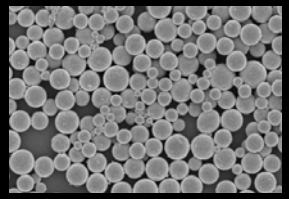
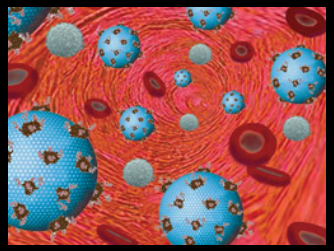
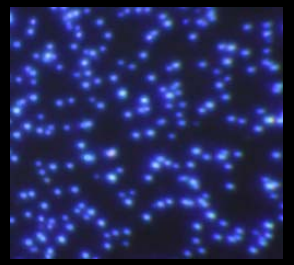


Instituto Universitario de Ciencia de Materiales Nicolás Cabrera

INTERNATIONAL SUMMER SCHOOL ON FLUORESCENT NANO-PARTICLES IN BIO-MEDICINE



Surface Plasmons in NPs
Applications in biomedicine



Miguel Angel García

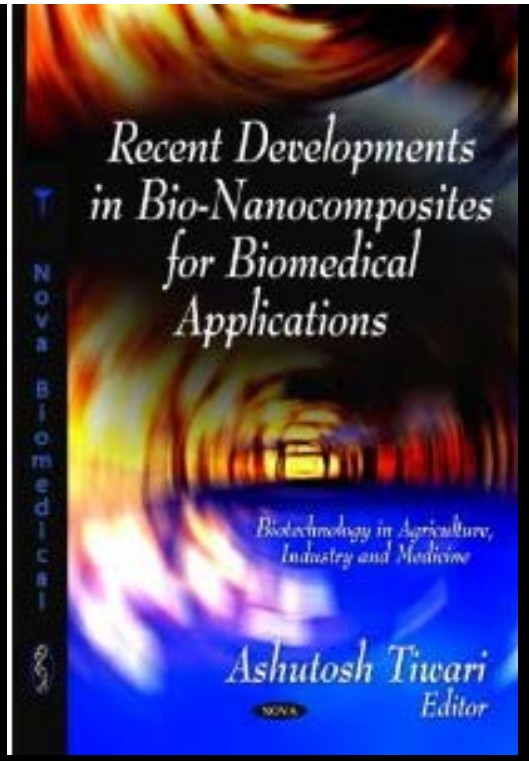
magarcia@icv.csic.es

Dpt. de Electrocerámics, Institute for Ceramic and Glass, CSIC

& IMDEA Nanoscience

Surface Plasmon in biomedicine, MAG, in Recent Developments in Bio- Nanocomposites for Biomedical Applications , @Novascience Pub. 2010

ISBN: 978-1-61761-008-0 4.



IOP Publishing — Journal of Physics D: Applied Physics
J. Phys. D: Appl. Phys. 44 (2011) 283001 (20pp) — doi: 10.1088/0022-3727/44/28/283001

TOPICAL REVIEW

Surface plasmons in metallic nanoparticles: fundamentals and applications

M A Garcia

✓**TOPICAL REVIEW** *Surface Plasmons in metallic Nanoparticles: Fundamentals and Applications*, MAG, J. Phys. D. Appl. Phys, 44 (2011) 283001

✓See corrigendum !!

Outline

1. What are Surface Plasmons?
   - -The physics of SP
   - -Features
   - - Models and calculations

2. Applications of SP in biomedicine
   - -General strategies
   - -SP based applications
   - - Combination with other techniques

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

¿What are Surface Plasmons in nanoparticles?

➢**Condensed Matter Physics**

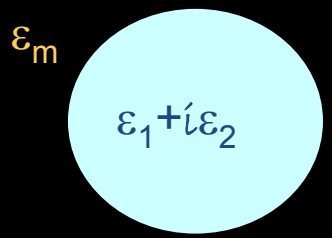
The plasmon is a quasiparticle resulting from the quantization of plasma oscillations.

➢**Solid State Physics**

Resonant coupling of conduction electrons with a electromagnetic field propagating in that region of the space.

➢**Material Physics (Science)**

A collective oscillation of conduction electrons at a metal dielectric interface excited by the electromagnetic field of the light.



$$\nabla \cdot E = \rho$$

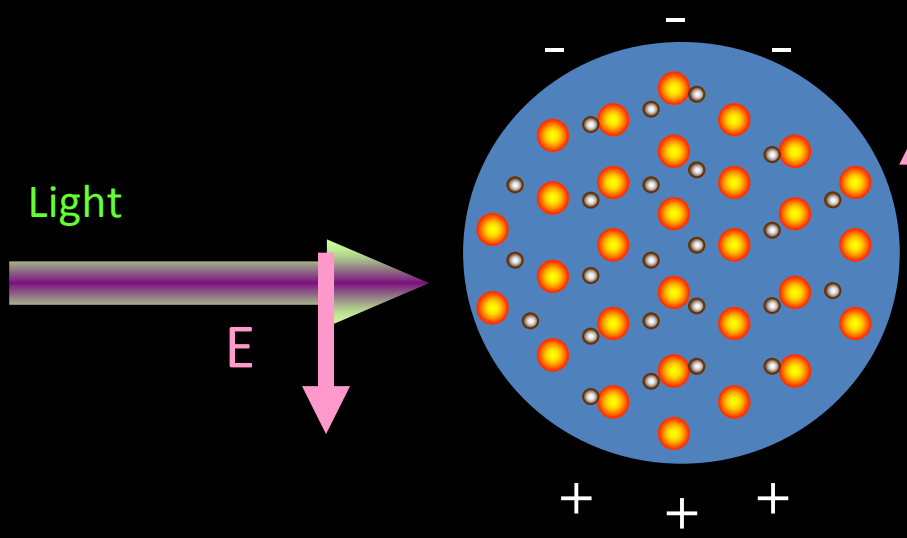
$$\nabla \cdot B = 0$$

$$\nabla \times E = -\sqrt{\varepsilon_0 \mu_0}\,\frac{\partial B}{\partial t}$$

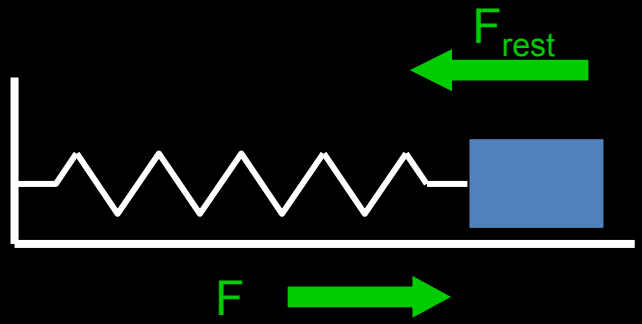
$$\nabla \times B = j + \sqrt{\varepsilon_0 \mu_0}\,\frac{\partial E}{\partial t}$$

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

¿What are Surface Plasmons in nanoparticles?



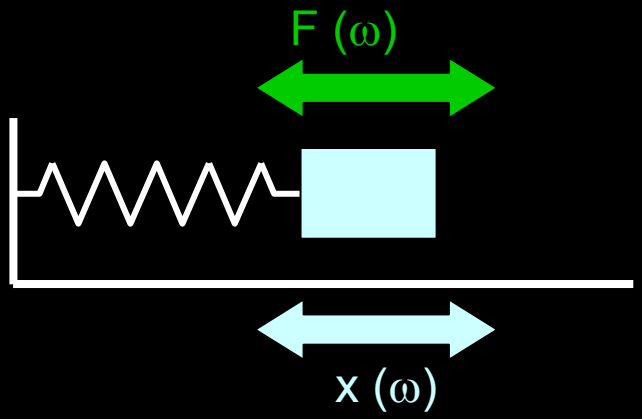
$$\omega_p = \sqrt{\frac{4\pi n e^2}{m}}$$

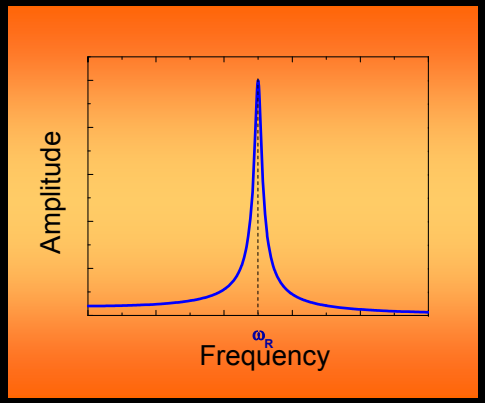


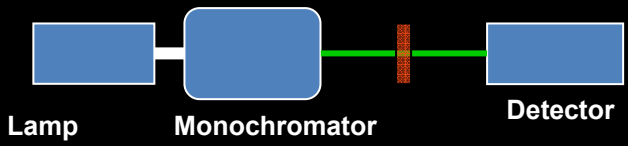
$$\omega = \sqrt{\frac{k}{m}}$$

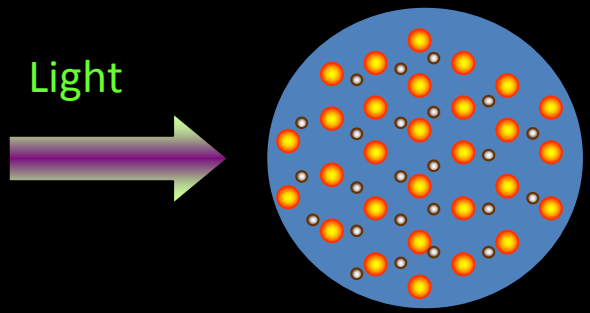
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

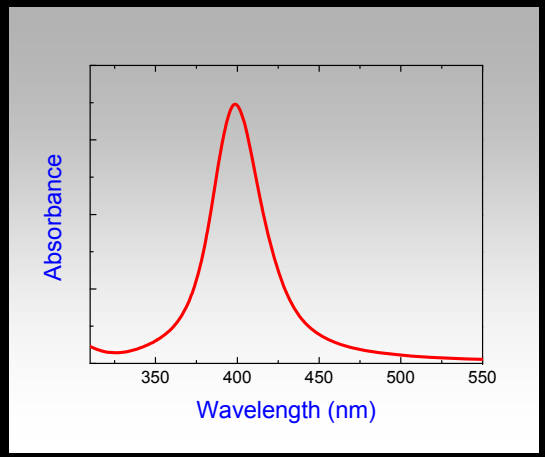
Forced oscillator











NPs Ag 10 nm

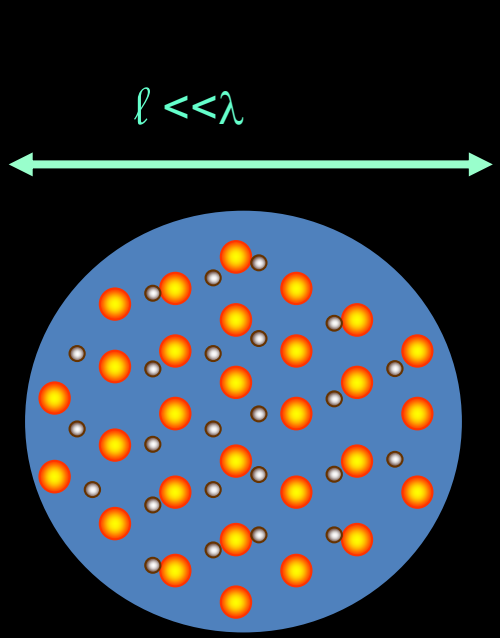
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

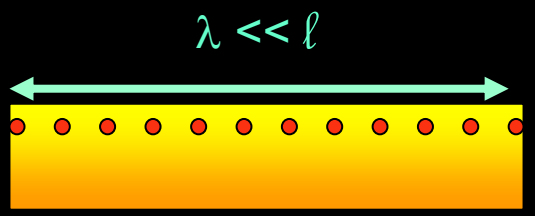
Resonance wavelength for SPs in NPs

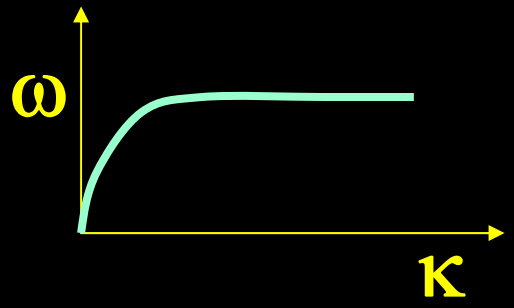
Element	Resonance λ (nm)
Li	450
Na	480
K	590
Rb	650
Eu	380
Mg	250
Ca	510
Au	490
Ag	410
Cu	550
Pt	215
Pd	210
Y	410

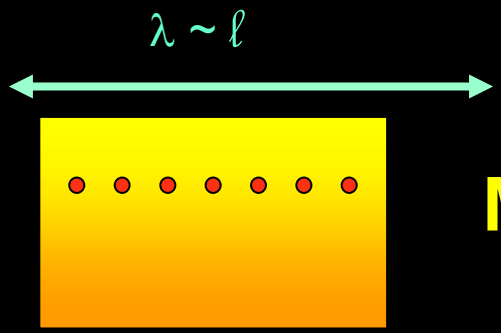
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Surface Plasmons in nanostructures







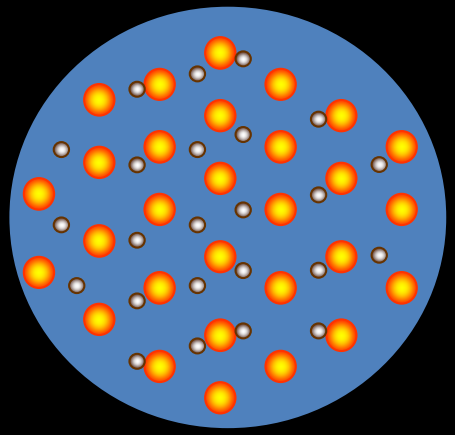


Modes: ω_n

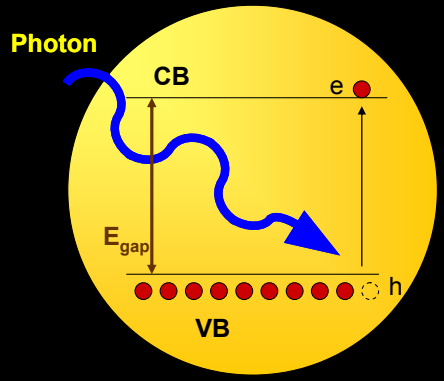
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Optical properties in nanomaterials

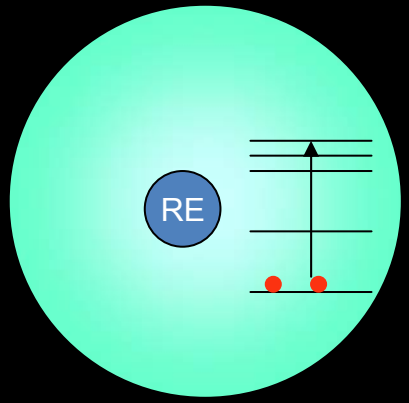
Metallic NPs



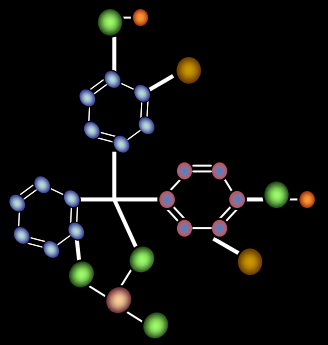
Semiconductor



Dielectric



Organics



(Noble) metals

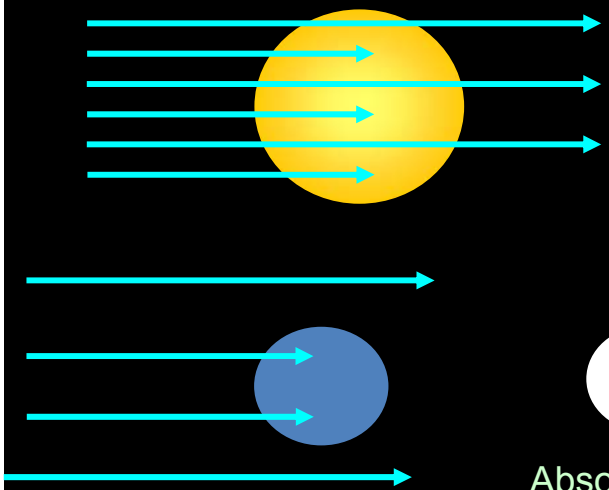
- ✓Highly biocompatible
- ✓Chemical stability
- ✓"Easy" functionalization

What is outstanding about SP?

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

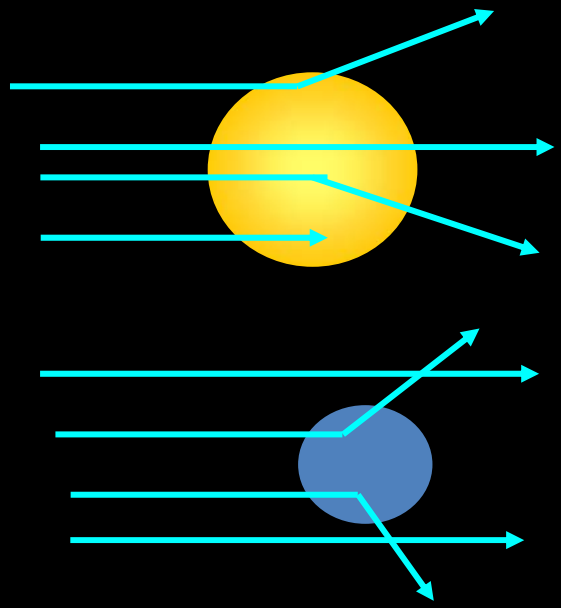
Intensity of Surface Plasmons Resonance in NPs

Absorption cross section (σ_{abs})



Absorption cross section

Scattering cross section (σ_{sca})



Scattering cross section

Extinction cross section

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

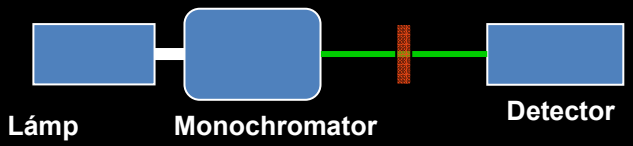
- ✓Bulk opaque particles: $\sigma_{ext} \cong \sigma_{geo}$
- ✓·Nanoparticles $\sigma_{ext} \leq 0.2 \cdot \sigma_{geo}$

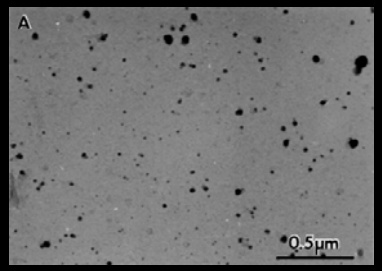
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

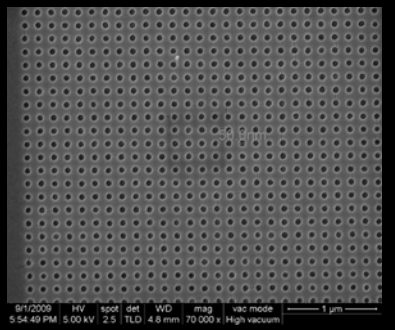
Intensidad de la Resonancia de PS

Extintion cross section

$\sigma_{ext} \leq 0.2\sigma_{geom}$

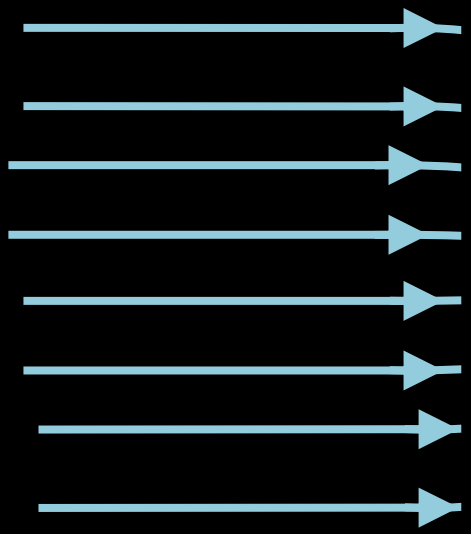






σ_{ext}~10 -100 Geometrical section

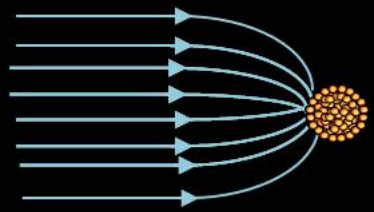
$$I = I_0 e^{-n\sigma}$$



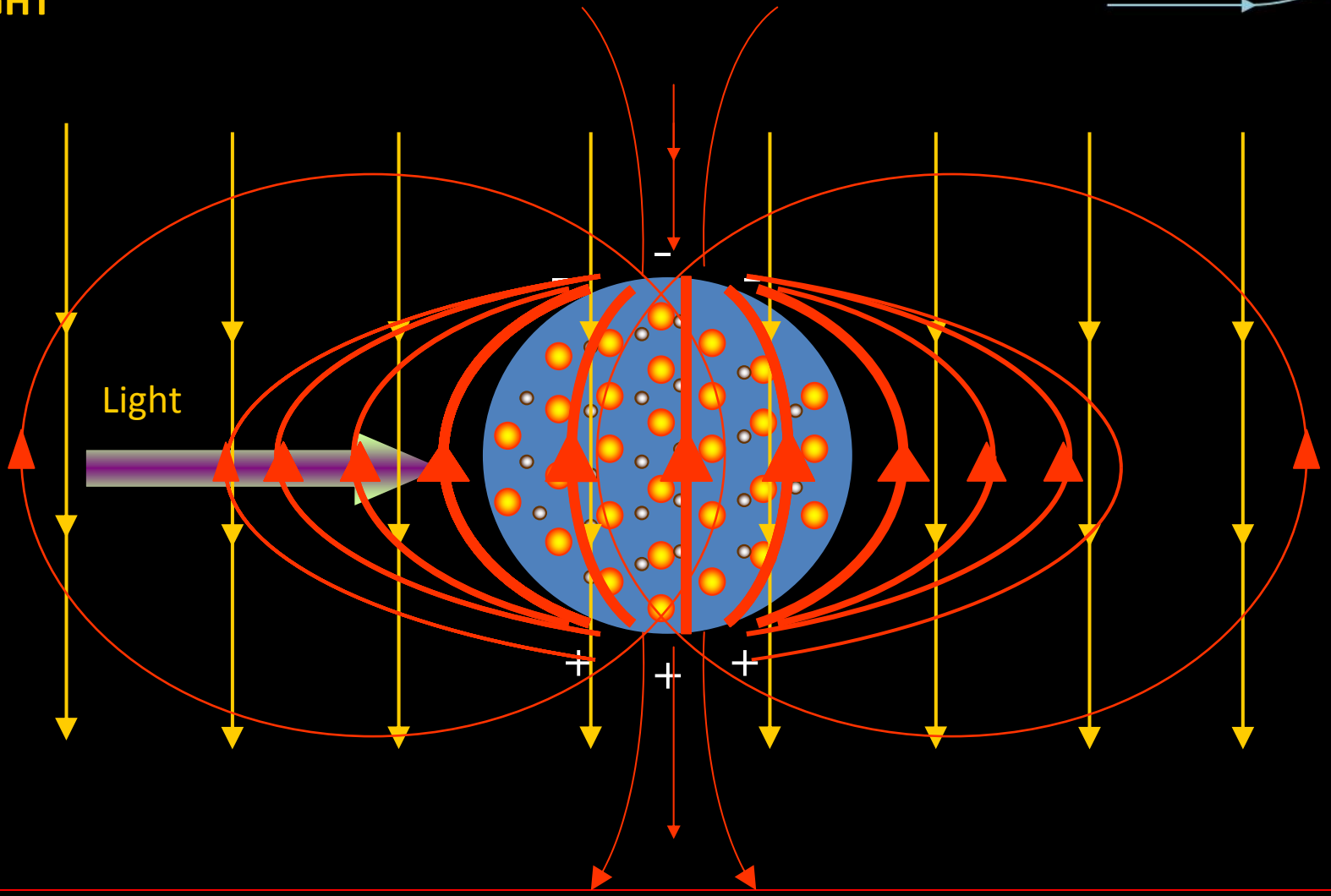
Diffraction limit ?

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Surface Plasmon Resonance process



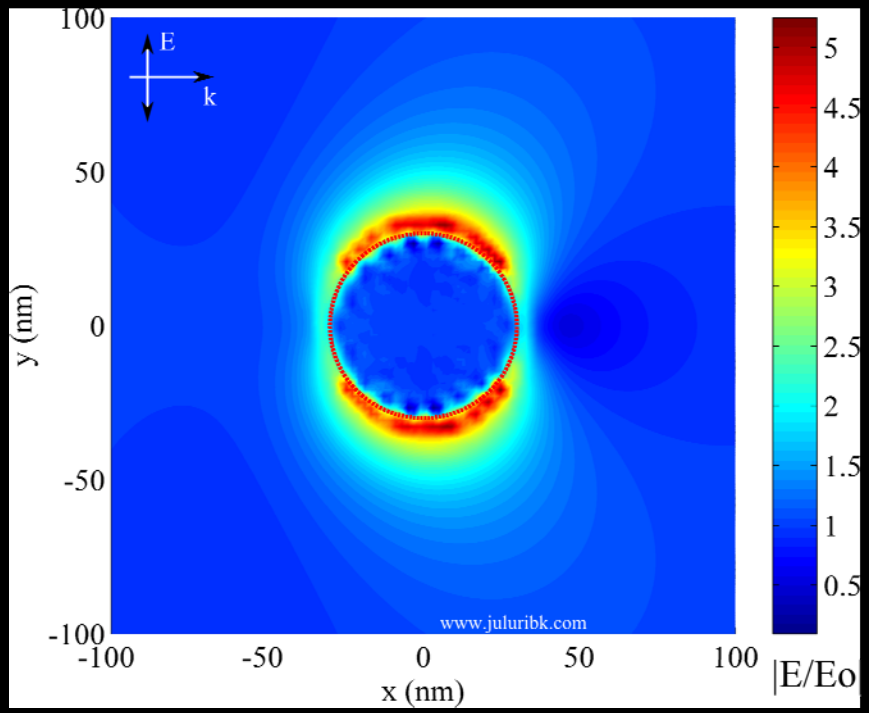
E_{LIGHT}

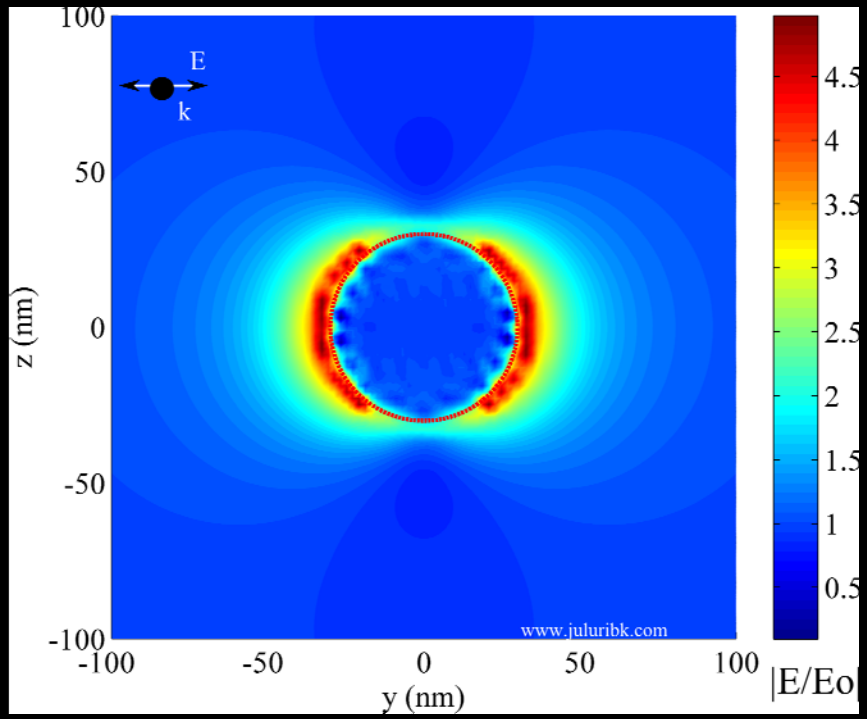


M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Electric fields in SPR

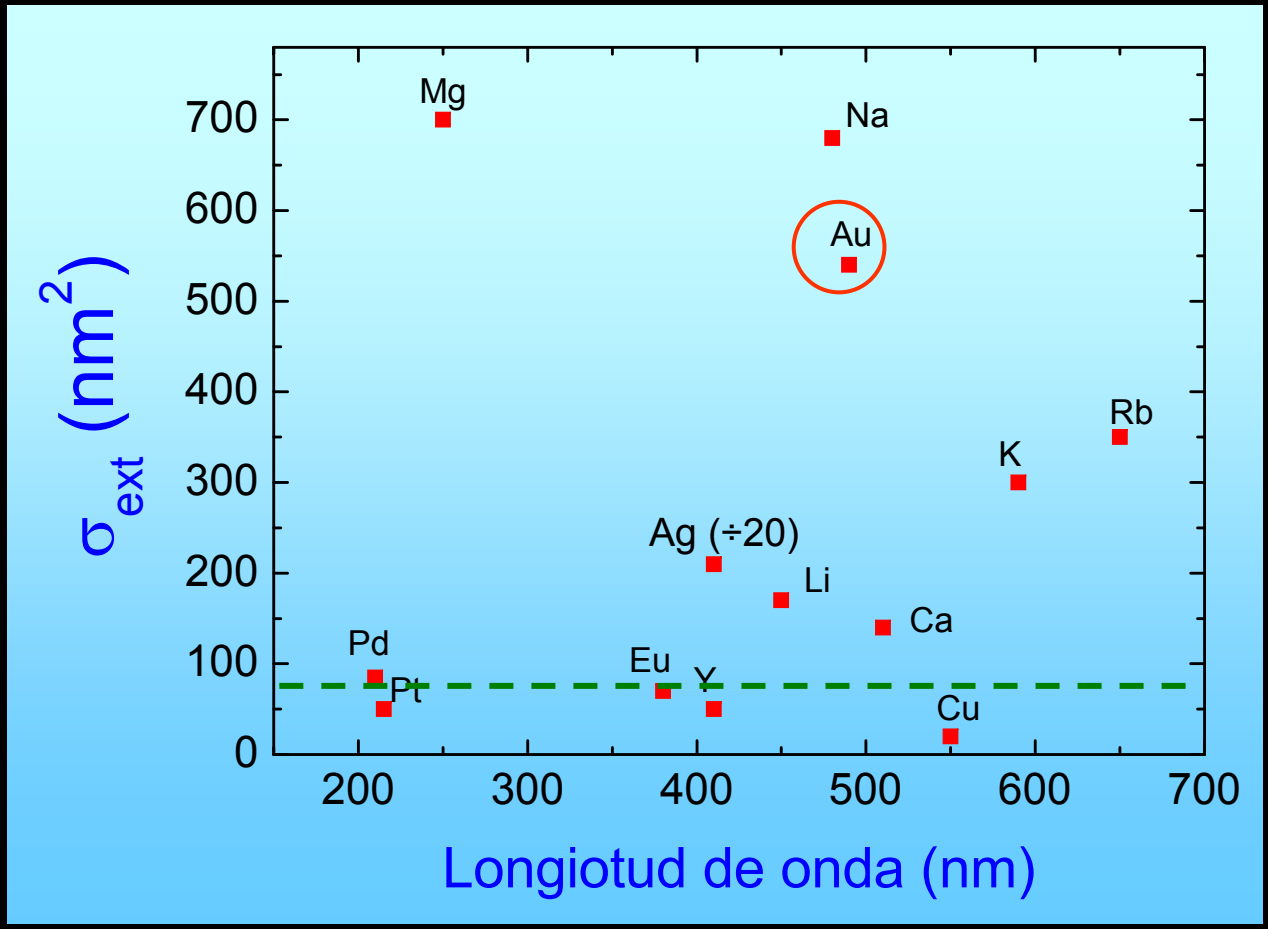
60 nm Au NP





M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

SPR for 10 nm diameter NPs (σ_{geo}=78 nm^2)



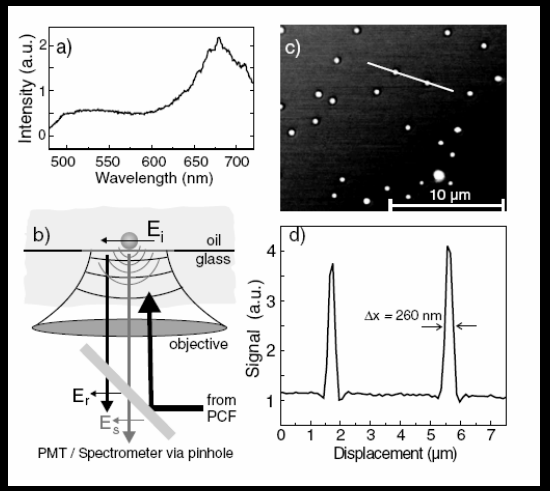
NOTE: σ for Ag has been divided by 20 !! (real value 4080 nm^2)

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

VOLUME 93, NUMBER 3 PHYSICAL REVIEW LETTERS week ending 16 JULY 2004

Detection and Spectroscopy of Gold Nanoparticles Using Supercontinuum White Light Confocal Microscopy

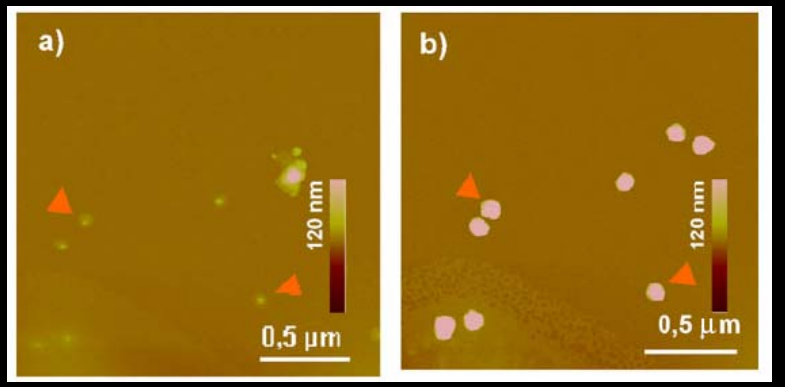
K. Lindfors,* T. Kalkbrenner,† P. Stoller, and V. Sandoghdar‡
Laboratory of Physical Chemistry, Swiss Federal Institute of Technology (ETH), CH-8093 Zurich, Switzerland
(Received 26 November 2003; published 15 July 2004)



INSTITUTE OF PHYSICS PUBLISHING NANOTECHNOLOGY
Nanotechnology **14** (2003) 1262–1268 PII: S0957-4484(03)65718-1

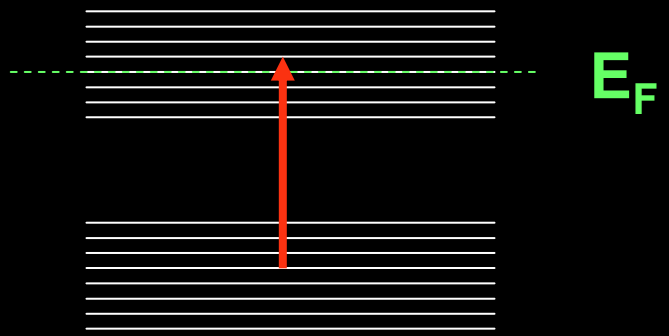
The optical detection of individual DNA-conjugated gold nanoparticle labels after metal enhancement

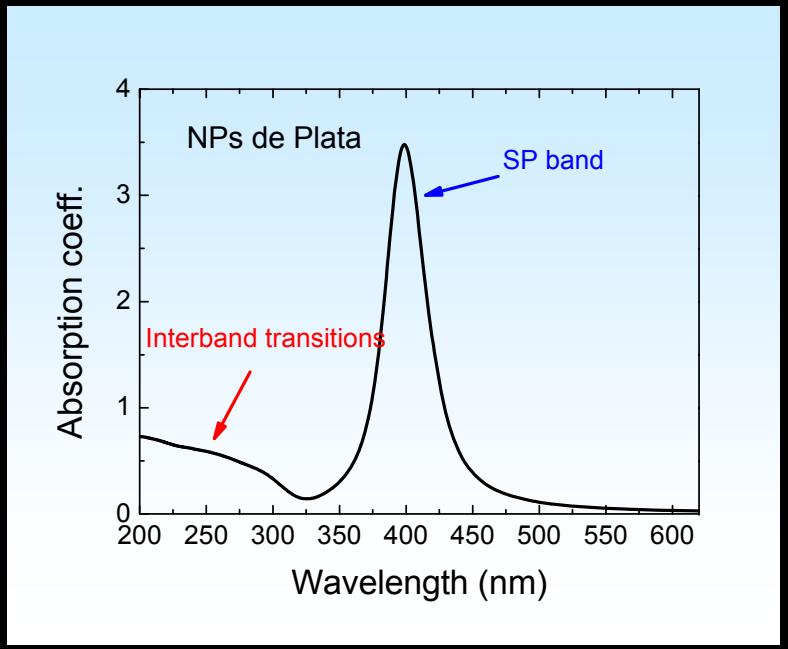
Andrea Csáki, Pia Kaplanek, Robert Möller and Wolfgang Fritzsche

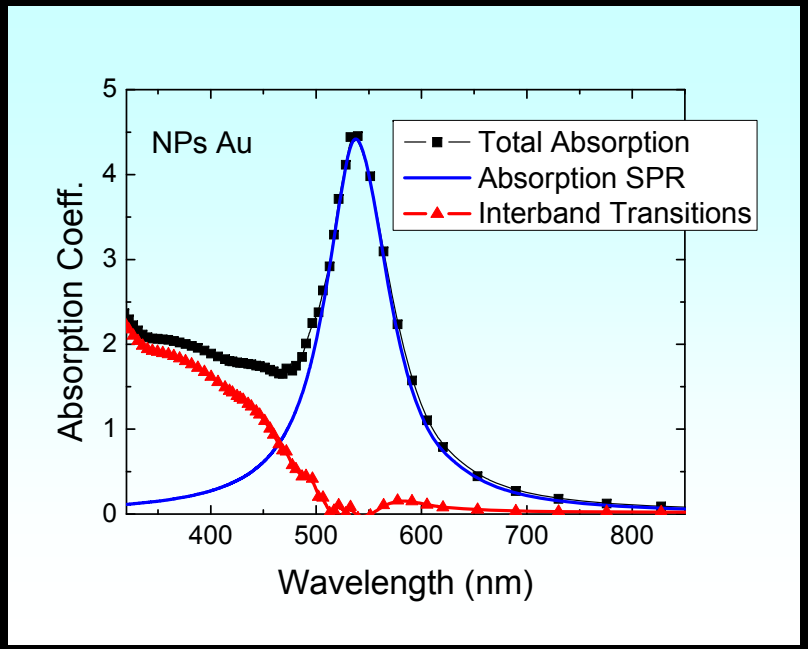


Surface plasmons resonance

Interband Transitions





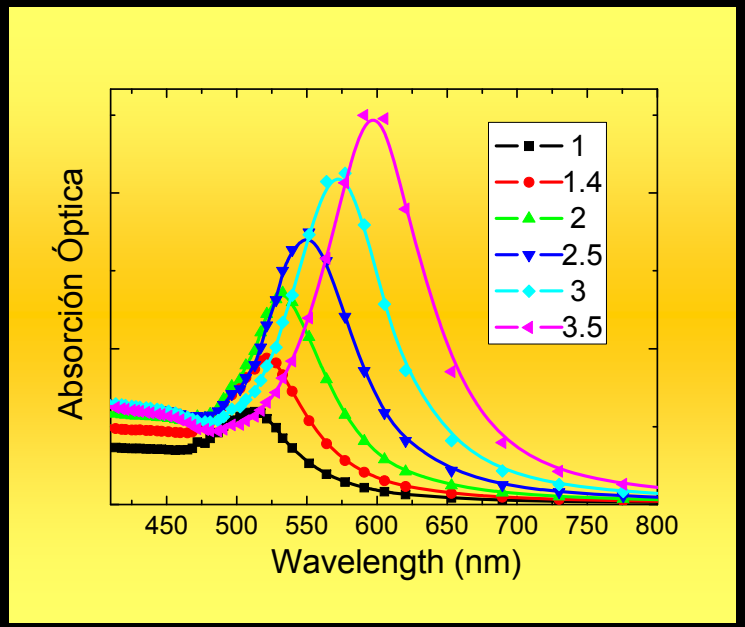


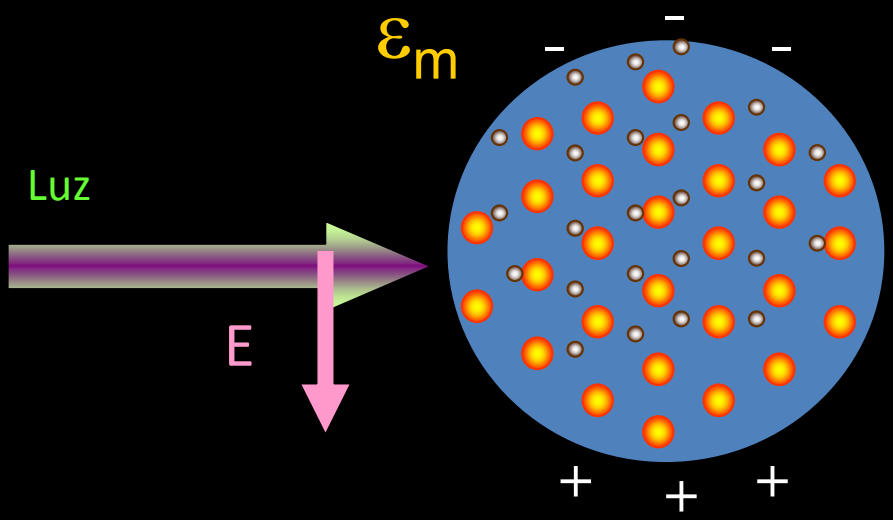
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

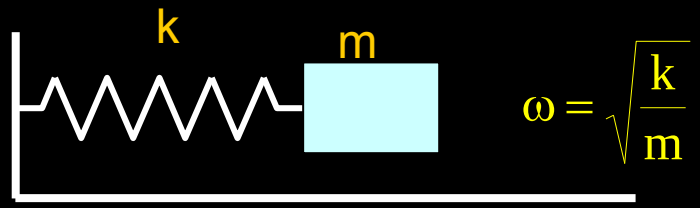
Surrounding medium

Au NPs - 10 nm

Absorption vs ε_m



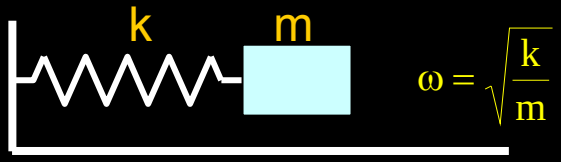




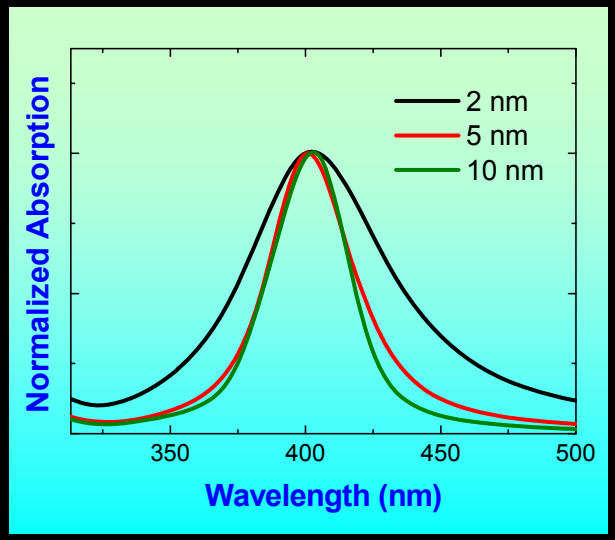
$$\omega = \sqrt{\frac{k}{m}}$$

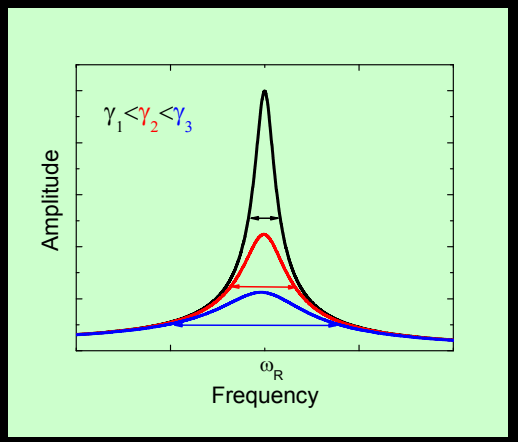
The dielectric permittivity of the medium shifts the SPR

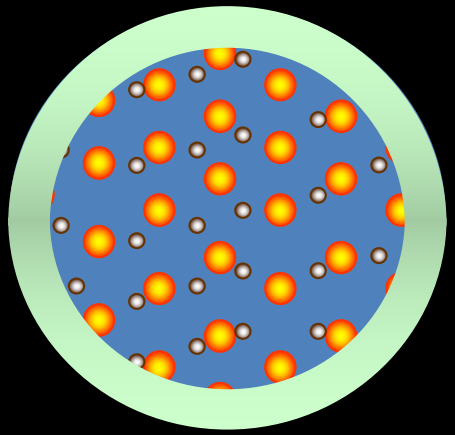
Size effects



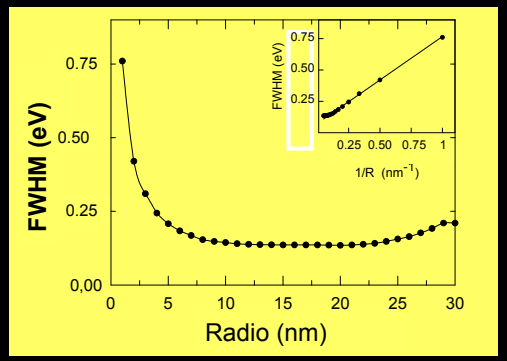
Ag NPs in a medium with ε_m=2.25







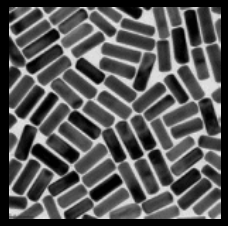
$$\gamma = \gamma_0 + \frac{v_F}{R}$$

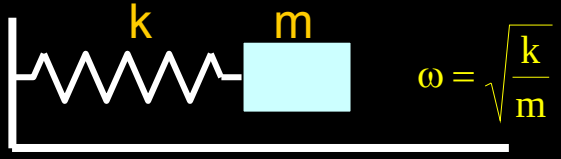


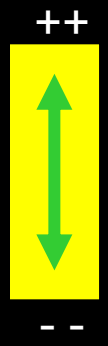
NPs size determines the width of the SPR band

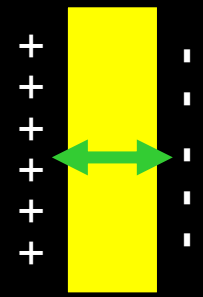
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

NPs shape



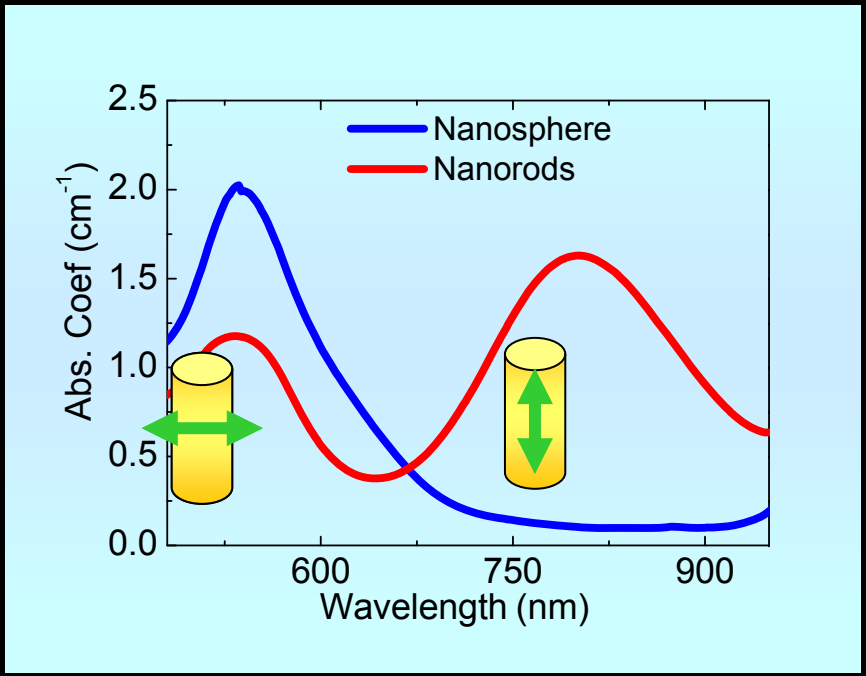






Longitudinal

Transversal

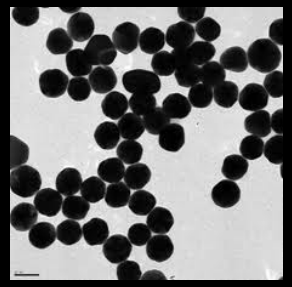


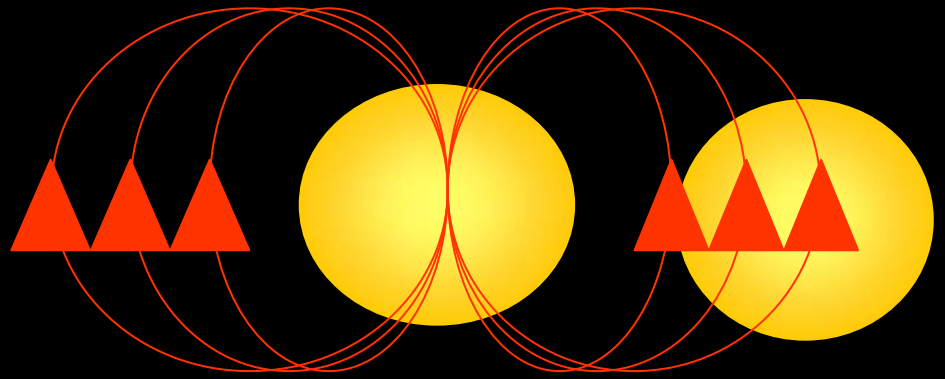
Longitudinal SPR shifts toward IR with increasing the aspect ratio

NP morphology allows tuning the resonance

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

NPs interactions





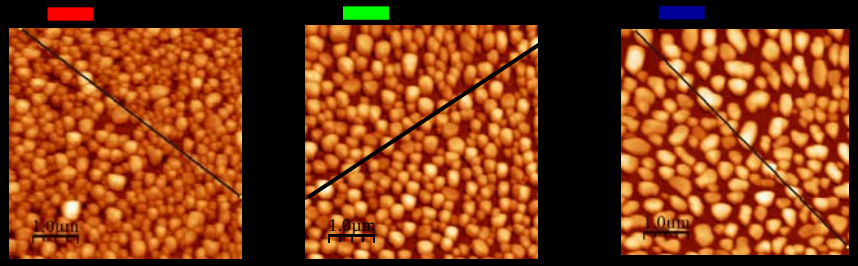
Interaction effects: Non homogeneous electric field

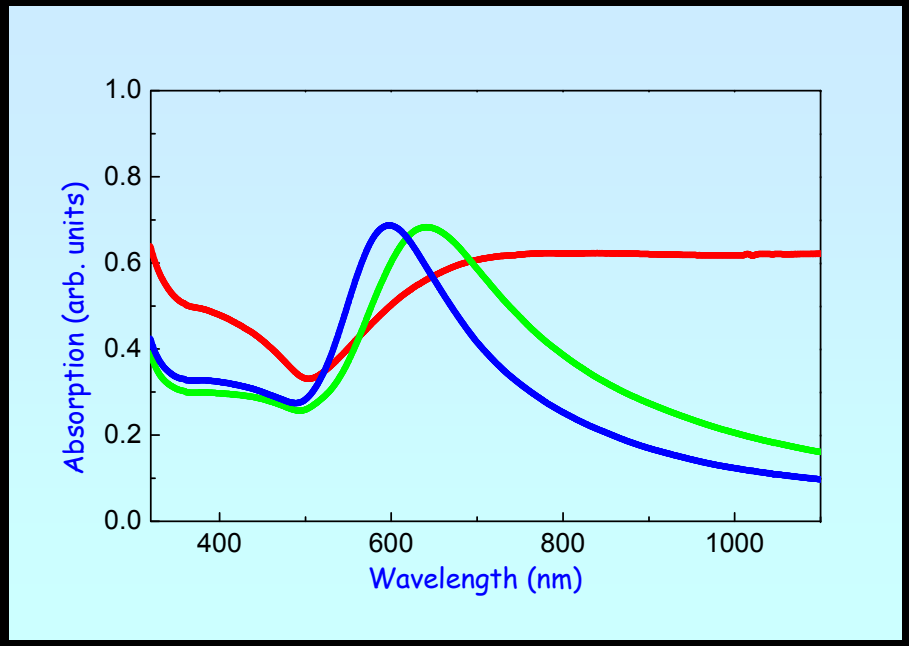
Damping of the SPR

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

NPs interactions

Damping: Widening & shift of the resonance



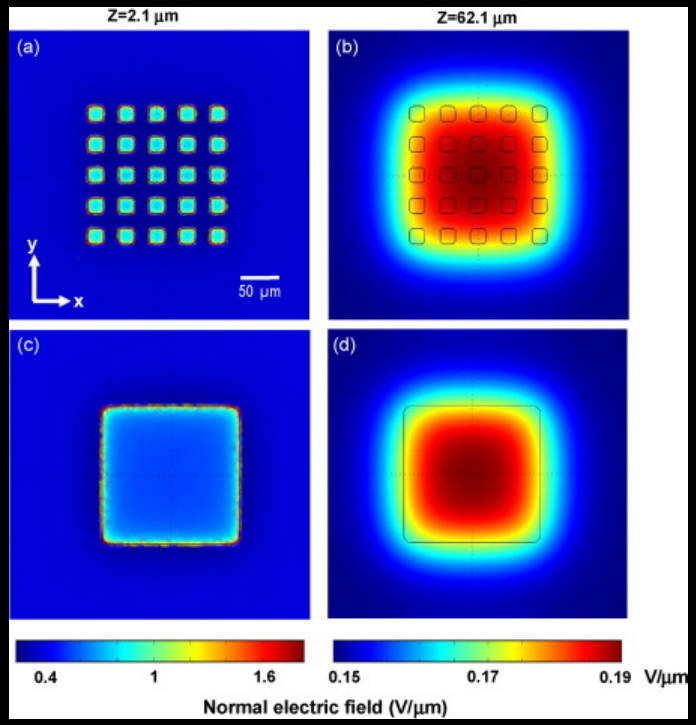


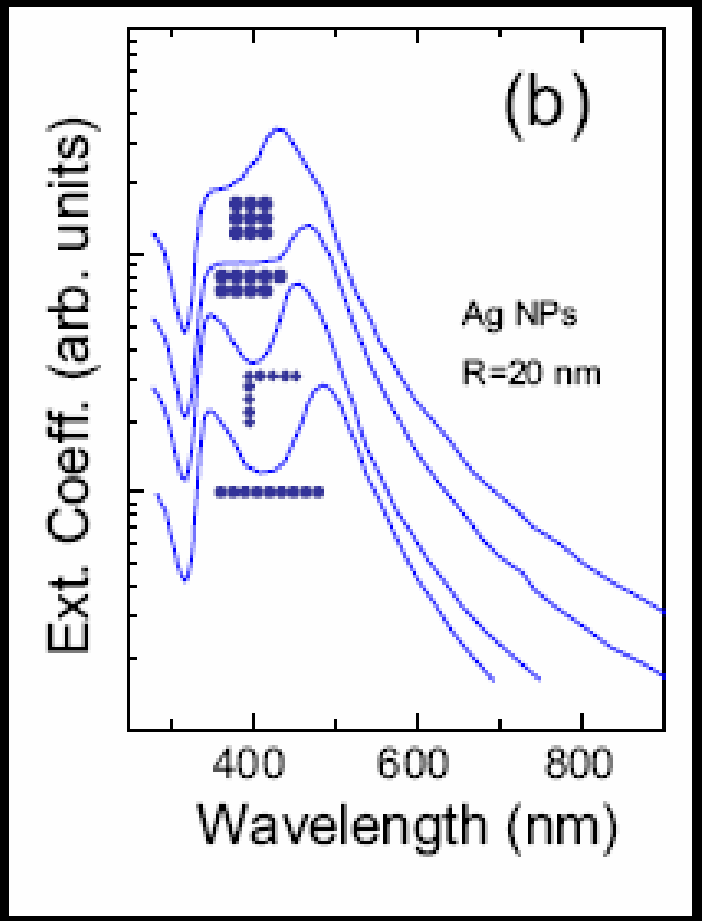
A. Serrano, O Rodriguez de la fuente, MAG, *J. Appl. Phys*. 108 074303 (2010)

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Ordered structures

New SPR modes

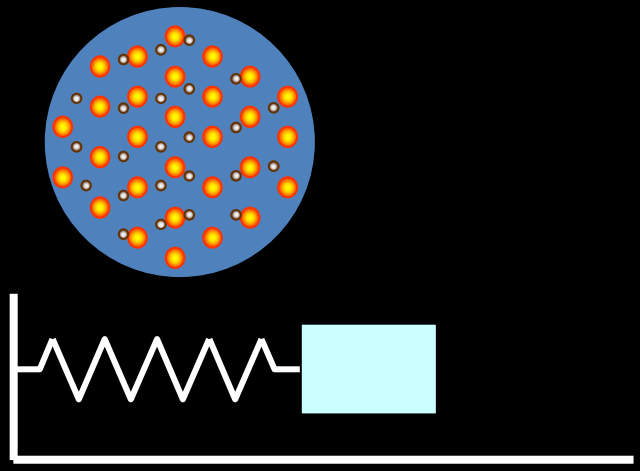




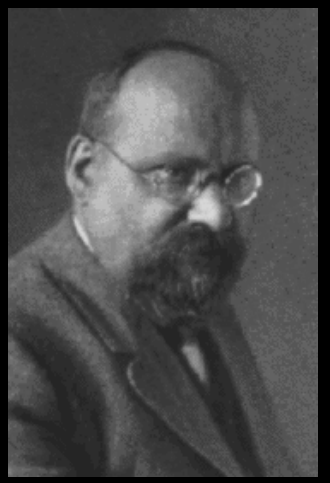
H. J. Lee et al Sens. & Act. B Sensors and Actuators B: Chemical 136 (2009) 320

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Calculation of the SPR spectra



* Gustav Mie, *"Beitrige zur Optik truber Medien, speziell kolloidaler Metallösungen,"* Ann Phys. (Leipzig) 25, 376-445 (1908).



Mie Theory

✓Spherical Nanoparticles
✓Isolated

U. Kreibig and M. Vollmer, *Optical properties of metal clusters* ed. Springer-Verlag, Springer Series in Material Science 25 (1995).

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

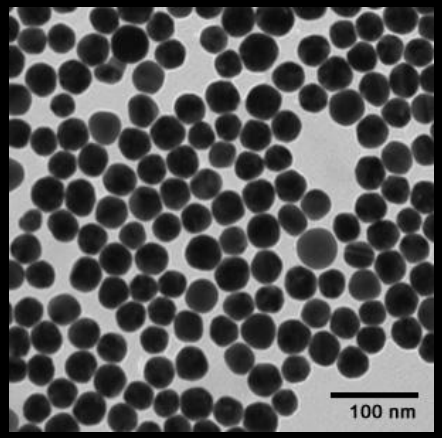
Calculation of the SPR spectra

$$\nabla \cdot \mathrm{E} = \rho$$

$$\nabla \cdot \mathrm{B} = 0$$

$$\nabla \times \mathrm{E} = -\sqrt{\varepsilon_0 \mu_0}\,\frac{\partial \mathrm{B}}{\partial t}$$

$$\nabla \times \mathrm{B} = \mathrm{j} + \sqrt{\varepsilon_0 \mu_0}\,\frac{\partial \mathrm{E}}{\partial t}$$



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

$$a_L = \frac{m\Psi_L(mx)\cdot\Psi_L'(x) - \Psi_L'(mx)\cdot\Psi_L(x)}{m\Psi_L(mx)\cdot\eta_L'(x) - \Psi_L'(mx)\cdot\eta_L(x)}$$

$$b_L = \frac{\Psi_L(mx)\cdot\Psi_L'(x) - m\Psi_L'(mx)\cdot\Psi_L(x)}{\Psi_L(mx)\cdot\eta_L'(x) - m\Psi_L'(mx)\cdot\eta_L(x)}$$

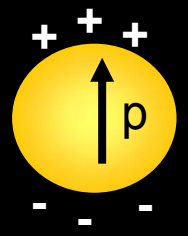
Aproximation

U. Kreibig and M. Vollmer, *Optical properties of metal clusters* ed. Springer-Verlag, Springer Series in Material Science 25 (1995).

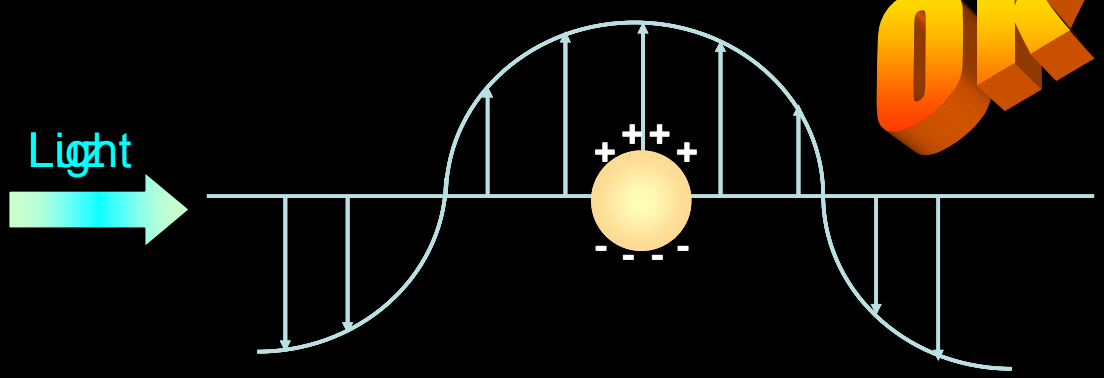
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Dipolar approximation

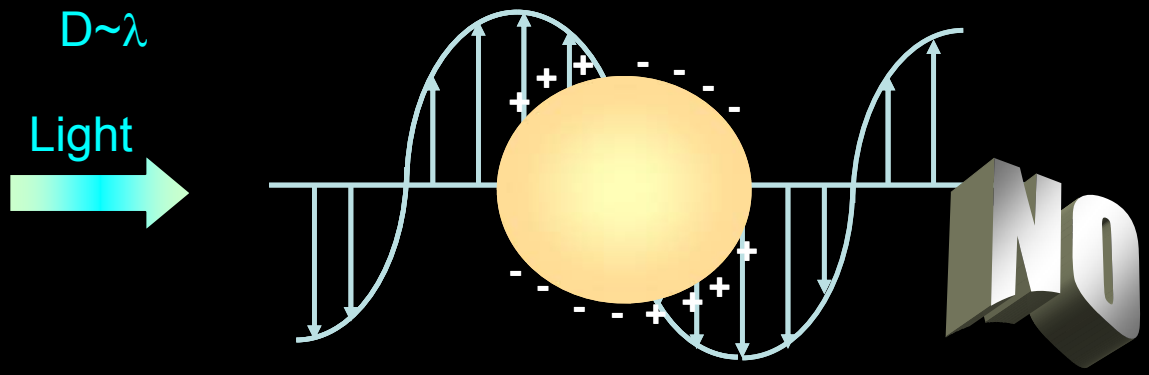
The NP behave as a dipole



D<<λ



D~λ



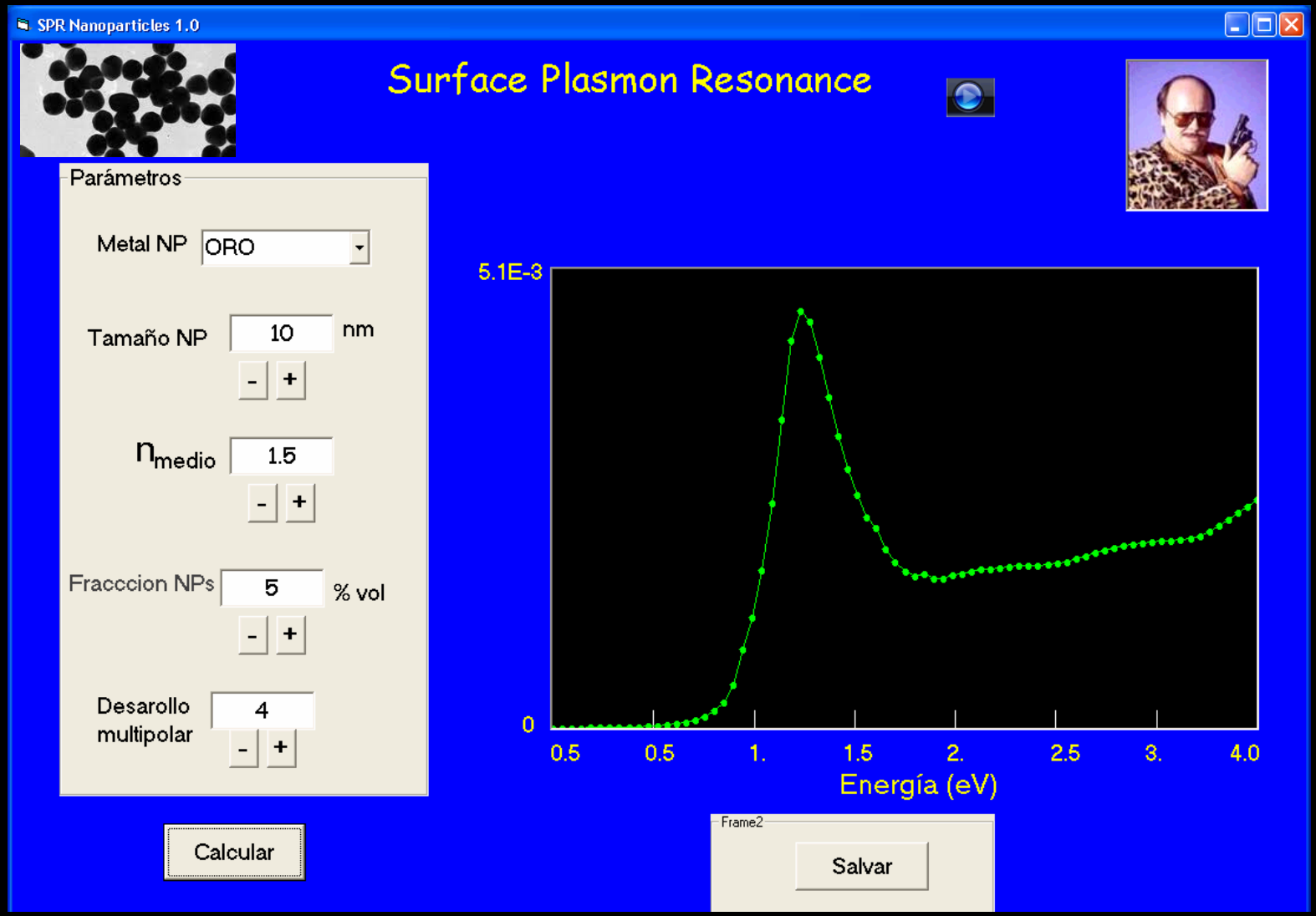
With this approximation

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

Interaction effects can be included

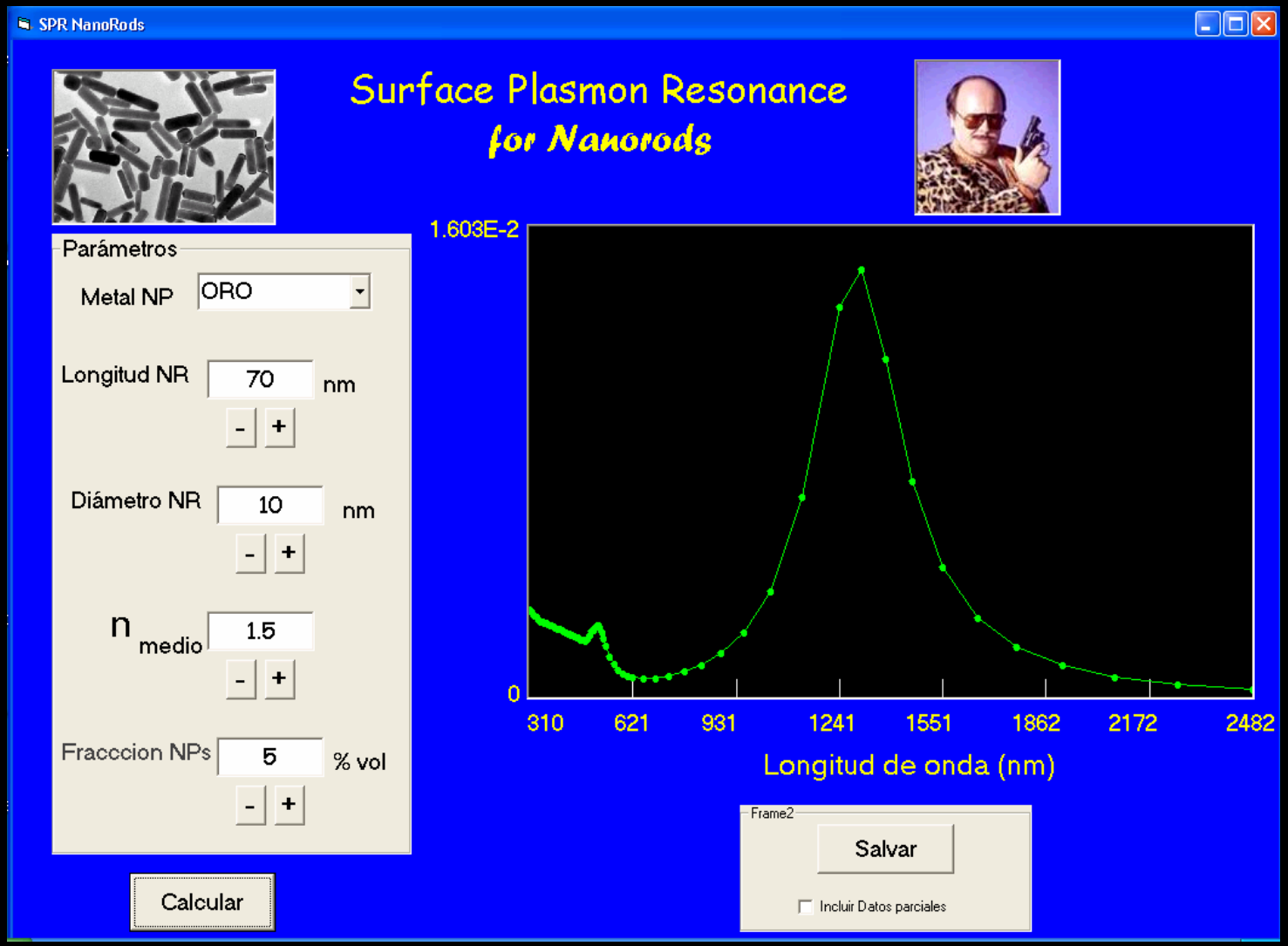
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Calculation of SPR Spectra



M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

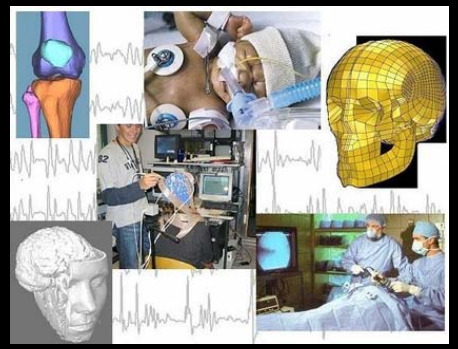
Calculation of SPR Spectra



M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Applications

Biomedicine

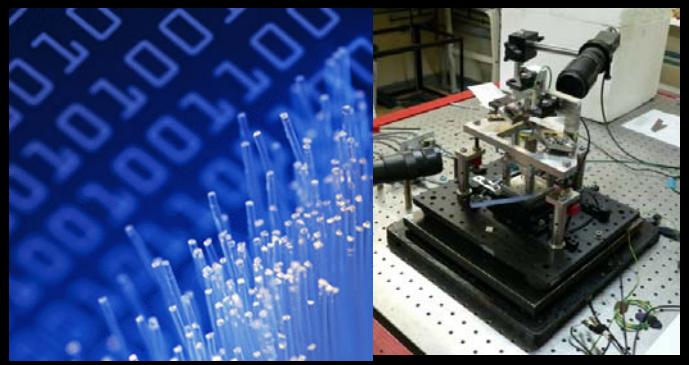


Energy

Environment

Technology of Information

Scientific Instrumentation



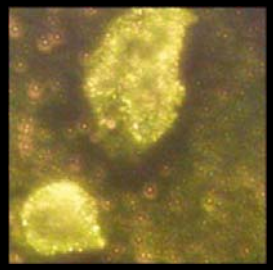
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Aplications in biomedicine

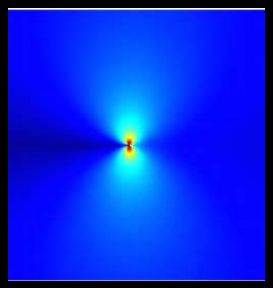
Strategy

✓Functionalization

✓Place the nanoparticles at targets

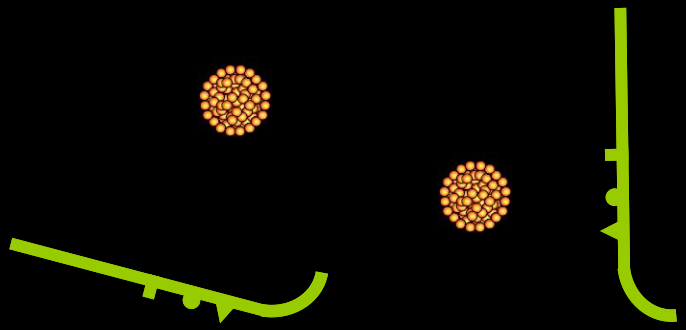


✓Excite SPR
- ✓Detection (optical)
- ✓Heating



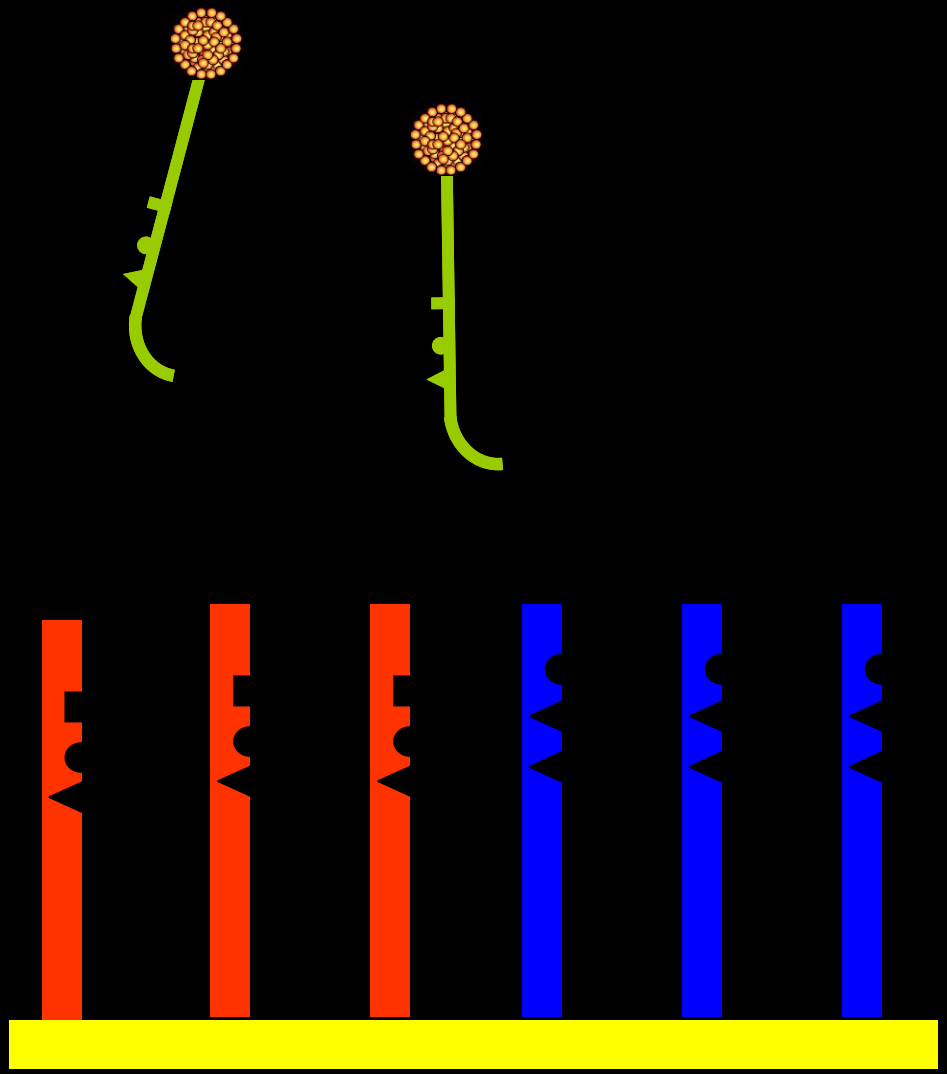
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

DNA sequencing



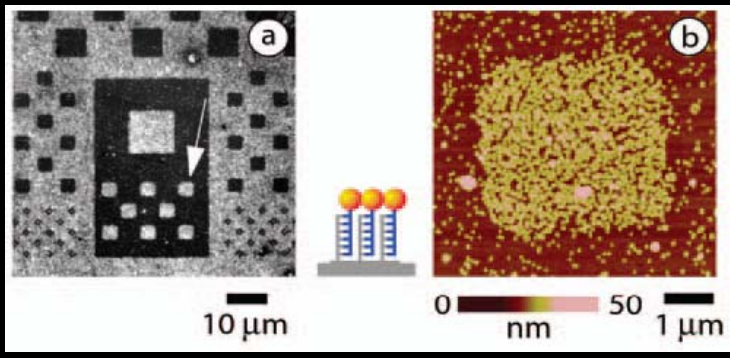
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

DNA sequencing

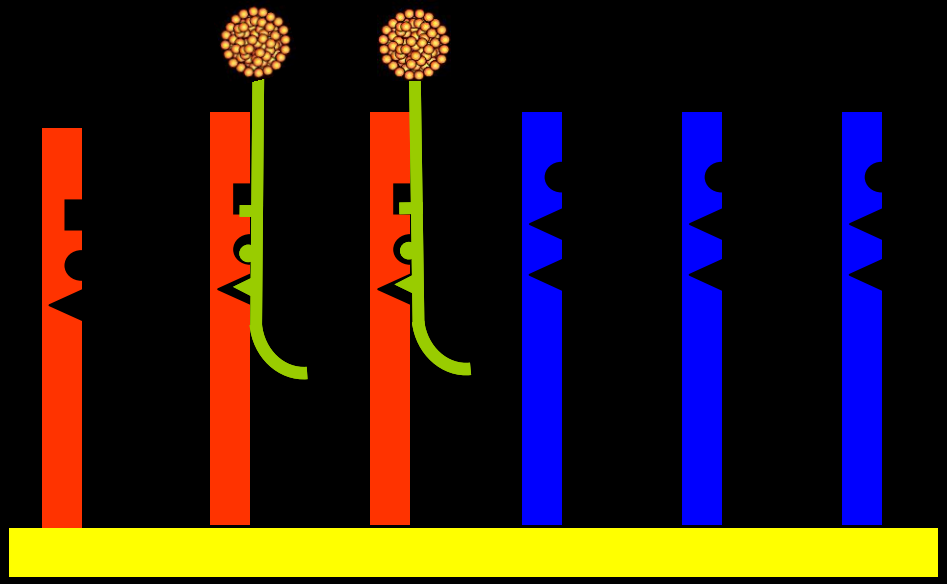


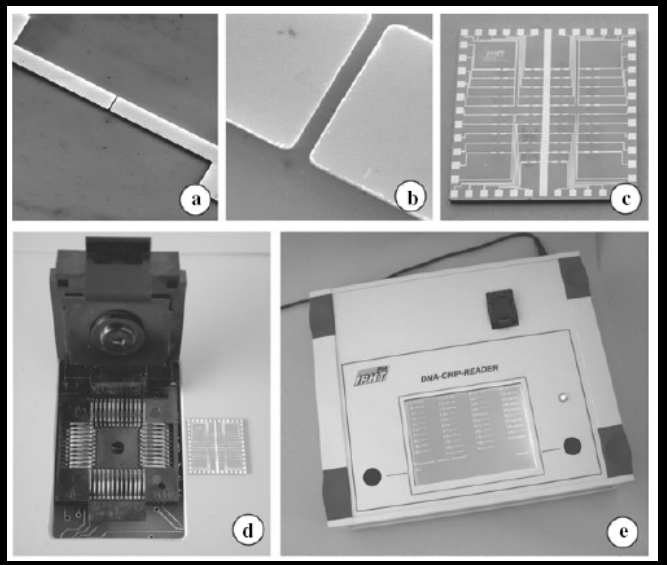
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

DNA sequencing



1.A. Csáki, G. M., D. Born, J. Reichert and W. Fritzsche *Single Mol.* 3, 275 (2002).





W. Fritzsche & T. A. Taton *Nanotechn.* 14 (2003) R63

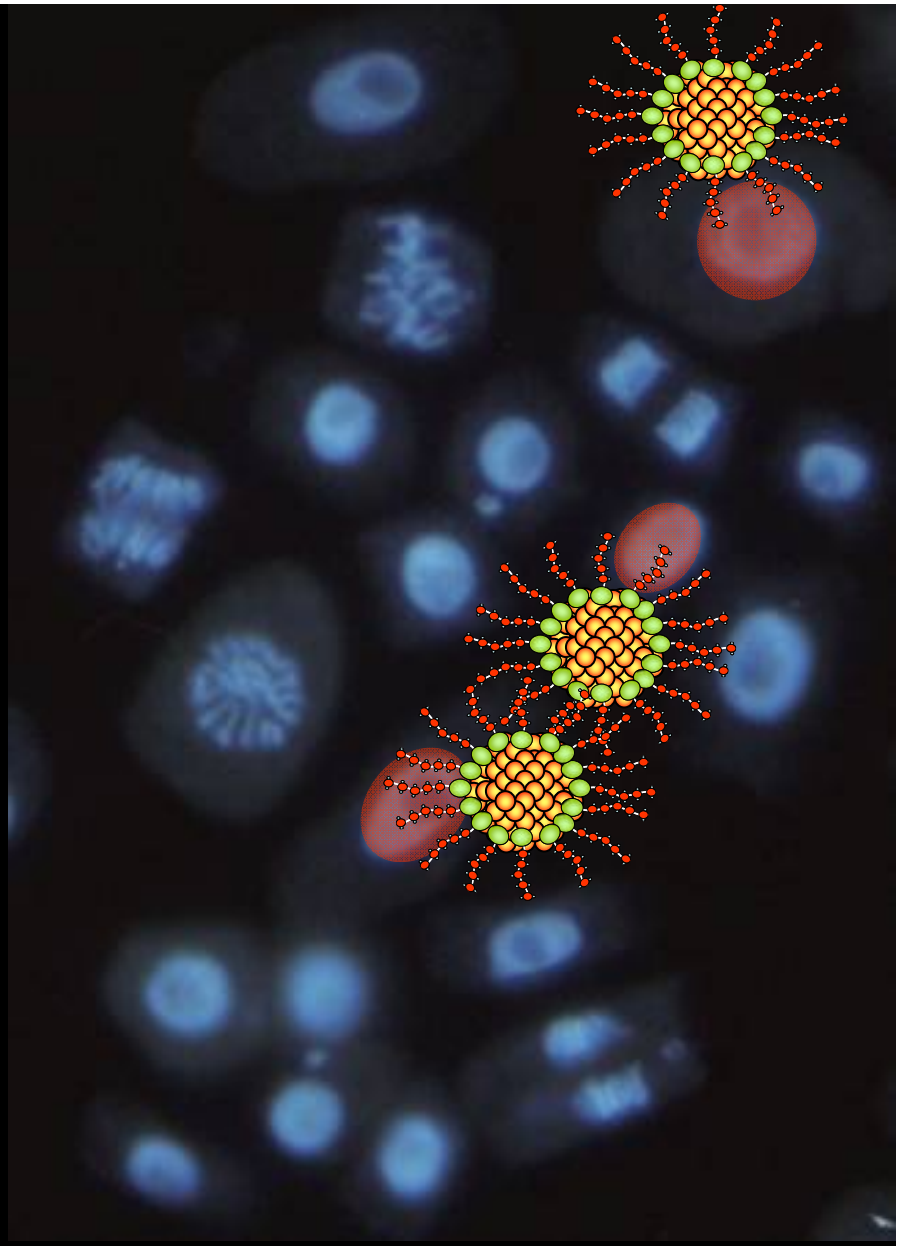
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Cell labelling

- Functionalization of the NPs with receptor of specific groups

- ✓The NPs will bind preferentially clls with certain features

- ✓The cells results labelled and can be identified with optical microscopy

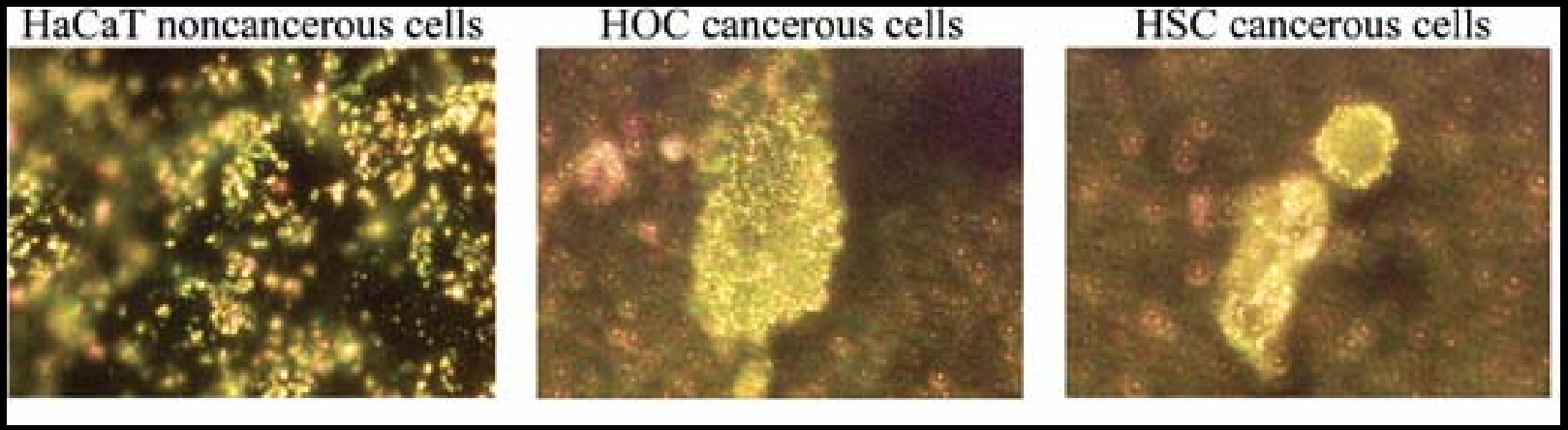


M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Cell labelling

Cancerous cells has overexpressed the epidermal growth factor (EGF)

Au NPs functionalized with the receptor of the EGF will bind preferentially cancerous cells



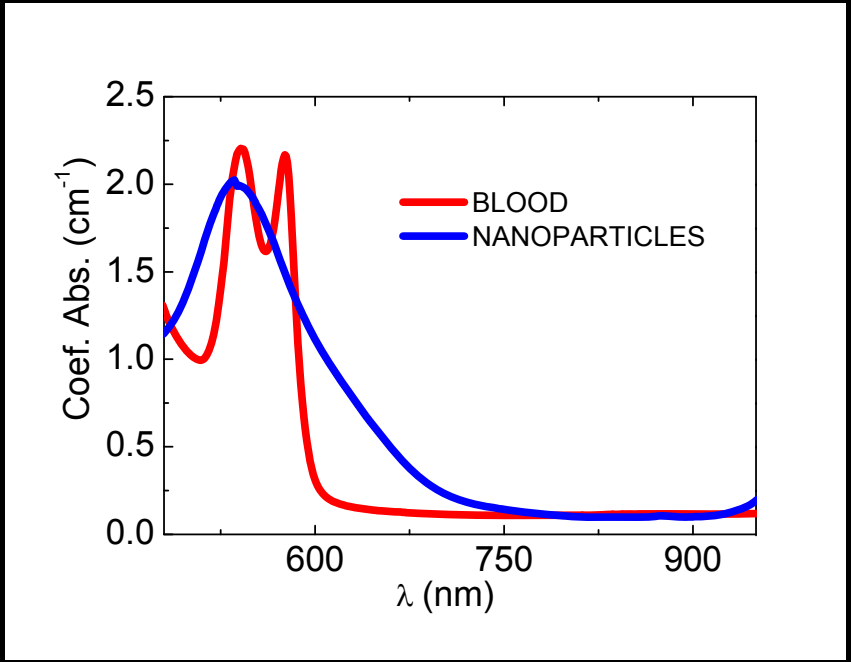
I. H. El-Sayed, X. Huang and M. A. El-Sayed, *Nano Letters* 5, 829 (2005).

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Biomedical Applications of SPR

In vivo applications

Au NPs absorption matches that of the human blood (hemoglobin)



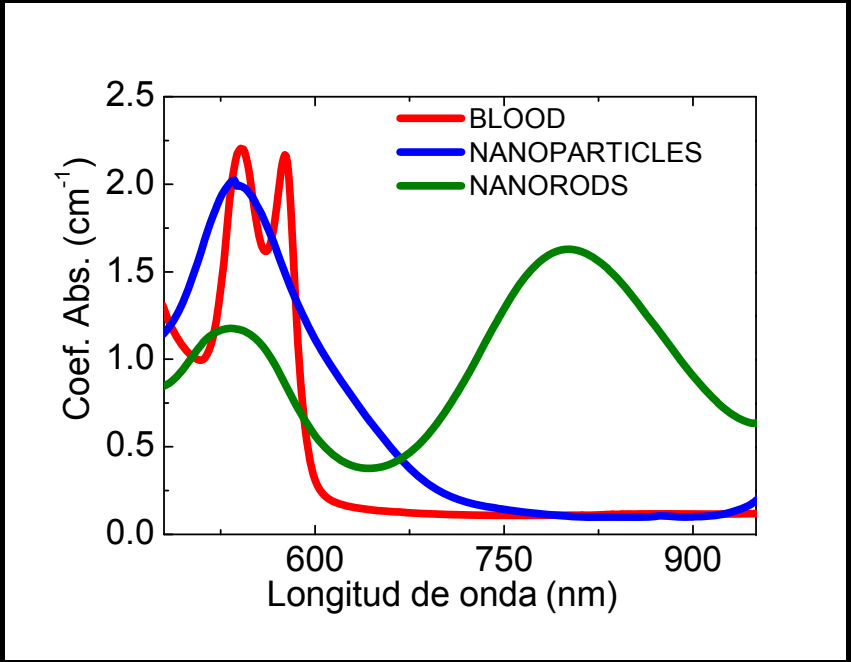
Limitation for *in vivo* applications

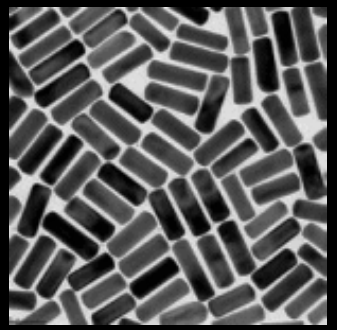
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Biomedical Applications of SPR

In vivo applications

Solution: Use of nanorods





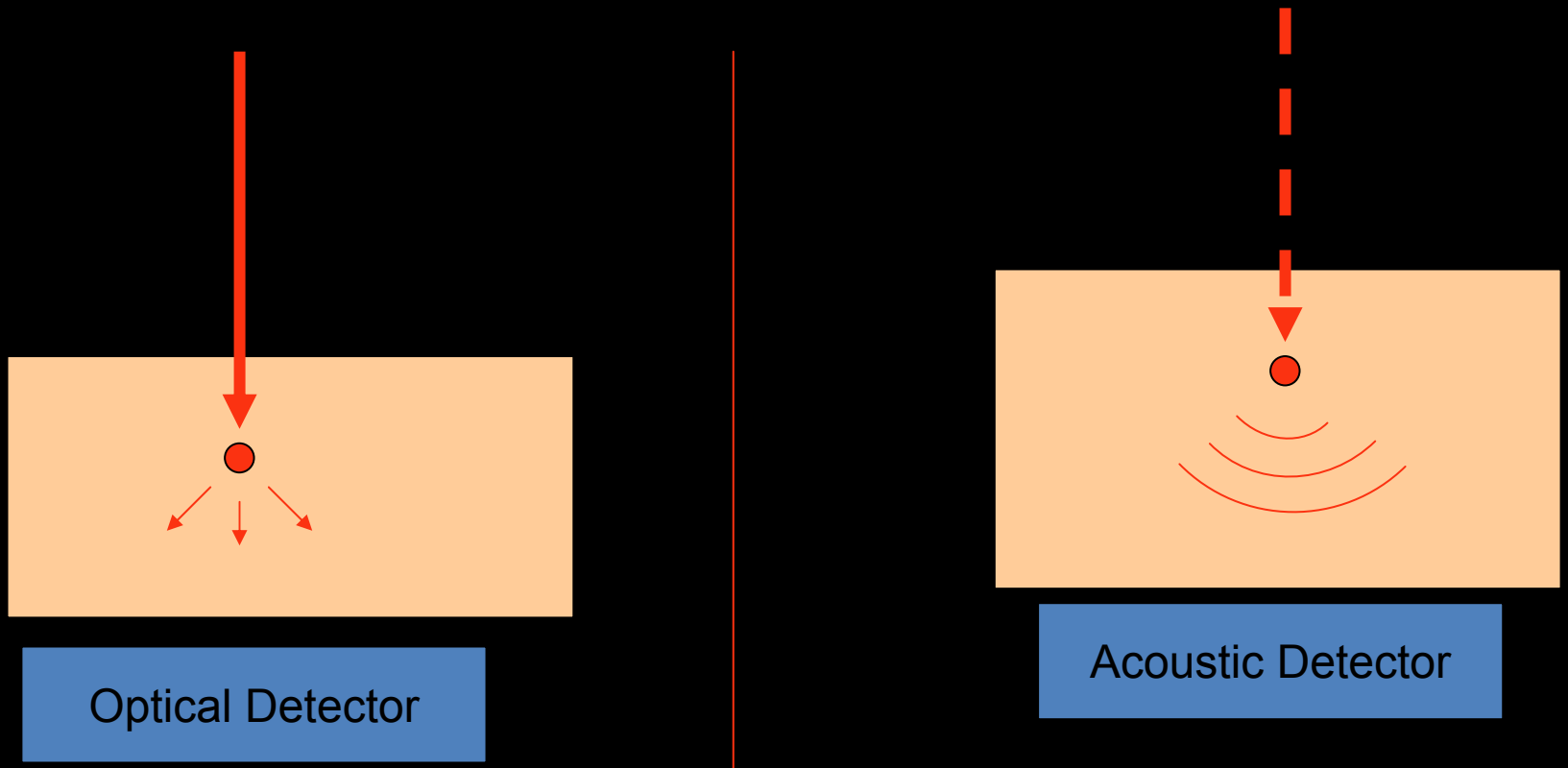
MAG, V. Bouzas, N.Carmona, *Mater. Chem. Phys.*, 127 (2011) 446

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Biomedical Applications of SPR

In vivo applications

In vivo SPR imaging is complicated (Scattering)

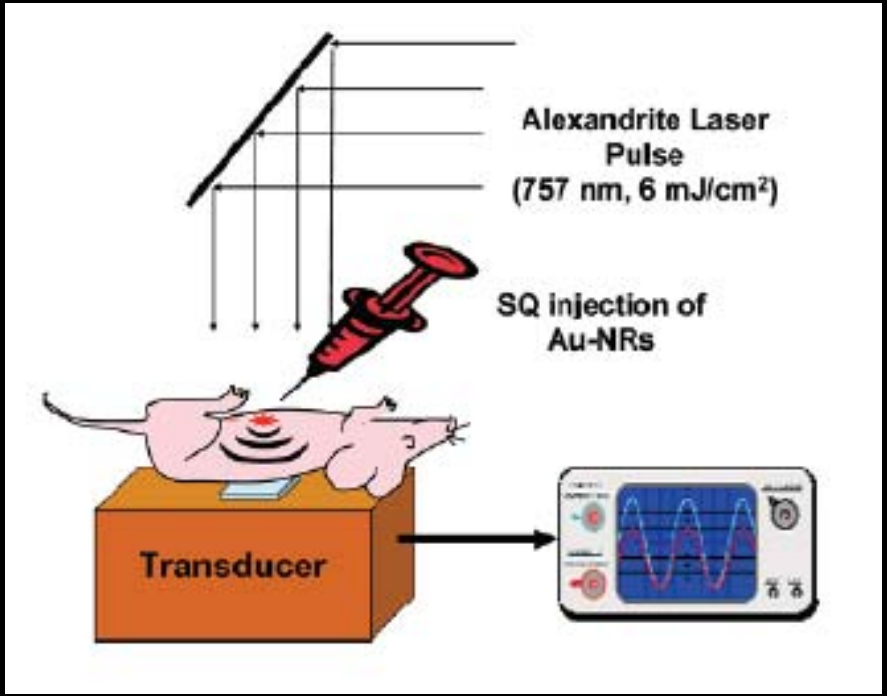


M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Biomedical Applications of SPR

In vivo Applications

Photoacustic imaging



M. Eghtedari, A. Oraevsky, J. A. Copland, N. A. Kotov, A. Conjusteau and M. Motamedi
Nano Letters, 7, 1914 (2007).

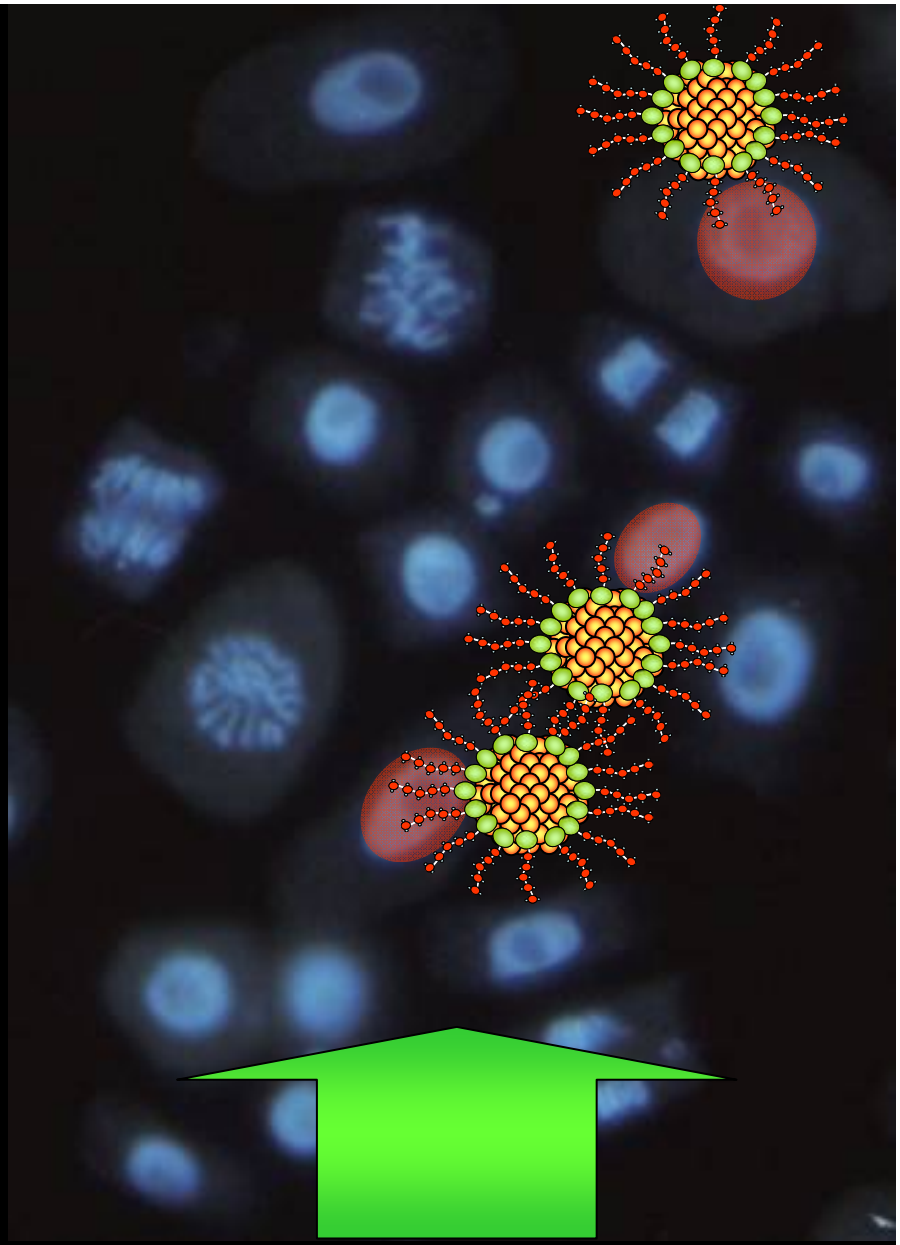
Biomedical Applications of SPR

- Hyperthermia & Thermolisis

✓Excitation of SPR induce a local heating of the NPs

✓"Temperature" locally increases

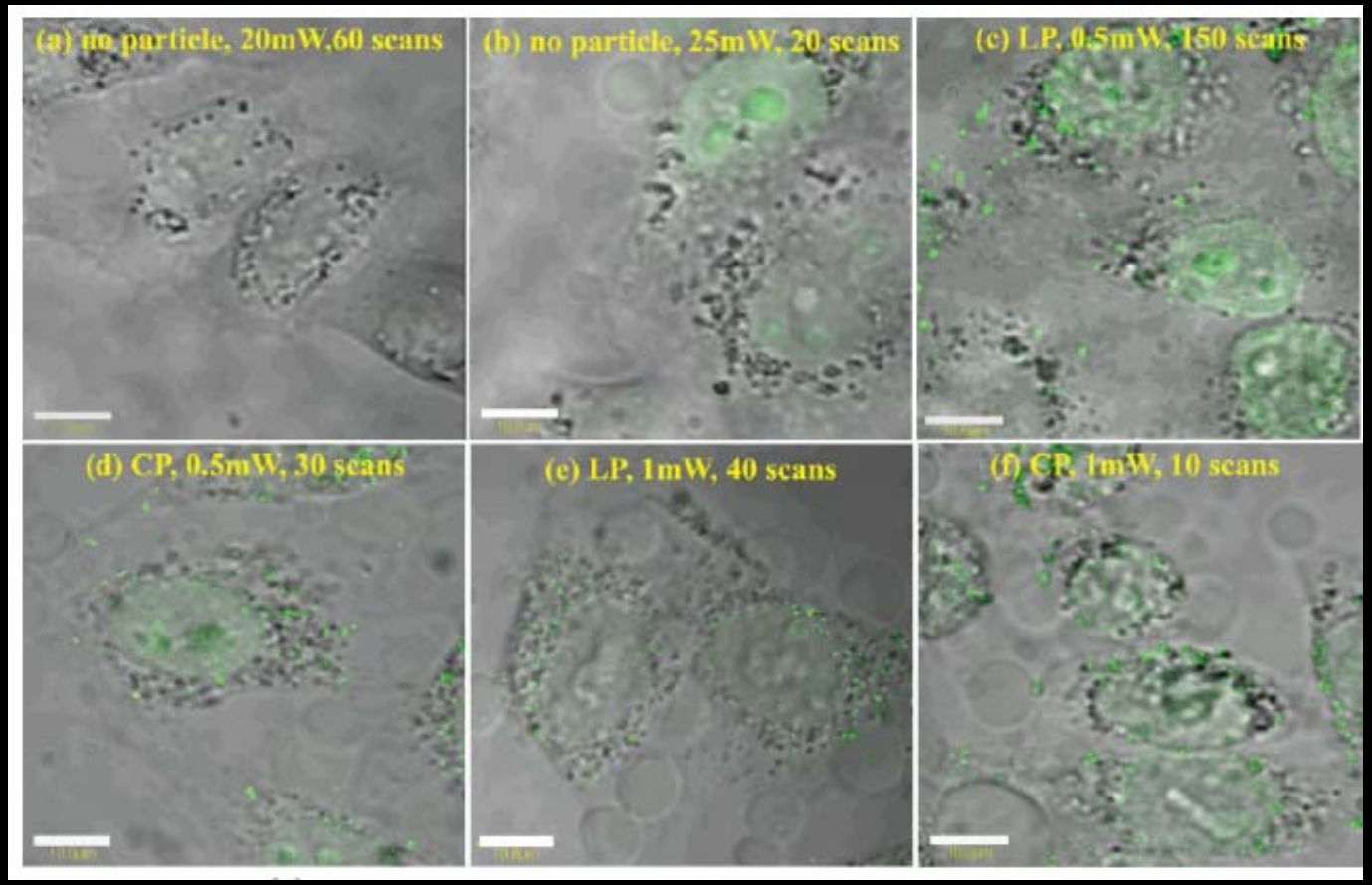
✓Selective cells elmination



M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Biomedical Applications of SPR

Thermolisis of cell membrane

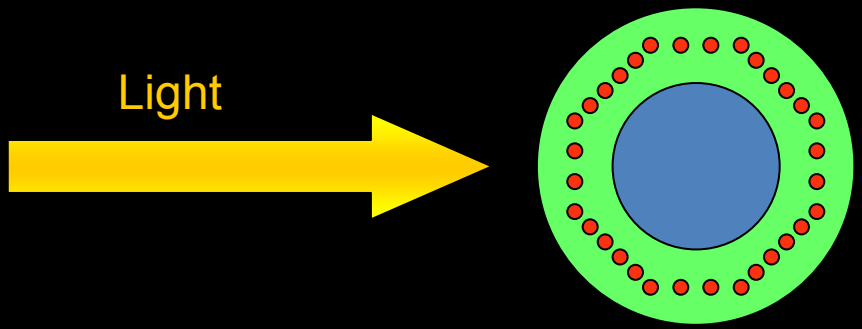


J. L Li, D. Day & M. Gu *Adv. Mat* 20 (2008) 3866

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Biomedical Applications of SPR

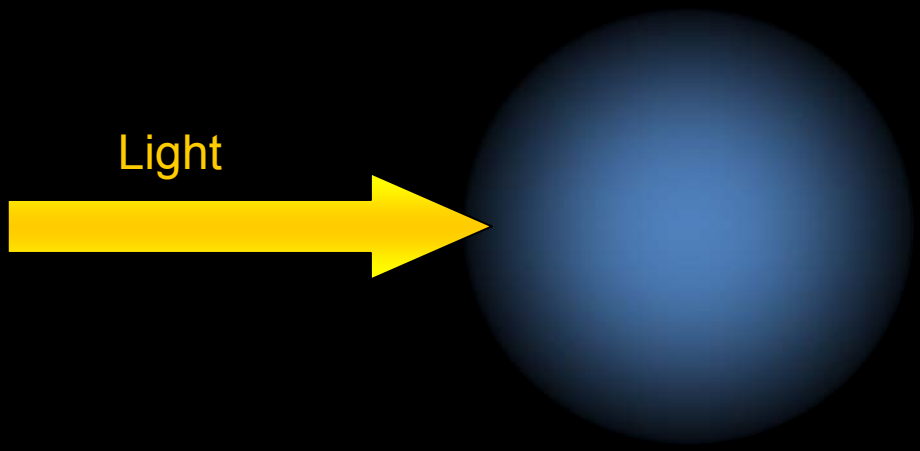
Drug Release



M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Biomedical Applications of SPR

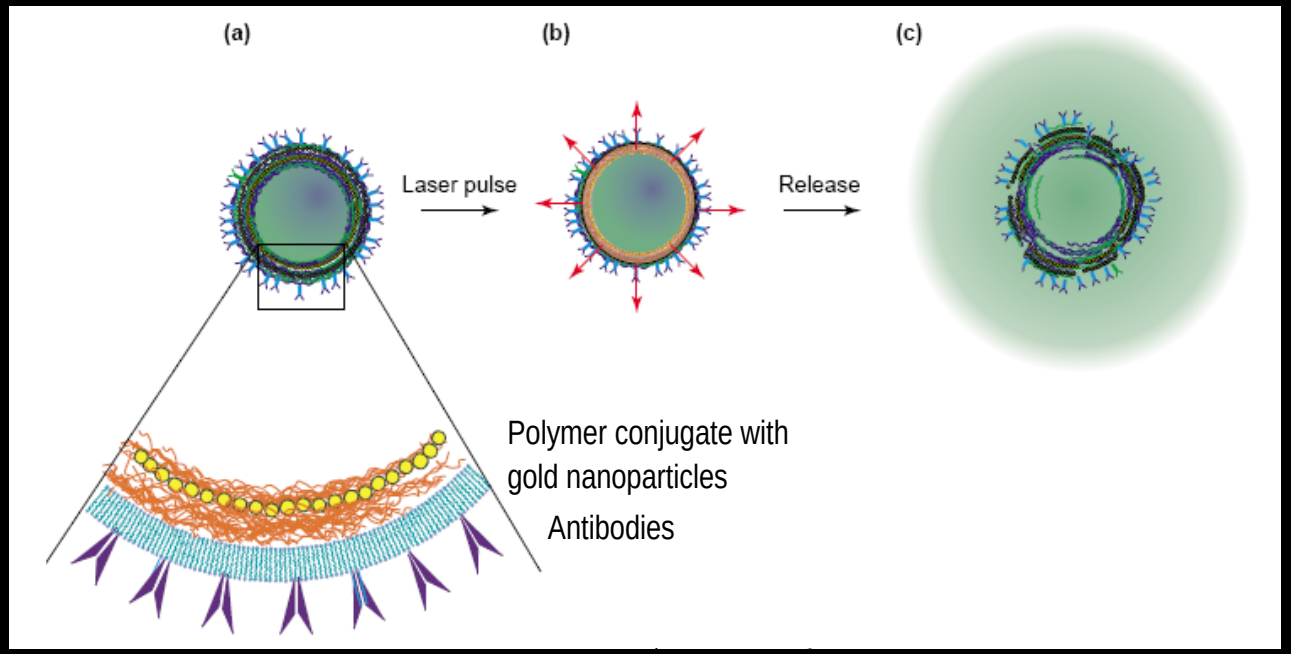
Drug Release



M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Biomedical Applications of SPR

Drug Release

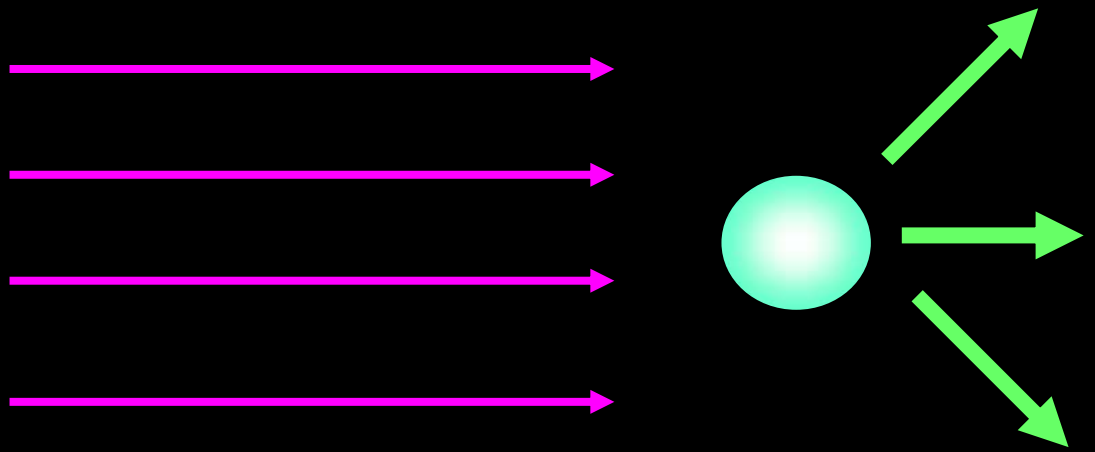


D. Pissuwan, S. M. Valenzuela and M. B. Cortie *TRENDS in Biotechnology* 24, 62 (2006).

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Biomedical Applications of SPR

Enhancement of Photoluminescence

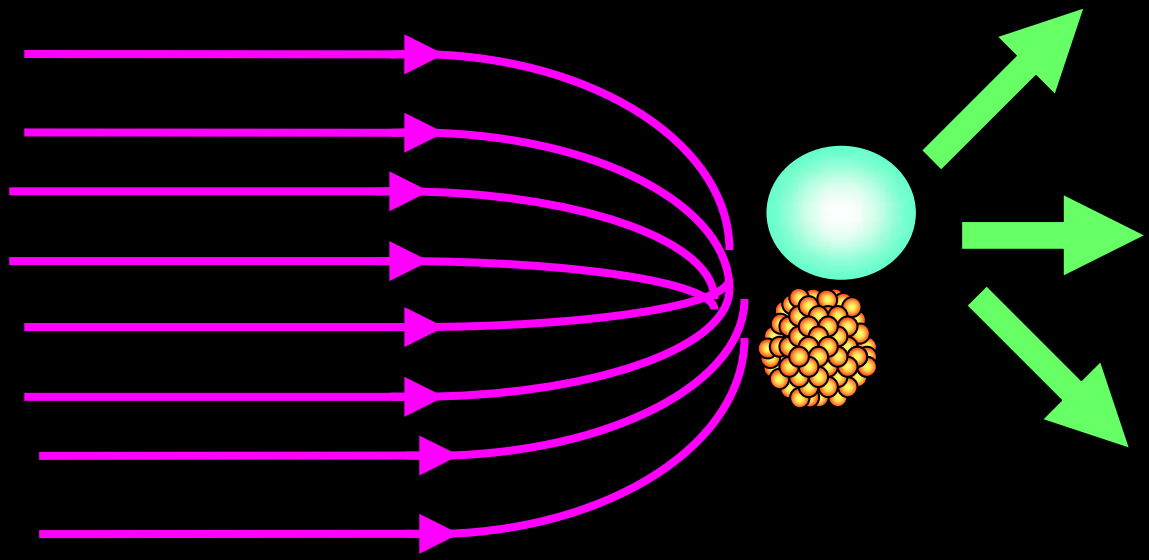


PL intensity is limited by the absorption cross section of the PL center

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Biomedical Applications of SPR

Enhancement of Photoluminescence

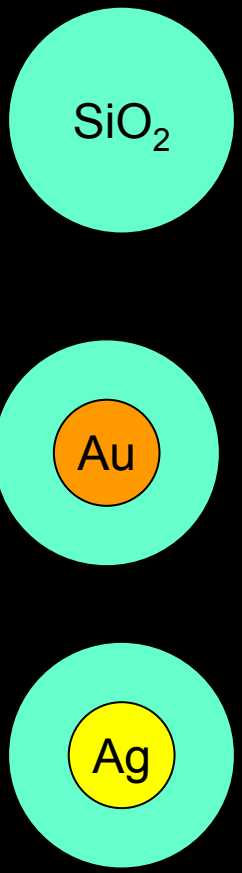


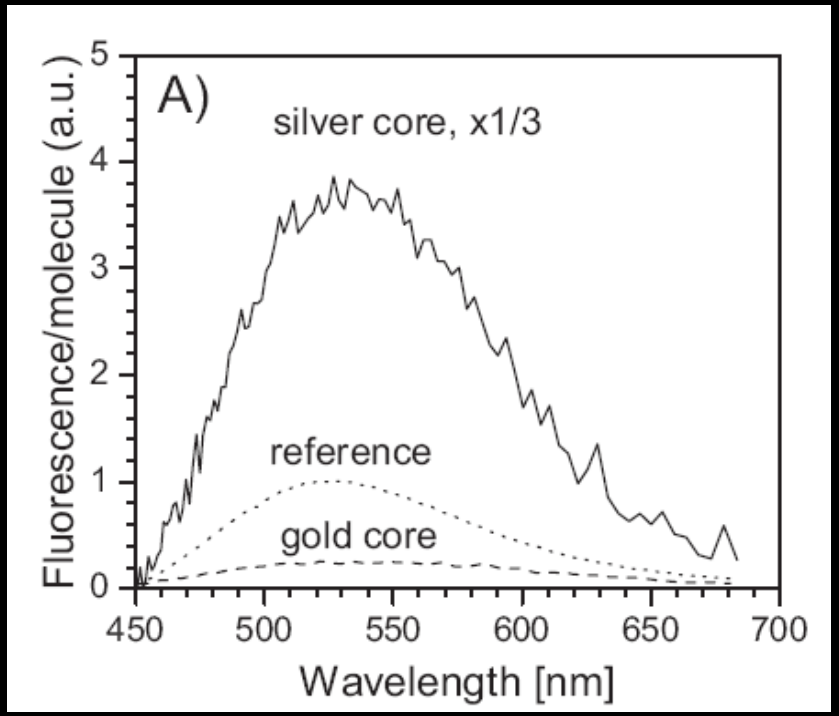
PL intensity extremely sensitive to distances

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Biomedical Applications of SPR

Enhancement of Photoluminescence



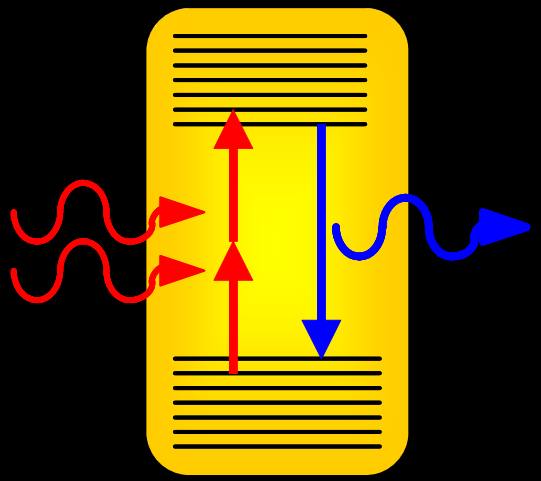


O. G.Tovmachenkoet al ,*Adv. Mat* **18** (2006) 91

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

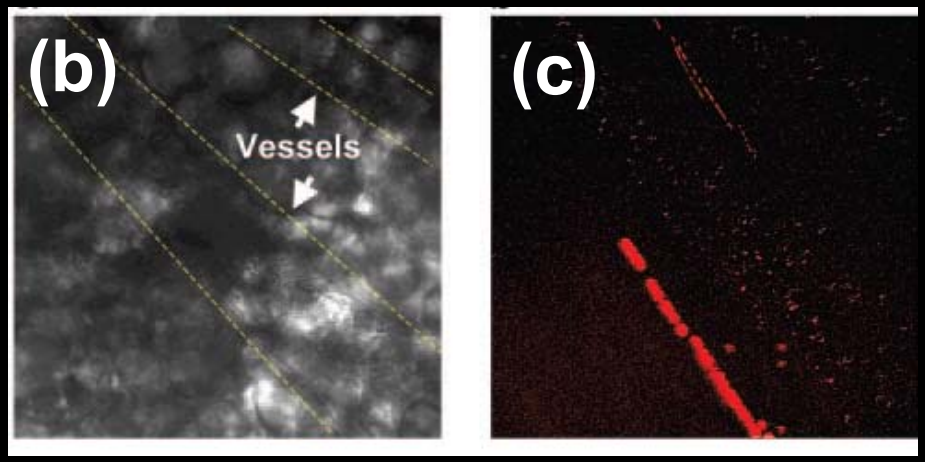
Biomedical Applications of SPR

Two photon Luminescence



Requires very large intensities & absorption coefficients at IR

Possible with Au nanorods



H. Wang et al, *Proc. Nat.Acad. Sci* 105 (2005) 15752

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Conclusions

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

"Physics is like sex: sure, it may give some practical results, but that's not why we do it. ".

Richard P. Feynman

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

Many thanks to…

José Llopis (UCM) PhD Supervisor

José Mª Fernández Navarro (ICV / FCNV / IFQ- RS)

Mª Angeles Villegas (ICV / CENIM /CCHS)

Paolo Mazzoldi (INFM- Padova)

Elisabetta Borsella (INFM Padova / ENEA)

Cesar de Julian (INFM-Padova /U. Florencia)

Istituto Nazionale per la Fisica della Materia
Consiglio Nazionale delle Ricerche

Antonio Hernando (IMA –UCM)

José de la Venta (UCM / ICV/ UCSD)

Enrique Fernandez Pinel (IMA-UCM)

Soledad Penadés (CSIC/Biomagune)

Instituto de **M**agnetismo **A**plicado
Laboratorio "Salvador Velayos"
U C M- ADIF

Noemi Carmona (FCNV / UCM)

Virginia Bouzas (UCM)

Oscar Rodríguez de la Fuente (UCM)

Aida Serrano (UCM/ICV)

Daniel Haskel (APS-ANL)

German Castro (Spline - ESRF)

…And more recently….

A.Lopez Cortajarena (IMDEA)

I. K .Schuller (UCSD)

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

...and thanks for the money....

EU 6th FP- Proyecto BONSAI

http://www.bonsai-project.eu

Proyecto FIS-2008-469

Project 200960I005

.....and user programs of:

Argonne NATIONAL LABORATORY

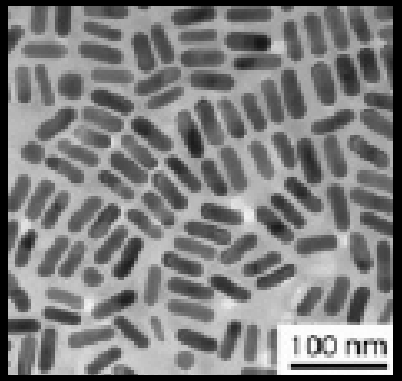
APS + IPNS

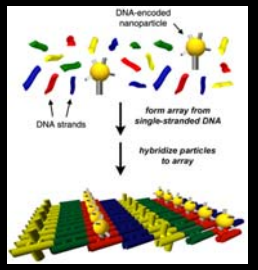
MAGNIFYCO

MAGNETIC NANOCONTAINERS FOR COMBINED HYPERTHERMIA AND CONTROLLED DRUG RELEASE

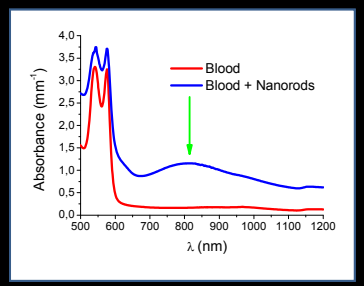
SEVENTH FRAMEWORK PROGRAMME - THEME 4 – NMP
Nanosciences, Nanotechnologies, Materials and new Production Technologies

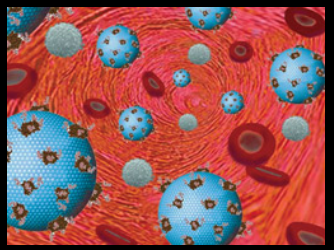
M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience

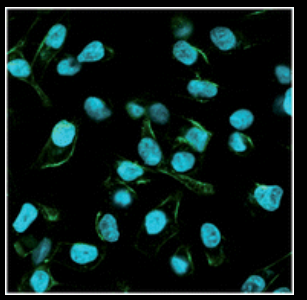




Thanks for your attention !!







INTERNATIONAL SUMMER SCHOOL ON FLUORESCENT NANO-PARTICLES IN BIO-MEDICINE
Madrid, July 2012

M. A. García
Institute for Ceramic and Glass, CSIC
& IMDEA NAnoscience