Quantum Plasmonics: Plasmon Enhanced Electron Transfer and Light Harvesting

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LABORATORY FOR NANOPHOTONICS

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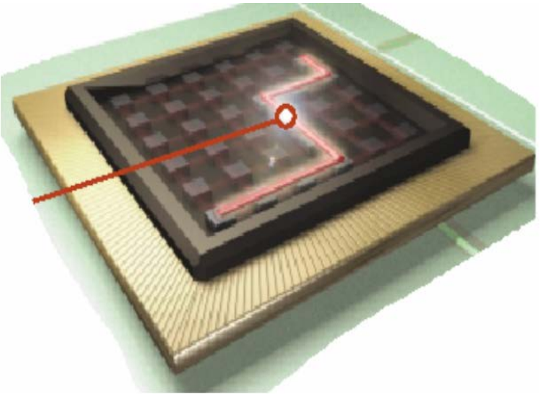
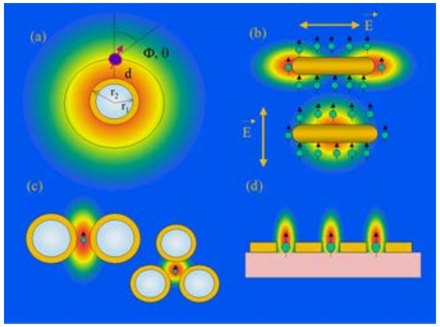
Plasmonics

Plasmons provide the mechanism for manipulating light at the nanoscale

Plasmonic waveguides

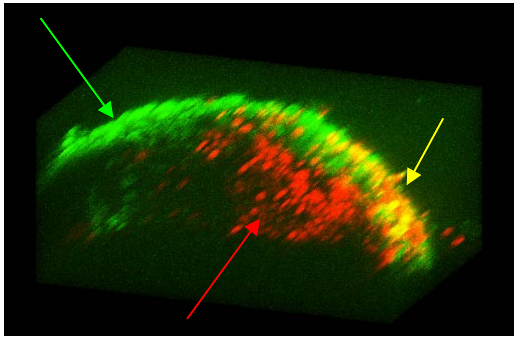


Plasmon enhanced spectroscopies



Plasmonic "hot spots"

Plasmonics in biomedicine

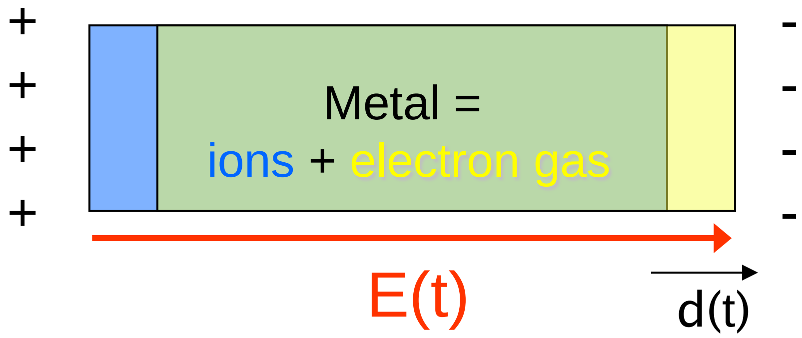


Outline

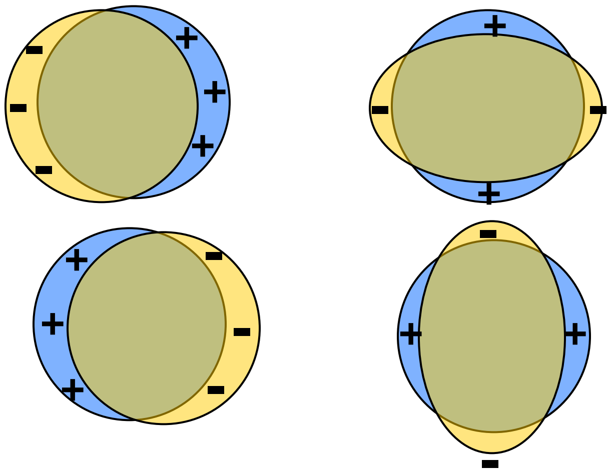
- **Introduction**
- **Quantum plasmonics**
- **Quantum Plexcitonics**
- **Plasmon-enhanced Light Harvesting**

Localized Surface Plasmons (LSPR)

Plasmons are incompressible oscillations of the conduction electron liquid

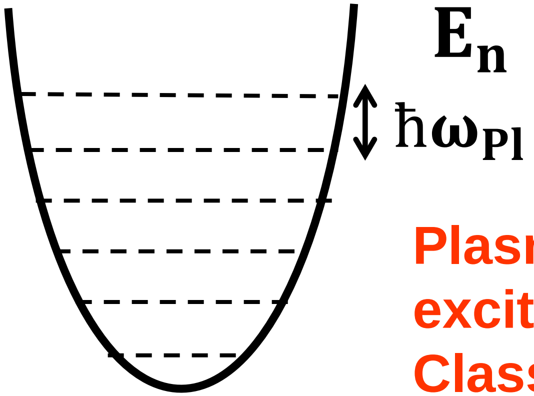


Dipolar **Quadrupolar**



Bright (superradiant) **Dark (subradiant)**

All conduction electrons are moving: Strong light coupling

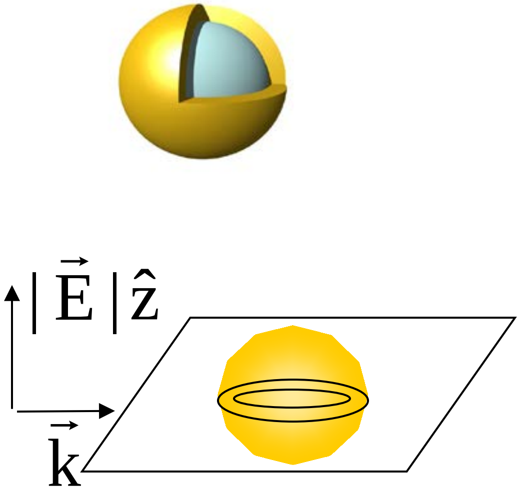


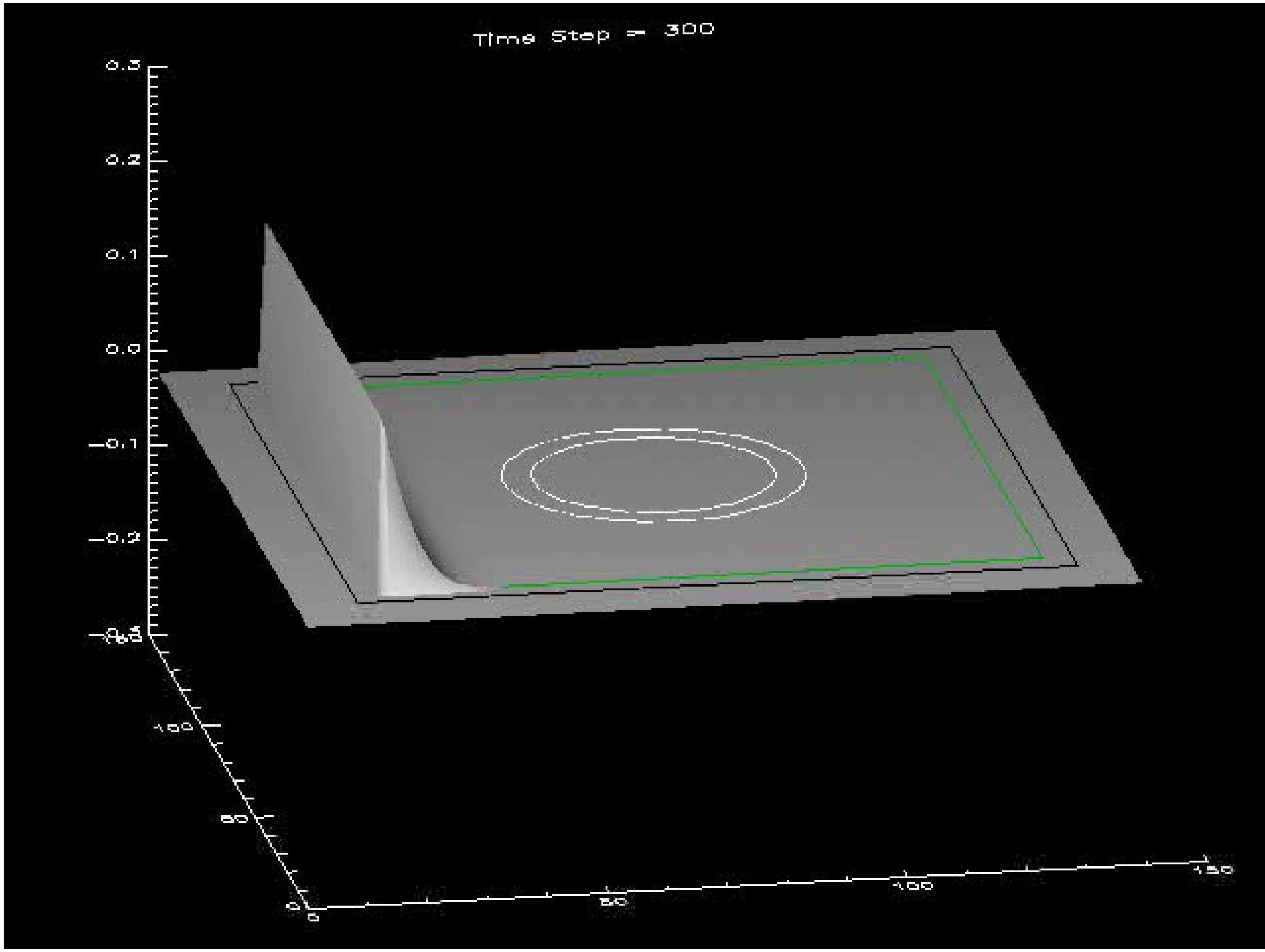
$$E_n = \hbar\omega_{Pl}(n + ½)$$

Plasmons typically excited to high n => Classical description

For resonant excitation, amplitude of motion becomes large. Large surface charges and field enhancements

Plasmons in real time, FDTD Simulations



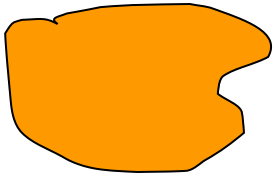


Electromagnetic pulse hitting an Au(40,50)nm nanoshell

Many different nanoshell plasmons are excited

The plasmon energies of a nanoparticle depend on its shape!

Bulk:

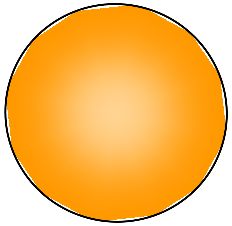


$$\omega_B = \sqrt{\frac{4\pi e^2 n}{m_e}}$$

Surface:

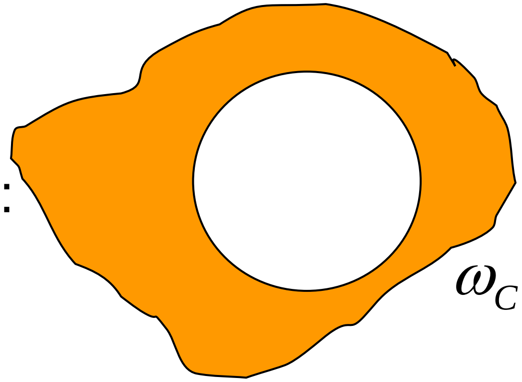
$$\omega_{surf} = \frac{\omega_B}{\sqrt{2}}$$

Sphere:



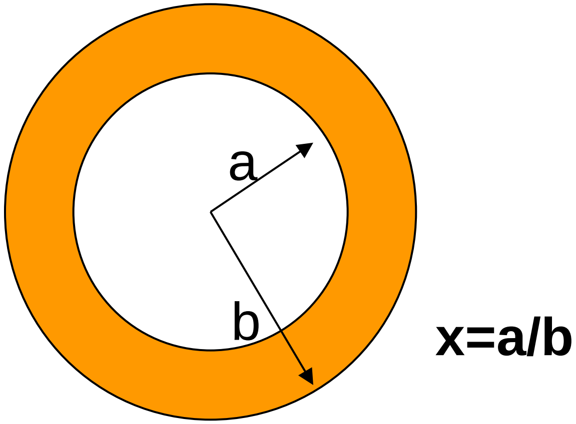
$$\omega_{S,l} = \omega_B\sqrt{\frac{l}{2l+1}}$$

Cavity:



$$\omega_{C,l} = \omega_B\sqrt{\frac{l+1}{2l+1}}$$

Nanoshell (N.J. Halas 1998)



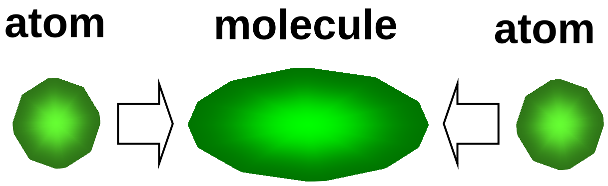
Nanorods

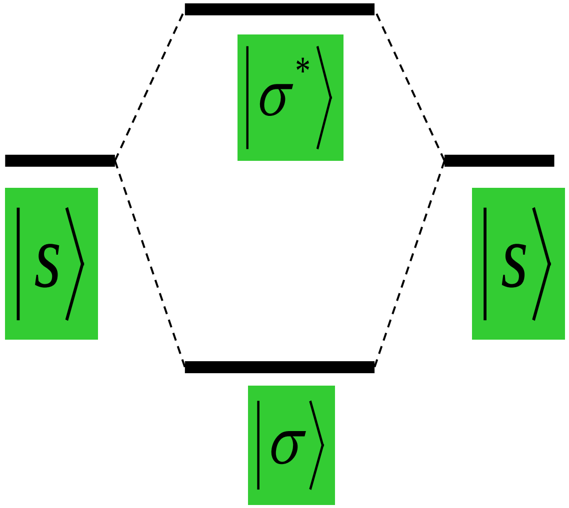
Plasmon energies depend on aspect ratio x and can be tuned from UV to the IR

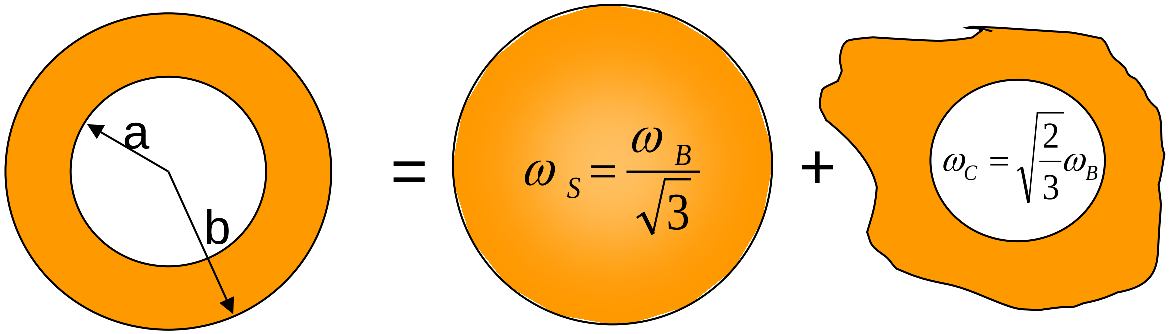
Physical origin of the tunability of nanoshell plasmons

Plasmon Hybridization (**Prodan *et al.* , Science 302(2003)319**)

Plasmons on different surfaces interact and hybridize like atomic orbitals in molecules

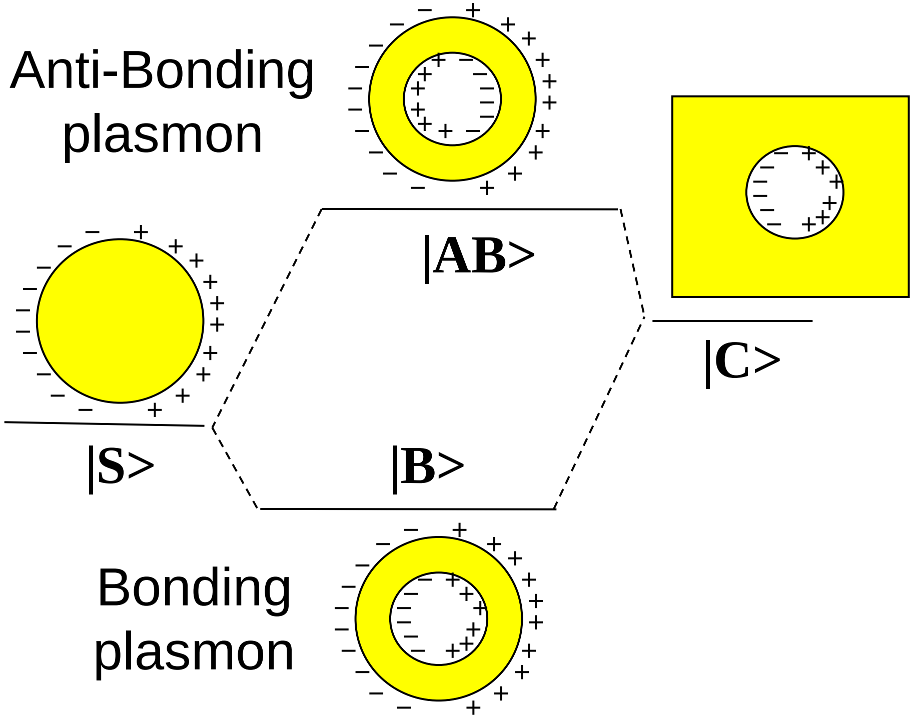






$$\omega_S = \frac{\omega_B}{\sqrt{3}}$$

$$\omega_C = \sqrt{\frac{2}{3}}\,\omega_B$$



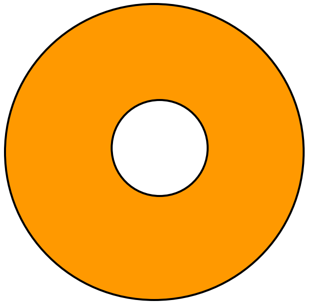
Anti-Bonding plasmon

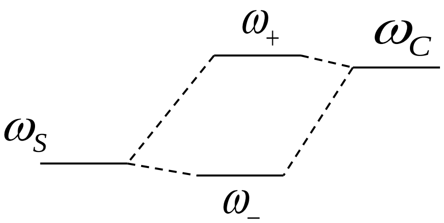
Bonding plasmon

Tunability of Nanoshells

Analogy with molecular orbital theory provides simple and intuitive understanding of plasmons in composite nanoparticles.

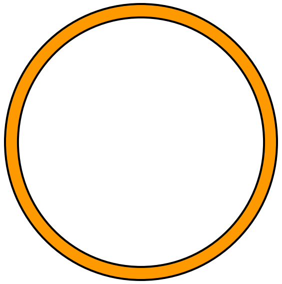
Thick shell => weak interaction:

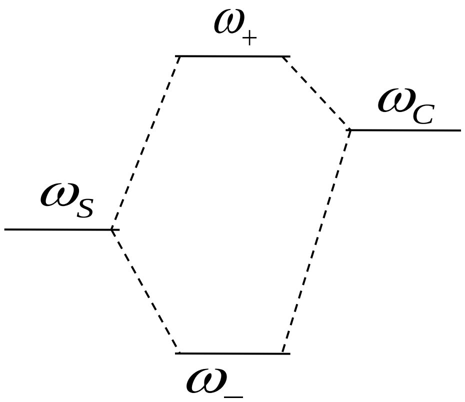




$$\omega_{l=1\pm} \xrightarrow{x\to 0} \frac{\omega_B}{\sqrt{2}}\sqrt{1\pm\frac{1}{3}} = \begin{pmatrix}\omega_C\\ \omega_S\end{pmatrix}$$

Thin shell => strong interaction:





$$\omega_{l=1\pm} \xrightarrow{\Delta\to 0} \begin{pmatrix}\omega_B\\ \omega_B\sqrt{\frac{2\Delta}{3}}\end{pmatrix}$$

where

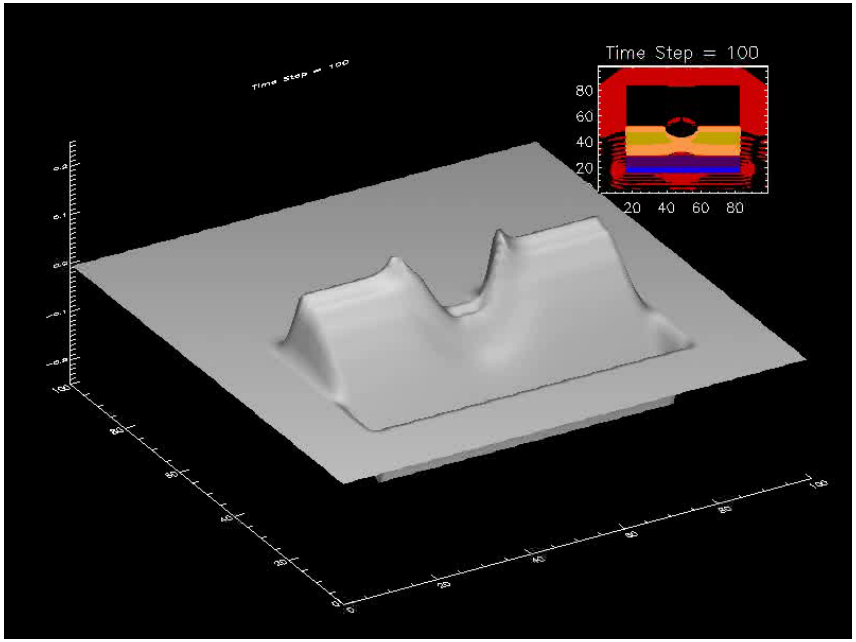
$$x=\frac{a}{b}=1-\Delta$$

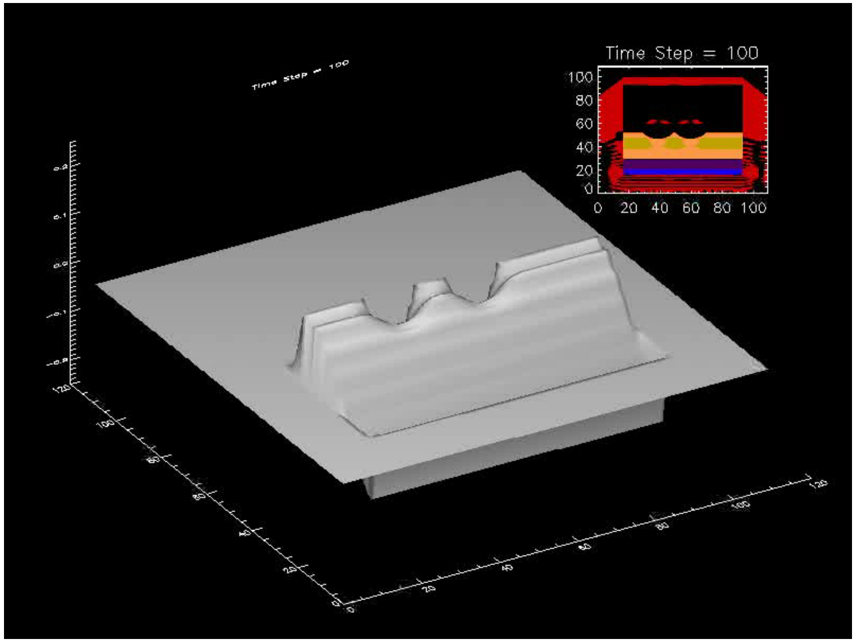
The ω_- plasmon can be tuned from far IR to UV

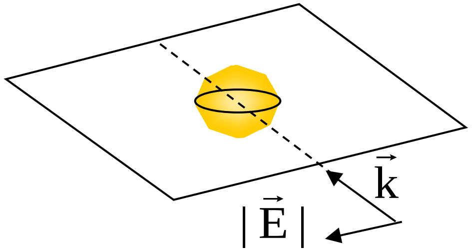
The coupling to light is proportional to the admixture of the |S> plasmon

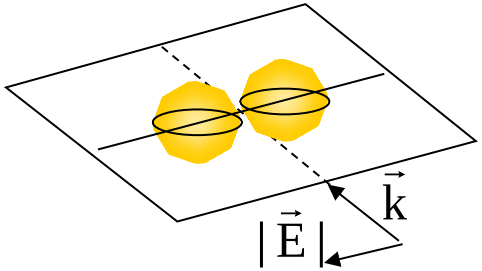
"Hot Spots": electromagnetic field enhancement in nanoparticle dimer junctions

Au sphere, D=60 nm; incident wavelength λ= 475 nm (l=1 plasmon resonance)







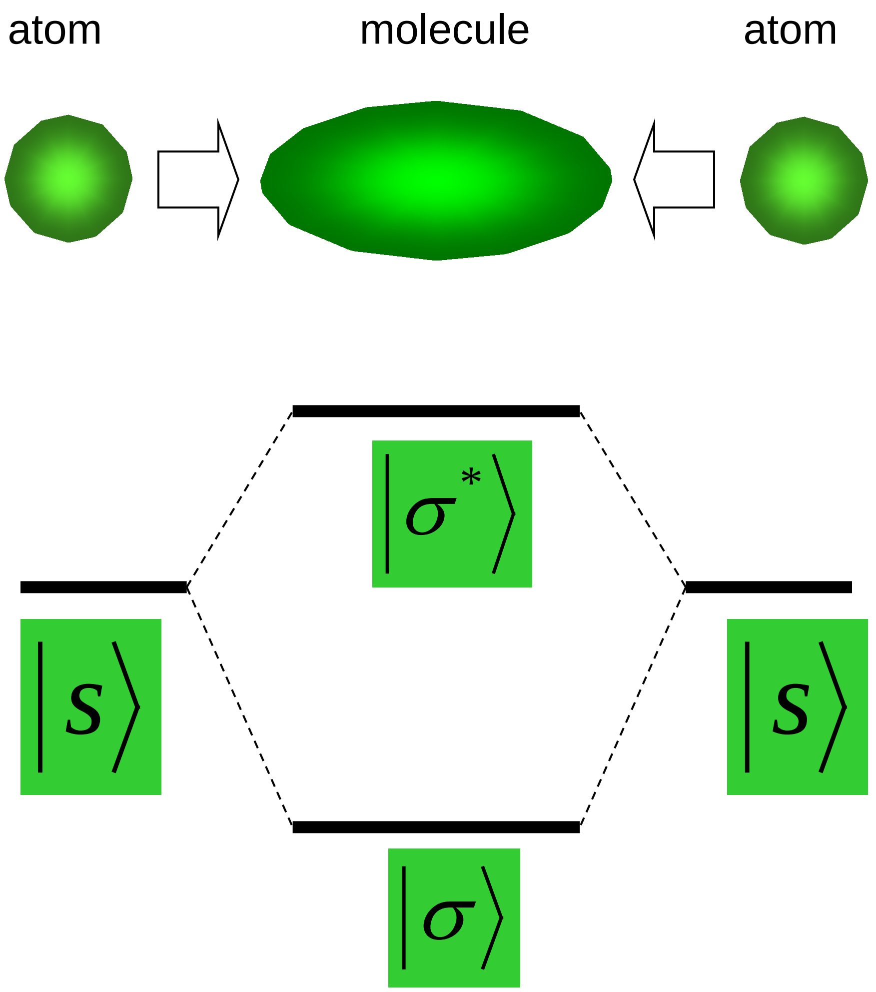


E field is enormously enhanced in the junction!

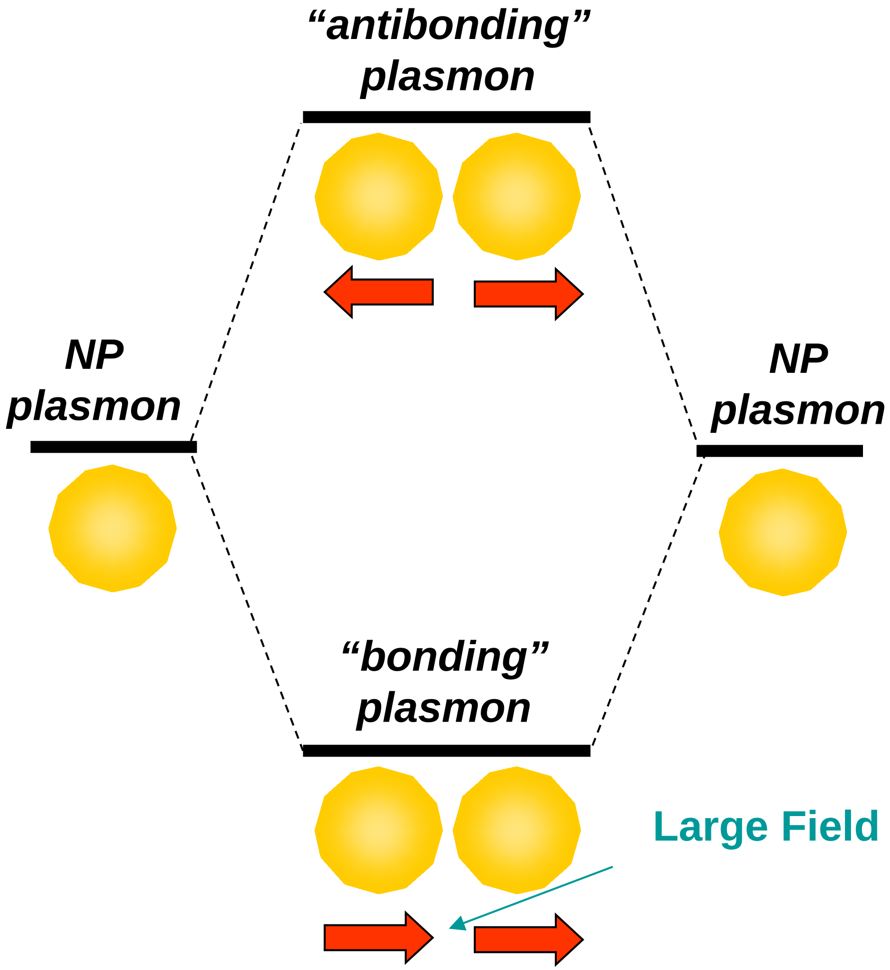
Enhancement is larger than sum of individual nanoparticles

=> Collective effect, Plasmon interactions!

Plasmon Hybridization **(Prodan *et al*, Science 302(2003)319)**



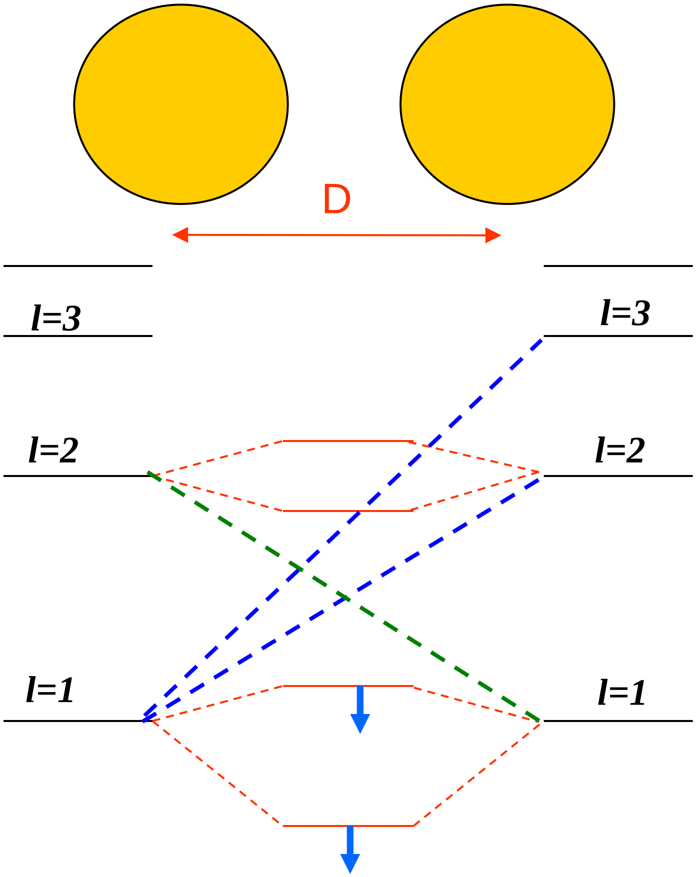
Nanoparticle “dimers”



Nanoparticle dimers: Plasmon Hybridization

(Nordlander *et al.*, NL 4(2004)899)

Nanosphere dimer:

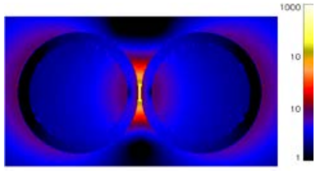


In the dimer geometry, NP plasmons of different *l* mix:

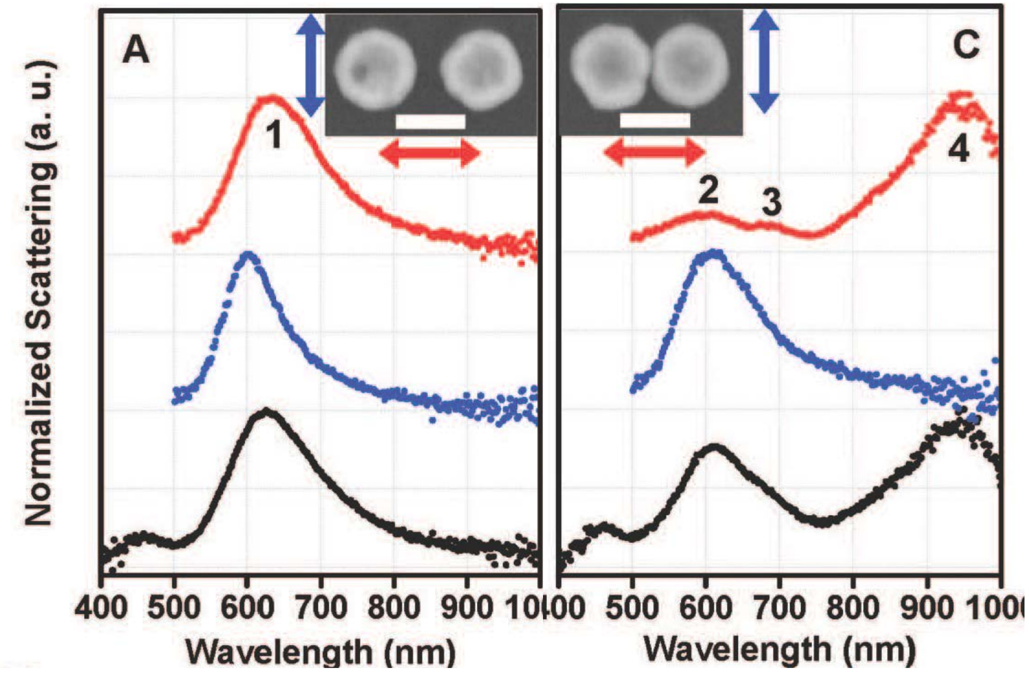
For large D, hybridization of modes of the same multipolar order *l*

For small D, hybridization of NP plasmons with different *l*: Multipolar modes appear and large fields are induced

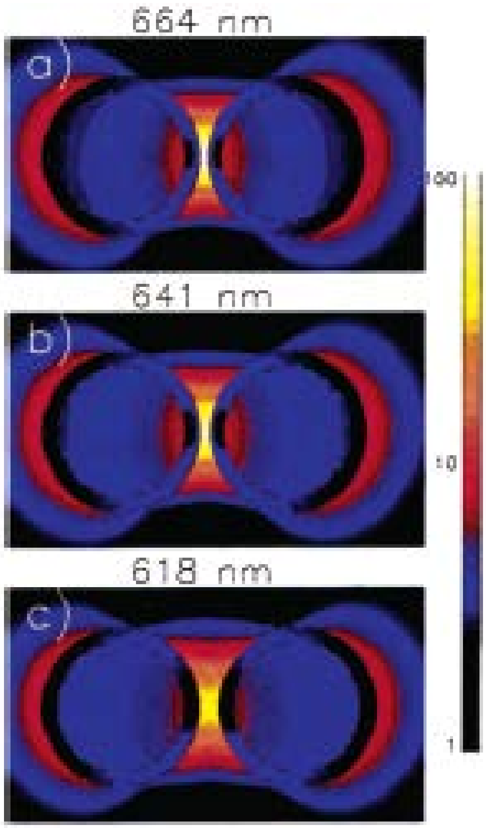
The large field enhancements are caused by admixture of high *l* individual NP modes



Nanoparticle dimers



Lassiter *et al.*, NL 8 (2008)1212



d=4.5nm

d=6.0nm

d=12.0nm

Oubre &PN, JPCB 109(2005)10042

Bonding dipole mode redshift and multipolar modes appear for small D

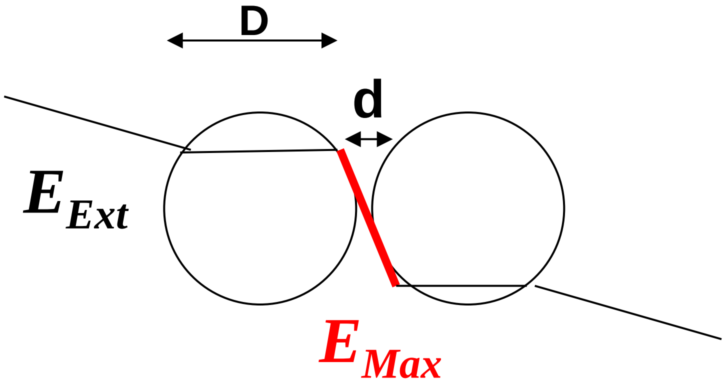
Large field enhancements for small D: Hot-Spots

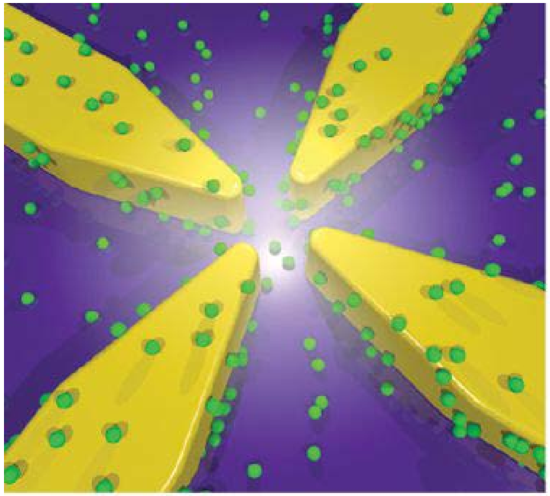
The dimer geometry is the canonical structure for SERS

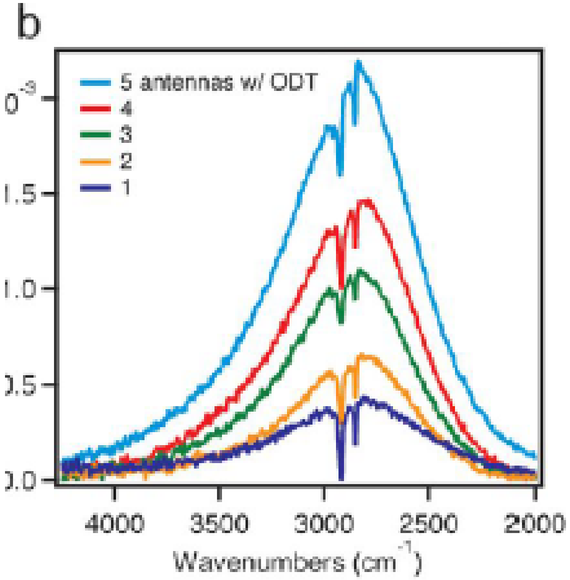
Surface Enhanced Infrared Absorption (SEIRA)

Field enhancement in the IR due to (nonplasmonic) lightning rod effect

$$E_{Max} = E_{Ext}\frac{2D+d}{d}$$







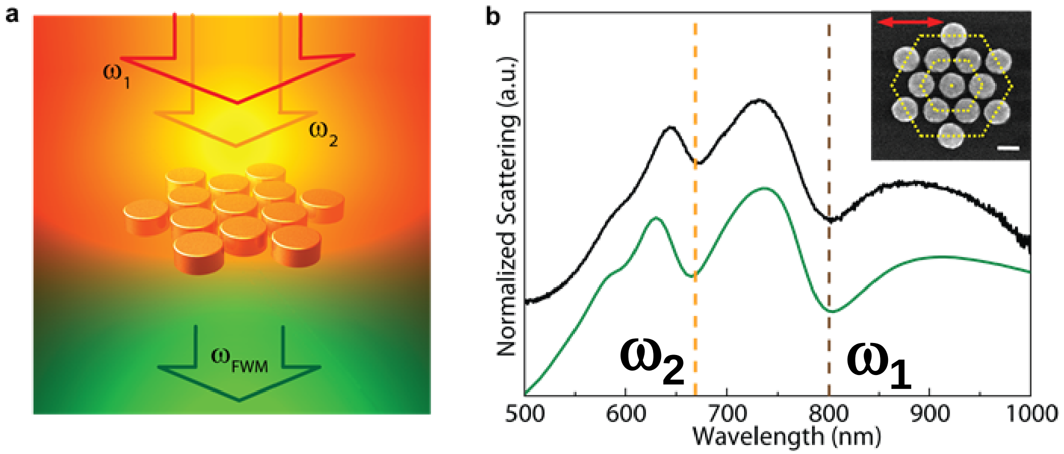
SEIRA using individual nanoatenna

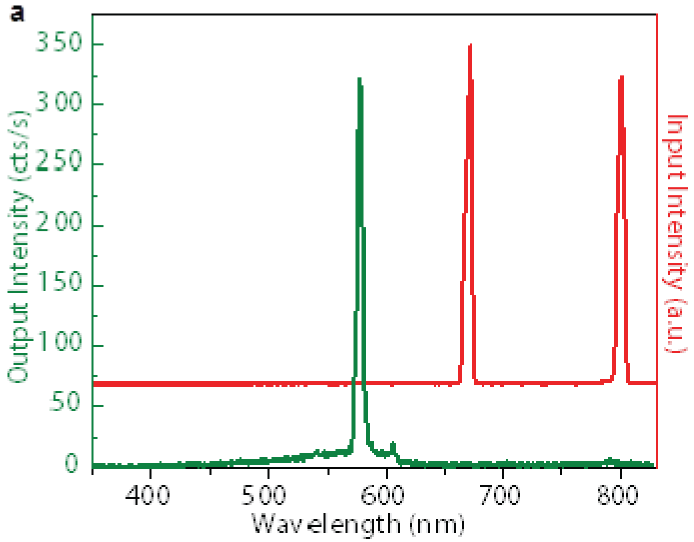
L.V. Brown *et al.*, JACS 135(2013)3688

Plasmon-Enhanced 4-wave mixing

(Y. Zhang *et al.*, PNAS 110(2013)9215)

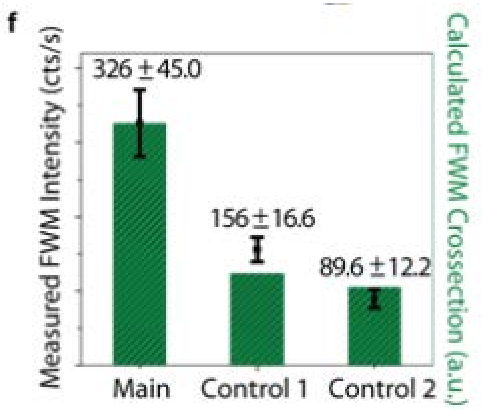
$$I(2\omega_2 - \omega_1) \propto |E(\omega_1)|^2 |E(\omega_2)|^4$$





Plasmonic oligomer with dual Fano resonances tuned to ω_1 and ω_2

$\omega_{FWM} = 2\omega_2 - \omega_1$



Control 1: only ω_1 tuned to FR
Control 2: only ω_2 tuned to FR

Main: Both ω_1 and ω_2 tuned to FRs
Strong enhancement!

Quantum Plasmonics

- **Plasmon Tunability of metallic nanorods**
- **Electron tunneling in NP dimer: Charge transfer plasmons**
- **Nonlinear effects**
- **Plasmon enhanced transport through conductive junctions**
- **Coupled Plasmonic and Excitonic systems: Quantum plexcitonics**
- **Graphene plasmons**

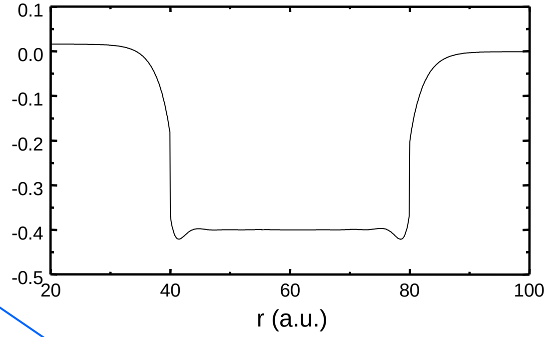
Time-dependent Local Density Approximation, RPA, jellium model,
Nonequilibrium Green functions, Anderson Model, ……

Time Dependent Local Density Approximation TDLDA

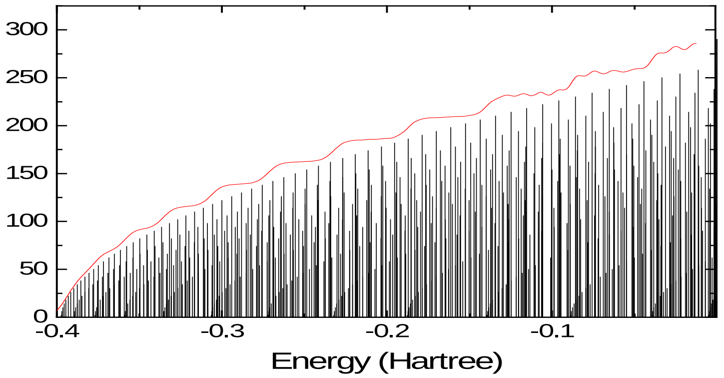
(Zangwill & Soven 1980)

1) Calculation of the electronic structure using the Local Density Approximation (LDA)

Effective electron potential

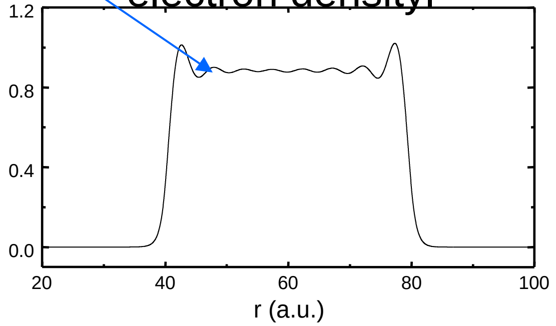


Density of states Au(40,80)a.u.



Friedel oscillations
Influence plasmon energies and optical properties

electron densityl



DOS is bulk like

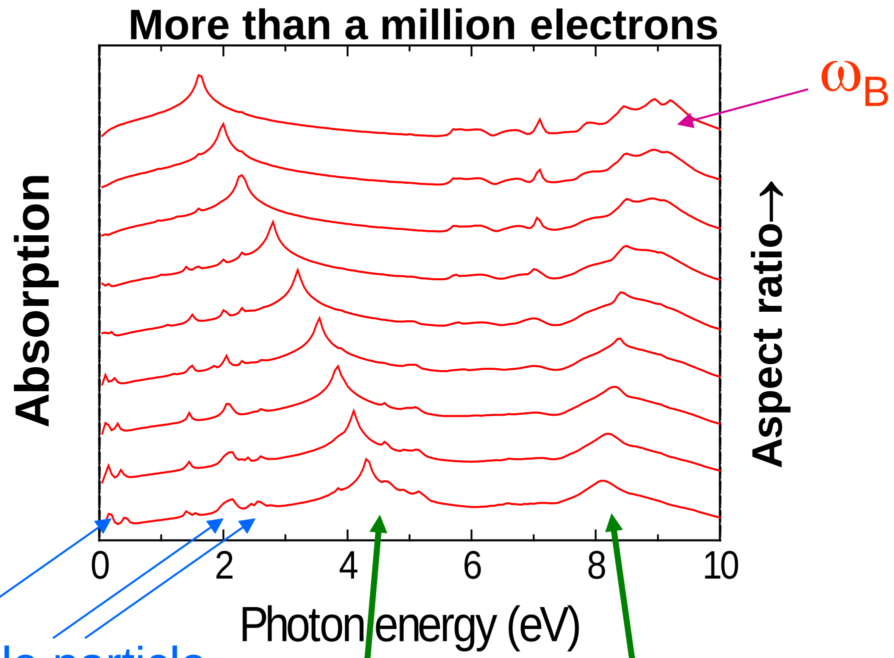
Prodan & PN, CPL 352(2002)140

2) Calculation of the frequency dependent dielectric function using the Random Phase Approximation (RPA)

Efficient implementation on Beowulf cluster for nanoshells
with more than a million inequivalent electrons

Quantum Plasmonics: Nanoshells

(Prodan & PN, CPL 360(2002)325, 368(2003)94, NL 3(2003)543, 1411)



Single particle excitations

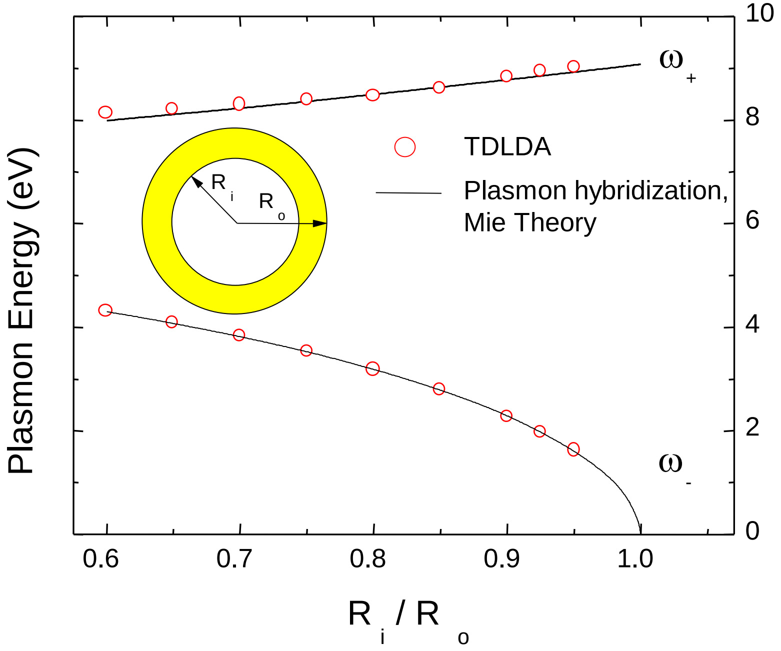
ω_-

ω_+

The spectral features around ω_B are due to Friedel oscillations.

Excellent agreement between TDLDA, and Mie theory for ω_+ and ω_- modes

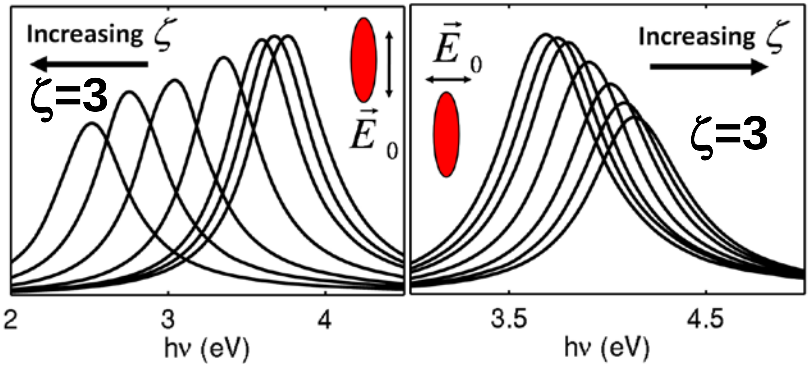
Tunability

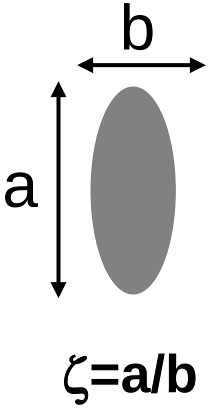


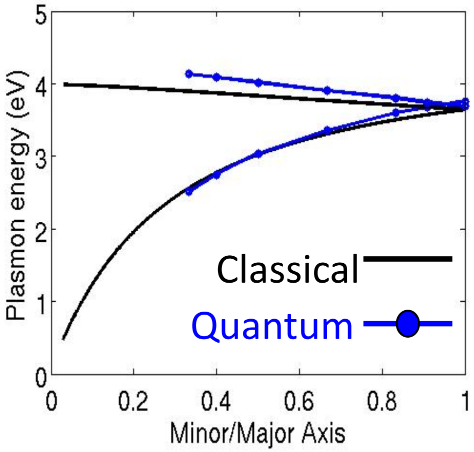
Quantum description of silver nanorod plasmons

(J. Zuloaga *et al.*, ACS Nano 4(2010)5269)

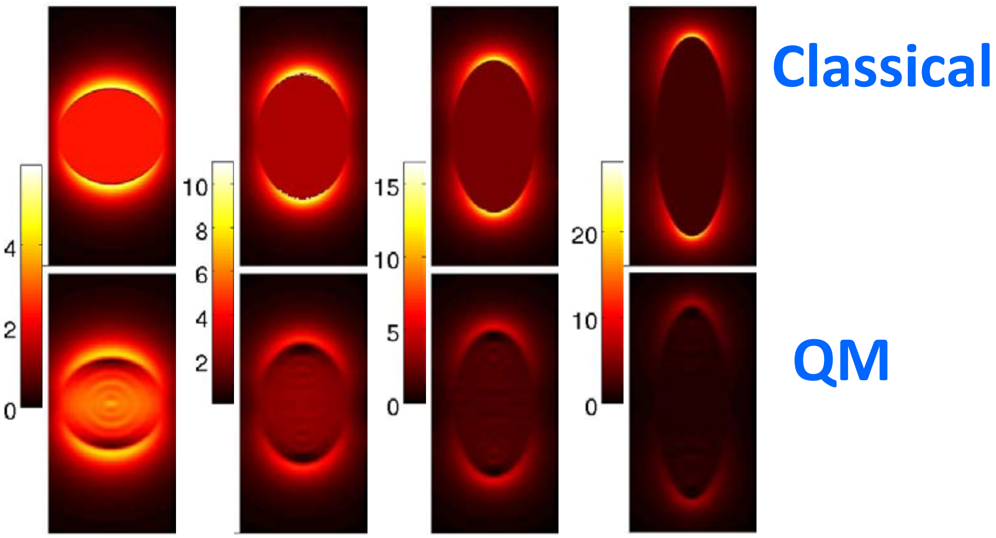
Longitudinal **Transverse**







Field enhancements



QM results for plasmon energies agree with classical theory!!

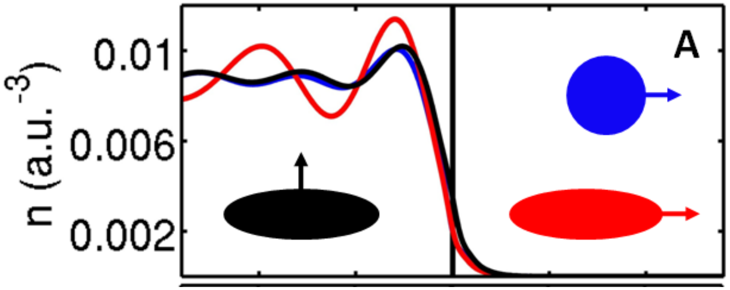
Quantum effects reduce the field enhancements near the NP surface

Enhancements agree <u>beyond 0.5 nm</u>

Physical origin of reduced field enhancements

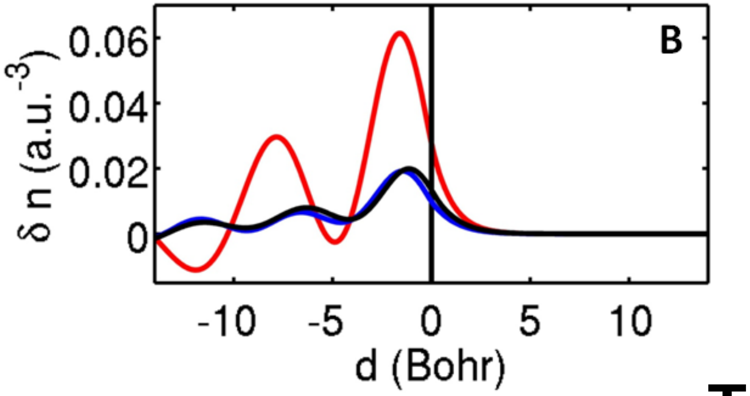
(J. Zuloaga et al., ACS Nano 4(2010)5269)

Equilibrium electron density $n(\vec{r})$



Electron density at NP surface varies continously, not abruptly "spill-out"

Plasmon-induced electron density $\delta n(\vec{r})$

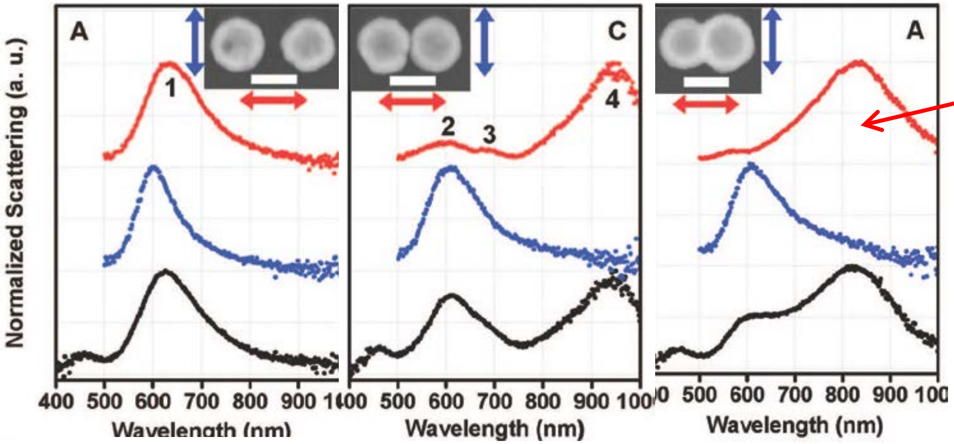


1 nm

Classical E&M predict δn=δ(d)
QM calculation give smeared volume charge distribution

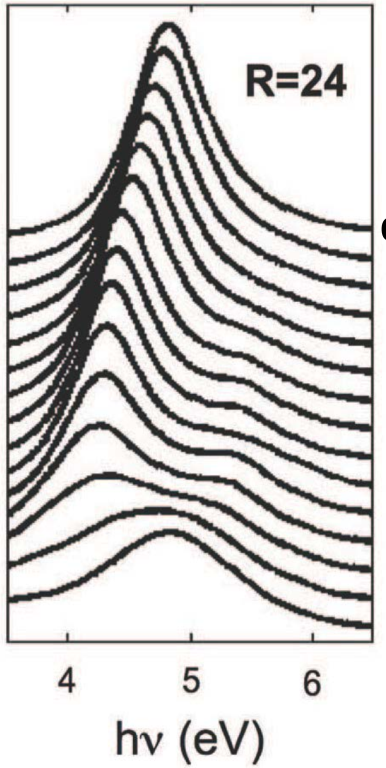
The effect can be modeled using nonlocal (k-dependent) permittivity

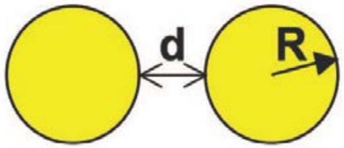
Quantum Plasmonics: Charge Transfer Plasmons (CTP)

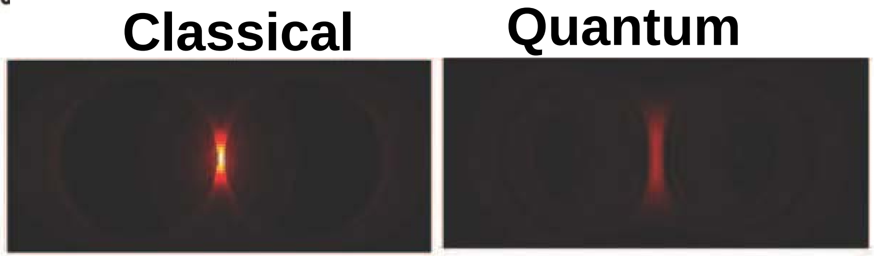


When nanoparticles near each other, a CTP appears

J.B. Lassiter *et al.*,
Nano Lett. 8 (2008)1212





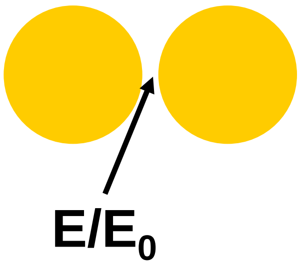


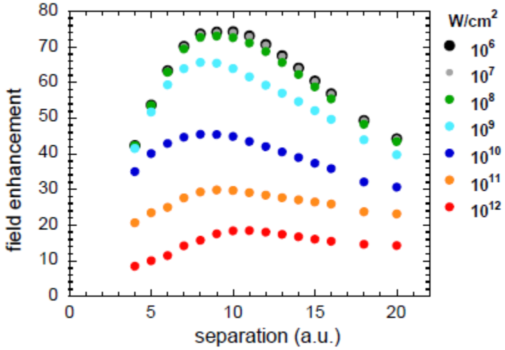
Quantum calculations show a CTP for d<1nm. Strong reduction of the field Enhancement. CANNOT be modeled using nonlocal description

J. Zuloaga *et al.*, Nano Lett. 9(2009)887;

Nonlinear optical response of a NP dimer

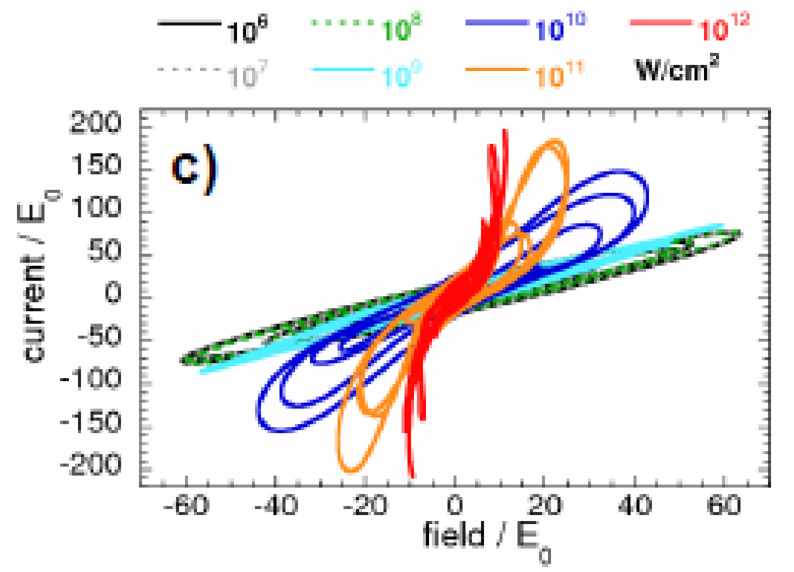
(C. Marinaca *et al.*, Nano Lett . 12(2012)1333)

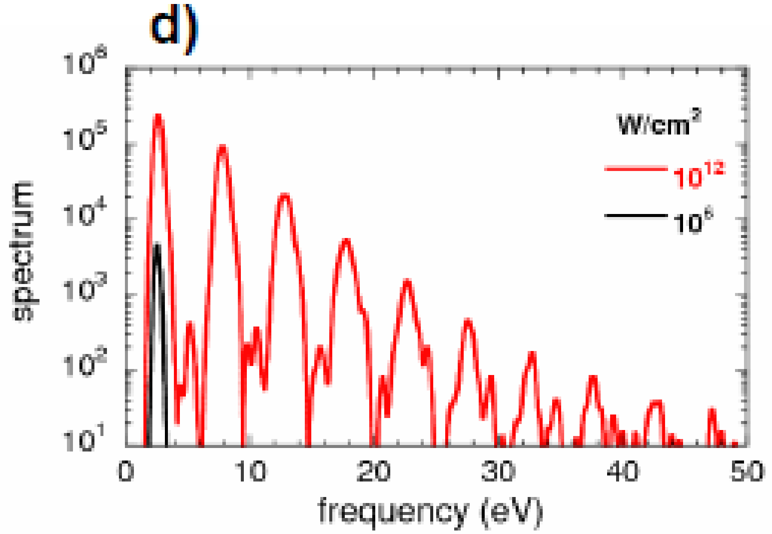




Field enhancement saturates due to electron tunneling!

Electron tunneling is nonlinear



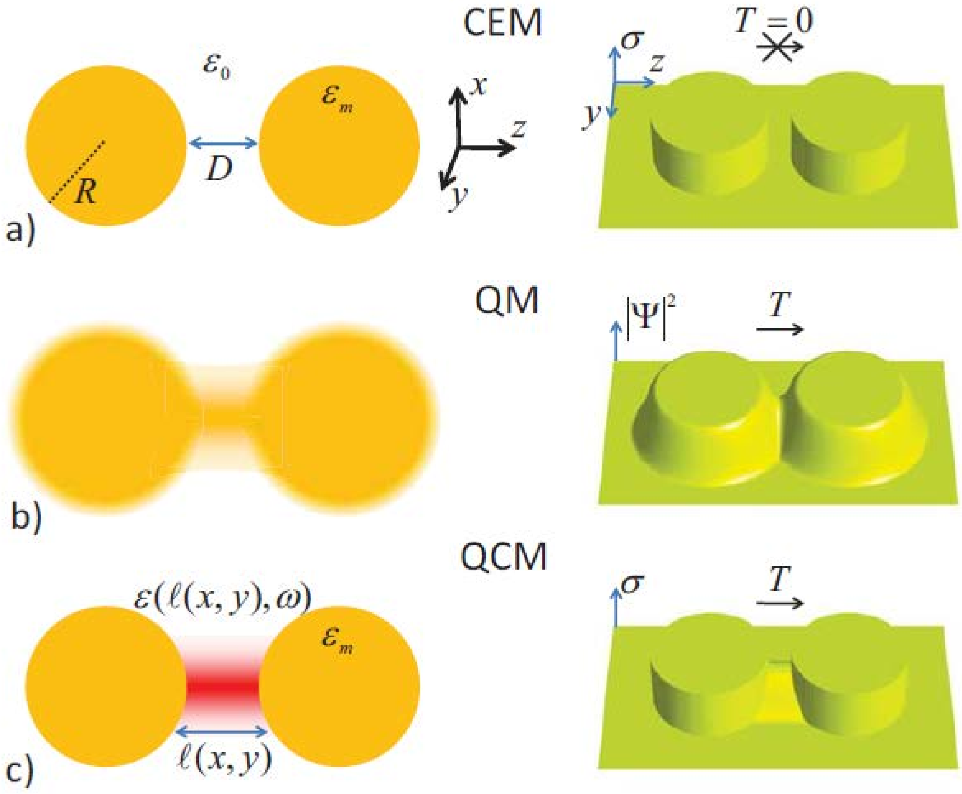


Low intensity: Ohmic (low G)
Intermediate: Ohmic (large G, HE)
High : Non Ohmic (HE, AC Stark)

High harmonics are generated!

Quantum Corrected Model (QCM)

(R. Esteban *et al.*, Nat Comm. 3(2012)825)

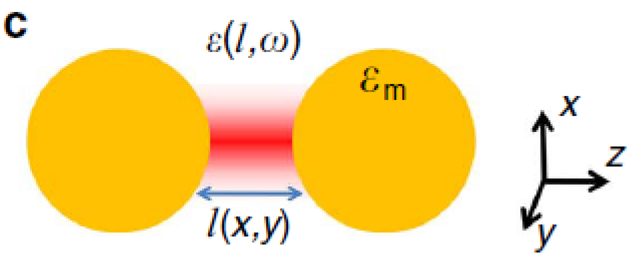


QM effects can be included in a classical E&M simulation by replacing the junction with a fictitious conductive material.

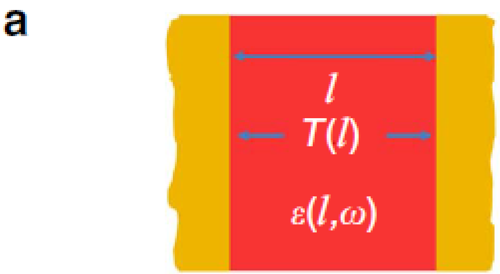
For typical timers, the field enhancement from QCM is an order of magnitude smaller than CEM!

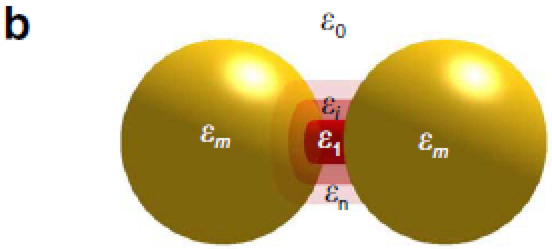
Implementation of QCM

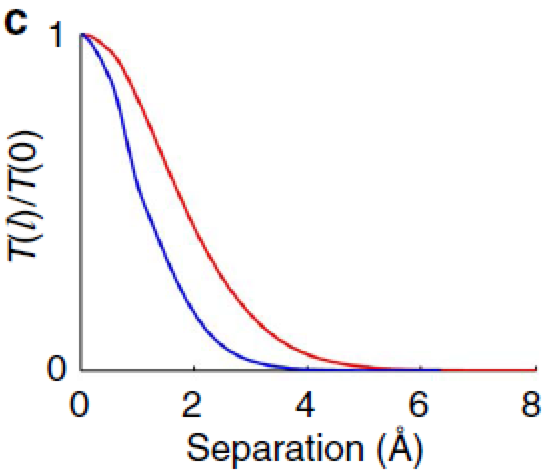
(R. Esteban *et al.*, Nat Comm. 3(2012)825)



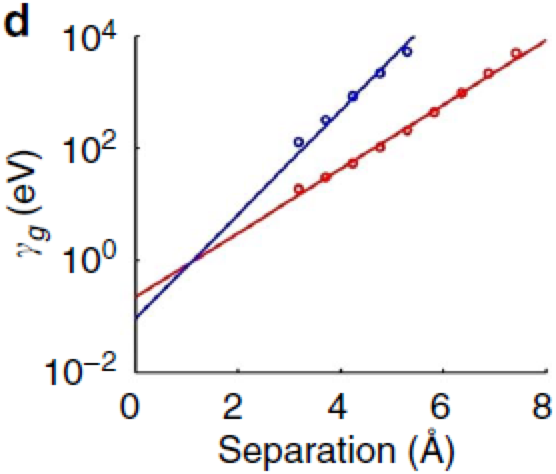
Local tunneling conductivity Im[ε] depends on *l(x,y)*





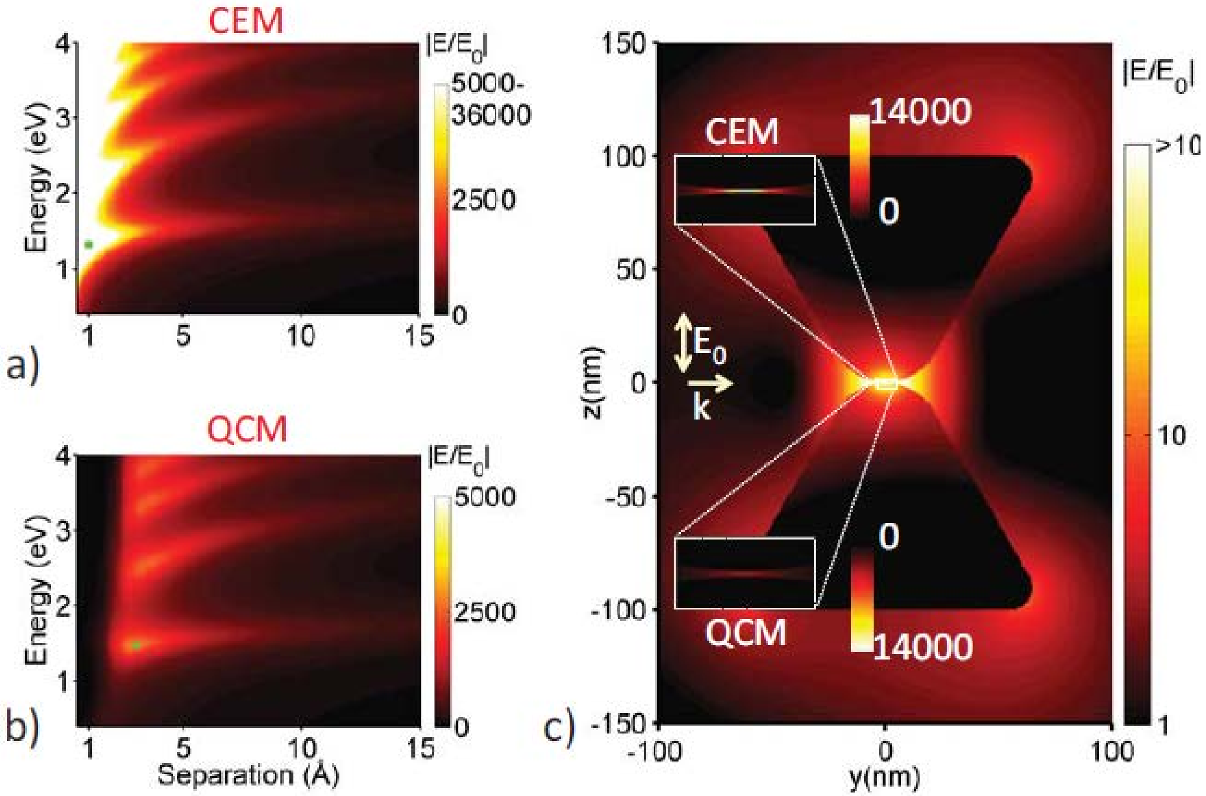


Tunneling rates calculated for planar junction



Practical implementation

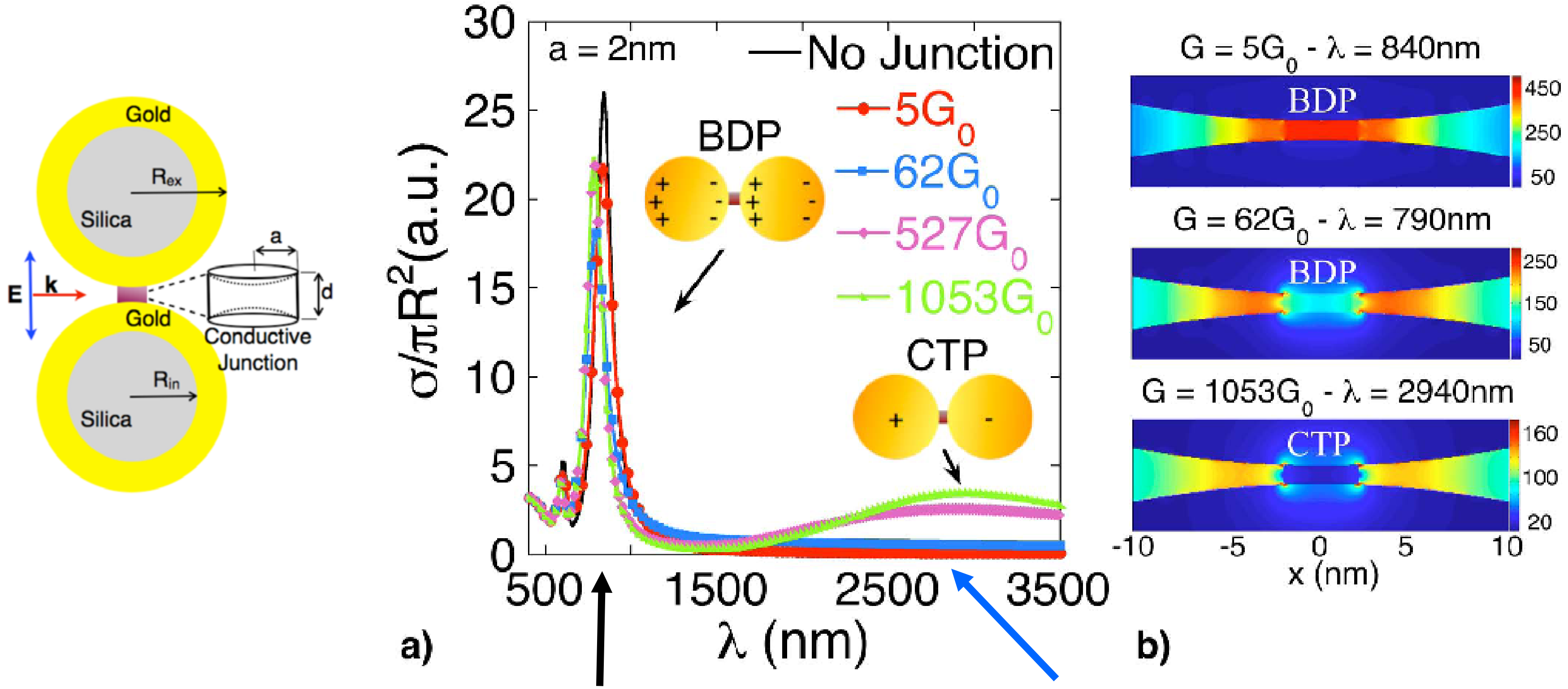
Application to realistic size bowtie antenna $>10^7$ electrons **(Esteban *et al.*, Nat. Comm. 3(2012)825)**



Field enhancement from QCM is an order of magnitude smaller than CEM due to electron tunneling and nonlocal screening!

Effects of conducting junctions

(O. Perez-Gonzalez *et al.*, NL 10(2010)3090)



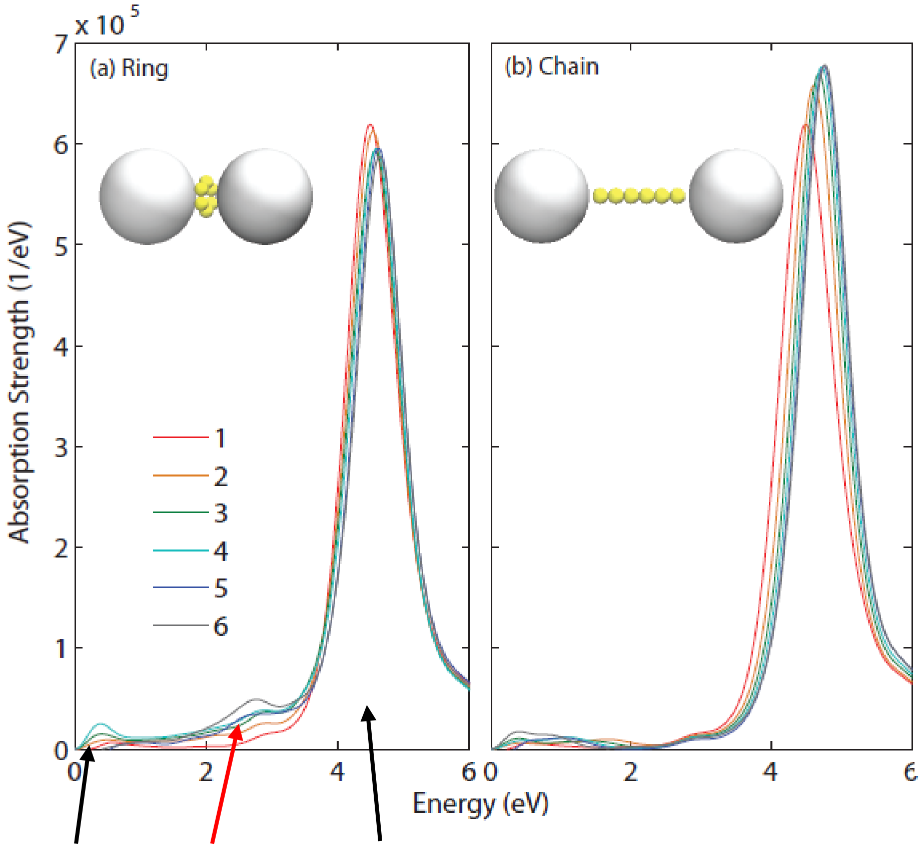
A conducting molecule blueshifts and broadens the dimer plasmon

For large conductance, a CTP appear in the mid IR

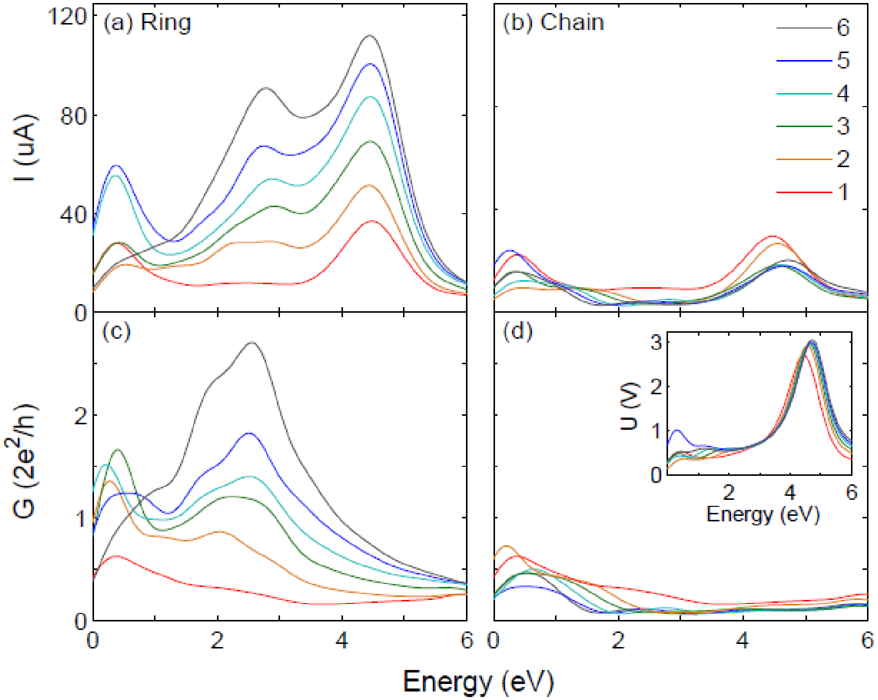
Extinction spectrum depend sensitively on junction conductance

Multi Na atom junctions

(P. Song, S.W. Gao *et al.*, JCP 134(2011)074701, PRB 86(2012)121410)

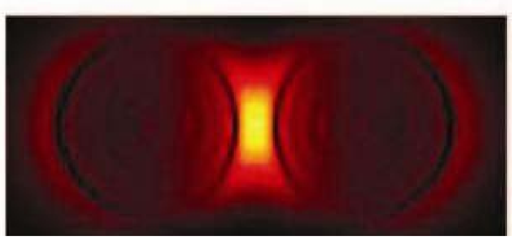


CTP **MR** **BDP**



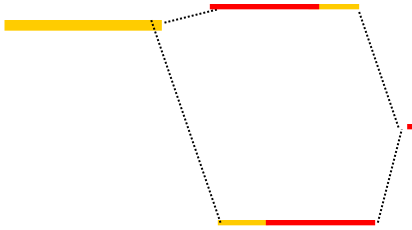
Electric currents are enormously enhanced because of E field

CTP and BDP as in classical EM. New molecular resonance (MR) appears depending on molecular structure.



Quantum Plexcitonics

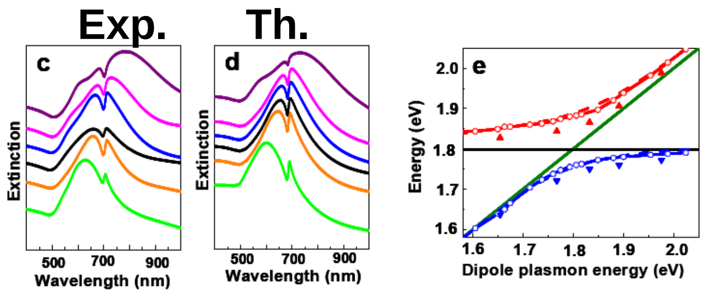
The electromagnetic coupling between excitonic and plasmonic systems results in hybrid "plexciton" states



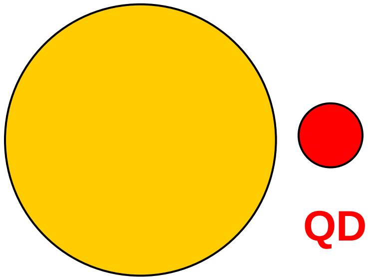
Plasmon

Exciton

Plexciton



(N. Fofang *et al.*, NL 8(2008)3481)



Bosonic operators: Plasmons, Photons, Phonons, …

Fermionic operators: Exciton, eh-pair excitations, ...

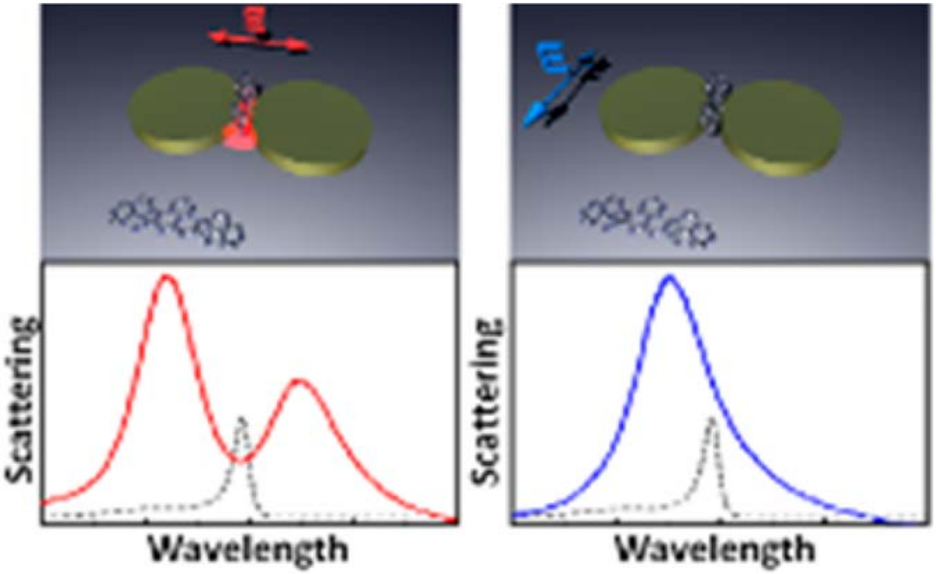
- **Nonlinear Fano effect** (Manjavacas *et al.*, Nano Lett. 11(2011)2318)
- **Plasmon blockade and antibunching**

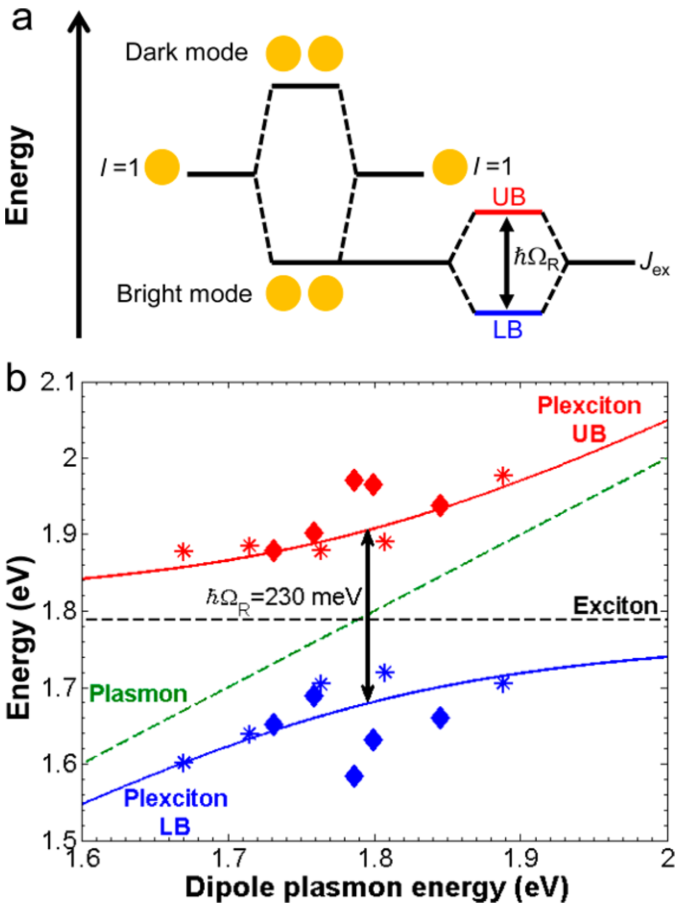
(Manjavacas *et al.*, ACS Nano 6(2012)1724)

Plexciton formation in individual NP dimer

(A.E. Schlather *et al.*, NL 13(2013)ASAP)

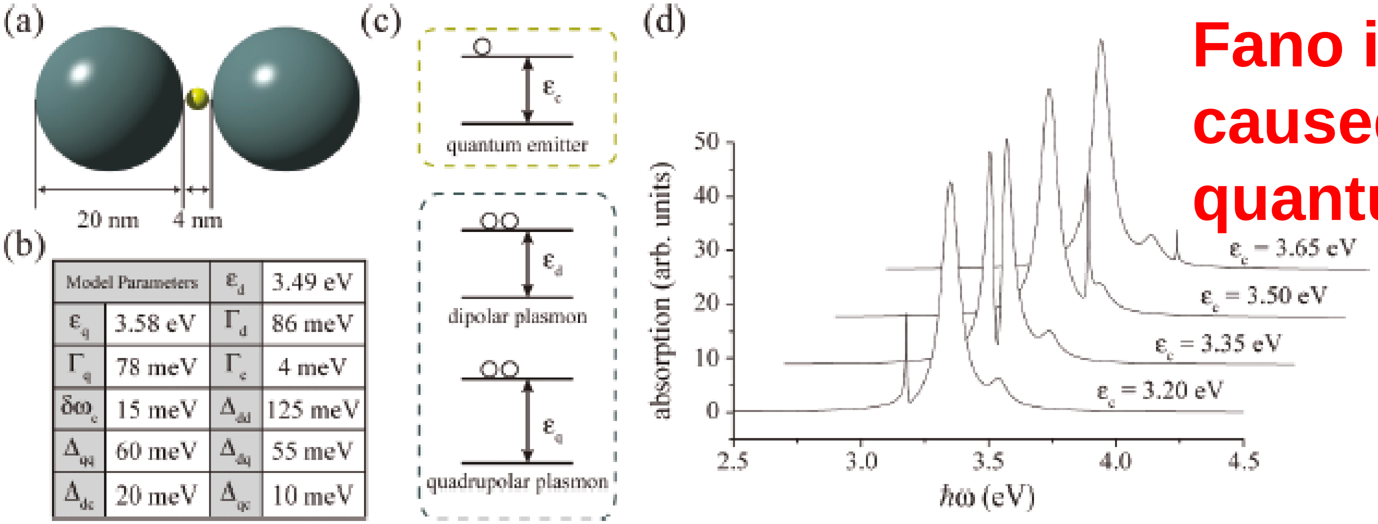
J-aggregates in NP junction





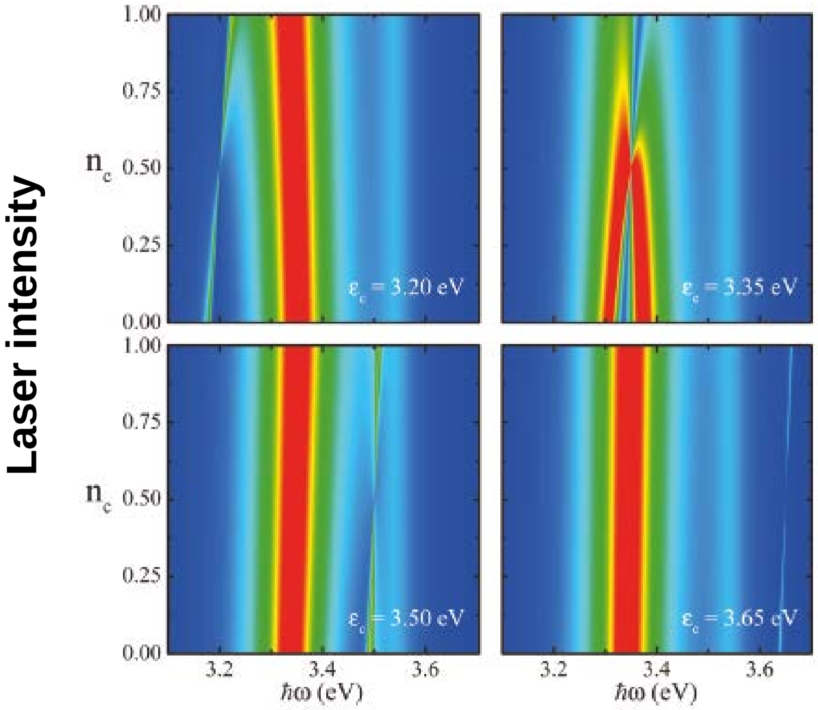
Giant Rabi splitting (250-400 meV) meV for longitudinal polarization

Quantum plexcitonics, (A. Manjavacas *et al.*, NL11(2011)2318)



Model Parameters		ε_d	3.49 eV
ε_q	3.58 eV	Γ_d	86 meV
Γ_q	78 meV	Γ_c	4 meV
$\delta\omega_c$	15 meV	Δ_{dd}	125 meV
Δ_{qq}	60 meV	Δ_{dq}	55 meV
Δ_{dc}	20 meV	Δ_{qc}	10 meV

Fano interference caused by a single quantum dot



Nonlinear absorption

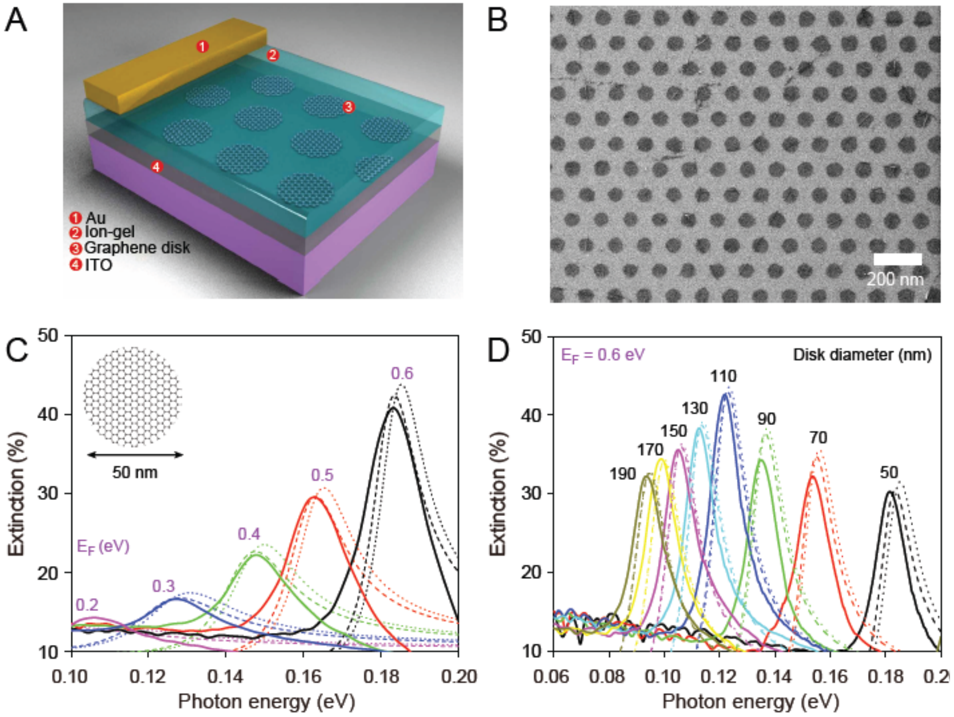
Due to the fermionic nature of quantum dot excitations (Pauli Principle)

Nonlinear Fano effect (Govorov 2008)

Graphene plasmonics

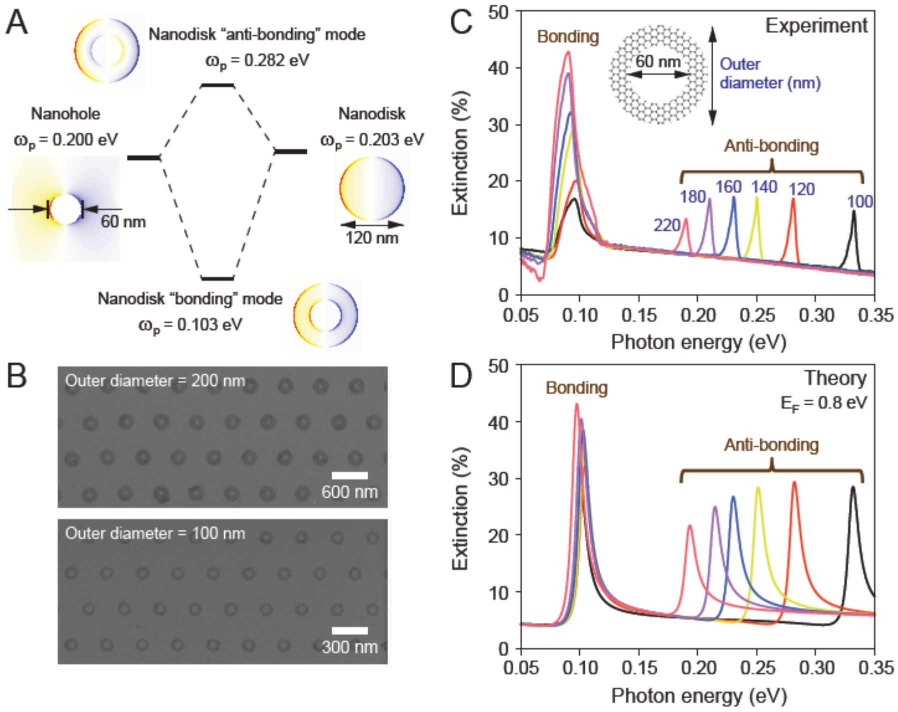
(Z.Y. Fang *et al.*, ACS Nano 7(2013)2388)

Nanodisks



Doping tunability **Diameter tunability**

Nanorings



Coupling tunability

Excellent agreement between experiments and theory

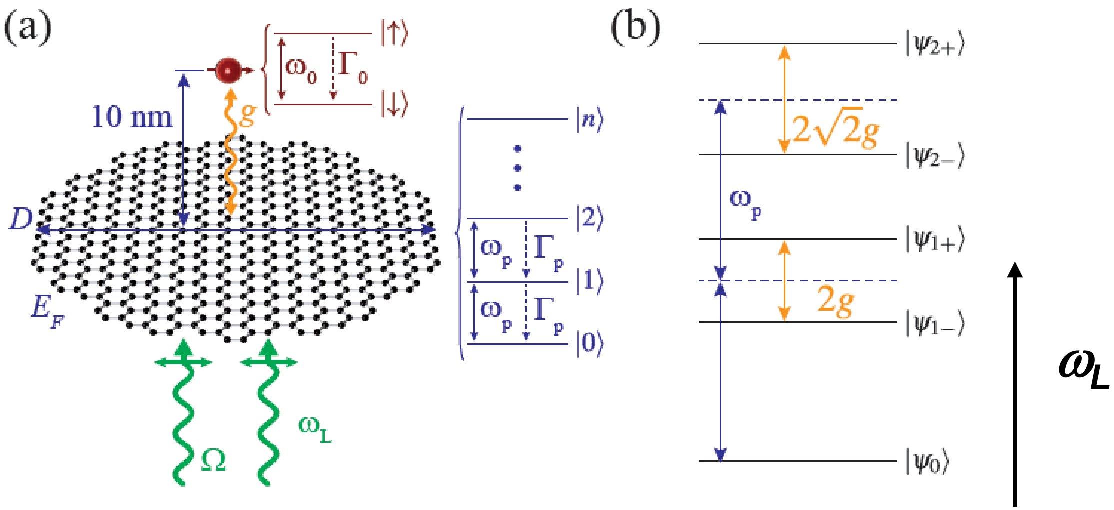
Q-factor for AB ring mode > 60!

Plasmon Blockade and antibunching

(A. Manjavacas *et al.*, ACS Nano 6(2012)1724)

**Graphene disks:
Ultranarrow and tunable
plasmon modes**

$g/\Gamma_p > 1$



The coupling to a quantum emitter (exciton) results in plexcitonic states, a Jaynes-Cummings ladder

$$E_{n\pm} = \hbar\left(n\omega_p + \frac{\delta}{2} \pm \sqrt{\frac{\delta^2}{4} + ng^2}\right)$$

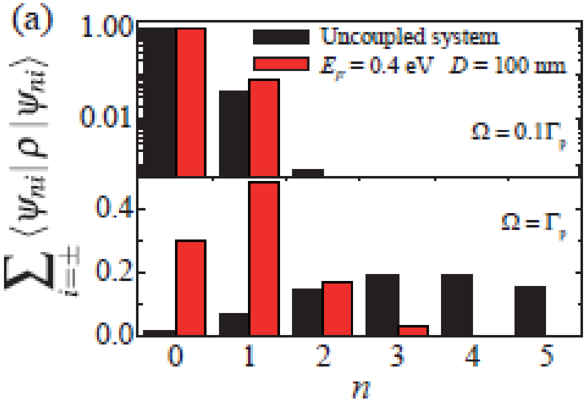
Energies no longer linear in *n*

⬄

Anharmonicity: $E_{n+1}-E_n \neq E_n-E_{n-1}$

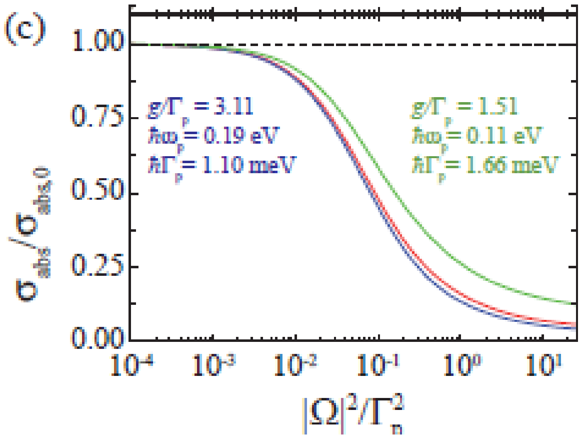
The presence of one plasmon quantum changes the energy of the next plasmon: Plasmon Blockade

Plasmon interaction changes many properties



Population of the different plexciton states
Black: w/o interaction
Red: interacting system

Plasmon Blockade restrict population of high *n* states



Normalized absorption cross section
Dashed: w/o interaction
Colored: increasing interaction
Plasmon blockade result in saturable absorbtion and plasmon antibunching ($<b^+b^+bb> < 1$)

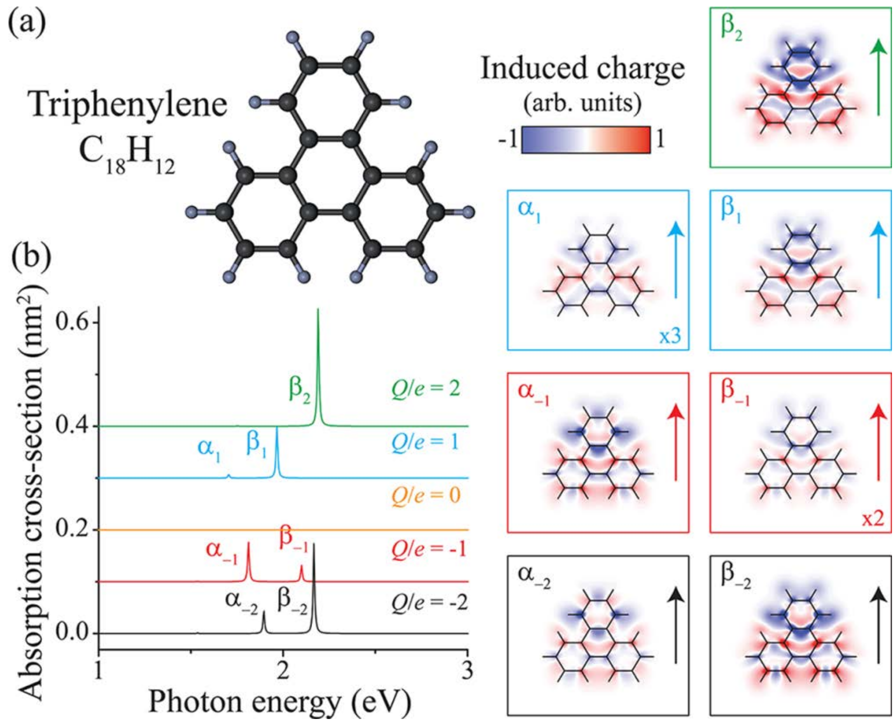
***g* (interaction), Ω intensity (Rabi frequency), Γ_p plasmon width, ω_p plasmon energy**

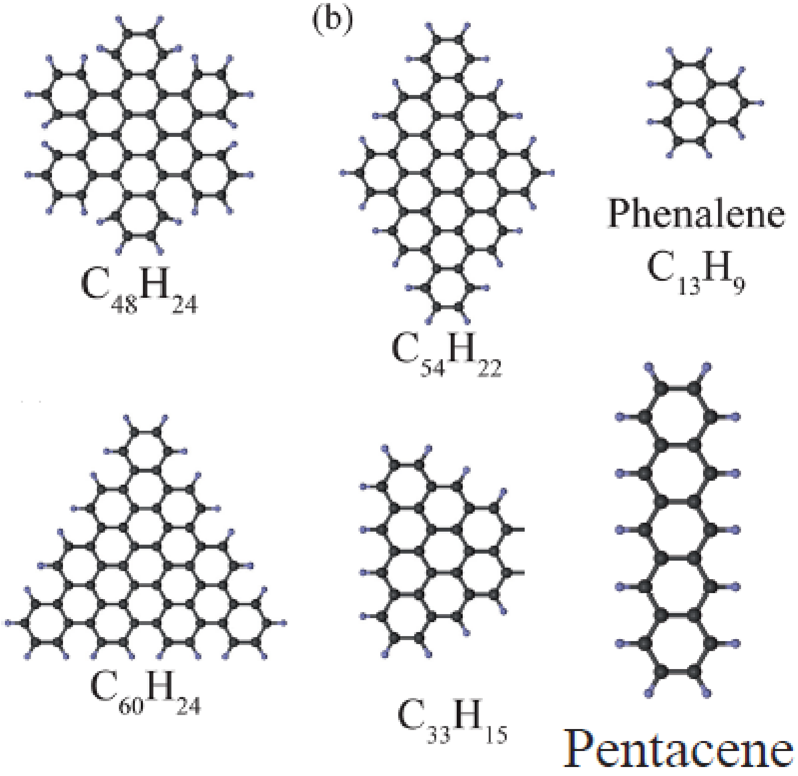
All realistic parameters from BEM and TDDFT calculations

Molecular Plasmons

(A. Manjavacas *et al.*, ACS Nano 7(2013)3635)

TDDFT studies of Polycyclic Aromatic Hydrocarbons: reveals “Molecular Plasmons”



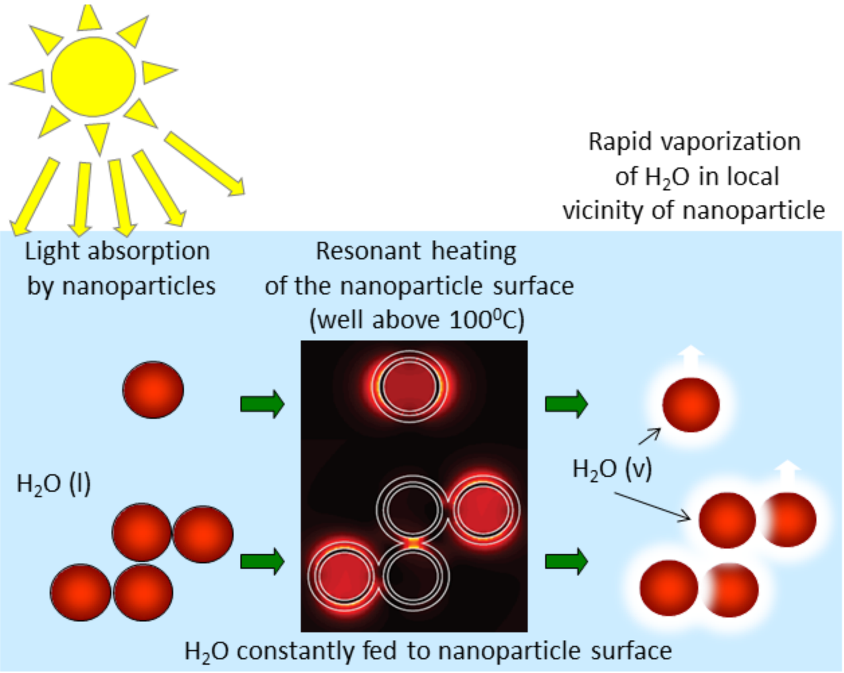


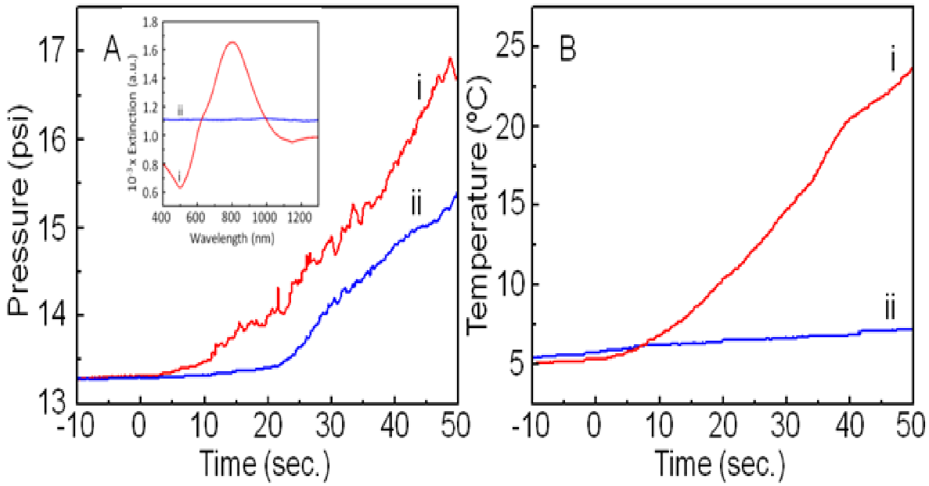
Highly tunable plasmon resonances in the visible
Stronger sensitivity to doping than graphene!

Plasmon-enhanced Light Harvesting

- Steam generation
- Hot electron generation and applications

Plasmon induced steam generation and distillation **(O. Neumann *et al.*, ACS Nano 7(2013)42)**

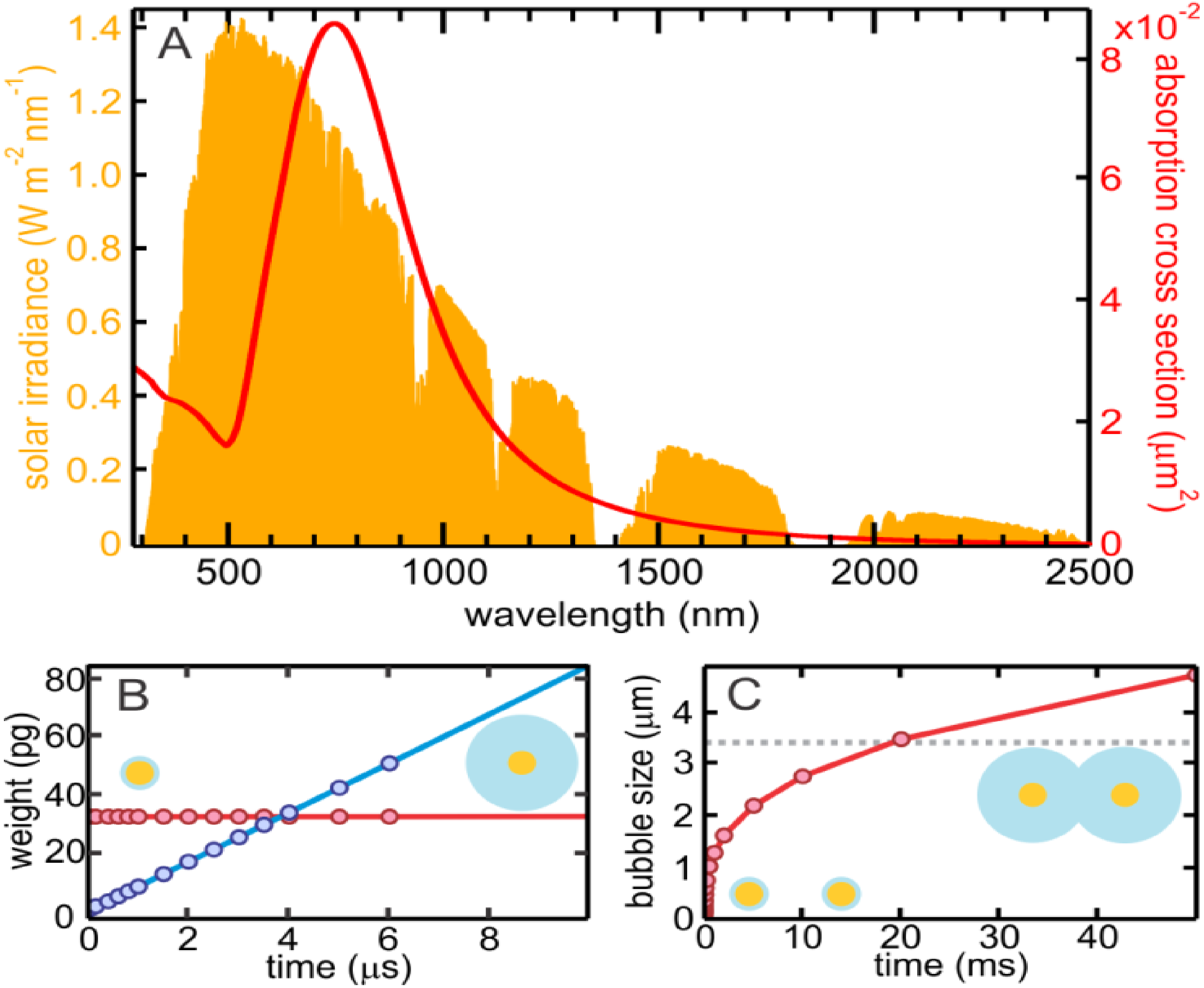




Solar light generate steam (T>150C) without heating the remaining liquid

Highly efficient process:

82% of light energy goes to direct vaporization of water; 18% goes to heating of the remaning liquid



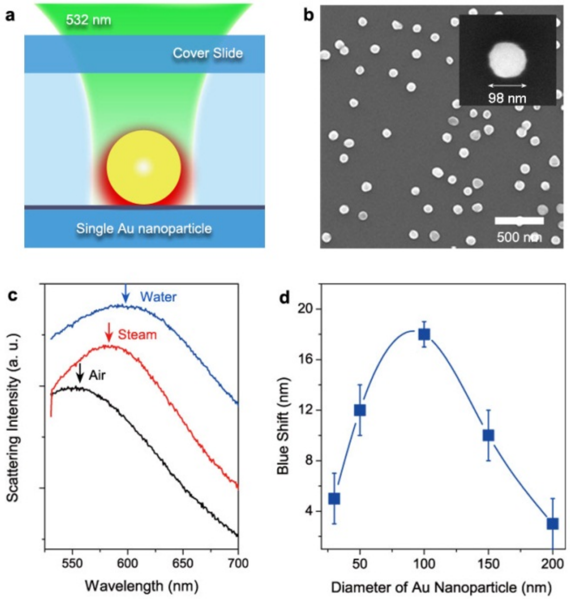
Nanoparticle tuned to solar spectrum

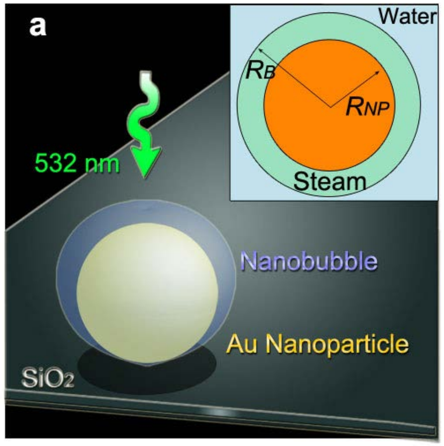
Nanoparticles surrounded by bubbles move to the the surface

Buoyancy after 4µs

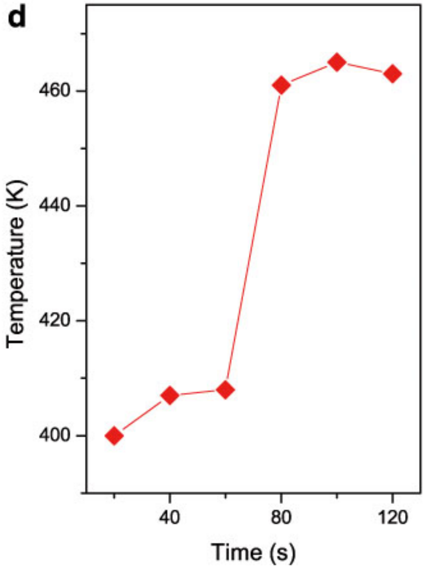
Bubble coalescence after 20 ms

Nanoparticle on a substrate studied with conventional light sources (Z.Y. Fang *et al.*, NL(2013)1736)





LSPR shift in steady State gives bubble thickness 10nm



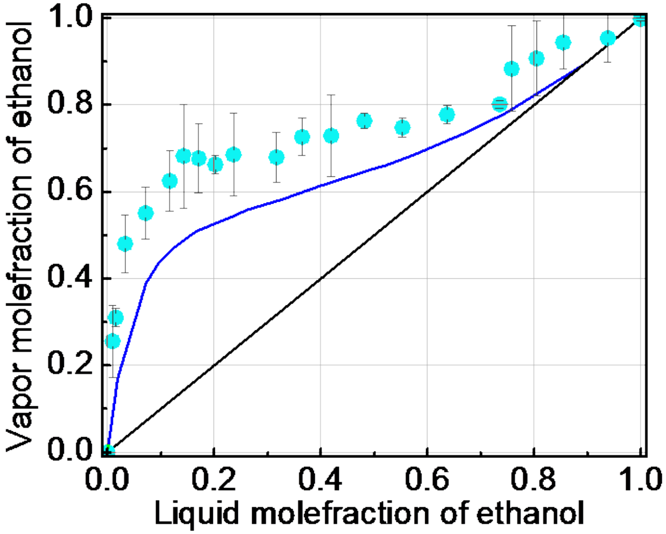
Bubble temperature from SERS Stokes anti-Stokes ratio

Once a complete nanobubble surrounds the NP, temperature increases drastically

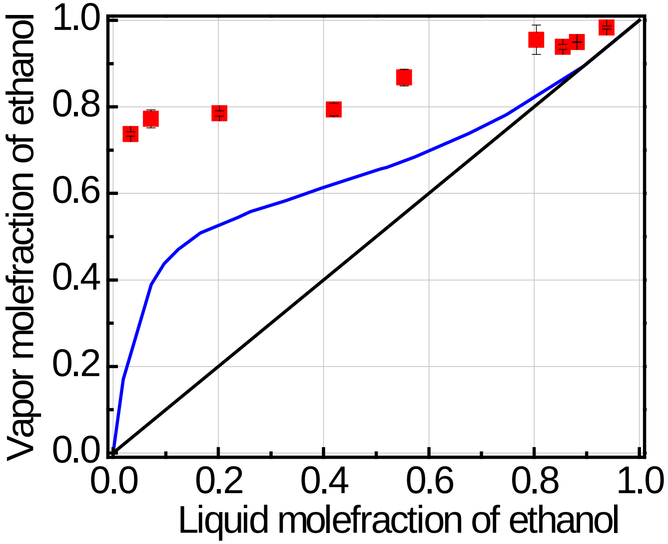
Applications

- Water purification, desalination, and remediation
- Sterilization and sanitation: Autoclave; waste management
- Distillation: Biofuels and chemical industry

Solar Distillation in "the field"



Laser Distillation in "dry" environment



Blue: Thermal Flash Distillation

Red: NP induced distillation

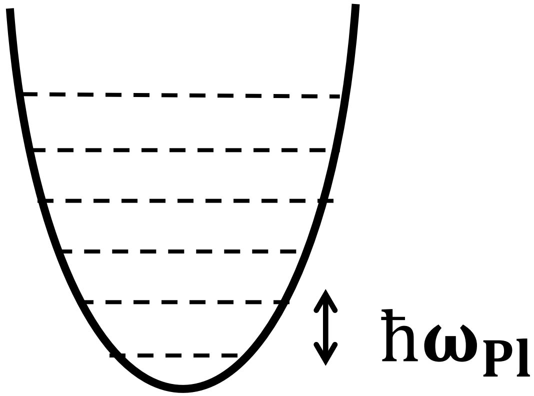
Distillate much richer than conventional distillation
Minimal heating of the remaining liquid

Plasmon decay

$$\mathbf{E_n} = \hbar\boldsymbol{\omega}_{\mathbf{Pl}}(\mathbf{n} + \tfrac{1}{2})$$

The decay of plasmons occur one quantum at a time

|n> -> |n-1> + Photon or eh-pair



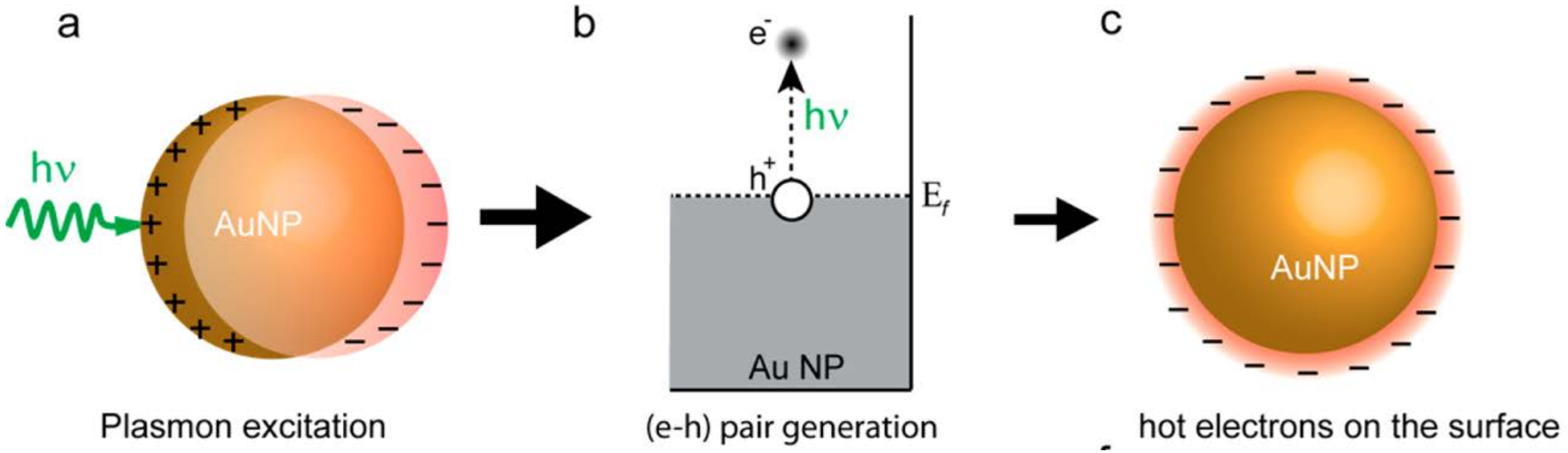
The branching ratio between photons and eh-pairs is determined by the radiance of the mode

i) Subradiant modes favors eh-pairs

ii) Superradiant favors photons

Since plasmon typically is excited to high n, many photons and eh-pairs are generated

Plasmon-induced Hot Electrons (HE)



Plasmon excitation

(e-h) pair generation

hot electrons on the surface

Each plasmon quantum decays into a single hot eh-pair.

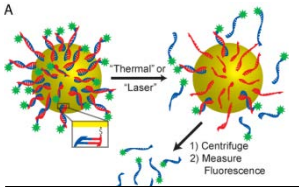
Most HEs end up at $\varepsilon_F+\hbar\omega$

Plasmon enhanced yield of HE is 10^6 times larger than for direct excitation ($Y_{Plasmon}=N_{el}\times Y_{DE}$)

HE ends up outside NP and can do things!

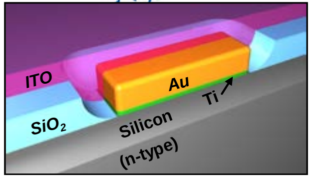
Hot electron applications

- **Chemical reactions**

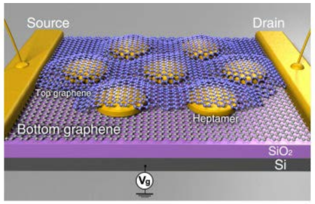


H_2+e -> 2H
D_2+e -> 2D
H+D -> HD

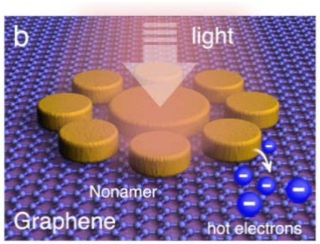
- **Photodetectors**



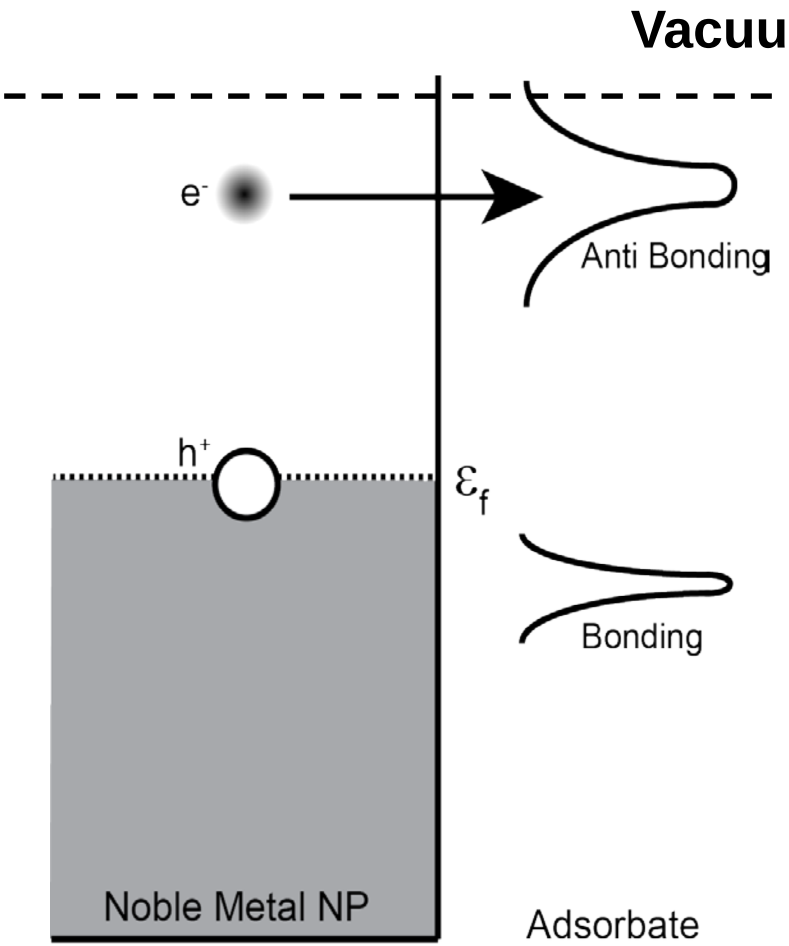
- **Photovoltaics**



- **Photoinduced graphene doping**



HE induced chemical reactions



Hot electrons are negative energy electrons and can transfer into specific molecular states.

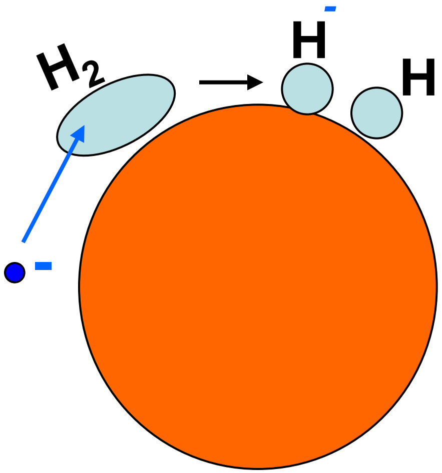
Chemical reactions can be steered optically!

C. Frischkorn *et al.*,
Chem. Rev. 106(2006) 4207

HE induced Dissociation of H_2/Au: The impossible reaction (S. Mukherjee *et al.*, NL 13(2013)240)

The dissociation of closed shell molecules is the entrance channel barrier in many important chemical reactions $3H_2 + N_2 = 2NH_3$

Dissociation of closed shell H_2 costs 4.6eV.
But H_2^- auto dissociates!

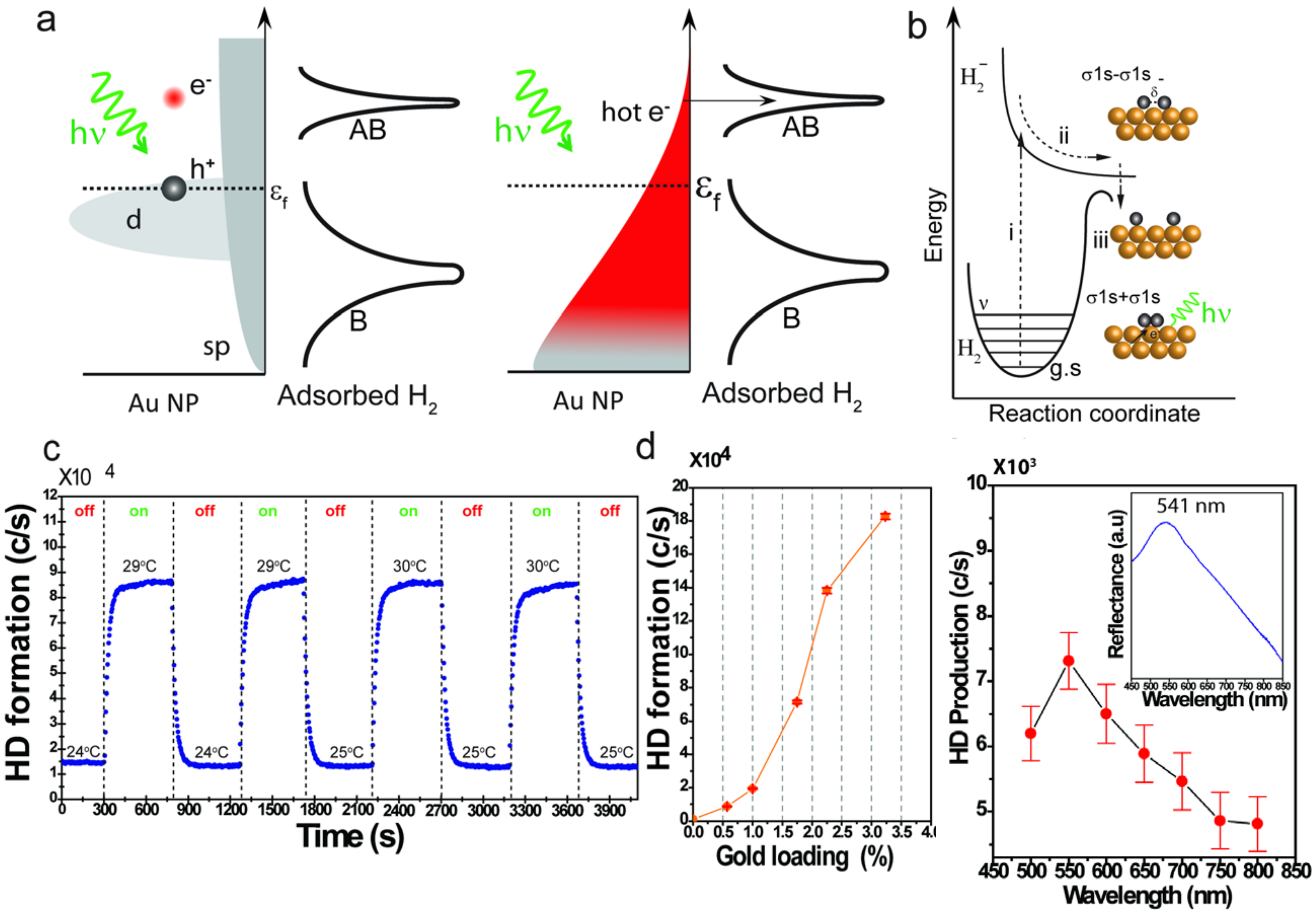


H_2+e -> 2H
D_2+e -> 2D
H+D -> HD

Hot electrons do the impossible, dissociation of H_2 on Au!

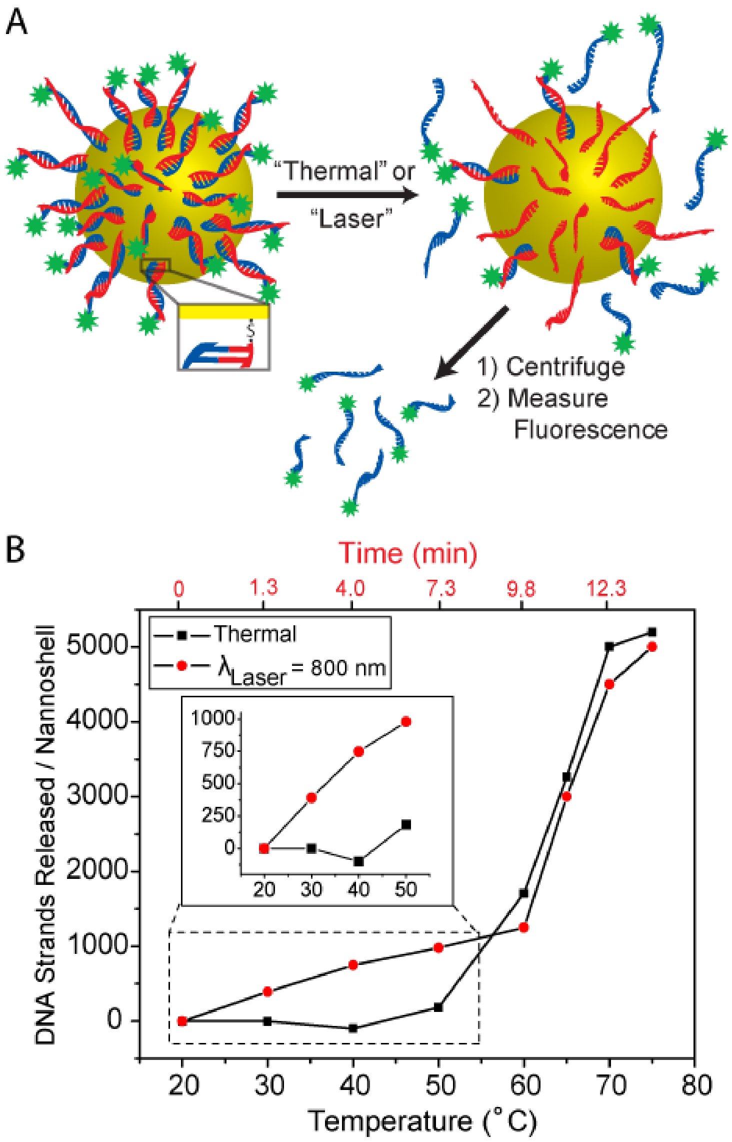
HE transfer into H_2 and induce dissociation!

Dissociation of H_2 on Au by plasmon-induced hot electrons (**S. Mukherjee *et al.*, NL 13(2013)240**)



HE triggered ssDNA release from Au nanoparticles

(R. Huschka *et al.*, JACS 133(2011)12247)



dsDNA with one strand anchored to a NP and the other strand tagged with a fluorophore

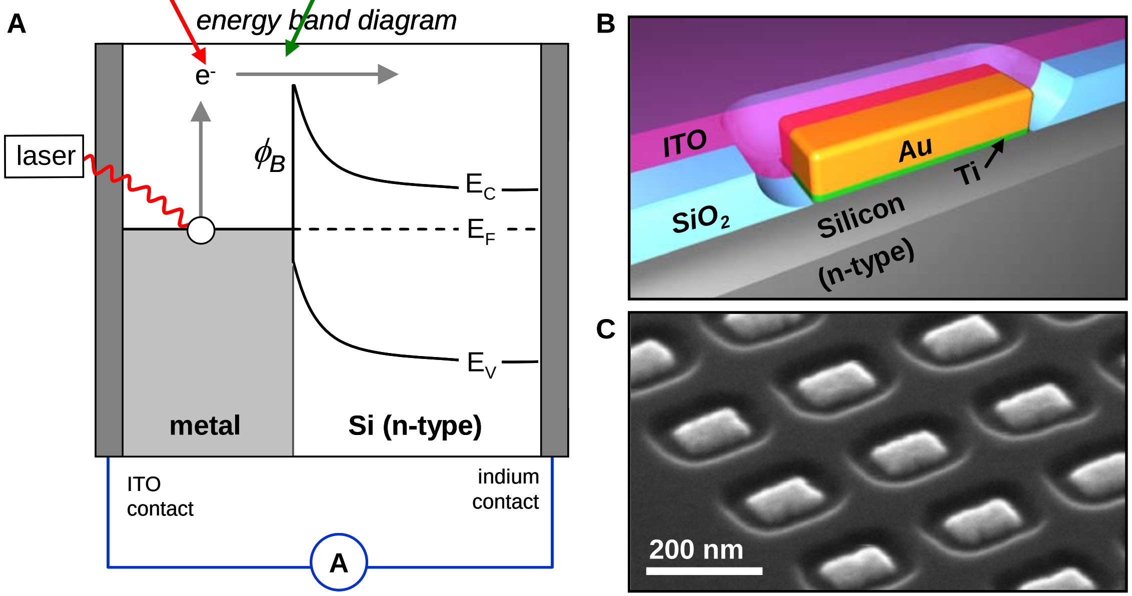
Hot electron transfer to DNA induce DNA melting at physiological temperatures

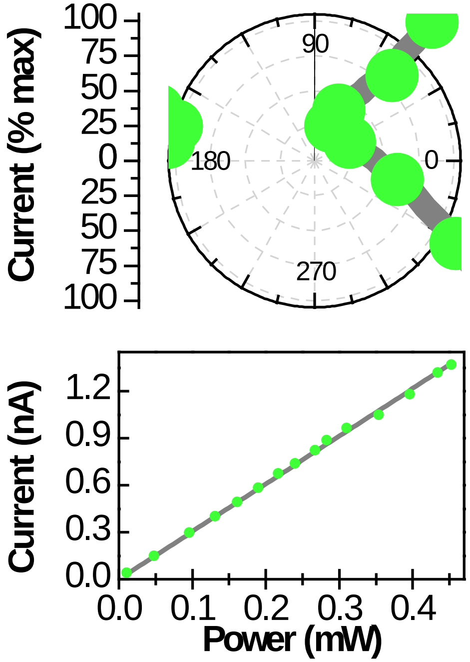
NP on semiconducting substrate

(M. W. Knight *et al.*, Science 332(2011)702)

Plasmon decay into hot electrons

Transport across the Schottky barrier





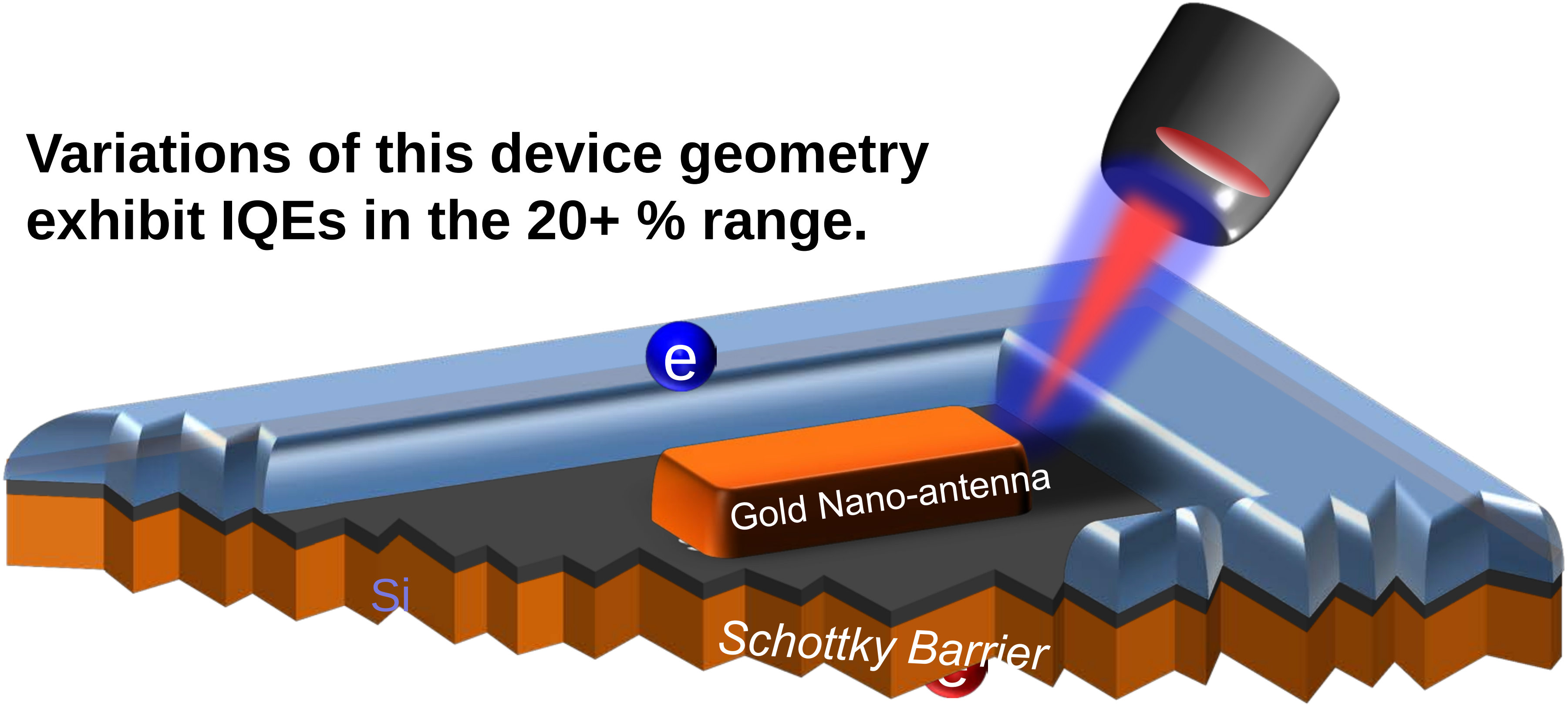
A nanoantenna-photodiode!

Simultaneous light collection and photocurrent generation

Hot-electron based photodetection

(M. W. Knight *et al.*, Science 332(2011)702)

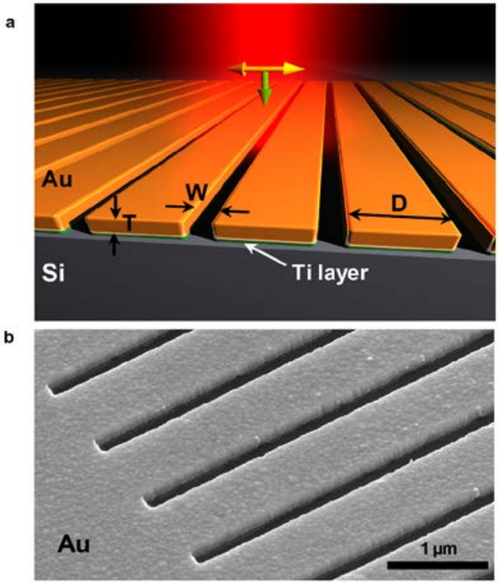
Variations of this device geometry exhibit IQEs in the 20+ % range.

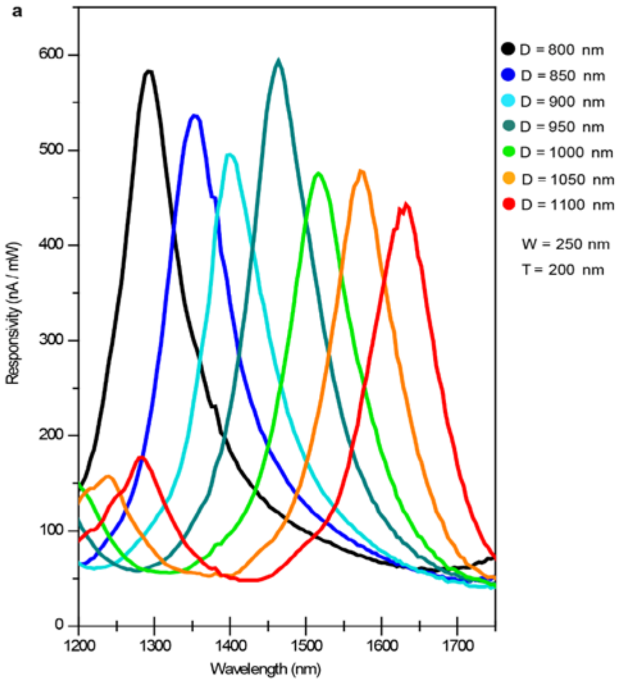


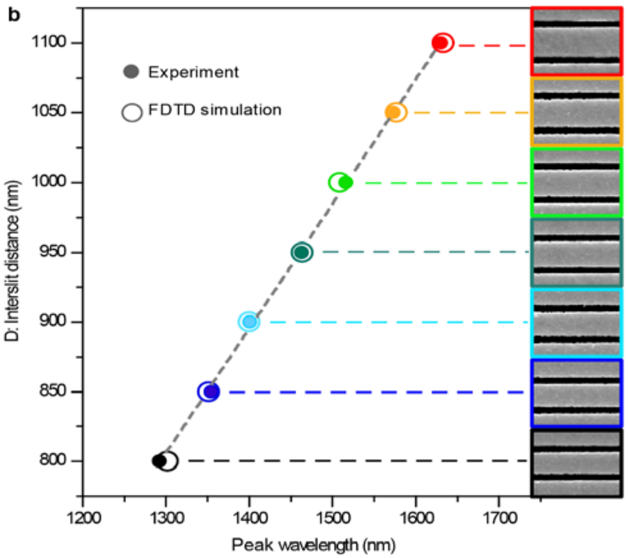
Device can be tuned into the visible.
Novel approach for photovoltaics!

EOT based Hot Electron Photodetector

(A. Sobhani *et al.*, Nature Comms. 4(2013)1643



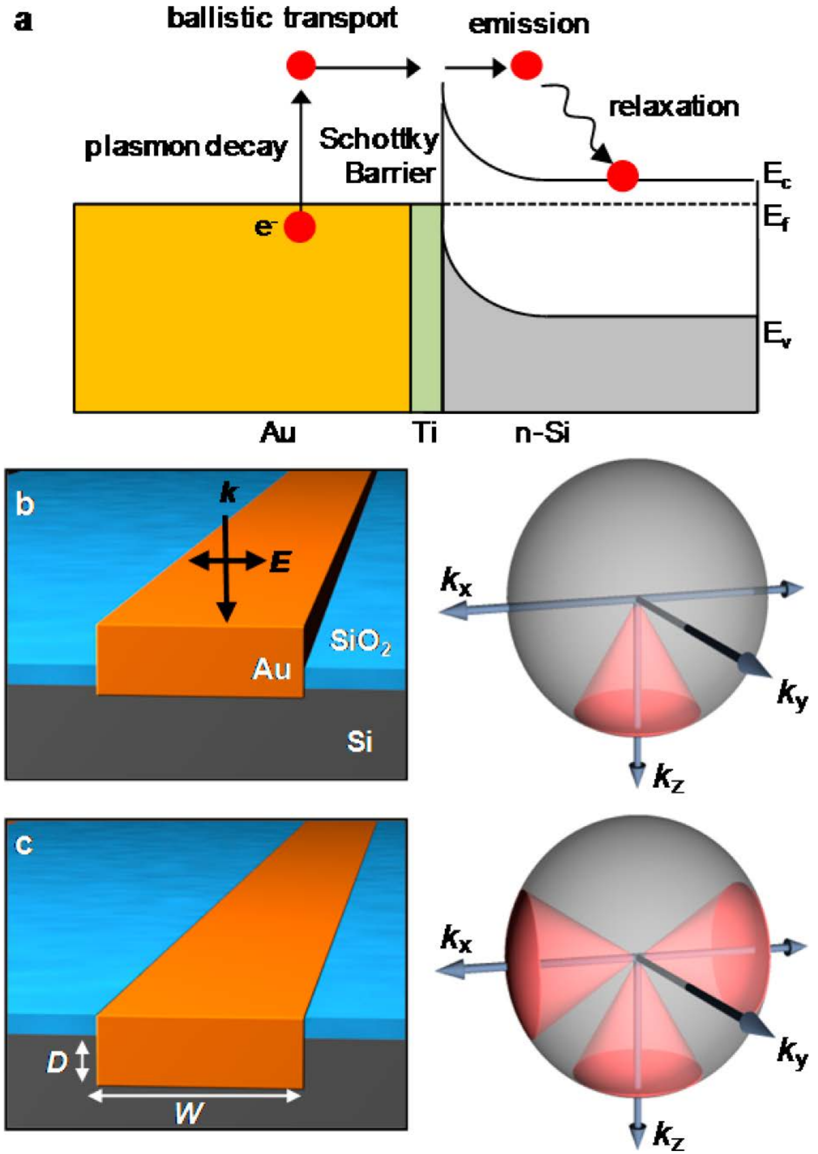


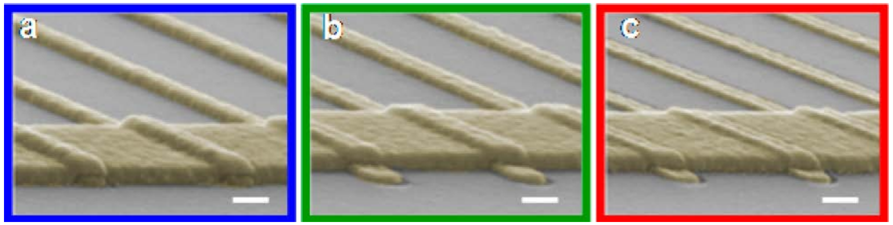


The use of a slit array enables the design of ultra narrow spectral photoresponse

No ITO needed: More efficient device

Embedding Plasmonic Nanostructure Diodes Enhances Hot Electron Emission, **(M. W. Knight *et al.*, Nano Lett 13(2013)1687)**



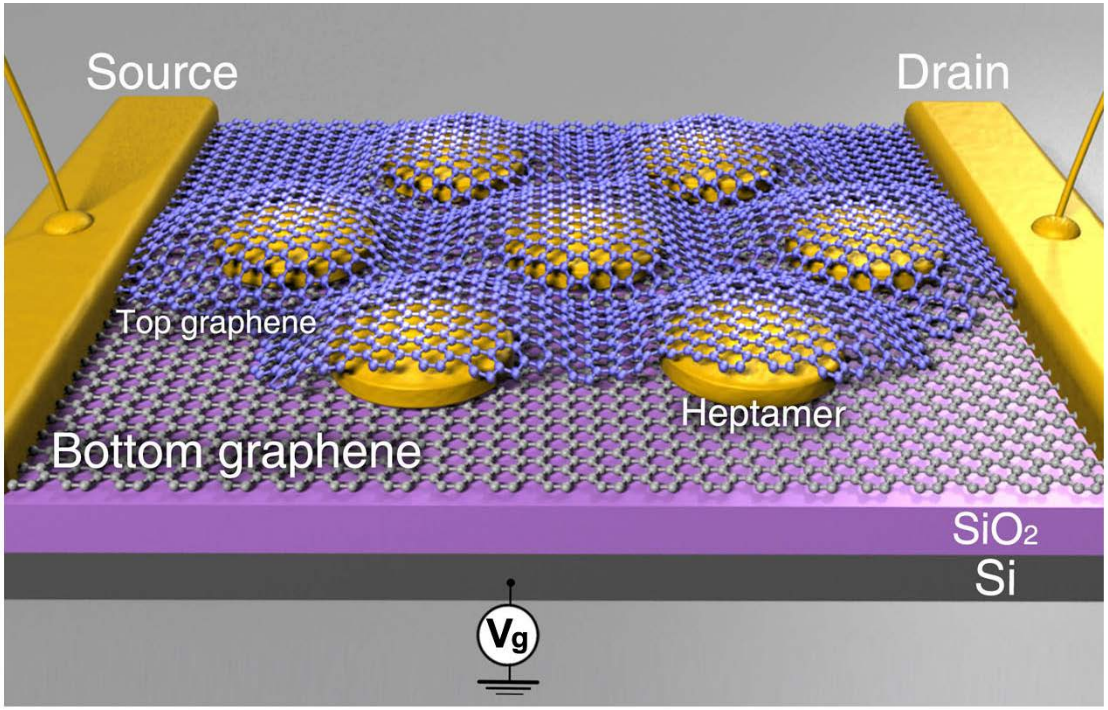


Embedding gold antenna in Si increases the quantum yield 25 times

HEs are emitted in the polarization direction!

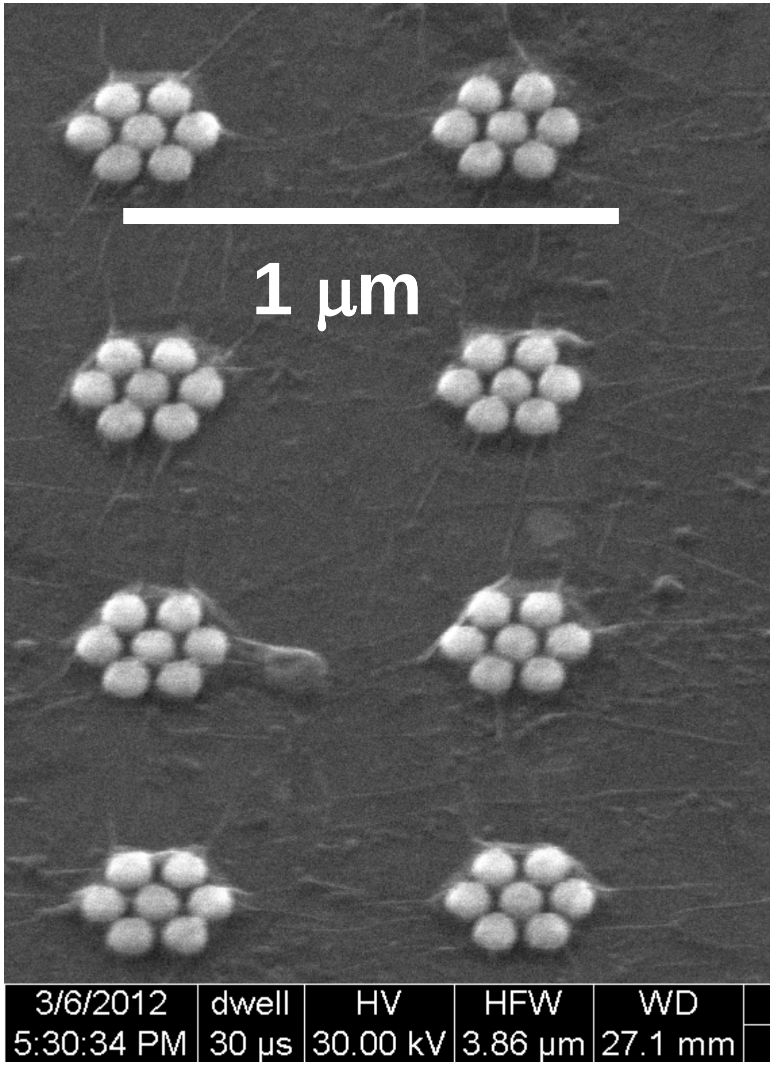
A Graphene-Antenna Sandwich Photodetector

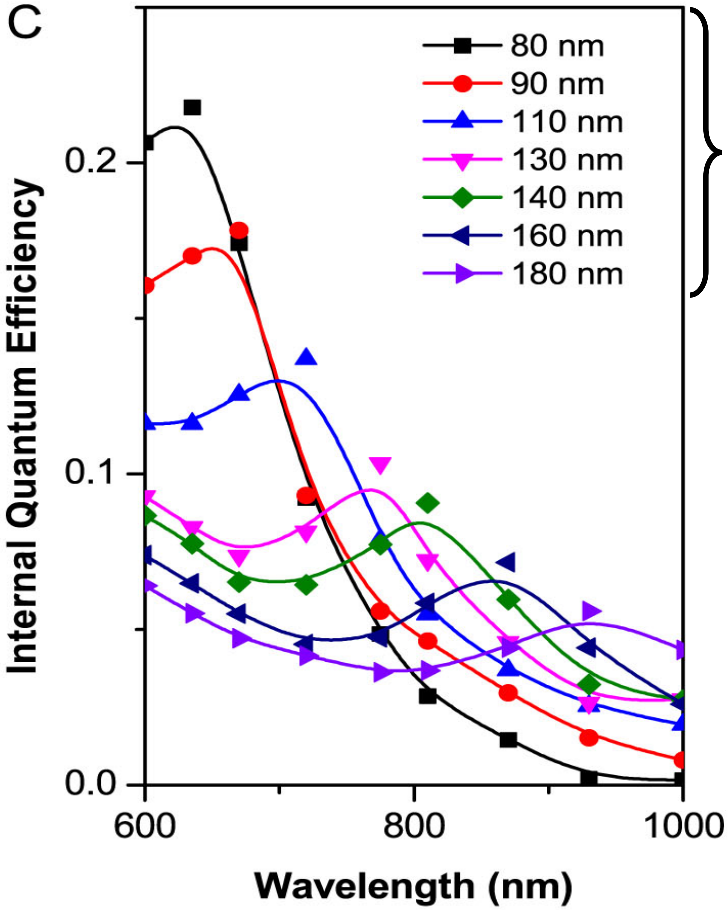
(Z.Y. Fang *et al.*, NL 12(2012)3808)



- **Efficient HE production at the heptamer Fano resonance**
- **Efficient HE collection because “wrapping”**
- **High tunability**

Primarily a hot e^- device:



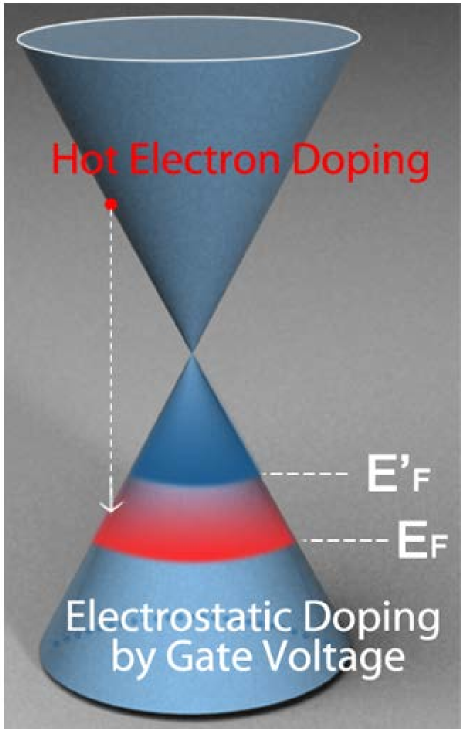


Disk Radii

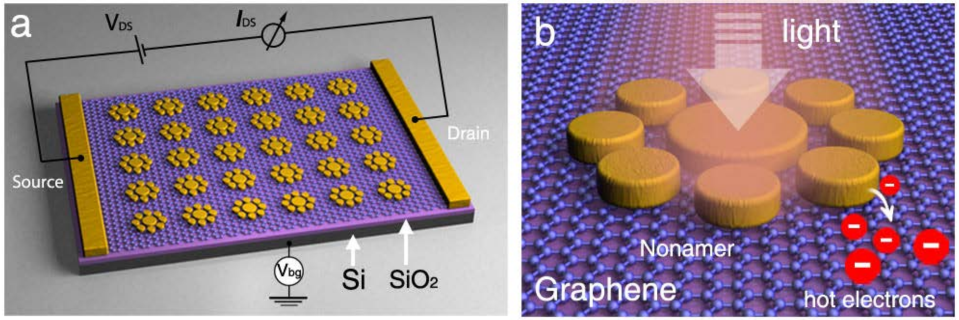
IQE is 22% at 600nm. Photovoltaic applications

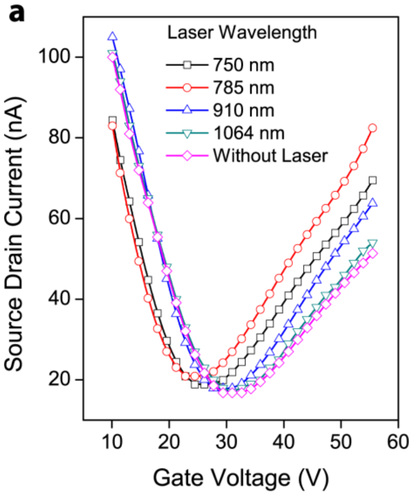
Hot electron doping of graphene

(Z.Y. Fang *et al.*, ACS Nano 6(2012)10222)

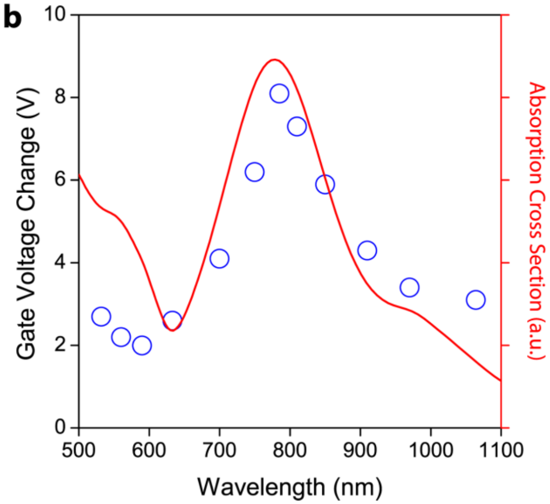


Conventional electrostatic doping





Dirac point changes with illumination



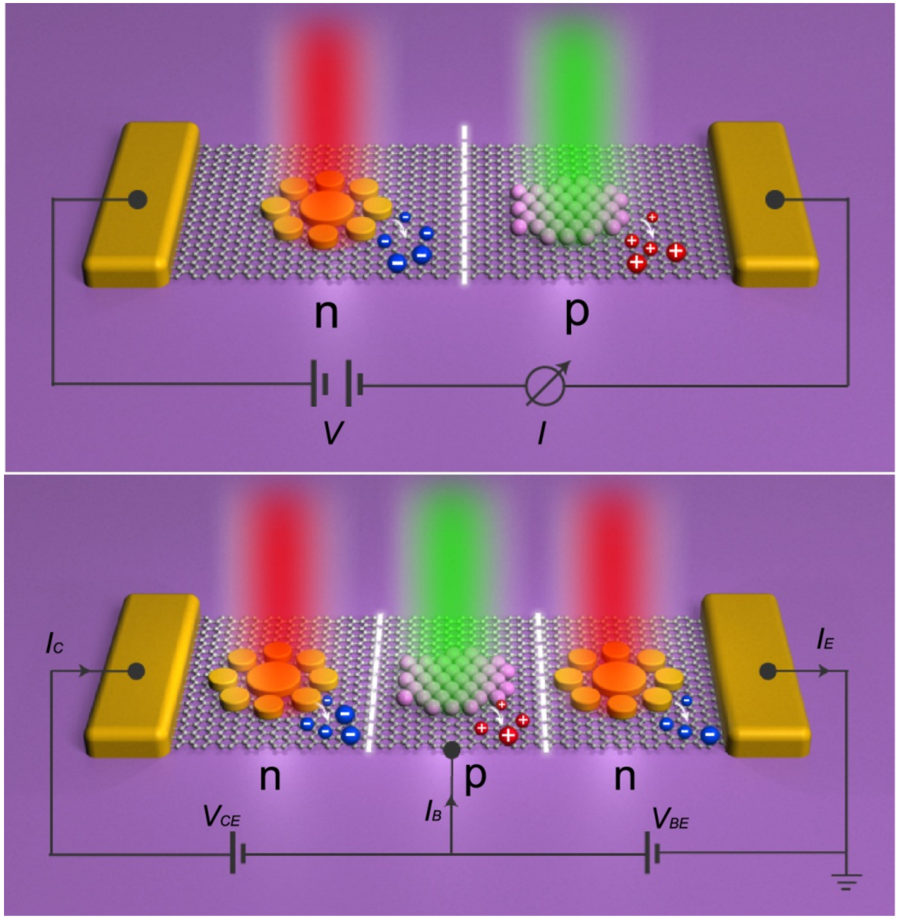
Doping proportional to absorption.

Large effect !

Plasmon induced doping equivalent to 10V gate voltage

Optically Induced Electronics

(Z.Y. Fang *et al*., ACS Nano 6(2012)10222)



Plasmons: n-doping

QDs: p-doping

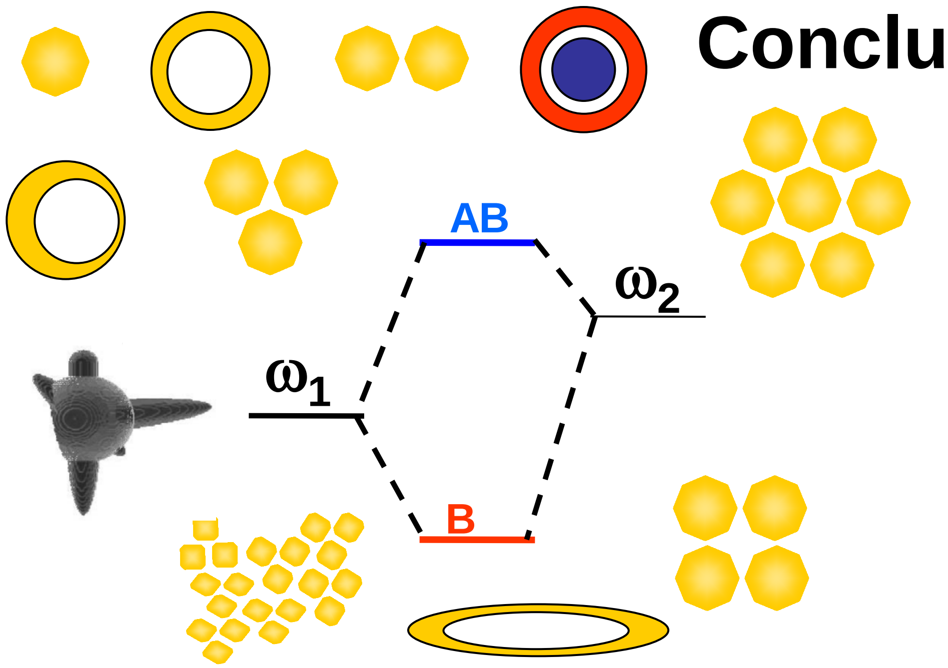
(G. Konstantatos *et al*., Nat. Nano. 7(2012)363)

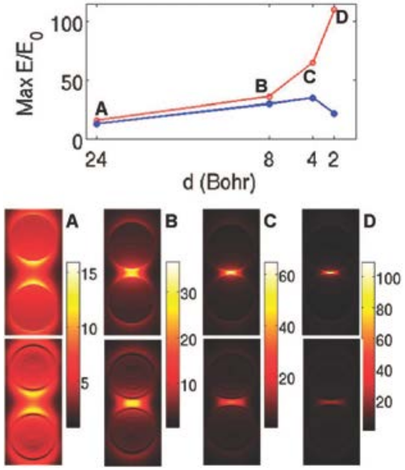
Electronic function only when ''right '' light is incident!

Tunable effect:

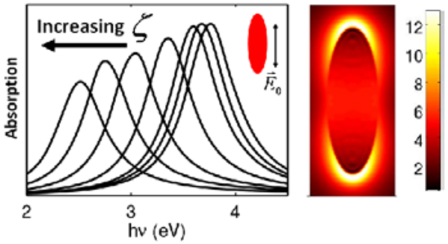
Wavelength, polarization incidence angle, …….

Conclusions

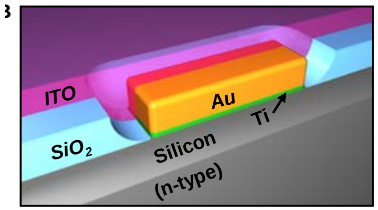


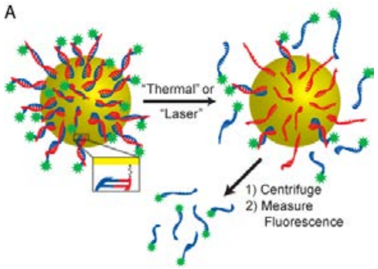


QM effects reduce field enhancements in narrow NP junctions and for NR



Plasmon-induced hot electron processes





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http://nordlander.rice.edu

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Further reading

nature materials

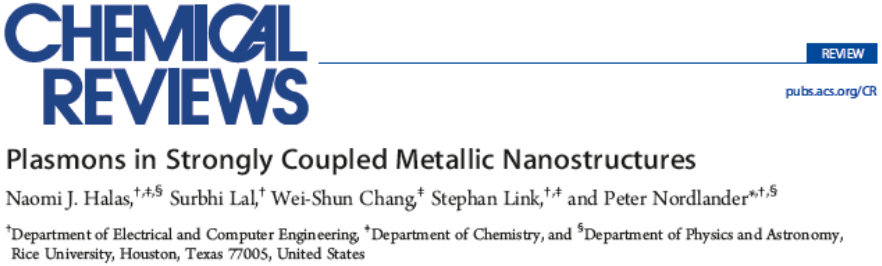
REVIEW ARTICLE

PUBLISHED ONLINE: 23 AUGUST 2010 | DOI: 10.1038/NMAT2810

The Fano resonance in plasmonic nanostructures and metamaterials

Boris Luk'yanchuk[1], Nikolay I. Zheludev[2], Stefan A. Maier[3], Naomi J. Halas[4], Peter Nordlander[5]*, Harald Giessen[6] and Chong Tow Chong[1,7]

Nature Mat., 9(2010)707



CHEMICAL REVIEWS

REVIEW

pubs.acs.org/CR

Plasmons in Strongly Coupled Metallic Nanostructures

Naomi J. Halas,[†,‡,§] Surbhi Lal,[†] Wei-Shun Chang,[‡] Stephan Link,[†,‡] and Peter Nordlander*[,†,§]

[†]Department of Electrical and Computer Engineering, [‡]Department of Chemistry, and [§]Department of Physics and Astronomy, Rice University, Houston, Texas 77005, United States

Chem. Rev., 111(2011)3913

Materials Views

www.MaterialsViews.com

ADVANCED MATERIALS

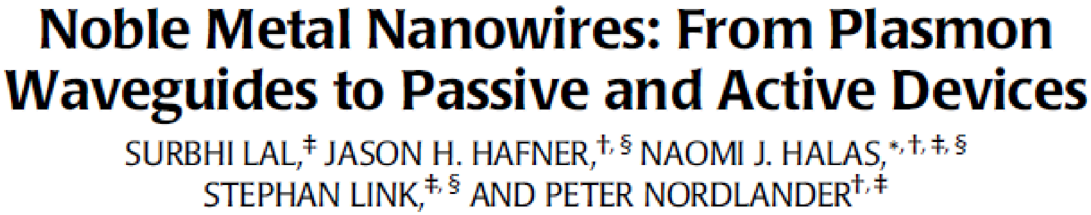
www.advmat.de

REVIEW

A Plethora of Plasmonics from the Laboratory for Nanophotonics at Rice University

Naomi J. Halas, Surbhi Lal, Stephan Link, Wei-Shun Chang, Douglas Natelson, Jason H. Hafner, and Peter Nordlander*

Adv. Mat., 24(2012)4842



Noble Metal Nanowires: From Plasmon Waveguides to Passive and Active Devices

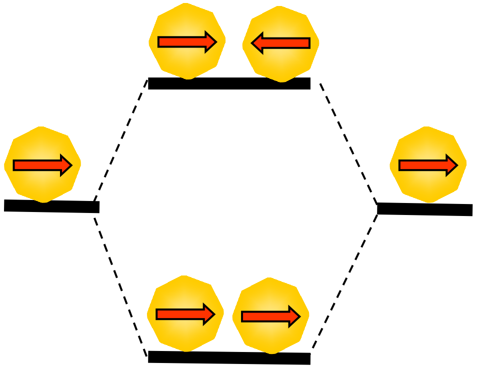
SURBHI LAL,[‡] JASON H. HAFNER,[†,§] NAOMI J. HALAS,[*,†,‡,§] STEPHAN LINK,[‡,§] AND PETER NORDLANDER[†,‡]

Acc. Chem. Res, 45(2012)1887

Dark and bright modes:

Homodimer

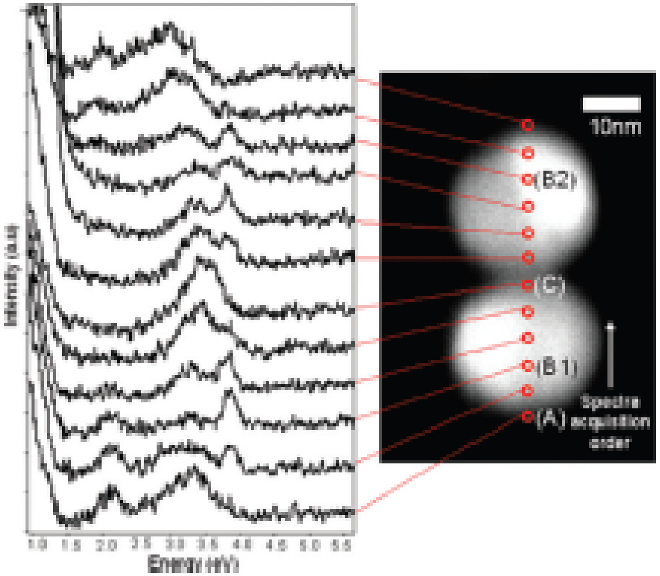
“antibonding”
Dark



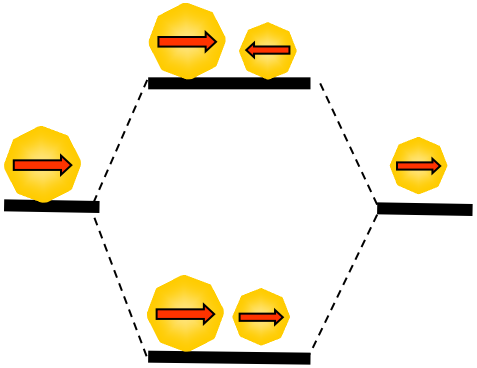
“bonding” Bright

AB mode cannot be excited with light but can be observed in EELS

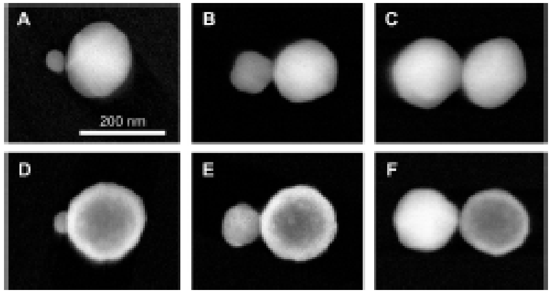
A.L. Koh *et al.*,
ACS Nano 3(2009)3015

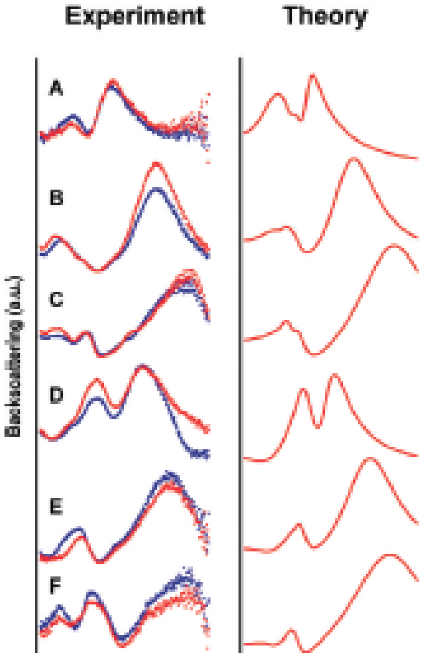


Heterodimer



Both B and AB can be excited by light.





L.V. Brown *et al.*,
ACS Nano 4(2010) 819)