From functional nanostructured surfaces to innovative optical biosensors

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Outline

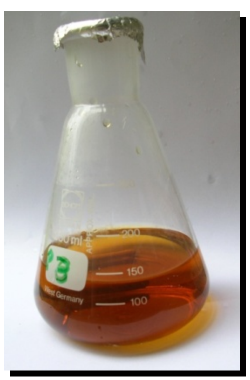
•Self-assembled monolayer (SAM) formation and growth

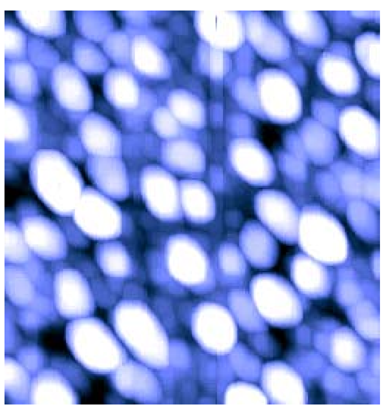
•Metal nanoparticles (NP) anchoring on SAM

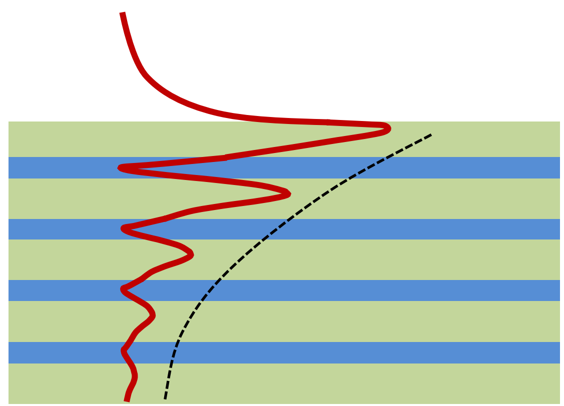
•Metal ions and NP SAM as antibacterial materials

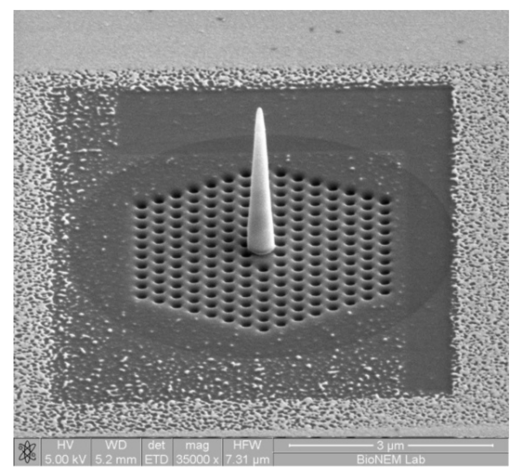
•Applications to photonic biosensors

•Plasmonic-photonic biosensor SENSe (surface-enhanced nanosensor)



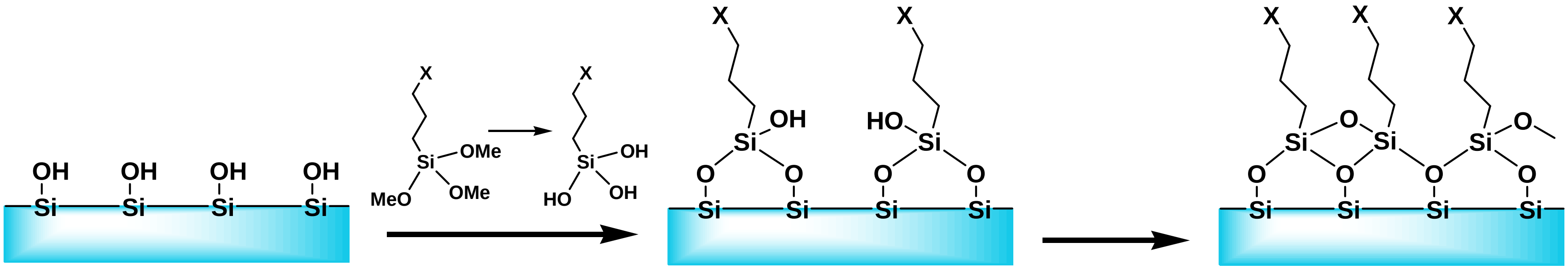




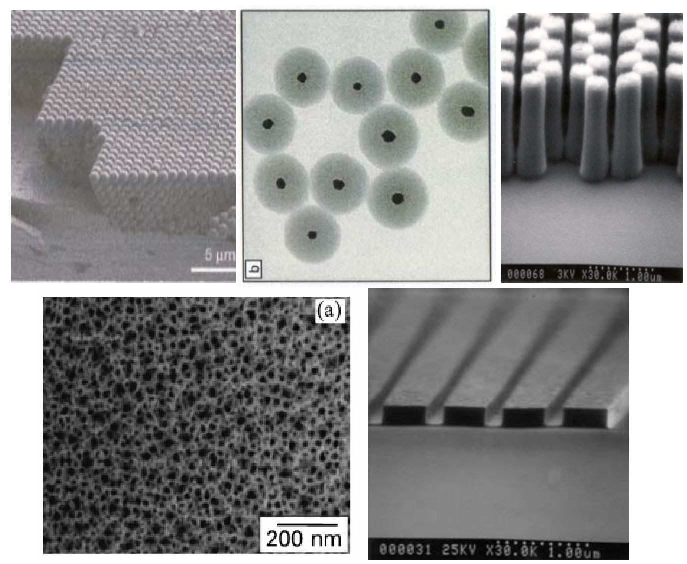


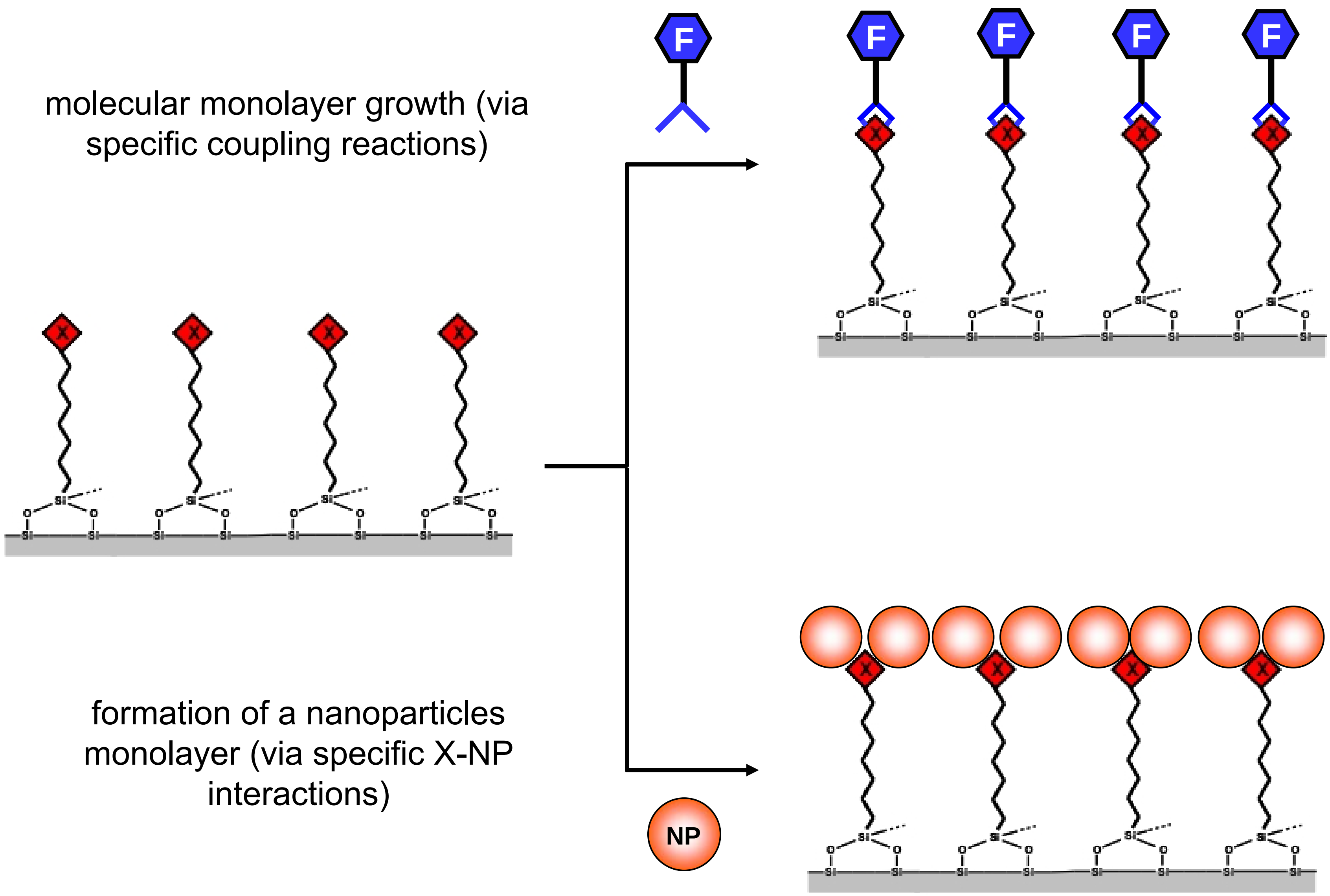
SAM formation and growth

1. SiO_2 surface cleaning/activation
2. Silanization
3. Further growth of the SAM



SiO_2 surfaces: glass, quartz, SiO_2/Si
Other surfaces: Si_3N_4, inorganic oxides




molecular monolayer growth (via specific coupling reactions)
formation of a nanoparticles monolayer (via specific X-NP interactions)
F
X
NP
Si
O

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Spectroscopic evaluation of surface functionalization efficiency in the preparation of mercaptopropyltrimethoxysilane self-assembled monolayers on glass

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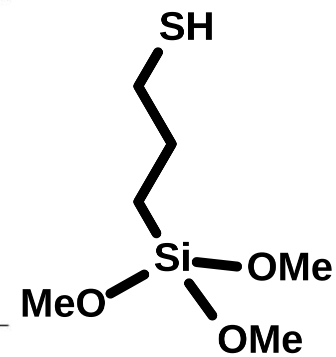
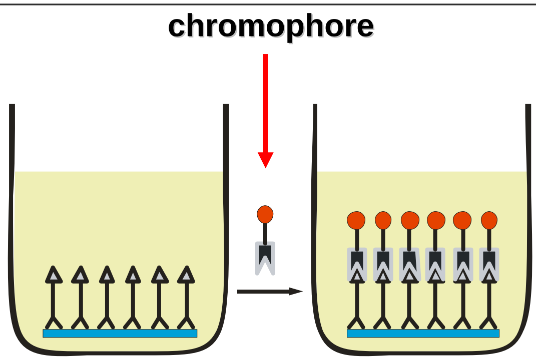
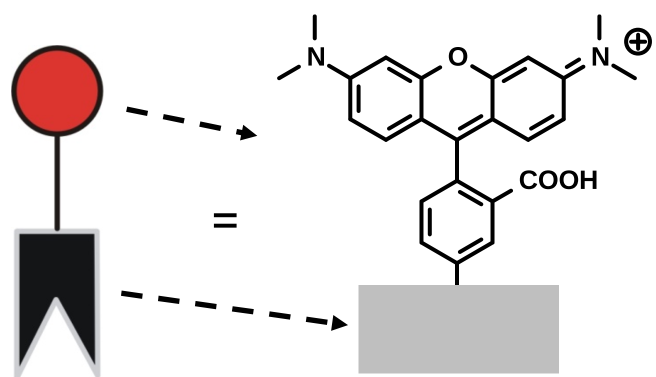
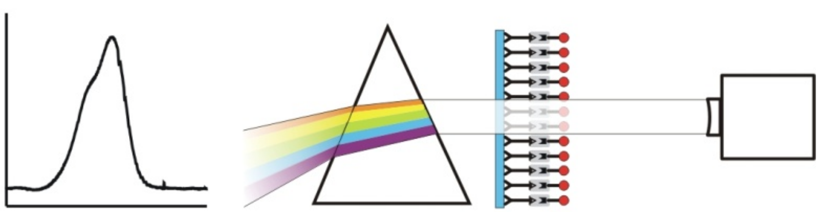
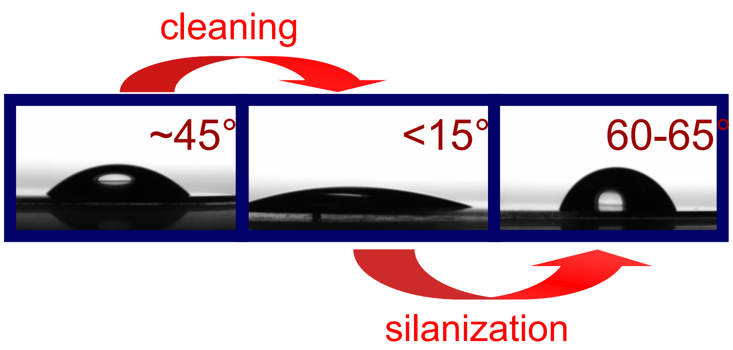






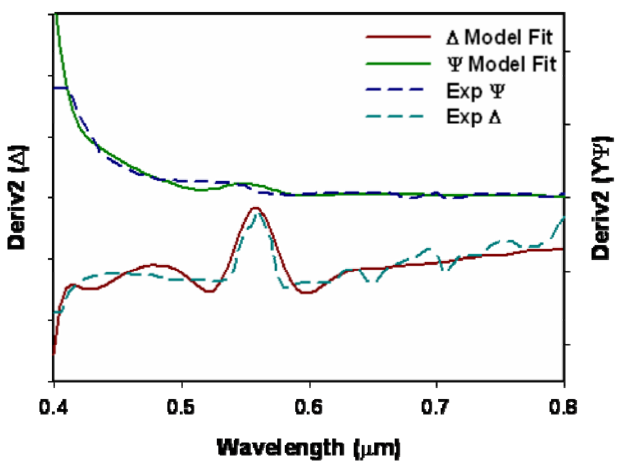


Contact Angle

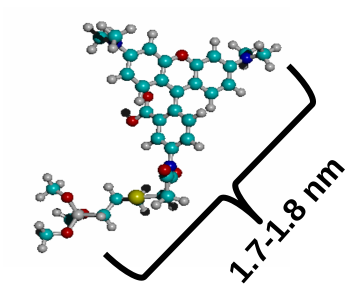


surface hydrophilicity/lipophilicity

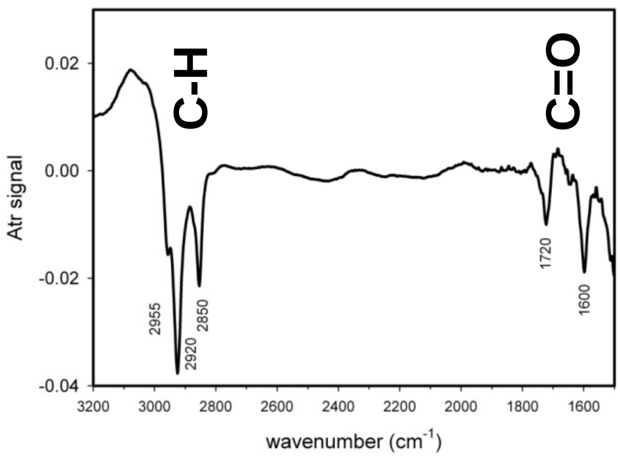
Spectroscopic Ellipsometry



Surface dielectric function changes
SAM thickness

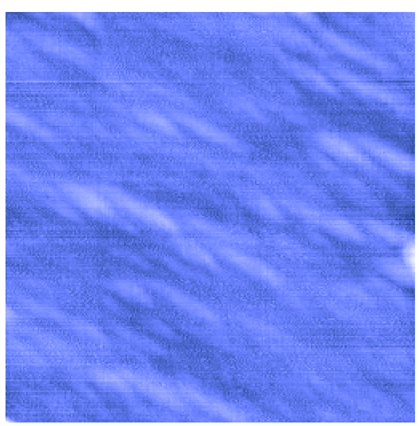


FTIR-Attenuated Total Reflectance (ATR)



Identification of chemical groups

Atomic Force Microscopy

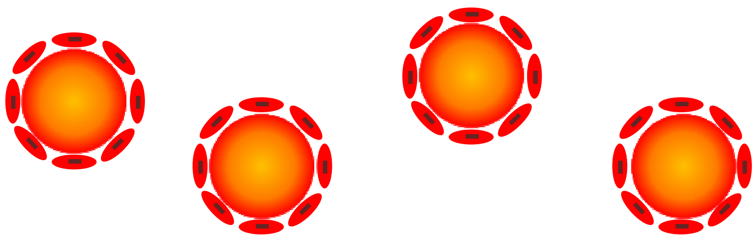


0.25 μm

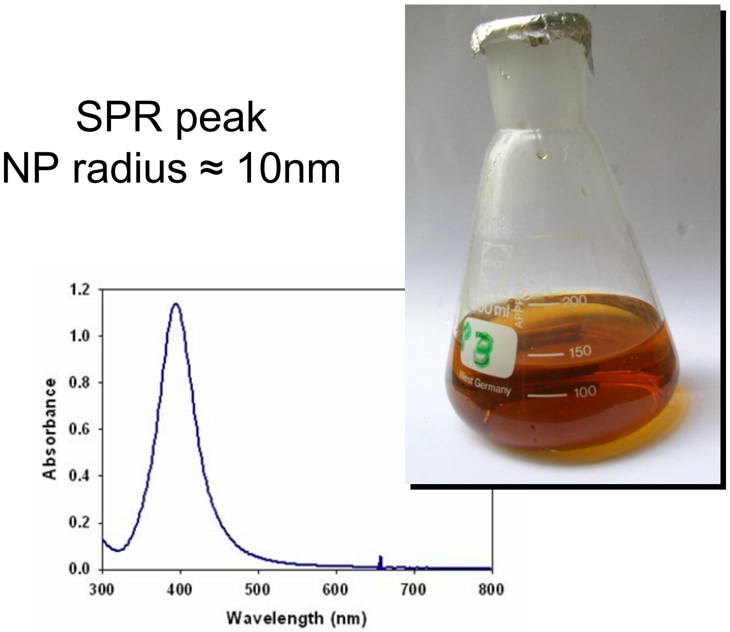
Sample topography, morphology
Roughness (rms roughness 0.31nm)

Synthesis and anchoring of Ag nanoparticles

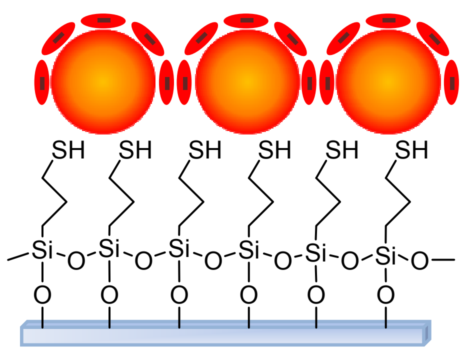
Silver salt: $AgNO_3$
Stabilizing agent: sodium citrate
Reducing agent: $NaBH_4$

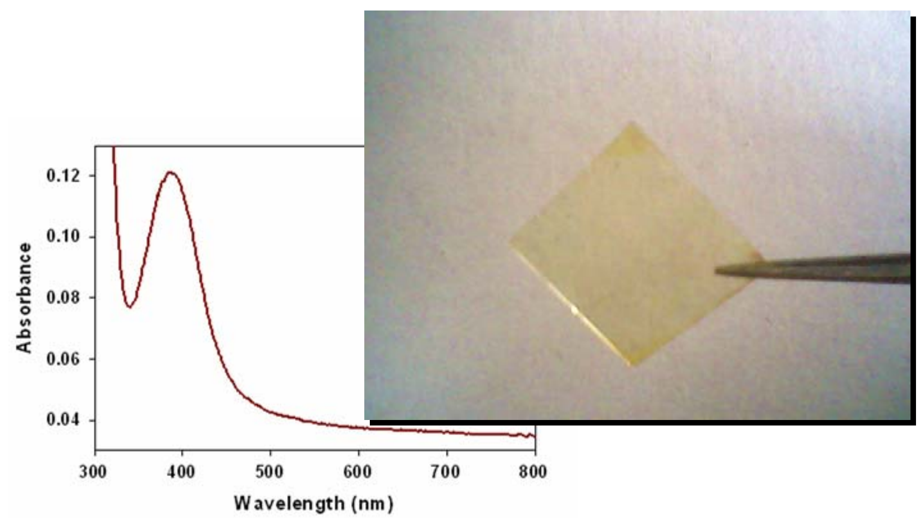


SPR peak
NP radius ≈ 10nm

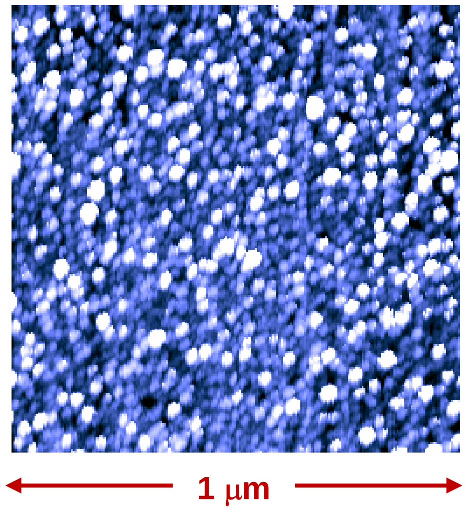


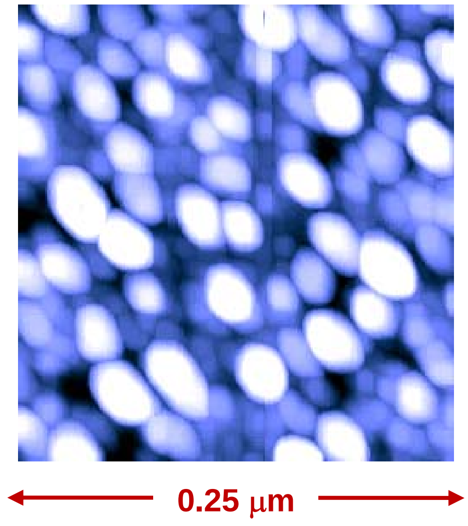
Functionalized glass dipped in
NP solution (rt, overnight)





Stability of Ag NP monolayer



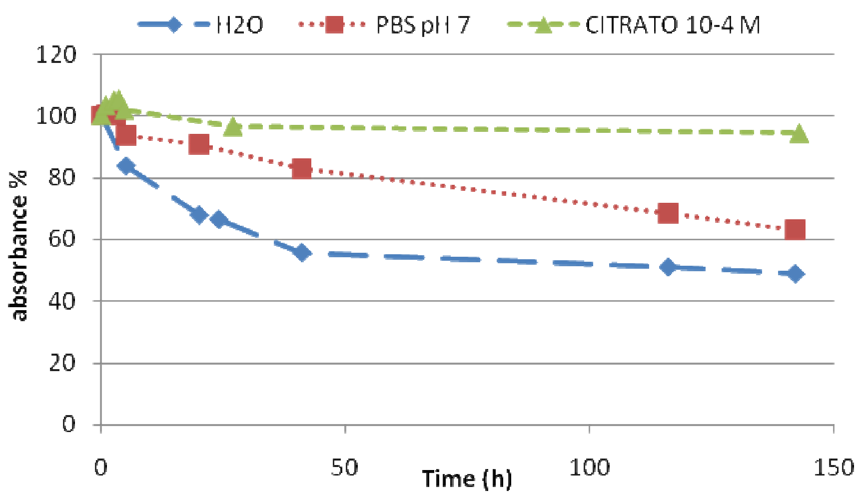


[Ag] = 4.84 μg/cm^2 (Neutron Activation Analysis)

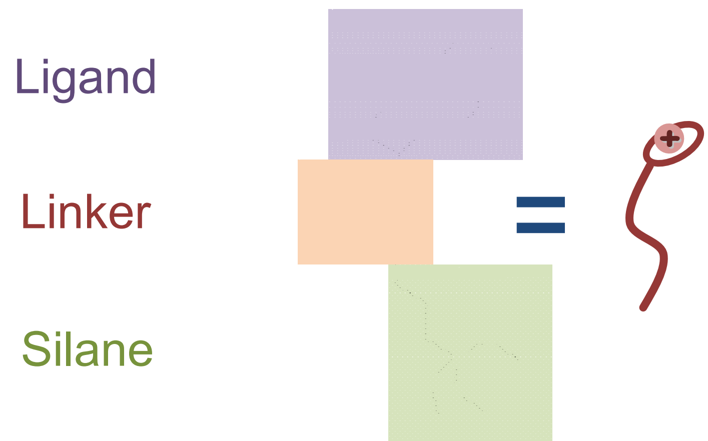
SAM is stable in air, water, PBS

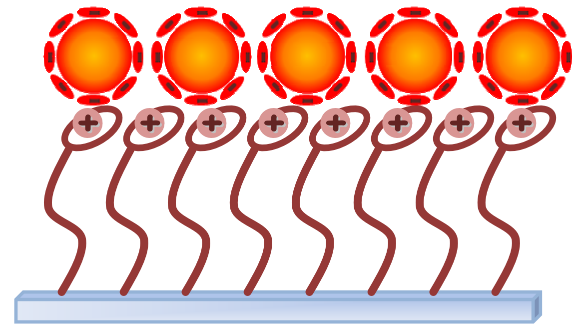
Ag release in water (ICP) ≈ 1.1 %

Time evolution of SPR peak intensity



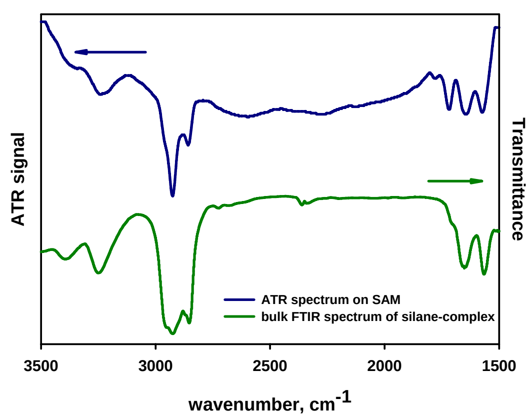
Anchoring of metal ion complexes



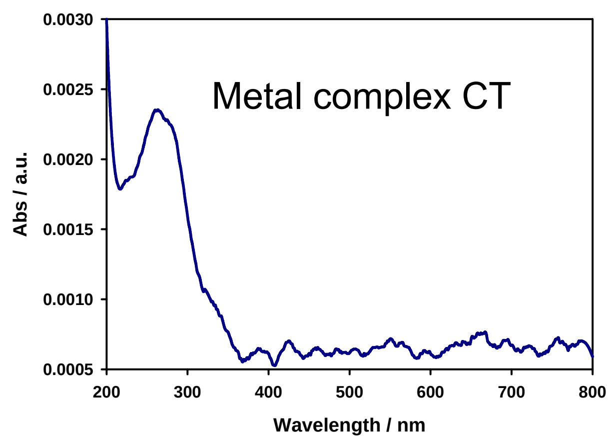


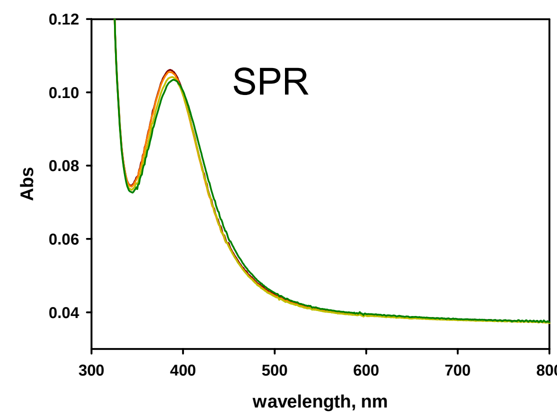
NP bound through weak (non covalent) interactions

FTIR-ATR



UV-Visible spectroscopy

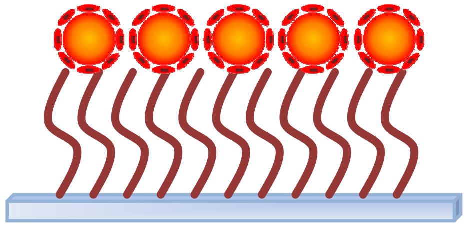




Antibacterial activity

Microbicidal Effect
$ME = \log N_C - \log N_E$

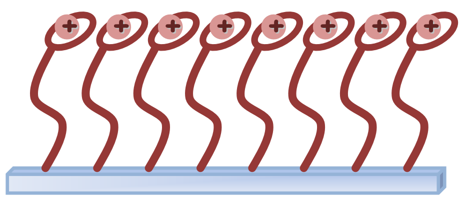
Ag NP on –SH SAM



Strands	ME	
	5 h	24 h
Staphylococcus aureus (Gram+)	**1.22**	**5**
Escherichia Coli (Gram-)	**3.24**	**4.12**

+

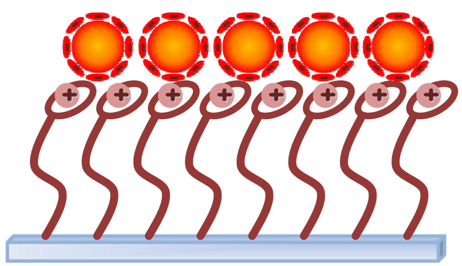
Cu complex SAM



Strands	ME	
	5 h	24 h
Staphylococcus aureus (Gram+)	**0.88**	**1.71**
Escherichia Coli (Gram-)	**2.29**	**2.5**

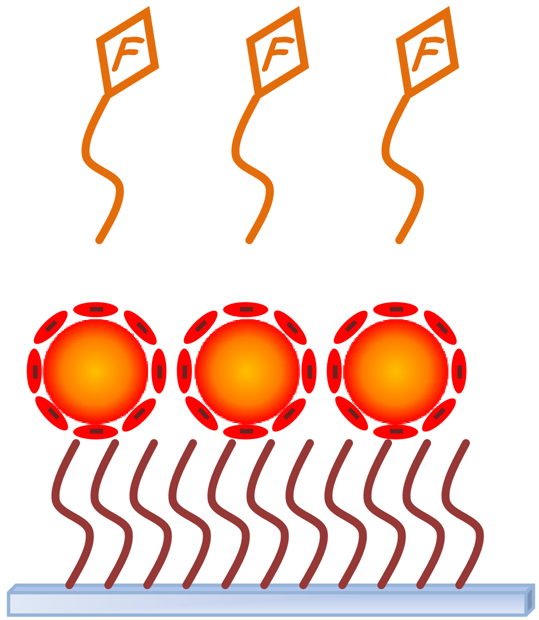
=

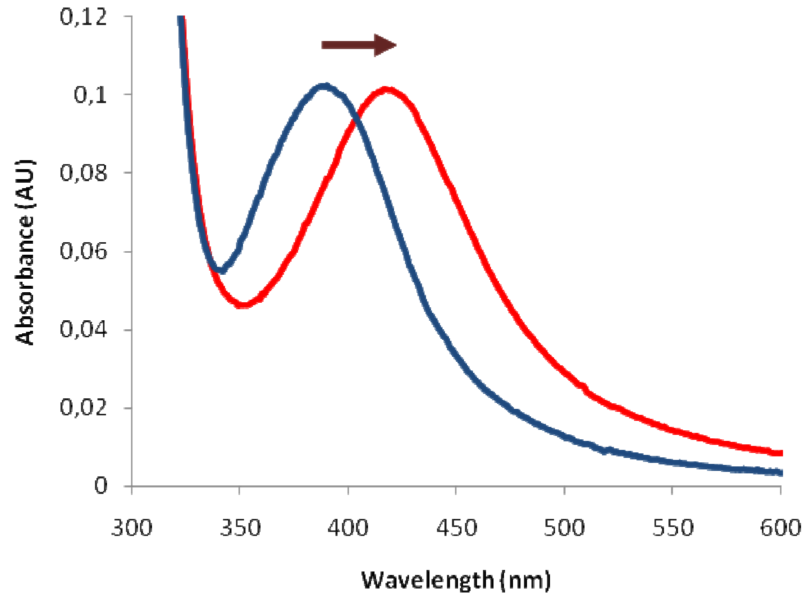
Cu complex SAM with Ag NP overlayer

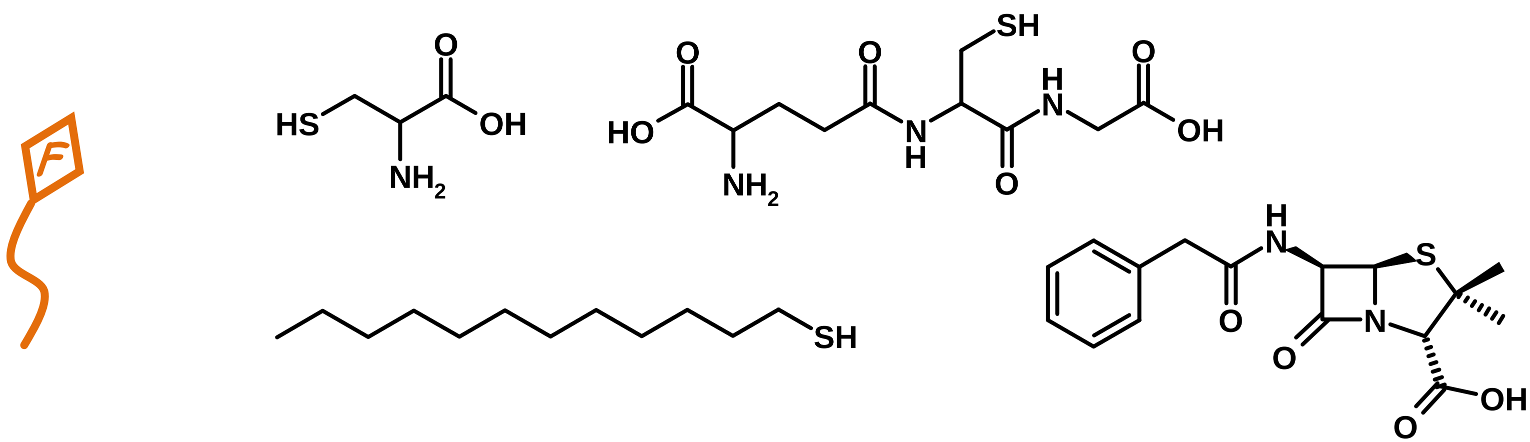


Strands	ME	
	5 h	24 h
Staphylococcus aureus (Gram+)	**2.33**	**6.60**
Escherichia Coli (Gram-)	**5.29**	**7.06**

A “tertiary” monolayer







Photonic biosensors

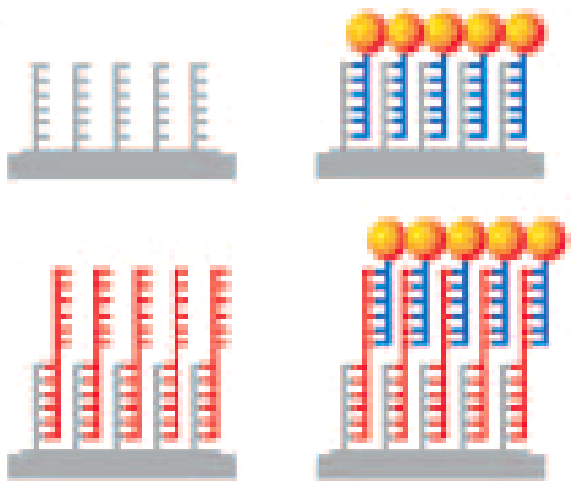
Nanofabrication Techniques to develop Sensitive Materials

photonic or plasmonic structures, porous substrates, nanoparticle deposits, light emitters

+

Spectroscopic Nano-optical Techniques

determine the optical response of the devices in presence of biomolecules



PB possess sensing ability due to the high specificity of the optical response of the environment

trough the ambient dielectric function

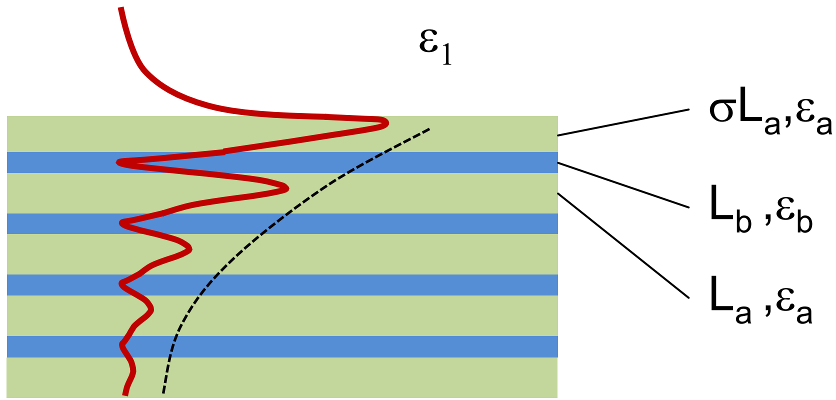
$\tilde{\varepsilon} = \tilde{n}^2 = (n + ik)^2$,

the absorption coefficient α

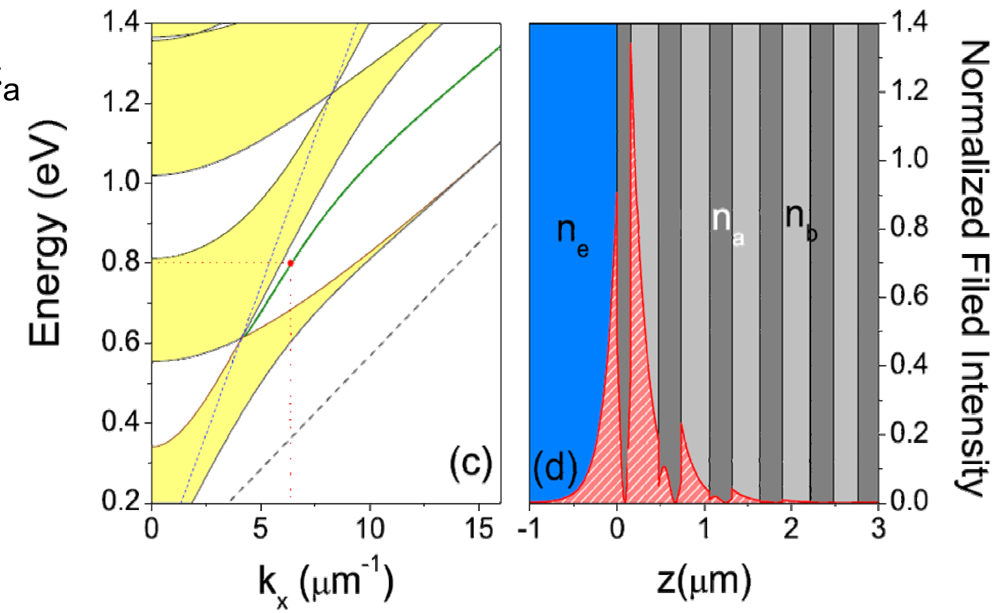
or absorption cross section σ

Bloch Surface Waves (BSW)

BSW can be considered as the dielectric analogues of SP



a-SiN:H 1D PhC

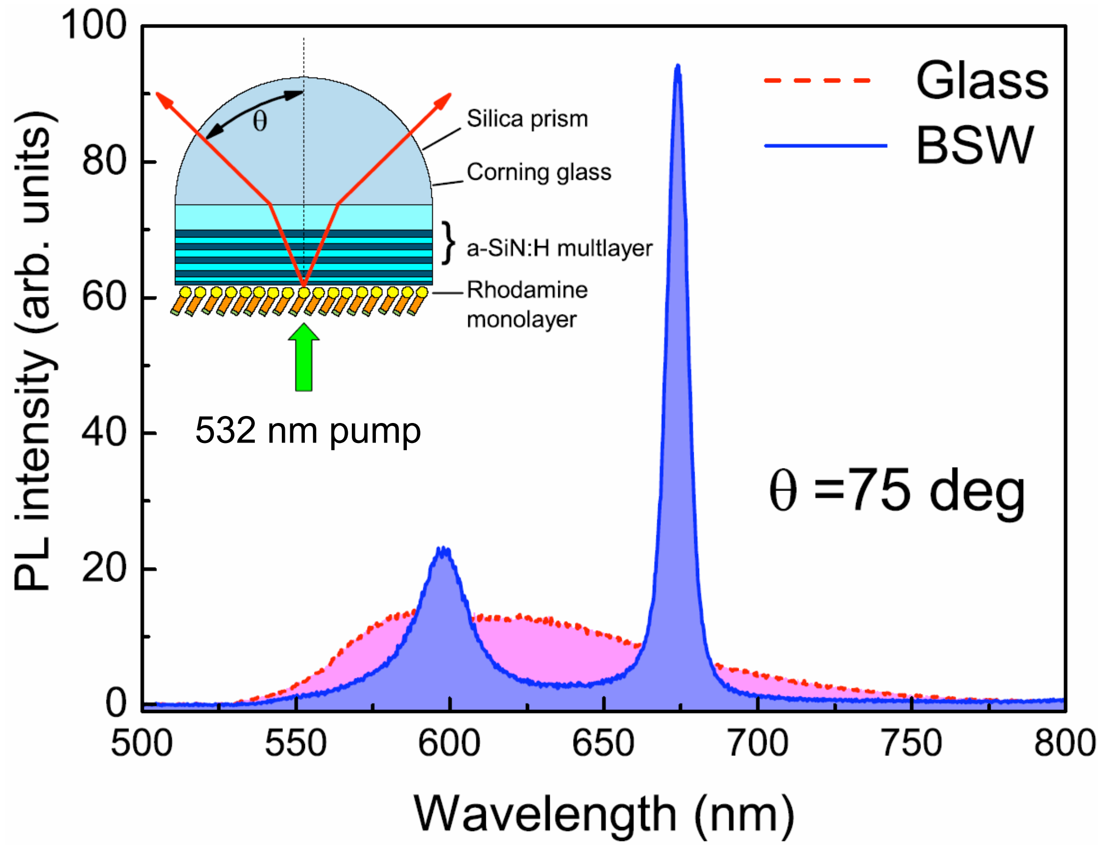


- Both TE and TM polarizations
- The mode can be excited through a propagating wave
- Dispersion can be tailored by changing layer thicknesses
- In principle they can be free from losses

M. Liscidini and J. E.Sipe, *JOSA b*, **2009**, 26, 279

Enhancement of emission by BSW

A rhodamine monolayer is covalently attached to the surface of the multilayer. A strong modification of Rhodamine emission spectrum is observed, due to the excitation of BSW



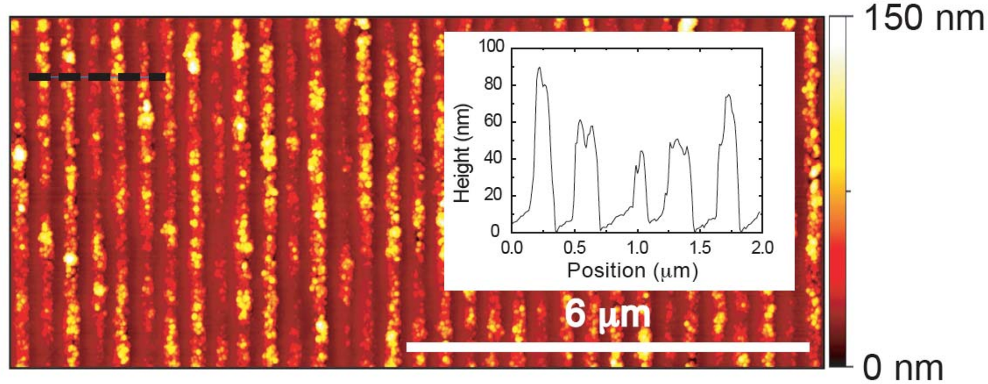
M. Liscidini et al., *APL*, **2009**, 94, 043117 M. Liscidini et al., *Optics Letters*, **2009**, 34(15), 2318

Towards the nanoscale chemical mapping

Microscale

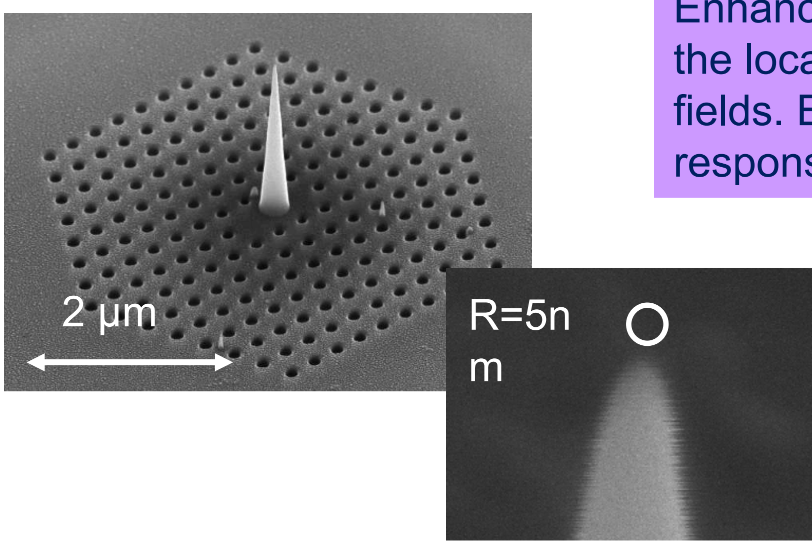
Delivery of energy to nanoscale:

adiabatic conversion of propagating EM wave to local fields



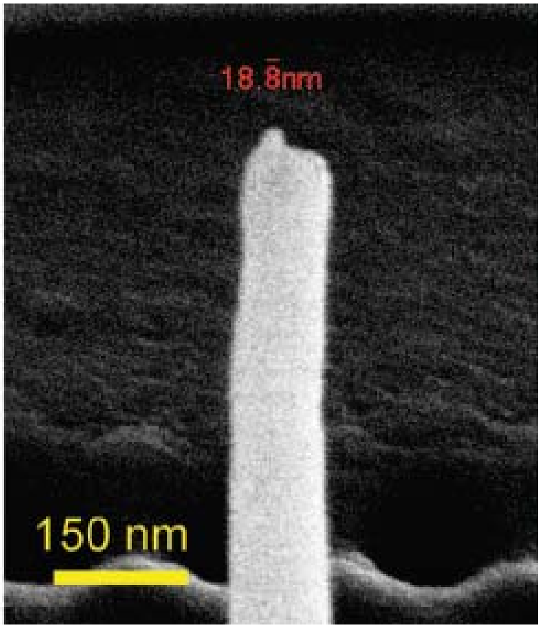
AFM topography at nanoscale resolution

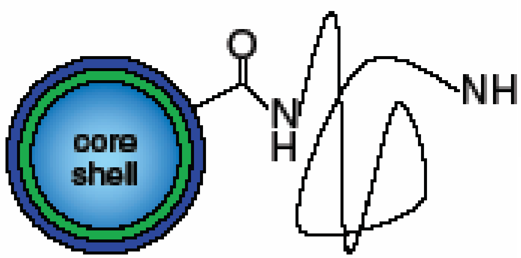
Enhancement and control of the local nanoscale e.m. fields. Enhanced near-field responses



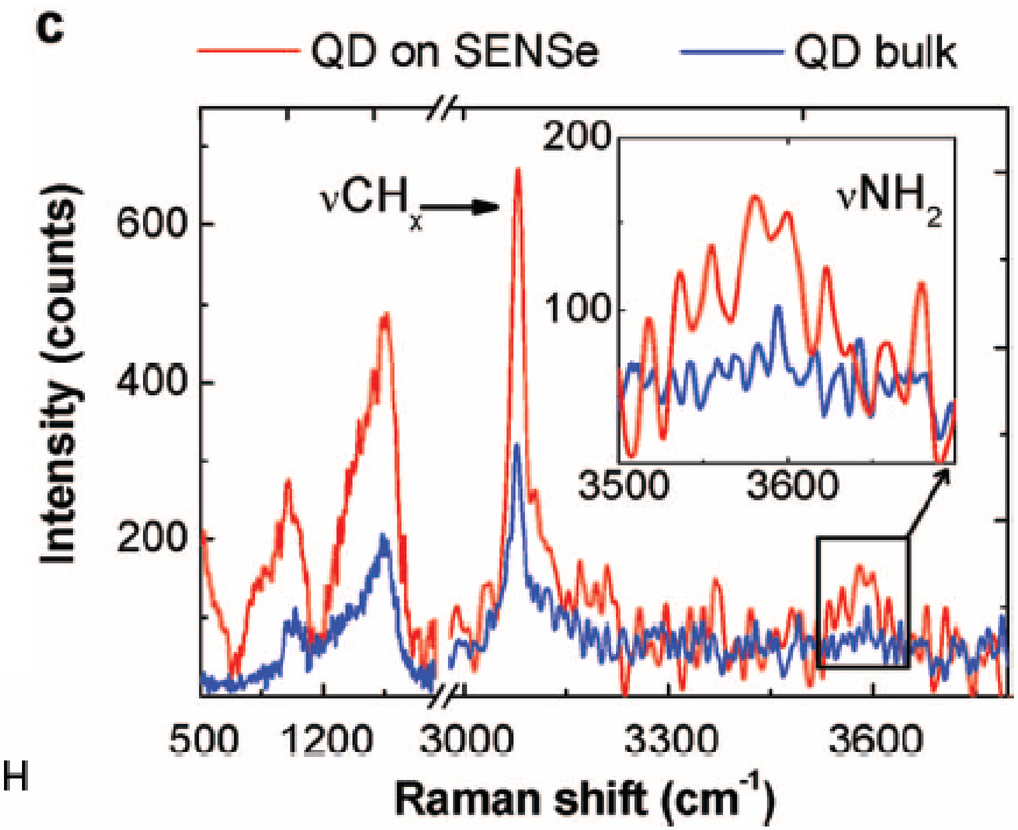
Far field optical collection - if possible

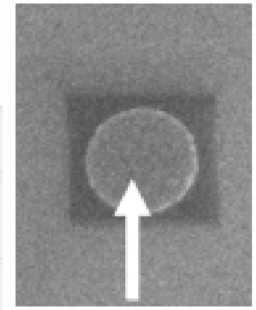
A single QD Raman spectrum - Few molecules sensitivity





Qdot® ITK™
amino (PEG) quantum dot

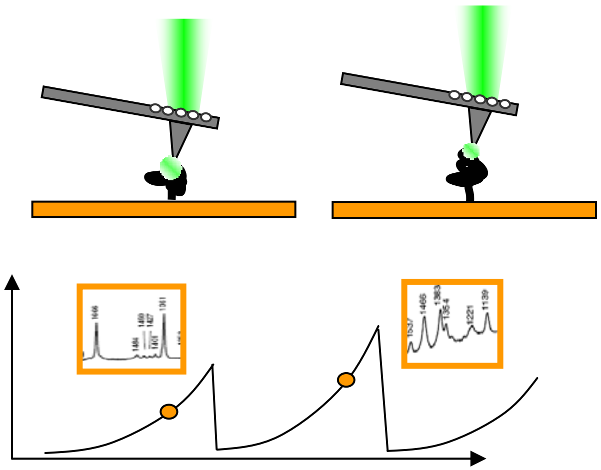




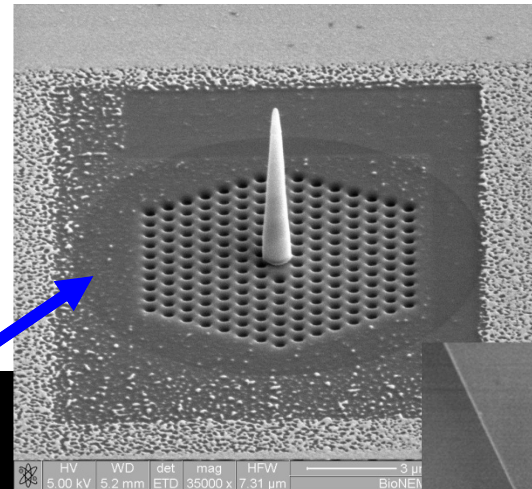
Amine peak ➔ estimated 10 NH_2 groups
(from company linkage data)
Maximum 80 NH_2 groups, SERS enh. 10^5

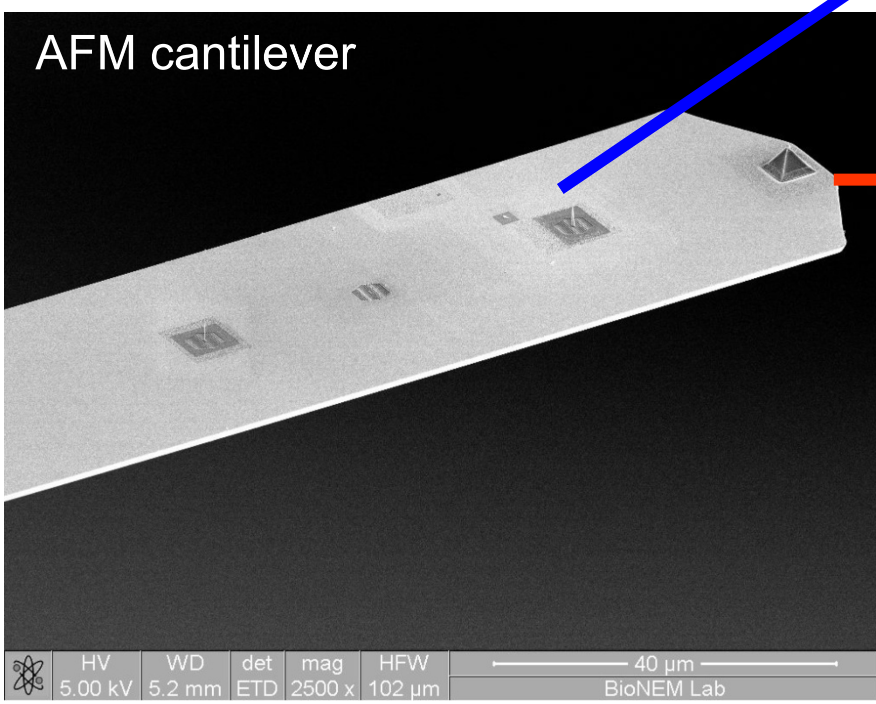
F. De Angelis et al. , *Nano Letters,* **2008**, 8, 2321

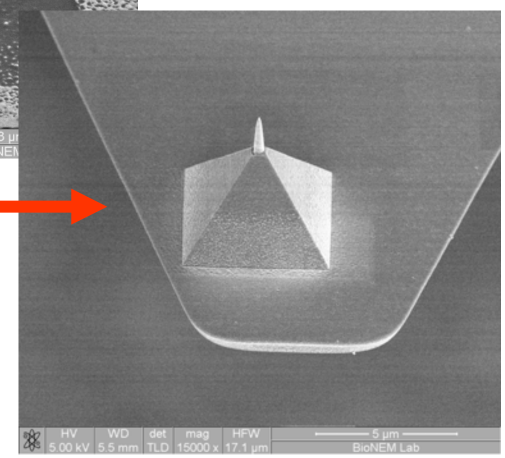
SENSe overall device



Nanometric resolution on real samples
AFM topography+ Raman Scattering signals







The **dual beam** @ BIONEM lab

FIB milling + e-beam induced deposition

Conclusions and perspectives

Goals

✓ "Smart", customizable, functional self-assembled materials
✓ High sensitivity optical biosensors
✓ Probes for nanoscale analysis and single-molecule detection

Starting point

Solution and surface chemistry
Optics and photonics

Perspective

Material science can provide powerful tools to bring medicine (diagnostics, drug delivery, targeting) to the molecular level

Thanks to

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