Applications of silicon nanoparticles to Electronics, Photonics and Nanomedicine

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

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

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silicon based nanoresonators

Theory.


Requirements

- Submicrometric silicon nanoparticles
- Monodisperse silicon nanoparticles
Silicon nanocavities. Processing methods

CVD.
Spherical particles
Polydisperse particles
Porous, amorphous & crystalline

Decomposition of Si$_3$H$_8$. Monodisperse (5%) and spherical particles + sintering process
Porous particles
n= 3.15

Texas University Collaboration
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 et al submitted
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Monodisperse Silicon colloids. Optical properties of single particles

Decomposition of $\text{Si}_3\text{H}_8 +$ sintering process

L. Shi, J. T. Harris, R. Fenollosa, I. Rodriguez, X. Lu, B. A. Korgel, and F. Meseguer
2D Silicon colloids based Photonic Crystal

Non-close packed 2D PC with omnidirectional photonic bandgap at $\lambda=1\mu m$

Light is fully transmitted at $\lambda>1200$- 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
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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.

See also Ge nanowires Brongersma et al., Nat. Mat 2008; Si nanowires Lieber Nature 2007

What about Infrared photons?
How to harvest them?
Silicon nano microspheres can absorb light very efficiently in the visible region. They can also absorb it in the IR region!!

Abs. Efficiency = 4 !!!

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 $\lambda = 1100$ nm

Q factor = $6 \times 10^3$

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

The time needed for traveling 0.3 mm in bulk silicon (the thickness of a silicon PV cell)!!

The PV cell processing (minimizing processing steps).

1. The CVD synthesis

2. The thermal diffusion

3. The ITO layer

M. Garin et al SPIE Newsroom DOI 10.1117/2.1201405.005483
& R. Fenollosa, et al submitted
I(V) measurements.

$\lambda=990 \text{ nm (1 sun)}$
$\eta=0.6\%$
$EQE=16\%$

Photocurrent spectral response.

Future work

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

\[ I_{\text{Raman}} \approx (E/\lambda)^4 <H> \]

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

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

- 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.

\[ I \alpha E^4 \]
\[ E = E_p + E_{ex} \]
\[ E_p >> E_{ex} \]

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

PABA affinity to gold vs silicon

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

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

SiNPs + dextran biodegradation in vivo assay.
Si NPs oxidizes violently. It may kill cancer cells. Silicon NPs biodegrades. 

R. Alvarez Puebla, RIV Tarragona Biochemistry. 
W. Parak, U. Marburg Biophysics. 
C. Villanueva, Medcomtech Medicine. 

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. SiO₂ removal (acidic media)
5. Violent silicon oxidation
6. The cancer cell dies
The strategy
The particles are coated with sugar and anti-HER-2

SiPs-anti-HER-2

Sugar
SiO₂
Silicon

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The cancer cell dies!

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!!

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 calculations 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.


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


THANK YOU VERY MUCH..

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