Conferința Diaspora in Cercetarea Ştiințifică şi Invățământul Superior din Romania

Bucuresti, 21-24 Septembrie 2010

Multifunctional Plasmonic Nanosensors for Bioanalytical Applications

Simion Astilean

Babes-Bolyai University
Faculty of Physics and Nanobiophotonics Center

Cluj-Napoca, Romania

Outline

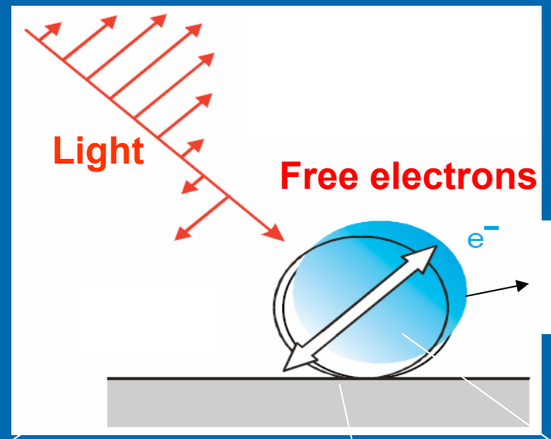
- **Optical Properties in Metallic Nanoparticles**
- **Plasmonics - a new emerging field of nanobiophotonics**

Our Results in Plasmonics:

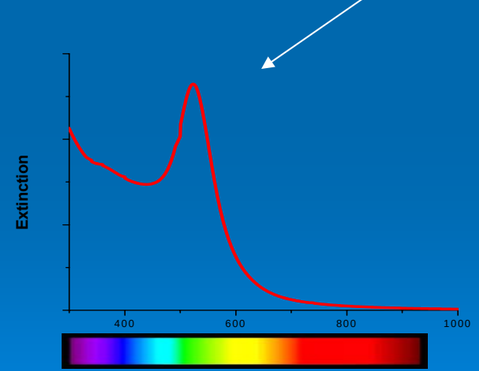
- **Methods for fabrication of plasmonic nanostructures**
- **Multifunctional sensors based on plasmonic nanostructures**

•Acknowledgement

Optical Resonance in Noble-Metal Nanoparticles

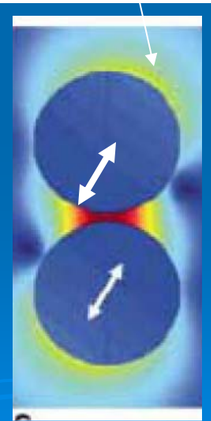


$$\sigma_{abs}(\omega) = 9\frac{\omega}{c}\varepsilon_H^{3/2}V_0\frac{\varepsilon_{1,M}(\omega)}{\left[\varepsilon_{1,M}(\omega)+2\varepsilon_H\right]^2+\varepsilon_{2,M}(\omega)^2}$$



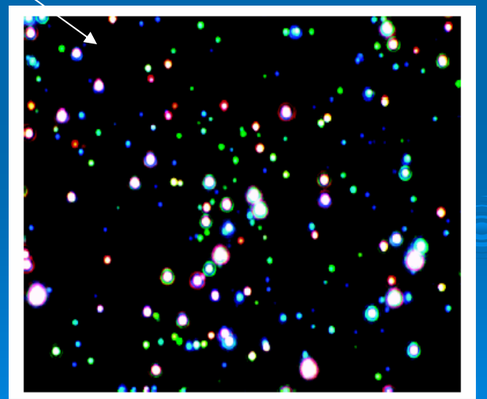
Selective Light Absorption

extinction coefficient of ~ 10^{11} M-1 cm-1



Enhanced Optical Field

~10^{3} times



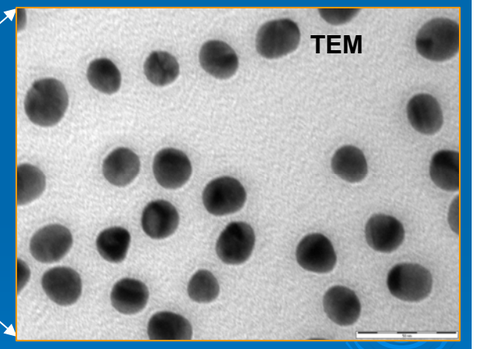
Selective Light Scattering

~10^{6} dye fluorophores

When the size of material makes the big difference…

Macroscale gold

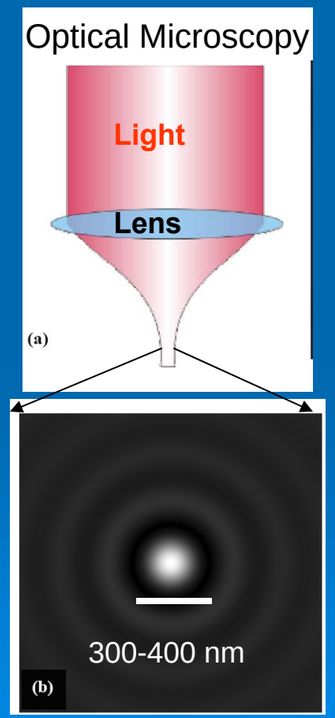
Nanoscale gold



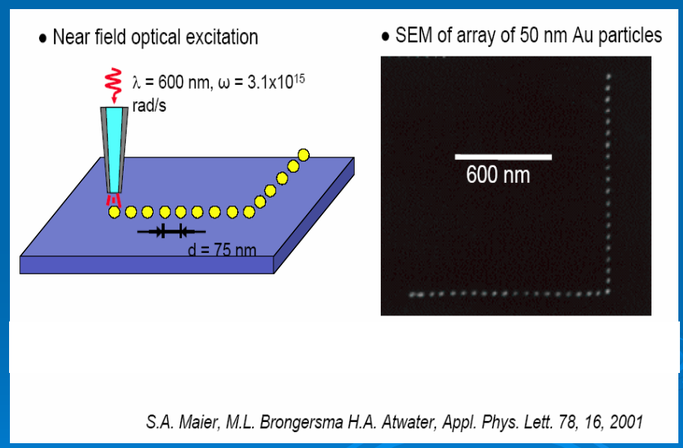
50 nm

Plasmonics might give solutions to problems other technology cannot solve

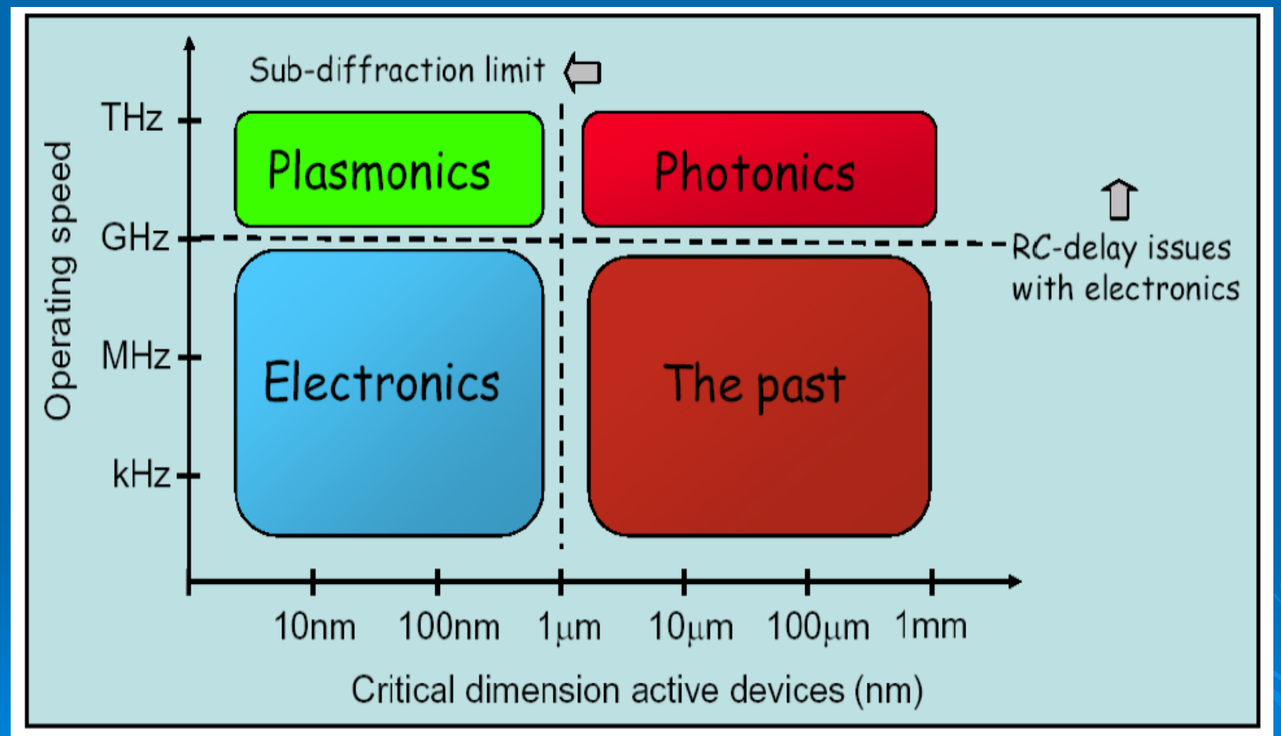
- **Clasical Optics and Photonics are Diffraction-Limited !**



- **Plasmon resonance is the only way to send, confine and address light on the nanoscale**

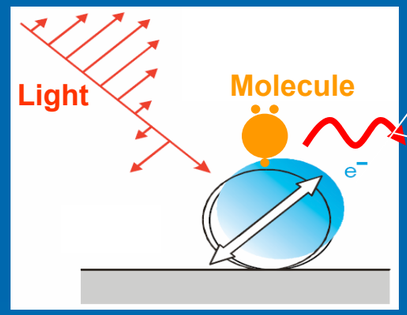


Plasmonics for Nanotechnology



- Plasmonics will enable an improved synergy between electronic and photonic devices
  - ➡ Plasmonics naturally interfaces with similar size electronic components
  - ➡ Plasmonics naturally interfaces with similar operating speed photonic networks

Plasmon – Assisted Molecular Spectroscopy



Raman Scattering

$$P = \alpha E$$

Surface Enhanced Raman Scattering (SERS): 10^6-10^7
10^{10}-10^{12} single molecule detection!

IR Absorbtion

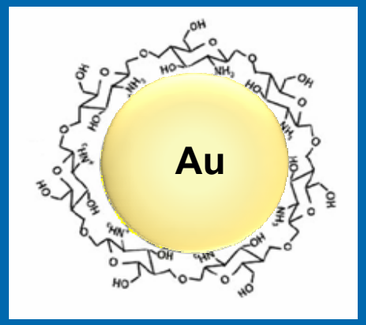
$$A = \left|\frac{\partial \mu}{\partial Q}\right|^2 |E|^2 \cos^2\theta$$

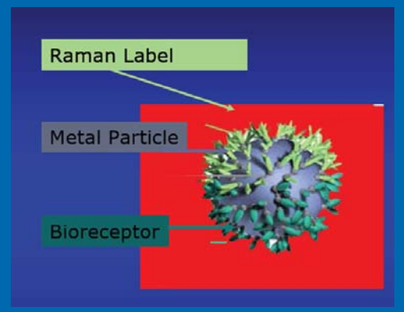
Surface Enhanced Infrared Absorption (SEIRA)
10^1-10^2 times

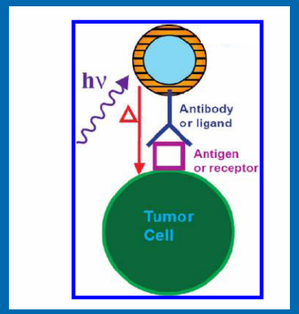
$$P_{12} = \frac{2\pi}{\hbar}\sum_f \left|\langle \Psi_f | \mu E(r) | \Psi_i \rangle\right|^2 \rho(\omega)$$

Metal - Enhanced Fluorescence (MEF)

Plasmon-Assisted Biomedical Sensing and Imaging



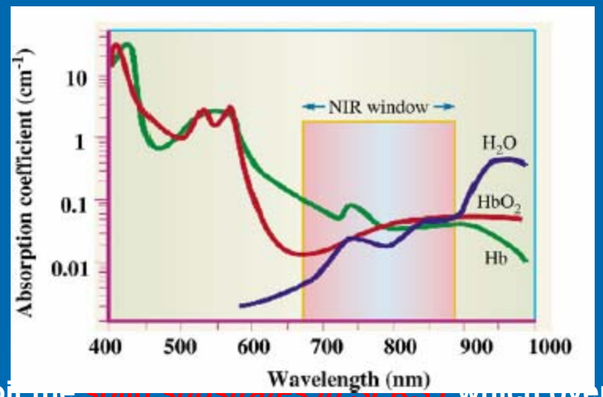




- Localized Surface Plasmon Resonance (LSPR) sensors
- Cancer therapy by plasmon-induced heating
- SERS Imaging and Diagnostic

Our Research Objectives

a) To fabricate plasmonic nanostructures that are highly responsive in the biological spectral window (NIR - Near Infra Red)



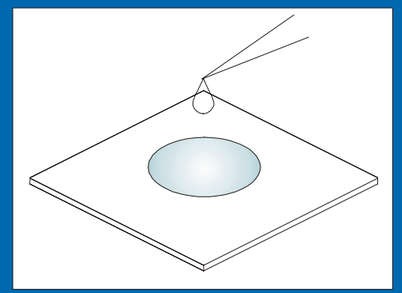
b) To exploit the solid substrates in SERS (which overcome a series of disadvantages of solution-phase nanoparticles, among the most critical aspects being *their stability, reproducibility and efficiency)*

b) To implement the concept of multifunctionality in biosensing: this is not only SERS but also for SEIRA, Localized Surface Plasmon Resonance (LSPR) sensors, Metal-Enhanced Fluorescent (MEF), Cell targeting and SERS Imaging.

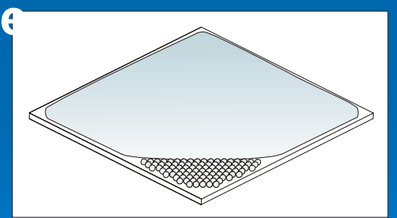
“Top – down” approach for substrate nanofabrication

(A) Self-assembling polystyrene nanospheres

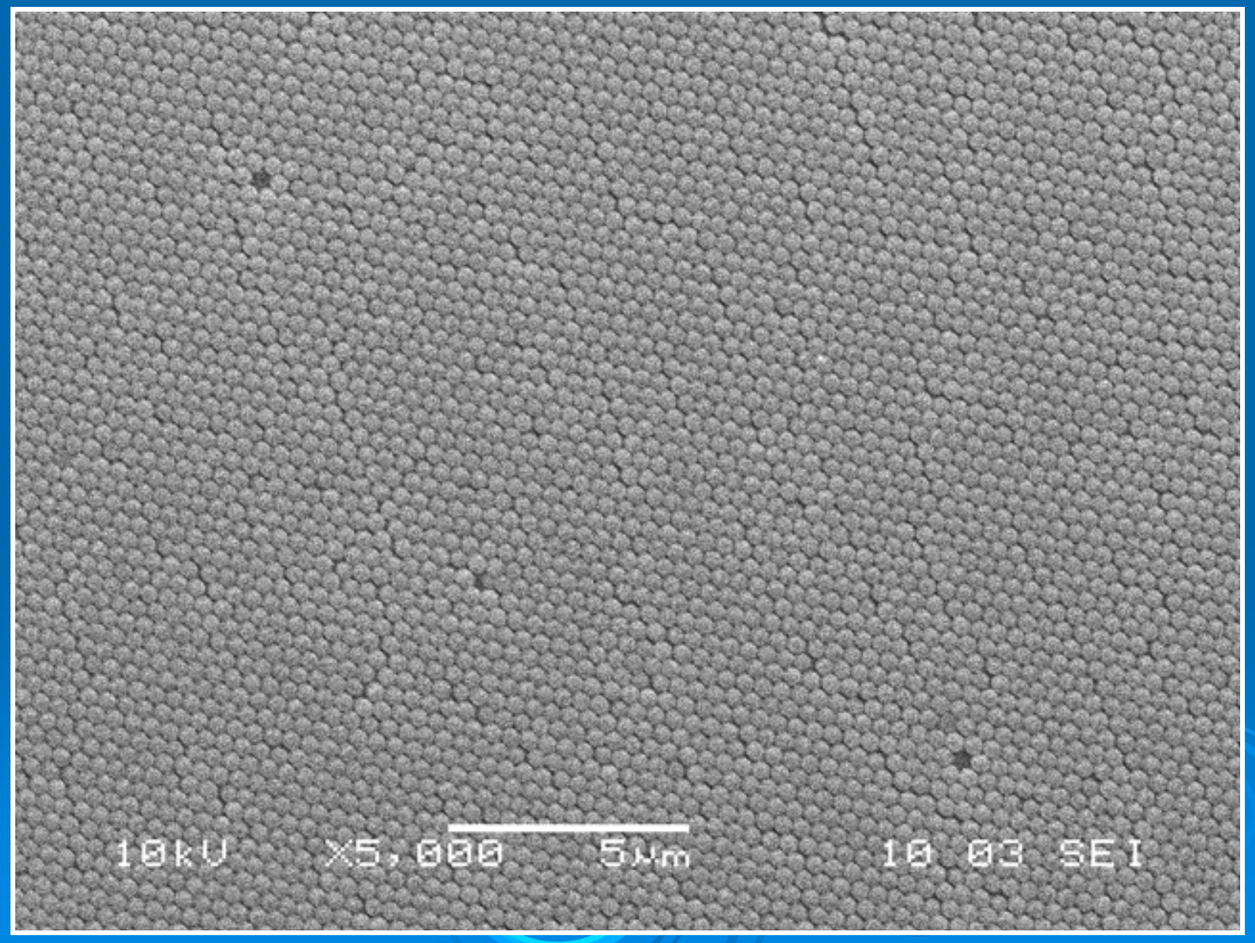
1. Drop ~10 μL colloid solution onto hydrophillic substrate



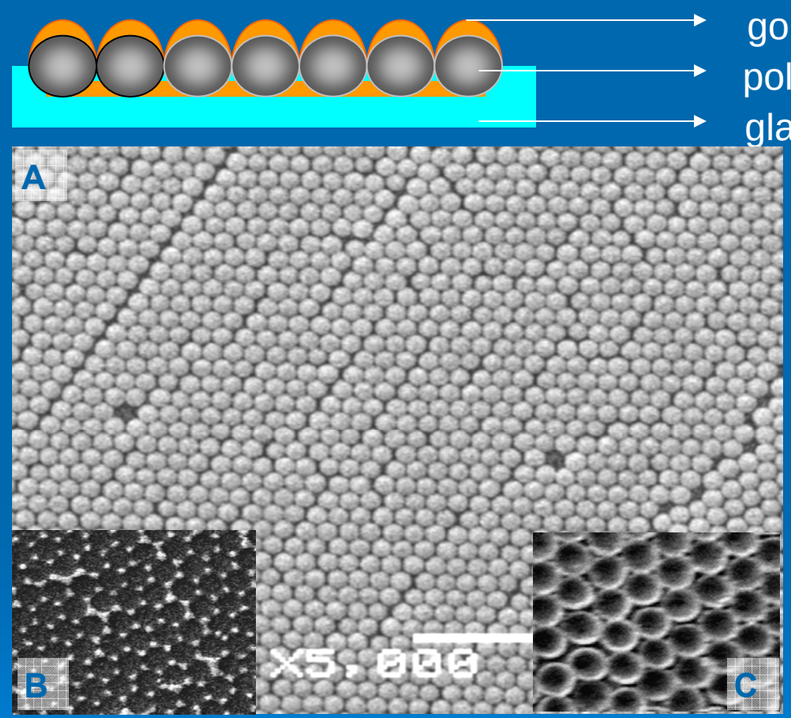
2. Dry in oven, spheres self-assemble at meniscus edge



Self-assembling polystyrene nanospheres on solid substrate (single layer)

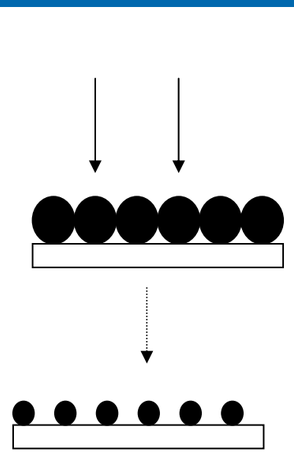


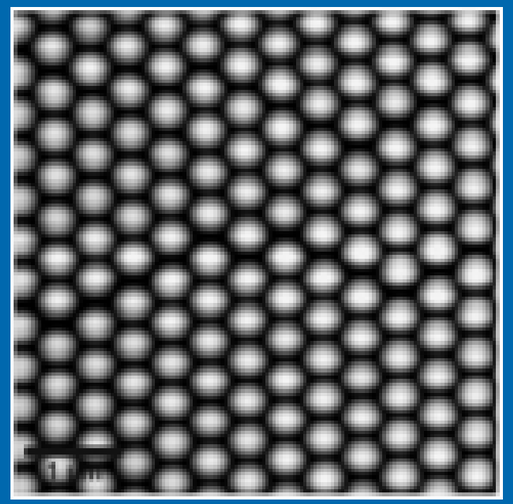
Metal deposition

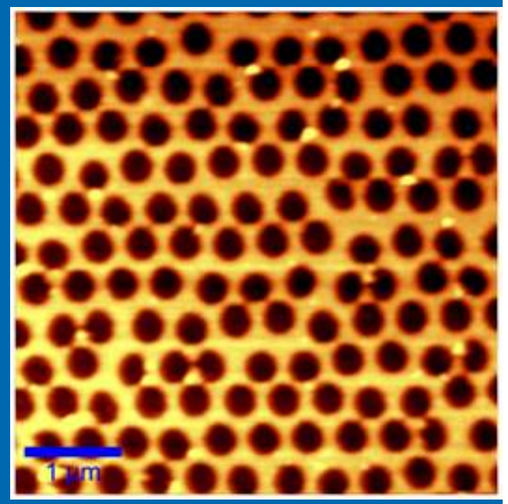


1. Thermally evaporate film of gold onto the polystyrene nanosphere array.

2. Remove nanospheres leaving a hexagonal array of nanoparticles and nano-cups







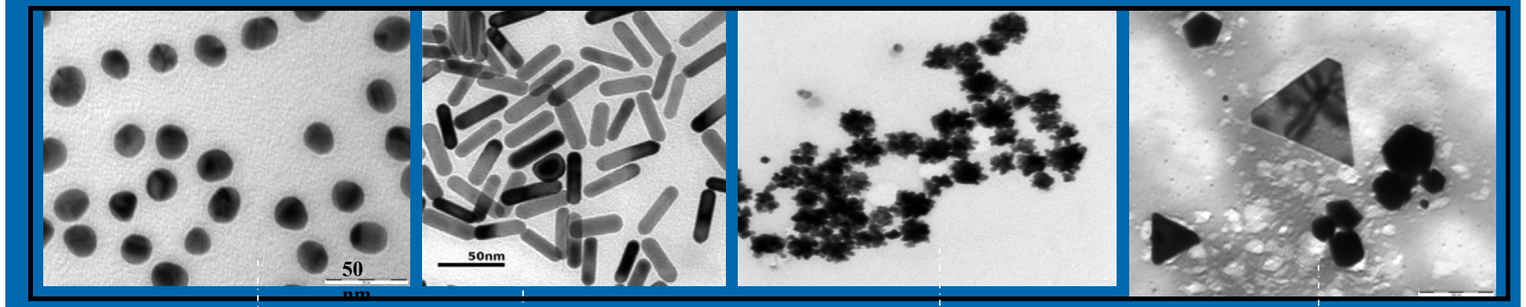
Reactive Ion Etching (RIE)

Metal deposition

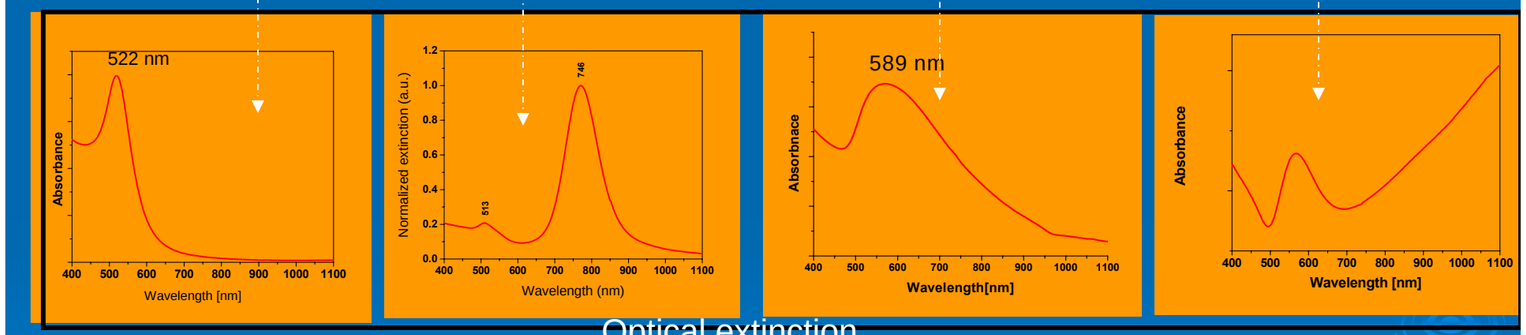
Template removing

“Bottom – up” approach of nanofabrication

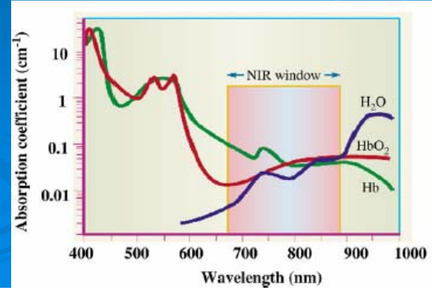
Tuning the size and shape of gold nanoparticles



TEM pictures

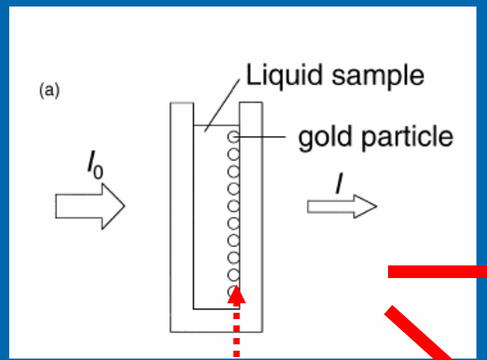


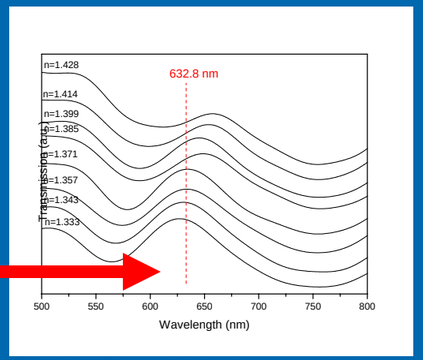
Optical extinction



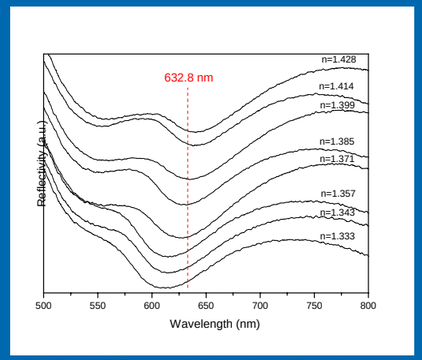
Multifunctional Plasmonic Sensors

Combining SERS and LSPR molecular detection on unique plasmonic substrate substrate



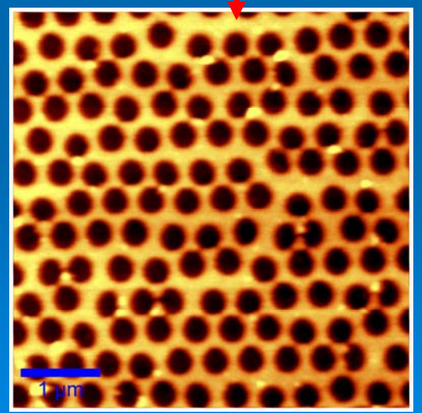


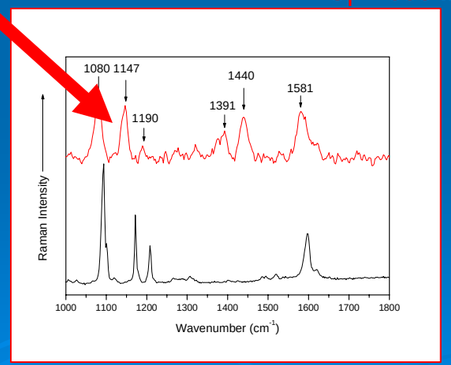
Bulk LSPR sensitivity in transmission



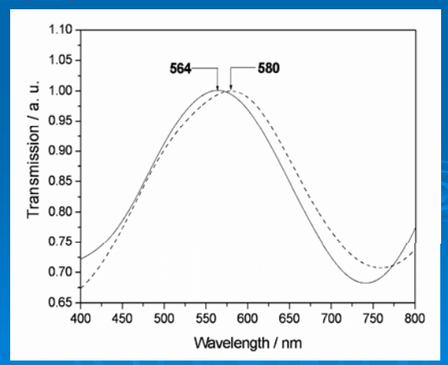
Bulk LSPR sensitivity in reflection

S_T ~ 338 nm/RIU





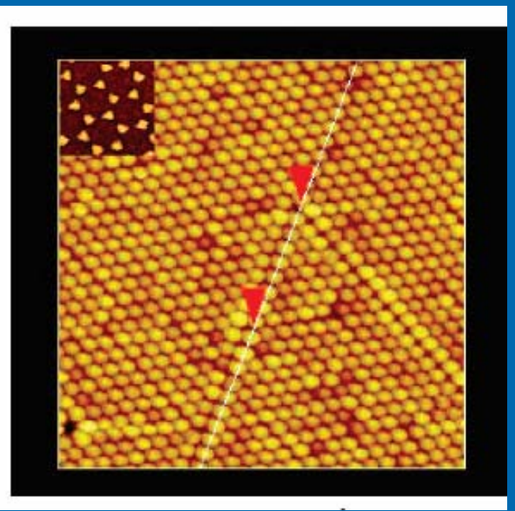
SERS sensitivity

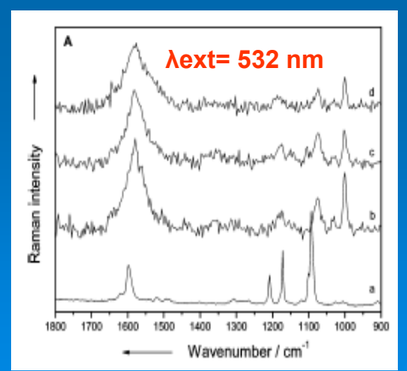


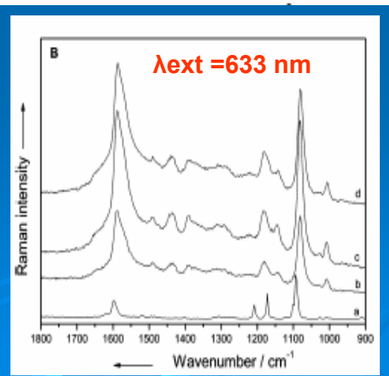
Molecular LSPR sensitivity in transmission

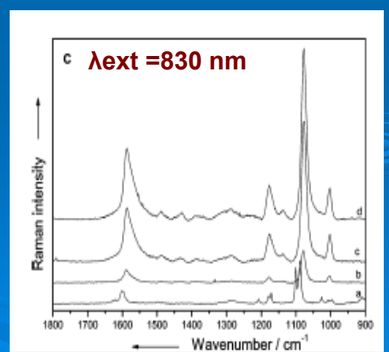
Canpean, V; Astilean, S, Lab on Chip 9 (2009) 3574-3579

Effective SERS substrates for multiple laser excitation in VIS-NIR





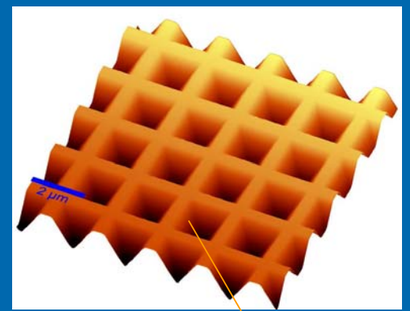




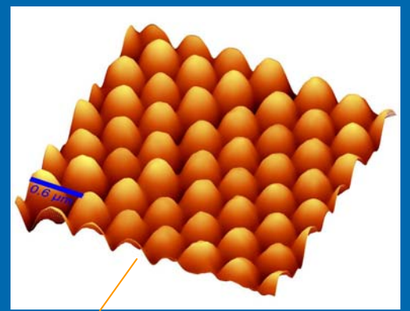
L. Baia, M. Baia, J. Popp, and S. Astilean, *J. Phys. Chem. B*, *110,* 23982, 2007

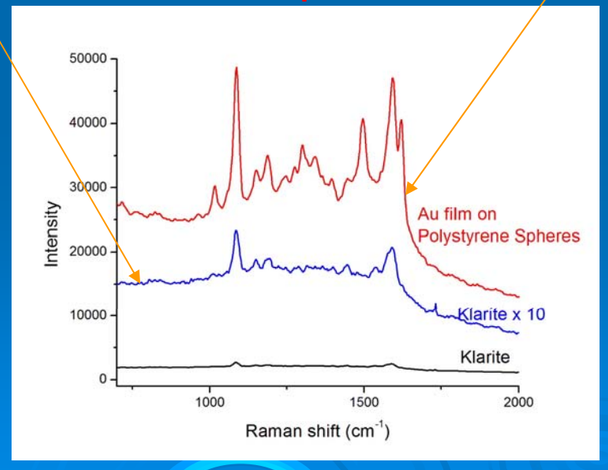
Comparison with other commercial SERS substrate

Klarite ®

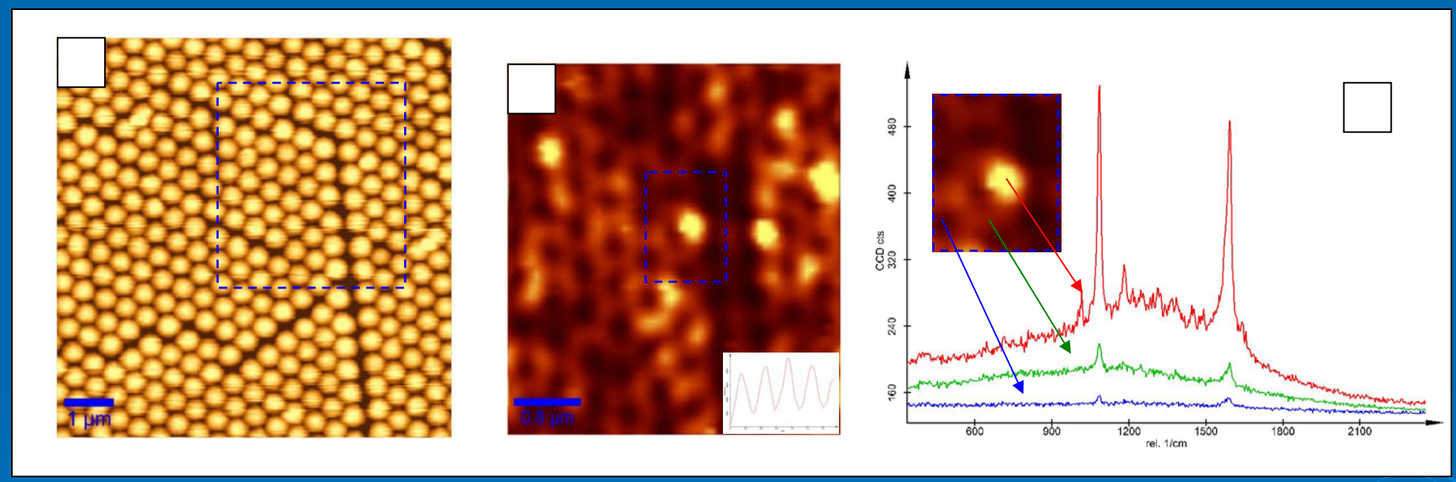


Our substrate





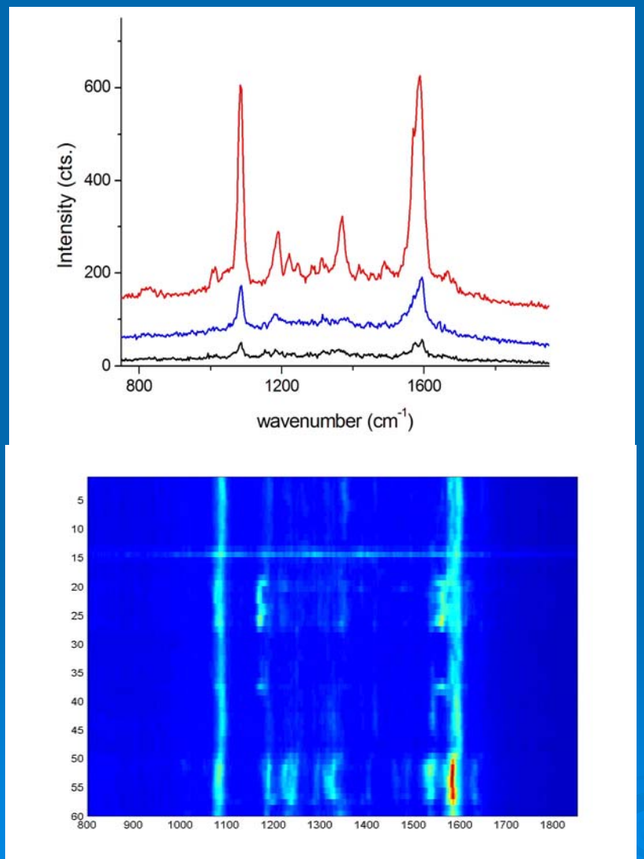
Imaging the distribution of *hot-spots* by scanning confocal Raman microscope



AFM imaging *SERS imaging* *local SERS spectra*

Cosmin Farcau, Simion Astilean, J. Phys. Chem. C, 114, 11717 (2010)

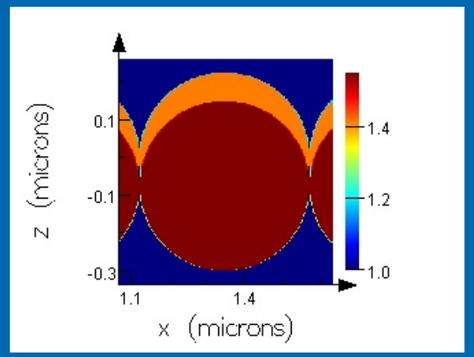
Single molecule SERS sensitivity

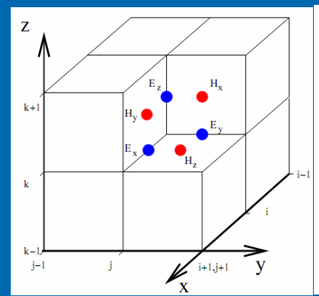


temporal series
of SERS spectra

Cosmin Farcau, Simion Astilean, J. Phys. Chem. C, 114, 11717 (2010)

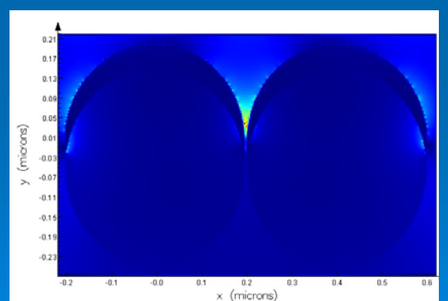
Finite difference time domain (FDTD) simulation

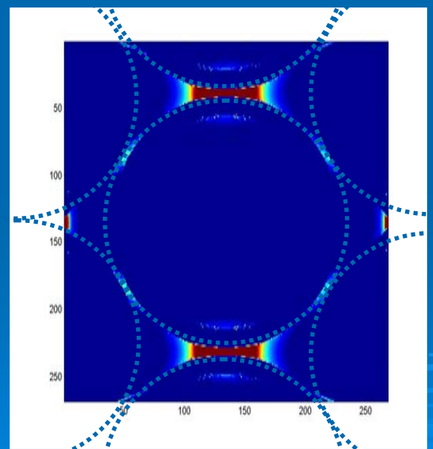




$$\nabla \times \vec{E} + \frac{1}{c}\frac{\partial \vec{H}}{\partial t} = 0$$

$$\nabla \times \vec{H} - \frac{\varepsilon}{c}\frac{\partial \vec{E}}{\partial t} = 0$$

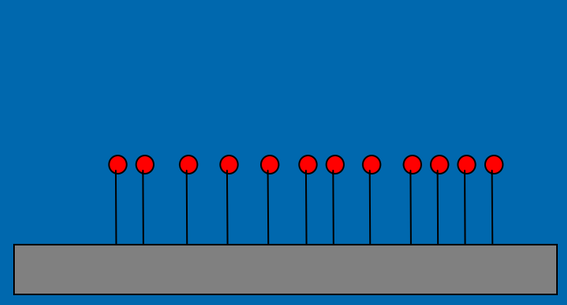




Cosmin Farcau, Simion Astilean, J. Phys. Chem. C, 114, 11717 (2010)

Metal film deposited over array of microspheres as fluorescence enhancement substrates

Sample preparation

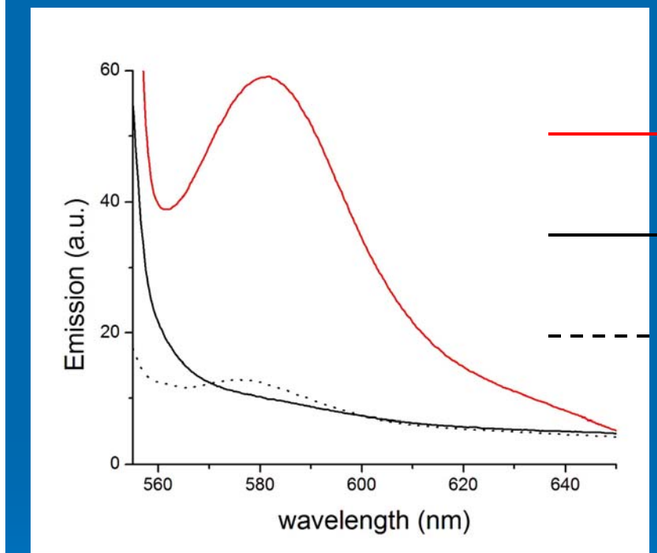


Rose Bengal fluorophore

Linker-spacer molecule

Nanostructured Au film

Metal-enhanced fluorescence

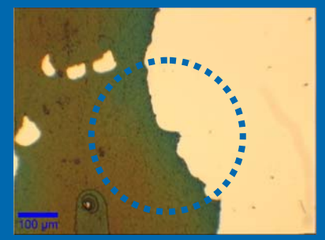


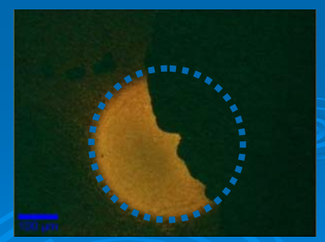
Emission spectra of Rose Bengal

nanostructured Au film

flat Au film

glass slide

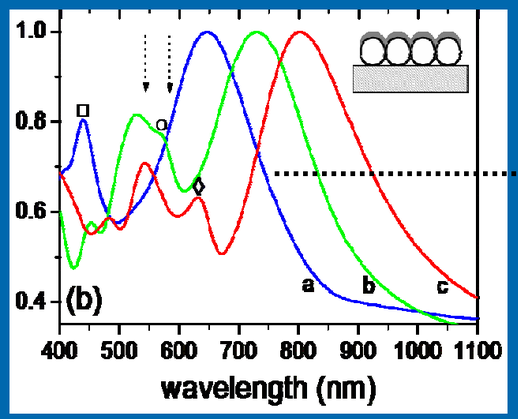


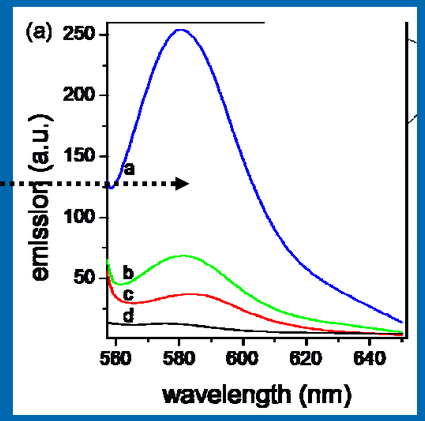


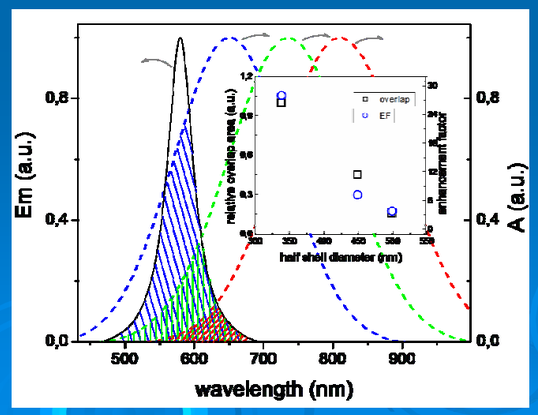
Optical images

C Farcau, S. Astilean, Appl. Phys. Lett. 95 (2009) 193110

Controlling the Fluorescence Enhancement



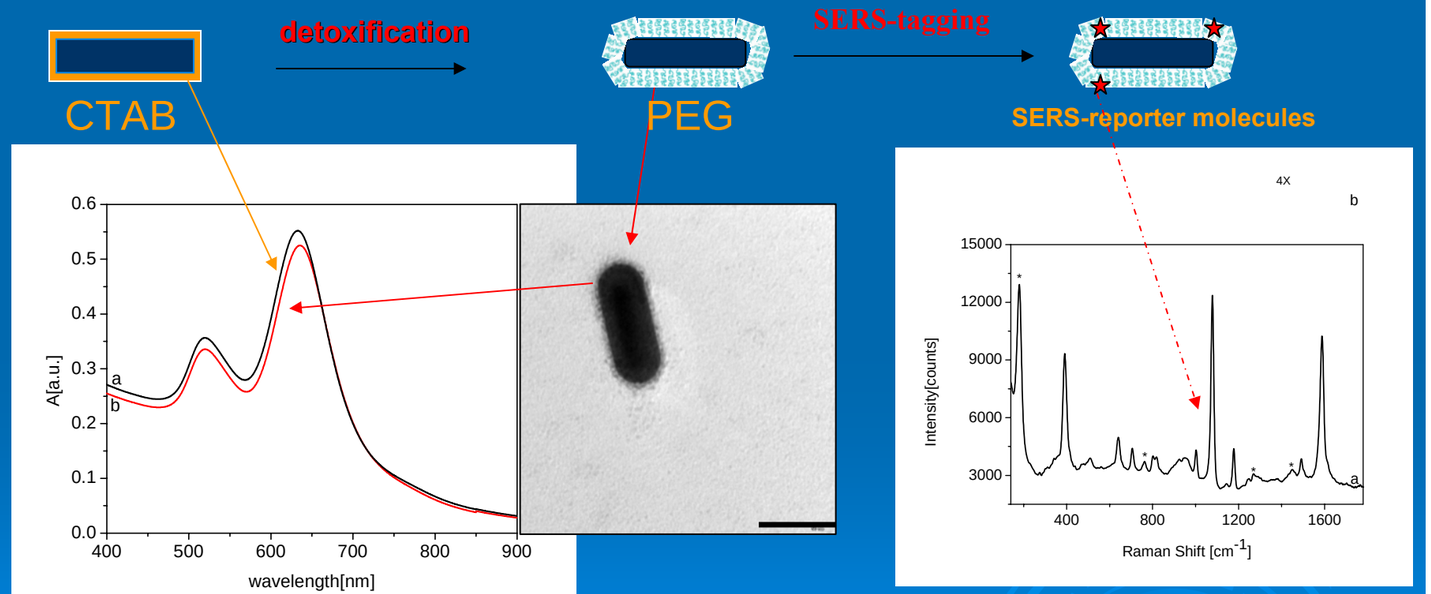




C Farcau, S. Astilean, Appl. Phys. Lett. 95 (2009) 193110

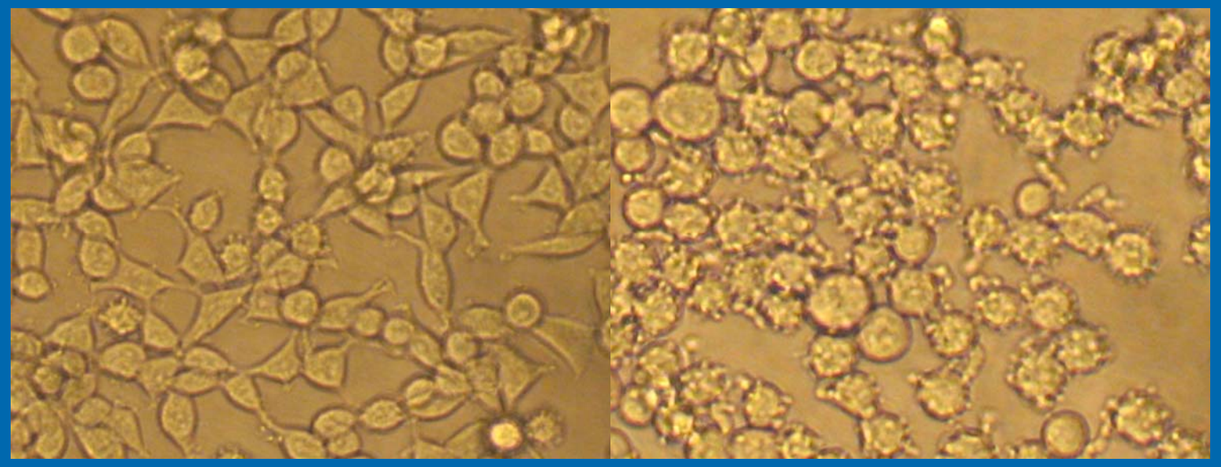
Recent results in bio - plasmonics

Detoxification, biofunctionalization and assessment of gold nanorods as SERS-active carriers of Raman tags



S. C. Boca, S. Astilean, Nanotechnology 21, 235601 (2010)

Uptake and biological effects of biopolymer-capped gold nanorods on living cells



Phase contrast images of Human Embryonic Kidney cells incubated for 24h in the presence of PEGylated nanorods (left) and CTAB as prepared nanorods (right)

Sanda C. Boca, Monica Potara, Felicia Toderas, Olivier Stephan, Patrice L. Baldeck and Simion Astilean,
Materials Science and Engineering: C, Article in Press, doi:10.1016/j.msec.2010.08.015

Conclusions

- We develop experimentally simple methods to control the plasmonic resonances of noble-metal nanostructures.
- We use as fabricated noble-metal nanostructures in multifunctional plasmonic sensors and ultrasensitive maolecular detection and imaging.

Acknowledgement

Financial support

1. Babes-Bolyai University
2. Project CEEX 71 /2006 (ANCS)
3. Project IDEI 407 / 2007 (CNCSIS)
4. Project IDEI COMPLEXE 129/2009 (CNCSIS)

Nanobiophotonics @ Molecular Spectroscopy Group

Permanents staff:

Simion Astilean, Prof.

Dana Maniu, Assoc Prof.

Simona Pinzaru, Assoc Prof.

Monica Baia, Assoc Prof.

Post-docs:

Monica Iosin, Dr

Valentin Canpean, Dr

PhD students:

Sanda Boca

Monica Potara

Ana-Maria gabudeam

Mircea Giloan

Previous staff and PhD students:

Iliescu Traian, Prof.

Felicia Toderas, Dr

Cosmin Farcau, Dr

Monica Potara, PhD

Sanda Boca, PhD

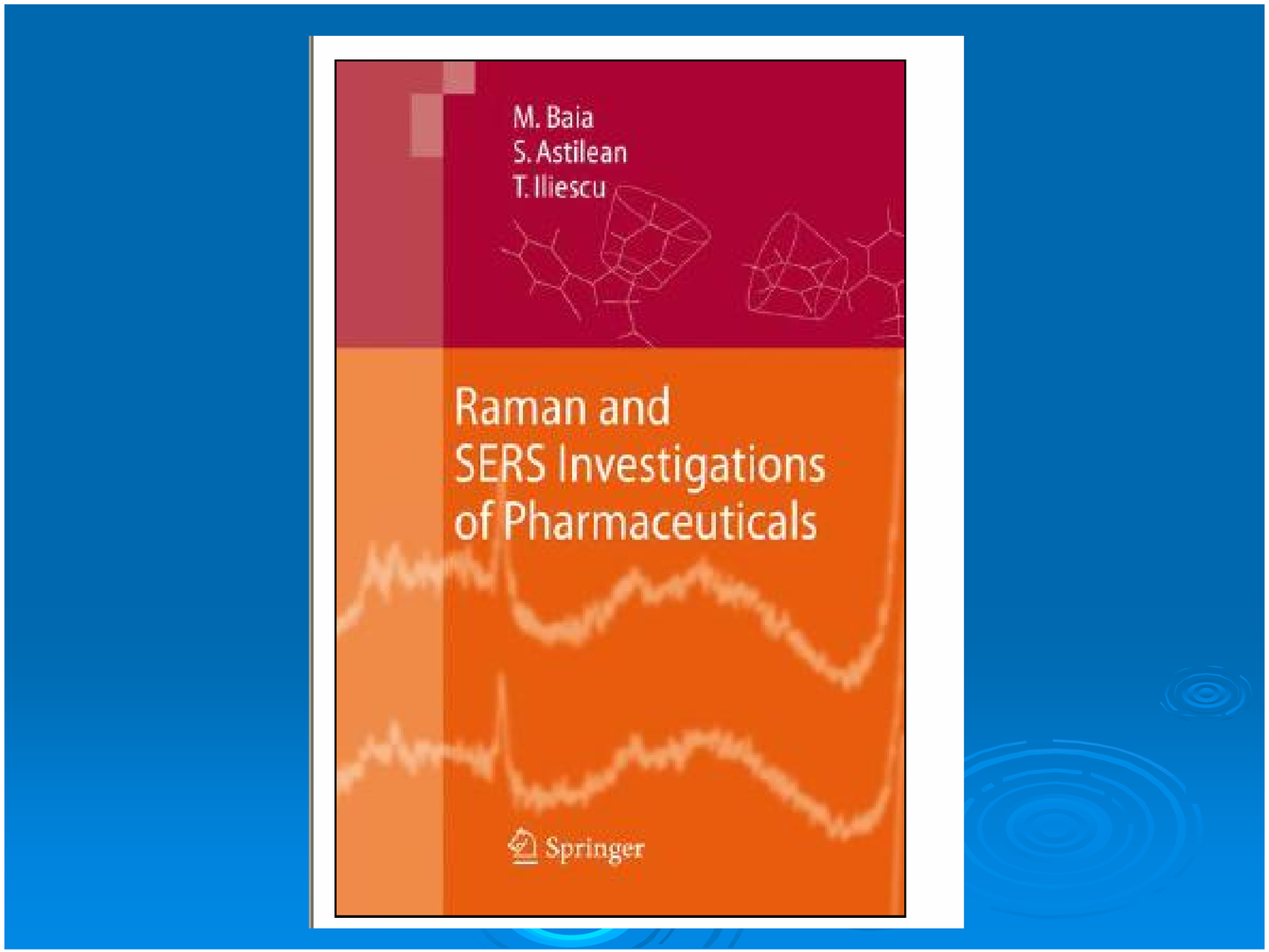
Dr Monica Iosin

Dr Vali Canpean

Dr Felicia Toderas,

Dr Cosmin Farcau,

Ana Gabudean, PhD


M. Baia
S. Astilean
T. Iliescu
Raman and
SERS Investigations
of Pharmaceuticals
Springer