Development of SERS nanostructures for biosensing

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BioNEM Laboratory – Main research lines

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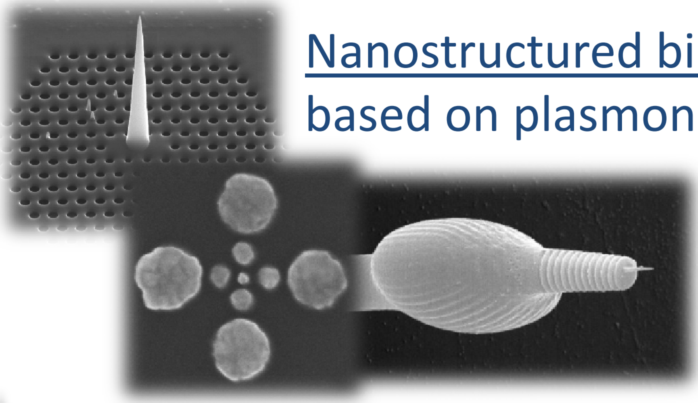
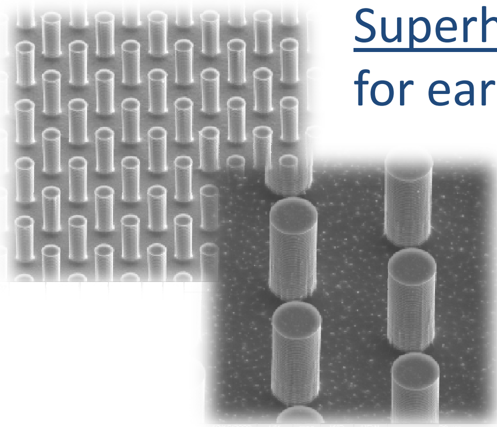
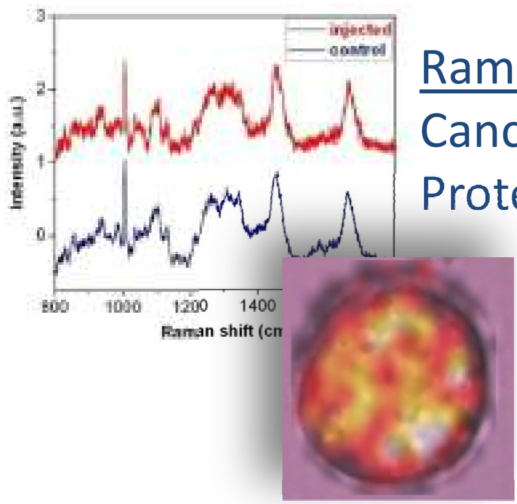


Nanostructured biosensors
based on plasmonic resonances



Superhydrophobic surfaces
for early diagnosis

Microfluidics:
cells screening,
proteins analysis,
biosensors integration



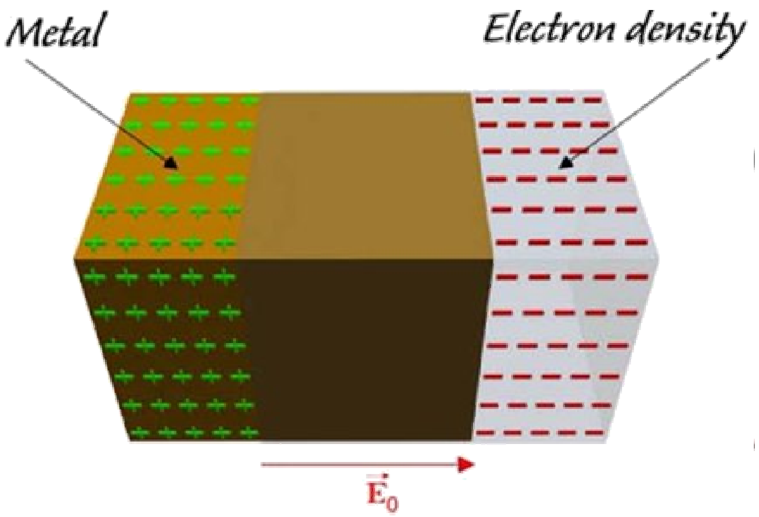
Raman spectroscopy:
Cancer Stem Cells studies,
Proteomics and Cellomics

Plasmonics and SERS: short introduction

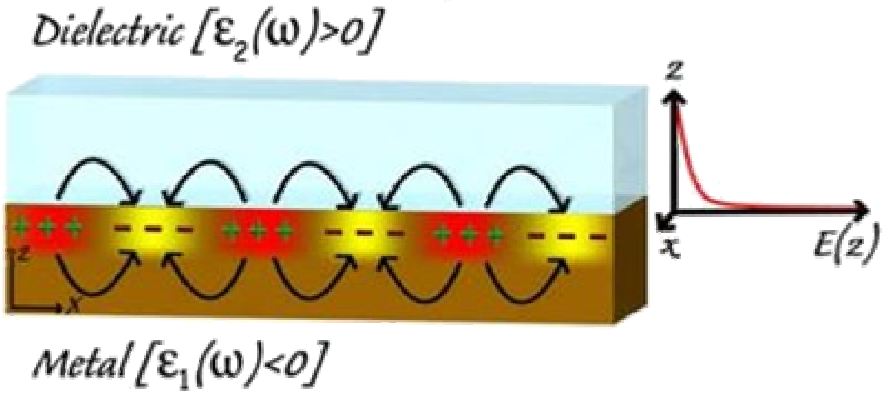
Plasmonics and SERS: short introduction

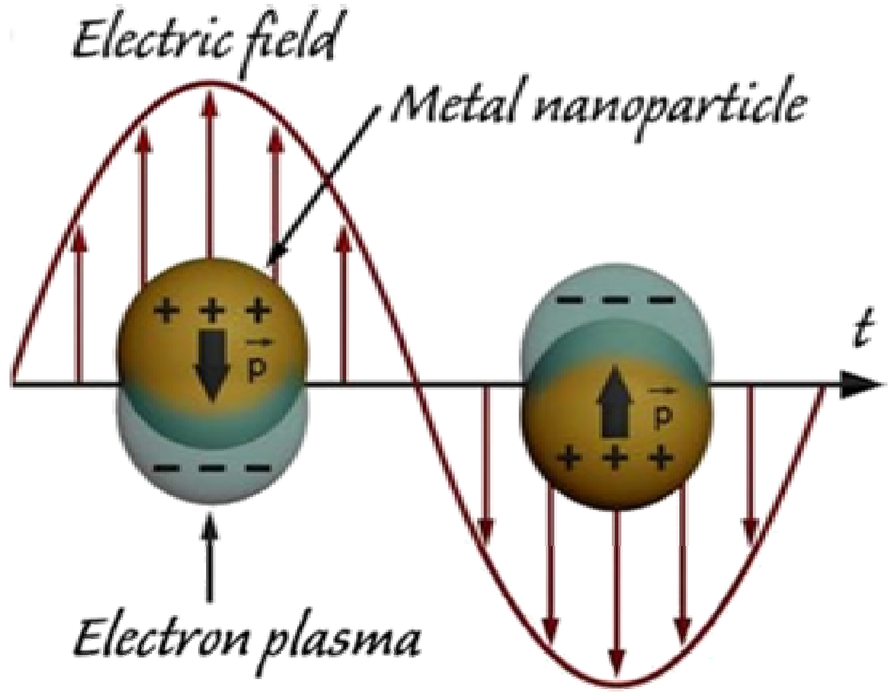
Plasmonic waves **(plasmons)** are collective oscillations of electrons cloud in conducting media

Starting from **bulk plasmons**…



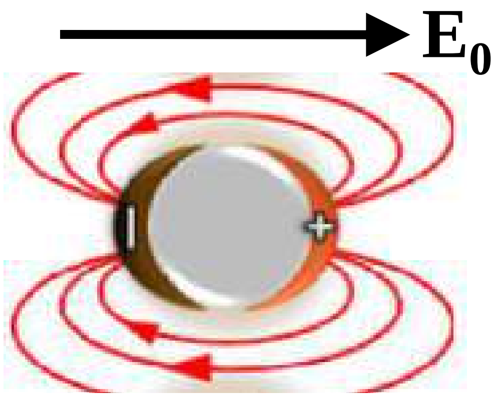
…**surface plasmons** are introduced…





…and finally **localized-surface-plasmon-resonances (LSPR)** in nanostructures.

Plasmonics and SERS: short introduction

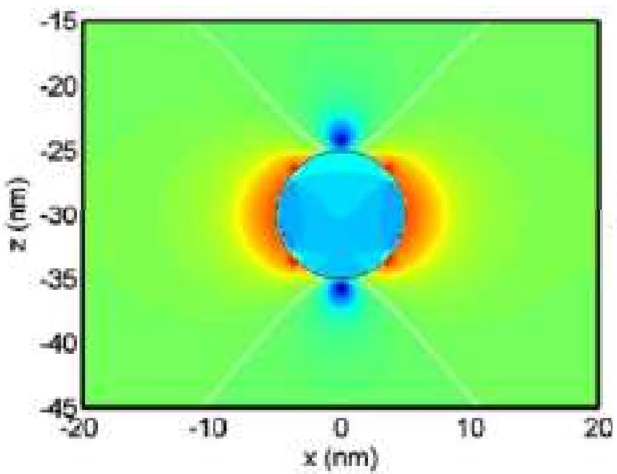


If an external field $\mathbf{E_0}$ is applied to a metal nanoparticle, dipolar fields $\mathbf{E_{LOC}}$ are generated close to the nanoparticle:

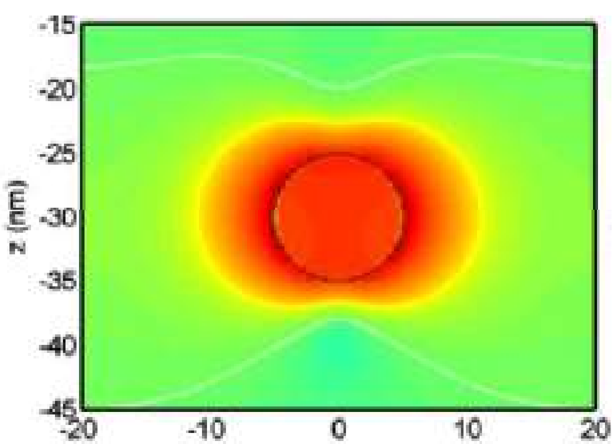
$$E_{tot}=E_0+E_{LOC}$$

- If the external field $\mathbf{E_0}$ is oscillating (laser source), the intensity of dipolar field $\mathbf{E_{LOC}}$ depends upon frequency
- At resonance, very strong oscillating dipolar fields are generated close to nanoparticle (localized plasmons)

Out of resonance



Plasmon Resonance



Localized surface plasmon resonance (LSPR) produces strong local electric fields (dipolar fields)

Plasmonics and SERS: short introduction

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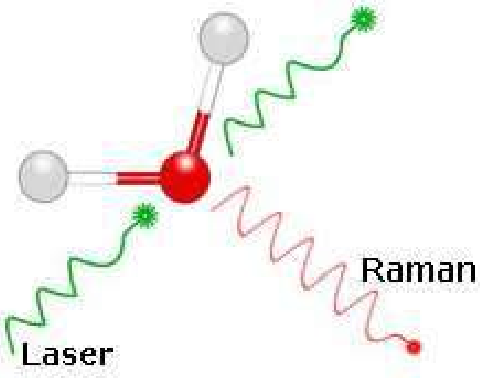
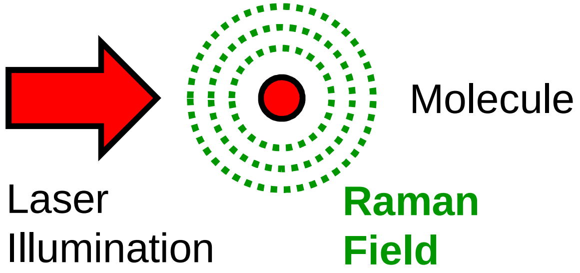
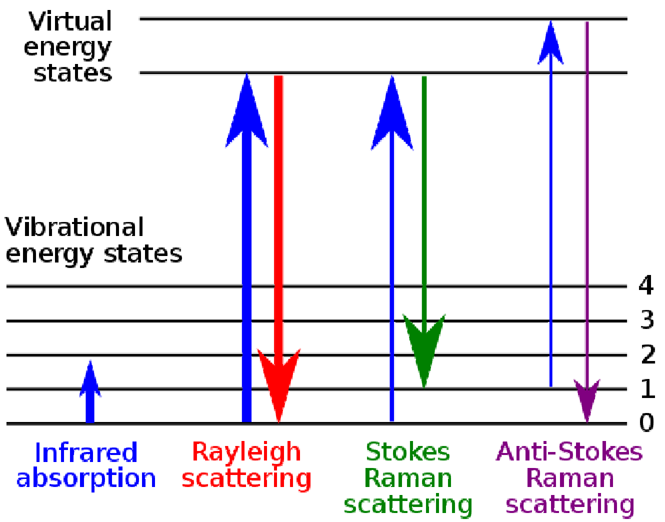
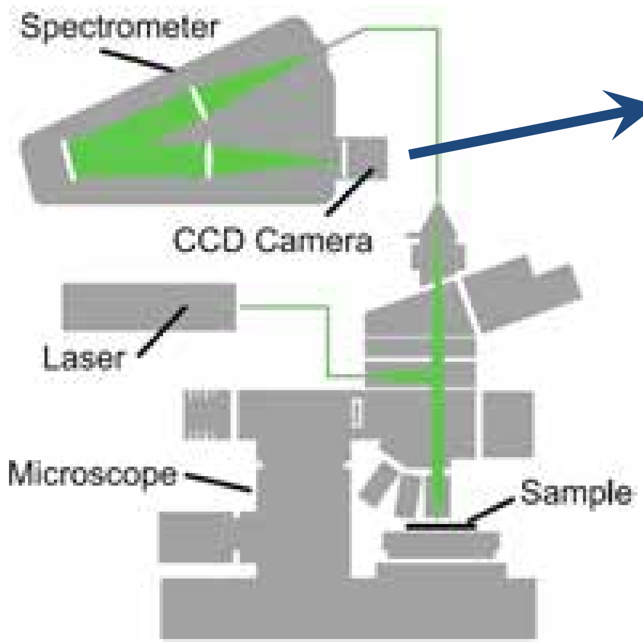
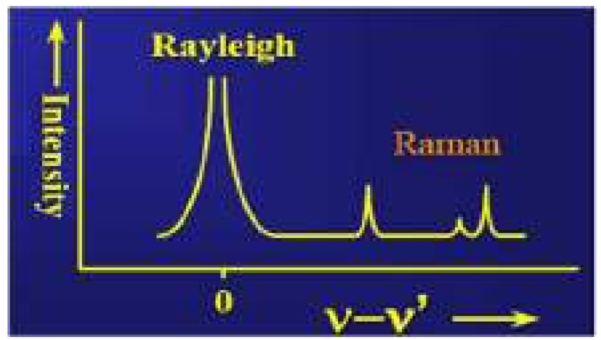






- In **Raman scattering**, the light of a laser source interacts with molecular vibrations, changing its energy (wavelength and frequency)
- The most of the laser light undergoes Rayleigh scattering, and only 1 photon over 10^5 leads to Raman scattering (low intensity)

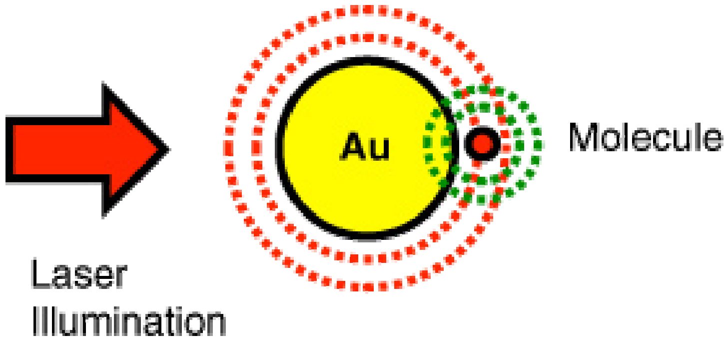




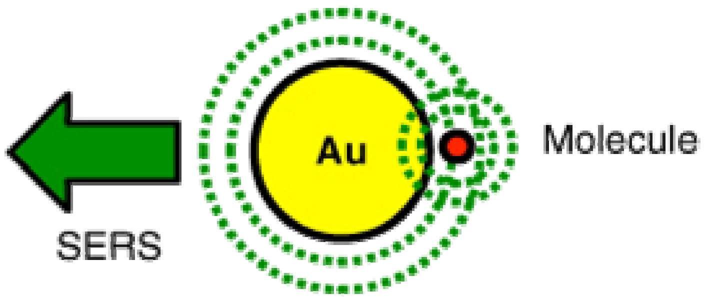
Spectral analysis of backscattered light reveals the energy of molecular vibrations, accounting for identification of molecules

Intensity Enhancement in SERS effect thanks to plasmonic local fields

Surface-enhanced-Raman-spectroscopy (SERS) achieves a large intensity enhancement due to a double amplification of the Local Electric Field



$$\leftarrow \begin{cases} E_{LOC} = f \cdot E_0 \quad \text{where } f\text{=enhancing factor} \\ E_{Raman} \propto E_{LOC} = f \cdot E_0 \end{cases}$$



$$\leftarrow \begin{cases} E_{SERS} = f \cdot E_{Raman} = f \cdot f \cdot E_0 \\ E_{SERS} = f^2 E_0 \end{cases}$$

SERS spectroscopic **intensity scales as the fourth power** of the field enhancing factor f

$$\left.\begin{cases} I_{Raman} \propto E_0^2 \\ I_{SERS} \propto E_{SERS}^2 = \left(f^2 E_0\right)^2 = f^4 E_0^2 \end{cases}\right\} \rightarrow \frac{I_{SERS}}{I_{Raman}} = f^4$$

Plasmonic Nanotriangles by means of NanoSphere Lithography

NanoSphere Lithography (NSL)

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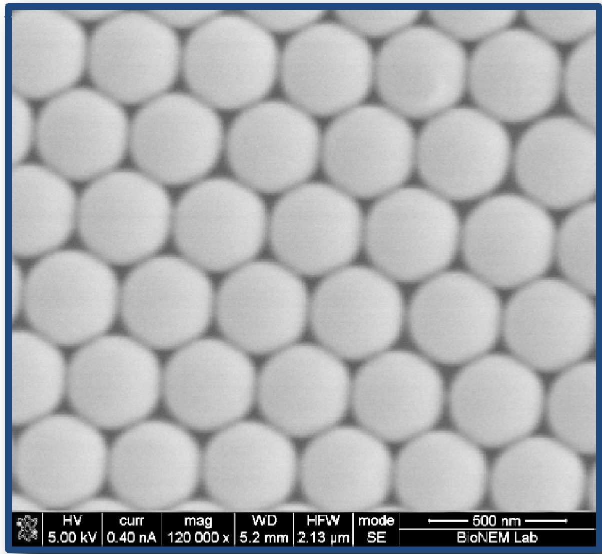
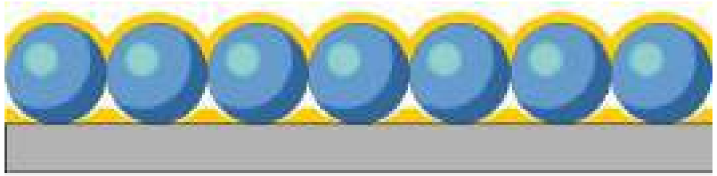
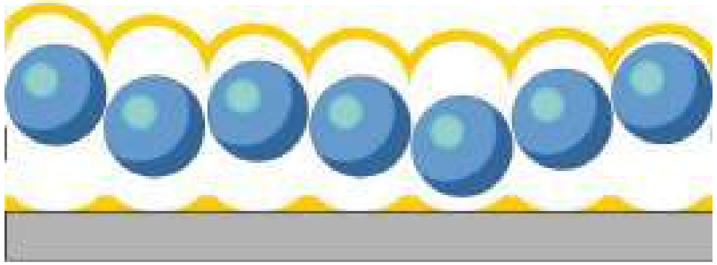
Nanosphere lithography (NSL) as a cheap approach to plasmonic triangular nanostructures

Single layer of Polystyrene nanobeads deposited over substrate

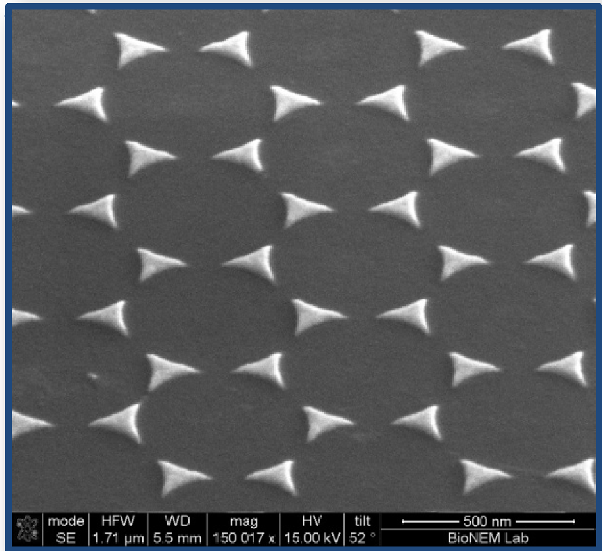




Thin Au layer deposited over the nanobeads array

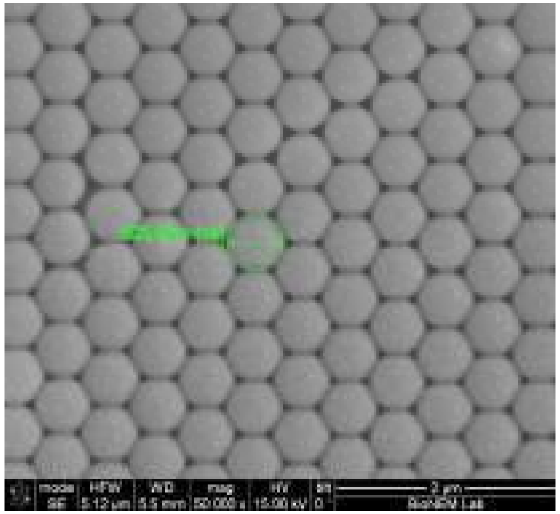


Nanobeads stripping for releasing the metal nanotriangles

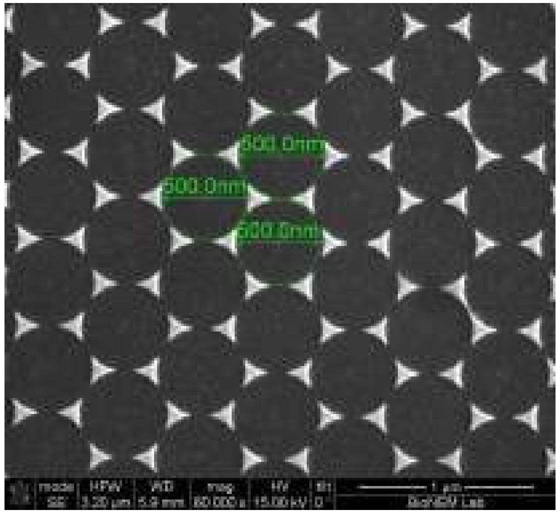


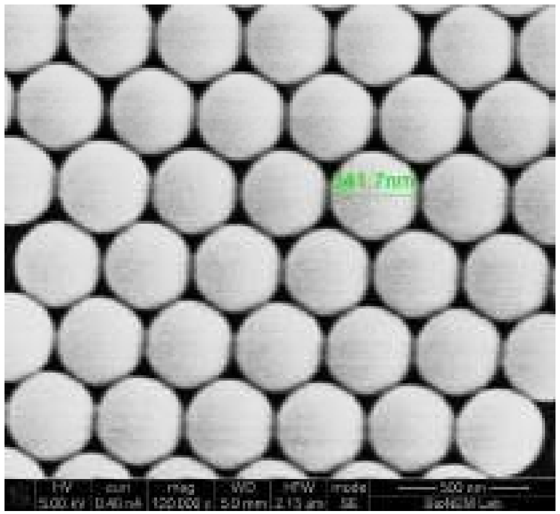
Nanosphere lithography combined with superhydrophobic substrates

500nm diameter beads

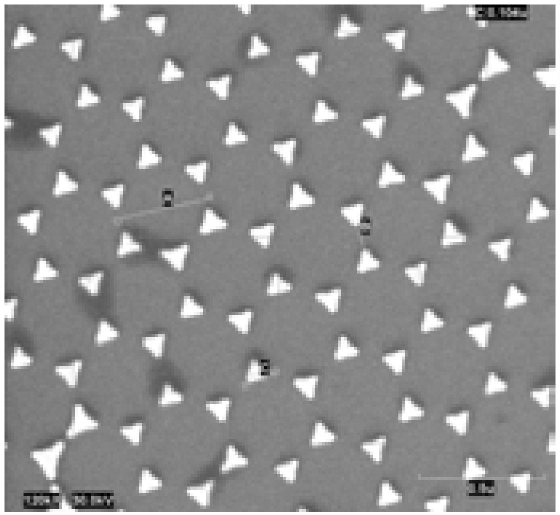


Sharper tips



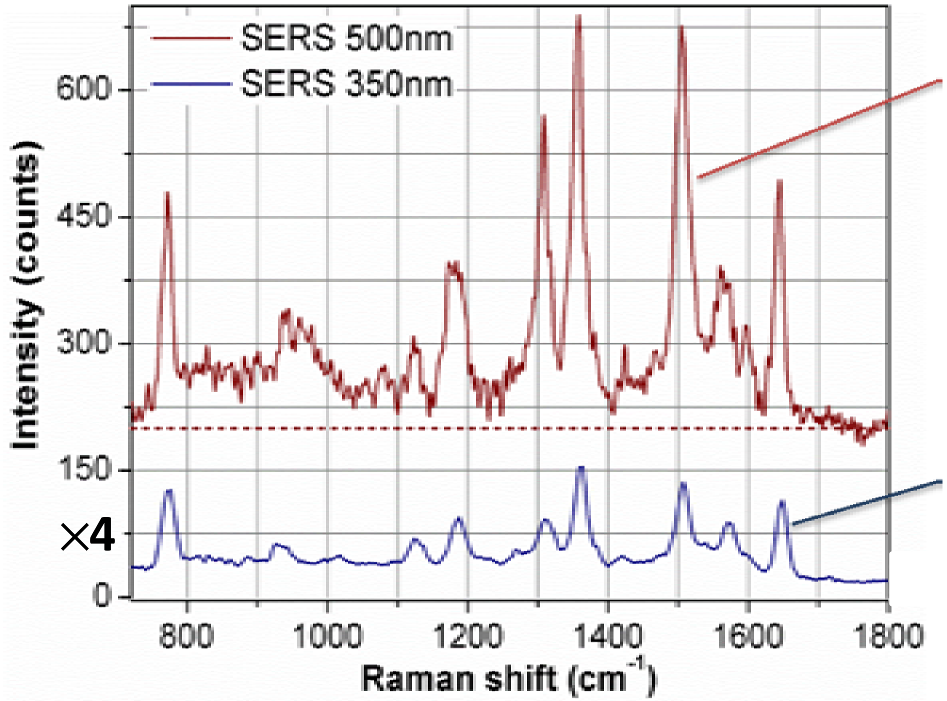


350nm diameter beads



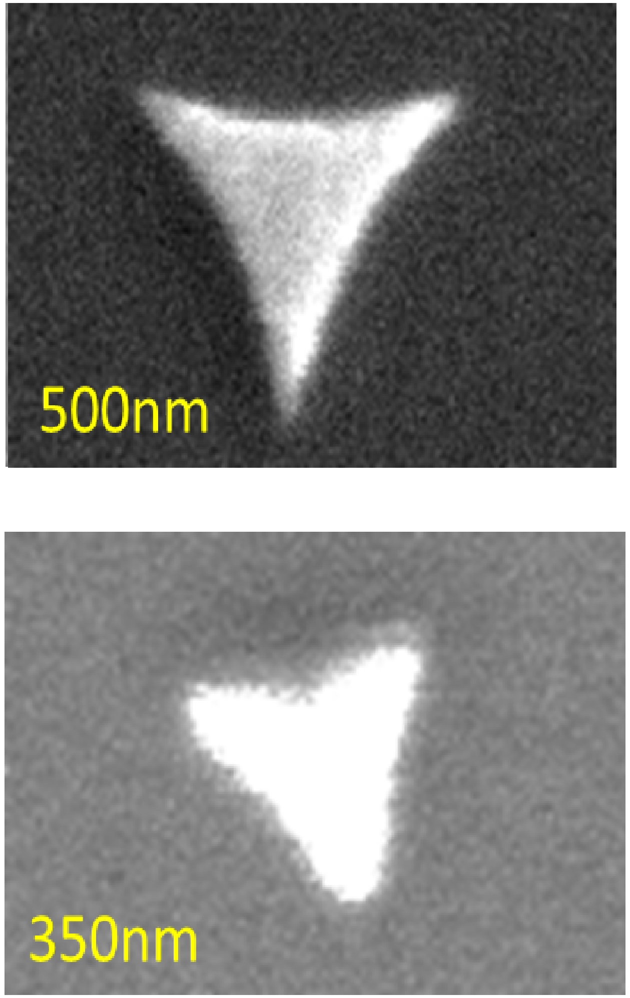
Smaller nanotriangles

SERS measurements

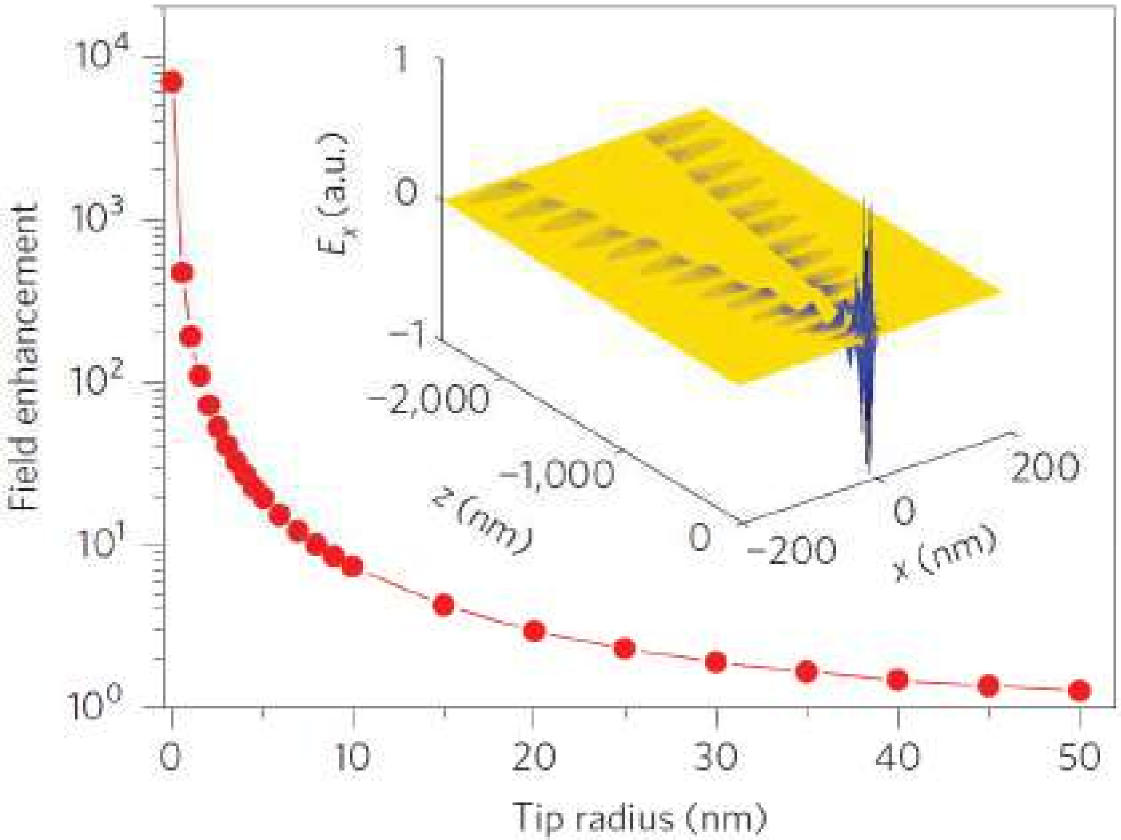


- Rhodamine-6G 10^{-8}M is deposited over the nanotriangles SERS substrate.
- SERS is performed with a 532nm laser wavelength and 75µW/cm^2 power

Dependence of the enhancing factor upon tip radius



Small variations in the tip radius can cause large differences in the enhancing factor



Plasmonic Nanoholes by means of Template Stripping technique

Template-stripping fabrication of plasmonic nanostructures on glass substrates

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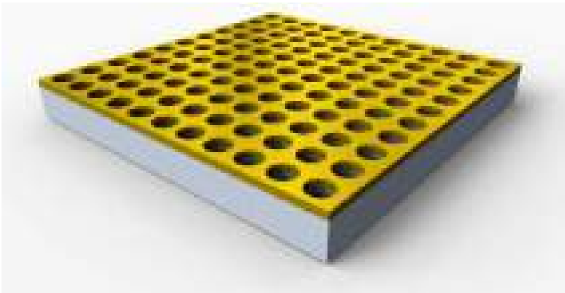
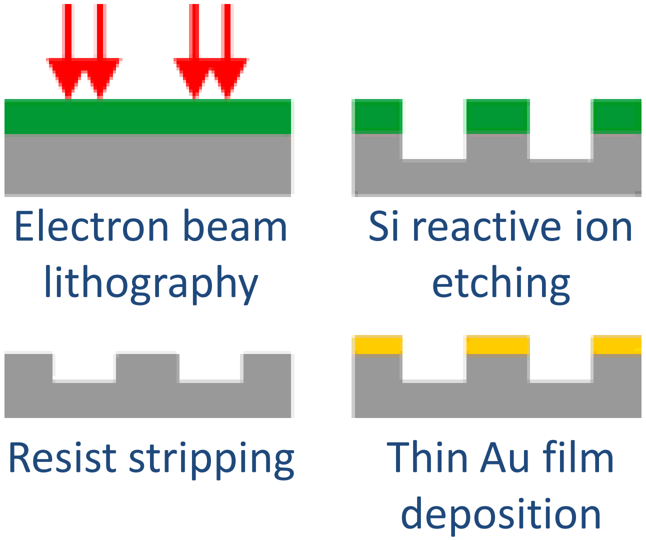
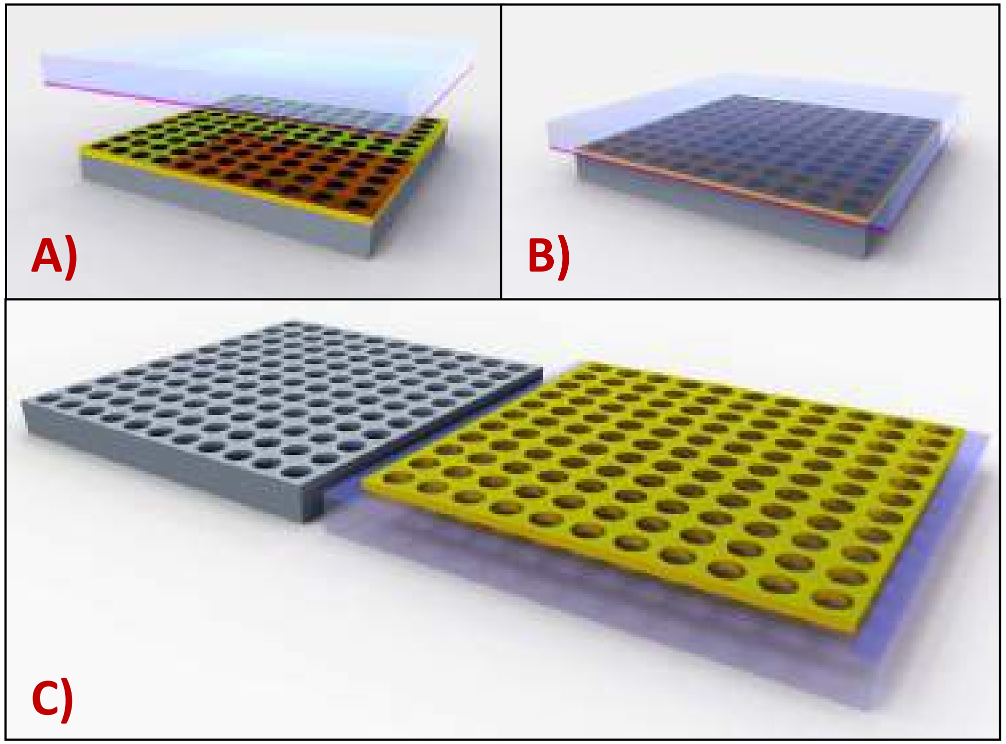
Fabrication of a Si template with nanoholes and Au thin layer





Template stripping replication



A) Glass slide with optical glue and Au+Si template
B) Glass slide is pressed over Au+Si template
C) Si template releases Au film sticking on glass slide

Template-stripping results

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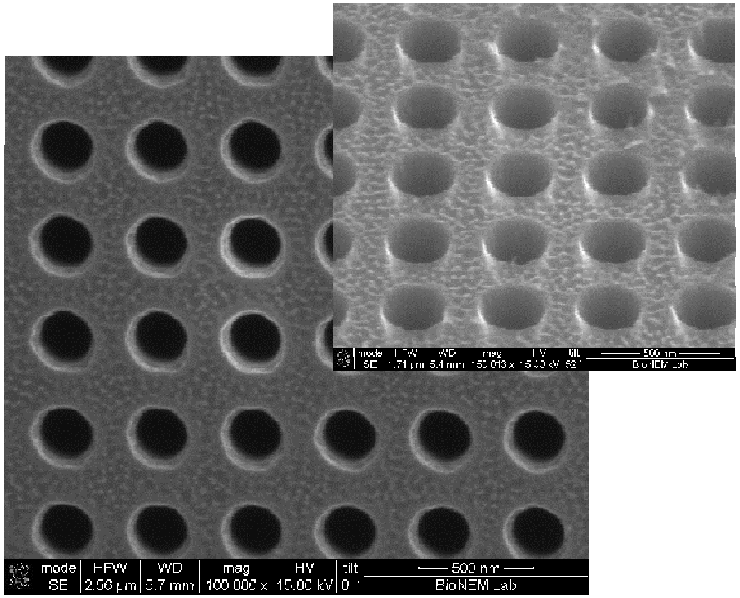
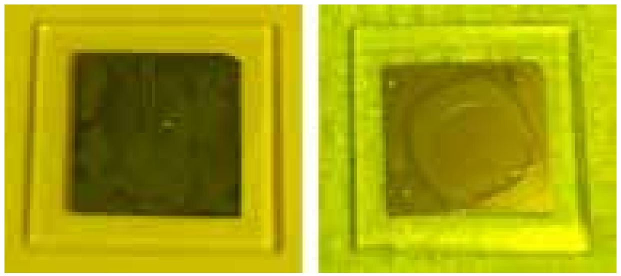
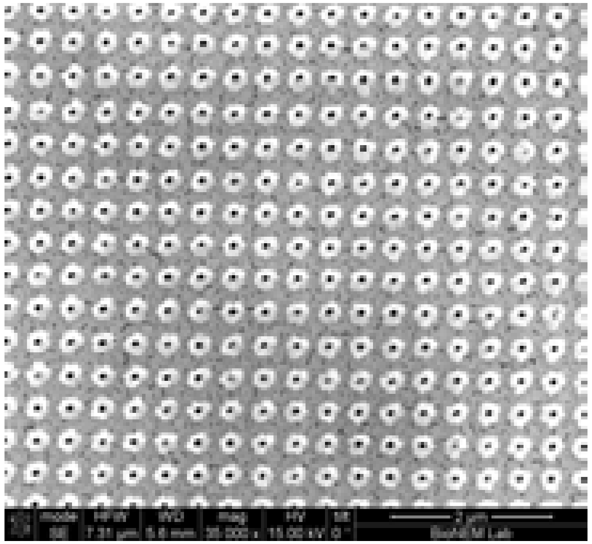
Fabricated Si templates

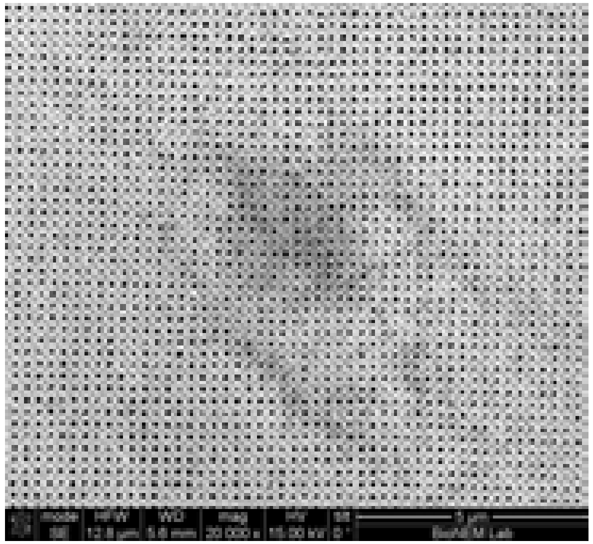


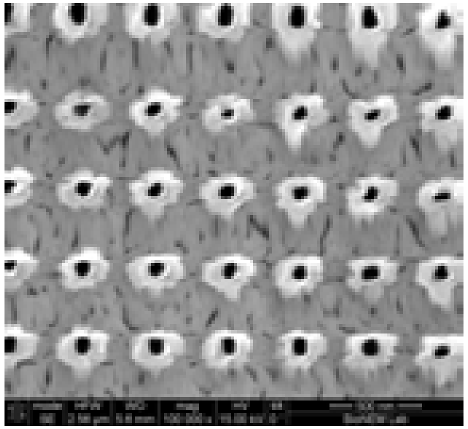


Template-stripping over glass substrates

Replicated patterns over glass substrates







- SEM pictures of Au-Nanoholes on glass slides.
- Mass production of nano-structures on insulating slides.
- Well suited for nano-optic and opto-plasmonic elements

Plasmonic behavior of Au nanoholes: numerical simulation

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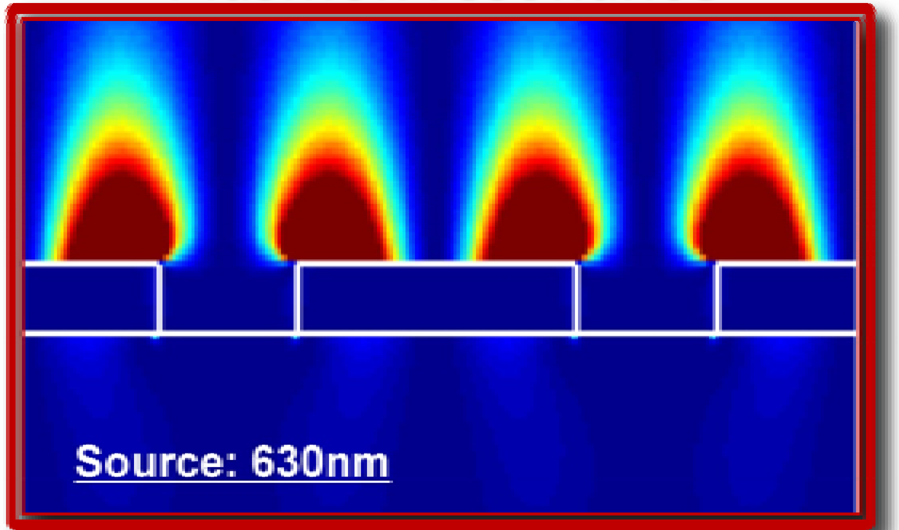
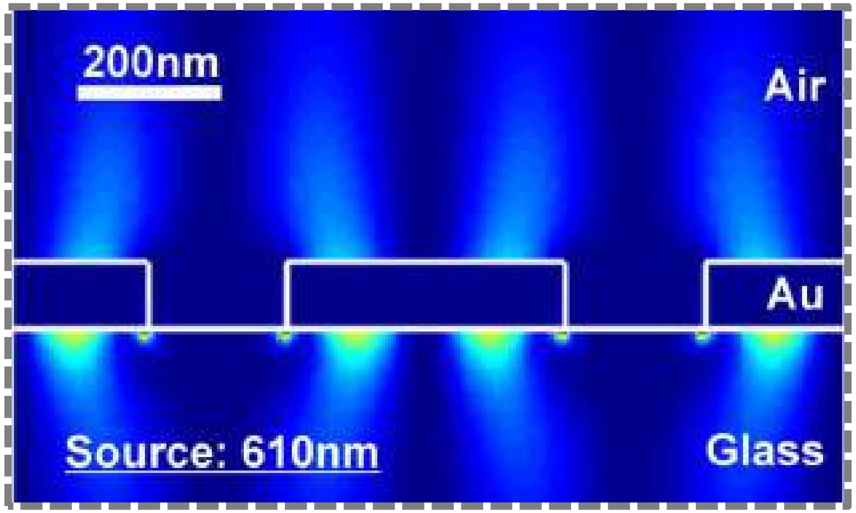
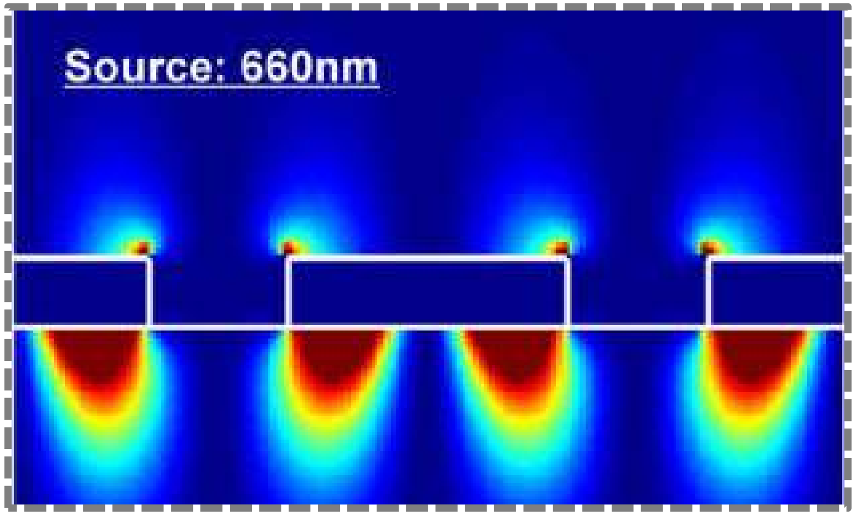
- Au Nanoholes laying on glass slides and immersed in air.
- Simulation of electric field distribution at different light source wavelengths.
- **Plasmon resonance on top side of nanoholes occurs at 630nm.**

Plasmon resonance







SERS spectra recorded over Nanoholes

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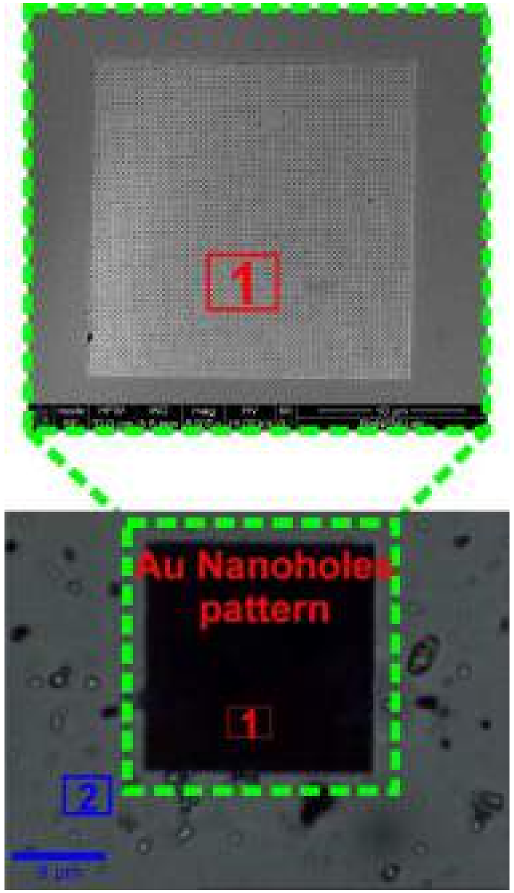
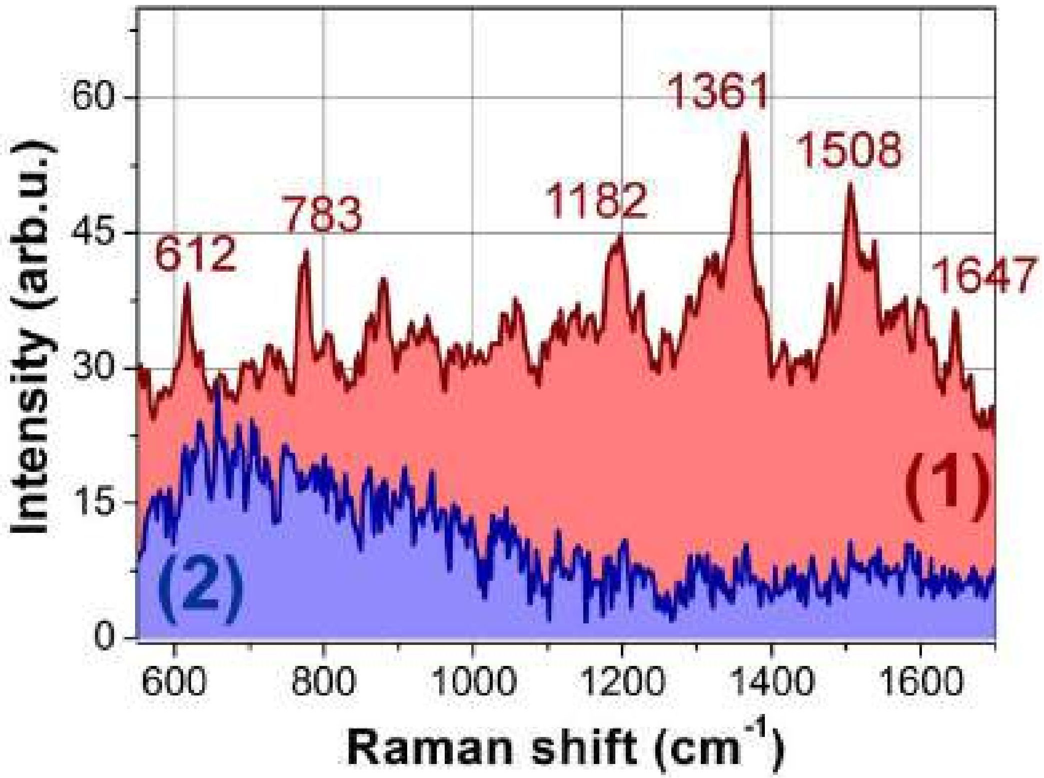


- Rhodamine-6G 10^{-8}M is deposited over patterned and surrounding area
- SERS is performed with a 633nm wavelength and 30mW/cm² power

SERS measurements



- **Red spectrum (1)** recorded inside the pattern shows clear Rhodamine-6G peaks
- **Blue spectrum (2)** outside is a background signal
- Subdiffraction pitch of Au Nanoholes prevents the arising of any signal from bottom glass

Plasmonics meets Superhydrophobicity

Plasmonics meets Superhydrophobicity for few biomolecules detection

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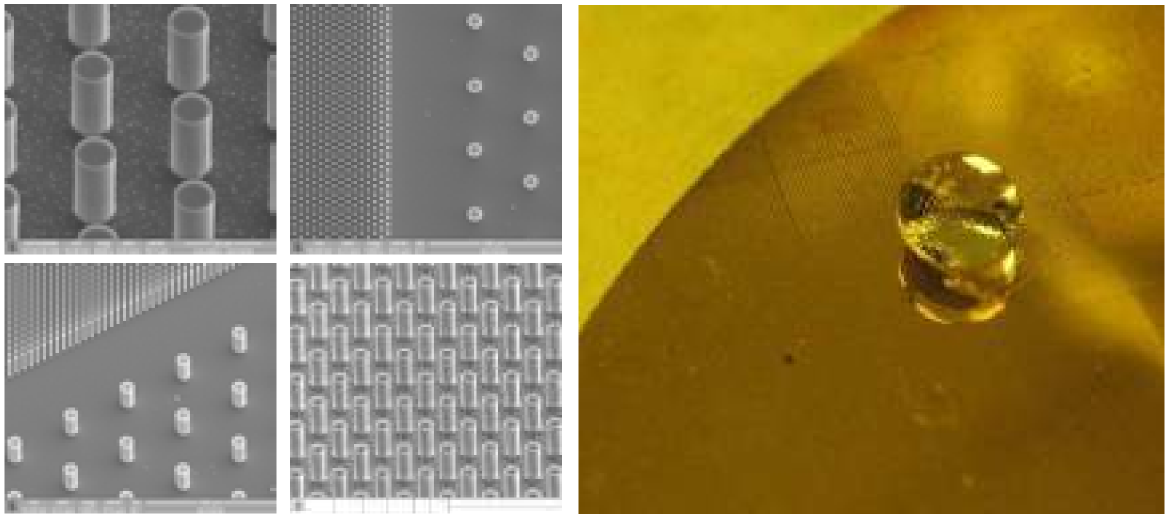
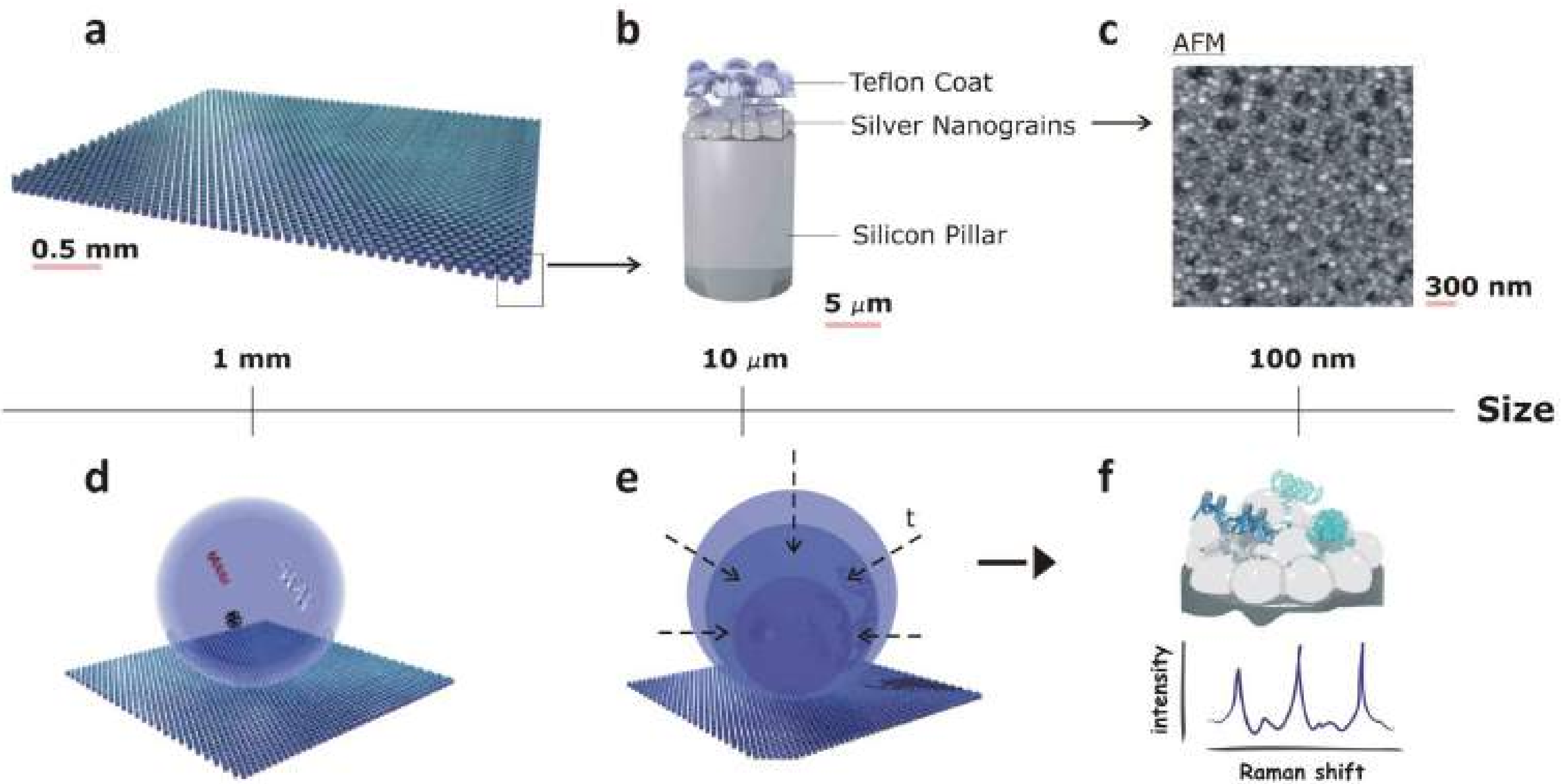
When a drop is placed upon a micro- or nano-patterned surface it experiences a contact angle which can easily exceed 150°.

This phenomenon is commonly referred to as the **lotus effect** and is widely observed in nature



Micro and nano fabrication techniques allow to *artificially* reproduce the natural superhydrophobicity

Working mechanism



Superhydrophobic microstructures for few biomolecules confinement

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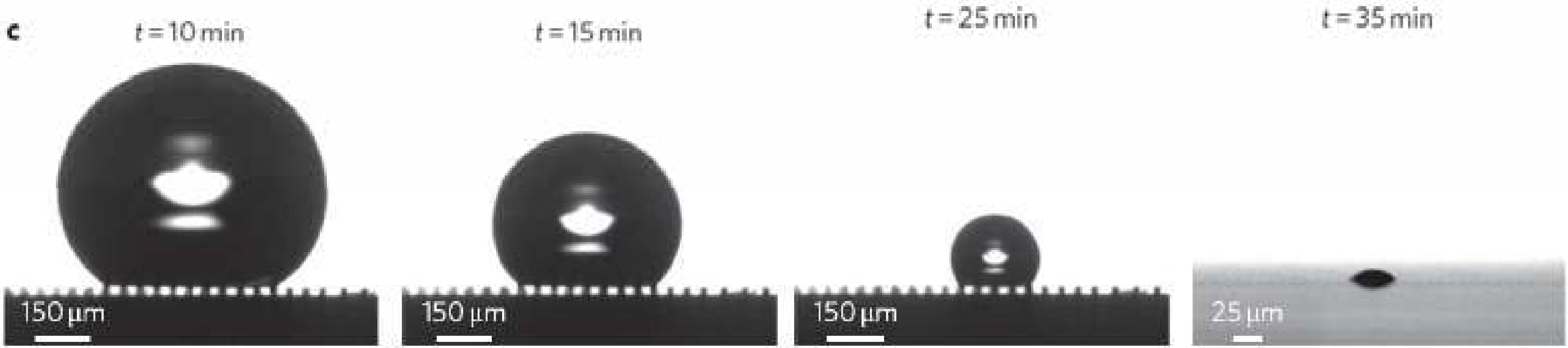
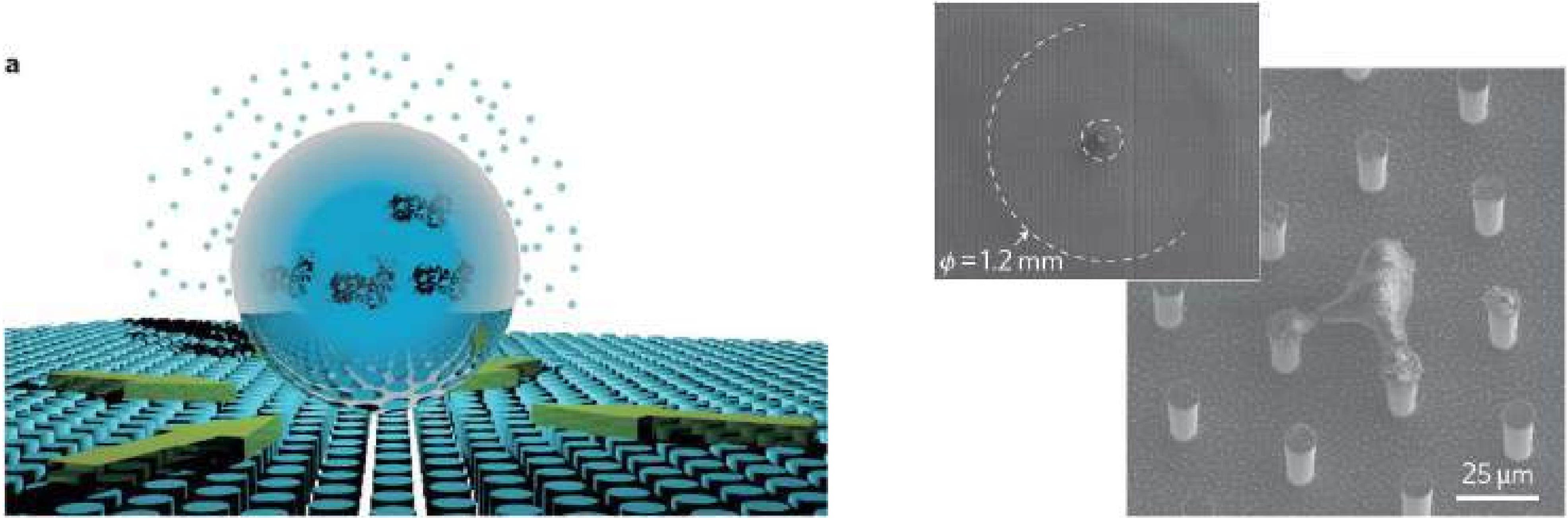
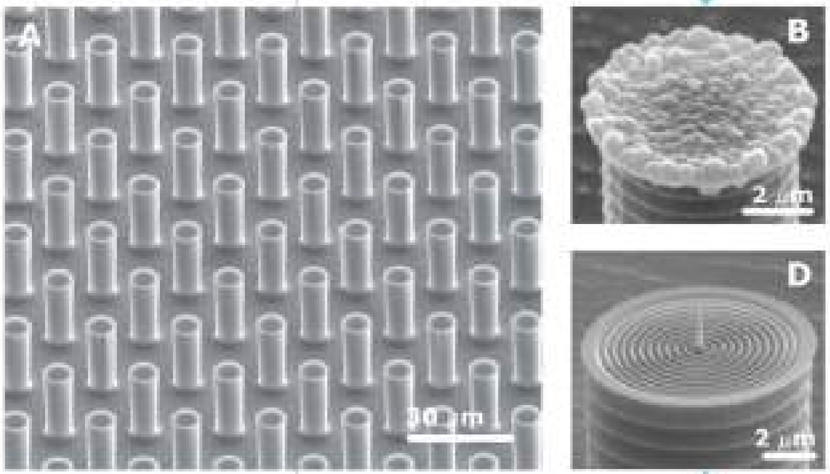
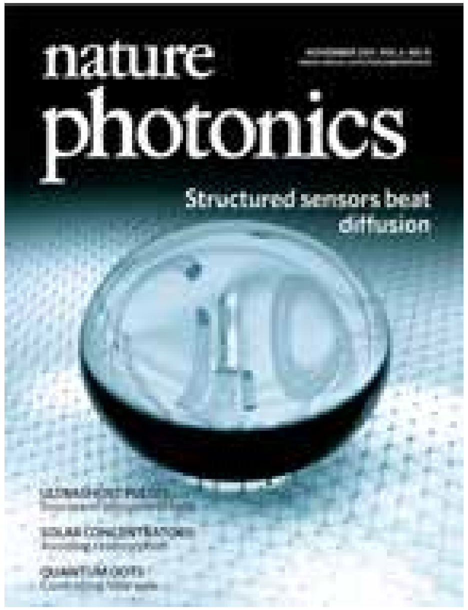




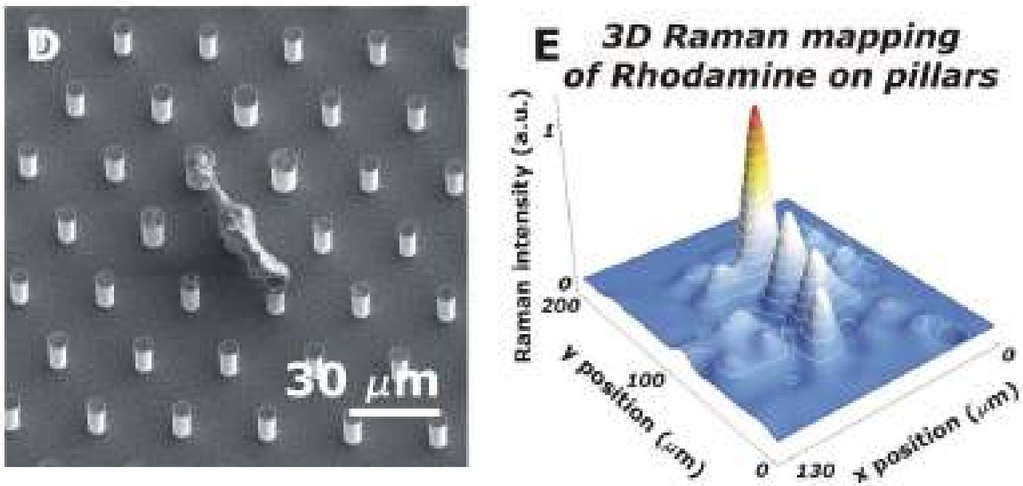
Plasmonics meets Superhydrophobicity for few biomolecules detection



Micro- and nano-fabricated superhydrophobic surfaces



Nature Photonics cover page



Rhodamine attomolar (10^{-18} M) deposition and detection

Thanks to **BioNEM Lab**:

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Luca Tirinato
Francesco Guzzi

THANKS FOR YOUR ATTENTION

www.bionem.unicz.it