Hot spots and confinement in metal nanoparticles and assemblies

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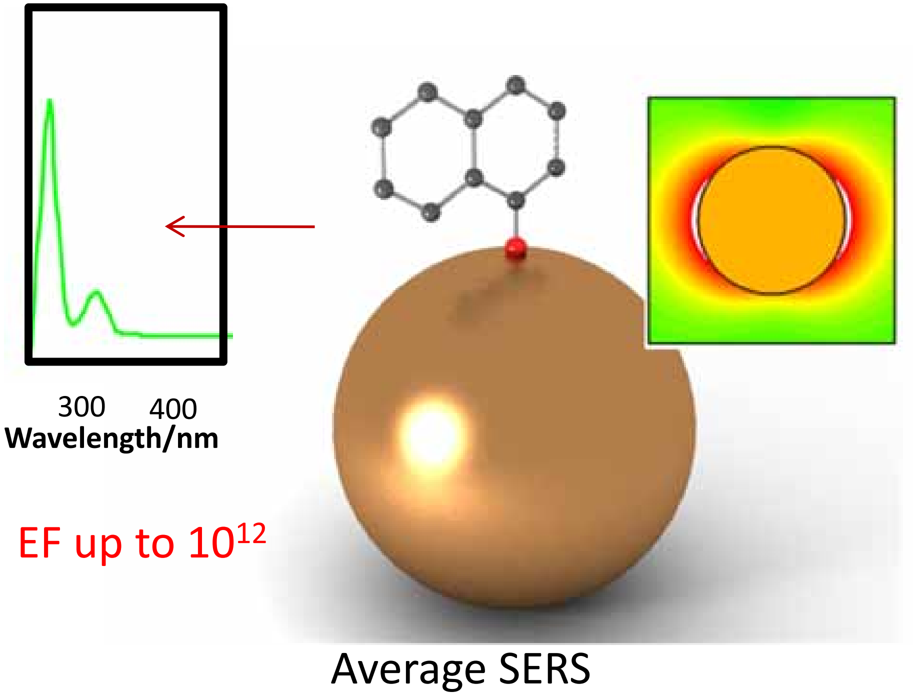
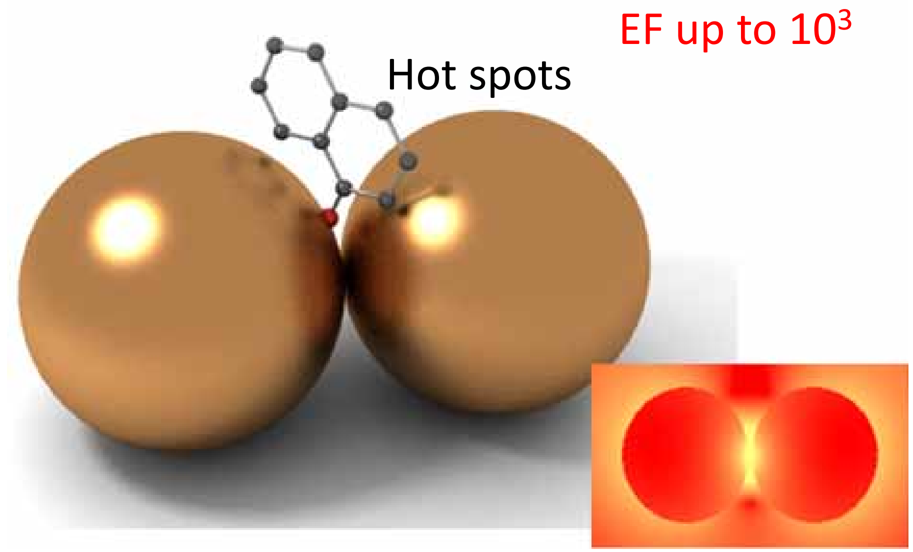
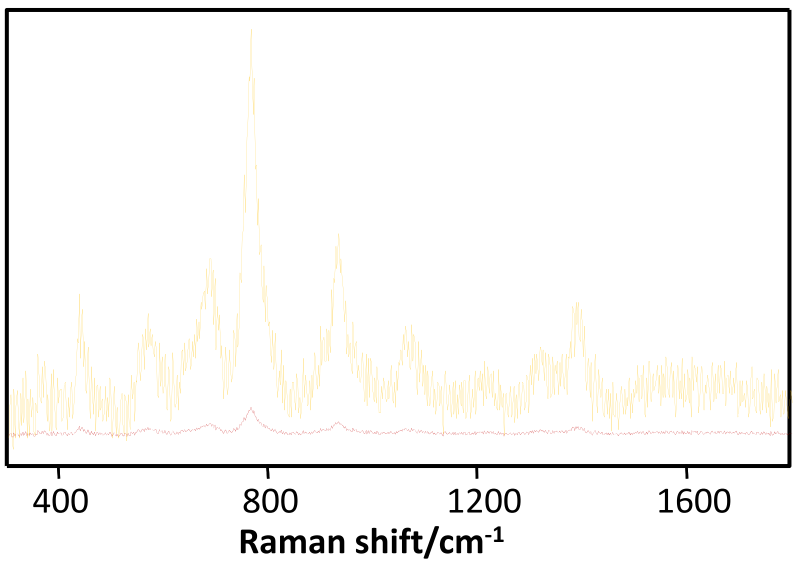
http://webs.uvigo.es/coloides/nano/

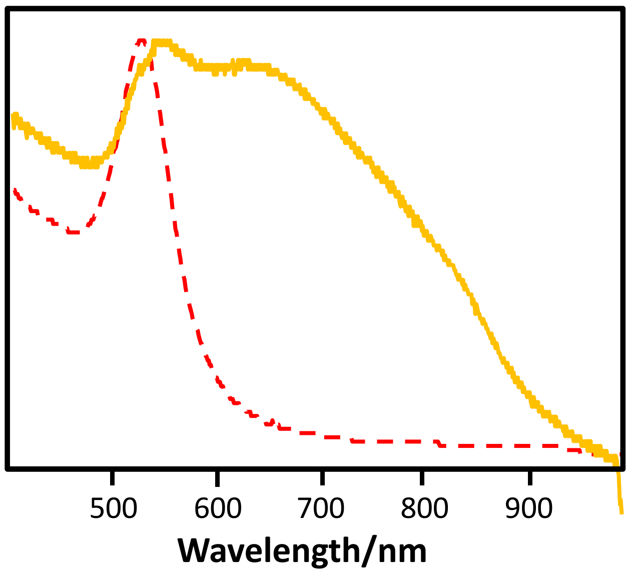
Surface Enhanced Raman Scattering

see: *Chem. Soc. Rev.* **2008**, *SERS issue*
Small **2010**, *6*, 604

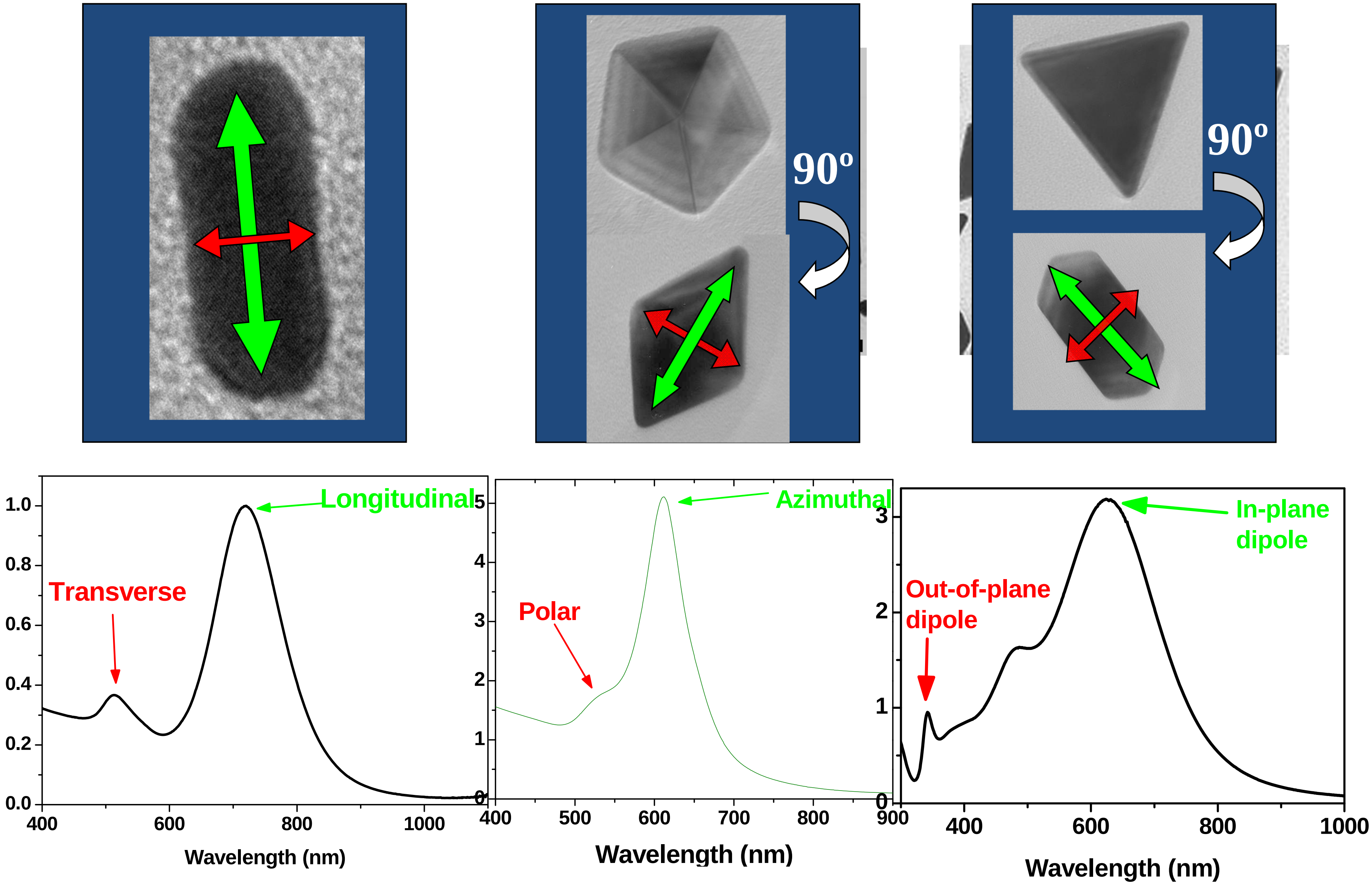








Plasmon modes in anisotropic nanoparticles



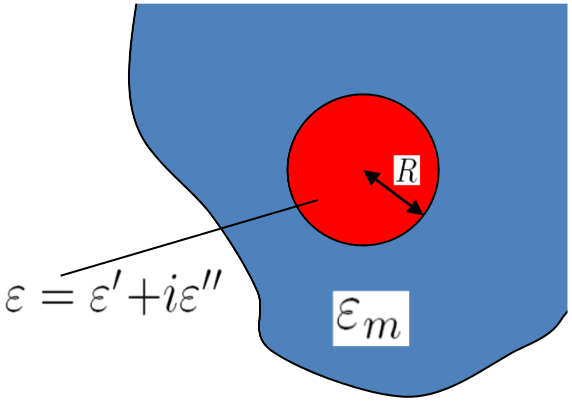
Optical Modelling – Theoretical Background

-Analytical method - Mie Theory

$$\boxed{C_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon''}{(\varepsilon' + 2\varepsilon_m) + \varepsilon''^2}}$$

$$\boxed{\varepsilon' = -2\varepsilon_m}$$

Spheres,
Spheroids,
Infinite cylinders



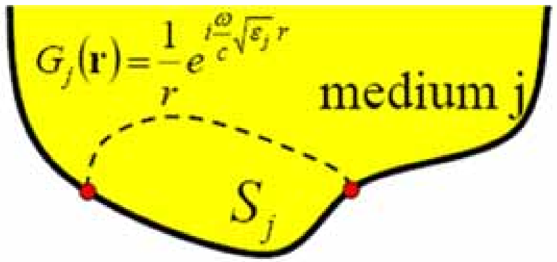
-Numerical methods:
Discrete **D**ipole **A**pproximation (DDA)
T-matrix
Finite **D**ifferences in the **T**ime **D**omain (FDTD)

Boundary **E**lement **M**ethod (BEM)

The boundary conditions lead to a set of surface integral equations with the interface currents $\mathbf{h}_j$ and charges σ_j as variables. For example, the continuity of ϕ leads to

$$\int_{S_j} ds' \left[G_1(\mathbf{s}-\mathbf{s}')\sigma_1(\mathbf{s}') - G_2(\mathbf{s}-\mathbf{s}')\sigma_2(\mathbf{s}')\right] = \phi_2^{ext}(\mathbf{s}) - \phi_1^{ext}(\mathbf{s}),$$

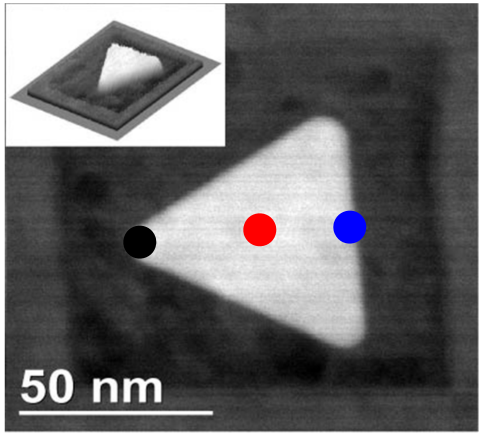
(1 and 2 refer to the interface sides). The surface integrals are now discretized using N representative points $\mathbf{s}_i$. This leads to a system of $8N$ linear equations with $\mathbf{h}_1(\mathbf{s}_i)$, $\mathbf{h}_2(\mathbf{s}_i)$, $\sigma_1(\mathbf{s}_i)$, and $\sigma_2(\mathbf{s}_i)$ as unknowns.

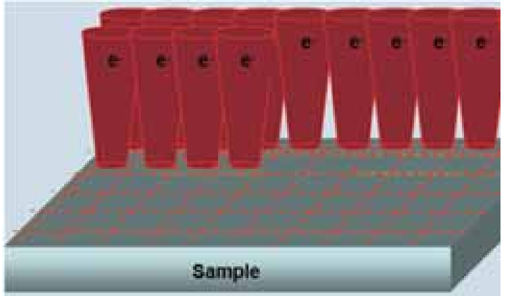


G.Mie, *Annalen der Physik*; **1908**, 25, 377
F. J. García de Abajo, A. Howie, *Phys. Rev. Lett.* **1998**, *80*, 5180
Chem. Soc. Rev. **2008**, *37*, 1792

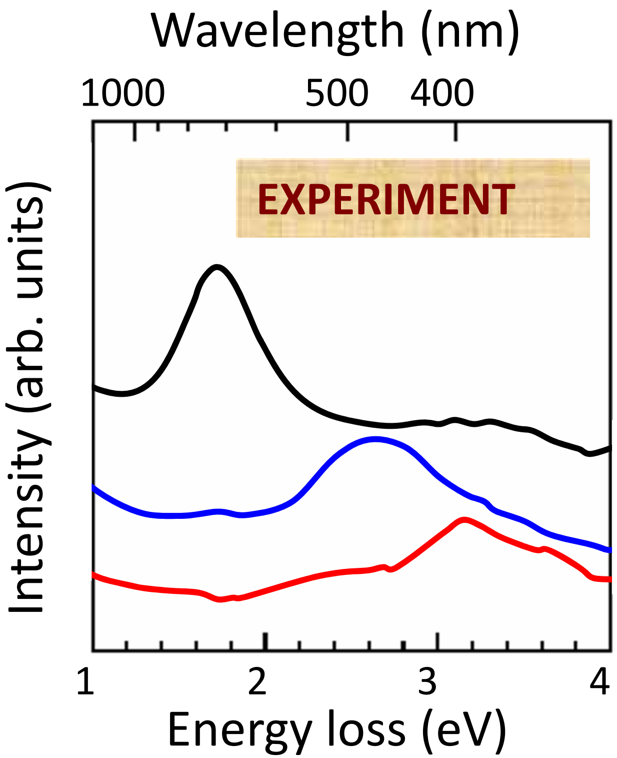
Plasmon modes in nanoprisms resolved by EELS

Ag nanotriangle on mica



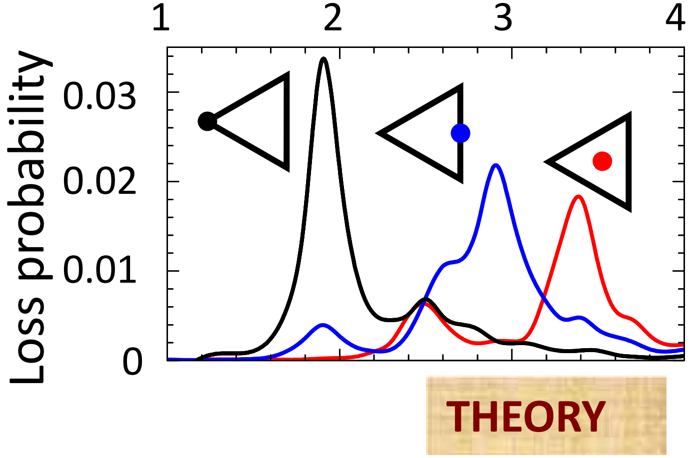


C. Colliex, CNRS Orsay



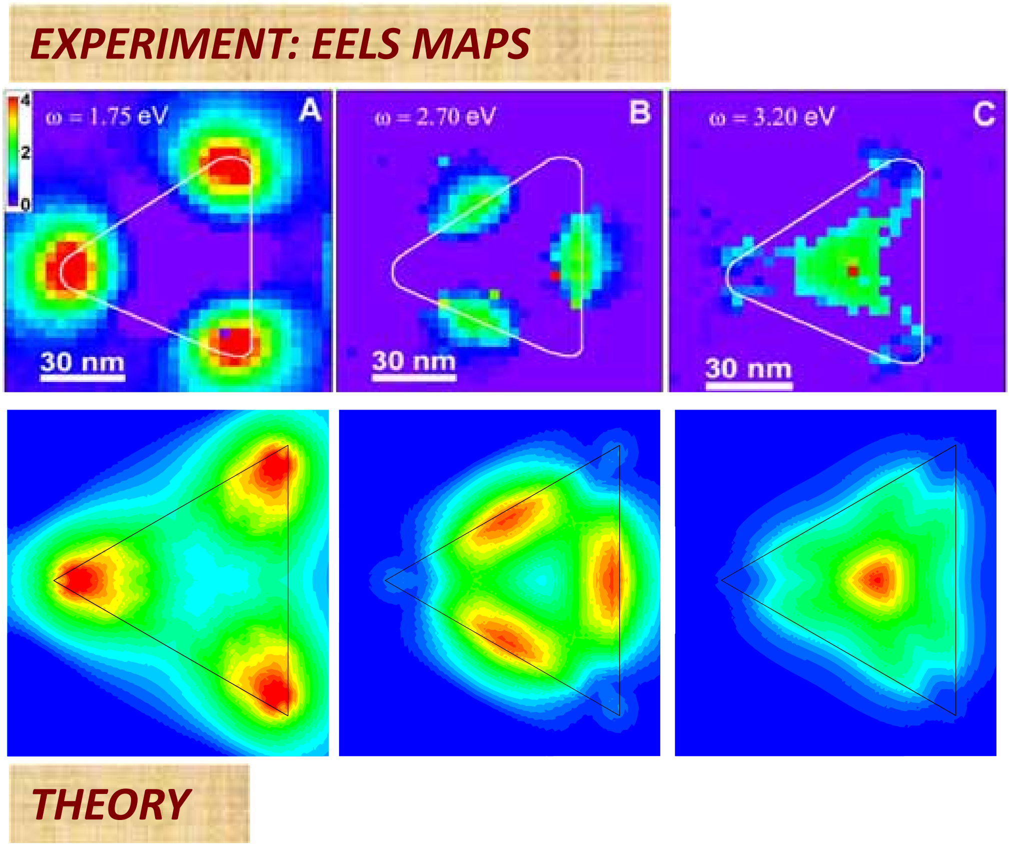
Electron energy: 100 keV
Beam size: 1 nm
Energy resolution: 0.3 eV

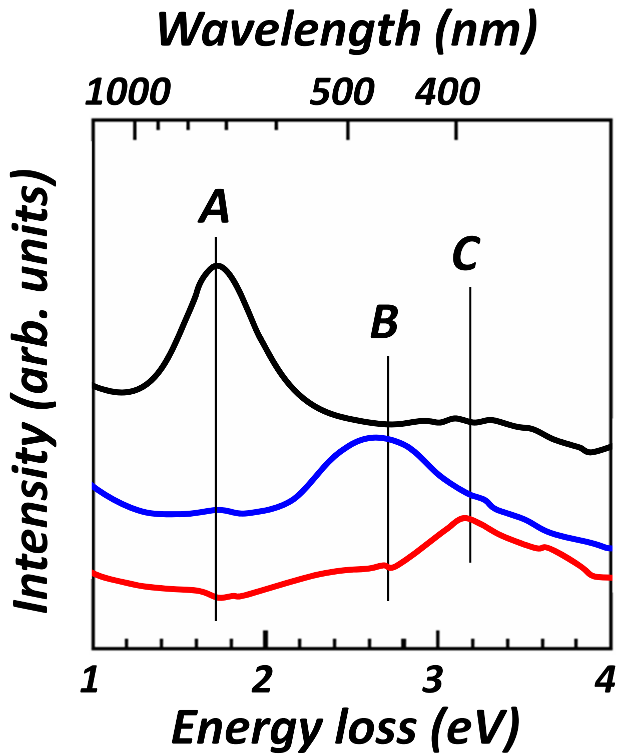
fraction of electrons that undergo an energy loss event per eV of energy loss range



Nature Phys. **2007**, *3*, 348 (col. C. Colliex)

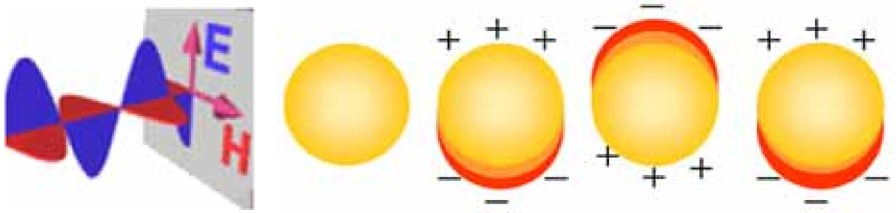
Plasmon modes in nanoprisms resolved by EELS

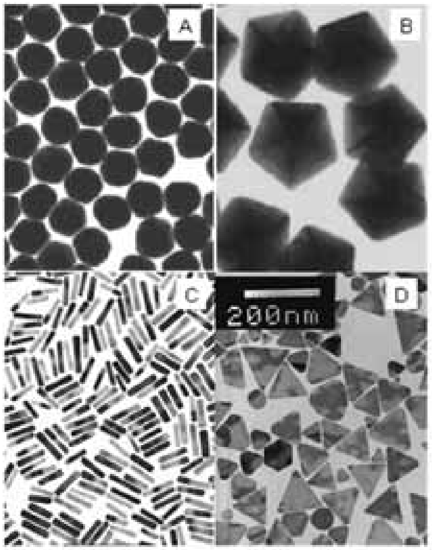


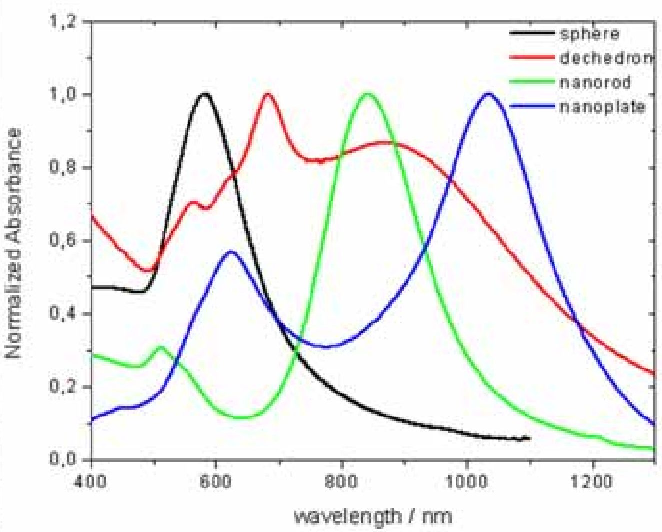


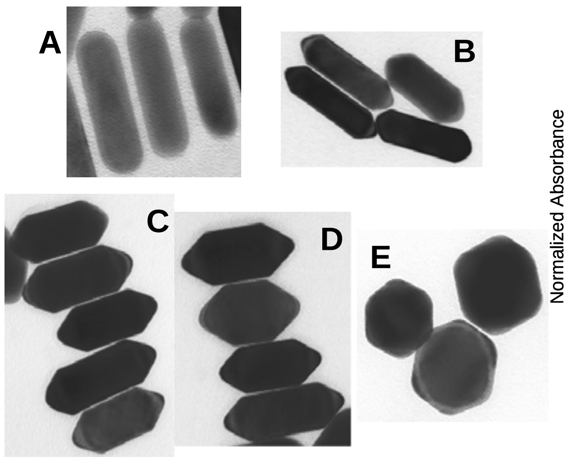
Nature Phys. **2007**, *3*, 348 (col. C. Colliex)

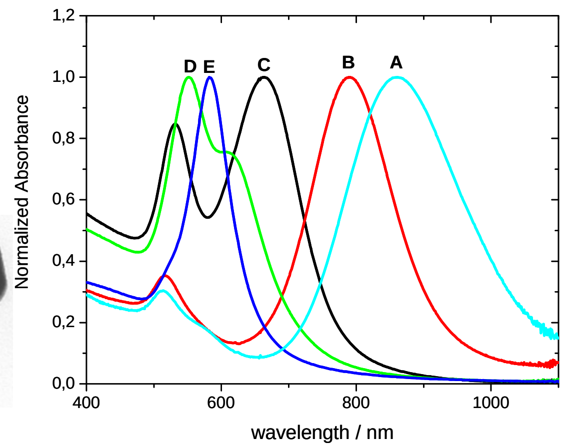
Localized SPRs in nanometals

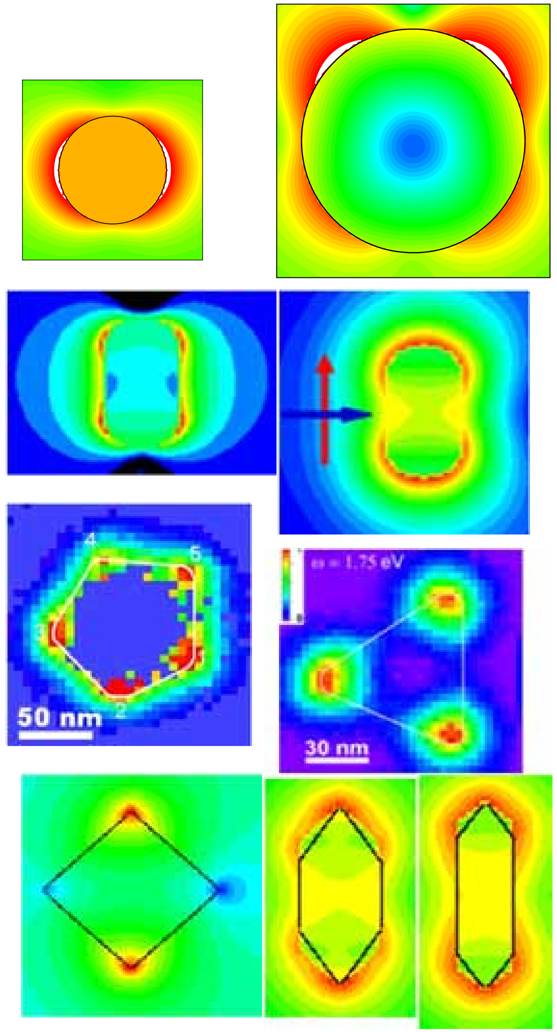










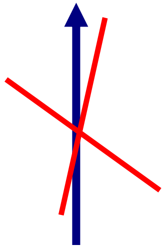


Coord. Chem. Rev. **2005**, *249*, 1870
Langmuir **2006**, *22*, 32
Adv. Mater. **2006**, *18*, 2529
Nature Phys. **2007**, *3*, 348
Angew.Chem.Int.Ed. **2007**, *46*, 8983
J. Mater. Chem. **2008**, *18*, 1724
Chem. Soc. Rev. **2008**, *37*, 1783
Chem. Soc. Rev. **2008**, *37*, 1792
Adv. Funct. Mater. **2009**, *19*, 679

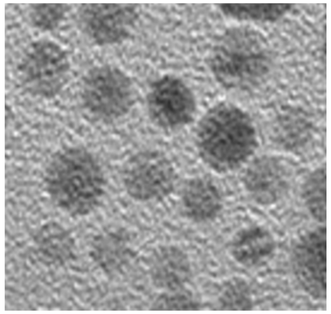
Seeded growth in DMF

Au^0

DMF



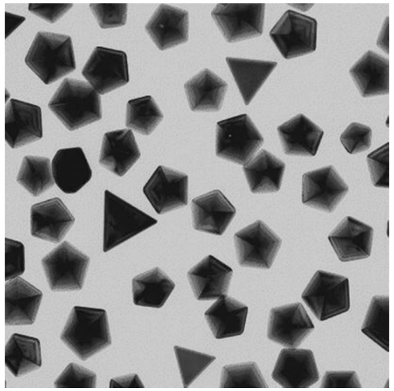
$AuCl_4^-$

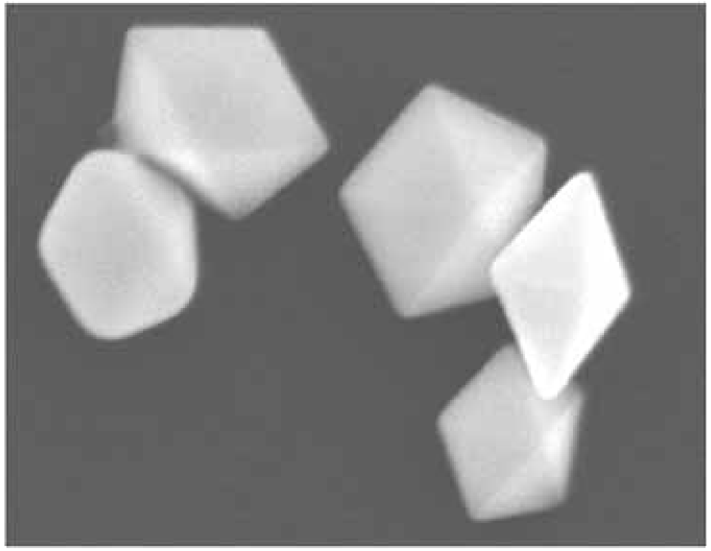


PTW seeds (2-3 nm)

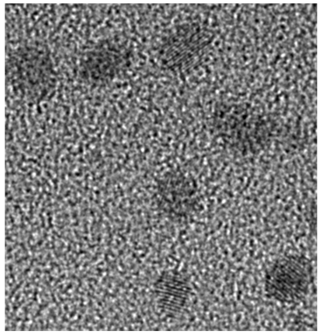
DMF, PVP

sonication

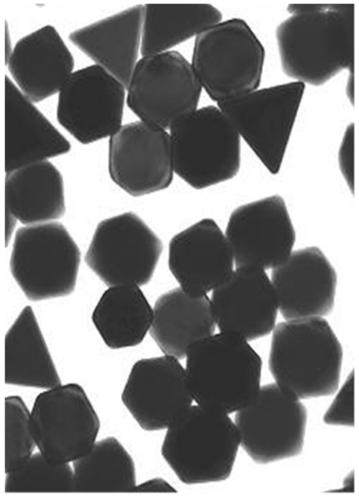


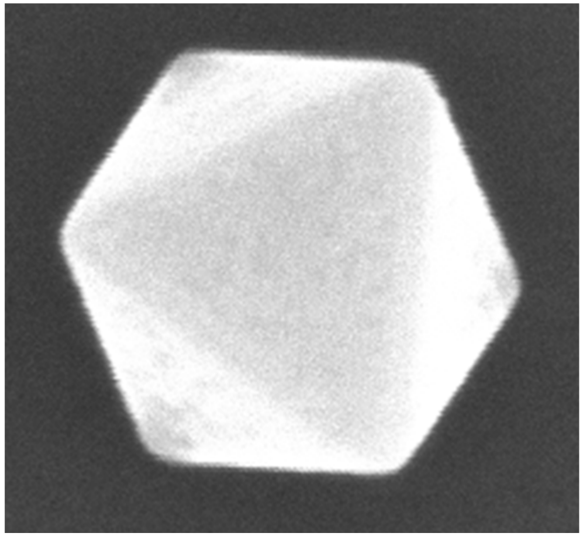


$AuCl_4^-$



SC seeds (2-3 nm)

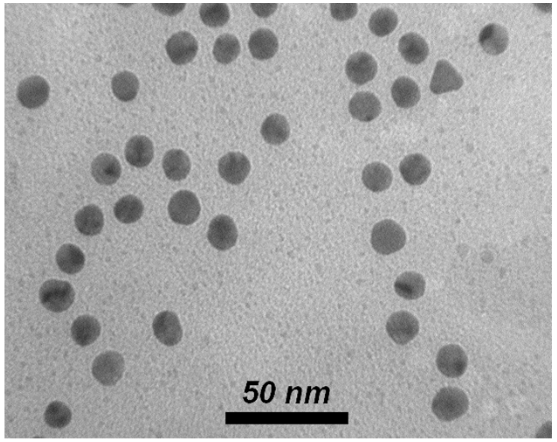




Adv. Funct. Mater. **2009**, *19*, 679

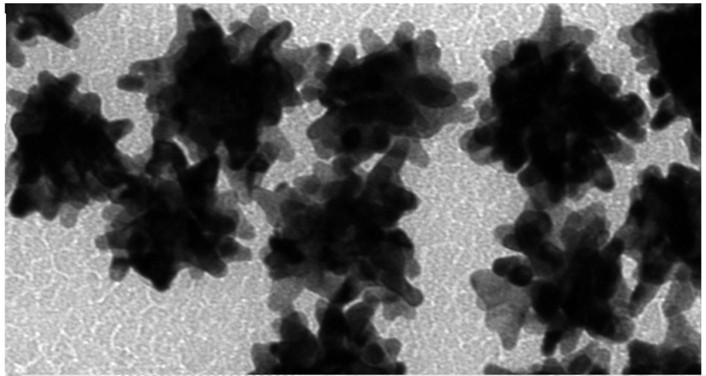
Sánchez-Iglesias et al., *Adv. Mater.* **2006**, *18*, 2529

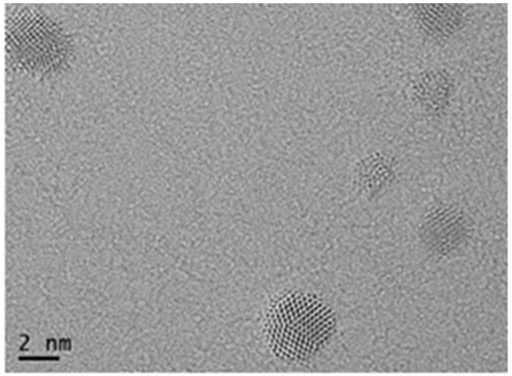
Au nanostars

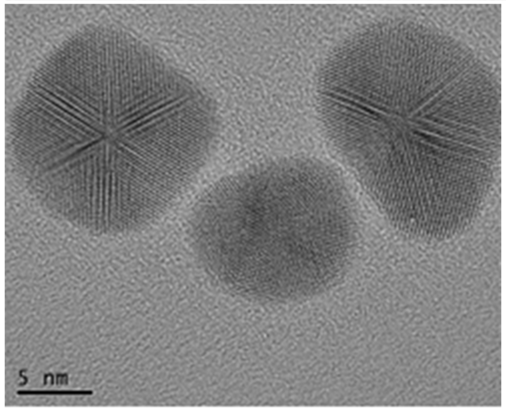


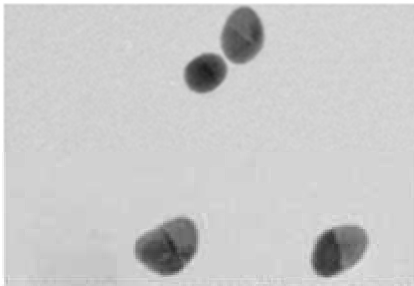
High [PVP] !!!

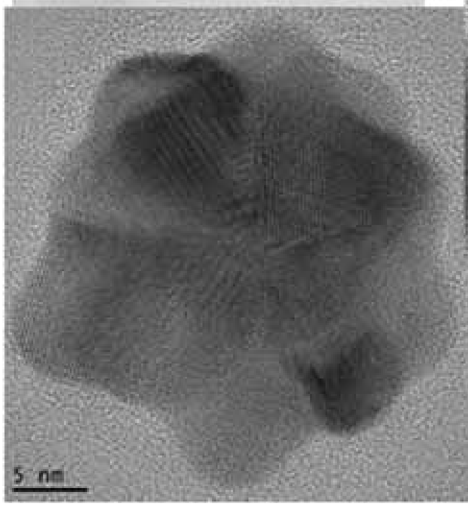
$$\xrightarrow[\text{DMF / PVP}]{HAuCl_4}$$

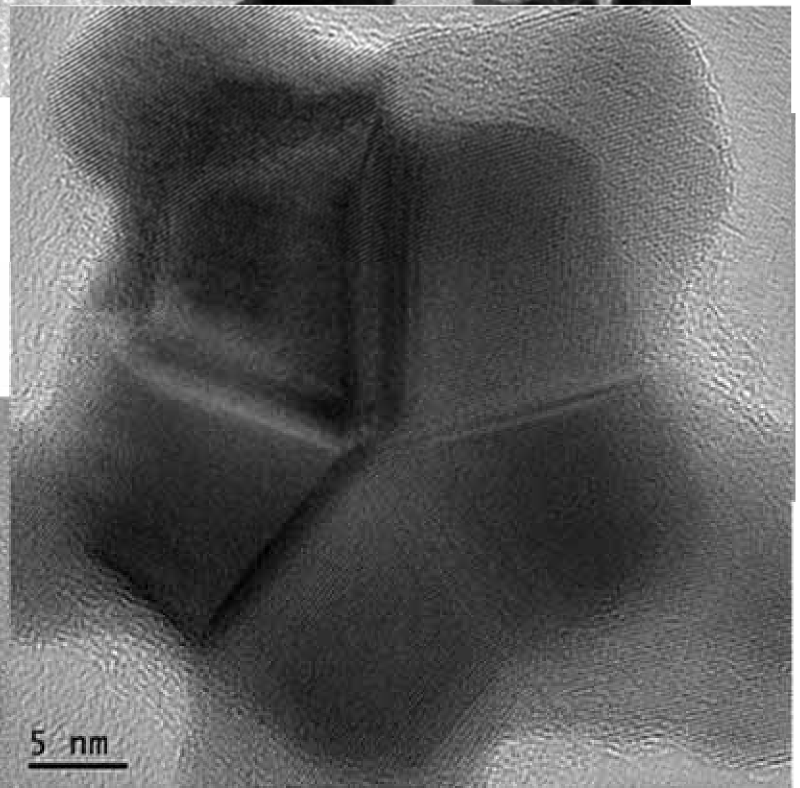






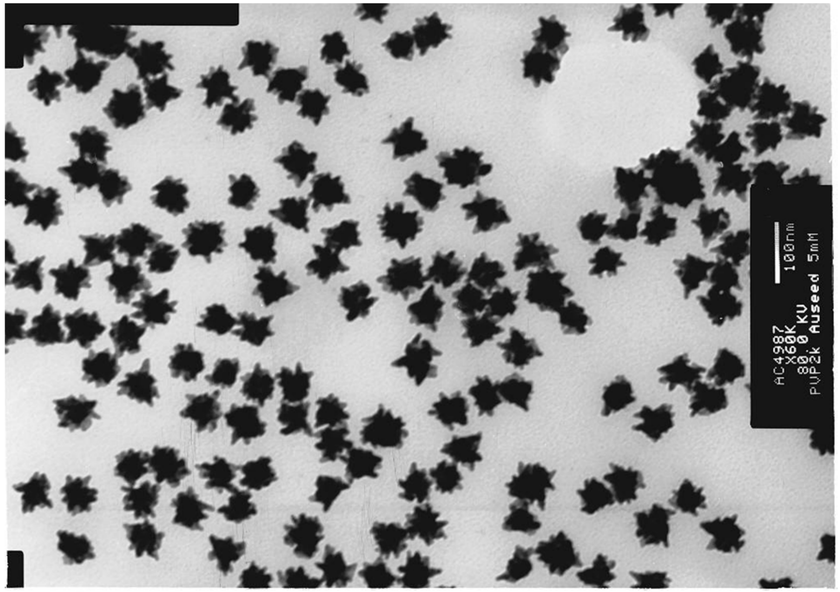


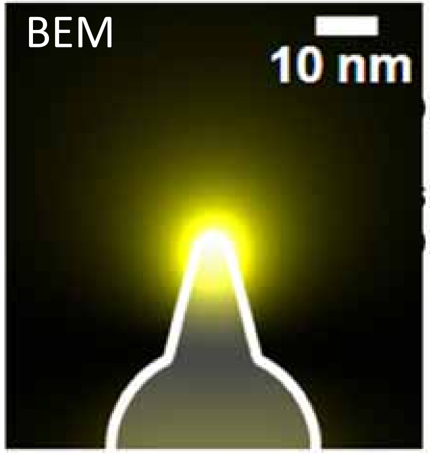


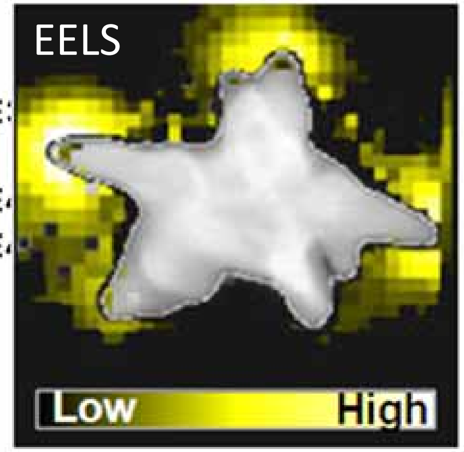


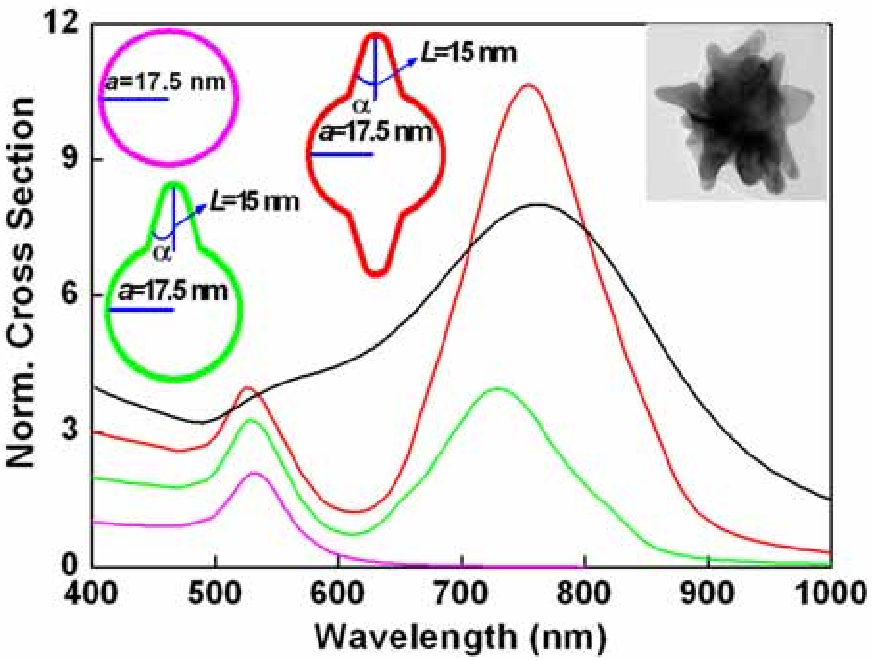
Kumar et al., Nanotechnology 2008, 19, 015606
Barbosa et al., *Langmuir* 2010, 26, 14943

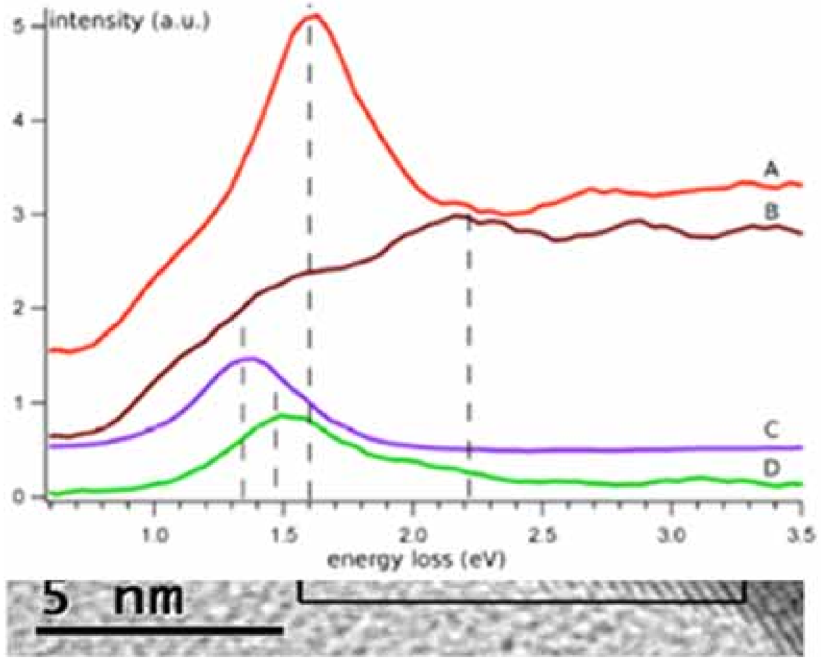
Au nanostars as SERS substrates







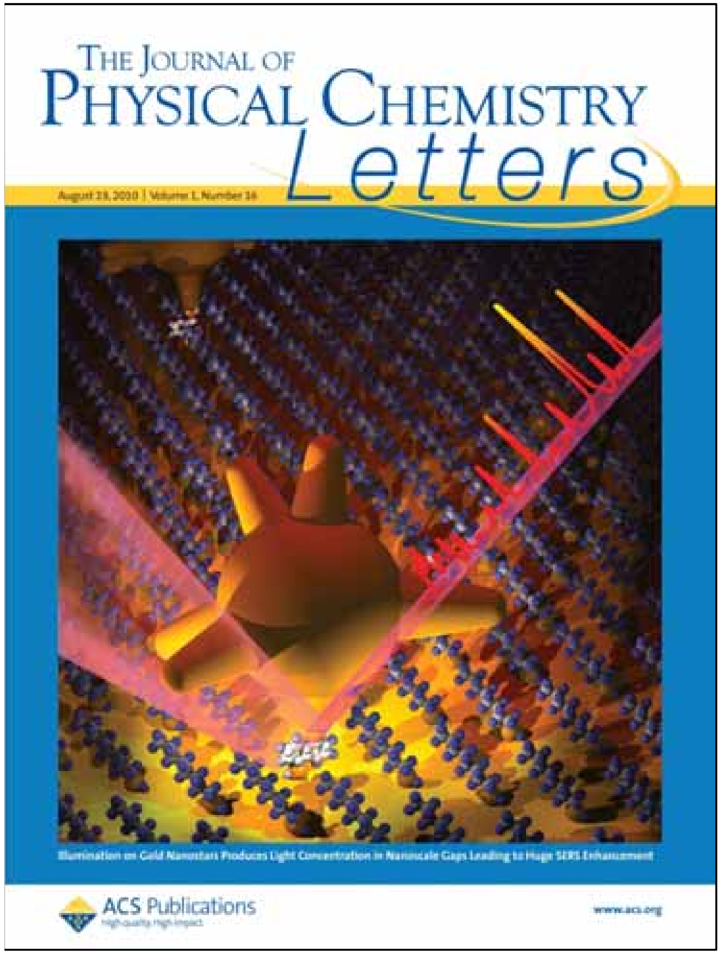




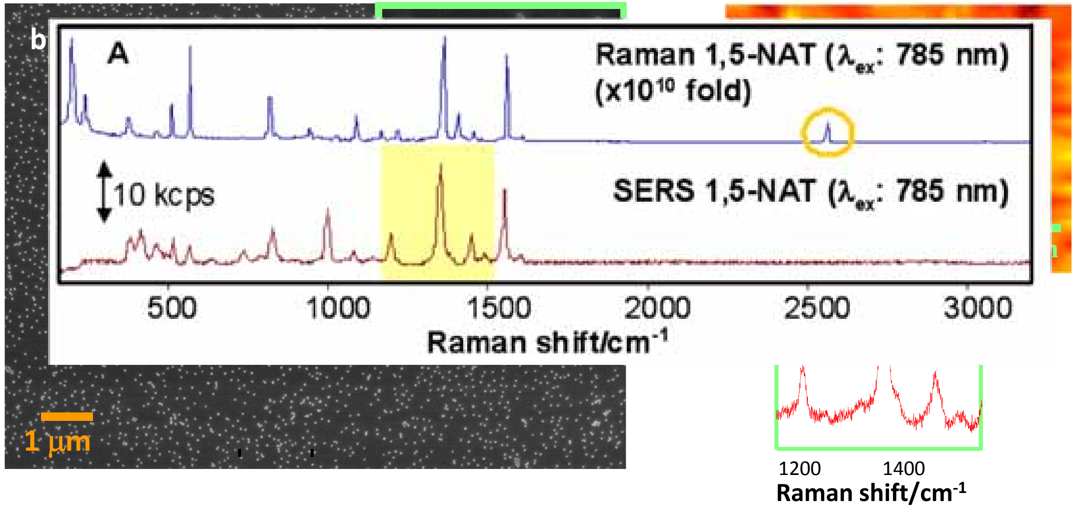
Nanotechnology **2008**, *19*, 015606

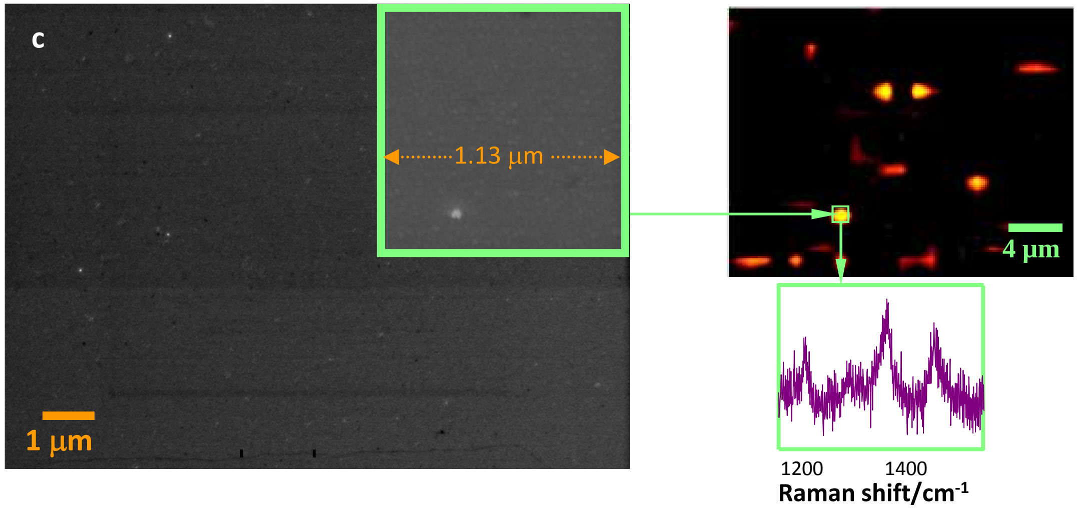
watch full perspective video at: http://www.youtube.com/user/AmerChemSoc

Single molecule detection using nanostars



$$EF = \frac{I_{SERS} / N_{surf}}{I_{Raman} / N_{vol}} \approx 10^{10}$$

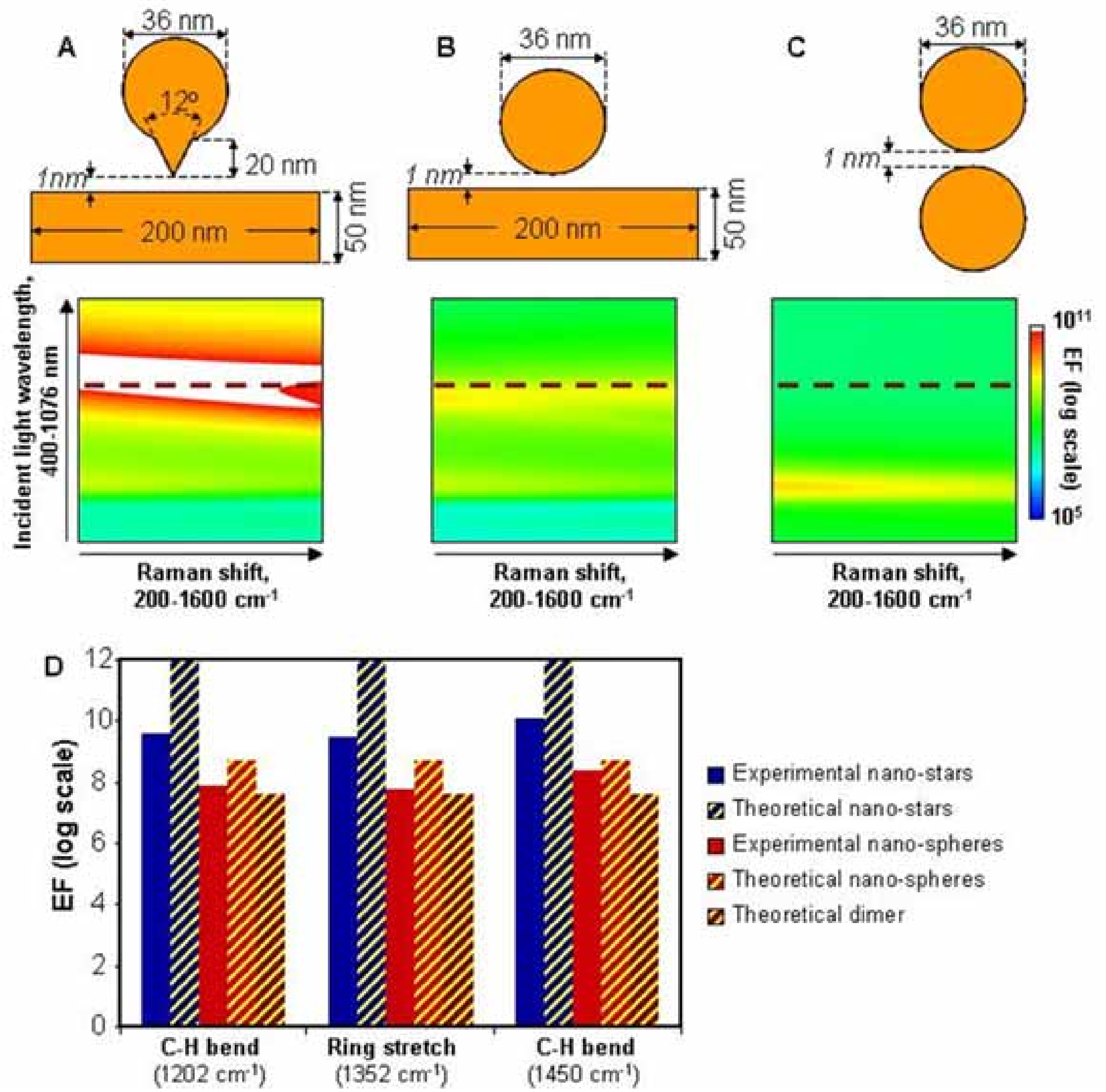




J. Phys. Chem. Lett. **2010**, *1*, 2428

J. Am. Chem. Soc. **2009**, *131*, 4616

The importance of using nanogaps



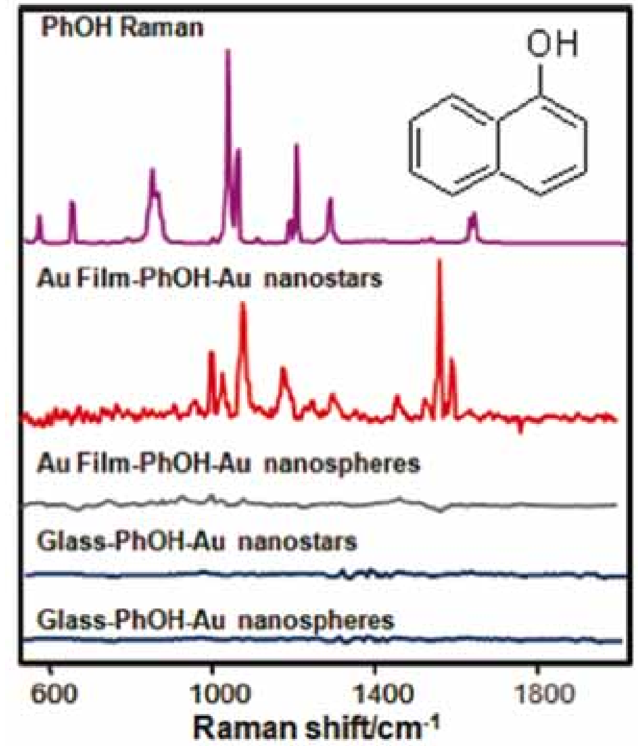
dip substrate in analyte

↓

drop casting AuNPs

↓

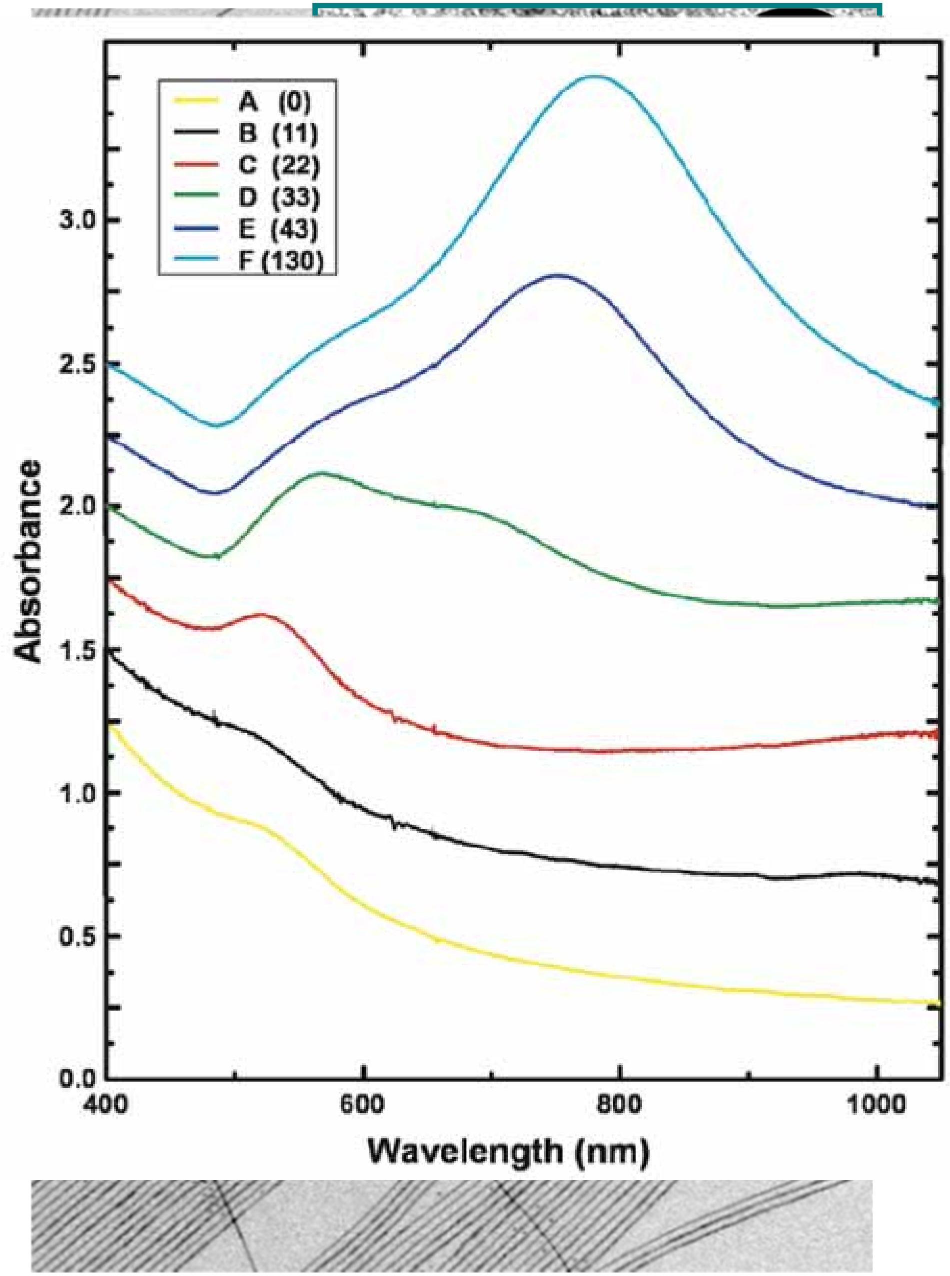
SERS analysis

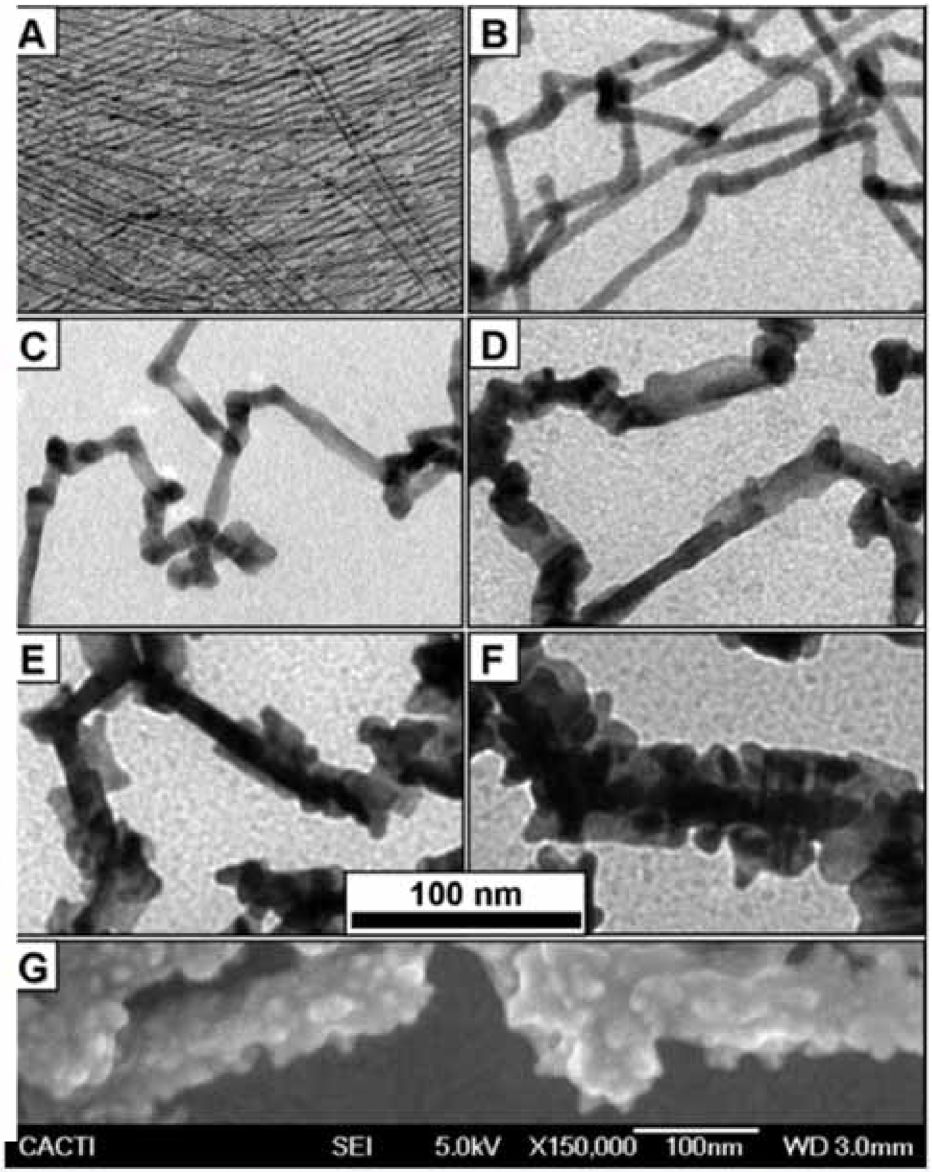


J. Am. Chem. Soc. **2009**, *131*, 4616

J. Phys. Chem. C **2010**, *114*, 7336

Tips also grow on nanowires…

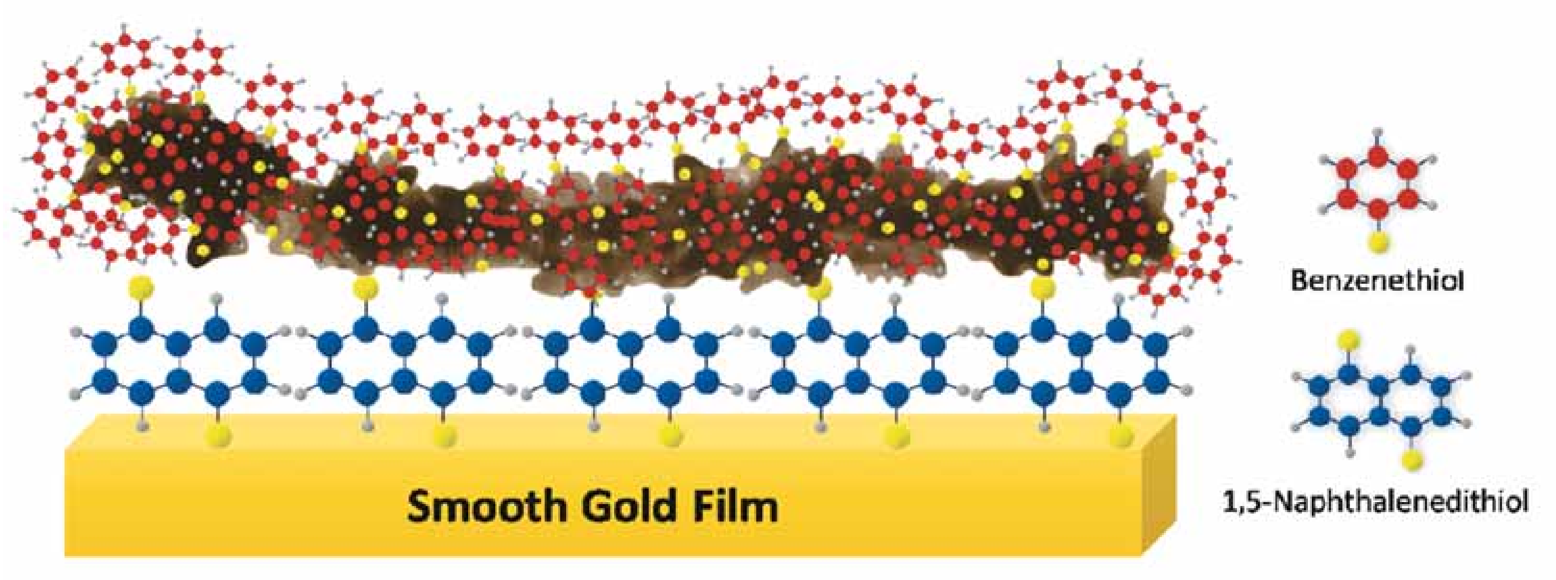


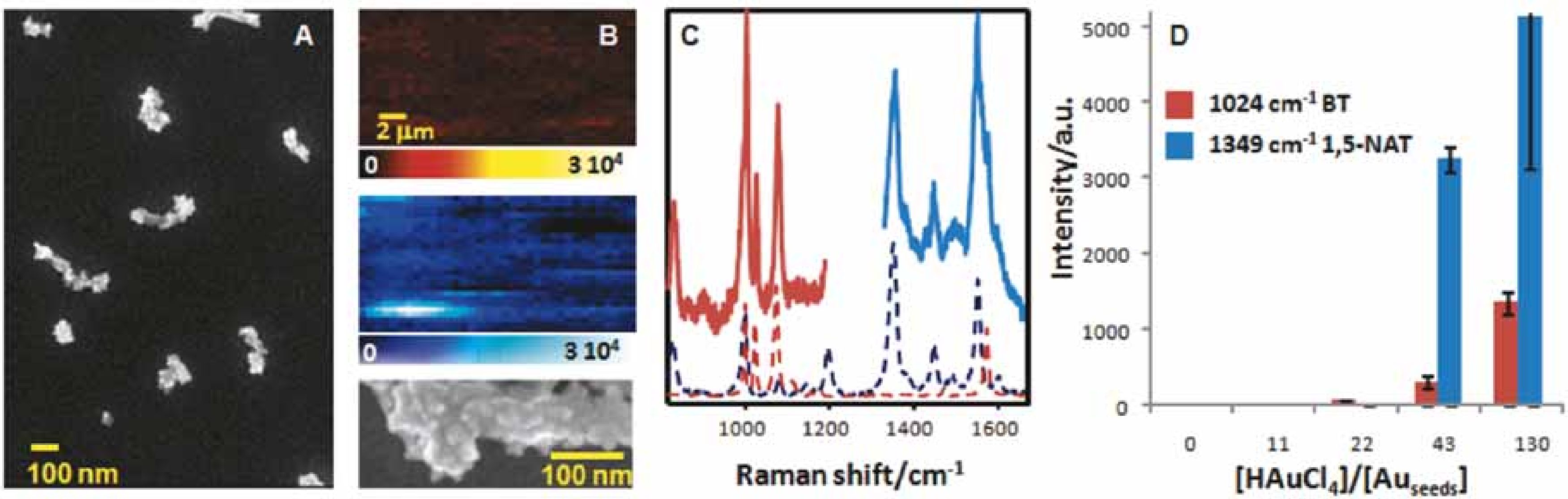


Pazos-Pérez et al. *Langmuir* **2008**, *24*, 9855

Pazos-Pérez et al. *J. Phys. Chem. Lett.* **2010**, *1*, 24

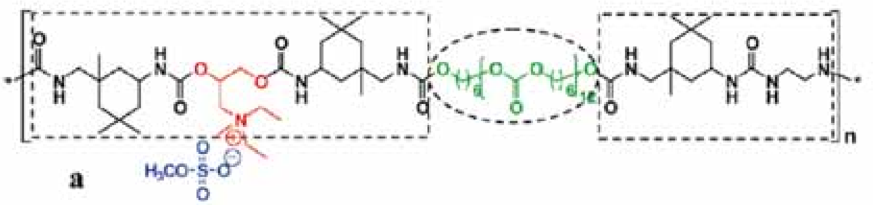
SERS enhancement at tips/gaps

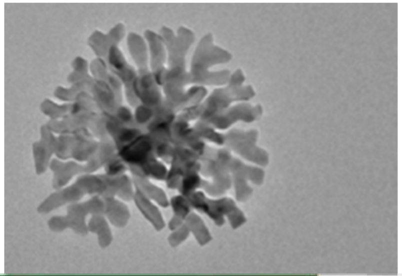


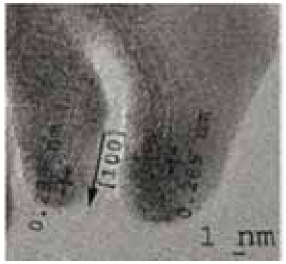


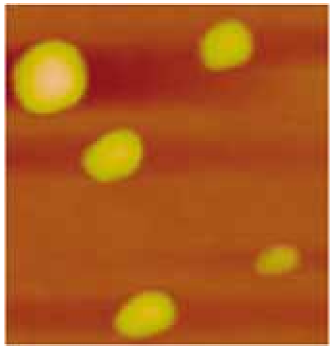
Pazos-Pérez et al. *J. Phys. Chem. Lett.* **2010**, *1*, 24

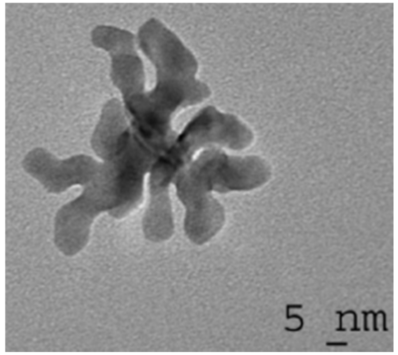
Intrinsic hot spots in Au nanolaces

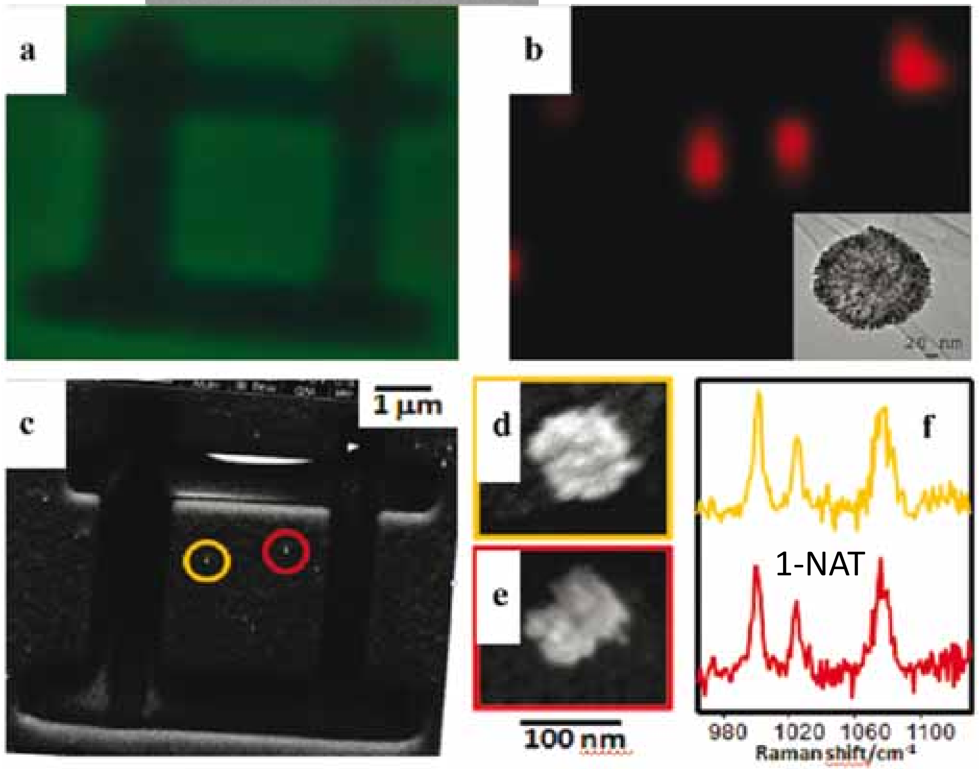


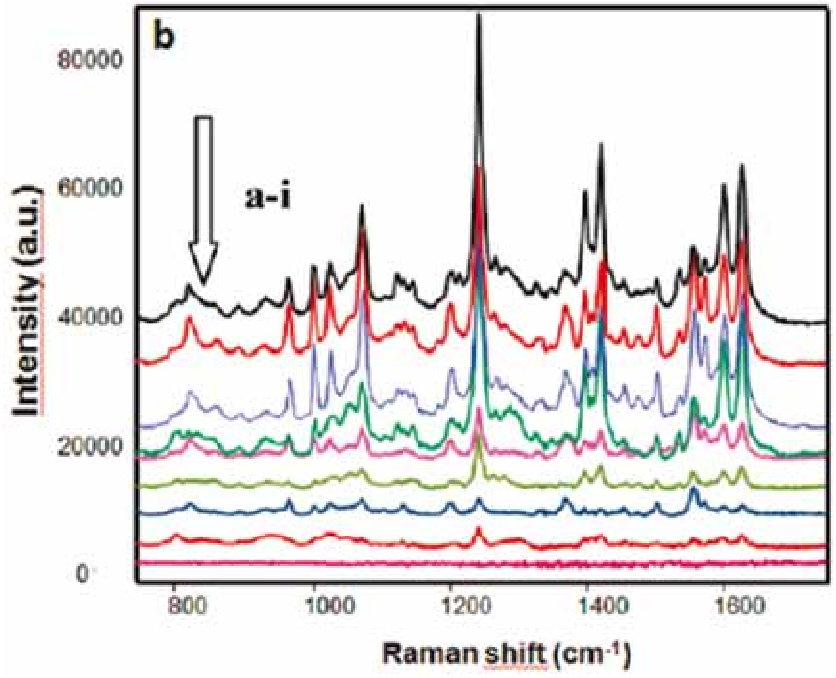








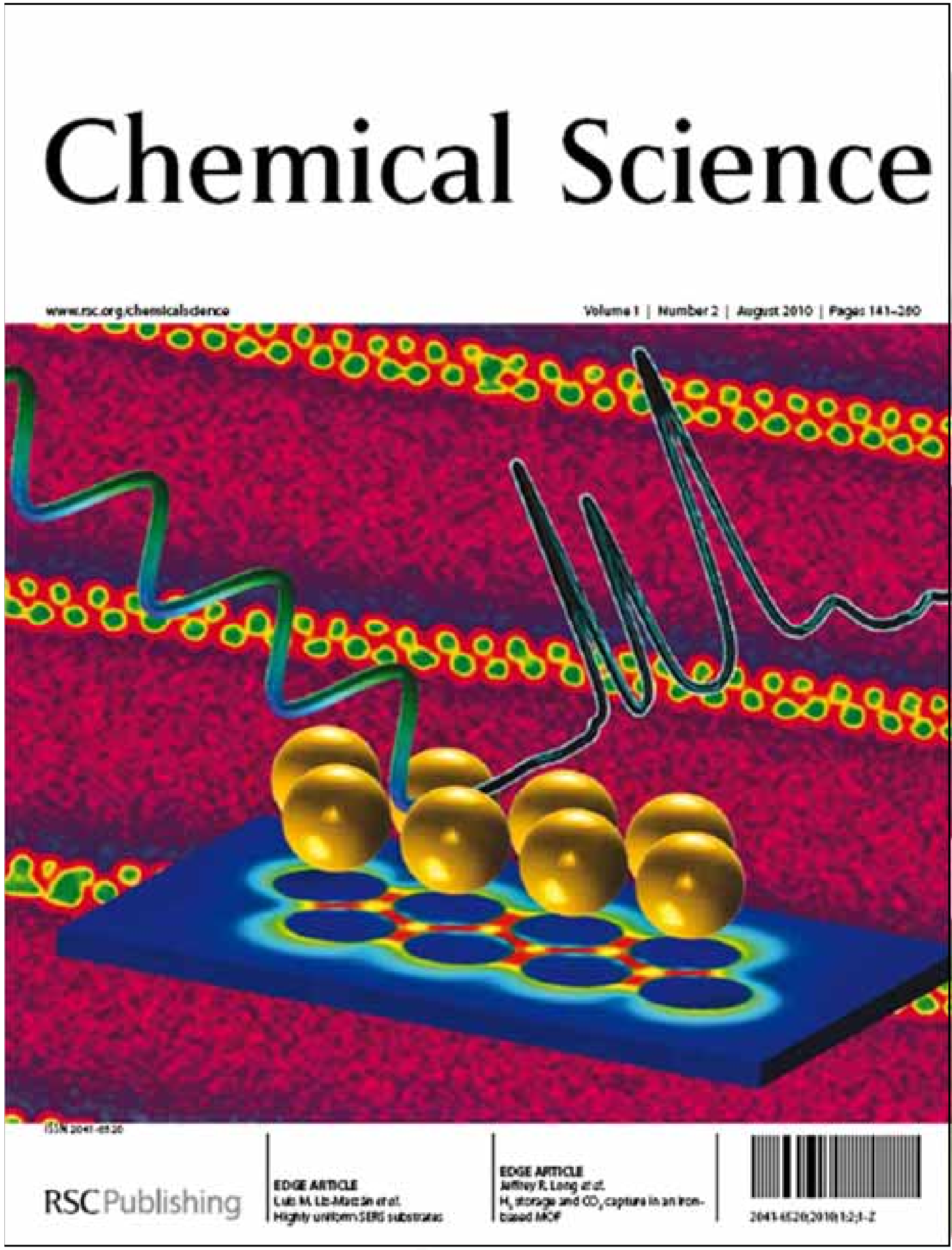


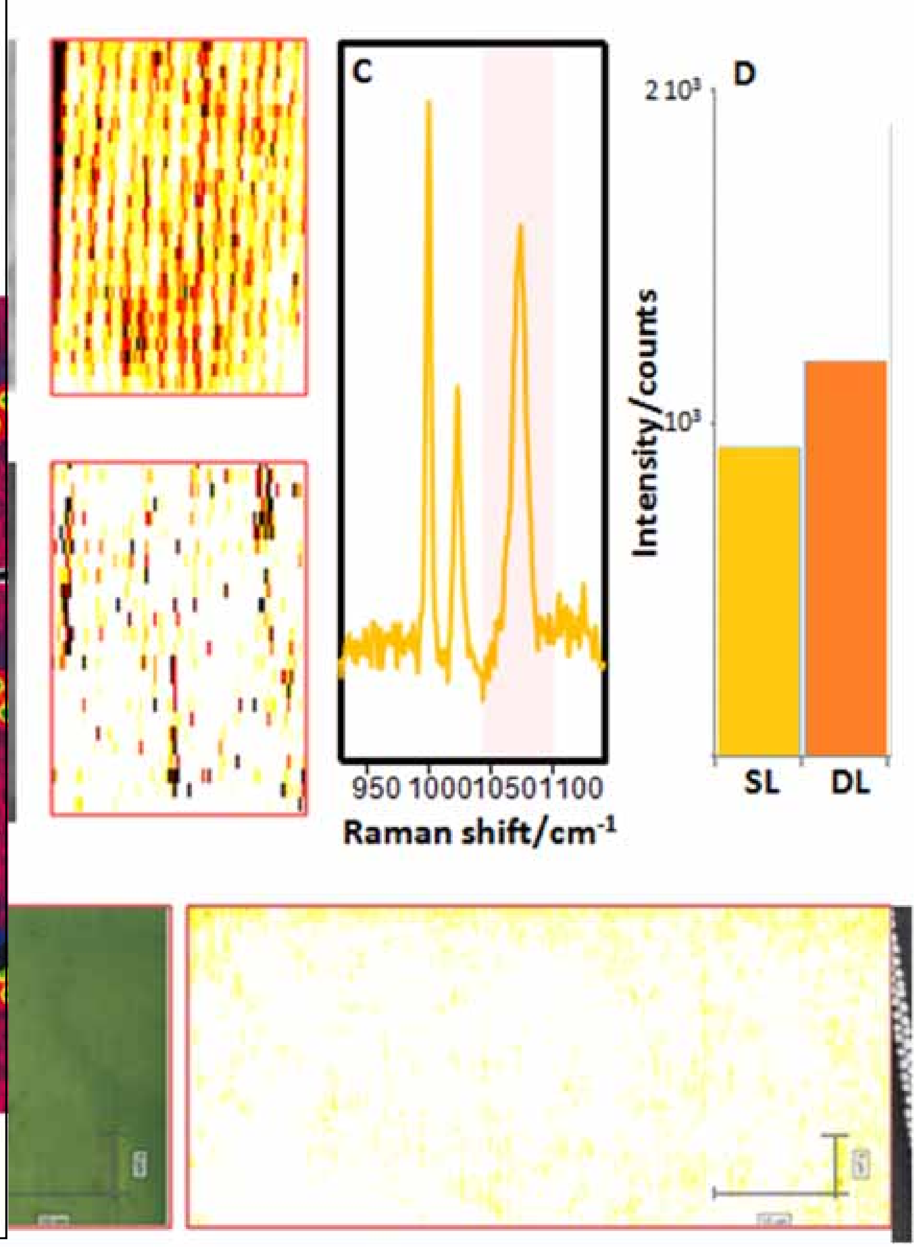


SERS monitoring pyrene release

Nano Lett. **2010**, *10*, 4013 (col.N. Kotov)

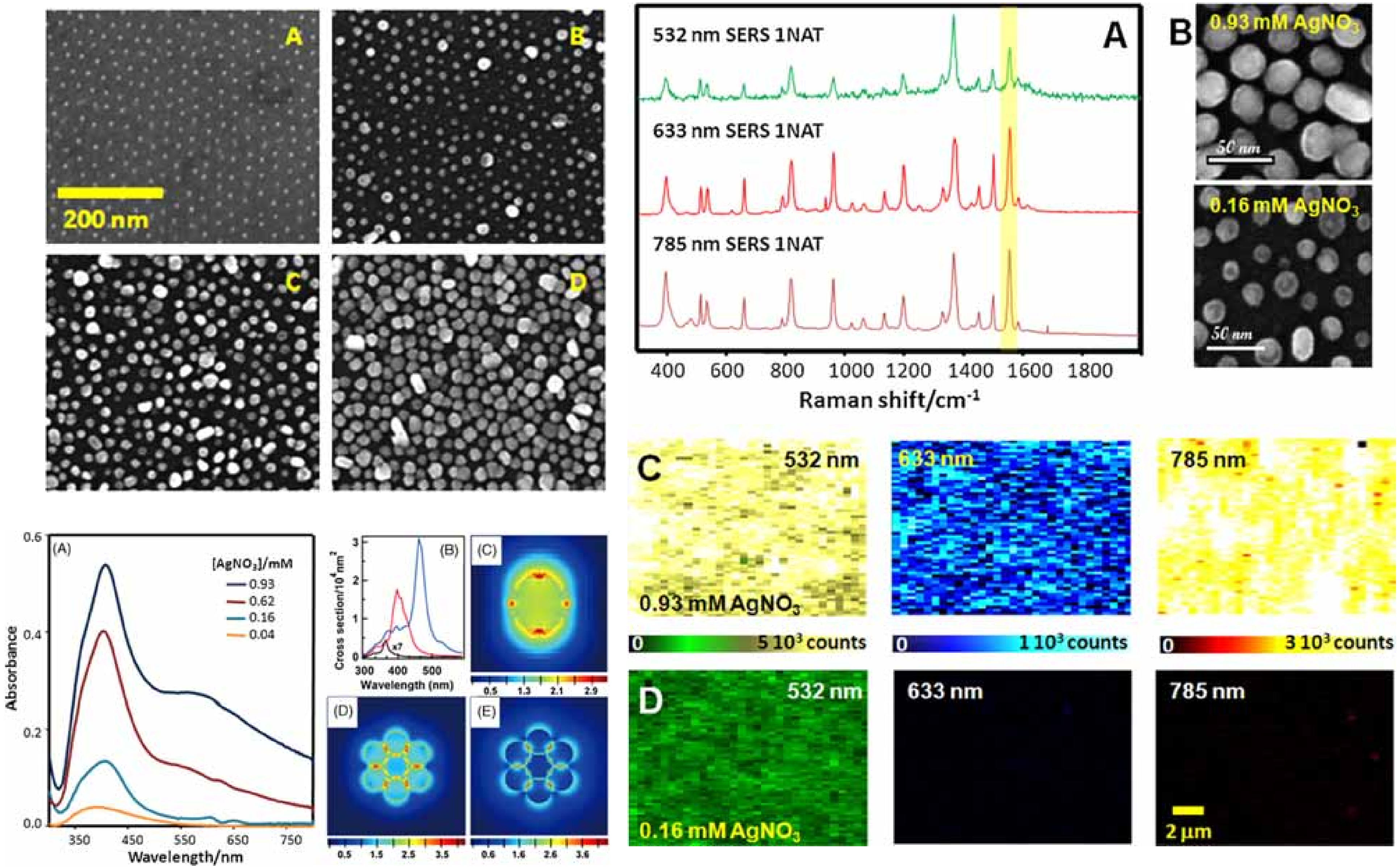
Controlled Fabrication of Hot Spots: Directed Assembly





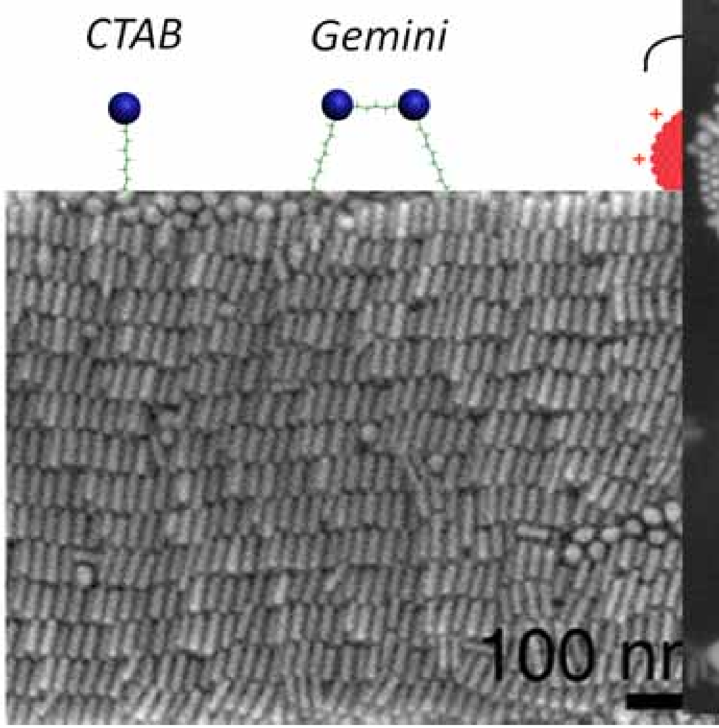
Chemical Science **2010**, *1*, 174 (col. A. Fery)

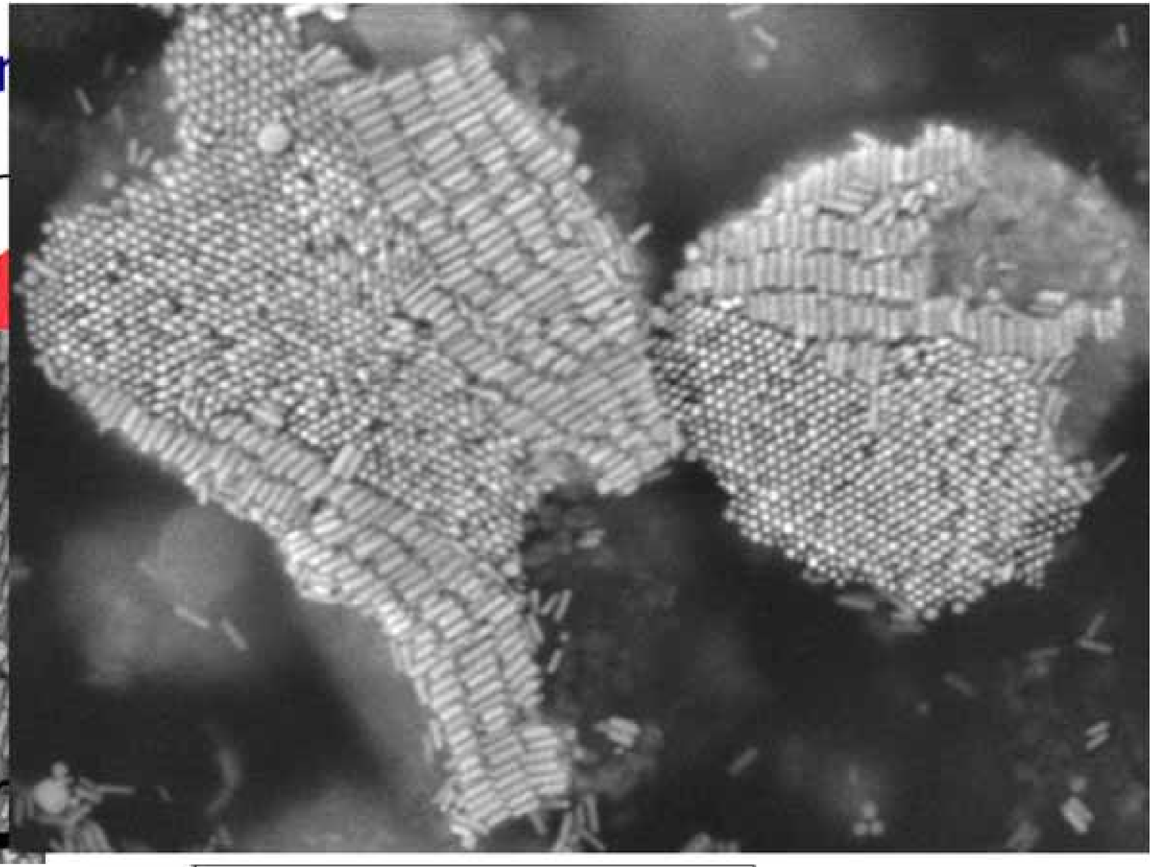
Controlled Fabrication of Hot Spots: Micelle nanolithography+chemical growth

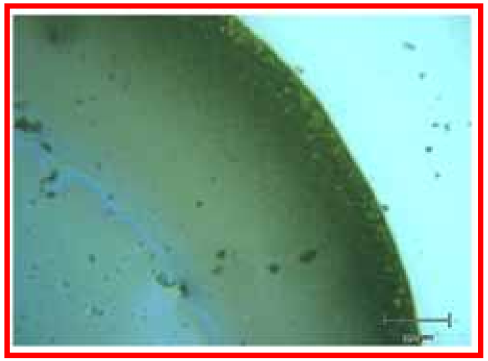


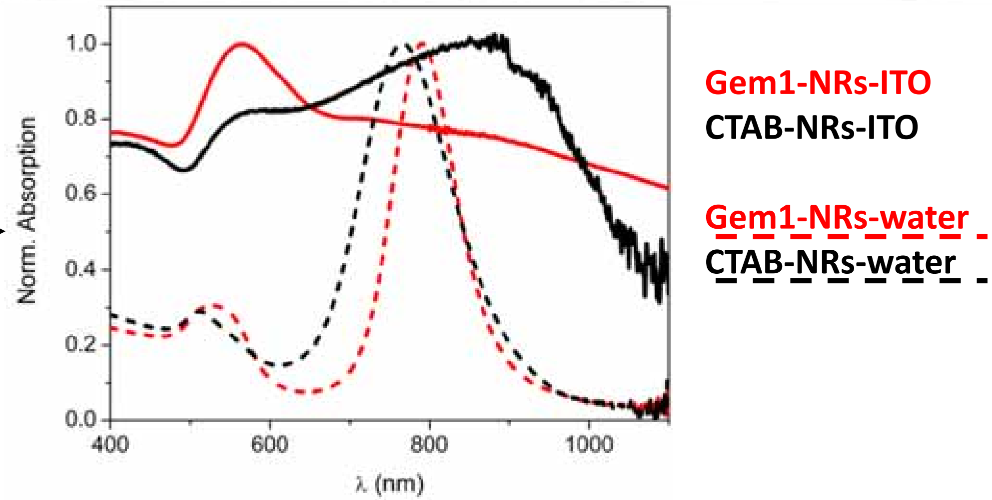
A. Sánchez-Iglesias et al., *Nano Today* **2010**, *5*, 21-27

Self-assembly of Au r



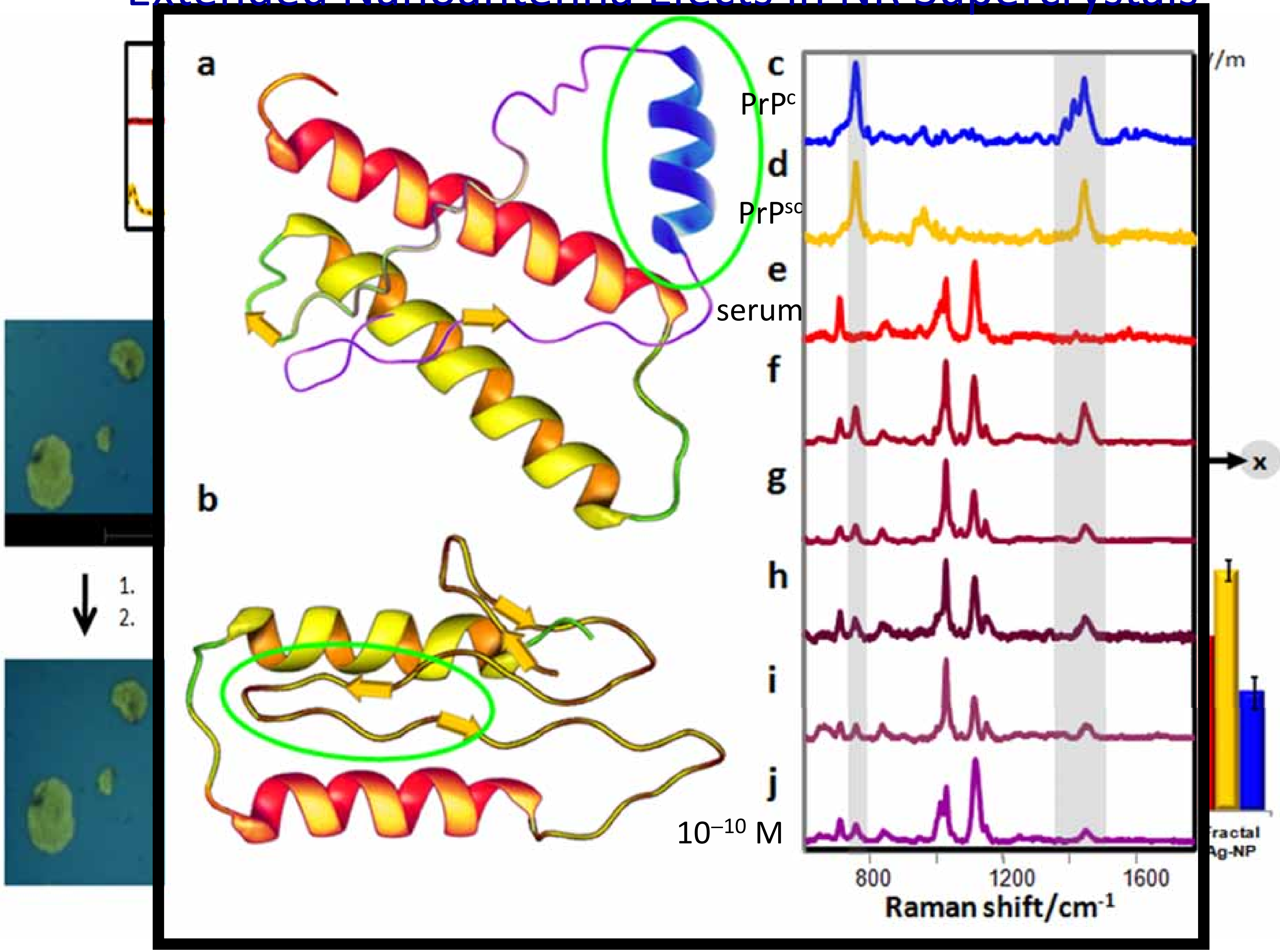






Angew. Chem. Int. Ed. **2009**, 48, 9484

Extended Nanoantenna Efects in NR Supercrystals



PNAS **2011**, in press (col. N. Kotov; E. Zubarev)

CONCLUSIONS

- Field enhancement can be achieved through shape optimization and directed assembly
- Growth of sharp tips can be achieved on a variety of gold surfaces
- Spiked gold nanoparticles are excellent SERS enhancers
- Gold nanorod supracrystals act as nanoantennas and promote huge SERS enhancements

Colloid Chemistry Group

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Thank you!

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