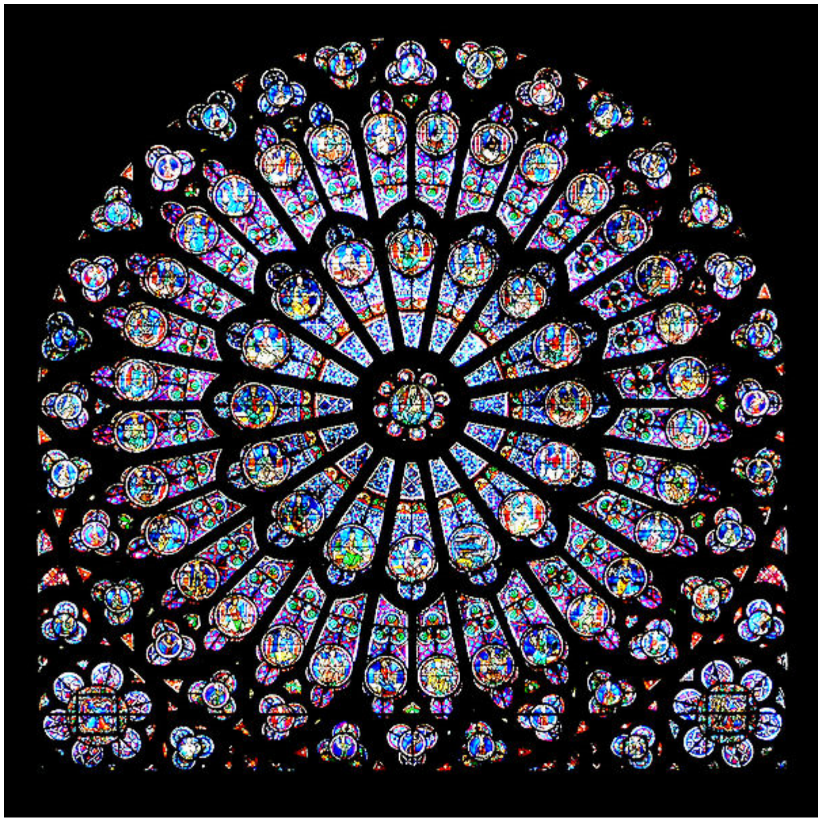
Selected Topics in Advanced Optics

Week 5 – part 1

Olivier J.F. Martin
Nanophotonics and Metrology Laboratory

EPFL

Optics of metals and plasmonics
Part I – Localized plasmon resonances



Notre Dame, Paris

The Lycurgus cup,
British Museum London

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Some references

- B.E.A. Saleh & M.C. Teich, Fundamental of photonics 2nd Ed. (Wiley, Hoboken, 2007), Chapter 5.
- C.F. Bohren & D.R. Huffman, Absorption and scattering of light by small particles (Wiley, New York, 1983).
- H. Raether, Surface Plasmons on Smooth and Rough Surfaces and on Gratings, Springer Tracts in Modern Physics **111** (Springer, New York, 1988).
- S.A. Maier, Plasmonics: Fundamentals and Applications (Springer, 2007).
- J. Homola, Surface plasmon resonance based sensors, SpringerSeries in Chemical Sensors and Biosensors **4** (Springer, Berlin, 2006).

Drude model

- The spring constant in Lorentz model is set to zero $K = 0$
- The real part of the permittivity can be negative:

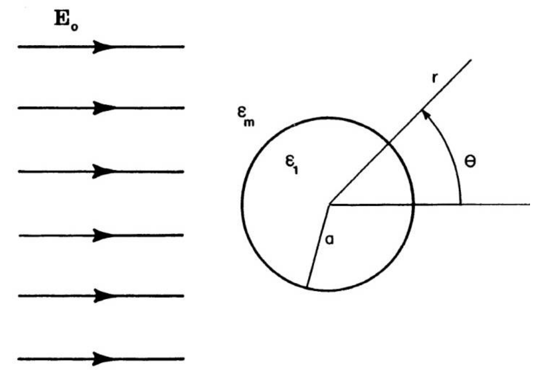
$$\varepsilon_r = 1 - \frac{\omega_p^2}{\omega^2 + j\gamma\omega}$$

$$\varepsilon' = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} \qquad \varepsilon'' = \frac{\omega_p^2 \gamma}{\omega\left(\omega^2 + \gamma^2\right)}$$

- The following website gathers the parameters for the Drude model for many metals: http://www.wave-scattering.com/drudefit.html

Scattering by a small particle in the electrostatic limit

- If the particle is small, it makes sense to assume that the incident field is homogeneous
- One can then use an electrostatic approach and the formulae simplify significantly:



$$Q_{abs} = 4x \operatorname{Im}\left\{\frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m}\right\}$$

$$Q_{scat} = \frac{8}{3} x^4 \left|\frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m}\right|^2$$

$$Q_{ext} = Q_{abs} + Q_{scat} \qquad x = ka = \frac{2\pi n a}{\lambda_0}$$

- When extinction is dominated by absorption, its spectrum goes with $1/\lambda$
- When it is dominated by scattering, its spectrum goes with $1/\lambda^4$

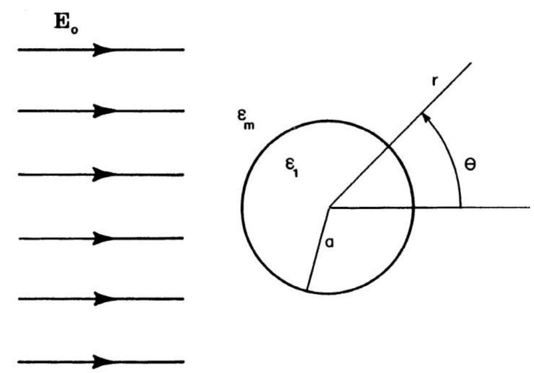
Scattering by a small particle in the electrostatic limit

- When the surrounding material is vacuum

$$\varepsilon_m = 1$$

$$Q_{abs} = 4x\,\mathrm{Im}\left\{\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\right\}$$

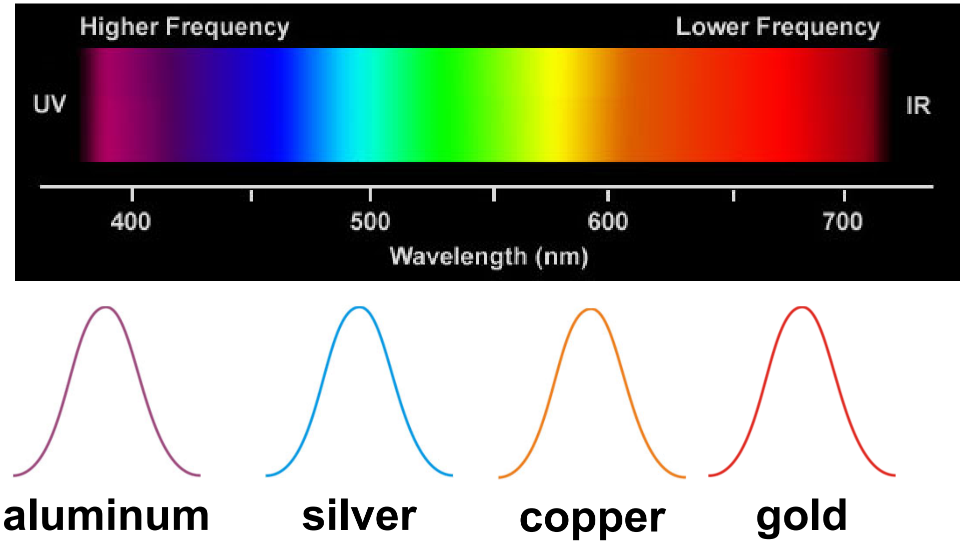
$$Q_{scat} = \frac{8}{3}x^4\left|\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\right|^2$$



- Which is resonant when $\varepsilon = -2$
- Plasmonic metals exhibit this condition in the visible part of the spectrum

Plasmonic metals

- Coinage metals (noble metals, group 11): Cu, Ag, Au
- Further plasmonic metals include Al, W, Pt and heavily doped semiconductors (density of electrons > $10^{22}/cm^3$)
- The plasma frequency determines the optical range where plasmonic effects can be observed



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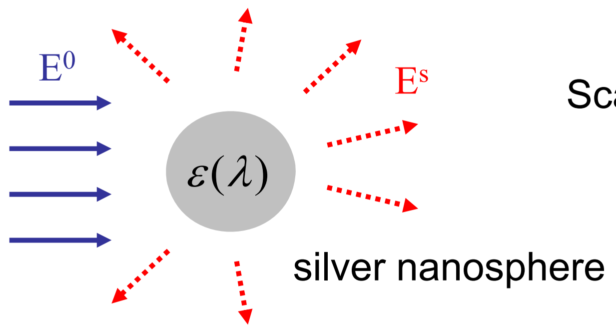
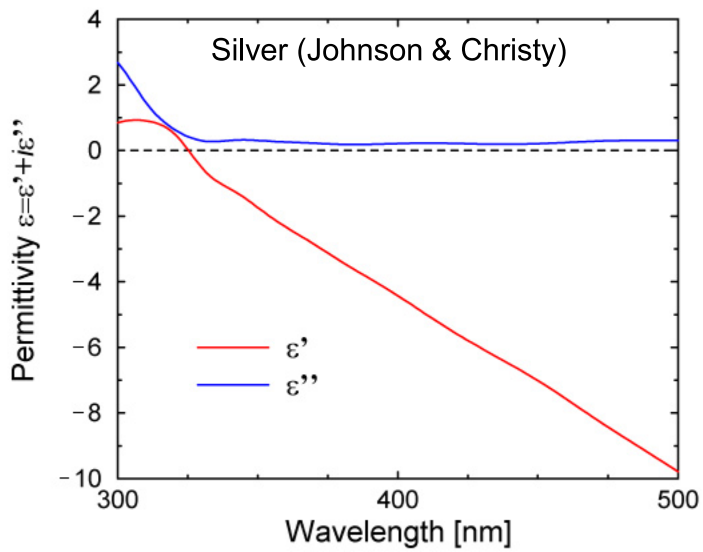
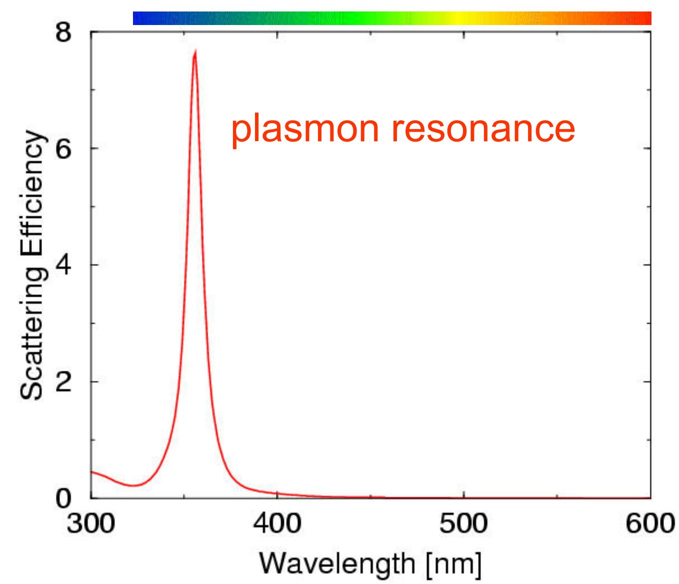
Plasmon resonant nanoparticle



Scattering efficiency: $$Q(\lambda) = \frac{8}{3} x^4 \left| \frac{\varepsilon(\lambda) - 1}{\varepsilon(\lambda) + 2} \right|^2$$

$$x = 2\pi R / \lambda$$





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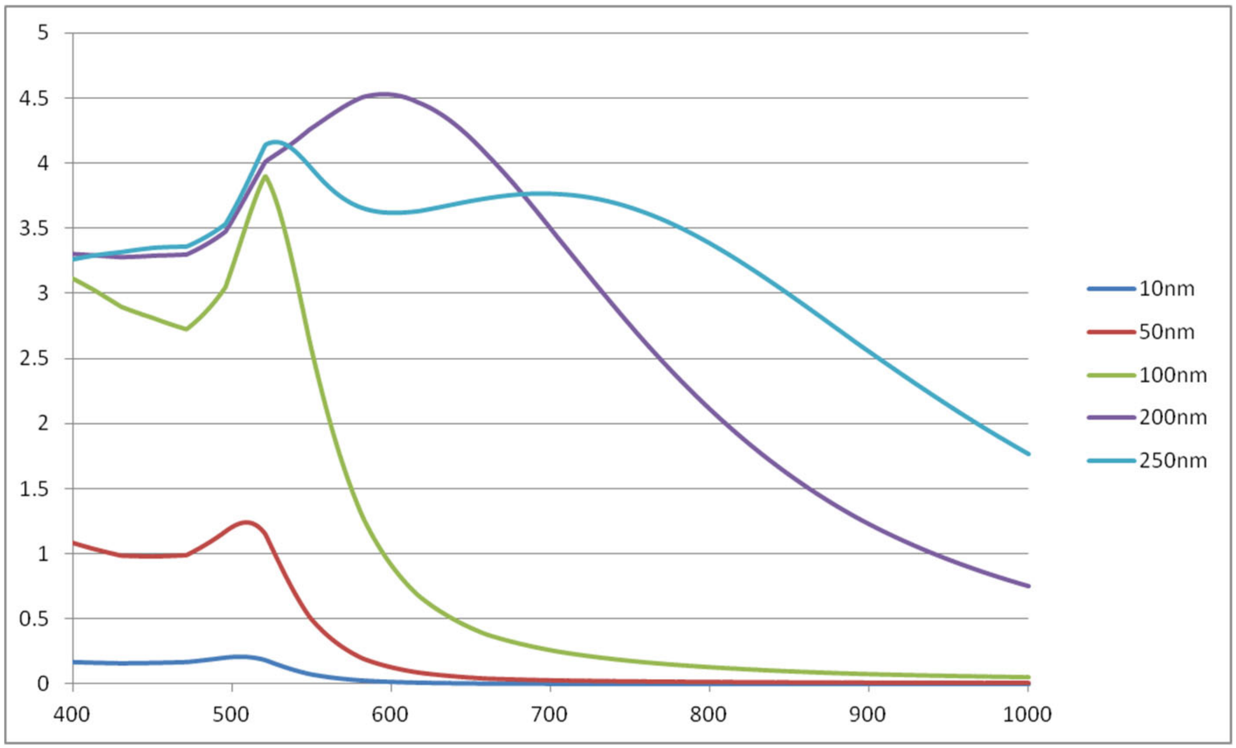
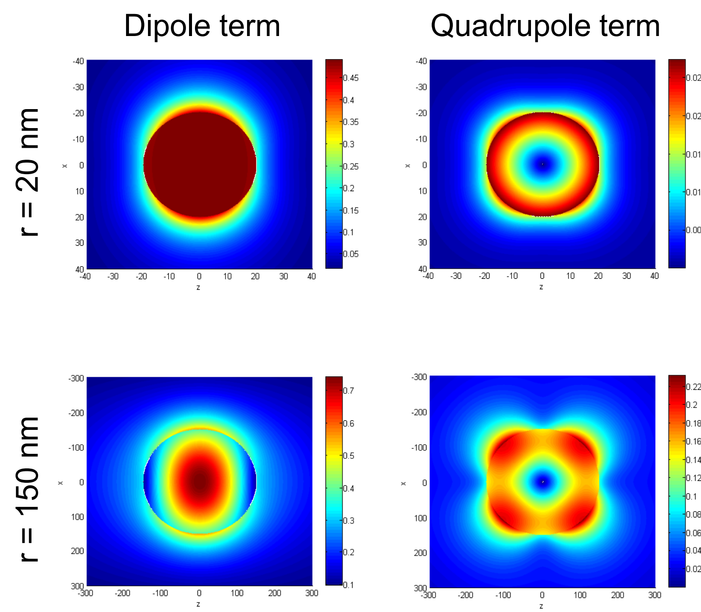
Size dependance and multipolar resonances

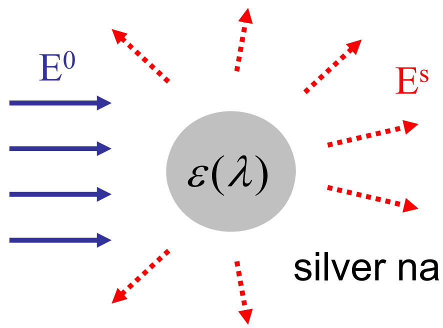
- Q_{ext} for different Au sphere diameters, in air





Dielectric sphere n=1.55, λ=600 nm

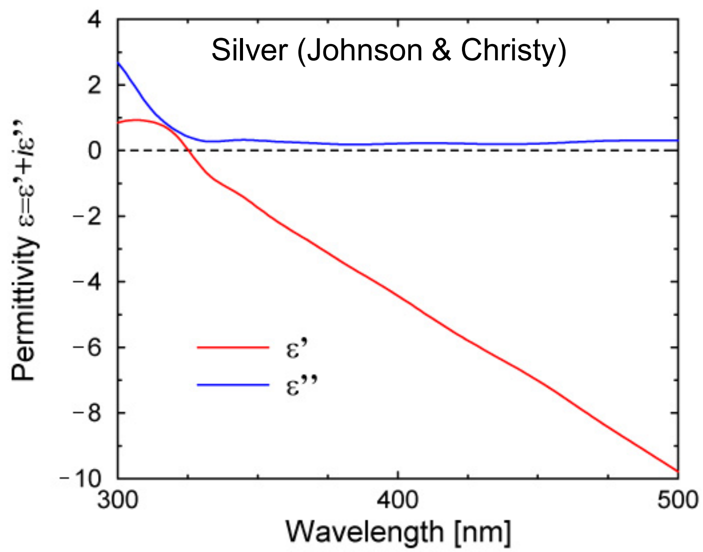
Plasmon resonant nanoparticle

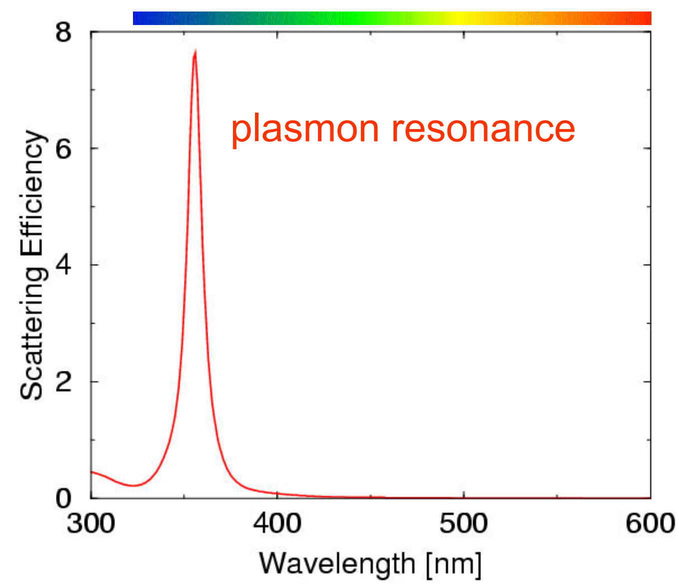


silver nanosphere

Scattering efficiency: $$Q(\lambda) = \frac{8}{3} x^4 \left| \frac{\varepsilon(\lambda) - 1}{\varepsilon(\lambda) + 2} \right|^2$$

$$x = 2\pi R / \lambda$$





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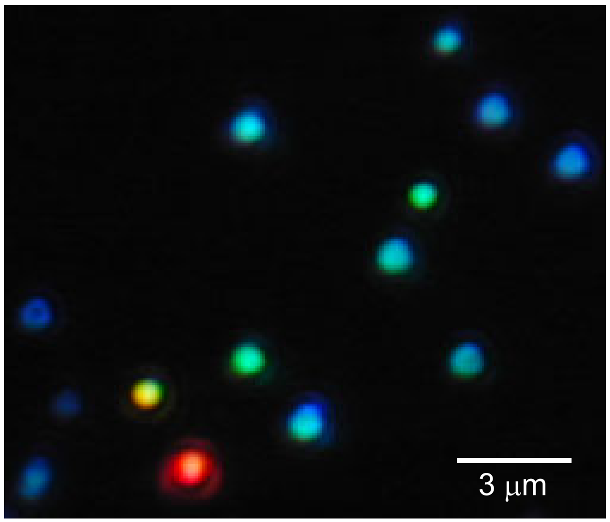
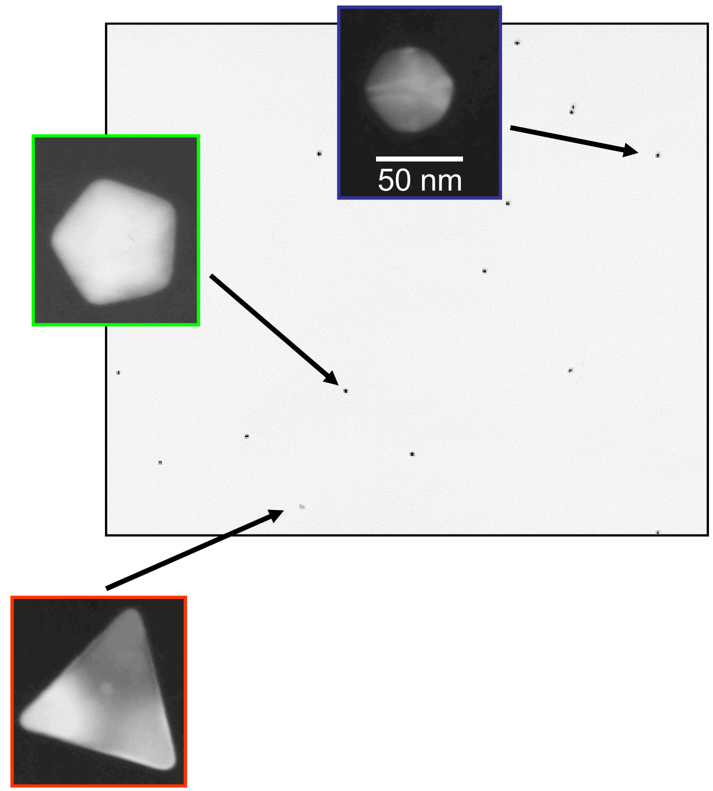
Plasmon resonances – Experimental observation

- Same material, similar sizes, but different colors ?



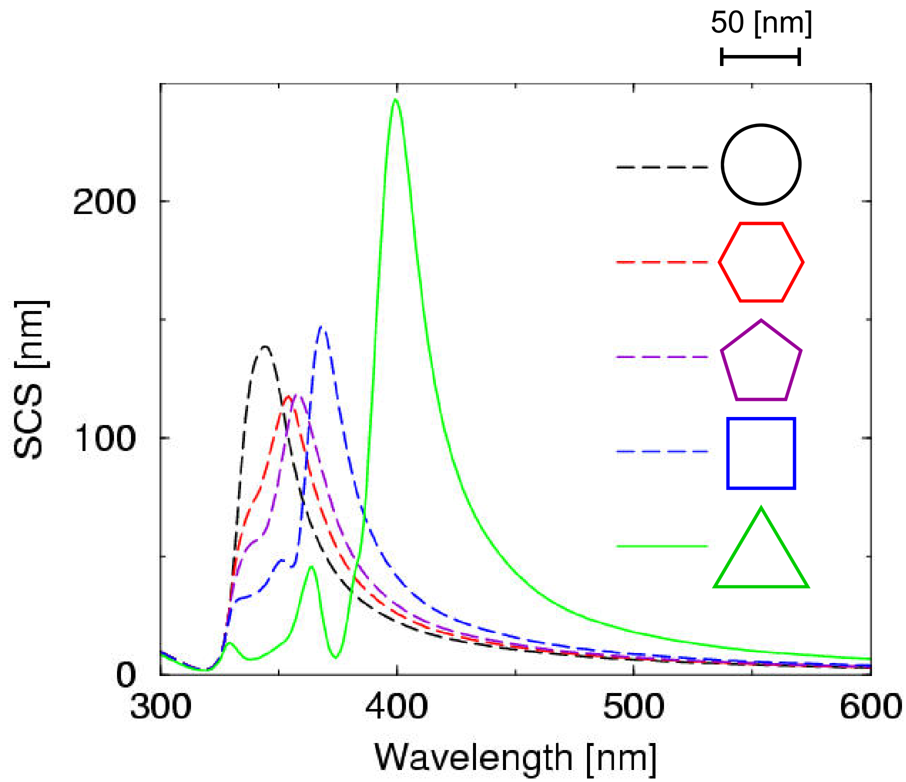


silver colloidal nanoparticles

J. Mock, Duke University

J. Chem. Phys. ***116****, 6755 (2002)*

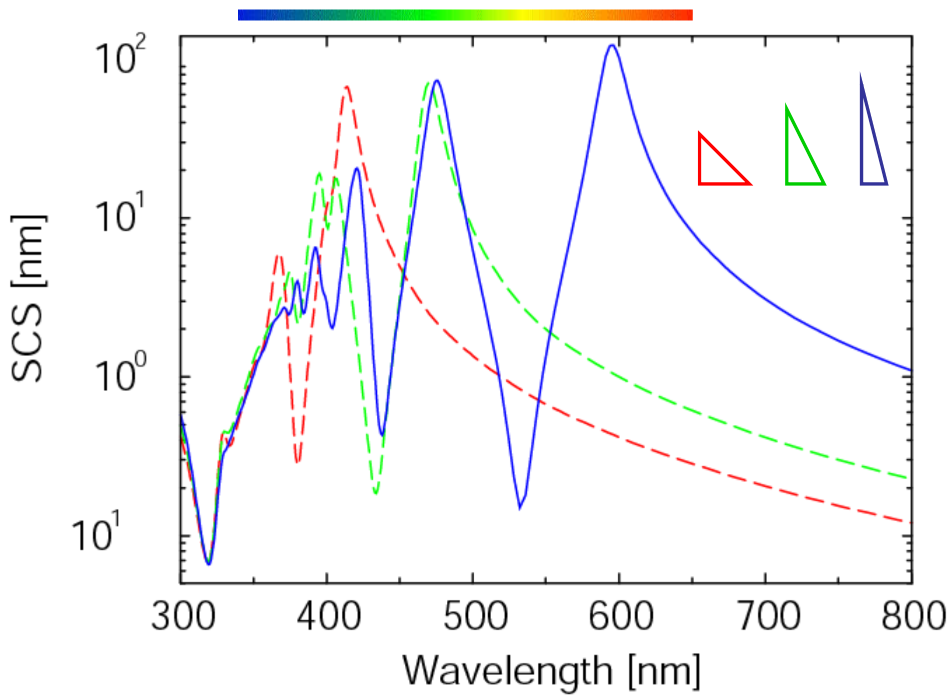
Plasmonic simplexes



• More complex spectrum as particle symmetry decreases

J. Kottmann et al., Applied Physics B vol. 73, p. 299 (2001)

Breaking the symmetry further



J. Kottmann et al., Applied Physics B vol. 73, p. 299 (2001)

Selected Topics in Advanced Optics

Week 5 – part 2

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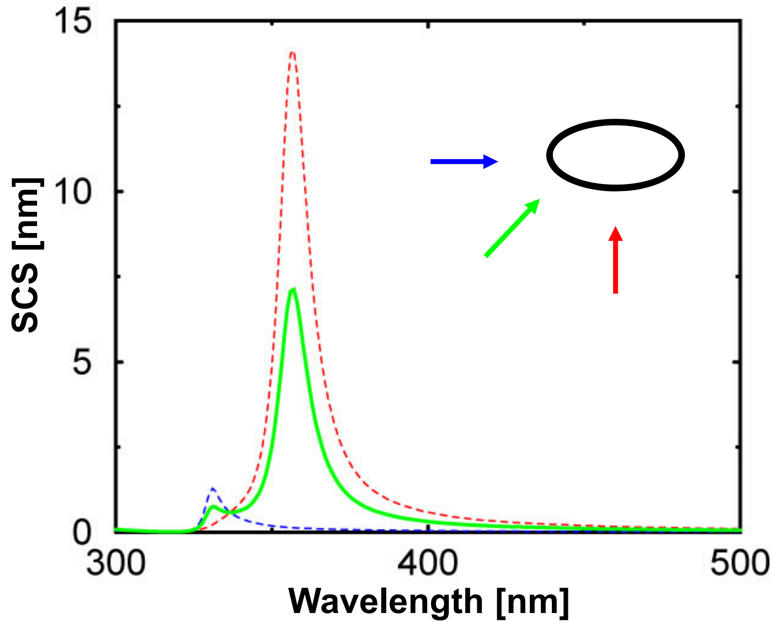
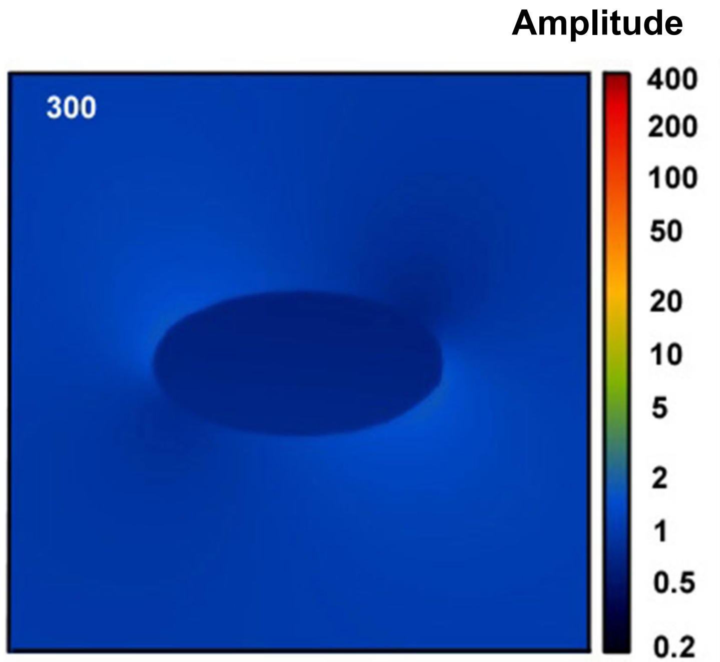
Elliptical particle

Ag, 20 x 10 [nm]

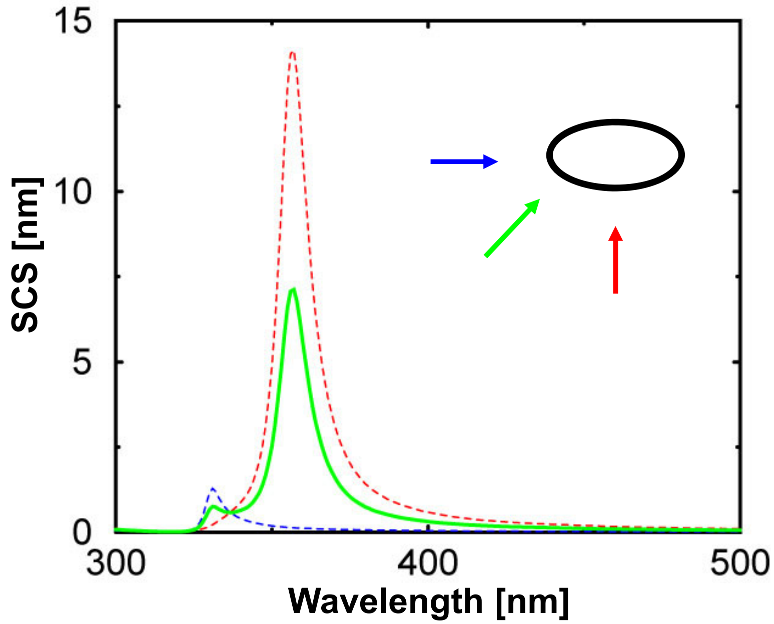


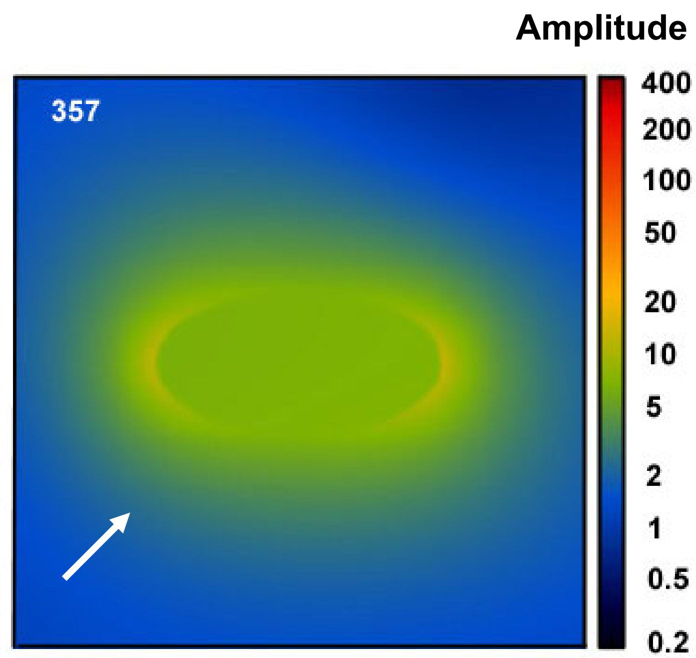


J. Kottmann et al., New Journal of Physics vol. 2, p. 27 (2000)

Elliptical particle

Ag, 20 x 10 [nm]

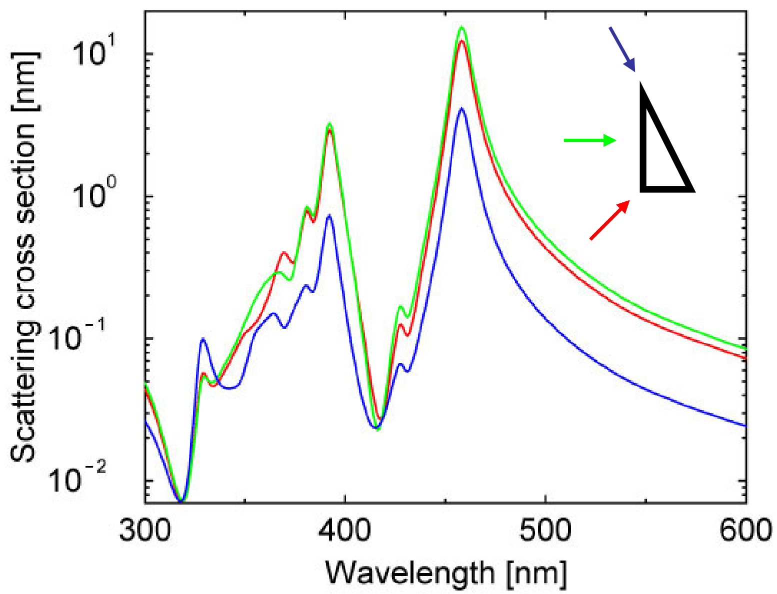


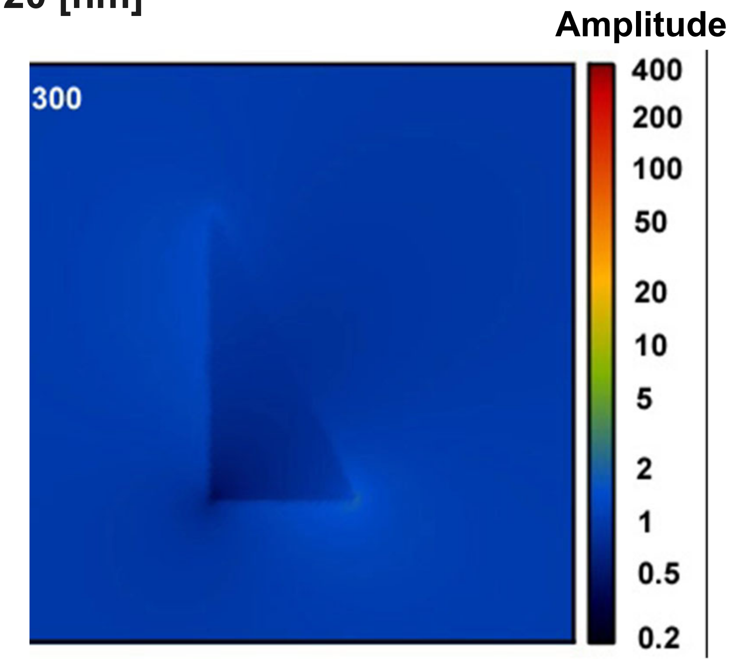


J. Kottmann et al., New Journal of Physics vol. 2, p. 27 (2000)

Near-field enhancement

Ag, 10 x 20 [nm]





- **Dramatic near-field enhancement**
- **At resonance, particle has dimensions λ/15…λ/30 !**

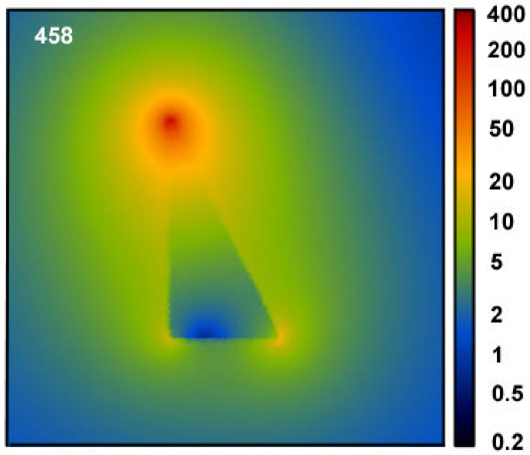
J. Kottmann et al., New Journal of Physics vol. 2, p. 27 (2000)

Near-field enhancement

20 x 10 [nm] particle:

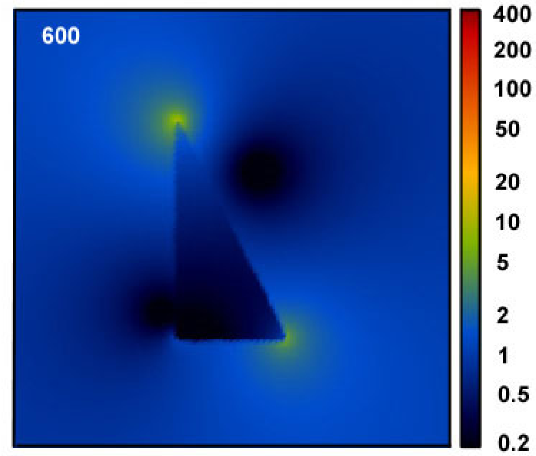
• Main resonance:

Amplitude



• Lightning rod effect:

Amplitude

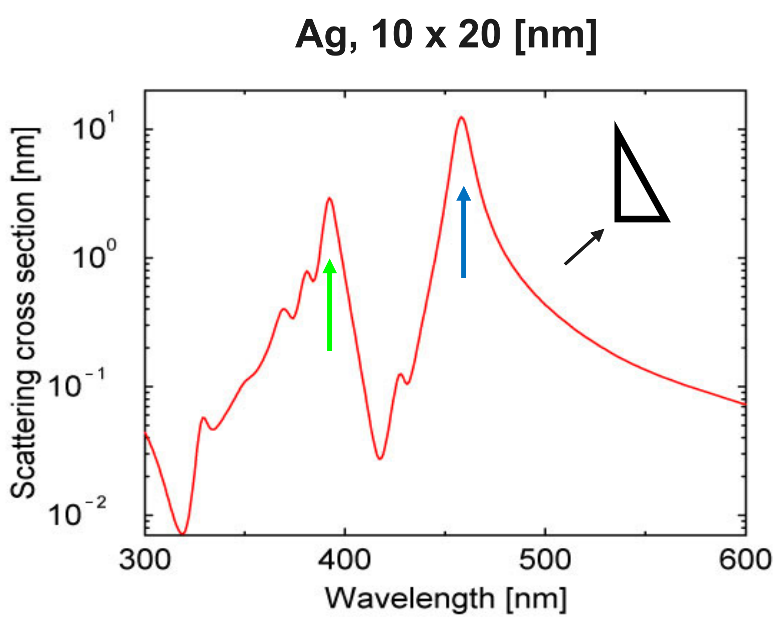


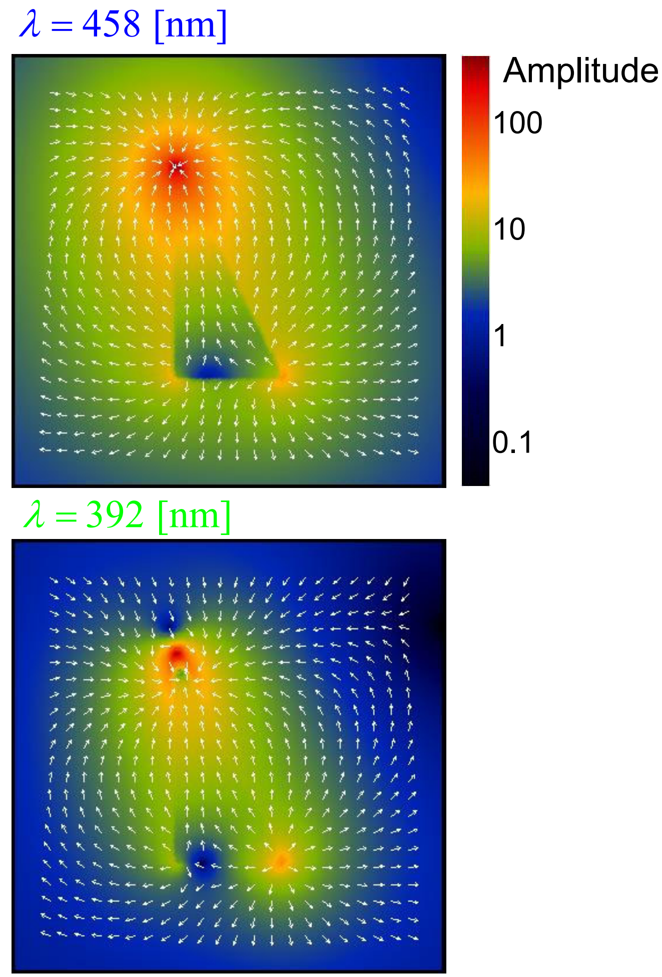
$$\varepsilon = -16 + i\ 0.4$$

- This is not a lightning rod effect (tip effect), but a resonance related to the overall particle shape!

J. Kottmann et al., New Journal of Physics vol. 2, p. 27 (2000)

Field distribution at different wavelengths



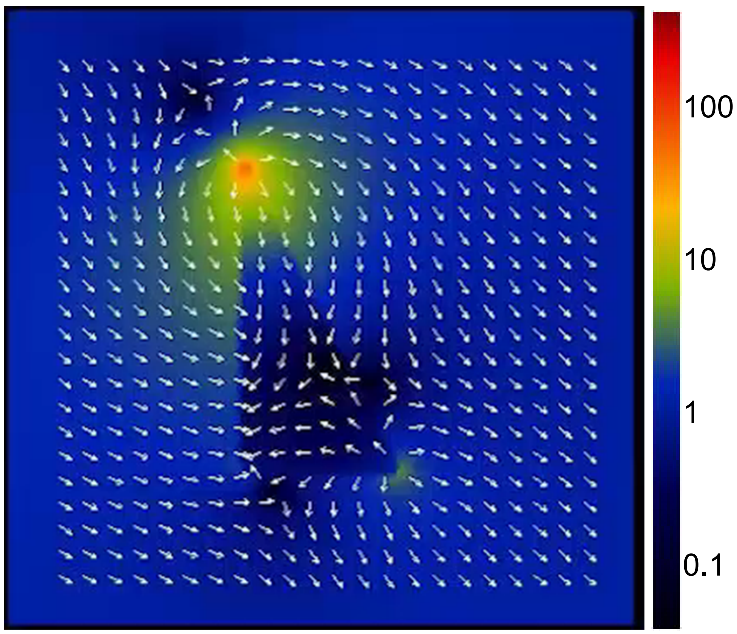


J. Kottmann et al., New Journal of Physics vol. 2, p. 27 (2000)

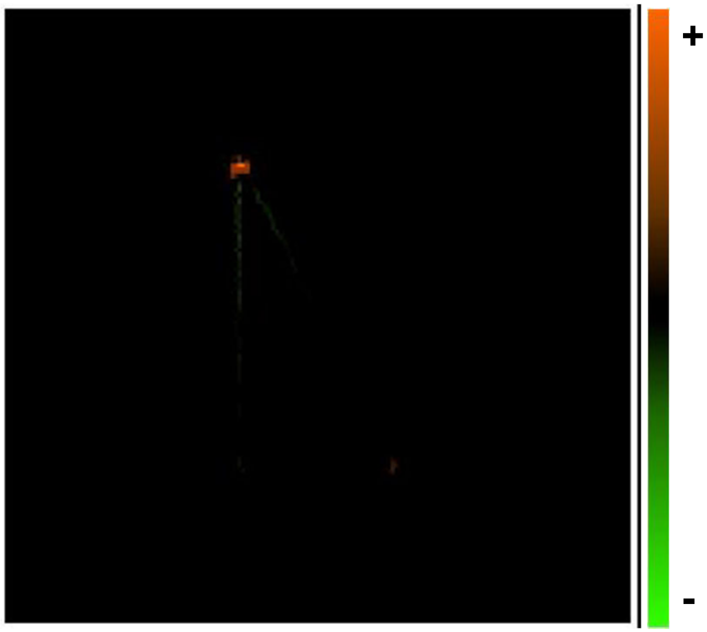
Field distribution at different wavelengths

Ag, 10 x 20 [nm] $\lambda = 458$ [nm]

Amplitude



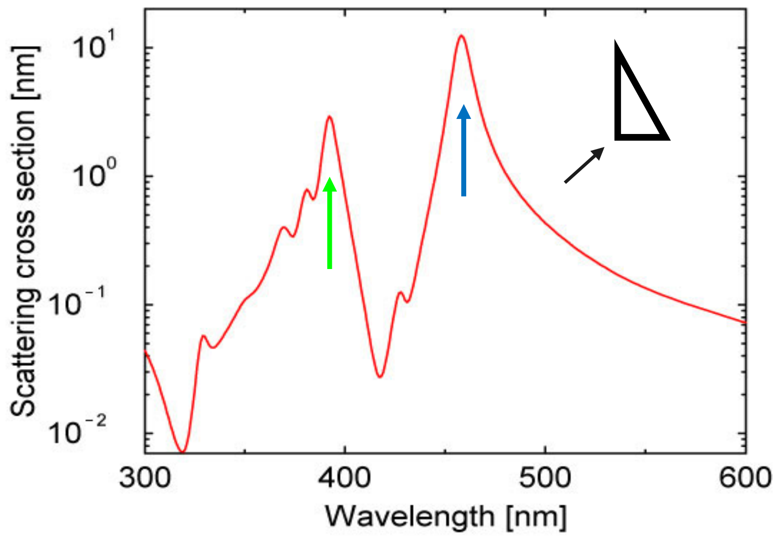
Polarization charge: $\nabla \cdot \mathbf{E}$



J. Kottmann et al., New Journal of Physics vol. 2, p. 27 (2000)

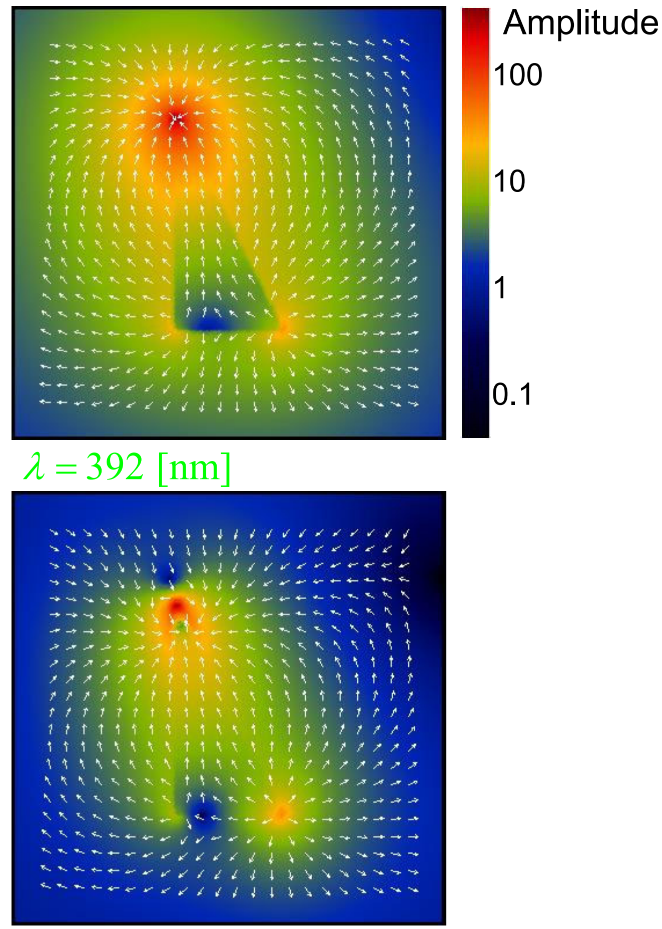
Field distribution at different wavelengths

Ag, 10 x 20 [nm]



$\lambda = 458$ [nm]

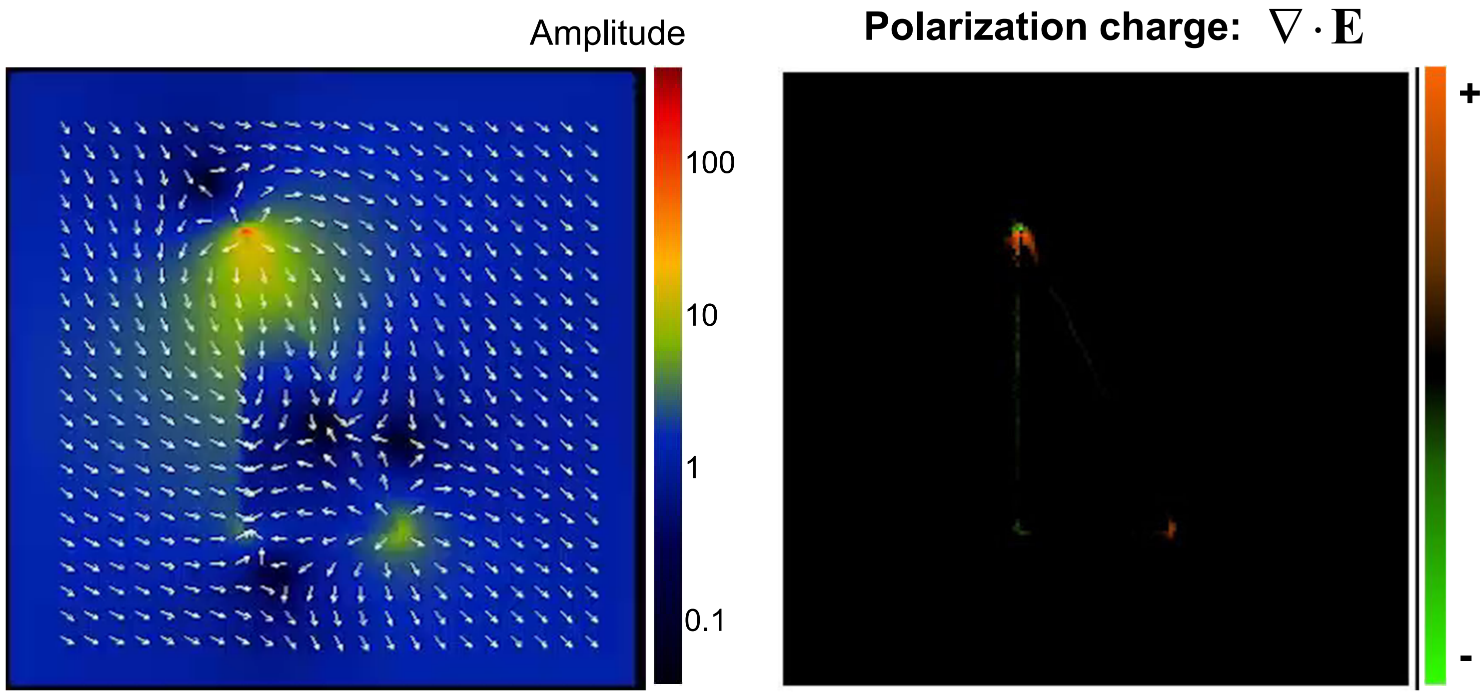
$\lambda = 392$ [nm]



J. Kottmann et al., New Journal of Physics vol. 2, p. 27 (2000)

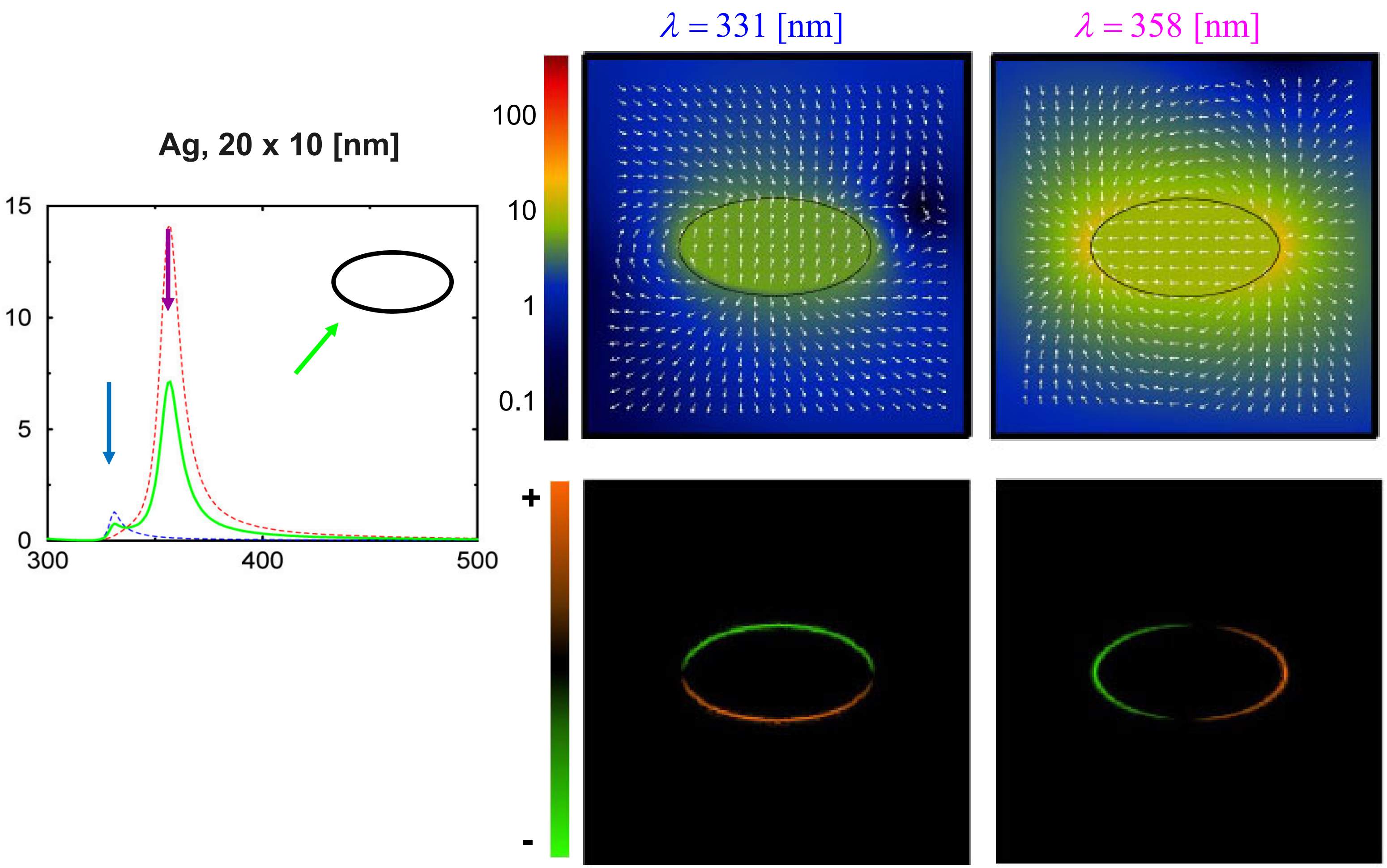
Field distribution at different wavelengths

Ag, 10 x 20 [nm] $\lambda = 392$ [nm]



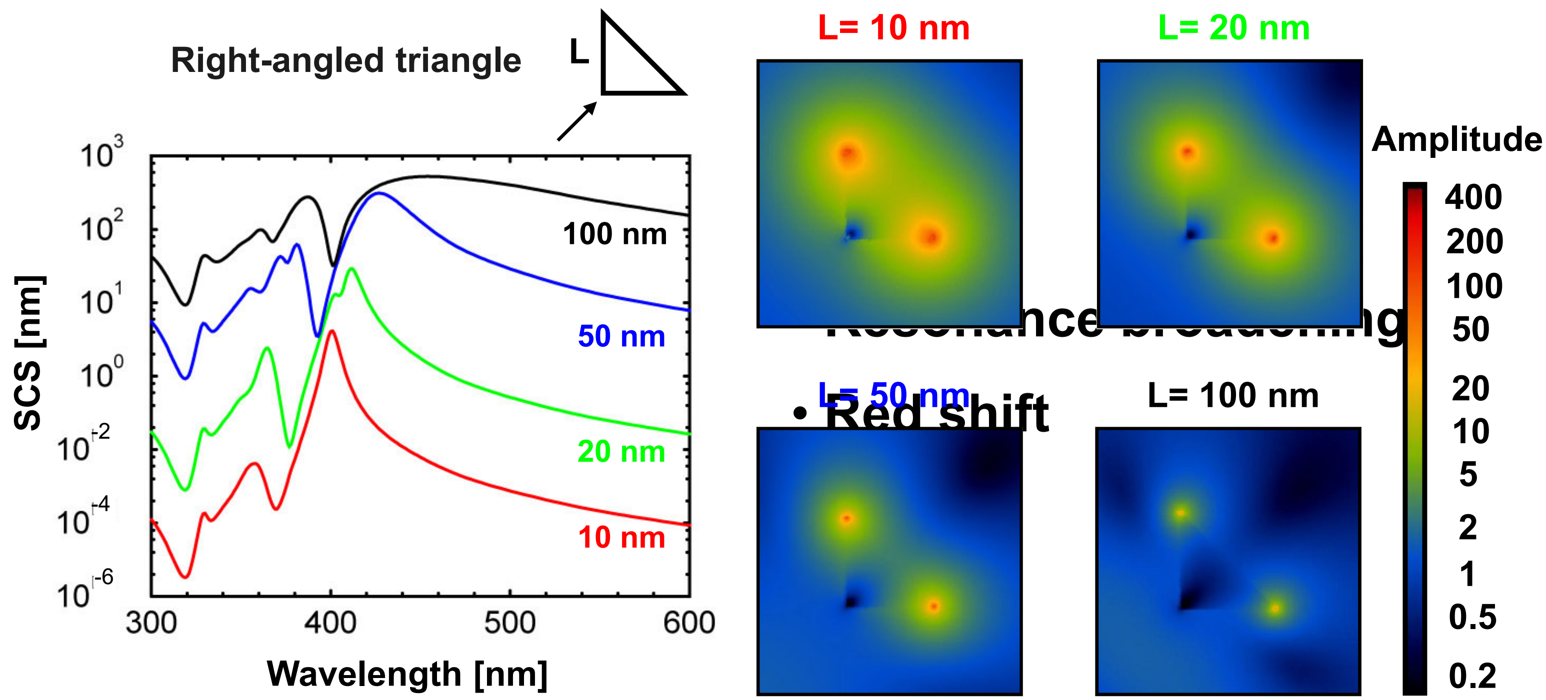
J. Kottmann et al., New Journal of Physics vol. 2, p. 27 (2000)

Elliptical particle



J. Kottmann et al., New Journal of Physics vol. 2, p. 27 (2000)

Size effect



- The maximum enhancement decreases for particles > 50 [nm]

J. Kottmann et al., New Journal of Physics vol. 2, p. 27 (2000)

In summary

- Plasmon resonances depend on the material and shape of the particle
- Each plasmon resonance is associated with a specific polarization charges distribution
- The field enhancement can be extremely significant
- The lower the symmetry of a particle, the more plasmon resonances and the strongest field enhancement

Selected Topics in Advanced Optics

Week 5 – part 3

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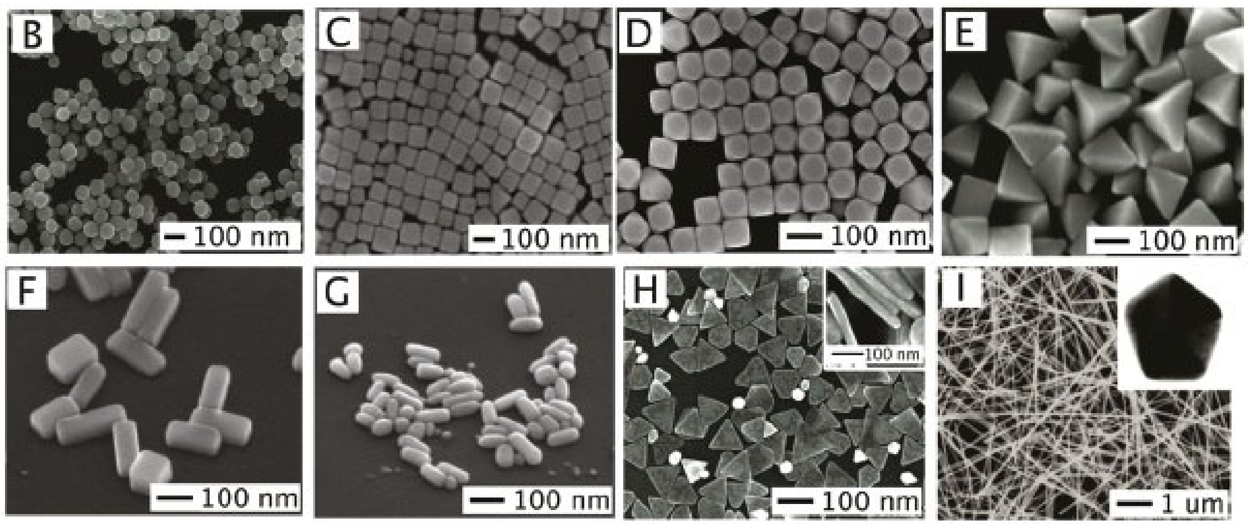
Different types of plasmonic nanostructures

- Two approaches exist for fabricating plasmonic nanostructures:
  - Top-down nanofabrication (conventional clean-room fabrication)
  - Bottom-up (chemical, self-assembled fabrication):

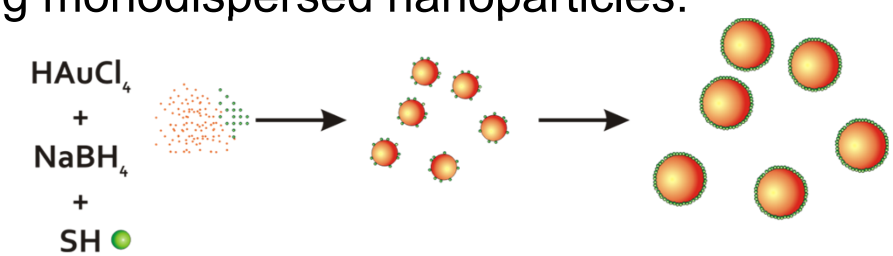


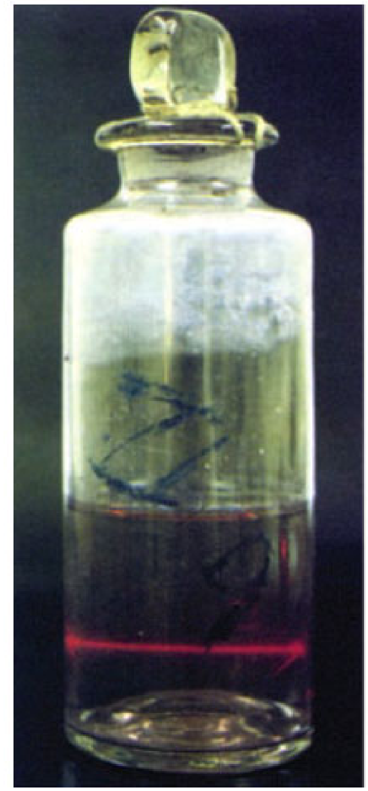
M. Rycenga, Chemical Reviews vol. 111, p. 3669 (2011)

Conventional gold nanoparticle synthesis

- Reduction of Au^{III} compounds to form metallic Au (e.g. with Sodium borohydride)
- Ostwald ripening process: over time small particles dissolve and redeposit onto larger particles, which are more favorable energetically → one single large particle:

- A capping agent (thiol-based for Au) stabilizes the process, producing monodispersed nanoparticles:





Faraday's colloidal suspension of gold or « gold fluid »

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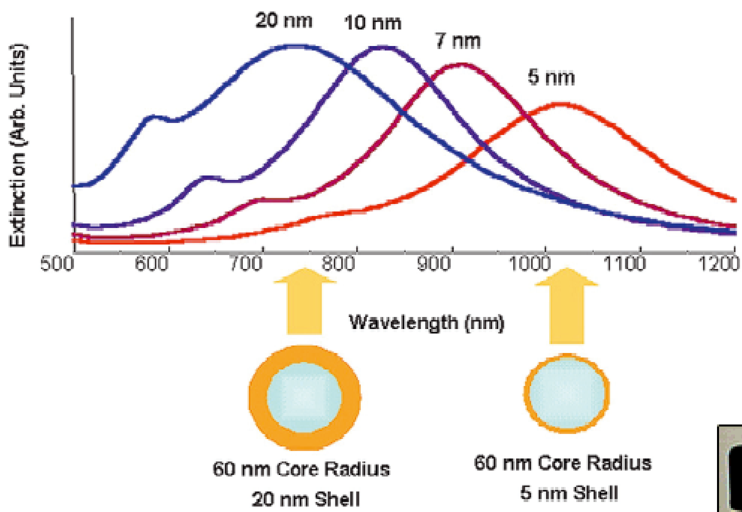
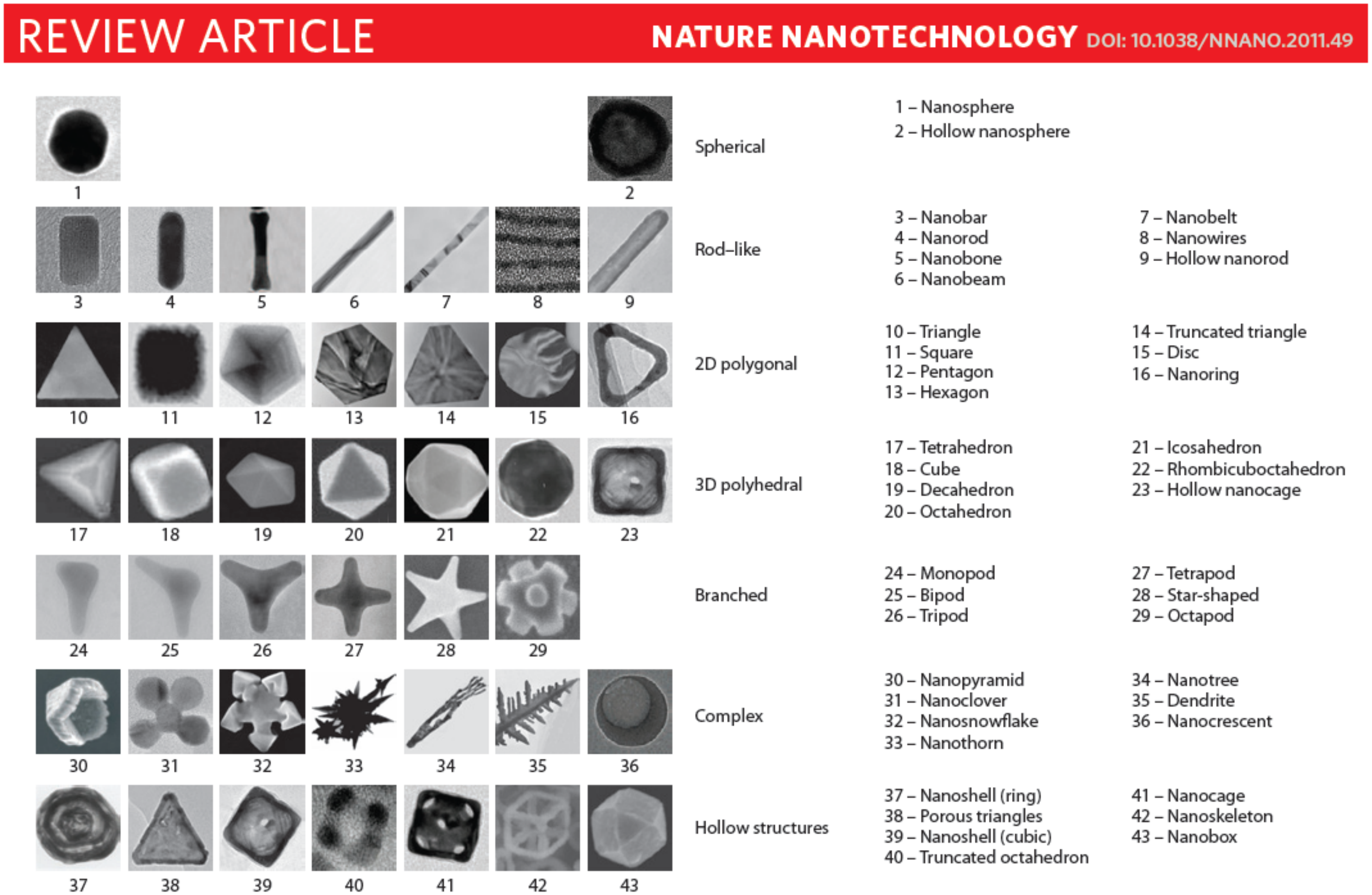
Different types of plasmonic nanostructures

- Core-shell nanoparticles are highly tunable:



N.J. Halas, Rice University

A broad variety of plasmonic "atoms" can be fabricated



S.J. Tan, Nature Nanotechnology vol. 6, p. 268 (2011)

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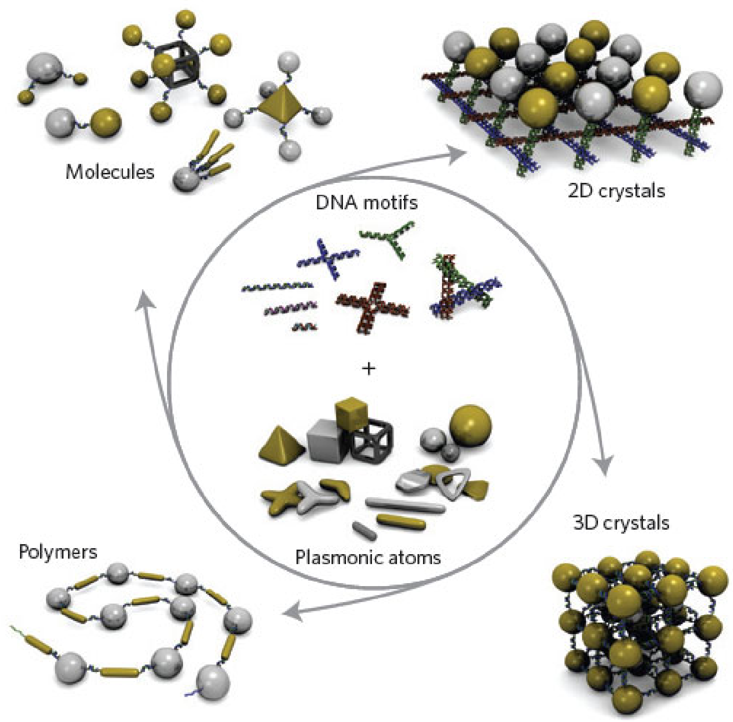
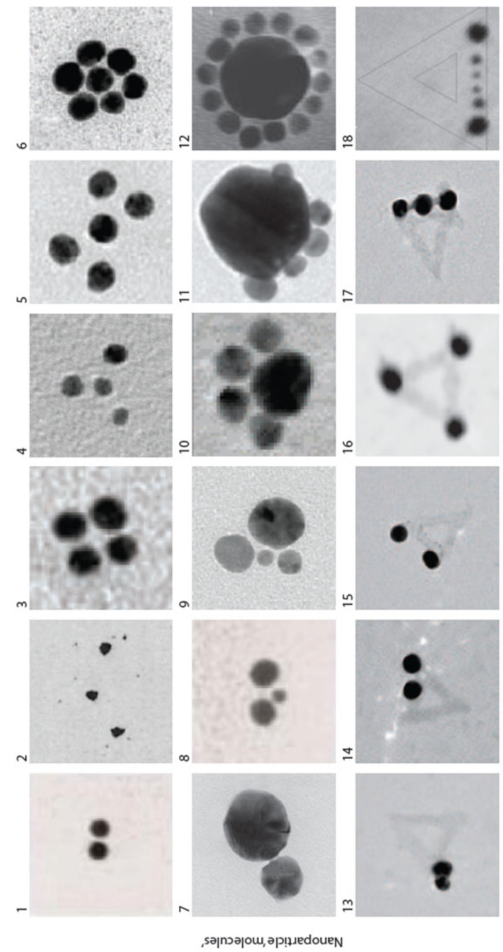
Larger structures can be ralized from these "atoms"

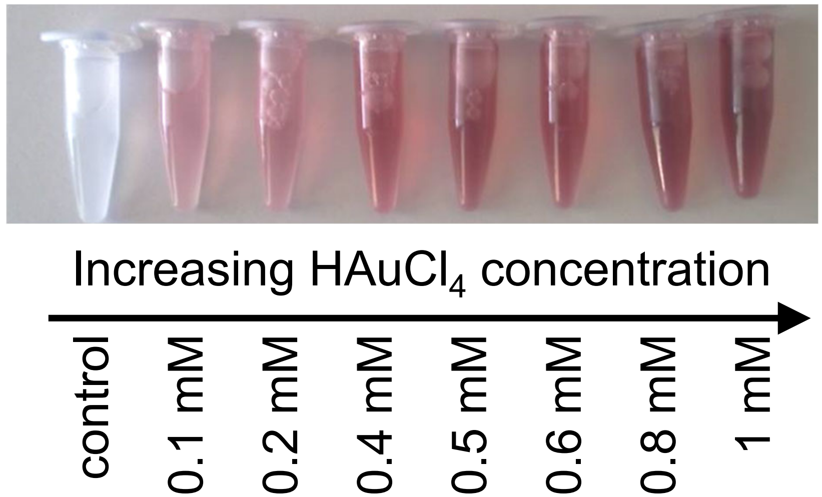




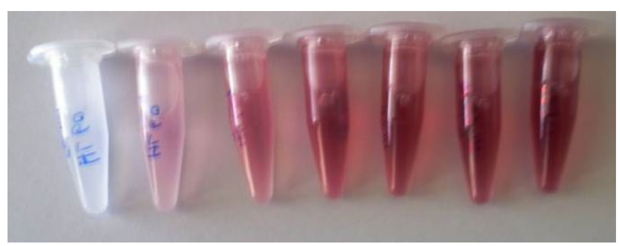
S.J. Tan, Nature Nanotechnology vol. 6, p. 268 (2011)

Nanoparticle biosynthesis in human cells

- Human cerebral endothelial cells (HCEC, adherent cells):

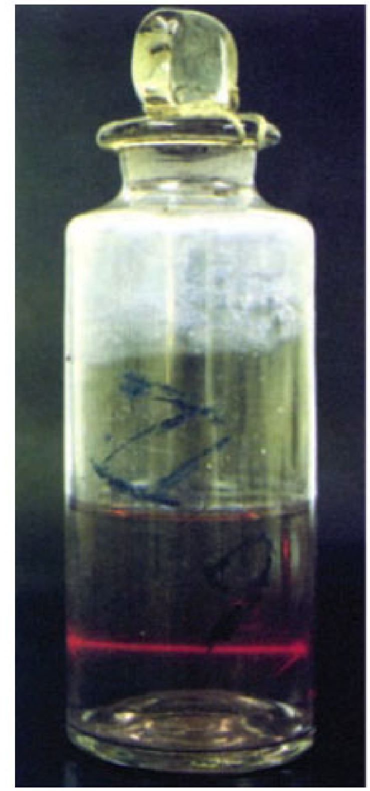


- Leukaemia HL60 cells (circulating cells):



Nanoparticle biosynthesis in human cells

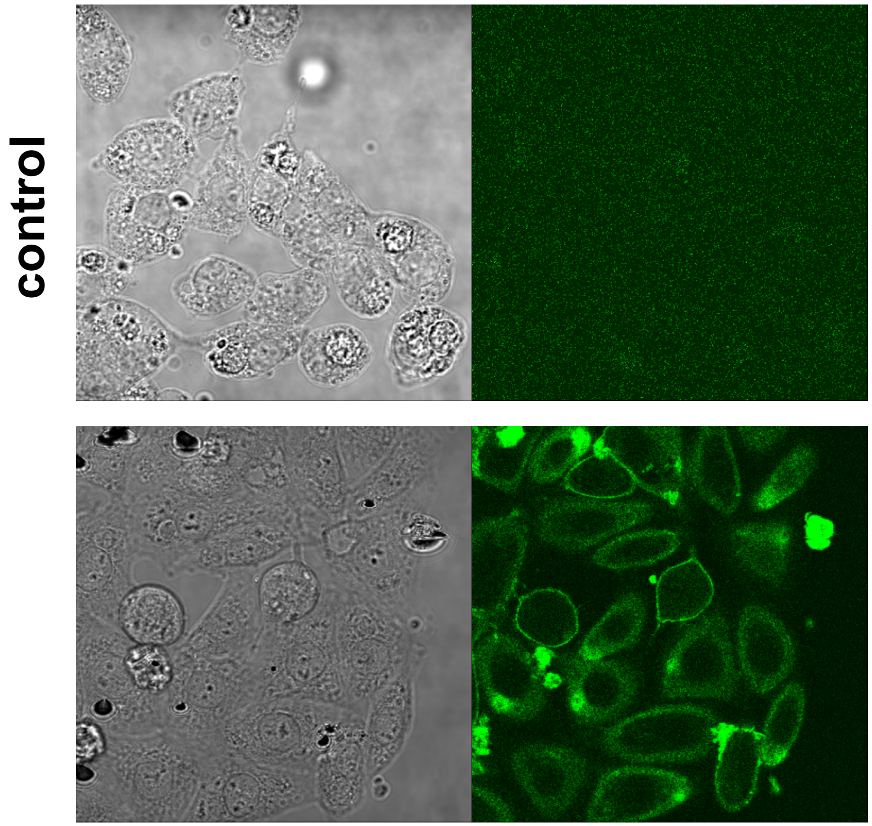
- Many open questions:
  - What is the reducing agent ?
  - What is the capping agent ?
  - Where are the nanoparticles produced ?
  - Are biosynthesized particles just like conventionally synthesized particles ?
  - Does the cell metabolism influence this biosynthesis ?



Faraday's colloidal suspension of gold or « gold fluid »

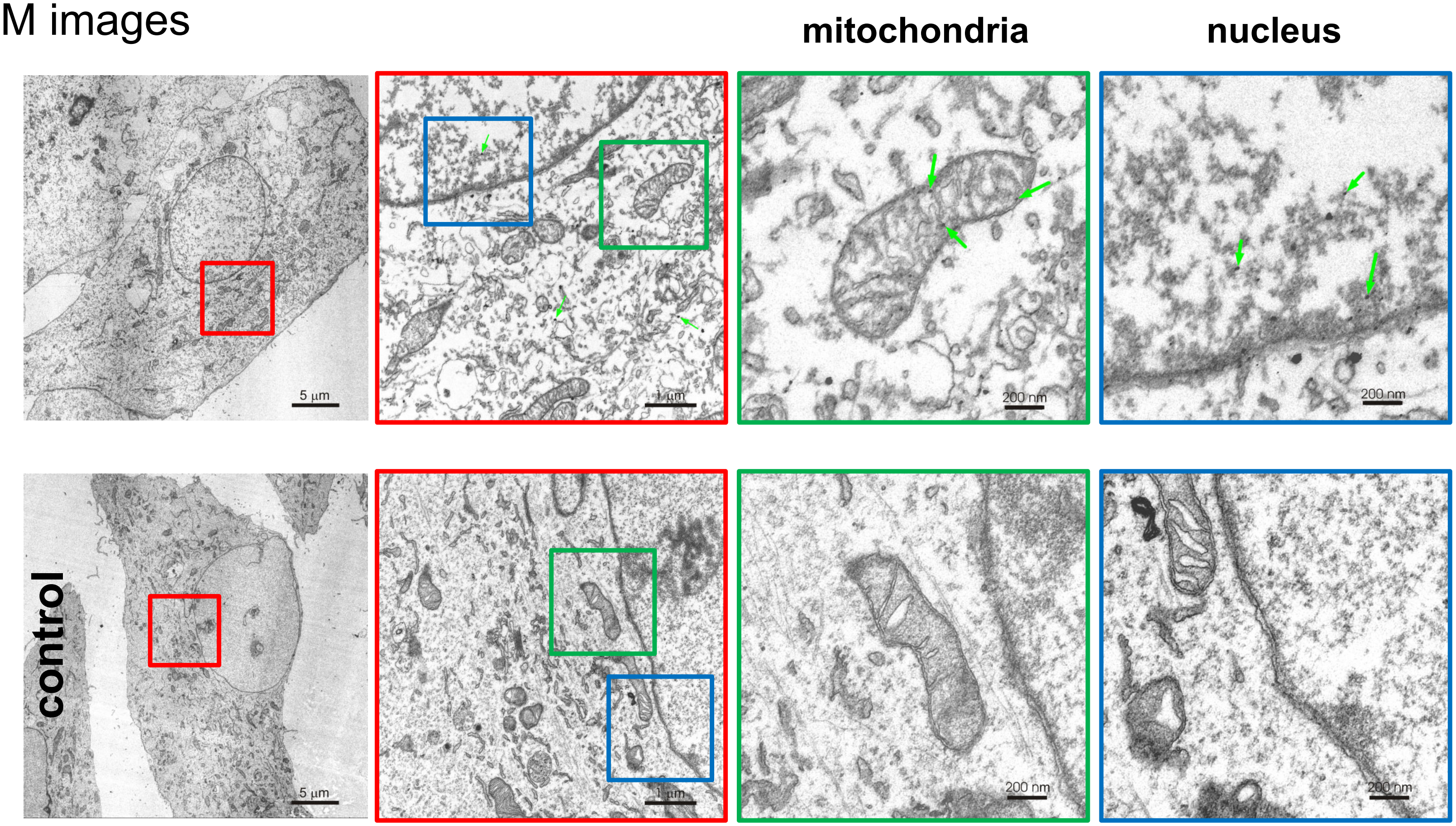
Where are the particles found in the cell?

- 2-photon microscopy (fluorescence of gold nanoparticles)



Where are the particles found in the cell?

- TEM images



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Selected Topics in Advanced Optics

Week 5 – part 4

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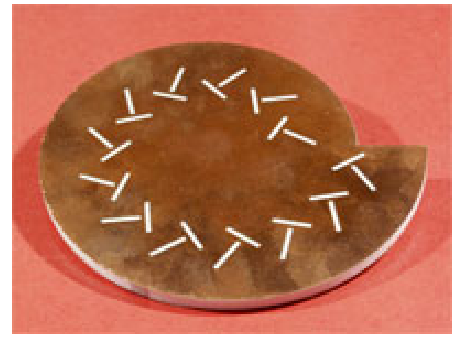
Plasmonic antennas – The microwave antenna gallery

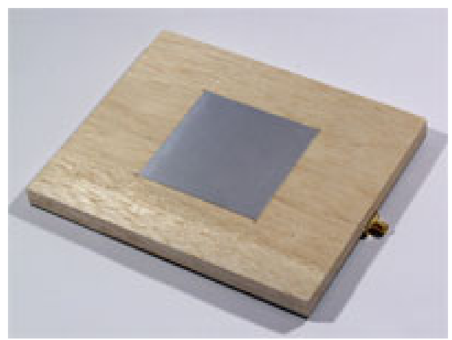
Dipolar

Fractal

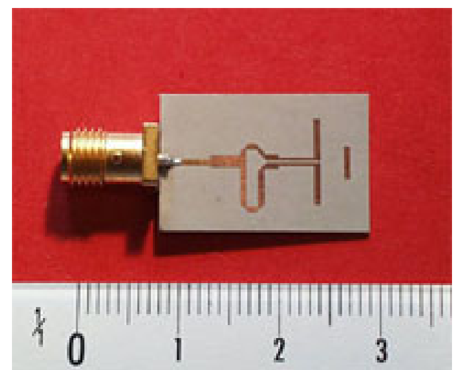


Radial line slots

Coplanar-fed slot bowtie



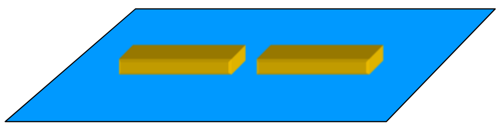
Patch



Printed Yagi

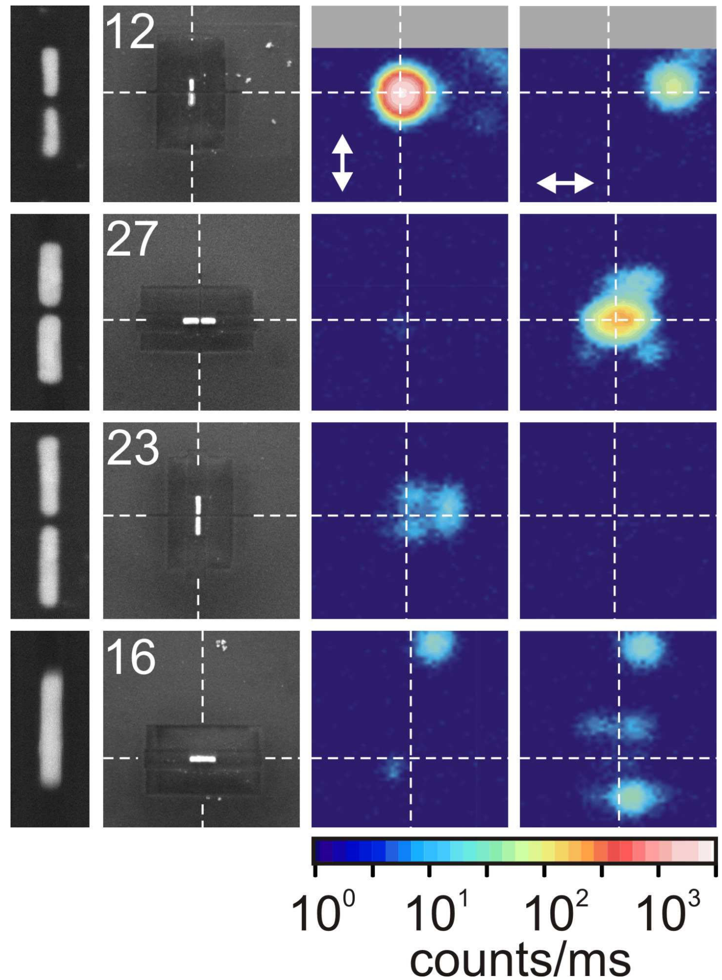
Electromagnetics laboratory EPFL

Plasmonic antennas – The dipole antenna



Focused ion beam fabrication:

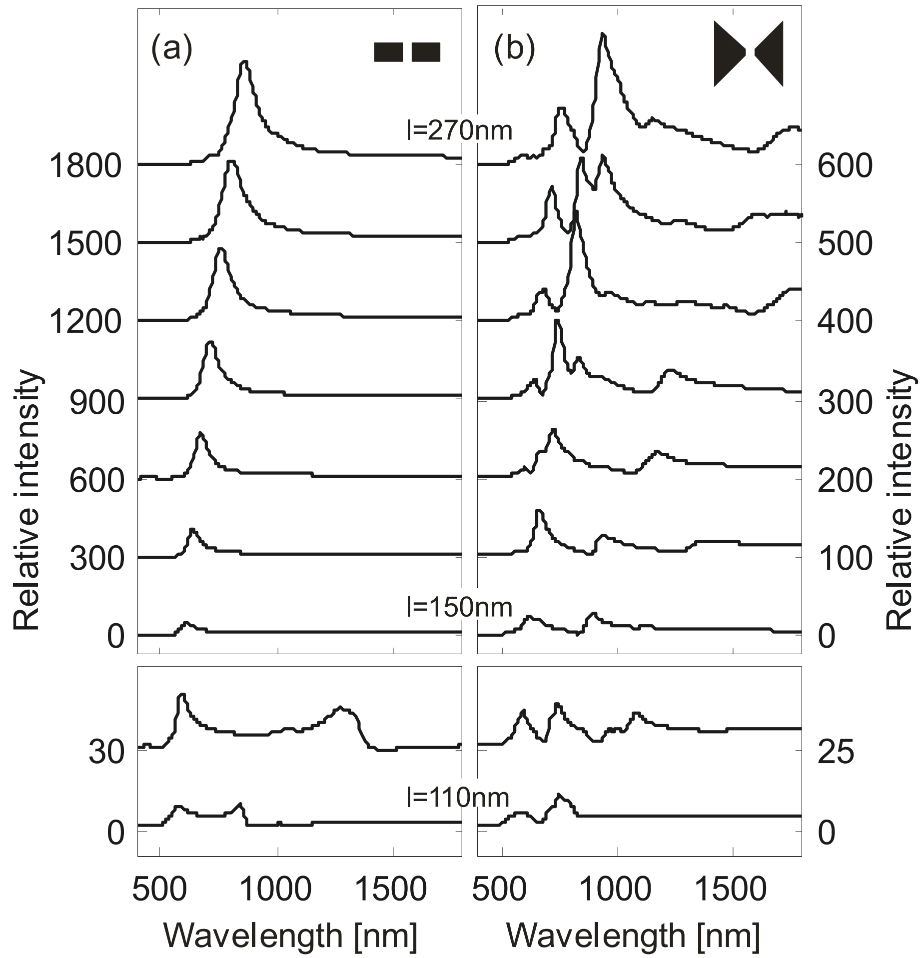
- 40nm thick gold
- Length: 190…400nm
- Width: 45nm
- Gap: 20nm
- Glass substrate



F. Mühlschlegel et al. Science vol. 308, p. 1607 (2005)

The dipole antenna – Tuning properties

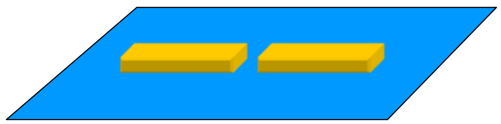
- Excellent tunability
- The bowtie antenna has multiple resonances

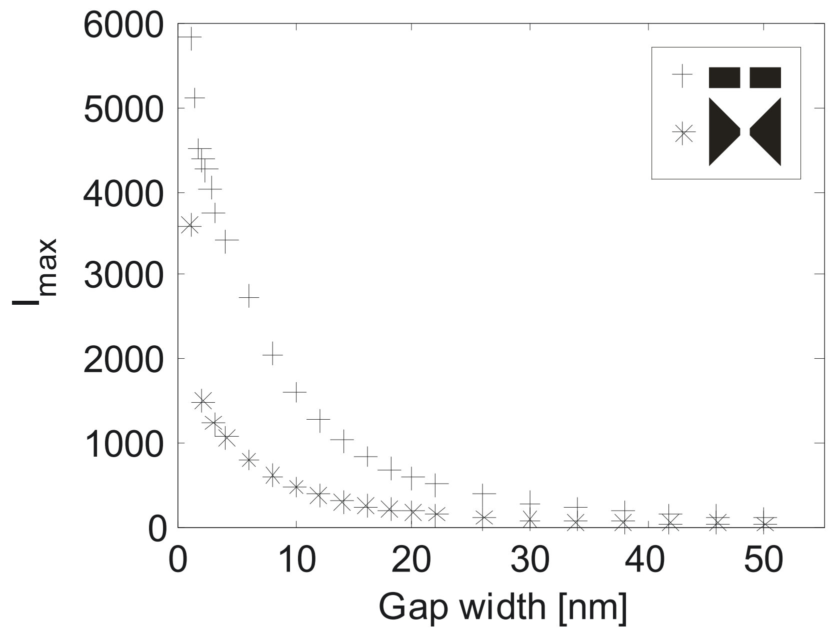


H. Fischer, Optics Express vol. 16, p. 9144 (2008)

The dipole antenna – Tuning properties

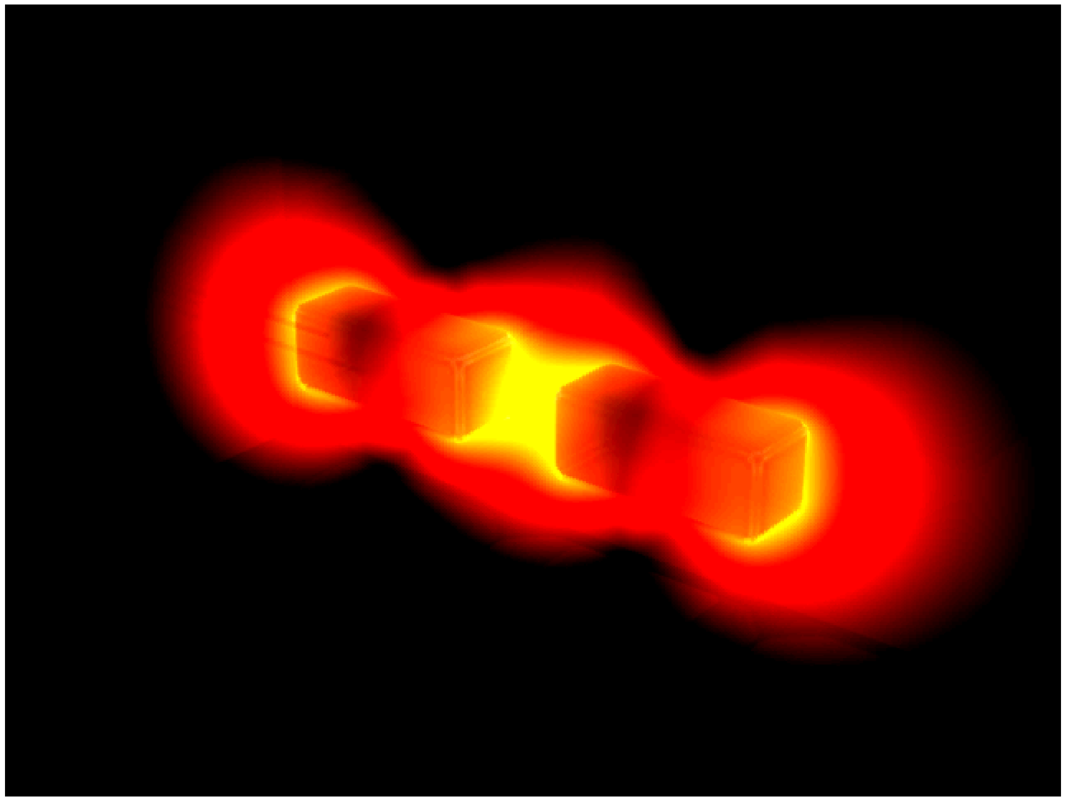
- The gap plays a crucial role for the field enhancement





H. Fischer, Optics Express vol. 16, p. 9144 (2008)

The dipole antenna – Field enhancement and localization



40x40x90 nm3 , gap=50...20 nm, λ=660 nm, in free space

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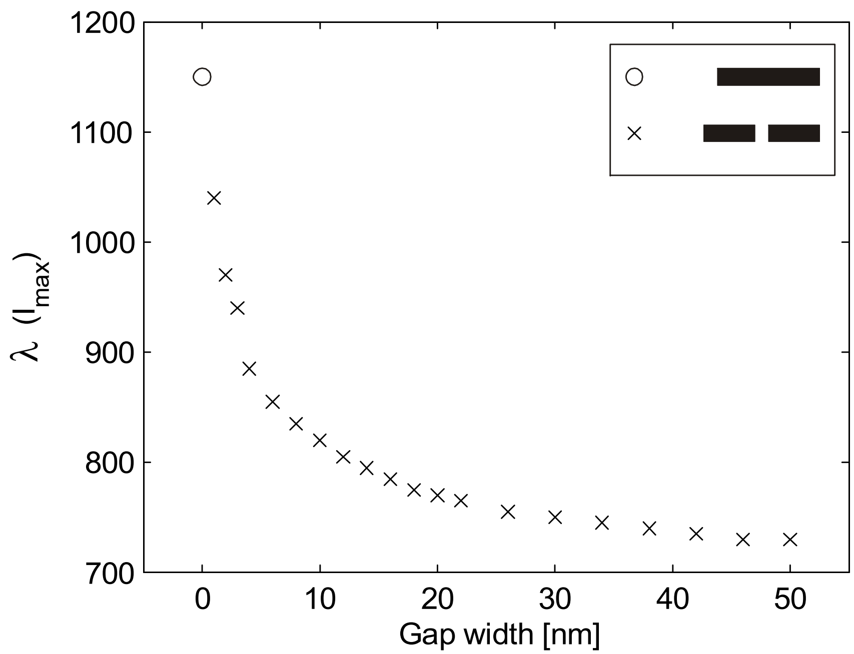
The dipole antenna – Role of the gap

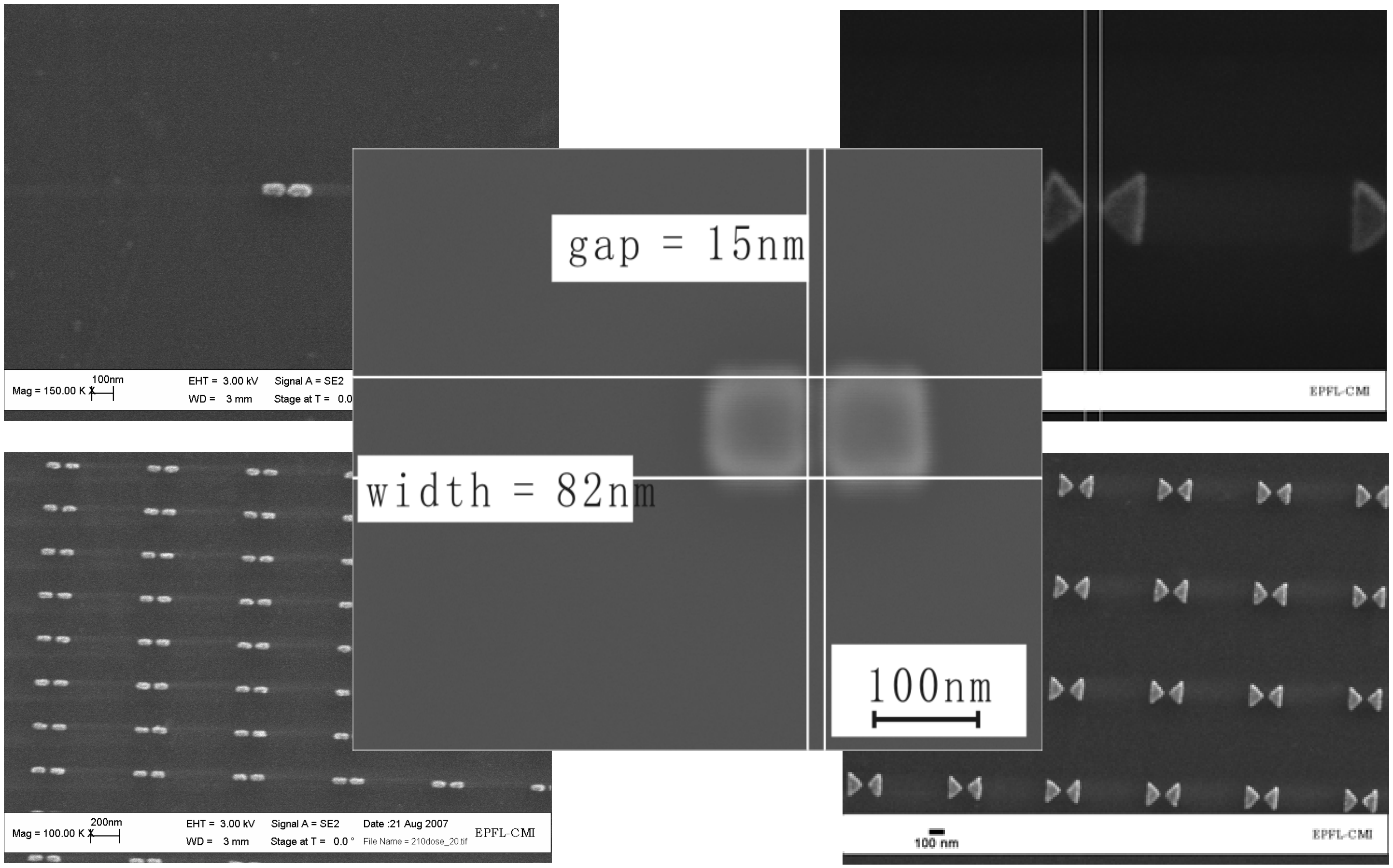
- The dipole antenna resonance frequency converges to that of the monopole "short-circuited" antenna



H. Fischer, Optics Express vol. 16, p. 9144 (2008)

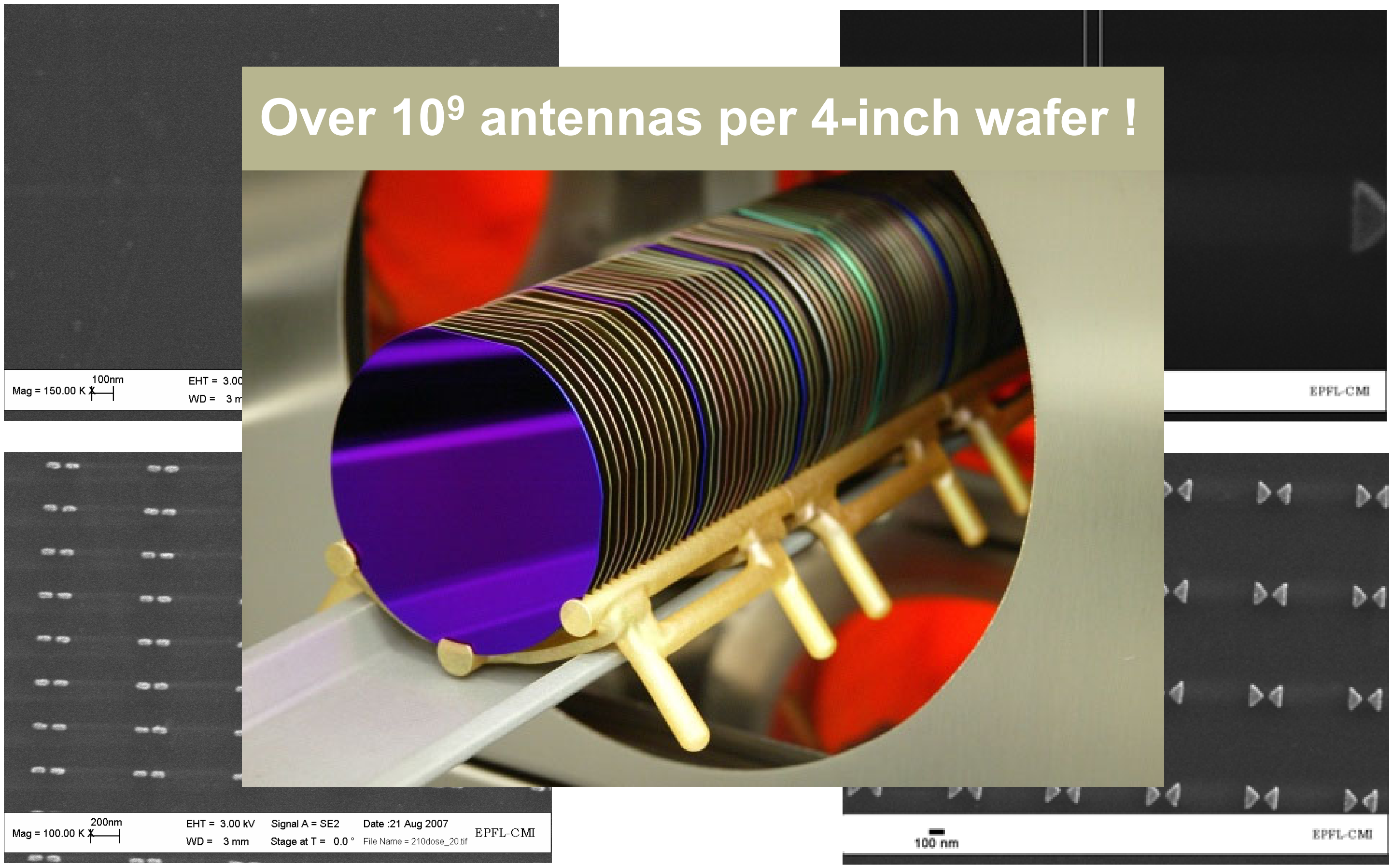
Top-down nanofabrication with e-beam

- Dipole antennas:
- Bowtie antennas:



Top-down nanofabrication with e-beam

- Dipole antennas:
- Bowtie antennas:



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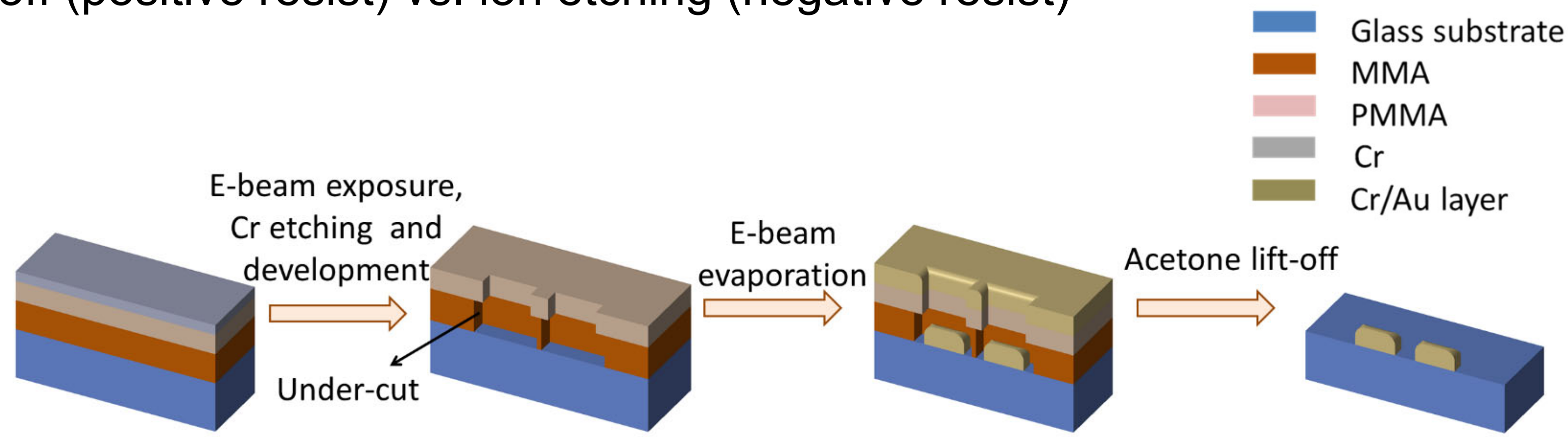
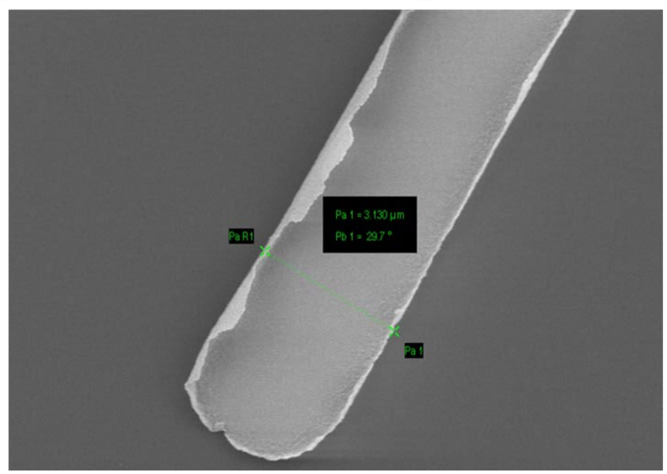
Top-down nanofabrication with e-beam

- Lift-off (positive resist) vs. ion etching (negative resist)

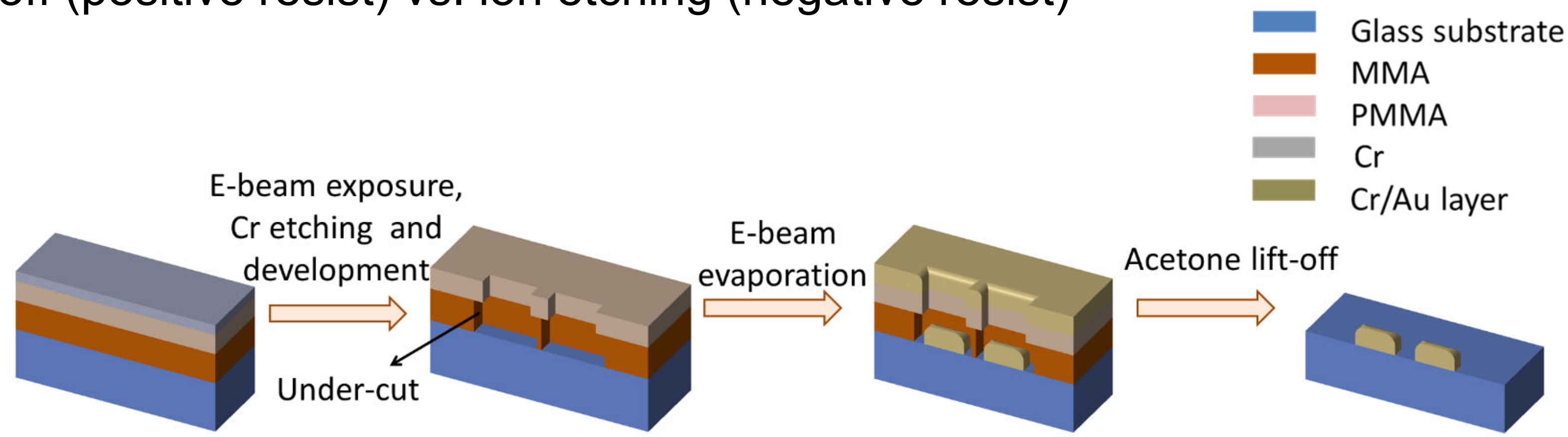


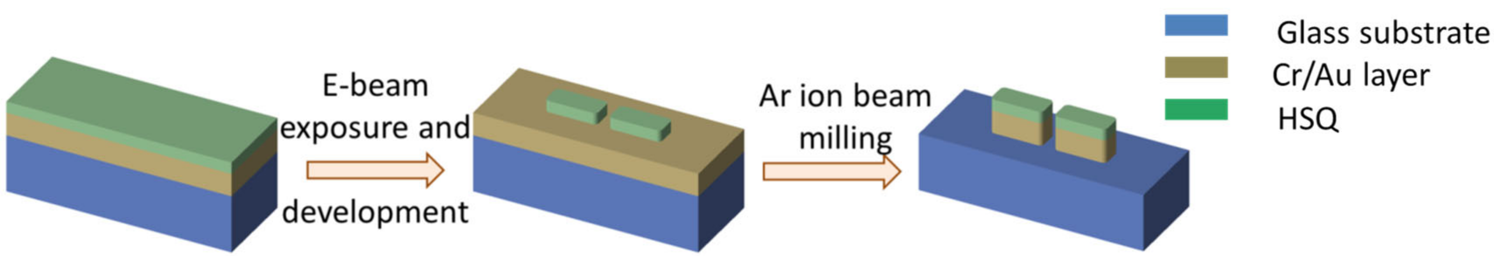


B. Abasahl, Nanotechnology vol. 32, p. 475202 (2021)

Top-down nanofabrication with e-beam

- Lift-off (positive resist) vs. ion etching (negative resist)

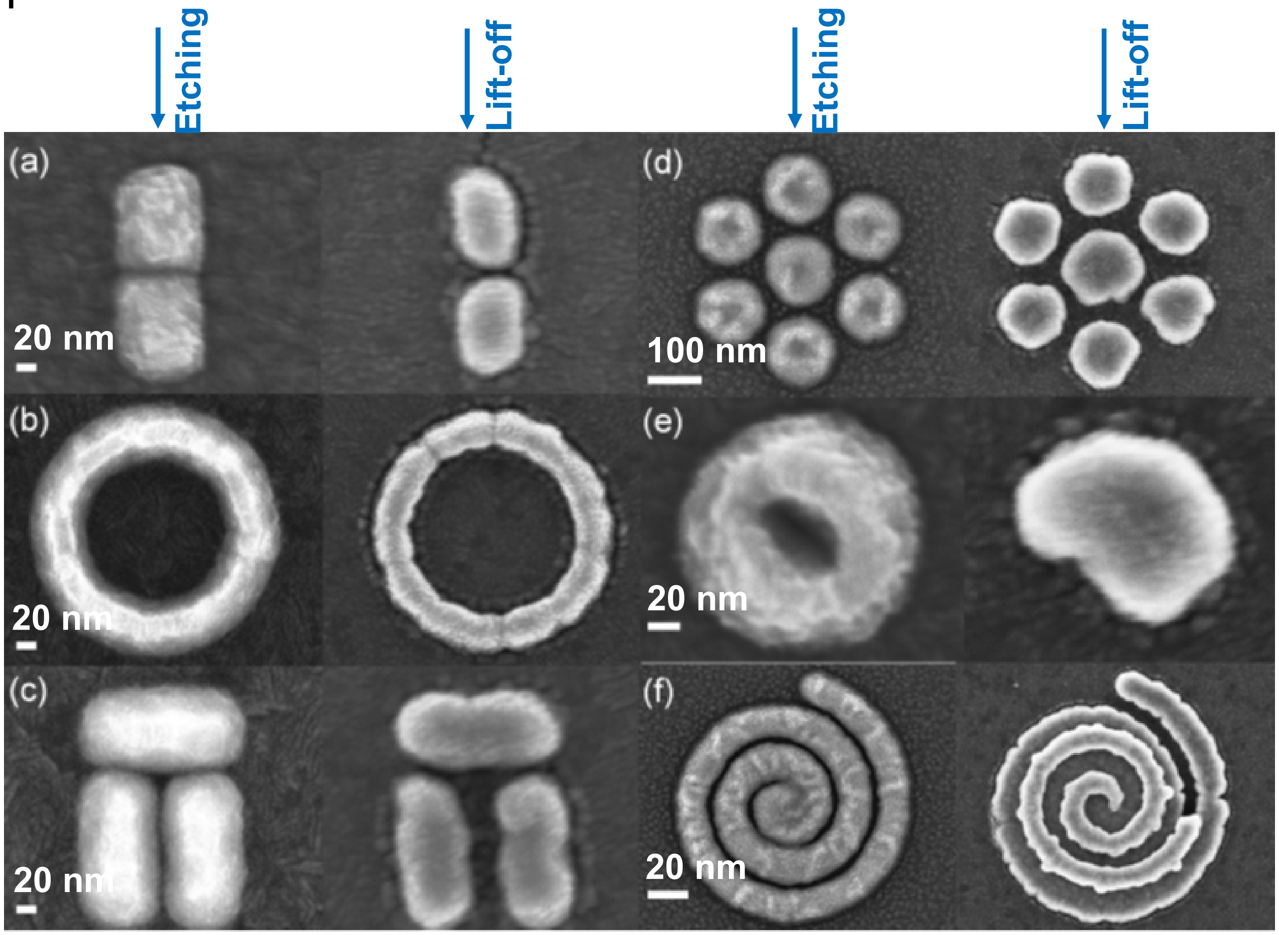




B. Abasahl, Nanotechnology vol. 32, p. 475202 (2021)

Top-down nanofabrication with e-beam

- Ion etching provides smaller features and better control

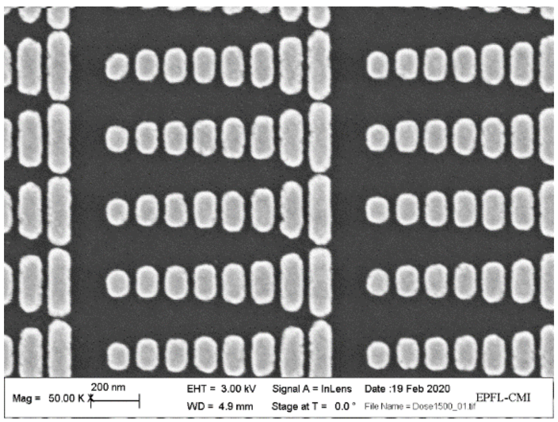


B. Abasahl, Nanotechnology vol. 32, p. 475202 (2021)

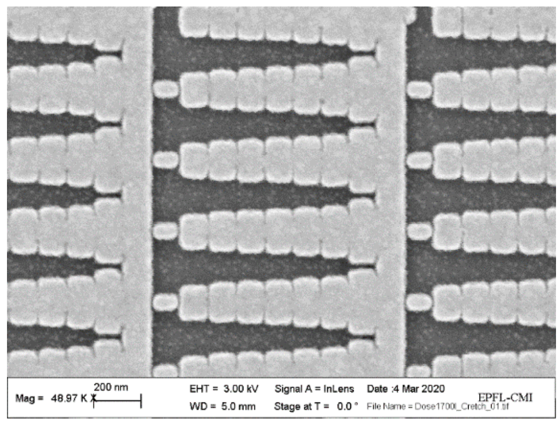
Dose test

- Both positive and negative resists require to perform a series of tests with different doses (for each sample geometry)

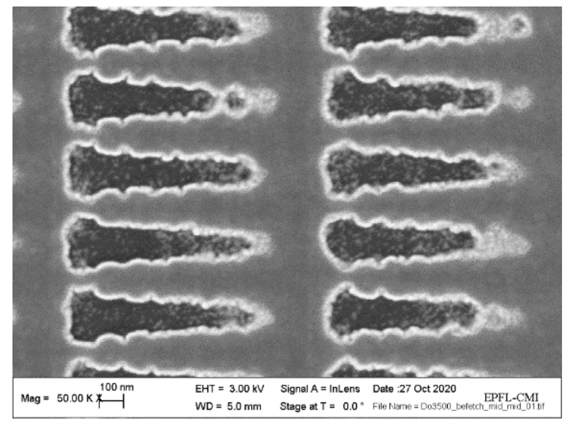
1'500 μC/cm^2



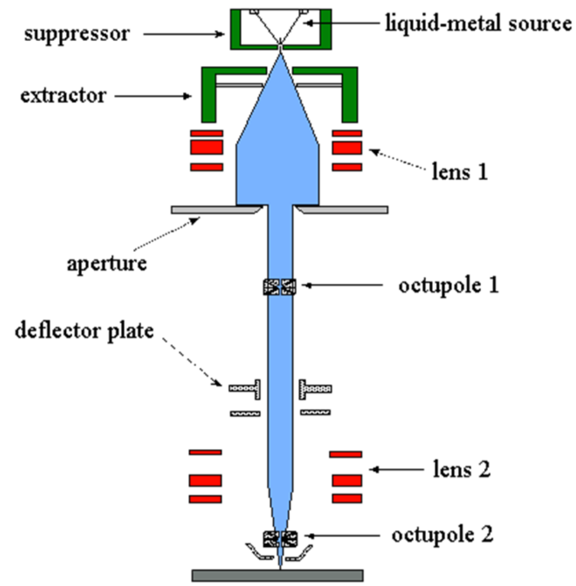
1'700 μC/cm^2

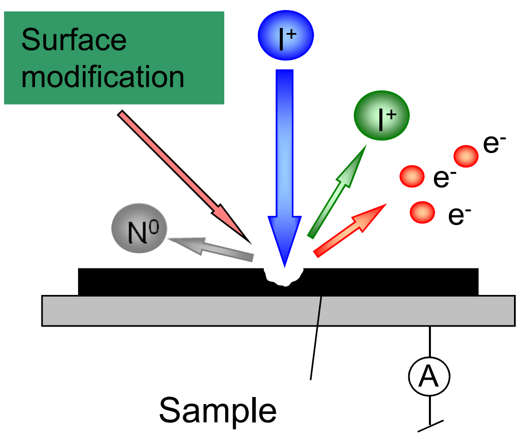


3'500 μC/cm^2



Top-down nanofabrication with focused ion beam (FIB)





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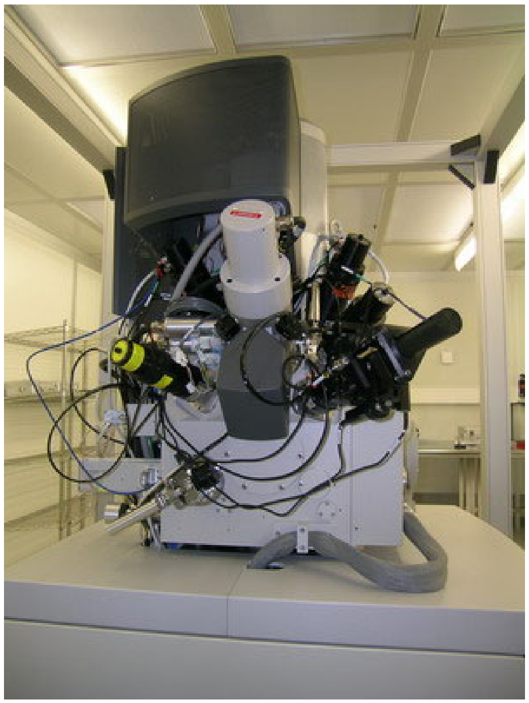
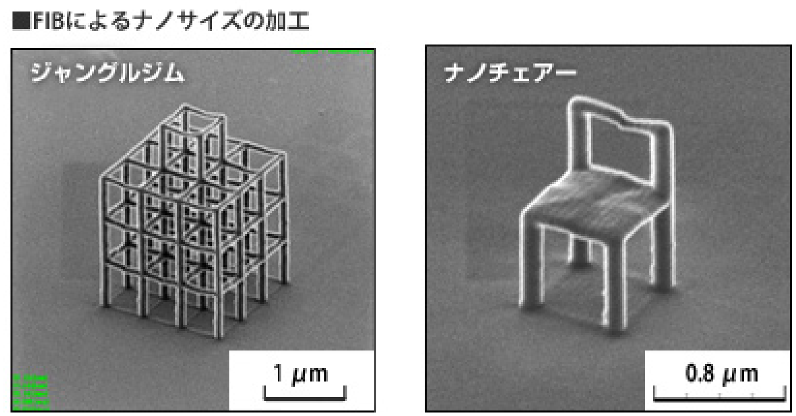
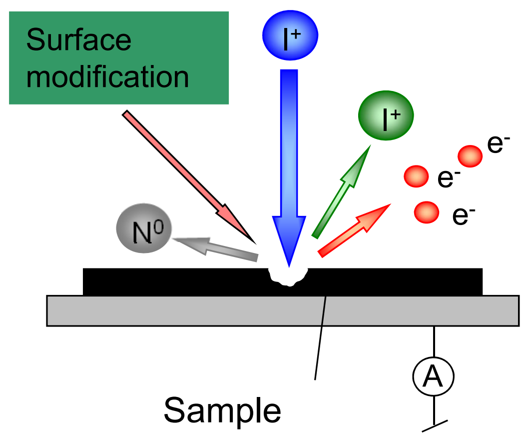
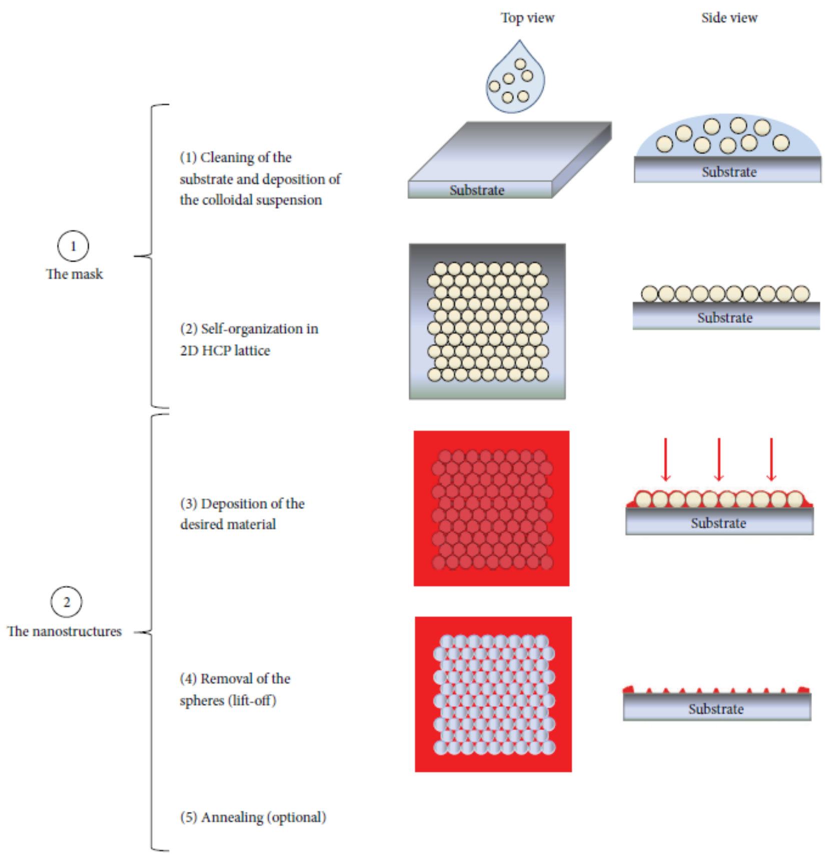
Top-down nanofabrication with focused ion beam (FIB)

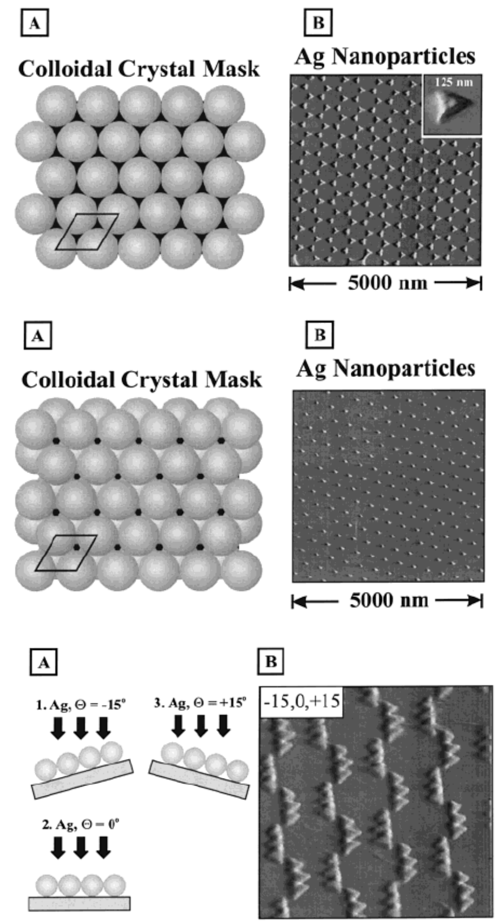






Top-down nanofabrication with colloidal lithography





P. Colson, J. Nanomaterials, vol. 2013, p. 948510 (2013)
C.L. Haynes, J. Phys. Chem. B vol. 105, p. 5599 (2001)

Selected Topics in Advanced Optics

Week 5 – part 5

Olivier J.F. Martin
Nanophotonics and Metrology Laboratory

EPFL

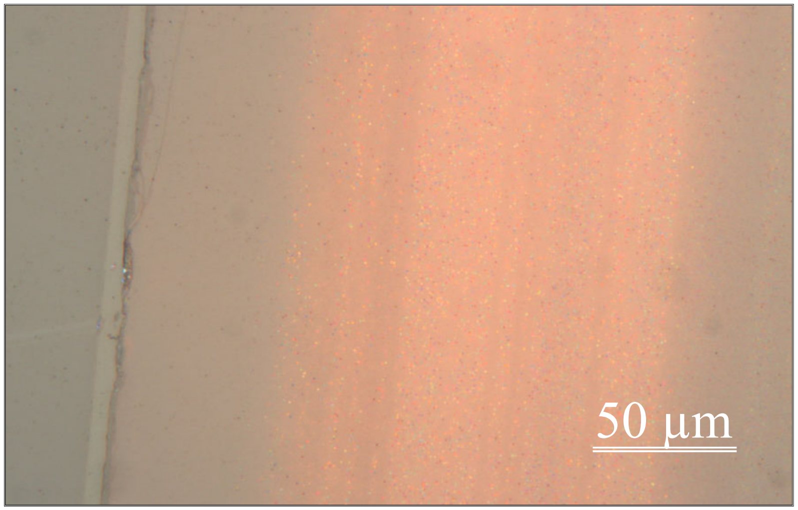
Medieval stained-glass windows

Stained-glass window
ca 1480

Ulm minster
built from 1377
wikipedia

Olivier J.F. Martin

Medieval stained-glass windows

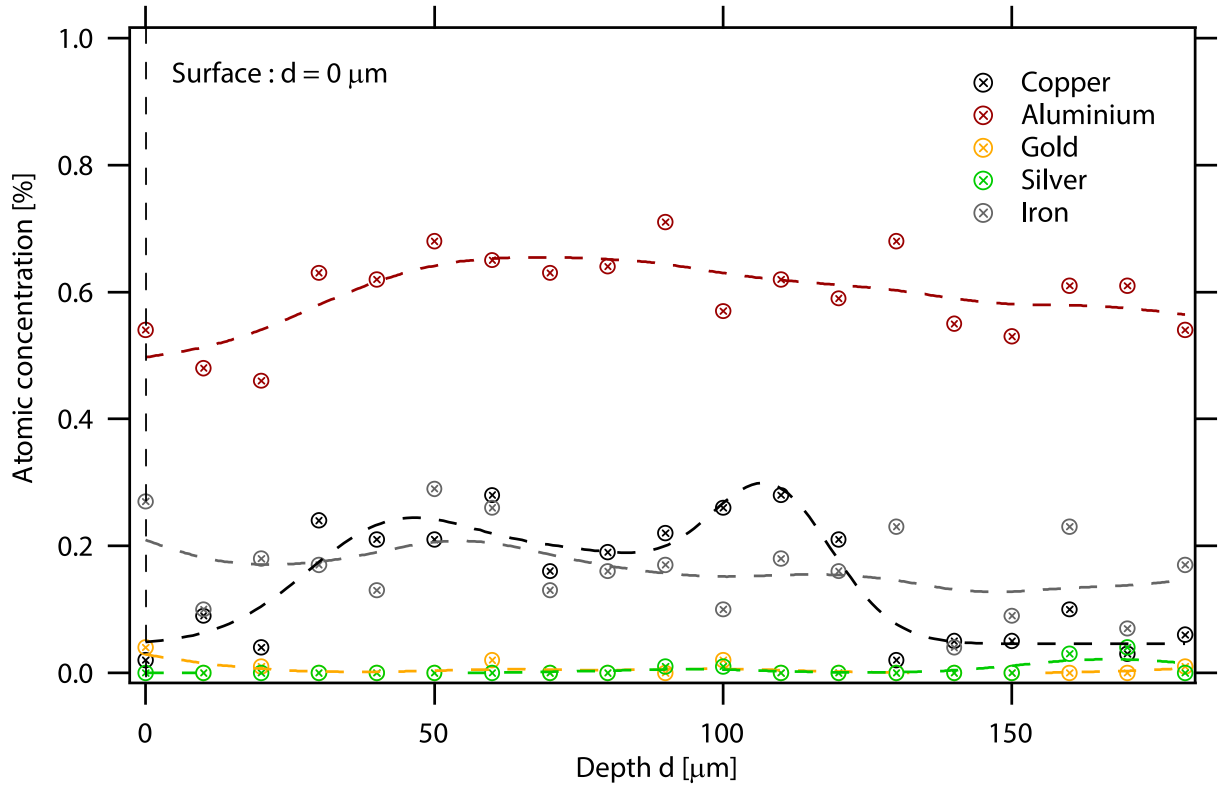


Colored layer, approx. 150 µm

Interfacial layer, approx. 65 µm

Glue

Medieval stained-glass windows



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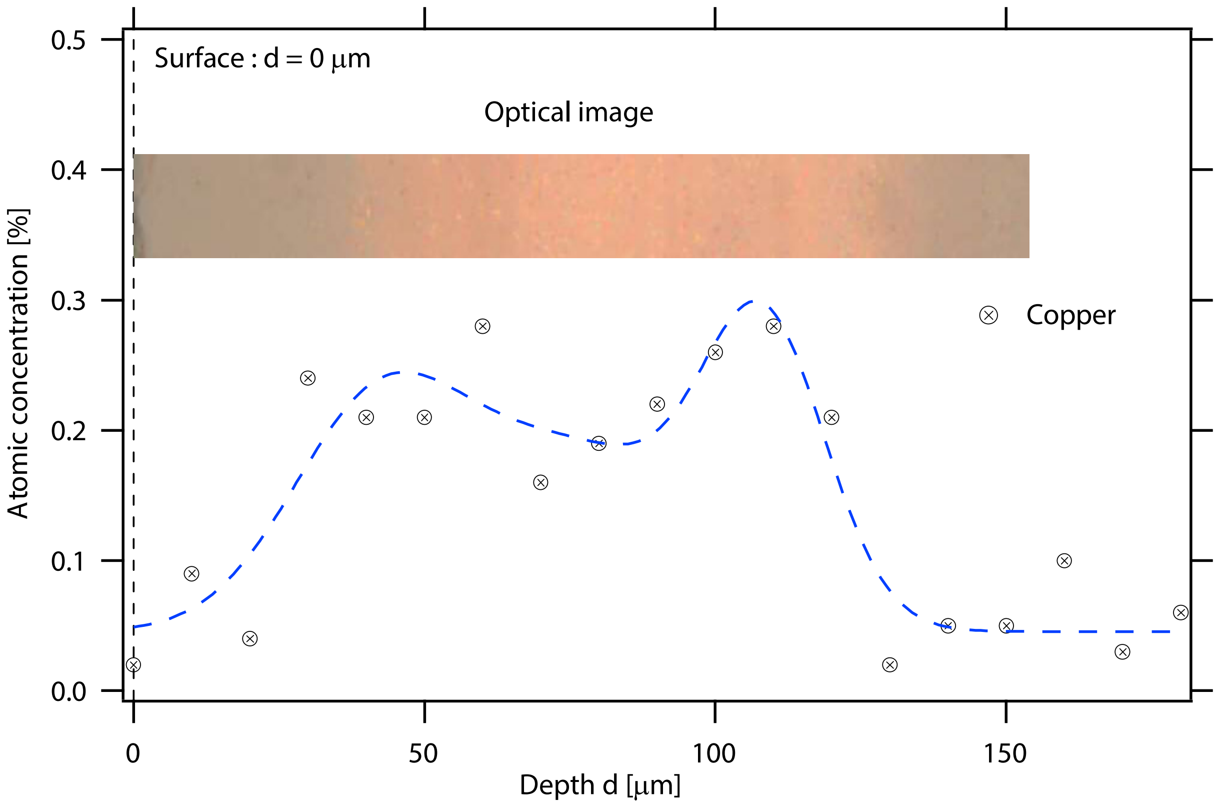
Medieval stained-glass windows



Cu particles: – size: 63 nm ± 15 nm

– density: 0.38 μm^{-3}

– average distance between particles 3.6 μm