UNIVERSIDAD DE LAS PALMAS DE GRAN CANARIA

UNIVERSIDAD DE CANTABRIA

Imperial College London

Enhancing and controlling light with plasmonic and non-plasmonic nanoantennas

Pablo Albella
Nanophotonics and Material science
University Institute for Intelligent Systems and Numerical Applications (SIANI)

Pablo.Albella@ulpgc.es
p.Albella@imperial.ac.uk

Acknowledgements (People)

Imperial College London
- **Stefan Maier**
- T. Shibanuma
- Rupert Oulton
- Joshua Edel
- T. Roschuk
- M. Rahmani (now in ANU)
- E. Cortes and G. Grinblat
- F. Bresme
- T. Matsui
- S. Hanham

Universidad de Buenos Aires
- Andrea Bragas et al
- Fernando Stefani et al

CSIC
- **Javier Aizpurua**
- M. Nieto-Vesperinas
- Juan Jose Saenz
- J. Sanchez-Gil

Nanogune
- **Rainer Hillenbrand**
- Pablo Alonso (now in UniOvi)

Universidad de Cantabria
- **Fernando Moreno**
- **Francisco Gonzalez**
- J.M. Saiz
- J.M. Sanz
- R. Alcaraz

Duke University
- Henry Everitt et al

Army Research Lab
- Gorden Videen

Fresnel Institute
- Jean Michel Geffrin

Univerity of Lyon
- Rodolphe Vaillon

University of Southampton
- Otto Muskens

University of Heidelberg
- Annemarie Pucci
- Frank Neubrech

University of Windsor
- Ricardo F. Aroca

University of Sao Paolo
- Osvaldo de Oliveira Jr.
- Ricardo Mejía

University of Liverpool
- Colin Crick

ICFO, Spain
- J. Canet-Ferrer

Acknowledgements (Funding)

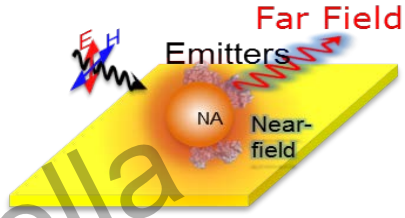
The Leverhulme Trust

Consejería de Economía,
Industria, Comercio y Conocimiento
Agencia Canaria de Investigación,
Innovación y Sociedad
de la Información

Outline

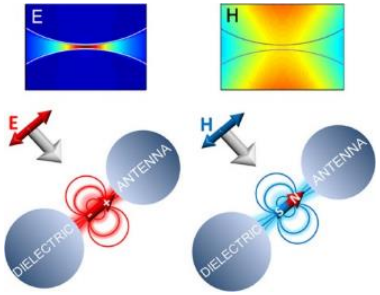
Part I:

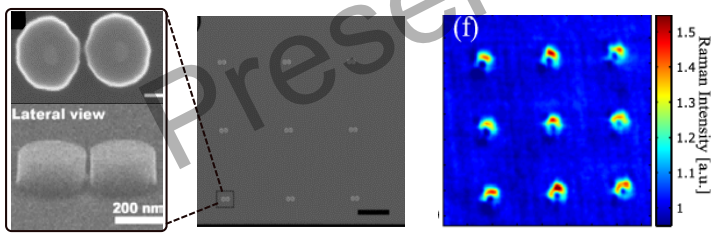
- **Surface Enhanced Spectroscopies (SES)**
  - Introduction to plasmonic nanoantennas and its limitations

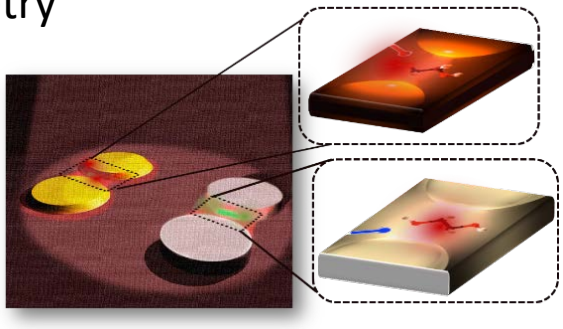


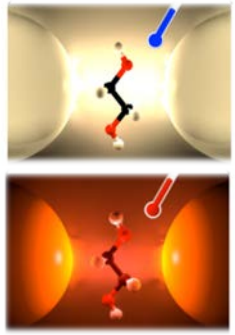
Part II:

- **Non-plasmonic HRI dielectric nanoantennas as an alternative to plasmonics for enhancing light (in near and far field) with low losses**
  - Electric and Magnetic Hot Spots
- **Experimental demonstration of these novel type of nanoantennas able to enhance Raman and Fluorescence:**
  - Heat assessment based on thermometry





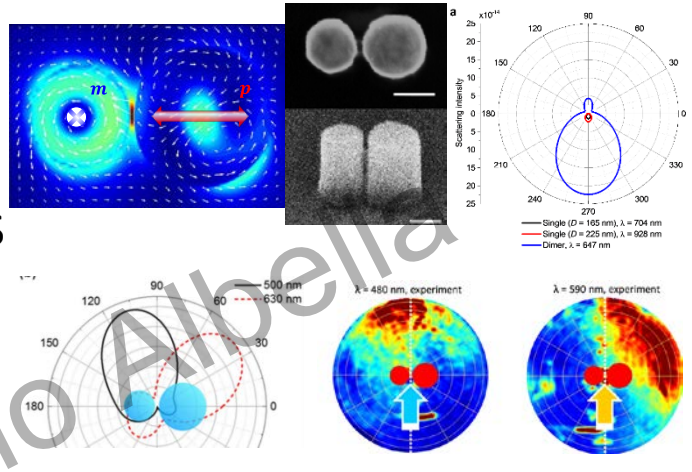




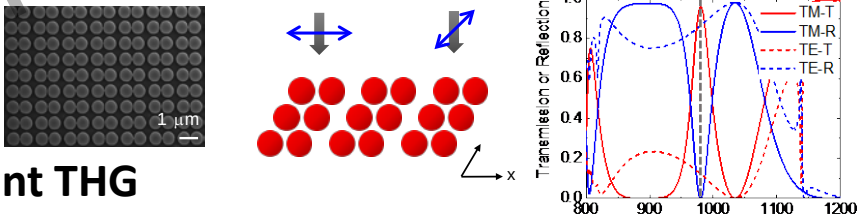
Outline

Part III:

- **What about enhancing light with directional control? or switchable steering of light?**
  - Possible direct application in Selective sensing or SES
  - Application in optical nano-circuitry

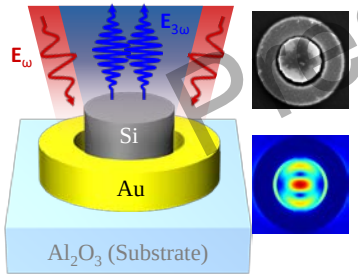


- **Polarization control of high transmission / reflection switching by all-dielectric metasurfaces**



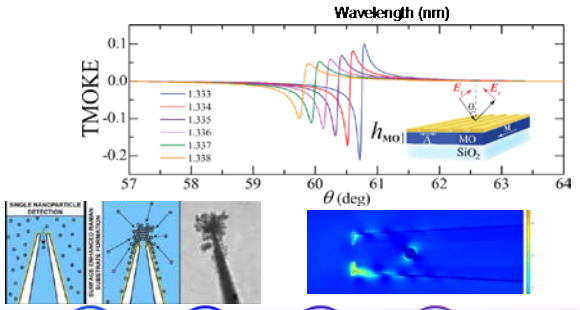
Part IV:

- **Dielectric - Metal hybrid structures for efficient THG**



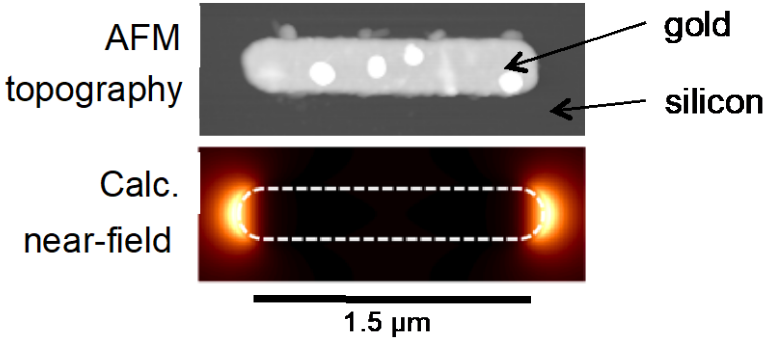
Part V:

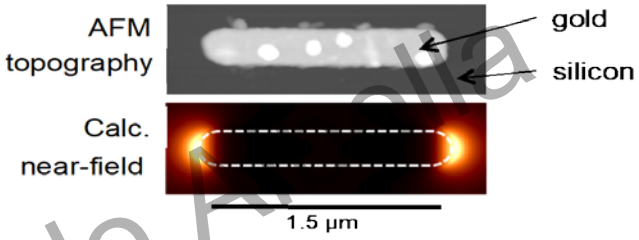
- **Examples of (bio) - sensors**
  - MO-Kerr effect in magnetoplasmonic crystals
  - DNA mapping with nanopipetes (SERS,SEF)



Part I: Introduction to SES and plasmonic nanoantennas

- Plasmonic antennas are widely studied due to their capability to convert free propagating radiation into highly enhanced-localized fields.

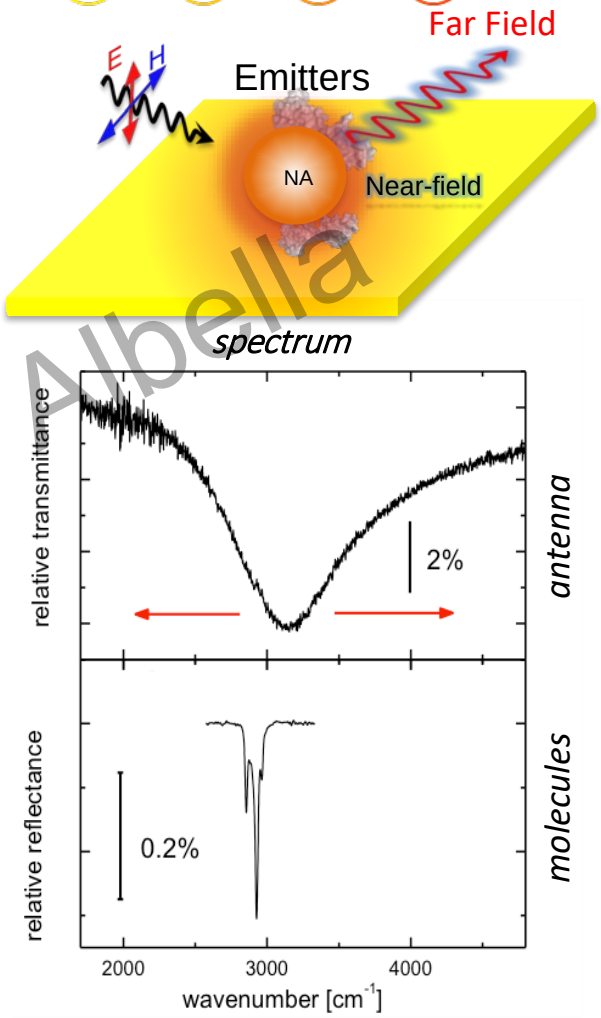




Neubrech, Aizpurua, et.al, PRL 101, 157403 (2008)

Part I: Introduction to SES and plasmonic nanoantennas

- **Idea in SES:** Using the enhanced electromagnetic near and far field of a nanostructure oscillating in resonance
- Pre-condition for SES[#,*]: Matching molecular vibration of interest and resonant excitation of the nanoantenna
- Very important to tune the resonance precisely! And with strong near and Far field enhancement!!

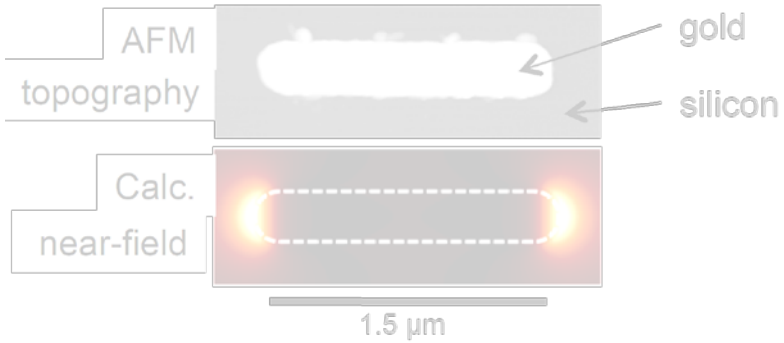


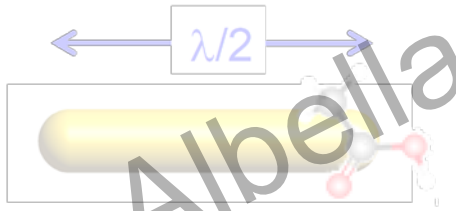
[*] L. Novotny, PRL 98, 266802 (2007)

[#] F. Neubrech, Aizpurua et al., PRL 101, 157403 (2008)

Surface Enhanced Spectroscopy (plasmonic nanoantennas)

- Plasmonic antennas are widely studied due to their capability to convert free propagating radiation into highly enhanced-localized fields.





mid-IR molecular spectroscopy

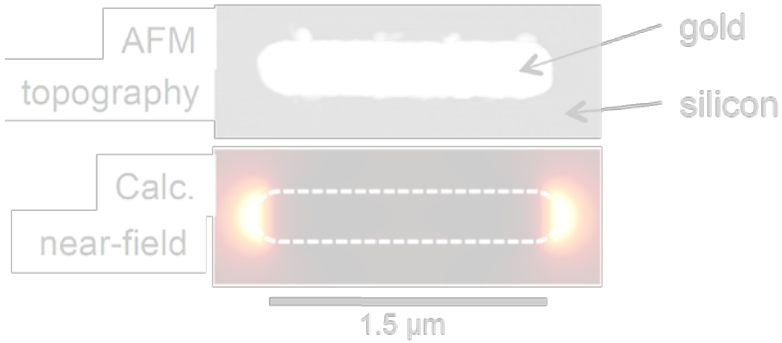
Neubrech, Aizpurua, et.al, PRL 101, 157403 (2008)

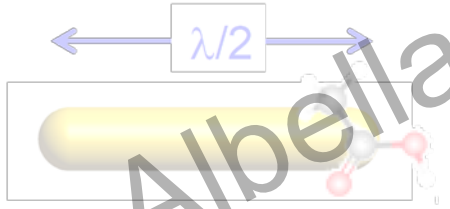
- Shape of nanoantenna very important!!

"Shape Matters: Plasmonic Nanoparticle Shape Enhances Interaction with Dielectric Substrate", **Nano Letters 11**, 3531–3537 (2011).

Surface Enhanced Spectroscopy (plasmonic nanoantennas)

- Plasmonic antennas are widely studied due to their capability to convert free propagating radiation into highly enhanced-localized fields.



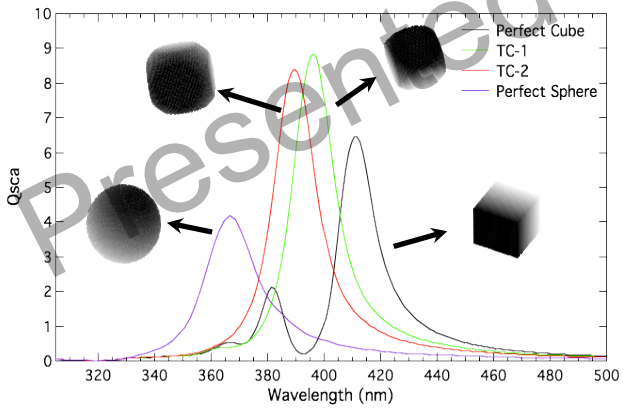


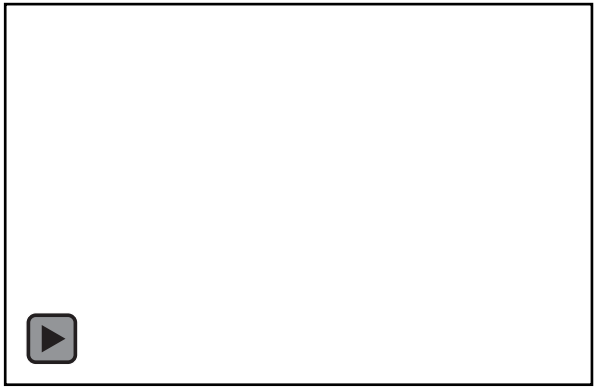
mid-IR molecular spectroscopy

Neubrech, Aizpurua, et.al, PRL 101, 157403 (2008)

- Shape of nanoantenna very important!!

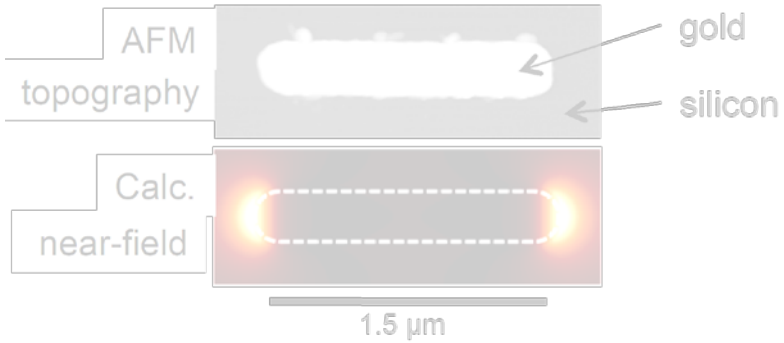
"Shape Matters: Plasmonic Nanoparticle Shape Enhances Interaction with Dielectric Substrate", **Nano Letters 11**, 3531–3537 (2011).





Surface Enhanced Spectroscopy (plasmonic nanoantennas)

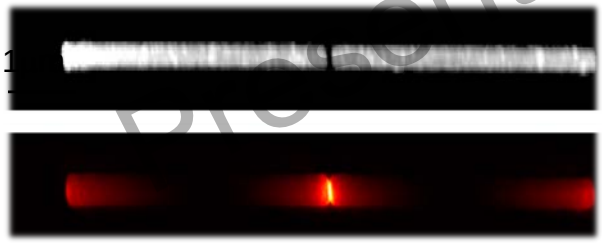
- Plasmonic antennas are widely studied due to their capability to convert free propagating radiation into highly enhanced-localized fields.

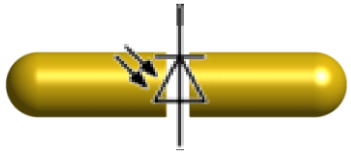


mid-IR molecular spectroscopy

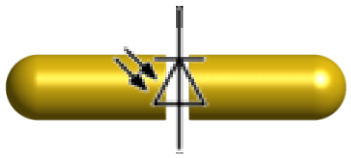
Neubrech, Aizpurua, et.al, PRL 101, 157403 (2008)

- Gap Antennas excel among other antenna structures due to the appearance of coupled oscillation modes which lead to interesting characteristics:
  - *Distinct Spectral Shifts and strong local field enhancements (broadly applied in SES)*





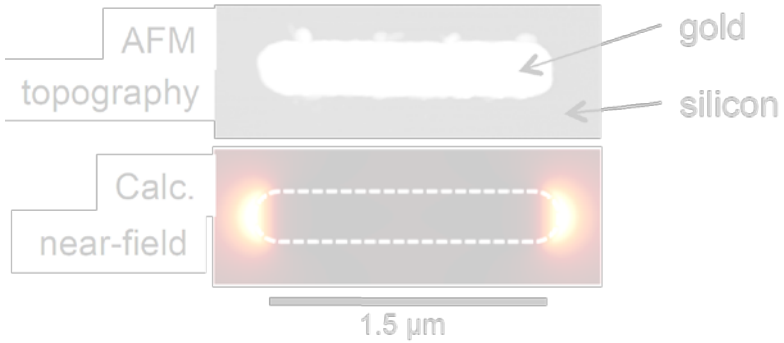
near-IR photodetector
Tang et al. Nature Photon. 2 (2008)



near-IR photodetector
Tang et al. Nature Photon. 2 (2008)

Surface Enhanced Spectroscopy (plasmonic nanoantennas)

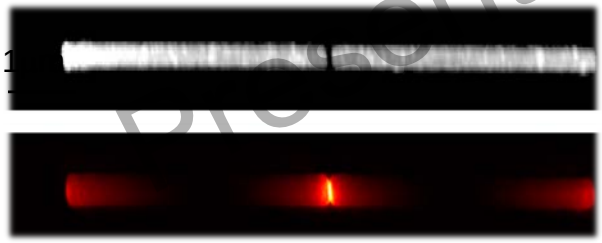
- Plasmonic antennas are widely studied due to their capability to convert free propagating radiation into highly enhanced-localized fields.

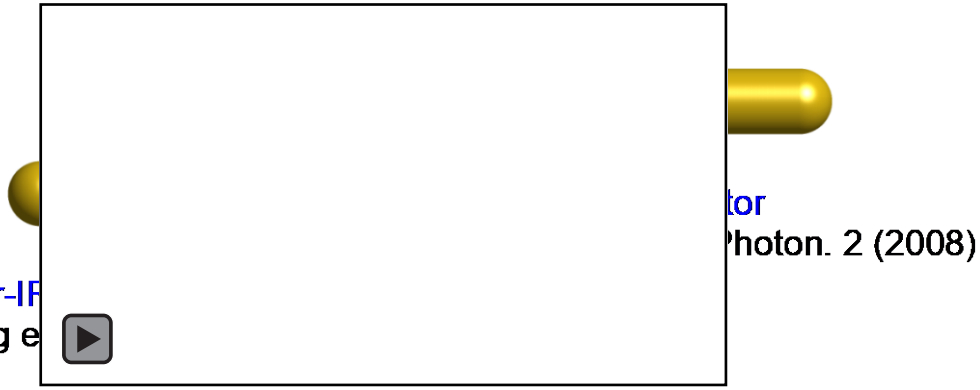


mid-IR molecular spectroscopy

Neubrech, Aizpurua, et.al, PRL 101, 157403 (2008)

- Gap Antennas excel among other antenna structures due to the appearance of coupled oscillation modes which lead to interesting characteristics:
  - *Distinct Spectral Shifts and strong local field enhancements (broadly applied in SES)*





near-IR

Tang e

tor

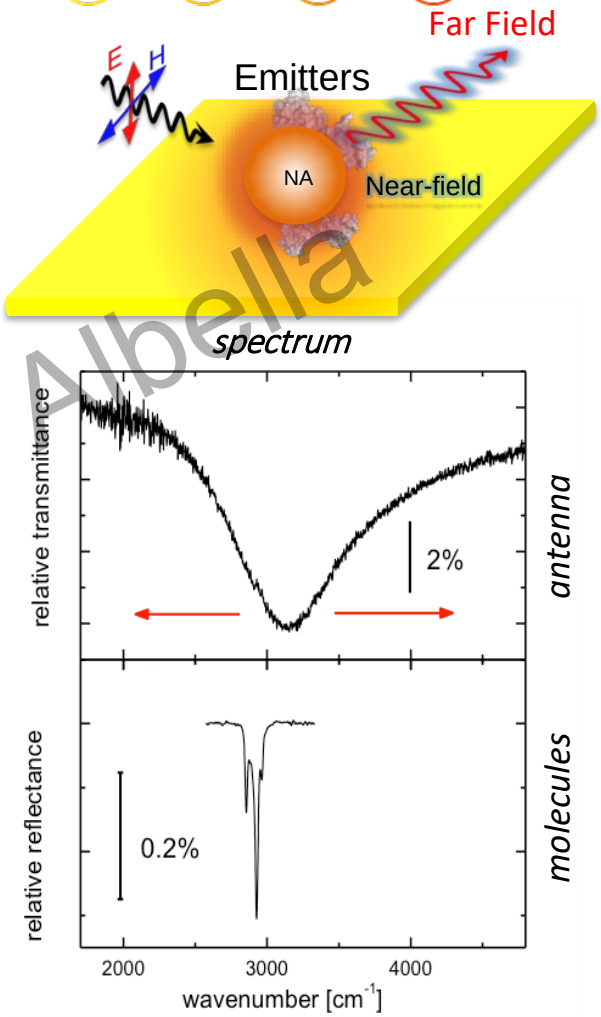
Photon. 2 (2008)

Part I: Introduction to SES and plasmonic nanoantennas

- **Idea in SES:** Using the enhanced electromagnetic near and far field of a nanostructure oscillating in resonance

- Pre-condition for SES[#,*]: Matching molecular vibration of interest and resonant excitation of the nanoantenna

- Very important to tune the resonance precisely! And with strong near and Far field enhancement!! **Why?**



[*] L. Novotny, PRL 98, 266802 (2007)

[#] F. Neubrech, Aizpurua et al., PRL 101, 157403 (2008)

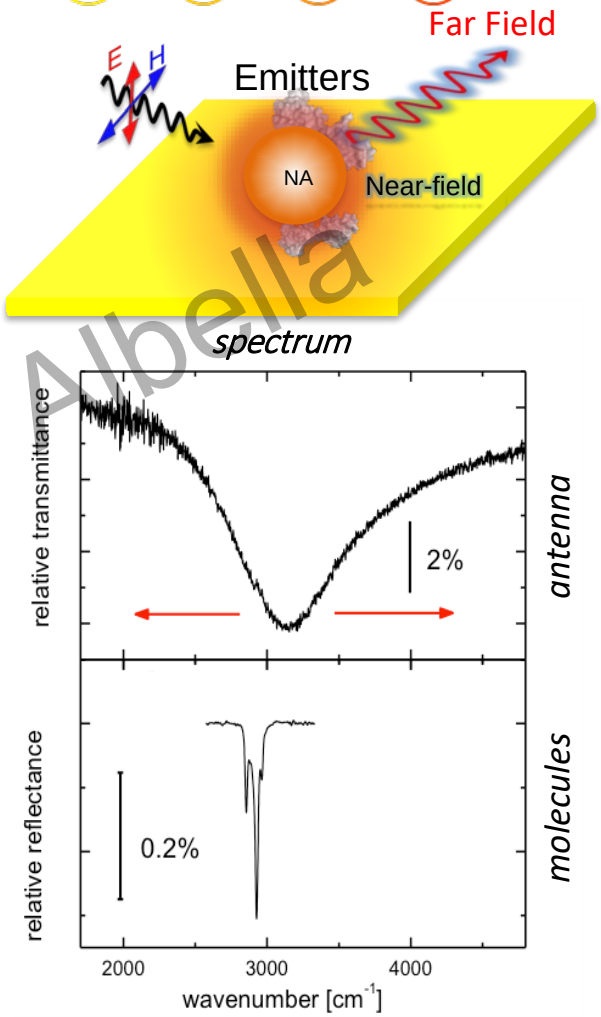
Part I: Introduction to SES and plasmonic nanoantennas

- **Idea in SES:** Using the enhanced electromagnetic near and far field of a nanostructure oscillating in resonance

- Pre-condition for SES[#,*]: Matching molecular vibration of interest and resonant excitation of the nanoantenna

- Very important to tune the resonance precisely! And with strong near and Far field enhancement!! **Why?**
  - Scattering will follow the **4th power SERS law**
  - Widely accepted, but not clearly shown why, until 2012*

* P. Alonso-González, P. Albella et. Al, ***Nature Comms 3, 684 (2012).***



[*] L. Novotny, PRL 98, 266802 (2007)

[#] F. Neubrech, Aizpurua et al., PRL 101, 157403 (2008)

Part I: Introduction to SES and plasmonic nanoantennas

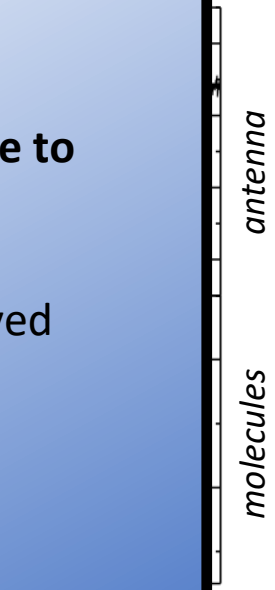
- **Idea:** Using the enhanced electromagnetic near and far field of a nanostructure oscillating in resonance

- All that is possible, because the Scattered intensity I scales with the 4th power of the local field enhancement at the metal surface.

- Direct and Quantitative verification of this law and its **underlying electromagnetic scattering mechanism was more than a challenge to tackle.**

- Why? Difficulties arise from the complex processes typically involved in surface-enhanced spectroscopies:
  - Chemical bonding
  - Charge transfer between object and metal nanostructures

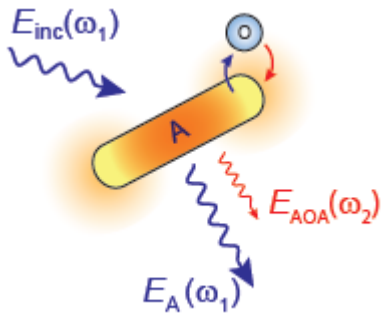
- ***How can we isolate the electromagnetic mechanism?***



[#] F. Neubrech, Aizpurua et al., PRL 101, 157403 (2008)

Surface Ehnanced Spectroscopy
Schematics of a surface-enhanced light scattering Process

Schemmatics of typical Antenna-enhanced Raman process (SERS)



Inelastic scattering process from an object (O) in the presence of a metal nanostructure

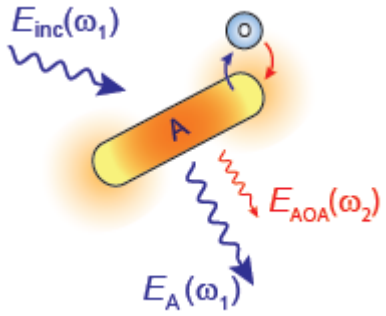
Elastic antenna-enhanced scattering process

We rely on

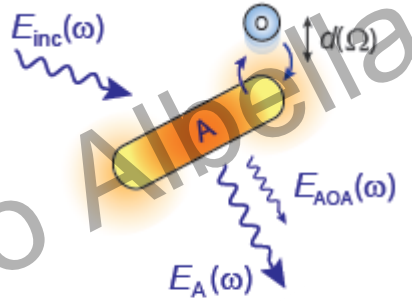
The underlying electromagnetic mechanism of the signal enhancement is challenging to trace experimentally.

Surface Ehnanced Spectroscopy
Schematics of a surface-enhanced light scattering Process

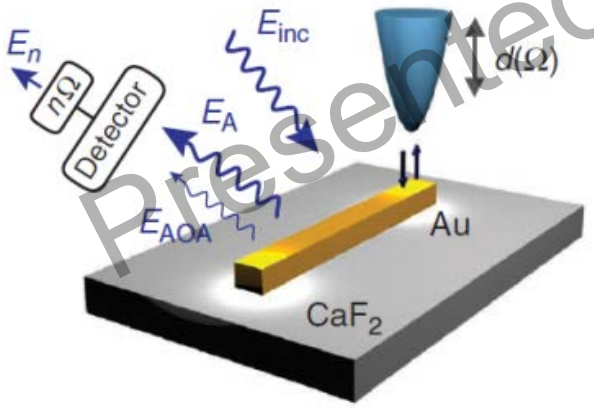
Schemmatics of typical Antenna-enhanced Raman process (SERS)



Elastic antenna-enhanced scattering process



Inelastic scattering process from an object (O) in the presence of a metal nanostructure

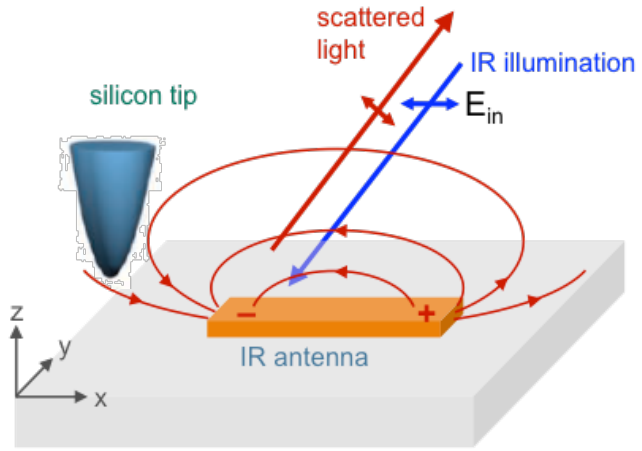


($\omega 1 = \omega 2 = \omega$)

By relying on elastic scattering (s-SNOM) we were able to isolate the electromagnetic effect!!

* P. Alonso-González, P. Albella et. Al, ***Nature Comms 3, 684 (2012).***

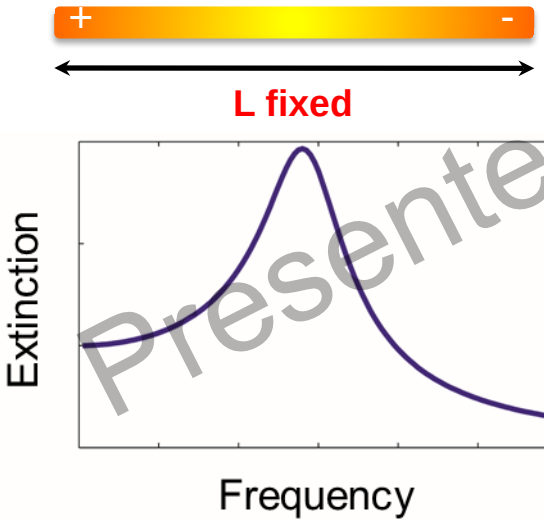
IR Spectroscopy of plasmonic antennas with S-SNOM. How?

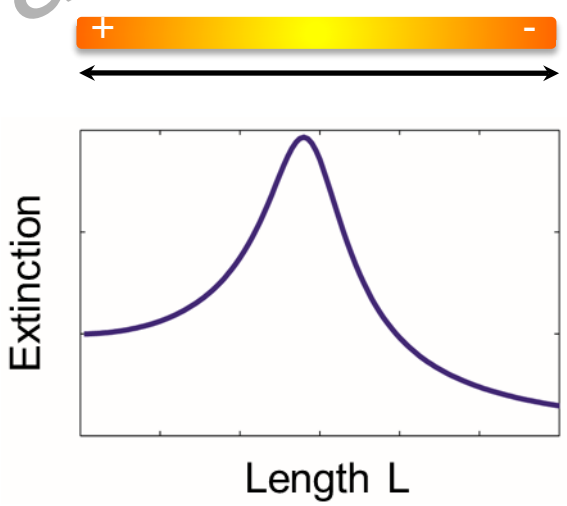


Spectroscopy in frequency is equivalent to spectroscopy in length.

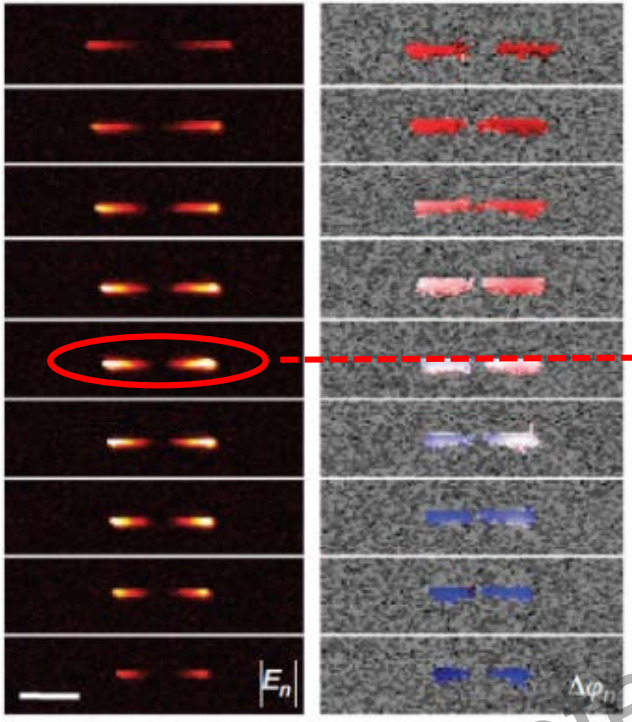
IR Light λ = 11.1 μm **fixed**

E_{in}

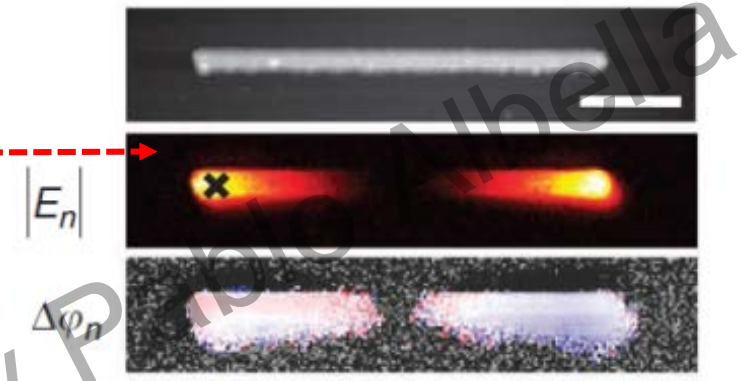


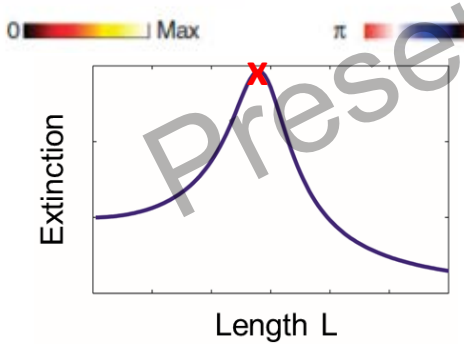


Surface Ehnanced Spectroscopy - Near Field Mapping



We clearly see the resonance behaviour, with the resonance appearing at L = 3.7 µm.





AIM: To relate the scattered field E_n with the local field enhancement f and proof that $E_n = f^2 \rightarrow I_n = f^4$

1. We measure $|En|$ and $\Delta\varphi_n$ at the hot spot (x)

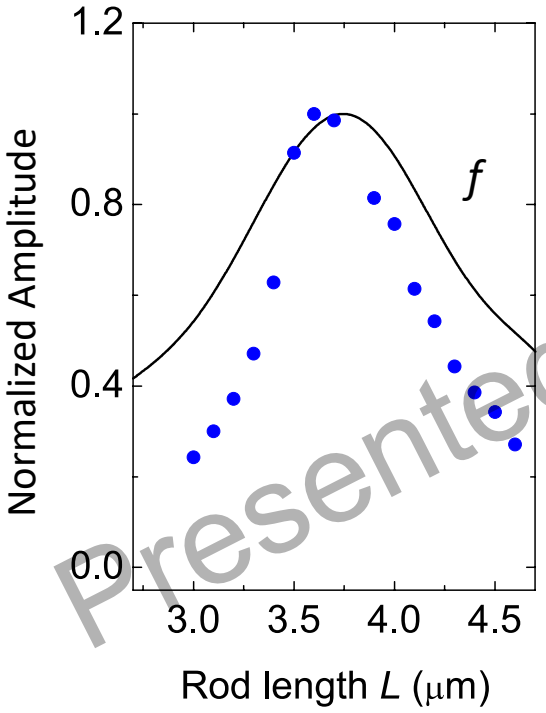
2. We compare them to the numerically calculated $|f|$ and $\Delta\varphi_f$ of the local field enhancement.

s-SNOM spectra do not agree with calculated near-field spectra!!

Single Rod

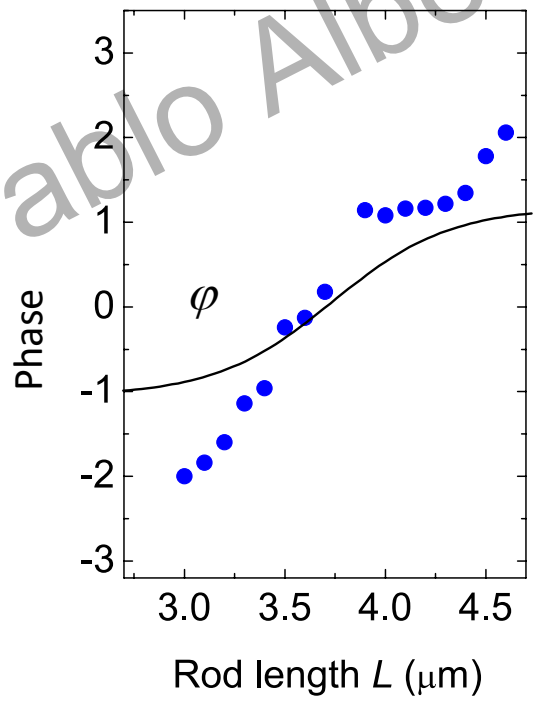
Calculated near-field enhancement f

Measured s-SNOM amplitude



Calculated near-field phase φ

Measured s-SNOM phase



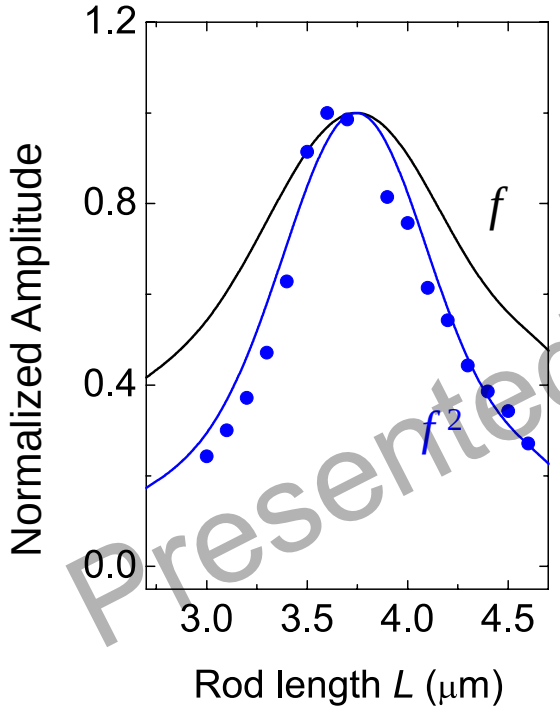
Square of the near field agrees well with s-SNOM data

Single Rod

Calculated near-field enhancement f

Measured s-SNOM amplitude

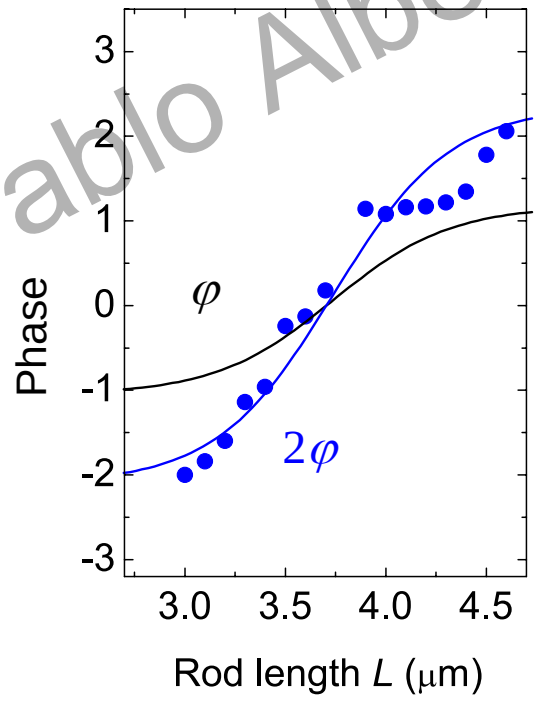
Squared calc. near-field enhancement f^2



Calculated near-field phase φ

Measured s-SNOM phase

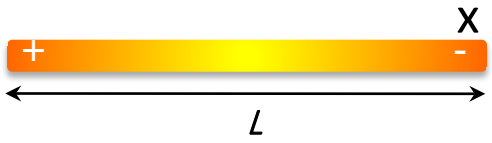
Doubled calc. near-field phase 2φ



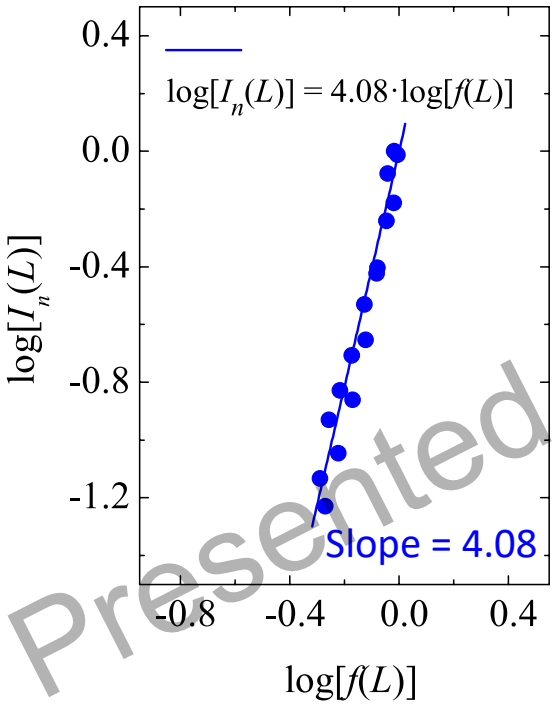
* P. Alonso-González, P. Albella et. Al, *Nature Comms 3, 684 (2012).*

Parametric representation (Intensity and Phase)

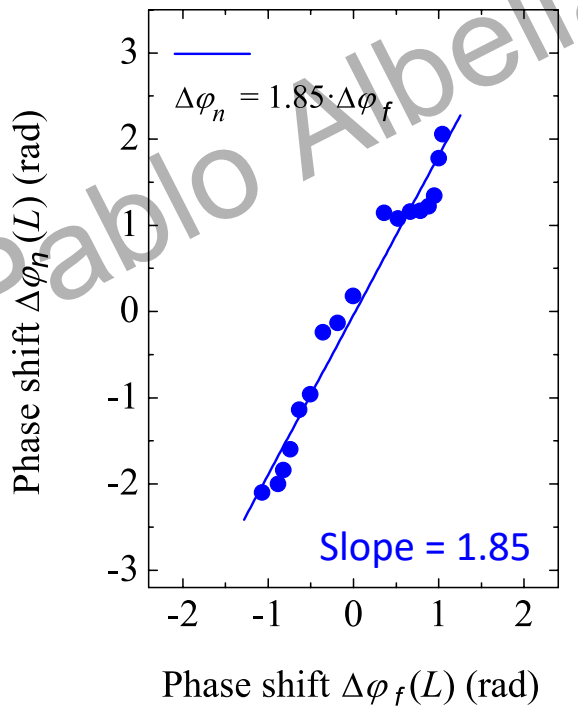
Single Rod



Intensity



Phase Shift

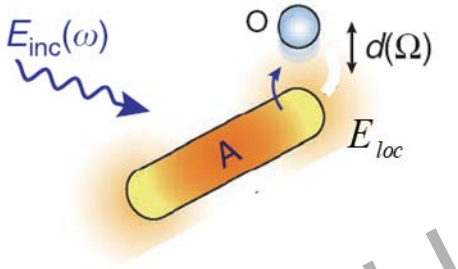


* P. Alonso-González, P. Albella et. Al, *Nature Comms 3, 684 (2012).*

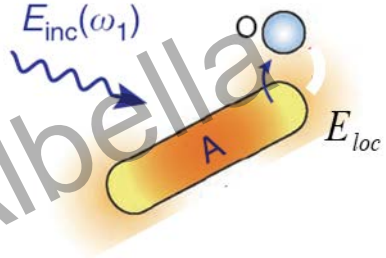
How we can understand this observation?

$$E_{loc} = f\,E_{inc}$$

Elastic antenna-enhanced scattering process



Antenna-enhanced Raman (**inelastic**) process (SERS)



* P. Alonso-González, P. Albella et. Al, *Nature Comms 3, 684 (2012).*

How we can understand this observation?

$$E_{loc} = f\,E_{inc}$$

$$E_{AOA} \propto f^2 E_{inc}$$

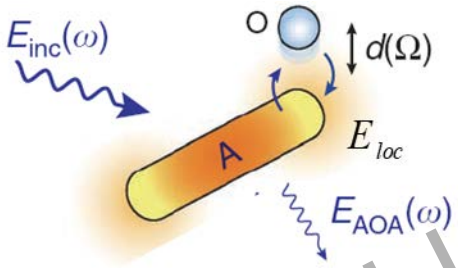
$$f = |f| e^{i\varphi}$$

field enhancement *f* is a complex value !

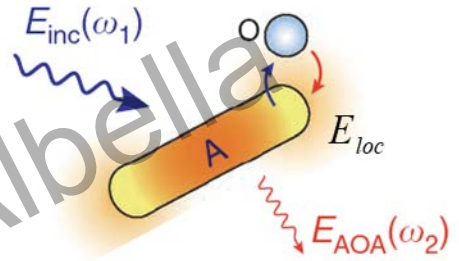
$$|E_{AOA}| \propto |f|^2 \quad \Rightarrow \quad I_{AOA} \propto |f|^4$$

$$\varphi_{AOA} = 2\varphi$$

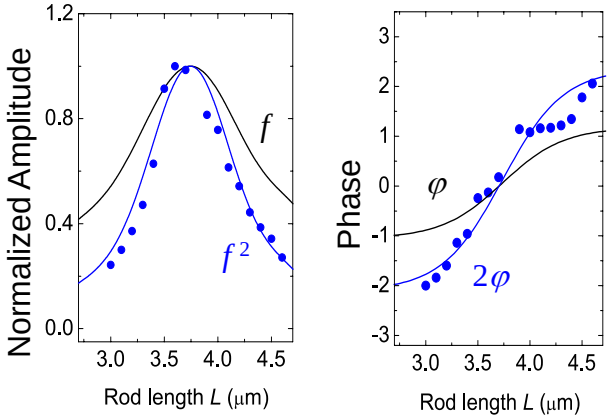
Elastic antenna-enhanced scattering process



Antenna-enhanced Raman (**inelastic**) process (SERS)

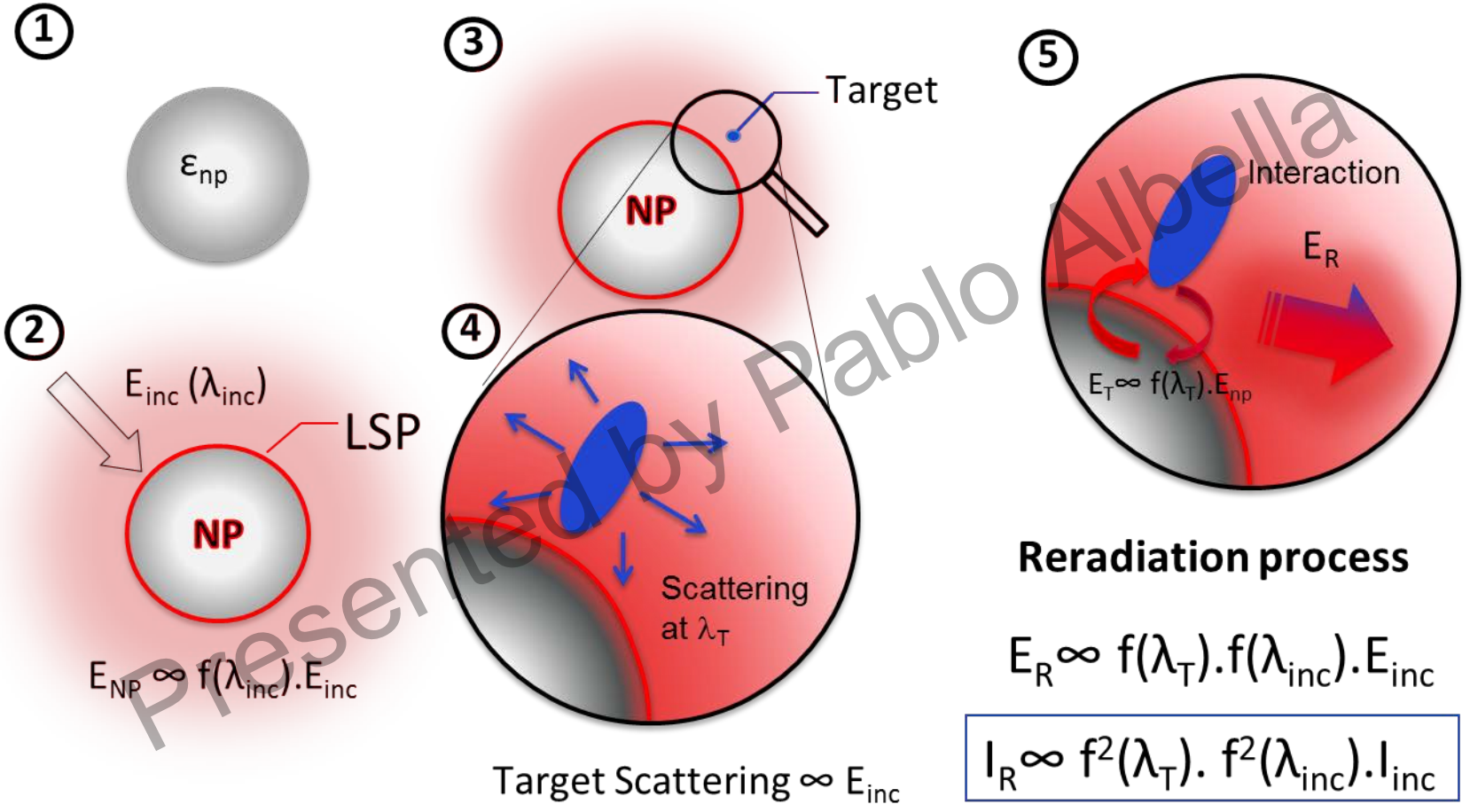


Double role of the antenna: illuminating the object and scattering off the object.



* P. Alonso-González, P. Albella et. Al, *Nature Comms 3, 684 (2012).*

How we can understand this observation? Other view…



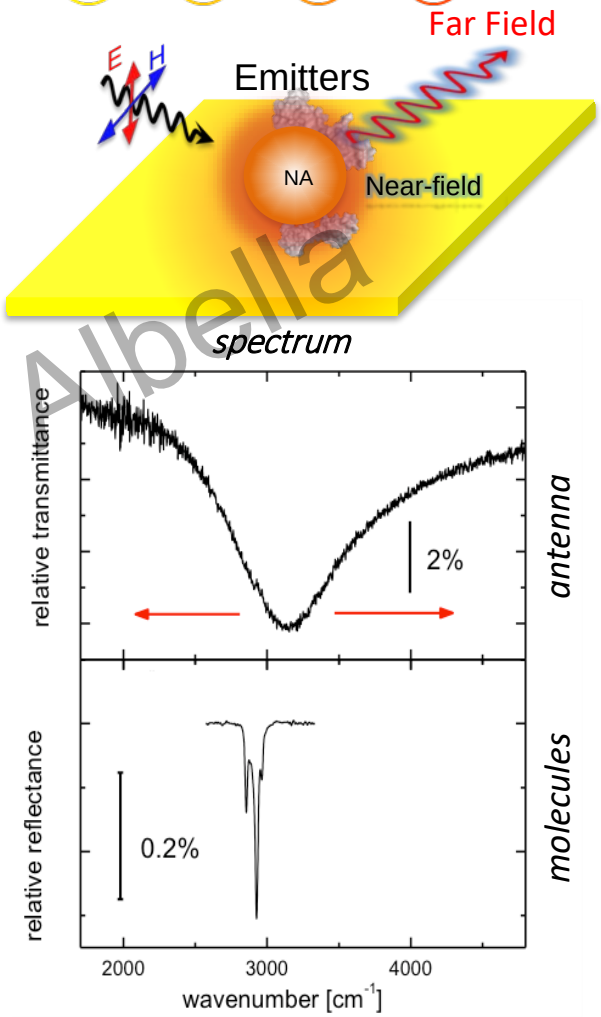
Part I: Introduction to SES and plasmonic nanoantennas

- **Idea in SES:** Using the enhanced electromagnetic near and far field of a nanostructure oscillating in resonance

- Pre-condition for SES[#,*]: Matching molecular vibration of interest and resonant excitation of the nanoantenna

- Very important to tune the resonance precisely! And with strong near and Far field enhancement!! **Why?**
  - Scattering will follow the **4th power SERS law**
  - Widely accepted, but not clearly shown why, until 2012*

* P. Alonso-González, P. Albella et. Al, ***Nature Comms 3, 684 (2012).***



[*] L. Novotny, PRL 98, 266802 (2007)

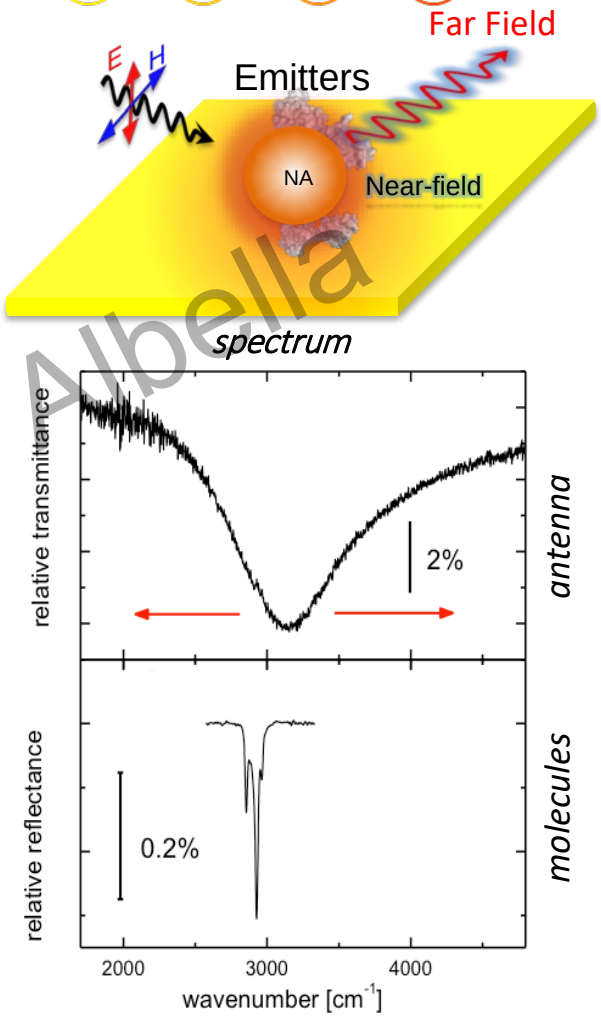
[#] F. Neubrech, Aizpurua et al., PRL 101, 157403 (2008)

Part I: Introduction to SES and plasmonic nanoantennas

- **Idea in SES:** Using the enhanced electromagnetic near and far field of a nanostructure oscillating in resonance

- Pre-condition for SES[#,*]: Matching molecular vibration of interest and resonant excitation of the nanoantenna

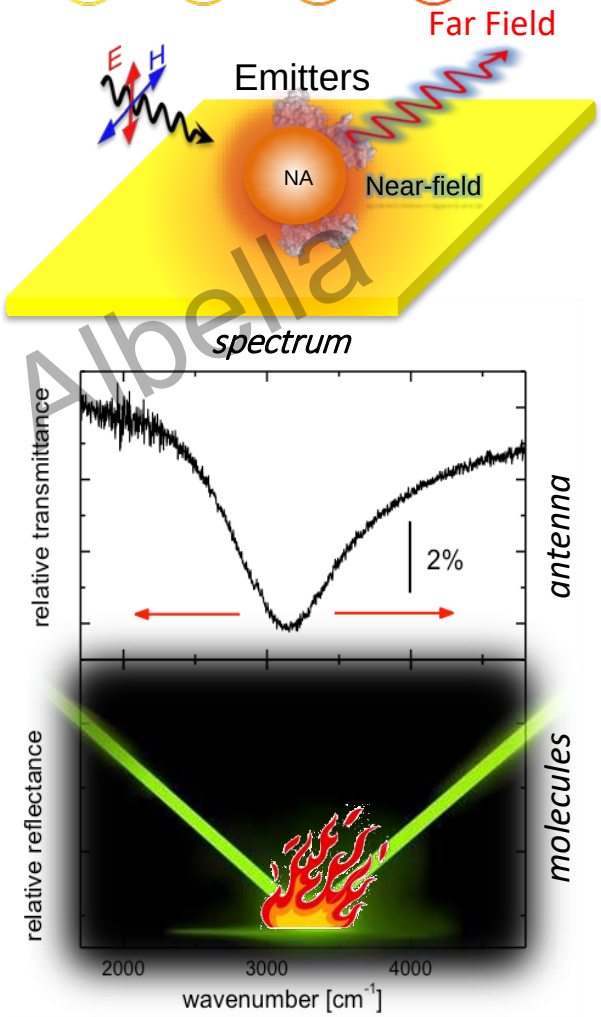
- Very important to tune the resonance precisely! And with strong near and Far field enhancement!! **Why?**
  - Scattering will follow the **4th power SERS law**
  - Widely accepted, but not clearly shown why, until 2012*
- *Good results in SERS, SEIRA and SEF applications, have been reported over the last 20 years…*
- All these is well known!



[#] F. Neubrech, Aizpurua et al., PRL 101, 157403 (2008)

Part I: Introduction to SES and plasmonic nanoantennas

- **Idea in SES:** Using the enhanced electromagnetic near and far field of a nanostructure oscillating in resonance
- Pre-condition for SES[#,*]: Matching molecular vibration of interest and resonant excitation of the nanoantenna
- Very important to tune the resonance precisely! And with strong near and Far field enhancement!! **Why?**
  - Scattering intensity will follow the **4th power SERS law**
  - Widely accepted, but not clearly shown why, until 2012*
- *Good results in SERS, SEIRA and SEF applications, have been reported over the last 20 years…*
- All these is well known! But what about losses and Heating issues in the nanoantennas?
- **Can dielectric nanoantennas play a new role in SES?...**



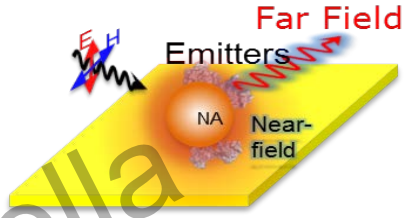
[*] L. Novotny, PRL 98, 266802 (2007)

[#] F. Neubrech, Aizpurua et al., PRL 101, 157403 (2008)

Outline

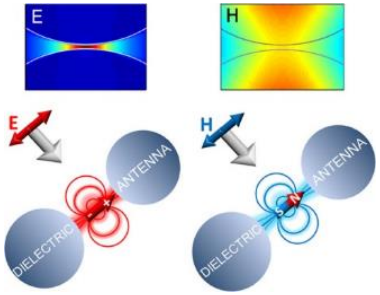
Part I:

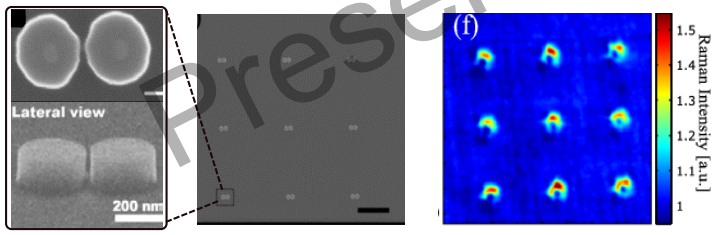
- **Surface Enhanced Spectroscopies (SES)**
  - Introduction to plasmonic nanoantennas and its limitations

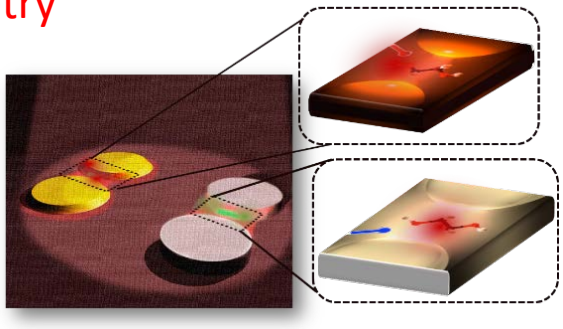


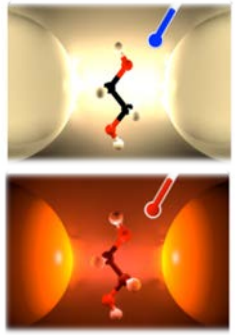
Part II:

- **Non-plasmonic HRI dielectric nanoantennas as an alternative to plasmonics for enhancing light (in near and far field) with low losses**
  - Electric and Magnetic Hot Spots
- **Experimental demonstration of these novel type of nanoantennas able to enhance Raman and Fluorescence:**
  - Heat assessment based on thermometry









Influence of losses/heat radiation to the efficiency of Surface Enhance Spectroscopies

- An effect of the losses in plasmonic structures, and an aspect quite often neglected with respect to SES, is the **local heating** of the particle due to the absorption of incident radiation and the transduction into thermal energy.

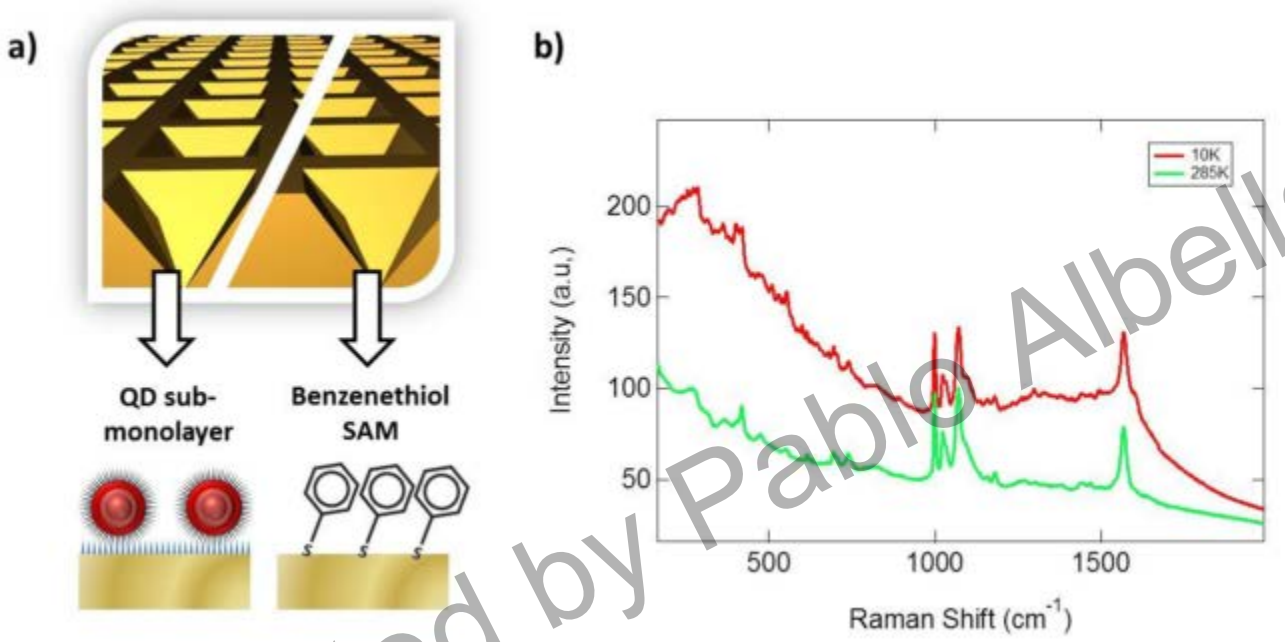
- Theoretical and experimental studies have reported temperature increases ranging from 50 K under continuous excitation to as high as 1000 K using pulsed light sources [#].

[*] M. D. King, J. Phys. Chem. C 2008, 112, 11751

Influence of losses/heat radiation to the efficiency of Surface Enhance Spectroscopies

- An effec … lected with res … of incident …

- Theoreti … s ranging from 50 … t sources [#].



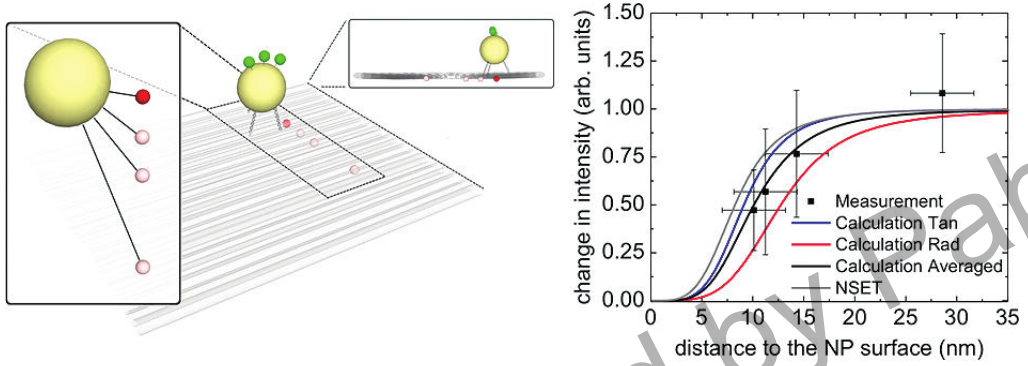
- *This increase in the particle T, and in turn in the T of the surrounding medium, can directly influence the SERS and SEF signals.*

  - *This fact has been attributed to several processes (thermal annealing, modified adsorption/desorption kinetics of surface molecules, and changes in the dielectric properties of the medium and NP) [*].*

[*] M. D. King, J. Phys. Chem. C 2008, 112, 11751

Plasmonic nanoantennas show strong hot spots but…

- **Metals (plasmonics) can offer very high relative field enhancements**
  - However, they exhibit high Ohmic losses that lead to local heating
    - Fluorescence quenching without spacer layers [*]
    - Can cause localised damage to the sample or molecules under study [**]

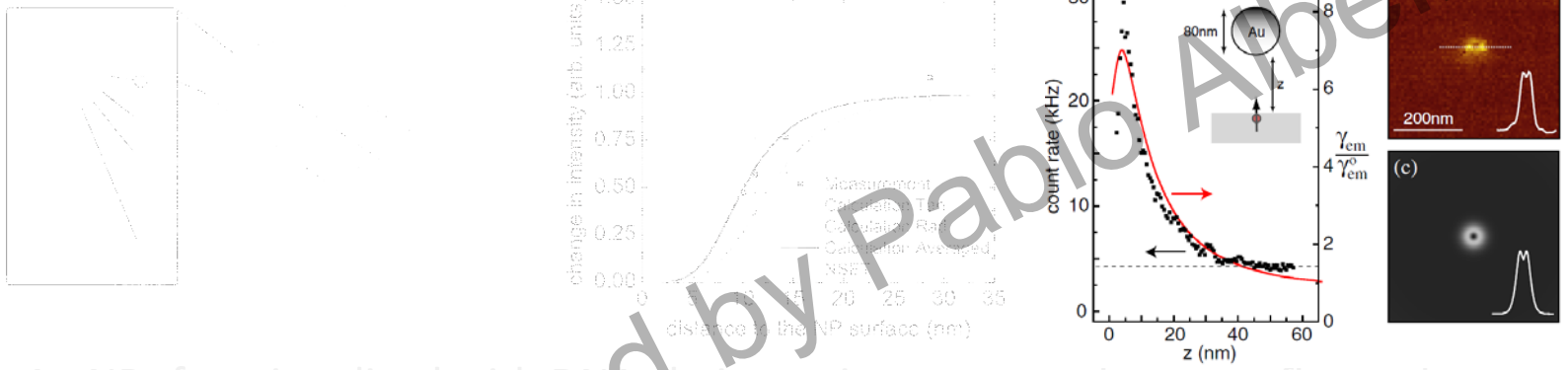


- Au NPs functionalised with DNA chains acting as spacer between fluorophore and nanoantenna.
  - SEF significant for distances larger than 10nm

[*] P. Holzmeister et al. *Nano Letters*, (4), 3189–3195, (2012).

[**] L. Novotny et al. *Phys Rev Lett. 96, 113002 (2006)*

Plasmonic nanoantennas show strong hot spots but…



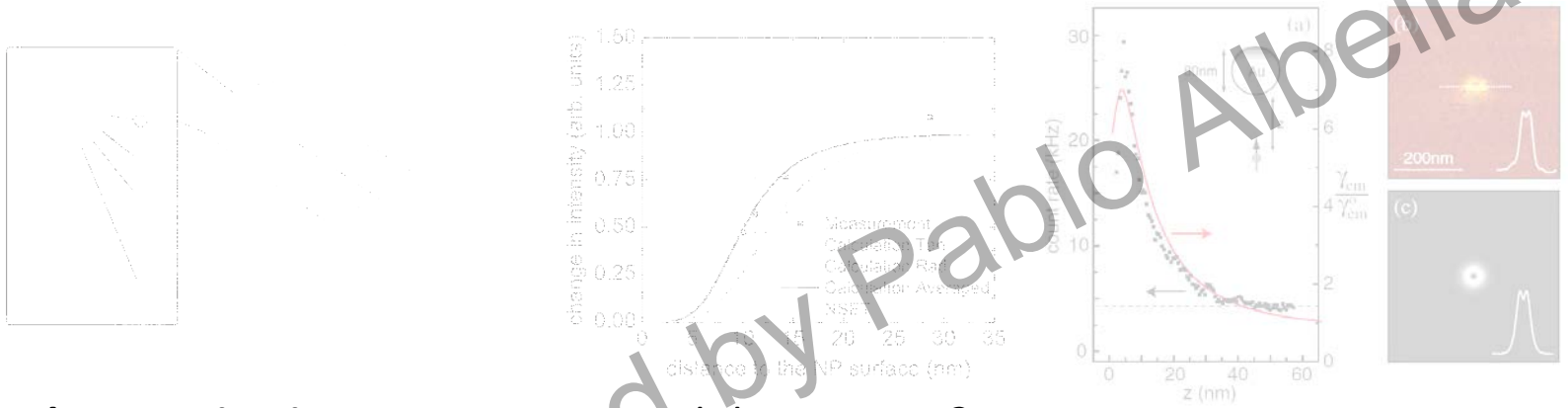
- *This would also damp the Raman strongly. Novotny quantitatively measured the continuous transition from fluorescence enhancement to fluorescence quenching on a single molecule.*

[*] P. Holzmeister et al. *Nano Letters*, (4), 3189–3195, (2012).

[**] L. Novotny et al. *Phys Rev Lett. 96, 113002 (2006)*

Alternatives to address this problem

- **Metals (plasmonics) can offer very high relative field enhancements**
  - However, they exhibit high Ohmic losses that lead to local heating
    - Fluorescence quenching without spacer layers [*]
    - Can cause localised damage to the sample or molecules under study [**]



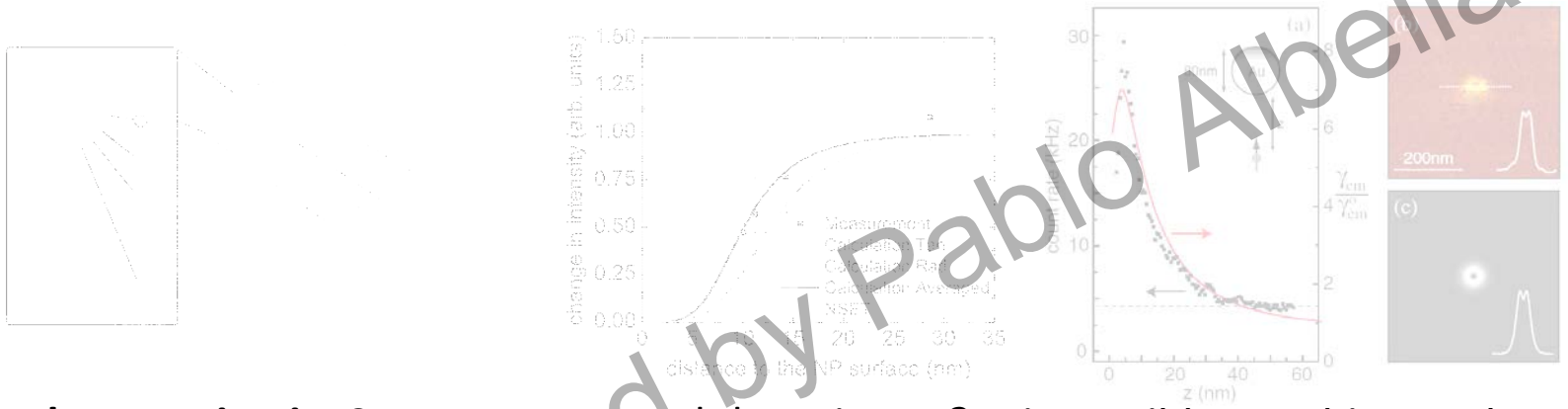
- **The question is:** Can we get around these issues? Is it possible to achieve enhanced NF and FF but under a low loss/heat response?

[*] P. Holzmeister et al. *Nano Letters*, (4), 3189–3195, (2012).

[**] L. Novotny et al. *Phys Rev Lett. 96, 113002 (2006)*

Alternatives to address this problem

- **Metals (plasmonics) can offer very high relative field enhancements**
  - However, they exhibit high Ohmic losses that lead to local heating
    - Fluorescence quenching without spacer layers [*]
    - Can cause localised damage to the sample or molecules under study [**]

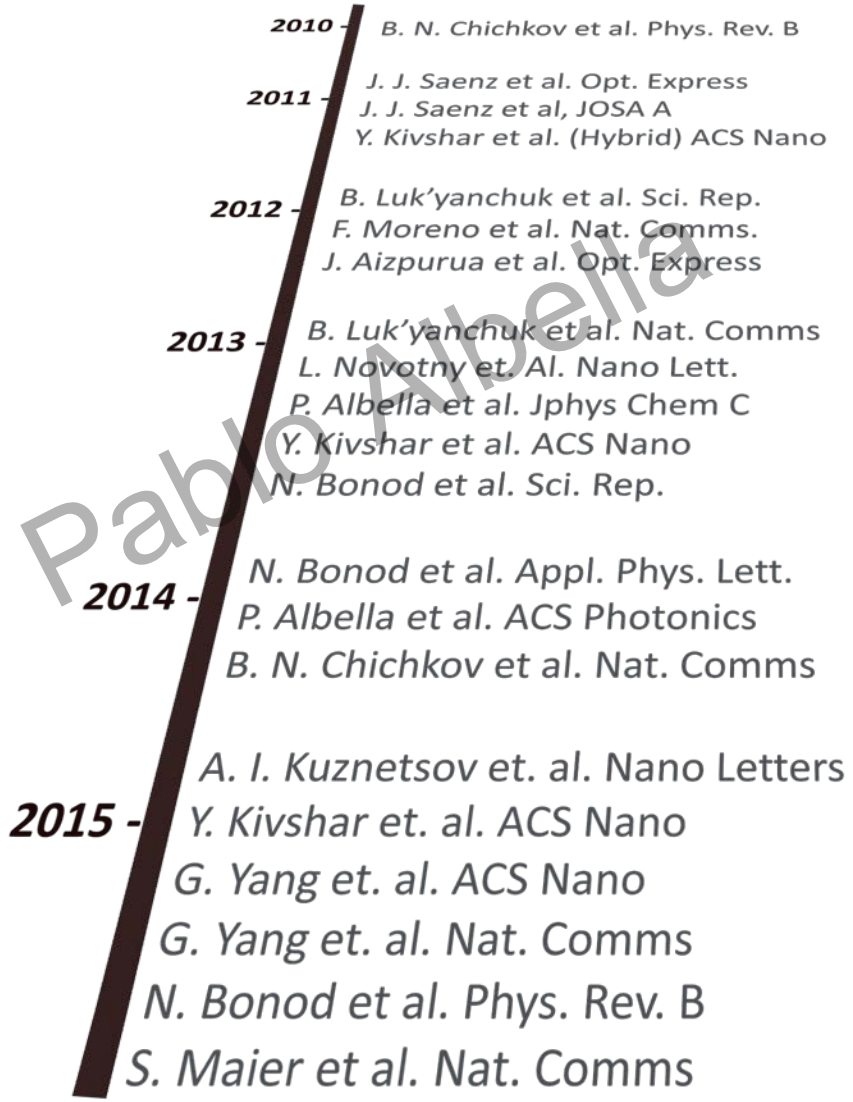


- **The question is:** Can we get around these issues? Is it possible to achieve enhanced NF and FF but under a low loss/heat response?
- **The answer is: Yes, Non-Plasmonic Nanoantennas can!**
  - Nanostructures made of dielectrics with high refractive index - Si, Ge, GaAs, GaP
  - *Important to note that we refer to individual structures, not metasurfaces!*

[*] P. Holzmeister et al. *Nano Letters*, (4), 3189–3195, (2012).

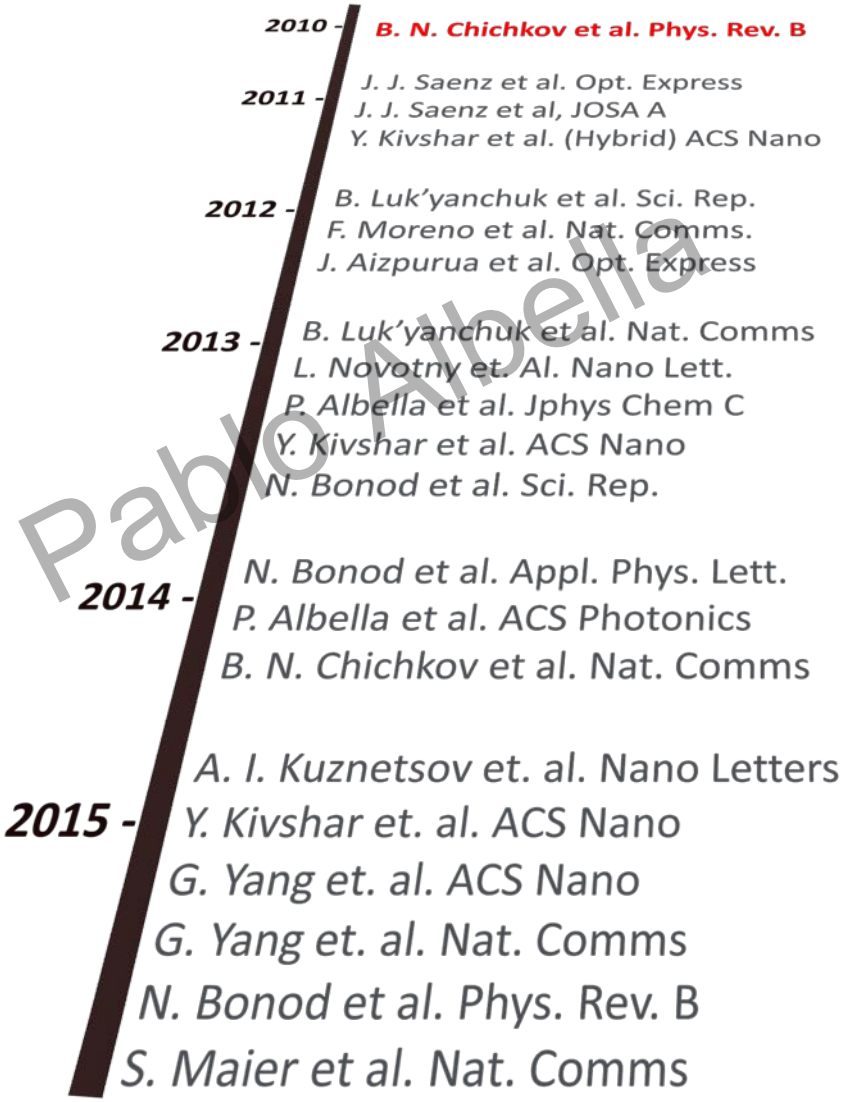
[**] L. Novotny et al. *Phys Rev Lett. 96, 113002 (2006)*

A bit of literature review on HRI dielectrics…



A bit of literature review on HRI dielectrics…

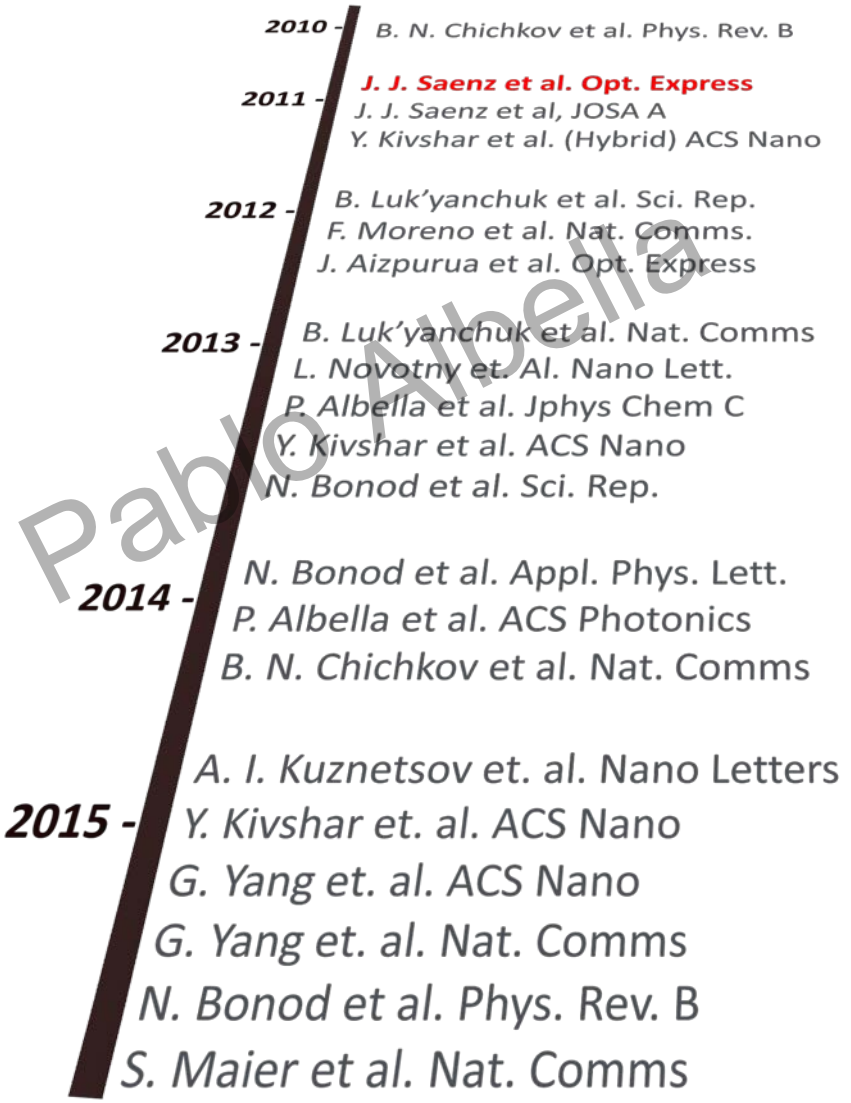
- Theoretically revealed magnetic dipolar response in silicon NP arrays…
- but no addressing NF or origin of this.



A bit of literature review on HRI dielectrics…

- Theoretically revealed magnetic dipolar response in silicon NP arrays…
- but no addressing NF or origin of this.

- Theoretically studied how the rotation of displacement current induces magnetic responses and analysed near fields with a single silicon sphere

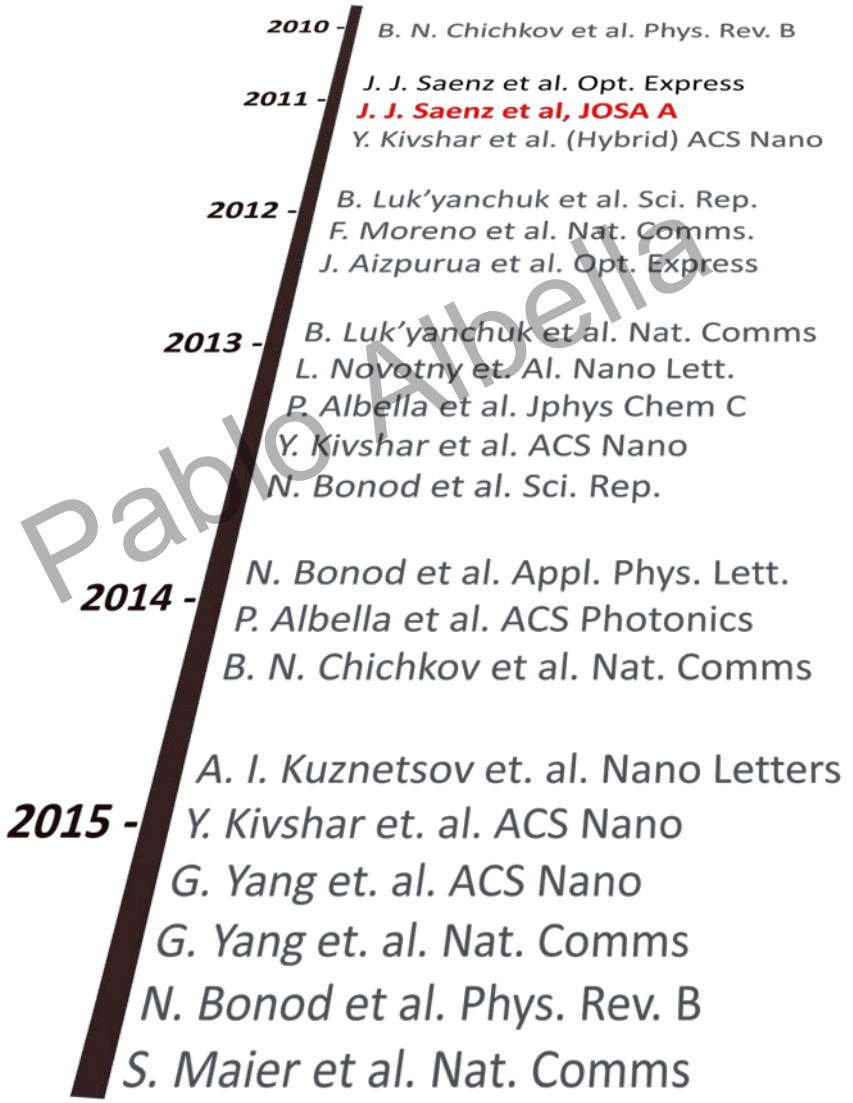


A bit of literature review on HRI dielectrics…

- Theoretically revealed magnetic dipolar response in silicon NP arrays…
- but no addressing NF or origin of this.

- Theoretically studied how the rotation of displacement current induces magnetic responses and analysed near fields with a single silicon sphere

- Theoretically revealed that silicon sphere can fulfil the Kerker's conditions



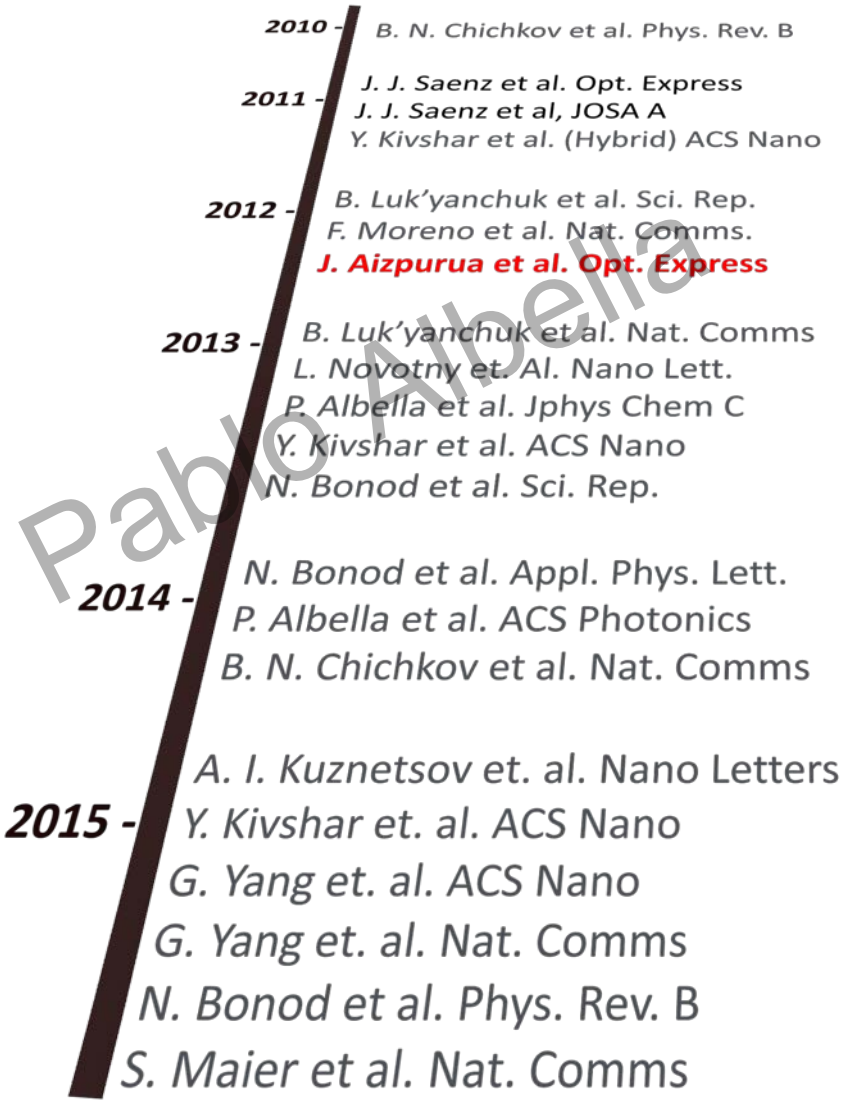
A bit of literature review on HRI dielectrics…

- Theoretically revealed magnetic dipolar response in silicon NP arrays…
- but no addressing NF or origin of this.

- Theoretically studied how the rotation of displacement current induces magnetic responses and analysed near fields with a single silicon sphere

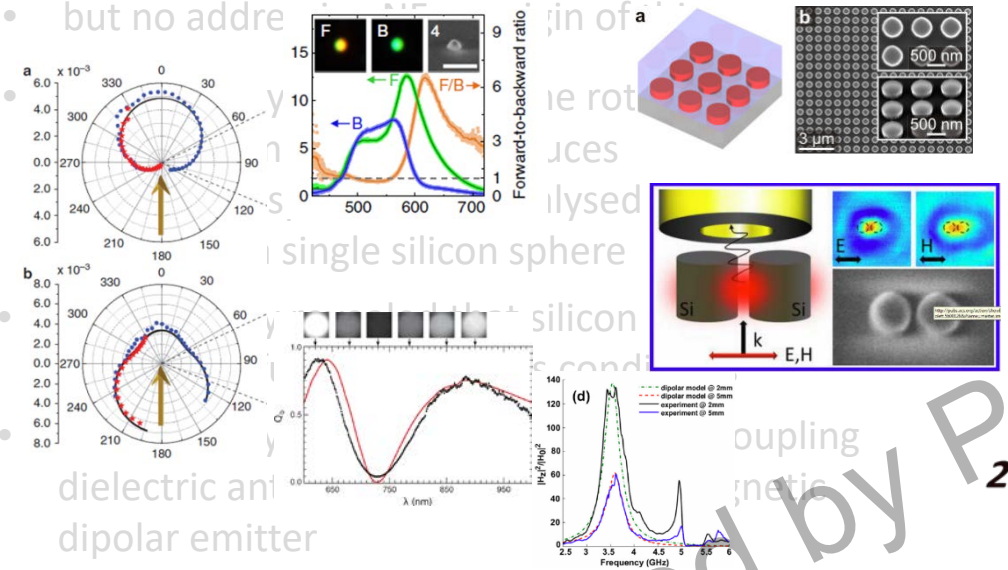
- Theoretically revealed that silicon sphere can fulfil the Kerker's conditions

- Theoretically explored the concept of coupling dielectric antennas with electric or magnetic dipolar emitter



A bit of literature review on HRI dielectrics…

- Theoretically revealed magnetic dipolar response in silicon NP arrays…
- but no addre… …gin of …
- … …e rot…
- … …uces …
- … …lysed …
- … single silicon sphere
- … …silicon …
- … …oupling …
- dielectric ant… …gnetic… dipolar emitter



- **Experimentally demonstrated those findings either in the visible, near IR or microwave…**

2010 - B. N. Chichkov et al. Phys. Rev. B

2011 - J. J. Saenz et al. Opt. Express
J. J. Saenz et al, JOSA A
Y. Kivshar et al. (Hybrid) ACS Nano

2012 - **B. Luk'yanchuk et al. Sci. Rep.**
F. Moreno et al. Nat. Comms.
J. Aizpurua et al. Opt. Express

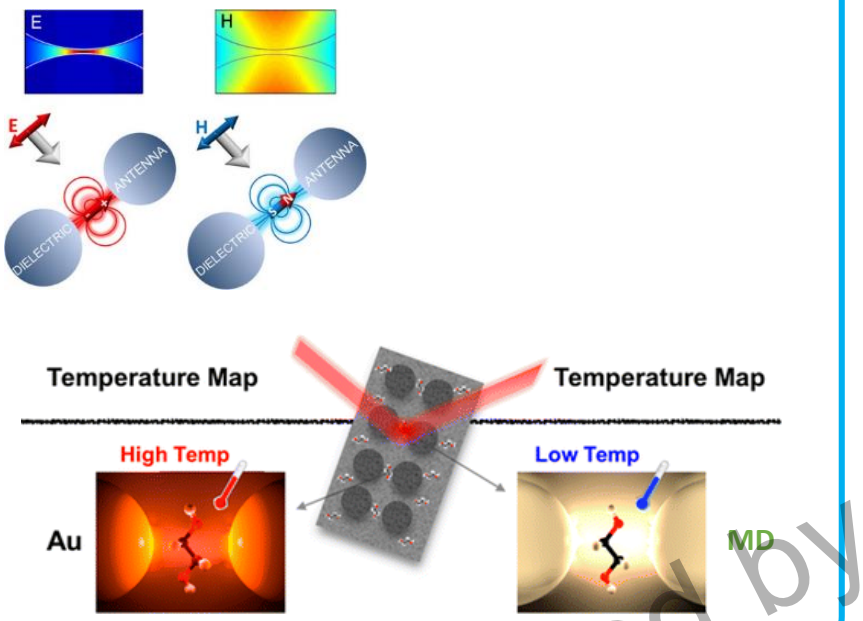
2013 - **B. Luk'yanchuk et al. Nat. Comms**
L. Novotny et. Al. Nano Lett.
P. Albella et al. Jphys Chem C
Y. Kivshar et al. ACS Nano
N. Bonod et al. Sci. Rep.

2014 - N. Bonod et al. Appl. Phys. Lett.
P. Albella et al. ACS Photonics
B. N. Chichkov et al. Nat. Comms

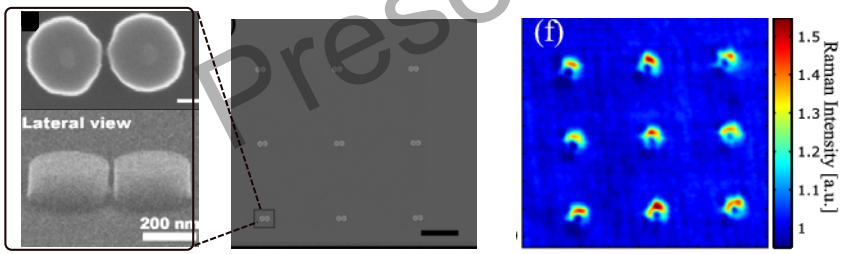
2015 - **A. I. Kuznetsov et. al. Nano Letters**
Y. Kivshar et. al. ACS Nano
G. Yang et. al. ACS Nano
G. Yang et. al. Nat. Comms
N. Bonod et al. Phys. Rev. B
S. Maier et al. Nat. Comms

Our aim is: Non-Plasmonic (all-dielectric) Nanoanntenas for SES

Theoretical Proposals



First Experimental Proof



2010 - B. N. Chichkov et al. Phys. Rev. B

2011 - J. J. Saenz et al. Opt. Express
J. J. Saenz et al, JOSA A
Y. Kivshar et al. (Hybrid) ACS Nano

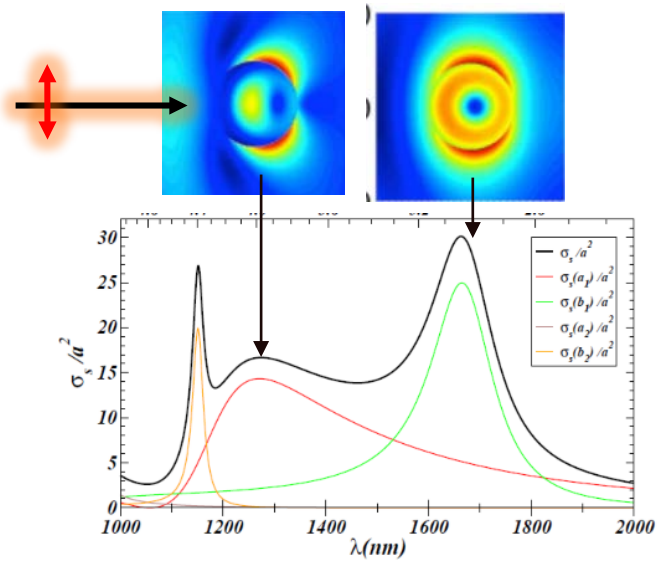
2012 - B. Luk'yanchuk et al. Sci. Rep.
F. Moreno et al. Nat. Comms.
J. Aizpurua et al. Opt. Express

2013 - B. Luk'yanchuk et al. Nat. Comms
L. Novotny et. Al. Nano Lett.
P. Albella et al. Jphys Chem C
Y. Kivshar et al. ACS Nano
N. Bonod et al. Sci. Rep.

2014 - N. Bonod et al. Appl. Phys. Lett.
P. Albella et al. ACS Photonics
B. N. Chichkov et al. Nat. Comms

2015 - A. I. Kuznetsov et. al. Nano Letters
Y. Kivshar et. al. ACS Nano
G. Yang et. al. ACS Nano
G. Yang et. al. Nat. Comms
N. Bonod et al. Phys. Rev. B
S. Maier et al. Nat. Comms

Non-Plasmonic HRI Nanoantennas

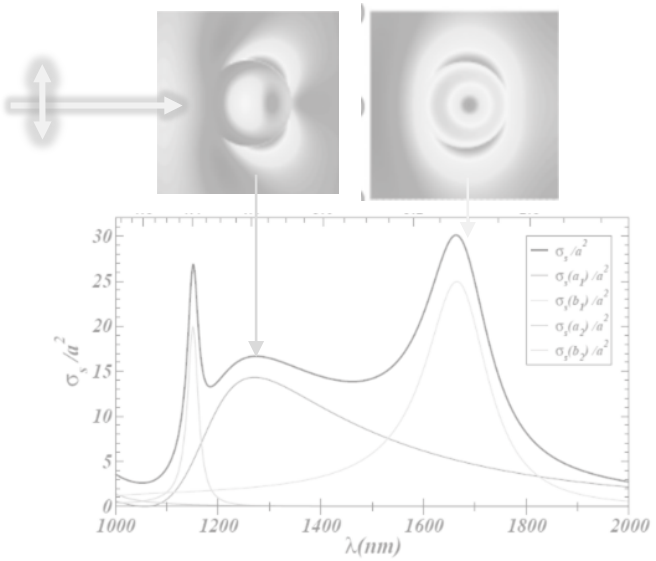


Scattering of Si particle (r = 230 nm)

- Strong magnetic resonances
- Field enhancement inside particle

*A. Garcia-Etxarri et al., Opt. Express. **19**, 4815 (2011)

Non-Plasmonic HRI Nanoantennas: Hot Spots and FF enhancement

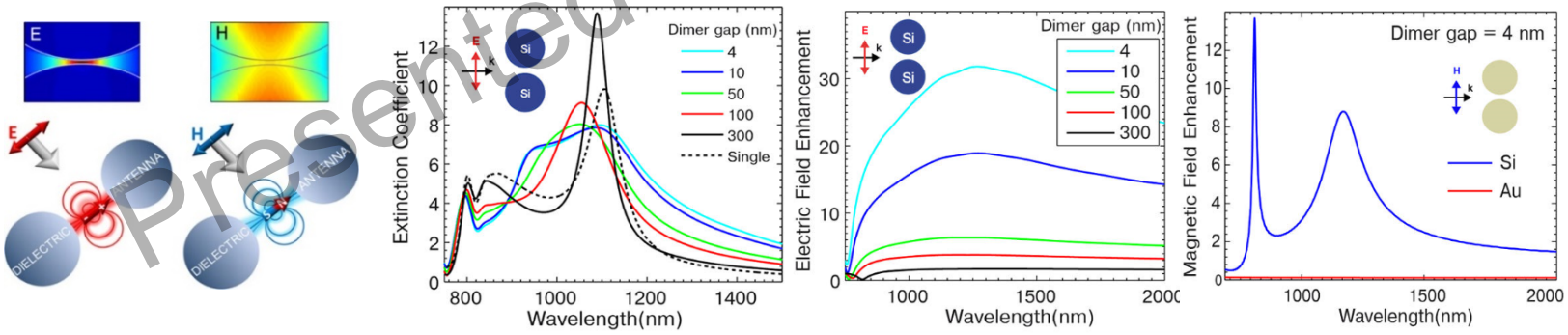


Scattering of Si particle (r = 230 nm)

- Low energy losses
- Strong magnetic resonances
- Field enhancement inside particle

*A. García-Etxarri et al., Opt. Express. **19**, 4815 (2011)

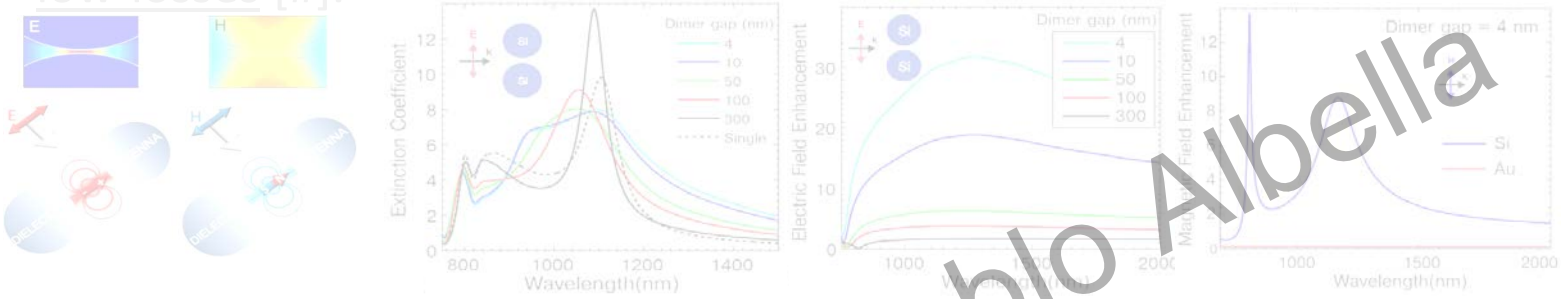
- In 2013 we theoretically showed how Silicon dimers offer not only, near and far field **electric** enhancement but also **magnetic**, <u>both under very low-losses</u> [#].



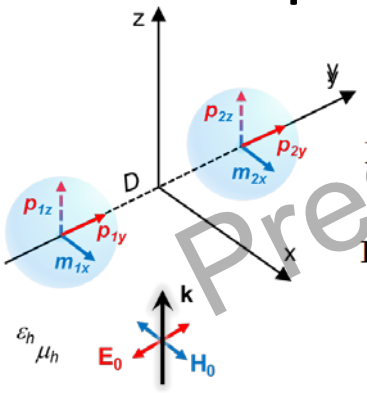
[#] P. Albella, M.A. Poyli, M.Schmidt, Stefan A. Maier, F. Moreno, J.J. Sáenz, J.Aizpurua, **J. Phys Chem C, 117, 13573 (2013)**

Non-Plasmonic HRI Nanoantennas: Hot Spots and FF enhancement

- In 2013 we theoretically showed how Silicon dimers offer not only, near and far field **electric** enhancement but also **magnetic**, both under very low-losses [#].

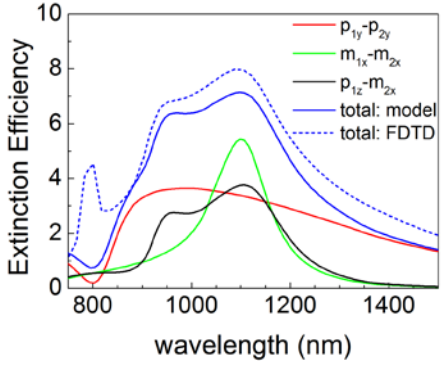


- The Near and Far Field Electric and Magnetic Field enhancements are due to the interaction between electric and magnetic Mie modes, **and can be spectrally tuned.**



$$\mathbf{E}_{scat}(\mathbf{r}) = \sum_{j=1,2} \left\{ \frac{k^2}{\epsilon_0 \epsilon_h} \overleftrightarrow{\mathbf{G}}_E (\mathbf{r}-\mathbf{r}_j) \cdot \mathbf{p}_j + iZk^2 \overleftrightarrow{\mathbf{G}}_M (\mathbf{r}-\mathbf{r}_j) \cdot \mathbf{m}_j \right\}$$

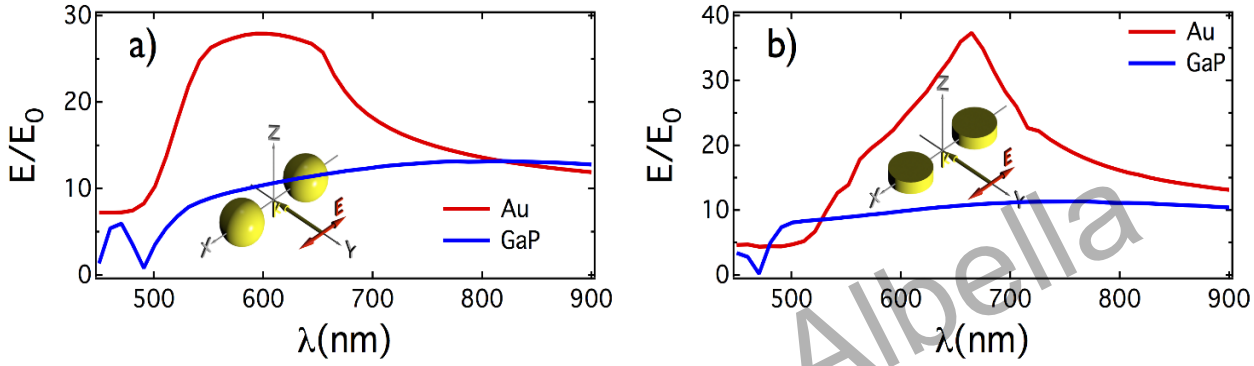
$$\mathbf{H}_{scat}(\mathbf{r}) = \sum_{j=1,2} \left\{ -i\frac{1}{Z}\frac{k^2}{\epsilon_0 \epsilon_h} \overleftrightarrow{\mathbf{G}}_M (\mathbf{r}-\mathbf{r}_j) \cdot \mathbf{p}_j + k^2 \overleftrightarrow{\mathbf{G}}_E (\mathbf{r}-\mathbf{r}_j) \cdot \mathbf{m}_j \right\}$$



[#] P. Albella, M.A. Poyli, M.K. Schmidt, Stefan A. Maier, F. Moreno, J.J. Sáenz & J. Aizpurua, **J. Phys Chem C, 117, 13573 (2013)**

HRI Nanoantennas in the VIS: Hot Spots and FF Enhancement

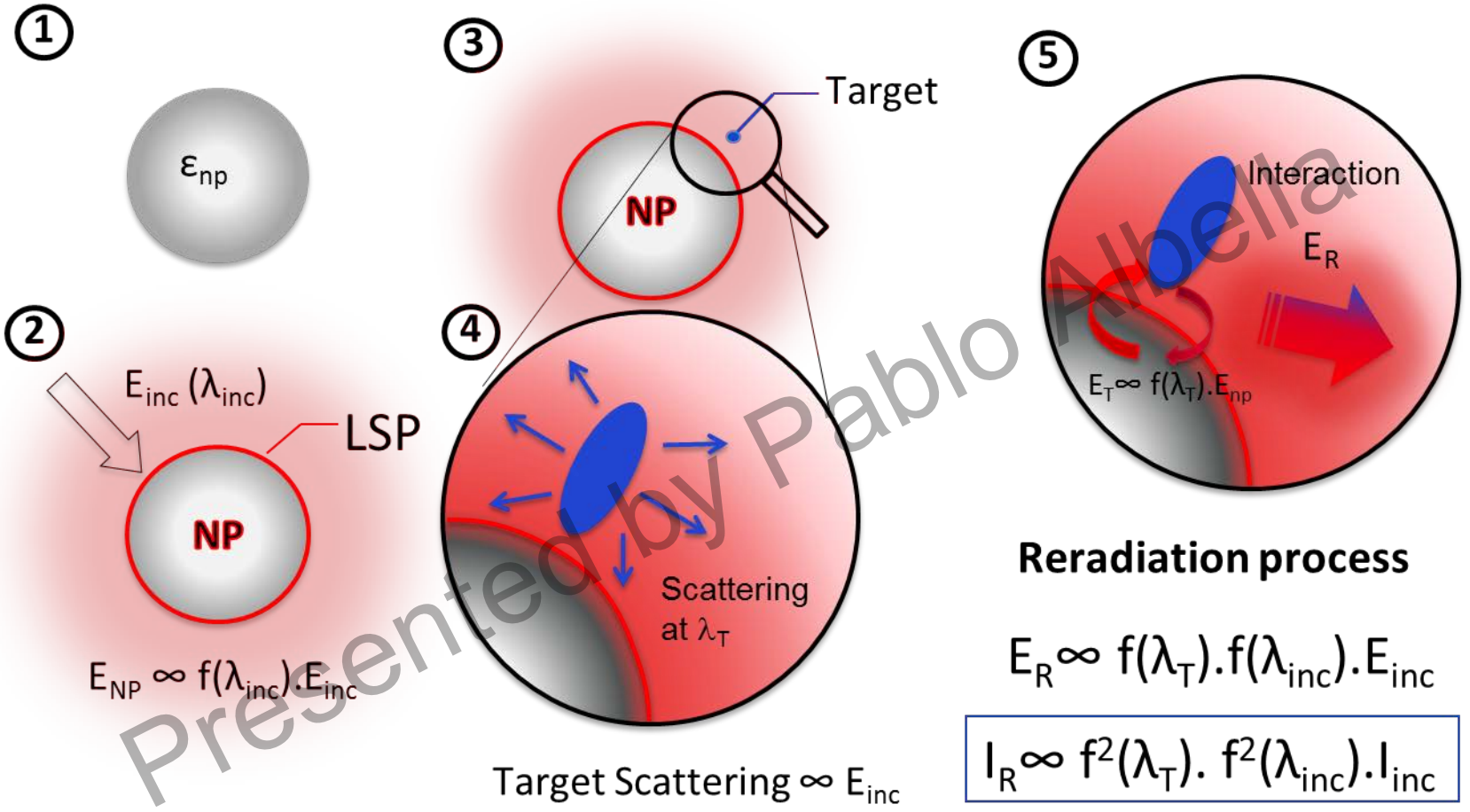
Near Field Response



- Au dimers offer better NF enhancement when compared with the Non-plasmonic ones.

*P. Albella, R. Alcaraz de la Osa, F. Moreno and S. A. Maier. **ACS Photonics** 1, 524-529 (2014)

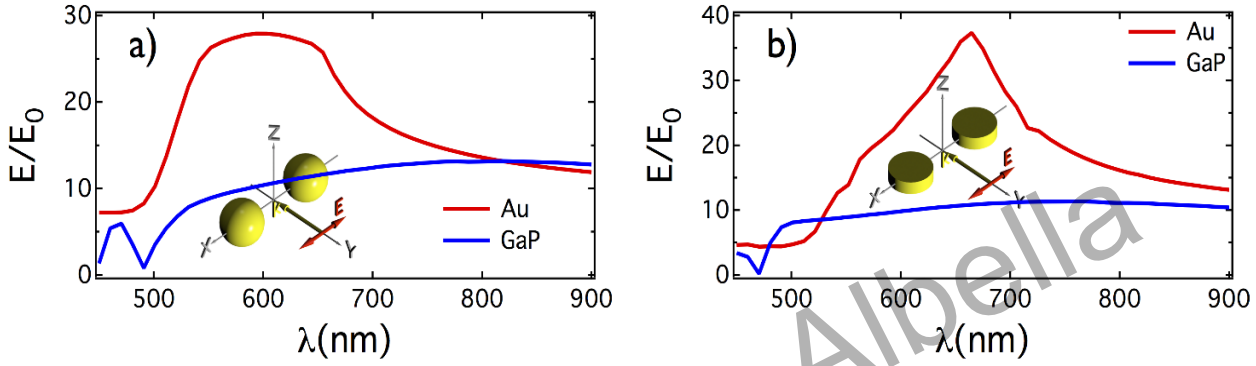
HRI Nanoantennas in the VIS: Hot Spots and FF Enhancement



* P. Alonso-González, P. Albella et. Al, *Nature Comms 3, 684 (2012).*

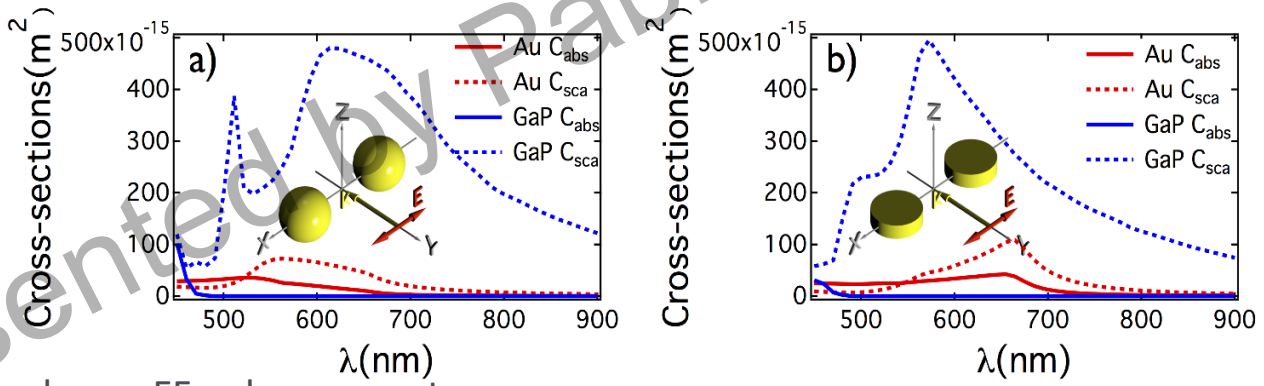
HRI Nanoantennas in the VIS: Hot Spots and FF Enhancement

Near Field Response



- Au dimers offer better NF enhancement when compared with the Non-plasmonic ones.

Far Field Response



- HRI antennas show larger FF enhancement.
- More Scattering efficiency together with the possibility of increasing the incident power can compensate the smaller NF enhancement in SES applications

*P. Albella, R. Alcaraz de la Osa, F. Moreno and S. A. Maier. ACS Photonics 1, 524-529 (2014)

Theoretical Proposal

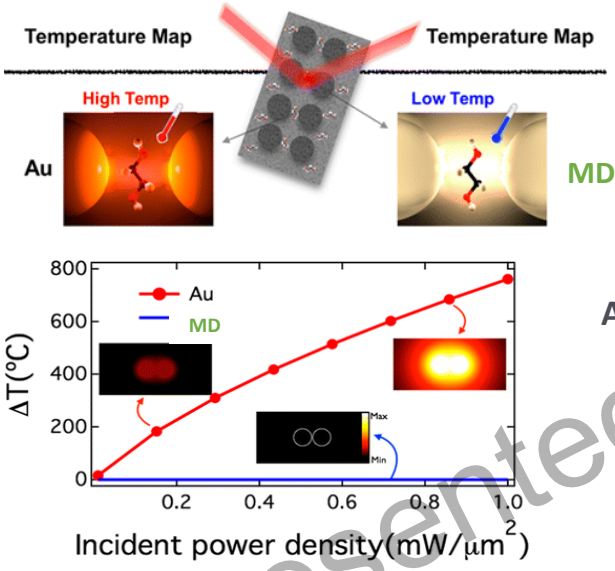
Non-Plasmonic nanoantenas: low local temperature

- We have seen that HRI dielectric nanoantennas can generate hot spots and good scattering efficiency.
- The idea of looking for alternatives to plasmonic nanoantennas came up from the large absorption and therefore heat that they generate in their surrounding

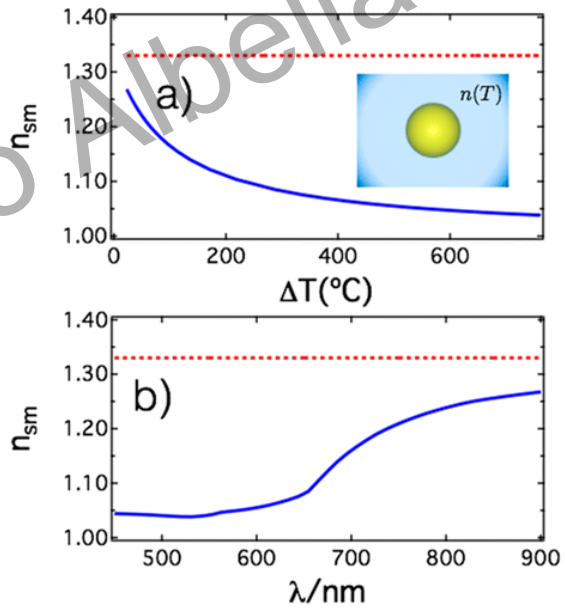
Theoretical Proposal

Non-Plasmonic nanoantenas: low local temperature

- We have seen that HRI dielectric nanoantennas can generate hot spots and good scattering efficiency.
- The idea of looking for alternatives to plasmonic nanoantennas came up from the large absorption and therefore heat that they generate in their surrounding



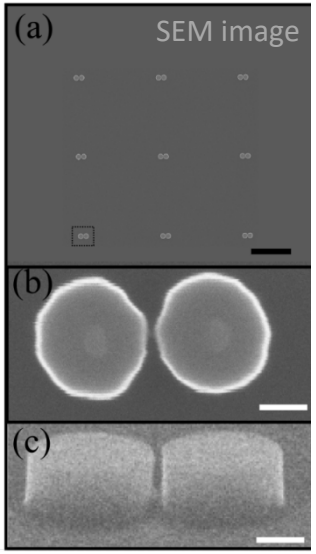
ACS Photonics 1, 524-529 (2014)



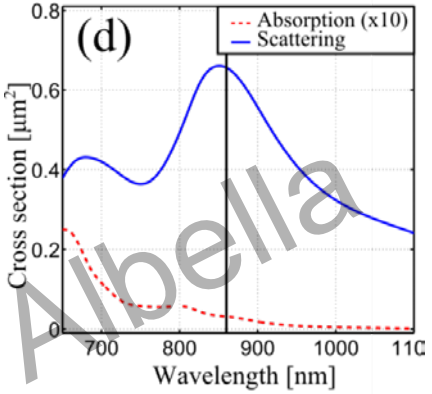
- Metals can produce extreme changes in local temperature (implications for SERS and SEF)
  - Damage to antennas and molecules
  - Can modify the local environment (n) and/or possibly degrade the performance

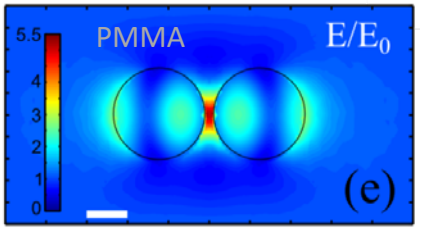
Experimental Demonstration:
Low-Heat SERS and SEF with Si-Dimers

Si Dimers D=220nm, h=200nm, gap~20nm fabricated with reactive ion etching on Si-on-insulator wafers



Far and Near Field Response



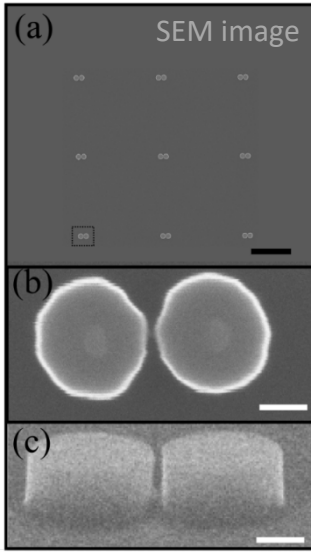


- Resonance is a mix between electric and magnetic modes in Si (purely electric in Au)
- Reasonable NF enhancement for Si, although not as high as Au (but FF enhancement and hot spot volume compensates this).

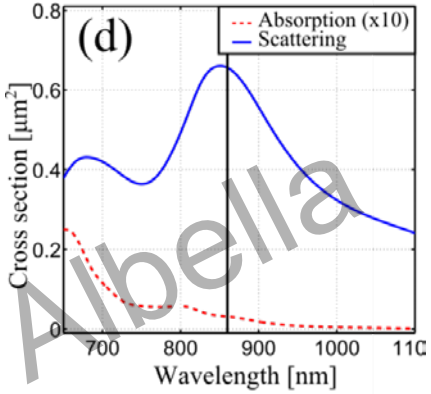
*M. Caldarola, P. Albella et al, Nature Comms 6:7915 (2015)

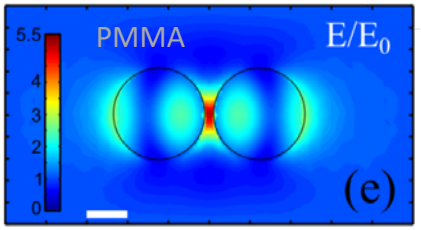
Experimental Demonstration:
Low-Heat SERS and SEF with Si-Dimers

Si Dimers D=220nm, h=200nm, gap~20nm fabricated with reactive ion etching on Si-on-insulator wafers



Far and Near Field Response



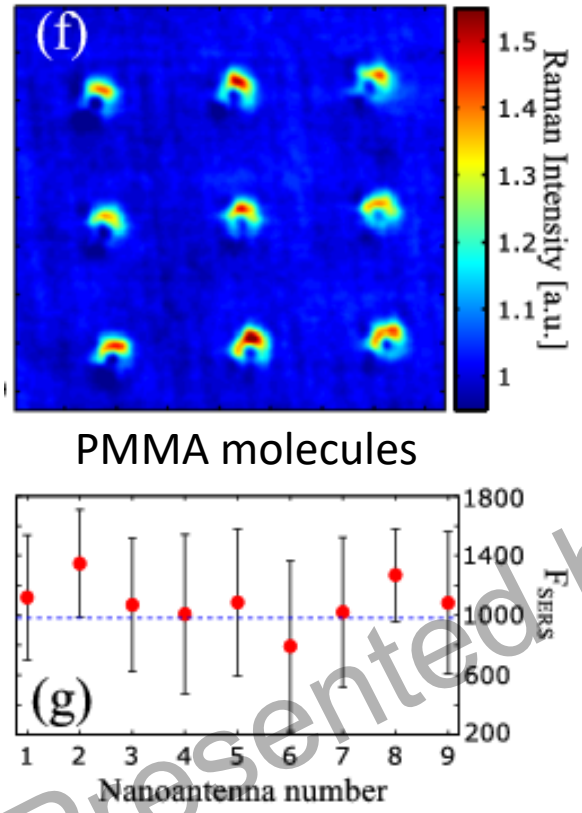


- Resonance is a mix between electric and magnetic modes in Si (purely electric in Au)
- Reasonable NF enhancement for Si, although not as high as Au (**but FF enhancement and hot spot volume compensates this**).
- **Higher E/E0 can be achieved by engineering future dielectric nanoantenna configurations**

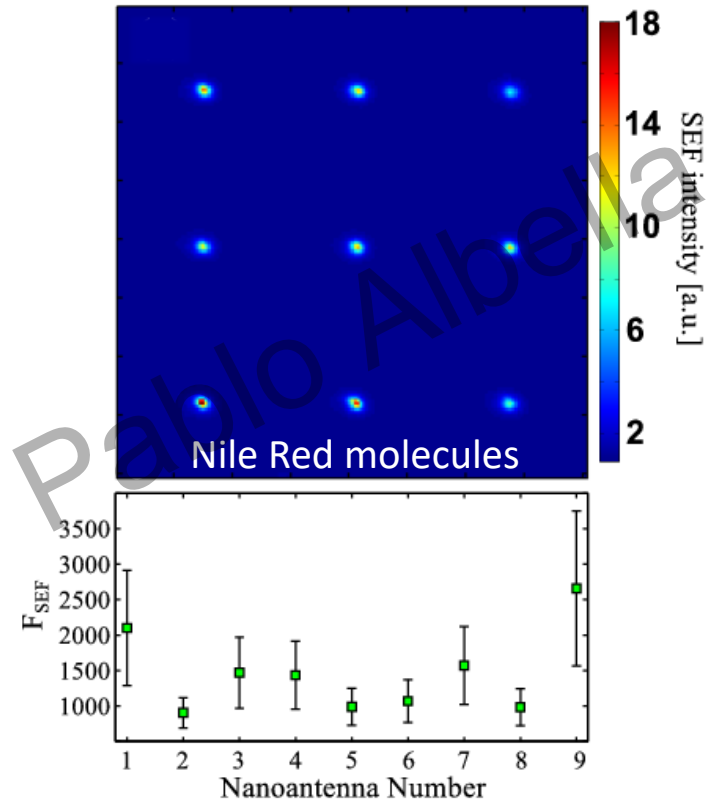
*M. Caldarola, P. Albella et al, Nature Comms 6:7915 (2015)

Experimental proof of SERS and SEF with the same Si-Dimers

Surface-Enhanced Raman (SERS)



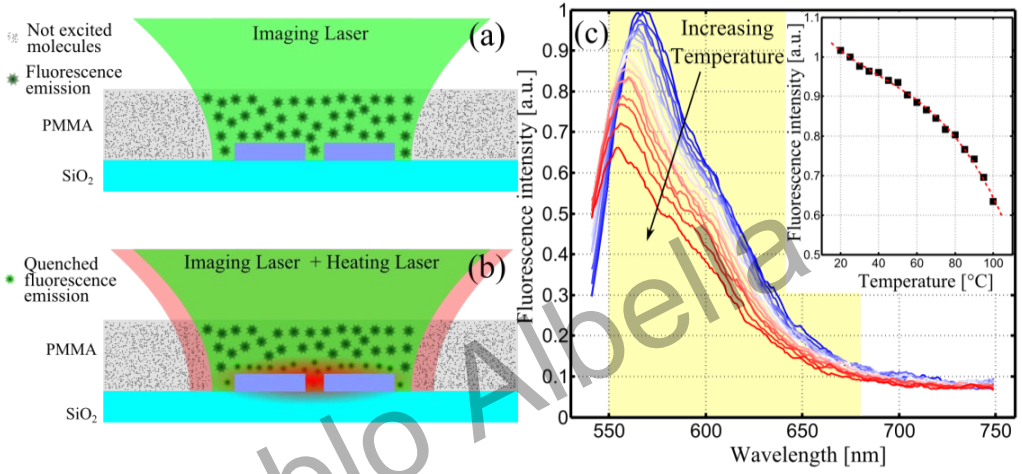
Surface-Enhanced Fluorescence(SEF)



- Sample shows both enhanced Raman scattering and enhanced fluorescence

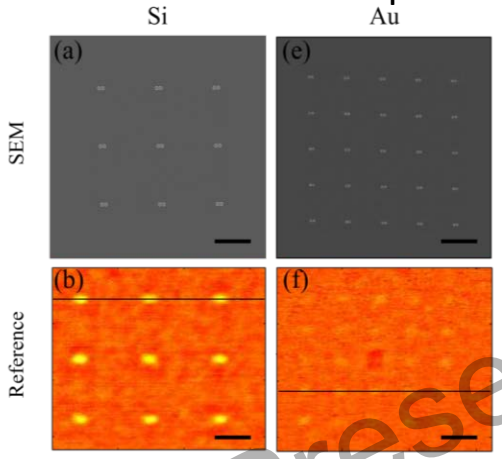
Assessment of Local Heat based on Molecular thermometry

- Local heat generation around the NA was determined using molecular thermometry.
- 2 lasers:
  - Heating laser on resonance with the NA.
  - Imaging laser
- Spectral shifts and reduction in intensity of nile red molecules upon increase in T.



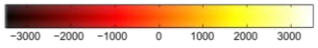
Heating laser λ=860-890nm

Low power Imaging laser λ=532nm



Reference: fluorescence images without the heating laser turned on.

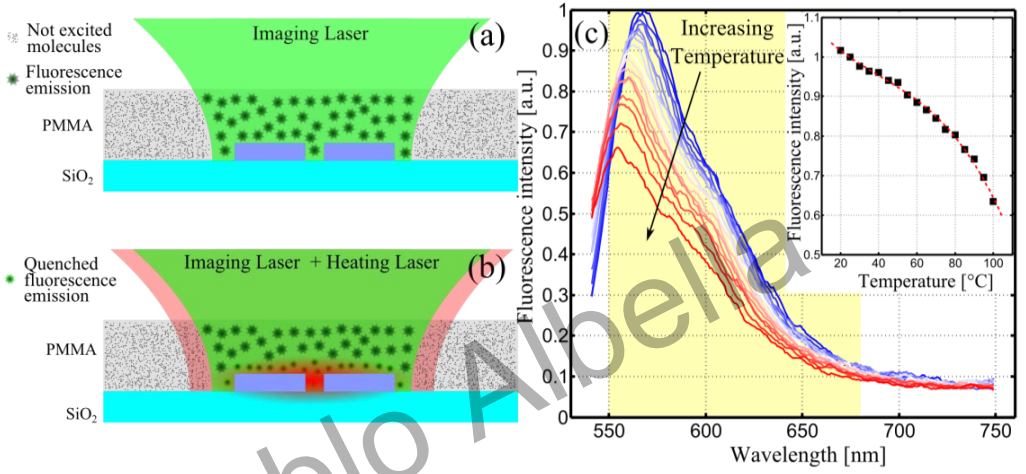
- Si produce enhanced fluorescence larger than Au



*M. Caldarola, P. Albella et al, Nature Comms 6:7915 (2015)

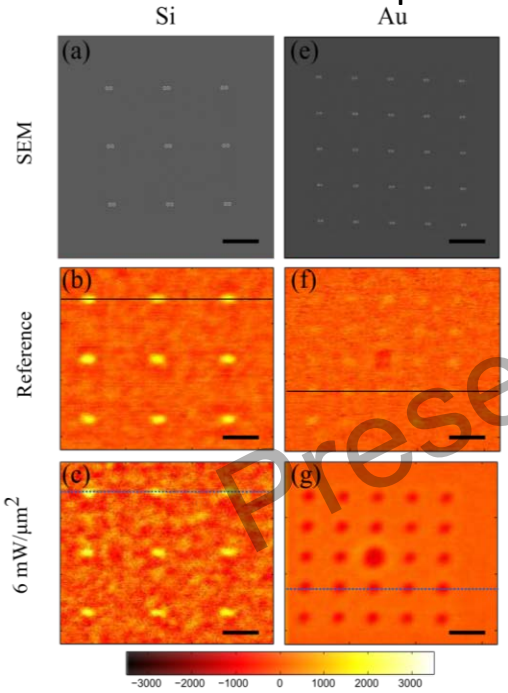
Assessment of Local Heat based on Molecular thermometry

- Local heat generation around the NA was determined using molecular thermometry.
- 2 lasers:
  - Heating laser on resonance with the NA.
  - Imaging laser
- Spectral shifts and reduction in intensity of nile red molecules upon increase in T.



Heating laser λ=860-890nm

Low power Imaging laser λ=532nm



Reference: fluorescence images without the heating laser turned on.

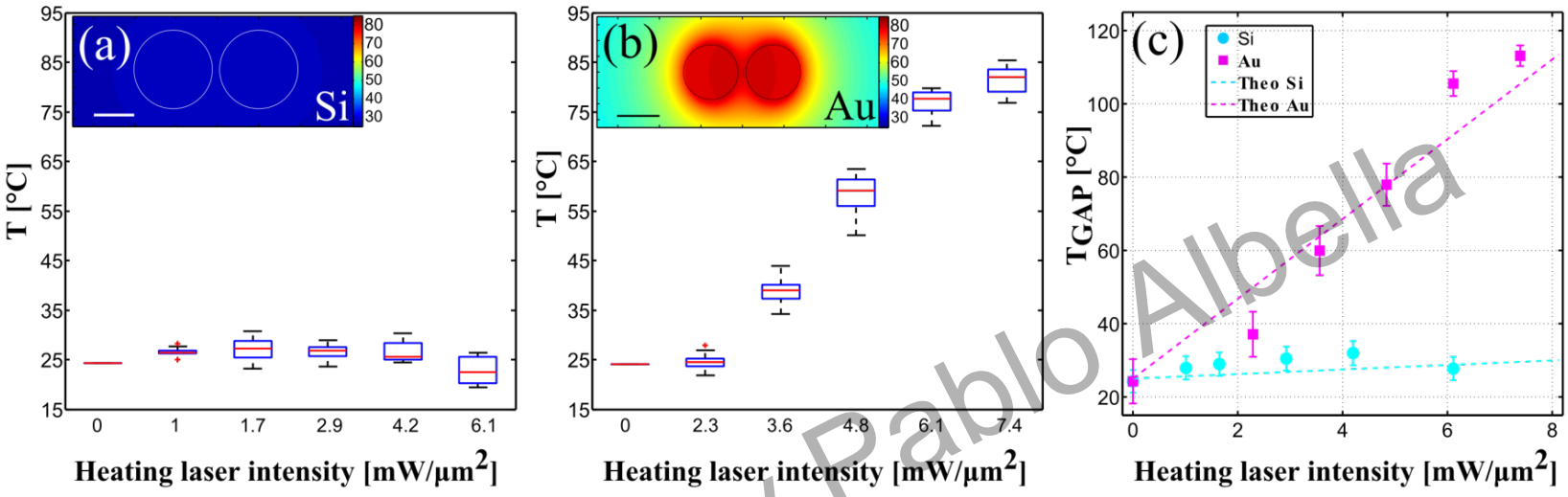
- Si produce enhanced fluorescence larger than Au

Fluorescence images with the heating laser on at 6 mW μm^{-2}

- Intensity clear drops for the Au antennas.

*M. Caldarola, P. Albella et al, Nature Comms 6:7915 (2015)

Local Heat Mapping results: Gold vs Si Nanoantennas



- Si antennas show little heating while substantial heating is observed for Au antennas
- Modelling the heating and extracting Tgap indicates local temperatures of > 100 °C at high powers.
- Very good agreement with theory (dotted lines).

Summary of Part II

- We have shown a novel type of nanoantenna based on all-dielectric materials (Si in this case)

- These nanoantennas enhanced the Raman scattering of a polymer thin film by a factor of ~10^3 and also allowed surface enhanced fluorescence by a factor of ~$2x10^3$

  - avoiding the well-known fluorescence quenching effects observed for metallic structures when no spacer layers are used.

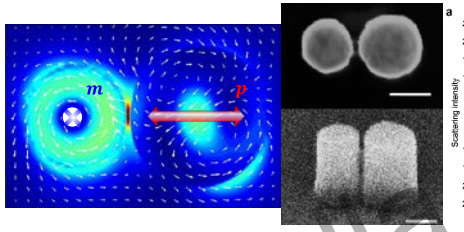
- Molecular thermometry demonstrate that dielectric nanoantennas produce ultra-low heating, thus overcoming one of the main drawbacks of traditional plasmonic materials.

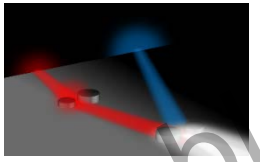
  - important advances in many fields can be foreseen due to almost no-restrictions in the power that can be delivered to these non-plasmonic nanoscale devices
  - Some examples: nanoelectronics or unperturbed sensing of nanoemitters behaviour by SES.

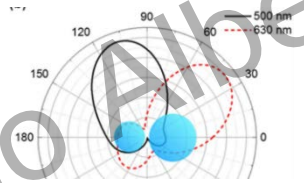
Outline

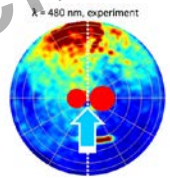
Part III:

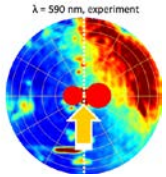
- **What about enhancing light with directional control? or switchable steering of light?**
  - Possible direct application in Selective sensing or SES
  - Application in optical nano-circuitry



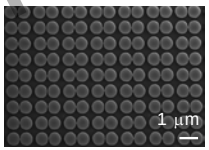


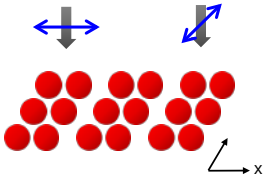


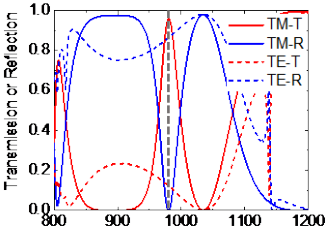




- **Polarization control of high transmission / reflection switching by all-dielectric metasurfaces**

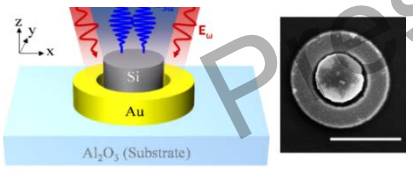






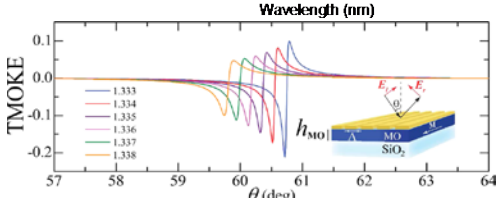
Part IV:

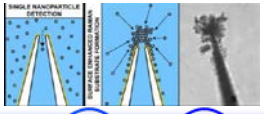
- **Dielectric - Metal hybrid structures for efficient THG**

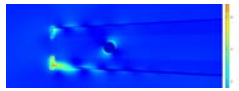


Part V:

- **Examples of (bio) - sensors**
  - MO-Kerr effect in magnetoplasmonic crystals
  - DNA mapping with nanopipetes (SERS,SEF)

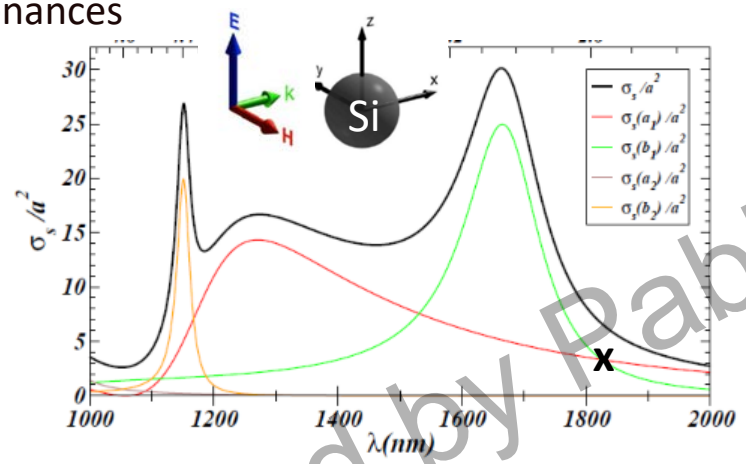






Introduction to Unidirectional forward scattering (Kerker's first condition)

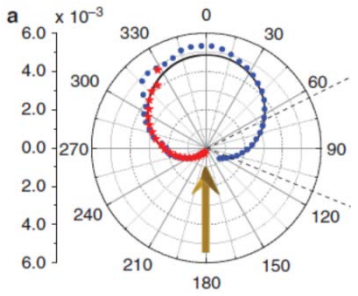
- When the first Mie coefficients, a1 and b1, corresponding to the electric and magnetic dipolar resonances are equal, the backward scattering is suppressed (1st Kerker condition)
  - Unidirectional forward scattering is achieved due to the interference between the electric and magnetic resonances

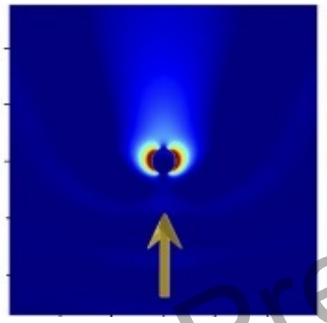


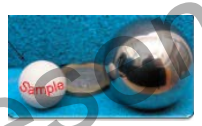
A. Gracia-Etxarri et al., Opt. Express. **19**, 4815 (2011)

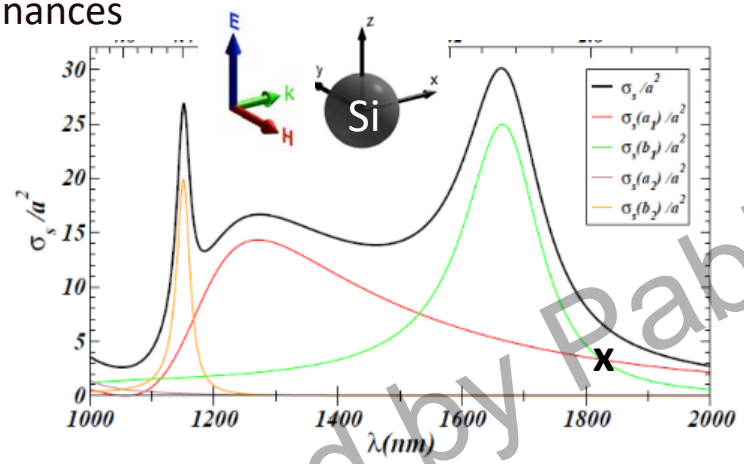
Introduction to Unidirectional forward scattering (Kerker's first condition)

- When the first Mie coefficients, a1 and b1, corresponding to the electric and magnetic dipolar resonances are equal, the backward scattering is suppressed (1st Kerker condition)
  - Unidirectional forward scattering is achieved due to the interference between the electric and magnetic resonances









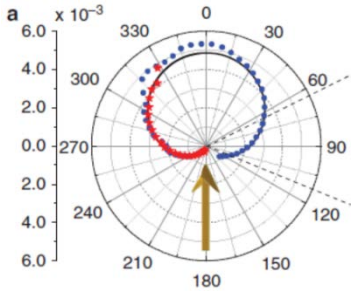
A. Gracia-Etxarri et al., Opt. Express. **19**, 4815 (2011)

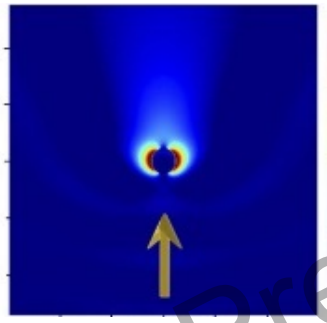
First demonstrated in the microwave
(radiation patterns measured in Fresnel Institute (anechoic chamber)

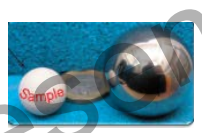
J.M. Geffrin, B. García-Cámara, R. Gómez- Medina, P. Albella, L.S. Froufe-Pérez, C.Eyraud, A. Litman, R. Vaillon, F. González, M. Nieto-Vesperinas, J.J. Sáenz and F. Moreno, ***Nat. Comm.* 3, 1171 (2012)**

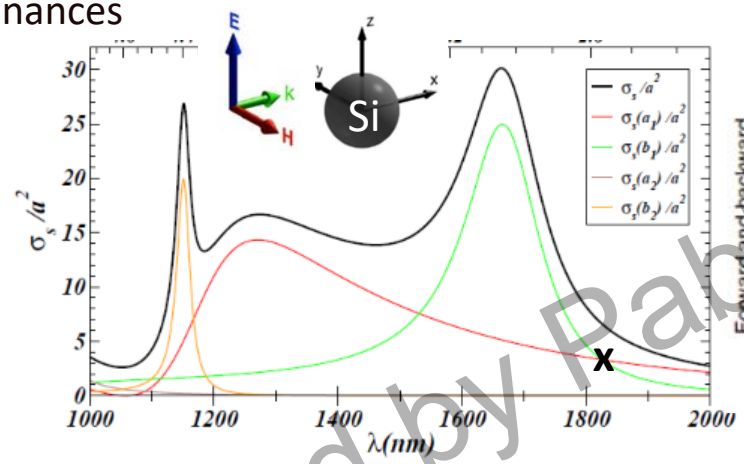
Introduction to Unidirectional forward scattering (Kerker's first condition)

- When the first Mie coefficients, a1 and b1, corresponding to the electric and magnetic dipolar resonances are equal, the backward scattering is suppressed (1st Kerker condition)
  - Unidirectional forward scattering is achieved due to the interference between the electric and magnetic resonances

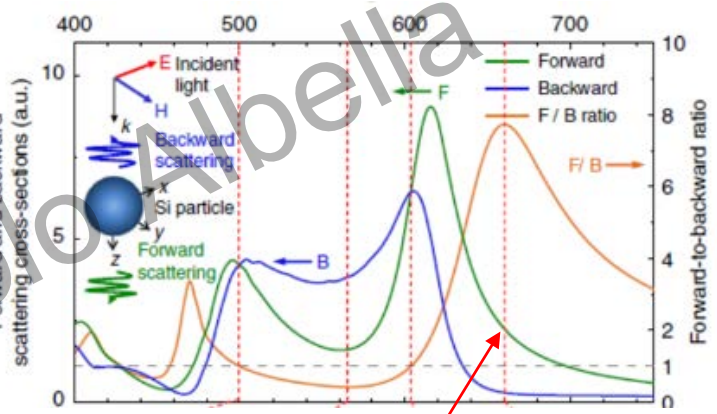








A. Gracia-Etxarri et al., Opt. Express. **19**, 4815 (2011)



Y. Fu et al. Nat. Comm. 4, 1527 (2013)

Low scattering efficiency

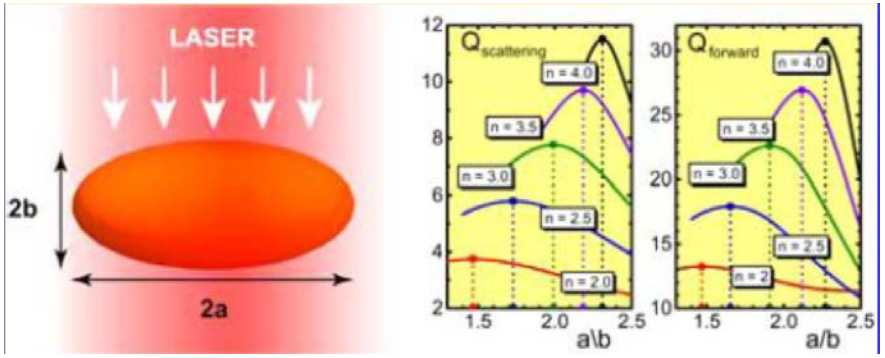
(electric and magnetic resonance far from each other)

First demonstrated in the microwave
(radiation patterns measured in Fresnel Institute (anechoic chamber)

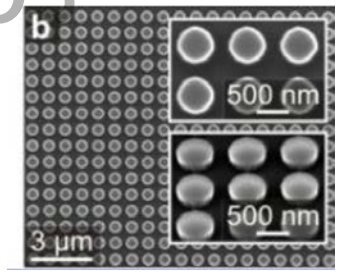
J.M. Geffrin, B. García-Cámara, R. Gómez- Medina, P. Albella, L.S. Froufe-Pérez, C.Eyraud, A. Litman, R. Vaillon, F. González, M. Nieto-Vesperinas, J.J. Sáenz and F. Moreno, ***Nat. Comm.* 3, 1171 (2012)**

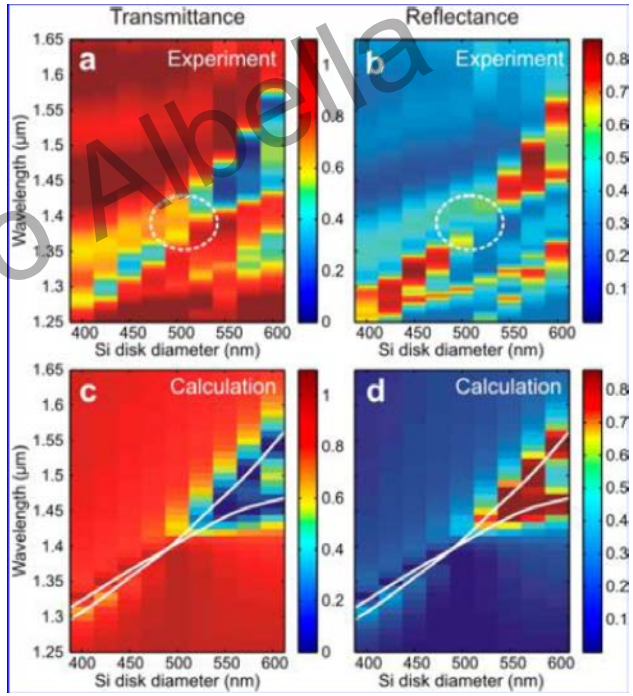
Some attempts to increase the scattering efficiency…

Spheroids and low aspect ratio disks can increase the efficiency



Boris S. Luk'yanchuk *et al. ACS Photonics 2015, 2, 993−999*

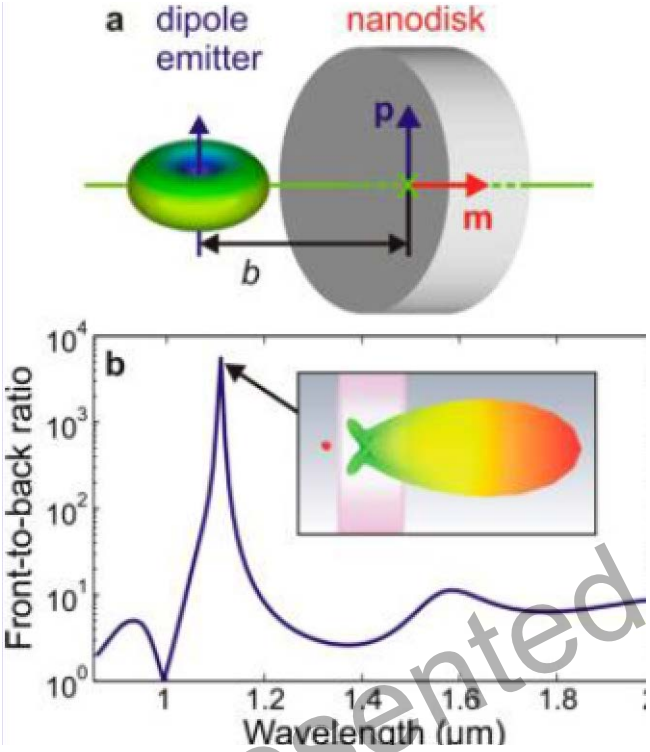




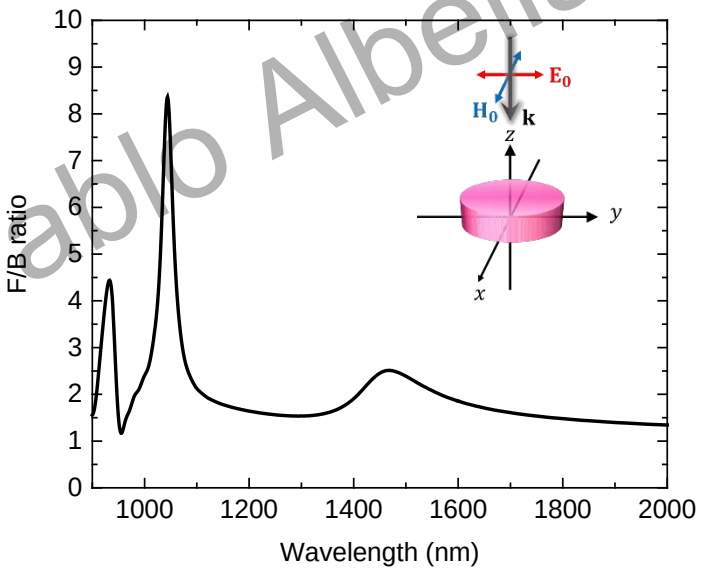
Measured optical transmittance and reflectance spectra for Si nanodisks embedded into a low-index medium.

I. Staude *et al. ACS Nano 2013, 7, 7824–7832*

F/B ratio based on optimized single disk with low aspect ratio



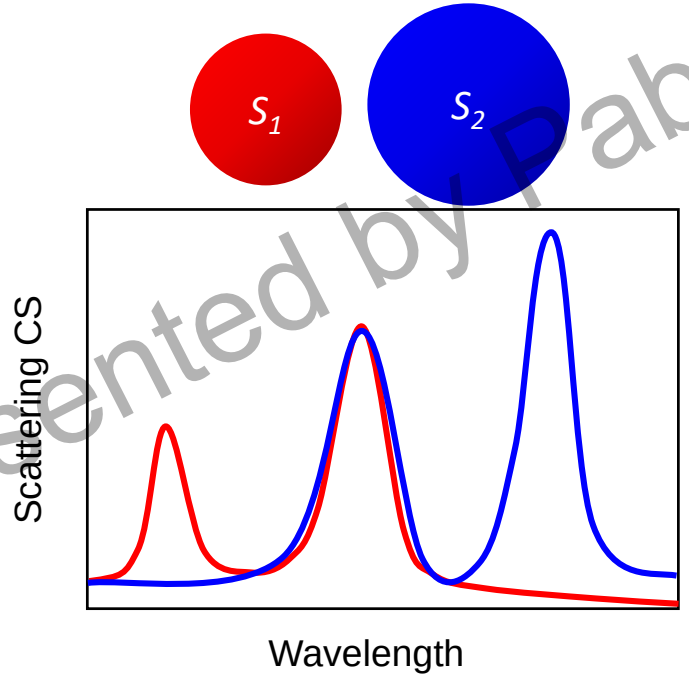
Optimised Single disk (Excited by PLANE wave instead)



I. Staude et al. ACS Nano 2013, 7, 7824–7832

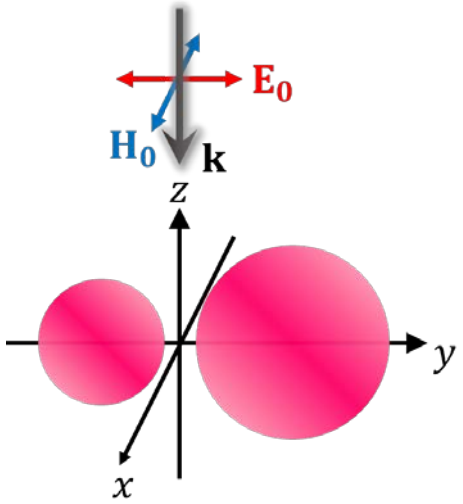
Asymmetric dimer configuration to enhance and direct light

- Idea: combine HRI dielectric nanoparticles of different sizes.
  - the position and intensity of the electric and magnetic resonance of dielectric particles strongly depend on their sizes.
  - Tuning them to achieve overlapping of those resonances could open up new possibilities for novel optical properties.



Optimizing dimer size to achieve first kerker condition

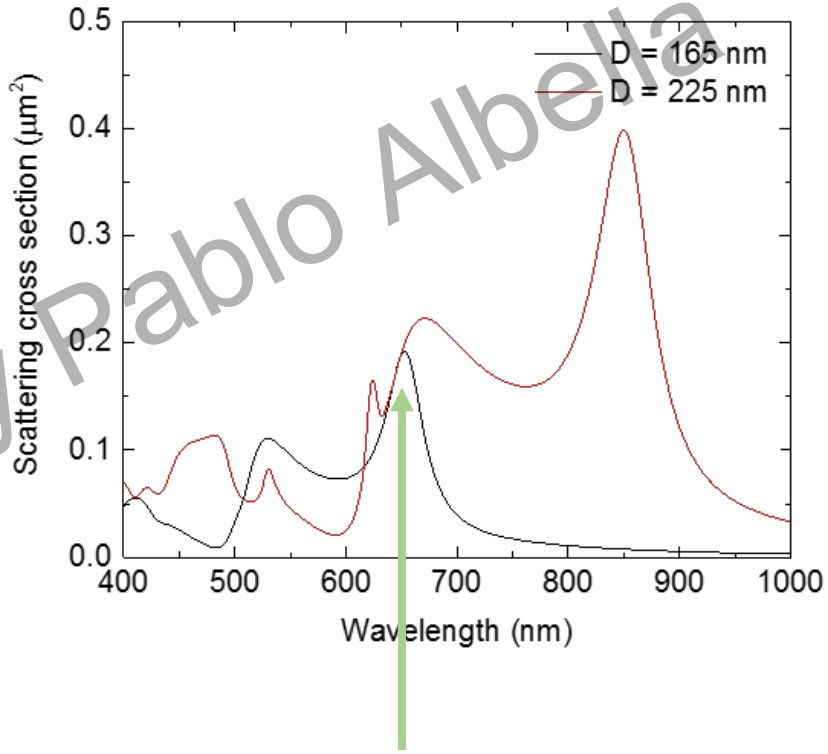
Asymmetric dimer



Silicon Dimer: D_1 = 165 nm, D_2 = 225 nm

Gap = 20nm

Scattering spectra of single spheres



Overlap of electric and magnetic resonance

Verification of the first Kerker condition

- Electric and magnetic dipoles were calculated considering the electric-electric, magnetic-magnetic and electric-magnetic dipole couplings.
  - Based on the Analytical dipole-dipole model proposed in [*]

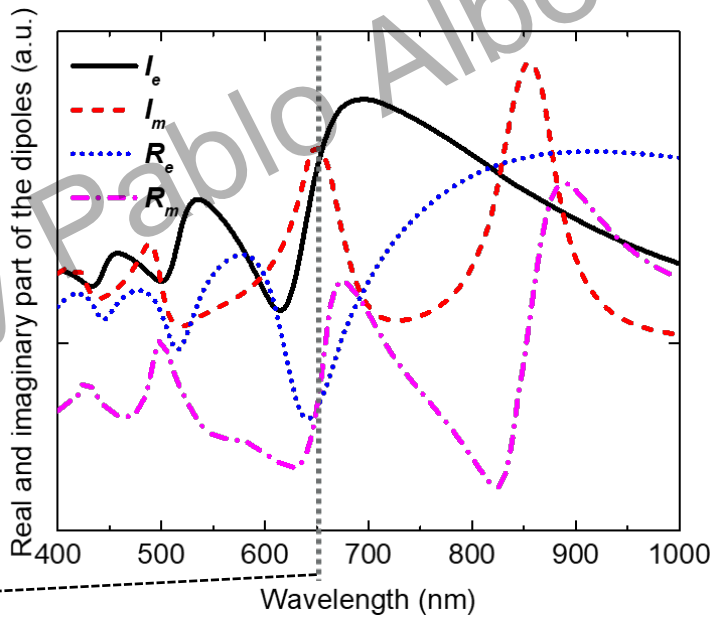
[*] P. Albella et al., J. Phys. Chem. C **117**, 13573 (2013)

$$R_e = \Re\left(\frac{1}{\varepsilon_0 \varepsilon}\left(p_{1y} + p_{2y}\right)\right)$$

$$R_m = -\Re\left(Z\left(m_{1x} + m_{2x}\right)\right)$$

$$I_e = \Im\left(\frac{1}{\varepsilon_0 \varepsilon}\left(p_{1y} + p_{2y}\right)\right)$$

$$I_m = -\Im\left(Z\left(m_{1x} + m_{2x}\right)\right)$$



$R_e = R_m$

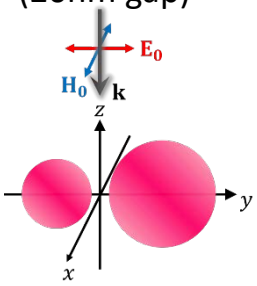
$I_e = I_m$

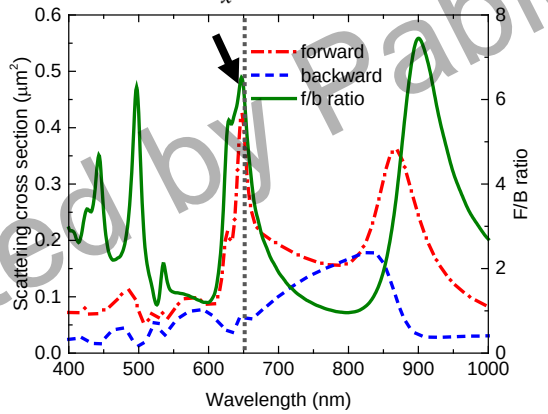
at λ = 650 nm, verifying the achievement of the first Kerker condition.

F/B ratio of the asymmetric dimer:
comparison to a single disk in low aspect ratio

- DF Scattering CS Calculation (Collection of scattered field on the forward and backward hemisphere)

Spherical asymmetric dimer
(20nm gap)





Basic Principle: No substrate

Forward / backward ratio comparable between the asymmetric dimer and optimised single disk.

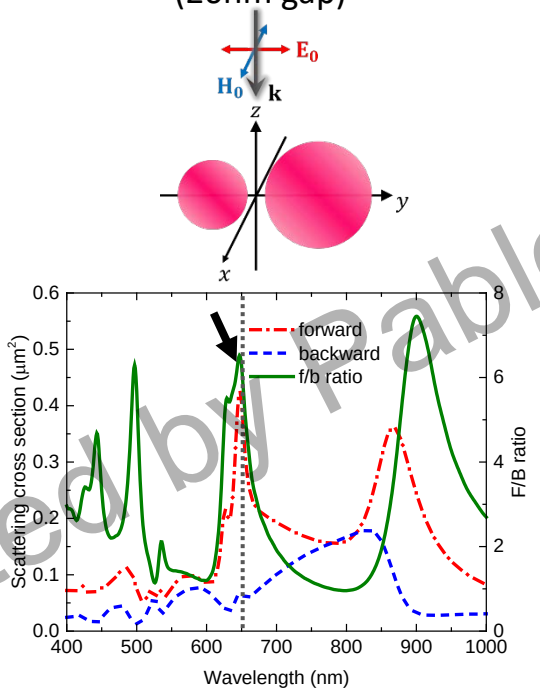
* I. Staude, A. E. et.al, ACS Nano, 2013, **7**, 7824–7832

T. Shibanuma, P. Albella and S. A. Maier. **Nanoscale**, 2016, 8 ,14184

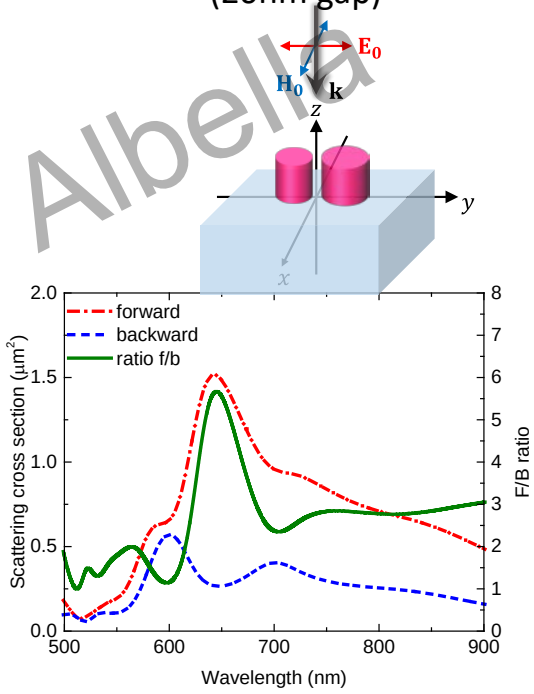
F/B ratio of the asymmetric dimer:
comparison to a single disk in low aspect ratio

- DF Scattering CS Calculation (Collection of scattered field on the forward and backward hemisphere)

Spherical asymmetric dimer
(20nm gap)



Cylindrical asymmetric dimer
(20nm gap)



* I. Staude, A. E. et.al, ACS Nano, 2013, **7**, 7824–7832

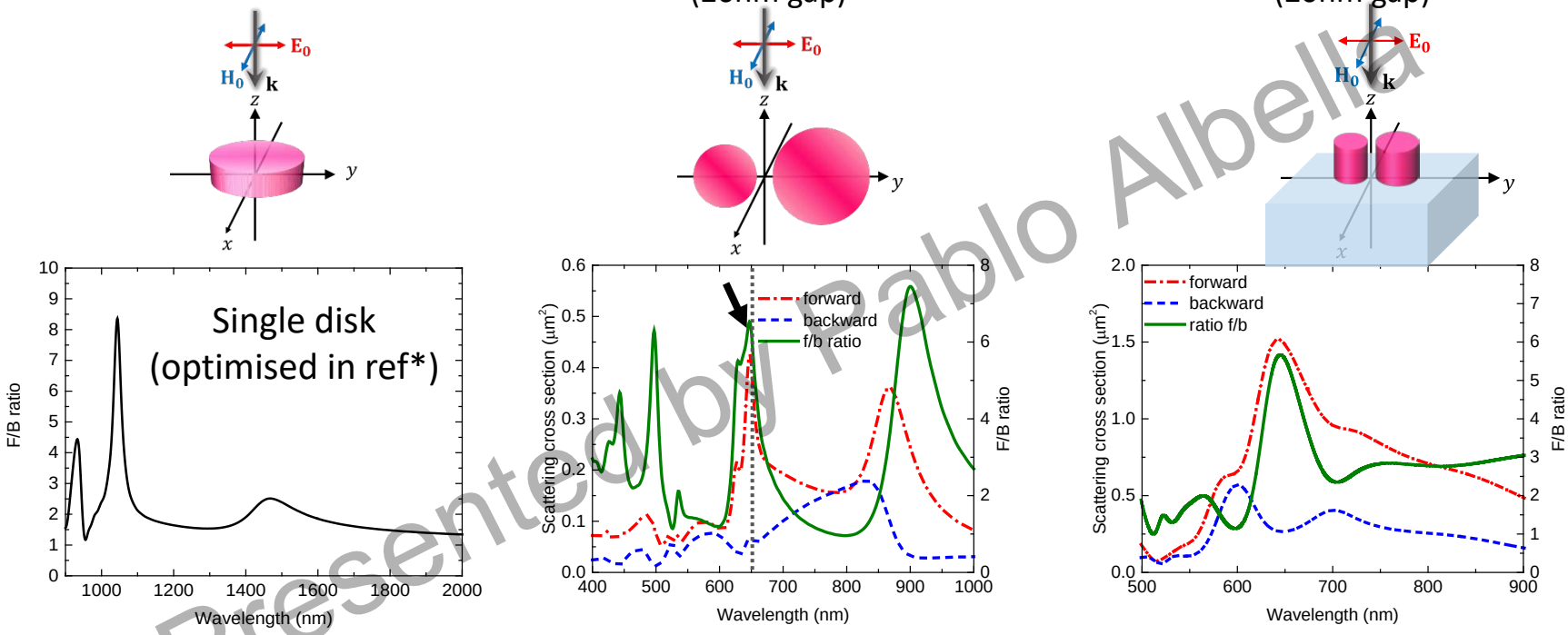
T. Shibanuma, P. Albella and S. A. Maier. **Nanoscale**, 2016, 8 ,14184

F/B ratio of the asymmetric dimer:
comparison to a single disk in low aspect ratio

- DF Scattering CS Calculation (Collection of scattered field on the forward and backward hemisphere)

Spherical asymmetric dimer (20nm gap)

Cylindrical asymmetric dimer (20nm gap)



Forward / backward ratio comparable between the asymmetric dimer and optimised single disk.

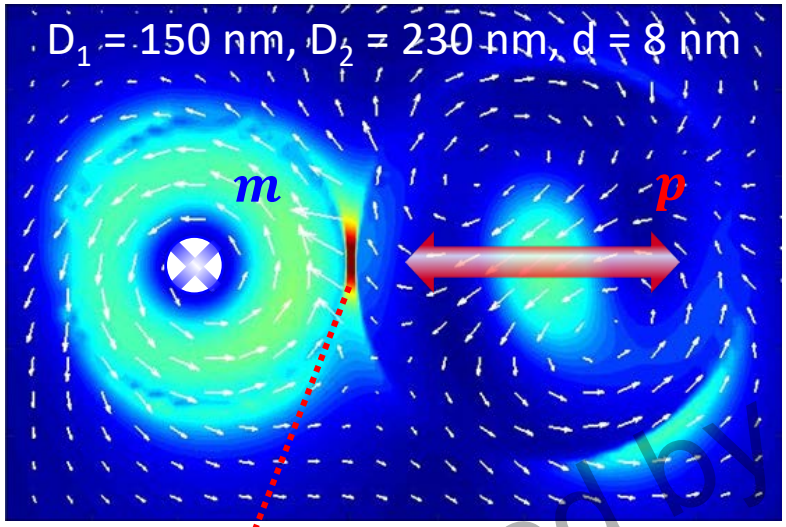
* I. Staude, A. E. et.al, ACS Nano, 2013, **7**, 7824–7832

T. Shibanuma, P. Albella and S. A. Maie. **Nanoscale**, 2016, 8 ,14184

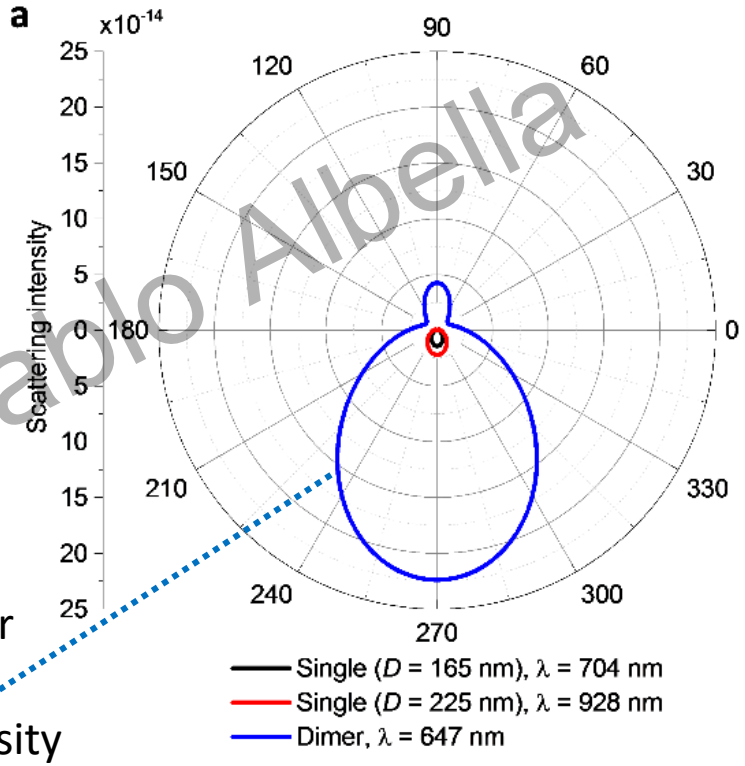
High F/B ratio of the asymmetric dimer and Presence of Hot Spot

Using asymmetric silicon dimer

Electric field mapping at λ = 647 nm



Scattering patterns

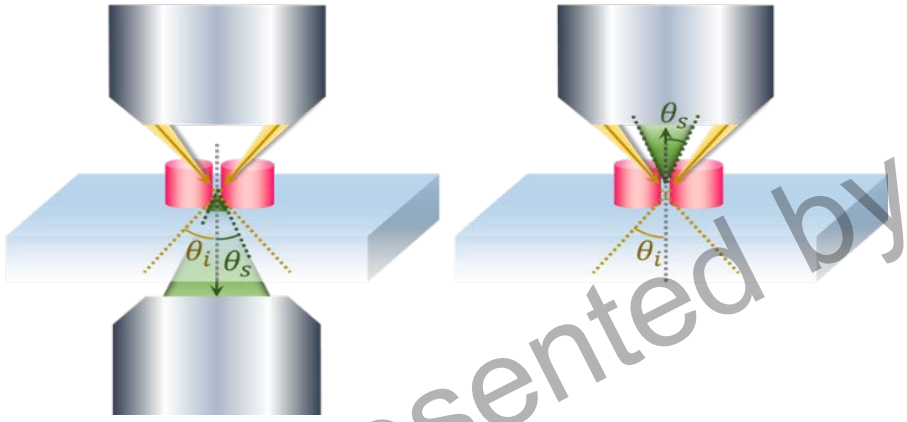


- This hot spot can not be obtained in single disk or spheroid cases.
- Unidirectional forward scattering with high intensity can be achieved
- It can be used as a novel nanoantenna for directional SERS or SEF

T. Shibanuma, P. Albella and S. A. Maier, **Nanoscale** 2016, 8 ,14184

Experimental demonstration

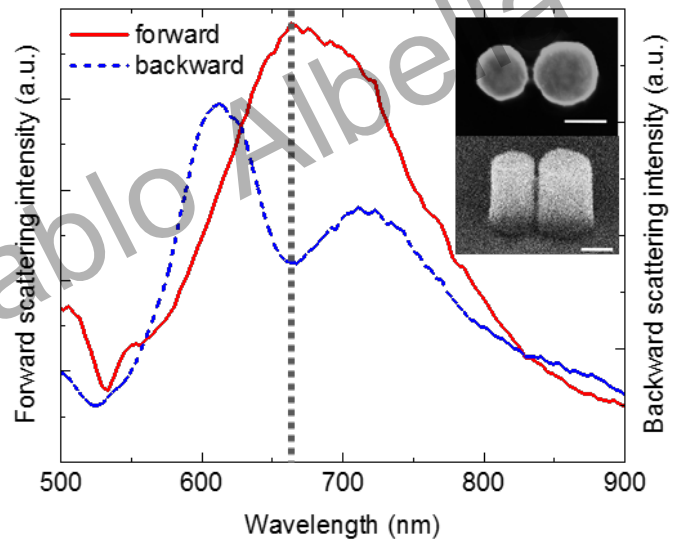
- Dark field spectroscopy for measurement of scattering from single nanoantenna
- This setup enables us to measure only scattering, excluding incidence.



Incidence: θ_i = 60-70 °

Scattering: θ_s = 0-53 °

- Fabricated sample and forward / backward scattering

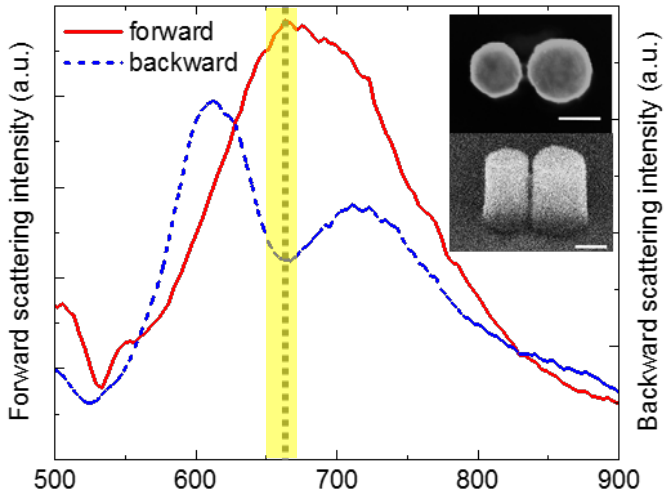


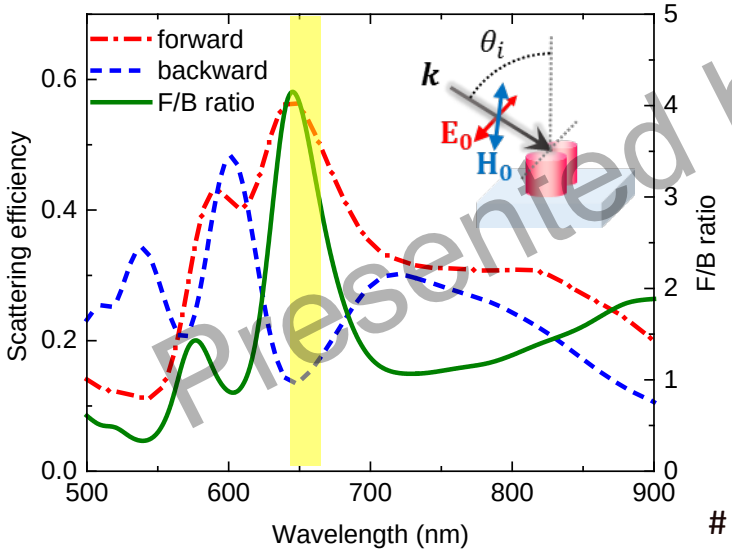
Peak and valley observed in forward and backward scattering, respectively.

→ Unidirectional forward scattering with high efficiency

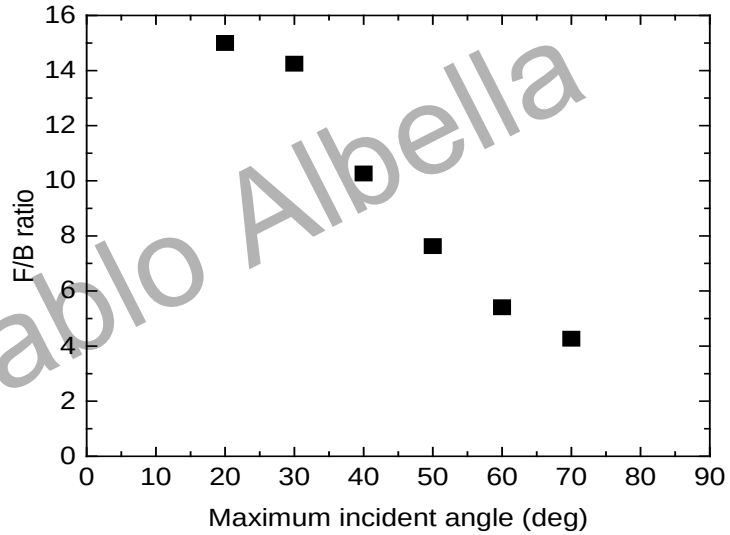
T. Shibanuma, P. Albella and S. A. Maier, **Nanoscale** 2016, 8 ,14184

Experimental demonstration: Comparison with theory and influence of incidence angle





Dependence with the Incident angle

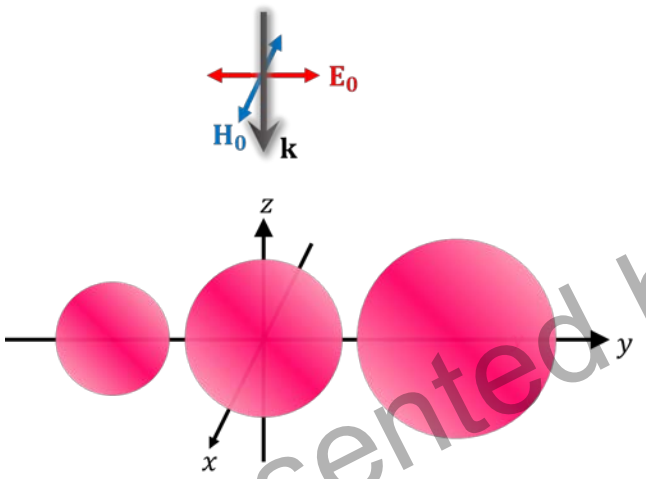


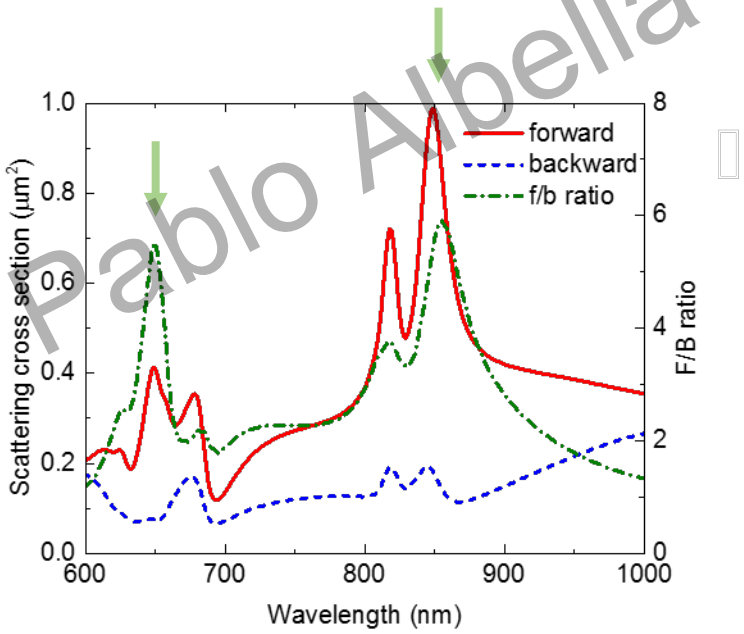
As incident angle decreased, the F/B ratio increased and reached around 15 with nearly normal incidence.

T. Shibanuma, P. Albella and S. A. Maier, **Nanoscale** 2016, 8 ,14184

Extending the idea for multi-wavelength and broadband response

Three Si spheres aligned with diameter of 165 nm, 225 nm, and 310 nm

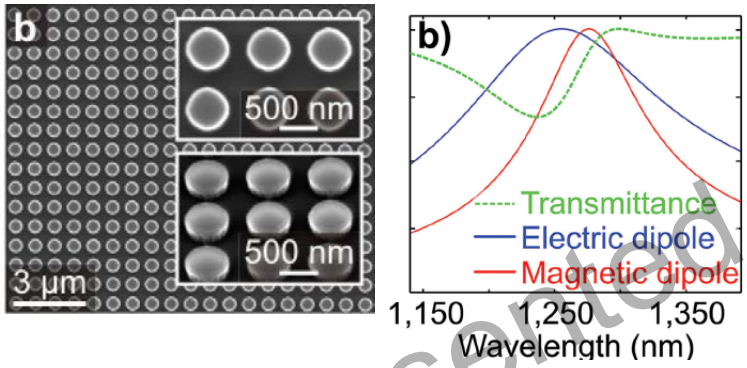




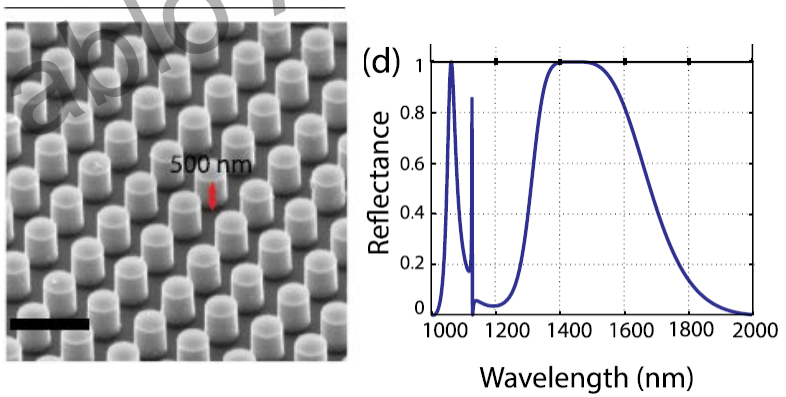
Polarization control of high transmission / reflection switching by all-dielectric metasurfaces

- When dielectric nanoantennas are aligned periodically, they can act as a metasurface providing with an effective permittivity.

When the two peaks overlap,
→ $\varepsilon \sim \mu$
→ High transmission



When the two peaks separate,
→ ε and μ have opposite signs
→ High reflection



I. Staude et al., ACS Nano, **7**, 7824 (2013)
M. Decker et al., Adv. Opt. Mater., **3**, 813 (2015)

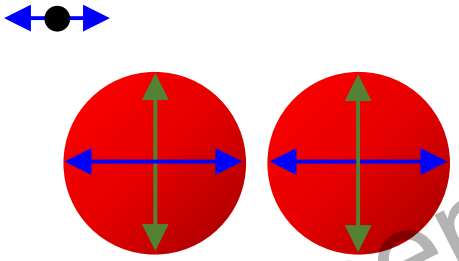
(ε, μ: effective permittivity and permeability of dielectric metasurface)

Polarization control of high transmission / reflection switching by all-dielectric metasurfaces

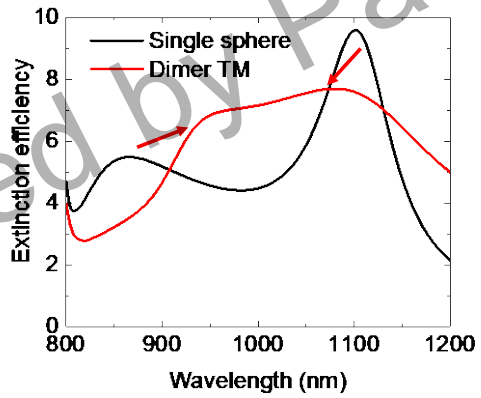
- Basic idea
  - **Spectral overlap** of electric and magnetic dipoles → **High transmission**
  - **Spectral separation** of electric and magnetic dipoles → **High reflectance**

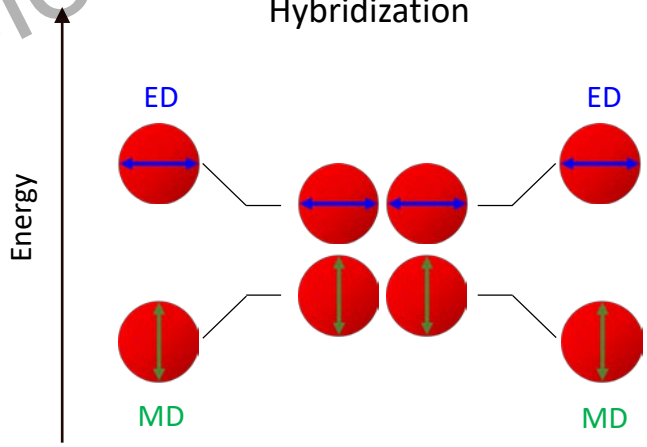
Polarization control of high transmission / reflection switching by all-dielectric metasurfaces

- Basic idea
  - **Spectral overlap** of electric and magnetic dipoles → **High transmission**
  - **Spectral separation** of electric and magnetic dipoles → **High reflectance**
- Array of the Si dimer
  - **Polarization along the dimer axis** → Mode hybridization induces spectral **overlapping**



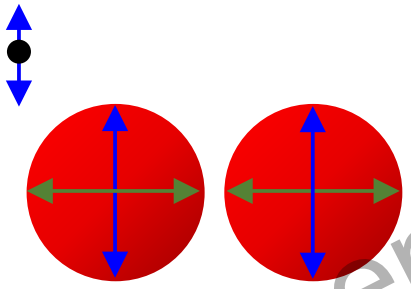
Scattering spectra of Si sphere dimer
Diameter: 300 nm, Gap: 10 nm



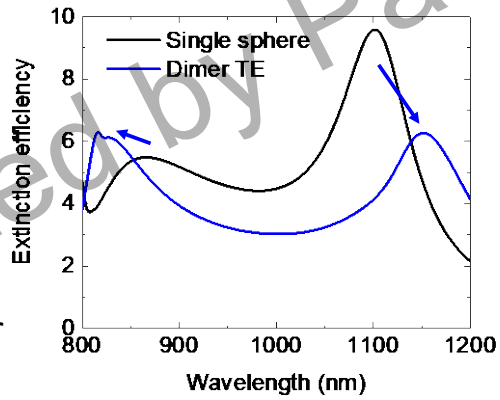


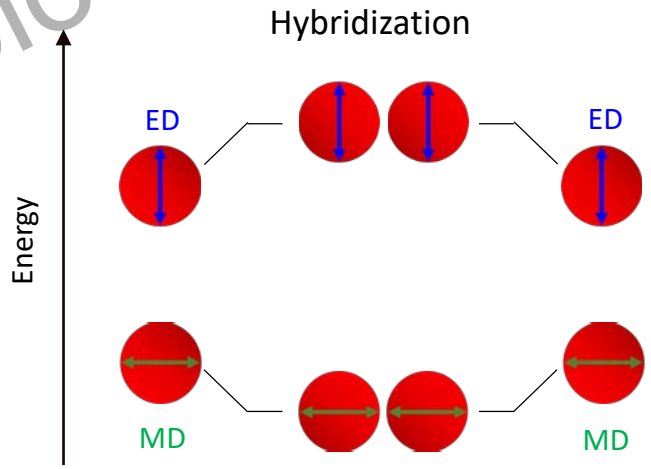
Polarization control of high transmission / reflection switching by all-dielectric metasurfaces

- Basic idea
  - **Spectral overlap** of electric and magnetic dipoles → **High transmission**
  - **Spectral separation** of electric and magnetic dipoles → **High reflectance**
- Array of the Si dimer
  - **Polarization perpendicular to dimer axis** → Mode hybridization induces spectral separation



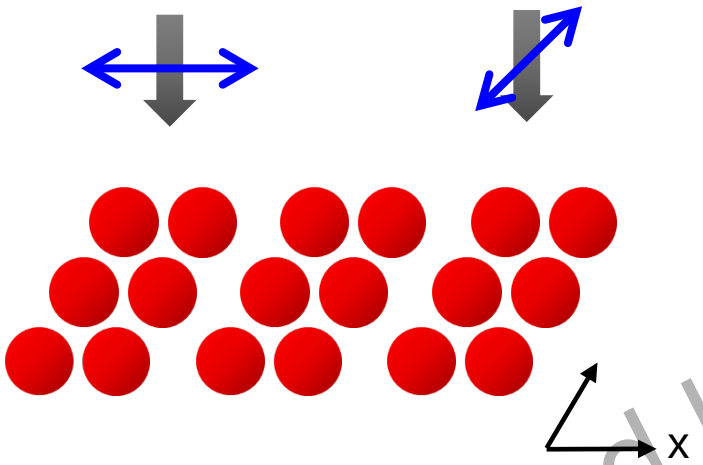
Scattering spectra of Si sphere dimer
Diameter: 300 nm, Gap: 10 nm



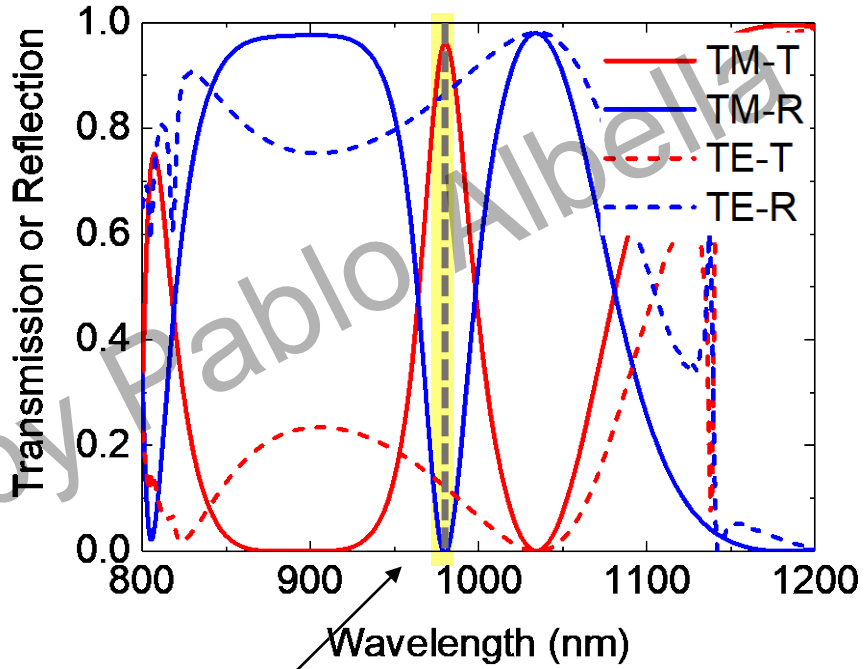


Proof of concept: array of nanospherical dimers

Si spherical dimer in air



FDTD calculation

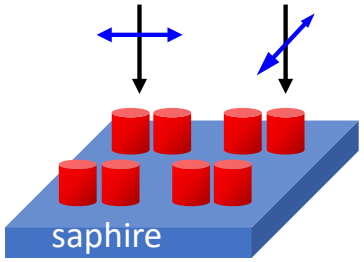


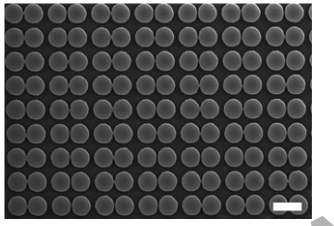
High R <-> High T switching around λ = 975 nm

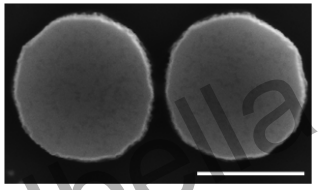
T. Shibanuma, Stefan A. Maier and P. Albella*. Appl. Phys. Lett 2018 (just accepted)

Experimental demonstration: array of nanocylindrical dimers

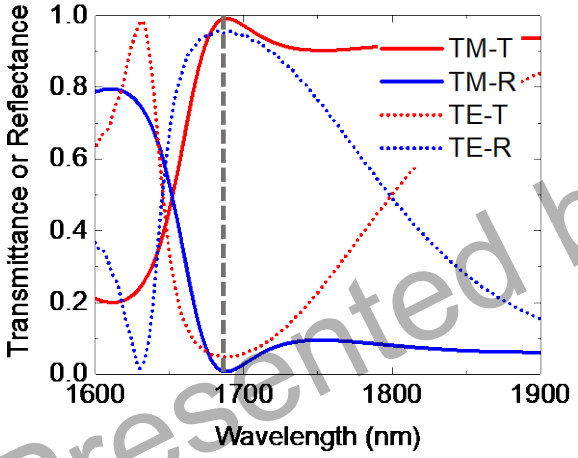
Array of cylindrical Si dimer on sapphire substrate





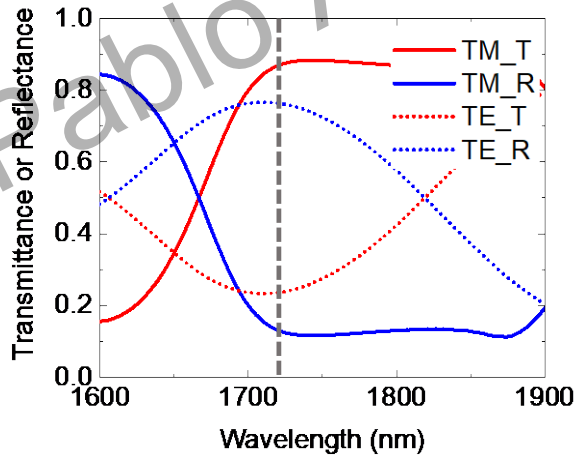


FDTD calculation



At λ = 1688 nm
TM: 99 % transmittance
TE: 95 % reflectance

Experiment (FTIR)



At λ = 1718 nm
TM: 86 % transmittance
TE: 77 % reflectance

T. Shibanuma, Stefan A. Maier and P. Albella*. Appl. Phys. Lett 2018 (just accepted)

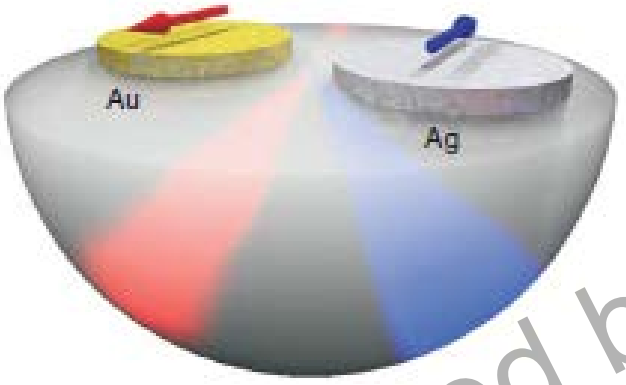
What about: switchable and tunable steering of light WITH Low Loss

- ***Theory and Basic Principle:*** **Sci. Rep 5:18322 (2015)**
- ***Experimental demonstration:*** **ACS Photonics 4, 489-494 (2017)**

Tuneable directional scattering either to left or right direction

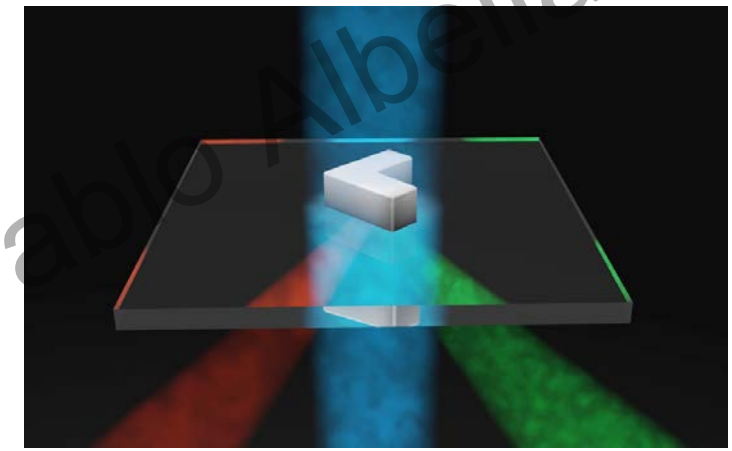
- Next topic is about directional control of scattering in the left or right direction from the incident axis

Bimetallic configuration



Mikael Käll et al. Nat. Commun. **2**, 481 (2011)

V shape nanoantenna

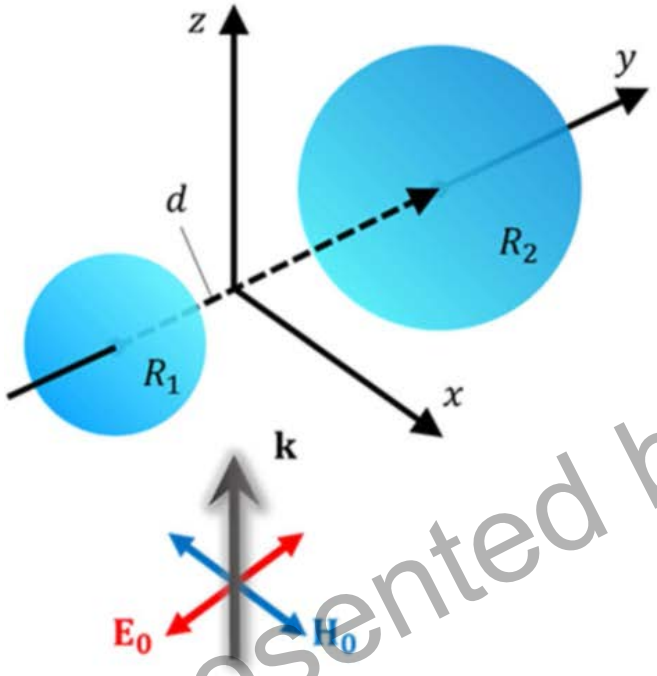


Paul van Dorpe et al. Nano. Lett. **16**, 4396 (2016)

- Most Scattering into the substrate.
- Control of the scattering light along the substrate would be preferable for some applications (e.g. optical nanocircuitry)

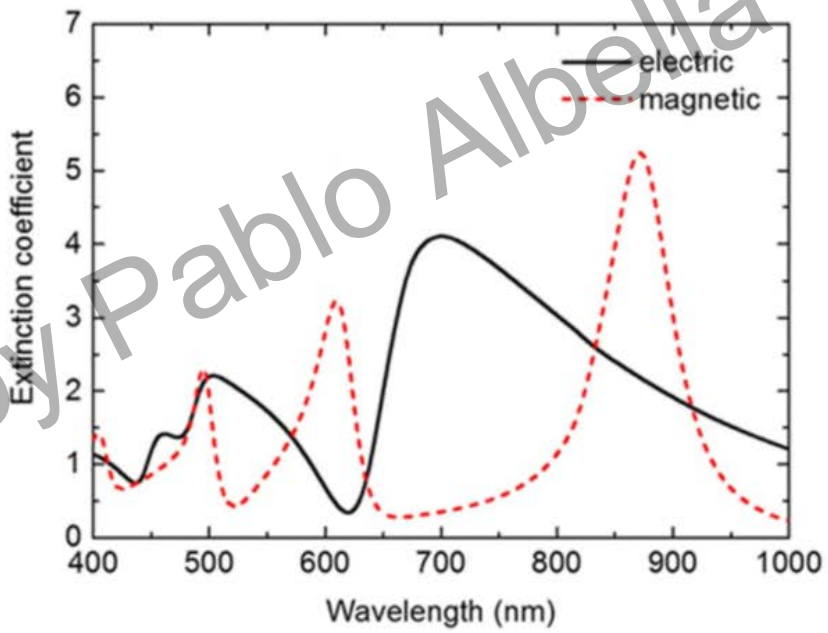
Basic idea to switch in-plane scattering either left or right

Using asymmetric dimer



Extinction Calculated by the dipole-dipole model [*]

[*] P. Albella et al., J. Phys. Chem. C **117**, 13573 (2013)

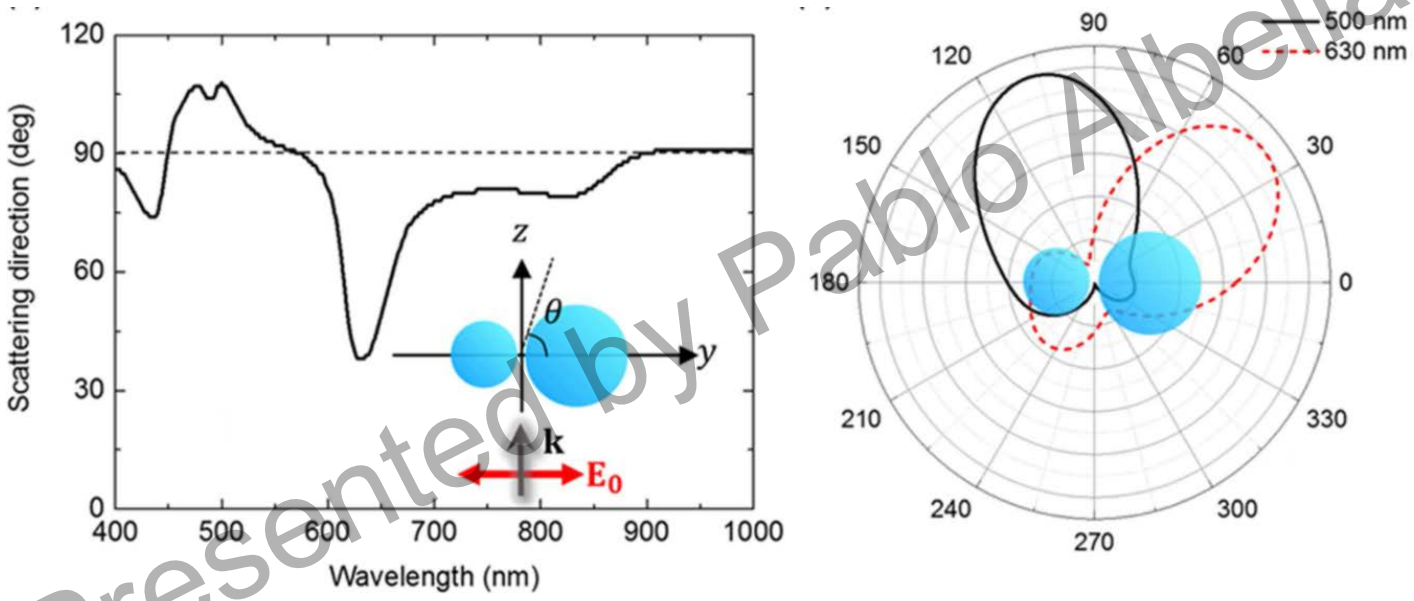


Dimer of Silicon Spheres:
D_1 = 150 nm, D_2 = 230 nm, d = 8nm

- Drastic phase shift by dimensions
- Tuneable from visible to microwave

Basic idea to switch in-plane scattering either left or right

- Scattering direction defined as the angle where maximum scattering is achieved.
- Direction can be changed depending on the wavelength of excitation.

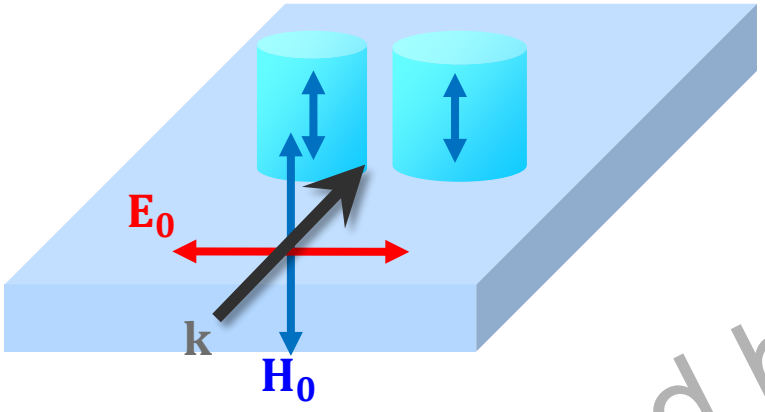


- Light scattered to either left (+18°) or right (-52°) depending on the wavelength.

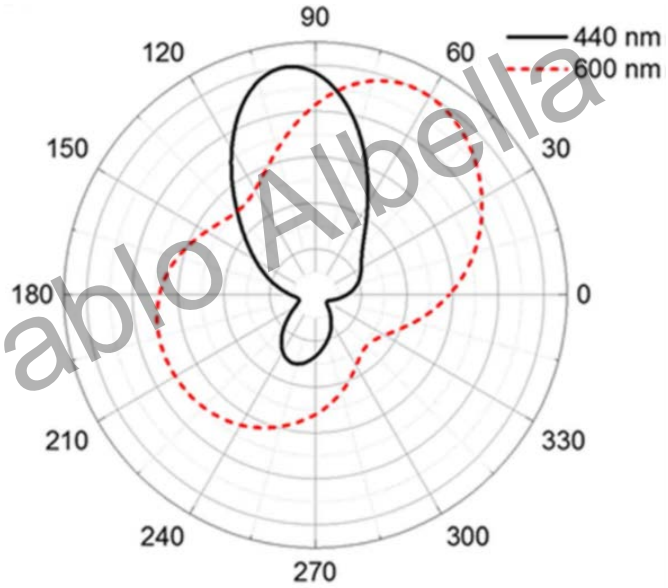
*P. Albella, T. Shibanuma, Stefan A. Maier. **Sci. Rep** 5:18322 (2015)

Asymmetric silicon dimer for tuneable scattering **along the substrate**

Si dimer on a silica substrate



Far field pattern in the xy plane calculated by FDTD

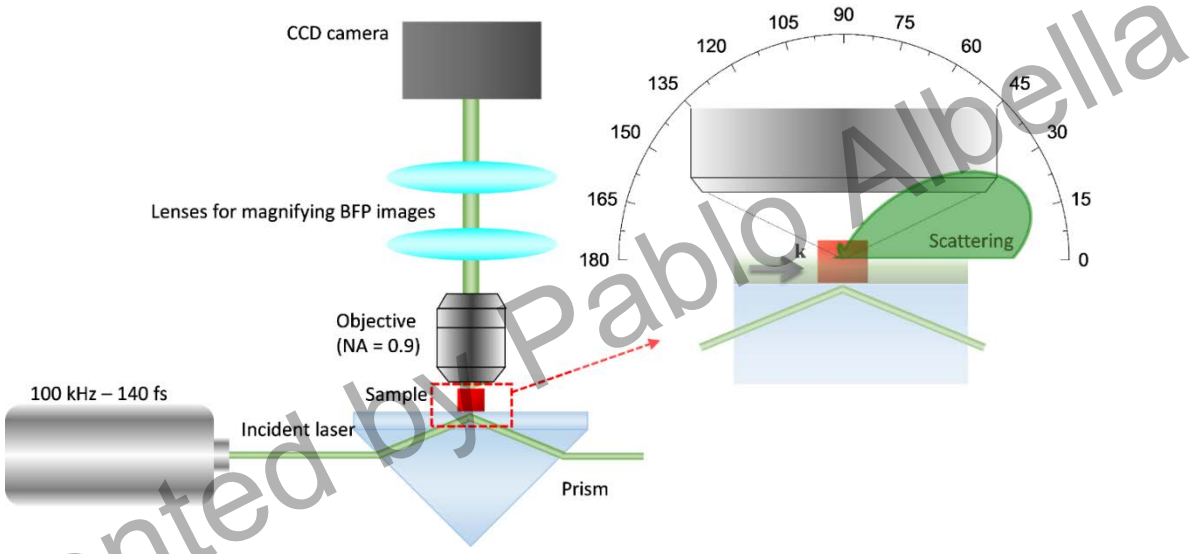


Interference between the excited magnetic dipoles results in the tuneable scattering

*P. Albella, T. Shibanuma, Stefan A. Maier. **Sci. Rep** 5:18322 (2015)

Experimental demonstration

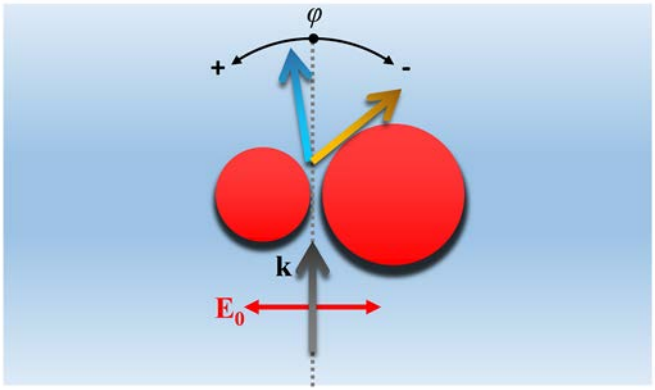
- To experimentally demonstrate the tunable directional scattering along the substrate, a BFP (Back focal plane imaging) technique combined with a prism coupling was designed.

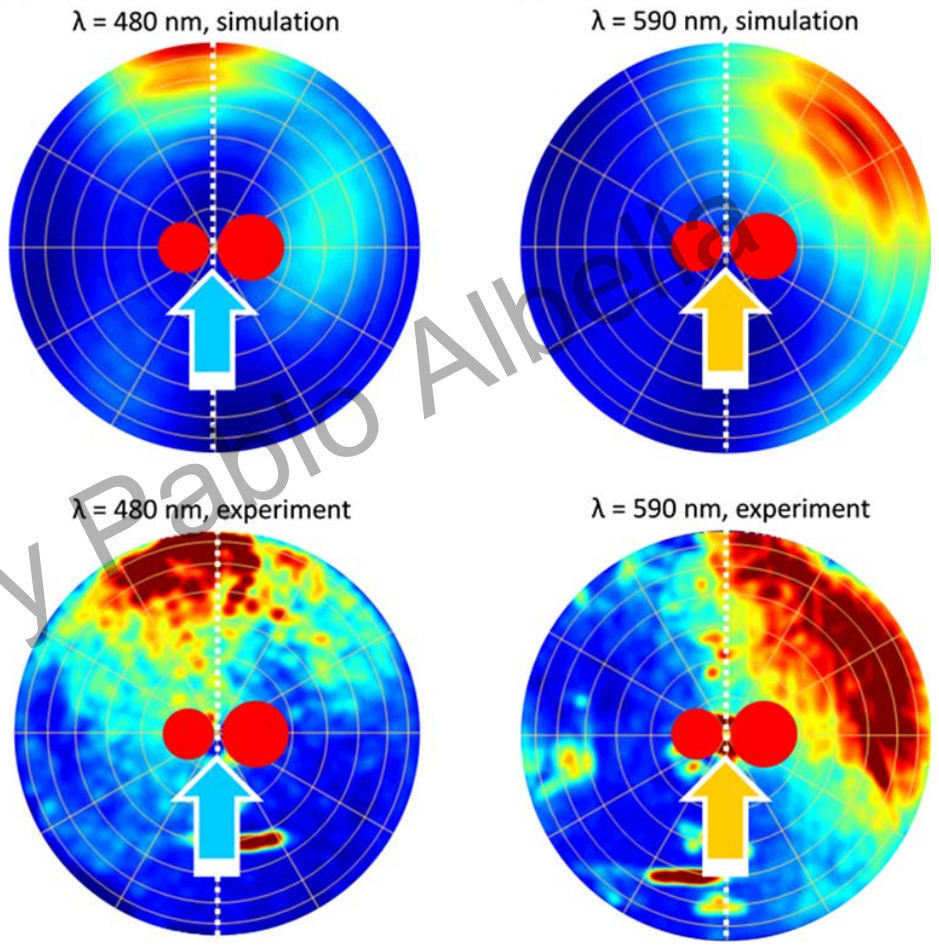


- Basically, an evanescent wave is generated by total internal reflection and travels along the substrate until it excites the nanoantenna.
- The scattering lobe is then observed with high NA objective.

T. Shibanuma, T. Matsui, T. Roschuk, J. Wojcik, P. Mascher, P. Albella and S. A. Maier, **ACS Photonics** 4, 489-494 (2017)

Experimental results vs numerical predictions





Scattering direction can be tuned by the excitation wavelength

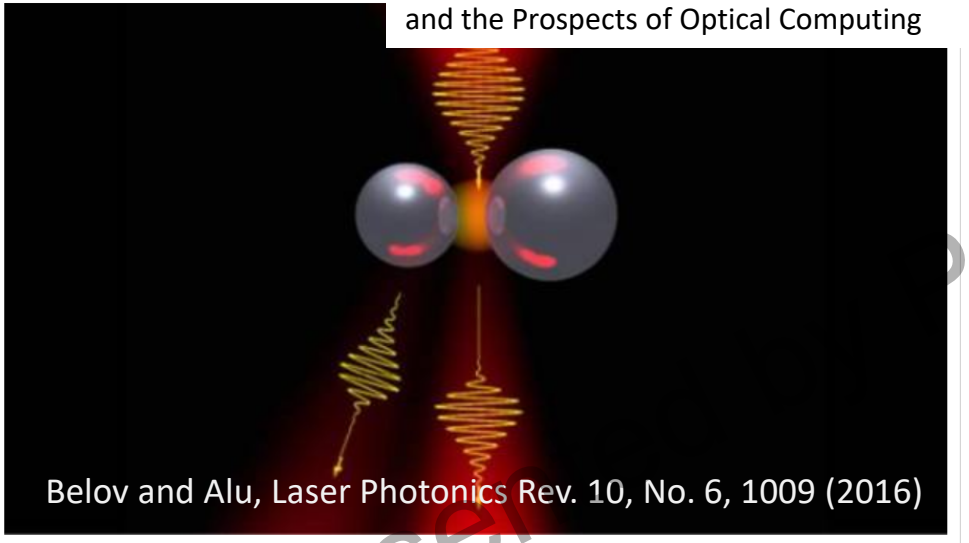
T. Shibanuma, T. Matsui, T. Roschuk, J. Wojcik, P. Mascher, P. Albella and S. A. Maier, **ACS Photonics** 4, 489-494 (2017)

This idea inspired recent works (optical computing)

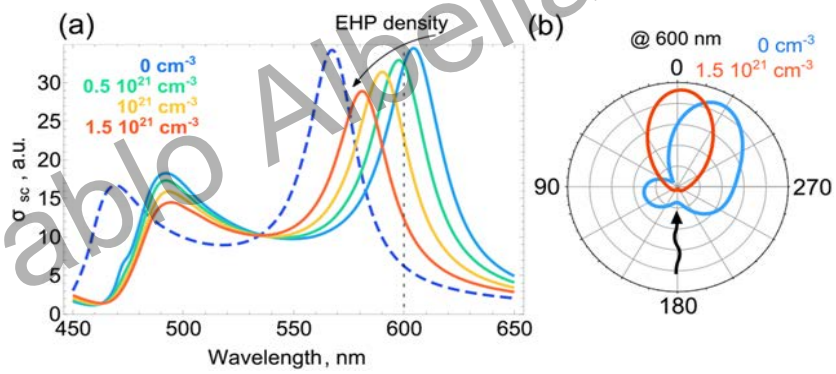
What a Twist: Silicon Nanoantennas Turn Light Around

Published: November 16, 2016.
Released by Moscow Institute of Physics and

Nanoantenna Changes Direction of Light and the Prospects of Optical Computing



A team of physicists from ITMO University, MIPT, and The University of Texas at Austin have developed an unconventional nanoantenna that scatters light in a particular direction depending on the intensity of incident radiation. The research findings will help with the development of flexible optical information processing in telecommunication systems.

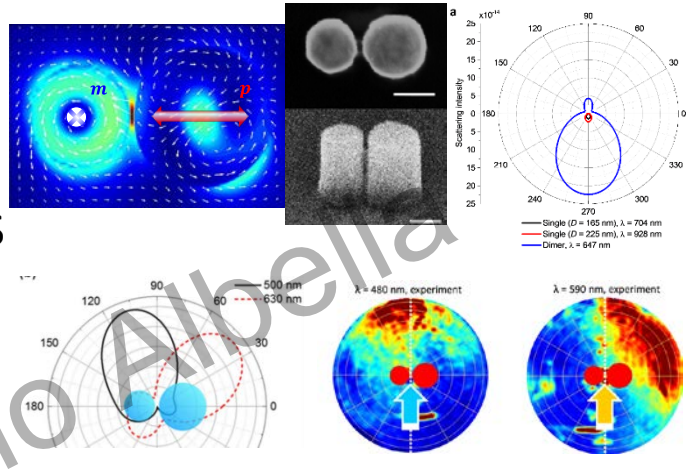


Scattering cross-section of isolated nanoparticles with increasing Electron Hole pair density in the resonant particle

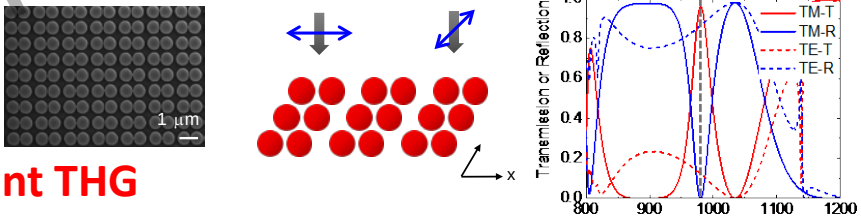
Outline

Part III:

- **What about enhancing light with directional control? or switchable steering of light?**
  - Possible direct application in Selective sensing or SES
  - Application in optical nano-circuitry

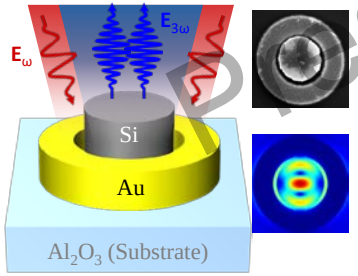


- **Polarization control of high transmission / reflection switching by all-dielectric metasurfaces**



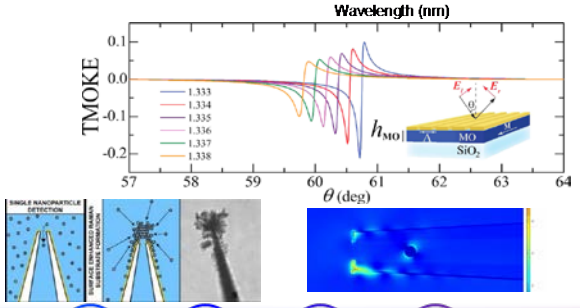
Part IV:

- **Dielectric - Metal hybrid structures for efficient THG**



Part V:

- **Examples of (bio) - sensors**
  - MO-Kerr effect in magnetoplasmonic crystals
  - DNA mapping with nanopipetes (SERS,SEF)



Introduction to THG

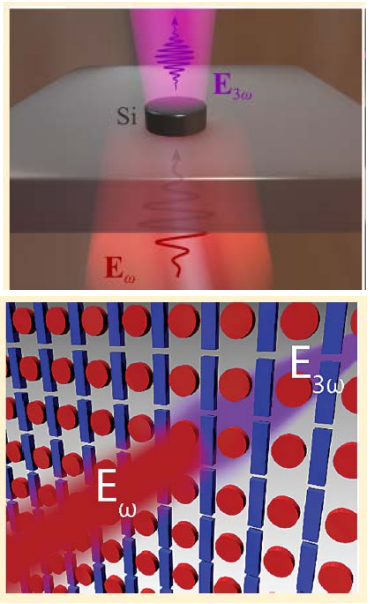
- Third-order susceptibilities of metals are among the highest in nature
  - enables, in principle, excellent THG performances.

- Skin depth of conductors is generally small
  - any third-order nonlinear effect from metals results in strongly reduced efficiencies.

- To further enhance the THG process, plasmonic nanostructures have been combined with non-metallic nm-scaled nonlinear materials.
  - For example, by placing an ITO nanoparticle at the hot spot of a metallic nanodimer

Metal – dielectric hybrid structures for efficient THG

- Third harmonic generation (THG) from high ref index dielectric nanostructures



Si

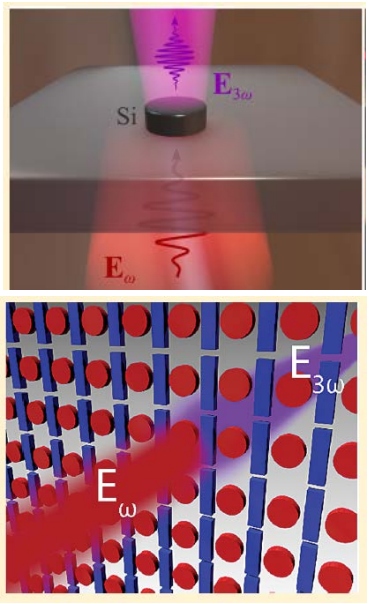
η_{TH} ~ 0.0002 %

M. R. Shcherbakov et al. Nano Lett., **14**, 6488 (2014)
Y. Yang et al. Nano Lett., **15**, 7388 (2015)
L. Wang et al. Nanoscale., **9**, 2201 (2017)

- Efficiency is still low, because of the low electric field enhancement in dielectric structures

Metal – dielectric hybrid structures for efficient THG

- Third harmonic generation (THG) from high ref index dielectric nanostructures

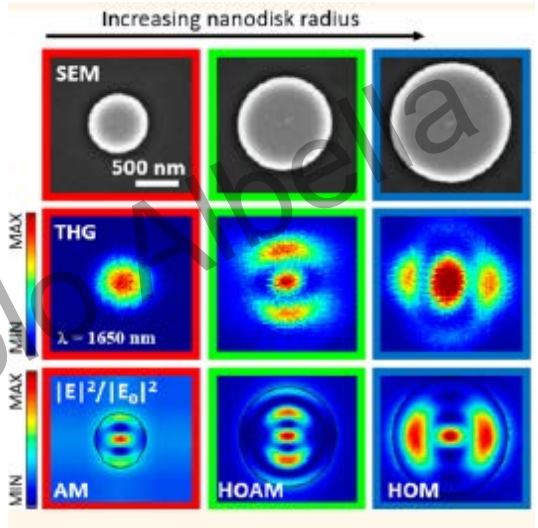


Si

η_{TH} ~ 0.0002 %

M. R. Shcherbakov et al. Nano Lett., **14**, 6488 (2014)
Y. Yang et al. Nano Lett., **15**, 7388 (2015)
L. Wang et al. Nanoscale., **9**, 2201 (2017)

Ge



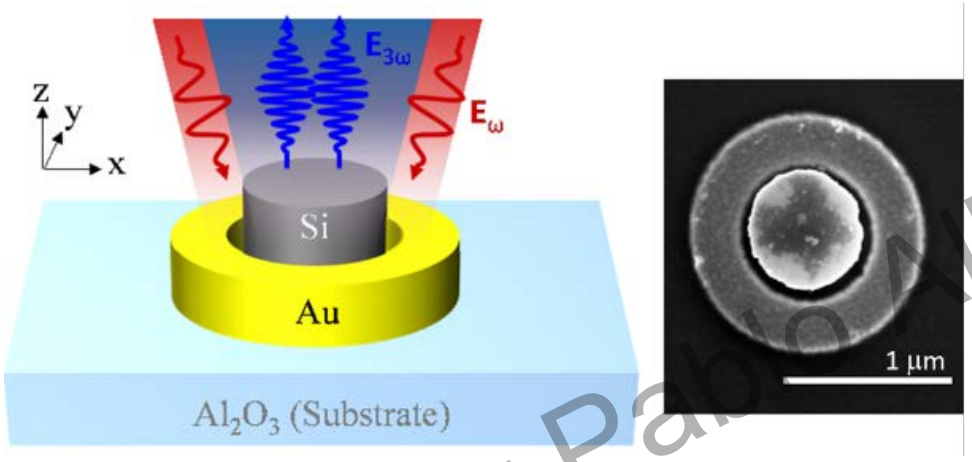
G. Grinblat et al. Nano Lett., **16**, 4635 (2016)
G. Grinblat et al. ACS Nano, **11**, 953 (2017)

η_{TH} ~ 0.001 %

- Efficiency is still low, because of the low electric field enhancement in dielectric structures
- **Ge** has shown conversion efficiencies of ~0.001% at 550 nm (green)
  - Performance cannot be extended to the blue region of the visible spectrum, due to high absorption of Ge below 1600 nm

How to improve the TH conversion efficiency?

Metal – dielectric hybrid structure

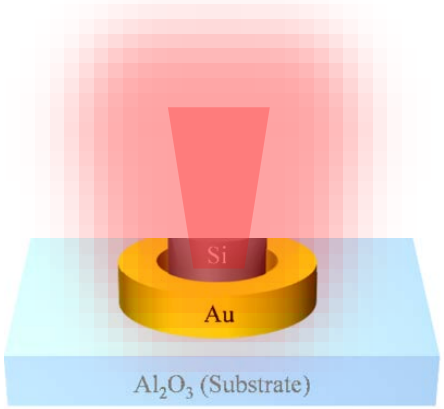


- In Third order nonlinear phenomena, the density of third harmonic dipoles are basically proportional to the third power of electric field (THG intensity is proportional to the 6th power of E).
- The idea is combining a metallic ring with a dielectric nanostructurecore to make hybrid one.
  - As we showed in [*] Plasmonic resonance of a Au nanoring can enhance the E field in a relatively large volume.
- This can boost the anapole mode supported by a Si nanodisk
  - strongly enhancing the electric field inside the large third-order susceptibility dielectric

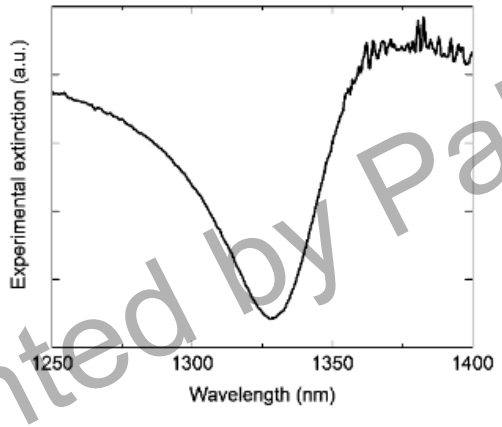
[*] A. Rakovich, P. Albella and S. A. Maier. **ACS Nano**, **9**, 2648 (2015)

Excitation of anapole mode for intense electric field

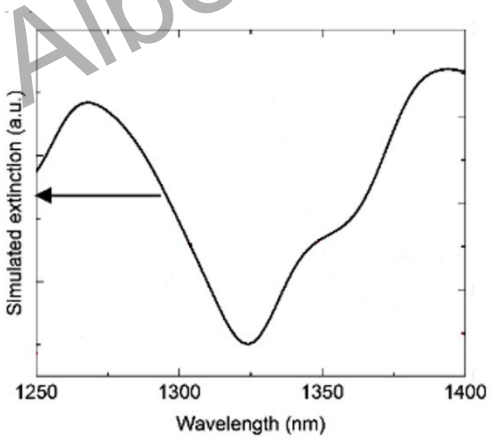
- To predict THG capabilities of the hybrid structure
  - we need to evaluate its ability to **concentrate the electric field inside the dielectric core**
  - by measuring and calculating first the extinction (a clear valley observed around 1325 nm)



Experiment

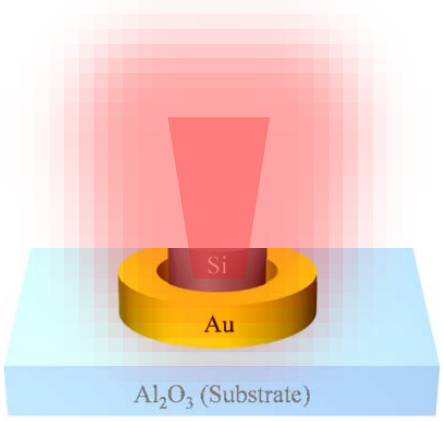


FDTD

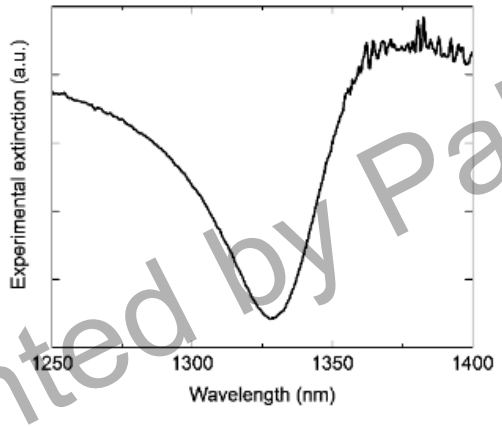


Excitation of anapole mode for intense electric field

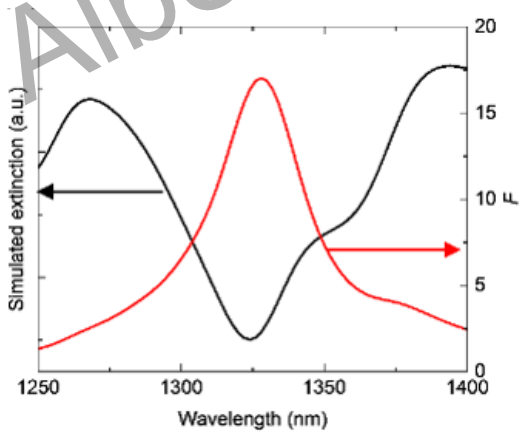
- To predict THG capabilities of the hybrid structure
  - we need to evaluate its ability to **concentrate the electric field inside the dielectric core**
  - by measuring and calculating first the extinction (a clear valley observed around 1325 nm)



Experiment



FDTD



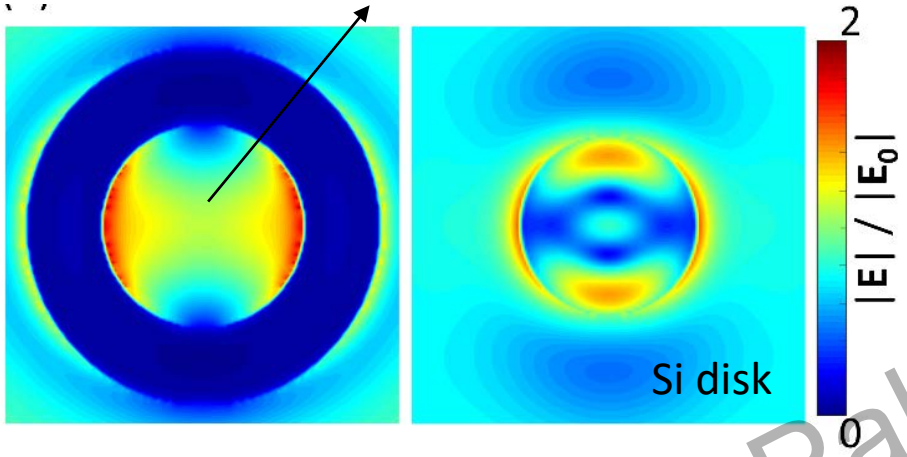
- we numerically explore the normalized electric field intensity ($|E|^2/|E0|^2$) averaged within the Si nanodisk volume, using the following expression:

$$F = \frac{\iiint |E|^2 dV}{|E_0|^2 V}$$

  - @ the wavelength of the extinction valley, drastically increased.

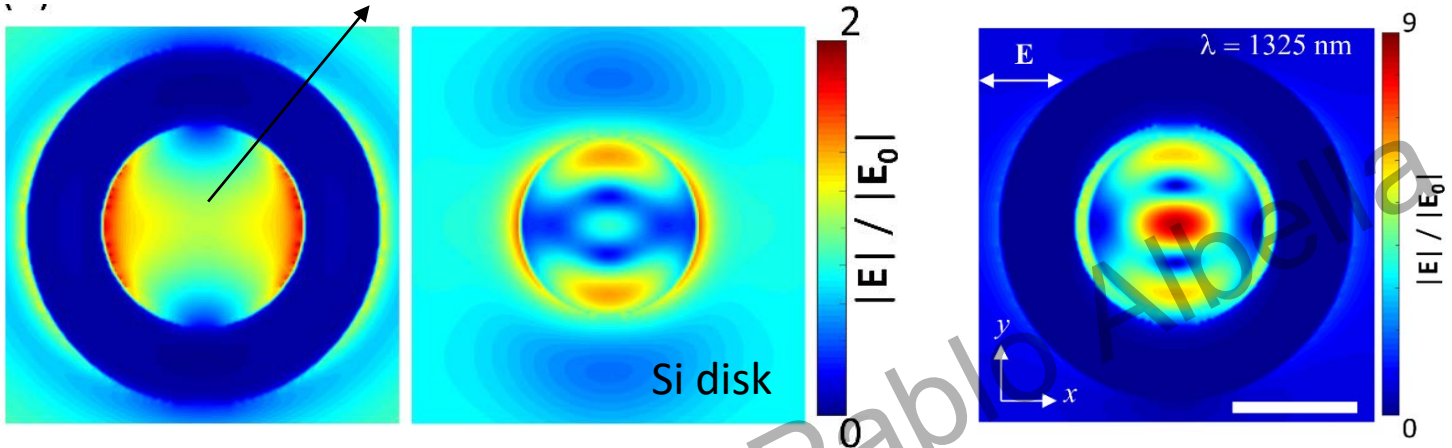
Let's double check the excitation of anapole mode and the increase in *F*

Au nanoring can enhance the electric field inside.

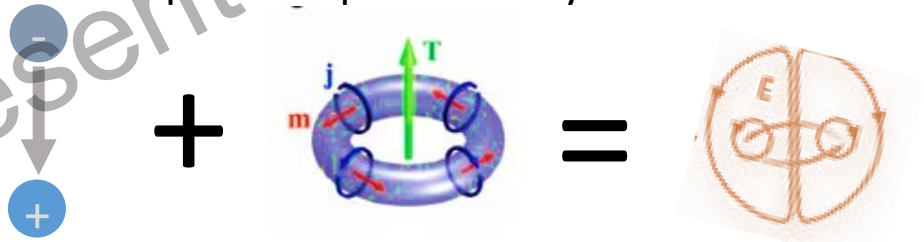


Let's double check the excitation of anapole mode and the increase in *F*

Au nanoring can enhance the electric field inside.



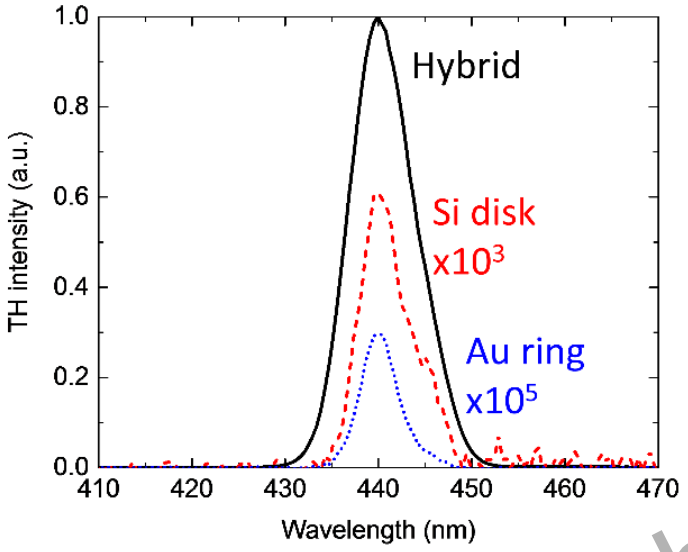
- Comparing the isolated structures with the hybrid structure shows E/E0 ~ 9.
- The shape of the distribution is quite unique, (anapole mode). Its physical origin has been theoretically attributed [*] to the destructive interference in the far field between the radiation patterns produced by the electric and toroidal dipole modes.



- **This provides a route to maximize the electric field energy inside the particle**

[*] Miroshnichenko, A. E et al. Nat. Commun. 2015, 6, 8069.

TH conversion efficiency

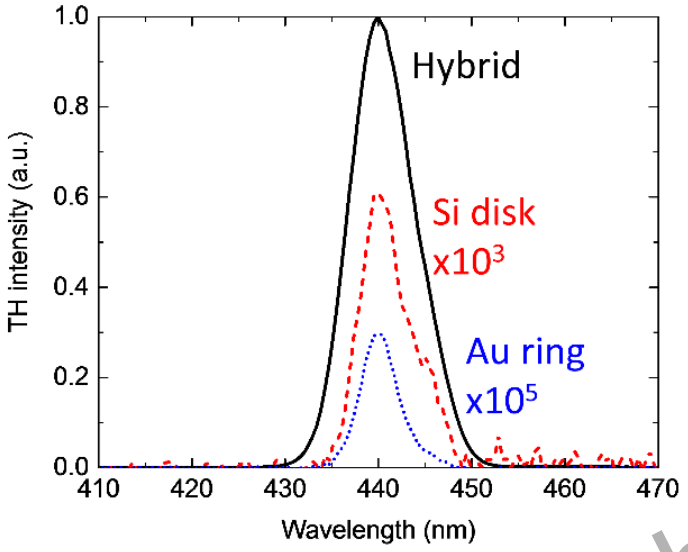


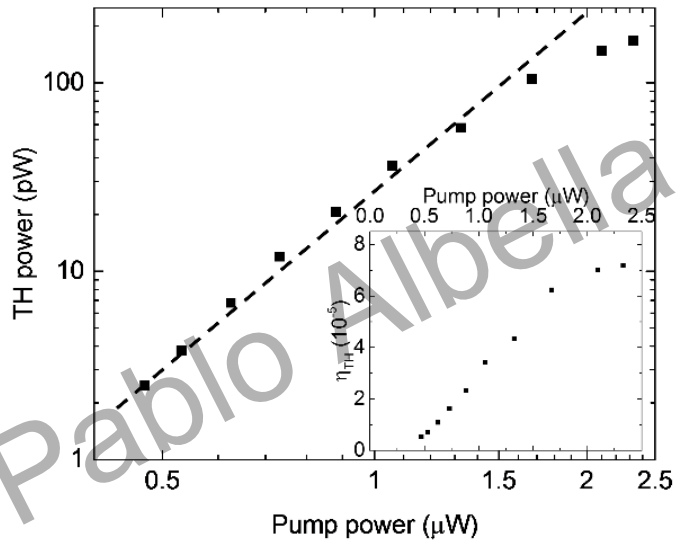
- The **hybrid structure shows very strong TH intensity**, 1000 times higher than single Si disks, and 100000 times higher than the Au ring

T. Shibanuma, G. Grinblat, P. Albella and S. A. Maier, **Nano Lett**. 2017, 17, 2647−2651

TH conversion efficiency

$$P^{(3)}(3\omega) = \chi^{(3)} E(\omega)E(\omega)E(\omega)$$



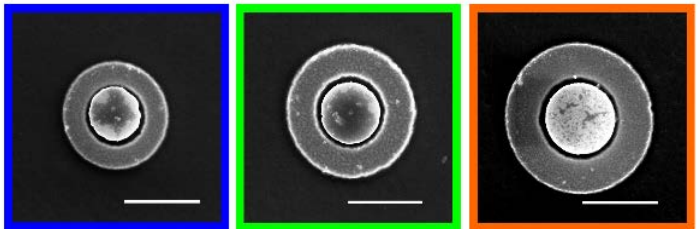


- The **hybrid structure shows very strong TH intensity**, 1000 times higher than single Si disks, and 100000 times higher than the Au ring

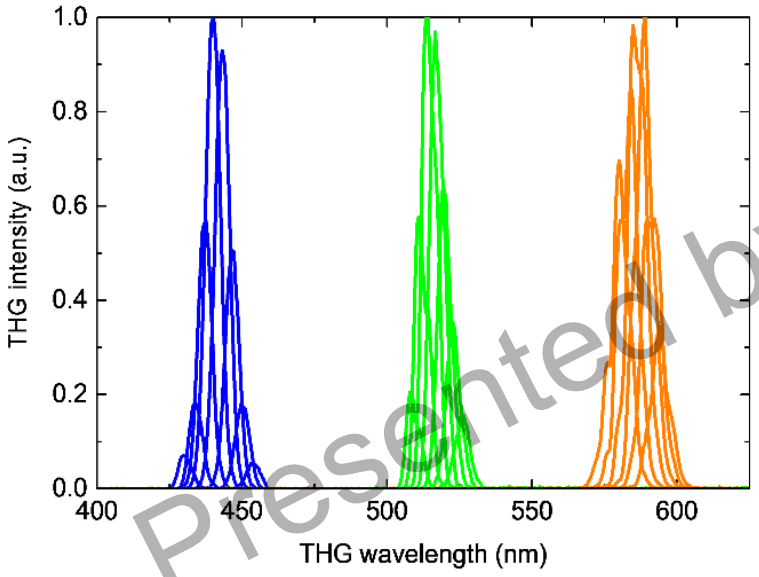
- By sweeping the pumping power, we found the slope of 3 in the logarithm scale of TH intensity, confirming that this is third harmonic generation
  - The TH conversion efficiency of the hybrid structure: η_{TH} ~ 0.007 %
  - This is as far as we know the largest TH efficiency from a nanoantenna.

T. Shibanuma, G. Grinblat, P. Albella and S. A. Maier, **Nano Lett**. **2017**, 17, 2647−2651

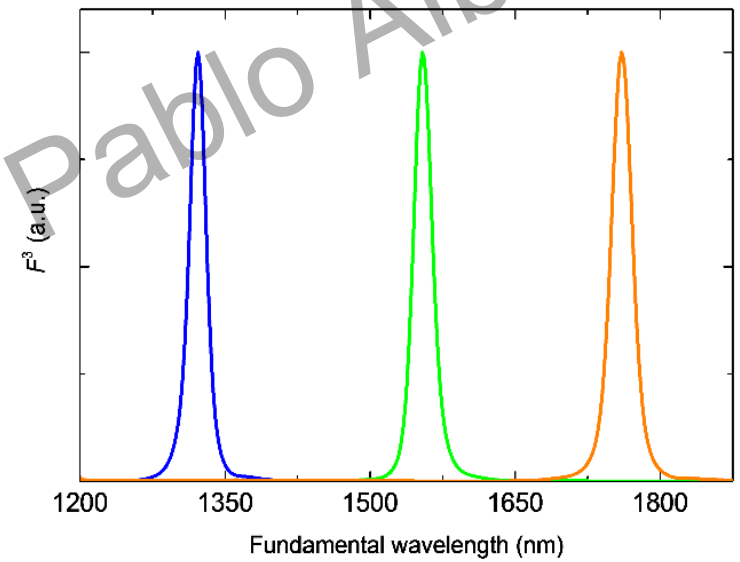
Very important: scalability offers THG throughout entire VIS



Experimental TH intensity



Simulated TH intensity (F^3)



THG enhancement can be achieved throughout the visible regime

T. Shibanuma, G. Grinblat, P. Albella and S. A. Maier, **Nano Lett**. 2017, 17, 2647−2651

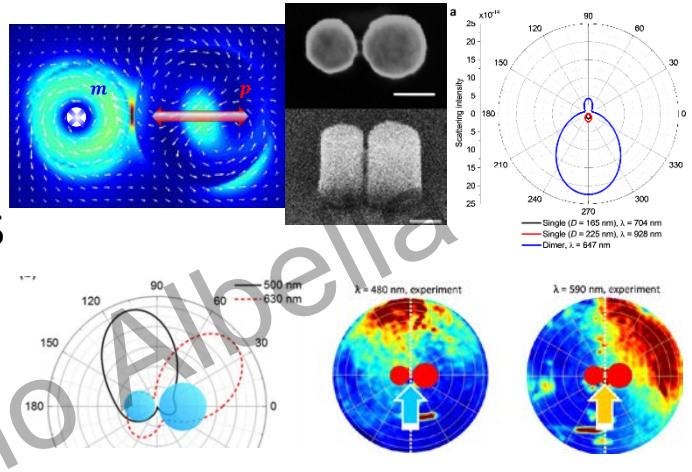
Summary of Part IV

- Hybrid structures can generate strong TH emission in the optical range.
- The anapole mode supported by the dielectric core, boosted by the plasmonic resonance of the surrounding metal nanoparticle, produced high electric field enhancement within the Si nanostructure.
- TH conversion efficiency can be drastically improved due to the coupling of the individual components defining the hybrid, (up to 0.007%).
- The optimum emission wavelength can be tuned from the blue to the red region of the visible spectrum by suitably adapting the nanosystem geometrical dimensions.

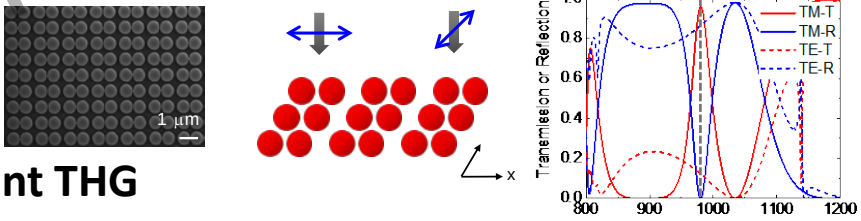
Outline

Part III:

- **What about enhancing light with directional control? or switchable steering of light?**
  - Possible direct application in Selective sensing or SES
  - Application in optical nano-circuitry

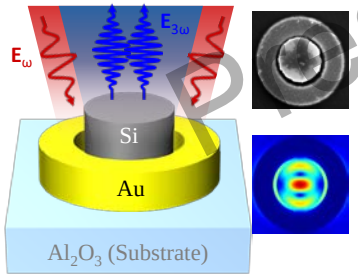


- **Polarization control of high transmission / reflection switching by all-dielectric metasurfaces**



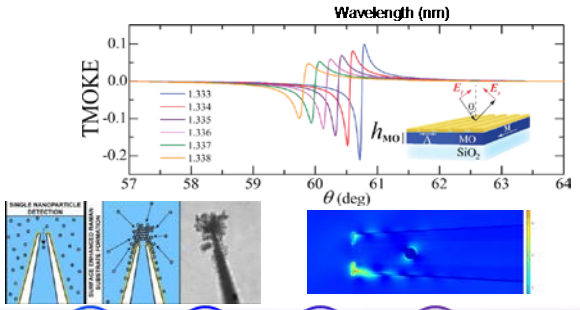
Part IV:

- **Dielectric - Metal hybrid structures for efficient THG**



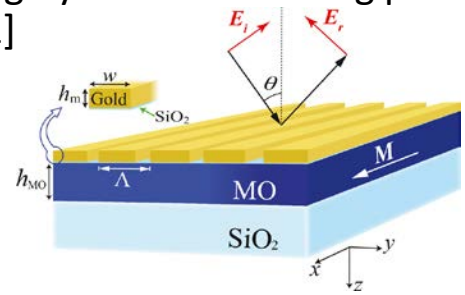
Part V:

- **Examples of (bio) - sensors**
  - MO-Kerr effect in magnetoplasmonic crystals
  - DNA mapping with nanopipetes (SERS,SEF)



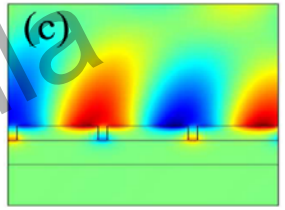
Magnetoplasmonic Crystals for the Design of Highly Sensitive Plasmonic (Bio)sensing Platforms

- An example of a simple yet highly sensitive sensing platform can be made as a one-dimensional magneto plasmonic crystal [1]

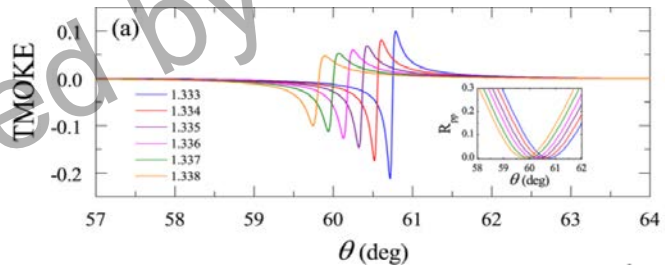


[1] B.F Diaz-Valencia et al. ACS Omega, 2 (11), 7682–7685, 2017

a 1D Au grating grown on a magneto-optical metallic substrate



- Sensitivity of an SPR-based sensor depends on where the EM field is most amplified
  - IDEA: develop a magnetoplasmonic crystal to excite SPRs mainly localized at the analyte region.
    - This is done optimizing the geometry of the grating and the MO metallic slab at the λinc [2].
- By using the optimization procedure in [3], enhanced TMOKE values with very narrow Fano-like resonant peaks can be achieved

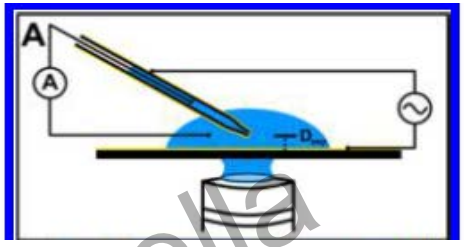


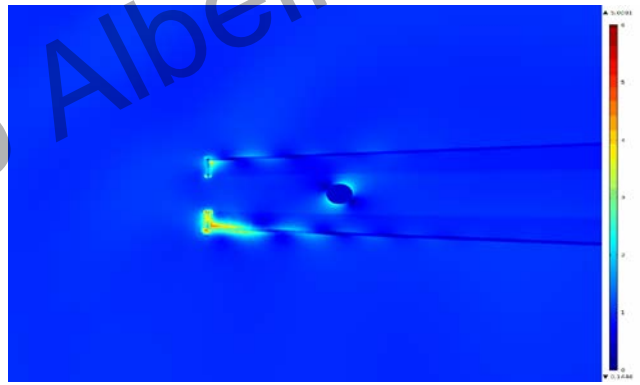
- These Fano-like resonances are extremely sensitive to the refractive index of the surrounding media, thus allowing to detect very small changes in the dielectric properties of the analyte.

[2] J. Pistora et al. Opt. Express 2013, 21, 21741.
[3] B. Caballero et al. ACS Photonics 2016, 3, 203−208

Another example: DNA mapping with nanopipete (SERS and TERS)

Gold-Glass nanopipete





ACS Photonics

Article

pubs.acs.org/journal/apchd5

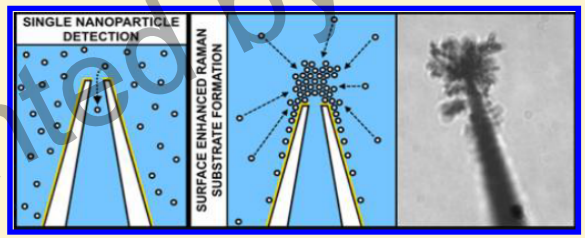
On-Demand Surface- and Tip-Enhanced Raman Spectroscopy Using Dielectrophoretic Trapping and Nanopore Sensing

Kevin J. Freedman,[†,⊥] Colin R. Crick,[†,⊥] Pablo Albella,[‡] Avijit Barik,[§,∥] Aleksandar P. Ivanov,[†] Stefan A. Maier,[‡] Sang-Hyun Oh,[§,∥] and Joshua B. Edel*[,†]

[†]Department of Chemistry and [‡]EXSS Group, Physics Department, Imperial College London, South Kensington, SW7 2AZ, London, United Kingdom

[§]Department of Electrical and Computer Engineering and [∥]Department of Biomedical Engineering, University of Minnesota, Minneapolis, Minnesota 55455, United States

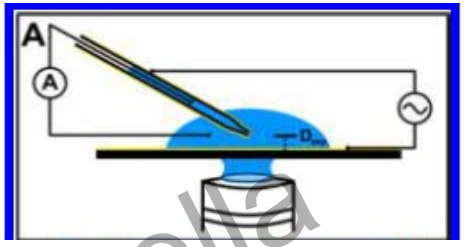
Supporting Information



ABSTRACT: Surface-enhanced Raman spectroscopy (SERS) and tip-enhanced Raman spectroscopy (TERS) have shown great promise in the detection and analysis of trace analytes throughout numerous fields of study. Both SERS and TERS utilize nanoscale plasmonic surface features to increase the intensity of observed Raman signals by many orders of magnitude (>10^8). One of the major factors limiting the wider and more routine implementation of the enhanced Raman phenomena is in the difficulty of forming consistent and reliable plasmonic substrates with well-defined "hot-spots". We address this limitation by designing a platform that can be used for both SERS and TERS. The presented technique allows for rapid, controlled, "on-demand", and reversible formation of a SERS substrate using dielectrophoresis at the end of a nanoscale pipet. This drives gold nanoparticles in solution to concentrate and self-assemble at the tip of the pipet, where analytes can be detected effectively using SERS. An additional benefit of the platform is that the nanopipet containing a nanopore can be used for detection of individual nanoparticles facilitated by the added enhancement originating from the nanopipet tip enhanced signal. Complementing the experimental results are simulations highlighting the mechanism for SERS substrate formation and TERS detection.

Another example: DNA mapping with nanopipete (SERS and TERS)

Gold-Glass nanopipete



ACS Photonics

Article

pubs.acs.org/journal/apchd5

On-Demand Surface- and Tip-Enhanced Raman Spectroscopy Using Dielectrophoretic Trapping and Nanopore Sensing

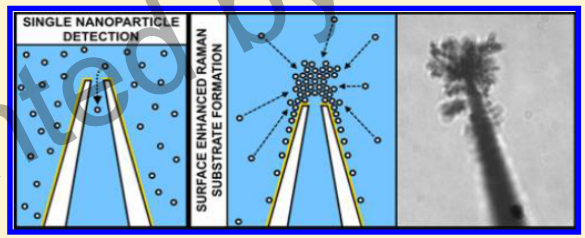
Kevin J. Freedman,[†,⊥] Colin R. Crick,[†,⊥] Pablo Albella,[‡] Avijit Barik,[§,∥] Aleksandar P. Ivanov,[†] Stefan A. Maier,[‡] Sang-Hyun Oh,[§,∥] and Joshua B. Edel*[,†]

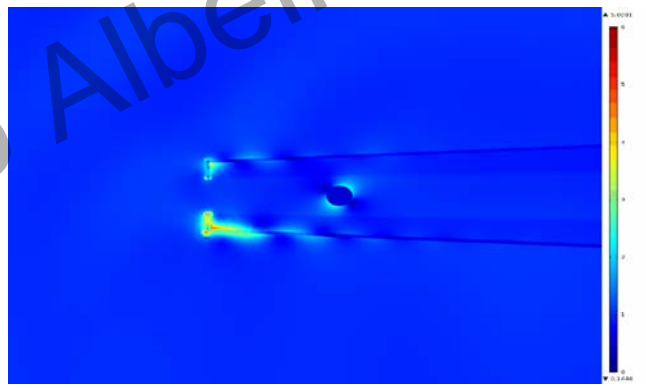
[†]Department of Chemistry and [‡]EXSS Group, Physics Department, Imperial College London, South Kensington, SW7 2AZ, London, United Kingdom

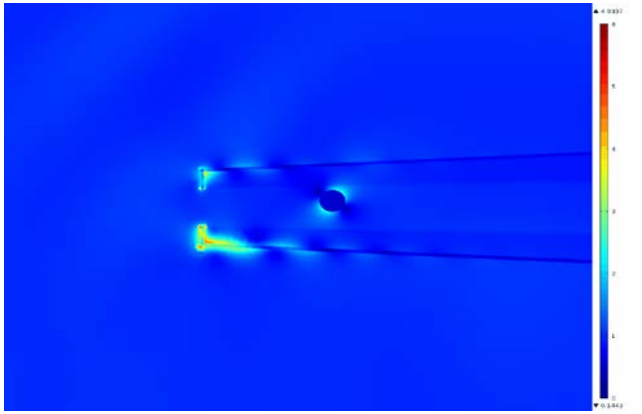
[§]Department of Electrical and Computer Engineering and [∥]Department of Biomedical Engineering, University of Minnesota, Minneapolis, Minnesota 55455, United States

Supporting Information

ABSTRACT: Surface-enhanced Raman spectroscopy (SERS) and tip-enhanced Raman spectroscopy (TERS) have shown great promise in the detection and analysis of trace analytes throughout numerous fields of study. Both SERS and TERS utilize nanoscale plasmonic surface features to increase the intensity of observed Raman signals by many orders of magnitude (>10^8). One of the major factors limiting the wider and more routine implementation of the enhanced Raman phenomena is in the difficulty of forming consistent and reliable plasmonic substrates with well-defined "hot-spots". We address this limitation by designing a platform that can be used for both SERS and TERS. The presented technique allows for rapid, controlled, "on-demand", and reversible formation of a SERS substrate using dielectrophoresis at the end of a nanoscale pipet. This drives gold nanoparticles in solution to concentrate and self-assemble at the tip of the pipet, where analytes can be detected effectively using SERS. An additional benefit of the platform is that the nanopipet containing a nanopore can be used for detection of individual nanoparticles facilitated by the added enhancement originating from the nanopipet tip enhanced signal. Complementing the experimental results are simulations highlighting the mechanism for SERS substrate formation and TERS detection.







Acknowledgements (People)

Imperial College London
- **Stefan Maier**
- T. Shibanuma
- Rupert Oulton
- Joshua Edel
- T. Roschuk
- M. Rahmani (now in ANU)
- E. Cortes and G. Grinblat
- F. Bresme
- T. Matsui
- S. Hanham

Universidad de Buenos Aires
- Andrea Bragas et al
- Fernando Stefani et al

CSIC
- **Javier Aizpurua**
- M. Nieto-Vesperinas
- Juan Jose Saenz
- J. Sanchez-Gil

Nanogune
- **Rainer Hillenbrand**
- Pablo Alonso (now in UniOvi)

Universidad de Cantabria
- **Fernando Moreno**
- **Francisco Gonzalez**
- J.M. Saiz
- J.M. Sanz
- R. Alcaraz

Duke University
- Henry Everitt et al

Army Research Lab
- Gorden Videen

Fresnel Institute
- Jean Michel Geffrin

Univerity of Lyon
- Rodolphe Vaillon

University of Southampton
- Otto Muskens

University of Heidelberg
- Annemarie Pucci
- Frank Neubrech

University of Windsor
- Ricardo F. Aroca

University of Sao Paolo
- Osvaldo de Oliveira Jr.
- Ricardo Mejía

University of Liverpool
- Colin Crick

ICFO, Spain
- J. Canet-Ferrer

Acknowledgements (Funding)

The Leverhulme Trust

Consejería de Economía,
Industria, Comercio y Conocimiento
Agencia Canaria de Investigación,
Innovación y Sociedad
de la Información


UNIVERSIDAD DE LAS PALMAS
DE GRAN CANARIA
UC
UNIVERSIDAD
DE CANTABRIA
Imperial College
London
Presented by Pablo Albella
Thank you!
Pablo Albella @ PHOTOPTICS 2018 (27 JAN 2018) - Madeira, Portugal