Introduction to surface plasmon coupled fluorescence

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Plan

1. Introduction: particular plasmonic effects and their applications.

2. How to excite surface plasmon waves? Nature of surface plasmon resonance.

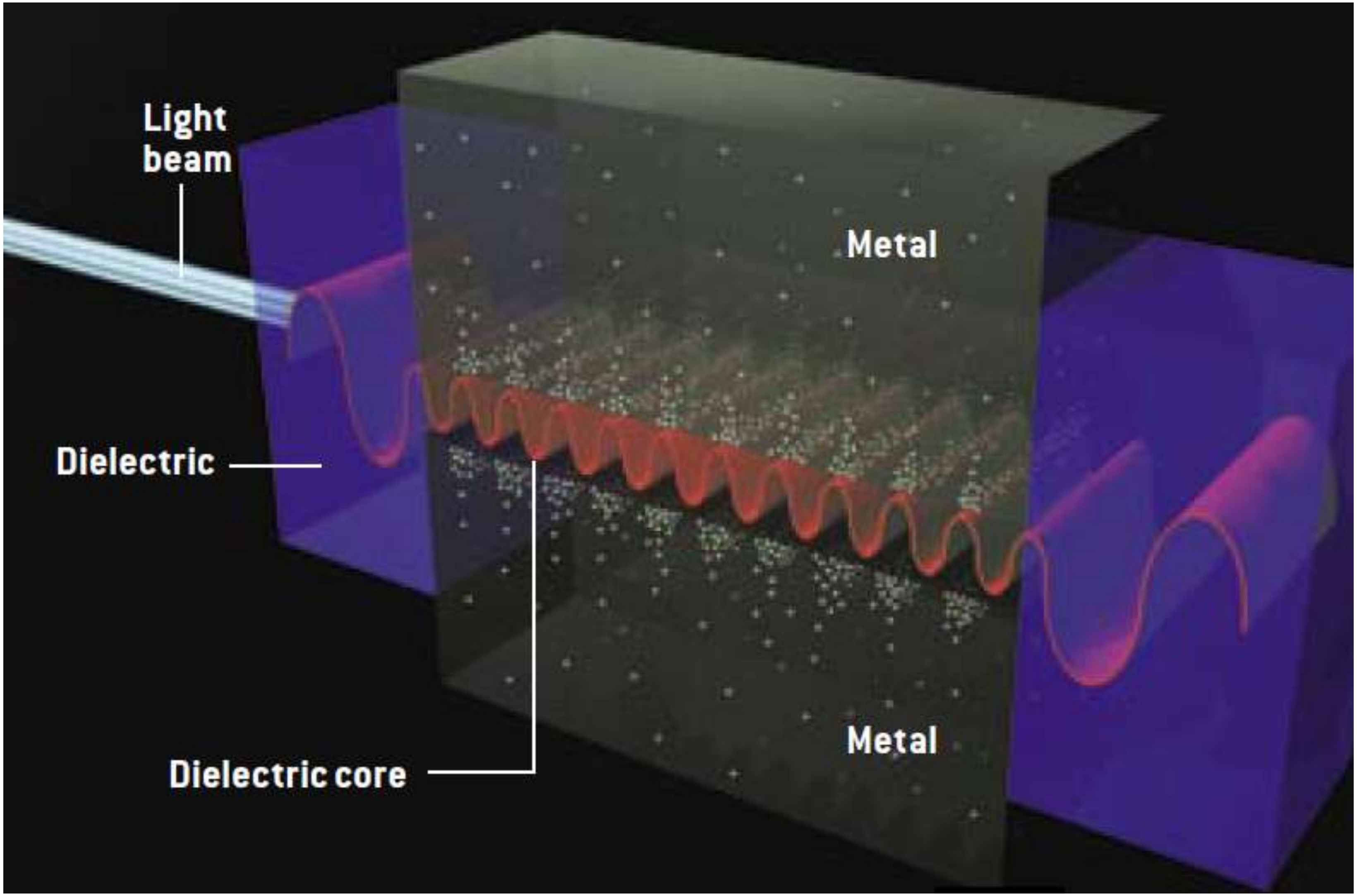
3. Excitation of plasmons by prism coupling scheme.

4. Modification of prism coupling scheme for the fluorescent materials.

5. Some knowledge about localized plasmons and different ways for excitation of plasmons.

1. Introduction: particular plasmonic effects and their applications.

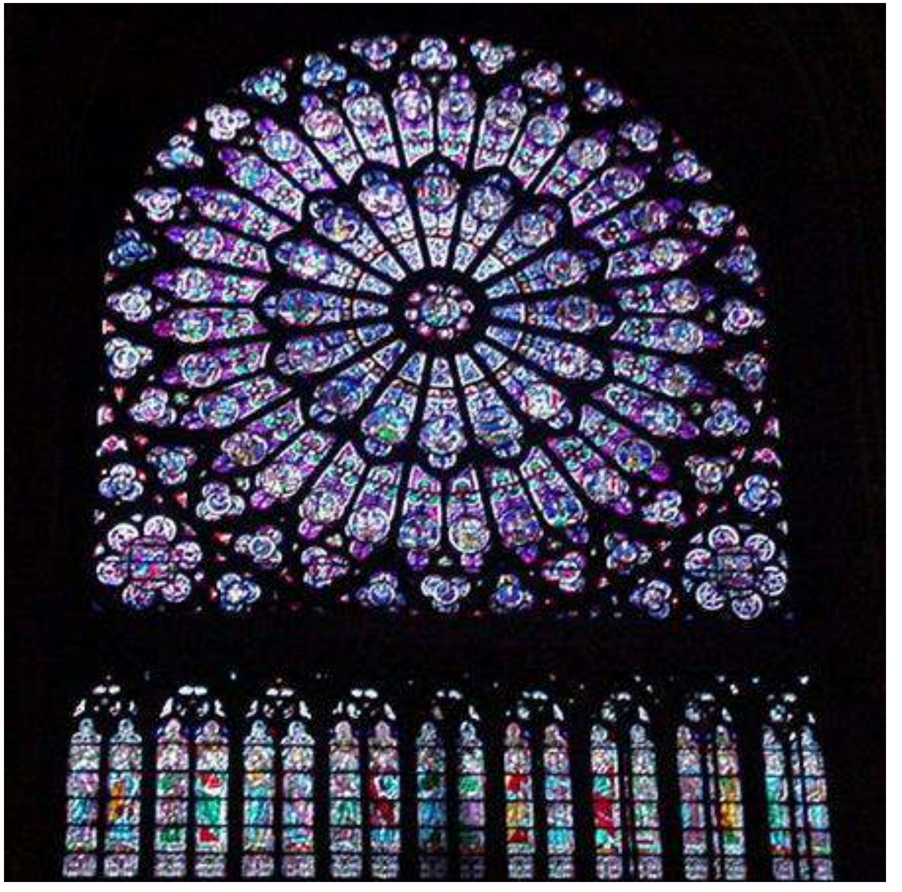
Metal-dielectric strusture: plasmon slot waveguide



Atwater H.A. / Scientific American (2007).

Ancient roots of plasmonics: Coloration effects caused by metal nanoparticles incorporated inside the glass

Lycurgus cup, 4thC AD, Rome

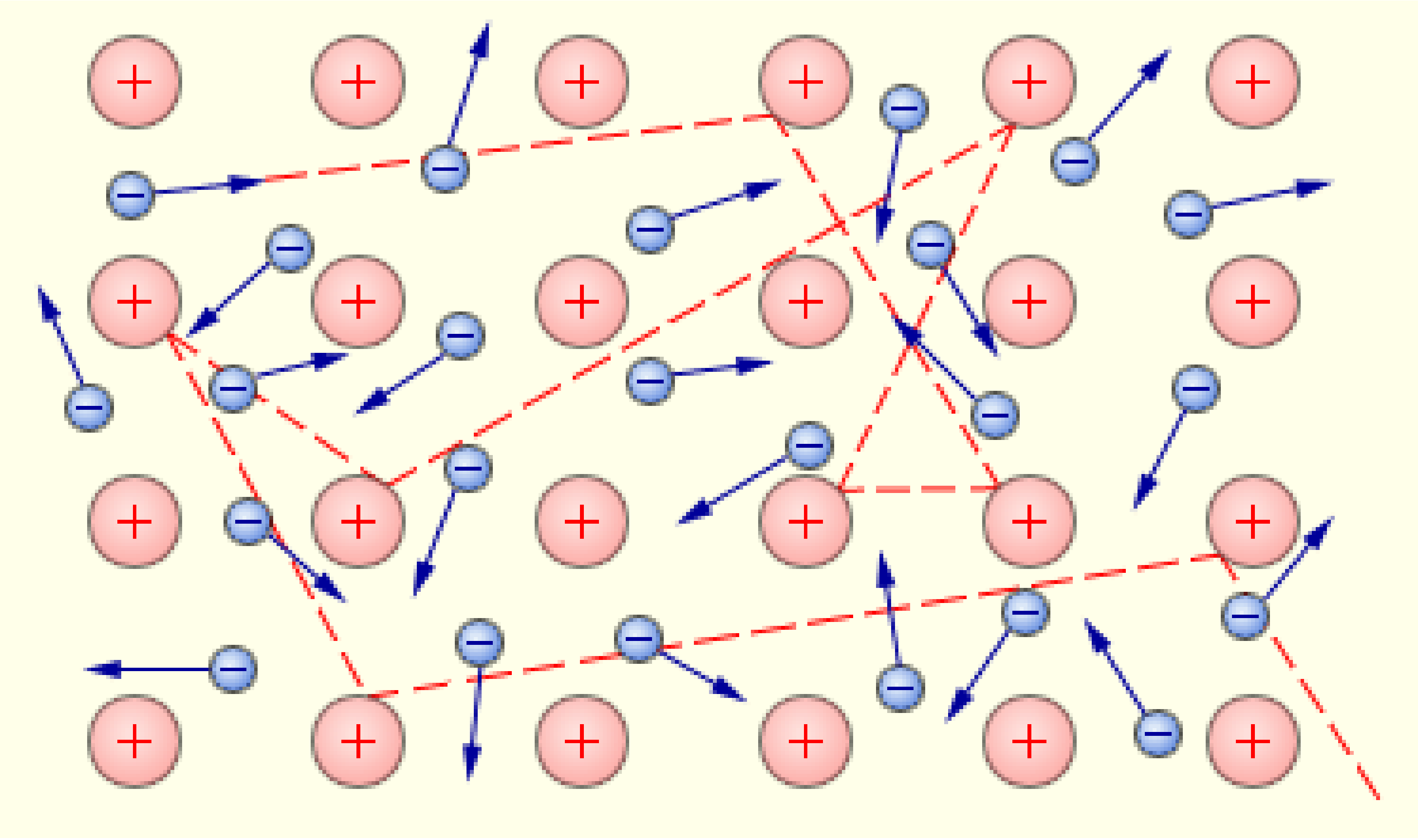


1268 CE, Notre Dame de Paris

Atwater H.A. / Scientific American (2007).

Lakowicz J. R. Plasmon-Controlled Fluorescence. A New Paradigm in Fluorescence Spectroscopy

Classical representation of electrons in the metal

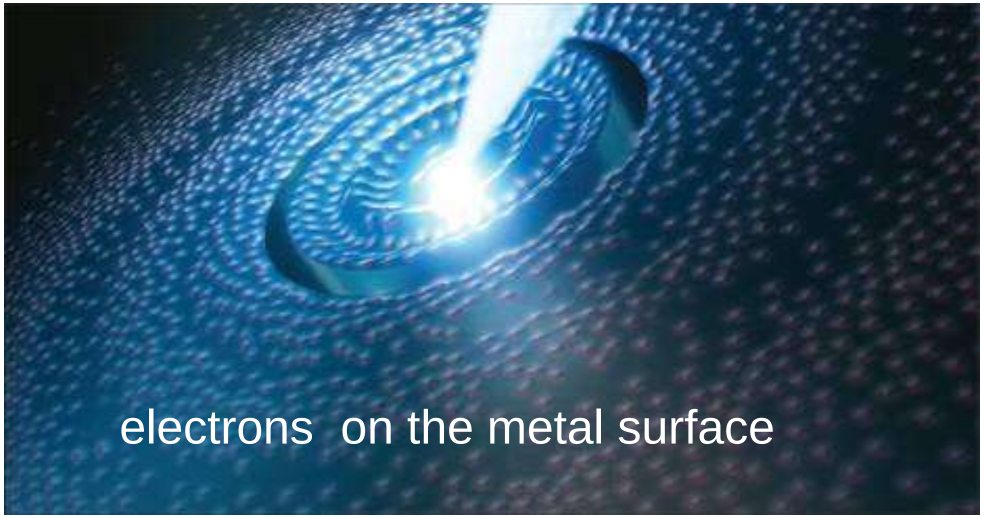


Imagine plasmons

Surface waves on the water

http://palscience.com

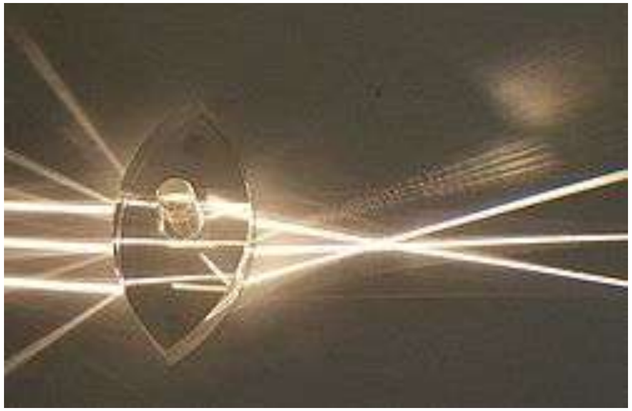
Scheme of electronic density waves in the circular metal groove



Atwater H.A. / Scientific American (2007).

Plasmons are the waves of electronic density on the metal surface

Lens

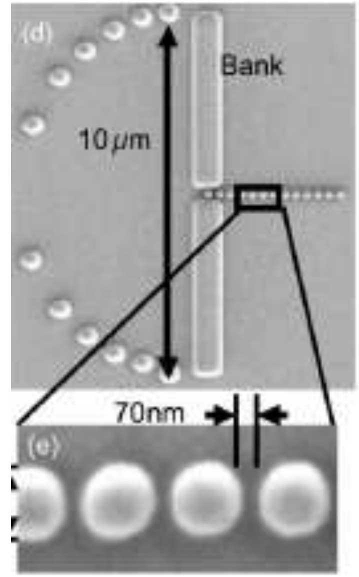


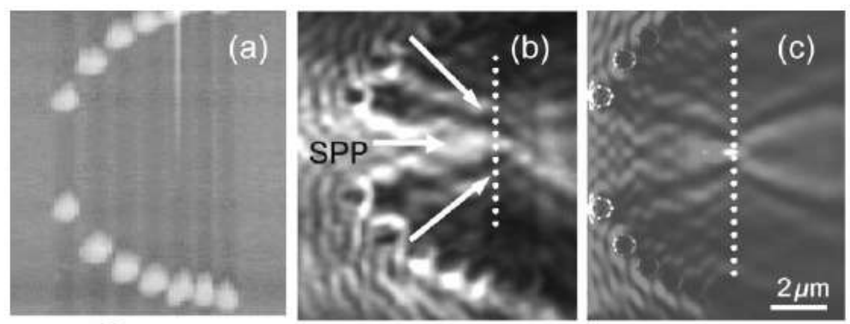
from wikipedia

Optical waveguide

A TOSLINK fiber optic audio cable being illuminated at one end

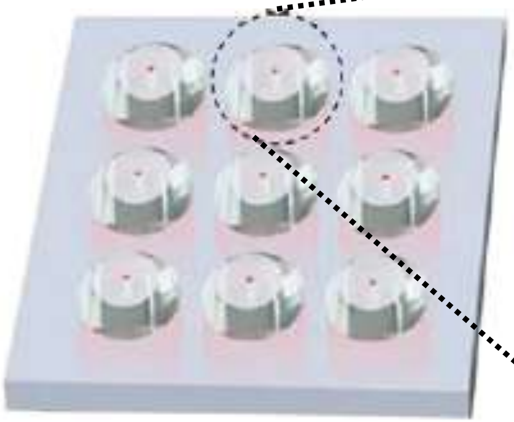
Plasmonic analog of condenser with waveguide

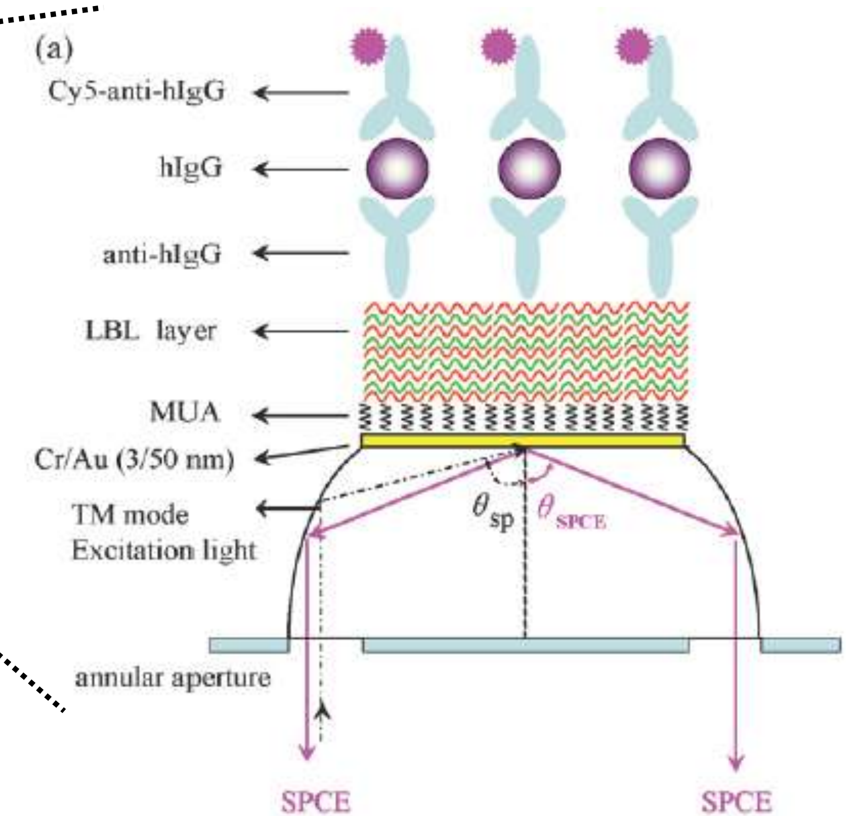


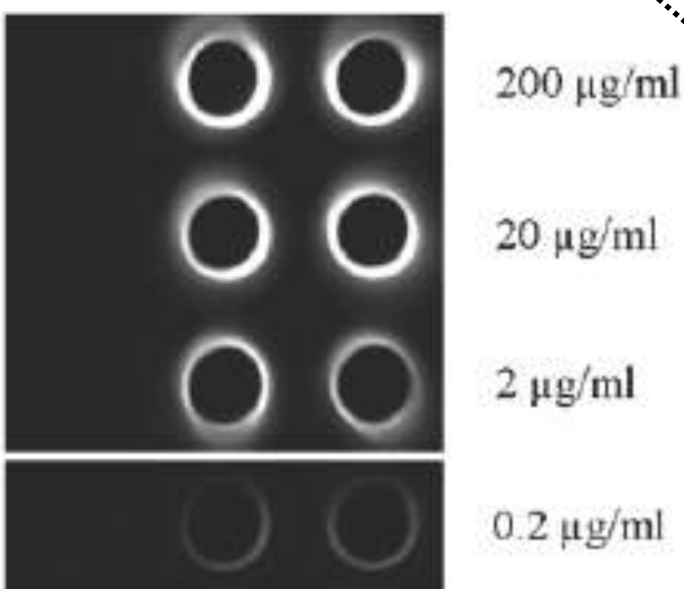


W. Nomura, M. Ohtsu, T. Yatsui, Appl. Phys. Lett. 86, 181108 (2005).

Plasmons for sensitive optical detectors





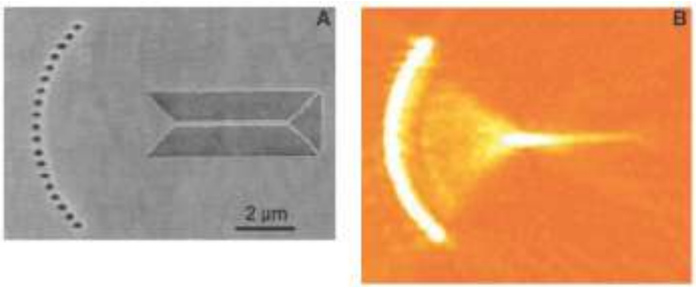


Yuk J.S., Trnavsky M., McDonagh C., MacCraith B. // Biosensors and Bioelectronics 25 (2010) 1344–1349.

Application of plasmons localized in nanoparticles

Enhanced electrical field of light near the nanoparticles

Focusing energy and its transfer to the subwavelength waveguides



W. Nomura, M. Ohtsu, T. Yatsui, Appl. Phys. Lett. 86, 181108 (2005).

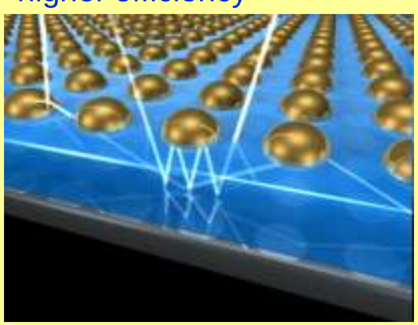
Enhanced absorption of light

Transformation of absorbed light into electricity

Nonradiative transfer of absorbed light to the fluorophore

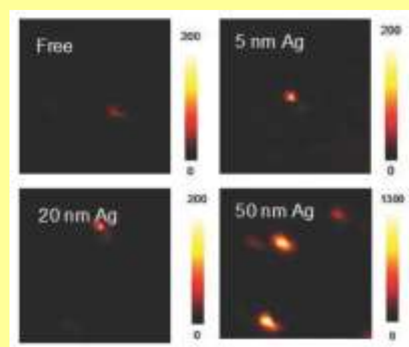
Transfer of absorbed light to heat

Plasmonic solar cells with higher efficiency



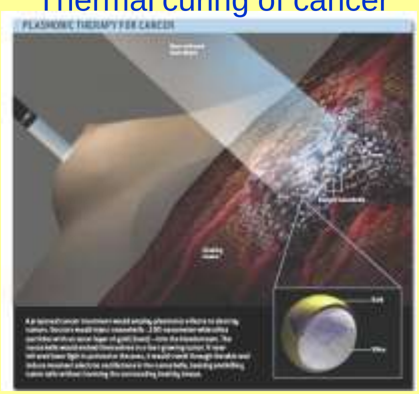
www.erbium.nl/research.html

Improved fluorescent materials



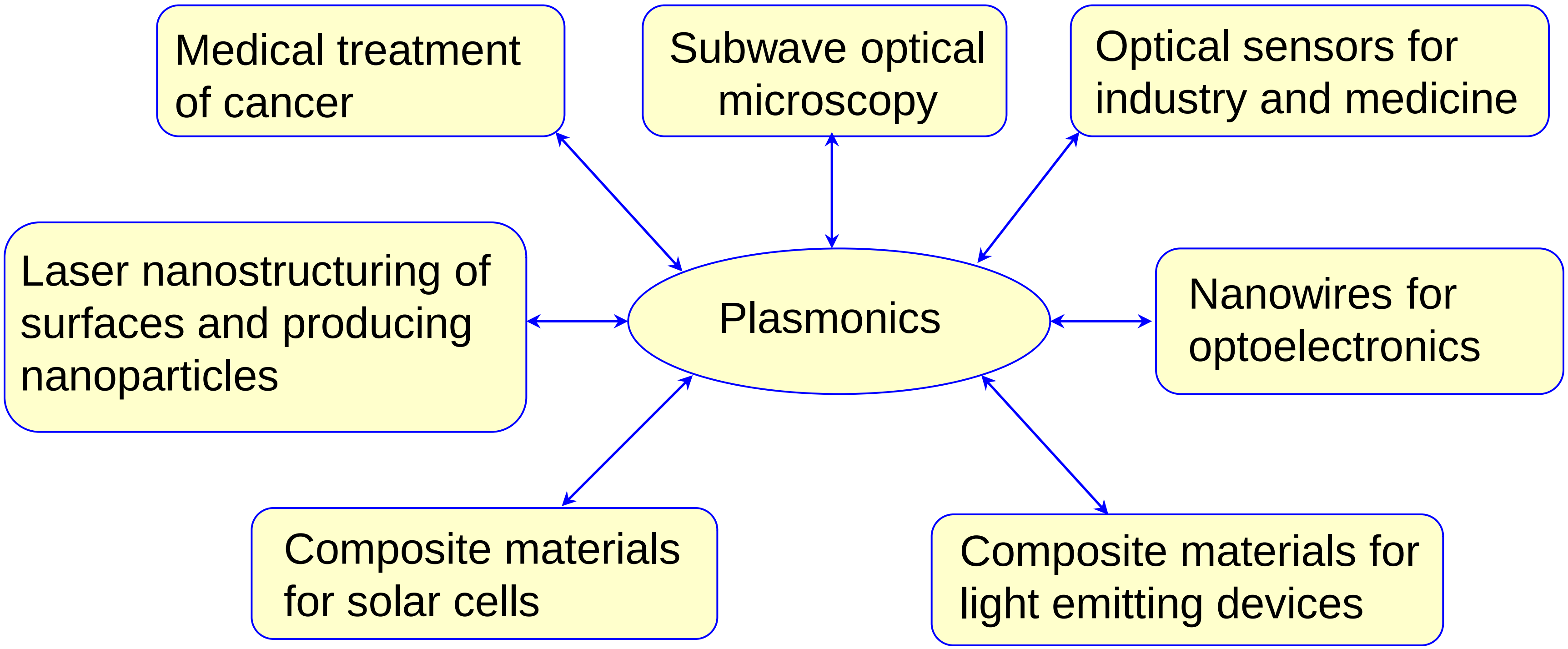
Lakowicz J. R. Plasmon-Controlled Fluorescence. A New Paradigm in Fluorescence Spectroscopy

Thermal curing of cancer



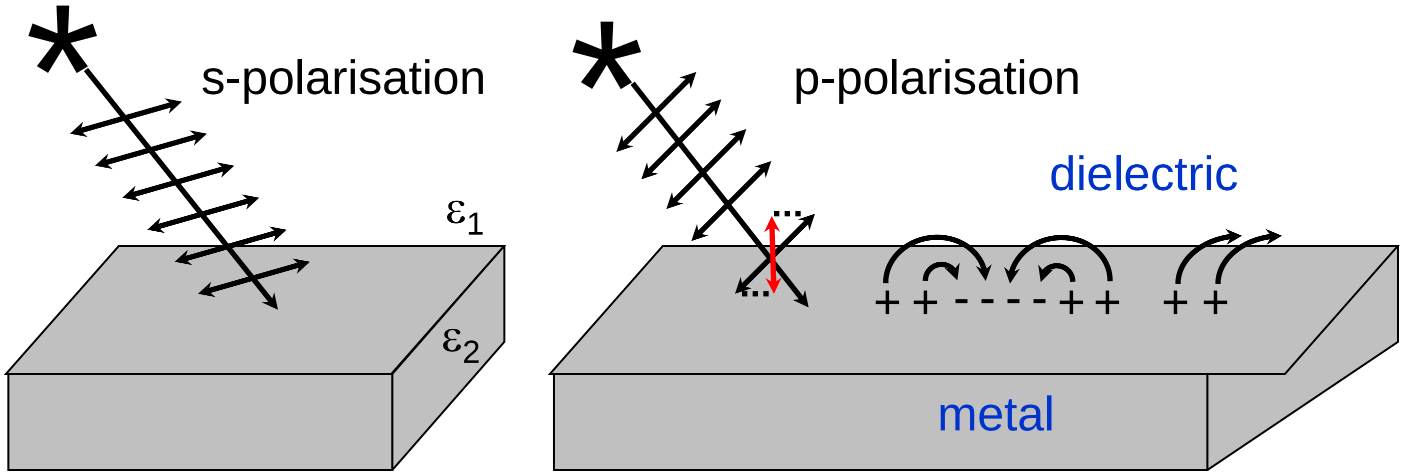
Atwater H.A. / Scientific American (2007).

Plasmons for…

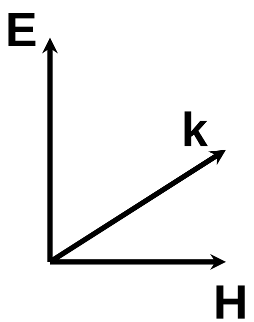


2. How to excite surface plasmon waves ? Nature of surface plasmon resonance.

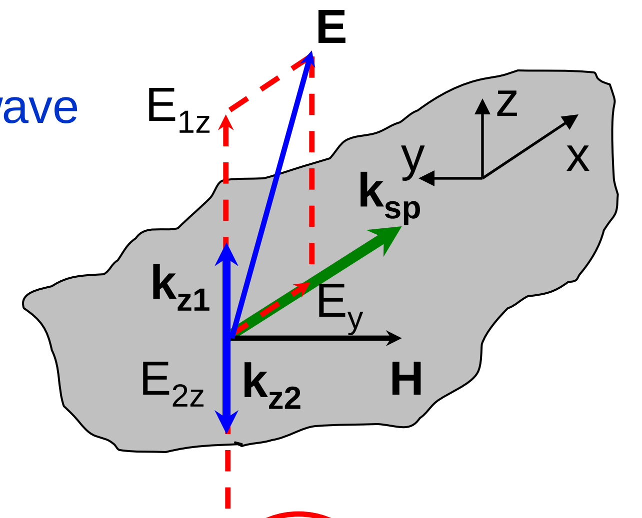
Surface plasmon waves are partially longitudinal



usual wave



surface wave



k – wave vector,
E – electric field strength,
H –magnetic strength

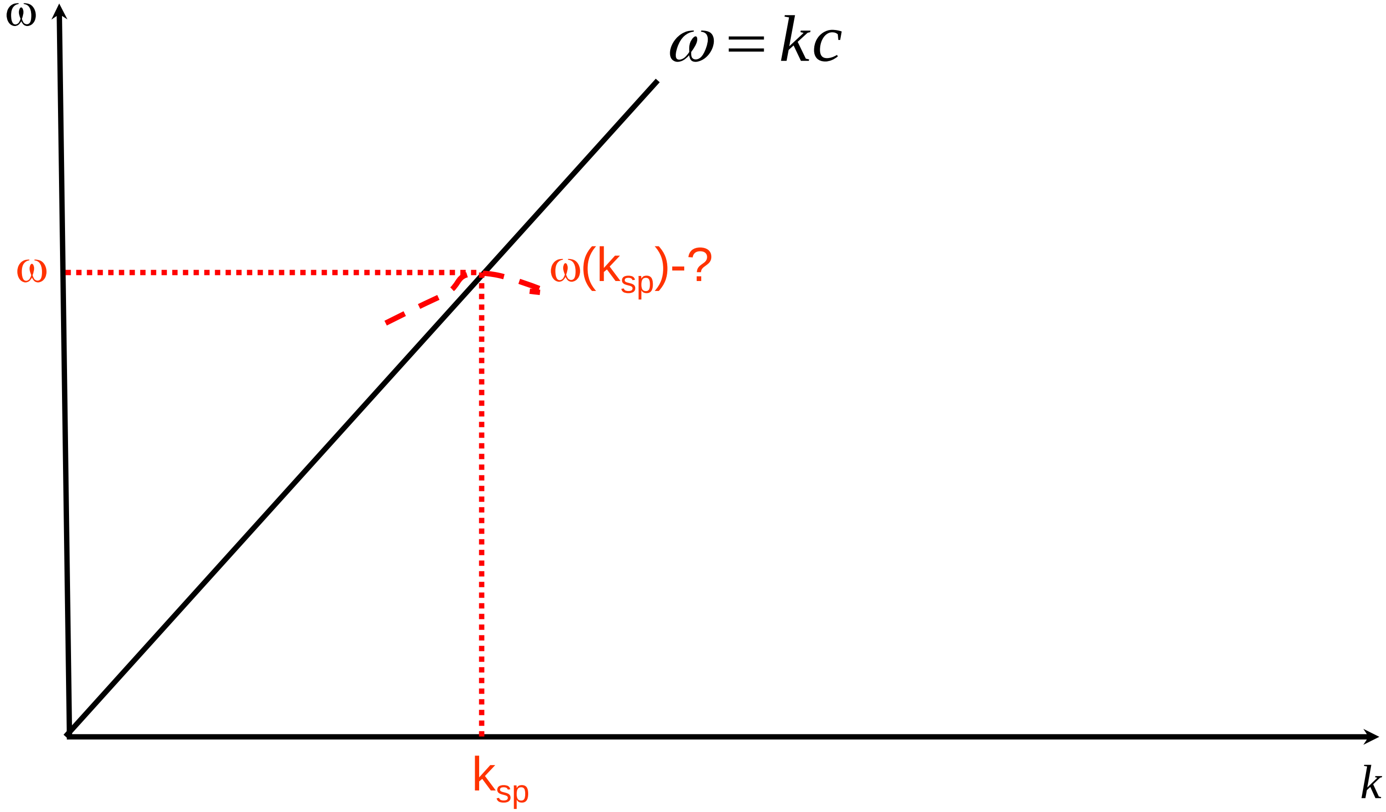
$$E = E_0 e^{\mp k_{z1,2} z} e^{i k_{sp} x - i\omega t}$$

Libenson M. N // Soros Journal, No. 10, pp. 92-98 (1996).

Dispersion relation for the wave vectors

$k=k_{sp}$ – surface plasmon resonance conditions

Light wave



Definition of wave vector for surface plasmon

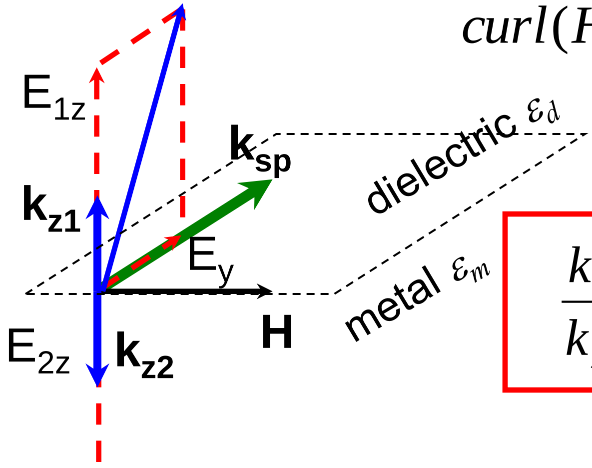
$$E = E_0 e^{\mp k_{z1,2} z} e^{ik_{sp}x - i\omega t}$$ - electric field of surface wave

$$H = H_0 e^{\mp k_{z1,2} z} e^{ik_{sp}x - i\omega t}$$ - magnetic field of surface wave

$$k_{z1}^2 + k_{sp}^2 = \varepsilon_d k^2 \qquad k_{z2}^{\ 2} + k_{sp}^2 = \varepsilon_m k^2$$

- connection between the components of the wave vectors

$$curl(\vec{H}) = \frac{1}{c} \frac{\varepsilon \cdot \partial \vec{E}}{\partial t}$$ - Maxwell's equation for magnetic field



$$\frac{k_{z1}}{k_{z2}} = \frac{\varepsilon_d}{\varepsilon_m}$$

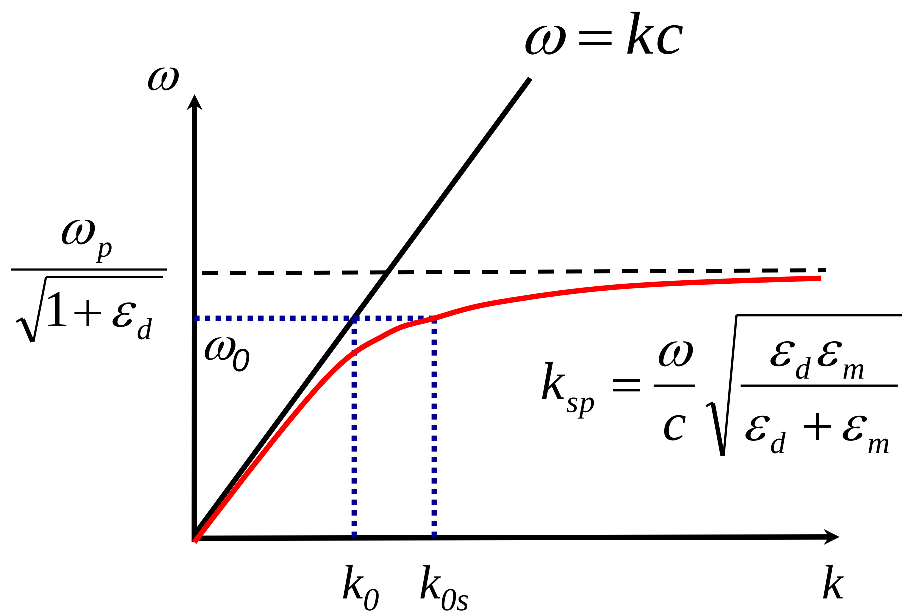
ε_d- real part of permittivity for dielectric

ε_m- real part of permittivity for metal

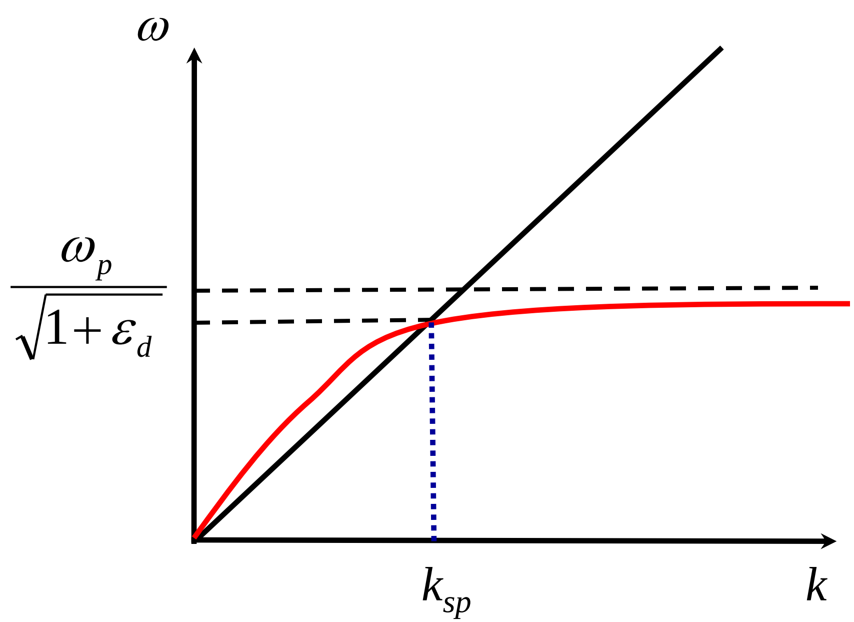
$$k_{sp} = k\sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}}$$ - wave vector of surface plasmon

Wave vector of light k_0 passing through the medium at fixed frequency ω_0 is smaller than wave vector of surface plasmon k_{0s}:

$$\omega_p = \frac{Ne^2}{m_e \varepsilon_0}$$ - volume plasmon frequency

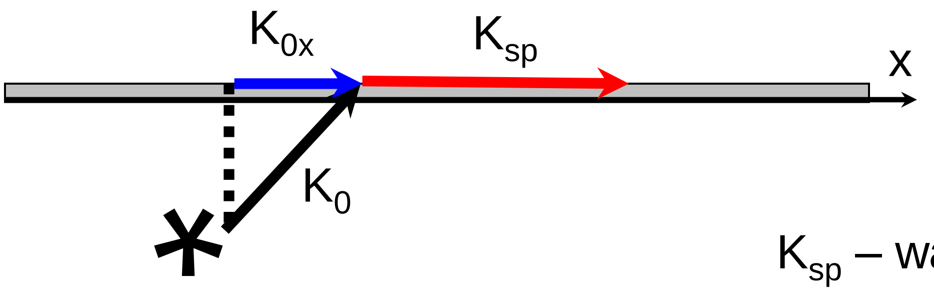


It is needed to increase the wave vector of light up to the wave vector of plasmon k_{sp}:



3. Excitation of plasmons by prism coupling scheme

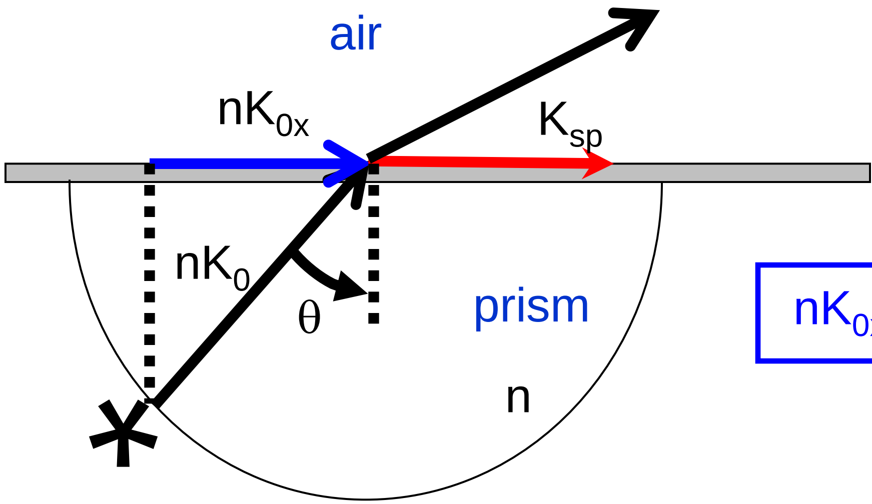
Hemispherical prism for increase wave vector of light



$K_0=\omega/v$ – wave vector of incident light

K_{0x} – projection of wave vector on the surface

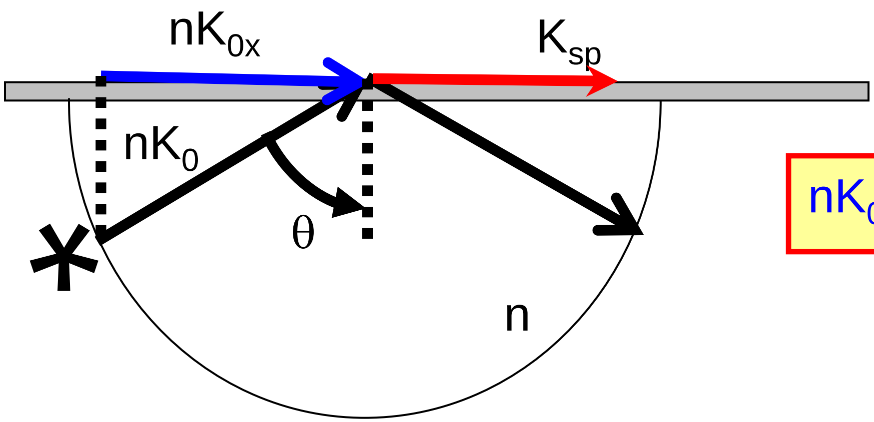
K_{sp} – wave vector of the surface plasmon wave



$K_{0x}<K_{sp}$ - there is no surface wave

sin $\theta<1/n$

$nK_{0x} \sin\theta < K_{sp}$ - there is no surface wave still

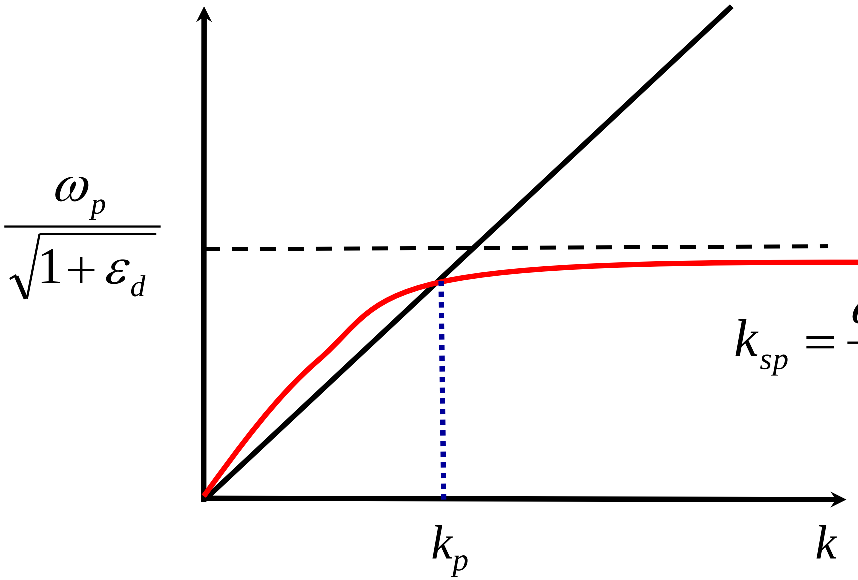


sin $\theta>1/n$

$nK_{0x} \sin\theta \sim K_{sp}$ - needed for surface wave

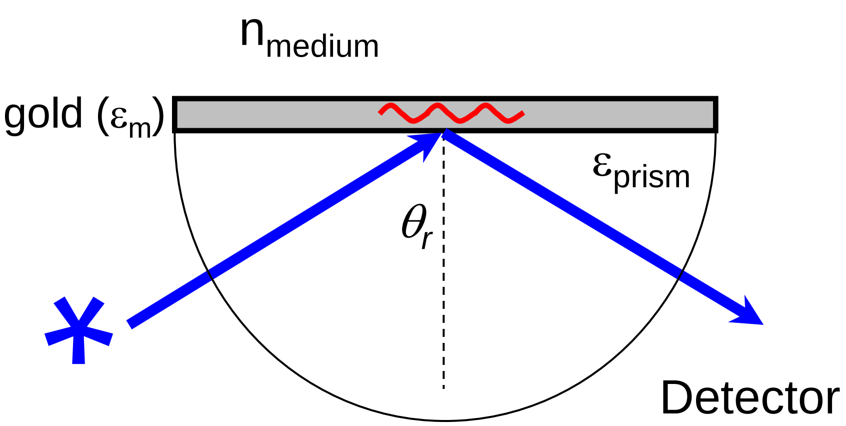
Dispersion relation for the wave vectors in case of surface plasmon resonance

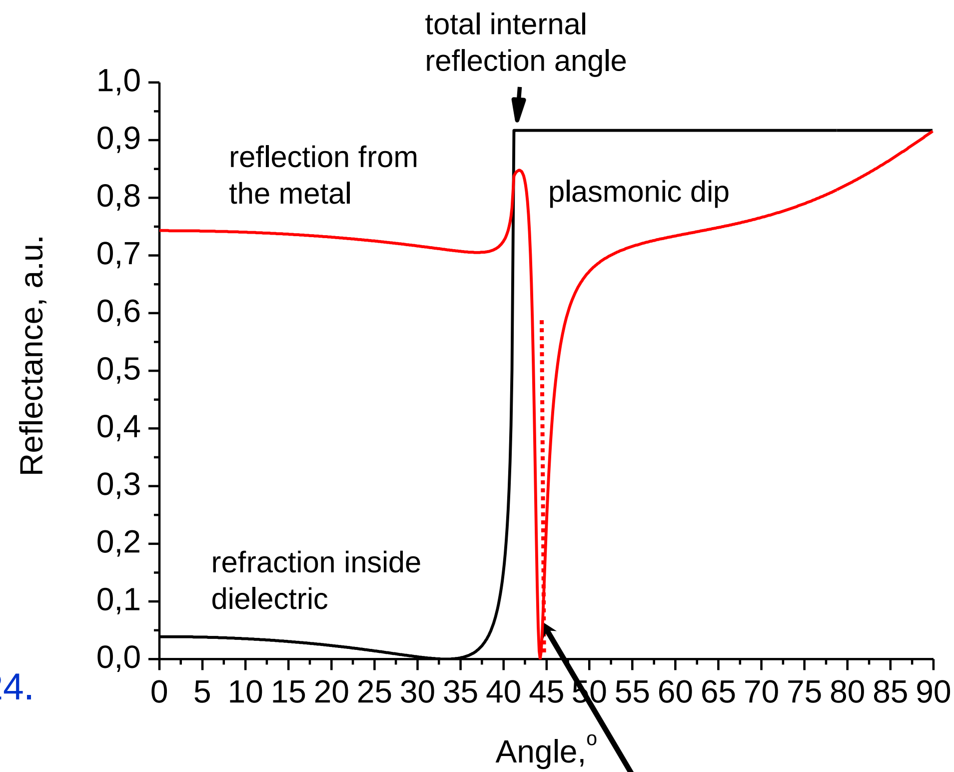
$$\omega = kcn\sin\theta$$ - light



$$k_{sp} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}}$$ - plasmons

Inducing of plasmons by Kretschmann scheme





Kretschmann geometry of experiment

Kretschmann E. // Z. Physik, 1971, B. 241, S 313-324.

$$k_{prism} = k_{sp}$$

$$kn \sin\theta = k\sqrt{\frac{\varepsilon_m \varepsilon_{air}}{\varepsilon_m + \varepsilon_{air}}} + \Delta\beta$$

$$\theta = \theta_r$$

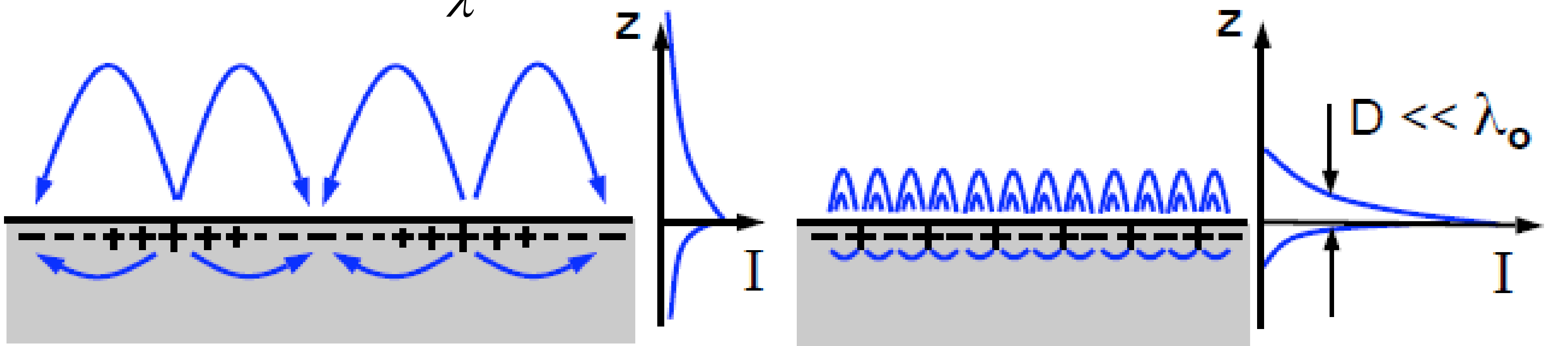
$$v = v_s$$

$$W_{reflected} = W_{incident} - W_{plasmon}$$

$\Delta\beta$ - parameter, which depends on the thickness of metal film

Plasmons with big and small wave vector k

small $k = \frac{2\pi}{\lambda}$ big k



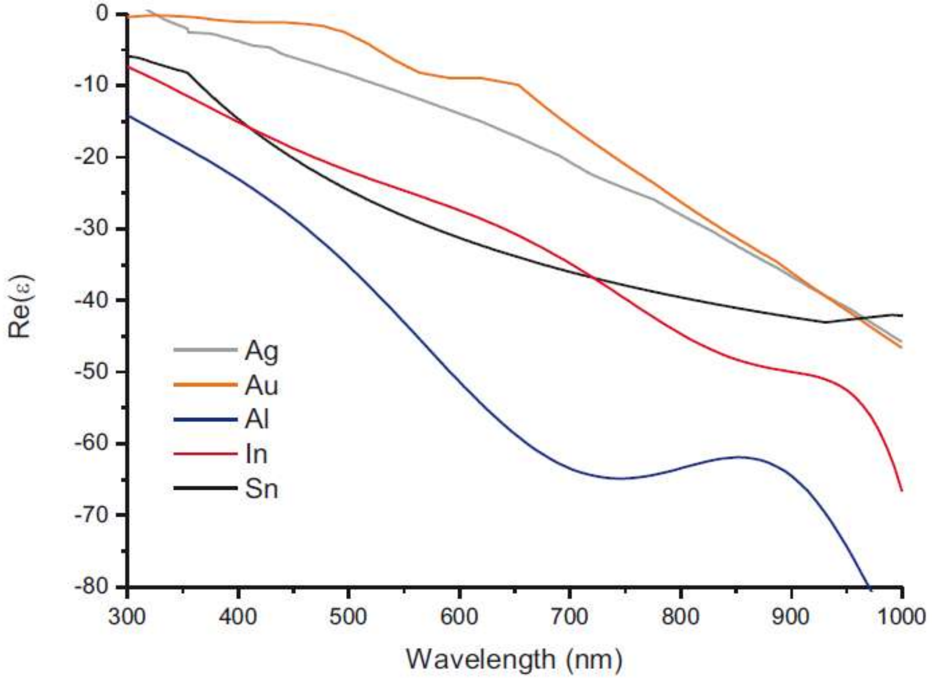
Long wavelength λ Short wavelength λ

At big *k:*

$$\omega = \omega_{sp} \, when: \varepsilon_m = 1 - \frac{\omega_p^2}{\omega^2} = -\varepsilon_d \rightarrow \omega^2 - \omega_p^2 = -\varepsilon_d \omega^2 \rightarrow \omega^2 = \frac{\omega_p^2}{1+\varepsilon_d} \rightarrow \omega = \frac{\omega_p}{\sqrt{1+\varepsilon_d}}$$

$$n \sin\theta = \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}}$$

Real part of metal permittivity vs the wavelength of light

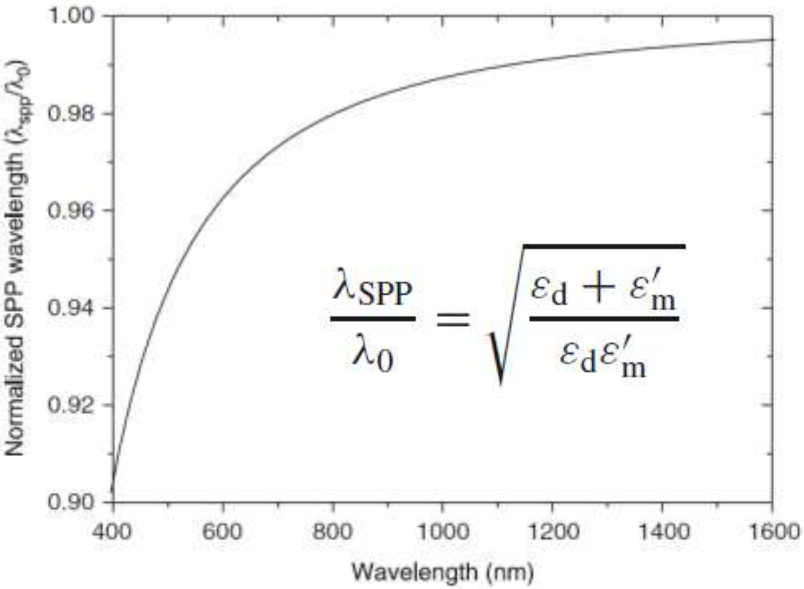


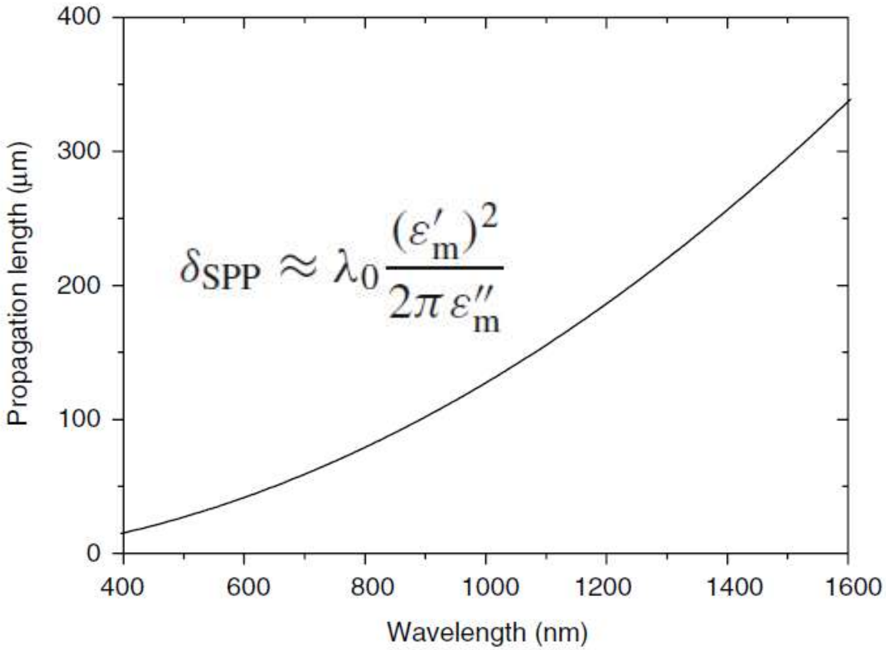
For metal-vacuum interface surface plasmon resonance must be at ε_m=-1

Oliver Benson Elements of Nanophotonics

Metal	Resonance wavelength of light, nm
Au	~520
Ag	~380
Al	<300

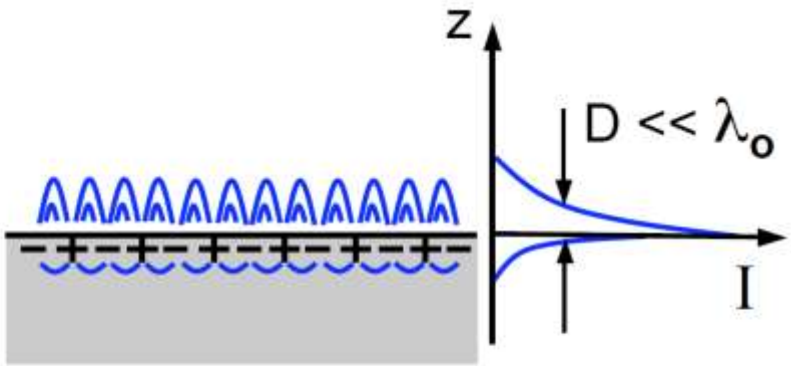
Wavelengths and propagation lengths of surface plasmons



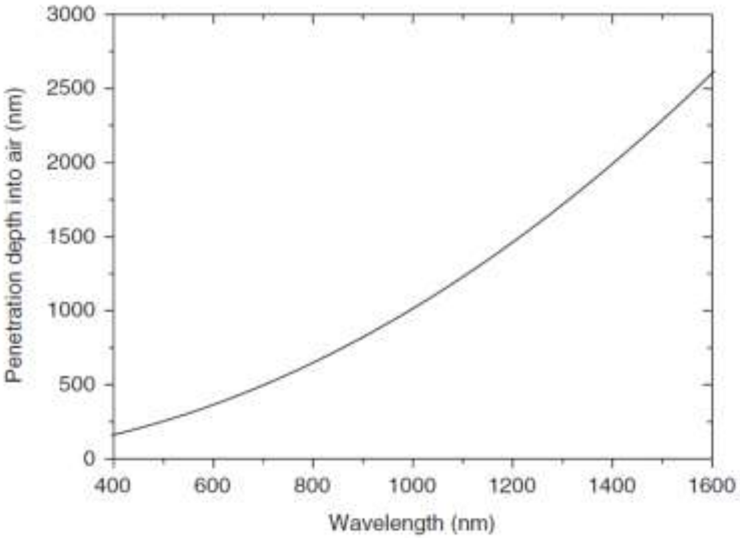


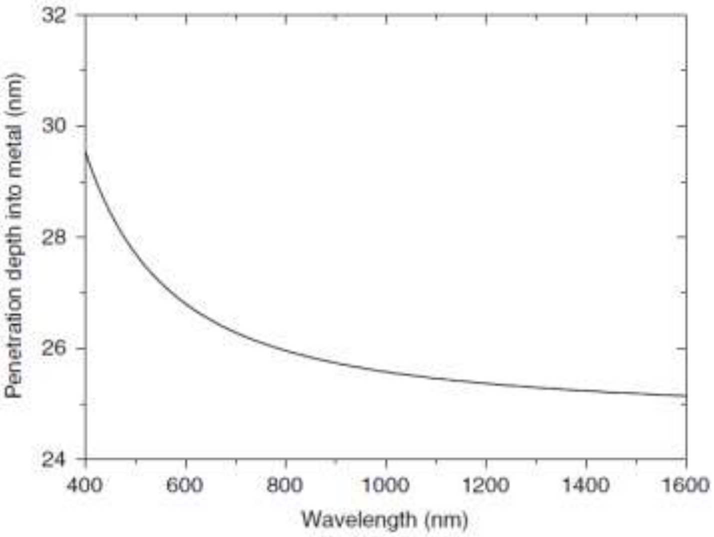
Barnes W. L. // J. Opt. A: Pure Appl. Opt., Vol. 8, p. S87-S93 (2006).

Surface plasmon penetration depths



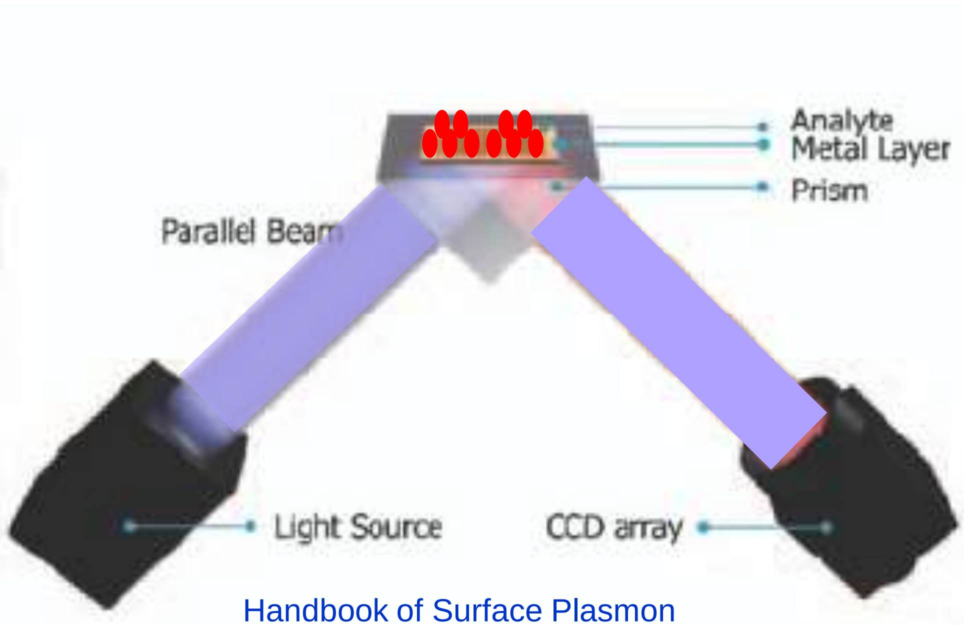
V. M. Shalaev Nanophotonics. Lectures





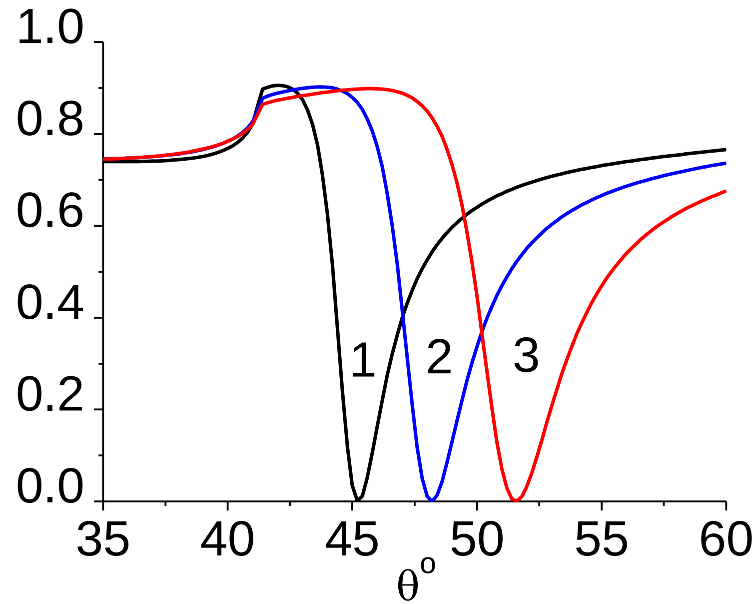
Barnes W. L. // J. Opt. A: Pure Appl. Opt., Vol. 8, p. S87-S93 (2006).

Plasmonics for the optical sensing



Handbook of Surface Plasmon Resonance / Editors R.B.M. Schasfoort and A. J. Tudos

Reflection



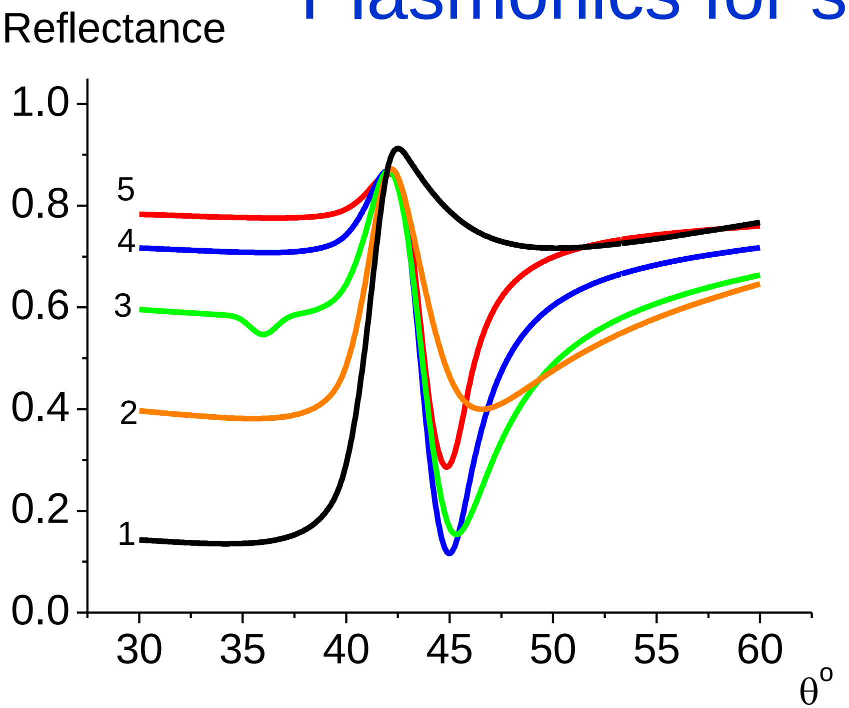
$n_{analyte}$	θ^o
1	45.23°
1.01	45.8°
1.05	48.2°
1.07	49.4°
1.1	51.4°

Prism is metallized by gold film (50 nm)

wavelength of incident light is 583 nm

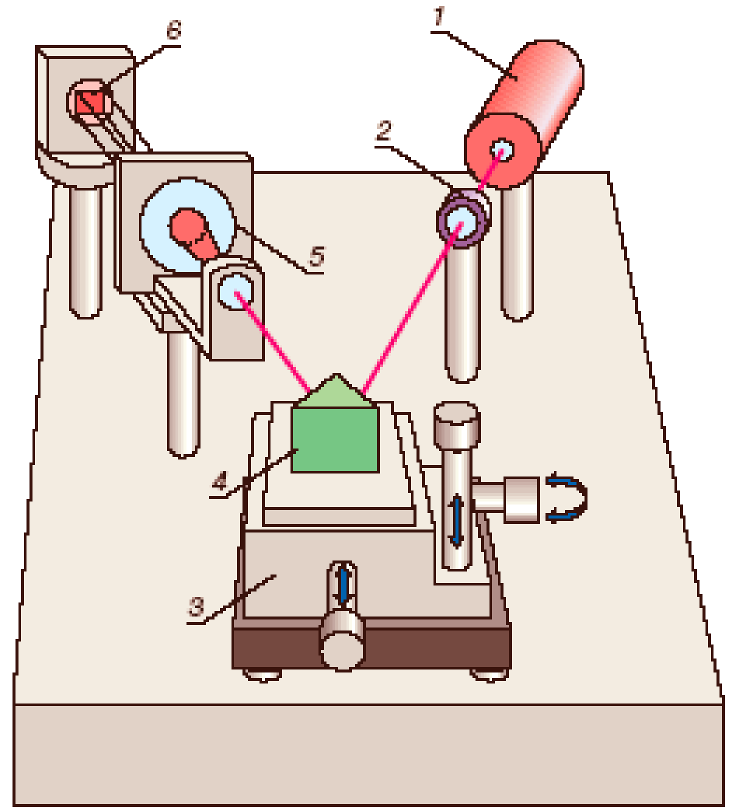
1) $n_{analyte}=1$,
2) $n_{analyte}=1.05$,
3) $n_{analyte}=1.1$.

Plasmonics for subwave microscopy

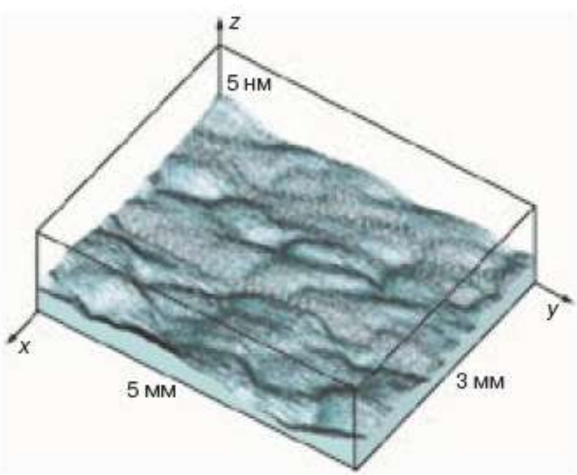


Reflectance for different thicknesses of metal films:
1) 10 nm, 2) 20 nm, 3) 30 nm, 4) 40 nm, 5) 50 nm
(λ=594 nm)

Optical subwave microscope



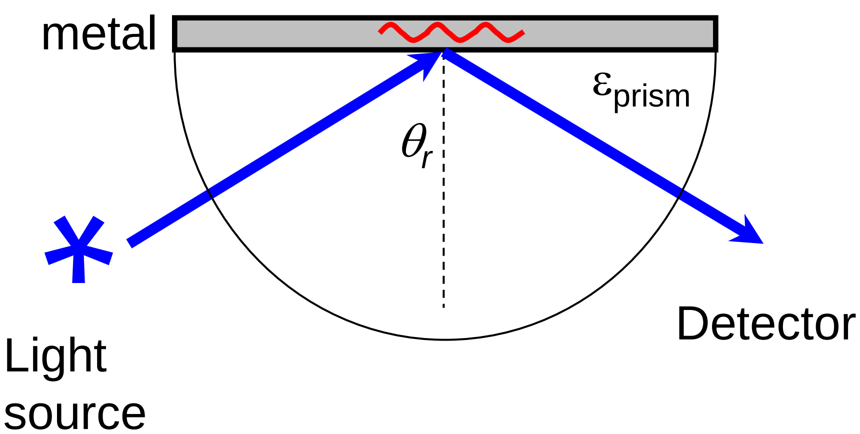
1 – laser, 2 – polarizer, 3 – presize stage, 4 – metallized prism, 5 – telescope, 6 – photodetector



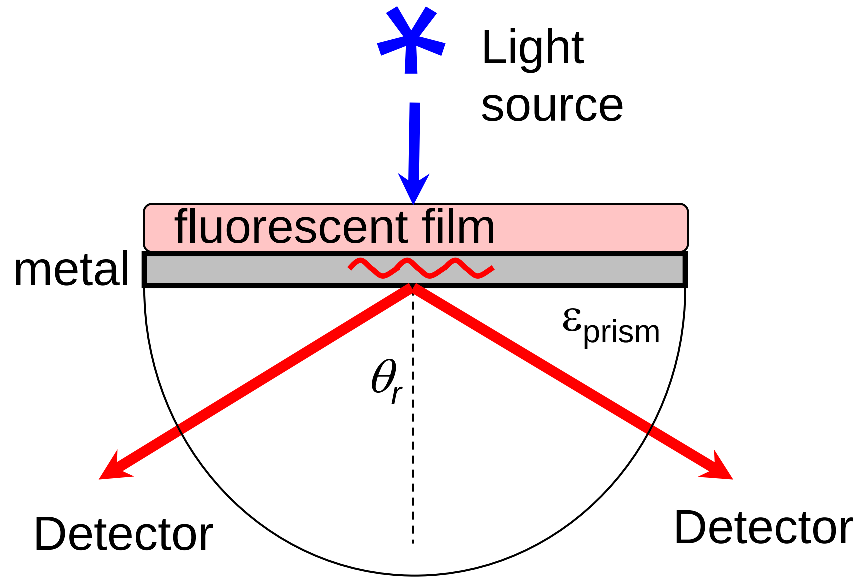
Valyansky // Soros Journal, No. 8, pp. 76-82 (1999).

4. Modification of prism coupling scheme for the fluorescent materials.

Kretschmann scheme



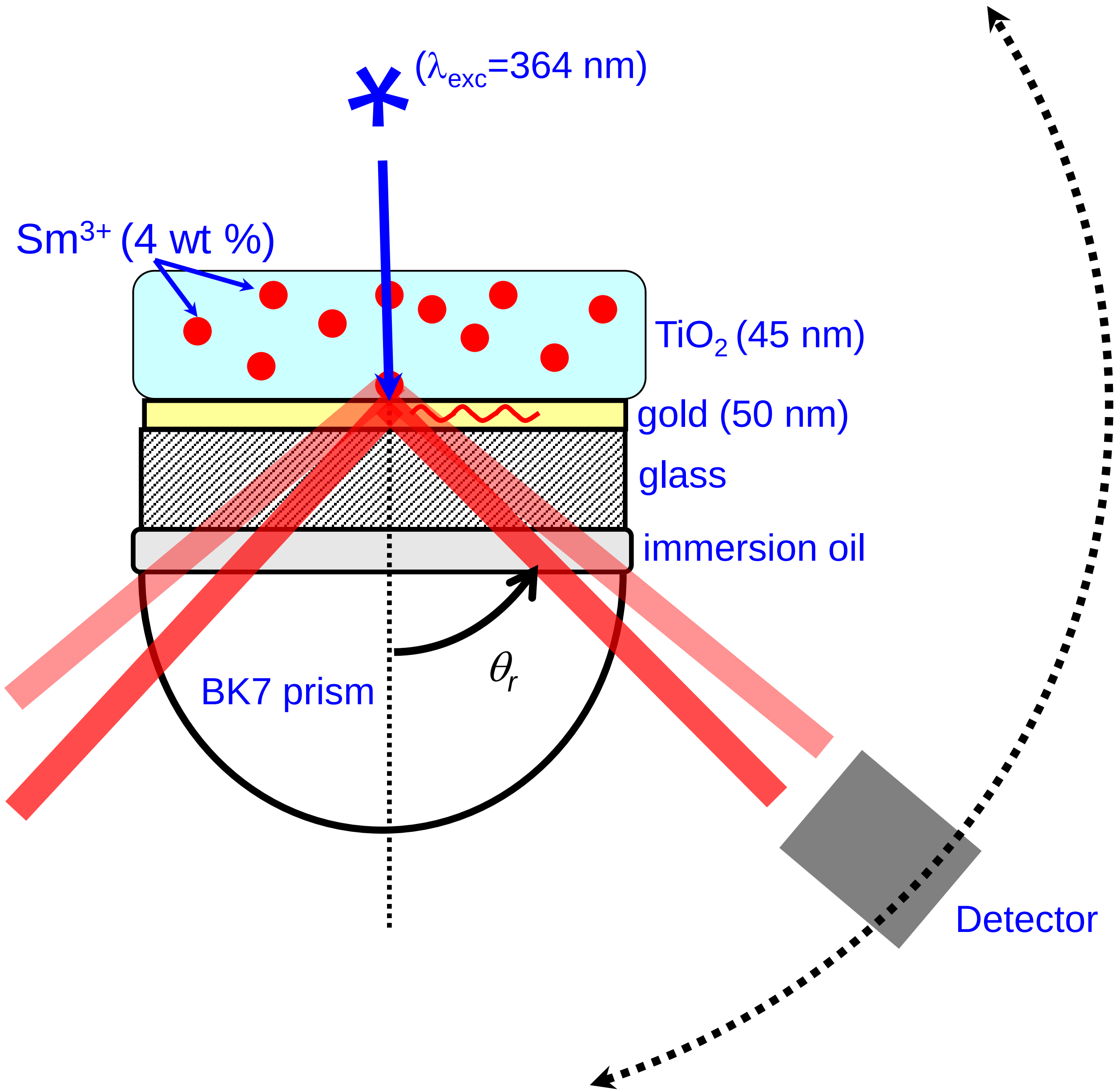
Reverse Kretschmann scheme



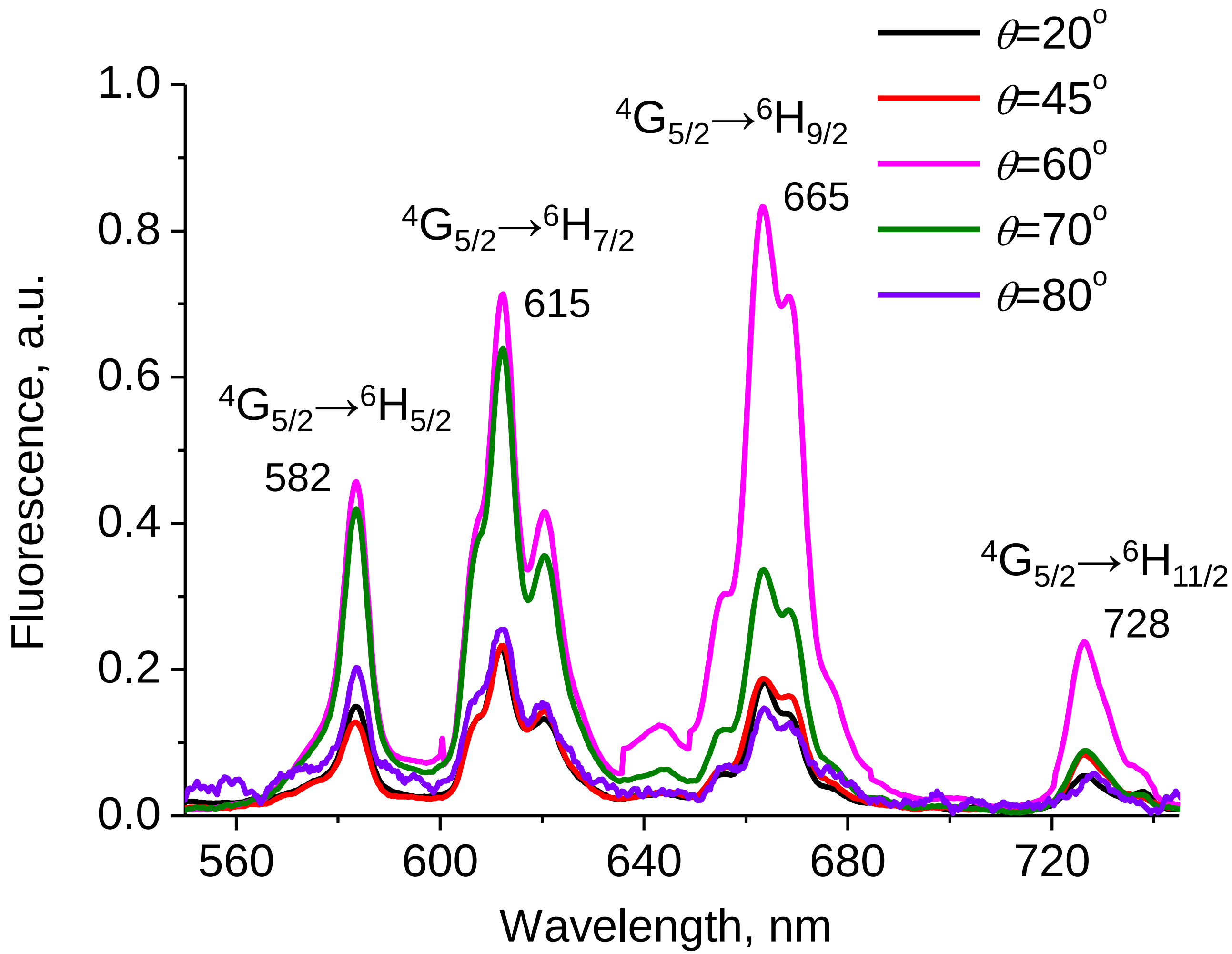
I. Gryczynski, J. Malicka, Z. Gryczynski, and J. R. Lakowicz // Anal. Biochem. Vol. 324, pp. 170-182, (2004).

Ray K. et al. / Advances in Biochemical Engineering/Biotechnology, Vol. 116 (2010).

Reversed Kretschmann scheme for control Sm^{3+} emission

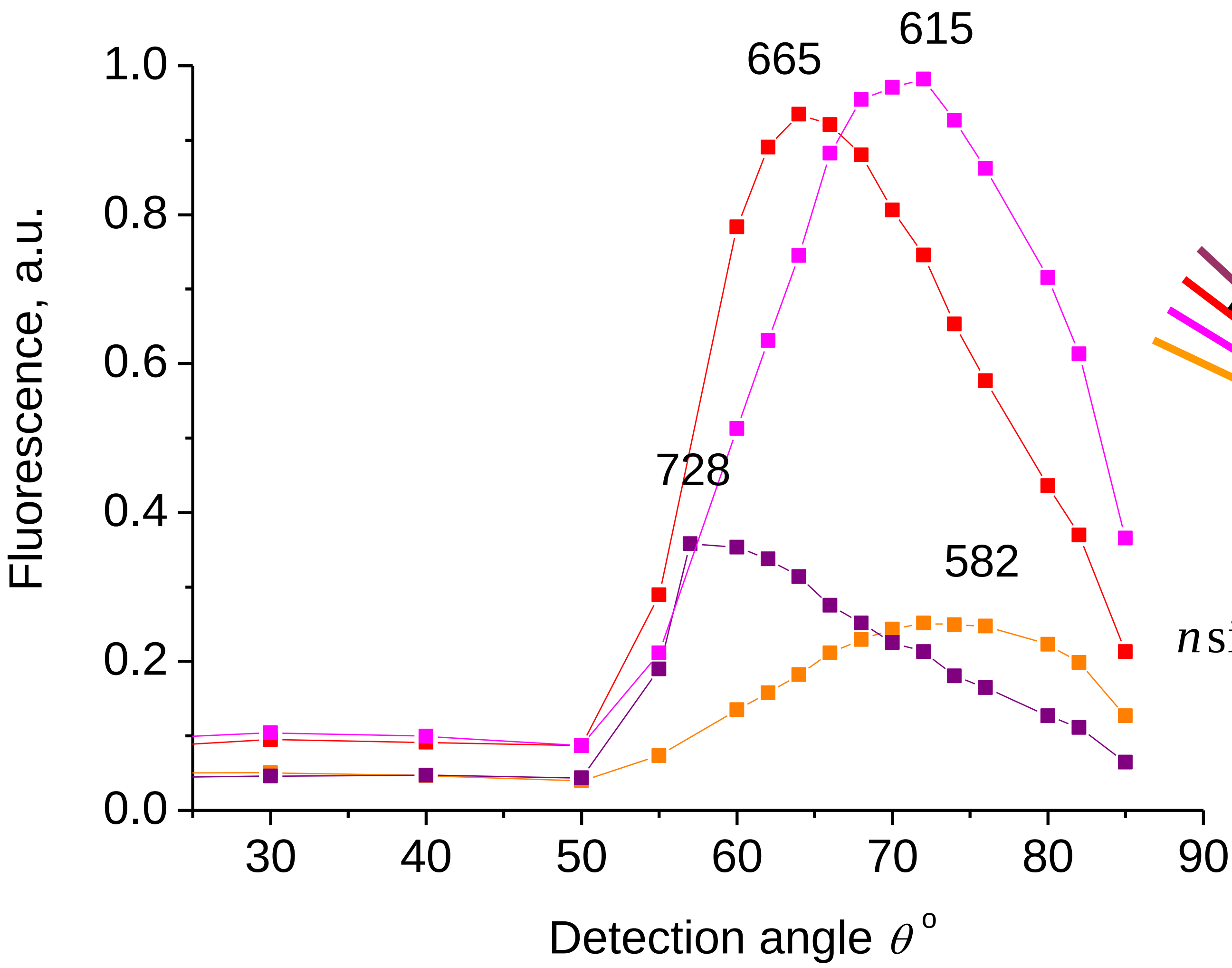


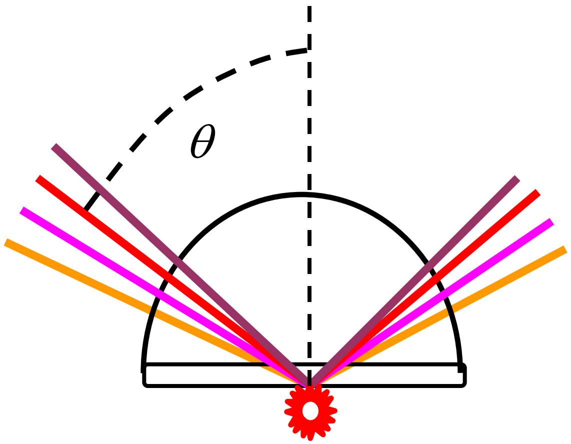
Spectral distribution of fluorescent bands



Fluorescence of Sm^{3+} ions embedded into TiO_2 films on the gold layer at different detection angles

Angular distribution of spectral bands

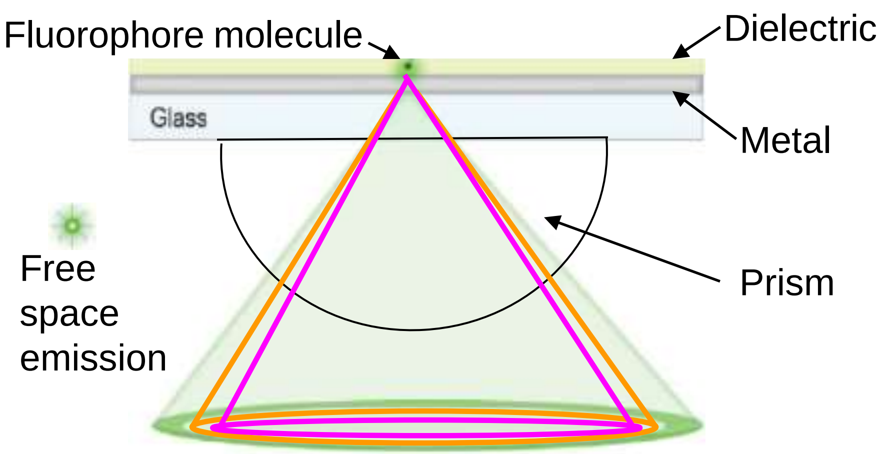




$$n \sin\theta_r = \sqrt{\frac{\varepsilon_m'(\lambda)\cdot\varepsilon'(\lambda)}{\varepsilon_m'(\lambda)+\varepsilon(\lambda)}} + \beta$$

Angular dependences of intensity for spectral bands at 582, 615, 665 and 728 nm detected from Sm^{3+} ions embedded into TiO_2 films on the gold layer

Plasmon coupled directional emission



I. Gryczynski, J. Malicka, Z. Gryczynski, and J. R. Lakowicz // Anal. Biochem. Vol. 324, pp. 170-182, (2004).

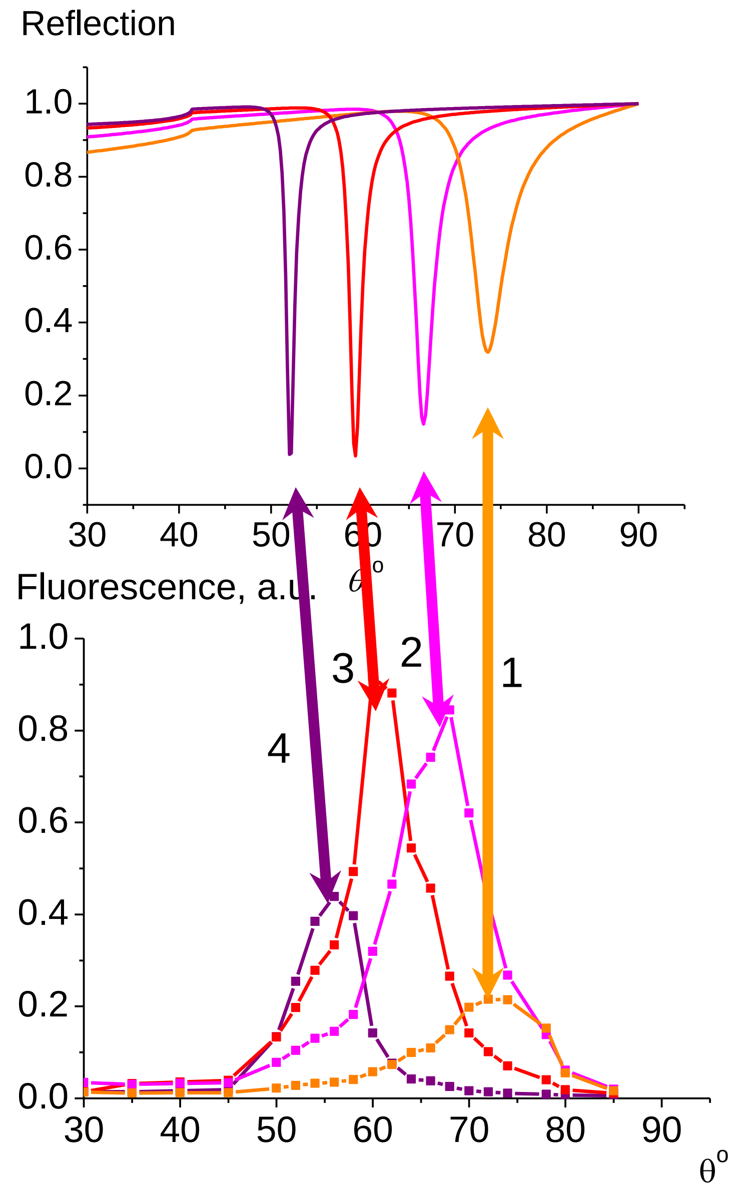
Correspondence between plasmonic dips and plasmon-coupled emission bands of Sm^{3+} ions in TiO_2 film (100 nm) deposited on the gold layer (50 nm):

1) 583 nm,

2) 616 nm,

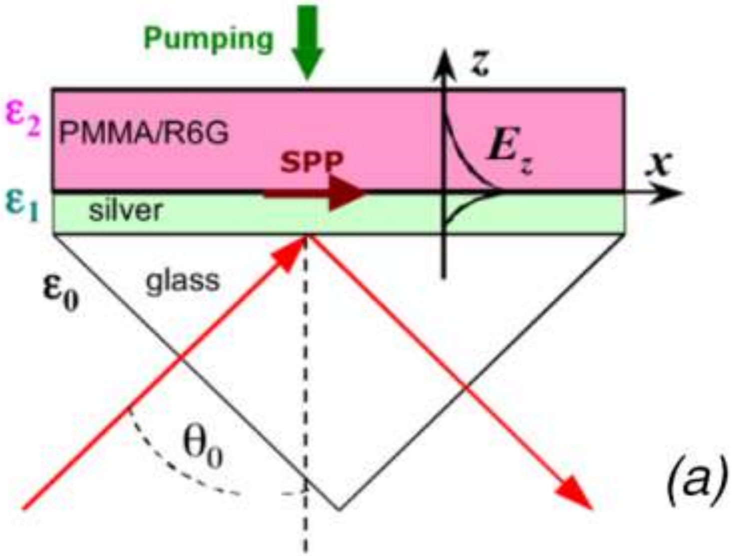
3) 665 nm,

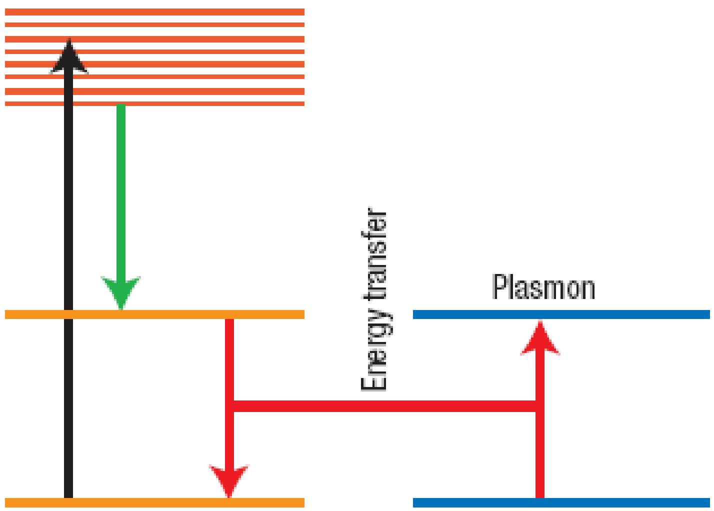
4) 728 nm



Our data, Dolgov L. et al. // Appl. Phys. B, Vol. 107, pp. 749-753 (2012)

Idea of SPASER: Surface Plasmon Amplification by Stimulated Emission of Radiation





Excitation of fluorophore

Non-radiative energy transfer to the plasmon

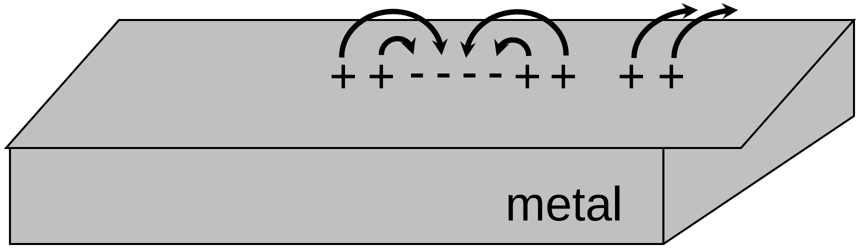
Stockman M. Spasers explained // Nature Photonics, Vol. 2, pp. 327-329 (2008)

Seidel J., Grafström S., and Eng L. // Phys. Rev. Lett. 94, 177401 (2005)

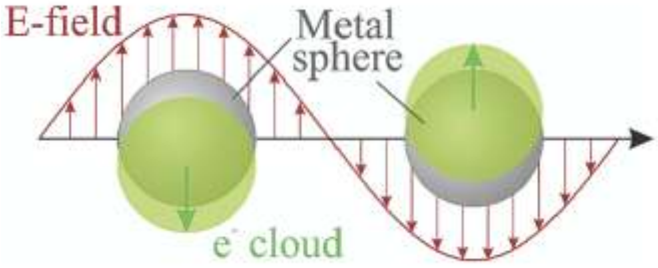
Noginov M. A. et al. // Phys. Rev. Lett., 101, 226806 (2008)

5. Some knowledge about localized plasmons

Plasmons propagating
in metal layer

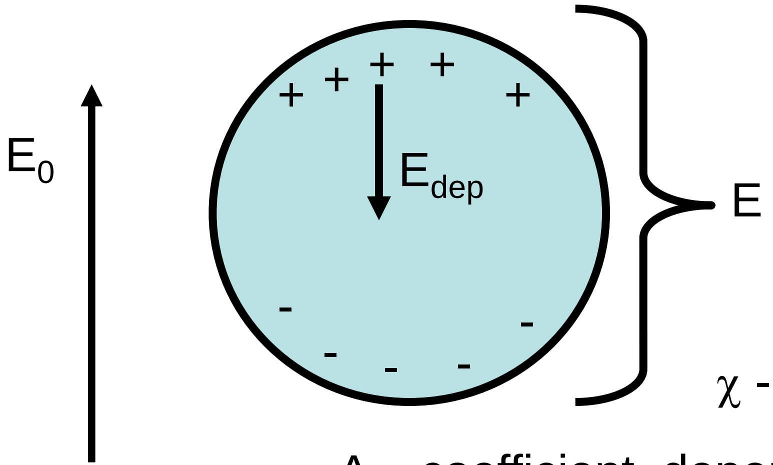


Plasmons localized in
metal nanoparticles



Lakowicz J. R. Plasmonics in Biology and Plasmon-Controlled Fluorescence // Plasmonics Vol. 1, pp. 5-33 (2006).

Plasmonic resonance in nanoparticle: basic idea



$E = E_0 – E_{dep}$

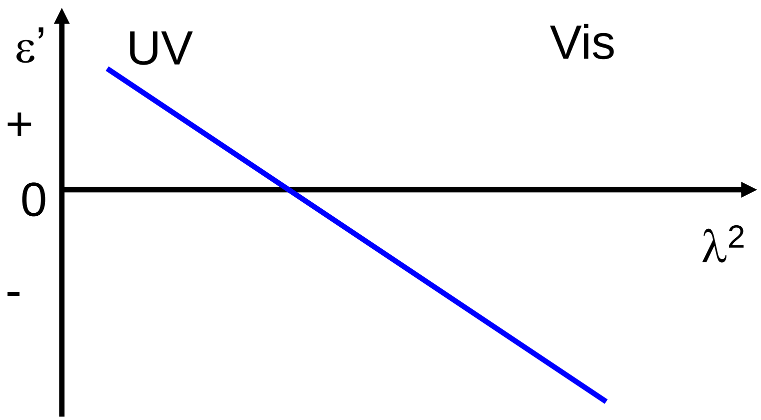
$E_0 = E + E_{dep}$

$E_0 = E + \chi AE$

χ - dielecrtical susceptibility, $\chi = \varepsilon - 1$

A – coefficient, dependent on the geometry of the particle

Wavelength dependence of ε' for noble metals



$E_0 = E + (\varepsilon-1)AE$

$E_0 = E\,(1 + (\varepsilon-1)A)$

$E = E_0/(1 + (\varepsilon-1)A)$

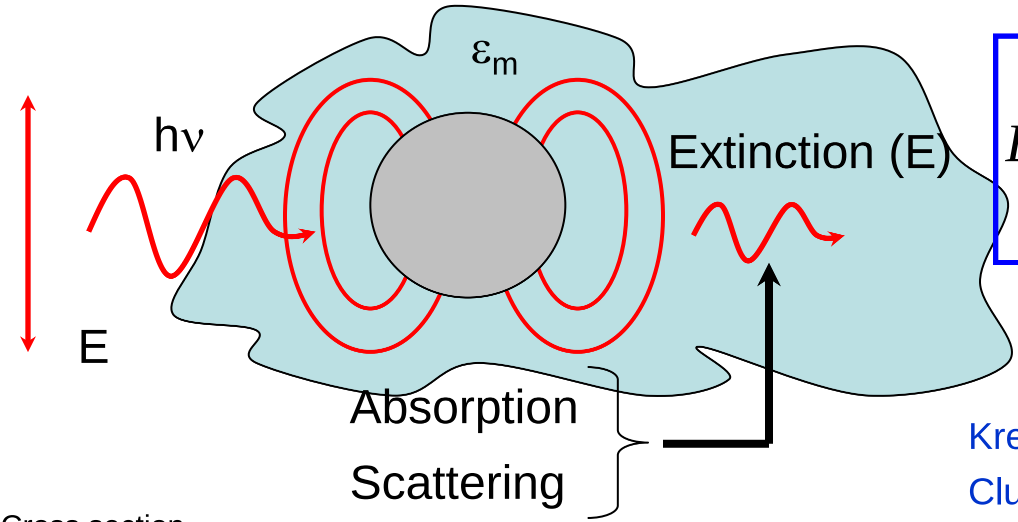
for spherical particle A=1/3 and

$E = 3E_0/(2+\varepsilon)$

For metals at some frequencies $\varepsilon \approx -2$ and **E increase increase strongly**

Kozuka H. Metal nanoparticles in gel-derived oxide coating films: control and application of surface plasma resonance // SPIE Proc., 3136, 304-314.

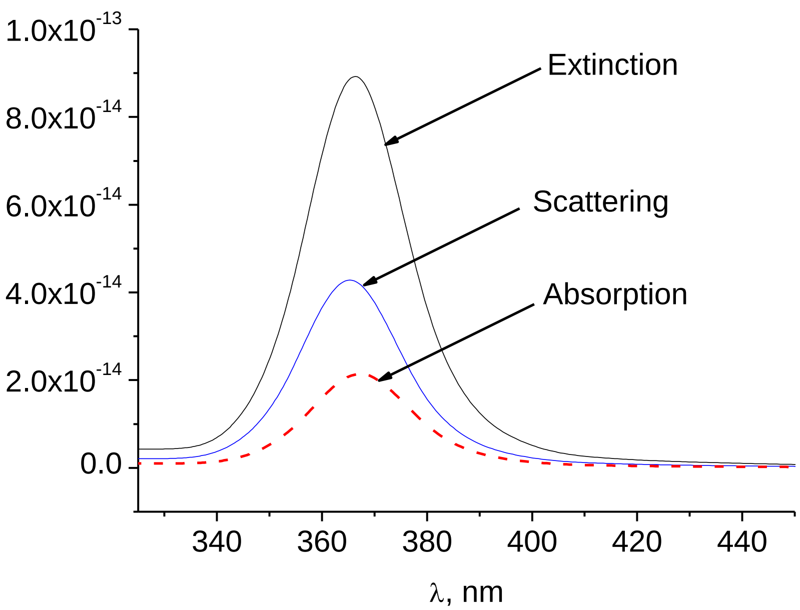
Interaction of incident light with silver nanoparticle: plasmonic effect



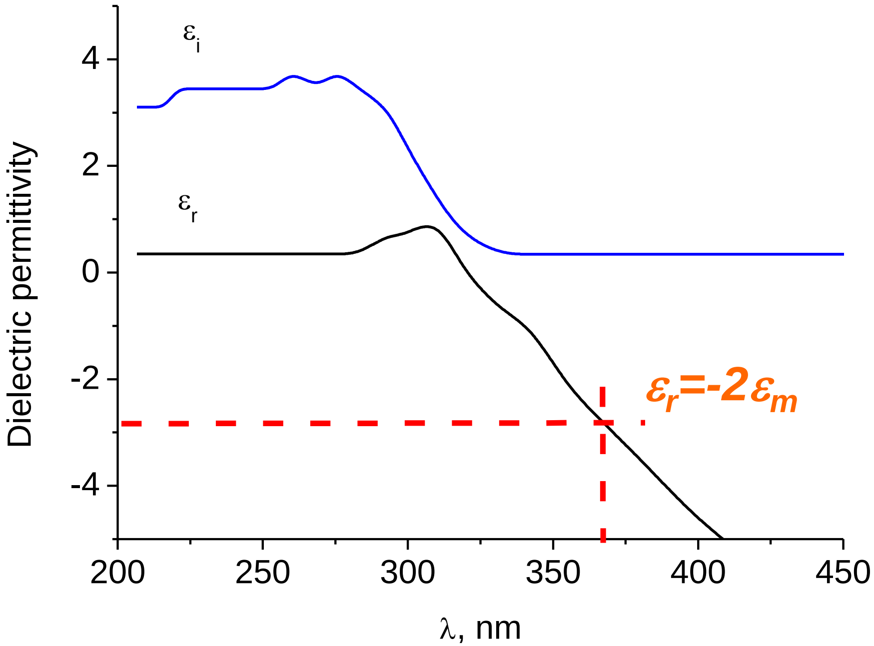
$$E = \frac{24\pi^2 N_A a^3 \varepsilon_m^{3/2}}{\lambda \ln(10)} \left[\frac{\varepsilon_i}{(\varepsilon_r + 2\varepsilon_m)^2 + \varepsilon_i^2} \right]$$

ε_r=-2ε_m - resonance

Kreibig U., Vollmer M. Optical Properties of Metal Clusters. Springer-Verlag: Germany, 1995, Vol. 25.

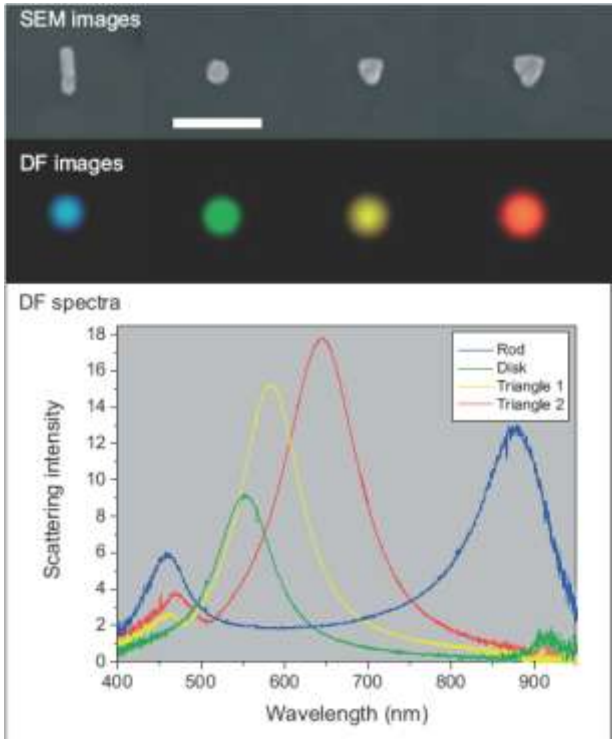


a= 40 nm, *ε_m=1.35*



Silver dielectric permittivities

How shape of nanoparticle can help in adjustment of spectral position of surface plasmon resonance



Relation between size, shape of nanoparticle and it’s extinction spectra

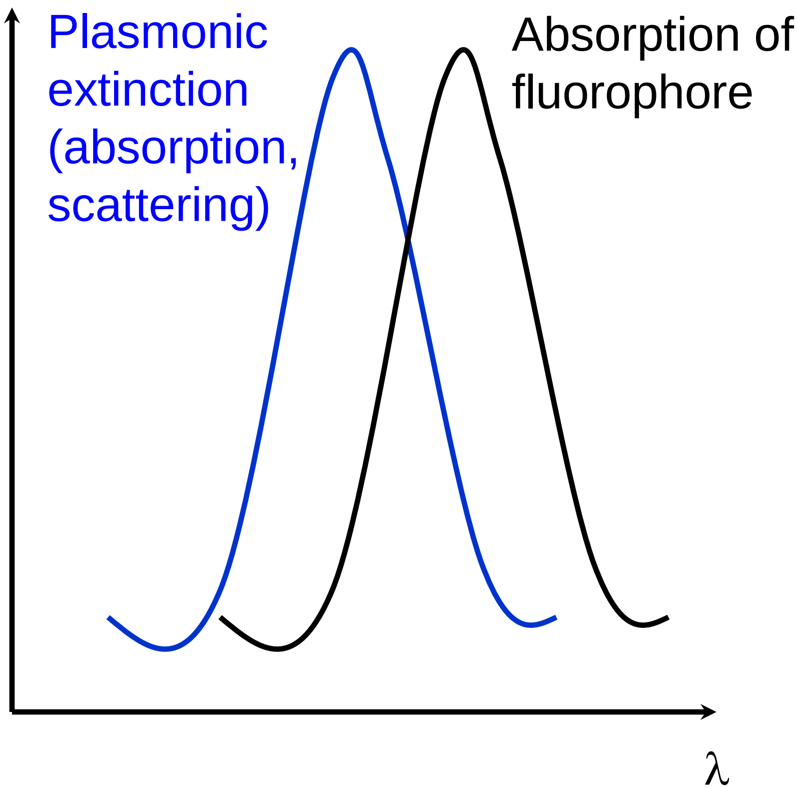
Murray W.A., Barnes W.L. // Adv. Mater., V. 19, pp. 3771-3782, (2007).

“Rainbow” from dispersions of silver nanoparticles

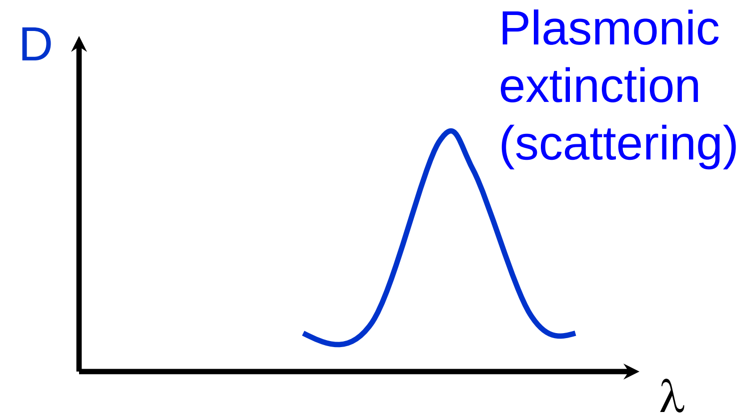
http://www.nanometer.ru/2008/04/06/nanochastici_serebra_plazmon_cvet_11224.html

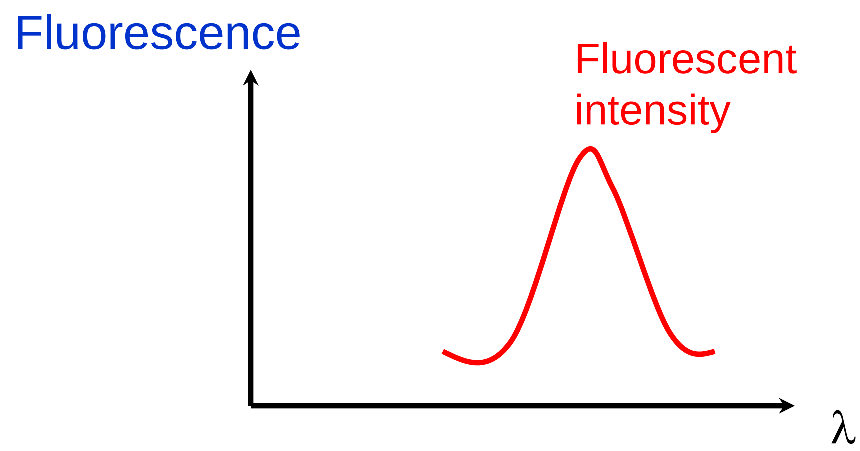
Two ways for the enhancement of plasmon coupled fruorescence

Plasmon resonance overlaps with fluorophore's light absoption D



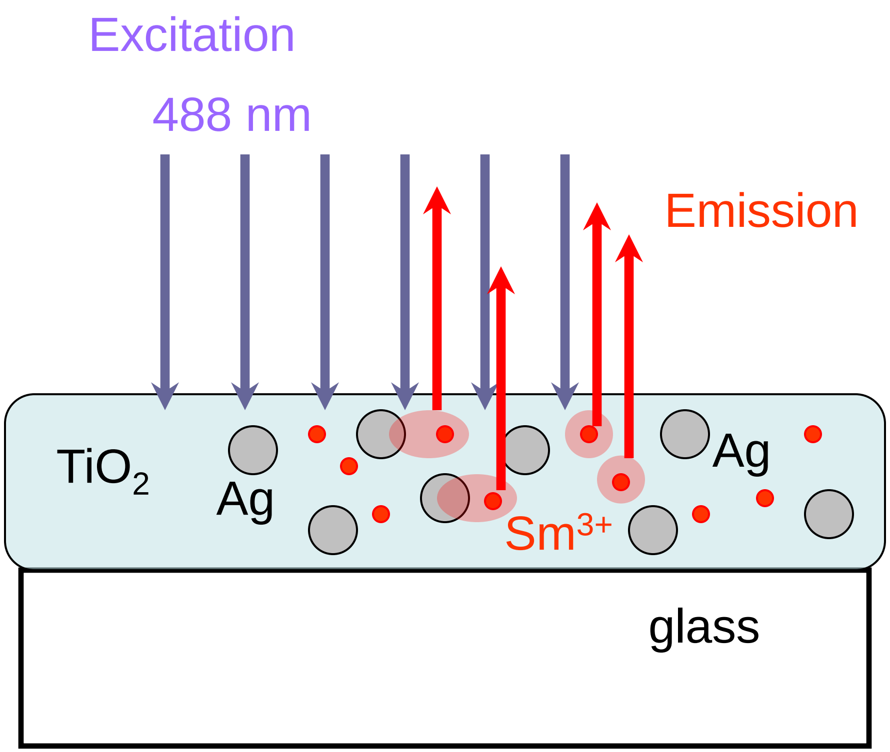
Plasmon resonance overlaps with fluorophore's light emission

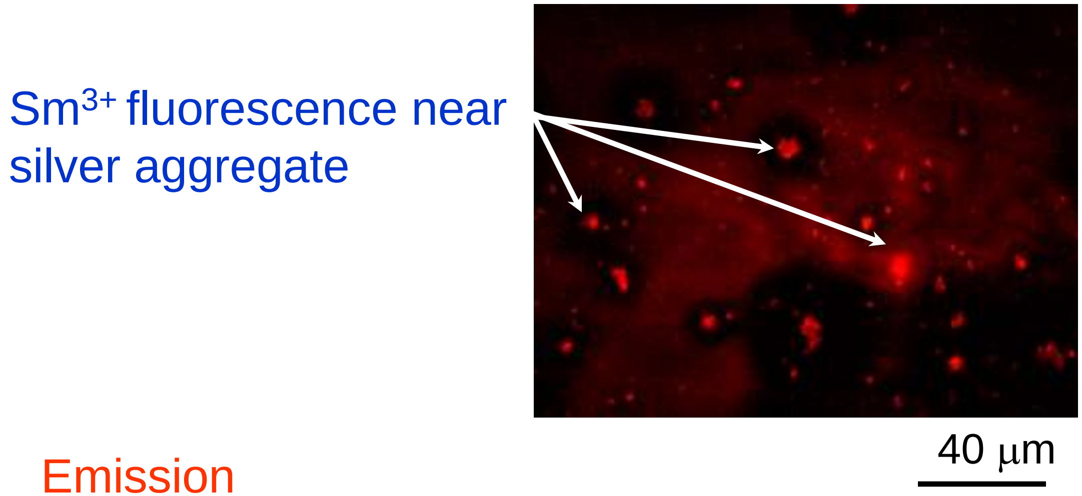


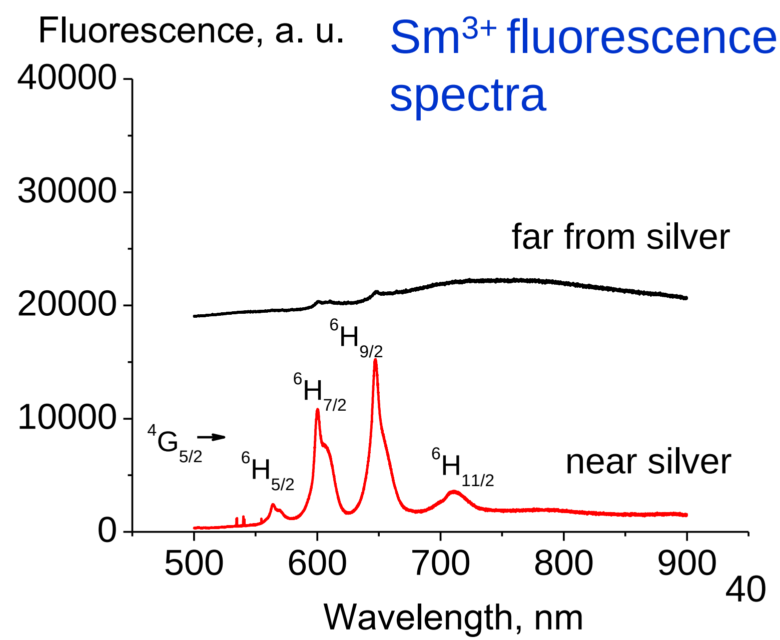


Kruszewski S. // ACTA PHYSICA POLONICA A, Vol. 113, No. 6, pp. 1599-1608 (2008).

Enhancement of Sm^{3+} fluorescence by silver particles

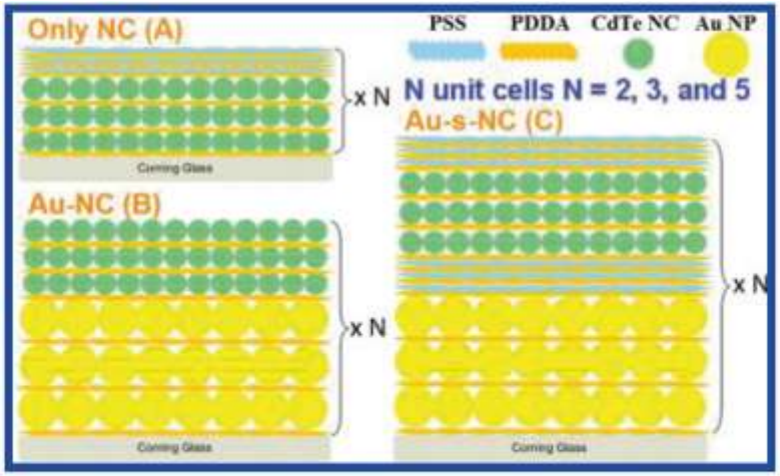


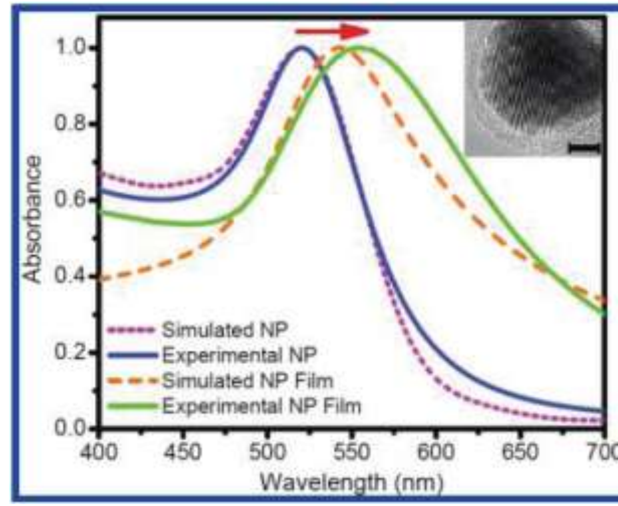


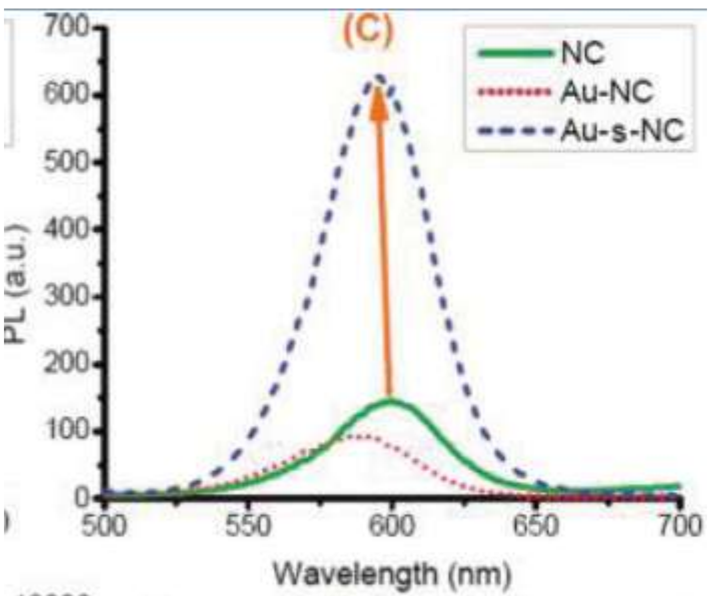


Dolgov L. et al. // Optical Materials Vol. 32, p. 1540–1544 (2010). 1540–1544.

Enhancement of quantum dots fluorescence by gold particles







Photoluminescence of Cd-Te quantum dots placed on the gold nanoparticles (15 nm) layer-by-layer (5 layers):

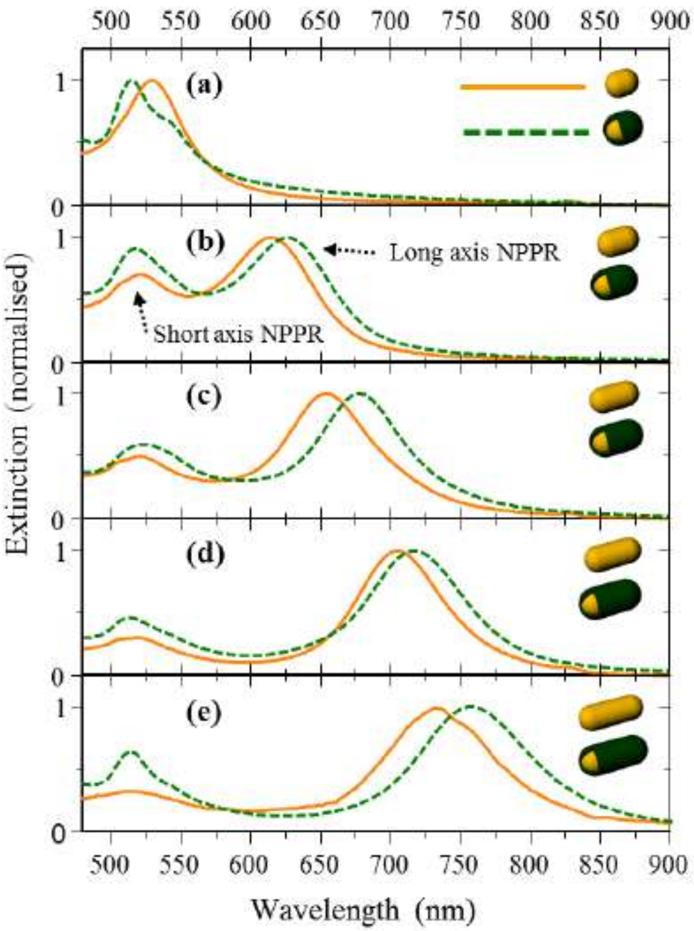
NC – quantum dots without gold,

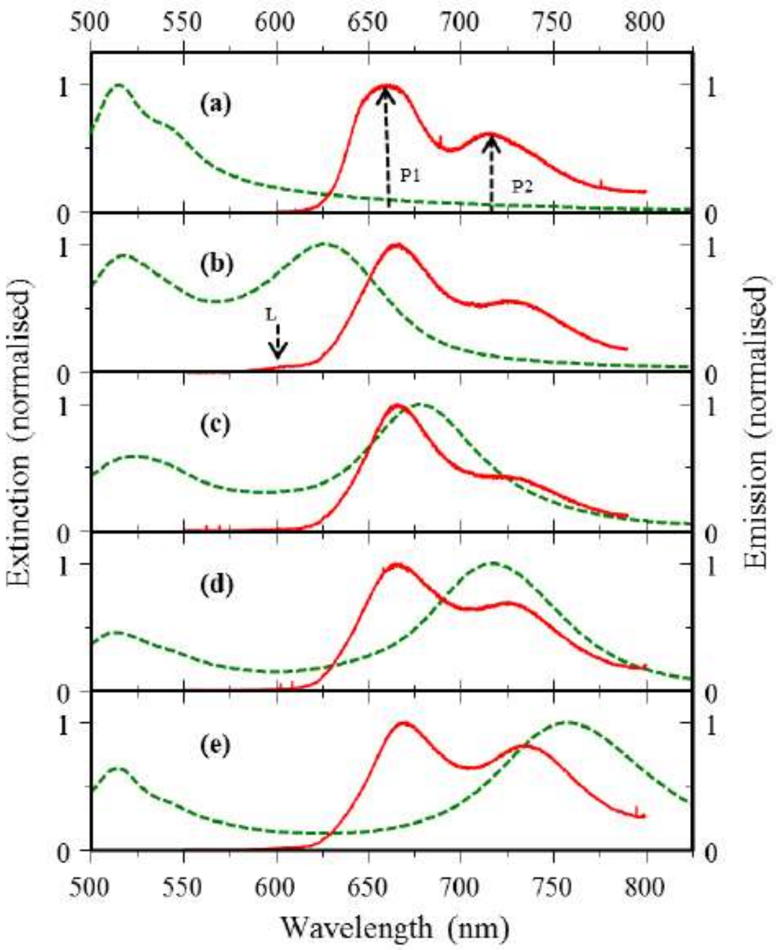
Au-NC – QDs with gold but without spacer layers

Au-NC - QDs with gold and spacer layers

Ozel T. et al. // ACS NANO, Vol.5(2), p. 1328-1334 (2011).

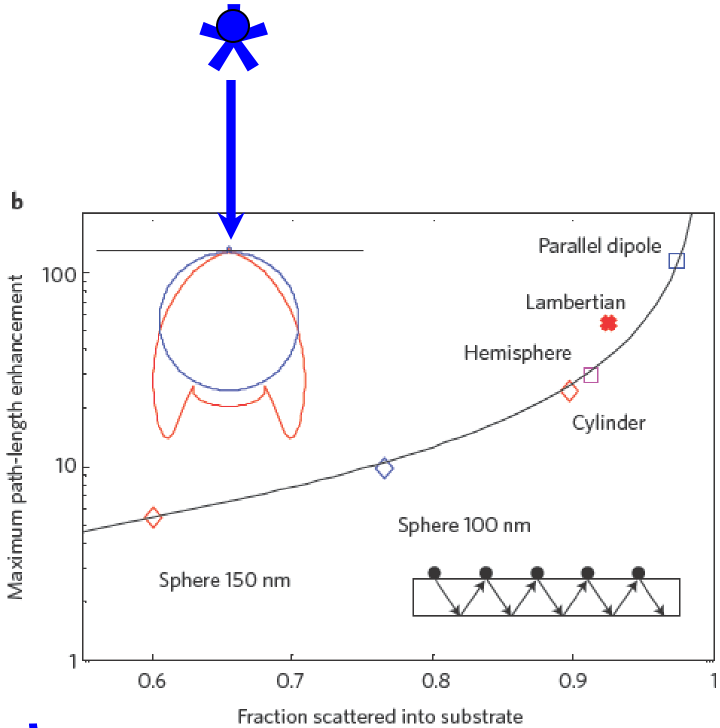
Enhancement of fluorescence by gold particles (example of porphyrin with several emission bands)

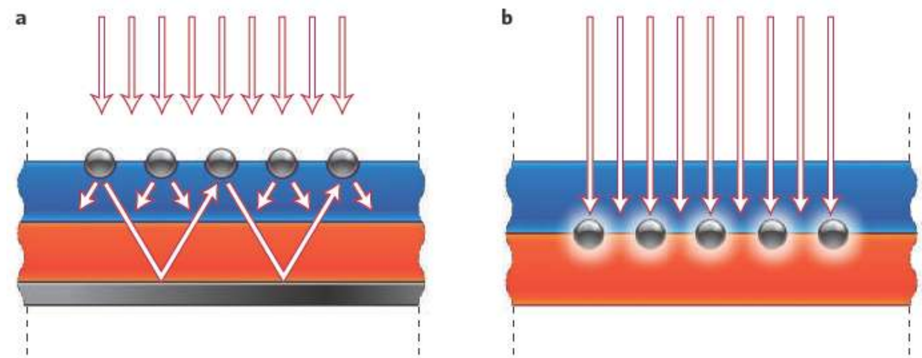




Djiango M., Ritter K., Müller R., Klar T. A. Spectral tuning of the phosphorescence from metalloporphyrins attached to gold nanorods // Optics Express, Vol. 20, No. 17 (2012).

How plasmonic particle can enhance light trapping in solar cell





Nanoparticle as scatterer

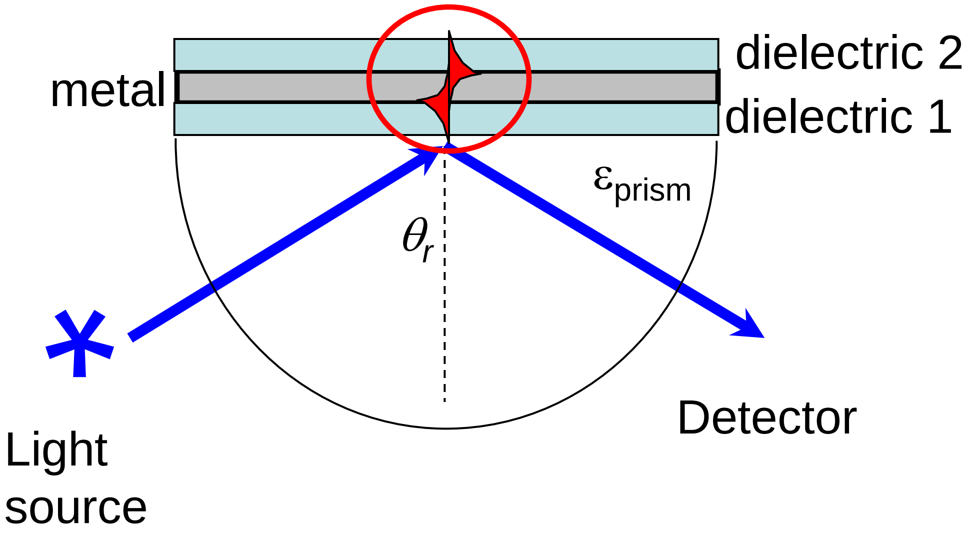
Nanoparticle as “antenna”

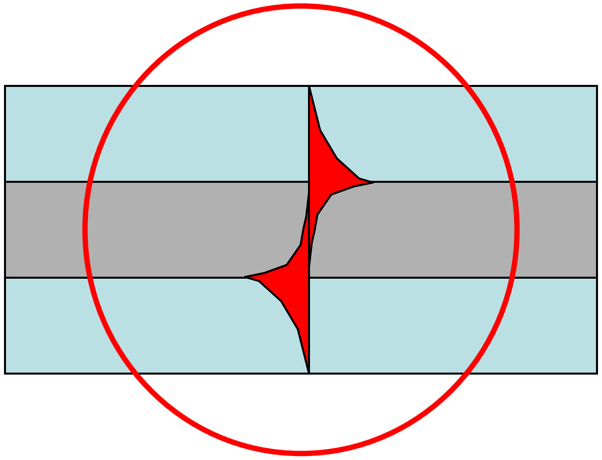
Atwater H. A., Polman A. Plasmonics for improved photovoltaic devices // Nature Materials, Vol. 9, pp. 205-213 (2010).

Different ways for excitation of plasmons.

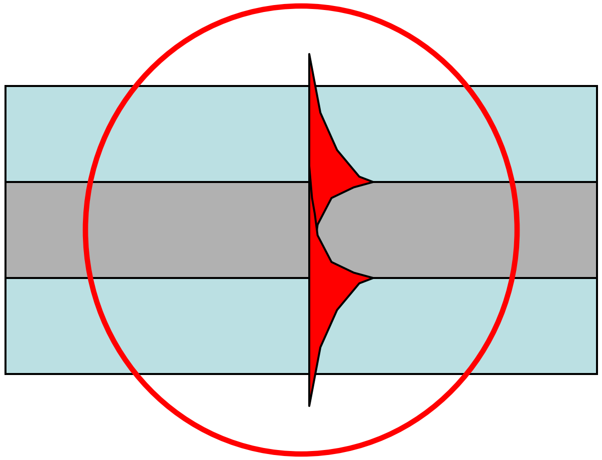
Other ways of excitation of surface plasmons and their application

Otto scheme for inducing plasmons



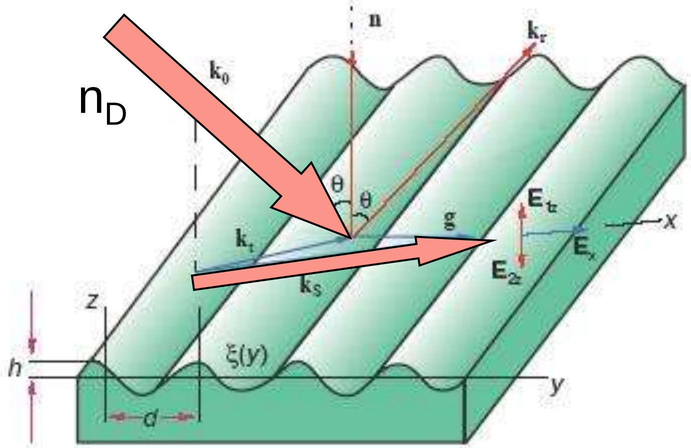


Antisymmetric distribution of the electric fields in the **short range plasmons**



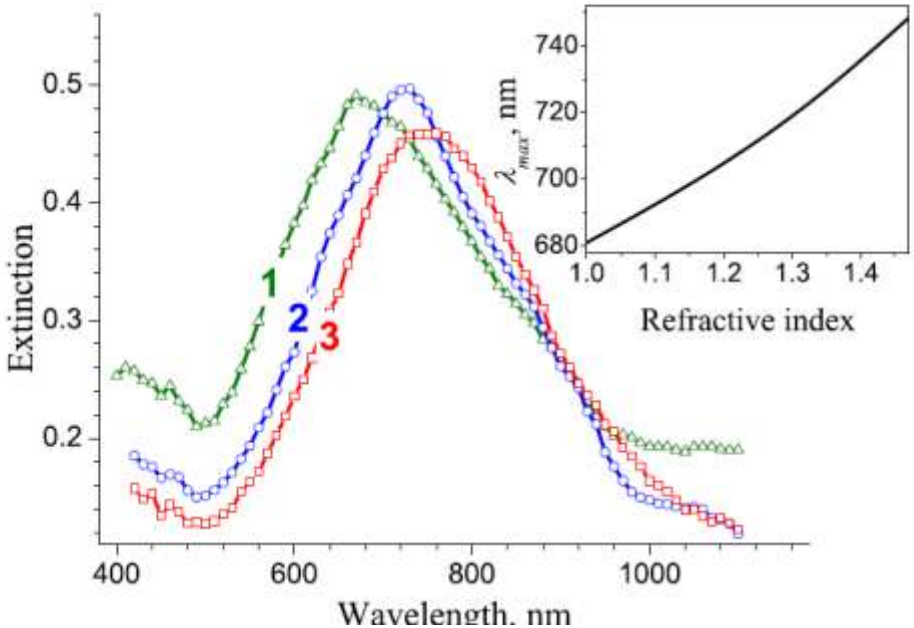
Symmetric distribution of the electric fields in the **long range plasmons**

Inducing of surface plasmons on periodic metal gratings



$$n_D \sin\theta + m\frac{\lambda}{d} = \pm\sqrt{\frac{\varepsilon_m n_D^{\ 2}}{\varepsilon_m + n_D^{\ 2}}}$$

Libenson M. N // Soros Journal, No. 10, pp. 92-98 (1996).

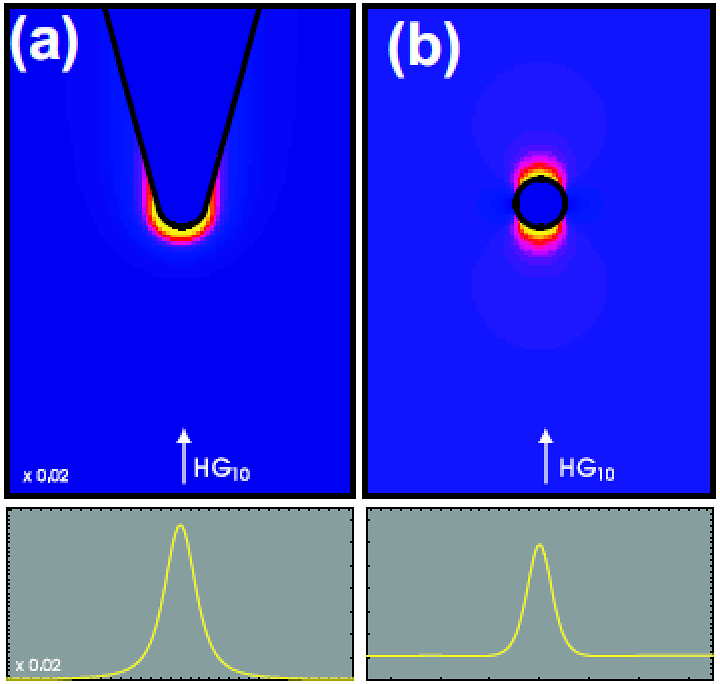


Sensitivity of the periodical array of golden nanowires deposited on the glass and immersed in different media:

1- air,2- water, 3 - glycerine

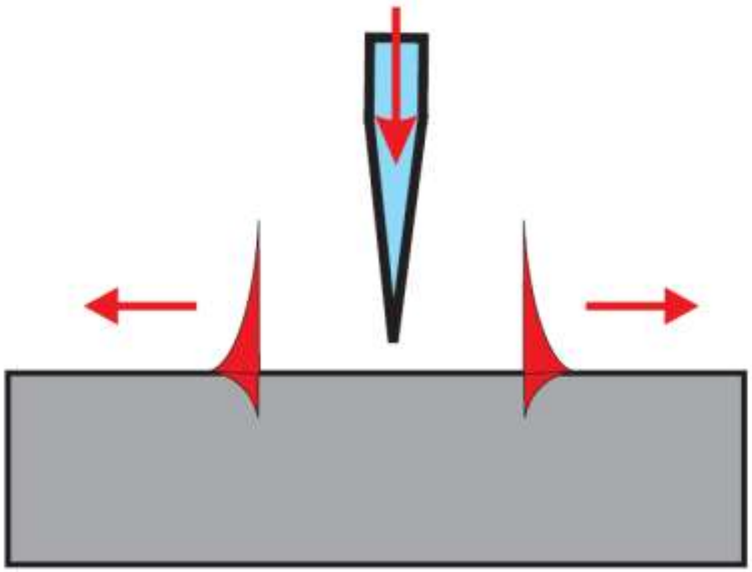
Sosnova et al. // Appl. Phys. B, Vol. 99, p. 493-497 (2010).

Localization of electric field near metal tip and metal nanoparticle



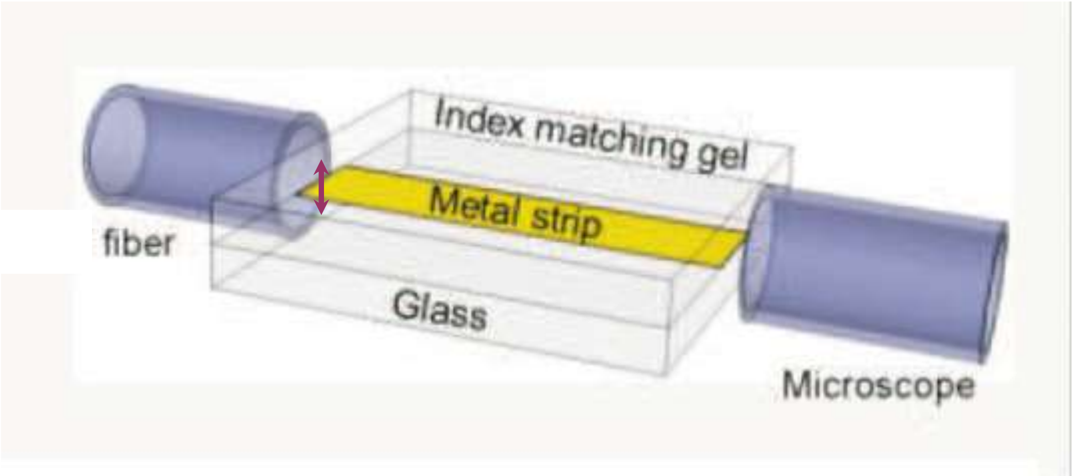
Surface Plasmon Nanophotonics. Series: Springer Series in Optical Sciences, Vol. 131 / Brongersma, Mark L.; Kik, Pieter G. (Eds.), 2007, VIII, 268 p.

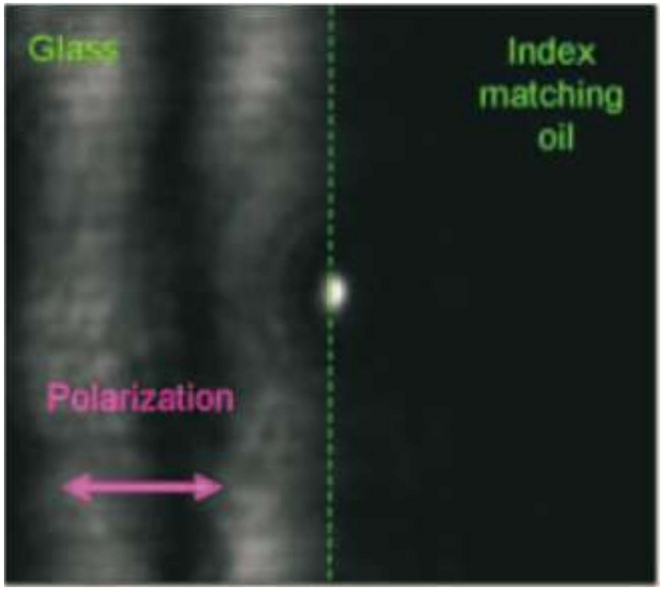
Near field excitation of surface plasmons

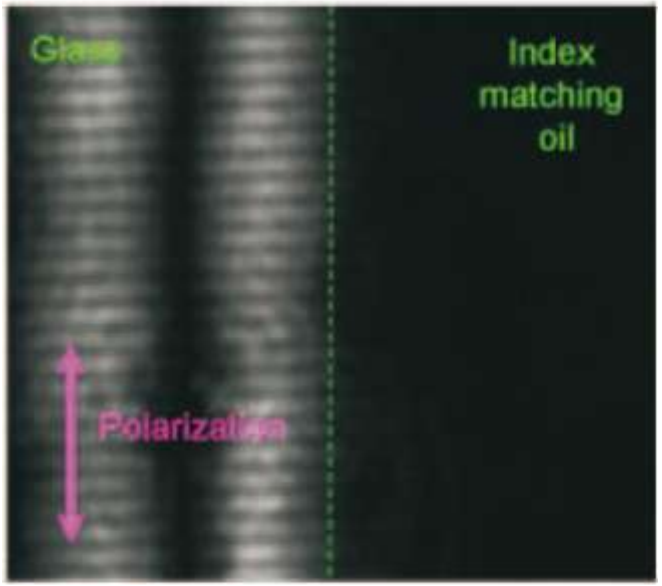


Zayats A.V. et.al. Nano-optics of surface plasmon polaritons // Physics Reports, Vol. 408, p. 131-314 (2005)

Excitation of plasmon wave by end-fire coupling







Oliver Benson Elements of Nanophotonics

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