New Trends in Computational Plasmonics

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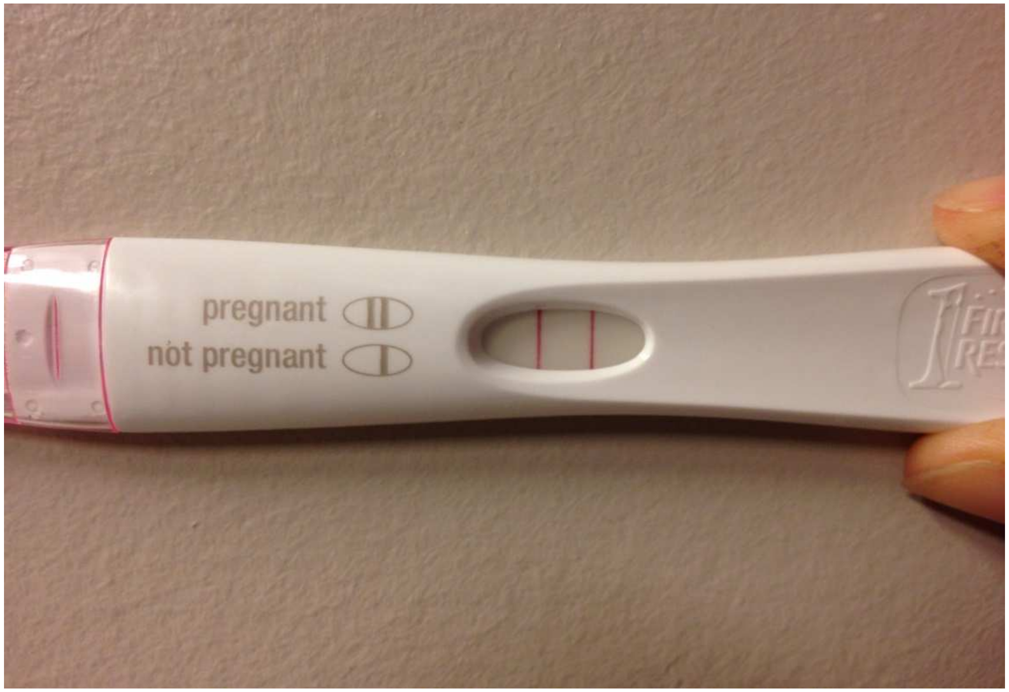
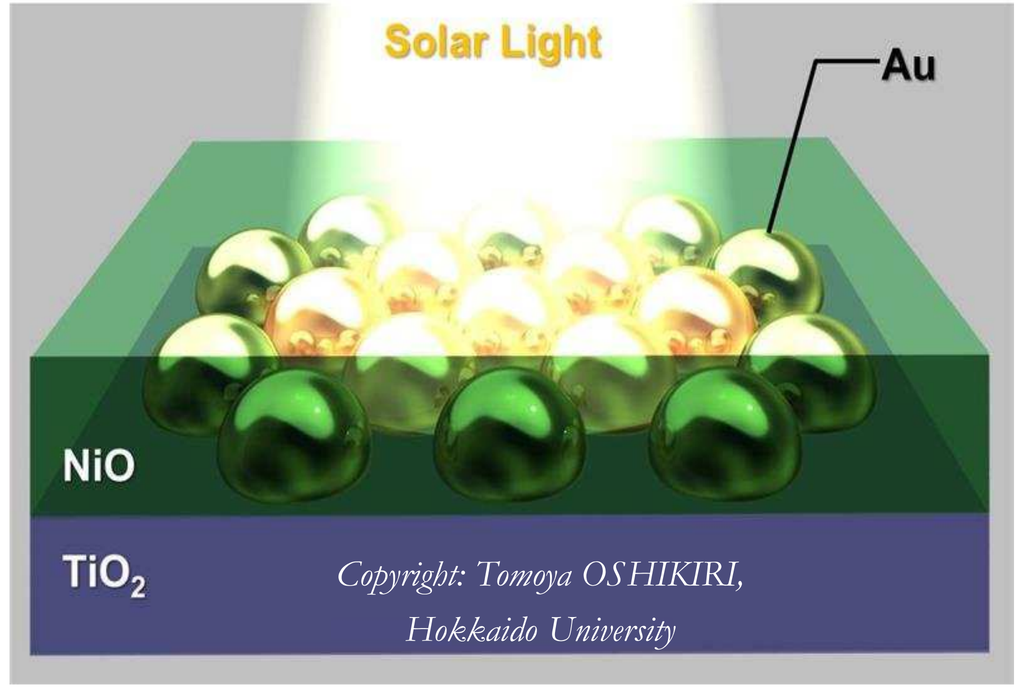
TNT2017 Conference - Trends in Nanotechnology, Dresden, June 7th 2017

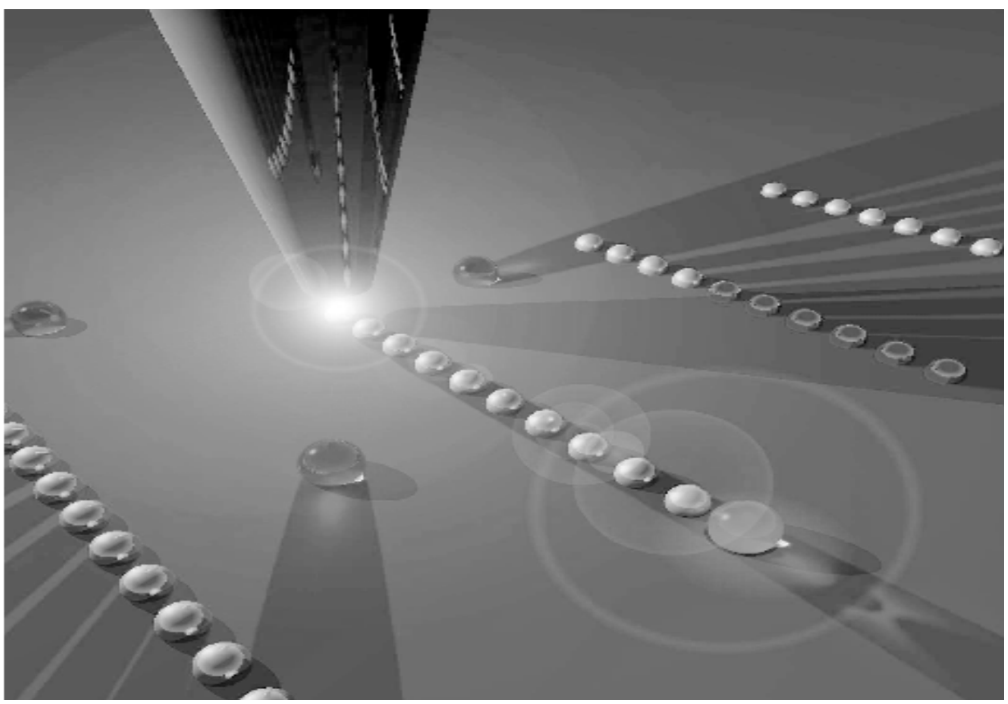
… the Romans Were Nanotechnology Pioneers

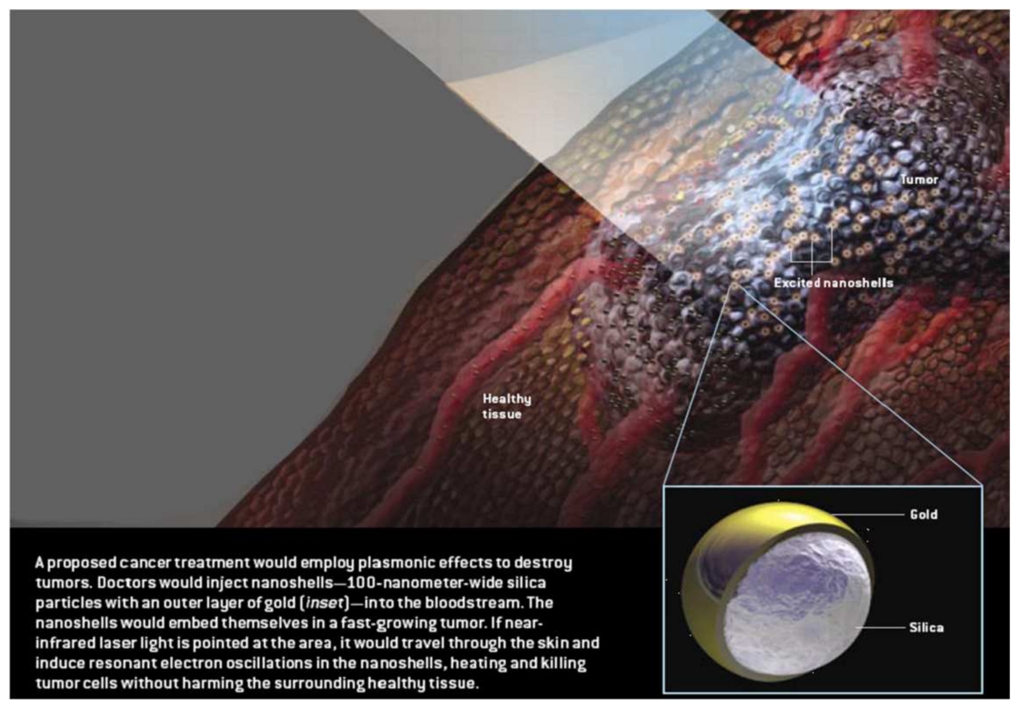
Lycurgus Cup, 4th century A. D.
(*British Museum*)

Nowadays Applications of Metal Nanoparticles (MNPs)





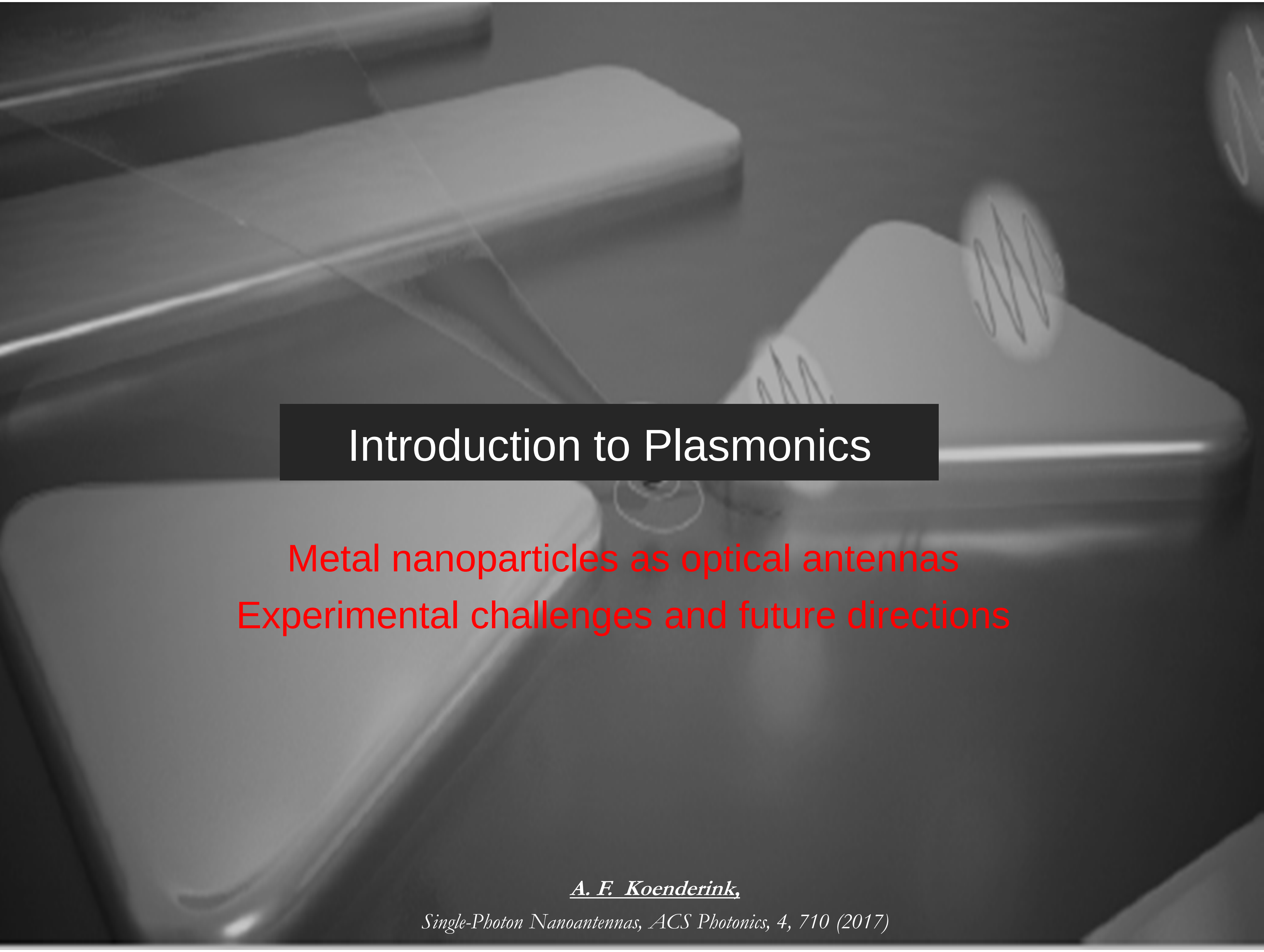




Outline

J. Fan, L. Sun,
Plasmonic nanostructures fabricated with templated self assembly

- Introduction to Plasmonics
  - Metal nanoparticles as optical antennas
  - Experimental challenges and future directions
- LSPs within the **Classical** Description
  - Strong coupling analysis example (DDA)
  - Plasmon blockade in the classical picture (BEM)
- LSPs in the **Semi-Classical** framework
  - TF-Hydrodynamic Models
  - Towards a Quantum Hydrodynamic Theory
- LSPs within the **Quantum-Mechanical** Scheme
  - Potentialities and limits of the Spherical Jellium Model
  - Advantages of Density Functional Tight Binding Method



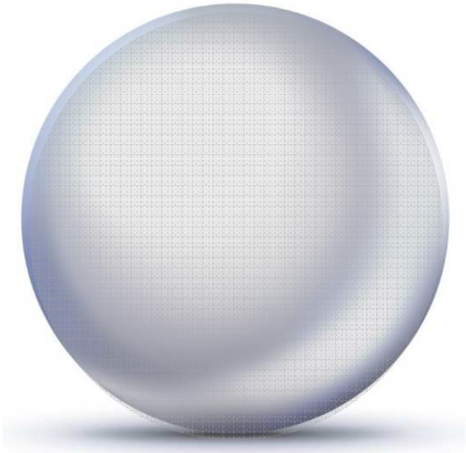
Introduction to Plasmonics

Metal nanoparticles as optical antennas
Experimental challenges and future directions

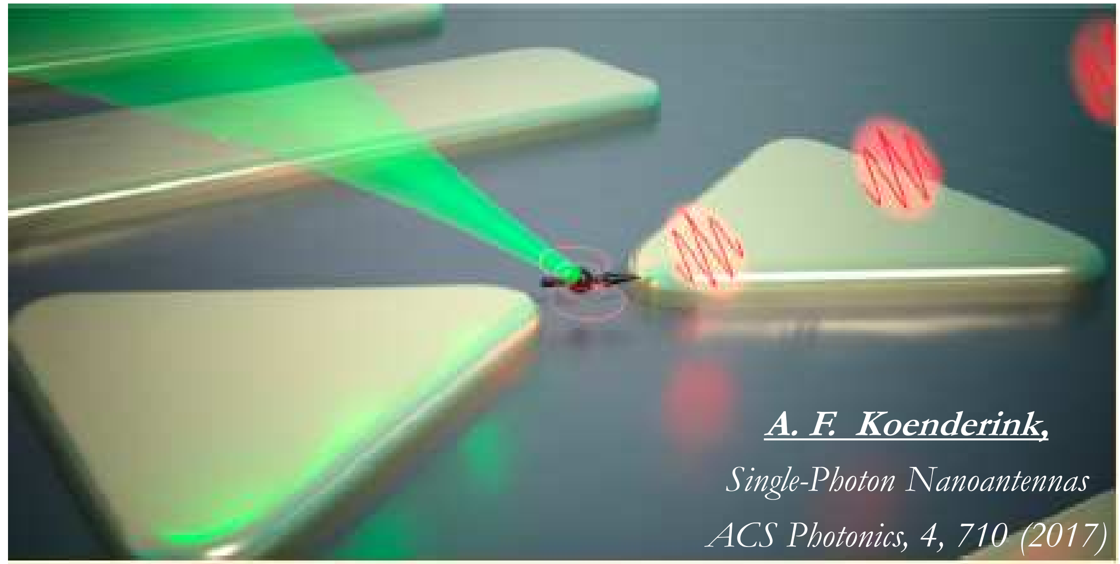
A. F. Koenderink,

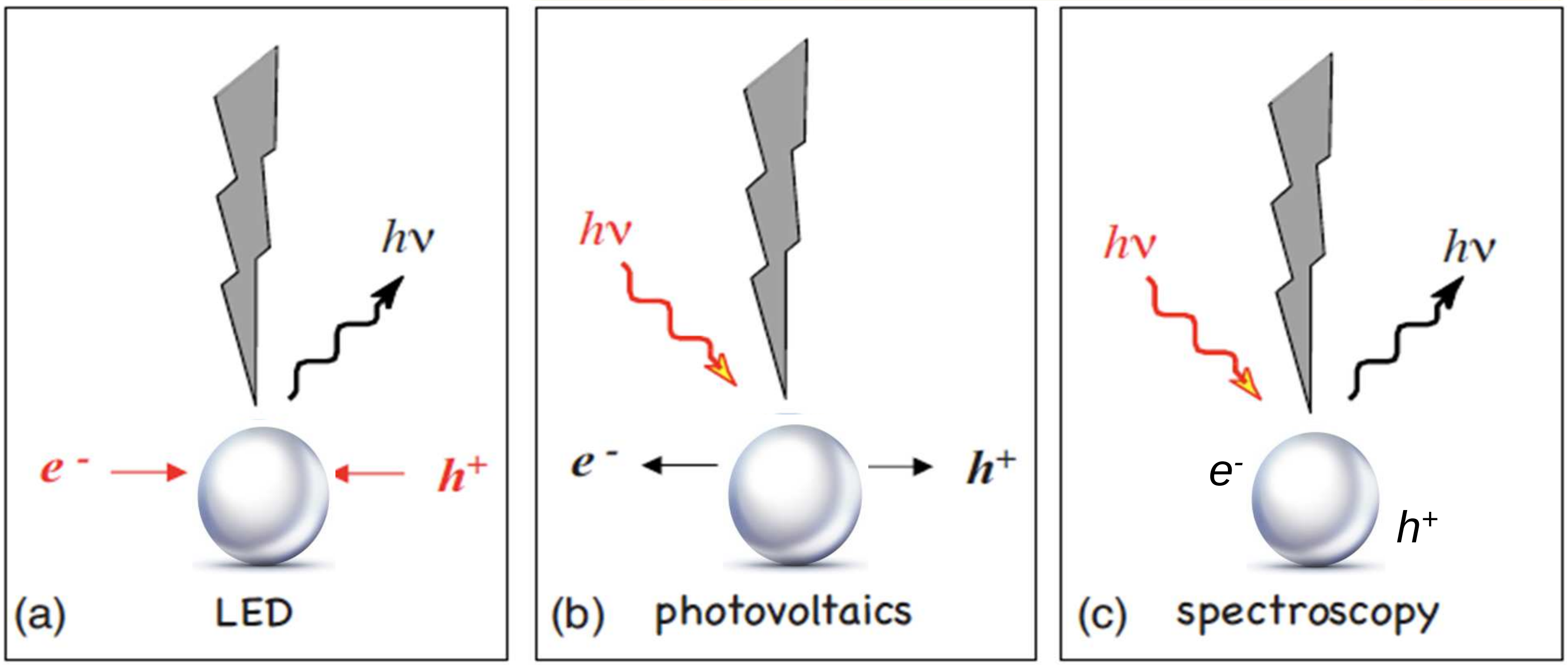
Single-Photon Nanoantennas, ACS Photonics, 4, 710 (2017)

MNPs *vs* Optical Antennas: the Physics Behind ..



$$\vec{E}(\vec{r},\omega) = \vec{E}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$





P. Bharadwaj et al., *Optical Antennas, Advances in Optics and Photonics* **1**, 438–483 (2009)

L. Novotny et al., *Antenna for light, Nature Photonics, 5, 83 (2011).*

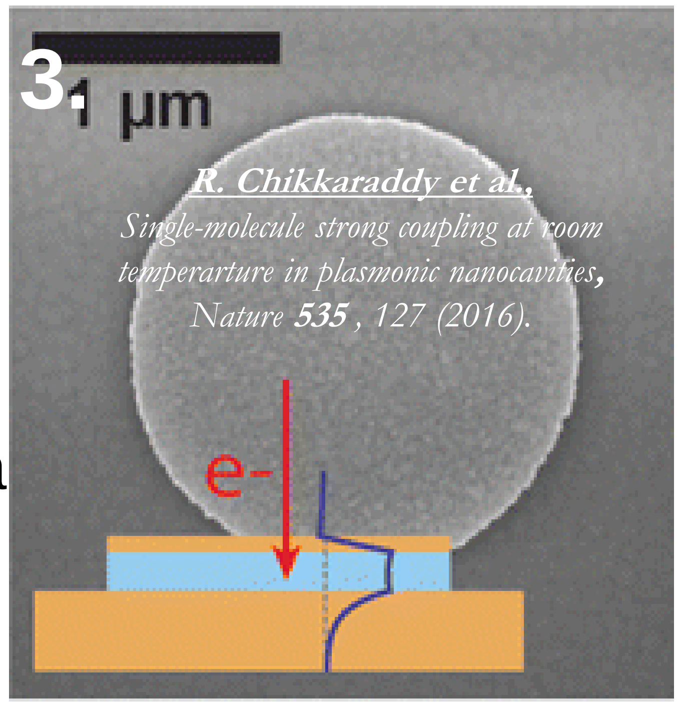
Optical Antennas Engineering and their FOM

A. Femius Koenderink, Single-Photon Nanoantennas, ACS Photonics 4, 710 (2017).

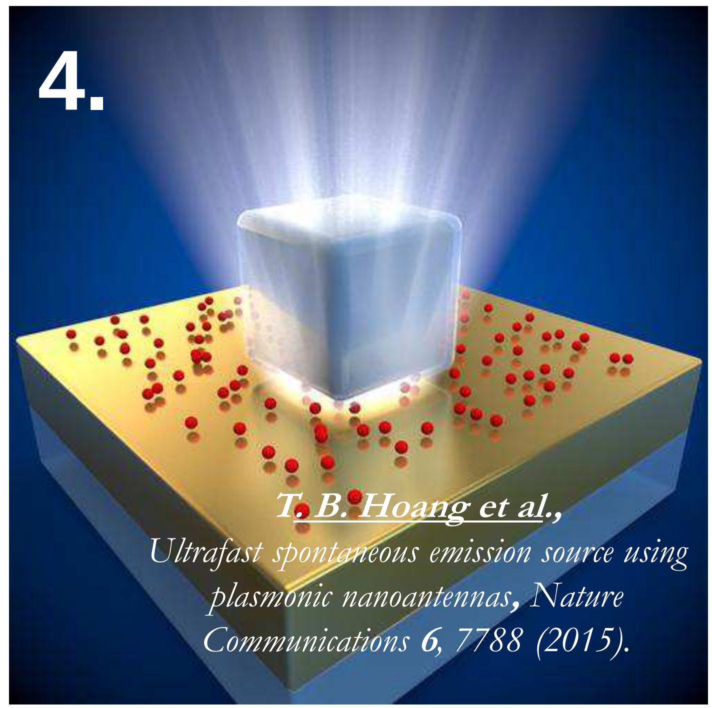
$$I\left(\vec{r},\omega_{pump},\omega_{em}\right)\propto P_{pump}\left(\vec{r},\omega_{pump}\right)\cdot\varphi\left(\vec{r},\omega_{em}\right)\cdot C_{NA}\left(\vec{r},\omega_{em}\right)$$

A. Ericson
A molecule being illuminated by two gold nanoantennas

P. Bharadwaj, B. Deutsch, L. Novotny,
Optical antennas, Adv. Opt. Photon. 1, 438 (2009).



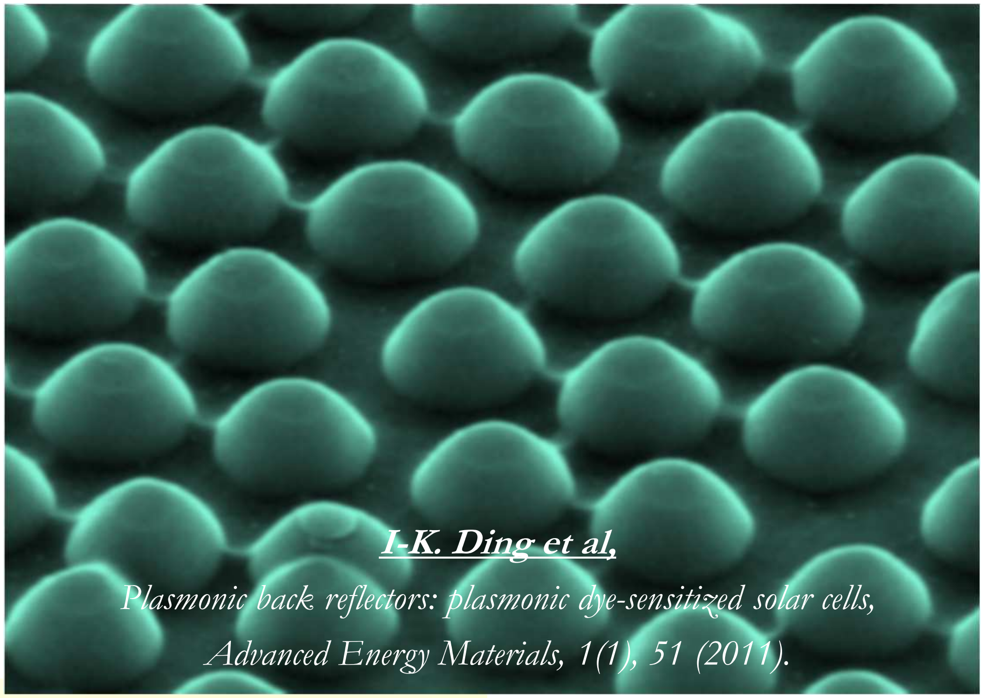
R. Chikkaraddy et al.,
Single-molecule strong coupling at room temperarture in plasmonic nanocavities, Nature **535** , 127 (2016).



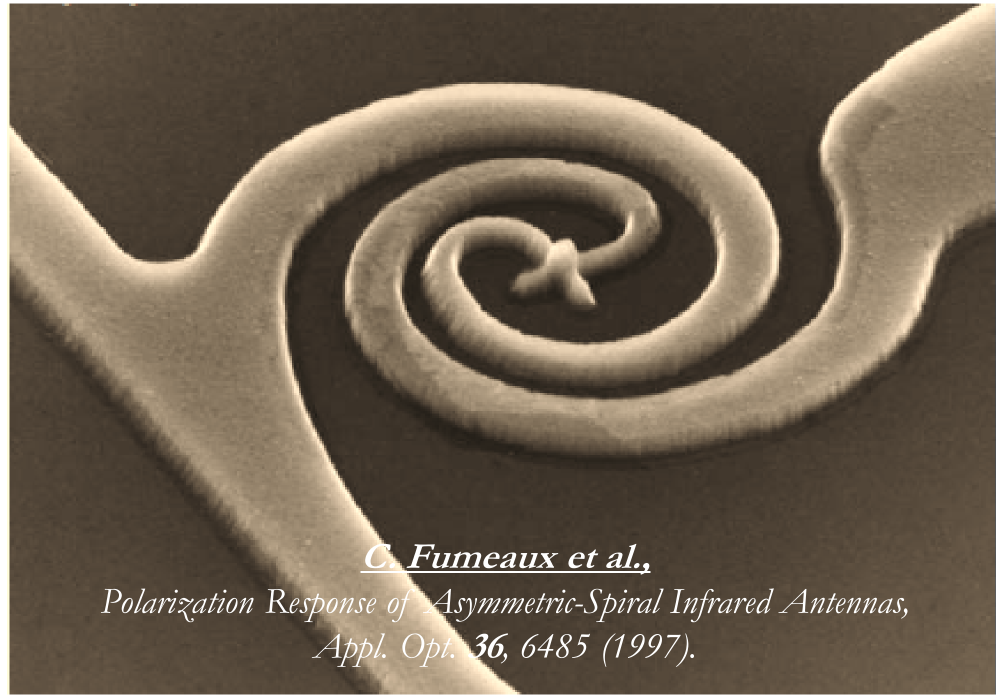
T. B. Hoang et al.,
Ultrafast spontaneous emission source using plasmonic nanoantennas, Nature Communications **6**, 7788 (2015).

1. Dipole resonator
2. Phased array
3. Patch/MIM-based
4. Nano-patch antenna

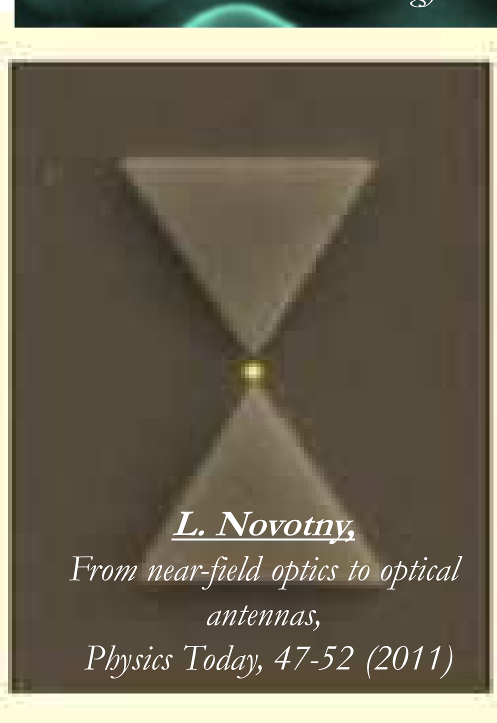
Optical Antannas Plethora: Current Challenges



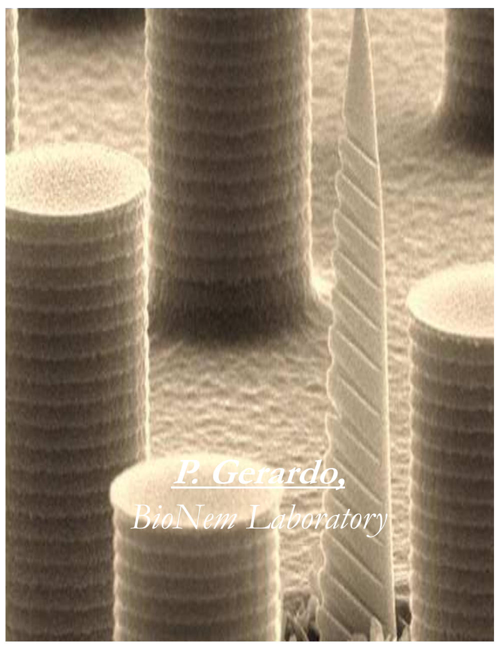
I-K. Ding et al,
Plasmonic back reflectors: plasmonic dye-sensitized solar cells,
Advanced Energy Materials, 1(1), 51 (2011).



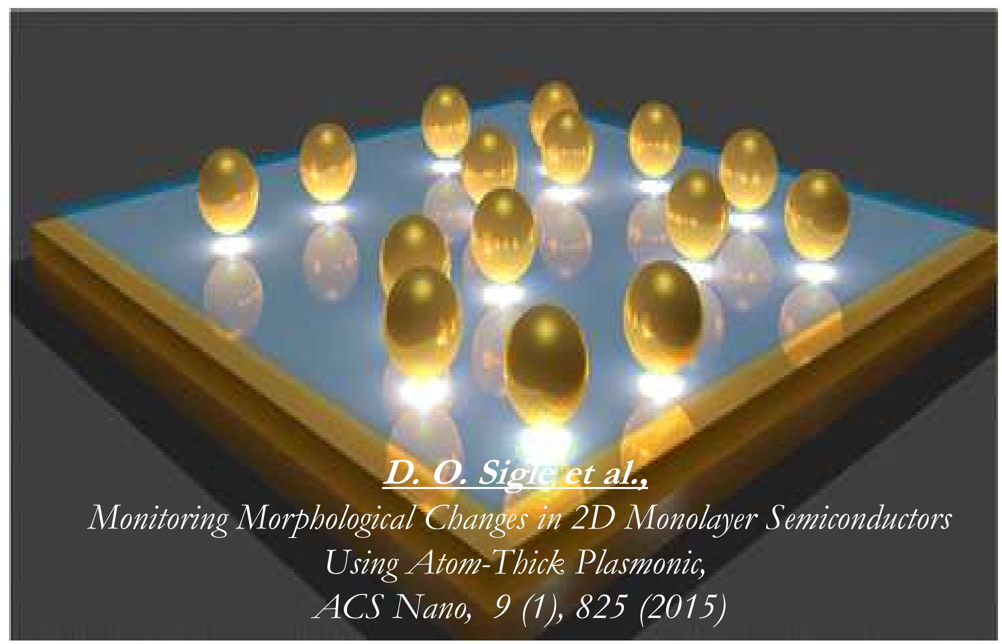
C. Fumeaux et al.,
Polarization Response of Asymmetric-Spiral Infrared Antennas,
Appl. Opt. ***36****, 6485 (1997).*



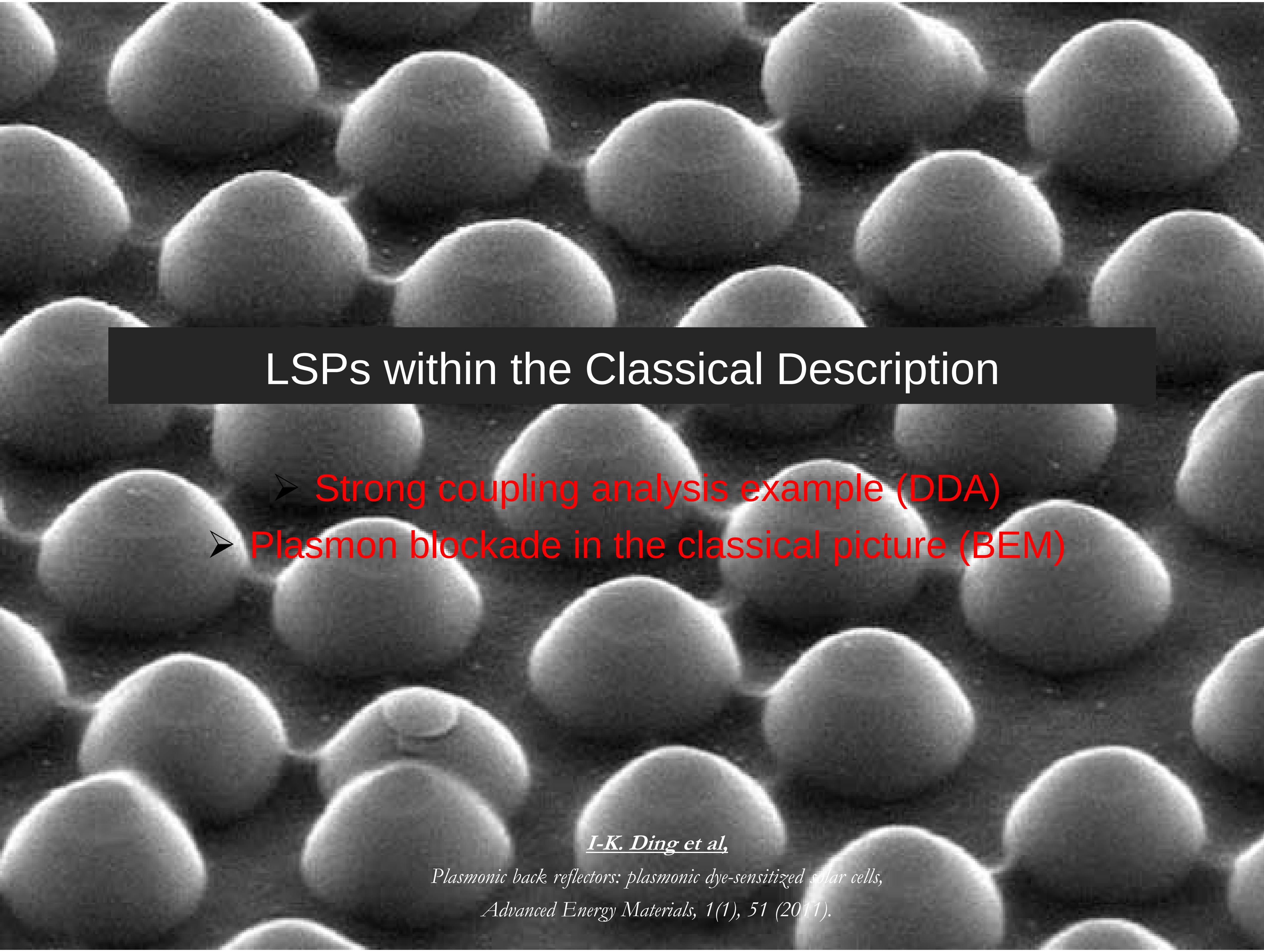
L. Novotny,
From near-field optics to optical antennas,
Physics Today, 47-52 (2011)



P. Gerardo,
BioNem Laboratory



D. O. Sigle et al.,
Monitoring Morphological Changes in 2D Monolayer Semiconductors Using Atom-Thick Plasmonic,
ACS Nano, 9 (1), 825 (2015)



LSPs within the Classical Description

- Strong coupling analysis example (DDA)
- Plasmon blockade in the classical picture (BEM)

<u>I-K. Ding et al,</u>

Plasmonic back reflectors: plasmonic dye-sensitized solar cells,

Advanced Energy Materials, 1(1), 51 (2011).

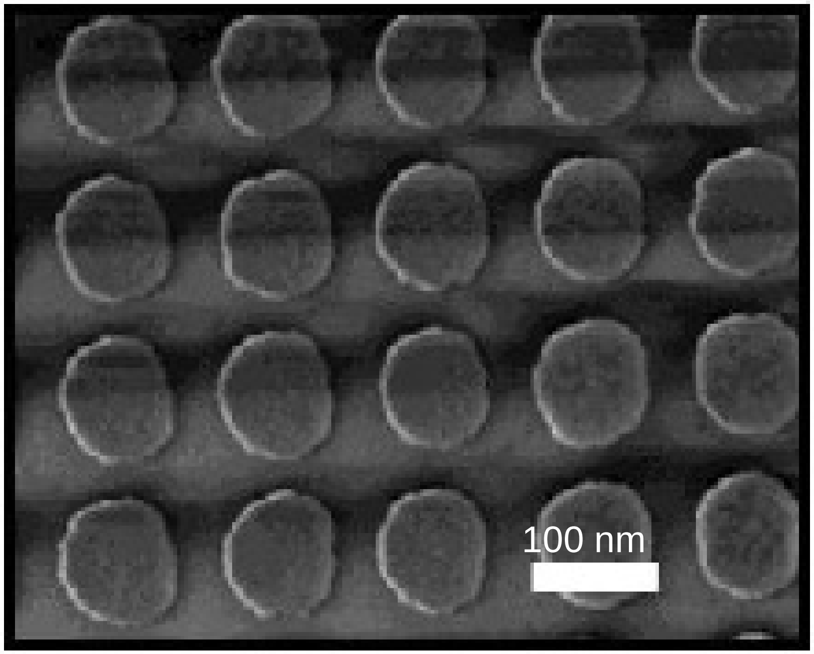
TDBC-LSPs Coupling: Effects of Oxide (DDA)

J-Aggregated cyanine dyes layer

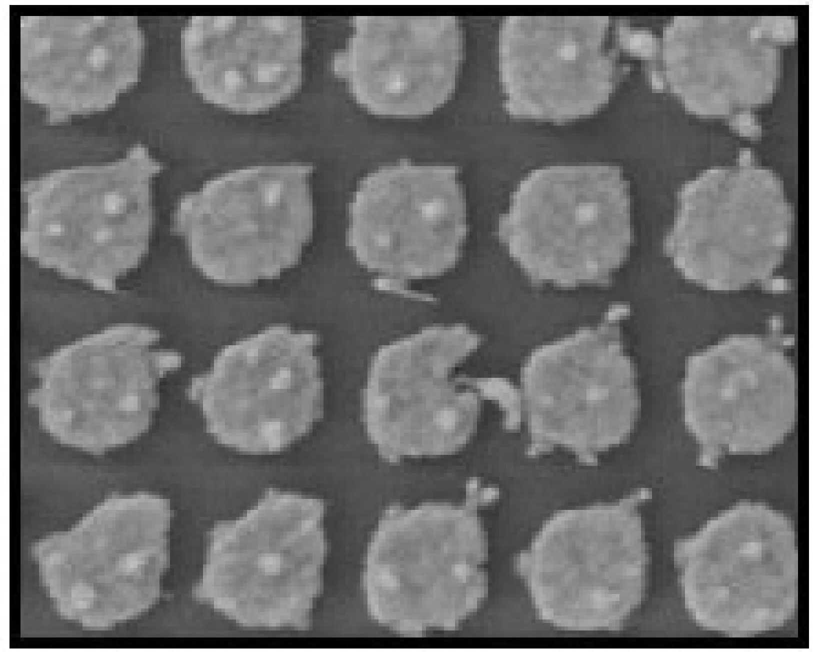
on

Ag Disks

Ag+Ag_2O Disks



SEM image (0 h)



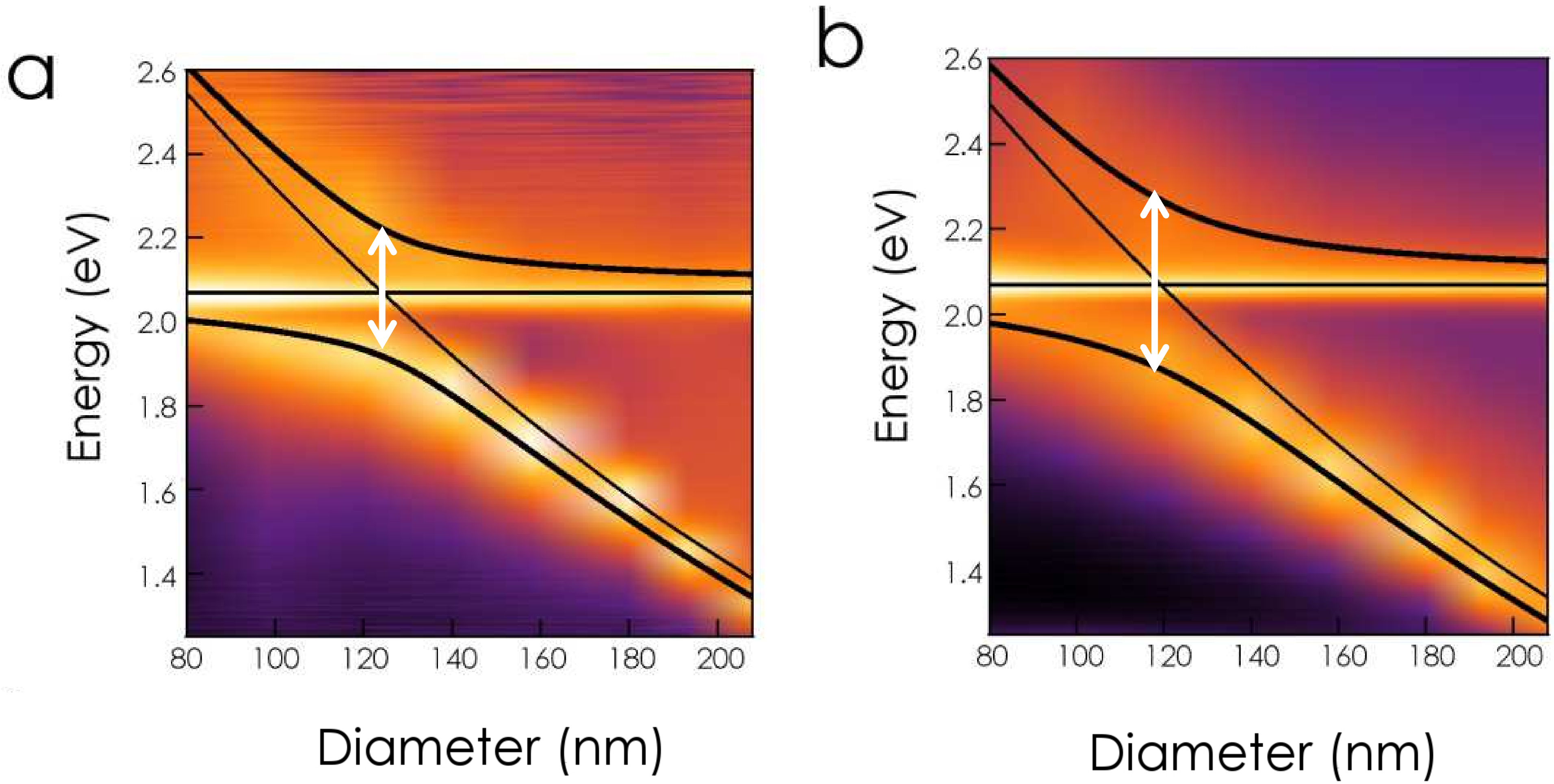
SEM image (72 h)

F. Todisco, S. D'Agostino et al. *Exciton–Plasmon Coupling Enhancement via Metal Oxidation, ACS Nano, 9 (10), 9691 (2015).*

TDBC-LSPs Coupling: Effects of Oxide (DDA)

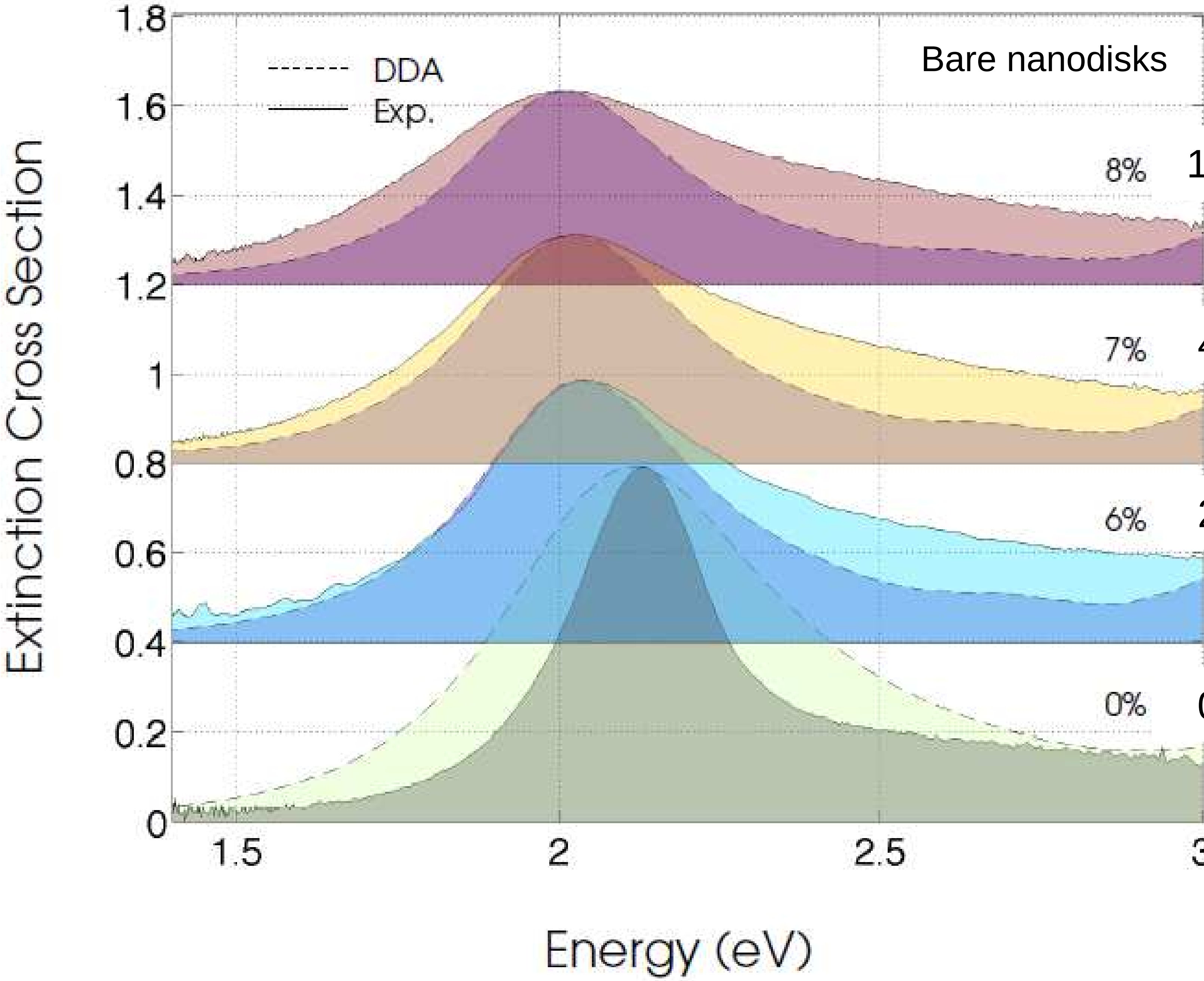
Aging Time = 0 h
g = 0.17 eV

Aging Time = 24 h
g = 0.20 eV



F. Todisco, S. D'Agostino et al. *Exciton–Plasmon Coupling Enhancement via Metal Oxidation, ACS Nano, 9 (10), 9691 (2015).*

TDBC-LSPs Coupling: Effects of Oxide (DDA)



120 h

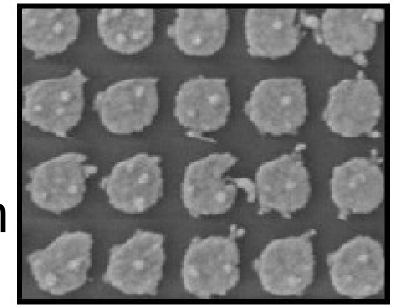
48 h

24 h

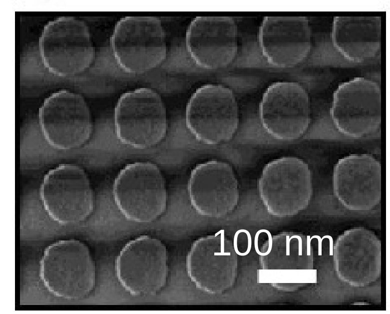
0 h

+

SEM (72 h)

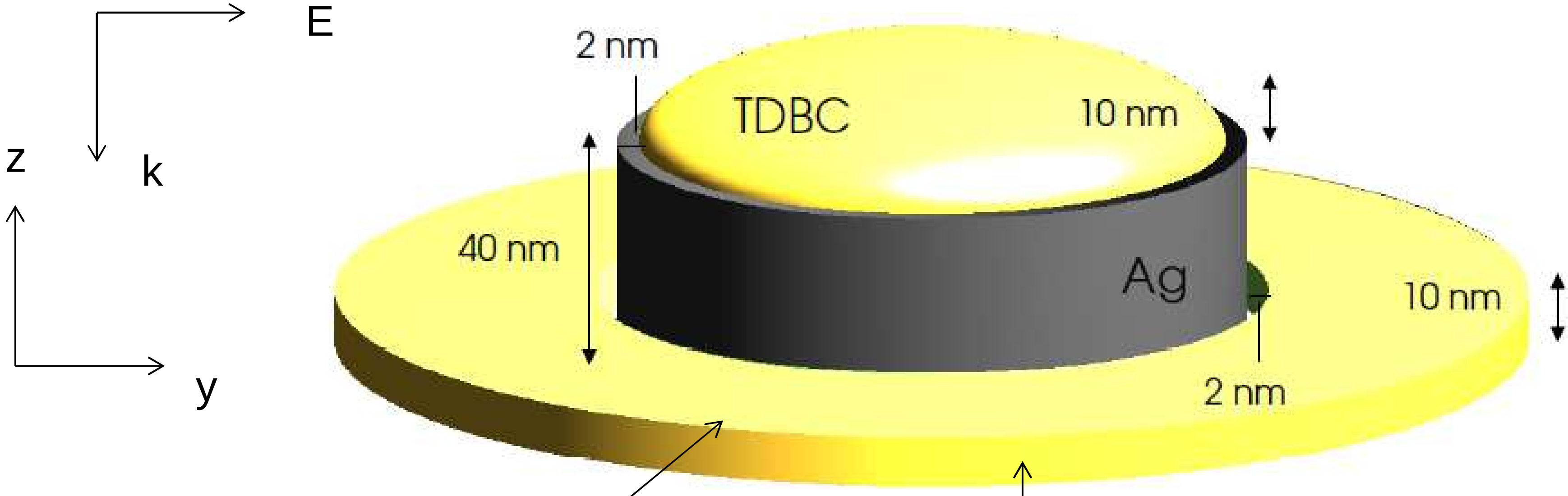


SEM (0 h)



F. Todisco, S. D'Agostino et al. *Exciton–Plasmon Coupling Enhancement via Metal Oxidation, ACS Nano, 9 (10), 9691 (2015).*

TDBC-LSPs Coupling: Effects of Oxide (DDA)



Complex dielectric function of the J-aggregated dyes

(b)

(a) Metal-oxide effective dielectric function

$$\varepsilon_{TDBC} = \varepsilon_{\infty} - f\frac{\omega^2_{exc}}{\omega^2 - \omega^2_{exc} + i\gamma_{exc}\omega}$$

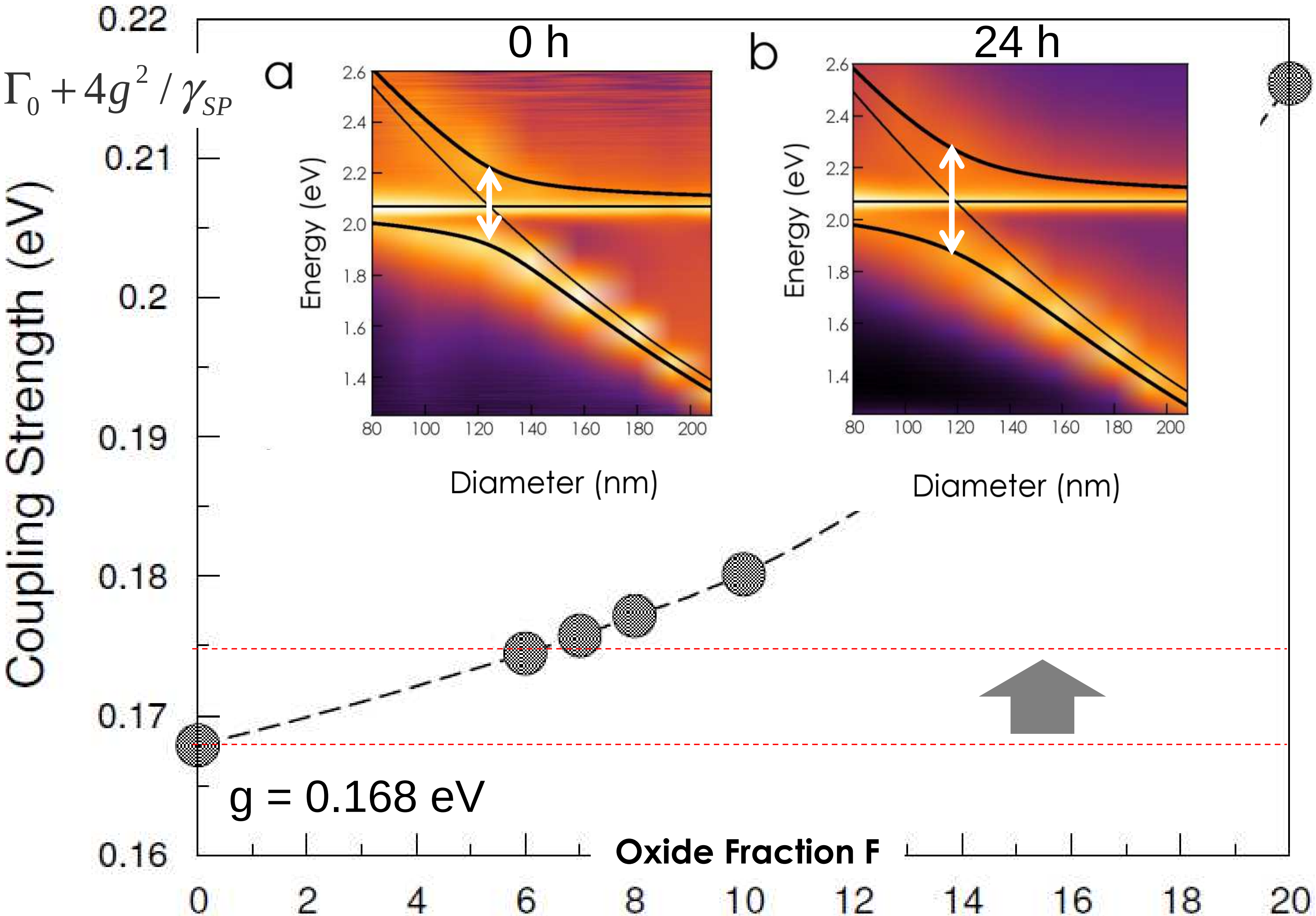
$$\varepsilon_{eff} = \varepsilon_{Ag}\frac{2F\left(\varepsilon_{Ag_2O} - \varepsilon_{Ag}\right) + \varepsilon_{Ag_2O} + 2\varepsilon_{Ag}}{2\varepsilon_{Ag} + \varepsilon_{Ag_2O} + F\left(\varepsilon_{Ag} - \varepsilon_{Ag_2O}\right)}$$

$$F = \frac{V_{Ag_2O}}{V_{Disk}}$$ Oxide volume fraction

<u>***F. Todisco, S. D'Agostino et al***</u>. *Exciton–Plasmon Coupling Enhancement via Metal Oxidation, ACS Nano, 9 (10), 9691 (2015).*

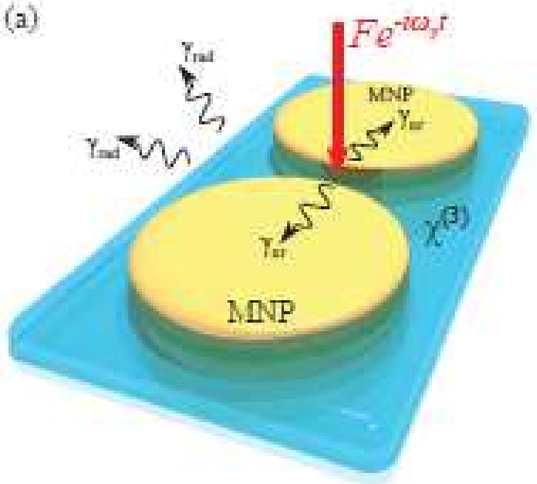
TDBC-LSPs Coupling: Effects of Oxide (DDA)

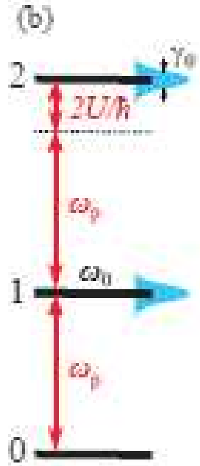
$$\Gamma = \Gamma_0 + 4g^2 / \gamma_{SP}$$



F. Todisco, S. D'Agostino et al. Exciton–Plasmon Coupling Enhancement via Metal Oxidation, ACS Nano, 9 (10), 9691 (2015).

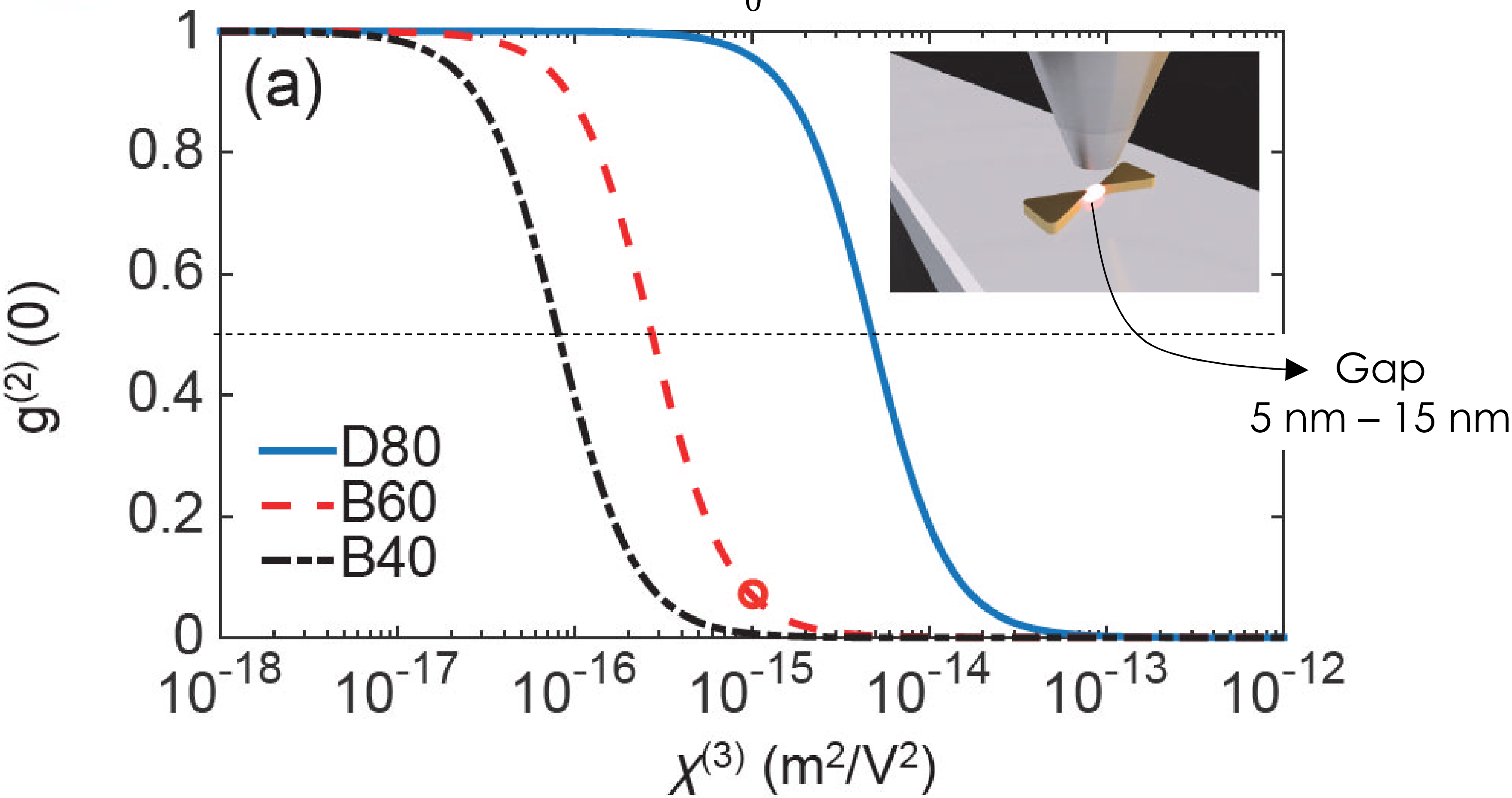
Plasmon Blockade with Au Dimers (BEM)





Nonlinear shift

$$U_{nl} = \frac{(\hbar\omega_0)^2}{\varepsilon_0}\int d\vec{r}\,\chi^{(3)}(\vec{r})\left|\xi(\vec{r})\right|^4$$

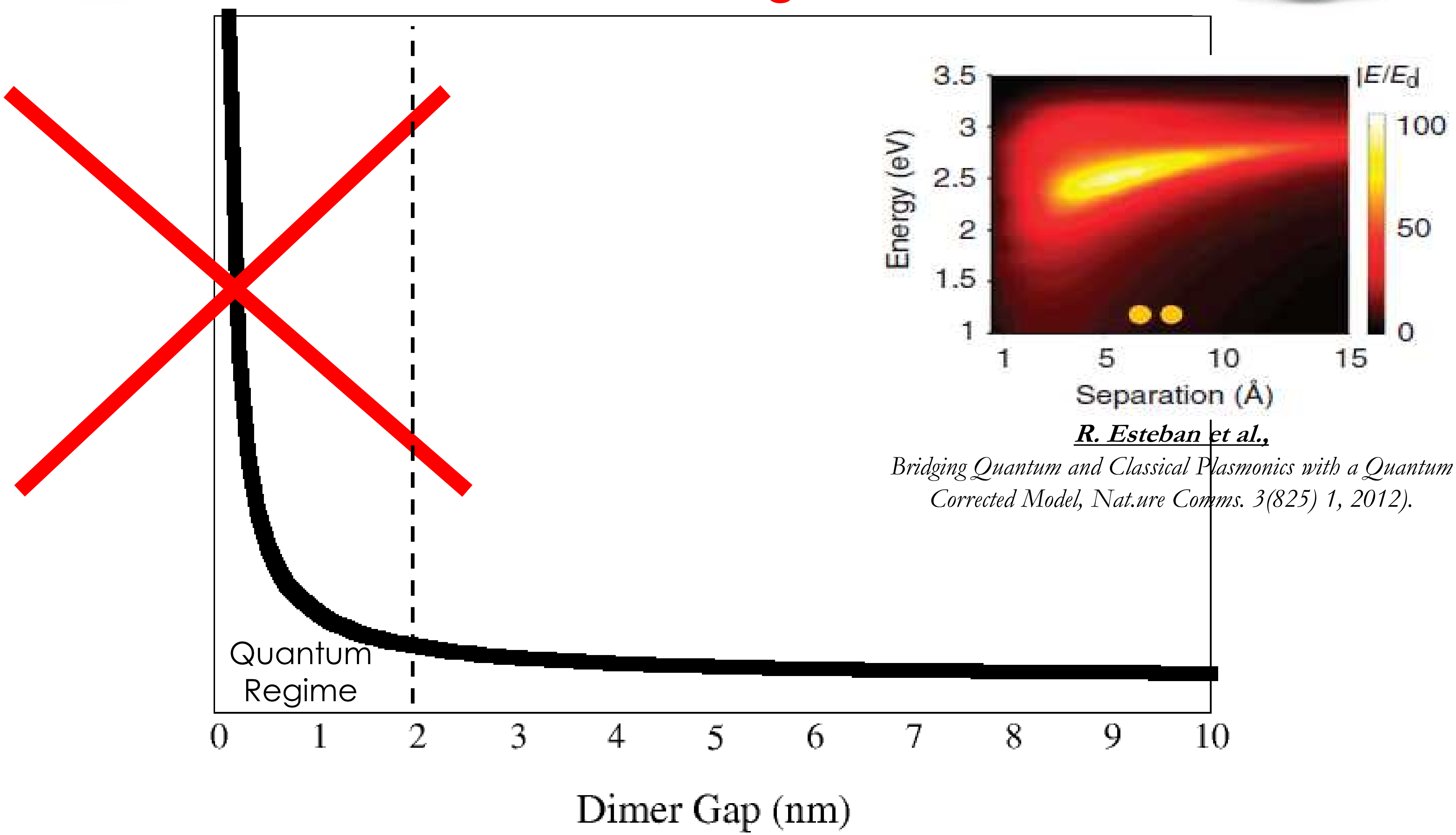


F. Alpeggiani , S. D'Agostino, D. Sanvitto and D. Gerace,

Visible Quantum Plasmonics for Metallic Nanodimers, Scientific Reports 6, 34772 (2016).

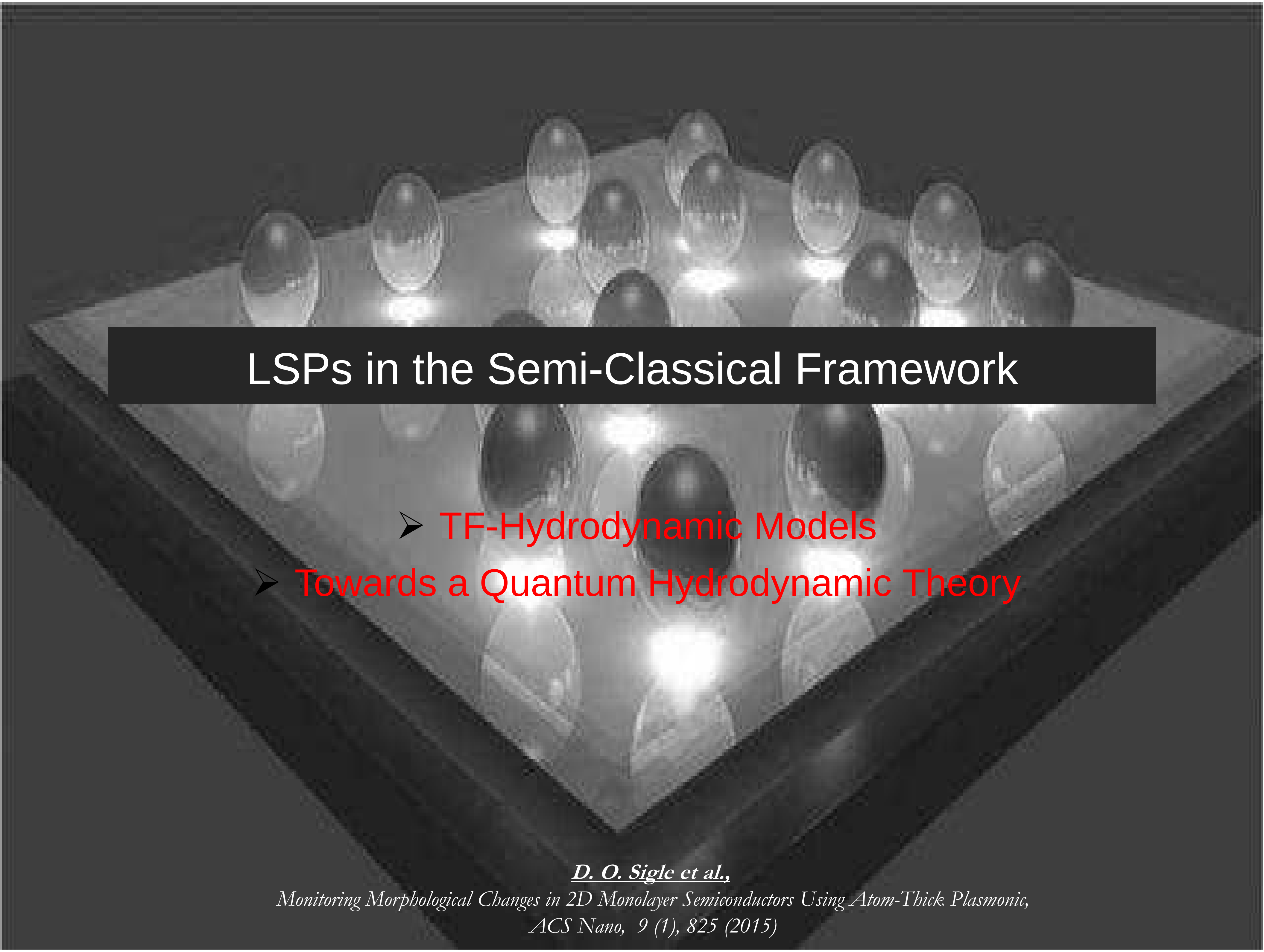
.. what about the classical field in the tunneling and contact regimes?

1/D divergence



R. Esteban et al.,

Bridging Quantum and Classical Plasmonics with a Quantum Corrected Model, Nat.ure Comms. 3(825) 1, 2012).



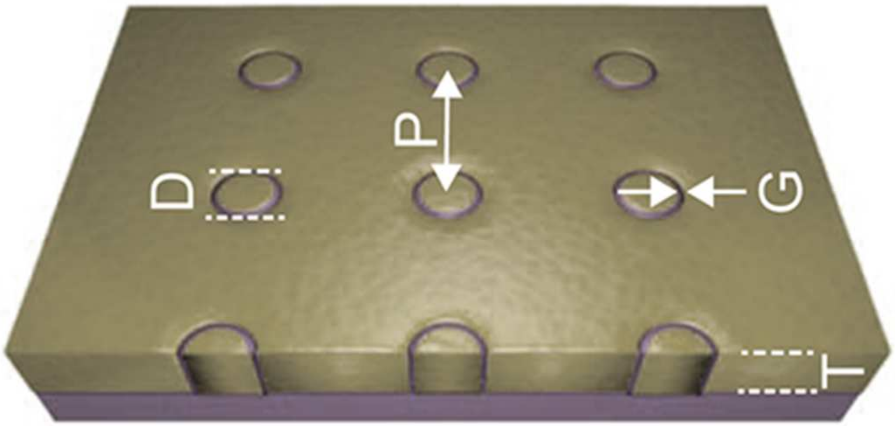
LSPs in the Semi-Classical Framework

- TF-Hydrodynamic Models
- Towards a Quantum Hydrodynamic Theory

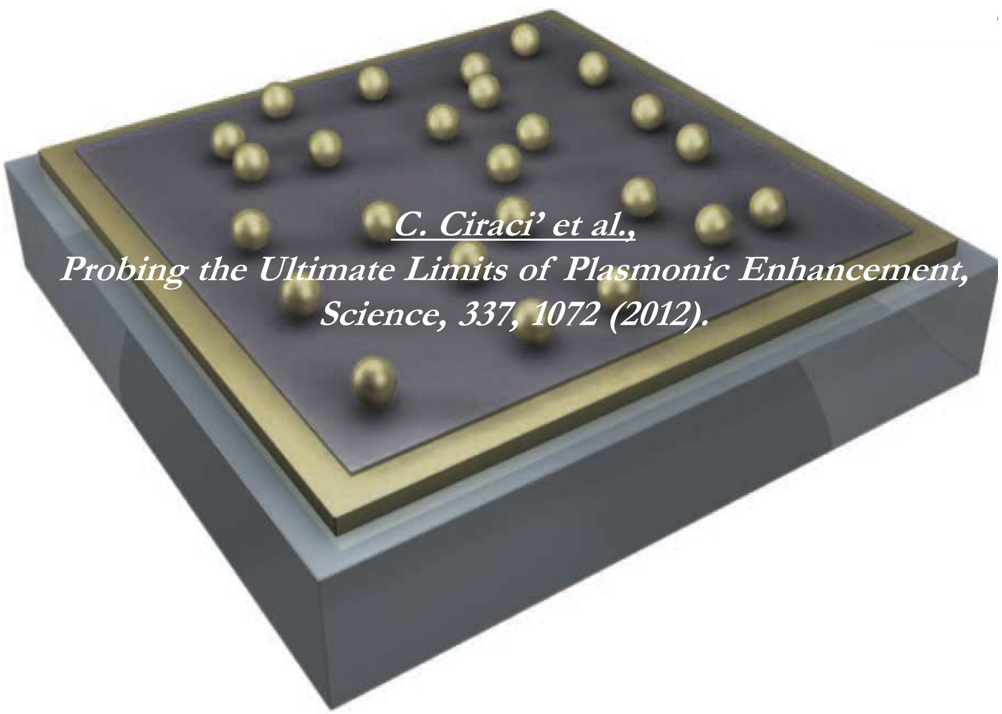
D. O. Sigle et al.,

Monitoring Morphological Changes in 2D Monolayer Semiconductors Using Atom-Thick Plasmonic,
ACS Nano, 9 (1), 825 (2015)

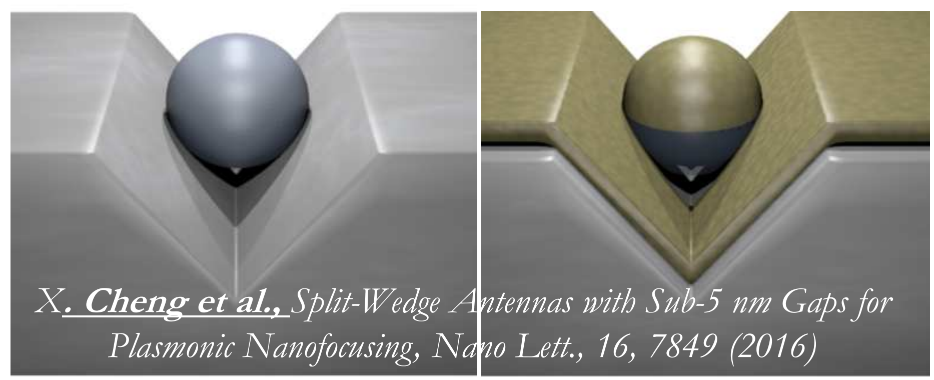
.. what about Multiscale Plasmonic Systems?



D. Yoo et al., High-Throughput Fabrication of Resonant Metamaterials With Ultrasmall Coaxial Apertures via Atomic Layer Lithography, Nano Lett. 16, 2040 (2016)



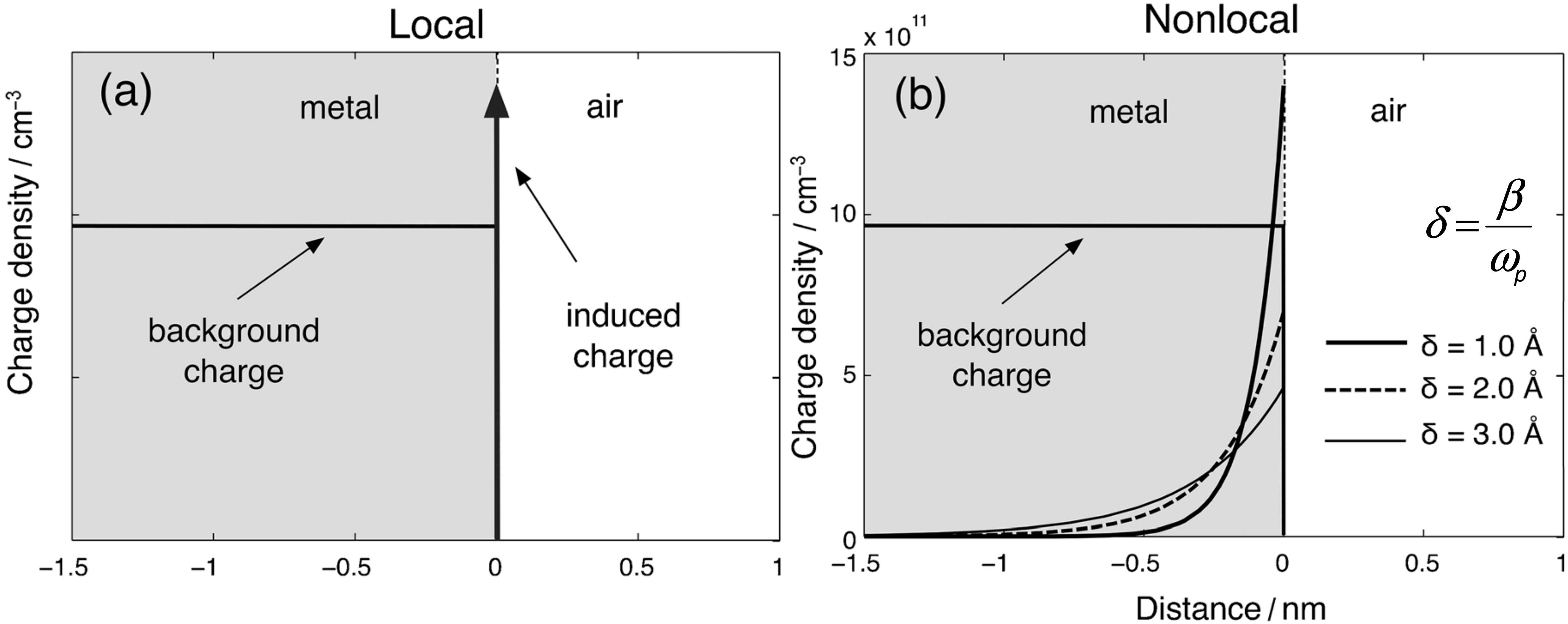
C. Ciraci' et al.,
Probing the Ultimate Limits of Plasmonic Enhancement, Science, 337, 1072 (2012).



*X. **Cheng et al.,** Split-Wedge Antennas with Sub-5 nm Gaps for Plasmonic Nanofocusing, Nano Lett., 16, 7849 (2016)*

TF-Hydrodynamic Models

C. Ciracì et al., *Hydrodynamic model for plasmonics: a macroscopic approach to a microscopic problem, Chem. Phys. Chem. 14, 1109 (2013).*



$$\varepsilon(\omega) = 1 - \frac{\omega^2{}_p}{\omega^2 + i\gamma\omega}$$

$$\varepsilon_L(\omega, k) = 1 - \frac{\omega^2{}_p}{\omega^2 + i\gamma\omega - \beta^2 k^2}$$

N. A. Mortensen et al., *A generalized non-local optical response theory for plasmonic nanostructures. Nature Communications 5, 3809 (2014).*

Generalized Nonlocal Optical Response model (GNOR)

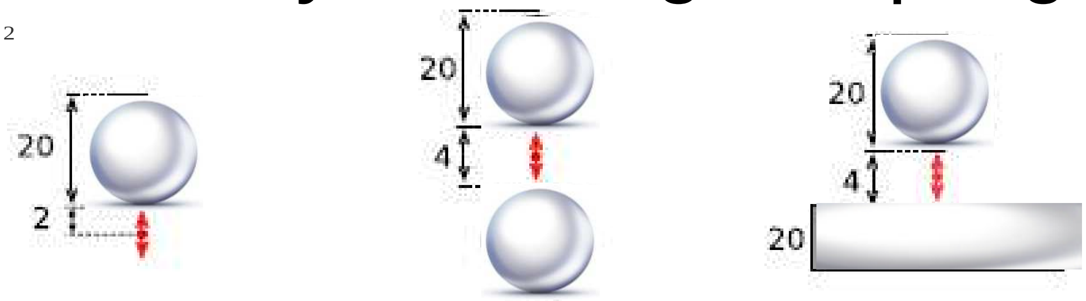
$$\beta^2 \rightarrow \xi^2 = \beta^2 + D(\gamma - i\omega) \approx \beta^2 - i\omega D$$

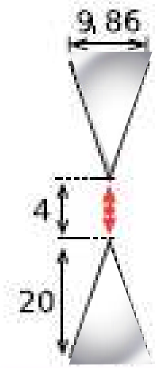
Nonlocality in Strong-Coupling

$$S(\omega)=\frac{\hbar\omega}{2\pi}q(\omega)\Gamma(\omega)S'(\omega)$$

$$S'(\omega)=\left|\frac{1}{i[\omega_0-\omega-\delta\omega(\omega)]+\frac{1}{2}\Gamma(\omega)}\right|^2$$

$$\delta\omega(\omega)=\frac{\omega^2}{\hbar\varepsilon_0 c^2}\,\tilde{p}_0\,\mathrm{Re}\left[\overline{G}_{sc}(\vec{r}_0,\vec{r}_0,\omega)\right]\cdot\tilde{p}_0$$





Local

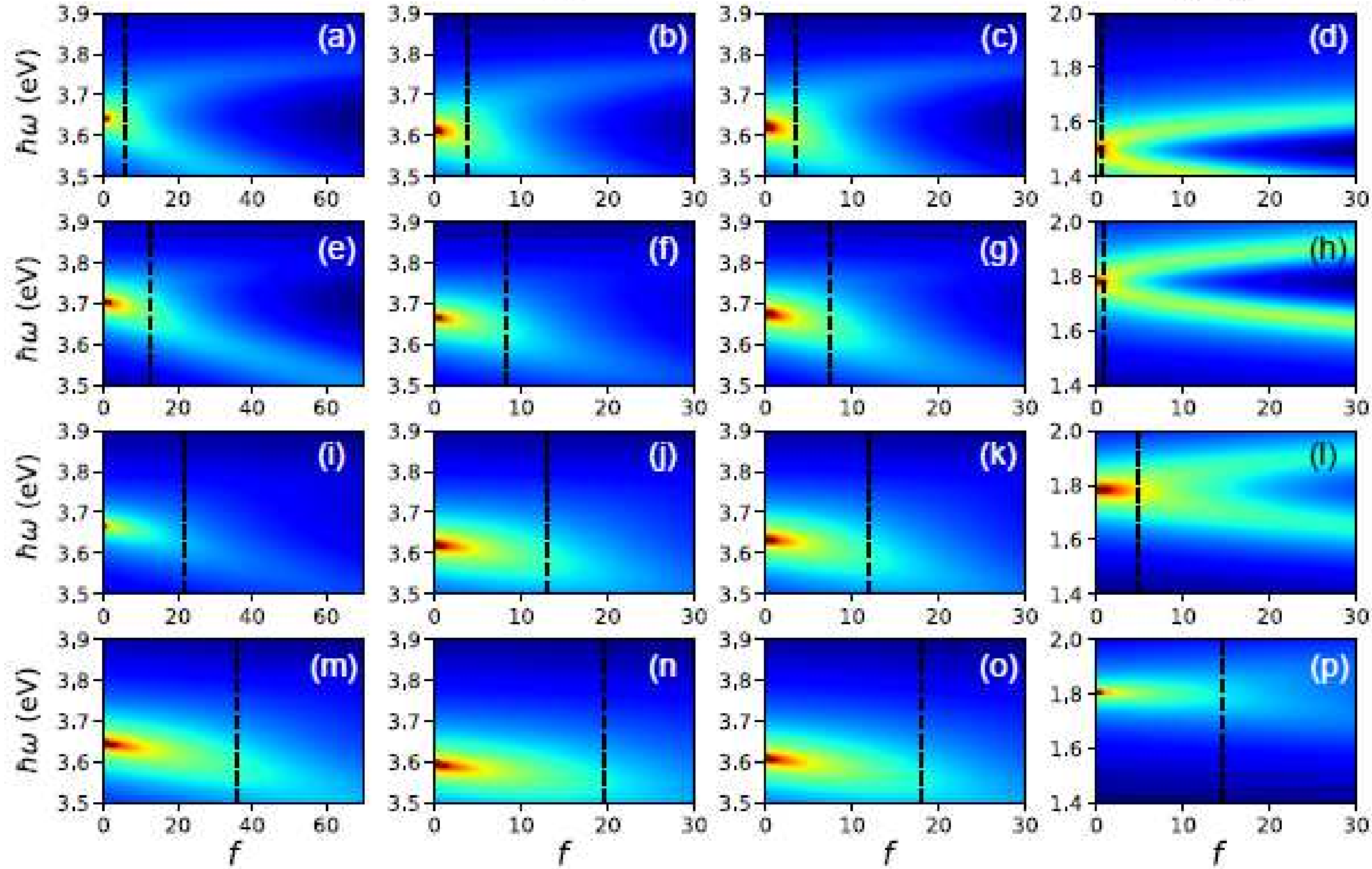
TF-HT

GNOR

(D = 3.61 x 10^{-4} m^2/s)

GNOR

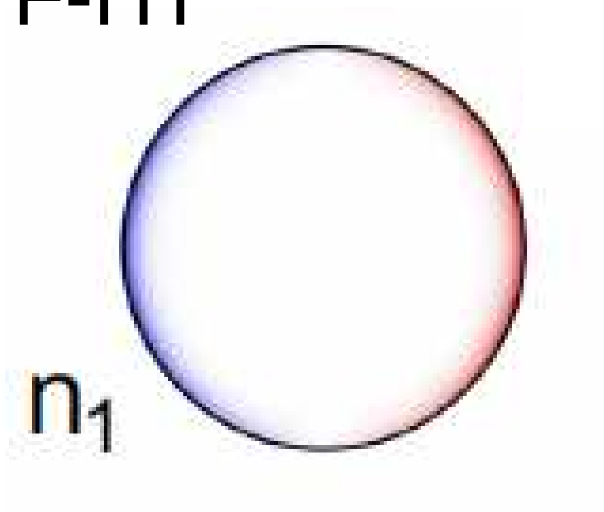
(D = 9.62 x 10^{-4} m^2/s)

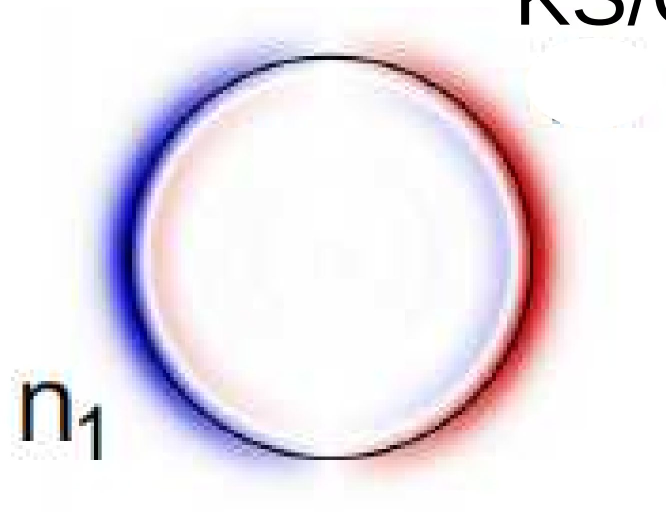


R. Jurga, S. D'Agostino, F. Della Sala and C. Ciraci', *Plasmonic nonlocal response effects on dipole decay dynamics in the weak and strong-coupling regimes, submitted to ACS Photonics (2017).*

Towards a Quantum Hydrodynamic Theory (QHT)

TF-HT | KS/QHT1





$$\nabla\times\nabla\times\mathbf{E}-\frac{\omega^2}{c^2}\mathbf{E}=\omega^2\mu_0\mathbf{P}$$

$$\beta^2\nabla(\nabla\cdot\mathbf{P})+\left(\omega^2+i\gamma\omega\right)\mathbf{P}=-\varepsilon_0\omega_p^2\mathbf{E}$$

$$\beta^2\rightarrow\xi^2=\beta^2+D(\gamma-i\omega)\approx\beta^2-i\omega D$$

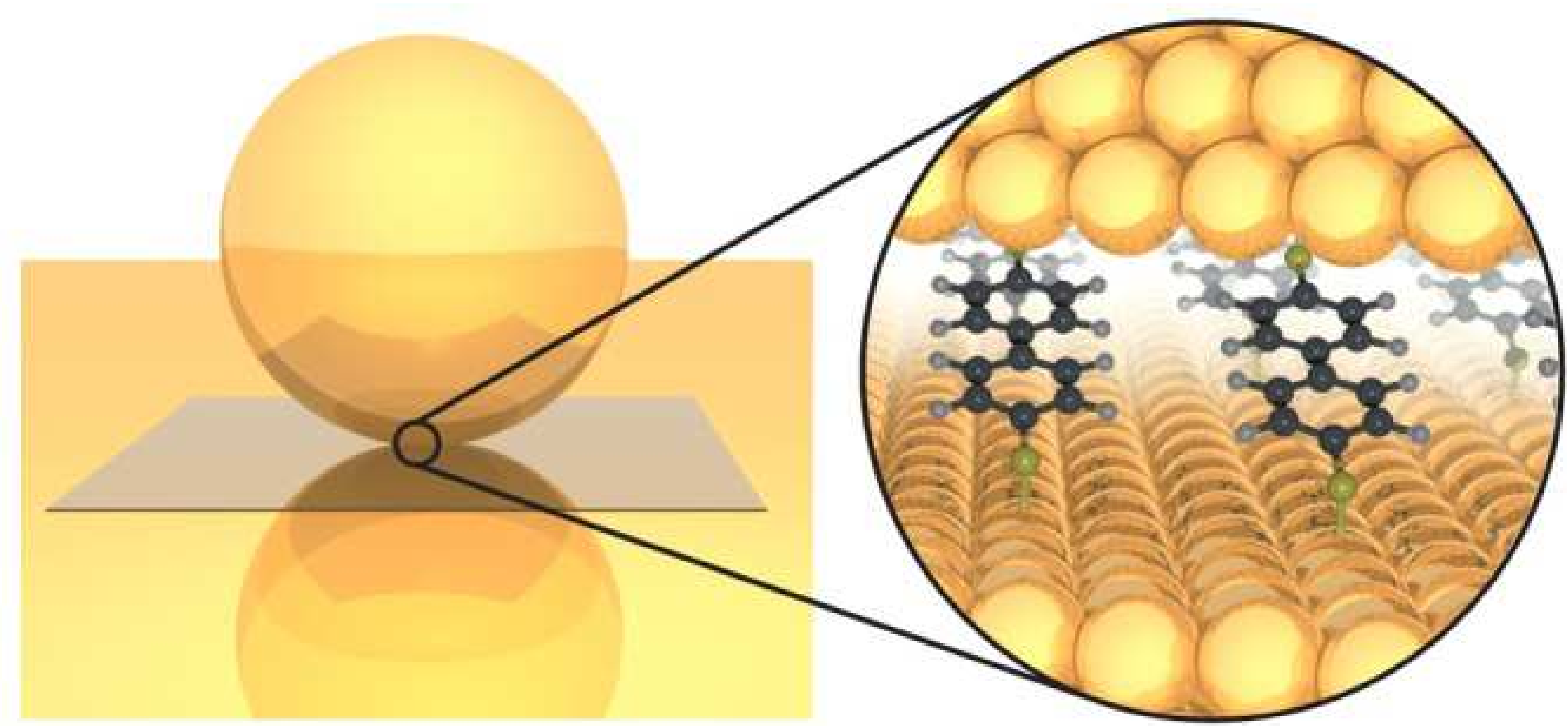
$$\frac{en_0}{m_e}\nabla\left(\frac{\delta G_n}{\delta n}\right)_1+\left(\omega^2+i\gamma\omega\right)\mathbf{P}=-\varepsilon_0\omega_p^2\mathbf{E}$$

$$G[n]\approx G_n[n]=\left(T_s^{TF}[n]+\frac{1}{\eta}T_s^{W}[n]\right)+E_{xc}^{LDA}[n]$$

G. Toscano et al., *Resonance shifts and spill-out effects in self-consistent hydrodynamic nanoplasmonics*, *Nature Comms* ***6****, 7132 (2015).*

C. Ciraci' and F. Della Sala, *Quantum hydrodynamic theory for plasmonics: Impact of the electron density tail*, *Phys. Rev. B 93, 205405 (2016)*

.. what about hybrid “organic-plasmonic” systems?



<u>F. Benz et al.</u>,
Nanooptics of Molecular-shunted Plasmonic Nanojunctions,
Nano Lett., 15, 669 (2015).

LSPs within the Quantum-Mechanical Scheme

- Potentialities and limits of the Spherical Jellium Model
- Advantages of Density Functional Tight Binding Method

R. Chikkaraddy *et al. Single-molecule strong coupling at room temperature in plasmonic nanocavities. Nature, 535, 127 (2016).*

The Electronic Structure Problem

A detailed comprehension of electronic phenomena in molecules and nanomaterials requires a detailed atomistic description of their electronic structure.
This is primarily achieved via the solution of the Schrödinger equation

$$H\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) = E\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)$$

With the electronic Hamiltonian being

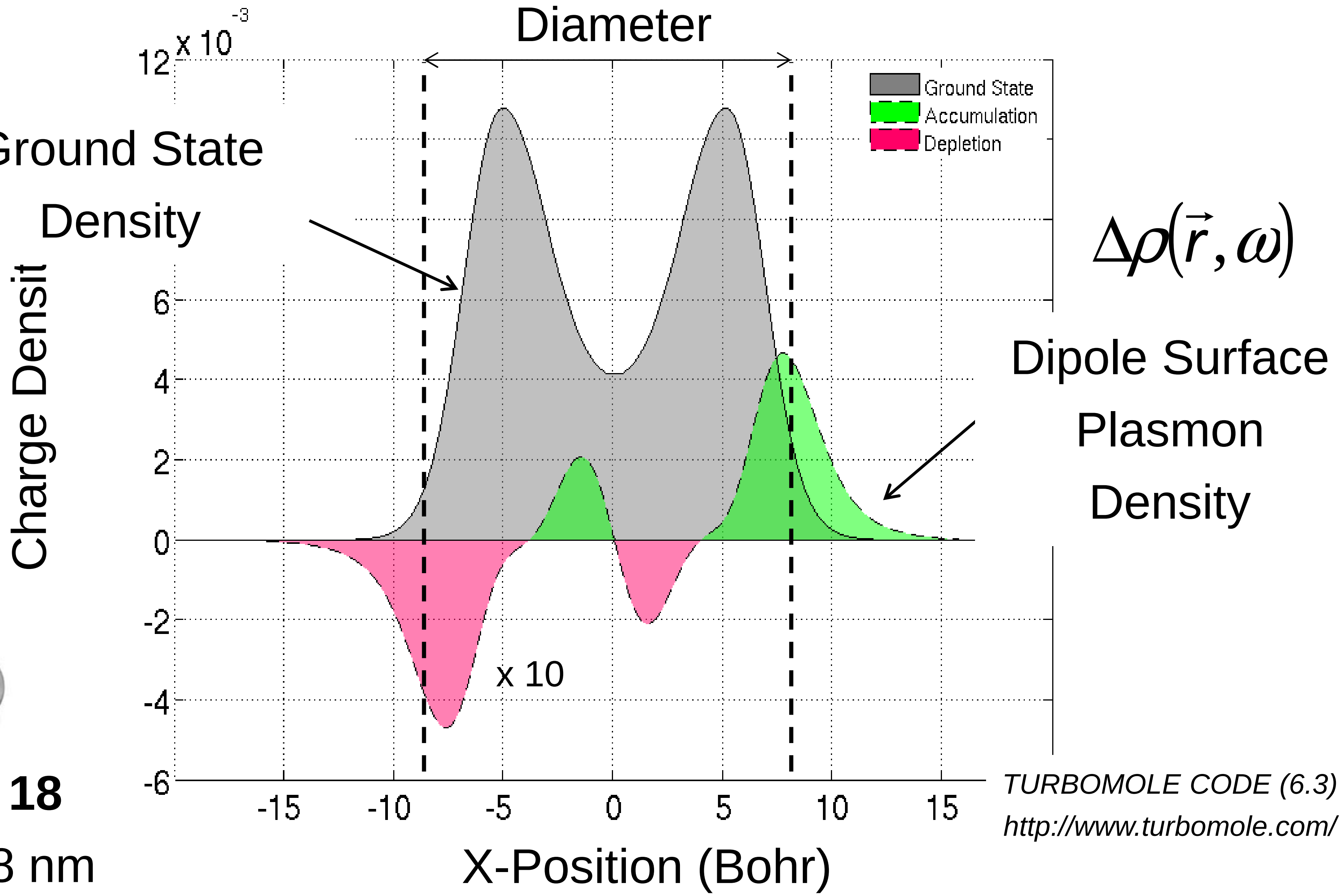
$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla^2_{\mathbf{R}_i} + V_{ext} + \sum_{i=1}^{N}\sum_{j\neq i}\frac{1}{|\mathbf{R}_i - \mathbf{R}_j|}$$

However, except for few simple cases, this problem is too complex to be solved directly (even numerically).

A large number of methods have then been developed to deal with the electronic structure problem:

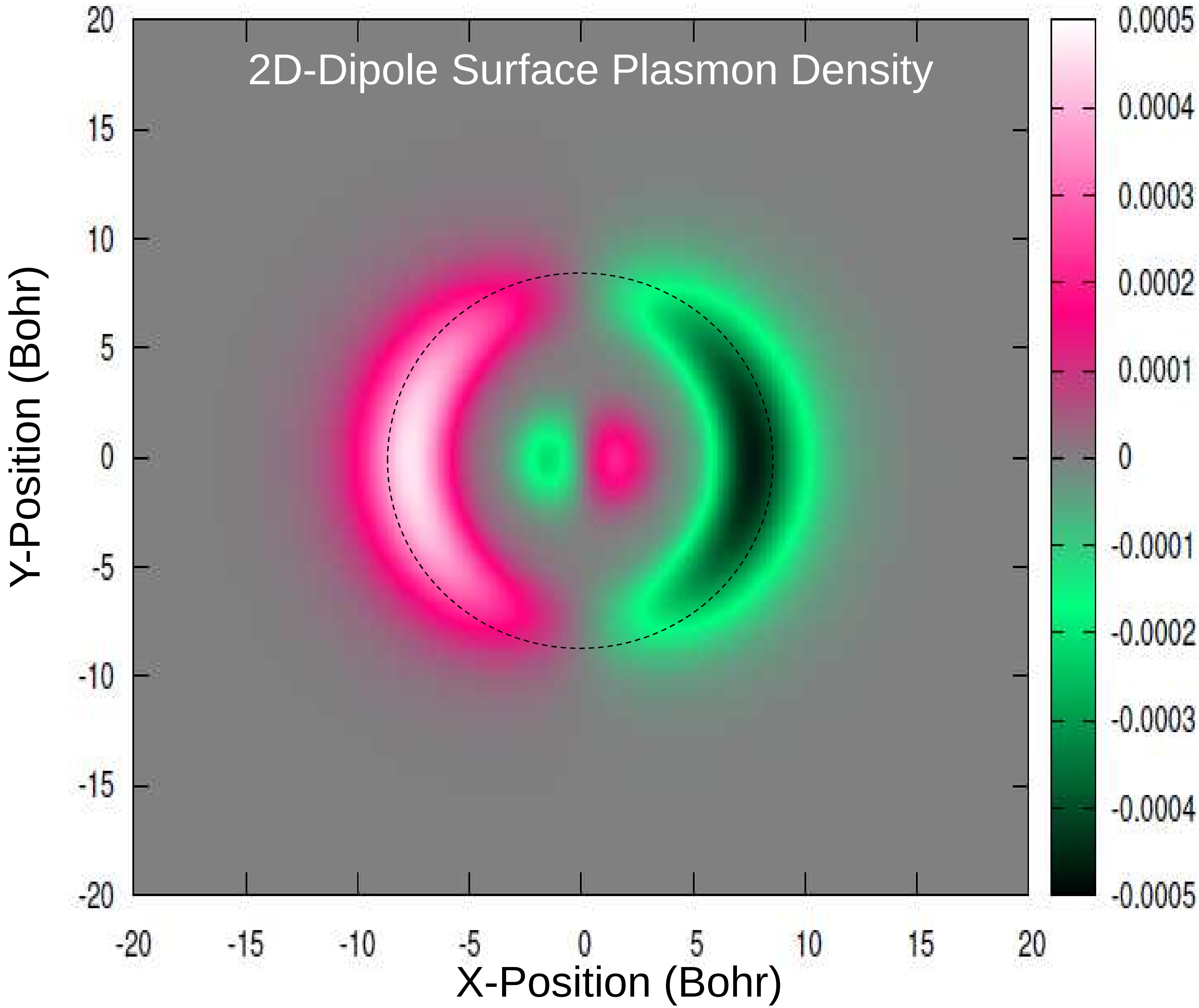
- *Wave function methods*
- *Density Functional Theory (DFT)*
- *Semiempirical methods*

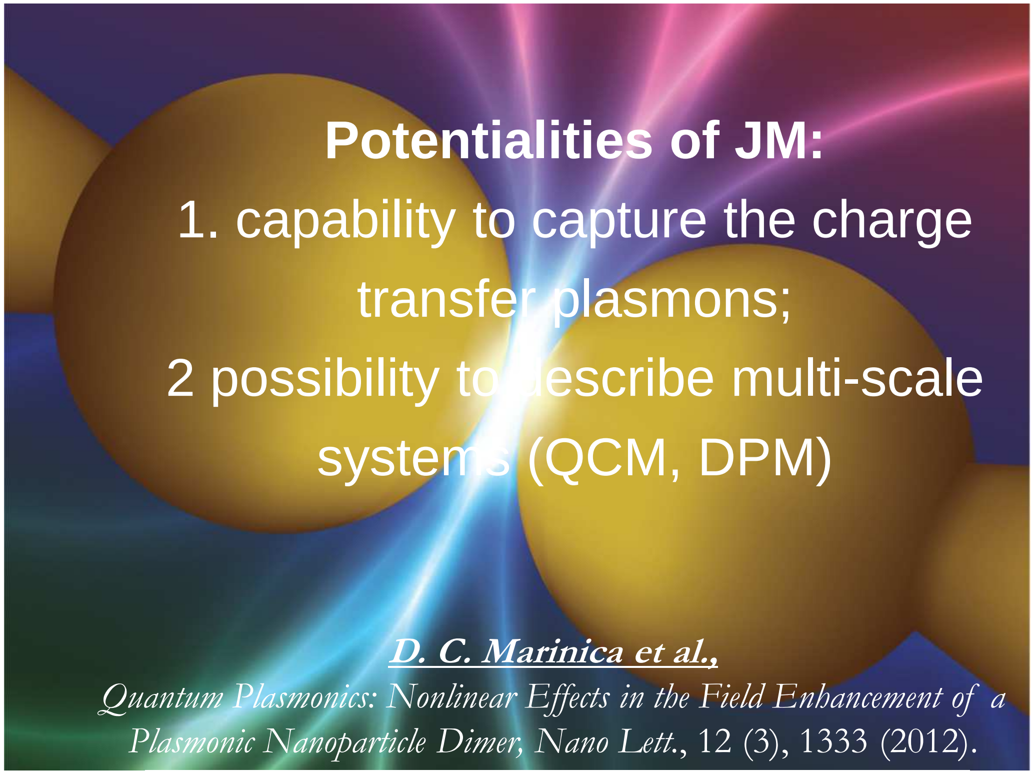
Density Functional Theory (DFT) and Time-Dependent DFT within the Jellium Model (JM)



Ne = 18

D = 0.8 nm


2D-Dipole Surface Plasmon Density
Y-Position (Bohr)
X-Position (Bohr)
20
15
10
5
0
-5
-10
-15
-20
0.0005
0.0004
0.0003
0.0002
0.0001
0
-0.0001
-0.0002
-0.0003
-0.0004
-0.0005

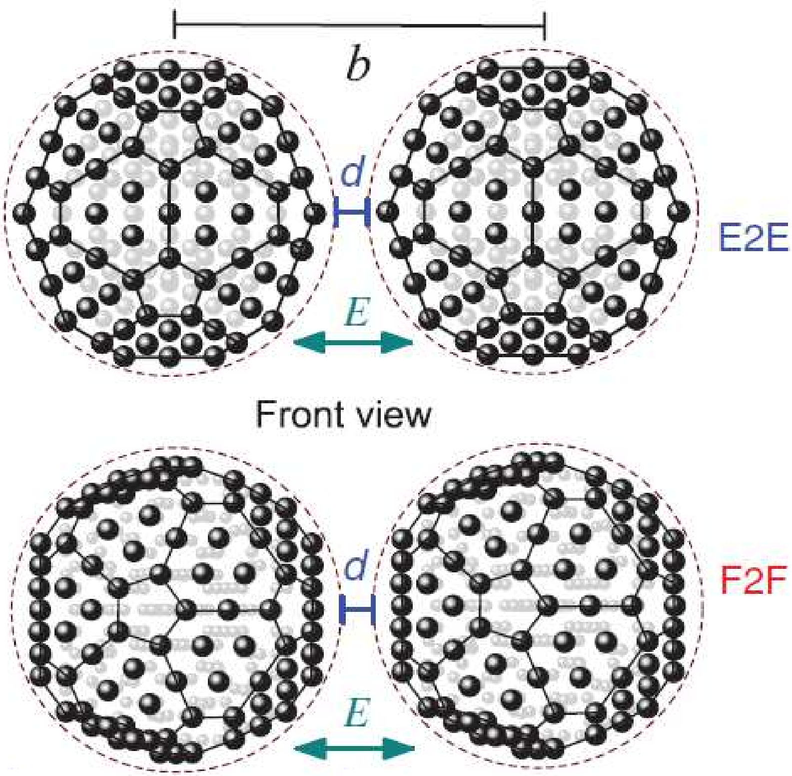


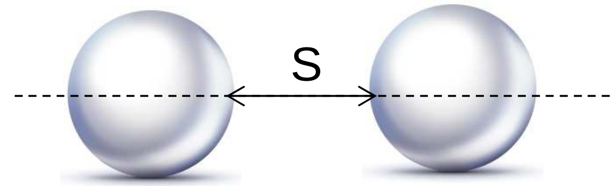
Potentialities of JM:

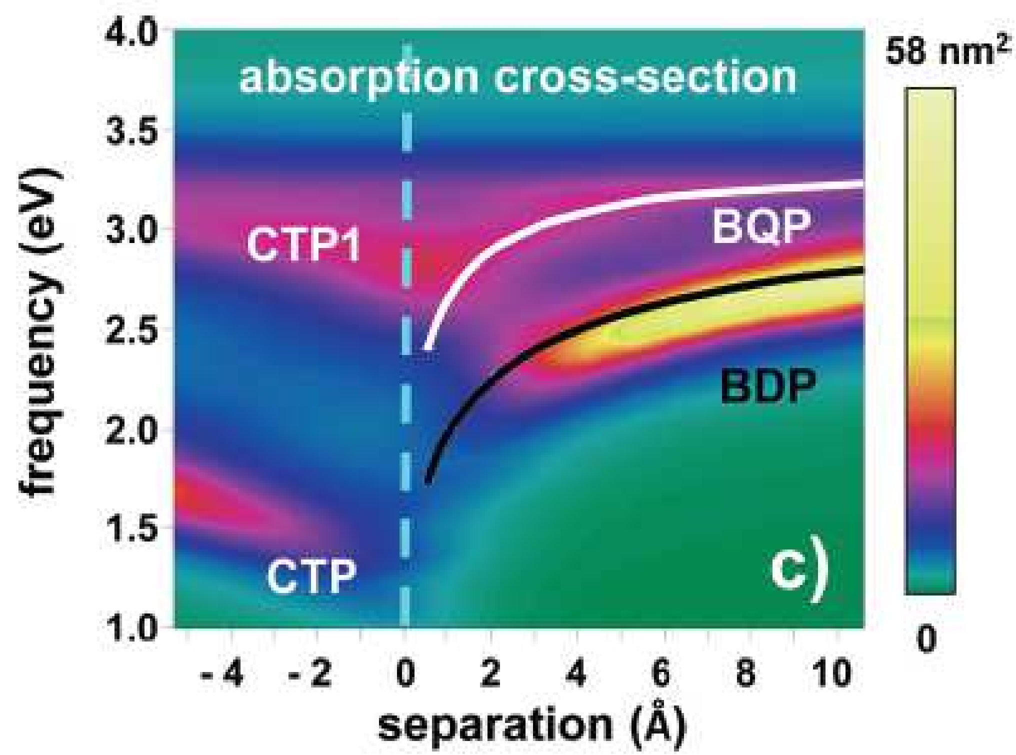
1. capability to capture the charge transfer plasmons;

2 possibility to describe multi-scale systems (QCM, DPM)

D. C. Marinica et al.,
Quantum Plasmonics: Nonlinear Effects in the Field Enhancement of a Plasmonic Nanoparticle Dimer, Nano Lett., 12 (3), 1333 (2012).







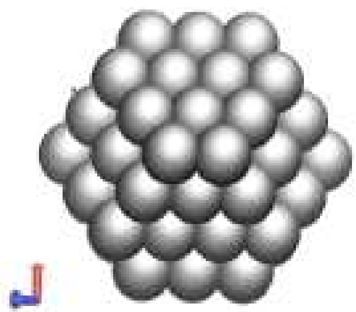
Limits of JM:

atomic structure is neglected (orientation and relaxation cannot be distinguished).

A. Varas et al., *Quantum plasmonics: from jellium models to ab initio calculations, Nanophotonics, 5(3), 409 (2016).*

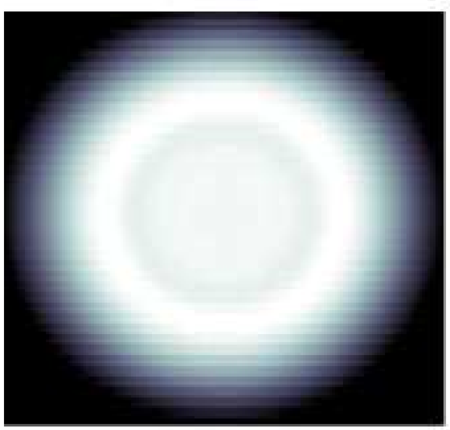
Density-Functional based Tight-Binding (DFTB)

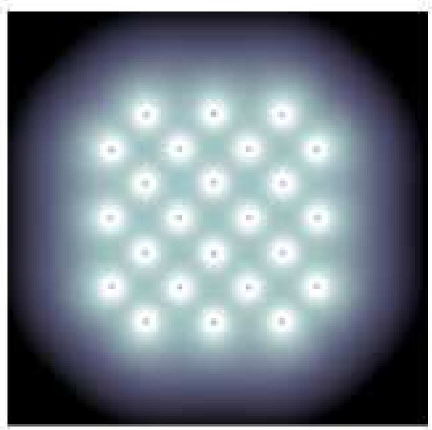
$$\phi_i = \sum_{\nu} c_{\nu}^{i} \psi_{\nu} \qquad \sum_{\nu} c_{\nu}^{i} \left(H_{\mu\nu} - \varepsilon_i S_{\mu\nu} \right) = 0 \quad \forall \mu, i$$



$$H_{\mu\nu} = H_{\mu\nu}^{0} + \frac{1}{2} S_{\mu\nu} \sum_{\xi} \left(\gamma_{\xi\mu} + \gamma_{\xi\nu} \right) q_{\xi}$$

Two-center Approximation:





$$H_{\mu\nu}^{0} = \left\langle \psi_{\mu} \middle| \hat{H}^{0} \middle| \psi_{\nu} \right\rangle = \begin{cases} \varepsilon_{\mu}^{free} & \mu = \nu \\ \left\langle \psi_{\mu} \middle| \hat{T} + V_{eff}^{AB} \middle| \psi_{\nu} \right\rangle & \mu \in A, \nu \in B, A \neq B \\ 0 & otherwise \end{cases}$$

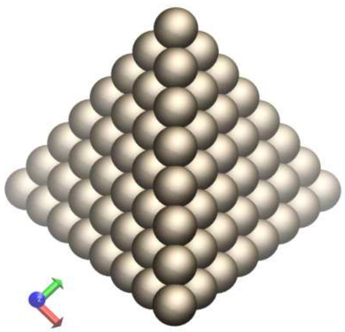
Potential Superposition: $V_{eff}^{AB} = V_0^A \left(\mathbf{r} - \mathbf{R}_A \right) + V_0^B \left(\mathbf{r} - \mathbf{R}_B \right)$

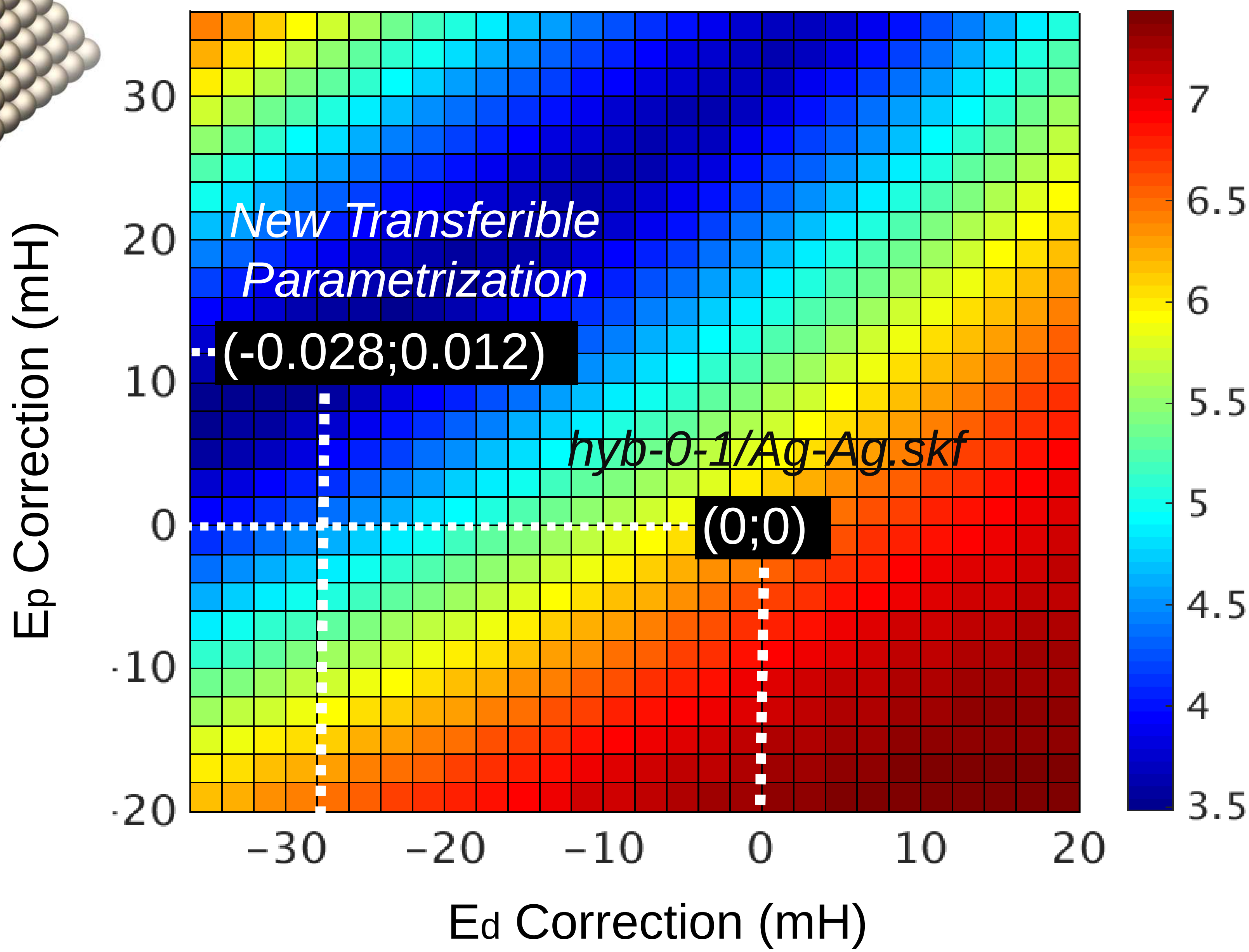
M. Wahiduzzaman et al.,

DFTB Parameters for the Periodic Table: Part 1, Electronic Structure, J. Chem. Theory Comput., 9, 4006 (2013).

Slater-Koster Parameters Optimization

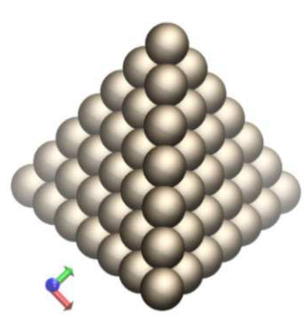
$$E_{\sigma} = \int \left| \sigma^{DFTB}_{abs} - \sigma^{DFT}_{abs} \right| d\omega$$



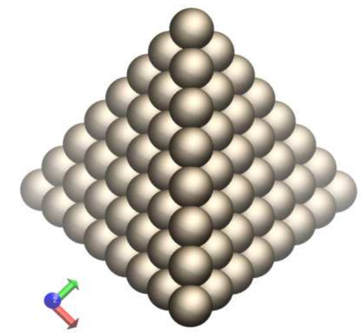


DFT/DFTB Comparison: Accuracy

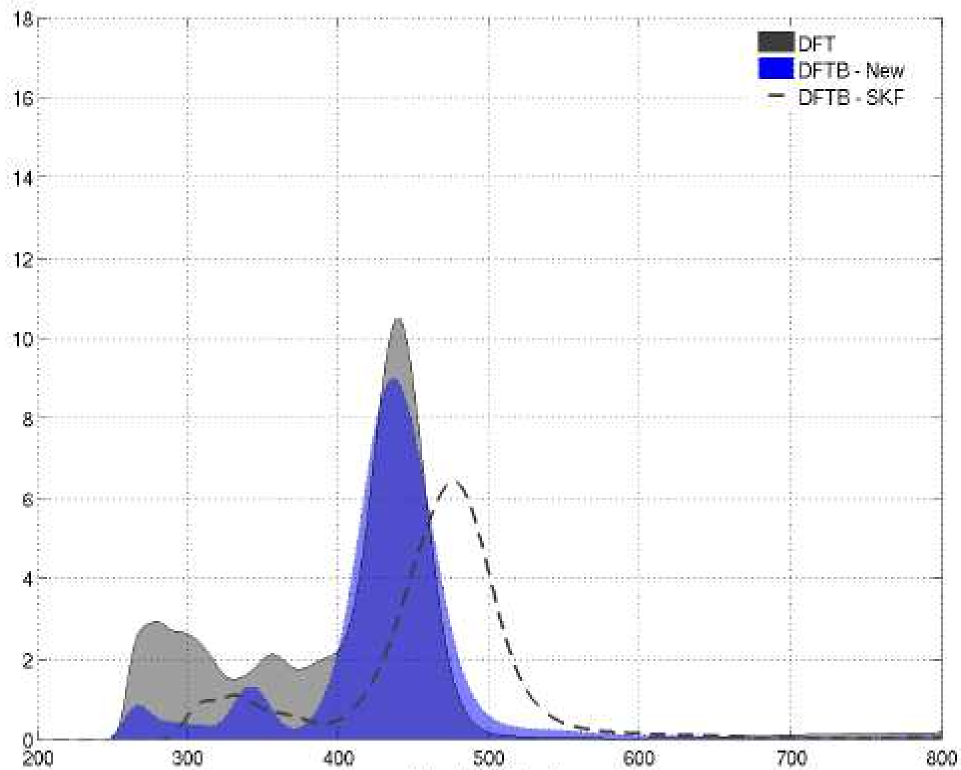
Ag_{84}

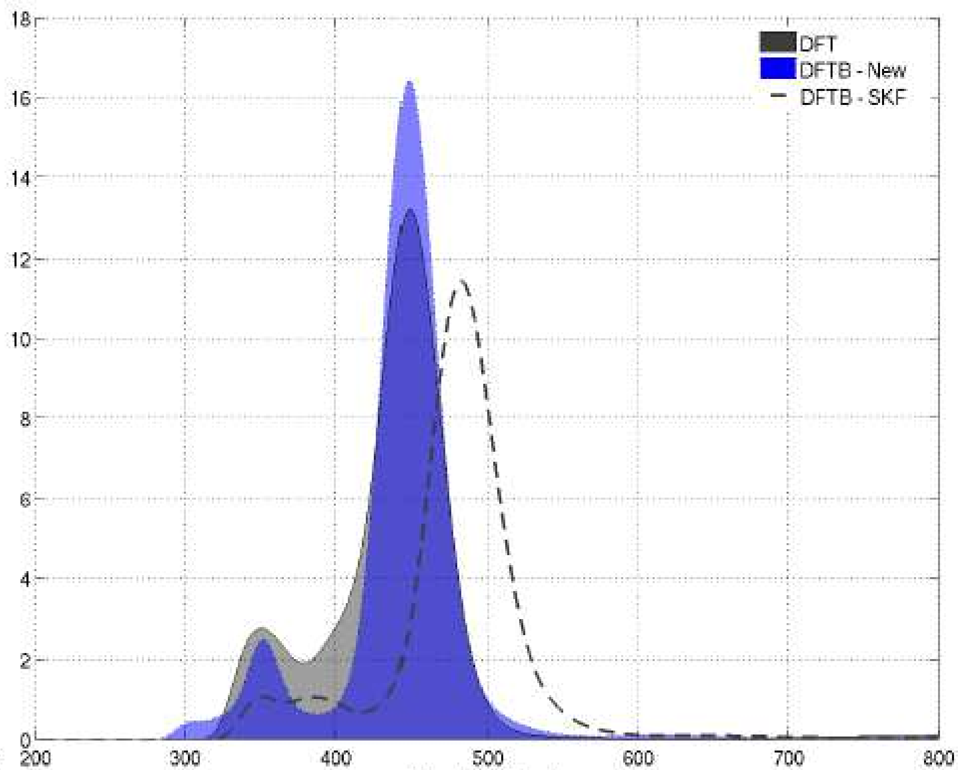


Ag_{120}



Absorption Efficiency (arb. u.)



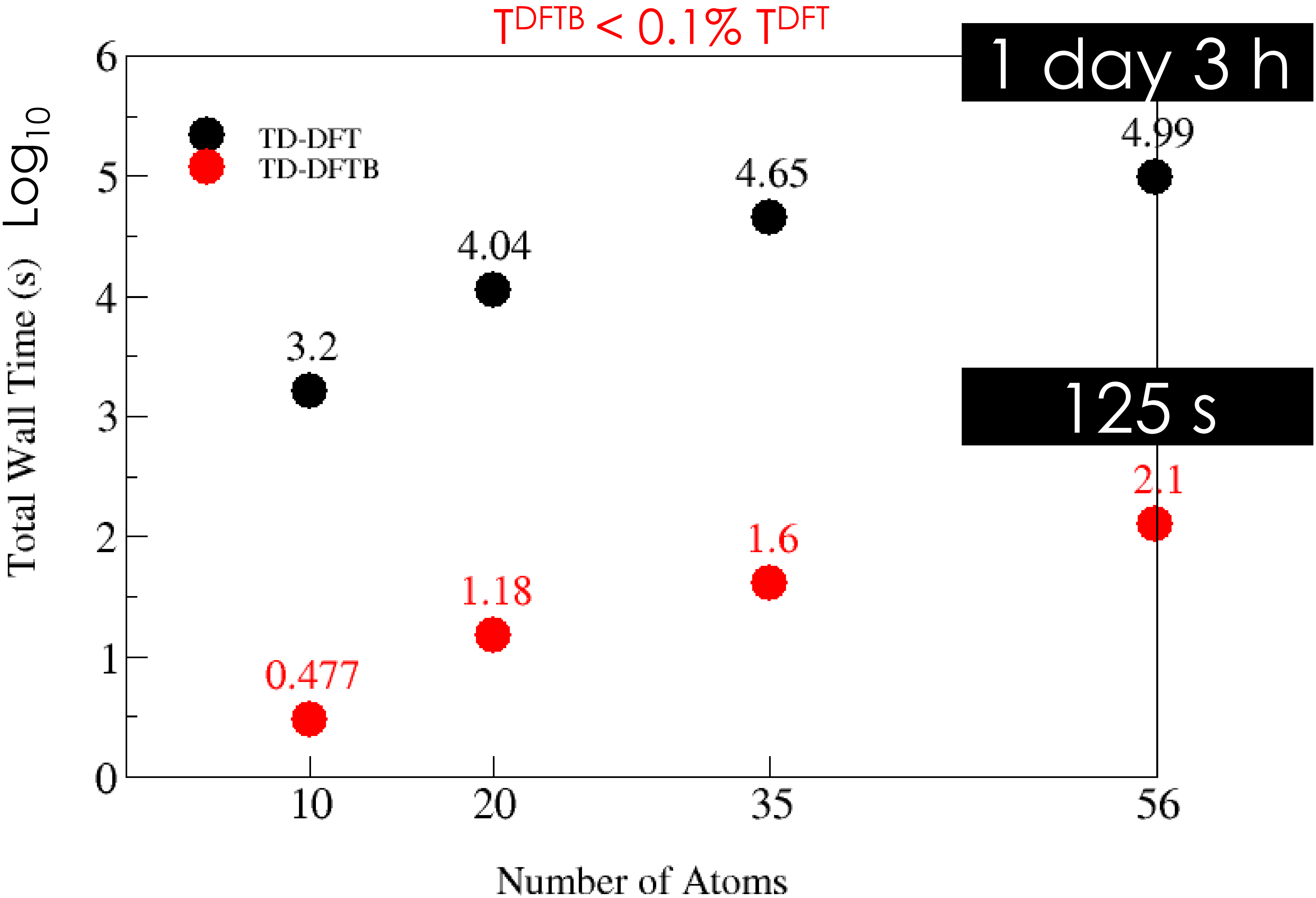


Wavelength (nm) Wavelength (nm)

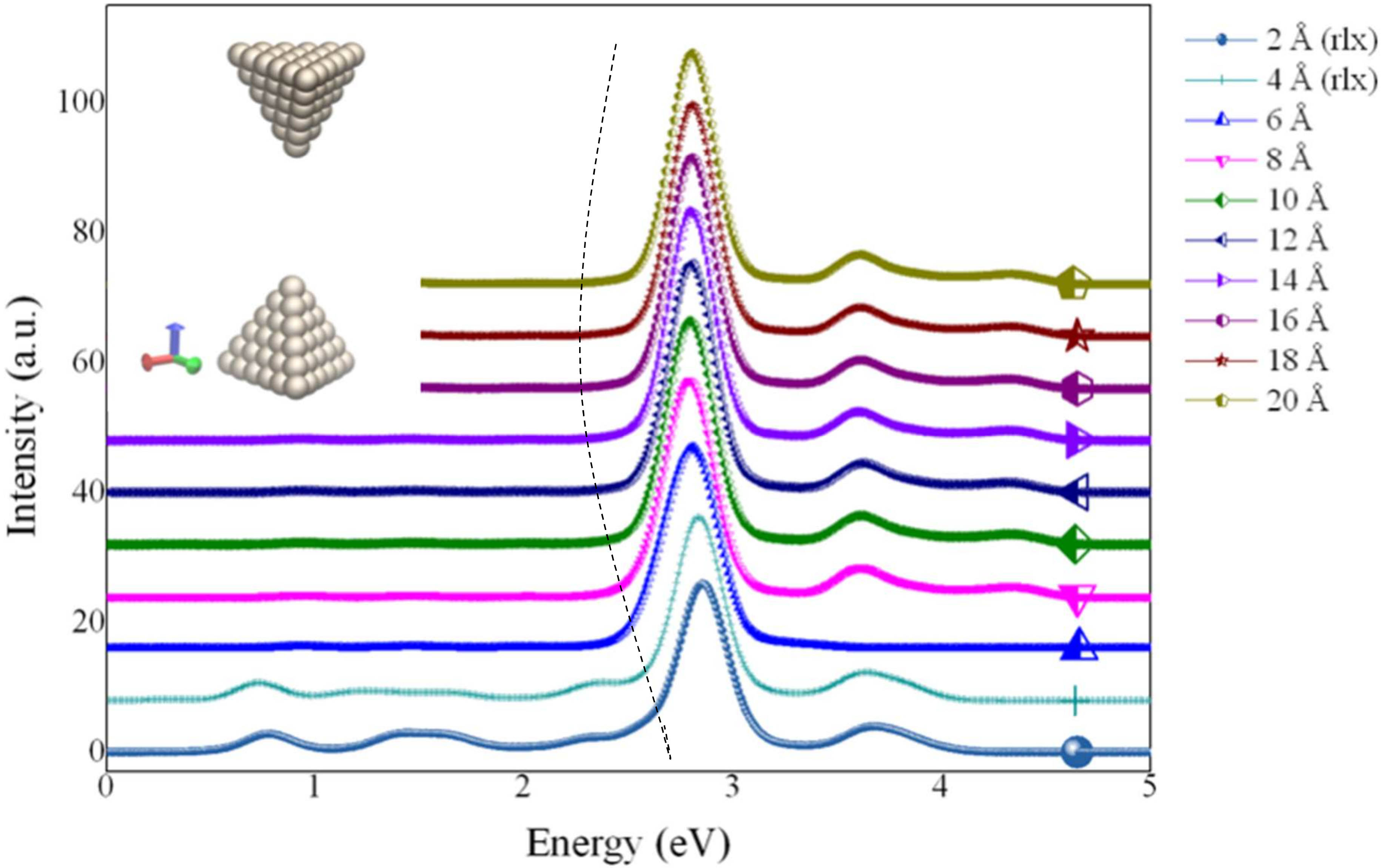
<u>S. D'Agostino, R. Rinaldi, G. Cuniberti and F. Della Sala,</u>

Density Functional Based Tight Binding for Plasmonics: Insights and Developments, in preparation (2017).

DFT/DFTB Comparison: Computational Cost



DFTB Analysis for Tetrahedral Ag Dimers



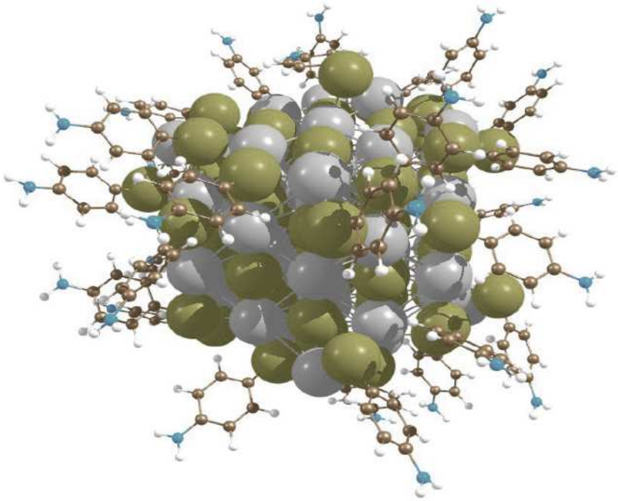
[TNT2017-POSTER] G. Giannone, R. Rinaldi, G. Cuniberti and S. D'Agostino,

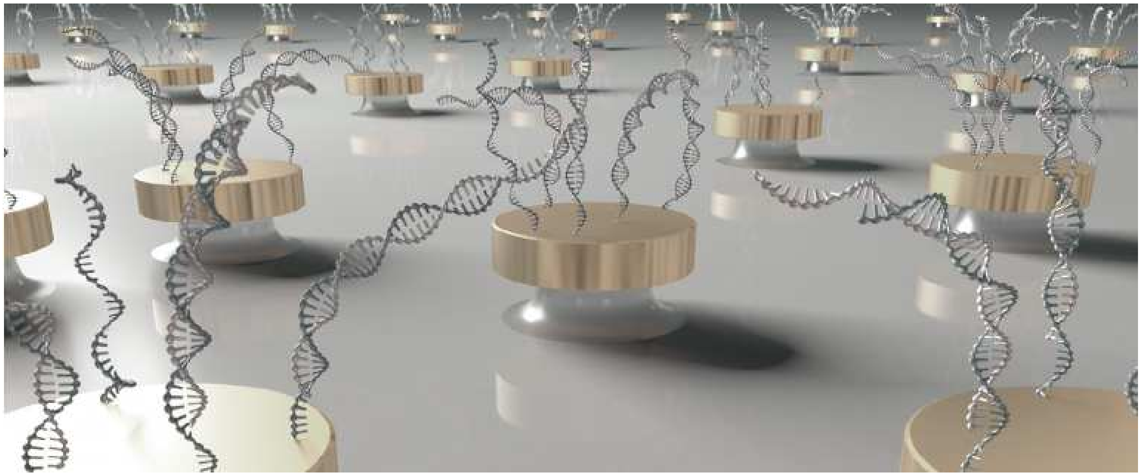
Density Functional Tight Binding Method for Plasmonics.

(Università del Salento, Italy)

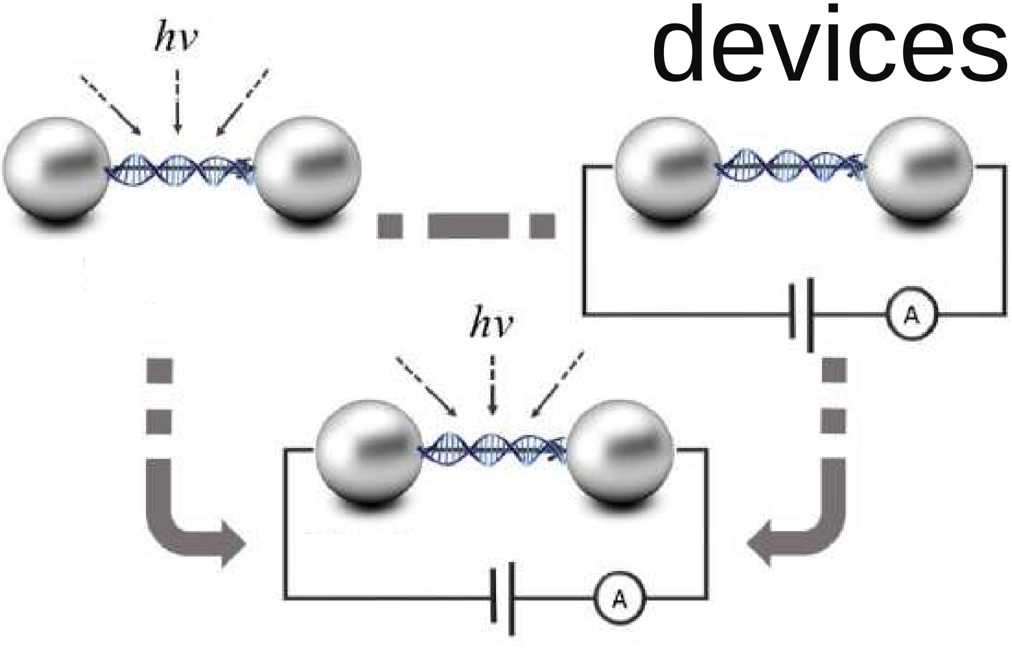
Future Perspectives

i. Plasmonic Switches



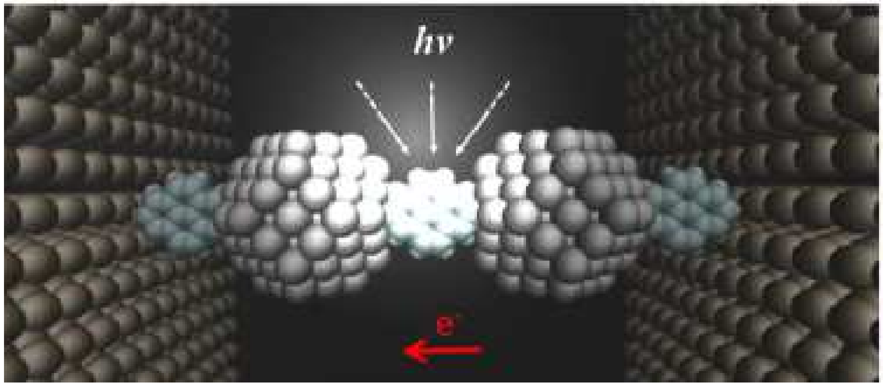


ii. Molecular electronic plasmonic devices (MEPs)



<u>T. Wang and C. A. Nijhuis,</u>

Molecular Electronic Plasmonics, Applied Material Today, 3, 73 (2016).



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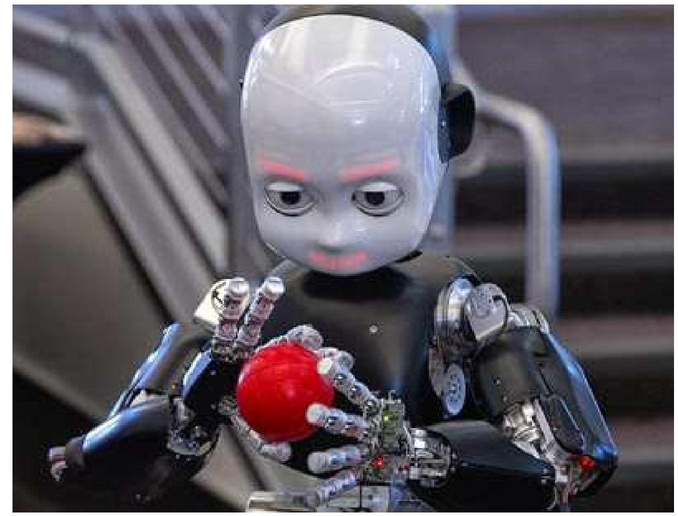

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… for your attention!

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