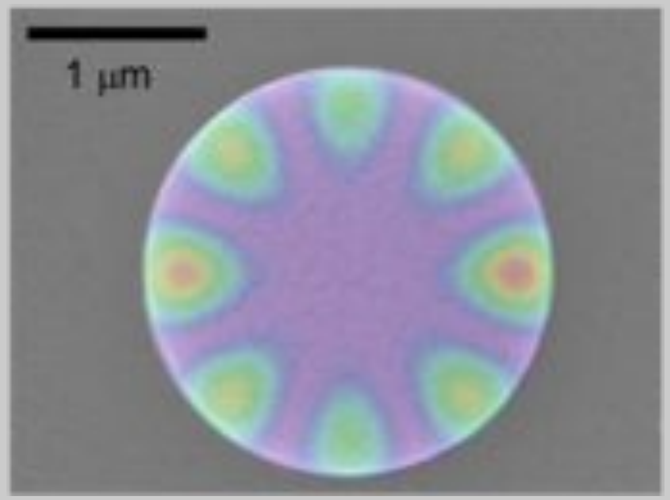
CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

UNIVERSITAT POLITÈCNICA DE VALÈNCIA

Applications of silicon nanoparticles to Electronics, Photonics and Nanomedicine



R. Fenollosa, I. Rodriguez & F. Meseguer

Instituto de Tecnología Química CSIC-UPV

Research National Council of Spain

Valencia, Spain

Nanolight, C. C. Benasque, March 7^{th}-March 11^{nt} 2016

Outline

- **Introduction & Motivation**
- **Optical properties of spherical microcavities. Mie Theory.**
- **Synthesis of silicon colloids.**
- **Applications of silicon colloids**
- **Monodisperse silicon nanocavities & Magnetic response**
- **Silicon colloids for electronic devices.**
- **Silicon colloids for sensing. Gold vs silicon SERS sensors.**
- **Silicon NPs for biomedicine.**

2

Silicon Colloids and NPs

They behave as spherical microcavities

They scatter/absorb very efficiently solar radiation.

They are semiconductors

They show a magnetic response

They are biocompatible & biodegradable

NPs & Porous silicon show explosive oxidation reactions

Photonics

Colloidal Chemistry

Electronics

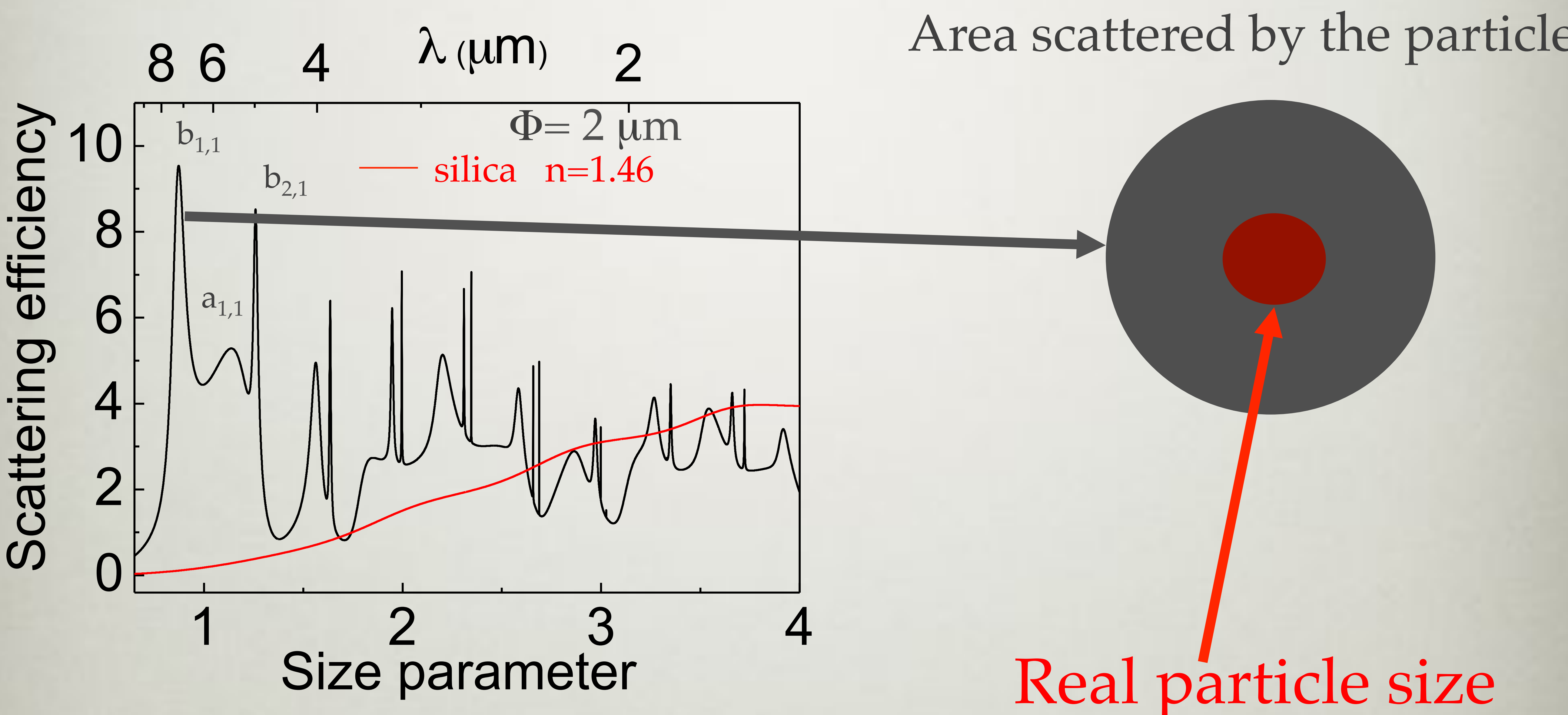
Medicine

Outline

- Introduction & Motivation
- **Optical properties of spherical microcavities. Mie Theory.**
- Synthesis of silicon colloids.
- Applications of silicon colloids
- Monodisperse silicon nanocavities & Magnetic response
- Silicon colloids for electronic devices.
- Silicon colloids for sensing. Gold vs silicon SERS sensors.
- Silicon NPs for biomedicine.

4

Microspheres can scatter light very efficently.
Scattering of Silicon vs. Silica microspheres



The size scattered by the particle can be 10 times larger than the real size!!

C. F. Bohren, D. R. Huffman, "Absorption and Scattering of Light by Small Particles, John Wiley 1998.

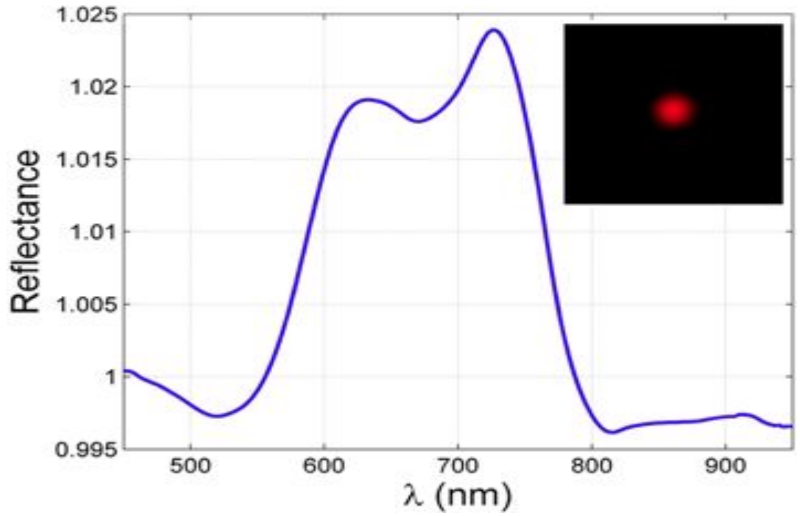
Outline

- Introduction & Motivation
- Optical properties of spherical microcavities. Mie Theory.
- **Synthesis of silicon colloids.**
- Applications of silicon colloids
- Monodisperse silicon nanocavities & Magnetic response
- Silicon colloids for electronic devices.
- Silicon colloids for sensing. Gold vs silicon SERS sensors.
- Silicon NPs for biomedicine.

6

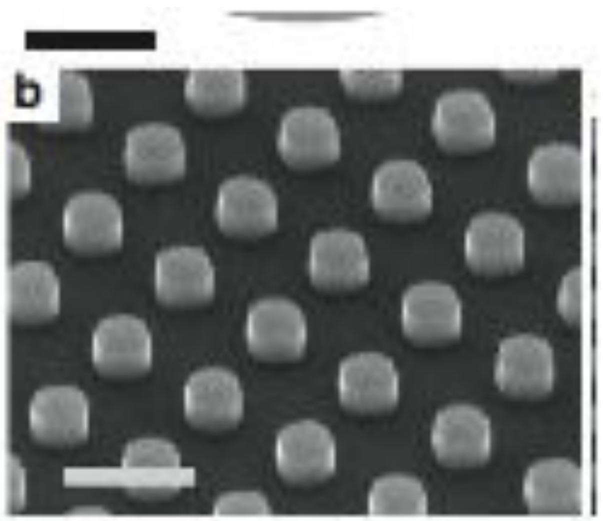
silicon based nanoresonators

Laser induced material transfer



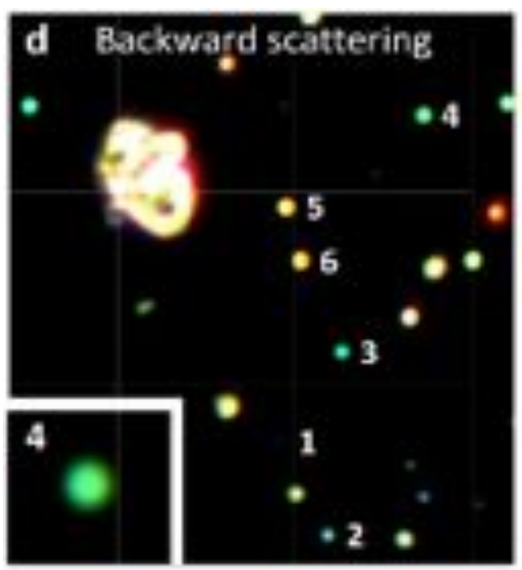
Evlyukhin,. et al. Nano. Lett. (2012).

Lithography induced black silicon



Polman. et al. Nat Comm. (2012).

Laser ablation



Luk'yanchuk et al et al. Nat Comm. (2013).

Theory.

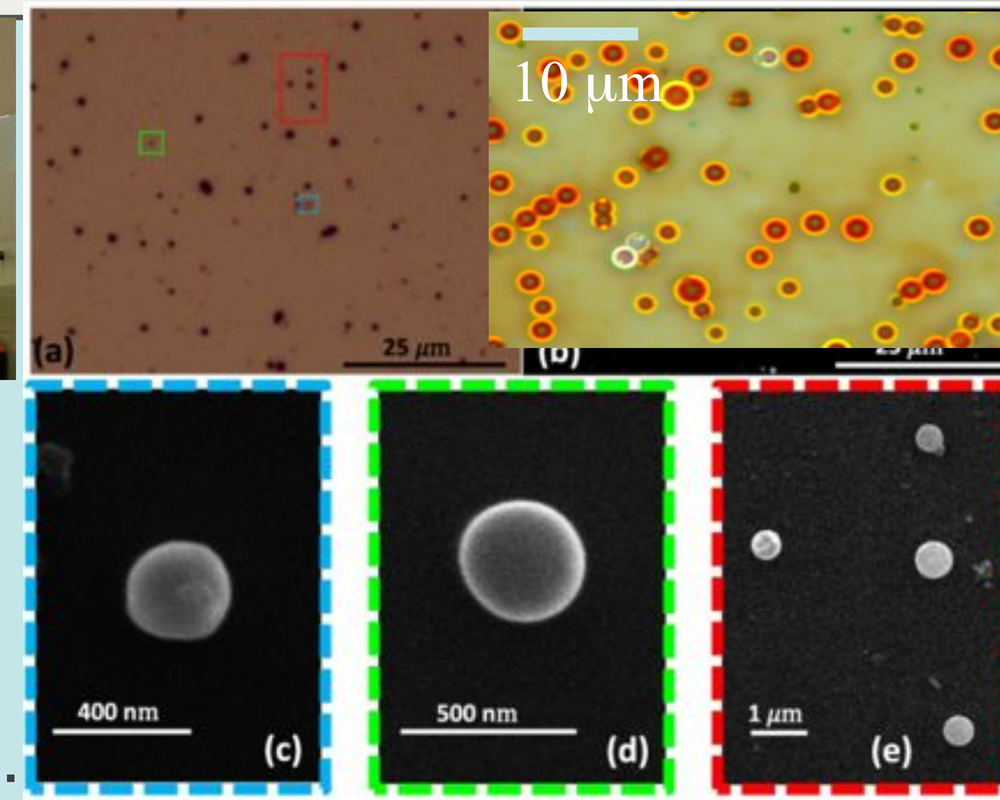
Pendry J. Phys. (2002), Luk'yanchuk et al Phys. Rev. B. 82, 045404,(2010); Garcia-Etxarri et al.,Opt. Express 19, 4815–4826 (2011). Kivshar et al., Opt. Express 20, 20599 (2012). Jian Zi,et al PRL 106, 203903 (2011); Kivshar ACSNano_2012_6_00837, A. Cummer et al.,PRL (2008), L. Brongersma et sl., PRL 2007

Requirements
Submicrometric silicon nanoparticles
Monodisperse silicon nanoparticles

Silicon nanocavities. Processing methods

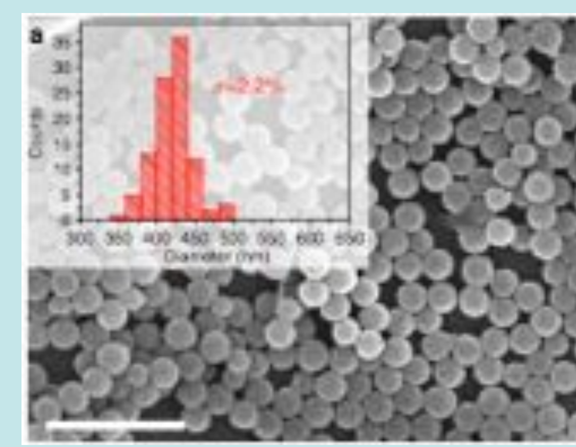
CVD .
Spherical particles
polydisperse particles
Porous, amorphous & crystalline

R. Fenollosa



L. Shi, et al Adv Mater. **24**, 5934, (2012).
R. Fenollosa, et al., *Adv. Mat.* **20**, 95 *(2008)*
R. Fenollosa, et *J. Mat Chem* 20, 5210, (2010).

Decomposition of Si_3H_8. Monodisperse (5%) and spherical particles + sintering process
Porous particles
n= 3.15
J. T. Harris et al , Chem. Mater. 22, 6378, (2010).
L. Shi, et al Nat Comm. 4, 1904, (2013)



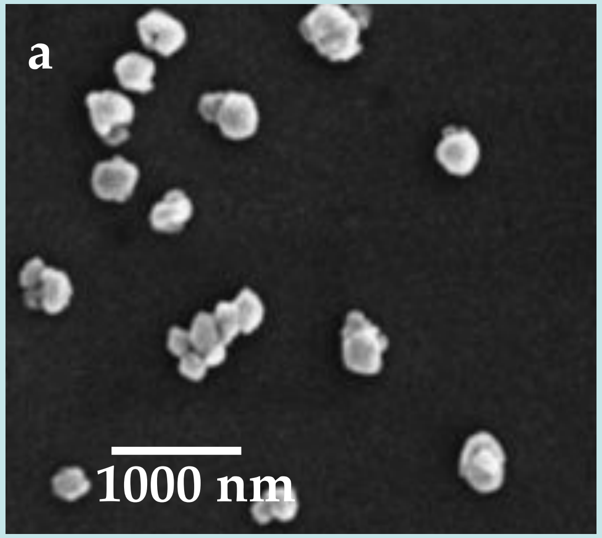
Texas University Collaboration

B. A. Korgel

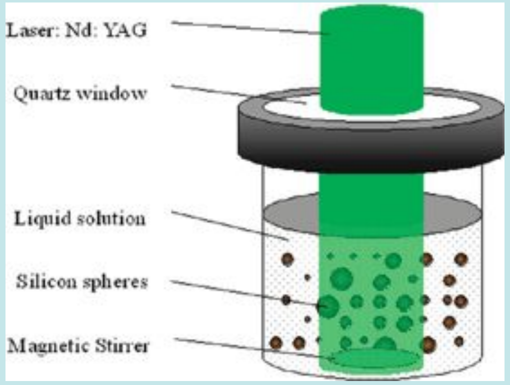
Silicon nanocavities through laser melting of NPs in suspension

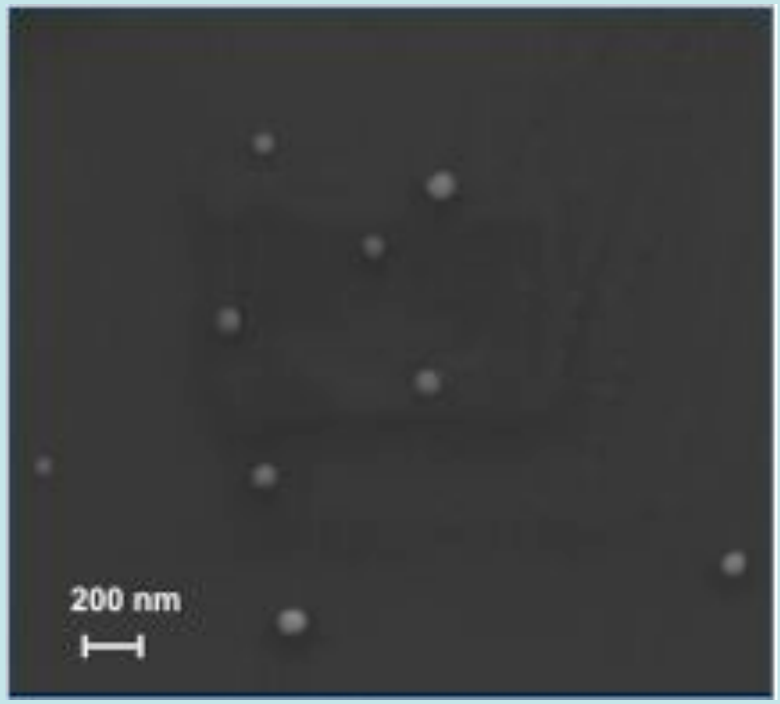
Arbitrary shape particles (non limited size values)
monodisperse (10%)
Grinding & sedimentation methods
I. Rodriguez et al., Nanoscale (2014).

I. Rodriguez



monodisperse (10%) (size. 100-500 nm)
Laser melting of monodisperse suspended NPs
.





X. Li, et al., Langmuir, 27, 5076, (2011)

I. Rodriguez, X. Lu, L. Shi, B Korgel, R. Alvarez-Puebla, and F. Meseguer, Nanoscale, 6, 5666, (2014).
I. Rodriguez et al submitted

Outline

- Introduction & Motivation
- Optical properties of spherical microcavities. Mie Theory.
- Synthesis of silicon colloids.
- Applications of silicon colloids
- **Monodisperse silicon nanocavities & Magnetic response**
- Silicon colloids for electronic devices.
- Silicon colloids for sensing. Gold vs silicon SERS sensors.
- Silicon NPs for biomedicine.

10

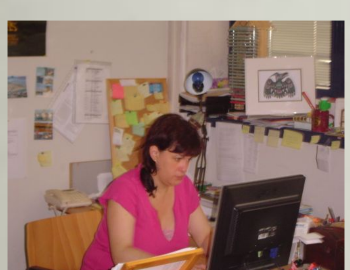
Monodisperse Silicon colloids. Optical properties of single particles

Decomposition of Si_3H_8 + sintering process

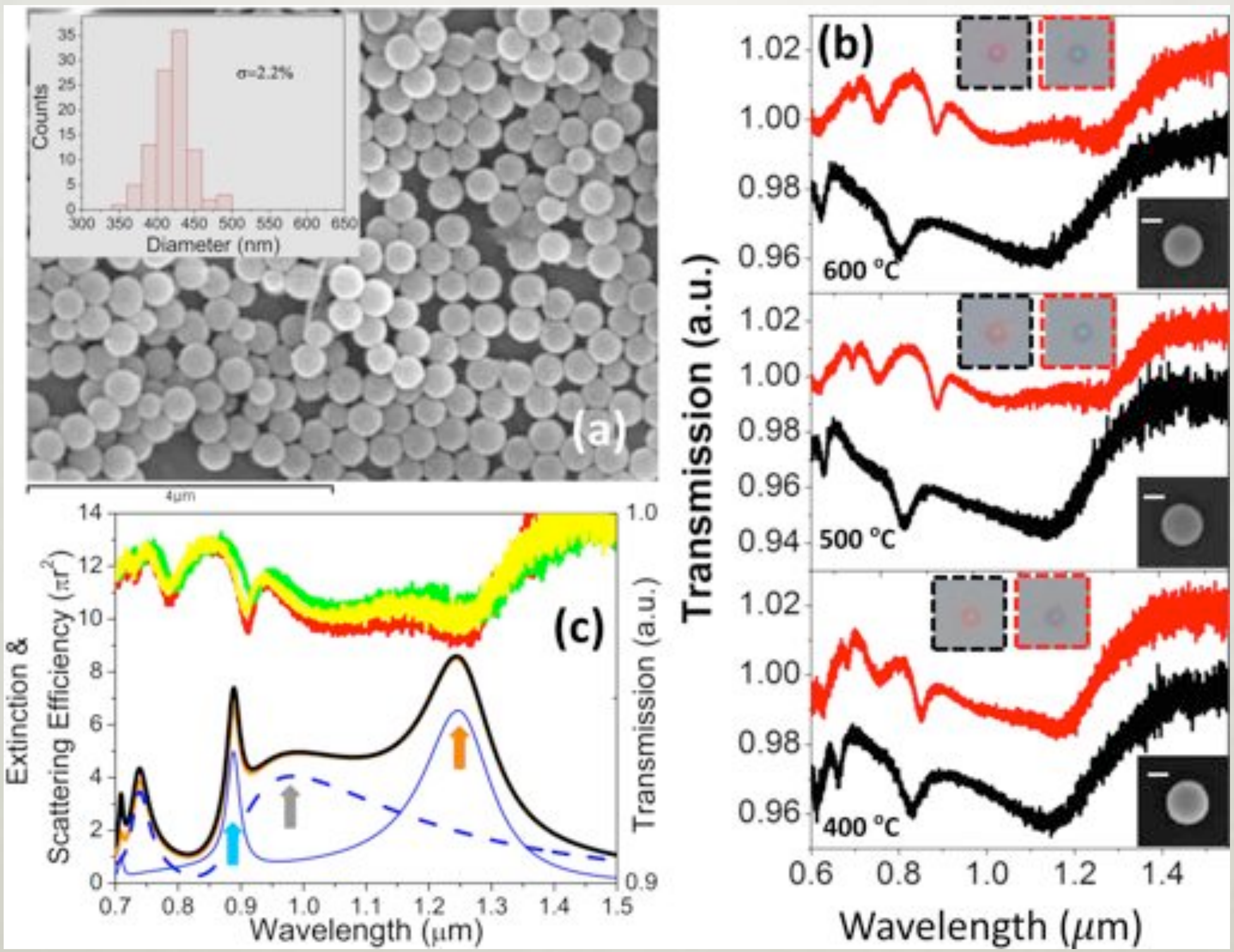
L. Shi

R. Fenollosa

B. A. Korgel



I. Rodriguez

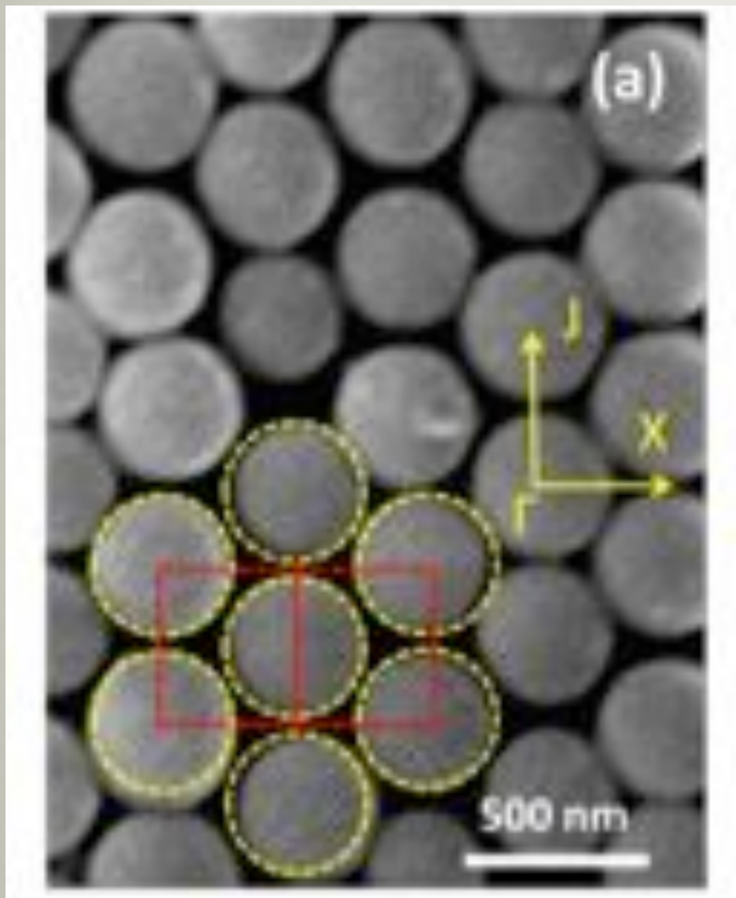


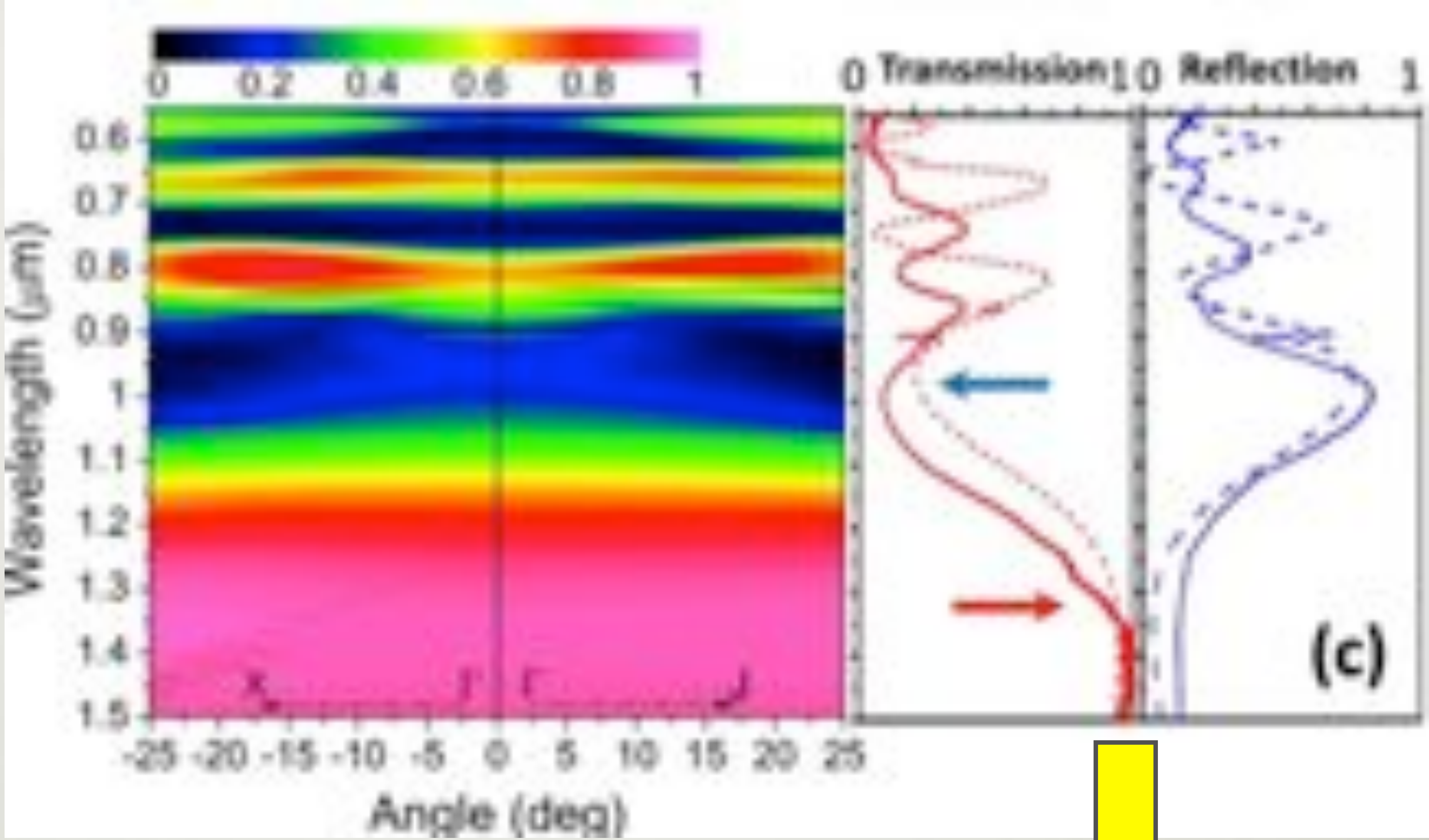
After sintering

Before sintering

L. Shi, J. T. Harris, R. Fenollosa, I. Rodriguez, X. Lu, B. A. Korgel, and F. Meseguer
Nature Communications 4, 1904 (2013).

2D Silicon colloids based Photonic Crystal





Non-close packed 2D PC
with omnidirectional photonic
bandagap at λ=1μm

Light is fully transmitted
At λ> 1200- forward scattering-
(Polman et al., Nat Comm 2012)

L. Shi, J. T. Harris, R. Fenollosa, I. Rodriguez, X. Lu, B. A. Korgel, and F. Meseguer
Nature Communications 4, 1904 (2013).

Outline

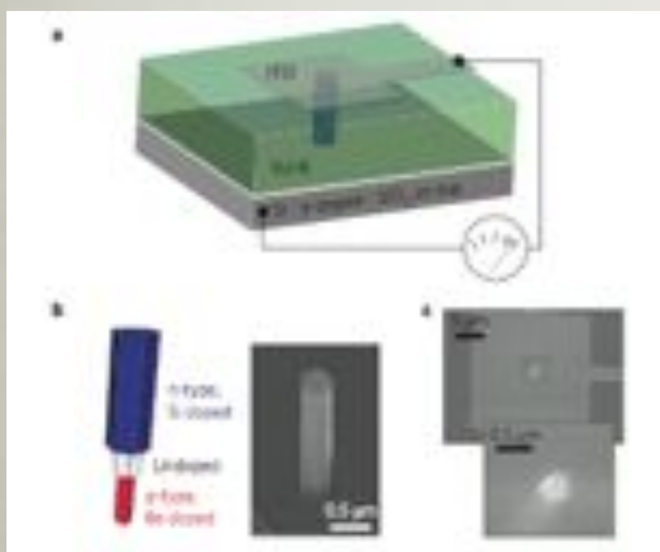
- Introduction & Motivation
- Optical properties of spherical microcavities. Mie Theory.
- Synthesis of silicon colloids.
- Applications of silicon colloids
- Monodisperse silicon nanocavities & Magnetic response
- **Silicon colloids for electronic devices.**
- Silicon colloids for sensing. Gold vs silicon SERS sensors.
- Silicon NPs for biomedicine.

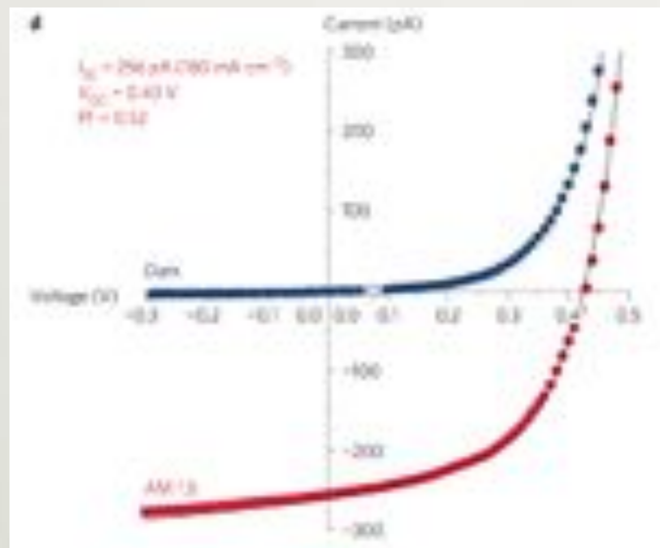
Rectifying junction in semiconductor nanowires

The effective optical area can be much larger than the device projected area !!

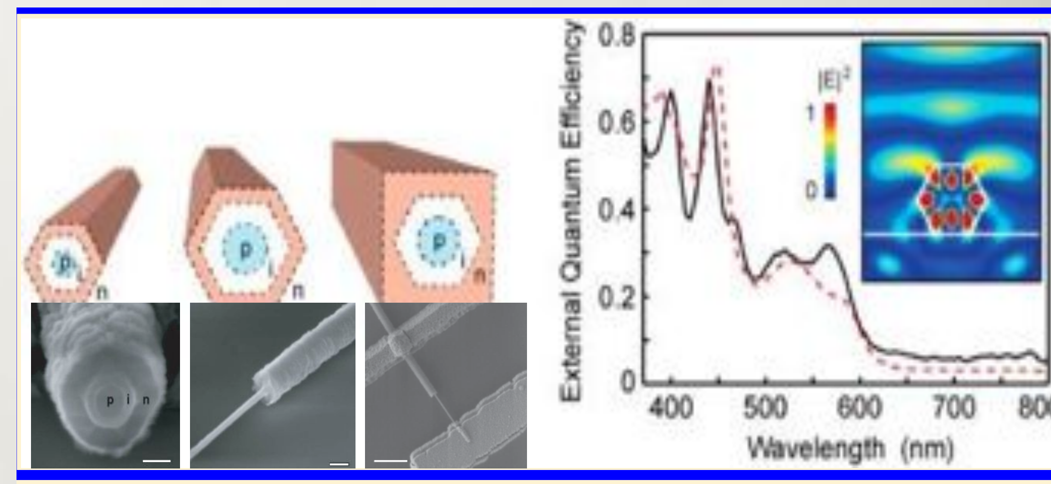
The absorption efficiency > 1

GaAs PVC nanowires beyond the S-Q limit
Fontcuberta et al. Nat Photonics 2013
Photocarriers generated near the collecting electrodes!!





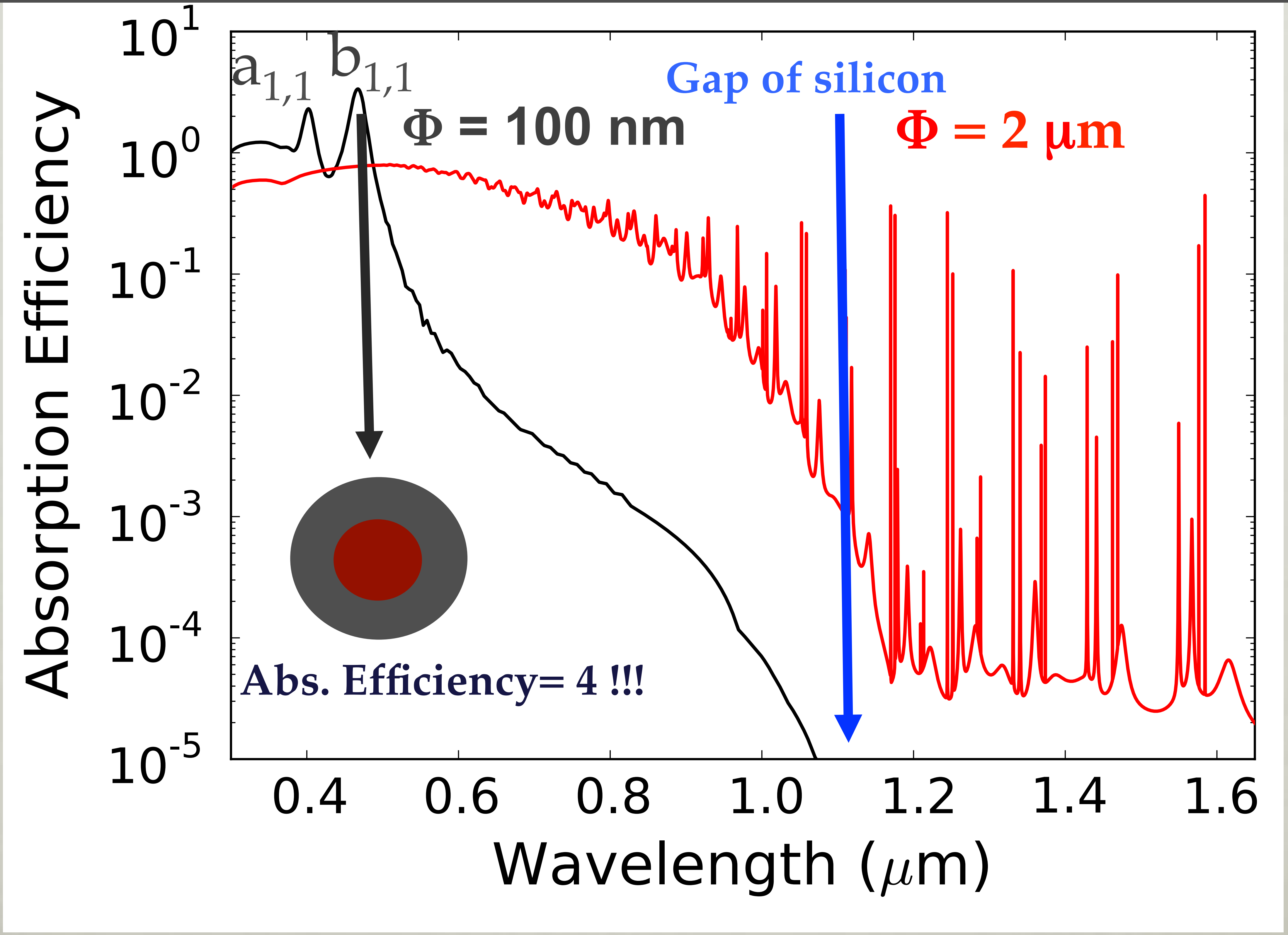
p-i-n PV cell on Silicon nanowires.
Lieber et al. Nature 2007, NL 2012



See also Ge nanowires Brongersma et al., Nat. Mat 2008;, Si nanowires Lieber Nature 2007 Kelzenberg, M. D. et al.. Nat. Mater. 9, 239–244 (2010) Kim, S. K. et al. Nano Lett. 12, 4971–4976 (2012). Fan, Z. et al., Nat. Mater. 8, 648–653 (2009). Wallentin, J. et al. Science 339, 1057–1060 (2013). Badding Adv. Mat 2013; S. Fan PNAS 2010

What about Infrared photons ?
How to harvest them?

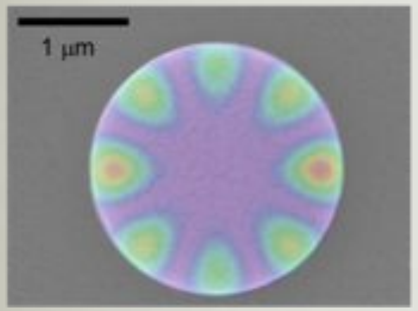
Silicon nano microspheres can absorb light very efficently in the visible region. They can also absorb it in the IR region!!

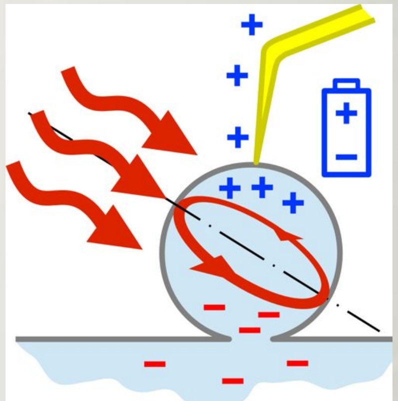


M. Garín, R. Fenollosa, P. Ortega, F. Meseguer, J. Appl. Phys. 119, 033101, (2016)

WHY A SILICON SPHERICAL PHOTODIODE MAY HARVEST INFRARED PHOTONS

Trapped photons stay in the cavity for long time enough to be absorbed

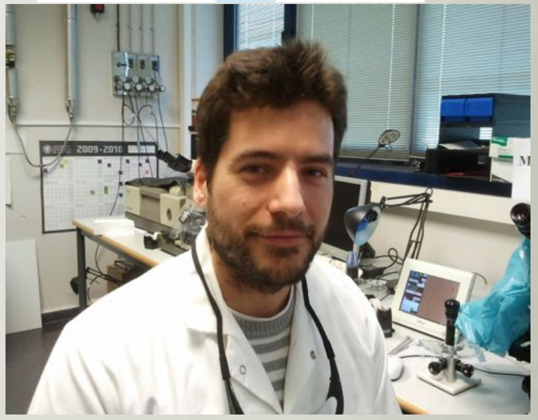




Optical mode at λ=1100 nm
Q factor = 6×10^3

R. Fenollosa

The photon stays for $\tau = 3 \times 10^{-12}$ sec



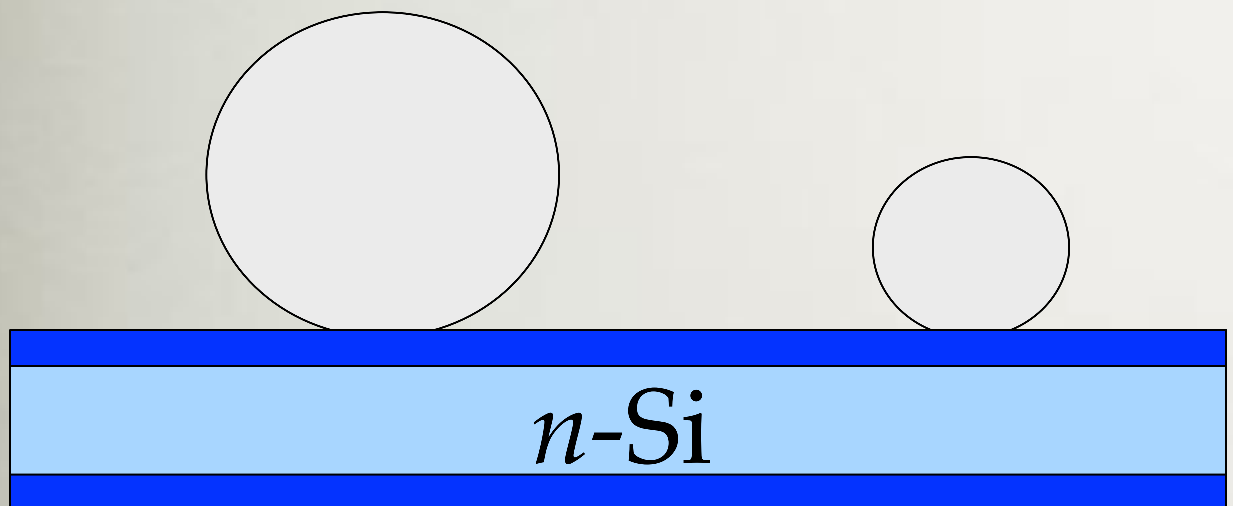
M. Garín

The time needed for traveling 0,3 mm in bulk silicon (the thickness of a silicon PV cell) !!

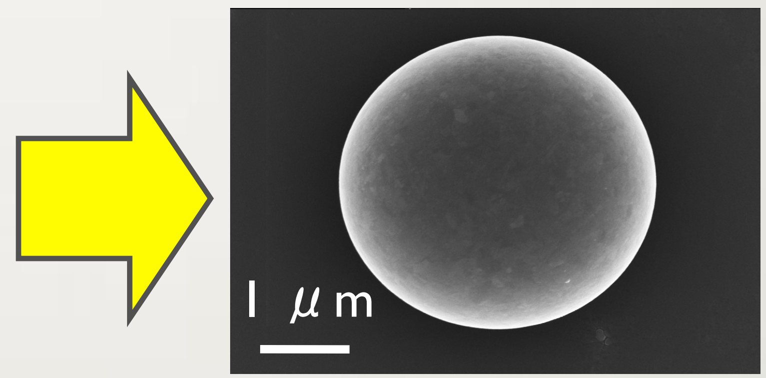
M. Garín, R. Fenollosa, L. Shi, R. Alcubilla, Ll. Marsal & F. Meseguer, Nature Comm. 5, 3440 (2014). SPIE Newsroom DOI 10.1117/2.1201405.005483

The PV cell processing
(minimizing processing steps).

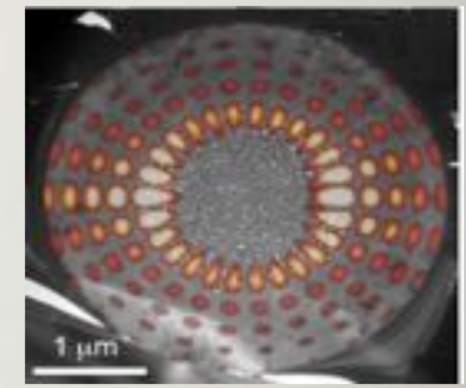
1. The CVD synthesis



CVD Poly-Si colloid

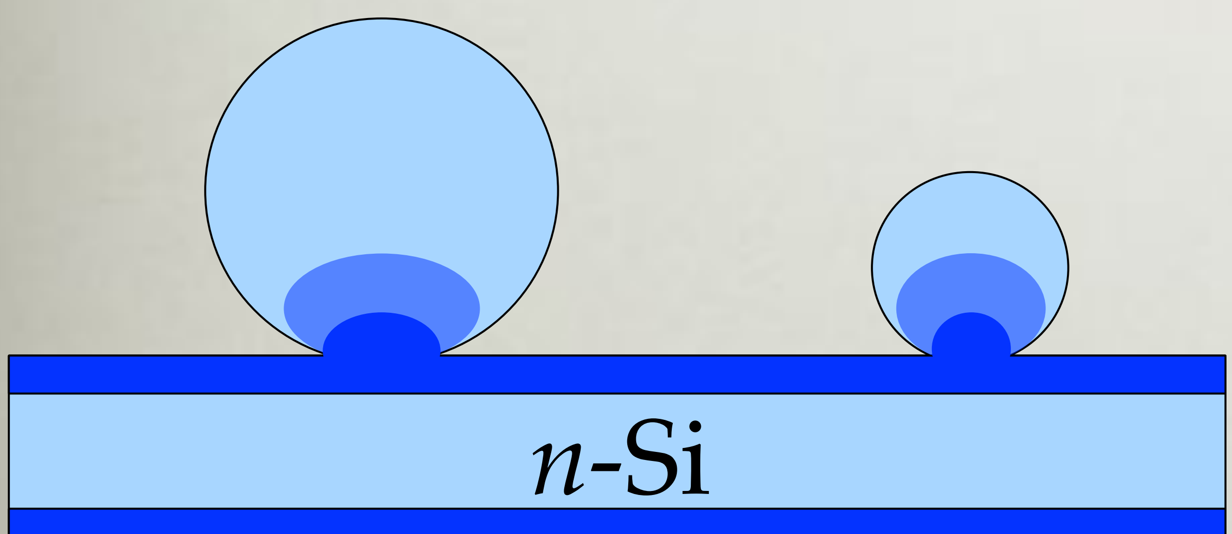


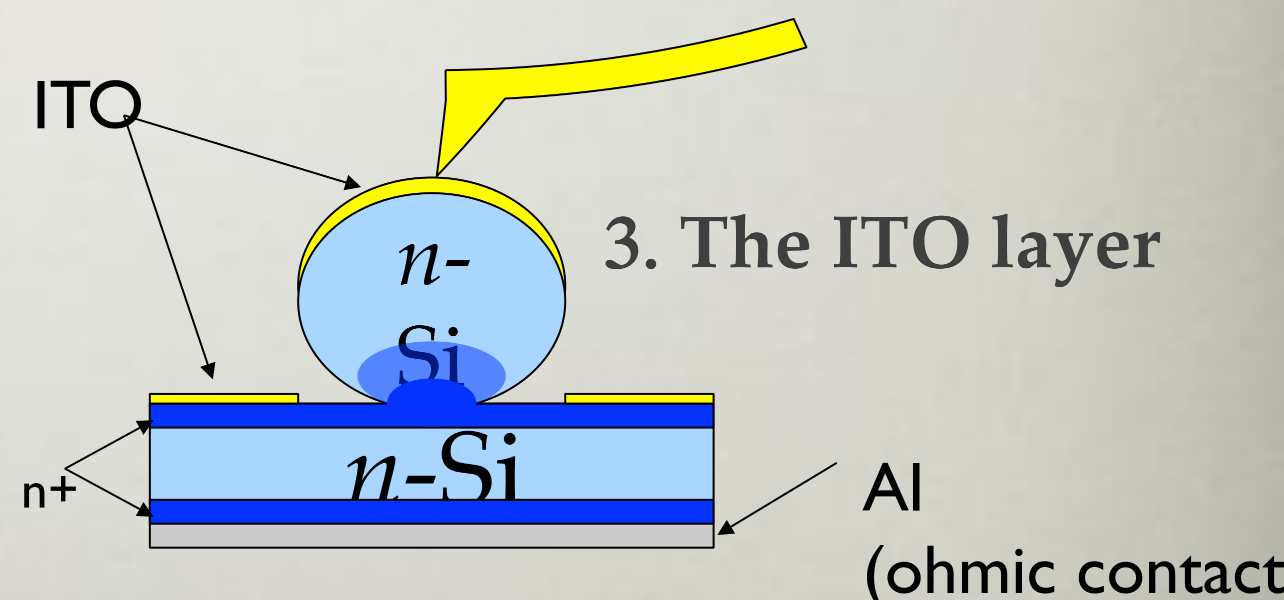
External view



Internal view
& Mie modes

2. The thermal diffusion

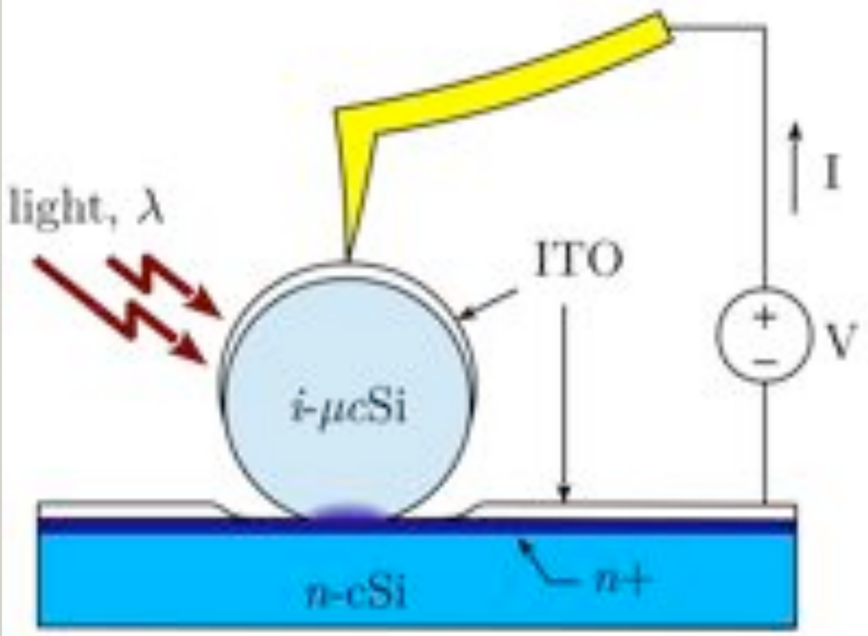


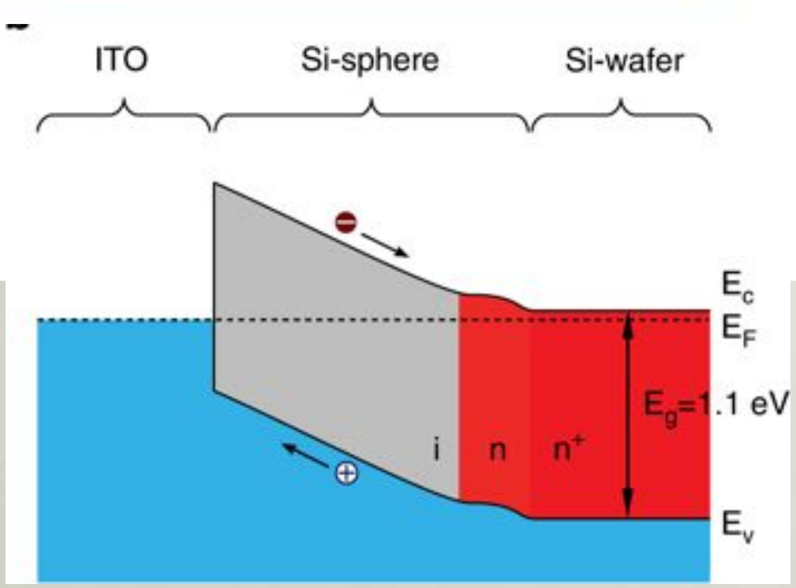


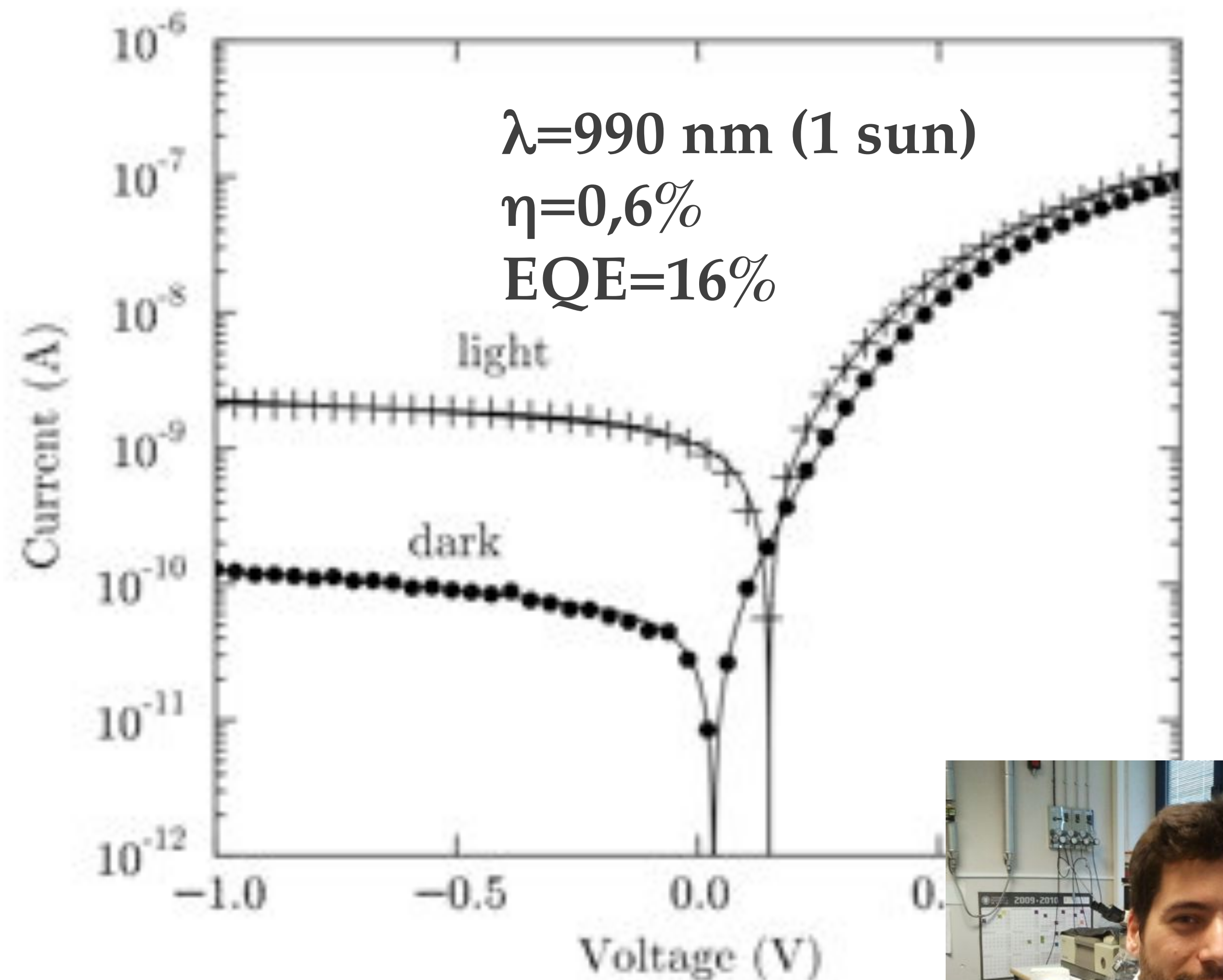
3. The ITO layer

M. Garín, et al Nature Comm. 5, 3440 (2014).
M. Garin et al SPIE Newsroom DOI 10.1117/2.1201405.005483
& R. Fenollosa, et al submitted

I(V) measurements.



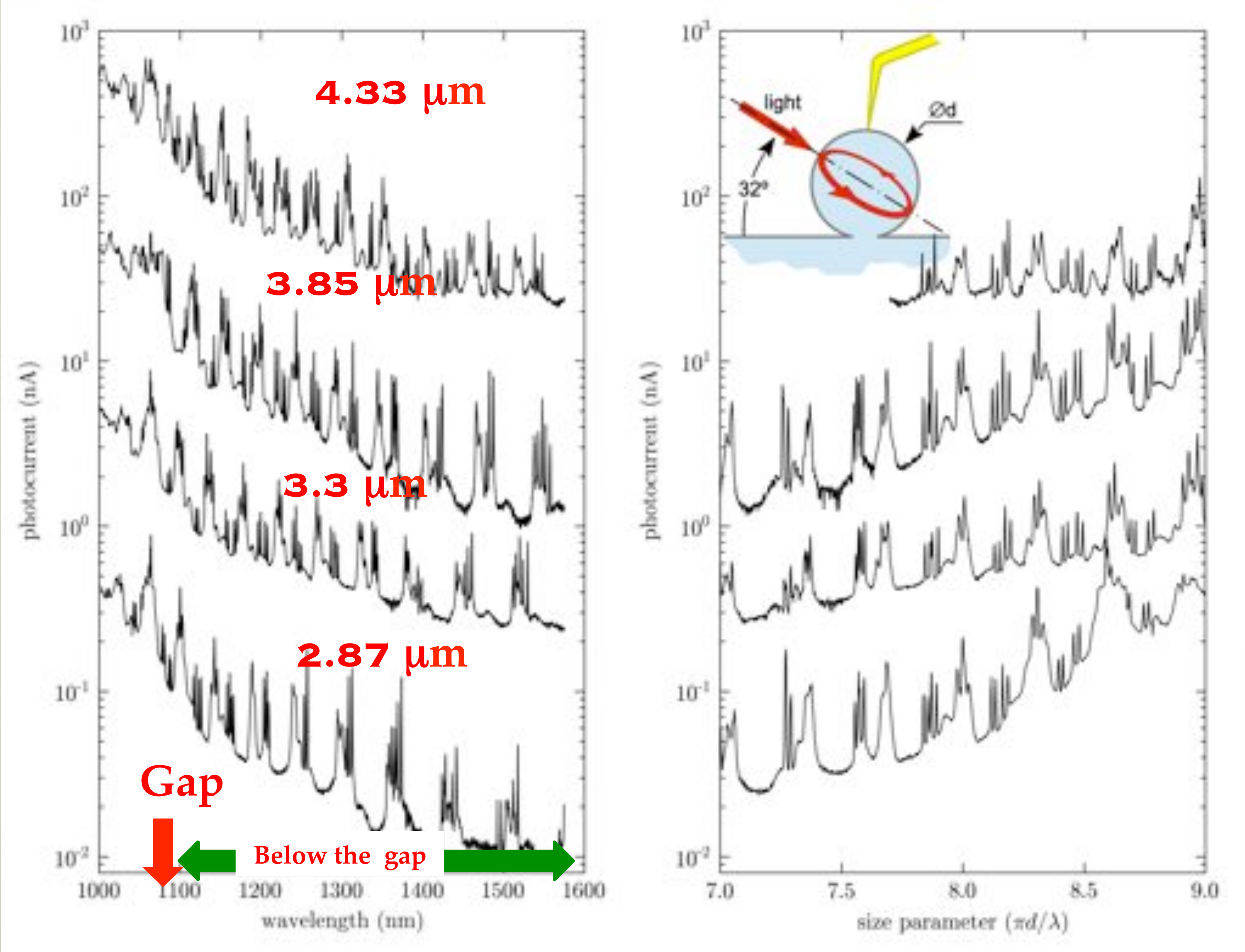


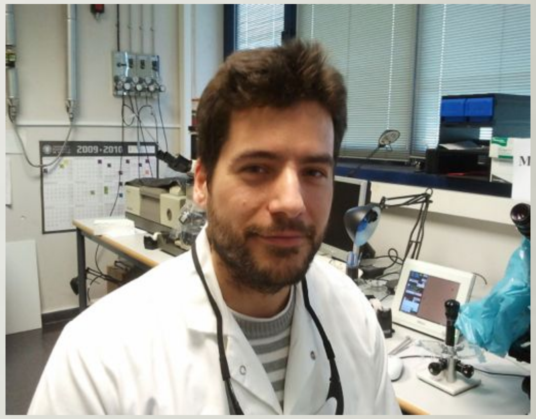


M. Garín

M. Garín, R. Fenollosa, L. Shi, R. Alcubilla, Ll. Marsal & F. Meseguer, Nature Comm. 5, 3440 (2014). SPIE Newsroom DOI 10.1117/2.1201405.005483

Photocurrent spectral response.

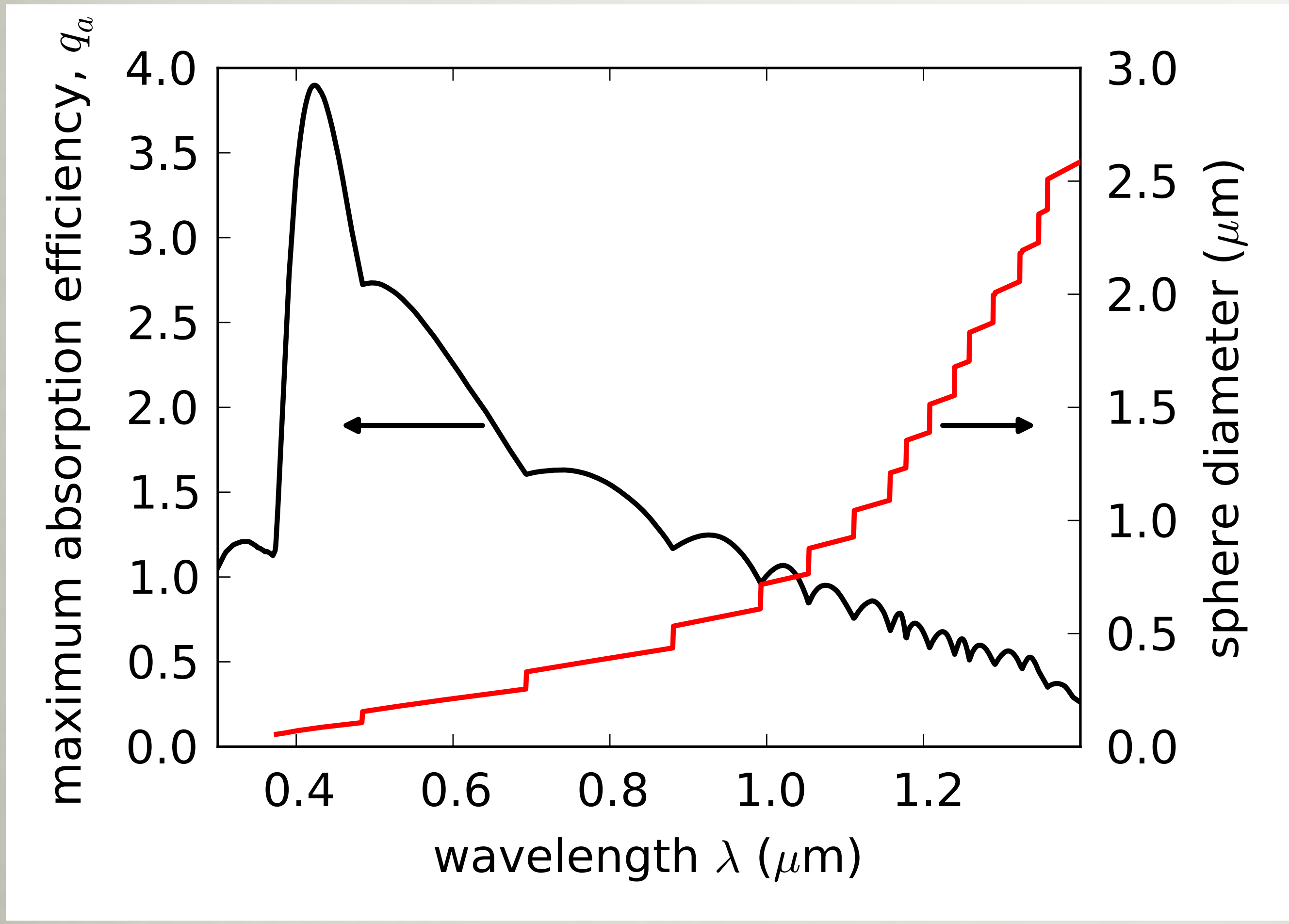


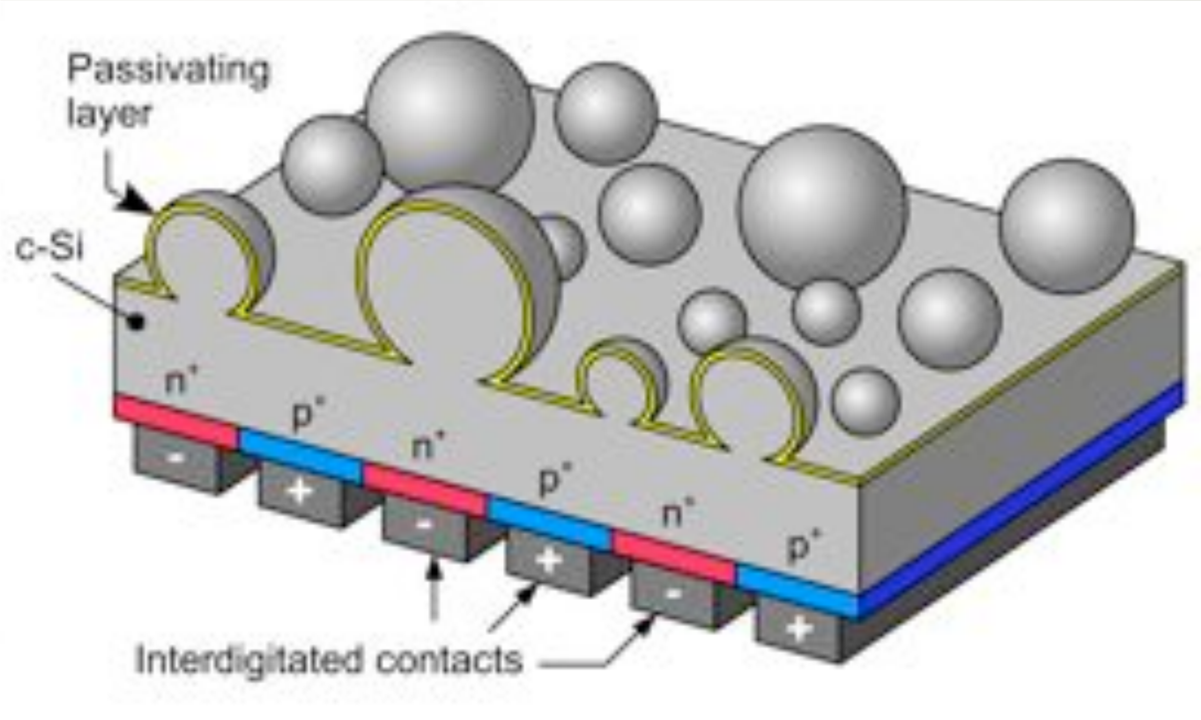


M. Garín

M. Garín, R. Fenollosa, L. Shi, R. Alcubilla, Ll. Marsal & F. Meseguer, Nature Comm. 5, 3440 (2014). SPIE Newsroom DOI 10.1117/2.1201405.005483

Future work





M. Garín, R. Fenollosa, P. Ortega, F. Meseguer, J. Appl. Phys. 119, 033101, (2016)

Outline

- Introduction & Motivation
- Optical properties of spherical microcavities. Mie Theory.
- Synthesis of silicon colloids.
- Applications of silicon colloids
- Monodisperse silicon nanocavities & Magnetic response
- Silicon colloids for electronic devices.
- **Silicon colloids for sensing. Gold vs silicon SERS sensors.**
- Silicon NPs for biomedicine.

21

LIGHT SCATTERING & RAMAN SCATTERING

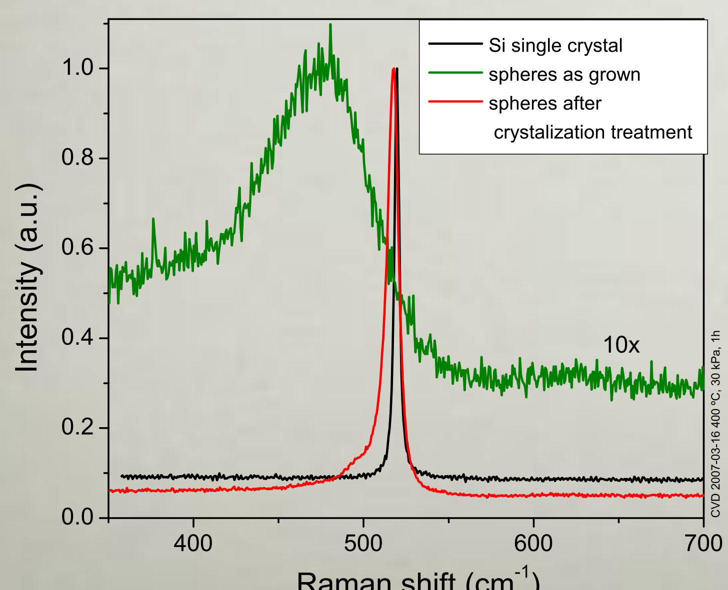
Crystal phonons (Ω)

Laser (λ)

Raman signal (λ-Ω)

Raman signal (λ+Ω)

Raman of bulk silicon

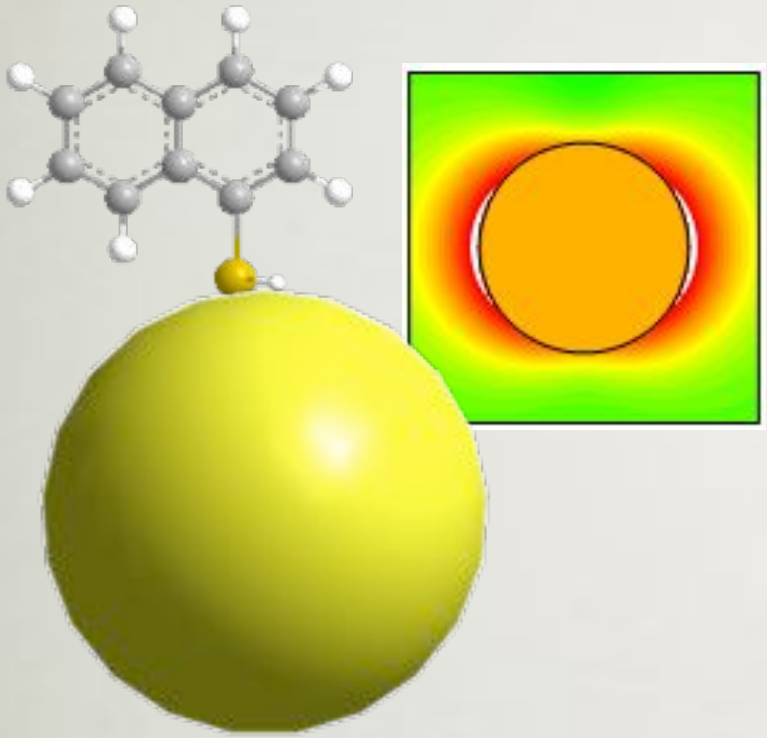


$$I\ (\mathrm{Raman}) \cong (E/\lambda)^4 <H>$$

The Raman scattering efficiency is very small (10^{-7})

The Raman Intensity is proportional to the fourth power of the EM field !!!

SERS overwiew



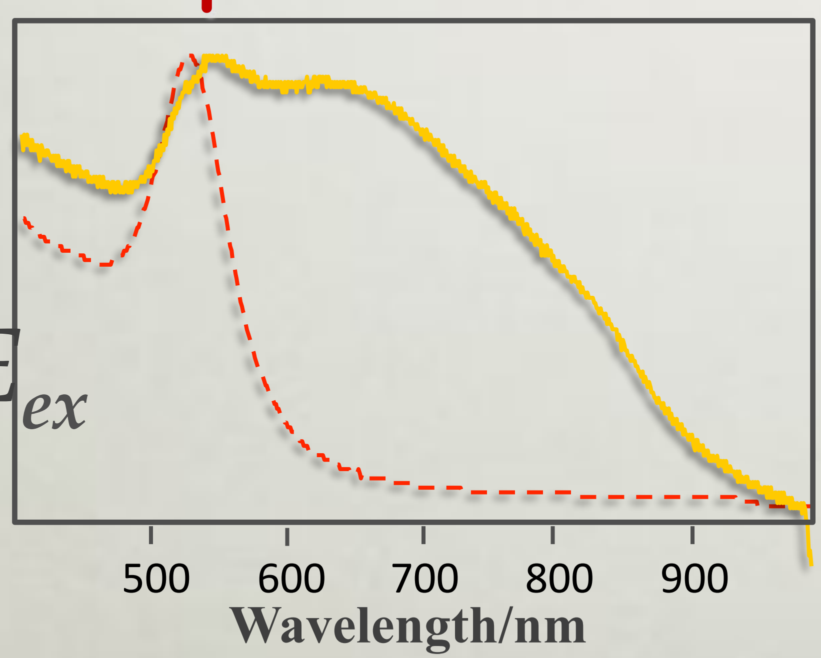
- **Plasmon modes of gold NPs show huge evanescent EM fields at the metal-air interface.**
- **The Raman signal of species near metal NPs is strongly enhanced.**

EF up to $10^{5\text{-}6}$

$I \,\alpha\, E^4$

$E = E_p + E_{ex}$

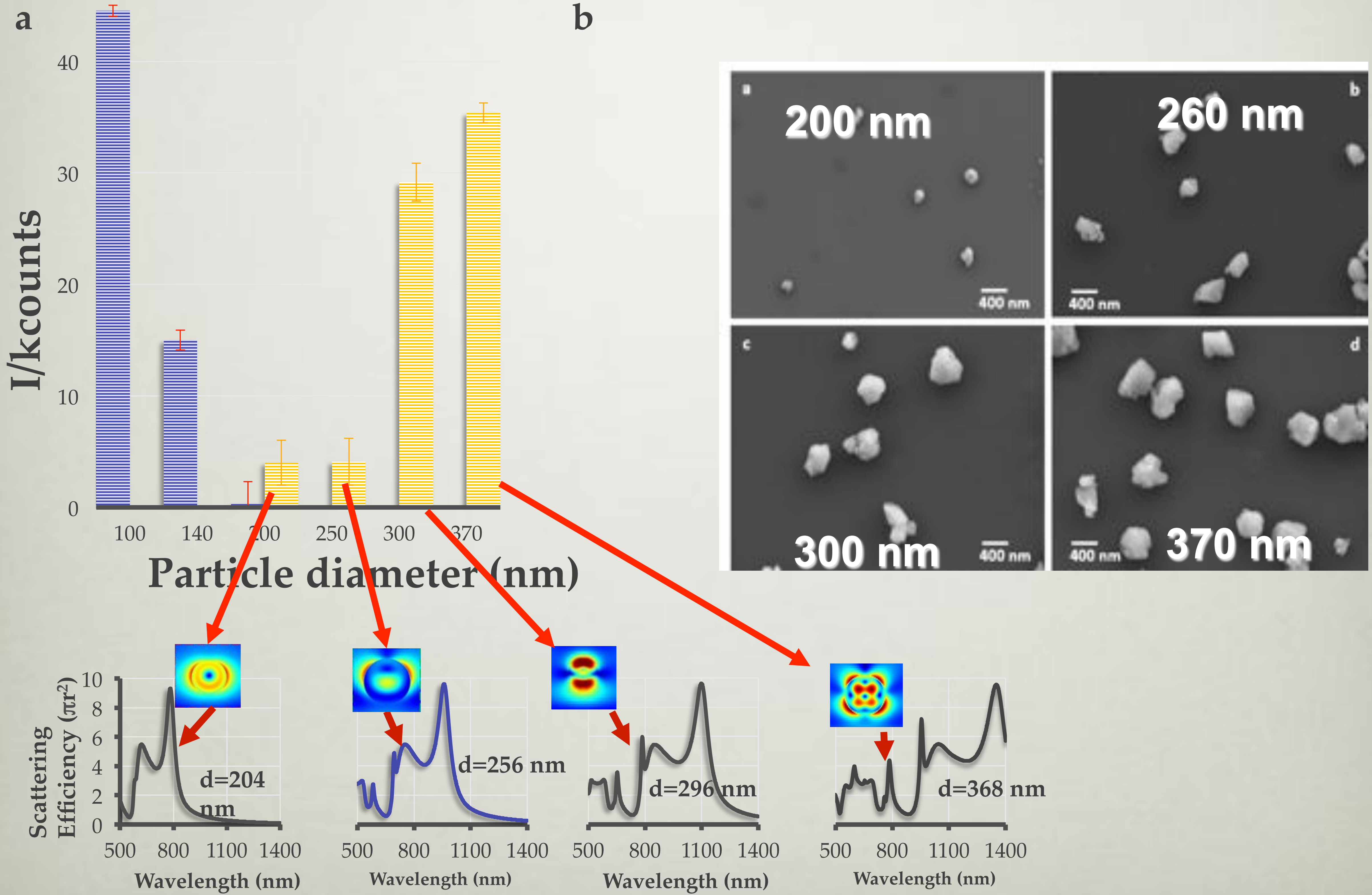
$E_p >> E_{ex}$



Surface induced Raman enhancement should appear for any other resonant systems like microcavities or high refractive index nanoparticles !!

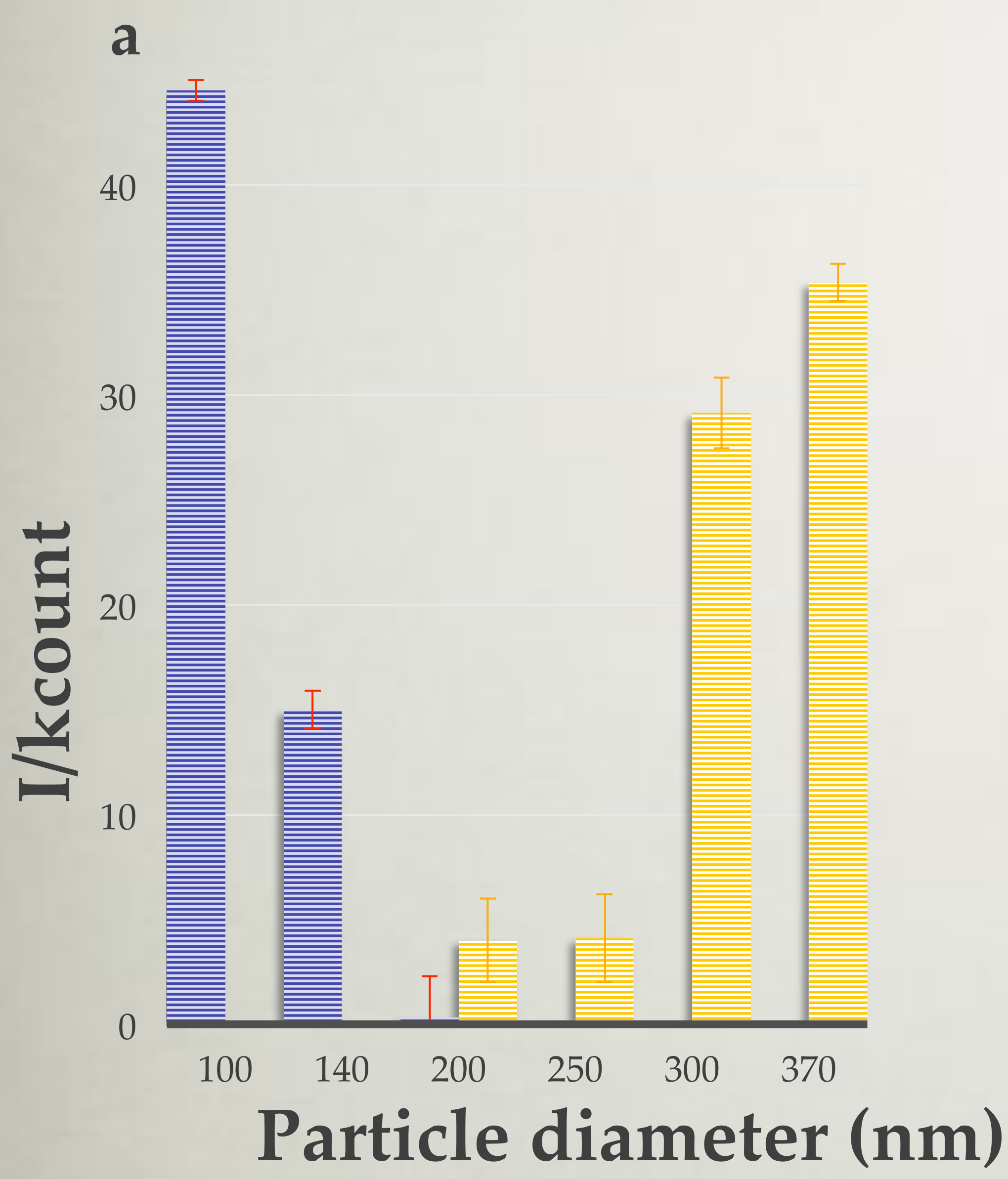
Energy Environ Sci *3 (2010) 1011–1017;* ***J Phys Chem Lett*** *1 (2010) 2428–2434;* ***J R S Interface*** *7 (2010) S435-S450;* ***Small*** *6 (2010) 604–610;* ***Chem Soc Rev*** *41 (2012) 43-51;* ***J Phys Chem Lett*** *3 (2012) 857–866; Ang. Chemie International Edition* ***2012****, 51, 11214*

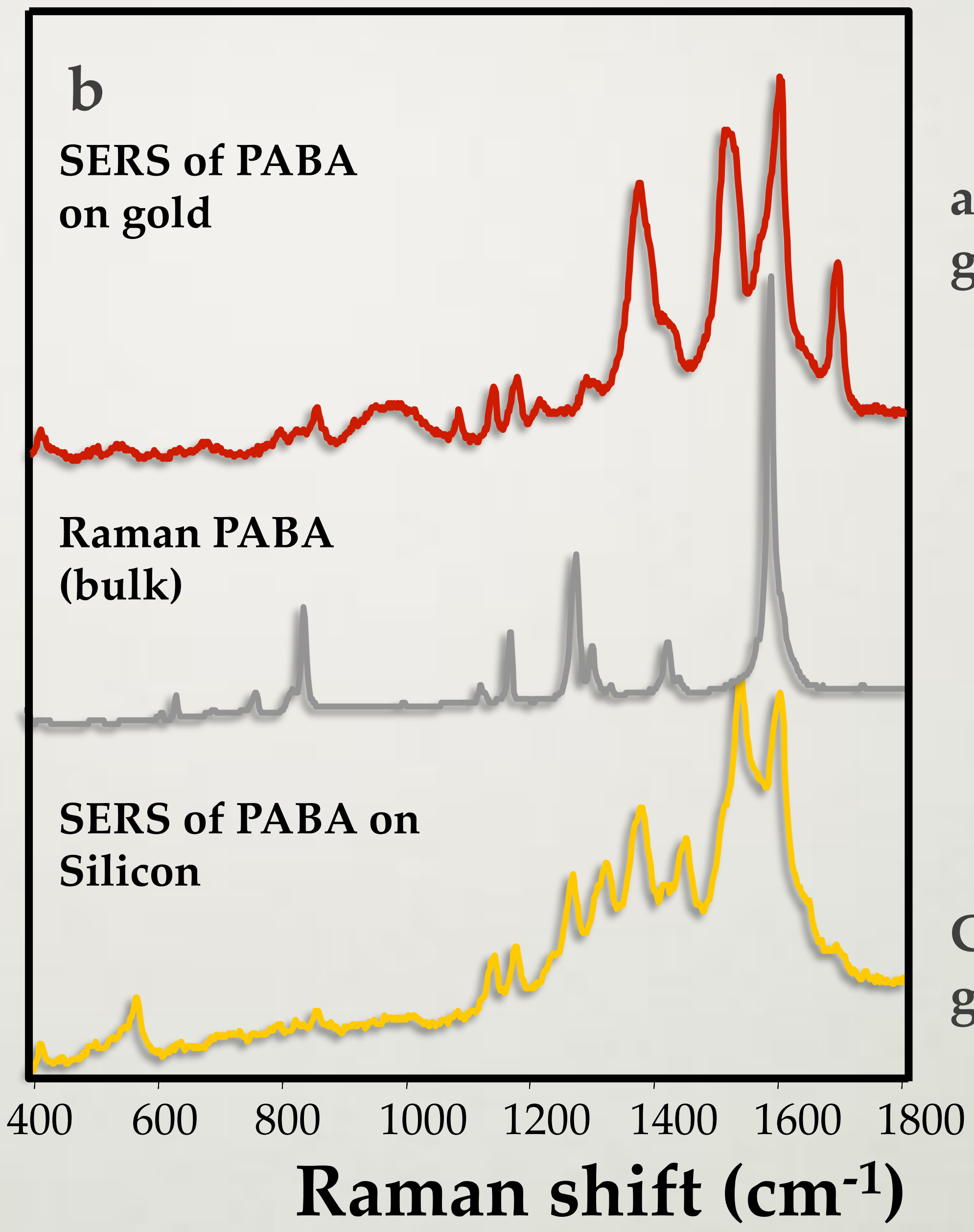
Raman spectra of PABA on gold vs silicon
(PABA: para-aminobenzoic acid)
Tuning Mie resonances to the laser line λ=785 nm

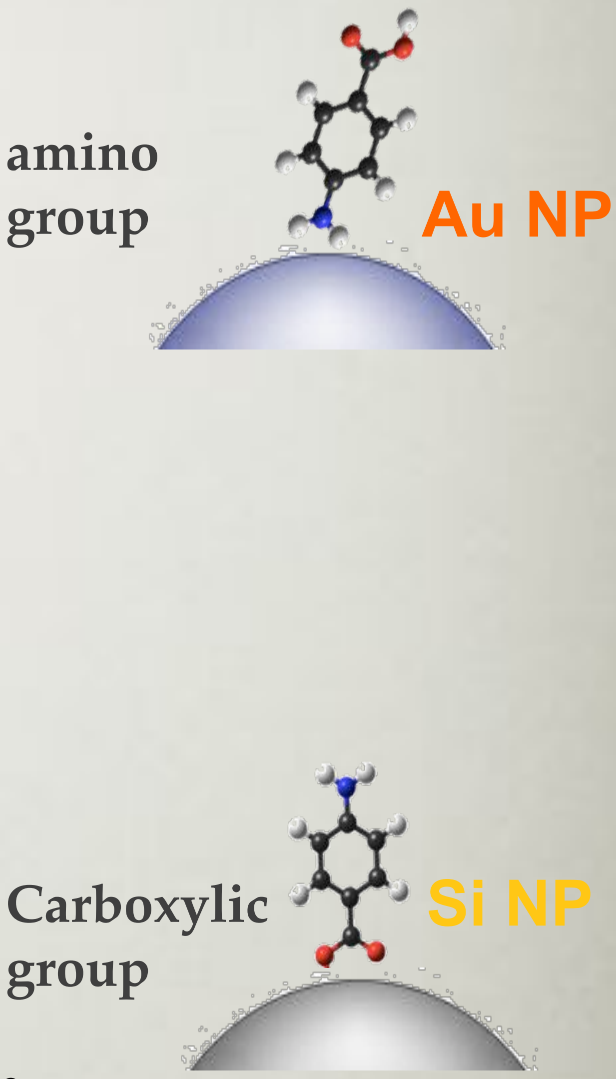


I. Rodriguez, X. Lu, L. Shi, B Korgel, R. Alvarez-Puebla, and F. Meseguer, Nanoscale, 6, 5666, (2014).

PABA affinity to gold vs silicon







PABA shows different affinity for silicon (carbolxylic) and gold (amino)

I. Rodriguez, X. Lu, L. Shi, B Korgel, R. Alvarez-Puebla, and F. Meseguer, Nanoscale, 6, 5666, (2014).

Outline

- Introduction & Motivation
- Optical properties of spherical microcavities. Mie Theory.
- Synthesis of silicon colloids.
- Applications of silicon colloids
- Monodisperse silicon nanocavities & Magnetic response
- Silicon colloids for electronic devices.
- Silicon colloids for sensing. Gold vs silicon SERS sensors.
- **Silicon NPs for biomedicine.**

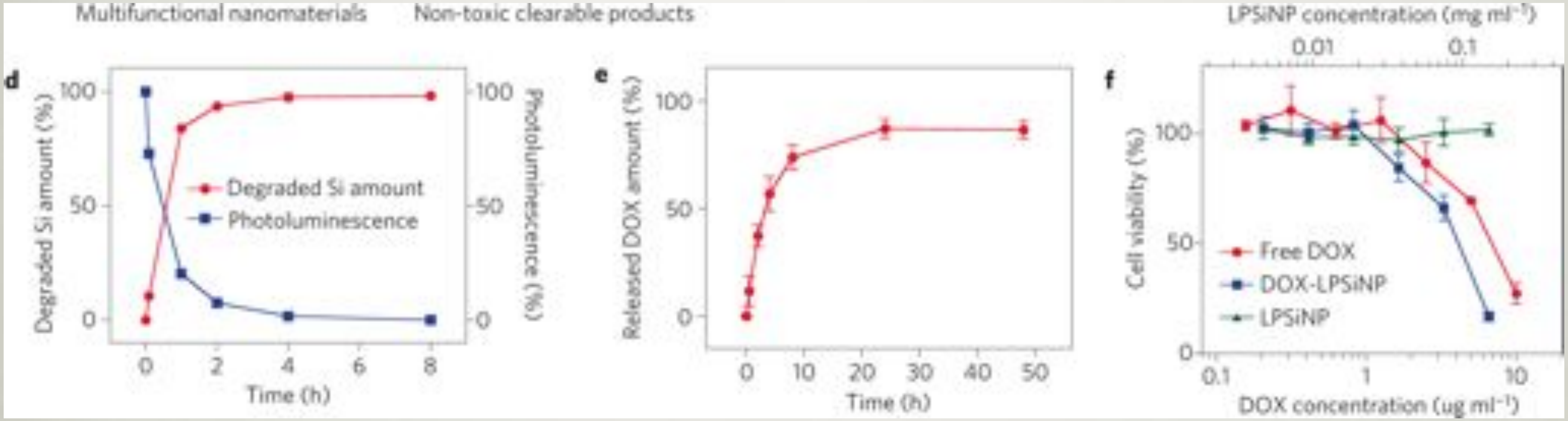
26

Biodegradable luminescent porous silicon for in vivo cancer therapy application. Porous silicon acts as a cancer drug carrier

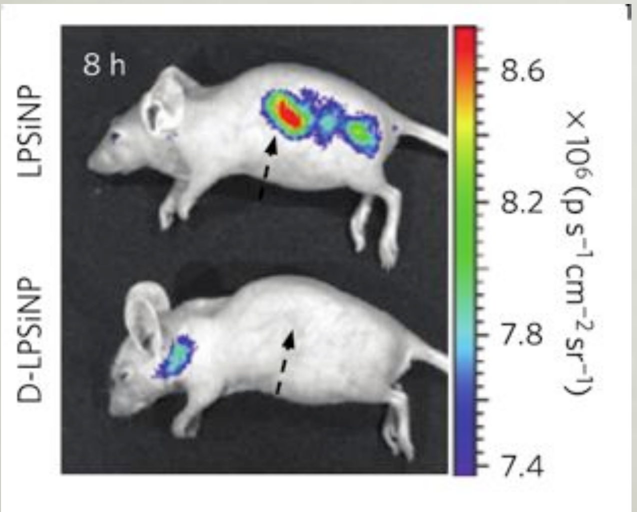
Cancer drug is delivered

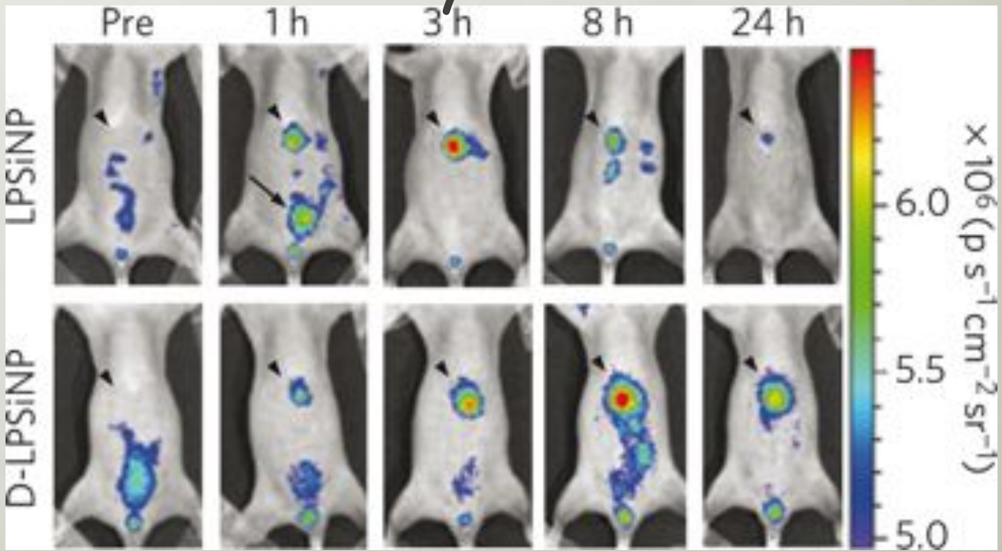
V.S. Lin, Nature Mat. 8, 252 - 253 (2009)

SiNPs & DOX(anti-cancer drug doxorubicin) cancer drug in vitro assay



SiNPs+dextran biodegradation in vivo assay



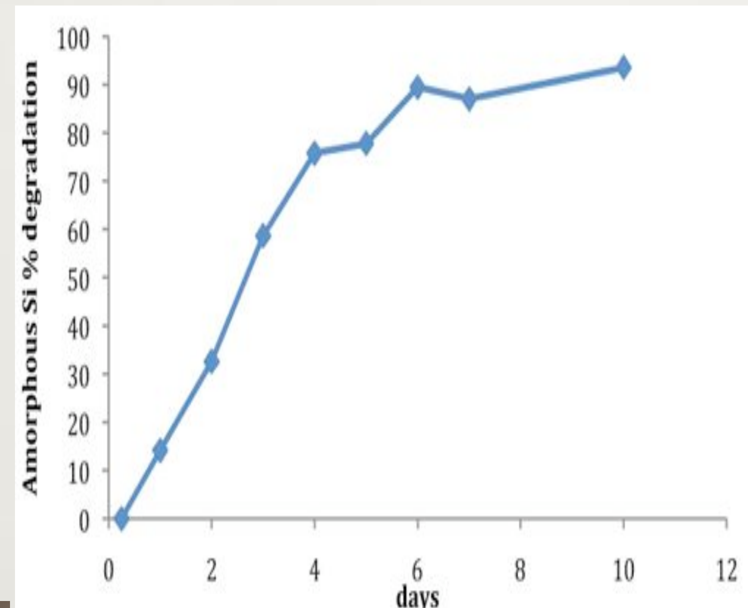


Sailor et al. Nature Materials 8, 331 (2009)

Chemical&Biochemical properties.
Si NPs oxidices; Si NPs biodegrades

Si NPs oxidices violently
It may kill cancer cells

Silicon NPs biodegrades



Cancer therapy drug

R. AlvarezPuebla
RIV Tarragona
Biochemistry

W. Parak
U. Marburg
Biophysics

A. de Lera
U. Vigo
Organic Chem

C. Villanueva
Medcomtech
Medicine

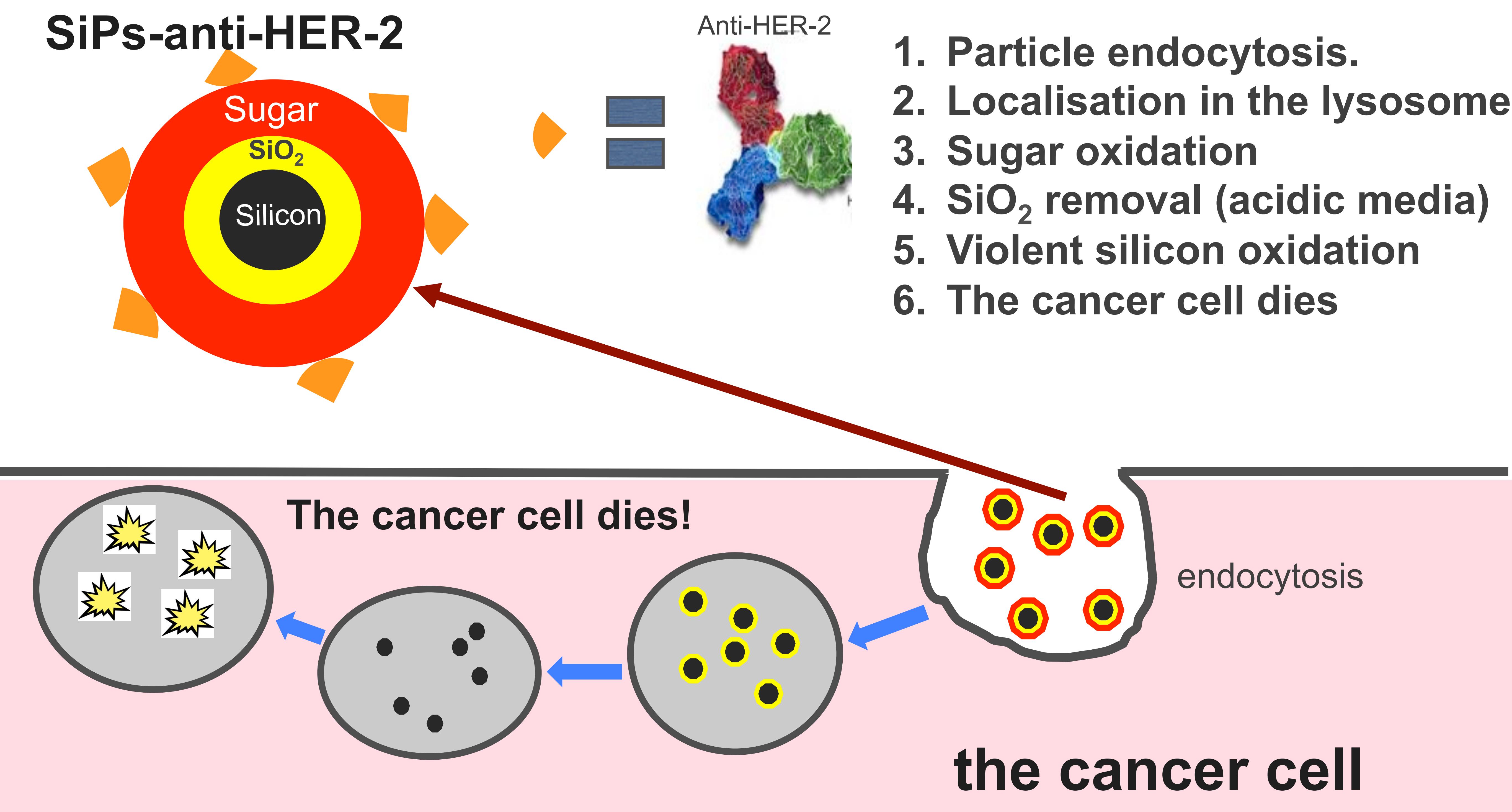
E. Garcia-Rico
Univ. Hosp. Madrid
Oncology

M. du Plessis, Prop, Explosives. & Piroth., 39, 348, (2014)
*R. Fenollosa, et al., Silicon **3**, 173 (2011).*
R. Fenollosa, et al.J. Nanobiotech, 12:35, (2014).

Outline of the strategy

1. **Particle endocytosis by the cancer cell.**
2. **Localisation in the cancer cell lysosome (pH = 4.0-4,5)**
3. **Sugar oxidation in the lysosome**
4. **SiO_2 removal (acidic media)**
5. **Violent silicon oxidation**
6. **The cancer cell dies**

The strategy
The particles are coated with sugar and anti-HER-2



1. Particle endocytosis.
2. Localisation in the lysosome
3. Sugar oxidation
4. SiO_2 removal (acidic media)
5. Violent silicon oxidation
6. The cancer cell dies

R. Fenollosa, et al. J. Nanobiotech, 12:35, (2014).

Steps

- **Immunotherapeutic material (SiPs+anti-HER-2)**

1. Processing of silicon coated with a native SiO_2 layer (**SiNPs**).
2. SiNPs coated with sugar (glucopyranoside) through a peptide bond (between APS and the glucopyranoside)
3. SiNPs are linked to a HER-2 antibody (**anti-HER-2**).

- **Test material. Bare SiNPs with NO anti-HER-2. (SiPs).**

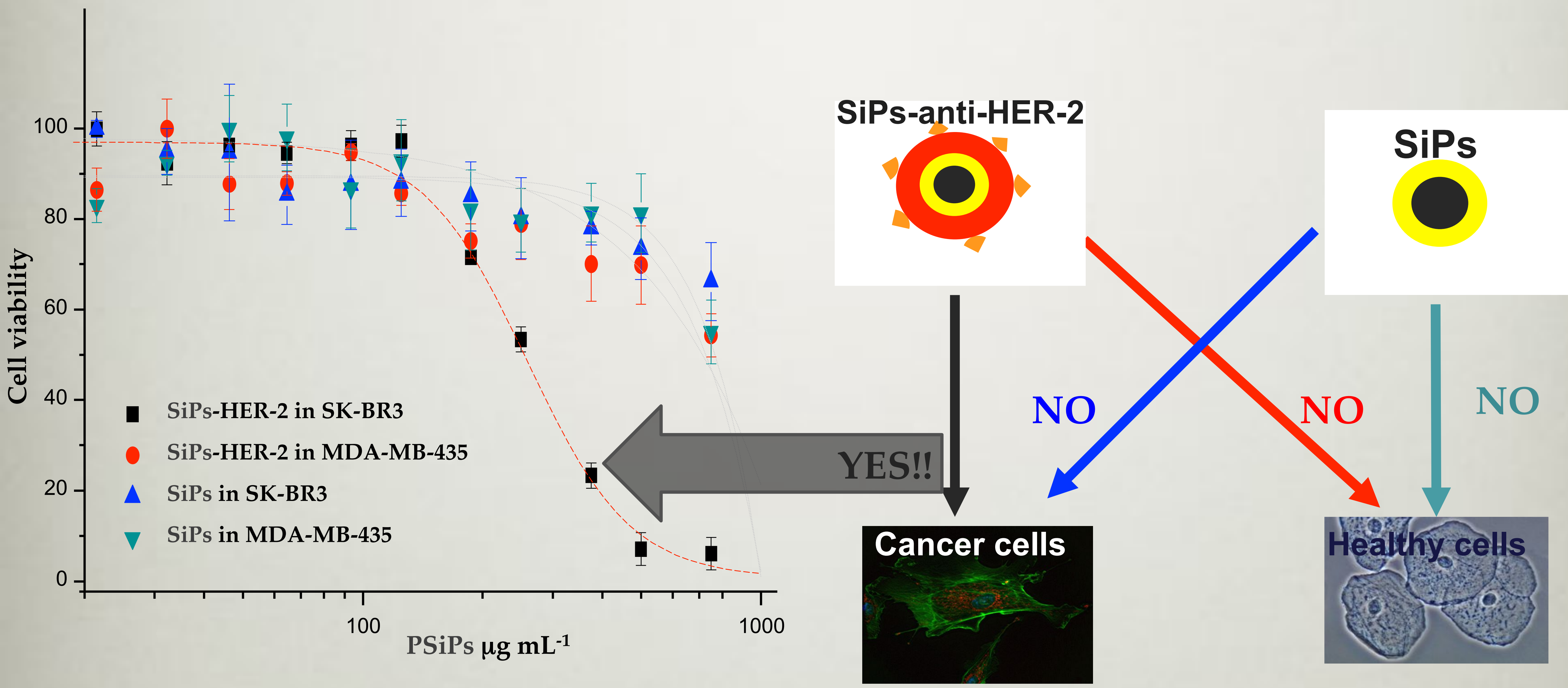
- **Two cell culture lines were developed.**

A. Breast cancer cells over-expressing HER-2 receptor **(SK-BR-3)**.
B. Human epithelial healthy cells **(MDA-MB-435)**.

- **Nanoparticle internalization into the cell cultures.**

- **Cell viability assay using a PL tag (Resazurin).**

The preliminary results (breast cancer cells)



SiPs+anti-HER-2 selectively recognize and destroy cancer cells!!

R. Fenollosa, et al. J. Nanobiotech, 12:35, (2014).

R. Fenollosa, et al. Patent Nr EP14382182.5, May 23rd, 2014.

Conclusions

High quality microcavities of amorphous, polycrystalline and porous silicon have been processed

We have developed a photodiode on a single silicon nanocavity with spectral response in the IR up to 1500 nm.

Recent calculatations show silicon micro and nanocavities are good candidates for harvesting solar energy in the visible and infrared ranges

We have processed SERS enhancers based on silicon nanoparticles

Silicon nanoparticles show potential applications for cancer therapy.

E. Xifré-Pérez, et al., ACSNano, 7, 664-668, (2013).

L. Shi, et al., Nature Comm., 4, 1904 (2013) DOI 10.1038/ncomms2934.

M. Garín, et al., Nature Comm., 5, 3440, (2014).
SPIE NewsRoom (2014) DOI 10.1117/2.1201405.005483

I. Rodriguez, et al., Nanoscale, 6, 5666, (2014).

L. Shi, et al., ACS Photonics, 1, 408, (2014)

R. Fenollosa, J. Nanobiotechnology 12:35, (2014).

M. Garín, R. Fenollosa, and F. Meseguer, J. Appl. Phys. 119, 033101, (2016)

THANK YOU VERY MUCH..

FUNDING
MINECO MAT2012, 2016
GV Prometeo 2015, 2016