2)}$$

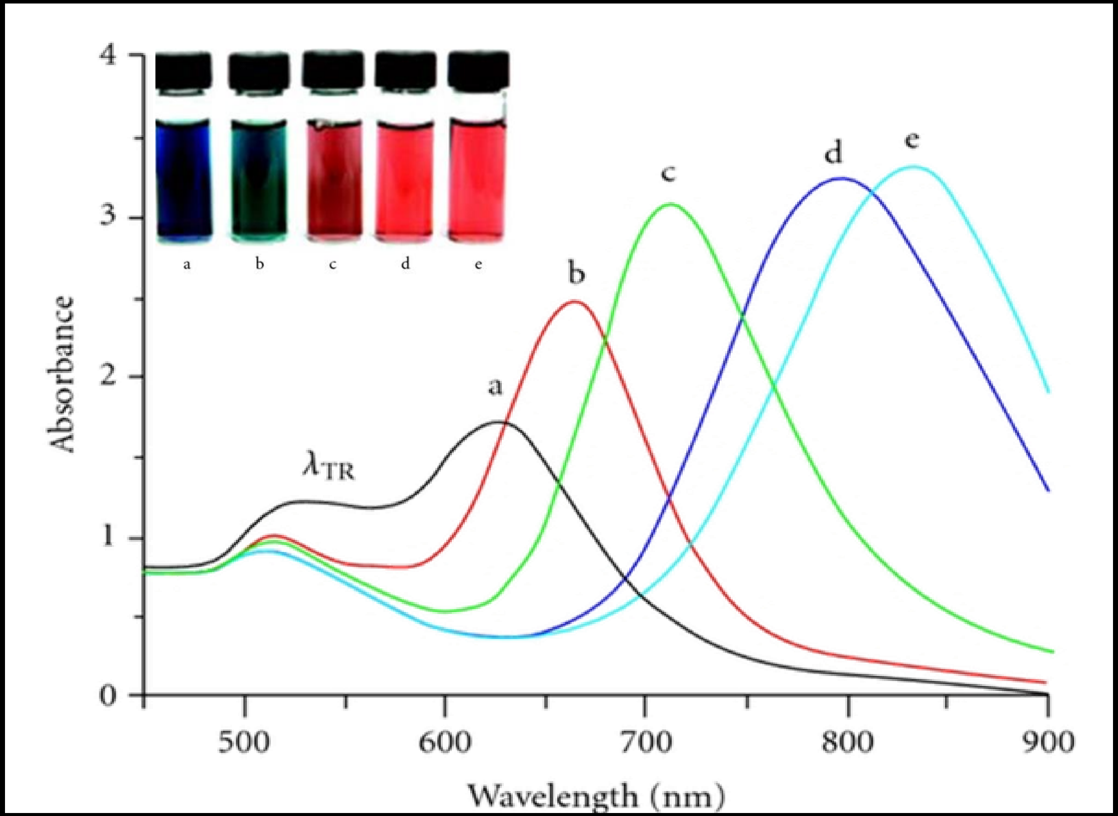
$$\omega = \frac{2\pi c}{\lambda}$$

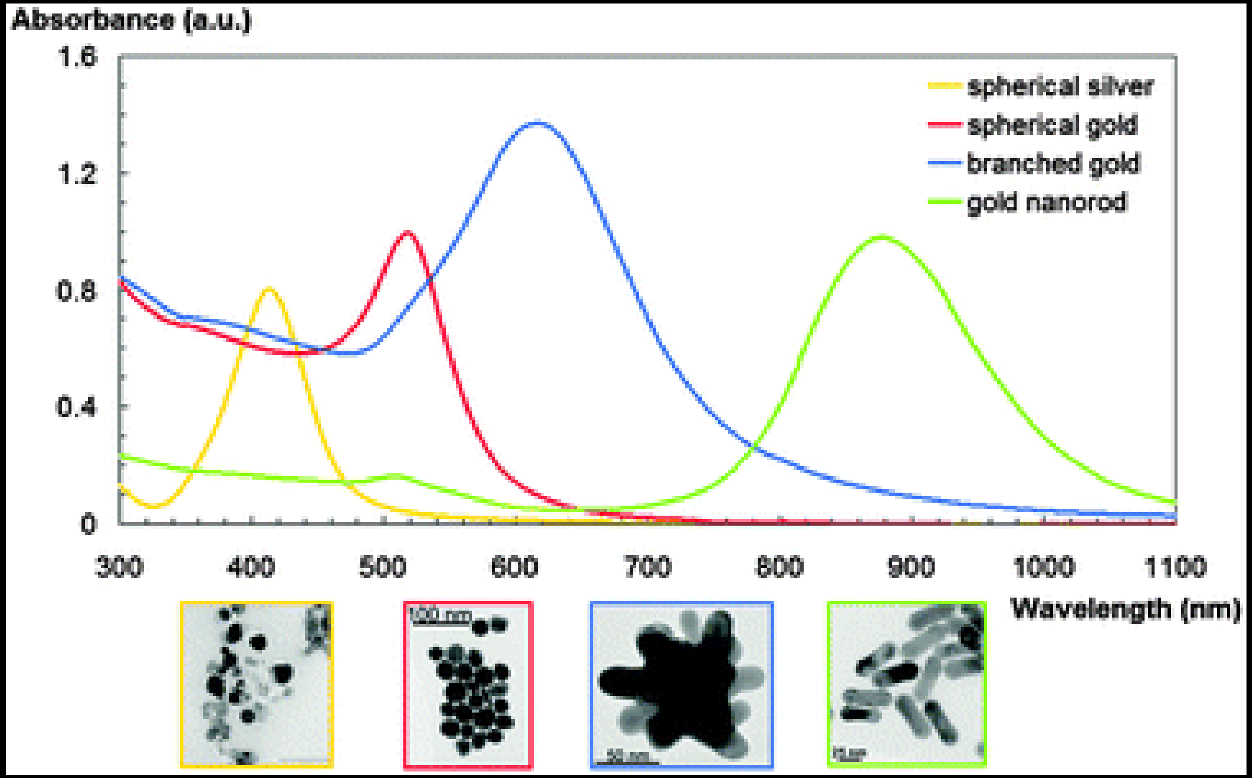
Shape effect



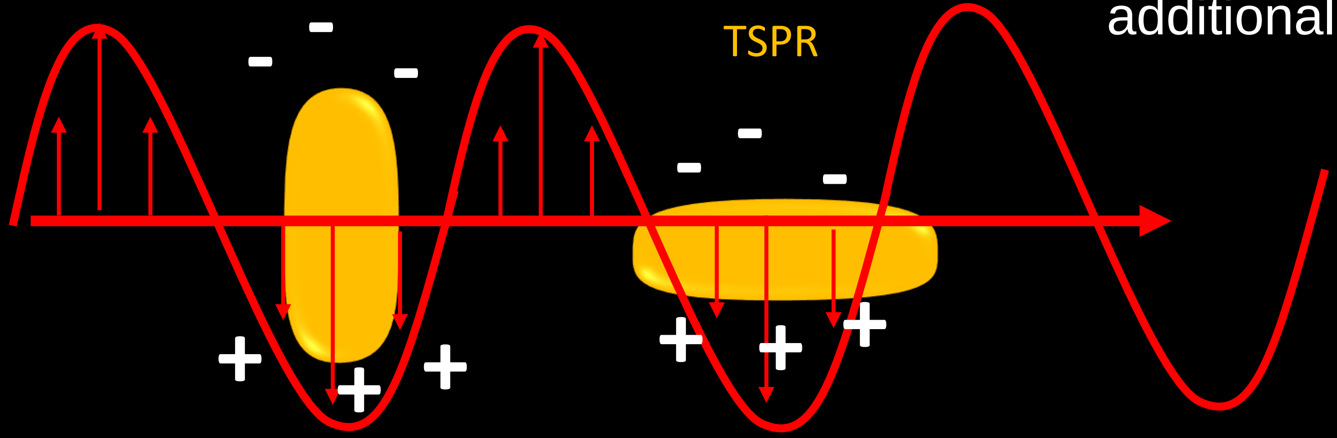
Au nanorods

nanoparticles of different shapes can show very different colors



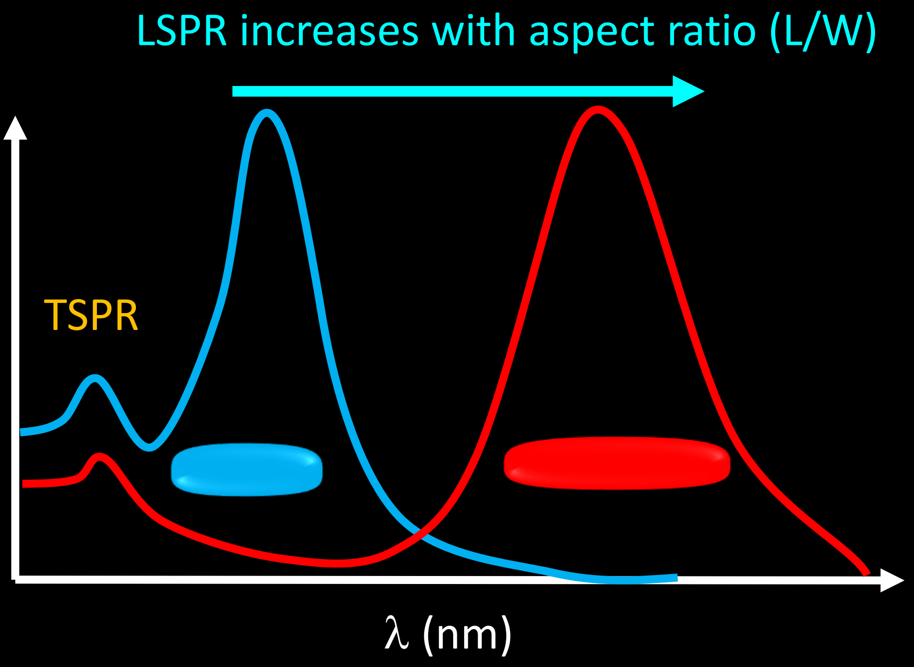


Shape effect: NanoRods



In particles without spherical symmetry there are additional modes of plasmon resonance (*Gans theory*)

Metal nanorods present two SPR modes: longitudinal and transversal



Metal nanorods are more easily polarized longitudinally: LSPR at lower energies, longer λ

Increasing the aspect ratio (*length/width*), the LSPR can be tuned from 550 to over 2000 nm, while the TSPR remains relatively constant at ~ 520 nm

Shape effect: NanoRods

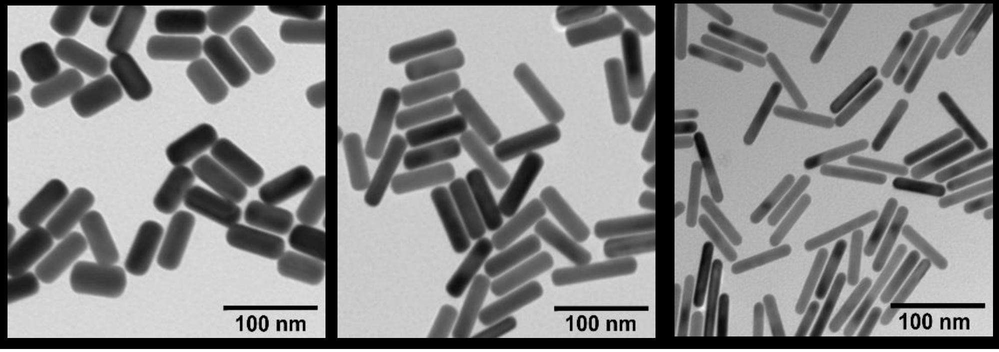
Variation of *longitudinal* and *transverse* SPR modes of gold nanorods (AuNR) with aspect ratio

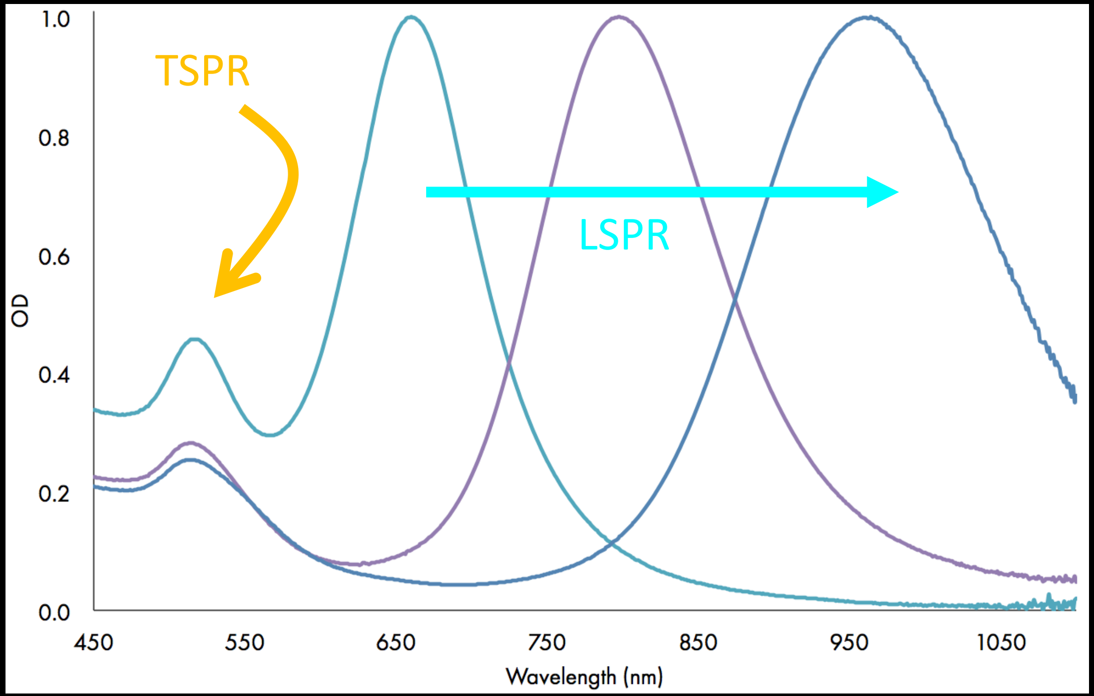
Resonance	Length	Width	Aspect Ratio
660 nm	50 nm	19 nm	2.7
800 nm	70 nm	19 nm	3.6
980 nm	70 nm	12 nm	6.1

Empiric expression

$$\lambda_{LSPR} = (K_1 D - K_2)\varepsilon_m + K_3$$

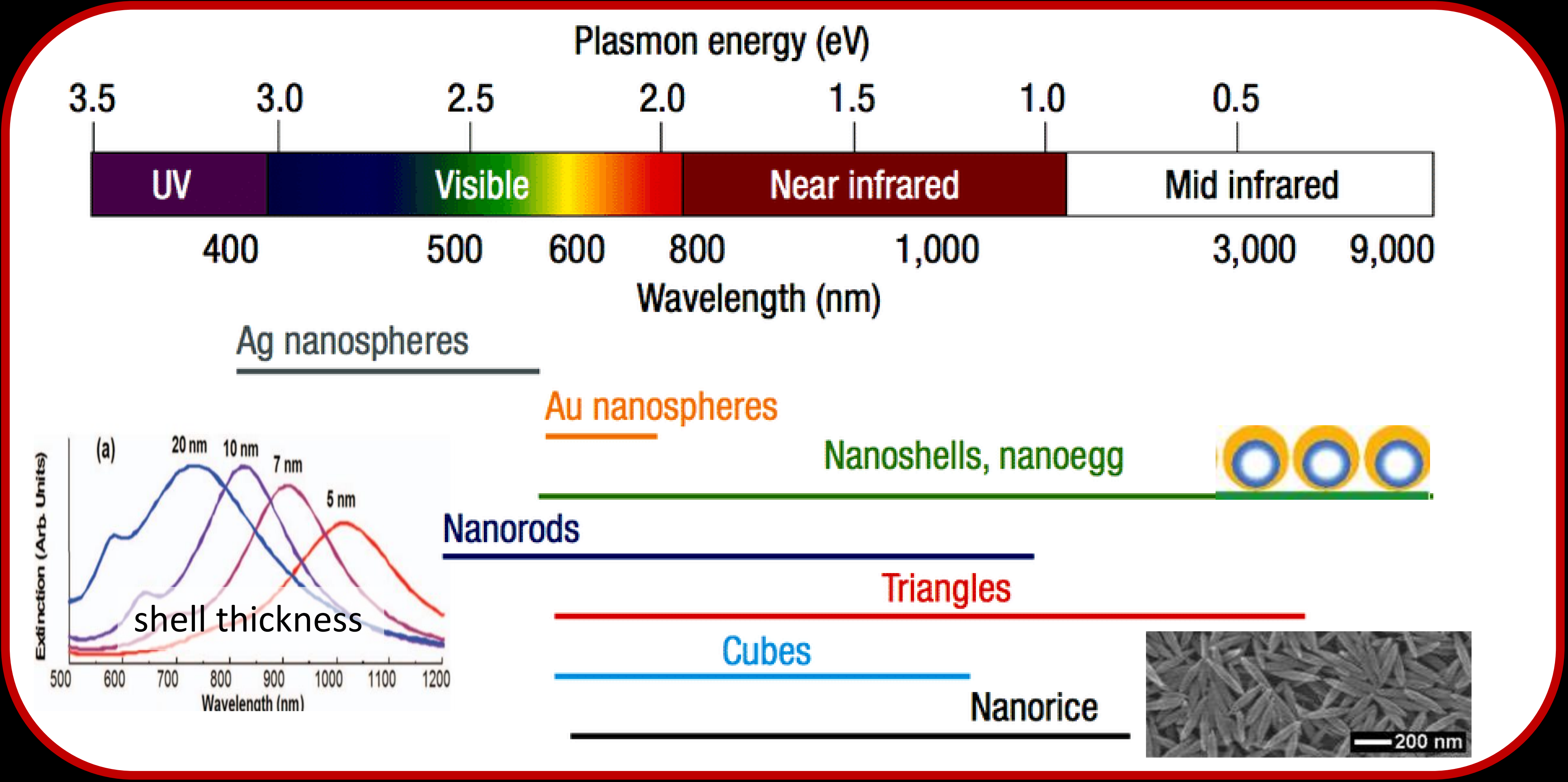
D = aspect ratio = main/minor axis





Shape effect

Range of SPR modes in metal nanoparticles with different morphology

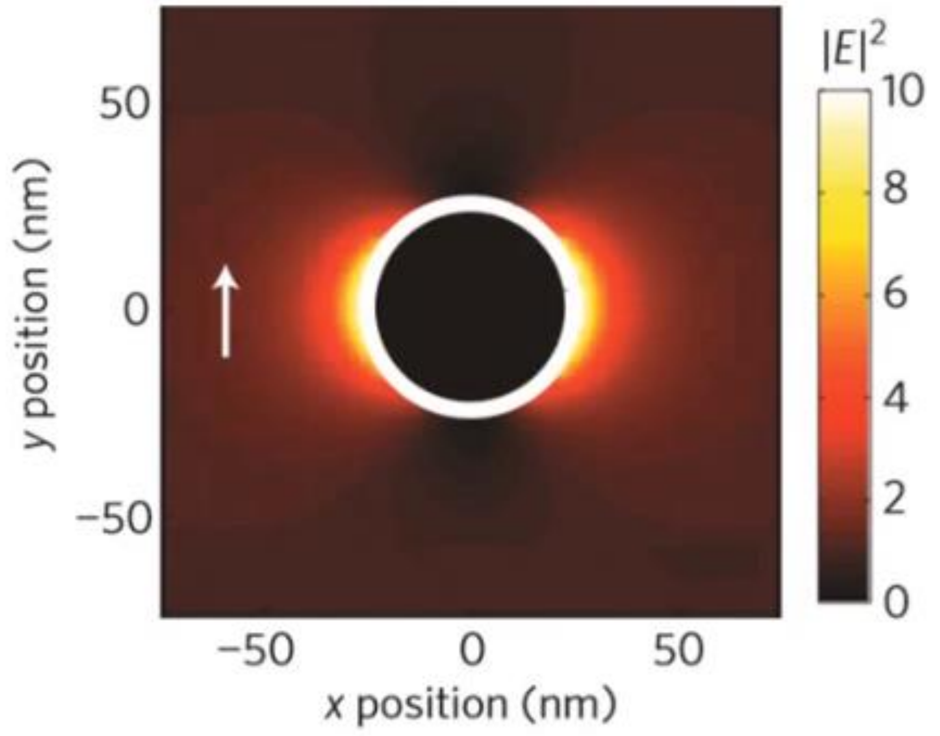


Field Enhancement

In NPs the plasmon field can couple with the incident electric field resulting in field enhancement

$$\frac{|E_{sphere}|}{|E_0|} = 1 + \left|\frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m}\right|$$

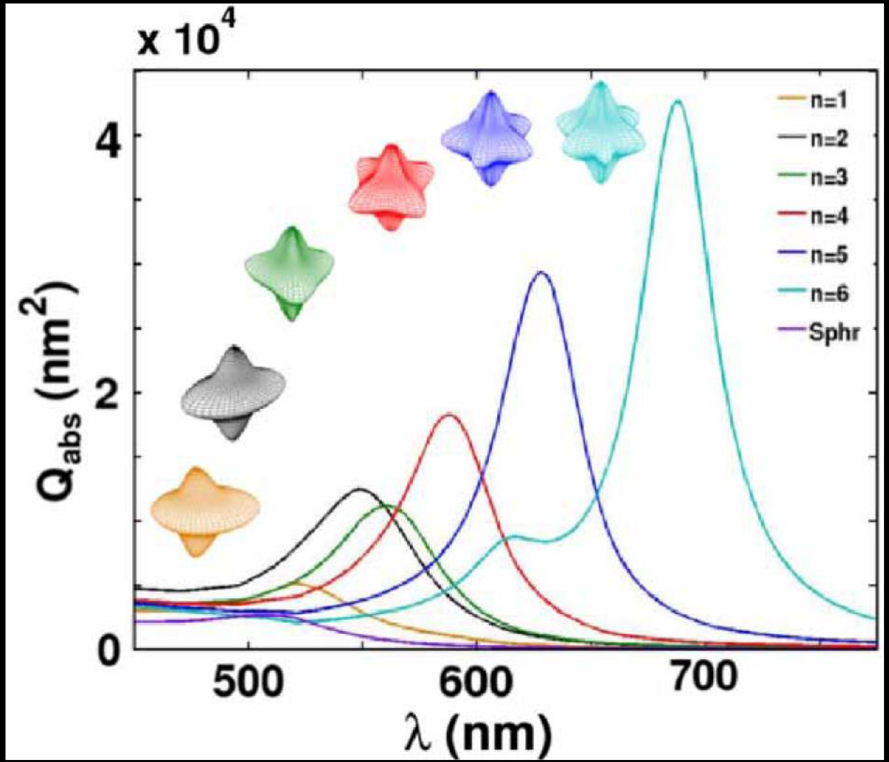
filed enhancement is maximized when the real part of the denominator vanishes



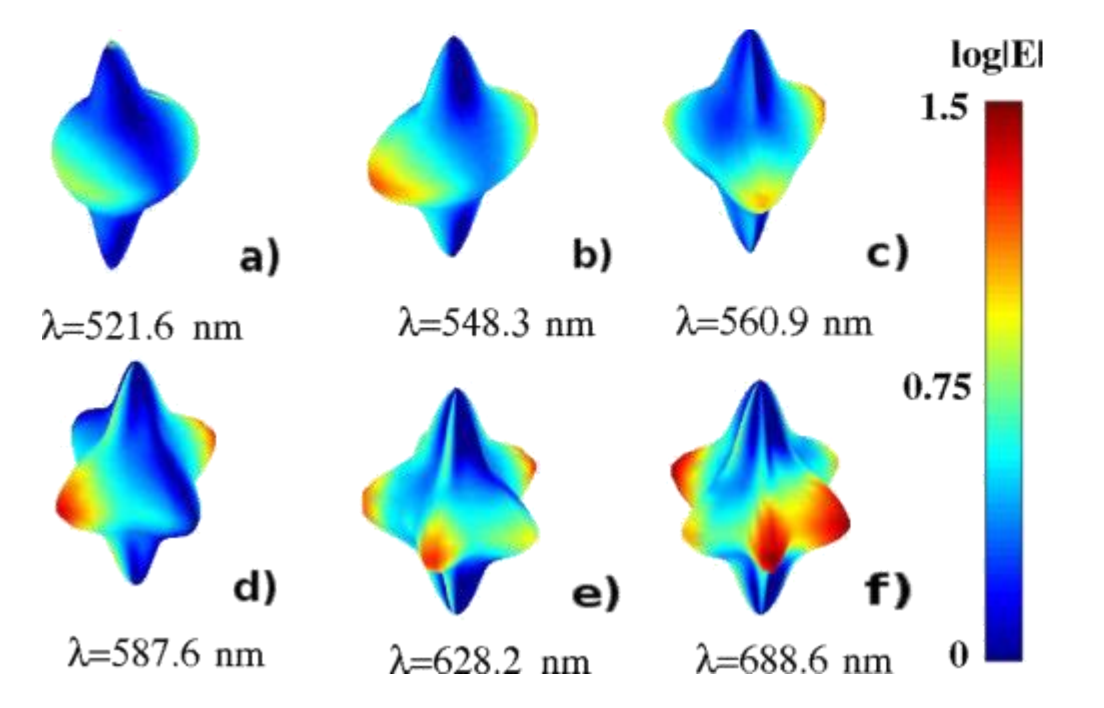
20 nm Ag spherical particle & electromagnetic field intensity

Field Enhancement: hotspots

Metal nanoparticles present surface electrical field enhancement due to the SPR. At high curvature points there are ***hotspots*** with higher reactivity and field enhancement

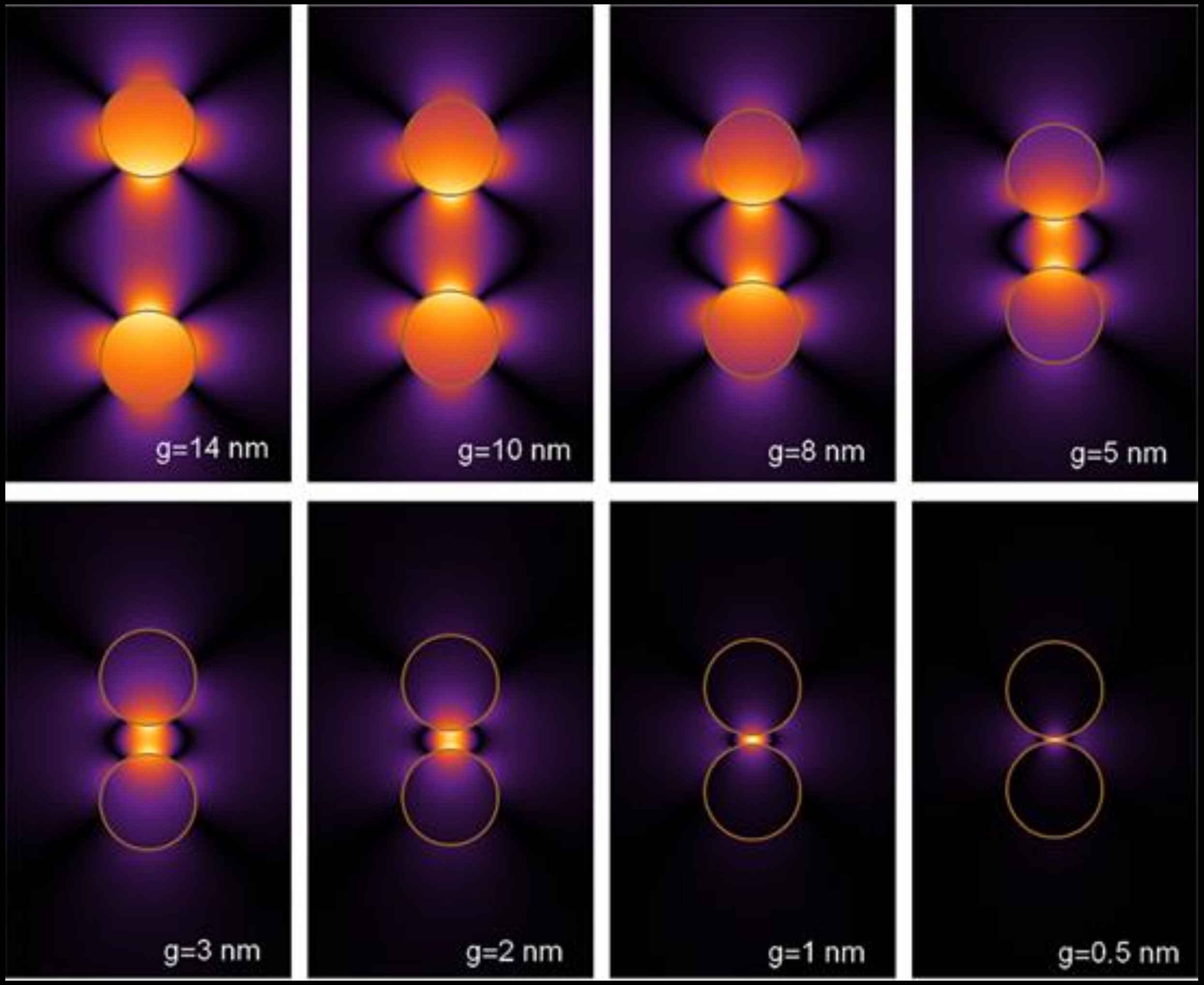


Variation of SPR modes of **gold nanostars** (AuNS) with morphology

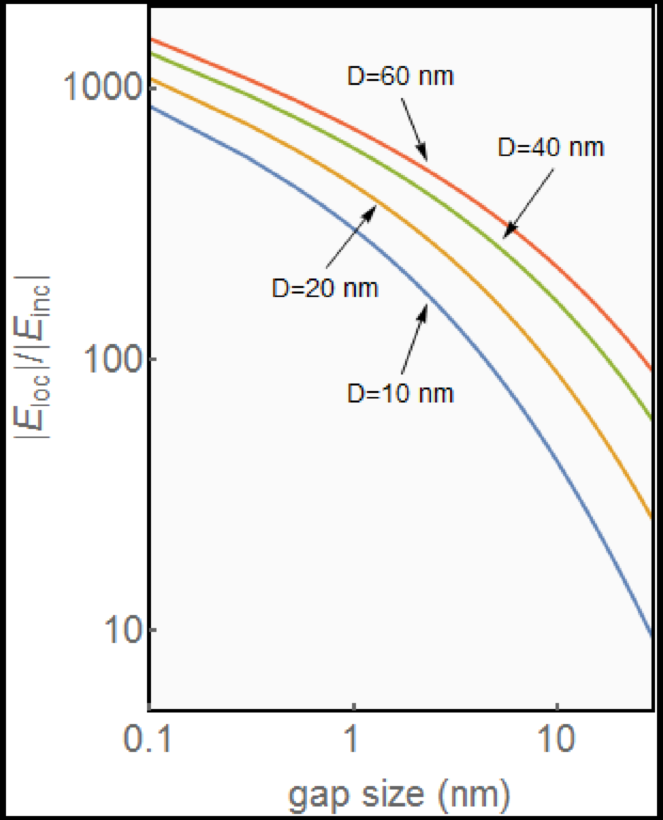


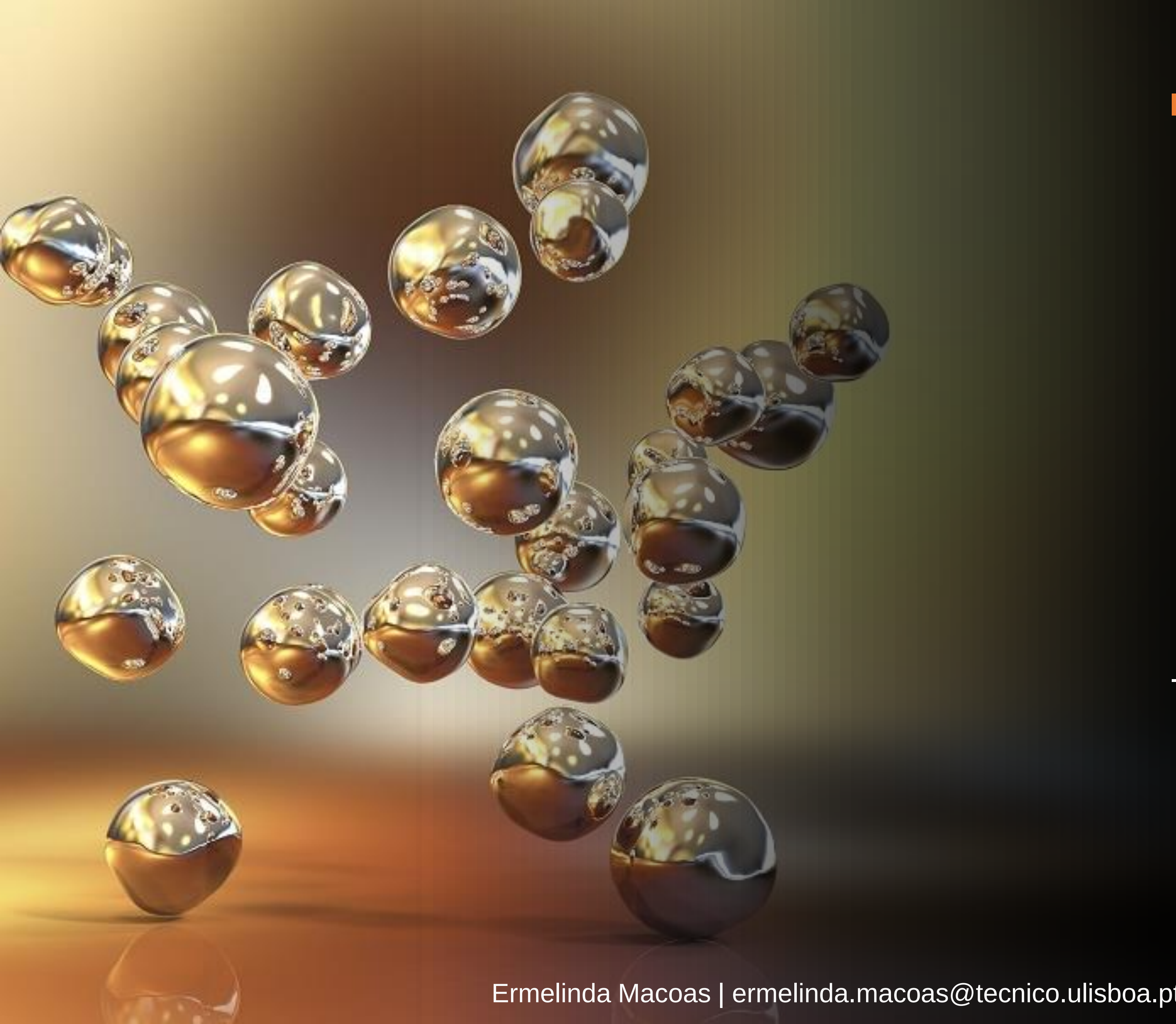
Distribution of electric field amplitudes on the surface of AuNSs, with corresponding LSPR wavelengths

Field Enhancement: coupled NPs



When NPs interact, the surface plasmon resonances couple, shifting the resonance frequencies and changing the field characteristics.

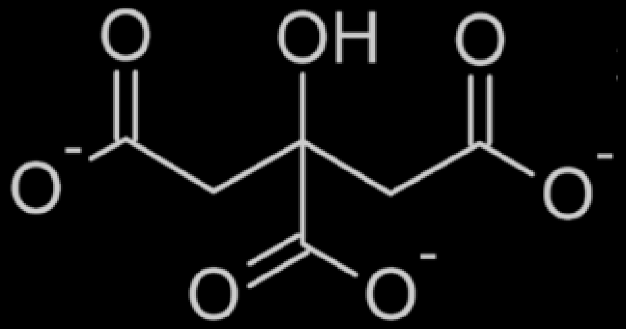




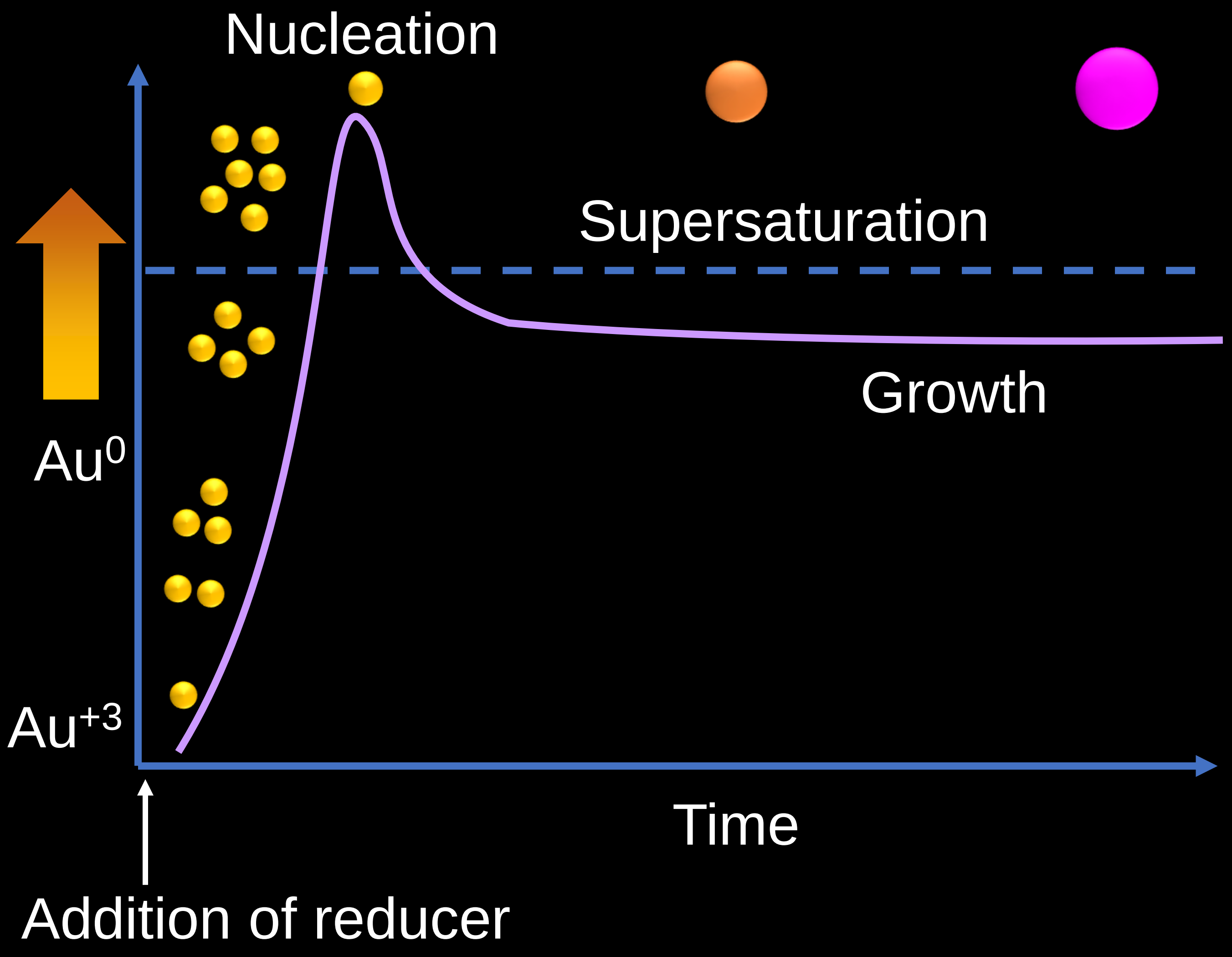
Metal nanoparticles: preparation

Metal NPs

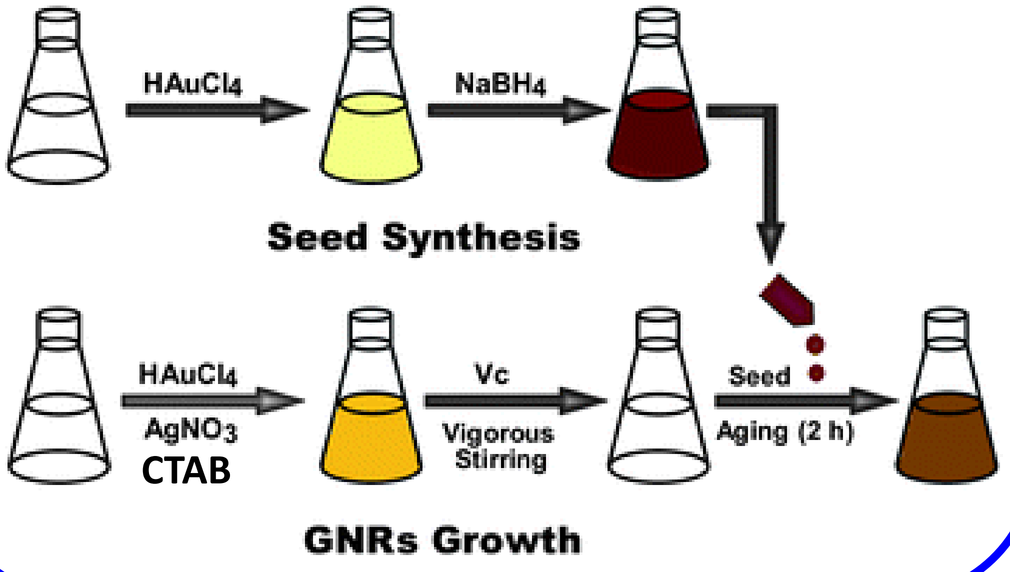
Au and Ag colloidal particles usually prepared in aqueous dispersion from $HAuCl_4$ and $AgNO_3$, in the presence of a reducer, for example of citrate

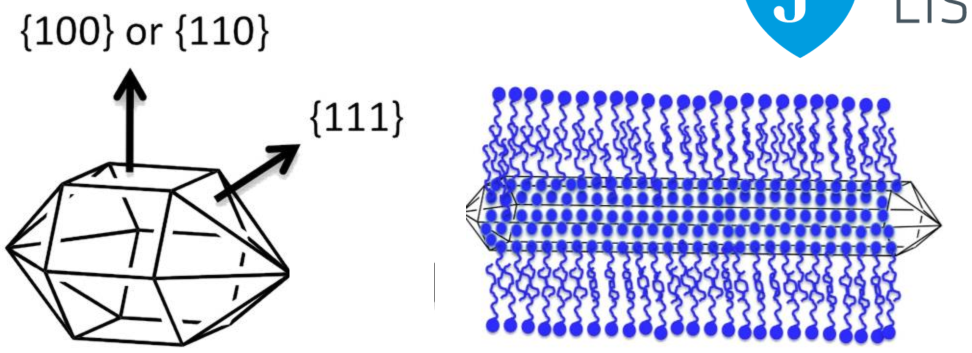


ascorbic acid, hydroxylamine, sodium borohydride ($NaBH_4$)

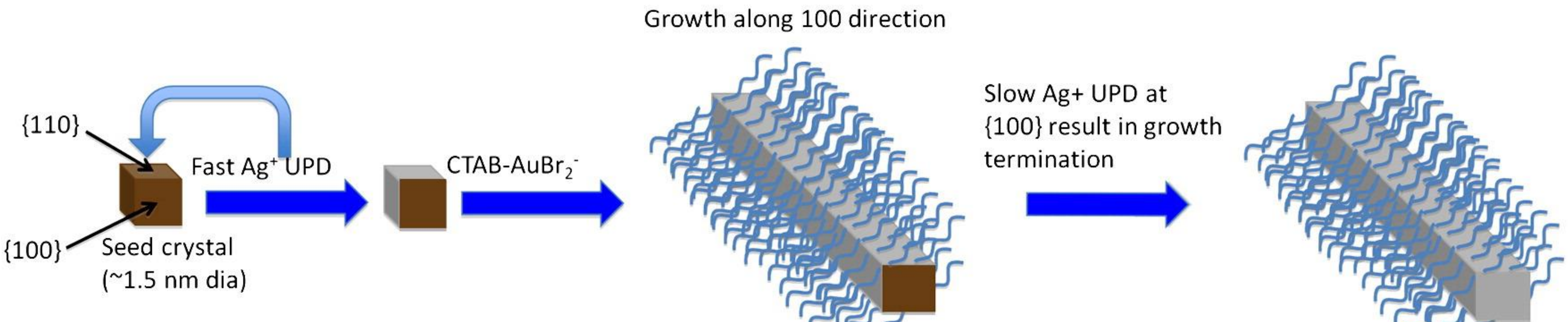


Nanorods
seed-mediated growth

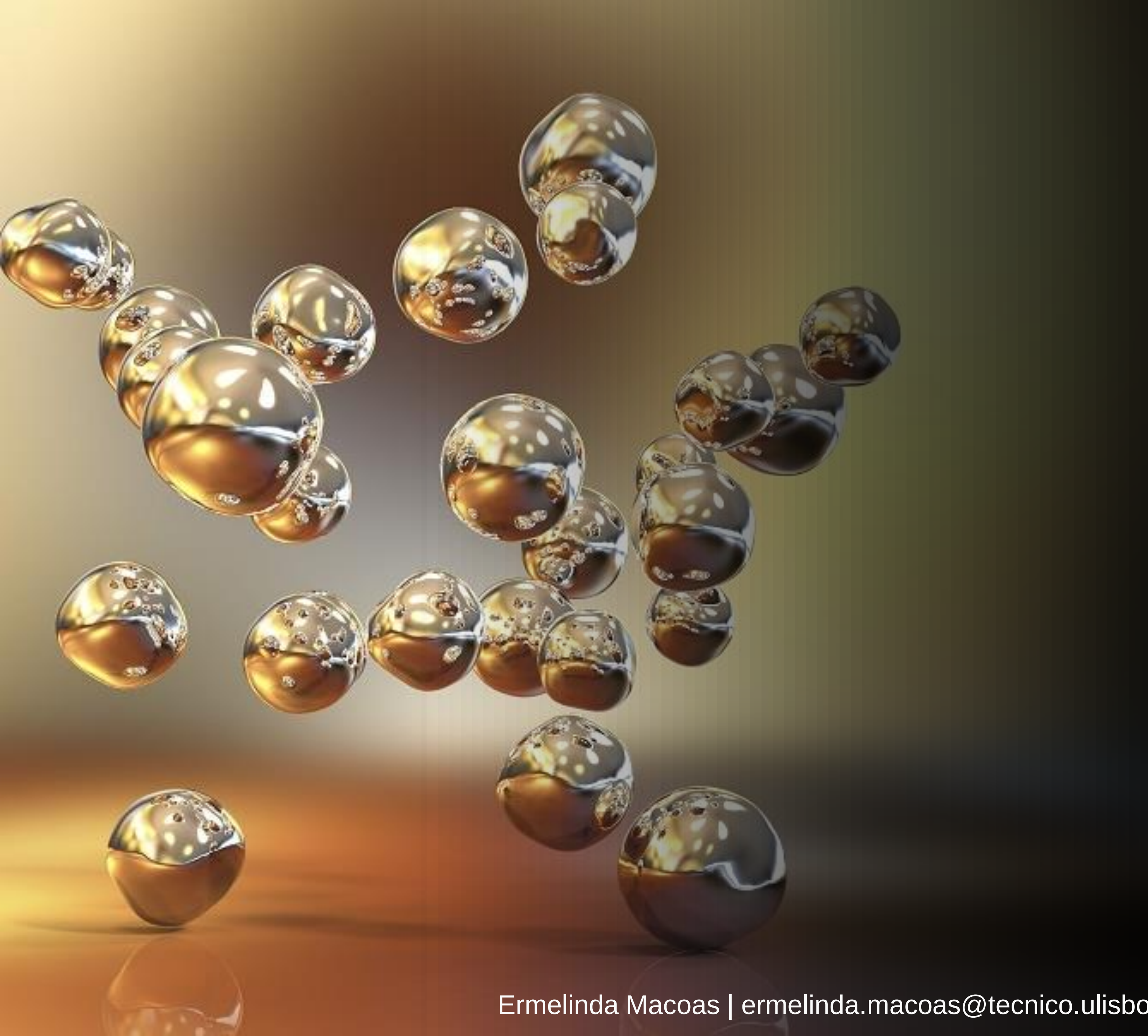




Bilayer packing density is lower near the tip due to its curvature
The probability for micellized gold ions to approach the tips is higher compared to the sides

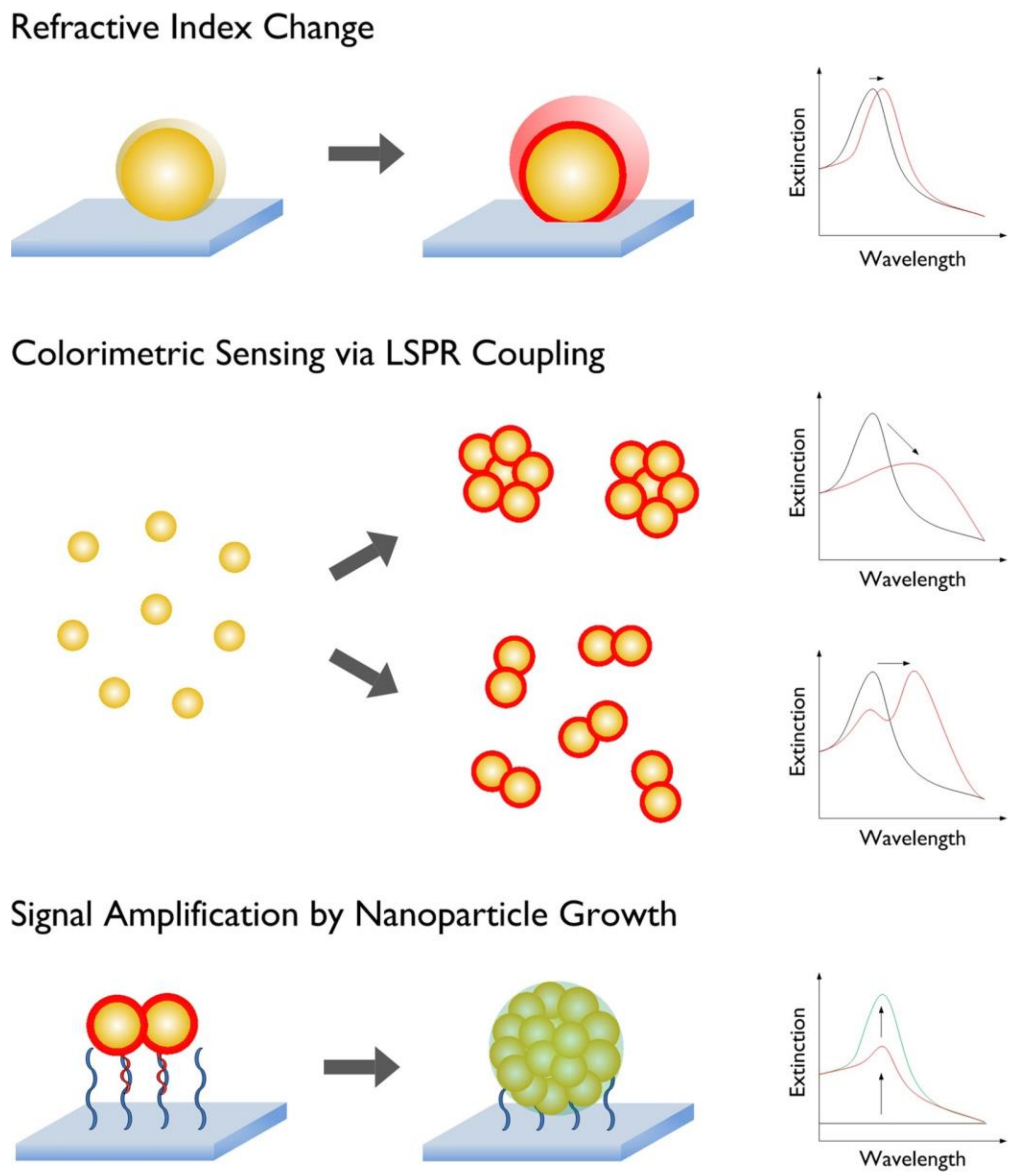


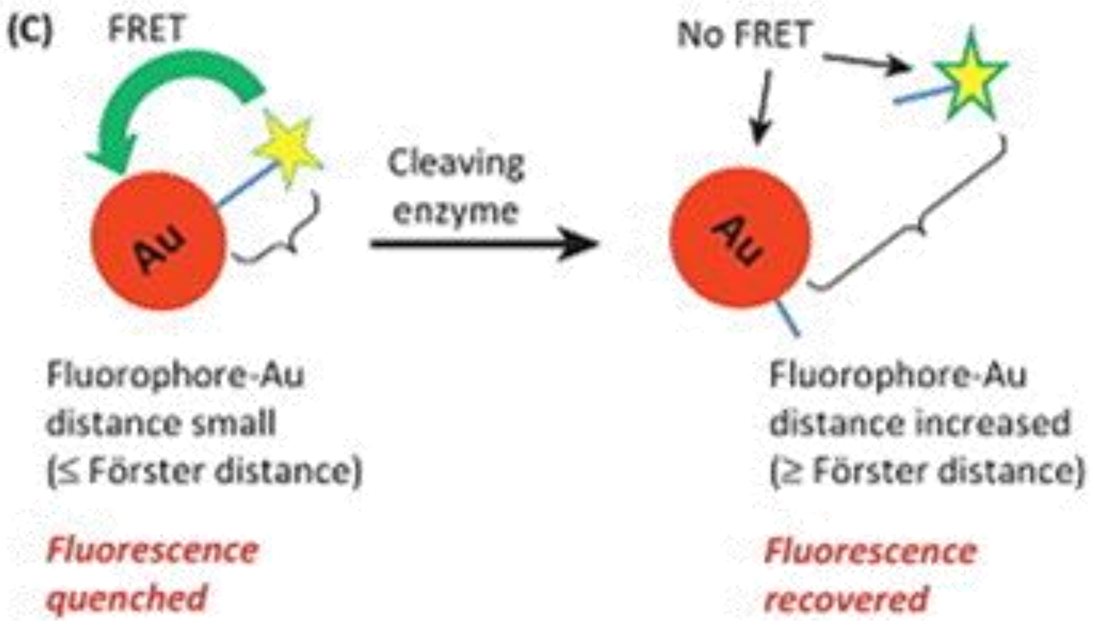
Murphy et al, 2011 https://doi.org/10.1016/j.cocis.2011.01.001



Metal nanoparticles: Application

Sensing

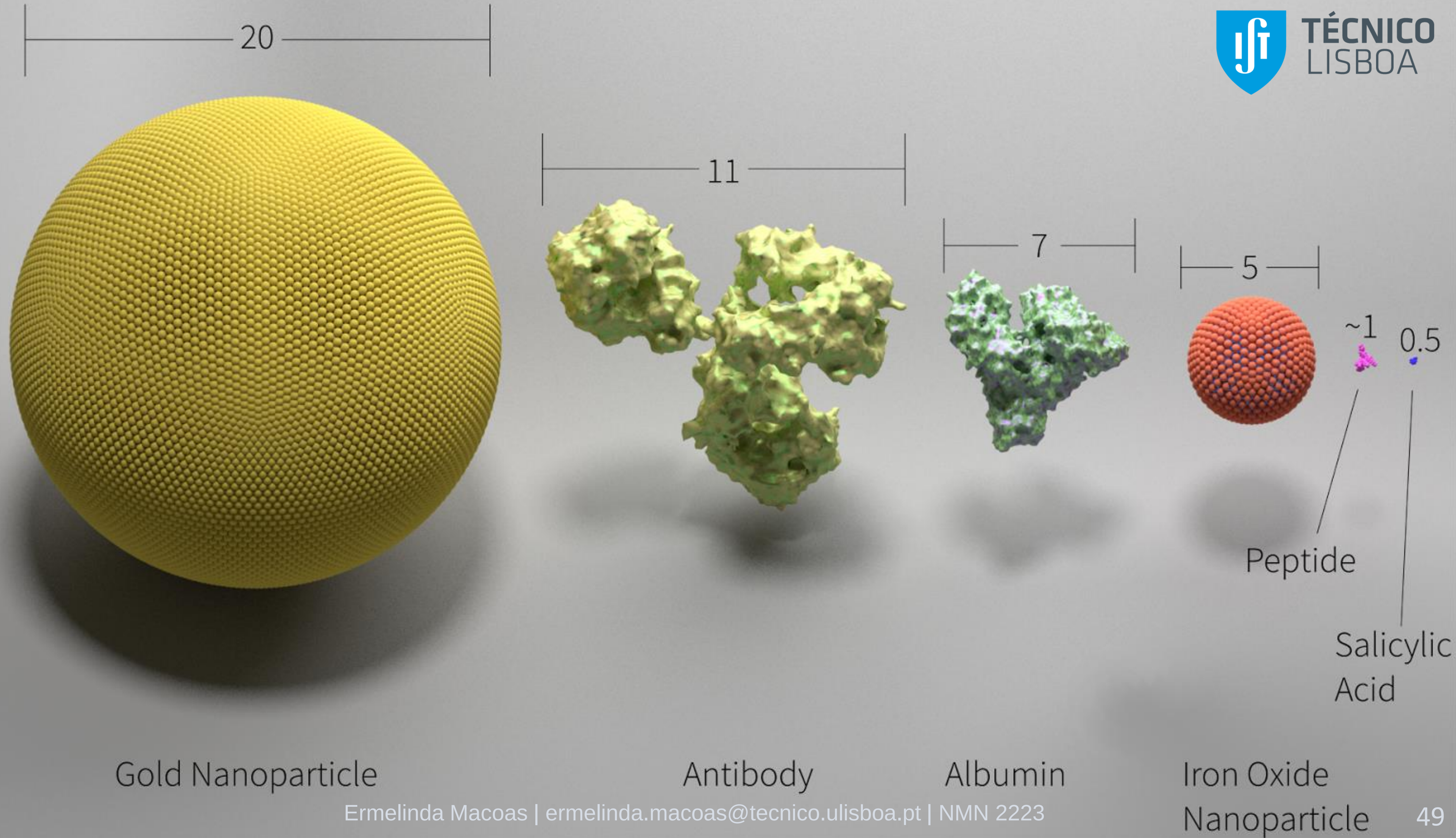




Distance between fluorophore and NP:
< 5 nm quenching effect
10-30 nm fluorescence enhancement

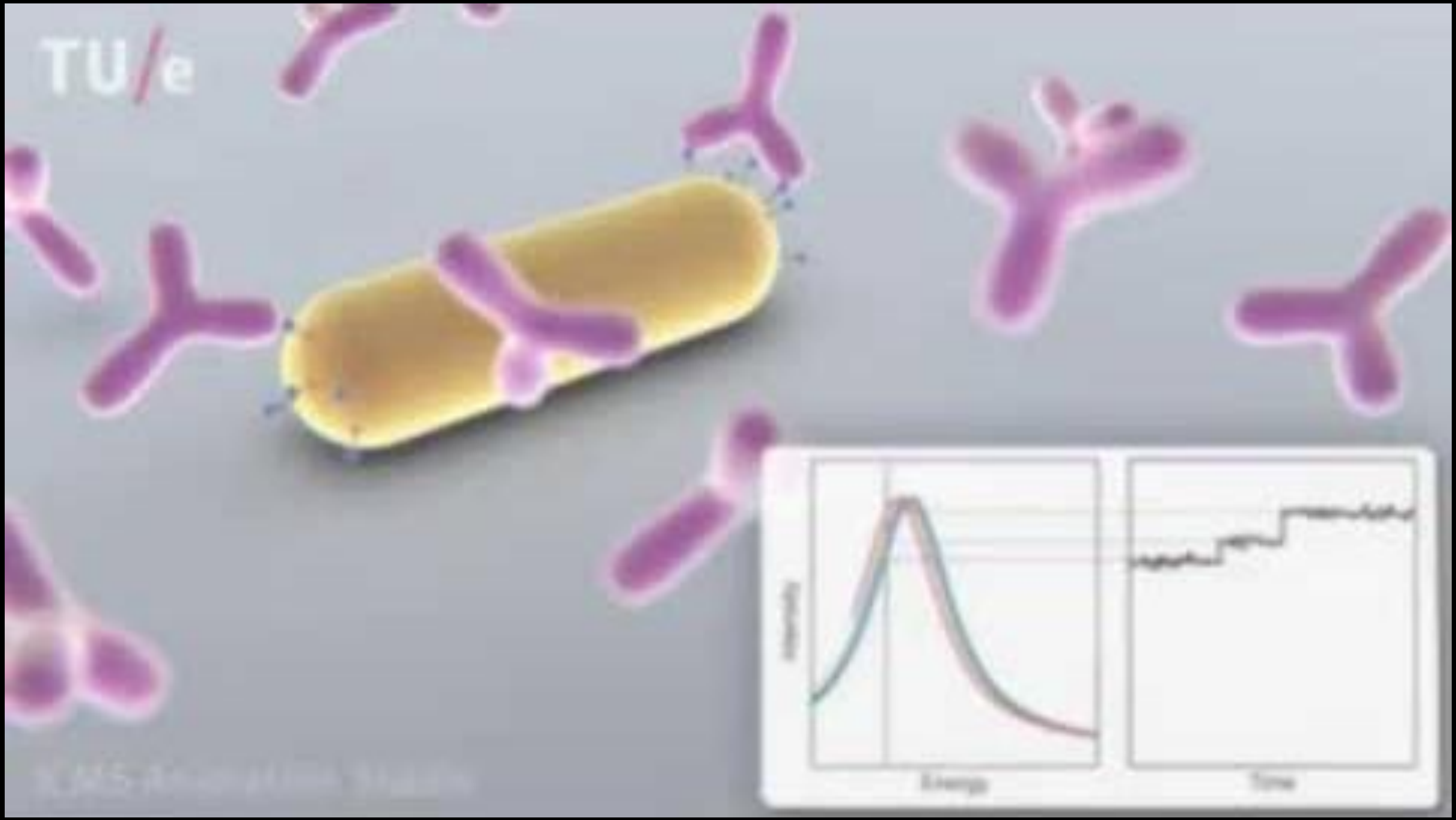
Trends in Pharmacological Sciences 2013, 34, 497

Nanotoday, 2015, https://doi.org/10.1016/j.nantod.2015.02.007


20
11
7
5
~1
0.5
Peptide
Salicylic Acid
Gold Nanoparticle
Antibody
Albumin
Iron Oxide Nanoparticle

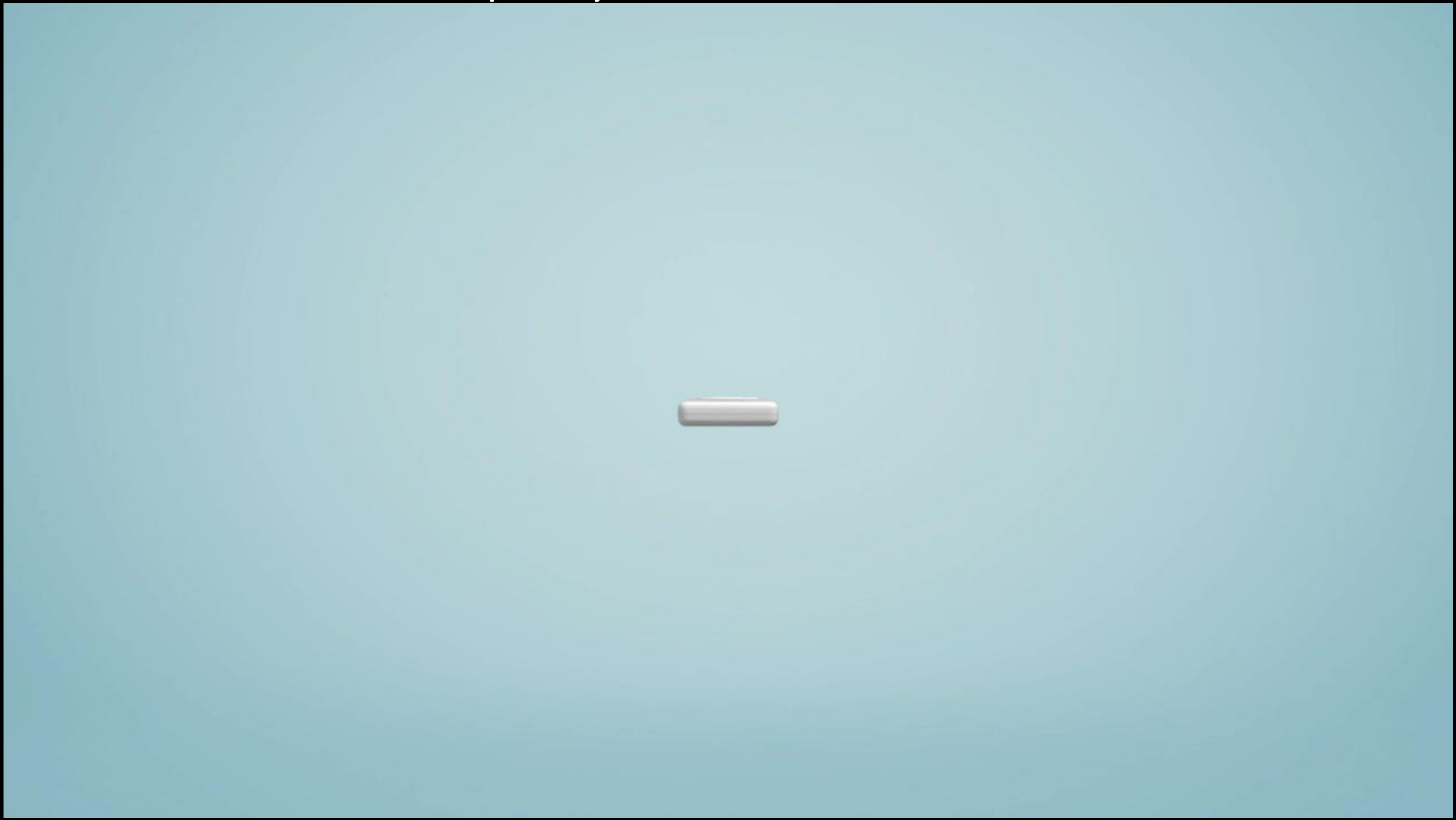
Single-Molecule Detection using Plasmons in Metal Nanoparticles

https://youtu.be/HCdMXhvRD9A



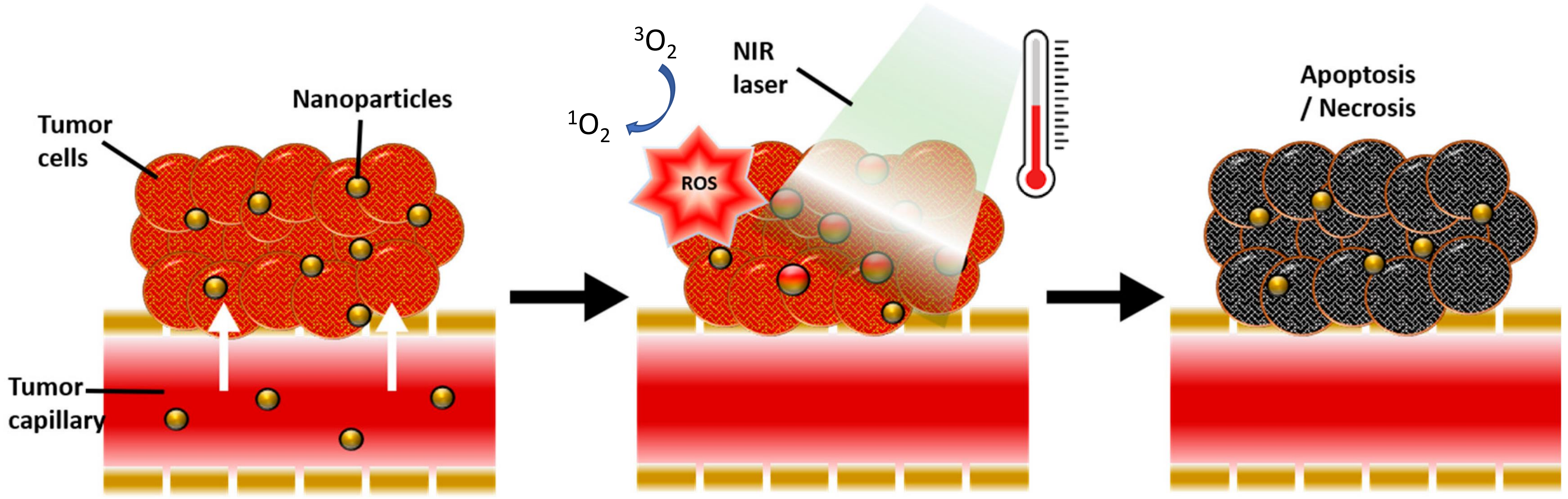
Lateral Flow Immunoassay

https://youtu.be/z07CK-4JoFo



Photothermal and photodynamic therapy

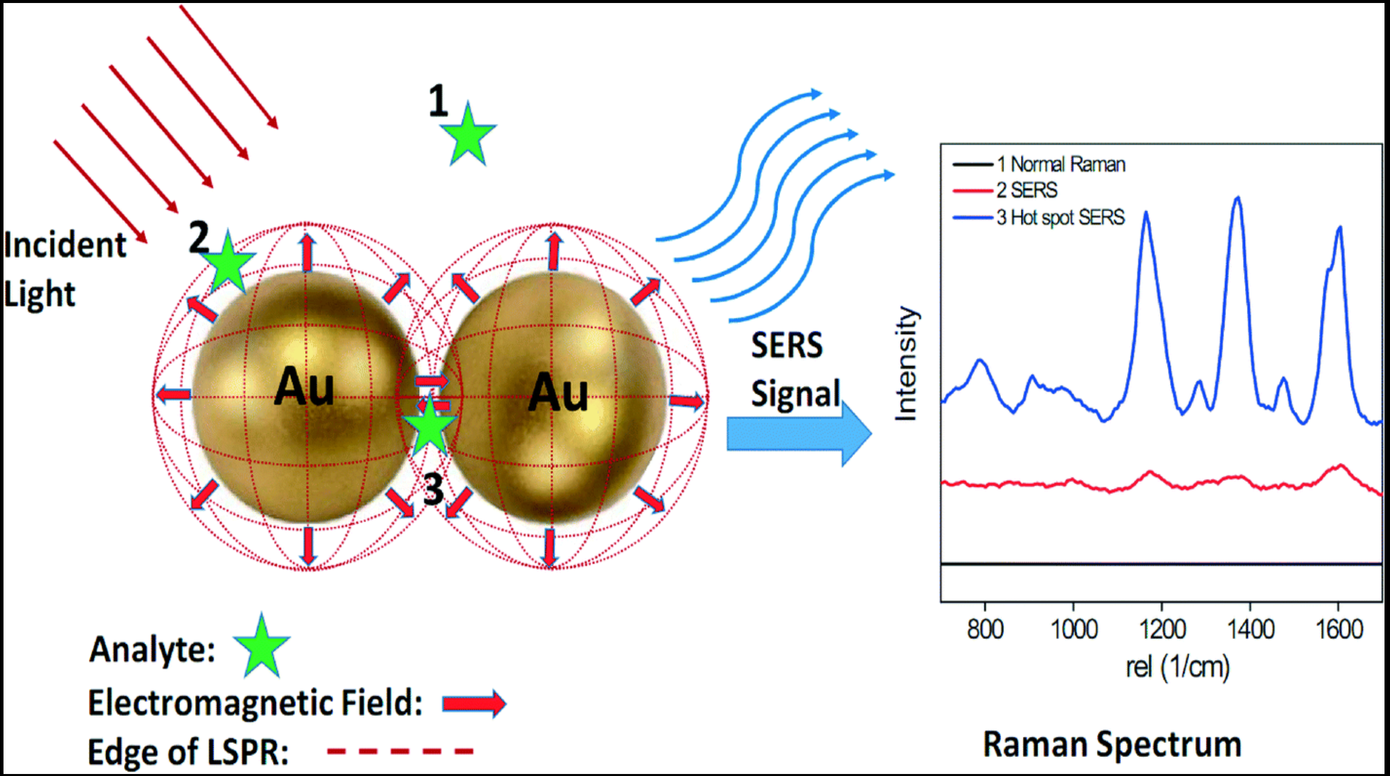
NPs with absorption in the NIR (typically NanoRods)
Most important effect comes from absorption of light



SERS (Surface Enhanced Raman Scattering)

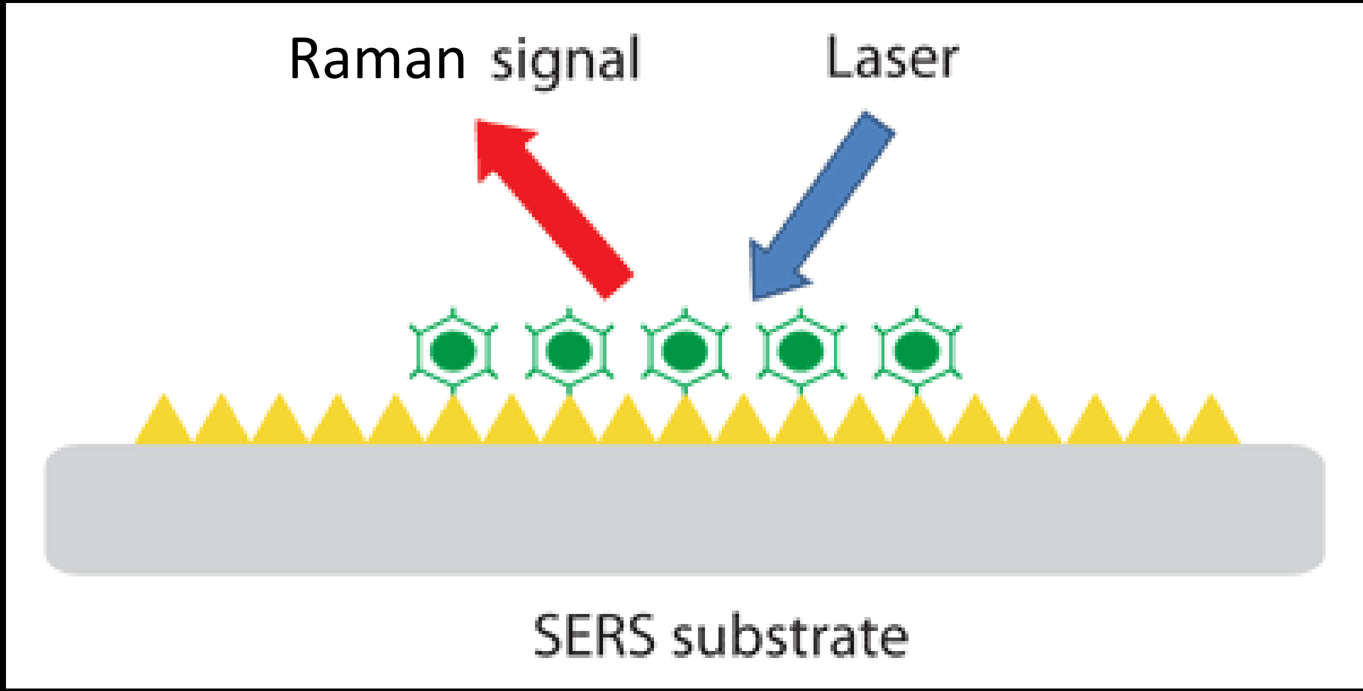
Raman spectroscopy

SERS
- 10^6 - 10^{14} amplification
- single molecule detection



Raman scattering cross-section is extremely small compared with fluorescence process, which is usually 15 orders of magnitude smaller.
SP is ideal for enhancing Raman scattering processes.

SERS



Coupling of LSPR with incident light (E_0)

$$\frac{|E_{sphere}|}{|E_0|} = 1 + \left|\frac{\varepsilon_1(\lambda_L) - \varepsilon_m}{\varepsilon_1(\lambda_L) + 2\varepsilon_m}\right|$$

Coupling of LSPR with the Raman scattered light (E_{mol})

$$\frac{|E_{sphere}|}{|E_0|} = 1 + \left|\frac{\varepsilon_1(\lambda_{Raman}) - \varepsilon_m}{\varepsilon_1(\lambda_{Raman}) + 2\varepsilon_m}\right|$$

SERS

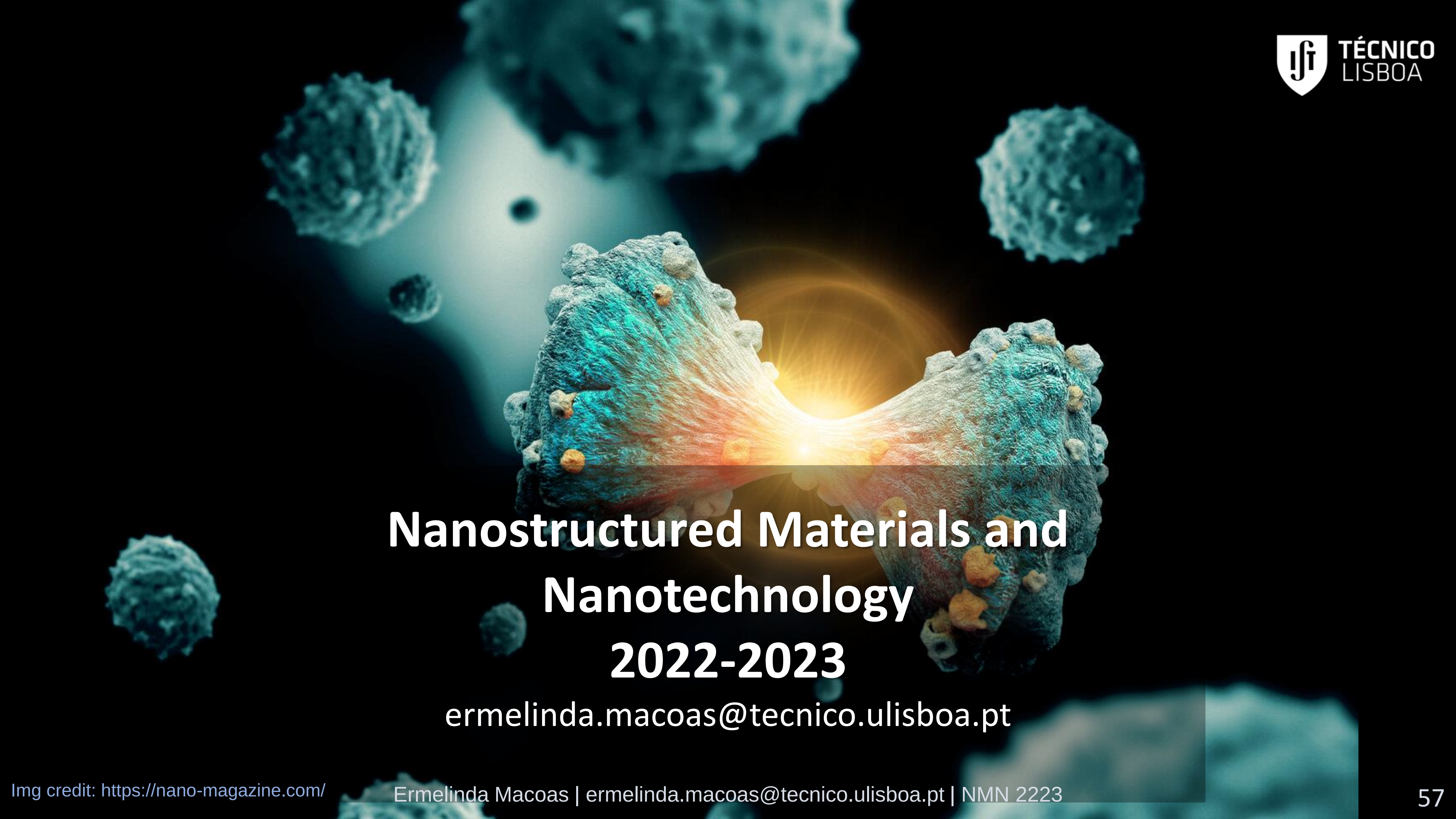
- 10^6 - 10^{14} amplification
- single molecule detection

λ_{Raman} and λ_L should both match the λ_{LSPR}

Chem. Soc. Rev., 2008, 37, 1067

Applications

	Size (nm)						shape
	5	10	20	40	60	80	
Lateral flow			X	X	X	X	sphere
Western blot			X	X	X	X	Sphere
Dark filed microscopy				X	X	X	Sphere
Electron microscopy	X	X	X				sphere
Metal enhanced fluorescence			X	X			Sphere/spiky surface
SERS				X	X		Non-spherical/spiky
FRET quenching	X	X	X	X			sphere
Photothermal therapy				X			Rod/hollow sphere
Photodynamic therapy				X			Rod/hollow sphere
Drug delivery	X	X	X	X			Rod/sphere



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Img credit: https://nano-magazine.com/