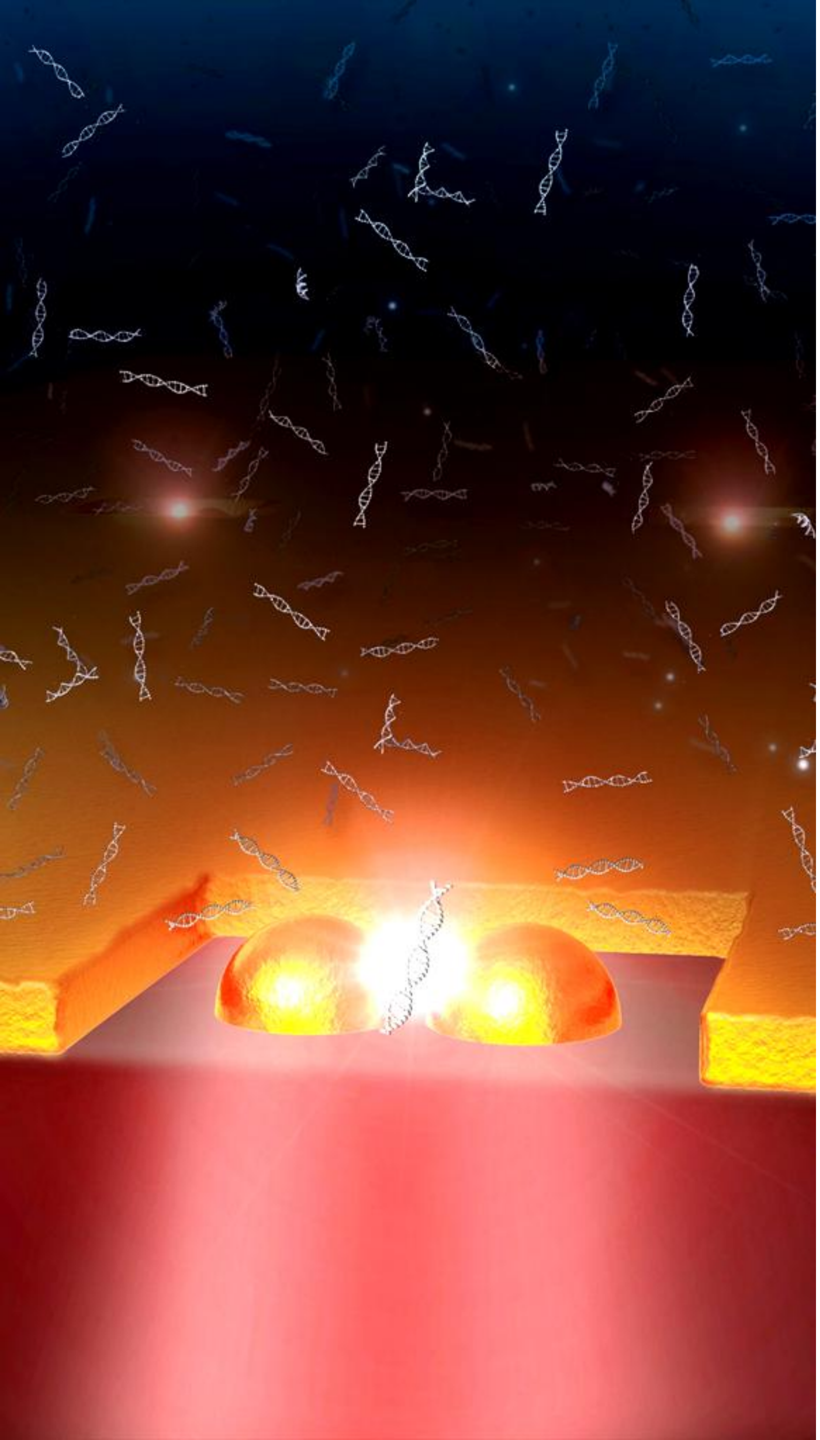


Concentrating Light at the Nanoscale: Plasmonics and Nano-Optics

Jérôme Wenger

INSTITUT FRESNEL
MARSEILLE

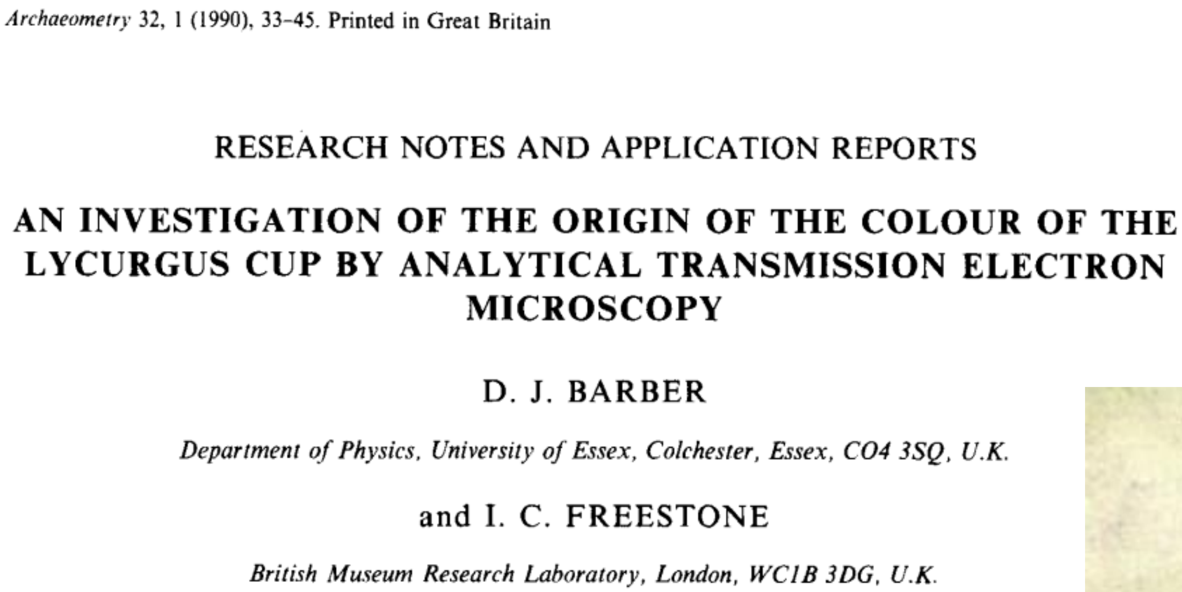
The Lycurgus cup (The British Museum) 4th century AD

➔ *Reflected light*

The Lycurgus cup (The British Museum) 4th century AD

➔ *Transmitted light*

The Lycurgus cup under the electron microscope



Archaeometry 32, 1 (1990), 33–45. Printed in Great Britain

RESEARCH NOTES AND APPLICATION REPORTS

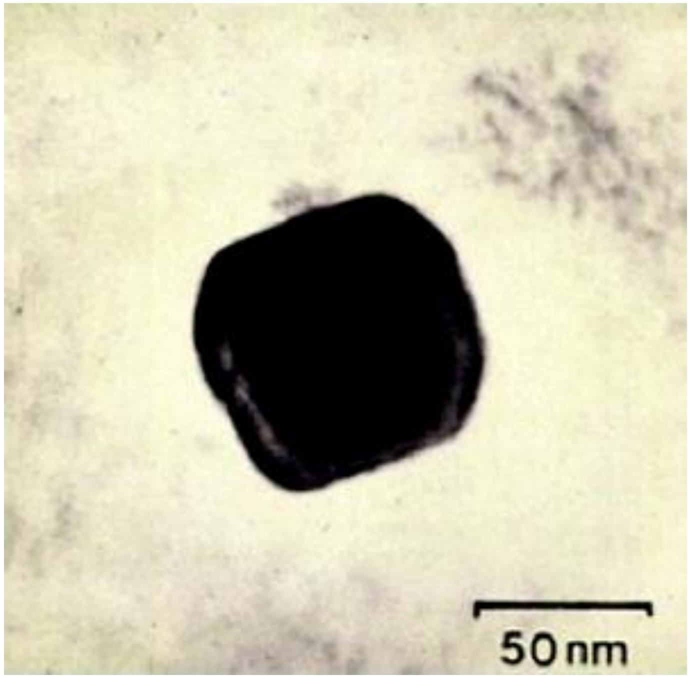
AN INVESTIGATION OF THE ORIGIN OF THE COLOUR OF THE LYCURGUS CUP BY ANALYTICAL TRANSMISSION ELECTRON MICROSCOPY

D. J. BARBER

Department of Physics, University of Essex, Colchester, Essex, CO4 3SQ, U.K.

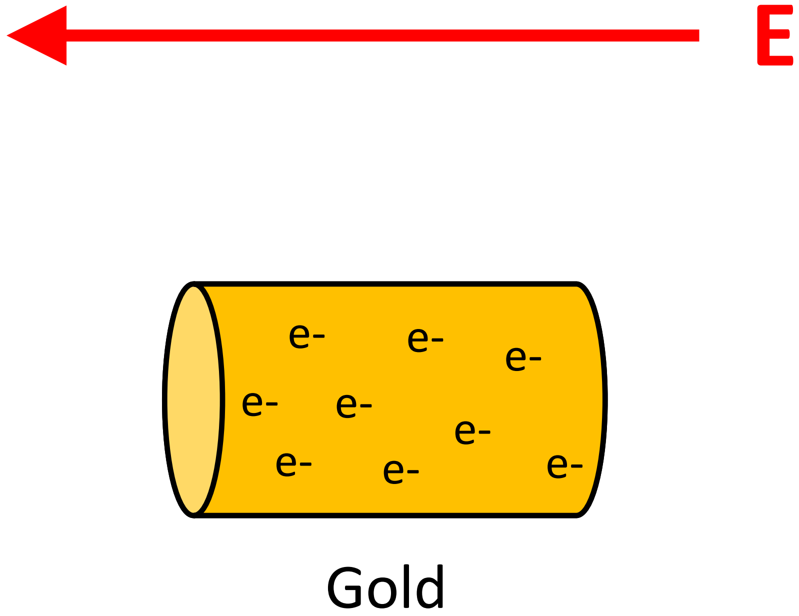
and I. C. FREESTONE

British Museum Research Laboratory, London, WC1B 3DG, U.K.

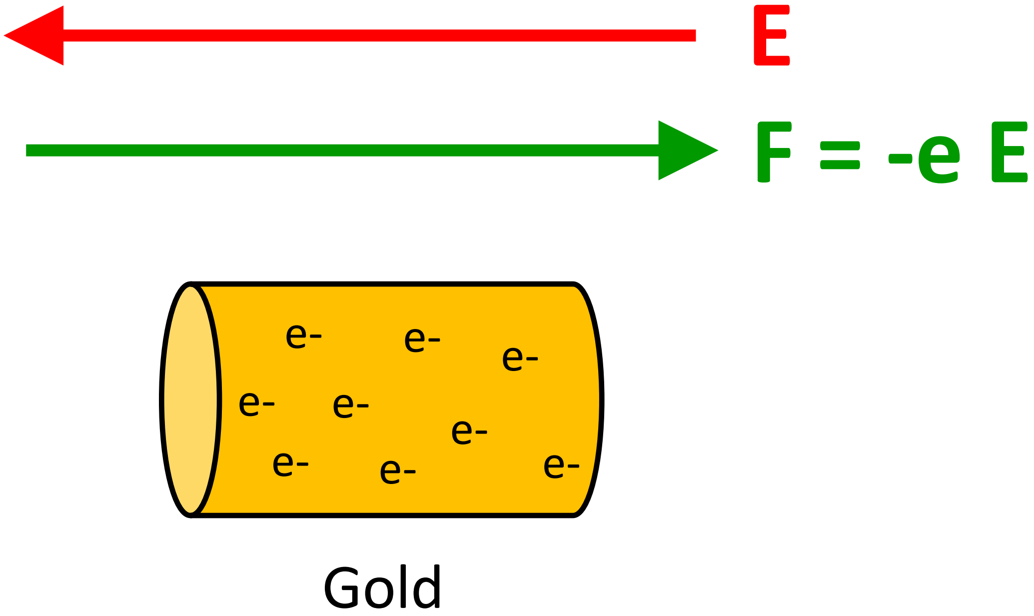


70nm alloy $Ag_{0.7}/Au_{0.3}$ nanoparticles

Free electrons (plasma) oscillations in a nanoparticle



Free electrons (plasma) oscillations in a nanoparticle

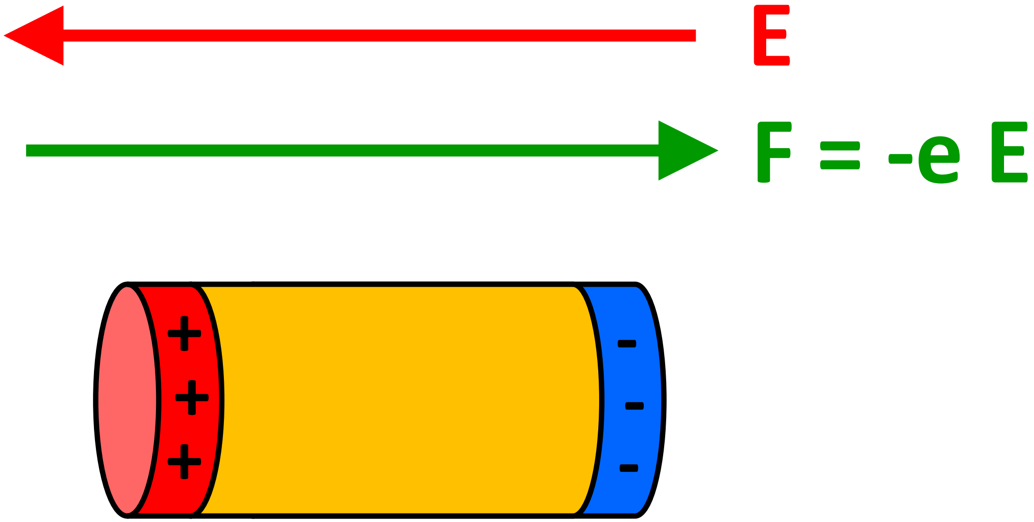


E

$F = -e E$

Gold

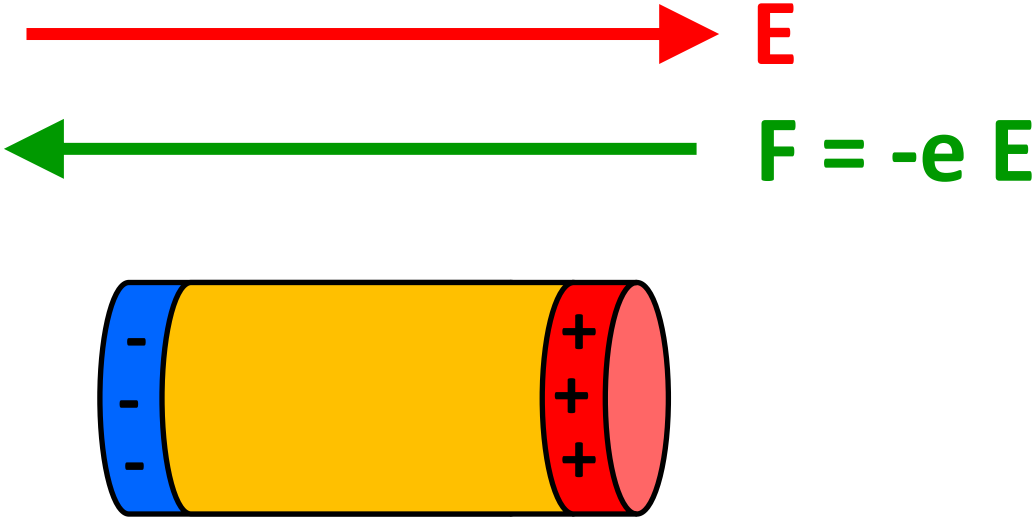
Free electrons (plasma) oscillations in a nanoparticle



E

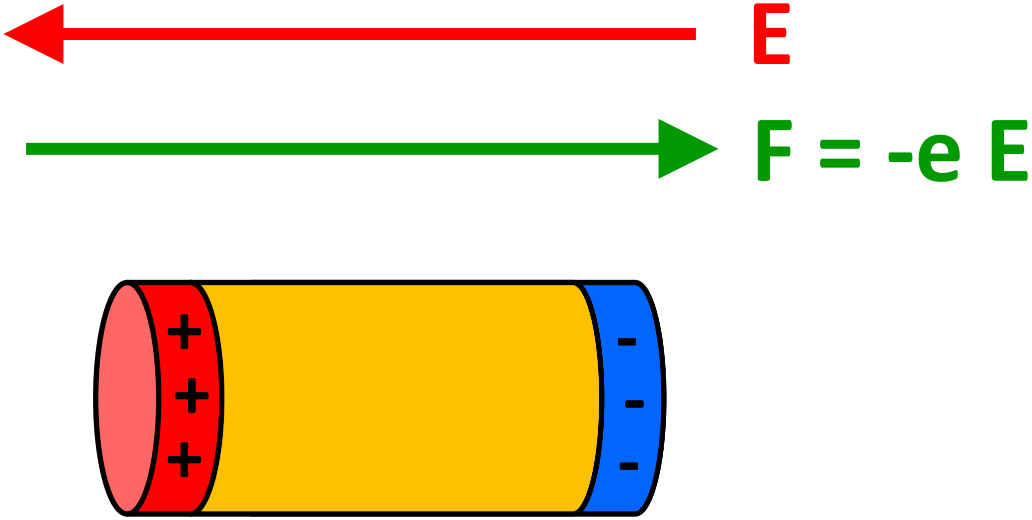
$F = -e E$

Free electrons (plasma) oscillations in a nanoparticle



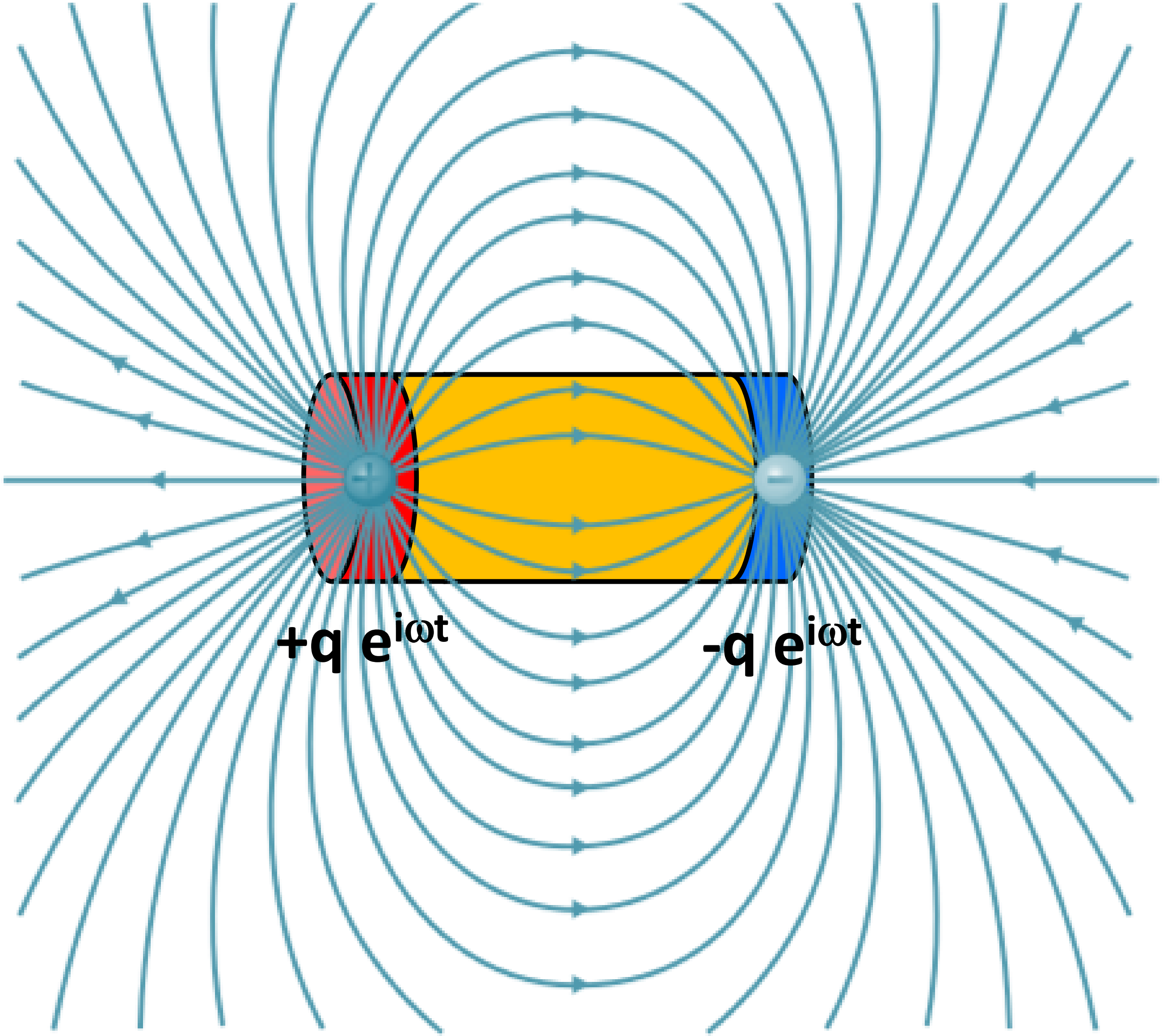
Half a period later....

Free electrons (plasma) oscillations in a nanoparticle

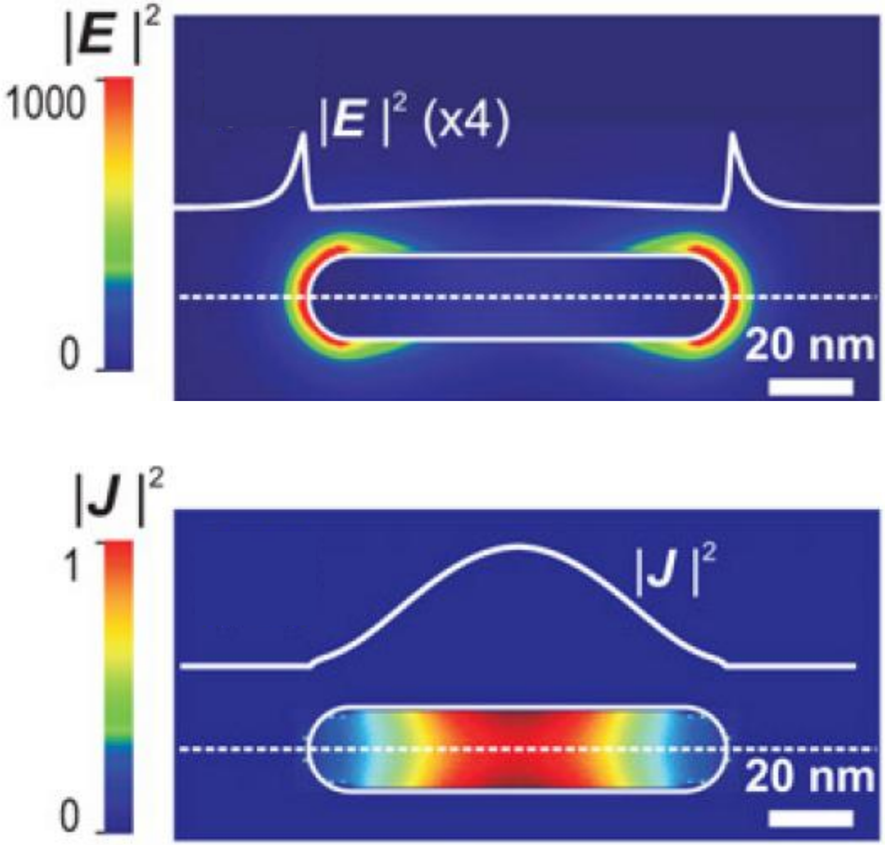


Another half a period later….

Oscillating charges in a nanoparticle at optical frequency



Oscillating charges in a nanoparticle at optical frequency



Intense fields

Nanoscale localization

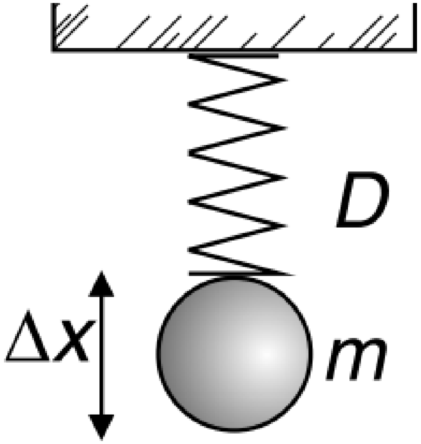
Coupling with light

Ohmic dissipation

Biagoni, Rep. Prog. Phys. 75 (2012) 024402

Oscillating charges in a nanoparticle at optical frequency

Spring & mass model



Resonance frequency

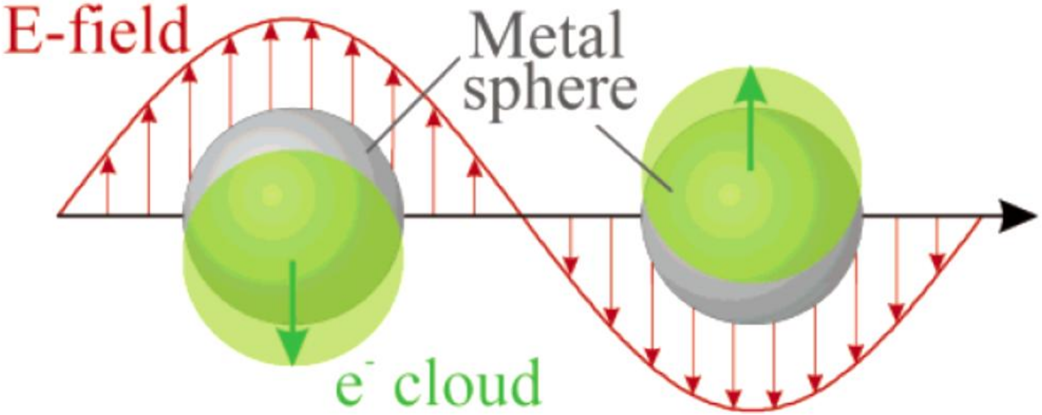
$$\omega_{\text{res}} = \frac{\omega_{\text{p}}}{2\sqrt{2}}\frac{1}{R}$$

→ Red-shift when aspect ratio *R* increases

→ There is always a resonance below ω_p for any size

Biagoni, Rep. Prog. Phys. 75 (2012) 024402

Polarisability of a spherical nanoparticle

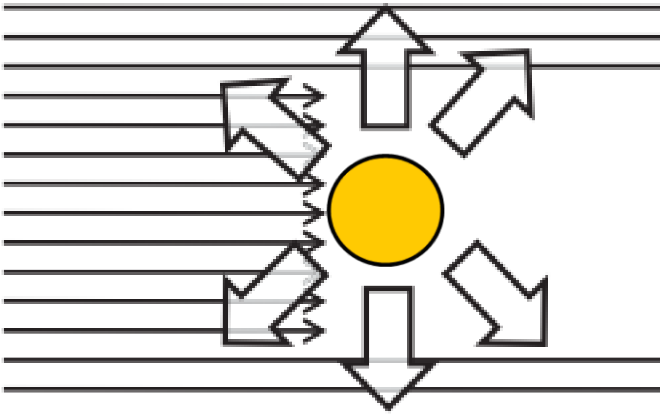


Schatz, JPCB 2003

For radius << λ, the quasi-static polarisability is

$$\alpha(\omega) = 4\pi\varepsilon_{ref}a^3 \frac{\varepsilon_{gold}(\omega) - \varepsilon_{ref}}{\varepsilon_{gold}(\omega) + 2\varepsilon_{ref}}$$

Polarisability of a spherical nanoparticle – Optical observables



Extinction = scattering + absorption

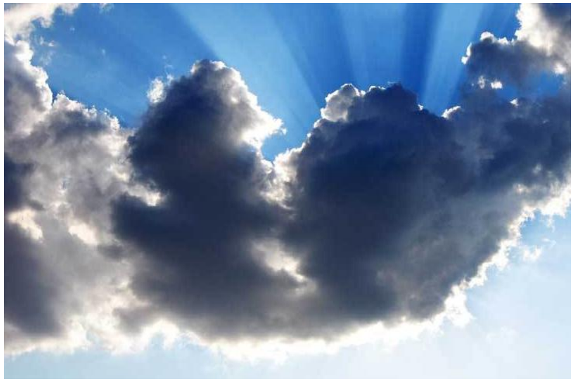
removed from the beam

Re-radiated into all angles

Lost as heat in the scatterer

Polarisability of a spherical nanoparticle – Optical observables

Absorption



$$\sigma_{\text{abs}} = \frac{k}{\varepsilon_0} \operatorname{Im}[\alpha(\omega)]$$

scales as d^3 / λ

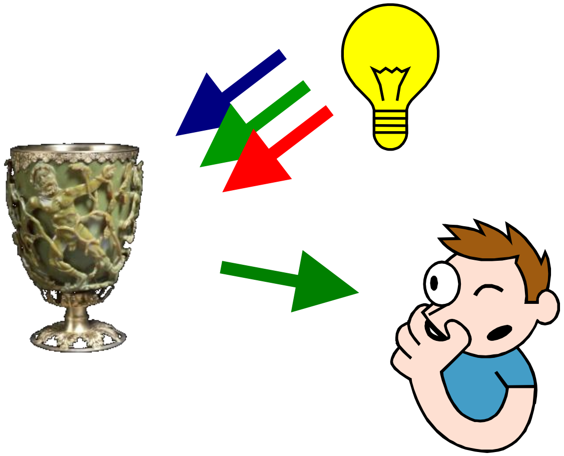
Scattering

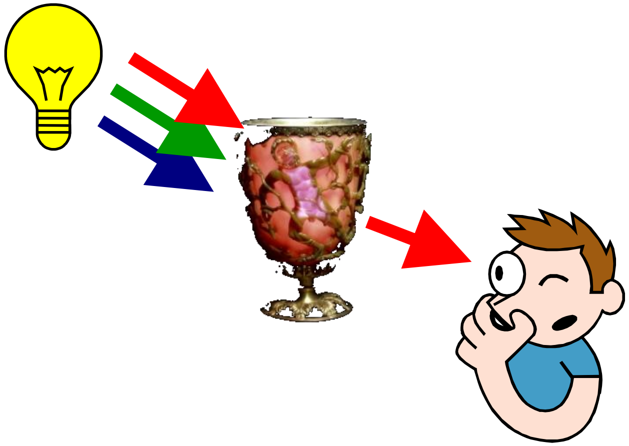
$$\sigma_{\text{scatt}} = \frac{k^4}{6\pi\varepsilon_0^2} |\alpha(\omega)|^2$$

scales as d^6 / λ^4

$$\alpha(\omega) = 4\pi\varepsilon_{ref} a^3 \frac{\varepsilon_{gold}(\omega) - \varepsilon_{ref}}{\varepsilon_{gold}(\omega) + 2\varepsilon_{ref}}$$

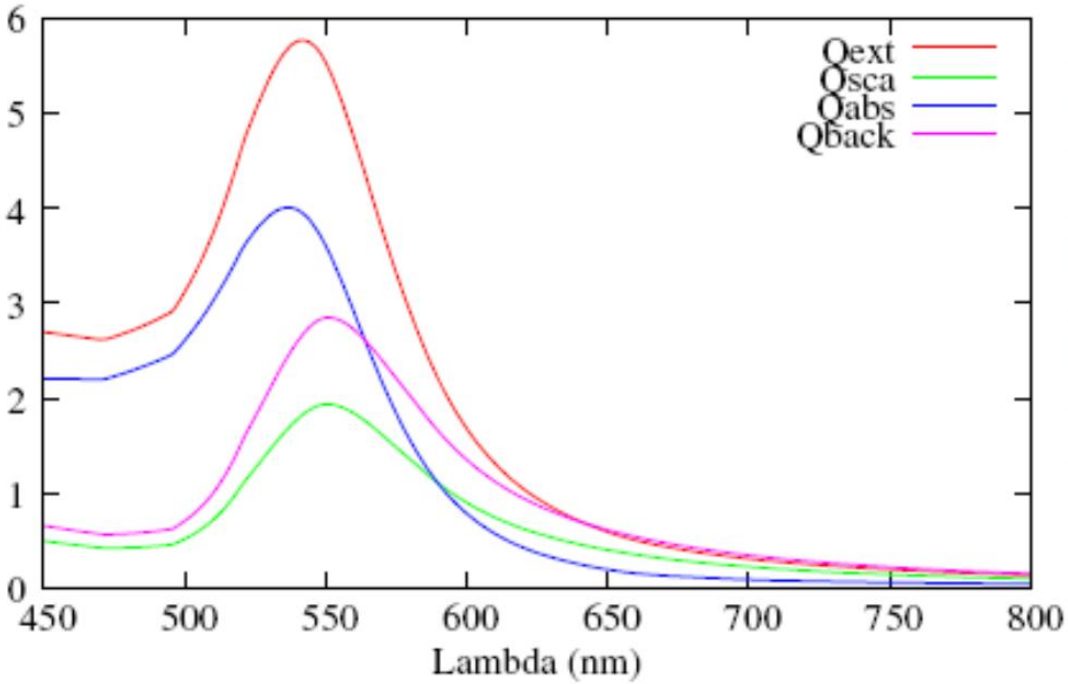
Back to Lycurgus cup





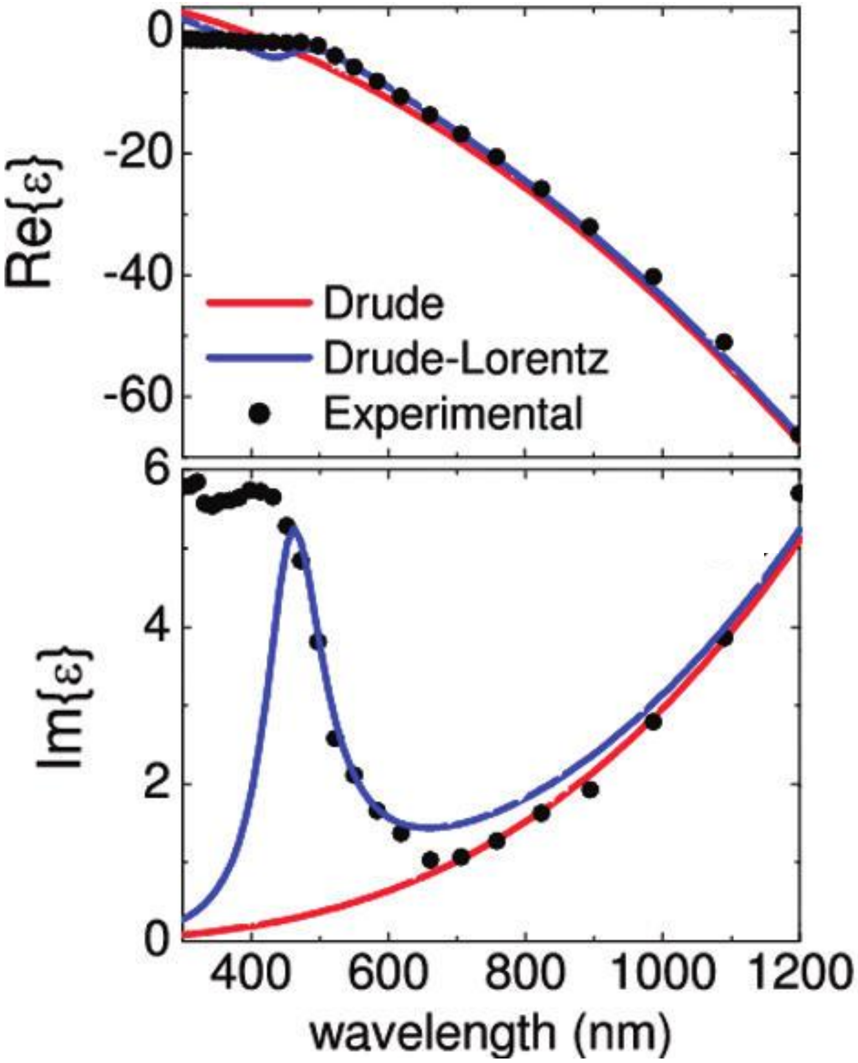
Absorption, Scattering and Extinction

of a 70nm gold sphere in glass



$$\alpha(\omega) = 4\pi\varepsilon_{ref}a^3 \frac{\varepsilon_{gold}(\omega) - \varepsilon_{ref}}{\varepsilon_{gold}(\omega) + 2\varepsilon_{ref}}$$

Optical properties of real metals

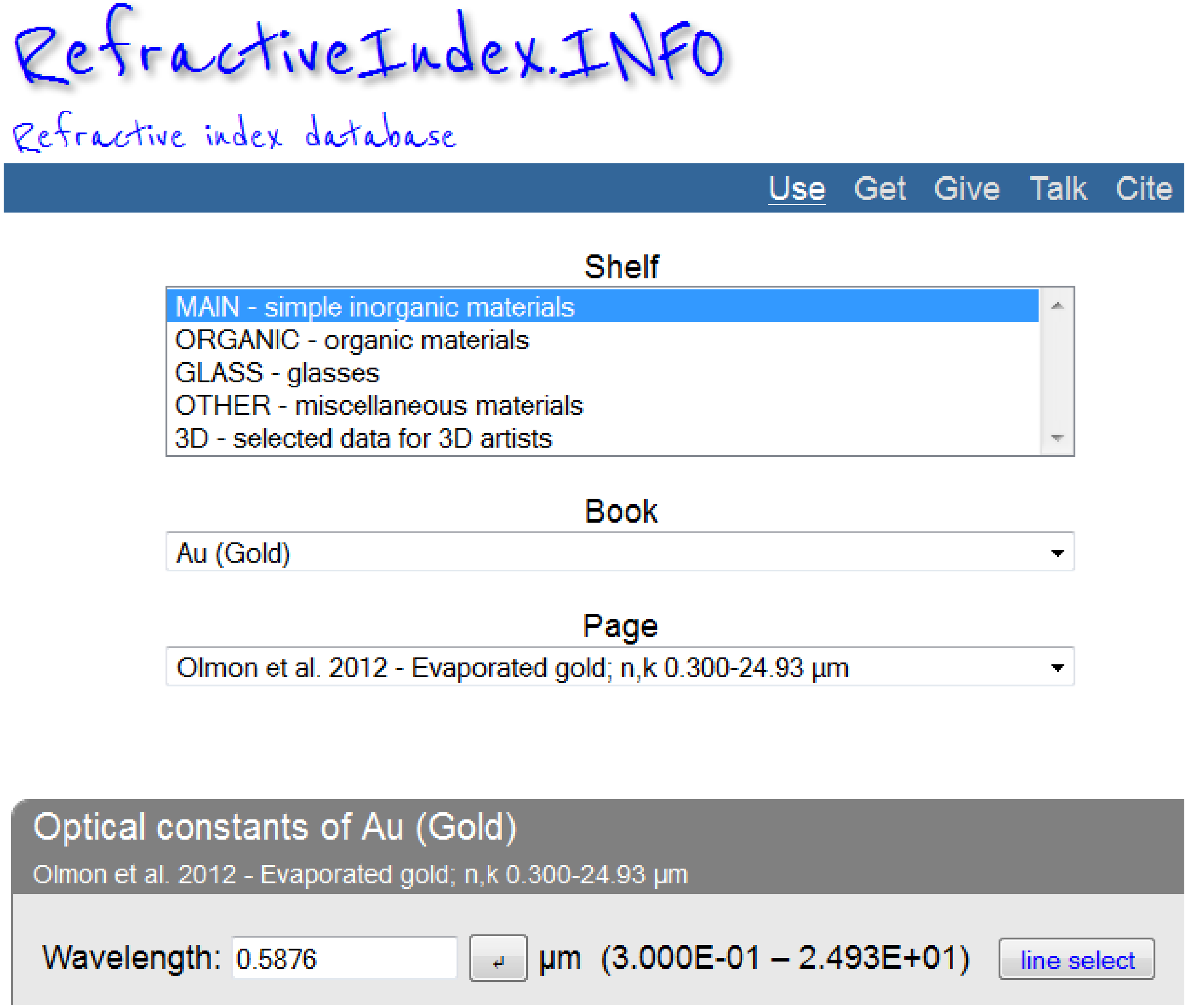


$$\varepsilon_{\mathrm{Drude}}(\omega) = 1 - \frac{\omega_{\mathrm{p}}^2}{\omega^2 + \mathrm{i}\gamma\omega}$$

$$\varepsilon_{\mathrm{Lorentz}}(\omega) = 1 + \frac{\tilde{\omega}_{\mathrm{p}}^2}{(\omega_0^2 - \omega^2) - \mathrm{i}\tilde{\gamma}\omega}$$

- Large negative real part
- Smaller imaginary part
- Interband transitions < 550 nm
- Depends on deposition method

Optical properties of real metals → www.refractiveindex.info



Shelf

MAIN - simple inorganic materials
ORGANIC - organic materials
GLASS - glasses
OTHER - miscellaneous materials
3D - selected data for 3D artists

Book: Au (Gold)

Page: Olmon et al. 2012 - Evaporated gold; n,k 0.300-24.93 µm

Optical constants of Au (Gold)

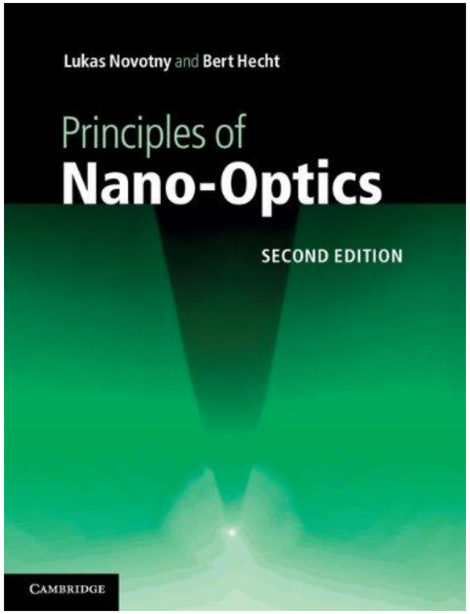
Olmon et al. 2012 - Evaporated gold; n,k 0.300-24.93 µm

Wavelength: 0.5876 µm (3.000E-01 – 2.493E+01)

What is a surface plasmon ?

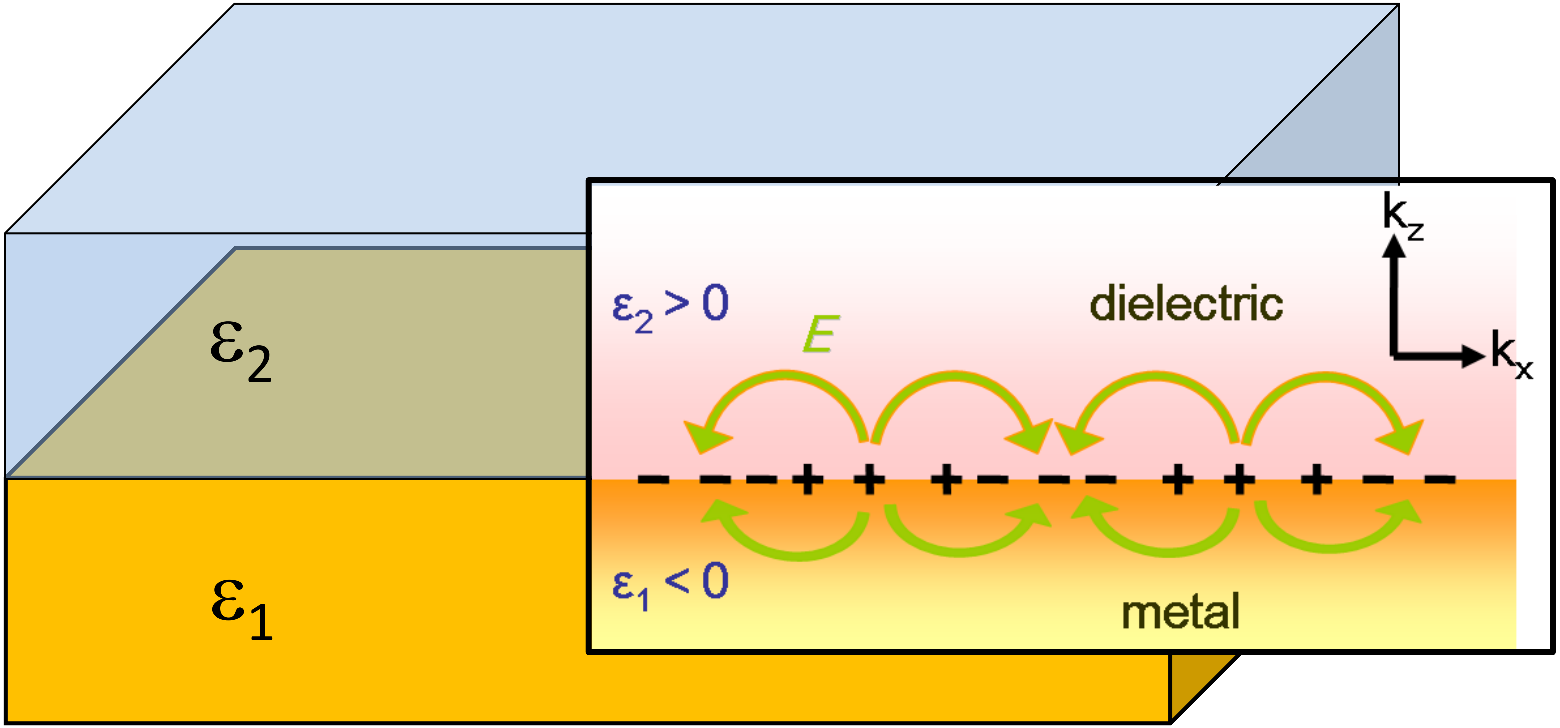
Surface plasmon polariton = quanta of surface charge oscillations

= surface mode solutions of Maxwell’s equations

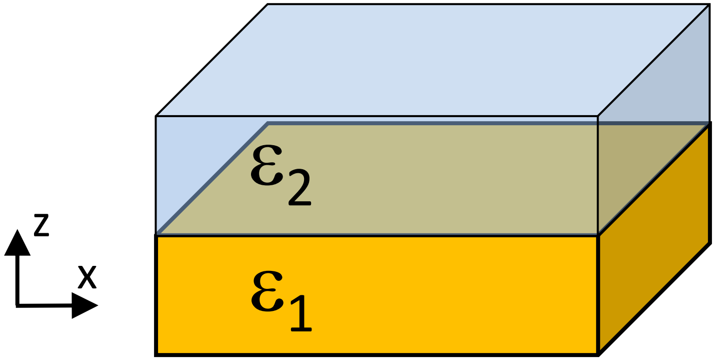


L. Novotny & B. Hecht, Principles of Nano-Optics

Surface plasmons at plane interfaces



Surface plasmons at plane interfaces



Conditions for Maxwell's equations solutions:

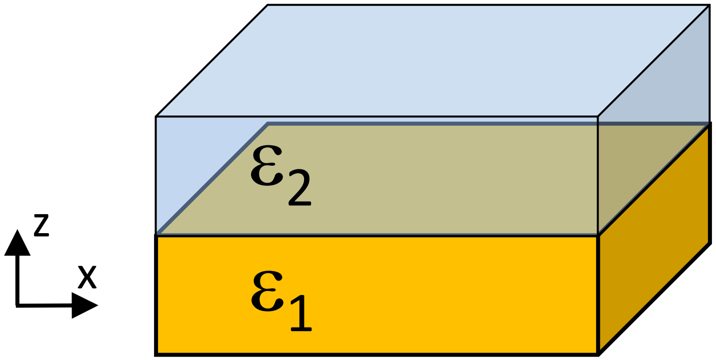
$$k_x^2 + k_{j,z}^2 = \varepsilon_j k^2$$

$$\varepsilon_1 k_{2,z} - \varepsilon_2 k_{1,z} = 0$$

$$\begin{aligned} \varepsilon_1(\omega) \cdot \varepsilon_2(\omega) &< 0 \\ \varepsilon_1(\omega) + \varepsilon_2(\omega) &< 0 \end{aligned}$$

- Surface solution exists for metal-dielectric interface
- Only for TM polarization

Surface plasmons at plane interfaces



Complex metal permittivity $\varepsilon_1 = \varepsilon_1' + \mathrm{i}\varepsilon_1''$

Dispersion relation

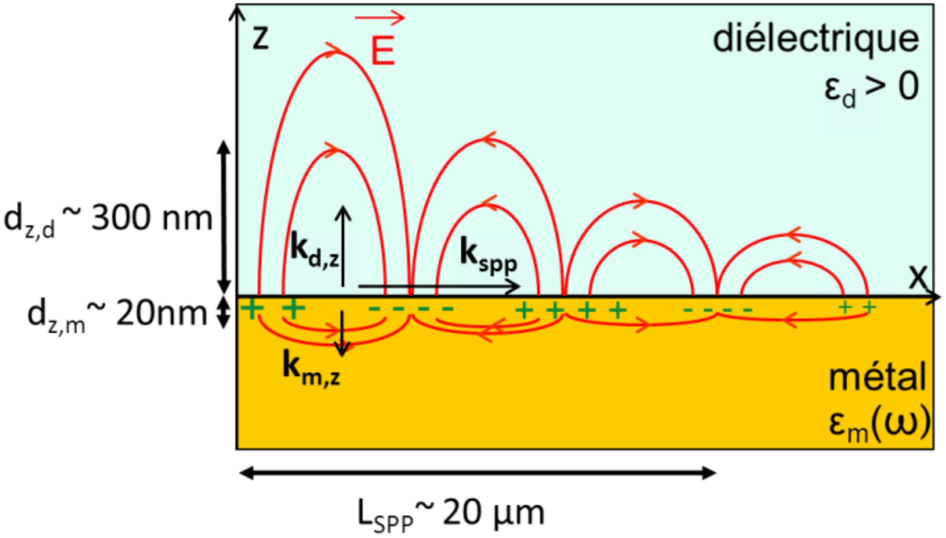
$$\boxed{k_x' \approx \sqrt{\frac{\varepsilon_1'\varepsilon_2}{\varepsilon_1' + \varepsilon_2}}\frac{\omega}{c}}$$

Surface plasmon wavelength $$\lambda_{\mathrm{SPP}} = \frac{2\pi}{k_x'} \approx \sqrt{\frac{\varepsilon_1' + \varepsilon_2}{\varepsilon_1'\varepsilon_2}}\lambda$$

Attenuation distance $$k_x'' \approx \sqrt{\frac{\varepsilon_1'\varepsilon_2}{\varepsilon_1' + \varepsilon_2}}\frac{\varepsilon_1''\varepsilon_2}{2\varepsilon_1'(\varepsilon_1' + \varepsilon_2)}\frac{\omega}{c}$$

Typical values for air/metal interface @ λ = 633 nm

	Gold	Silver
Permittivity	$\varepsilon = -11.6 + 1.2i$	$\varepsilon = -18.2 + 0.5i$
Propagation length	10 µm	60 µm
Decay into metal	28 nm	23 nm
Decay into air	330 nm	420 nm



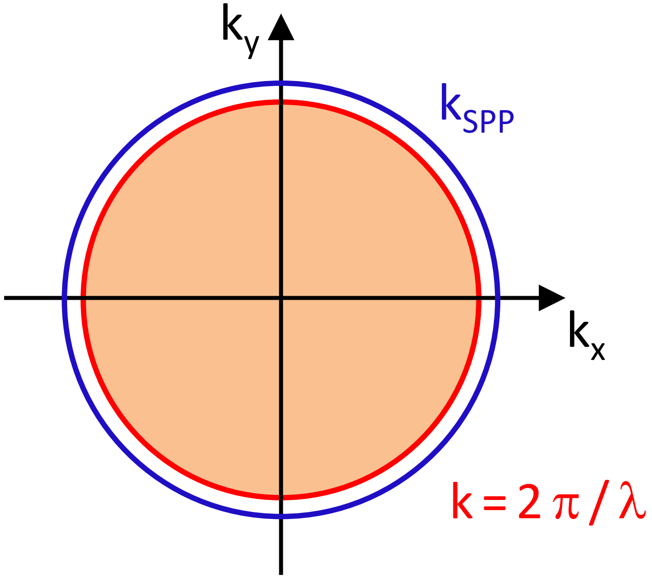
Excitation of surface plasmons at interfaces

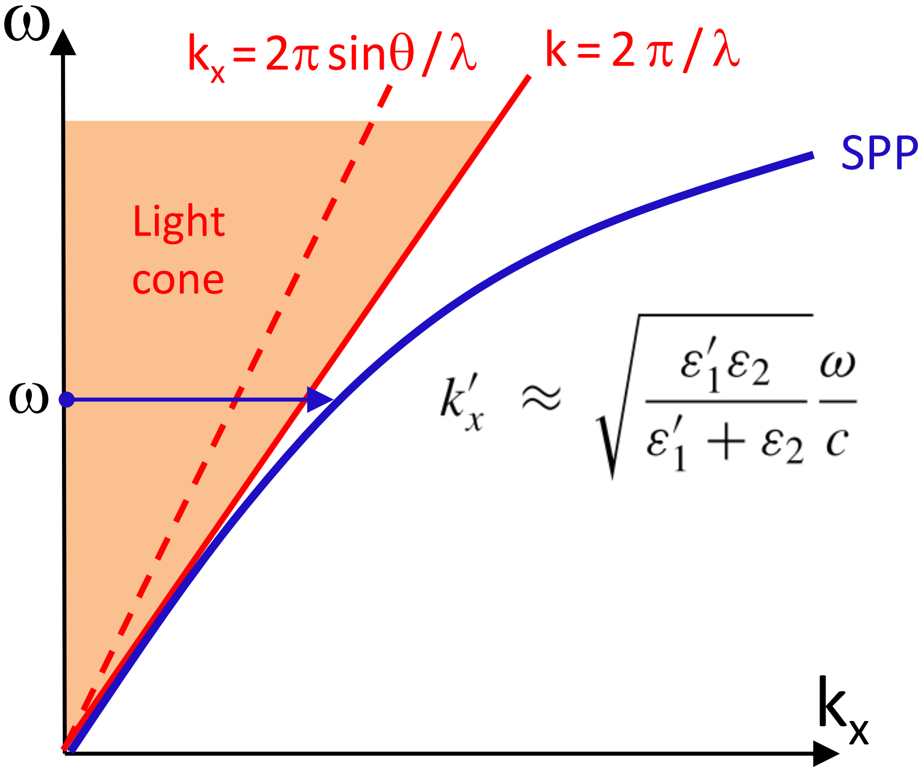
Momentum conservation :

$$\underbrace{k_x^2}_{\substack{\text{greater than } 2\pi/\lambda\text{ !} \\ \text{No direct coupling to light}}} + \underbrace{k_{j,z}^2}_{\substack{< 0 \\ \text{evanescent} \\ k_z \text{ imaginary}}} = \underbrace{\varepsilon_j k^2}_{\substack{\text{constant} \\ 2\pi/\lambda}}$$

Excitation of surface plasmons at interfaces

Momentum conservation : $k_x^2 + k_{j,z}^2 = \varepsilon_j k^2$

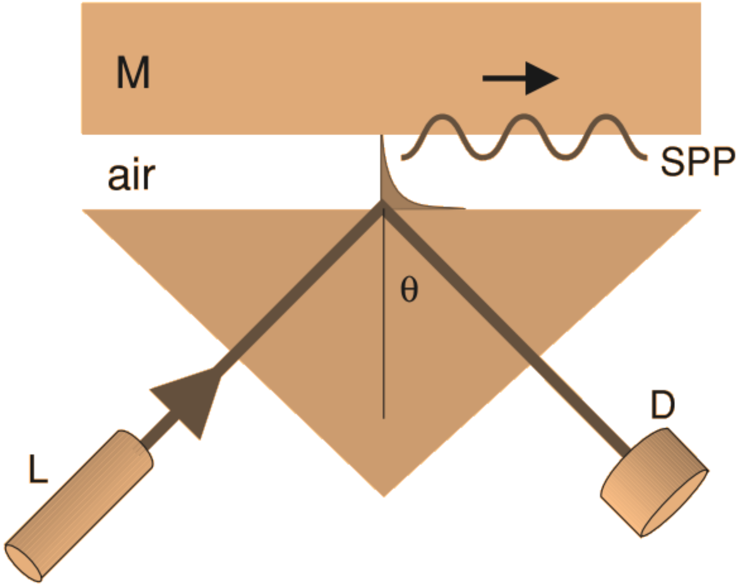


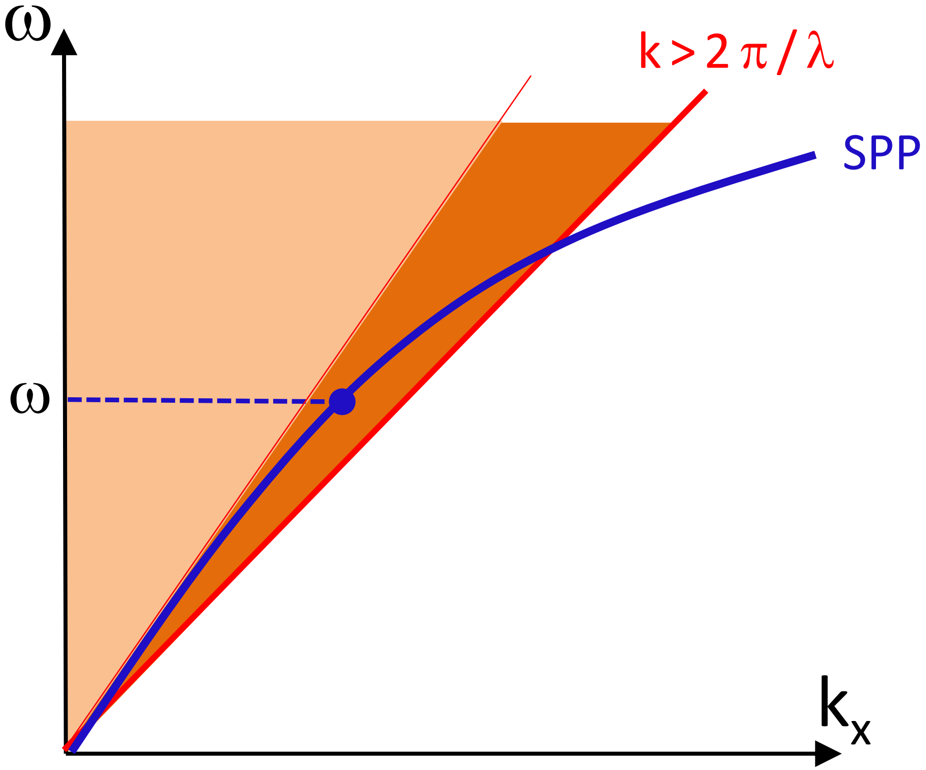


$$k_x' \approx \sqrt{\frac{\varepsilon_1' \varepsilon_2}{\varepsilon_1' + \varepsilon_2}} \frac{\omega}{c}$$

Solution #1: evanescent wave coupling via prism

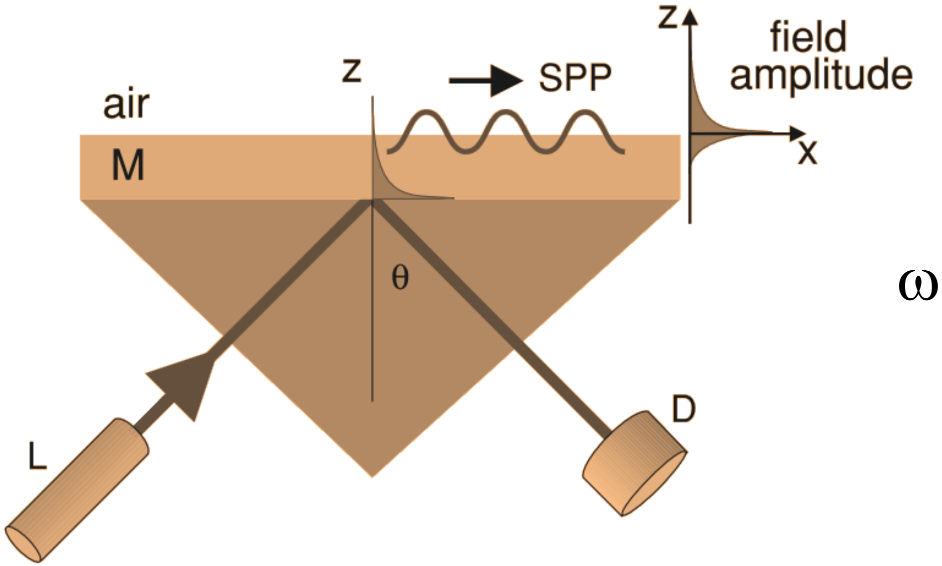
Otto configuration

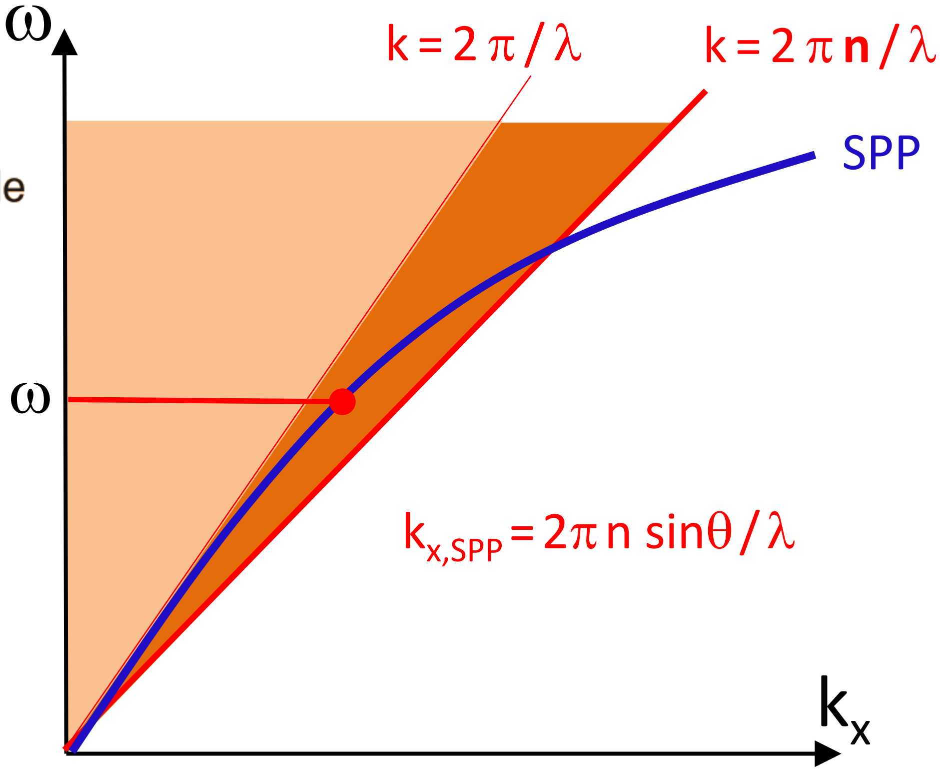




Solution #2: coupling via high refractive index substrate

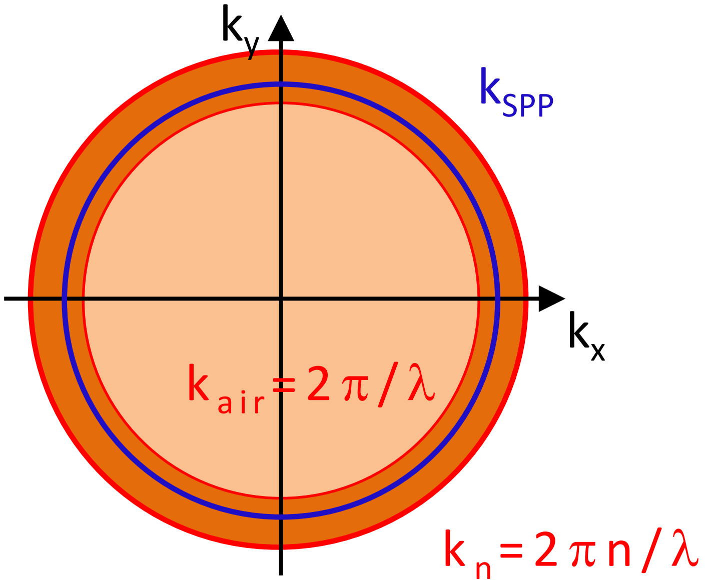
Kretschmann configuration

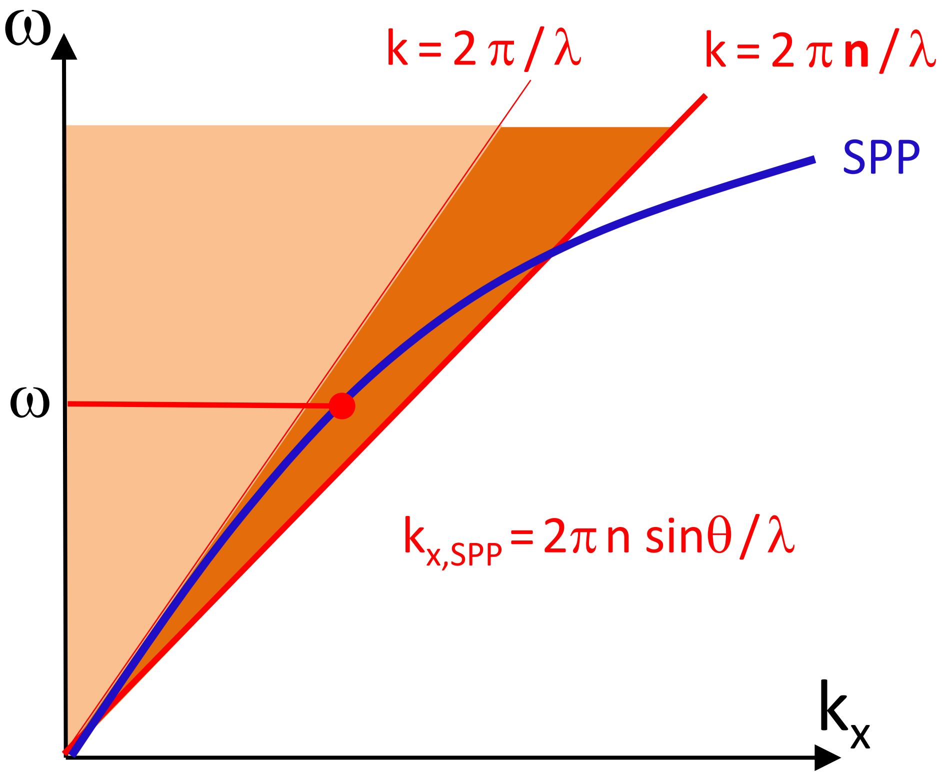




Solution #2: coupling via high refractive index substrate

Kretschmann configuration





Solution #2: coupling via high refractive index substrate

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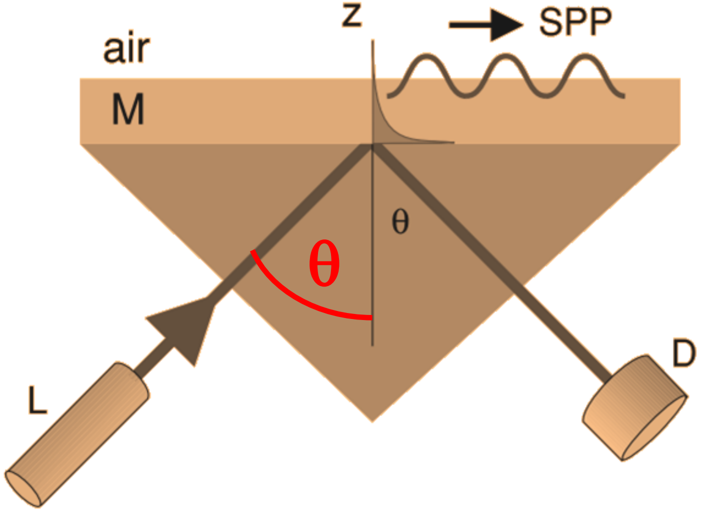
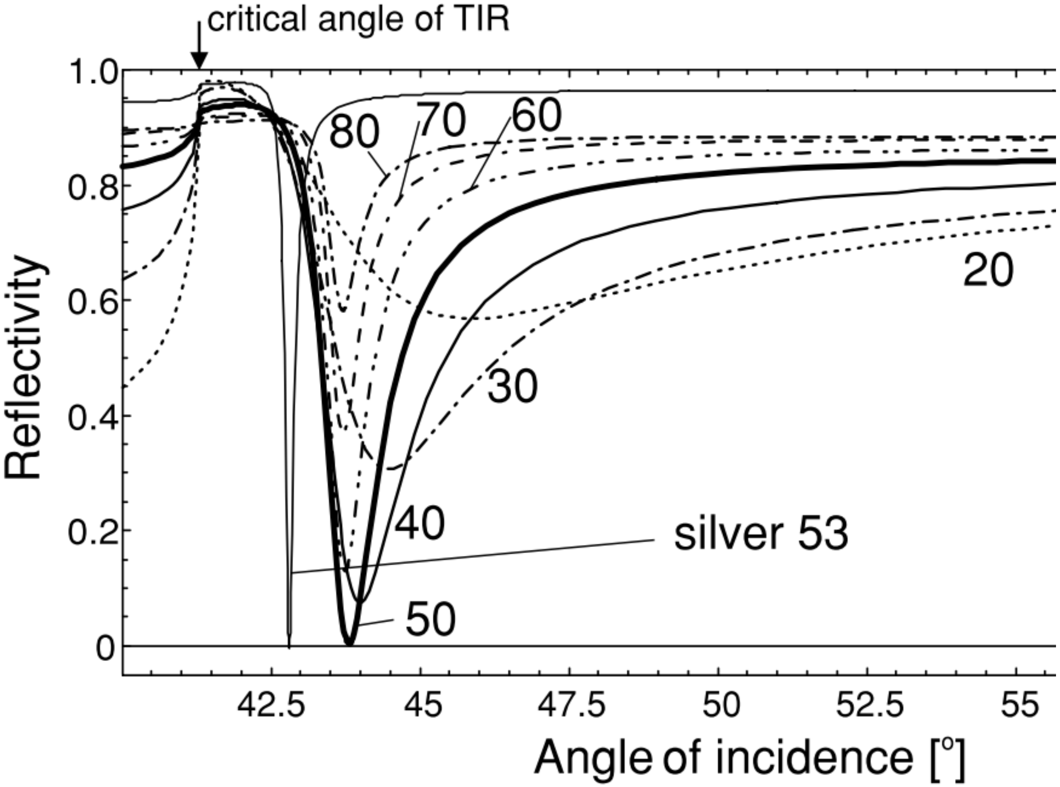
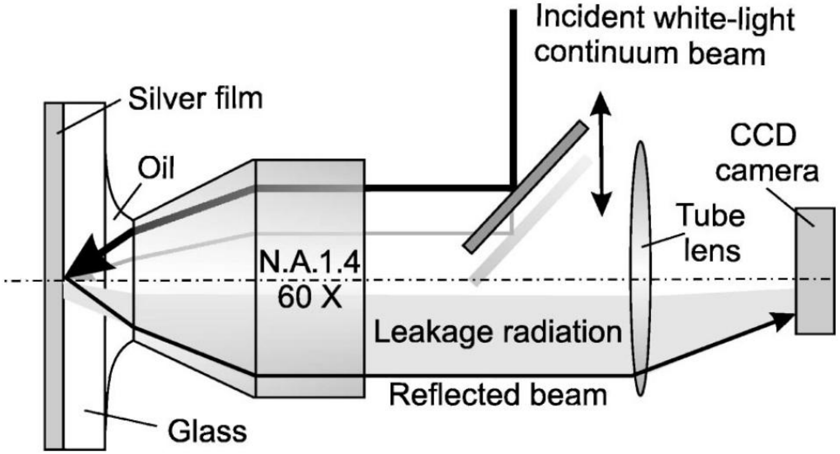
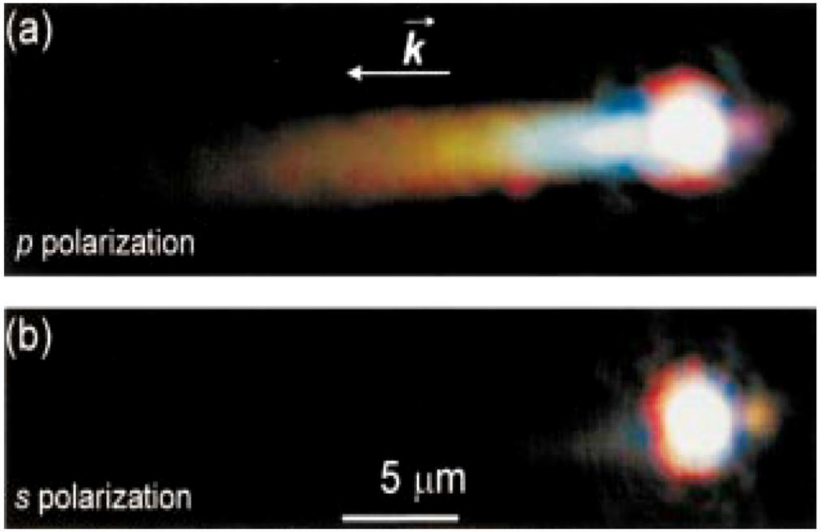




Solution #2: coupling via high refractive index substrate

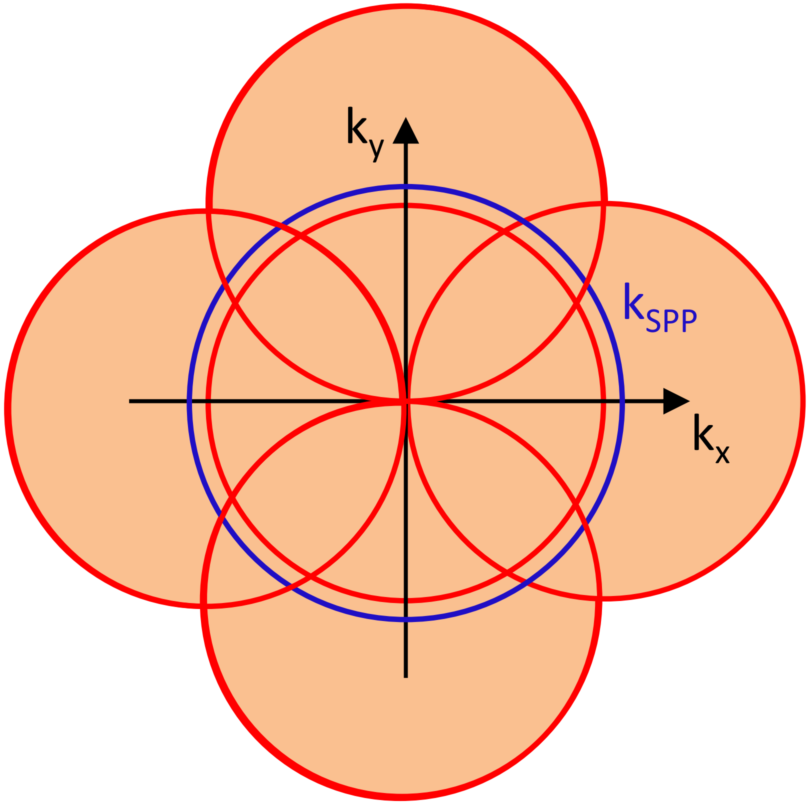


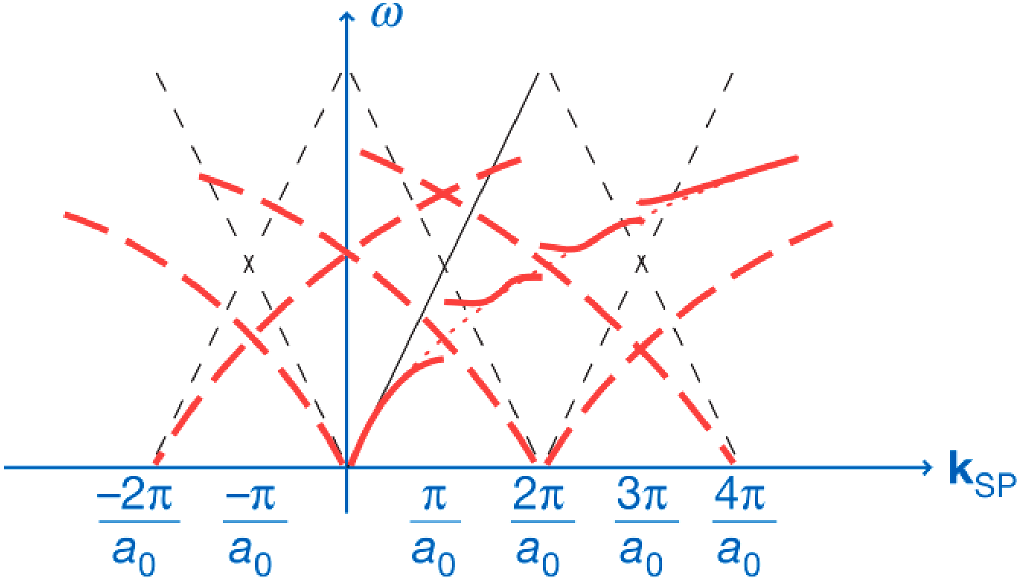


Bouhelier, Opt Lett 30, 884 (2005)

Solution #3: coupling via a grating

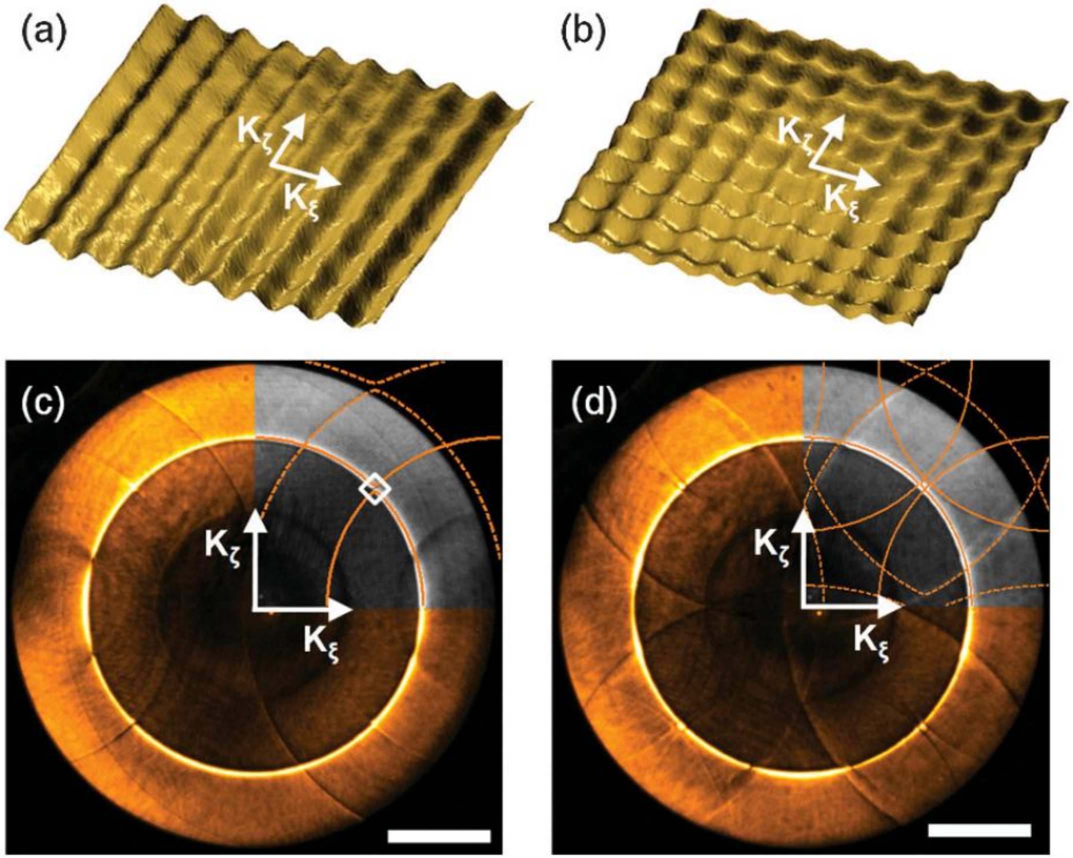
Extra momentum from grating lattice $k'_x = k_x + 2\pi n/a$





Genet *et al*, Nature 445, 39 (2007)

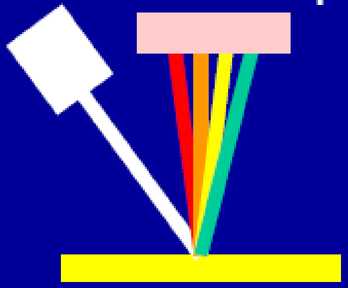
Solution #3: coupling via a grating



Stein, PRL 105, 266804 (2010)

Solution #3: coupling via a grating

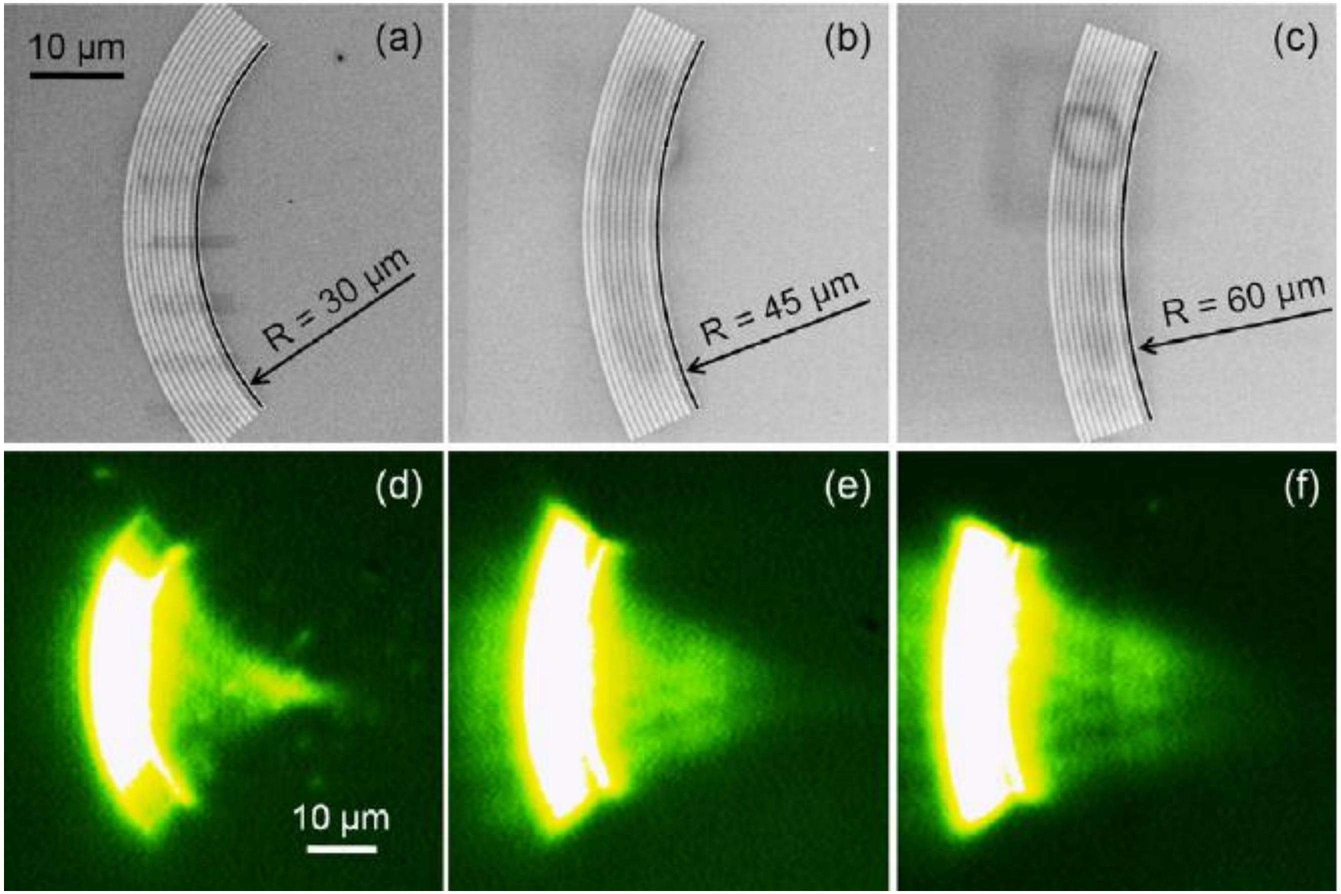
« One of the most interesting problems that I have ever met with »
R.W. Wood, 1902



« I was astounded to find that under certain conditions, the drop from maximum illumination to minimum, a drop certainly of from 10 to 1, occured within a range of wavelengths not greater than the distance between the sodium lines »

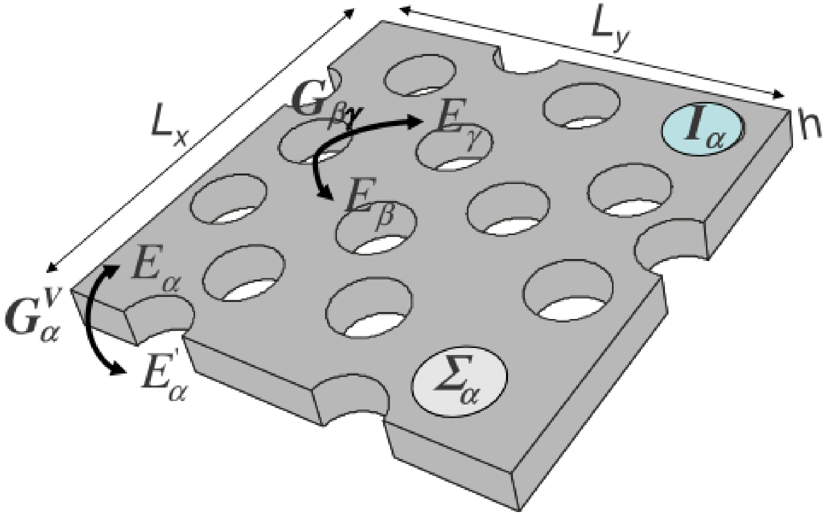
« The singular anomalies were exhibited only when the direction of electric field was at right angle to the ruling »

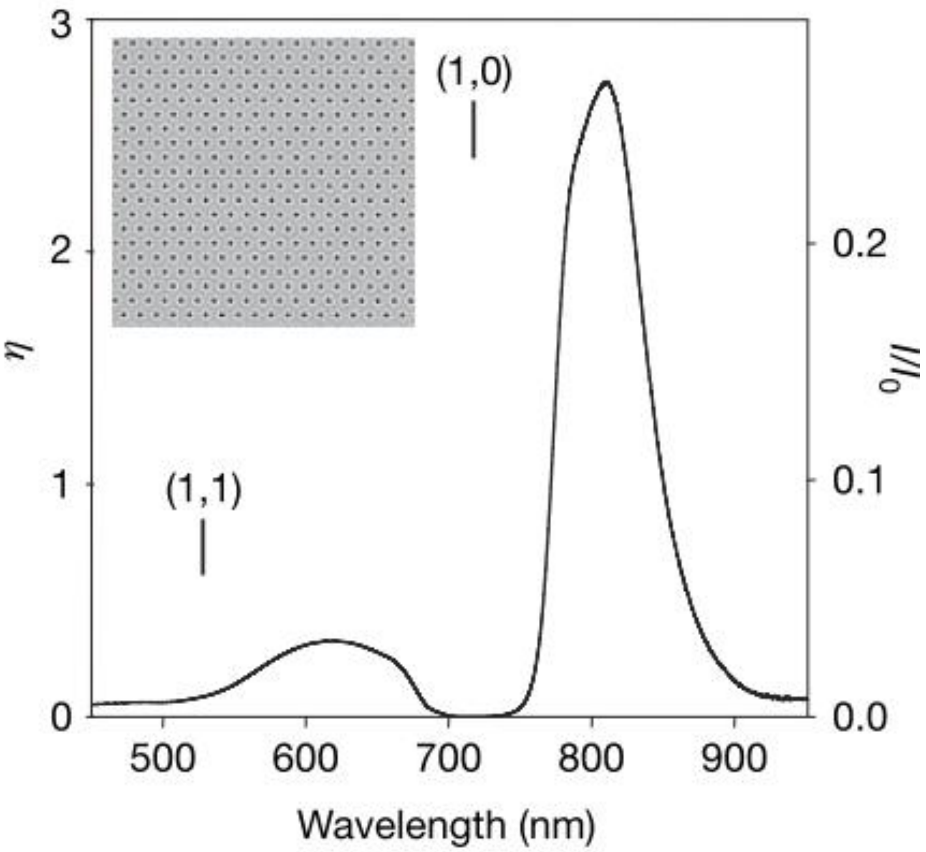
Solution #3: coupling via a grating



Lopez-Tejeira, New J. Phys. 10 (2008) 033035

Extraordinary optical transmission through aperture arrays





Ebbesen *et al*, Nature **391**, 667 (1998)

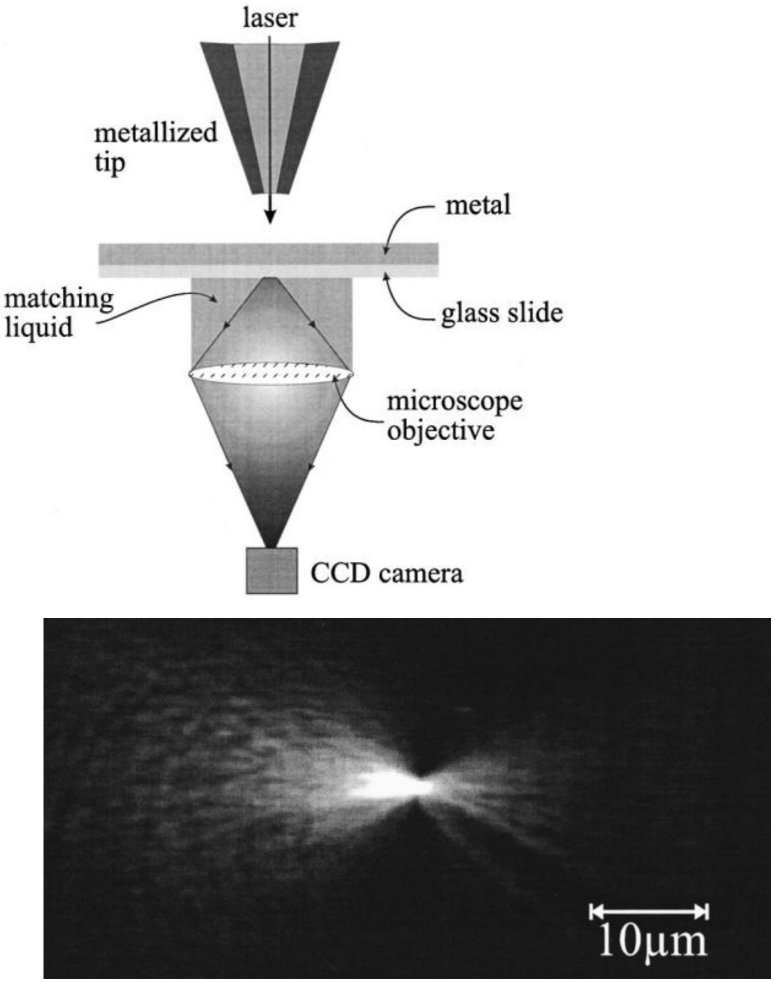
Genet *et al*, Nature **445**, 39 (2007)

Garcia-Vidal *et al*, Rev Mod Phys **82**, 729 (2010)

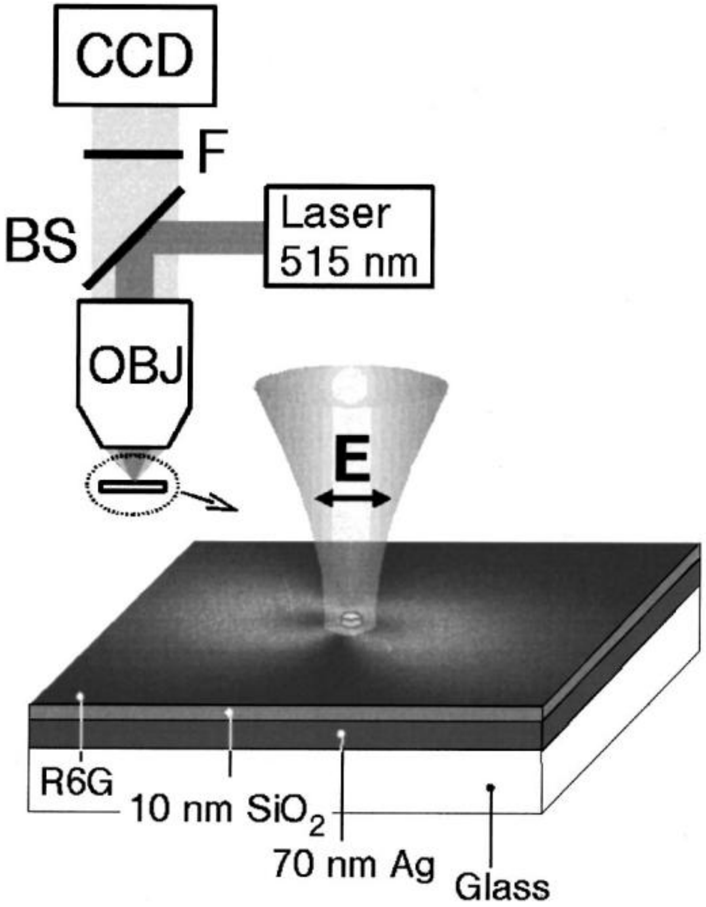
$$\lambda_{\max} = \frac{P}{\sqrt{\frac{4}{3}\left(i^2+ij+j^2\right)}}\sqrt{\frac{\varepsilon_{\mathrm{m}}\varepsilon_{\mathrm{d}}}{\varepsilon_{\mathrm{m}}+\varepsilon_{\mathrm{d}}}}$$

Solution #4: using sub-λ scatterer

NSOM probe, nanoparticle, hole, molecule…

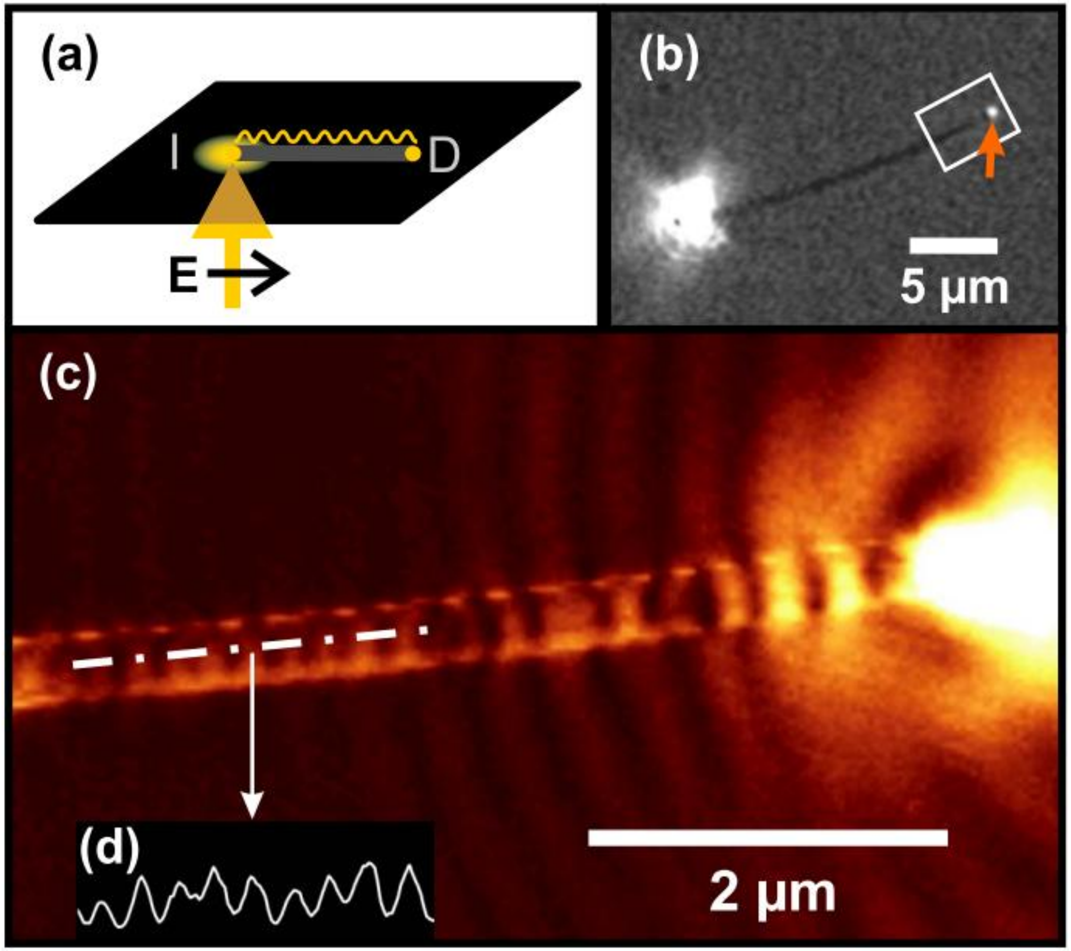


Baida, JOSA A 18, 1552 (2001)



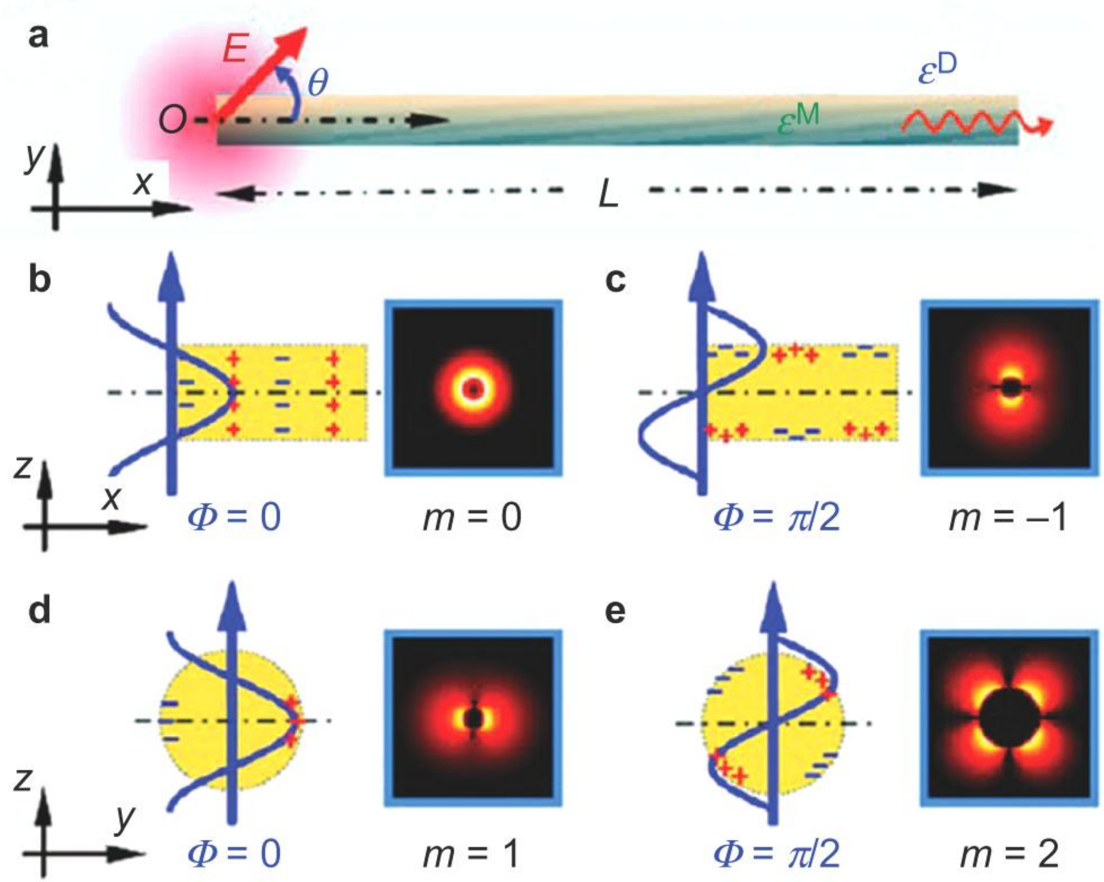
Ditlbacher, Appl Phys Lett 80, 404 (2002)

Plasmons on nanowires



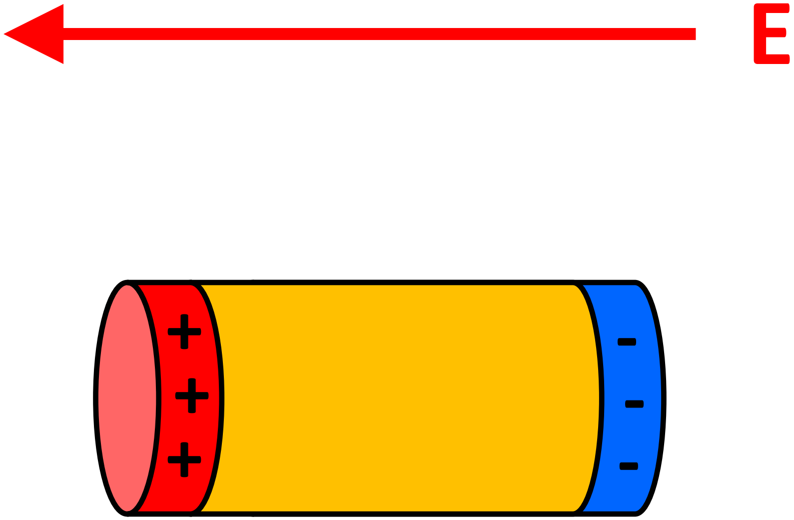
Ditlbacher, Phys Rev Lett 95, 257403 (2005)

Plasmons on nanowires

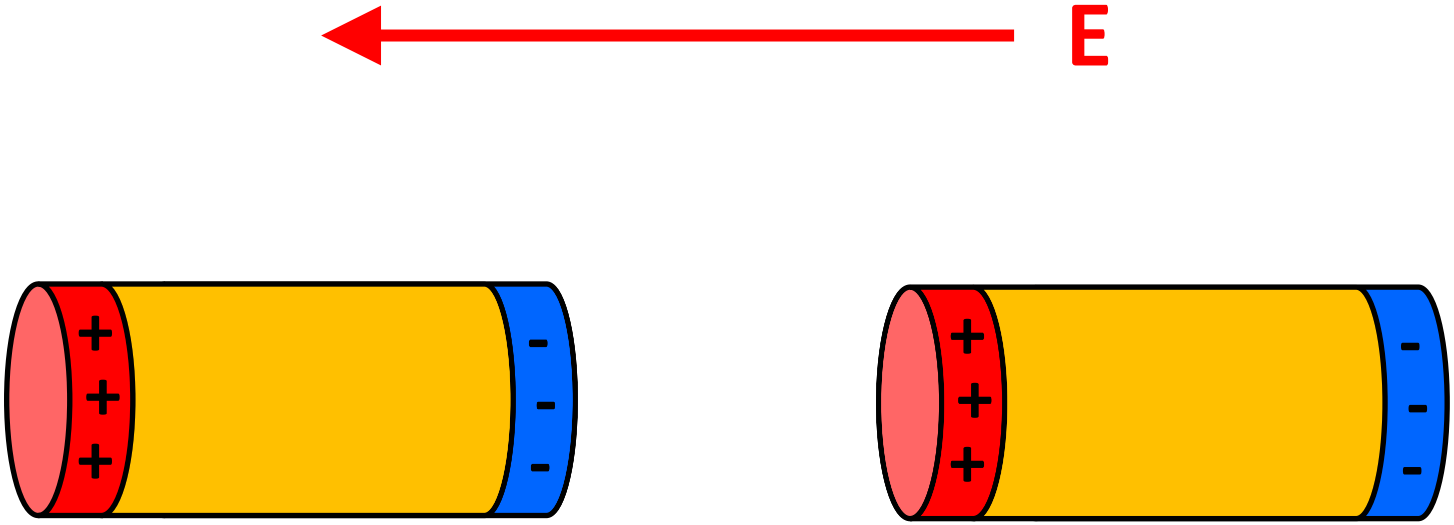


Zhang, Phys Rev Lett 107, 096801 (2011)

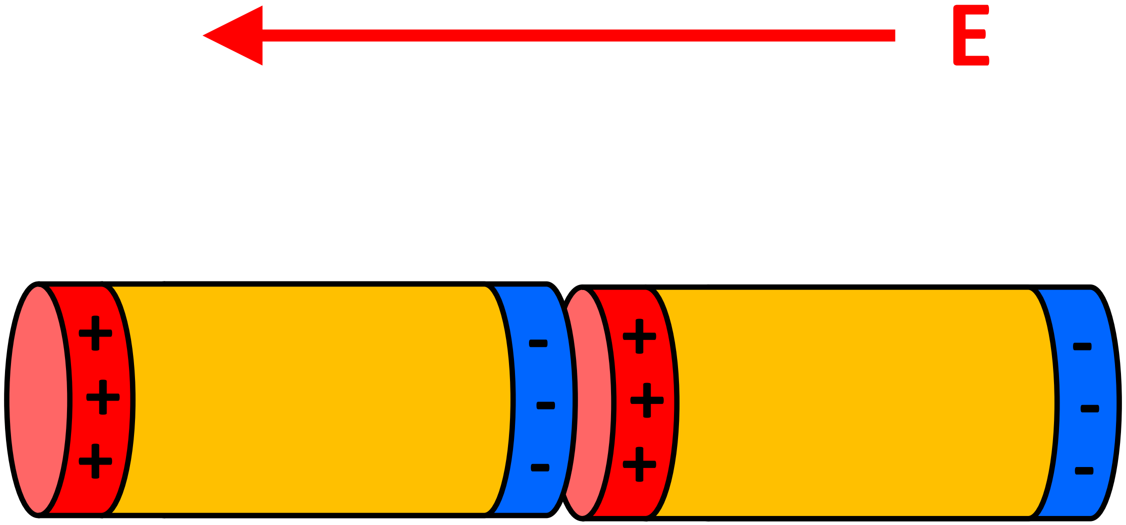
Local surface plasmon in a nanoparticle



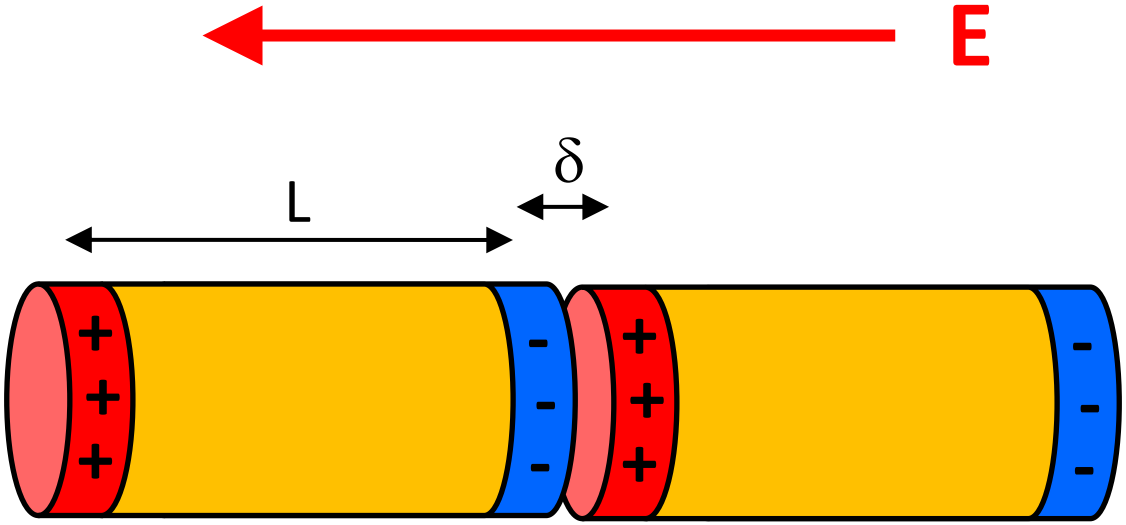
Local surface plasmon in two nanoparticles



Coupling between nanoparticles



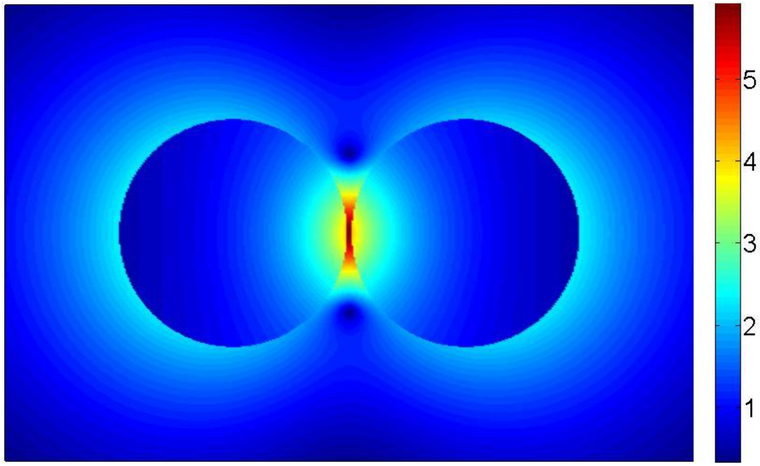
Coupling between nanoparticles



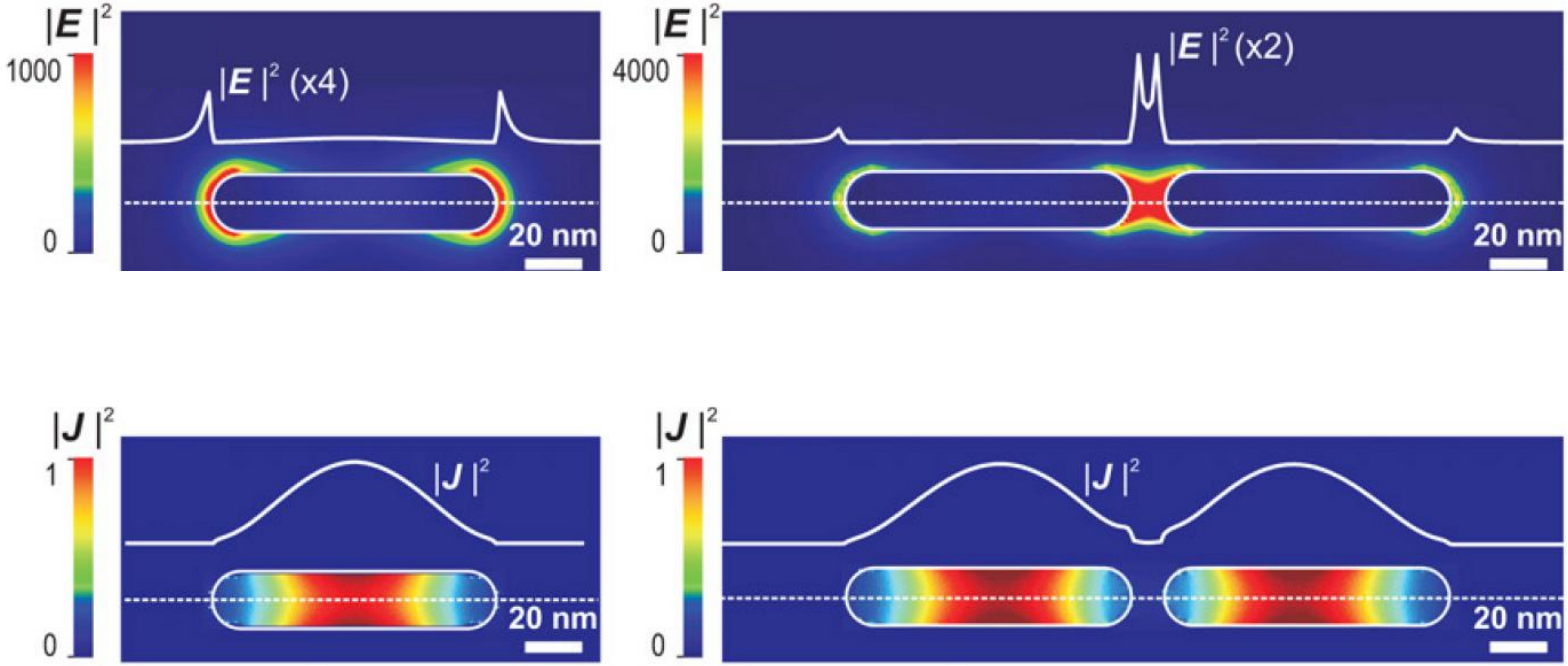
Local electric field enhancement:

$$\frac{E_{loc}}{E_o} = \frac{-\mathrm{Re}\,\varepsilon}{\mathrm{Im}\,\varepsilon}\;\frac{2\,L + \delta}{\delta} \;\sim 500$$

Intensity gain ~ $2\ 10^5$

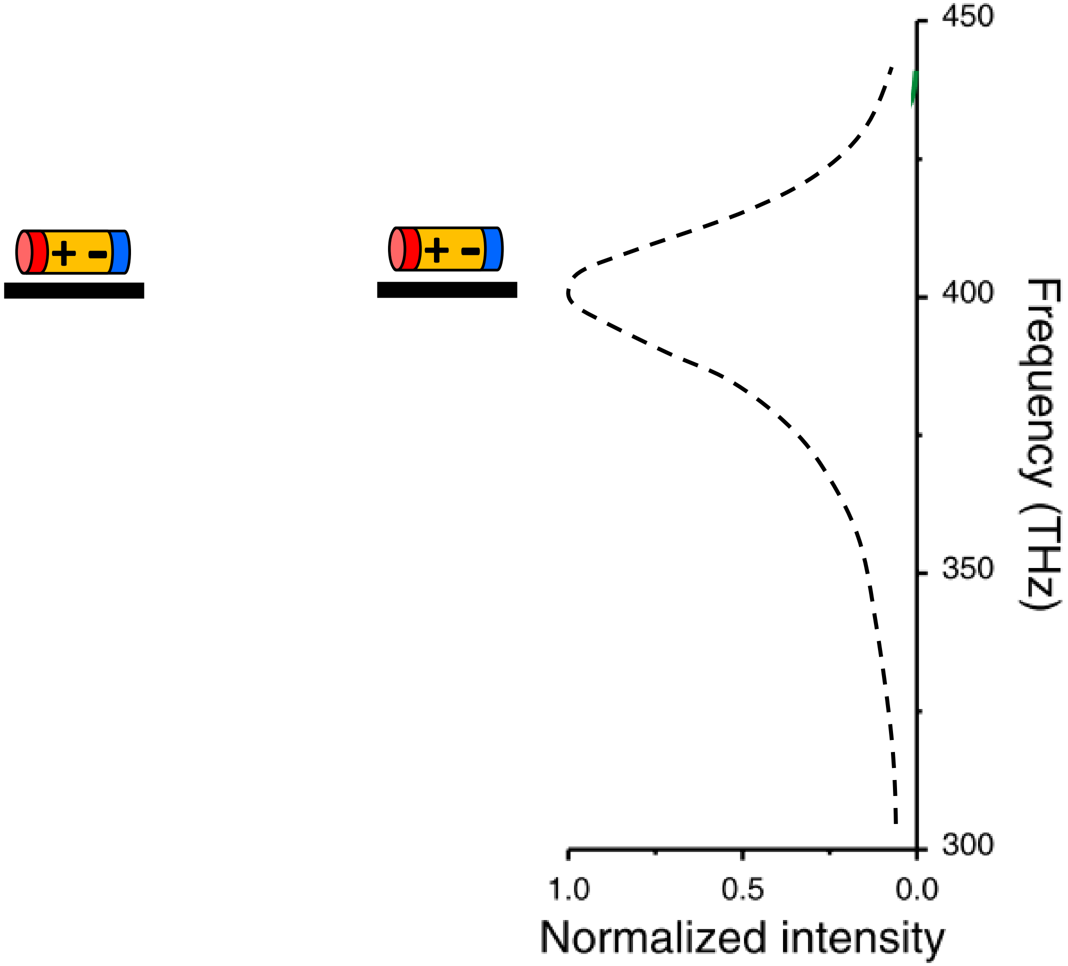


Intensity enhancement in coupled nanoparticles



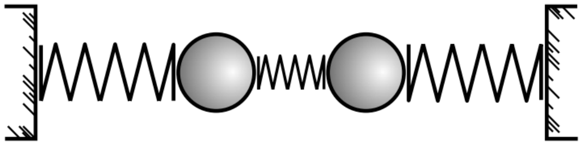
Biagoni, Rep. Prog. Phys. 75 (2012) 024402

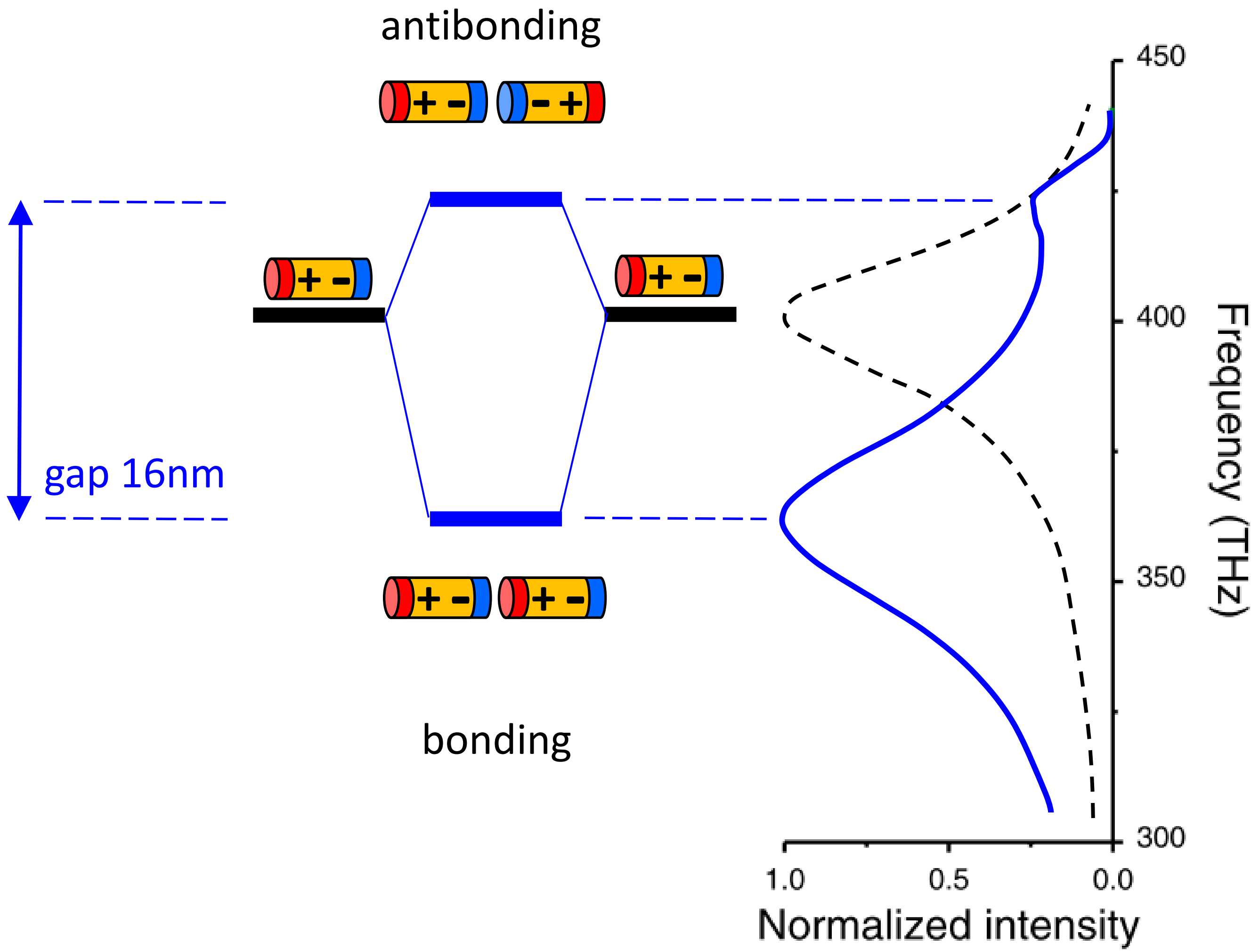
Spectral resonances in nanoparticle pairs



Biagoni, Rep. Prog. Phys. 75 (2012) 024402

Spectral resonances in nanoparticle pairs





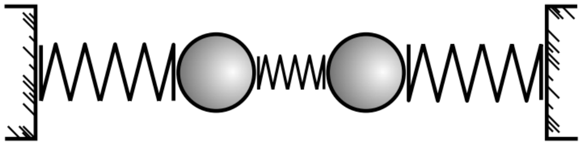
antibonding

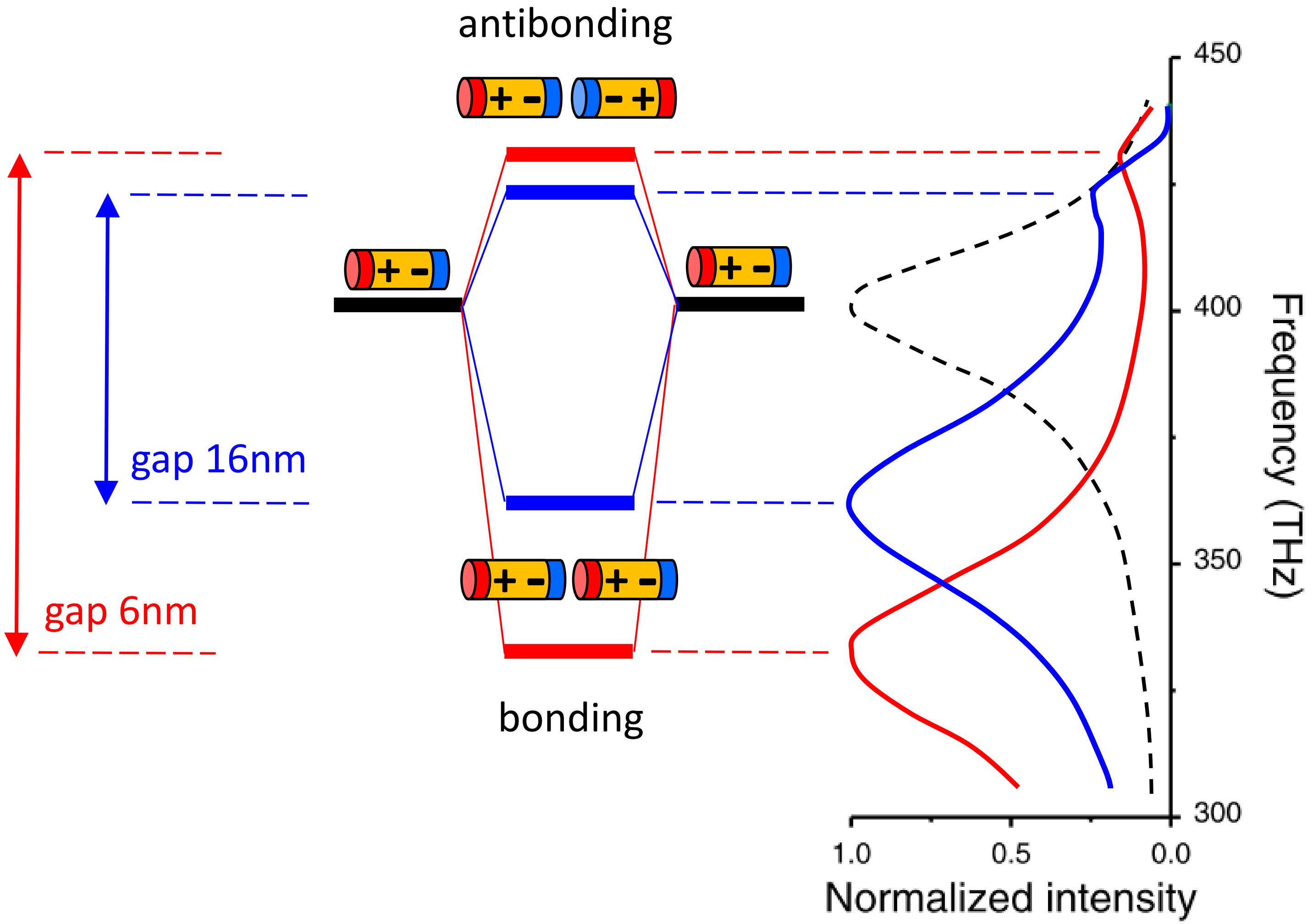
gap 16nm

bonding

Biagoni, Rep. Prog. Phys. 75 (2012) 024402

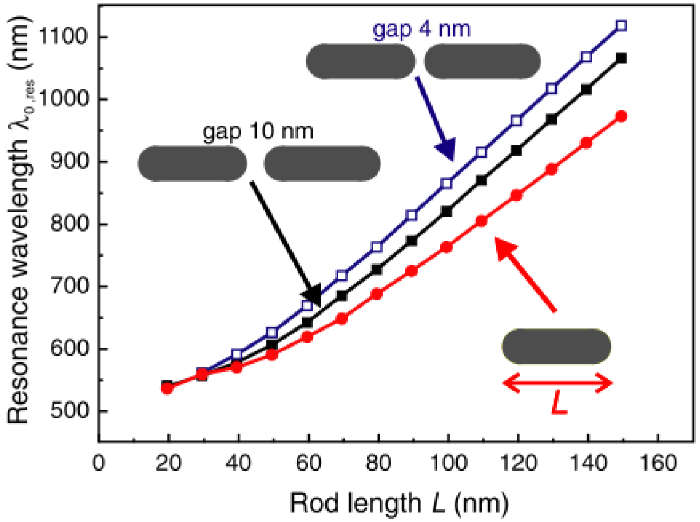
Spectral resonances in nanoparticle pairs

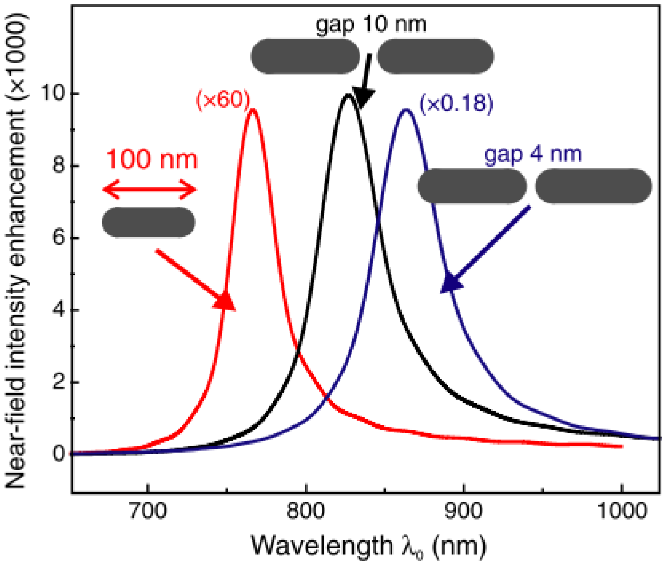




Biagoni, Rep. Prog. Phys. 75 (2012) 024402

Interacting plasmonic nanoparticles



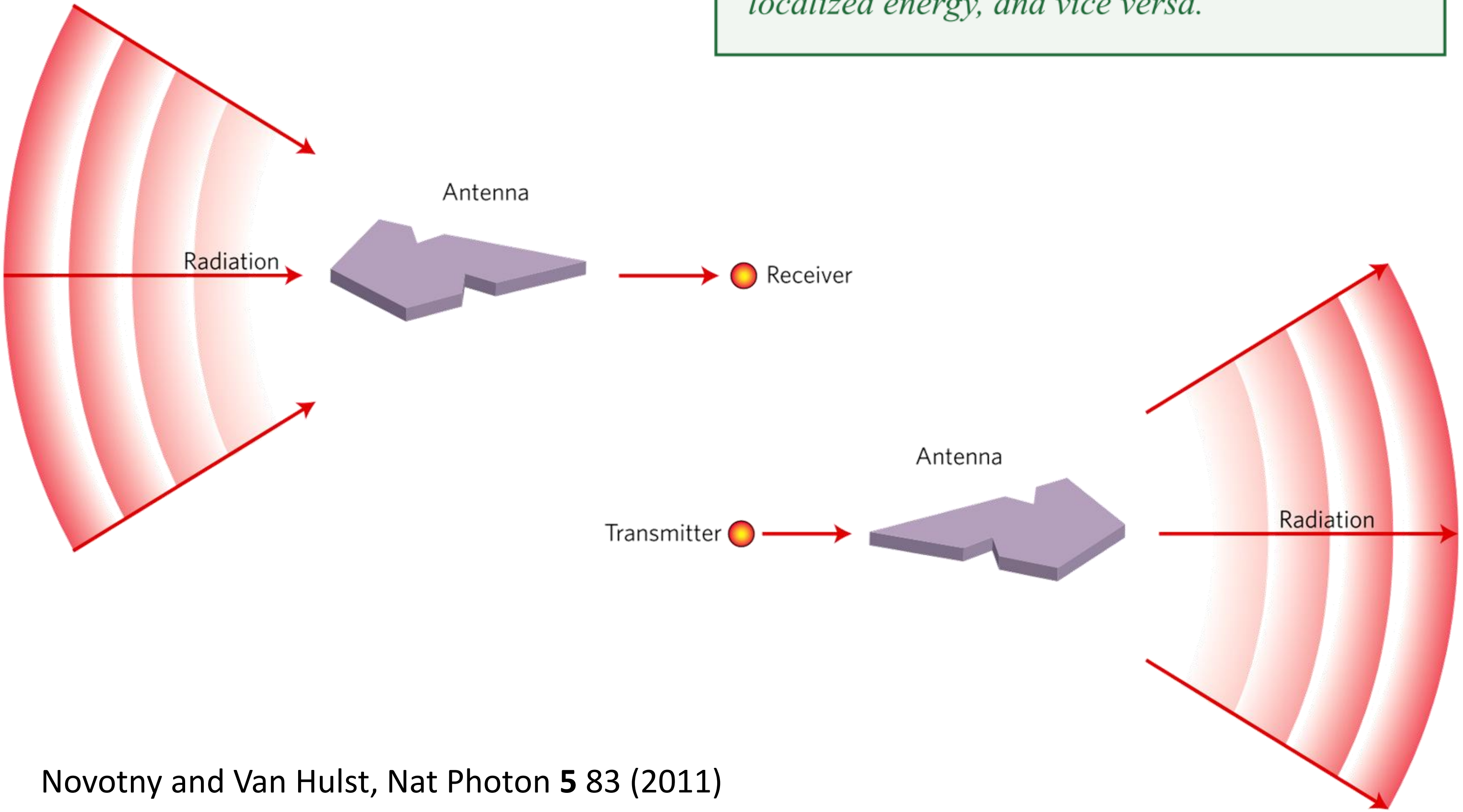


- Red-shift when length increases
- Red-shift when gap decreases
- Intensity increase when gap decreases

Biagoni, Rep. Prog. Phys. 75 (2012) 024402

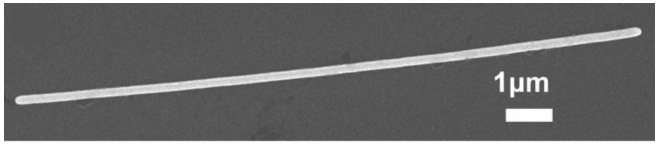
Plasmonic optical antennas

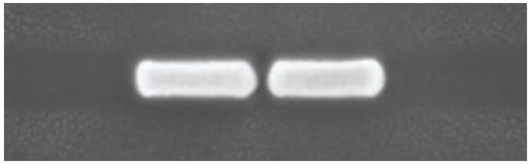
Optical antenna: a device designed to efficiently convert free-propagating optical radiation to localized energy, and vice versa.

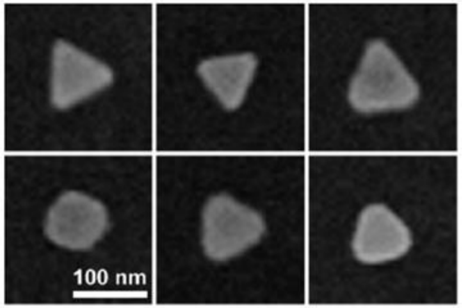


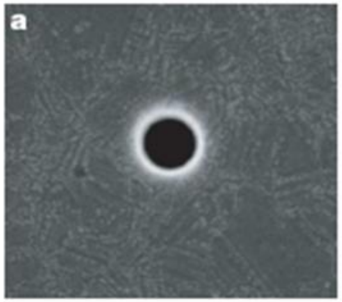
Novotny and Van Hulst, Nat Photon **5** 83 (2011)

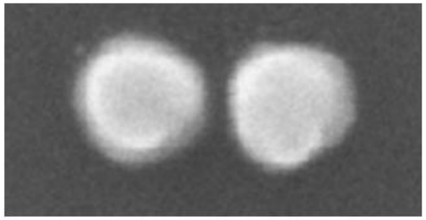
Plasmonic Optical Nanoantennas

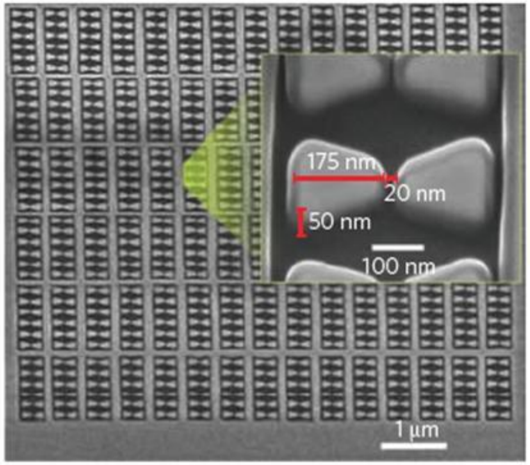


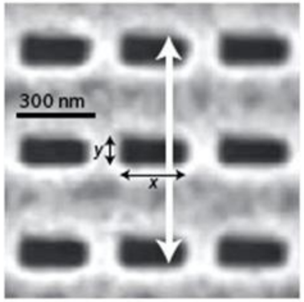


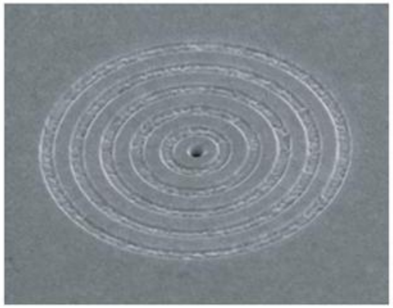


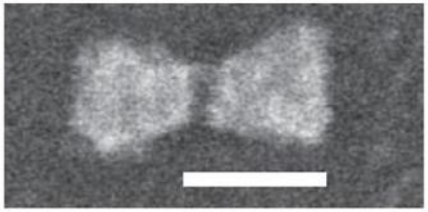


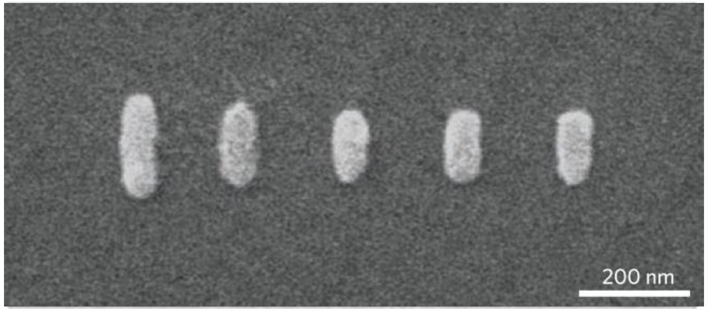


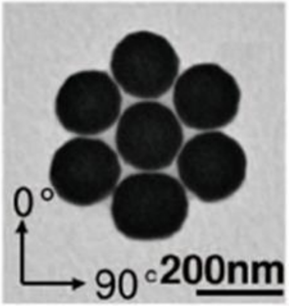


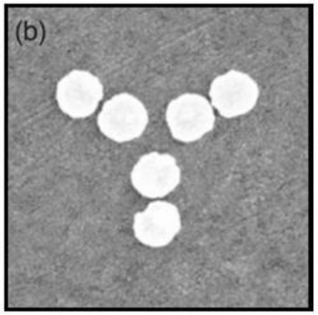


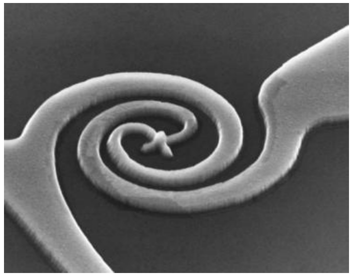


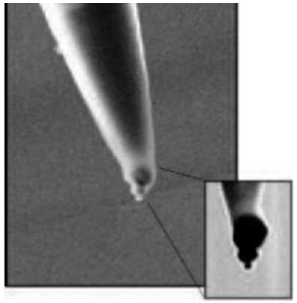


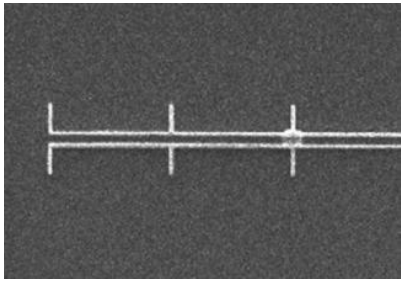


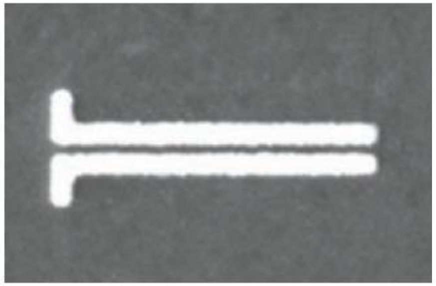


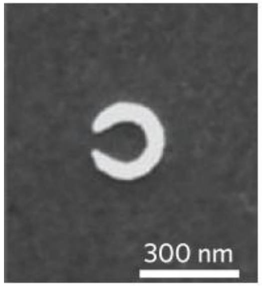


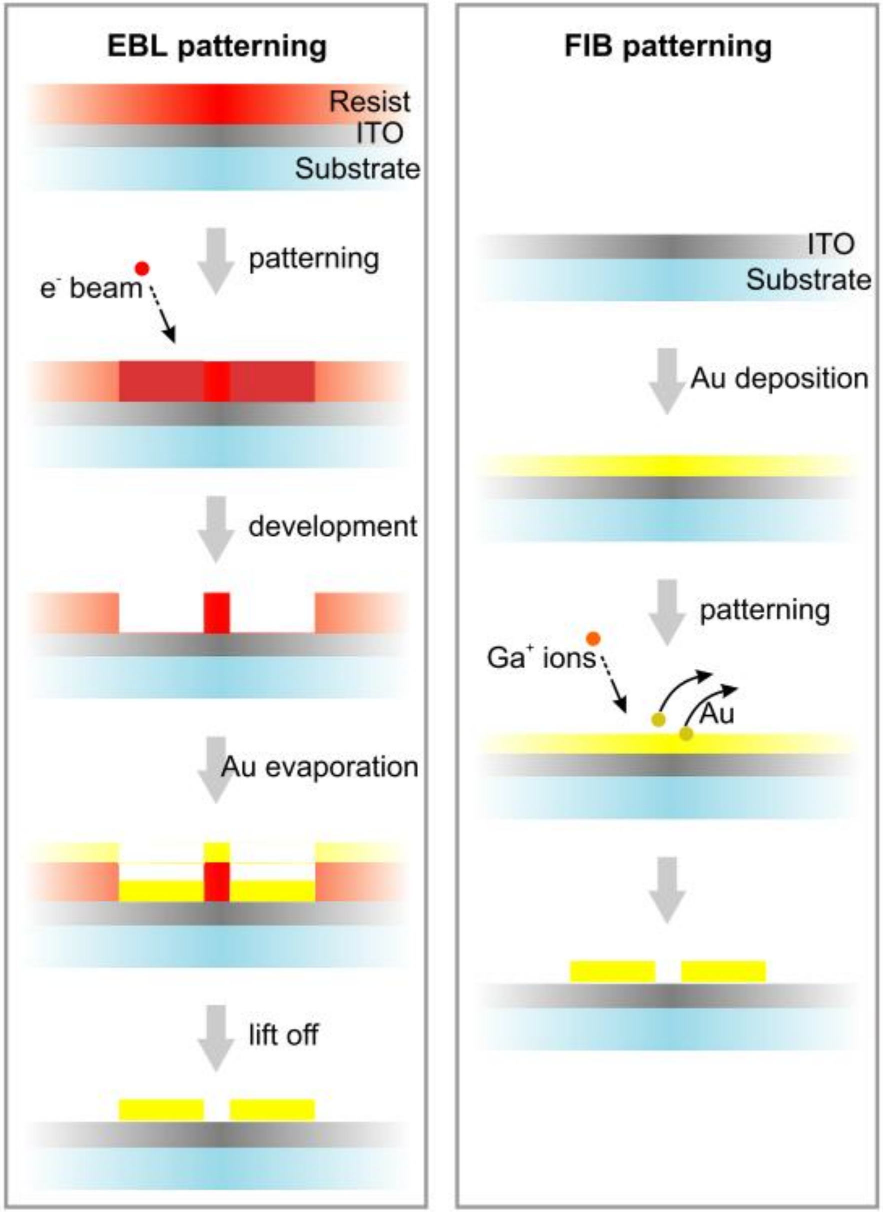






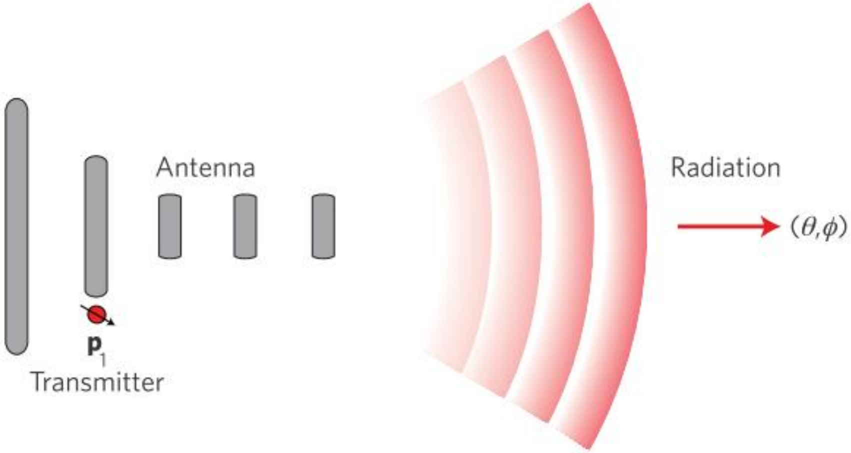


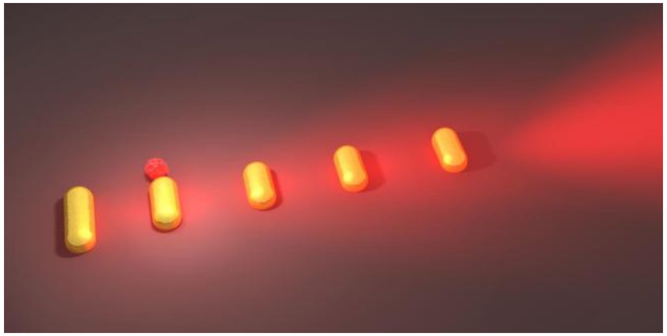


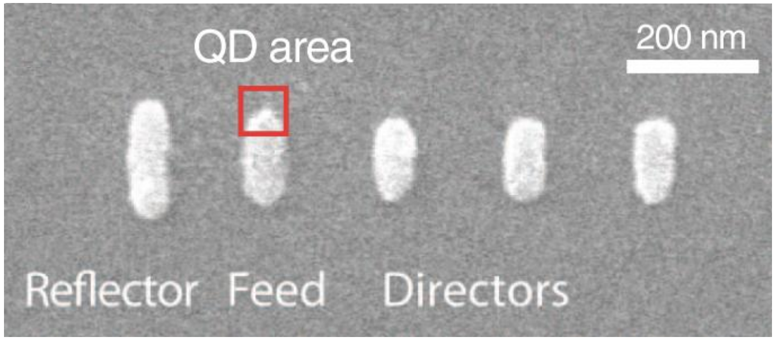


Biagoni, Rep. Prog. Phys. 75 (2012) 024402

Yagi-Uda antenna: directional emission from single emitter

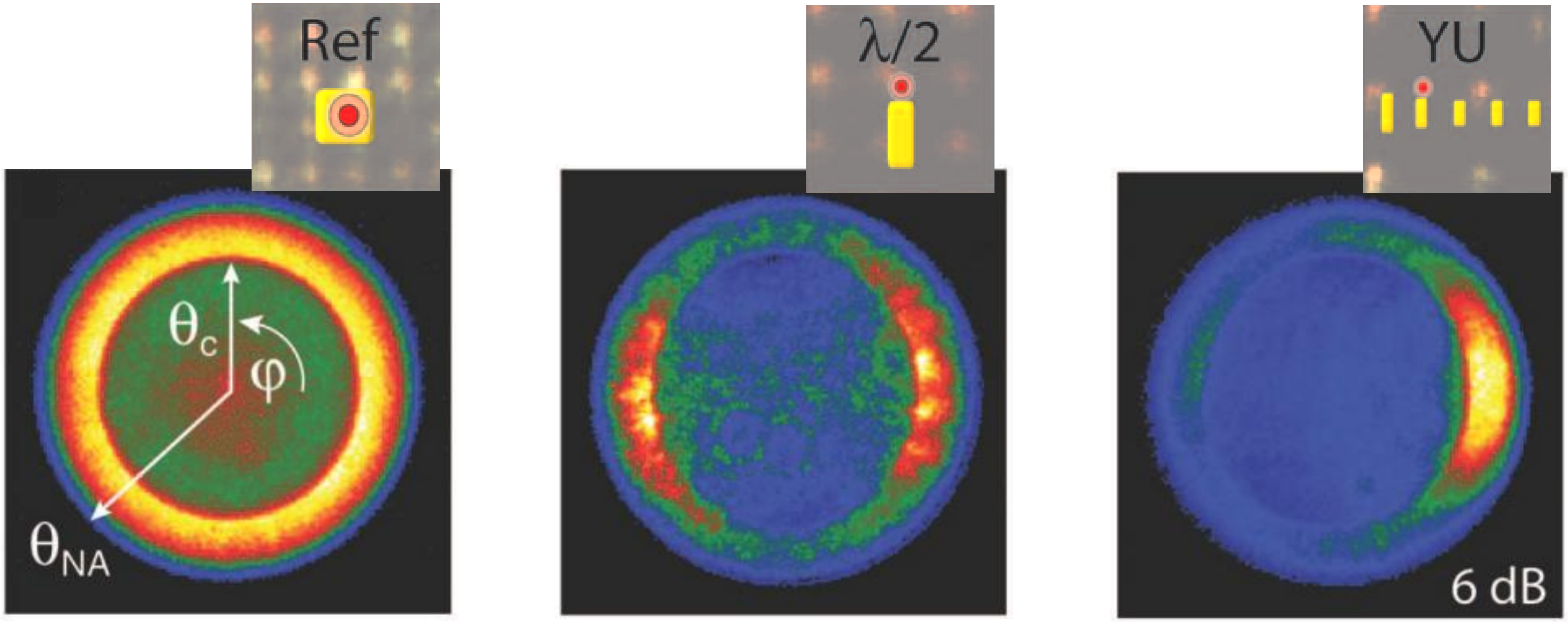


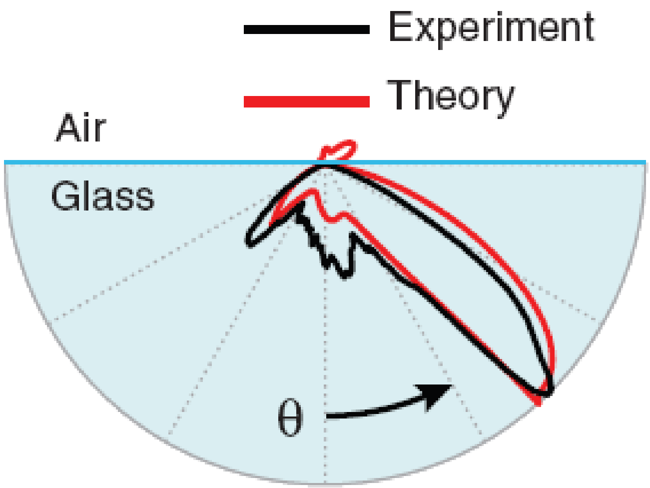




Curto, Science 329, 930 (2010)

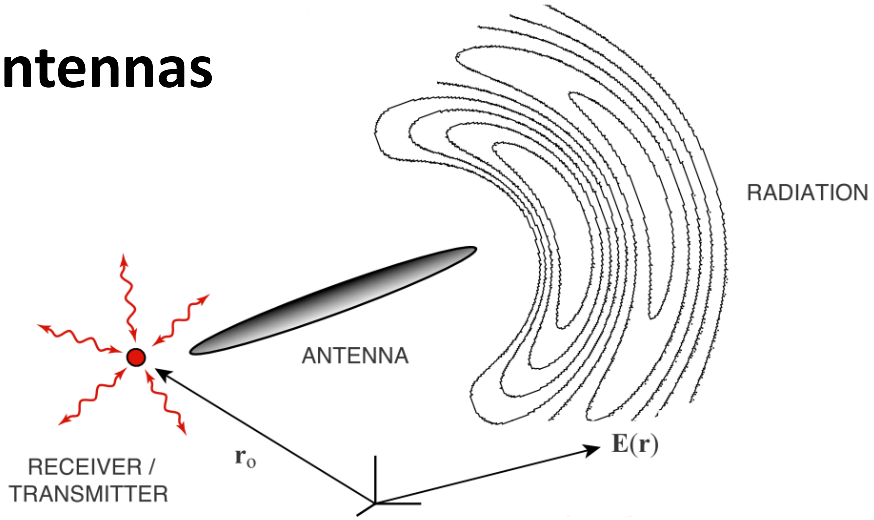
Yagi-Uda antenna: directional emission from single emitter

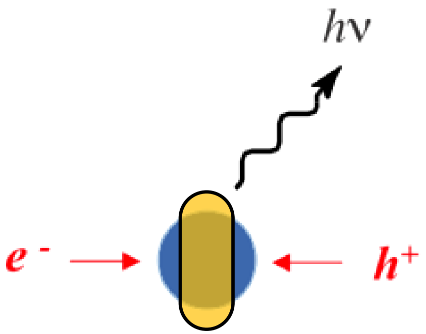




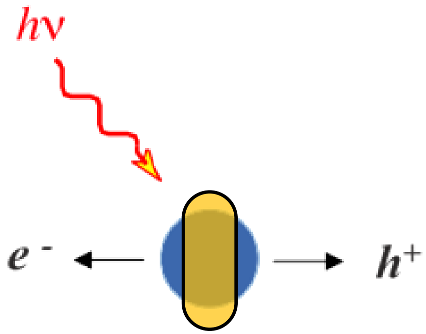
Curto, Science 329, 930 (2010)

Plasmonic Nanoantennas

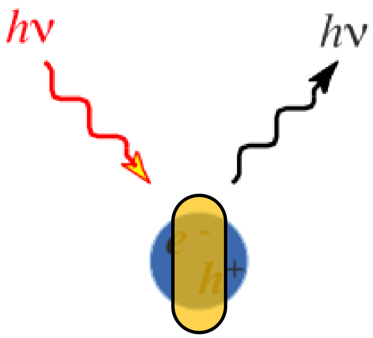




LED



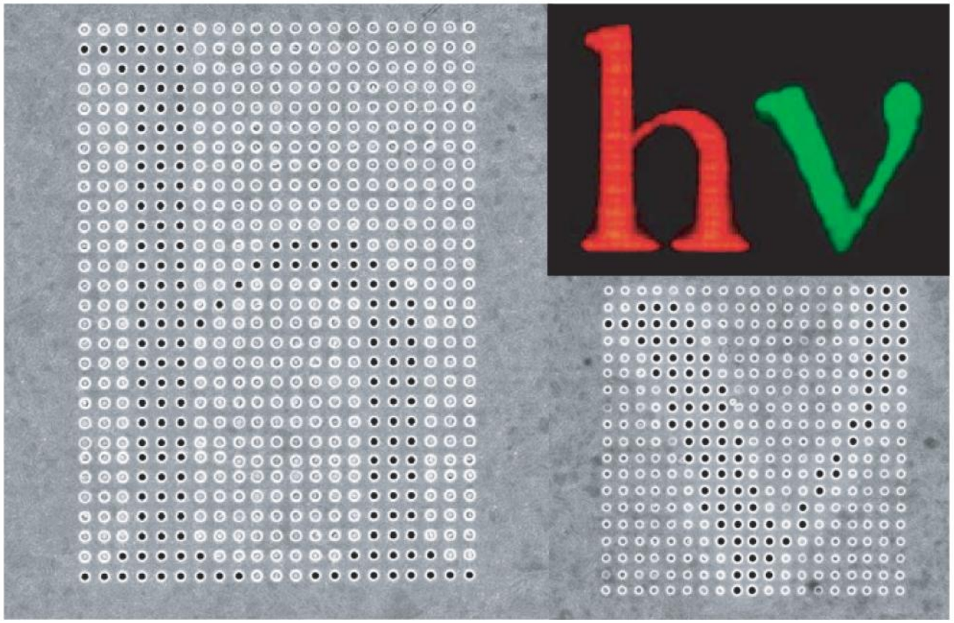
Photovoltaics

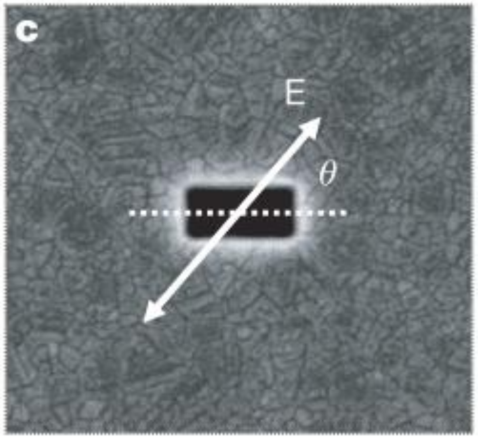


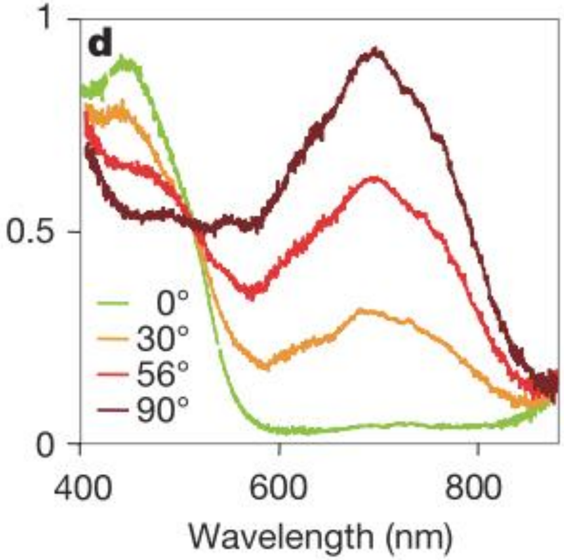
Spectroscopy

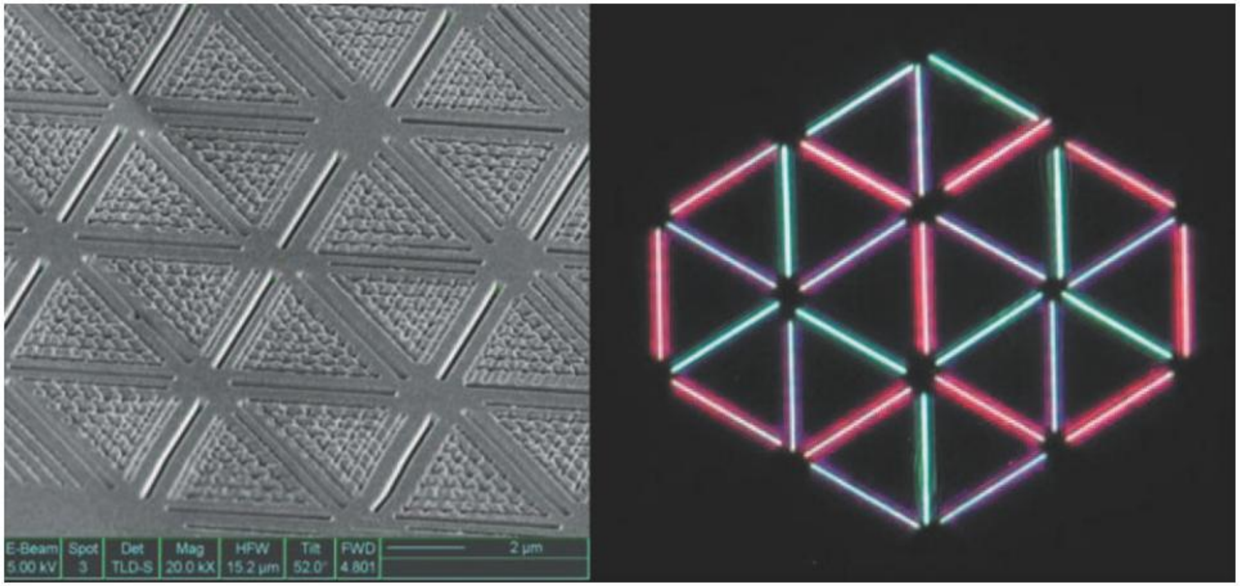
Bharadwaj, Advances in Optics and Photonics 1, 438 (2009)

Optical filters









Genet *et al*, Nature **445**, 39 (2007)

Garcia-Vidal *et al*, Rev Mod Phys **82**, 729 (2010)

Plasmonics = metal nano-optics

- Nanoparticles
- Metal-dielectric interfaces
- Nanowires
- Optical antennas
- Arrays & metasurfaces

Plasmonics for Biophotonics

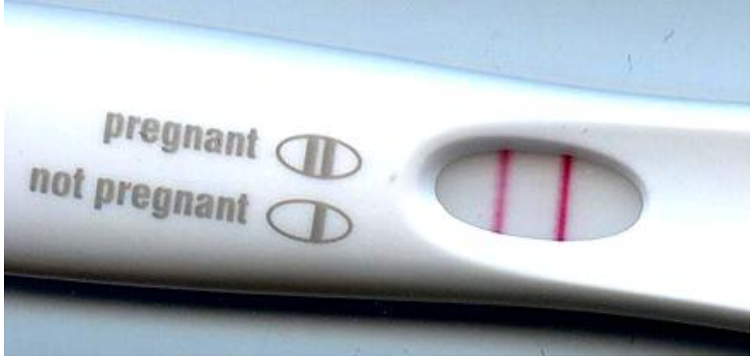
- Sensors
- Enhanced photoemission
- Thermoplasmonics
- Optical Tweezers

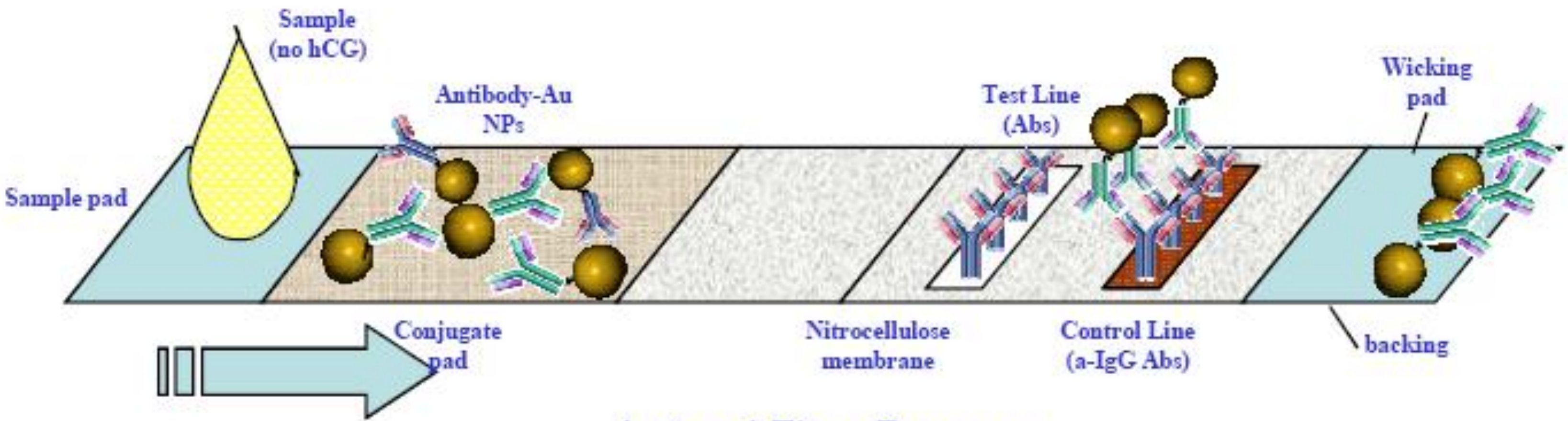
Plasmonics for Biophotonics

- Sensors
- Enhanced photoemission
- Thermoplasmonics
- Optical Tweezers

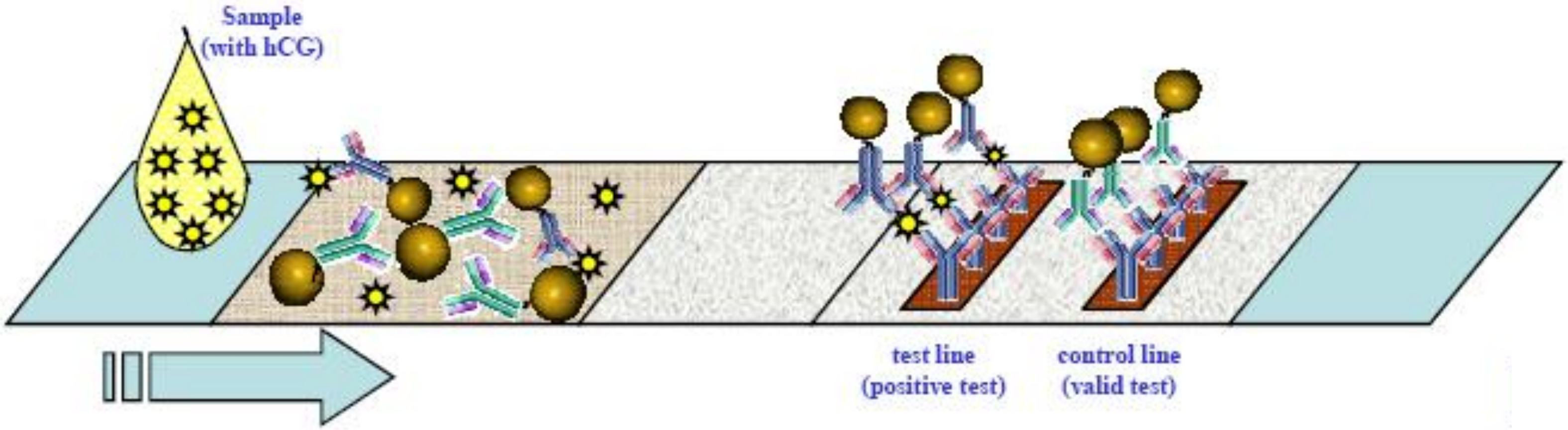
Pregnancy test:

Bioplasmonics best-seller





Lateral Flow Process

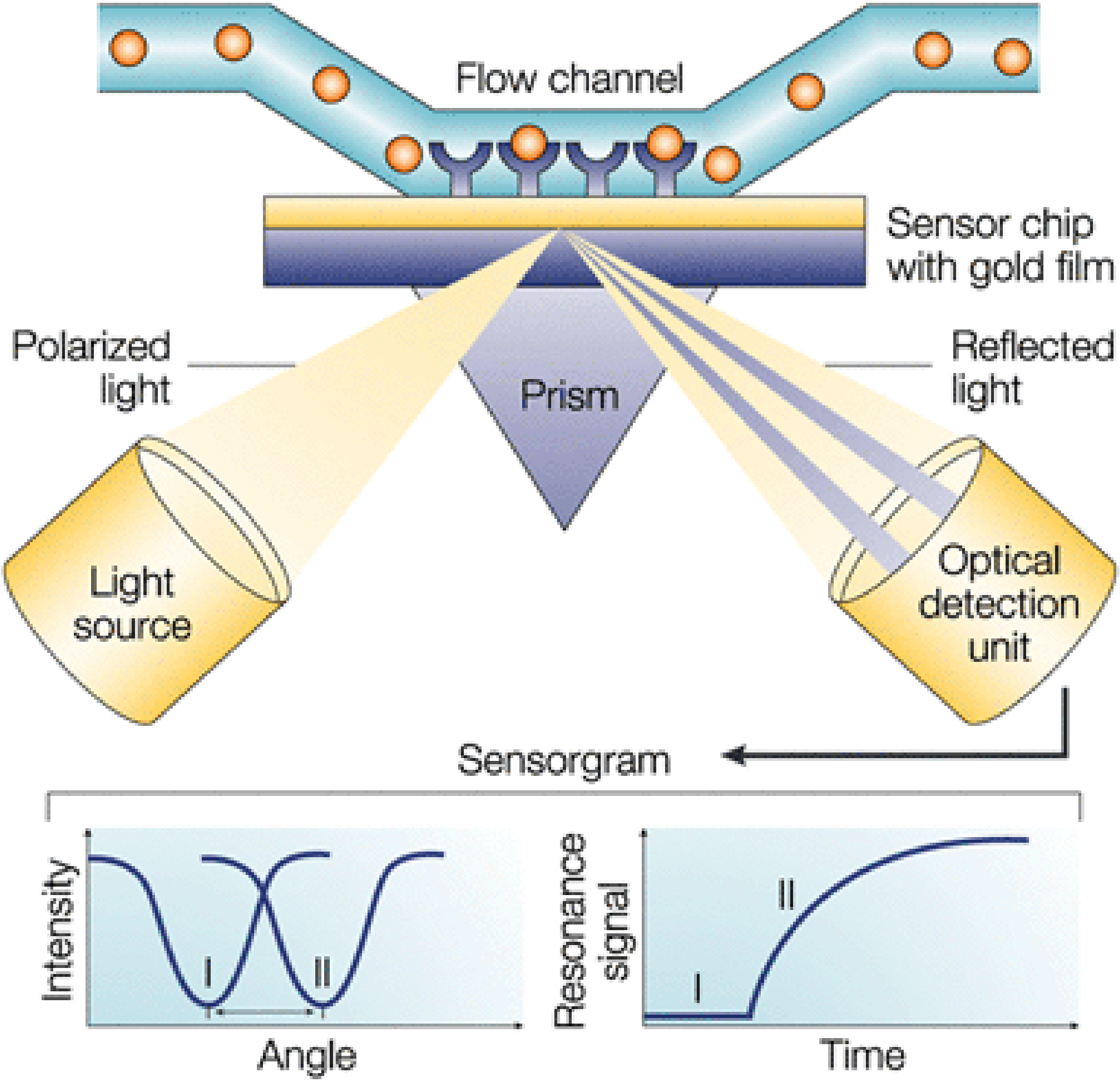


Lateral Flow Process

Surface plasmon resonance sensors

- Label-free molecular detection
- Real time
- Selective binding of biomolecules on gold surface

Surface plasmon resonance sensors

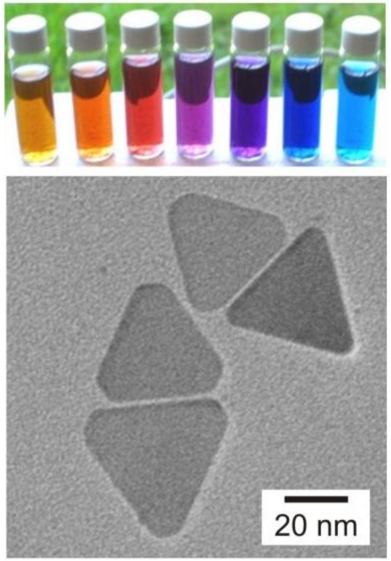


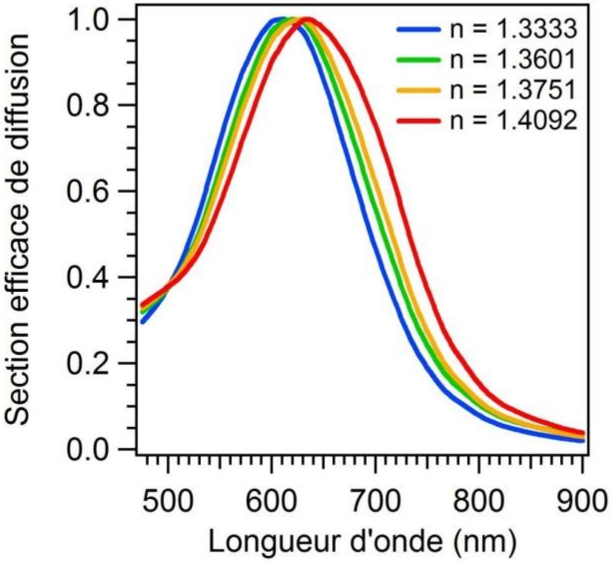
$$k_{x,SP} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}$$

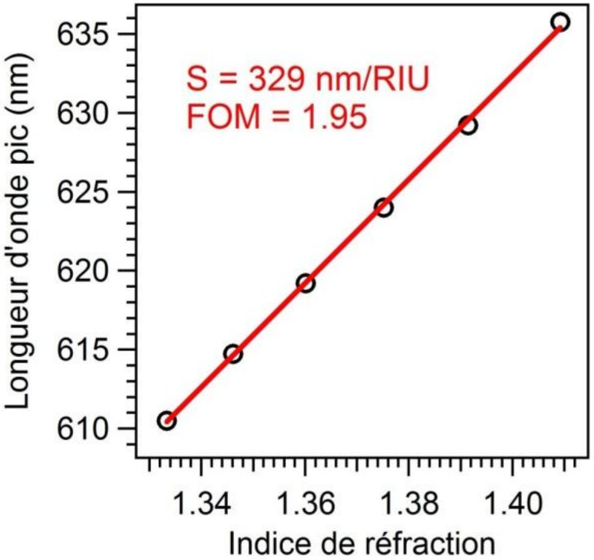
Local Surface Plasmon Resonance Sensor

Single colloidal nanoparticles

- Stronger localization of EM field on surface
- Ease-of-use





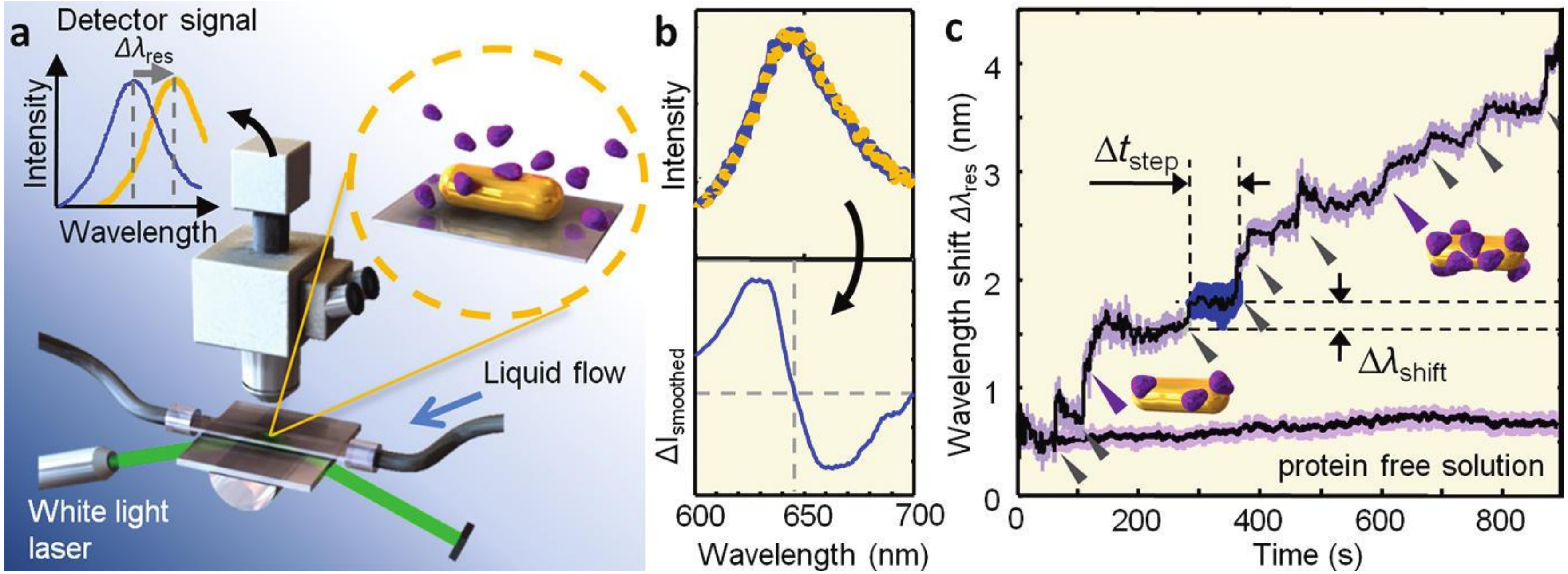


$$\alpha(\omega) = 4\pi\varepsilon_{ref}a^{3}\,\frac{\varepsilon_{gold}(\omega) - \boxed{\varepsilon_{ref}}}{\varepsilon_{gold}(\omega) + 2\boxed{\varepsilon_{ref}}}$$

Mayer and Hafner, Chem Rev **111** 3828 (2011)

Local Surface Plasmon Resonance Sensor

Single molecule detection with gold nanorods

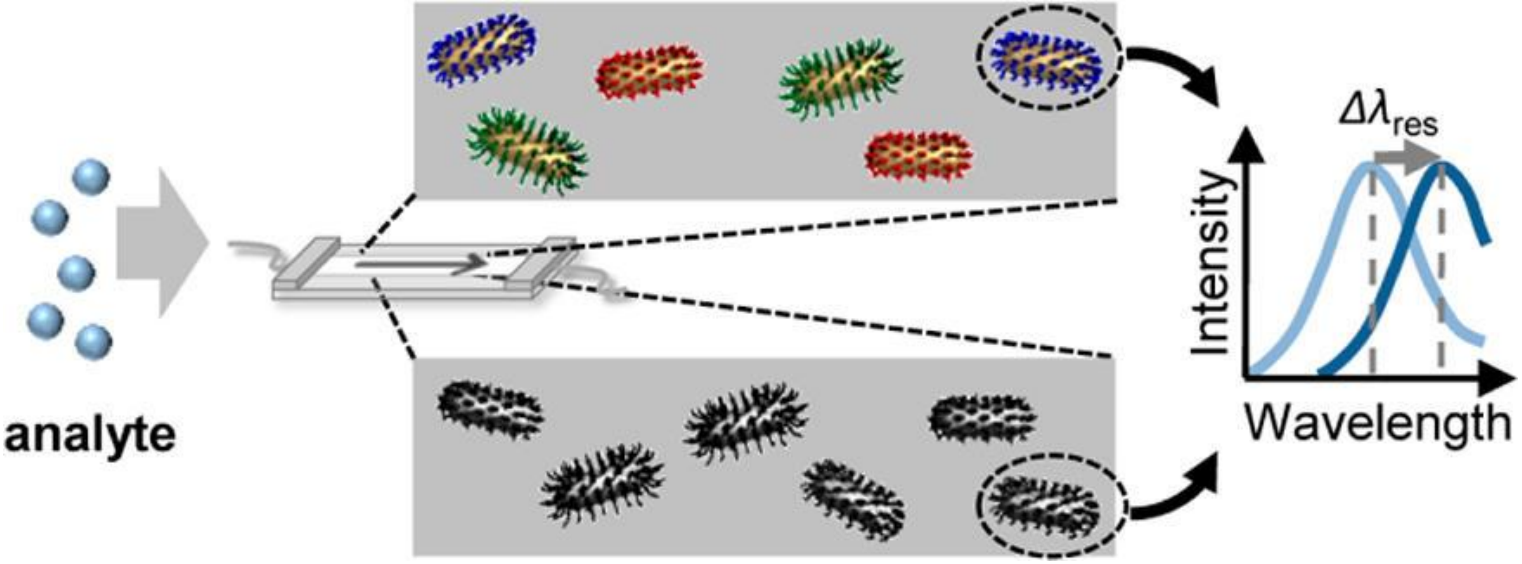


Ament et al, Nano Lett **12** 1092 (2012)

Local Surface Plasmon Resonance Sensor

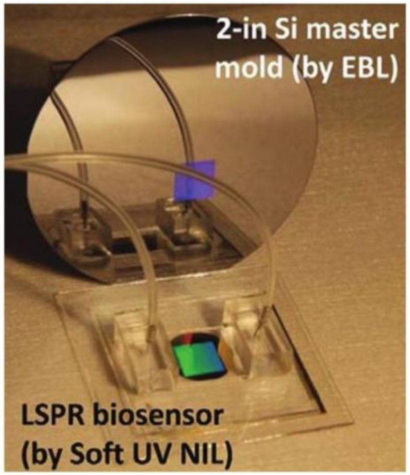
Current challenges

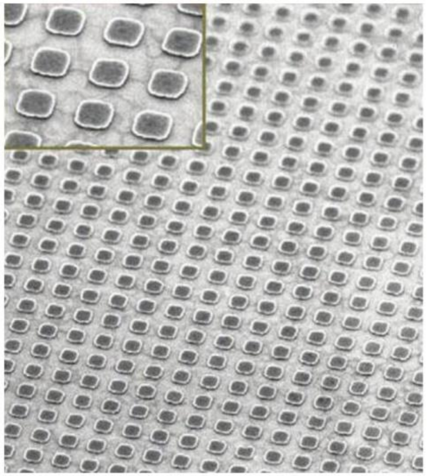
- Multiplexing / high throughput
- Recycling substrates
- Increasing speed

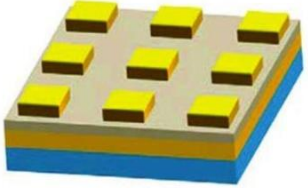


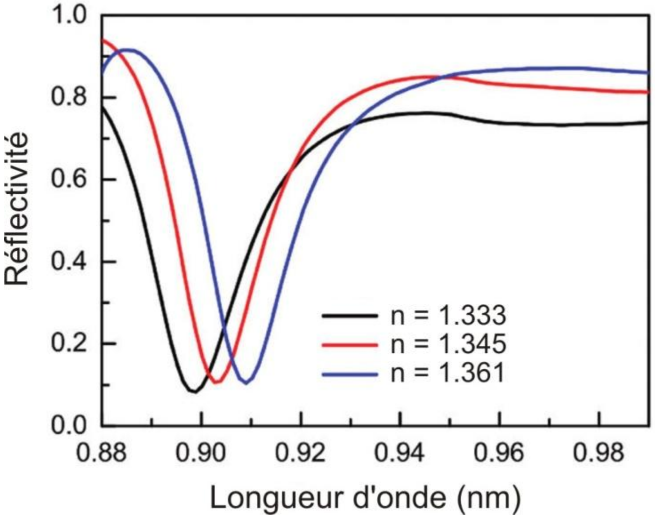
Rosman et al, Nano Lett **13** 3243 (2013)

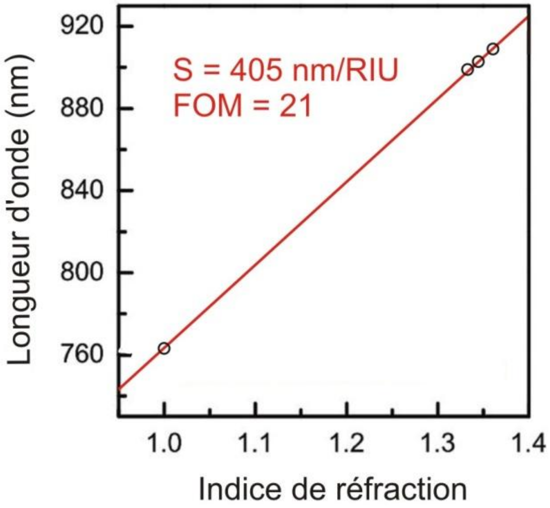
Combined structures – soft imprint lithography











Cattoni et al, Nano Lett **11** 3557 (2011)

Plasmonics for Biophotonics

- Sensors
- **Enhanced photoemission**
- Thermoplasmonics
- Optical Tweezers

A few typical figures…

Size of a molecule ~ 1 nm

Cross-section ~ 1 nm² = 10^{-14} cm²
for fluorescence σ ~ 10^{-16} cm²
for Raman scattering σ ~ 10^{-30} cm²

Excitation intensity : 1 mW = 2.5 10^{15} photons per second

Focus on a 500nm diameter spot : I = 10^{24} phot/s/cm²

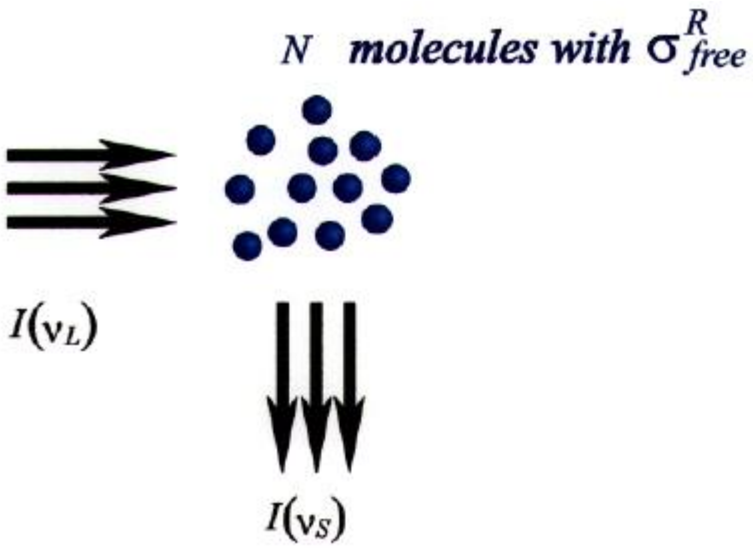
Max. single molecule fluorescence : σ I = 10^{8} phot/s = 40 pW

Max single molecule Raman signal : σ I = 10^{-6} phot/s = …

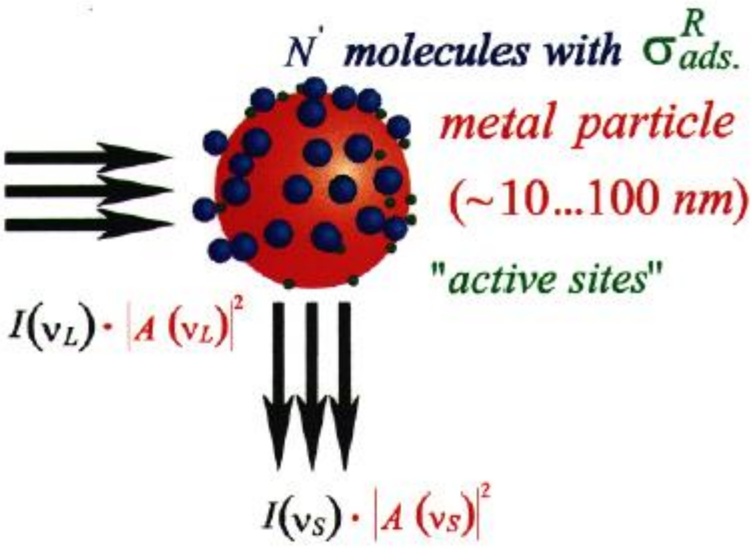
SERS : Surface Enhanced Raman Scattering

Free Molecules

Molecules on SERS clusters



$$I_{NRS}(\nu_S) = N \cdot I(\nu_L) \cdot \sigma^R_{free}$$



$$I_{SERS}(\nu_S) = N' \cdot I(\nu_L) \cdot |A(\nu_L)|^2 \cdot |A(\nu_S)|^2 \cdot \sigma^R_{ads.}$$

Enhancement of the excitation field

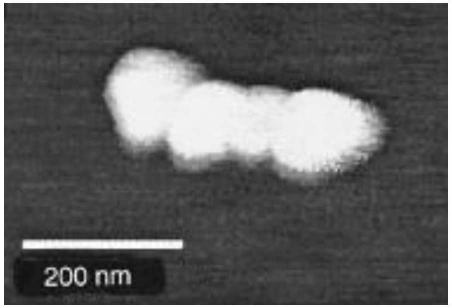
Enhancement of the signal field

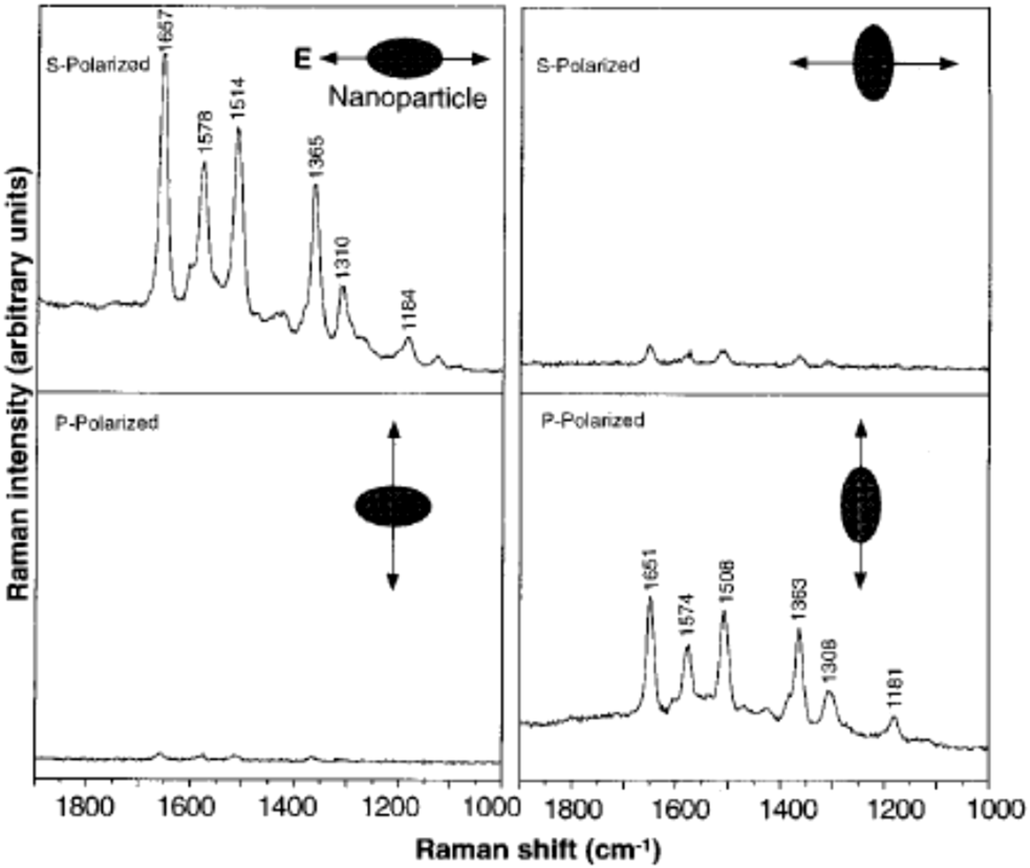
Enhancement of the absorption cross section

Kneipp et al,
J. Phys.: Condens. Matter
14 R597 (2002)

SERS : Surface Enhanced Raman Scattering

Electromagnetic enhancement ➔ towards single molecule detection

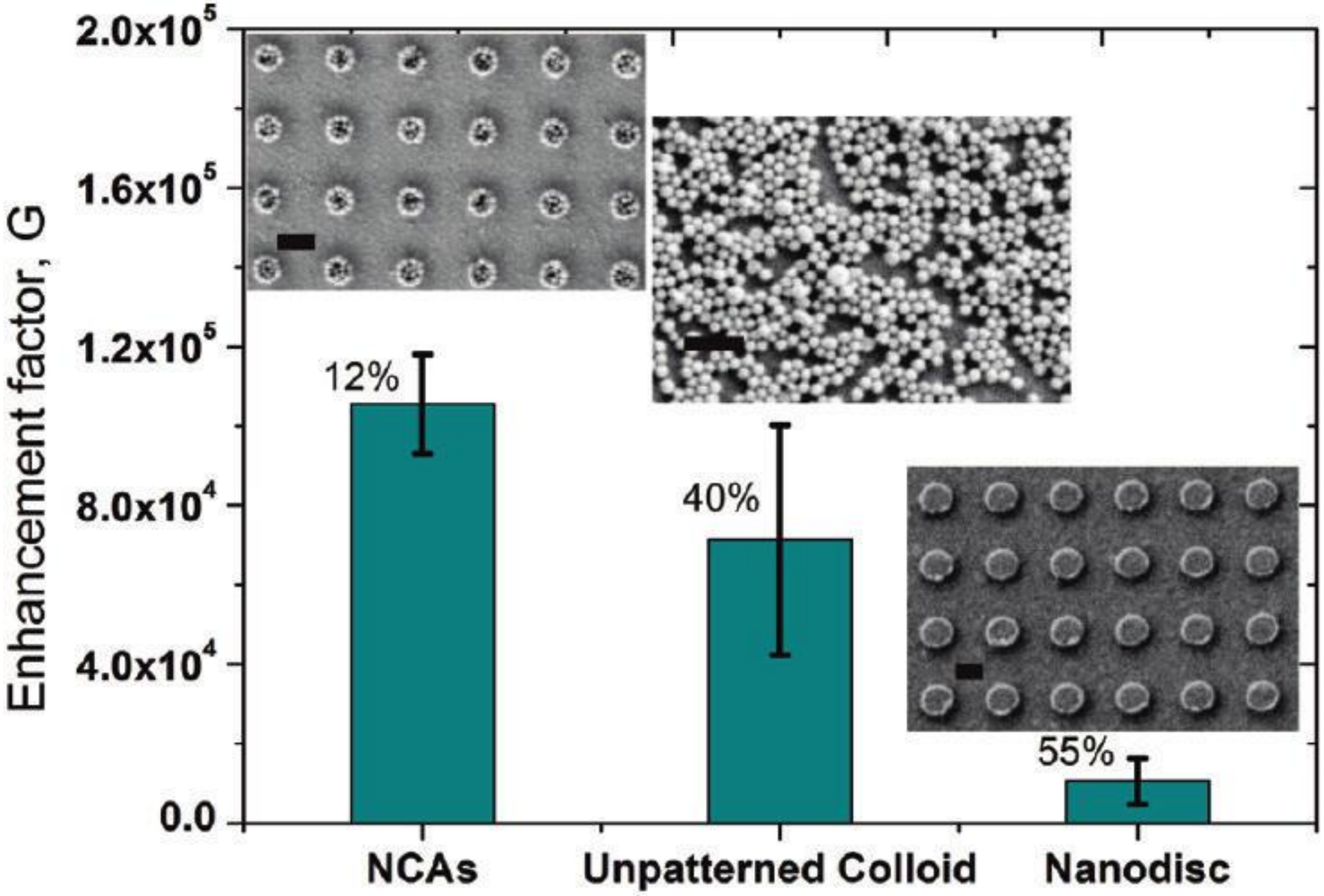




Nie and Emory
Science **275** 1102 (1997)

SERS : Surface Enhanced Raman Scattering

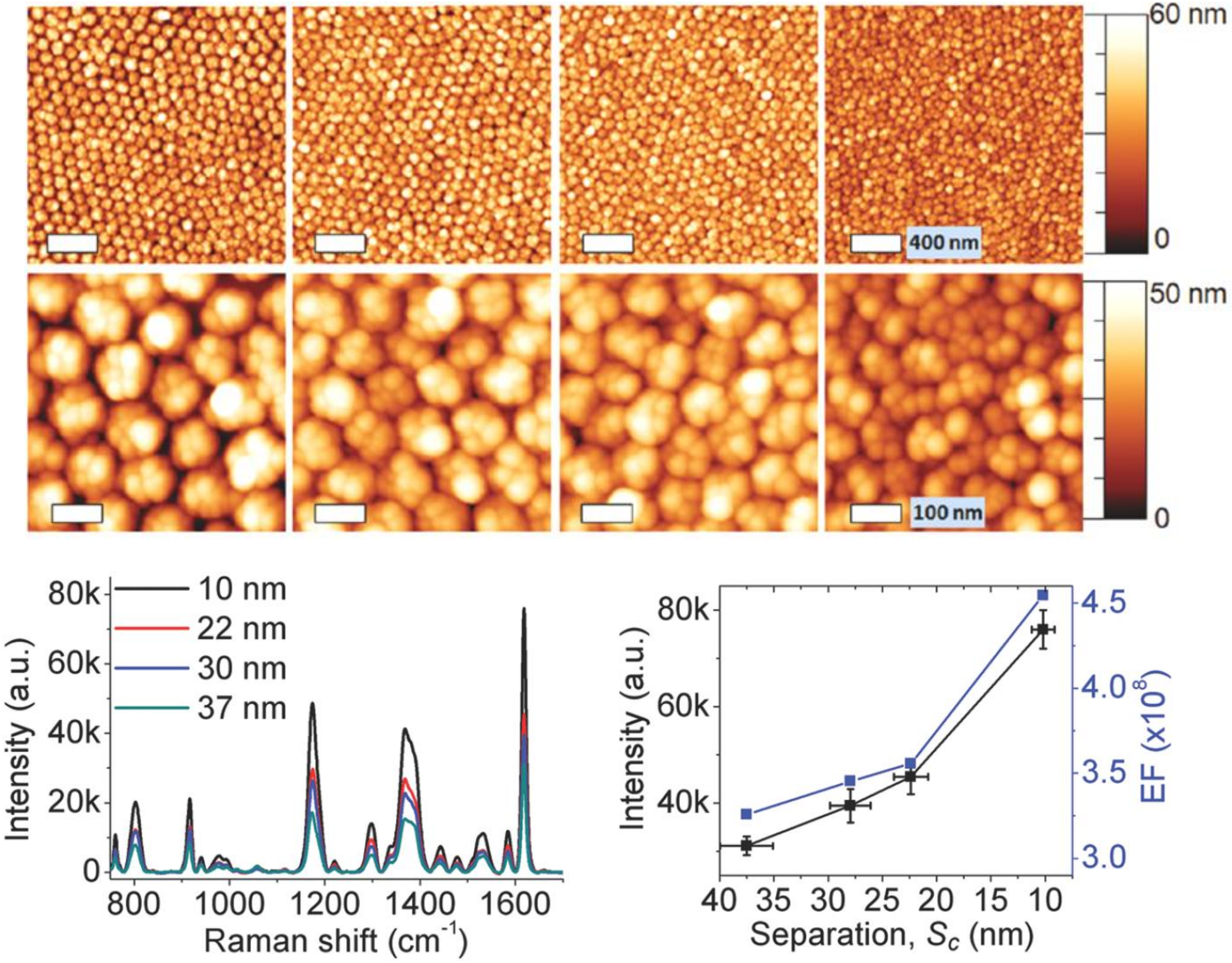
Reproducible substrates



B. Yan et al, ACS Nano **3** 1190 (2009)

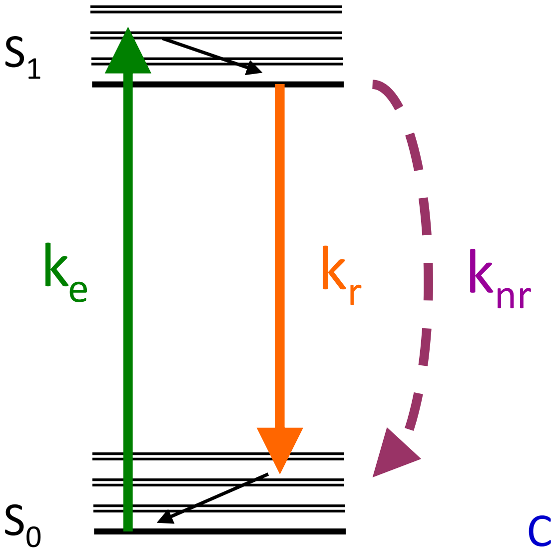
SERS : Surface Enhanced Raman Scattering

Reproducible substrates



Ling Yap al, ACS Nano **6** 2056 (2012)

Fluorescence



Detected fluorescence

$$F = \kappa\, k_r\, N_1$$

$$= \kappa \; \frac{k_r}{k_r + k_{nr}} \; \frac{k_e}{1 + k_e/(k_r + k_{nr})} \, N_{tot}$$

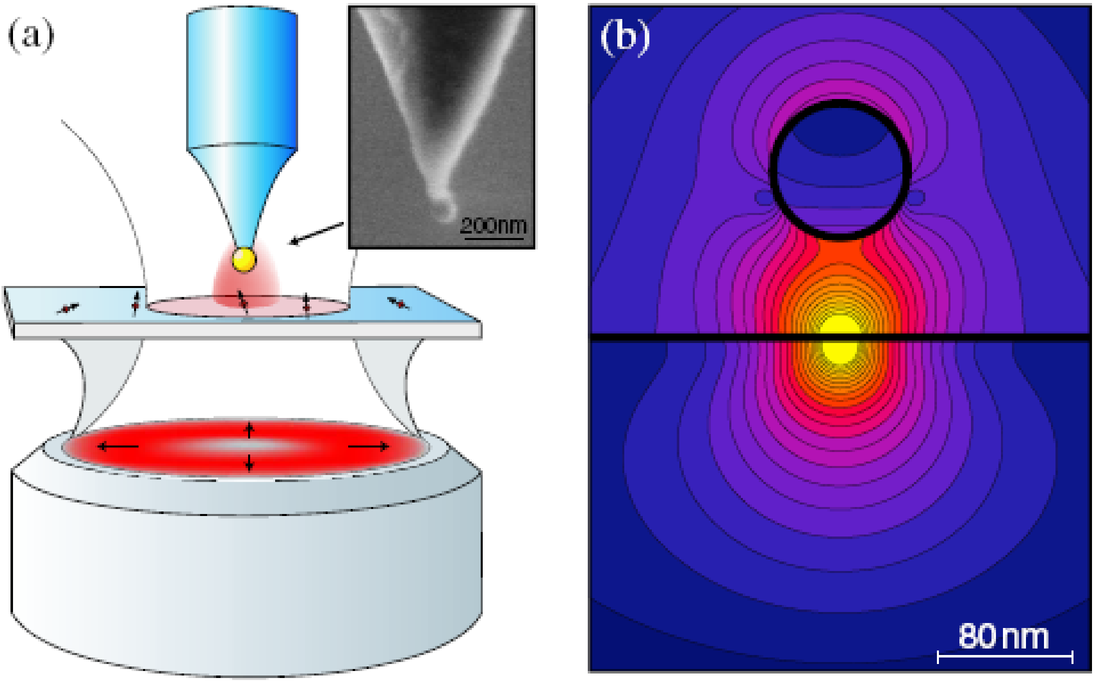
Collection efficiency

Quantum yield

Excitation intensity

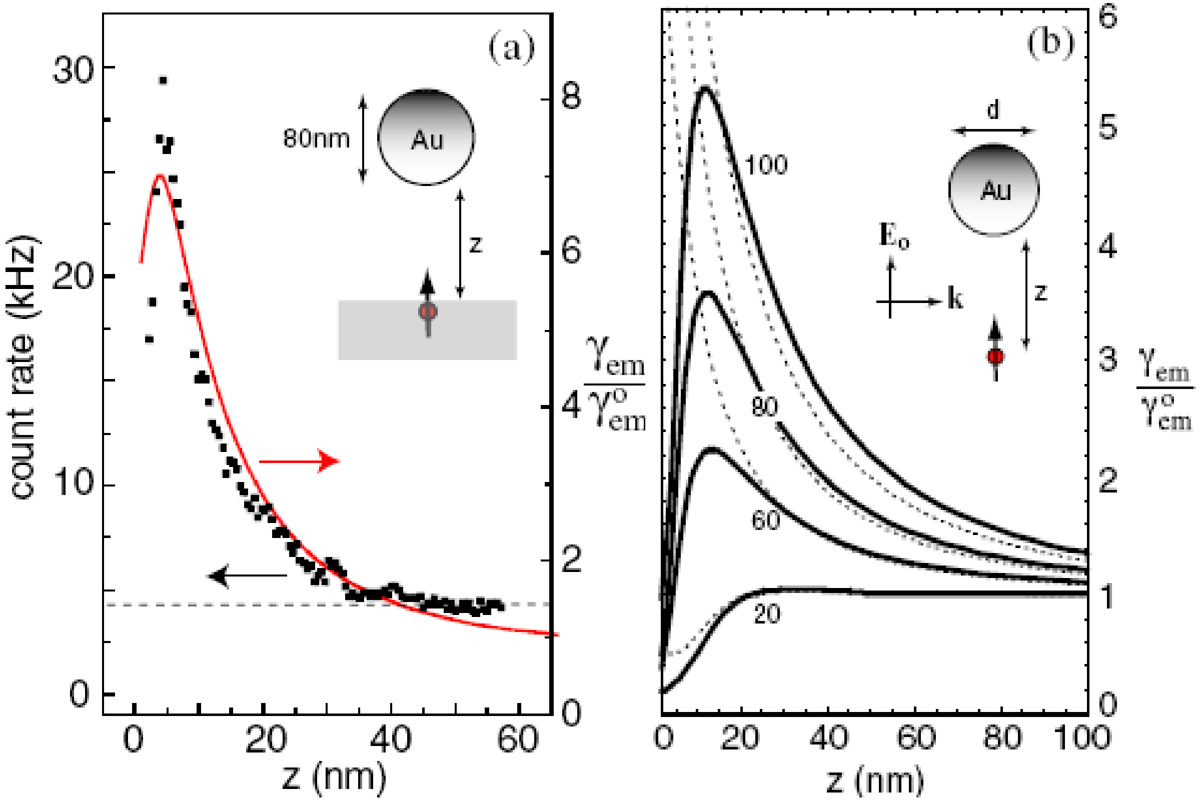
Affected by plasmonic structure

Single molecule fluorescence enhanced by a single gold nanoparticle



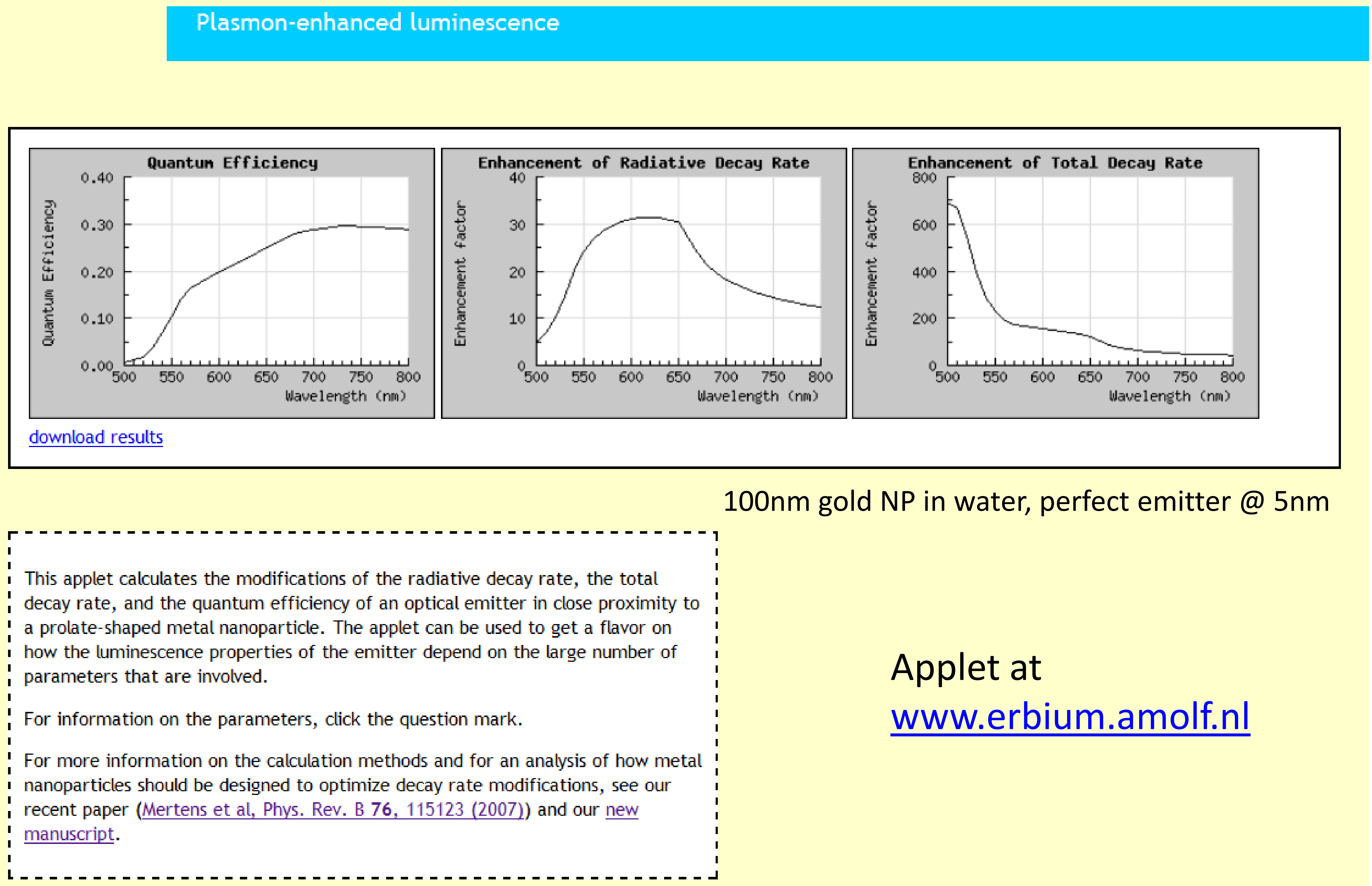
P. Anger et al, Phys Rev Lett **96** 113002 (2006)

Single molecule fluorescence enhanced by a single gold nanoparticle



P. Anger et al, Phys Rev Lett **96** 113002 (2006)

Single molecule fluorescence enhanced by a single gold nanoparticle



Plasmon-enhanced luminescence

This applet calculates the modifications of the radiative decay rate, the total decay rate, and the quantum efficiency of an optical emitter in close proximity to a prolate-shaped metal nanoparticle. The applet can be used to get a flavor on how the luminescence properties of the emitter depend on the large number of parameters that are involved.

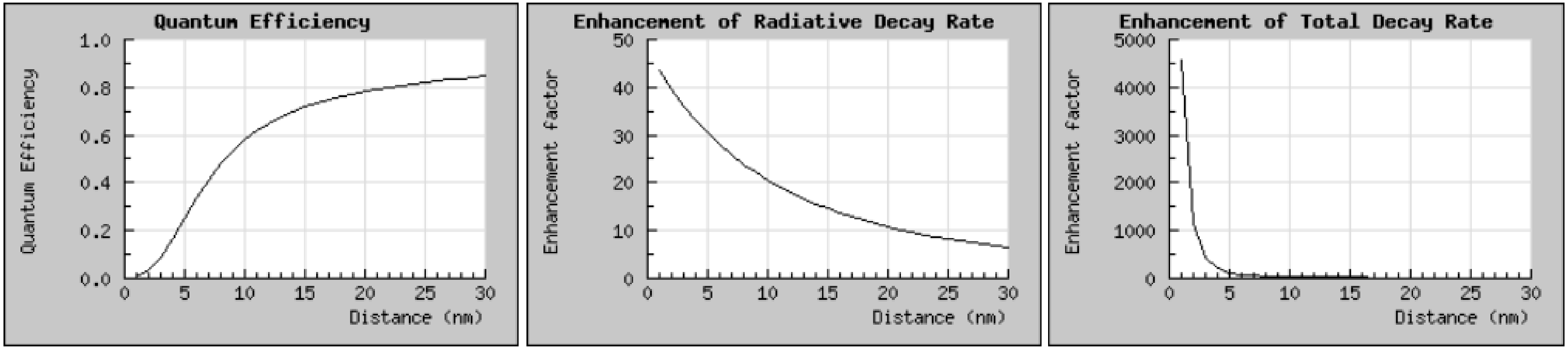
For information on the parameters, click the question mark.

For more information on the calculation methods and for an analysis of how metal nanoparticles should be designed to optimize decay rate modifications, see our recent paper (Mertens et al, Phys. Rev. B **76**, 115123 (2007)) and our new manuscript.

100nm gold NP in water, perfect emitter @ 5nm

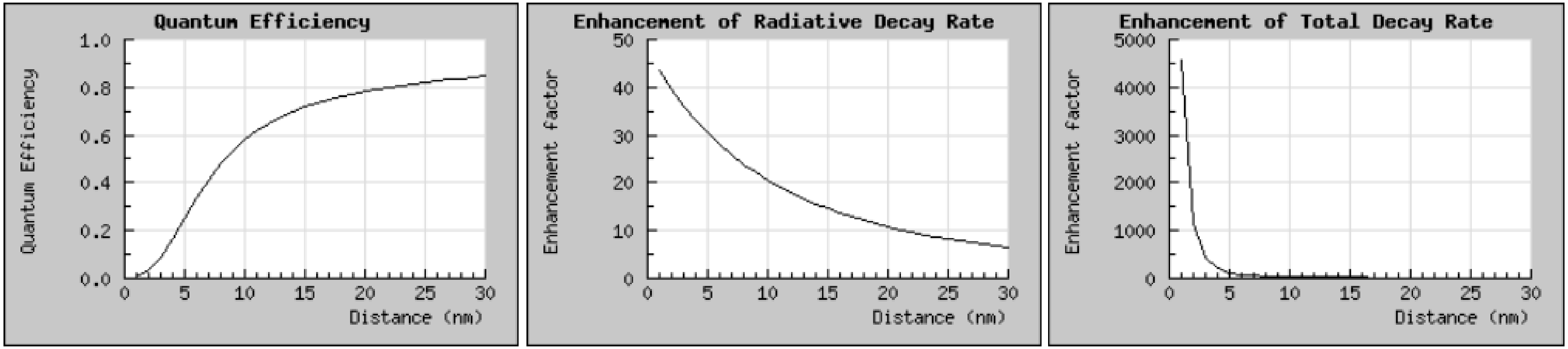
Applet at
www.erbium.amolf.nl

Single molecule fluorescence enhanced by a single gold nanoparticle

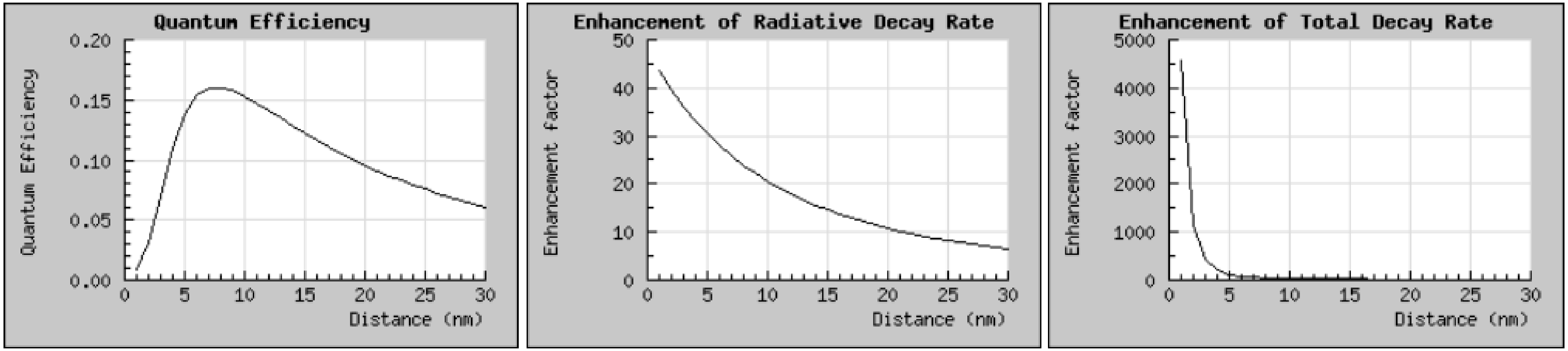


100nm gold NP in water, perfect emitter, parallel orientation, λ 650nm

Single molecule fluorescence enhanced by a single gold nanoparticle

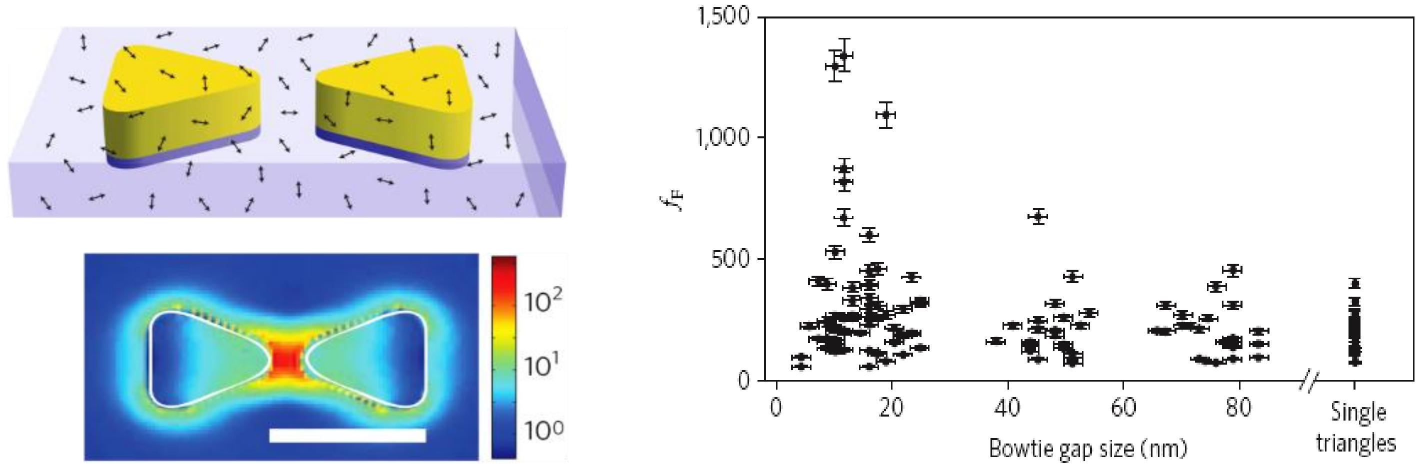


100nm gold NP in water, perfect emitter, parallel orientation, λ 650nm

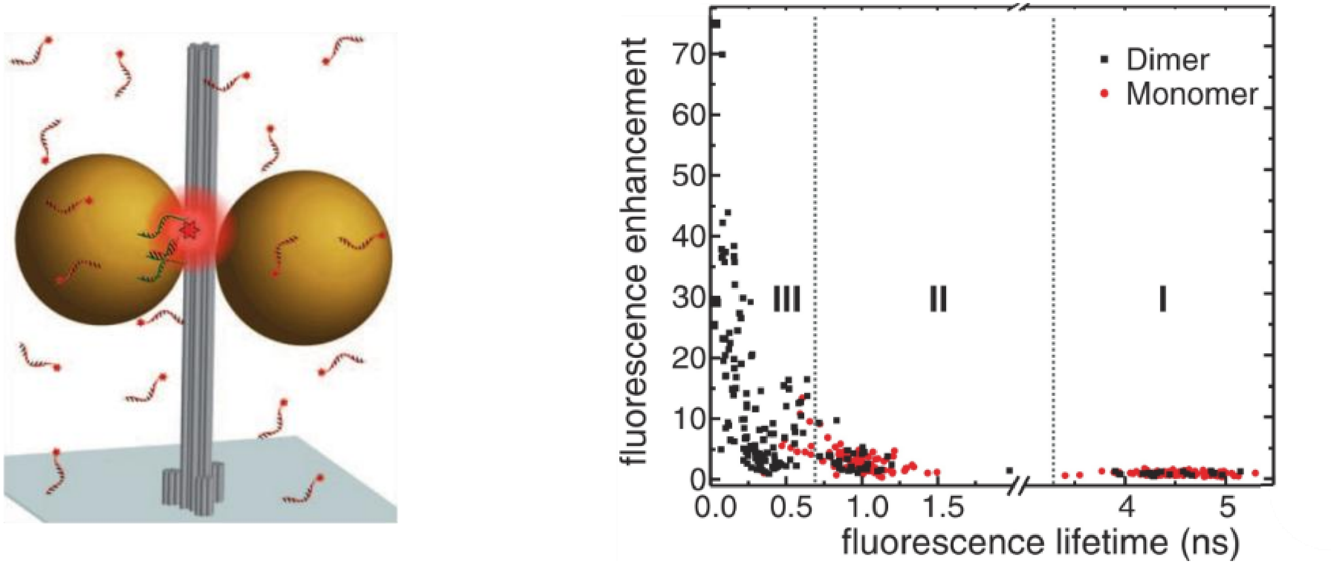


100nm gold NP in water, quantum yield 1%, parallel orientation, λ 650nm

www.erbium.amolf.nl

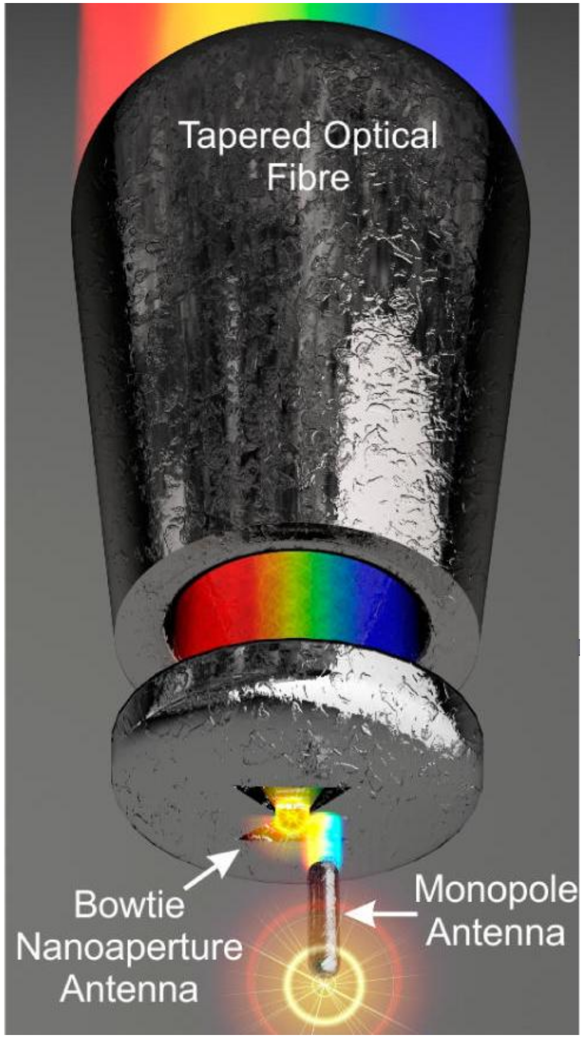


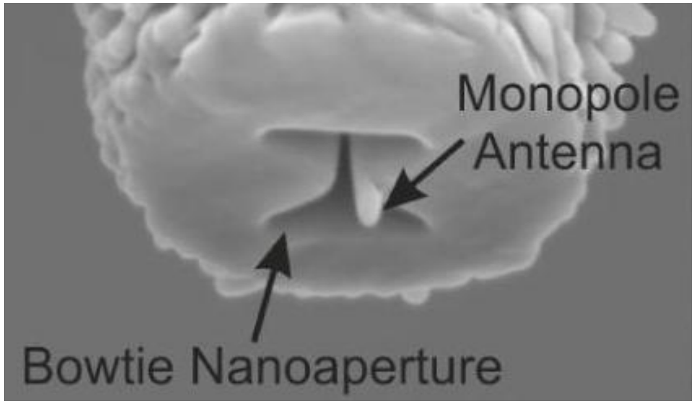
Kinkhabwala *et al*, Nature Phot. **3**, 654 (2009)

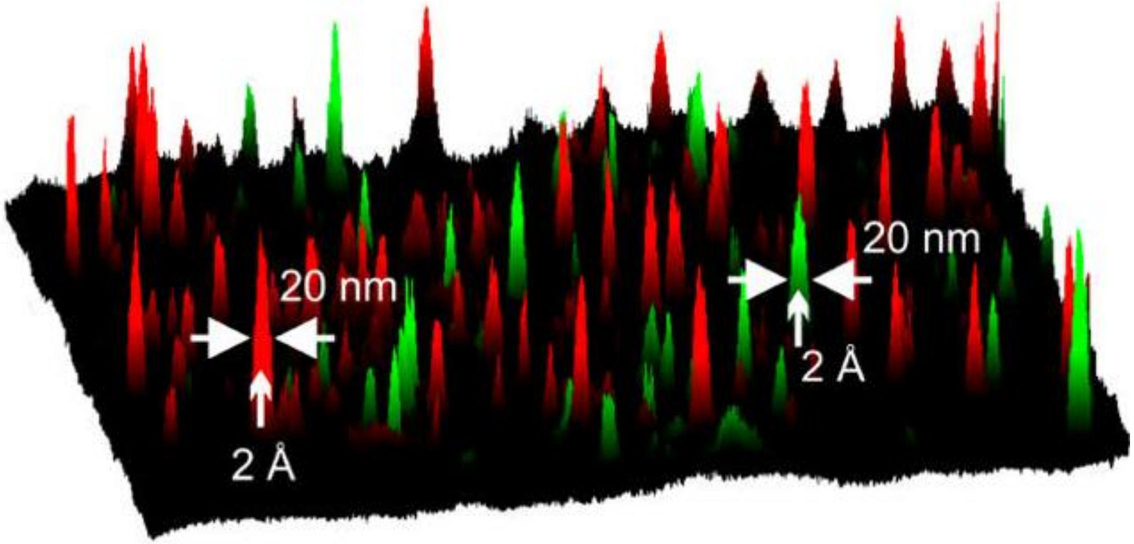


Acuna *et al*, Science. **338**, 506 (2012)

Nanoantennas combined with NSOM probes





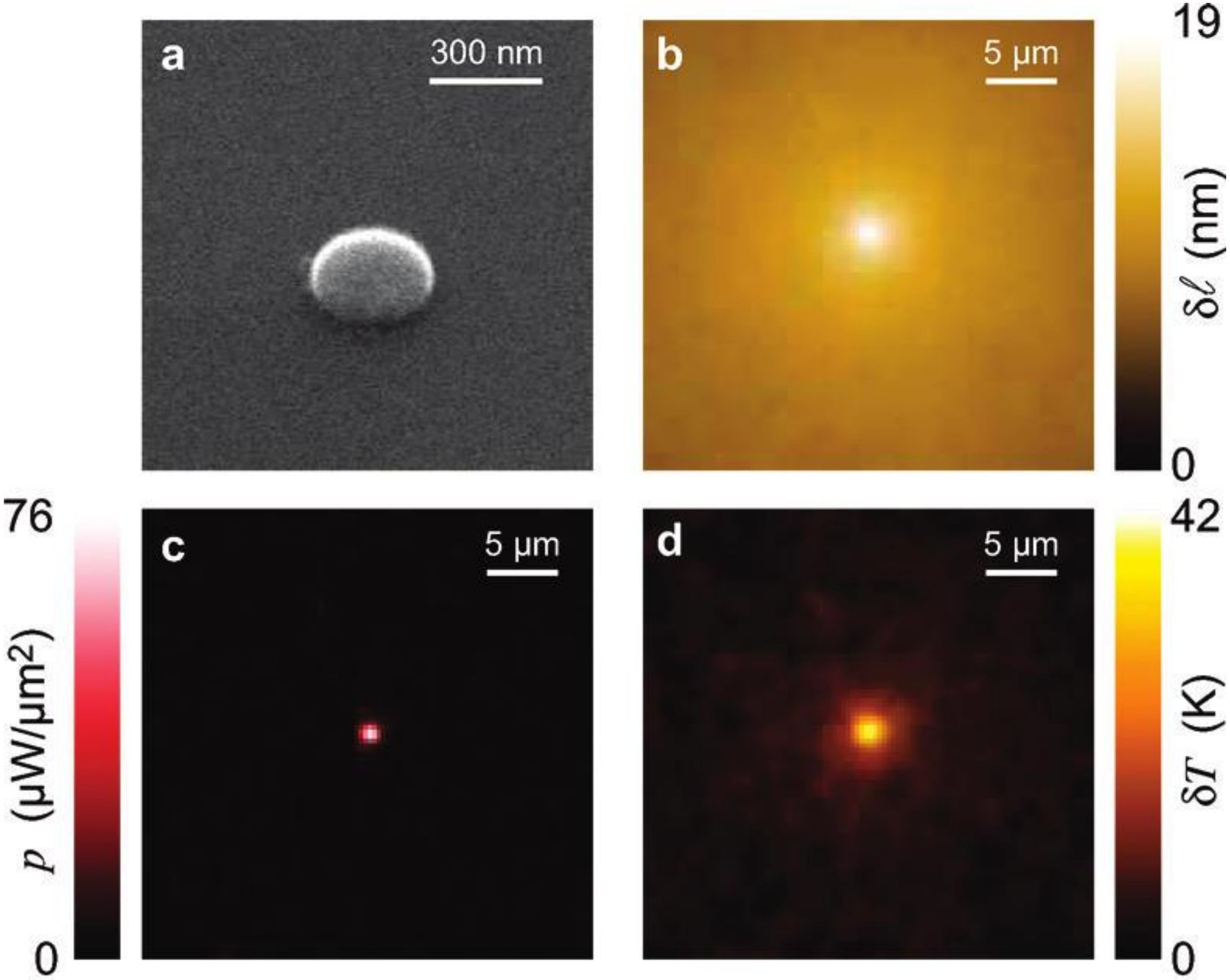


Mivelle et al, Nano Lett. **14**, 4895 (2014)

Plasmonics for Biophotonics

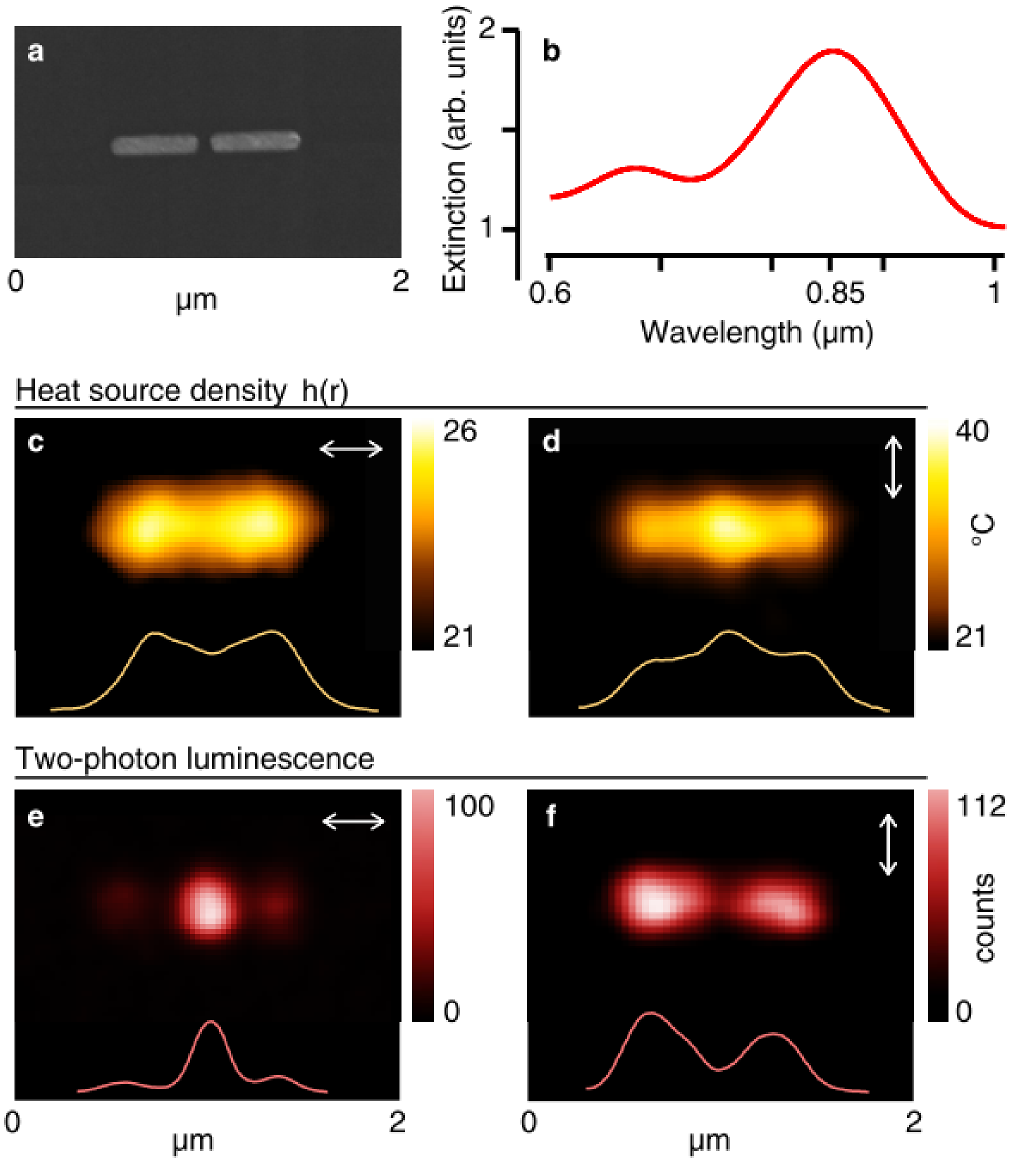
- Sensors
- Enhanced photoemission
- **Thermoplasmonics**
- Optical Tweezers

Nanosources of heat



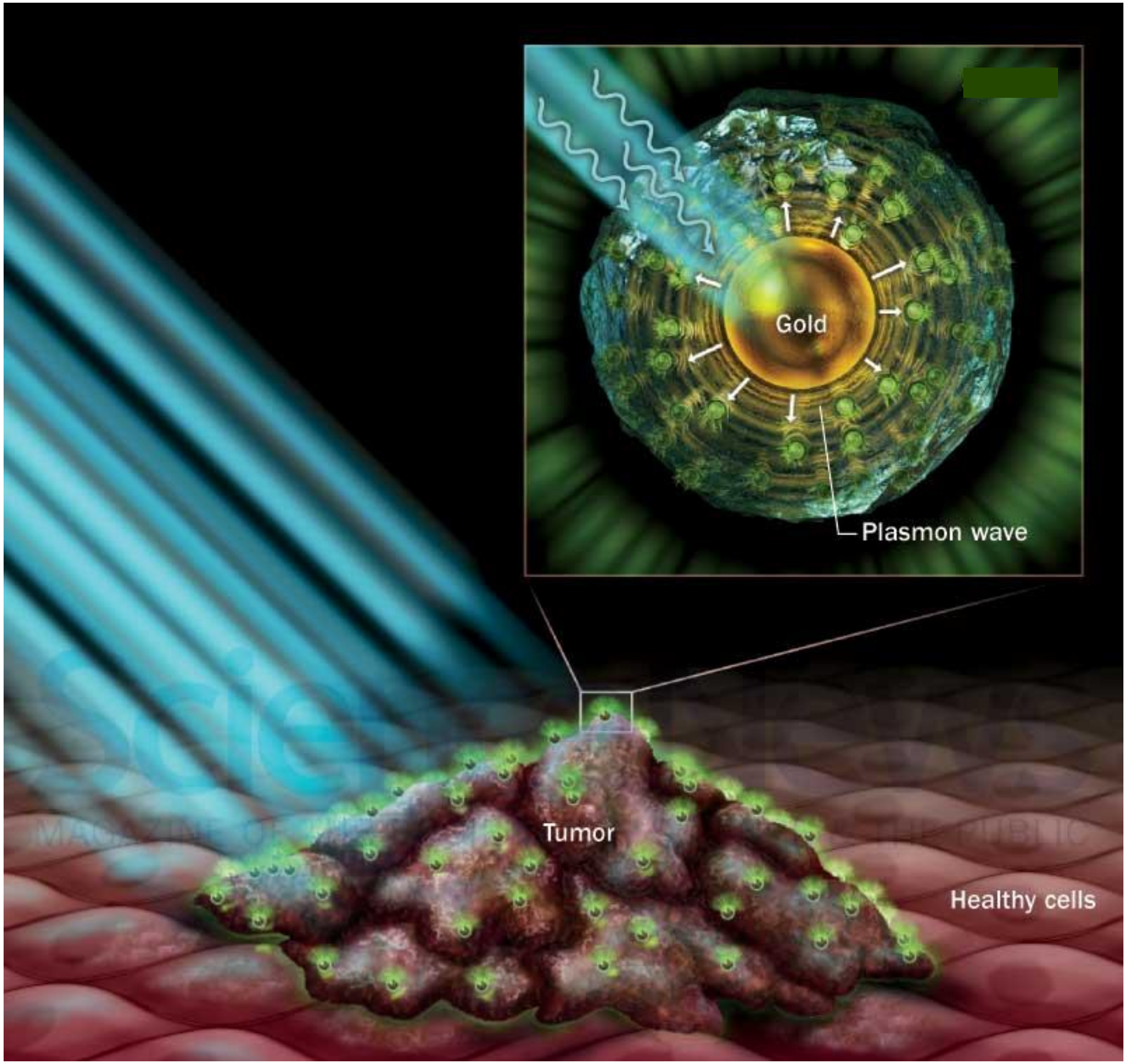
Baffou and Quidant, Laser Phot Rev. **2**, 171 (2013)

Nanosources of heat

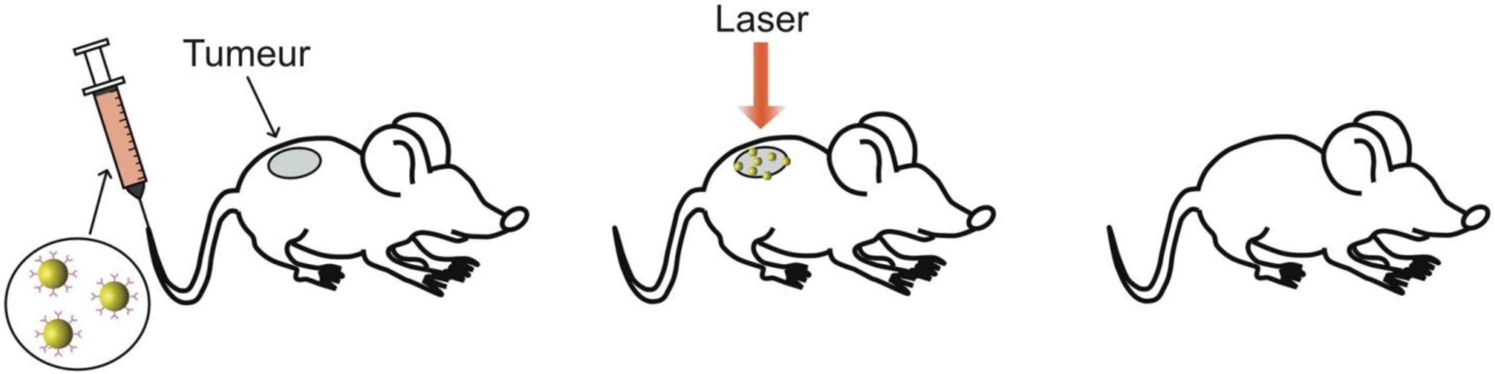


Baffou and Quidant, Laser Phot Rev. **2**, 171 (2013)

Cancer photothermal treatment



Cancer photothermal treatment

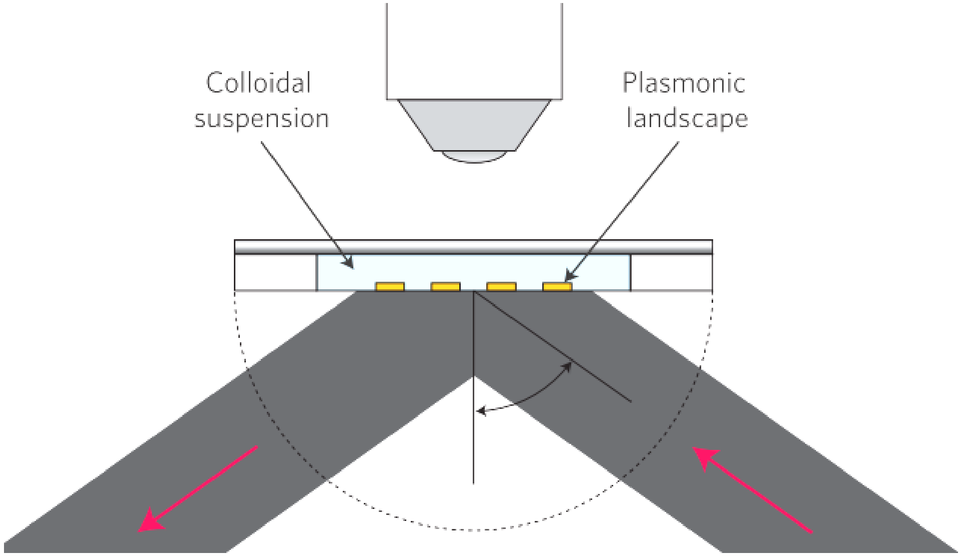


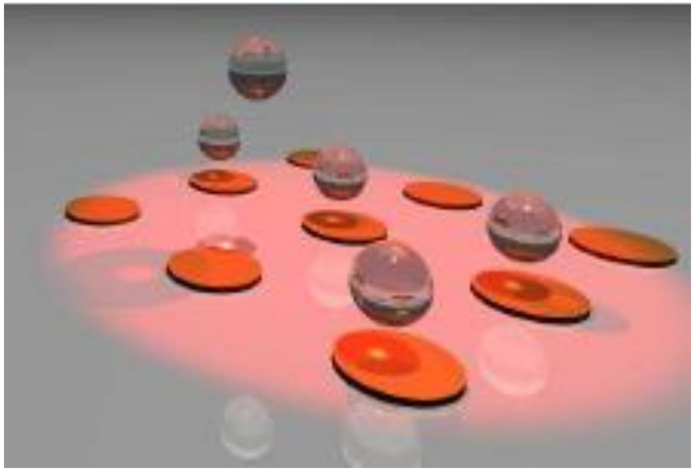
Stern et al, J Urol. **179**, 748 (2008)

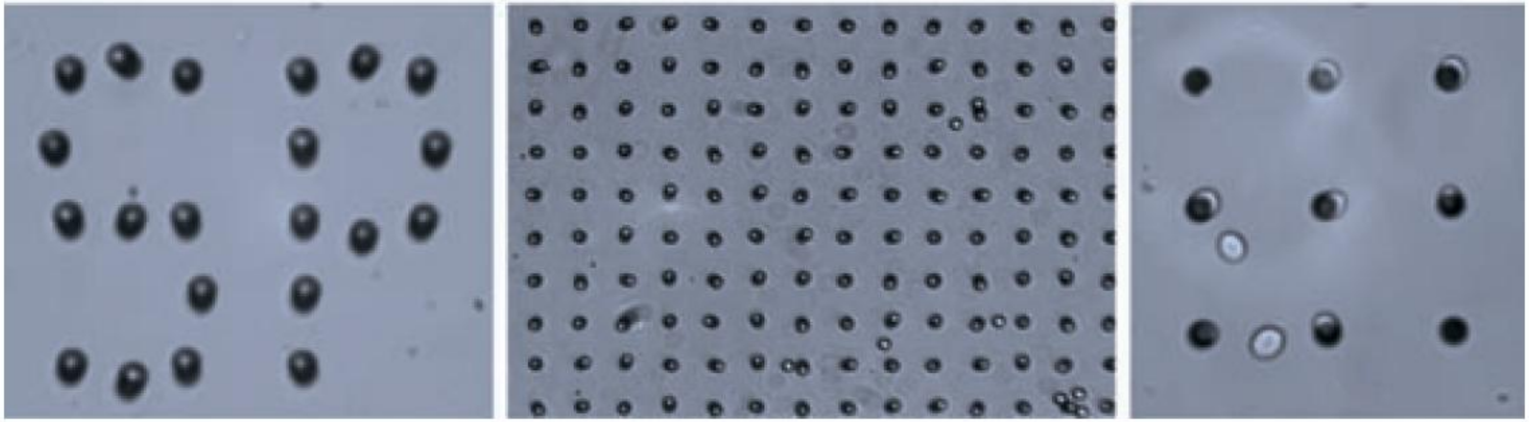
Plasmonics for Biophotonics

- Sensors
- Enhanced photoemission
- Thermoplasmonics
- **Optical Tweezers**

Local surface plasmon nano tweezers

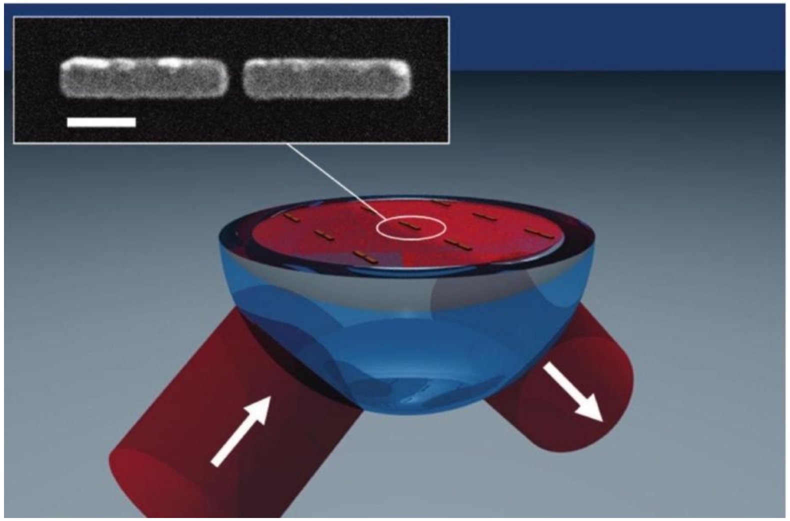


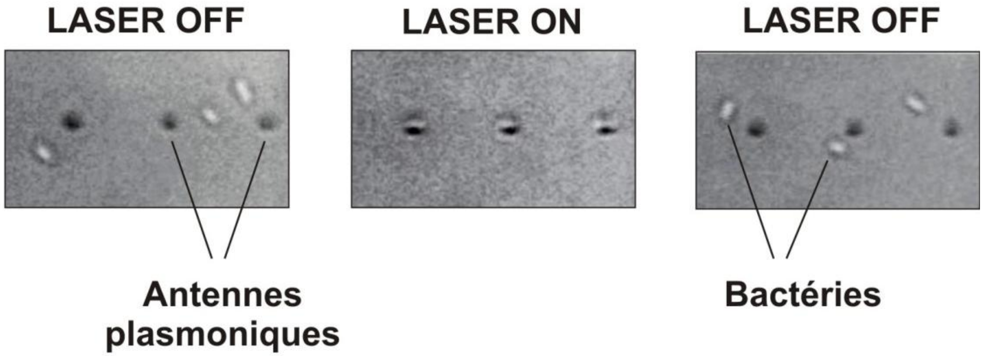


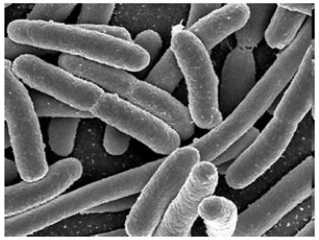


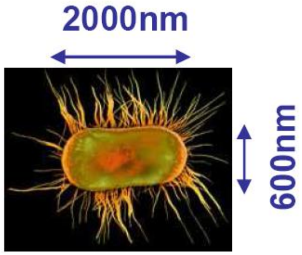
Righini et al, Nat. Phys. **3**, 477 (2007)

Bacteria trapping with nanoantennas





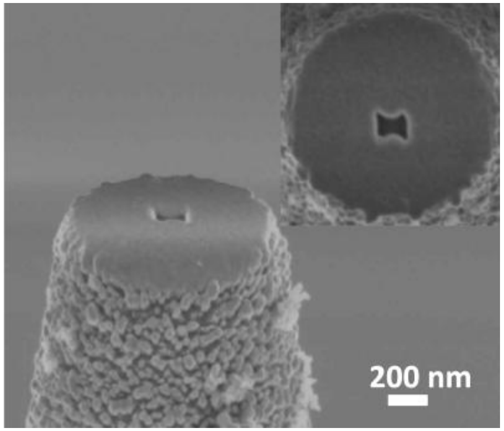


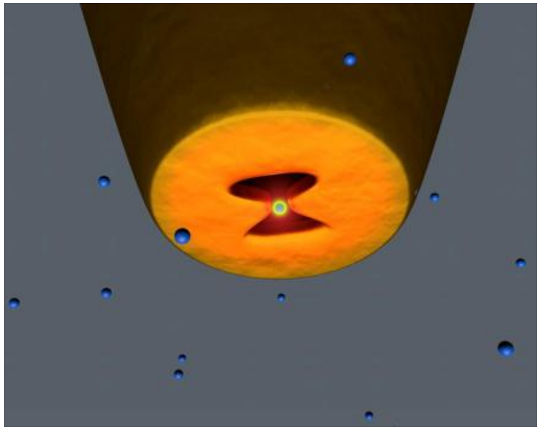


Righini et al, Nano Lett. **9**, 3387 (2009)

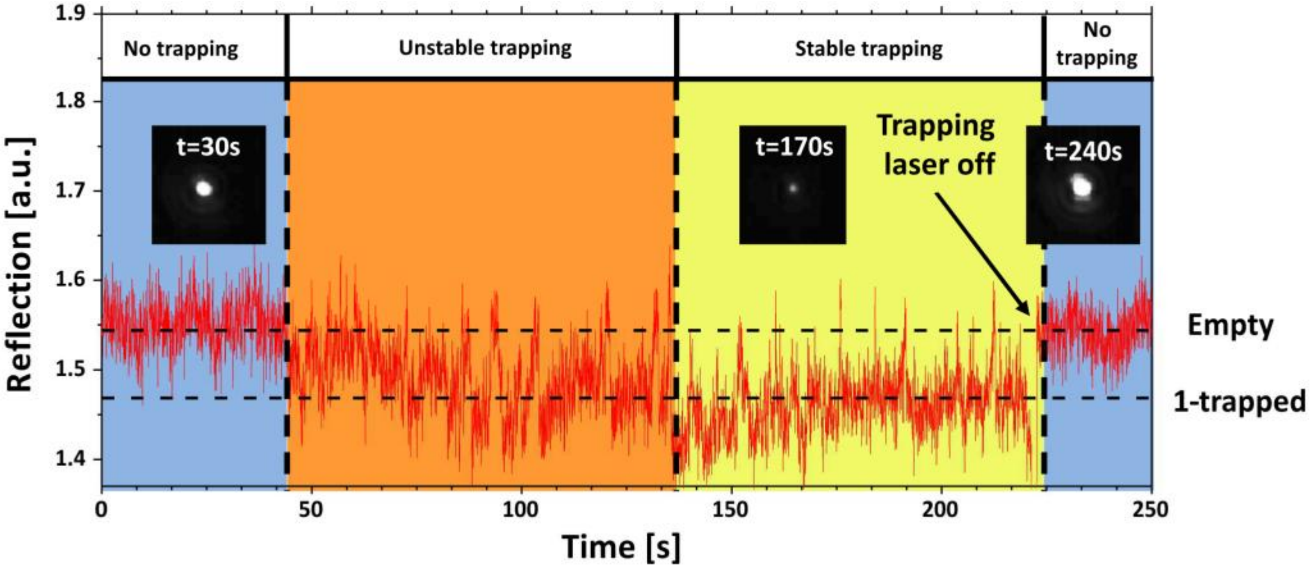
3D displacements with NSOM tweezers

Bowtie aperture at coated fiber tip





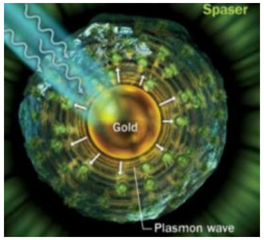
Trapping 50nm dielectric nanoparticles



Berthelot et al, Nat. Nanotech. **9**, 295 (2014)

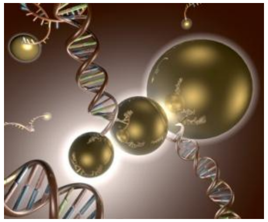
Plasmonics for Biophotonics

Main properties and applications :



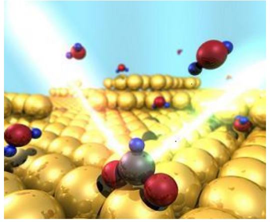
Confining light

→ trapping, photothermal effects



Intensity enhancement

→ enhanced optical emission



Sensitivity to local refractive index

→ label-free biosensors