Plasmonics in random media

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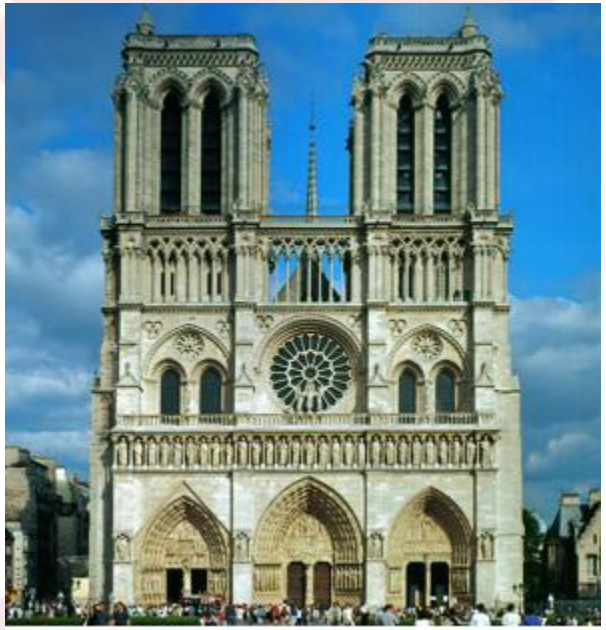
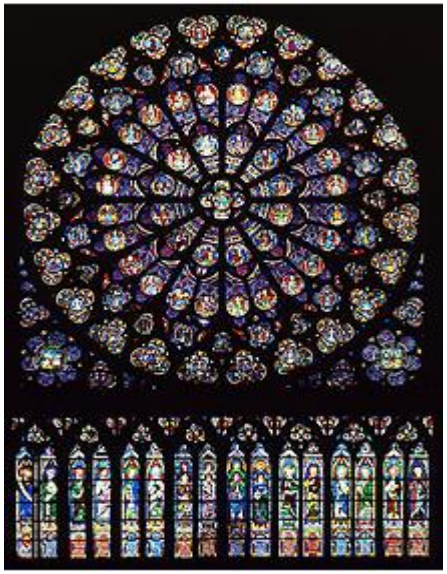
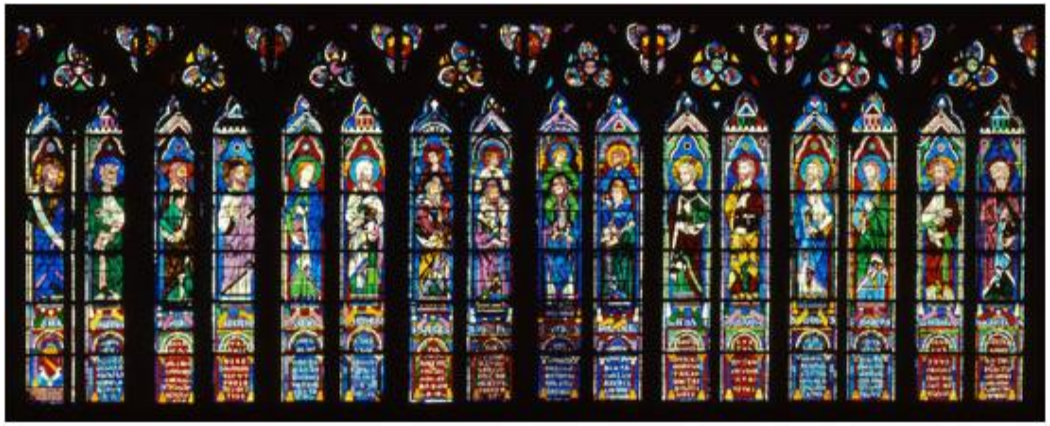
Plasmonics

"Science and technology that deals with the generation, control, manipulation, and transmission of plasmon excitation in metal nanostructures"

Surface plasmons in nanoparticles







Notre Dame de Paris

Cu, Ag, Au

Michael Faraday's Recognition of Ruby Gold: the Birth of Modern Nanotechnology

His 1857 Lecture to the Royal Society in London

David Thompson
DTThompson@aol.com

Figure 1
Faraday's colloidal ruby gold. Reproduced by Courtesy of the Royal Institution of Great Britain

From the paper in Philosophical Transactions entitled 'Experimental relations of gold (and other metals) to light' (1), based on his Bakerian lecture to the Royal Society in London on 5 February 1857, it is clear that Michael Faraday was fascinated by the ruby colour of colloidal gold. The objective of his investigations was to examine the interaction of light with metal particles, but much of this paper focused on various solution such as phosphorus in carbon disulfide in a two phase system. The yellow colour of sodium chloroaurate ($NaAuCl_4$) changes within minutes to the deep ruby colour of colloidal gold. Faraday concluded that the ruby fluid was gold dispersed in the liquid in a very finely divided metallic form not visible in any of the microscopes available in his day. Nearly 100 years later Turkevich et al (2, 4) used electron microscopic

Experimental Relations of Gold (and Other Metals) to Light, M. Faraday, *Philos. Trans. R. Soc. London*, 1857, **147**, 145

Gold-Doped Glass: A Maxwell-Garnett Composite

Red Glass Caraffe
Nurenberg, ca. 1700

Huelsmann Museum, Bielefeld

Developmental Glass, Corning Inc.

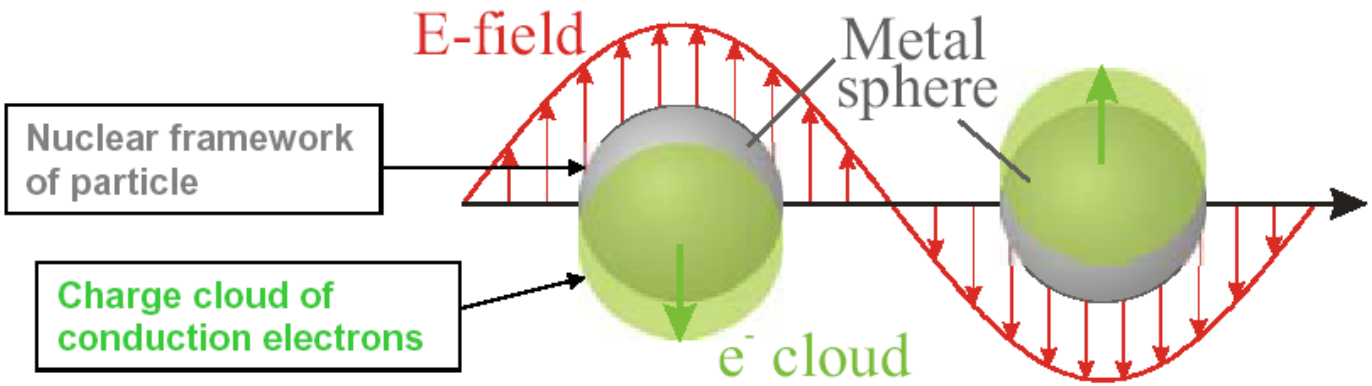
gold volume fraction approximately 10^{-6}
gold particles approximately 10 nm diameter

- Composite materials can possess properties very different from those of their constituents.
- Red color is because the material absorbs very strong in the blue, at the surface plasmon frequency

Boyd , Swieca School 2004

Surface Plasmon Resonance

collective excitation of the conduction electrons



Plasmon excitation influences the absorption and scattering of light from the surfaces of metals.

Surface plasmon frequency
(depend on shape, size and material)

$$E_{in} = \frac{3\varepsilon_0}{\varepsilon_{in} + 2\varepsilon_0} E_0$$

applied electric field

<u>nanosphere</u>

host dielectric function

$$\varepsilon_{in} = 1 - \frac{\omega_p^2}{\omega^2}$$

Drude dielectric function

SP frequency is therefore:

$$\omega = \frac{\omega_p}{\sqrt{1 + 2\varepsilon_0}}$$

(This assumes particle is small compared to wavelength.)

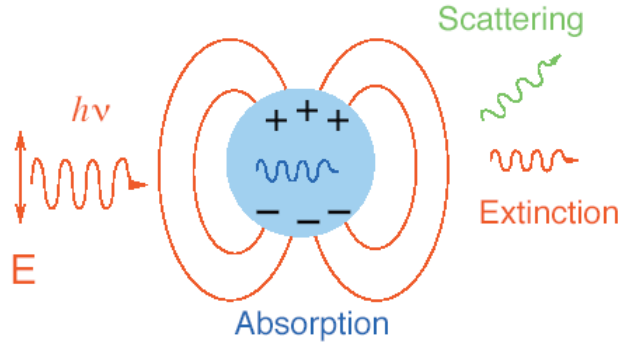
Extinction coefficient

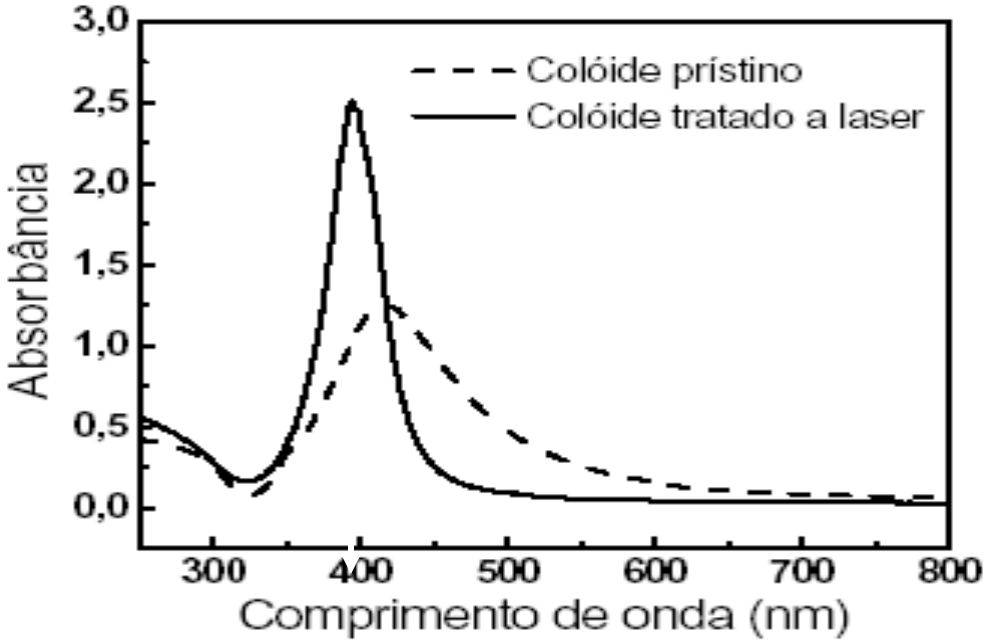
$$C_{ext} = 9\frac{\omega}{c}\varepsilon_m^{3/2}V\frac{\varepsilon_2}{\left[\varepsilon_1 + 2\varepsilon_m\right]^2 + \varepsilon_2^2}$$

nanospheres

Mie theory 1908 (dipole aproximation)

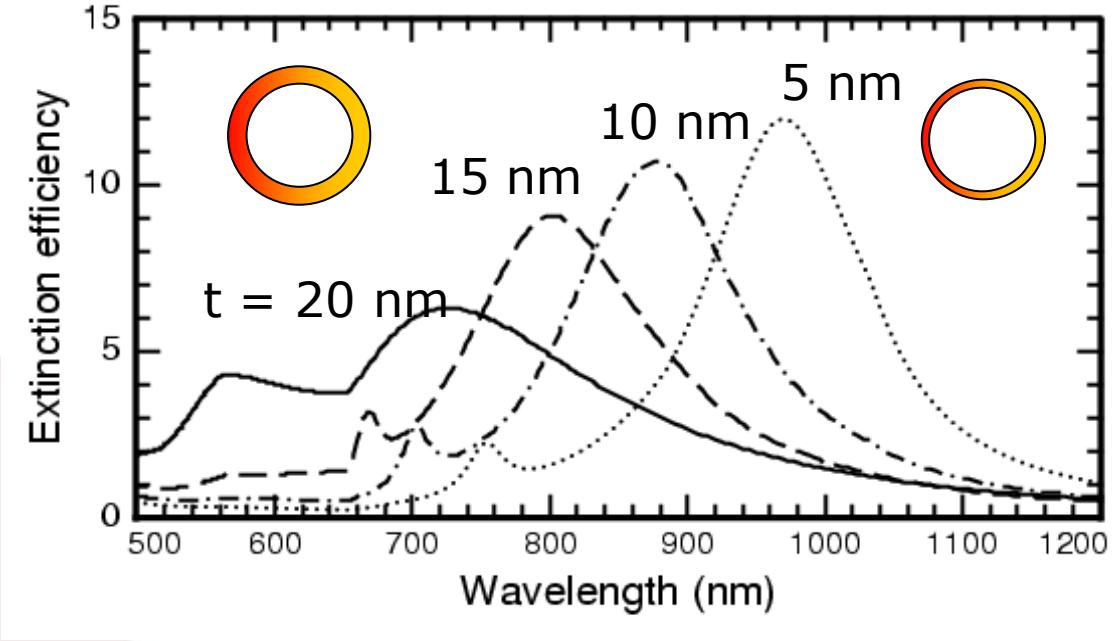
Silver in aqueous colloid



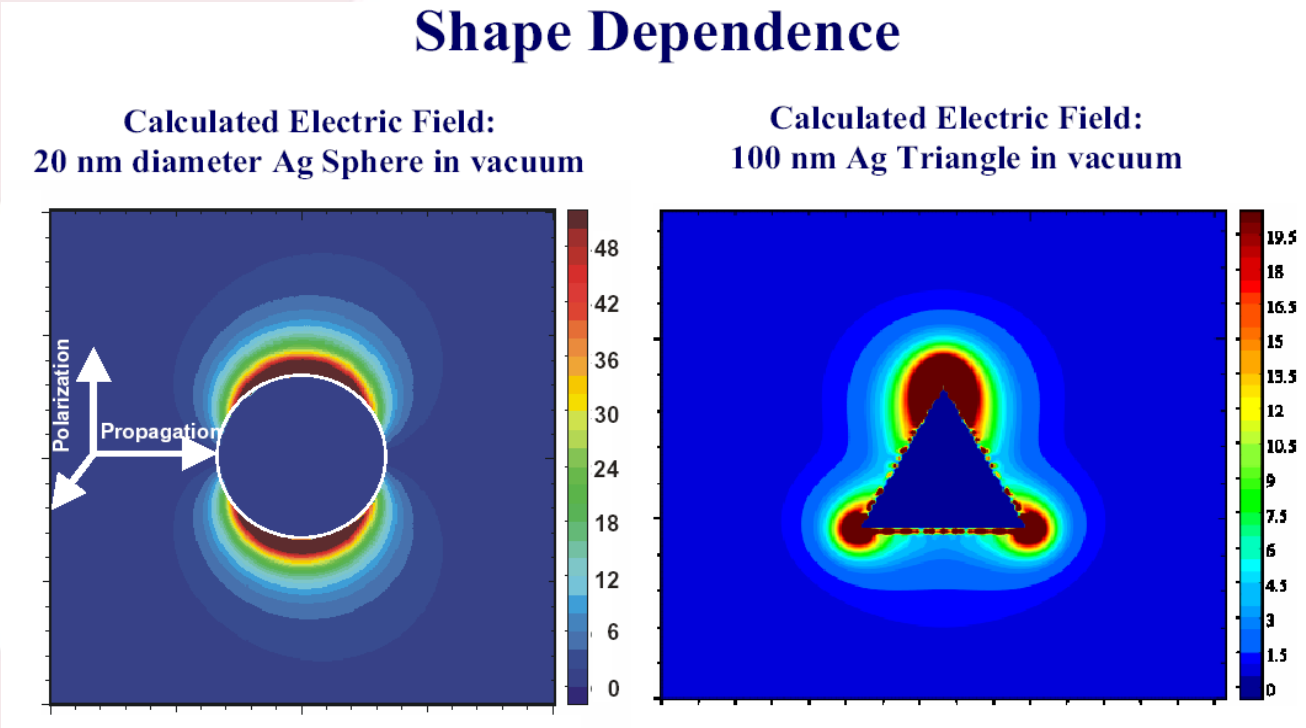


Metal nanoshell colloids

Plasmon resonance tunable by core and shell dimensions



Near-field intensity

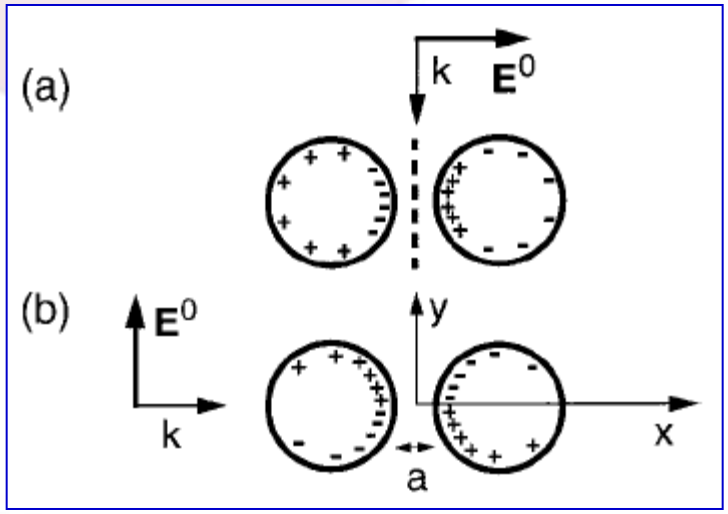


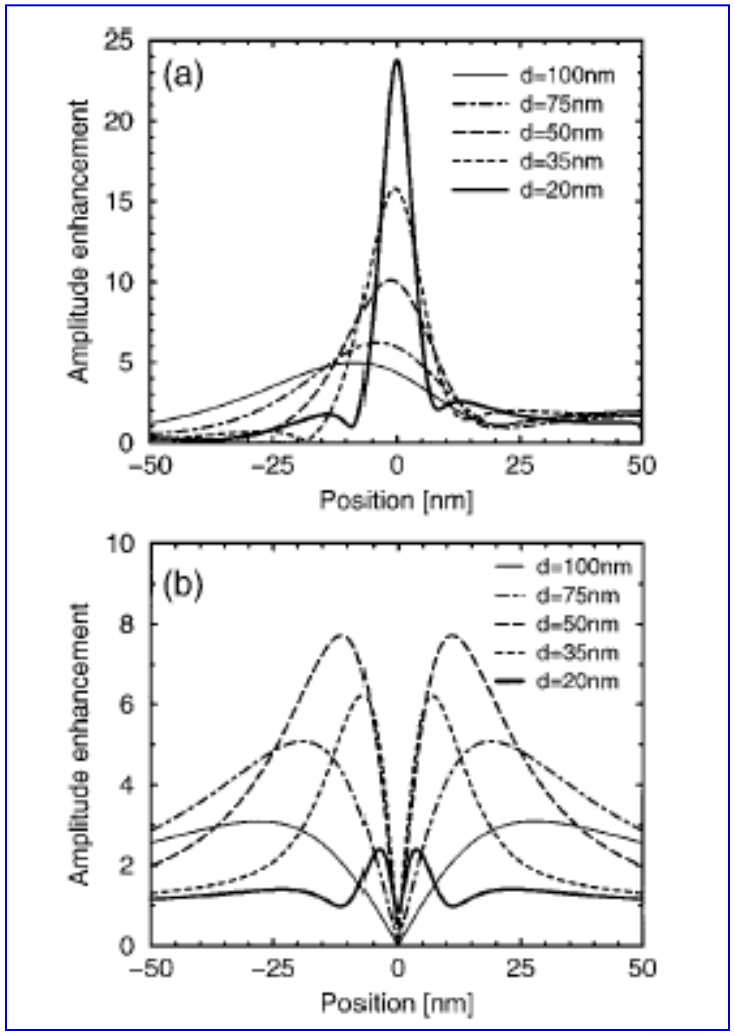
Schatz et al.

Spatial extension: 10-50 nm

Coupled nanoparticles

Kottmannn, Martin Opt. Lett 2001



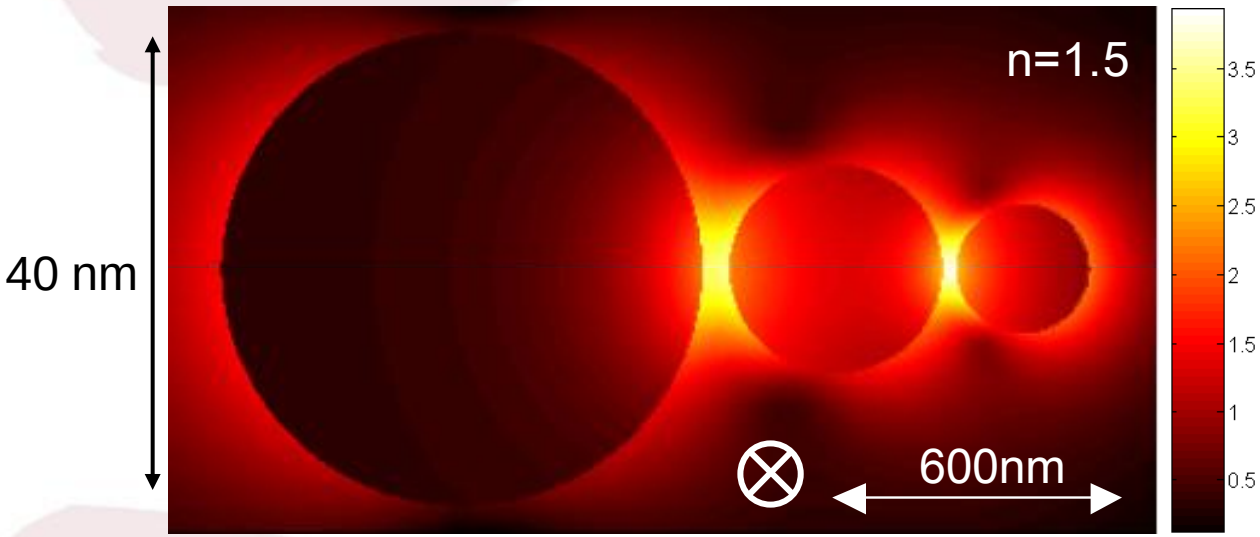


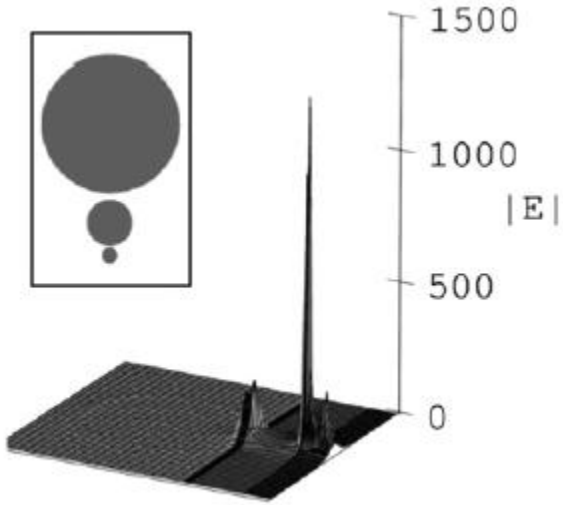
Field increases by 24 for particles with diameter of 20 nm.

Intensity enhancement > 500

More complex nano-structures

Log enhancement





Plasmonic nanolens:
First proposed by Li, Stockman & Bergman, PRL (2003)

Bidaut, JACS 2008

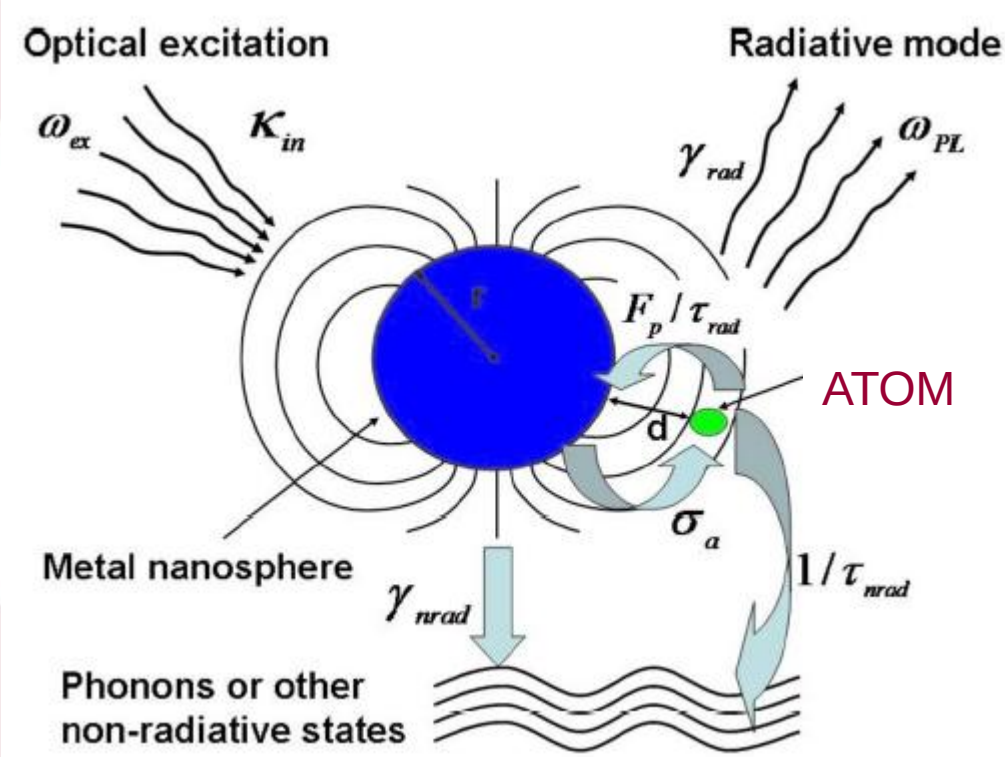
Metal-dielectric nanocomposites

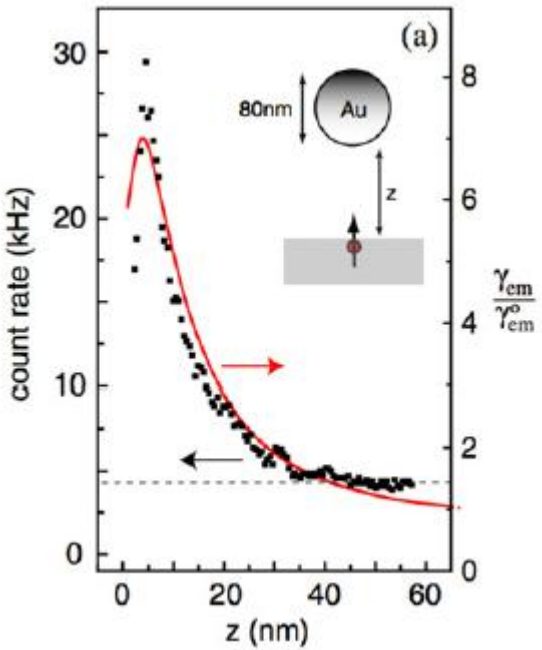
- Plasmon enhanced fluorescence
- Third-order nonlinear optics in plasmonic materials
- Random lasers

Surface plasmon resonances may increase NL response

Scale size of inhomogeneities << optical wavelength
Optical susceptibility can be described by volume averaged quantities

Plasmon enhanced luminescence





Novotny et al. PRL 2006

$$\sigma_{PL}(\omega_{ex}, \omega_{PL}) = \sigma_{abs}(\omega_{ex})\eta_{rad}(\omega_{PL})$$

Fractals structures and hot spots

Shalaev et al.
Marder et al.

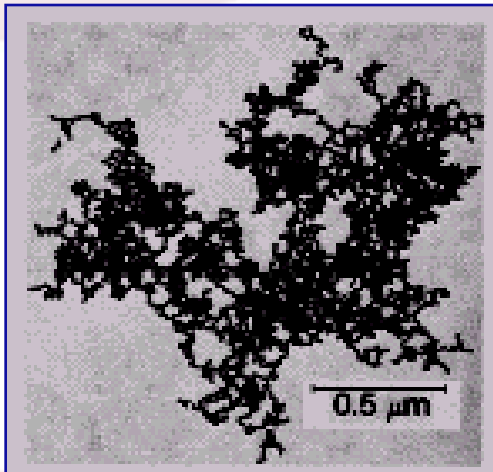
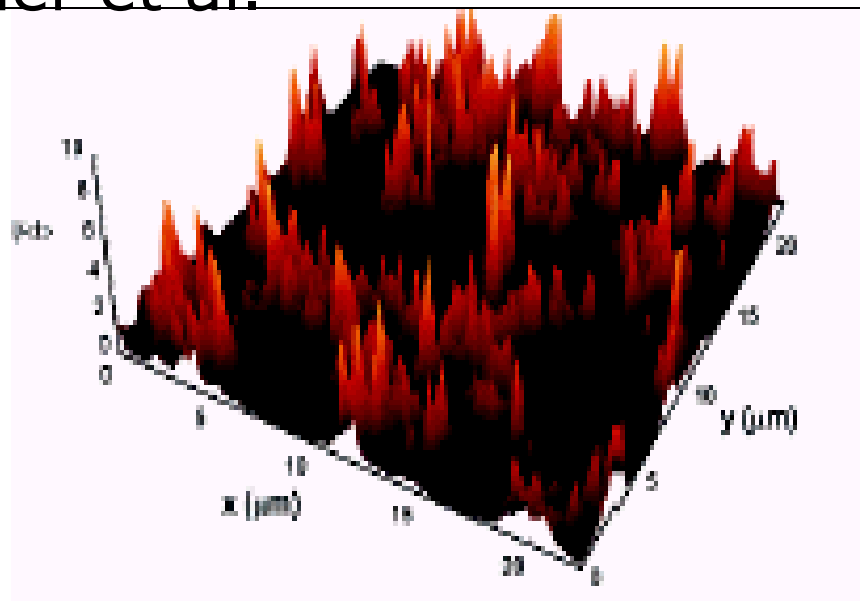


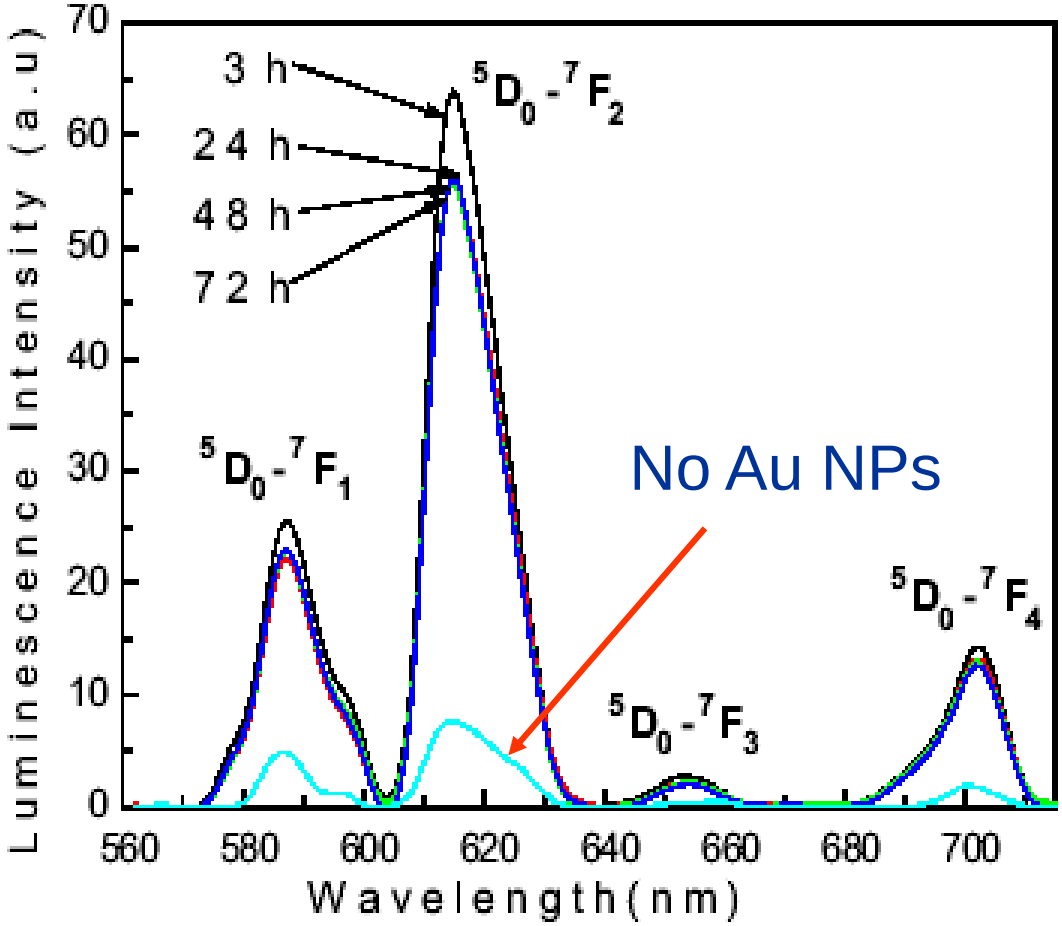
FIG. 1. TEM image of typical gold colloid aggregate. This cluster contains 4739 gold particles.

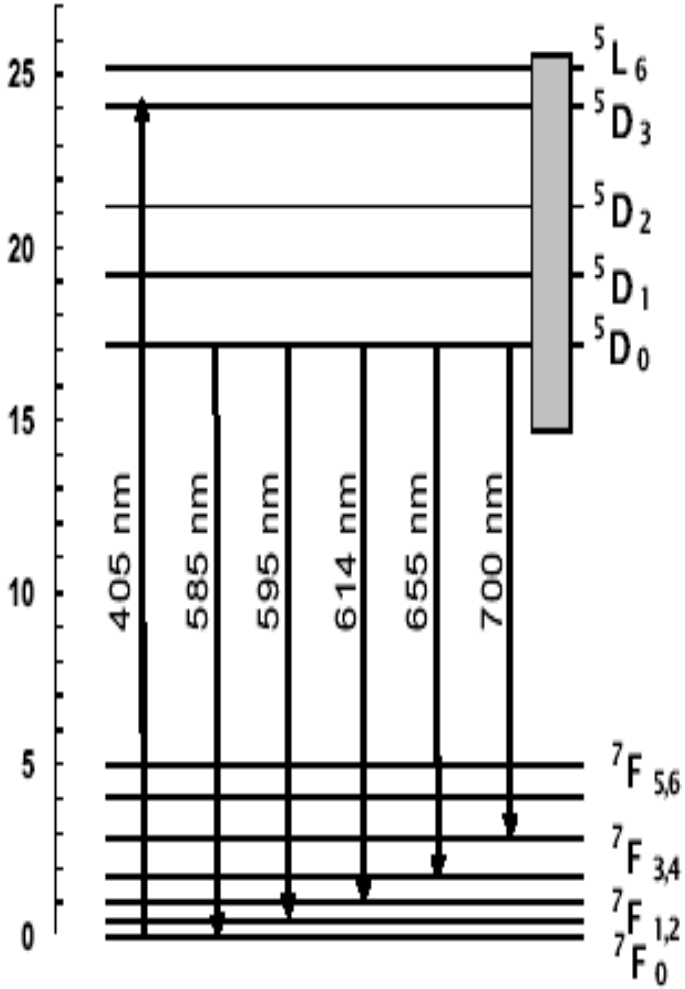


Optical glasses doped with trivalent rare earth ions containing silver or gold NPs

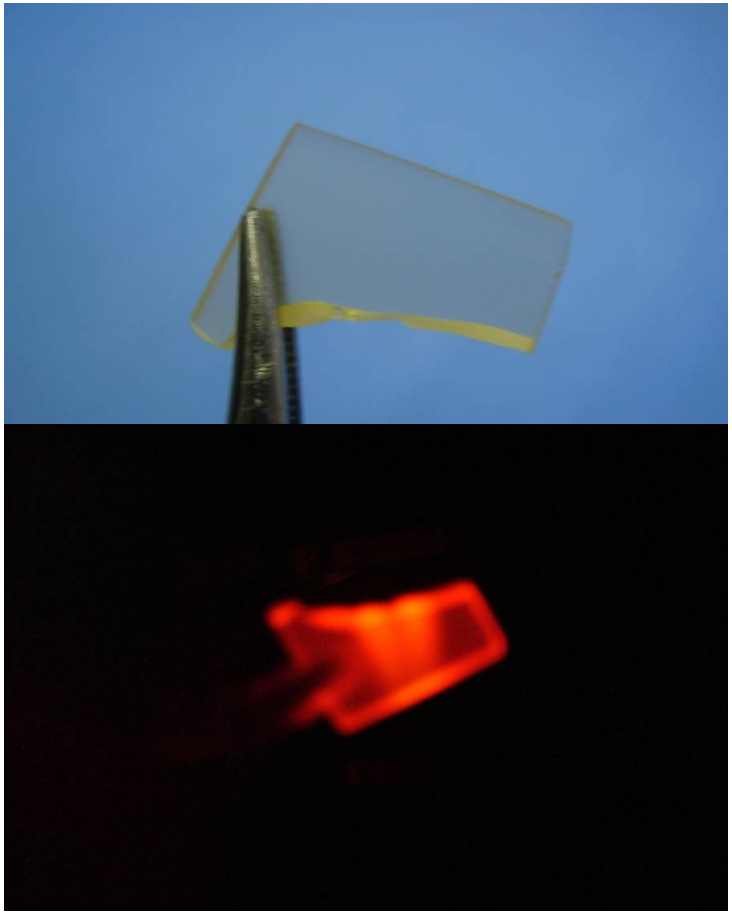
APPLIED PHYSICS LETTERS 94, 101912 (2009)

Photoluminescence enhancement by gold nanoparticles in Eu^{3+} doped $GeO_2-Bi_2O_3$ glasses



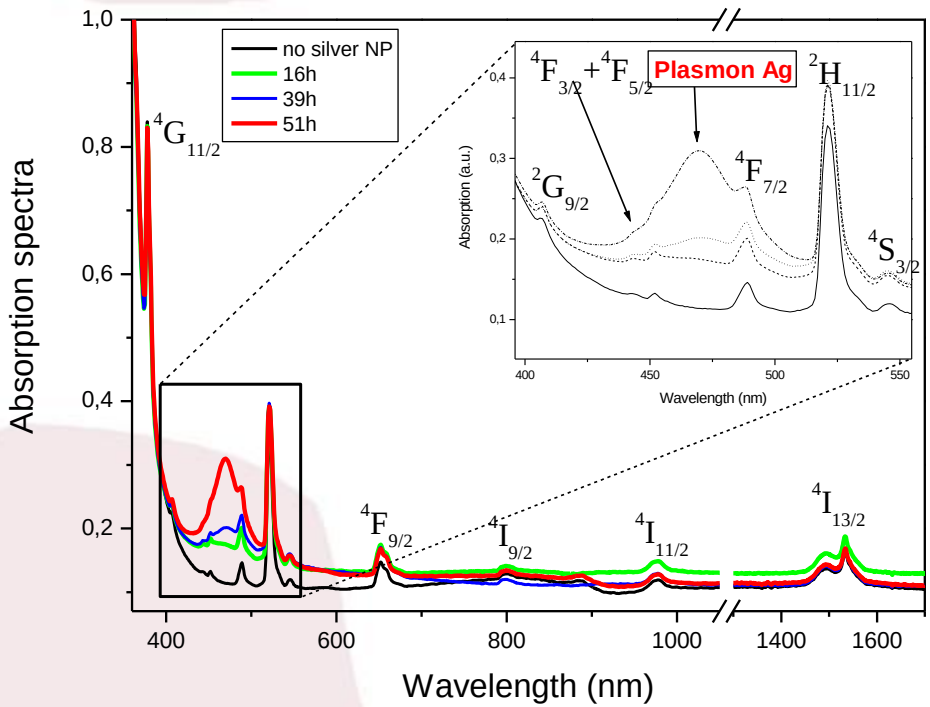


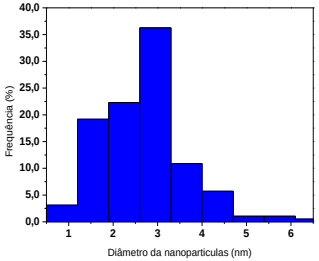
Enhanced luminescence at 614 nm (excitation at 405 nm)



Frequency upconversion in Er^{3+} doped $PbO-GeO_2$ glasses containing silver nanoparticles

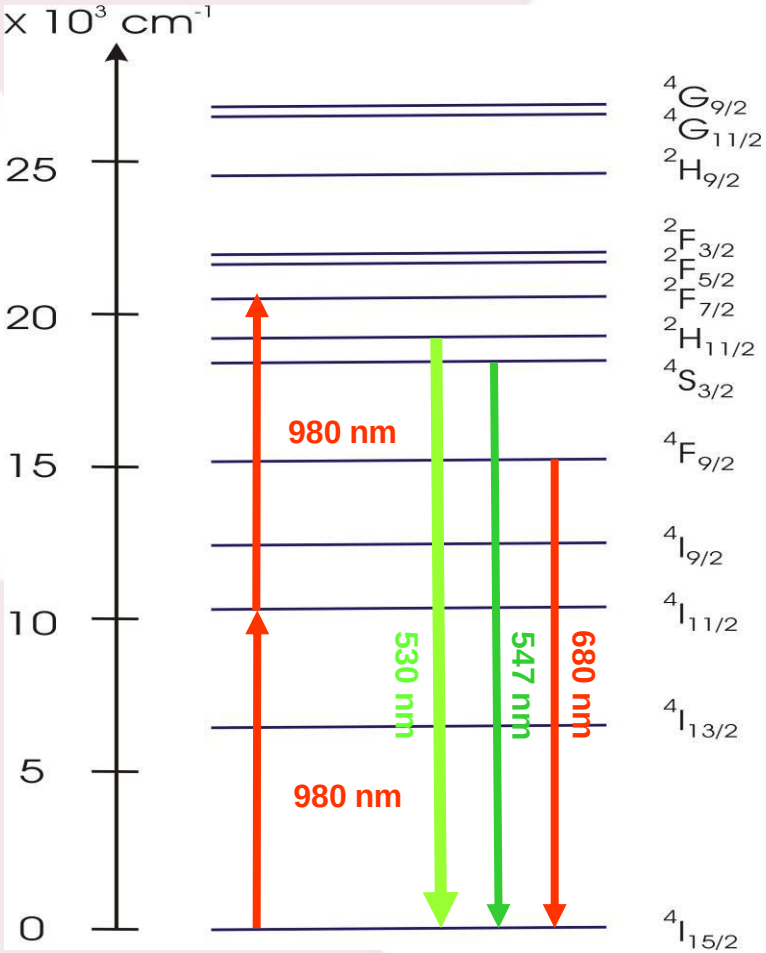
59 PbO – 41 GeO_2

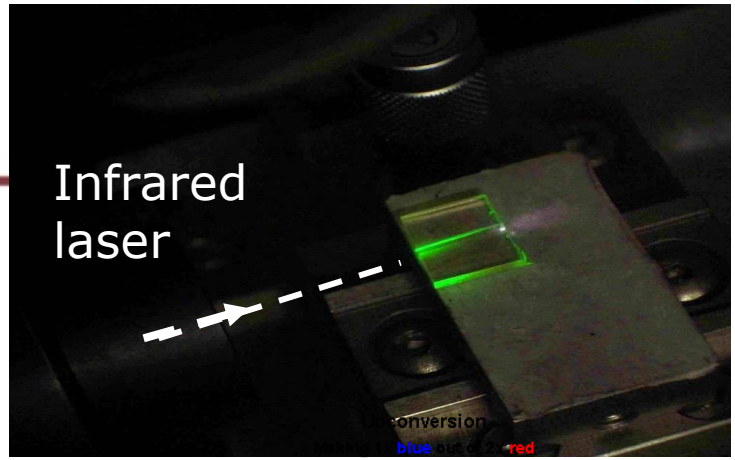


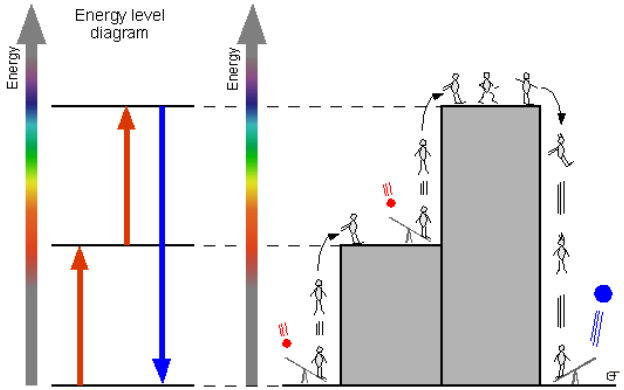


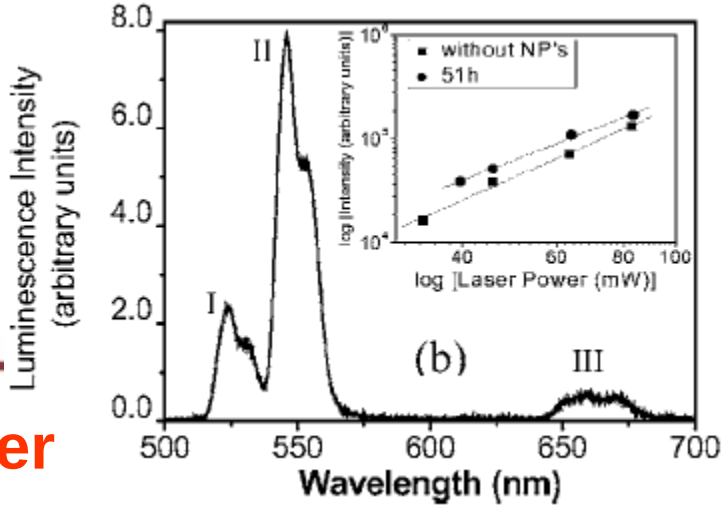
Appl. Phys. Lett. 90, 081913 (2007)

100% enhancement









Nanothermometer

Tellurium glass with silver NPs doped with Pr^{3+} or (Tb^{3+}-Eu^{3+}) or Tb^{3+}:

J. Appl. Phys. 105, 103505 (2009).
J. Appl. Phys. 104, 093531 (2008).
J. Appl. Phys. 103, 093526 (2008).

Gemanate glass doped with Eu^{3+} or (Yb^{3+}-Er^{3+}) containing silver, gold or copper NPs:

Appl. Phys. Lett. 94, 101912 (2009).
Appl. Phys. B 94, 239 (2009).
Appl. Phys. Lett. 92, 141916 (2008).

Nonlinear Optics

Interaction light-matter under circunstances that the linear superposition principle is violated

Optical polarization ≡ Dipole moment per unit volume

$$P = \varepsilon_o \left[\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \right]$$

$$\chi^{(n)} \equiv 0 \text{ , } n = \text{even (centro-symmetric media)}$$

P induces changes in the speed of light in the medium and new frequencies may be generated

Nonlinear Optics hold great promise for applications such as:

- All-Optical Switching
- Optical Limiting
- Optical Sensors
- Lasers and Amplifiers

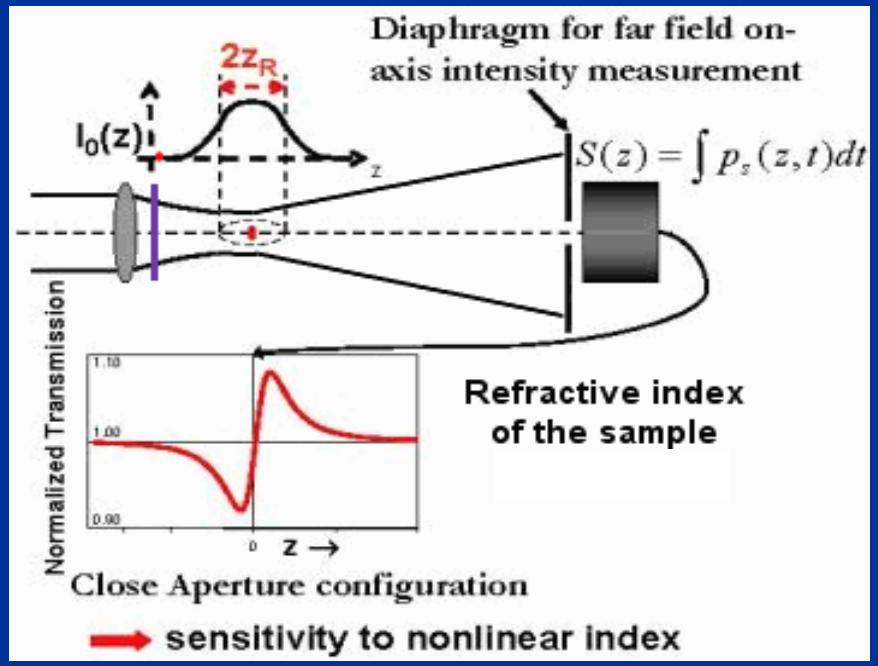
but the lack of appropriate materials do not allow the implementation of many ideas already presented

Z-scan technique

Nonlinear refraction

$$n = n_0 + n_2 I(r)$$

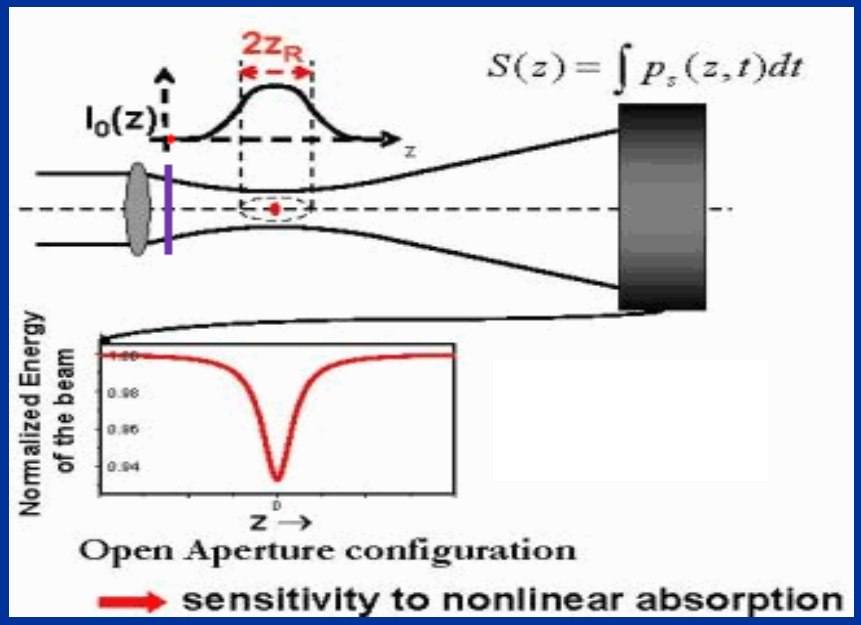
$n_2 > 0$ self focusing
$n_2 < 0$ self defocusing
$\Delta T \propto n_2 I$



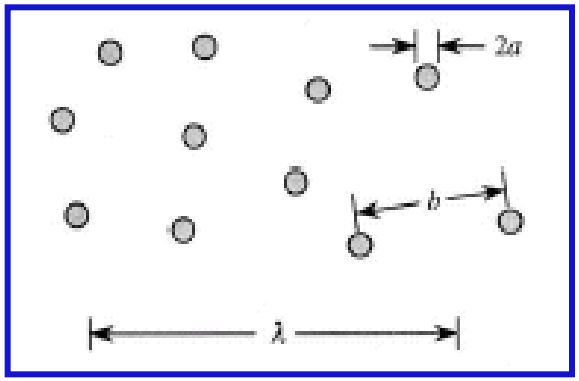
Nonlinear absorption

$$\alpha = \alpha_0 + \alpha_2 I(r)$$

$\Delta T \propto \alpha_2 I$



Colloids containing metallic nanoparticles



Local field enhancement

$$\chi_{eff}^{(3)} = f\,\eta^2 |\eta|^2 \chi_{NP}^{(3)} + \chi_{host}^{(3)}$$

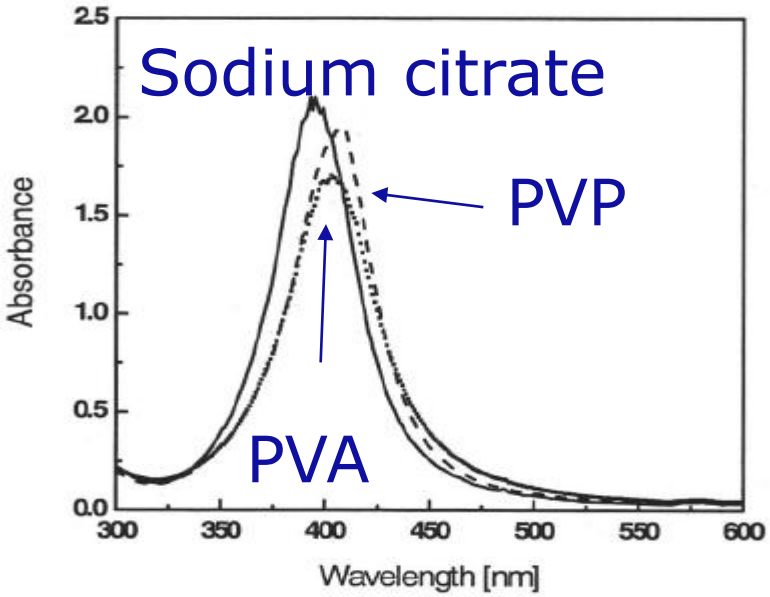
Filling fraction

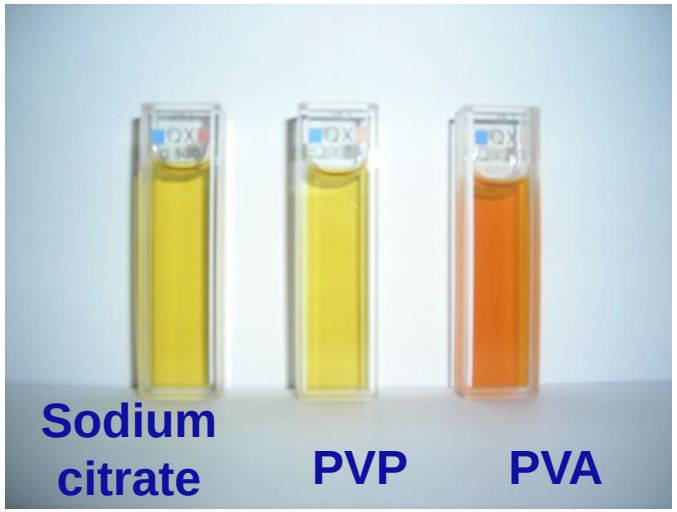
$$\eta = \frac{3\varepsilon_{NP}(\omega)}{\left[\varepsilon_{NP}(\omega) + 2\varepsilon_h(\omega)\right]}$$

Surface plasmon resonance

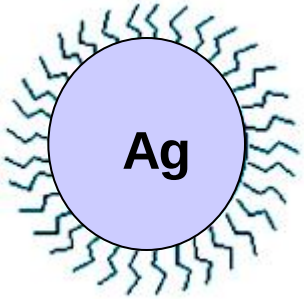
$$\mathrm{Re}\left[\varepsilon_{NP}(\omega_{sp}) + 2\varepsilon_h(\omega_{sp})\right] = 0$$

Third order susceptibility of silver colloids





Z – scan
532 nm
80 ps
5 Hz



Influence of stabilizing agents and dipole moment of solvents

Susceptibility changes by more that 100% for PVA and PVP

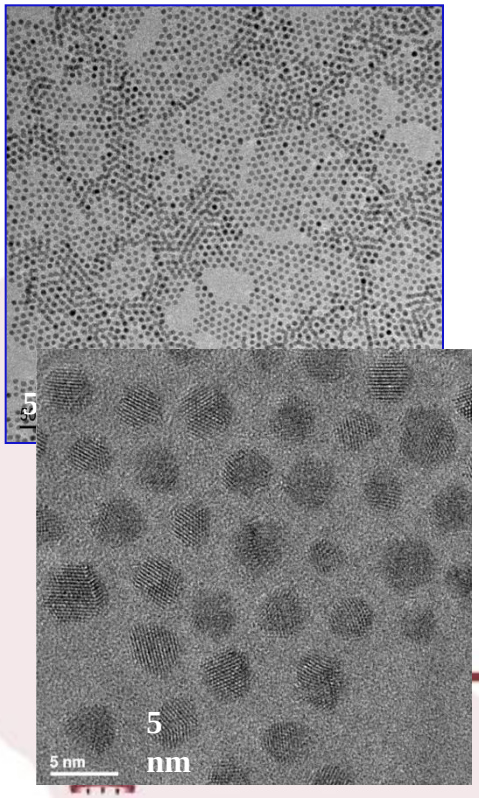
J.O.S.A. B 24, 2136 (2007)

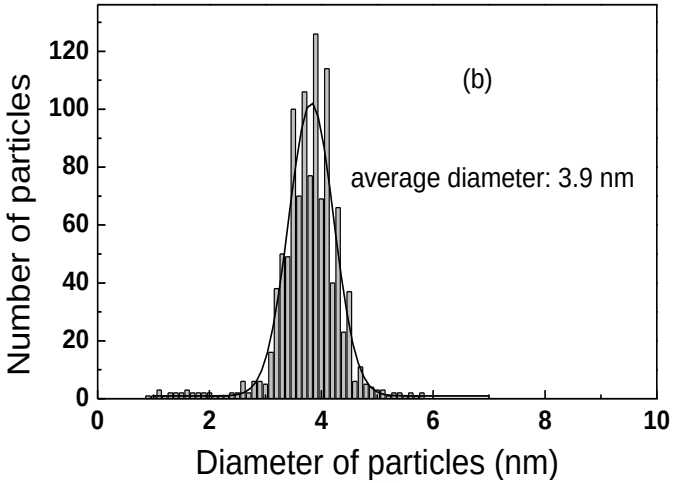
Applied Physics B 92, 61 (2008)

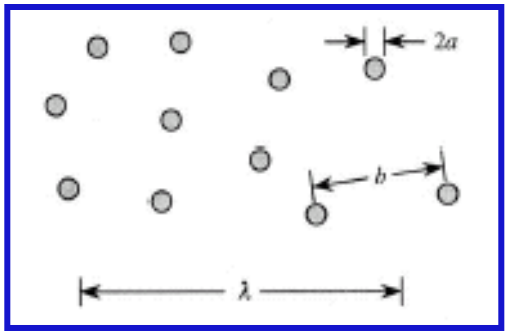
NL susceptibility of silver nanoparticles in CS_2

Competing processes between nonlinearities of the constituents

Silver NPs capped with dodecanethiol



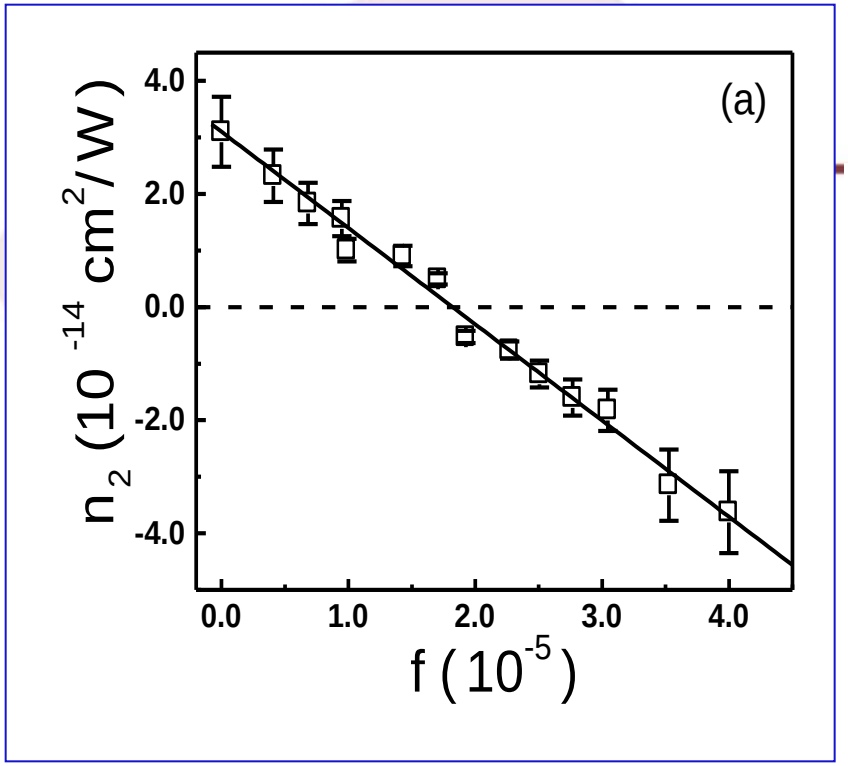




$$\beta = \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h}$$

$$\varepsilon_{eff} = \varepsilon_h \cdot \left[1 + \frac{3\beta f}{1 - \beta f} \right]$$

NL Maxwell Garnet model

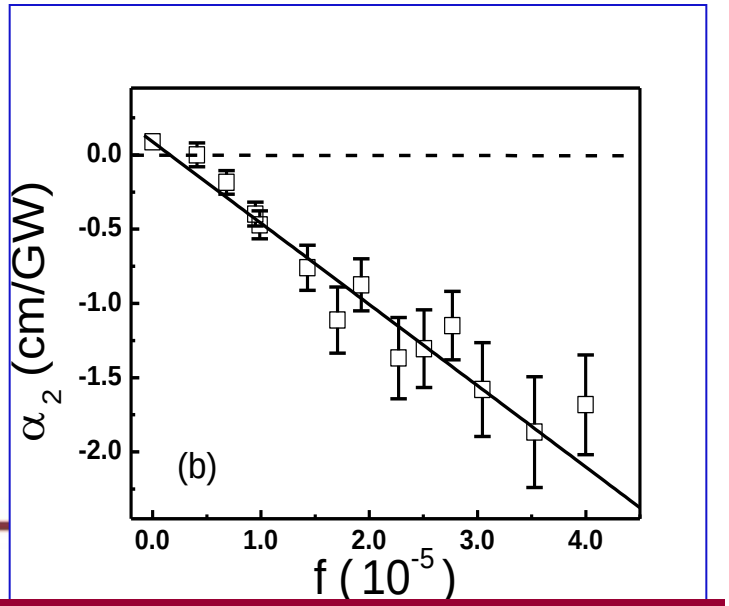


$$\chi_{eff}^{(3)} \cong \chi_h^{(3)} + f\,(a + i\,b)\,\chi_{NP}^{(3)}$$

$$\chi_{NP}^{(3)} = (-6.3 + i\,1.9) \times 10^{-16} \;\; m^2/V^2$$

$$\chi_h^{(3)} = 2.9 \times 10^{-20} + i\;3.5 \times 10^{-22}$$

m^2/V^2



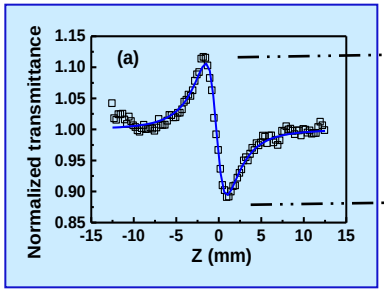
Control of spatial and temporal profile of optical beams (Space and temporal solitons)

J.O.S.A. B 22, 2444 (2005)

First observation of high-order nonlinearities in Ag aqueous colloids

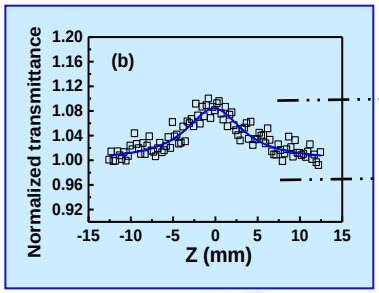
Z-scan 80 ps @ 532 nm (single pulses 5 Hz)

NL refractive behavior



$$\Delta T \propto n_2 I$$

Nonlinear absorption

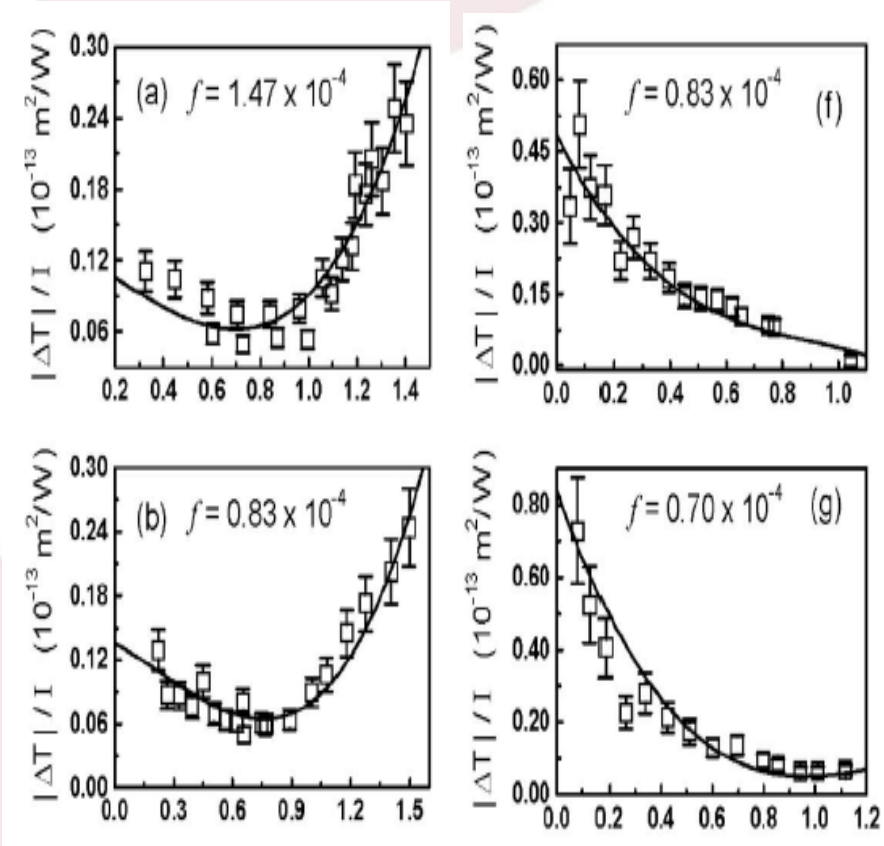


$$\Delta T \propto \alpha_2 I$$

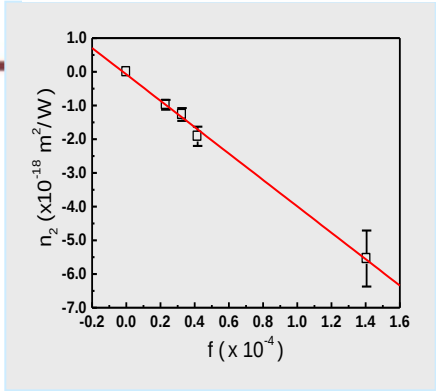
3rd order
$$\Delta T \propto I$$

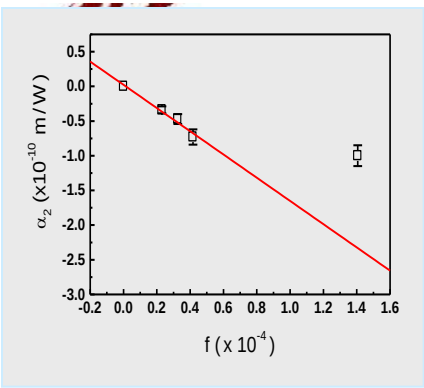
NL refraction

NL absorption

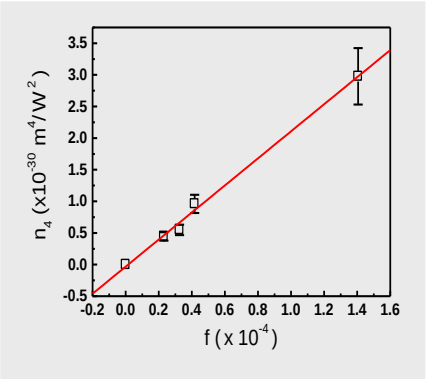


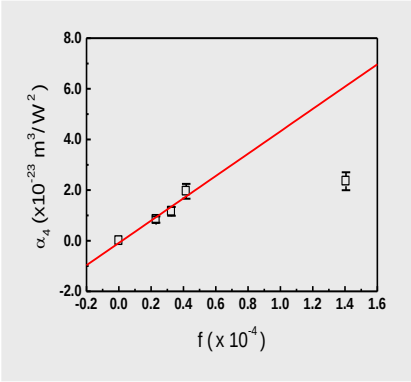
3rd. order nonlinearity





5th. order nonlinearity

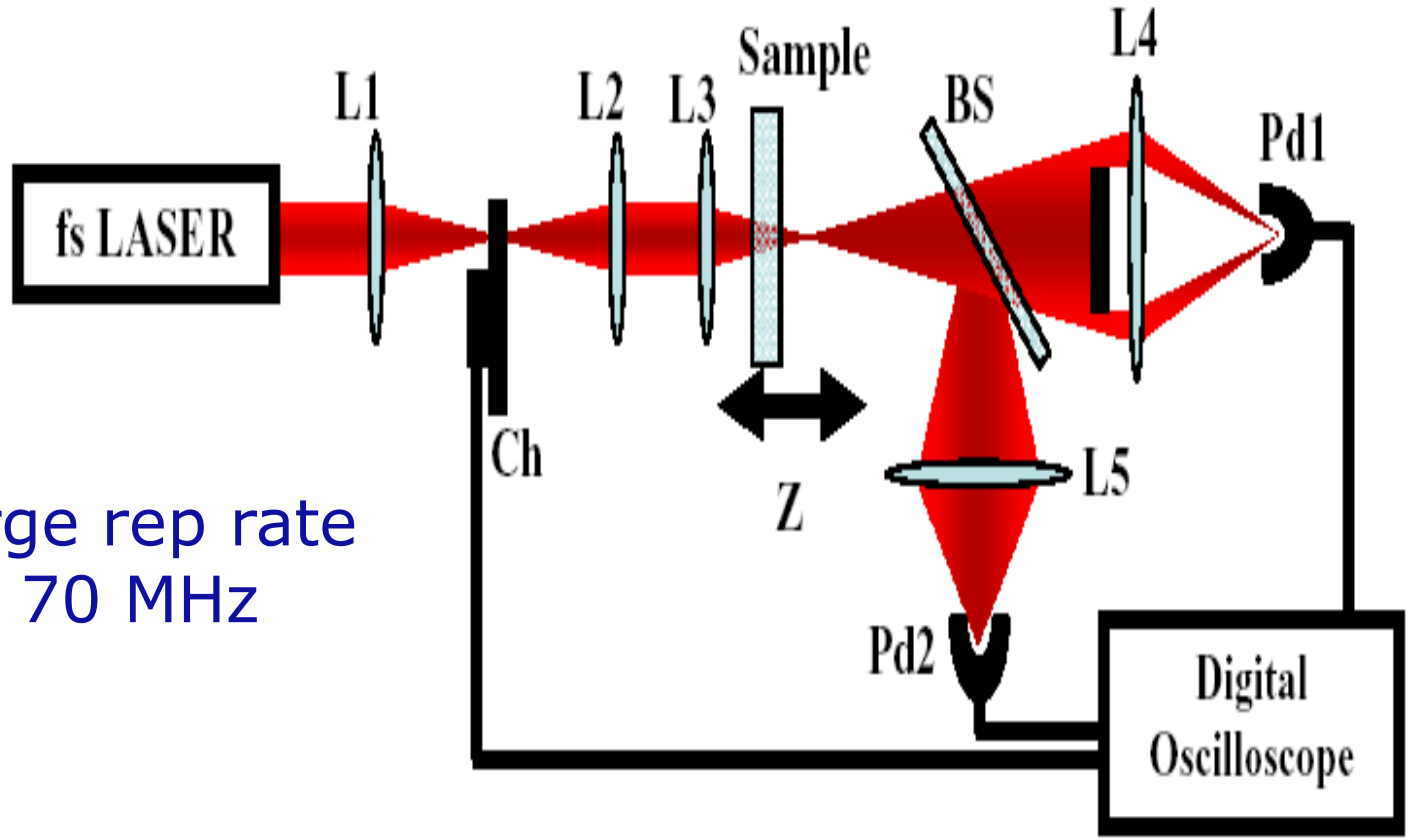




High order nonlinearities also depend linearly with *f*

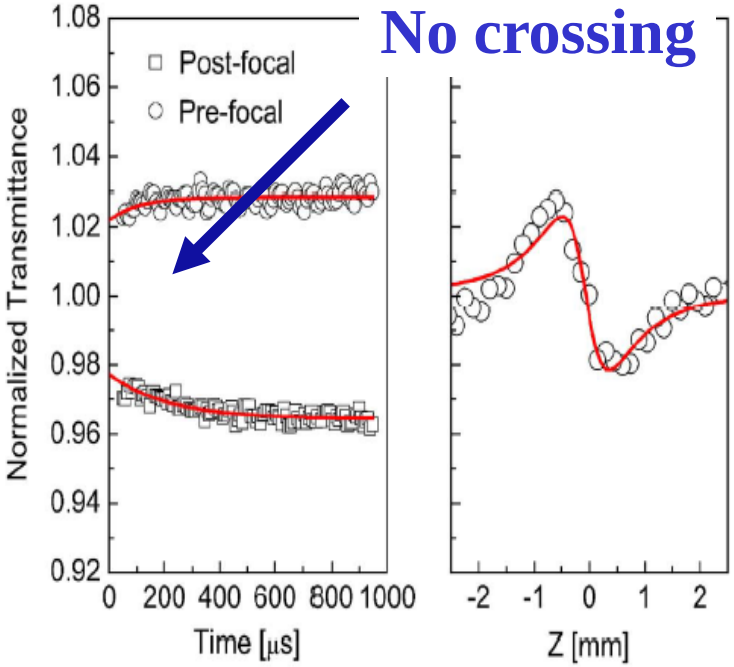
[Up to $\chi^{(9)}$]

Thermally managed eclipse Z-scan



Large rep rate
70 MHz

Opt. Express 15, 1712 (2007)



PbO-GeO_2 film with copper NPs

Influence of the Surface Plasmon Resonance

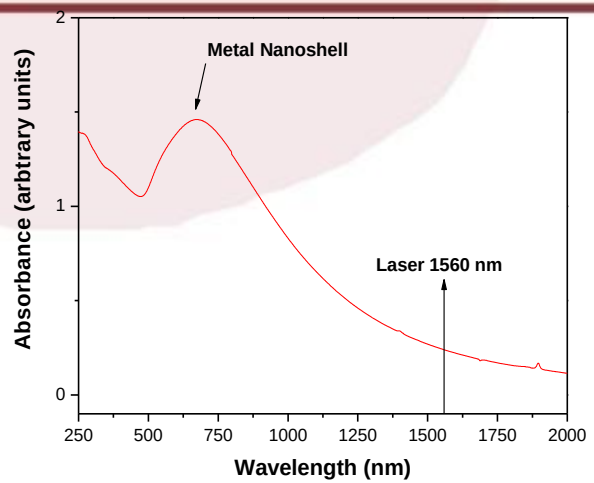
Laser pulses
150 fs

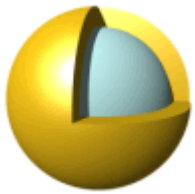
Material	λ (nm)	Pulse duration	n_2 (cm^2/W)	α_2 (cm/GW)	$n_2/\lambda\alpha_2$	Ref.
PGO film	1064	15 ps	6×10^{-12}	200	2.8×10^{-1}	9
PGO film	532	15 ps	6×10^{-12}	1200	9.4×10^{-2}	9
PGO film	800	150 fs	$(2\pm1)\times10^{-13}$	$(3\pm1)\times10^{-3}$	8.3×10^{-4}	10
PGO film with Cu and Cu_2O nanoparticles	800	150 fs	6.3×10^{-12}	<660	$>1.2\times10^{-1}$	This work
$Bi_2Nd_2Ti_3O_{12}$	532	35 ps	7×10^{-10}	3.1×10^{4}	4×10^{-1}	20
$Bi_{3.25}La_{0.75}Ti_3O_{12}$	532	35 ps	3.1×10^{-10}	3×10^{4}	1.9×10^{-1}	21

Appl. Phys. Lett. 92, 141916 (2008)

Nonlinear refraction at 1560 nm

Nanoshells silica-gold



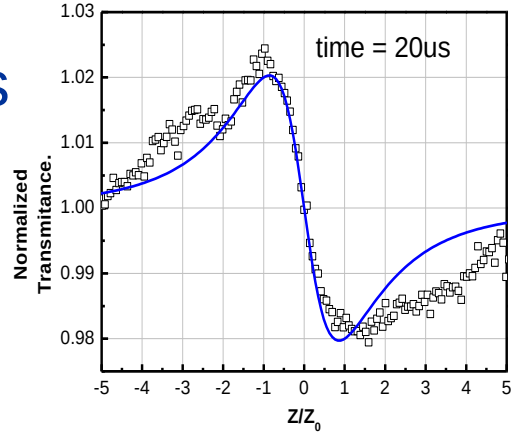


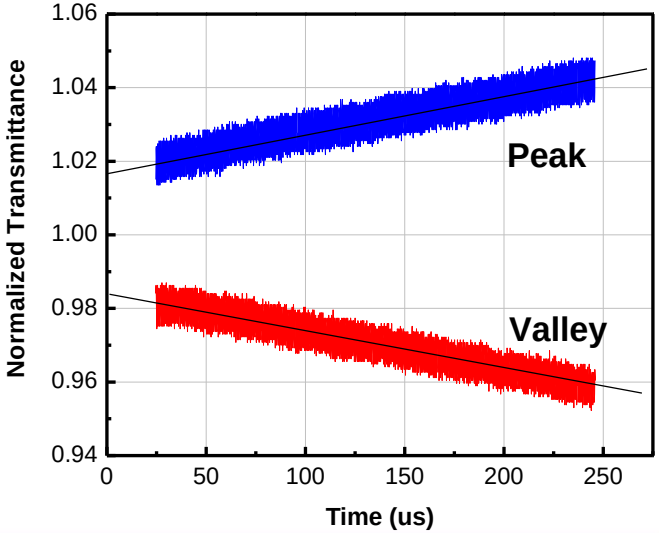
Thermally - managed eclipse Z-scan

Inner radius: 50 nm
Outer radius: 70 nm

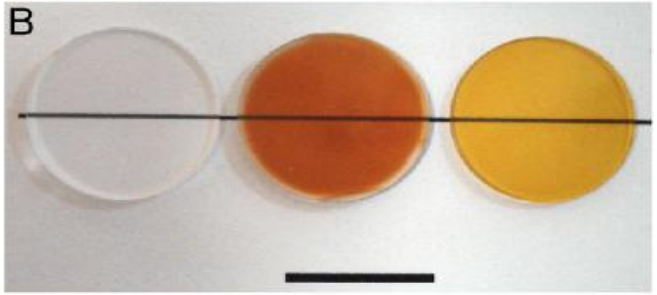
$n_2 = 20 \times 10^{-14}$ m^2/W

Laser pulses
60 fs



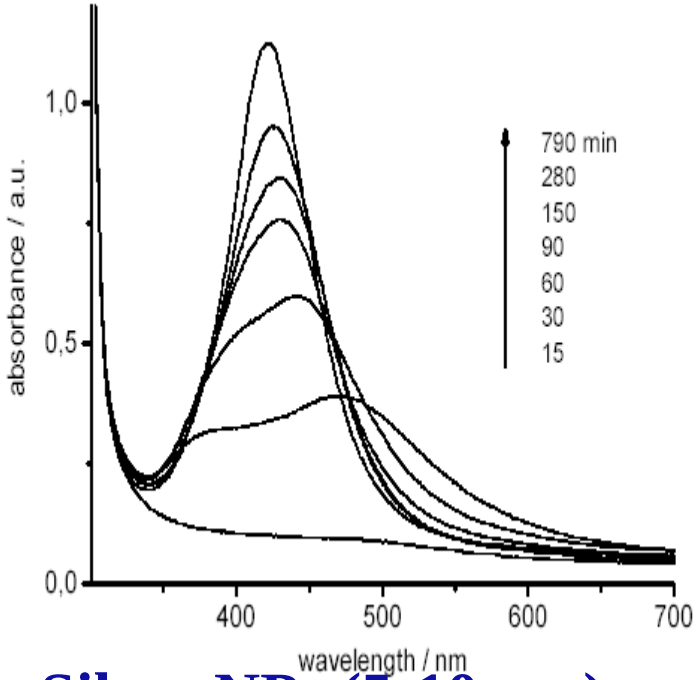


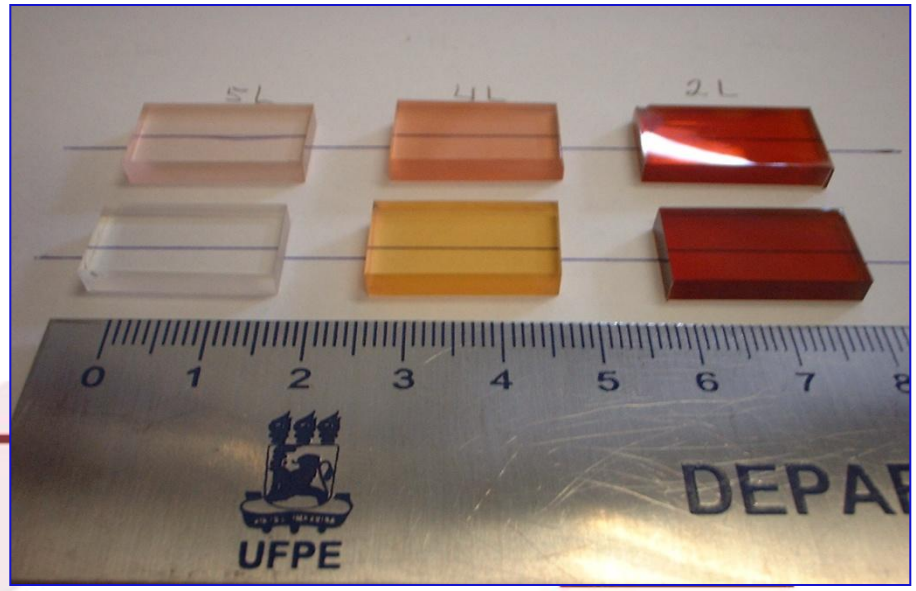
HYBRID COMPOSITES



Silver NPs in-situ growth within crosslinked poly (ester – co - styrene) induced by UV irradiation aggregation control with exposition time

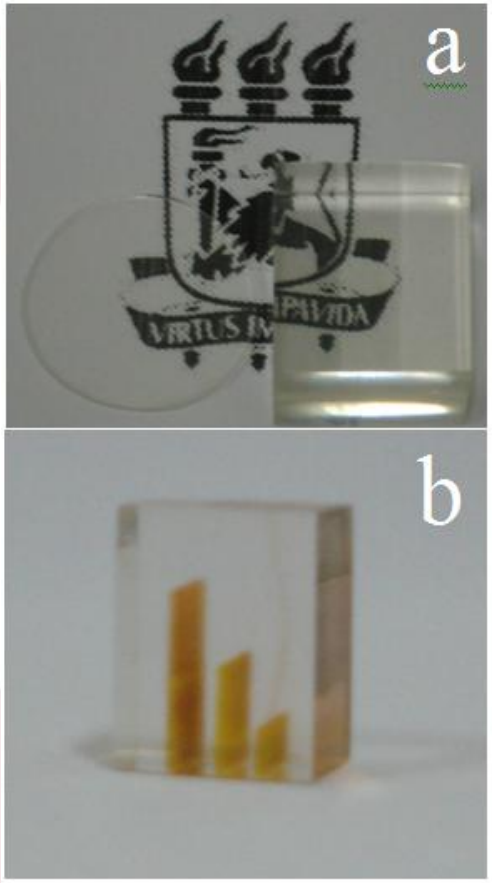
J. Phys. Chem. Solids 68, 729 (2007)

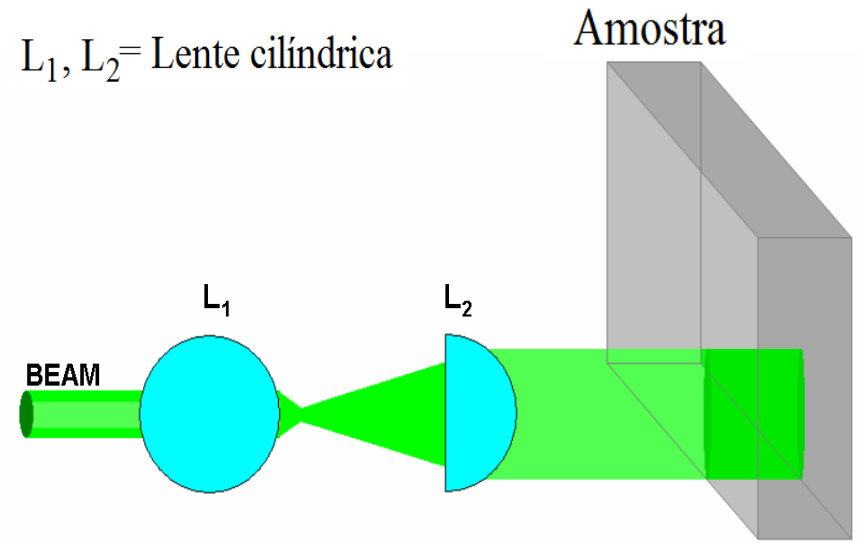


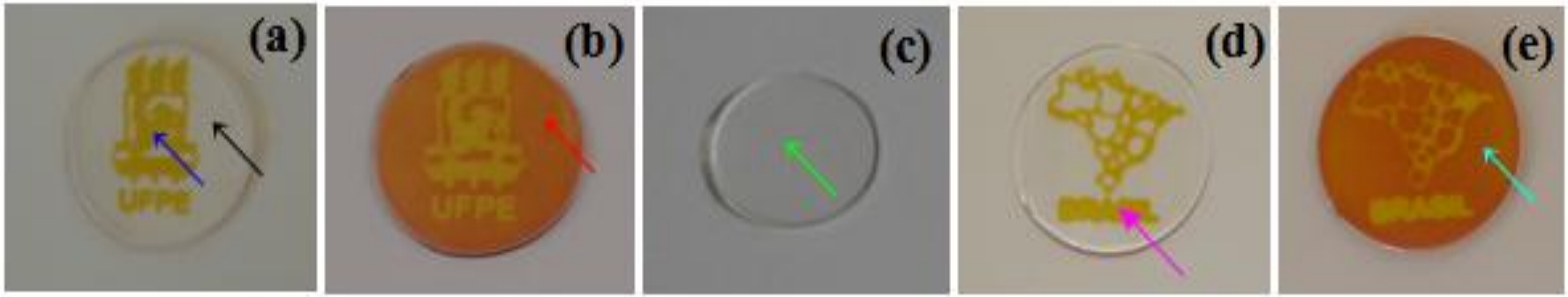


Silver NPs (5-10 nm)

Lithography

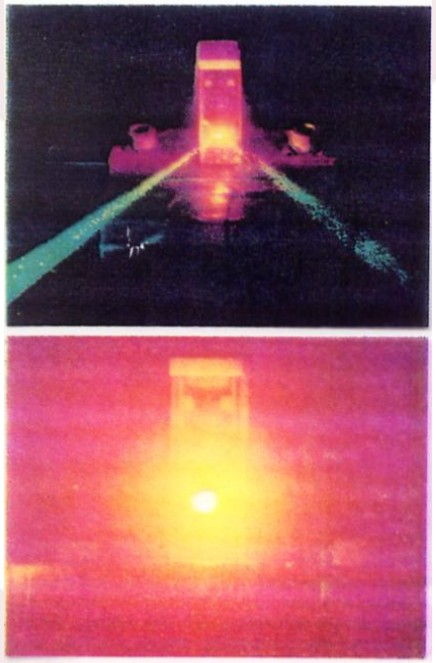






Random lasers (lasers without mirrors)

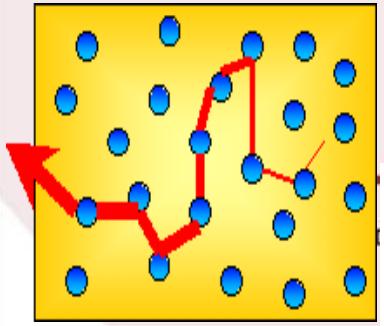
Lawandy et al. Nature 1994



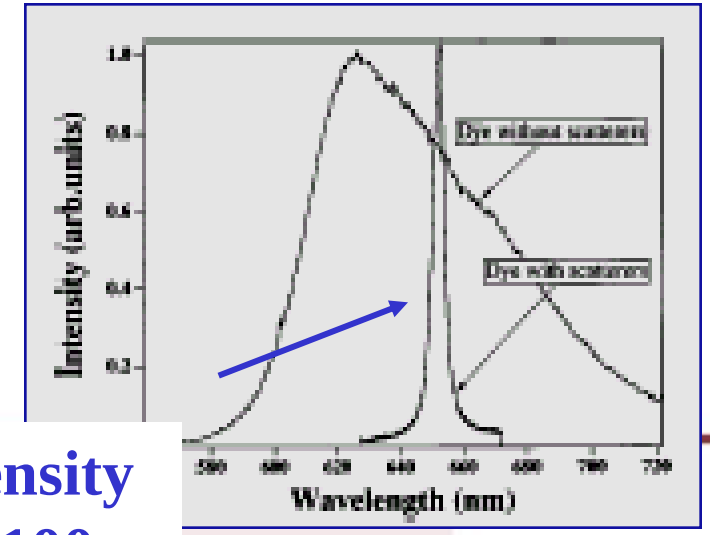
Generated photons make a random pathway due to reflection by the TiO_2 particles

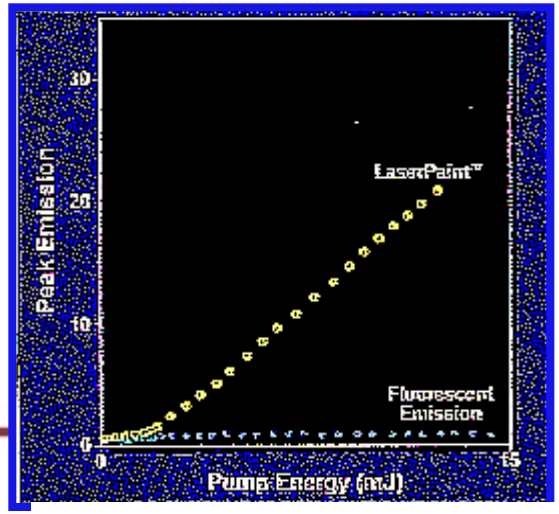
2×10^{-3} M 10^{11} particles / cm^3

Mean free path: 120 μ m @ 532 nm and 140 μ m @ 650 nm



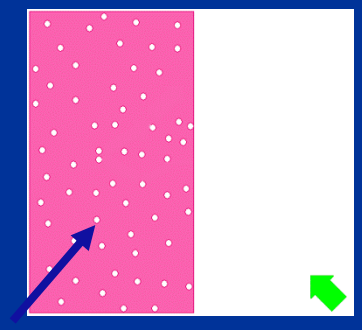
Intensity ÷ 100





0 mJ 15

Rh6G

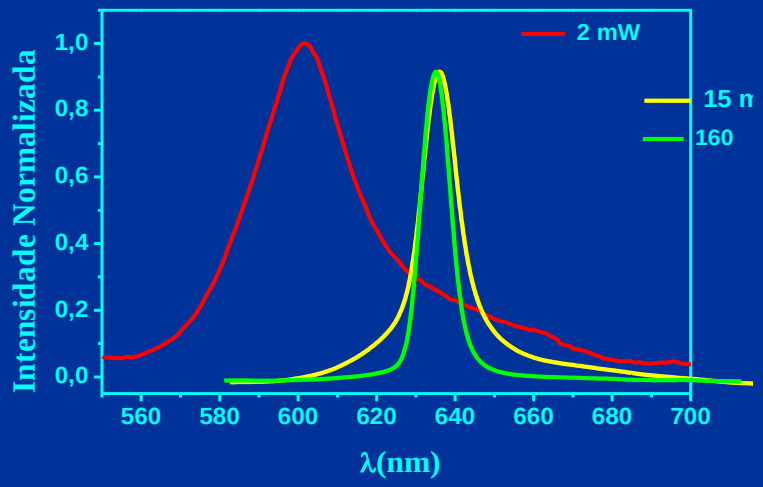


TiO_2 particles

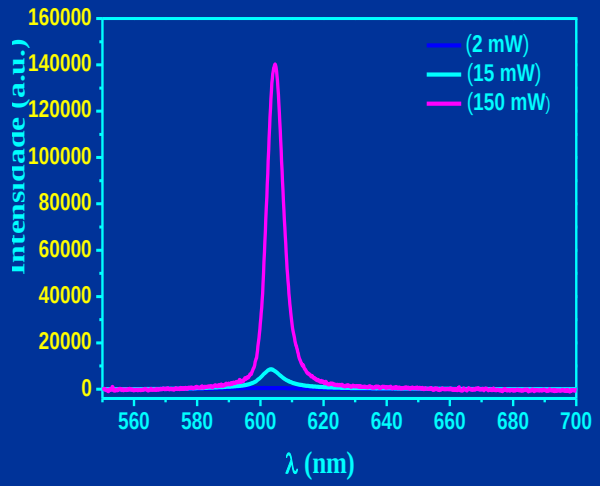
Our polymers with TiO_2 particles

Rhodamine 6G 2×10^{-3} M 10^{11} particles / cm^3

Mean free path: 120 μ m @ 532 nm and 140 μ m @ 650 nm



Line narrowing

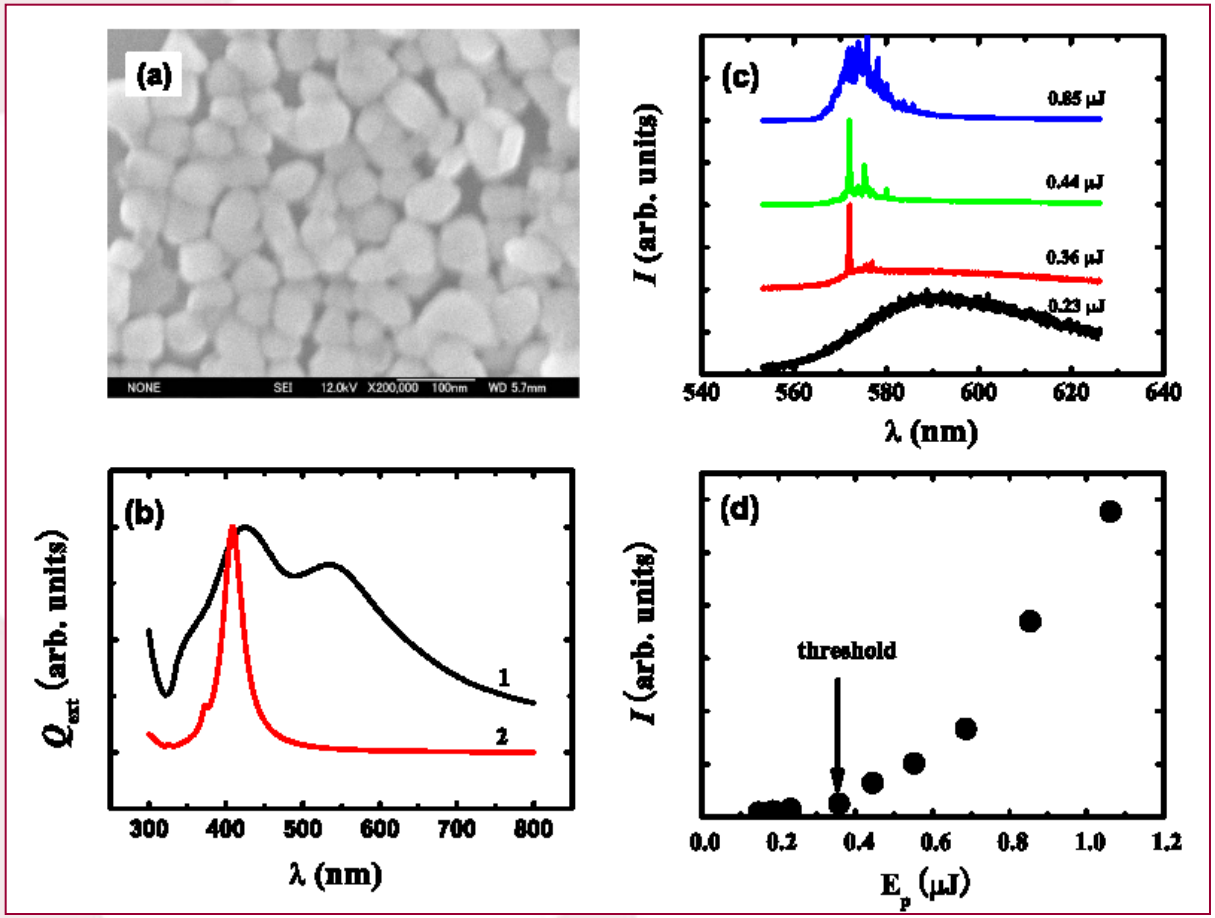


Threshold like behavior

PHYSICAL REVIEW A **79**, 053817 (2009)

Coherent random lasers in weakly scattering polymer films containing silver nanoparticles

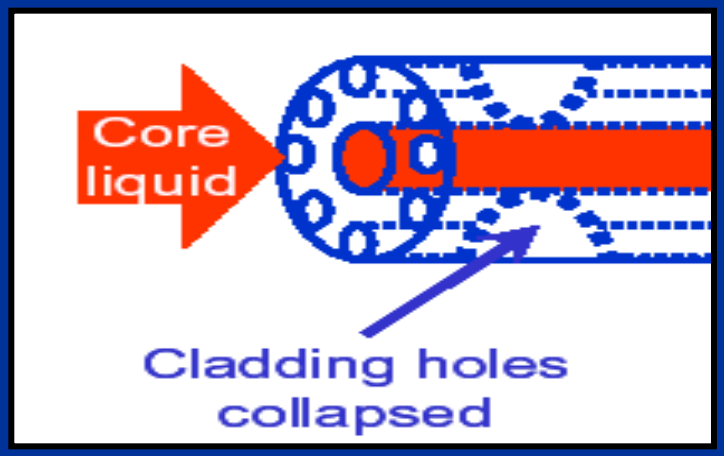
Xiangeng Meng,[1] Koji Fujita,[1,2,*] Shunsuke Murai,[1] and Katsuhisa Tanaka[1]



Is it possible to operate a random laser with directional emission but using no mirrors?

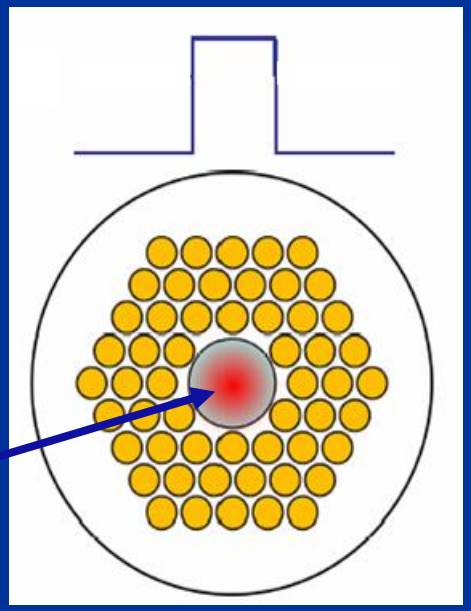
Photonic band gap fiber

Hollow core fiber



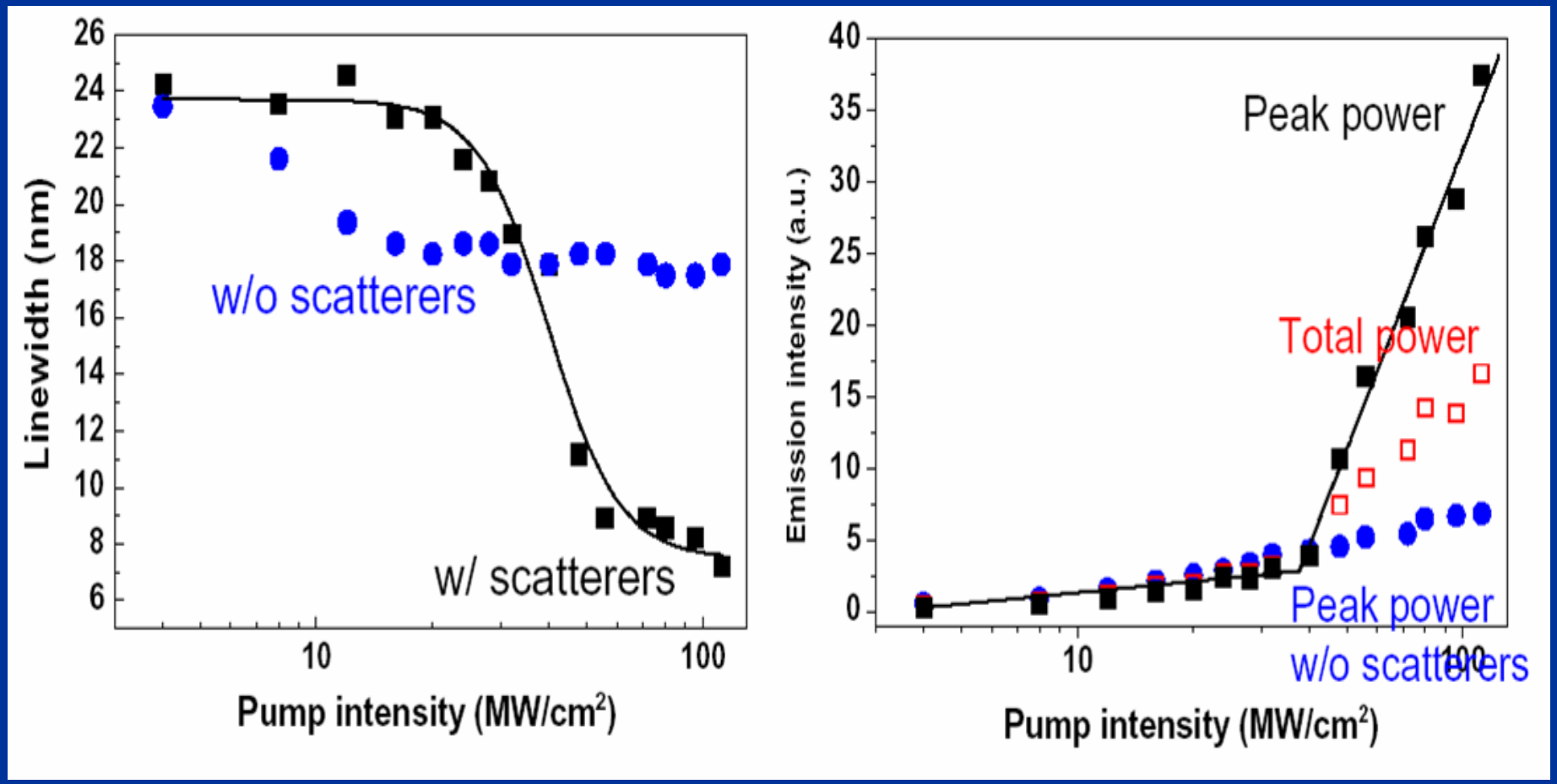
Colloid with Rh 6G +TiO_2

Refractive index profile



Transverse feedback: total internal reflection
Axial feedback: multiple scattering

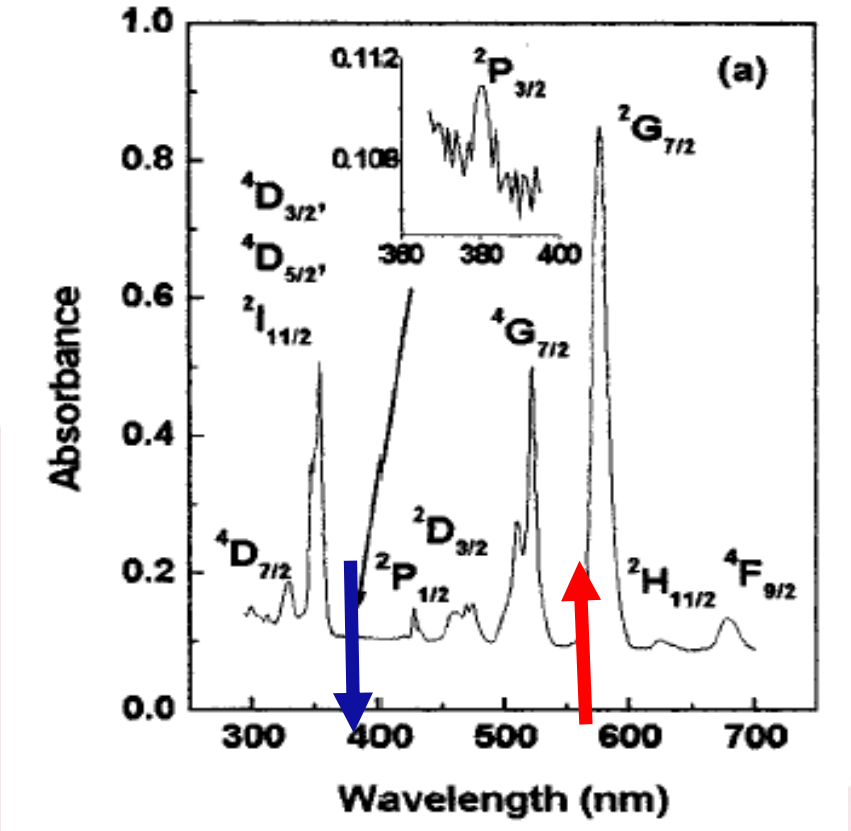
First Random Fiber Laser

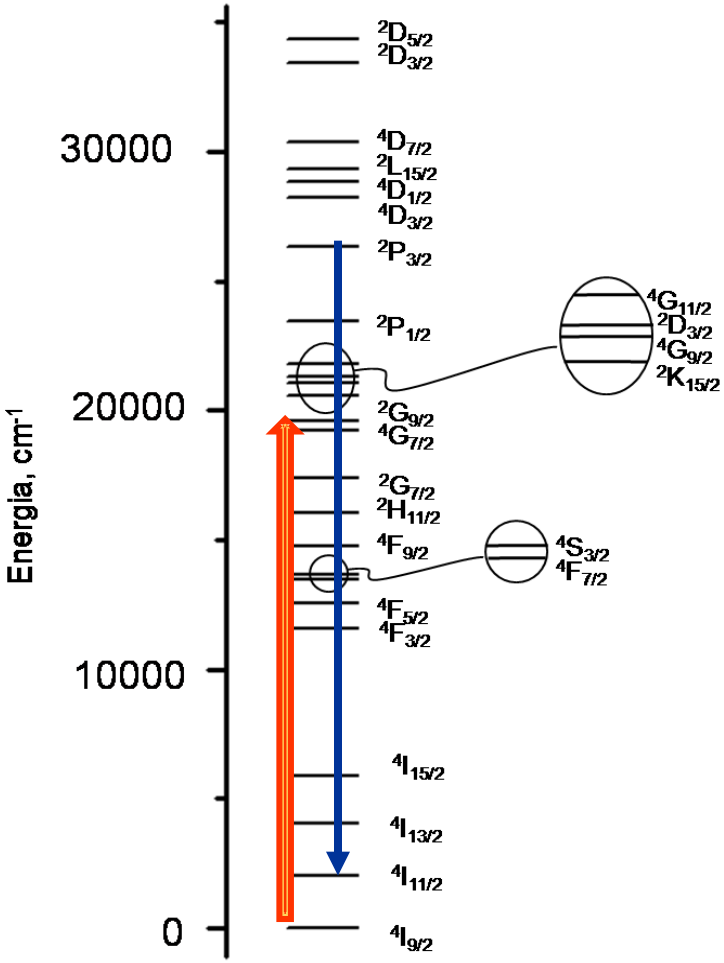


100 times more efficient than conventional random lasers

Phys. Rev. Lett. 99, 153903 (2007)

Nd^{3+} doped fluoroindate glass



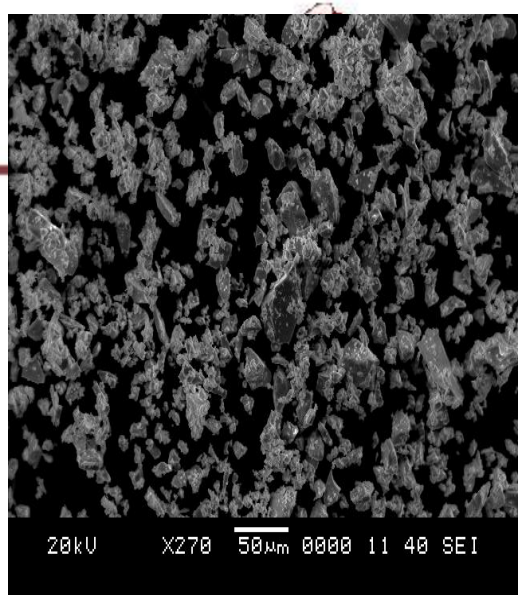


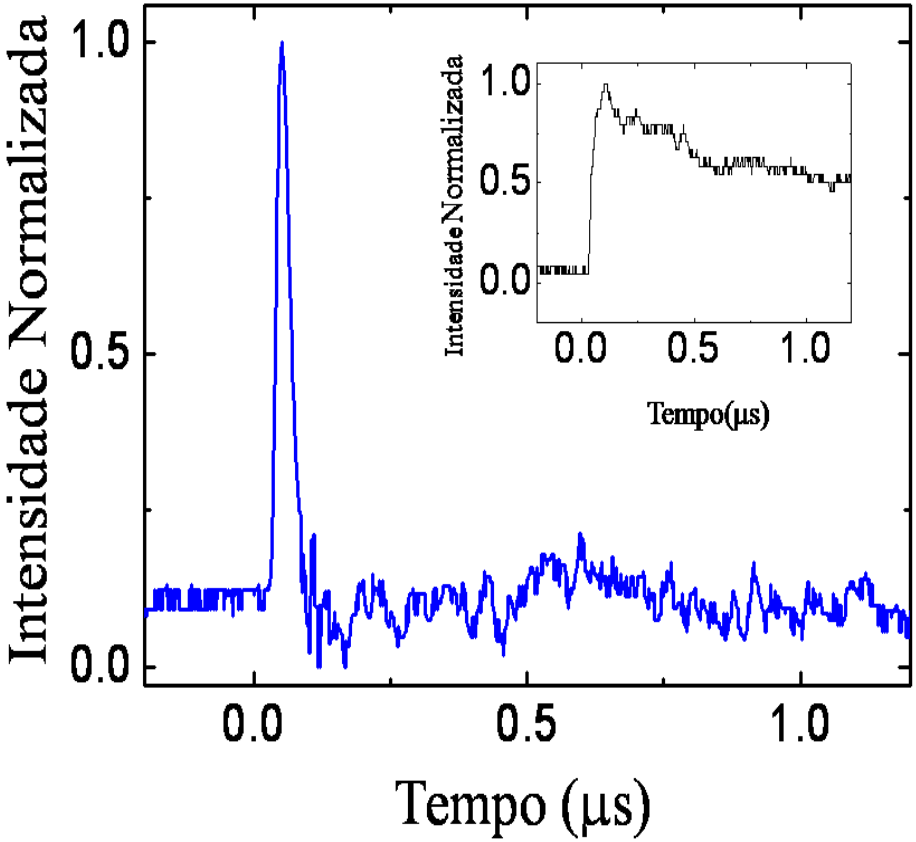
Upconversion Random Laser

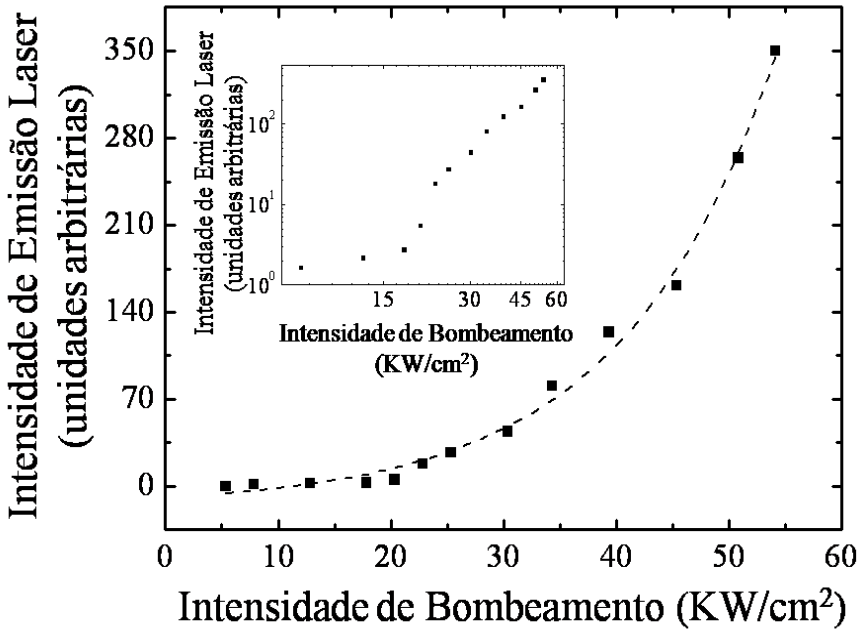
Fluoroindate glass powder

Normalized UV signal 381 nm
Above threshold

≈ 30 μm







NEXT STEP

Random fiber laser

based on

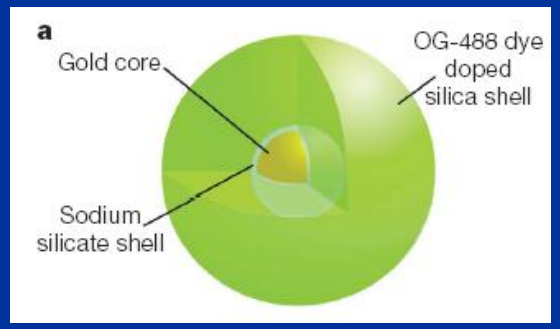
Nd^{3+} doped nanocrystals + metal nanoparticles

combined effects of multiple light scattering with local field enhancement due to surface plasmons

reduced threshold

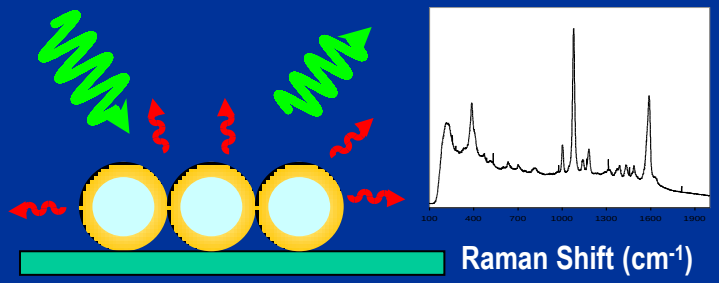
Plasmonics: a fundamentally multidisciplinary enterprise

Fundamental science of metallic nano-optical components

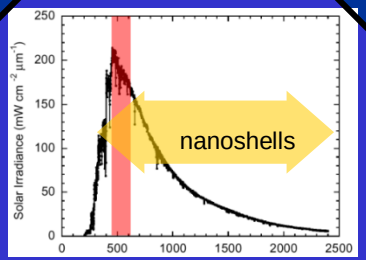


SPASER

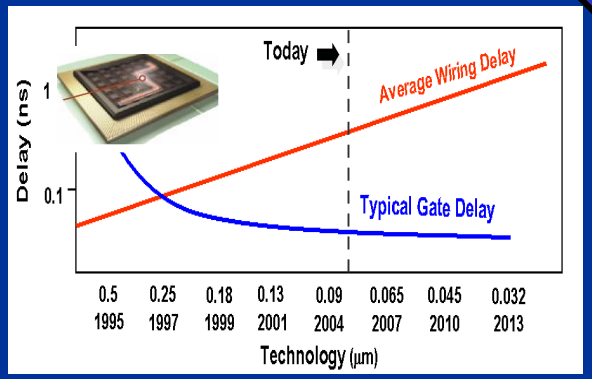
Plasmon-enhanced spectroscopies for chemical & biodetection



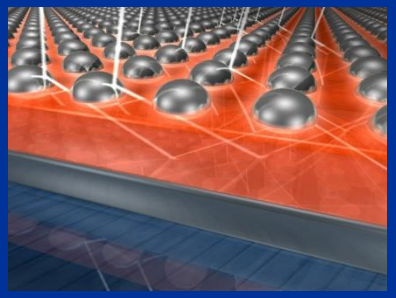
In vitro and in vivo Biomedical applications



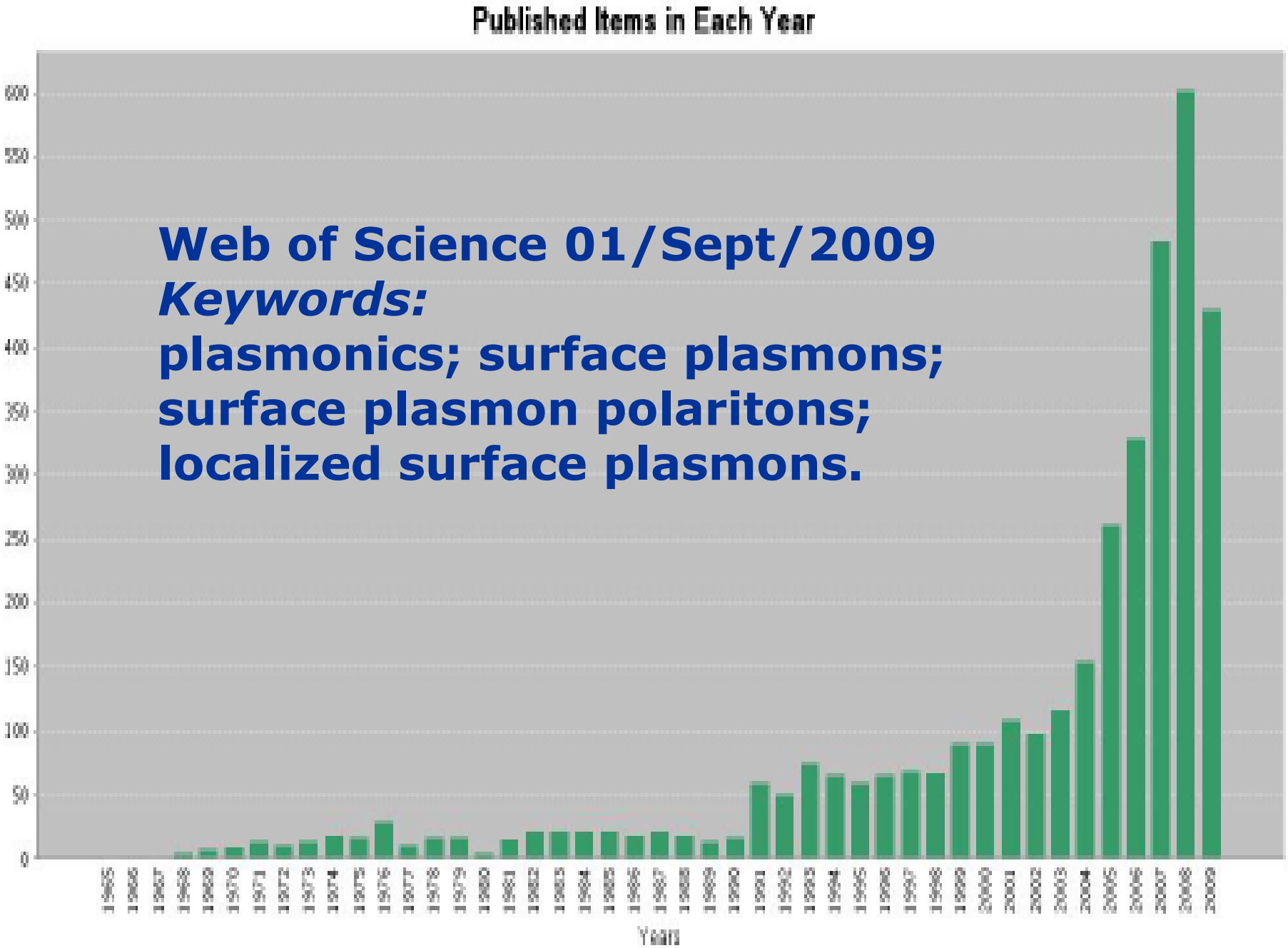
Light harvesting for energy conversion



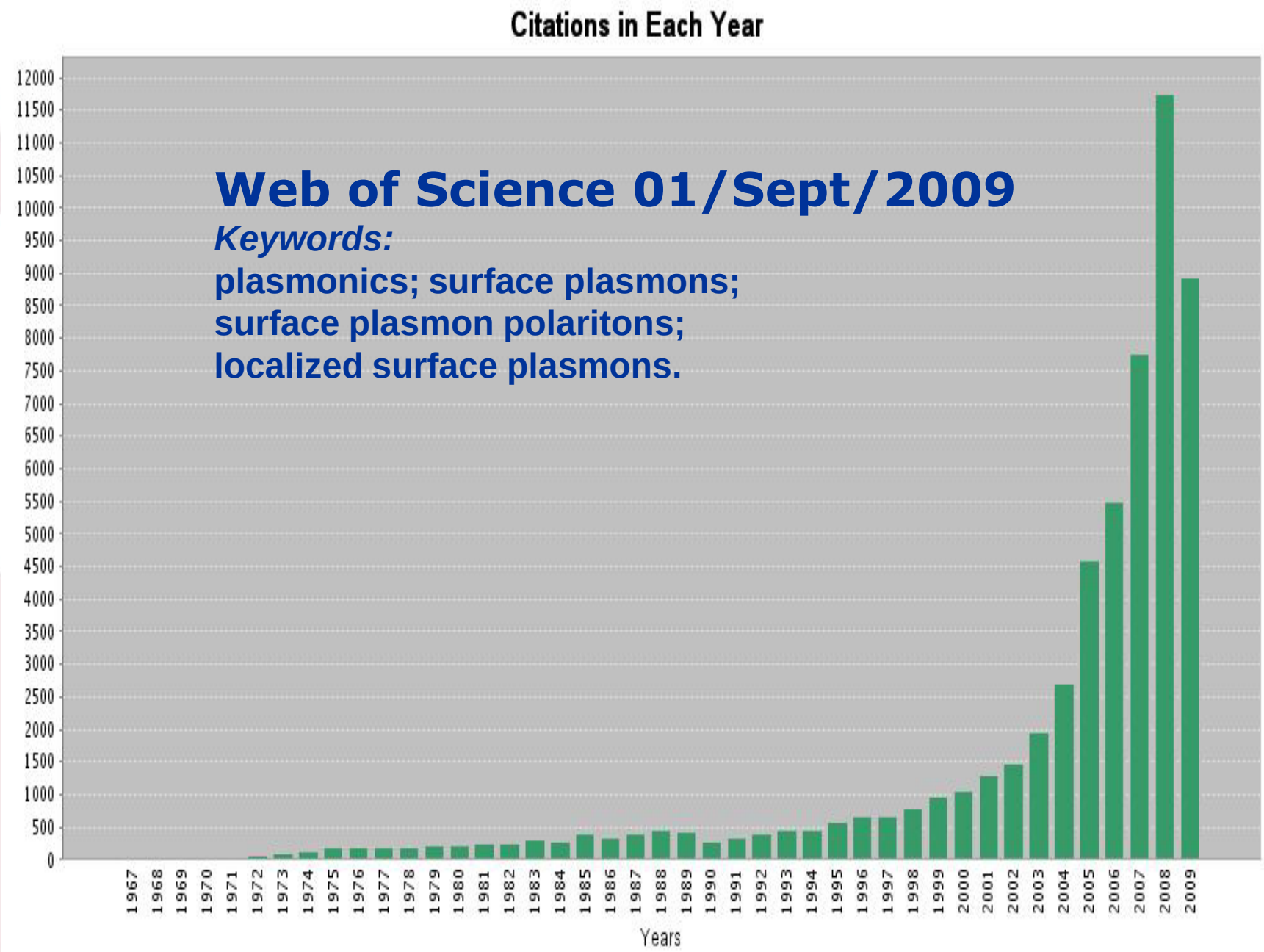
Optical interconnects in next-generation computer chips



Plasmonic solar cells



Web of Science 01/Sept/2009
Keywords:
plasmonics; surface plasmons; surface plasmon polaritons; localized surface plasmons.


Citations in Each Year
Web of Science 01/Sept/2009
Keywords:
plasmonics; surface plasmons;
surface plasmon polaritons;
localized surface plasmons.
Years

Ernesto Valdez Rodriguez (D. Sc. 2007) – Research Associate

Antonio Marcos Brito-Silva – D. Sc. student - Materials Science

Denise Valença – M. Sc. student – Physics

Euclides C. Lins de Almeida - D. Sc. student - Physics

Gemima Barros Correia – D. Sc. student – Materials Science

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Jamil Saade – D. Sc. Student – Materials Science

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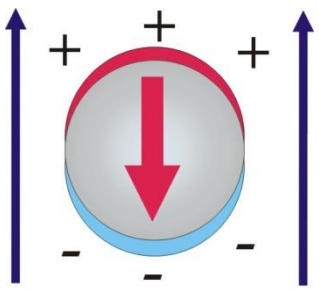
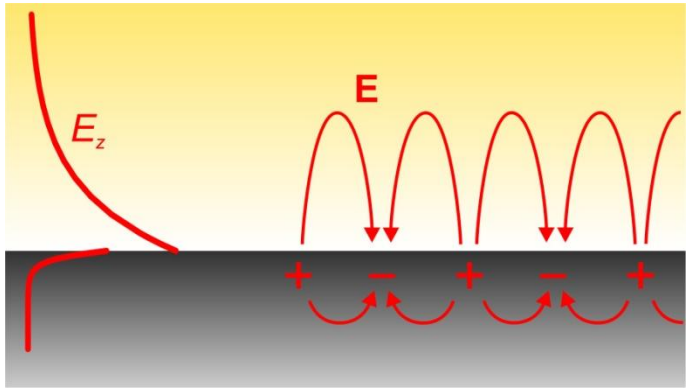
L. Kassab – FATEC – SP
M. Poulain – Rennes – France
Y. Messaddeq – UNESP - SP

Surface plasmons: electromagnetic resonances in the visible

Localized plasmon oscillation



Propagating surface plasmon polariton (SPP)



dielectric

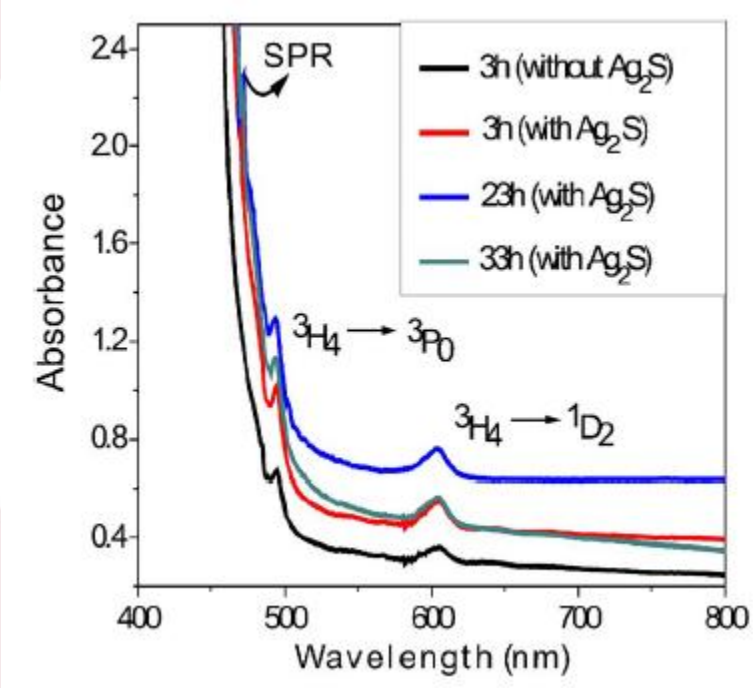
metal

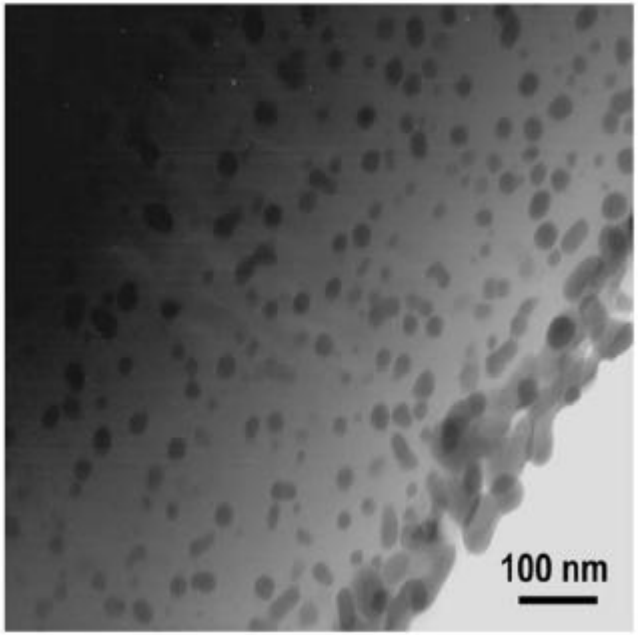
$$\alpha = 4\pi\varepsilon_0 R^3 \frac{\varepsilon - \varepsilon_m}{\boxed{\varepsilon + 2\varepsilon_m}}$$

dielectric metal

$$k_x = \frac{\omega}{c}\left(\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}\right)^{1/2}$$

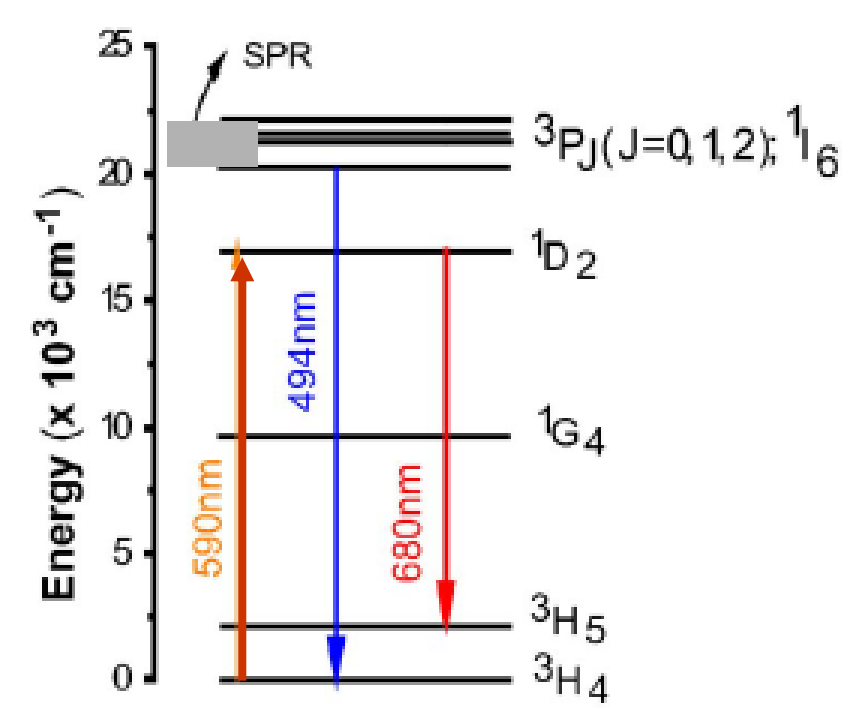
Pr^{3+} in $Ga_{10}Ge_{25}S_{65}$ with Ag nanoparticles

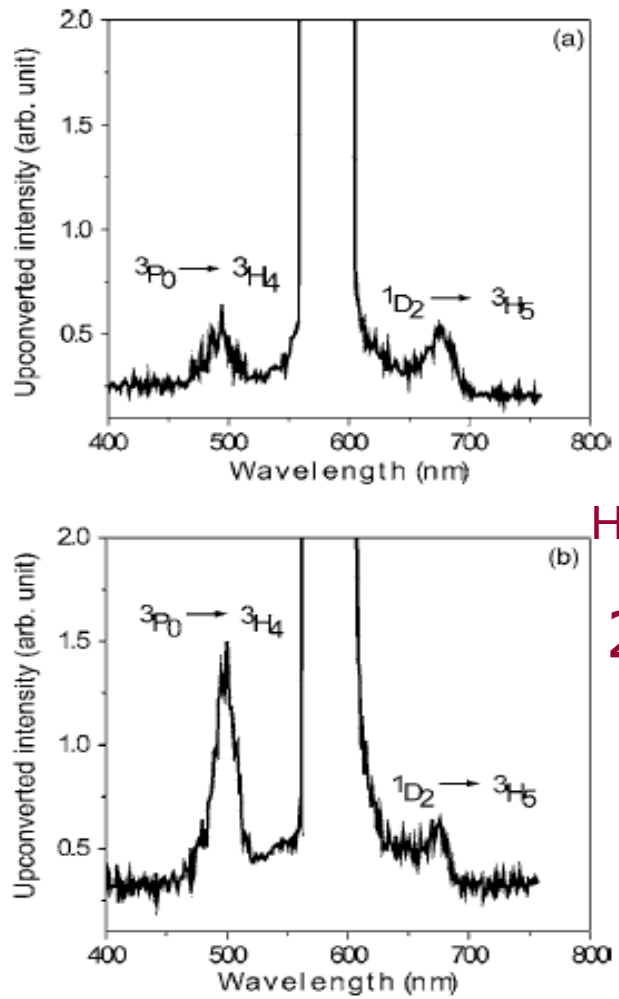




Heat treatment: 23 h

JAP **103**, 103526 (2008)





Heat treatment

23 hours

$$(^3P_0 \rightarrow {}^3H_4) \div (^1D_2 \rightarrow {}^3H_4)$$

Increase by 130 %