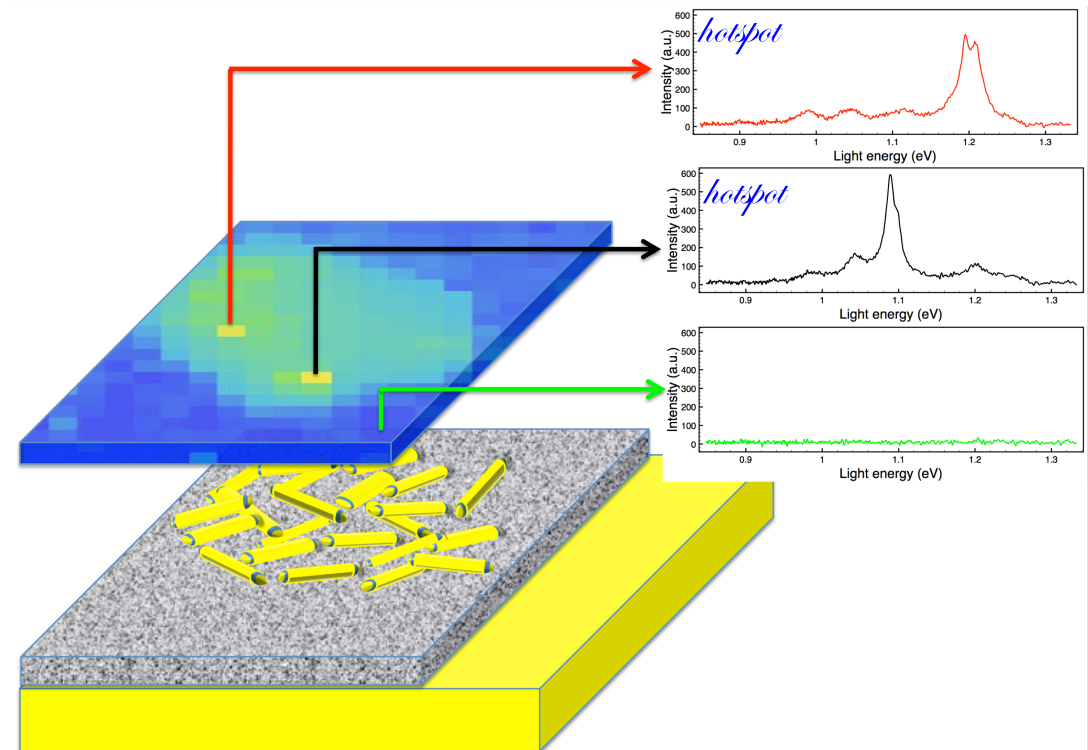


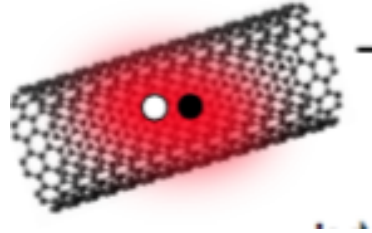
Enhancing carbon-nanotubes luminescence With the help of resonant hotspots

E. Rousseau
C. Beaufils
G. Cassabois

*Laboratoire Charles Coulomb
CNRS- Université de Montpellier
FRANCE*



Carbon nanotubes

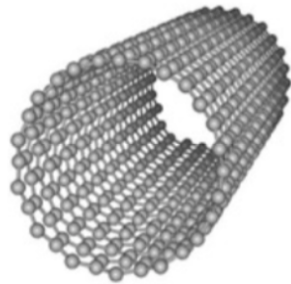


Well-defined exciton peak @ Room temperature

Telecom-window range : *wavelength* ~ 1200 nm

Small in diameter but quite long \rightarrow **single CNT**

(Can be excited by current injection)



CNT are attractive light source

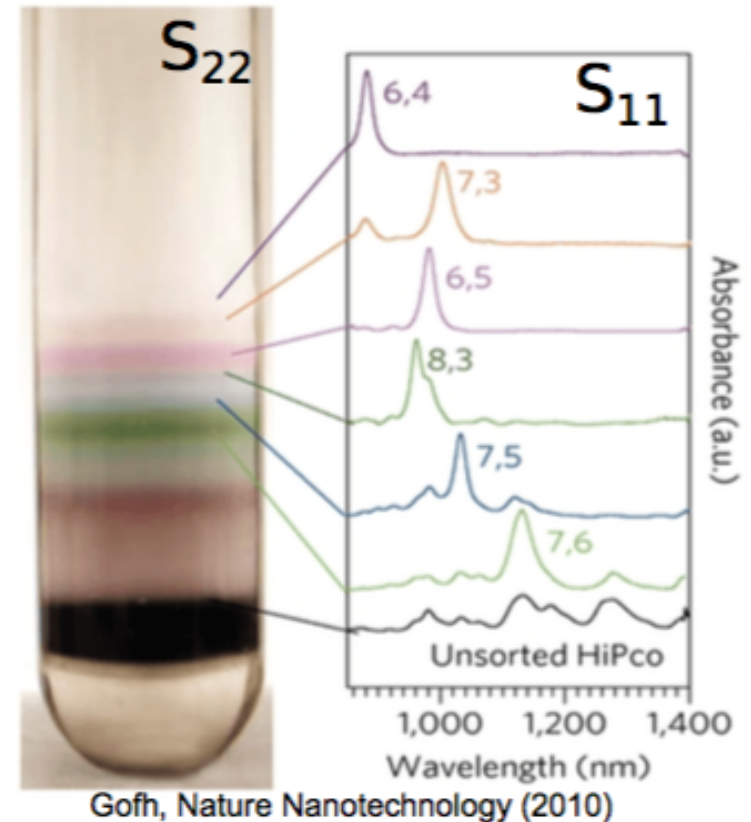
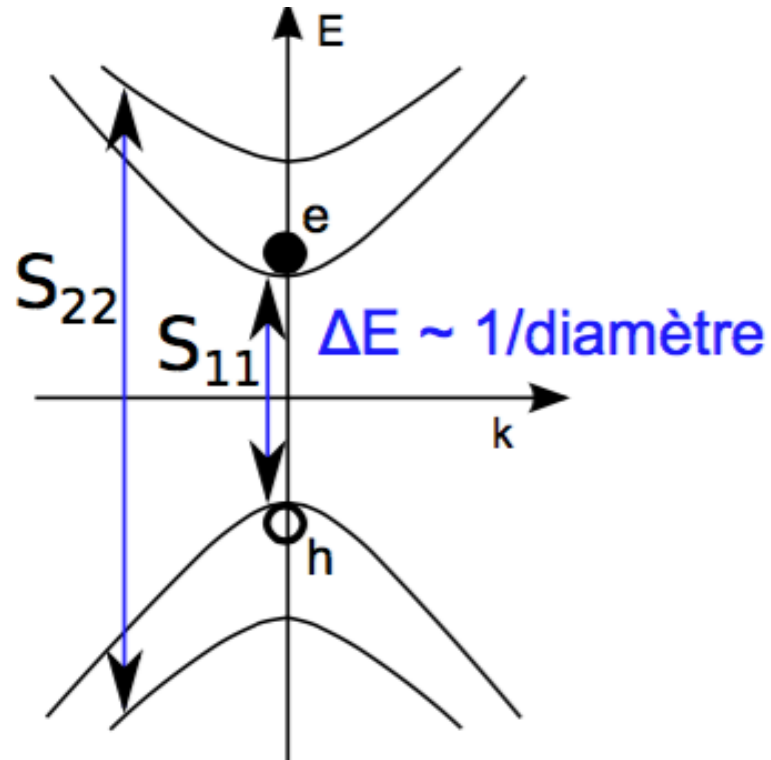
But...

with a very small quantum yield (less than 1%) !

Nanotube

$d \sim \text{nm}$

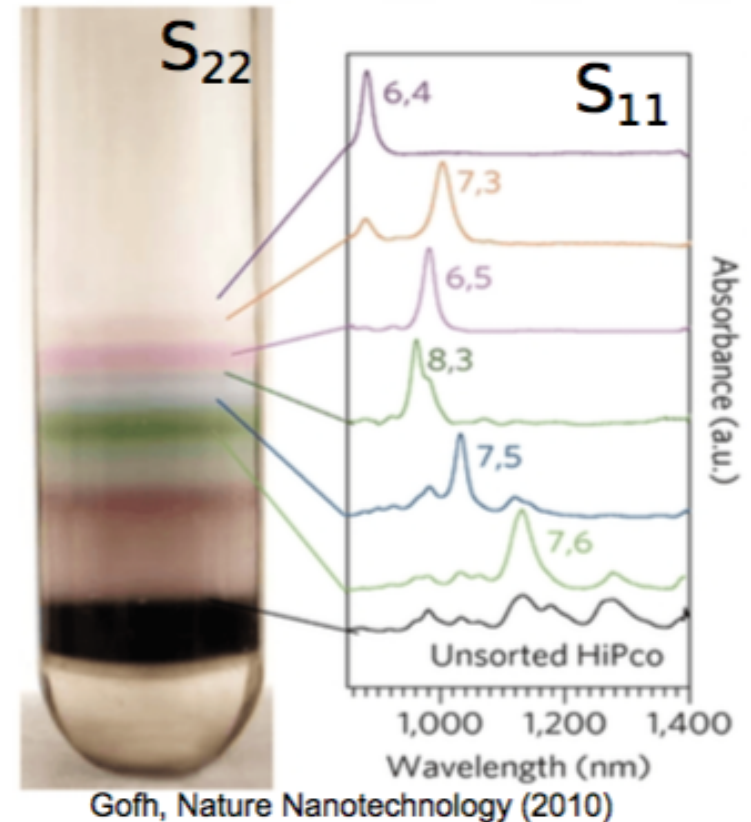
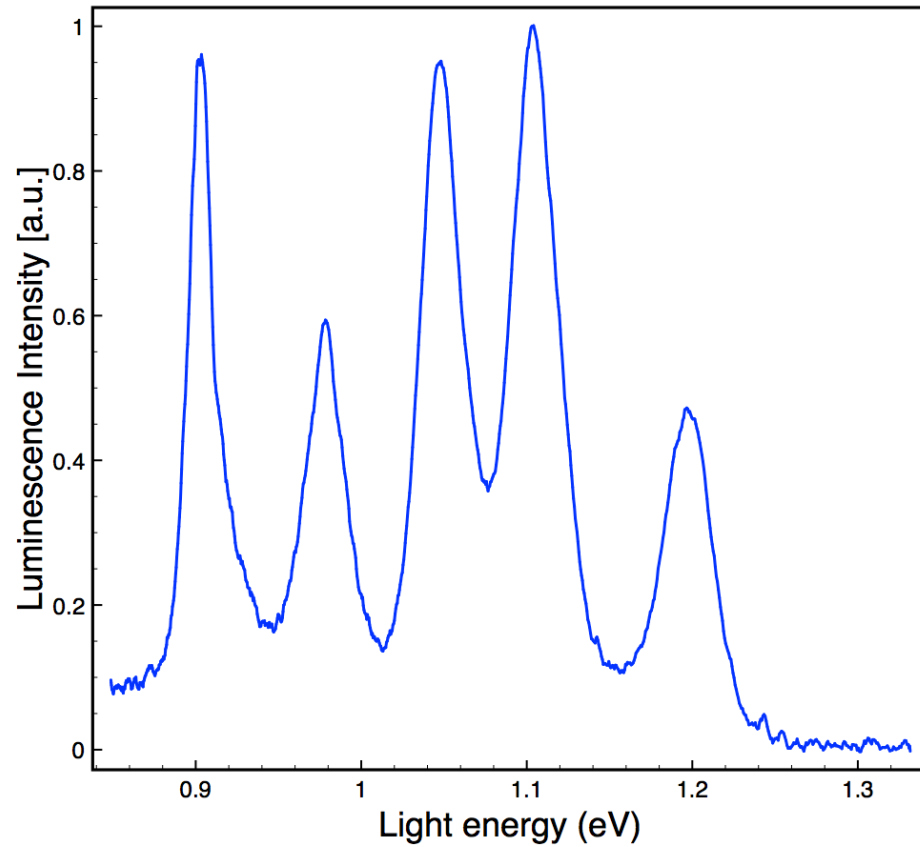
$L \sim \mu\text{m}$



Typically : in the sample 5 families of semiconducting carbon nanotubes

Characterized by a well-defined exciton peak

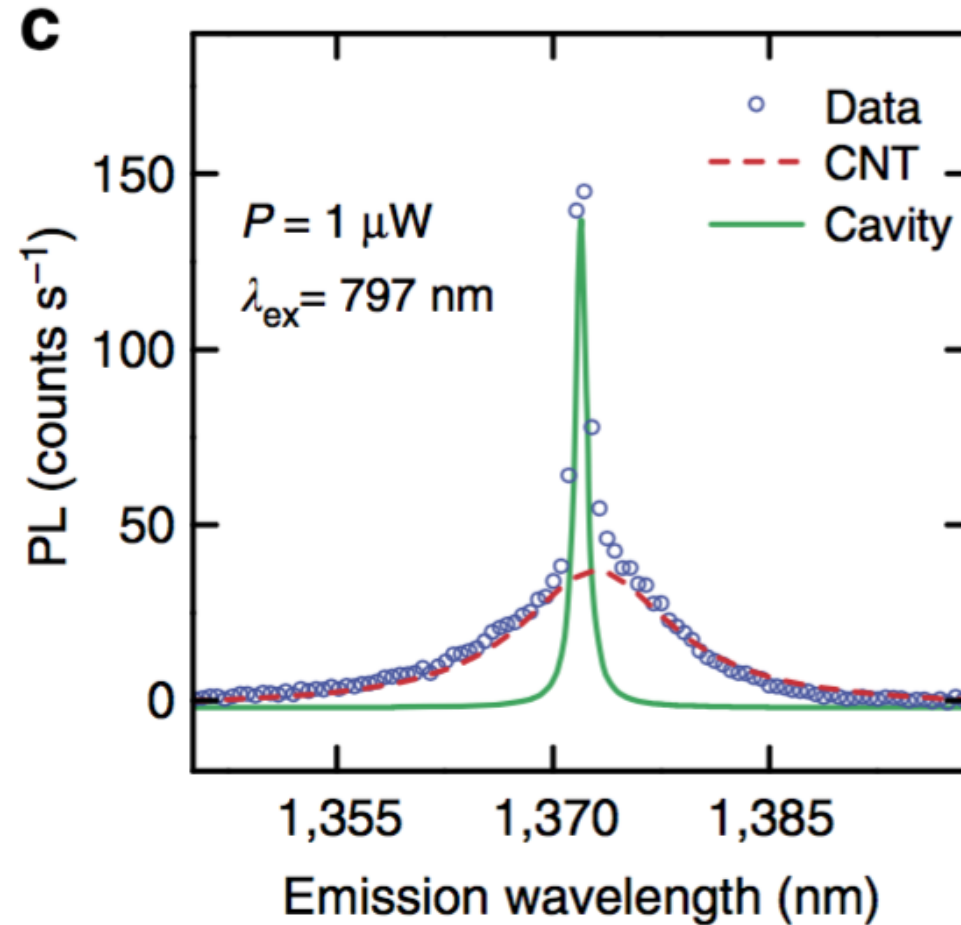
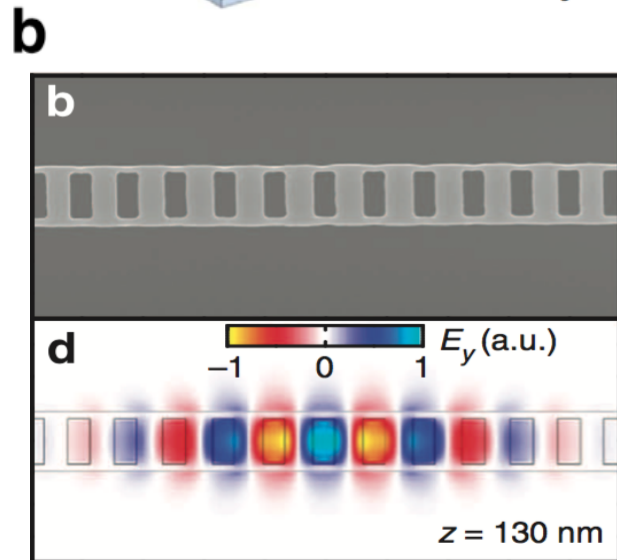
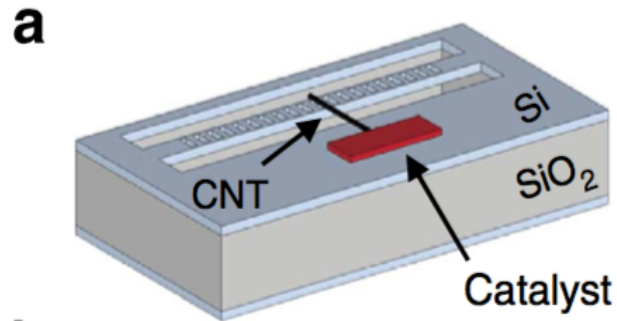
Carbon nanotubes



Typically : in the sample 5 families of semiconducting carbon nanotubes

Characterized by a well-defined exciton peak

Carbon nanotubes + photonics crystals



Radiative
Enhancement ~ 200

R. Miura et al.
Nature communications 6580 (2014)

Radiative Enhancement :

→ demonstration of the Purcell Effect

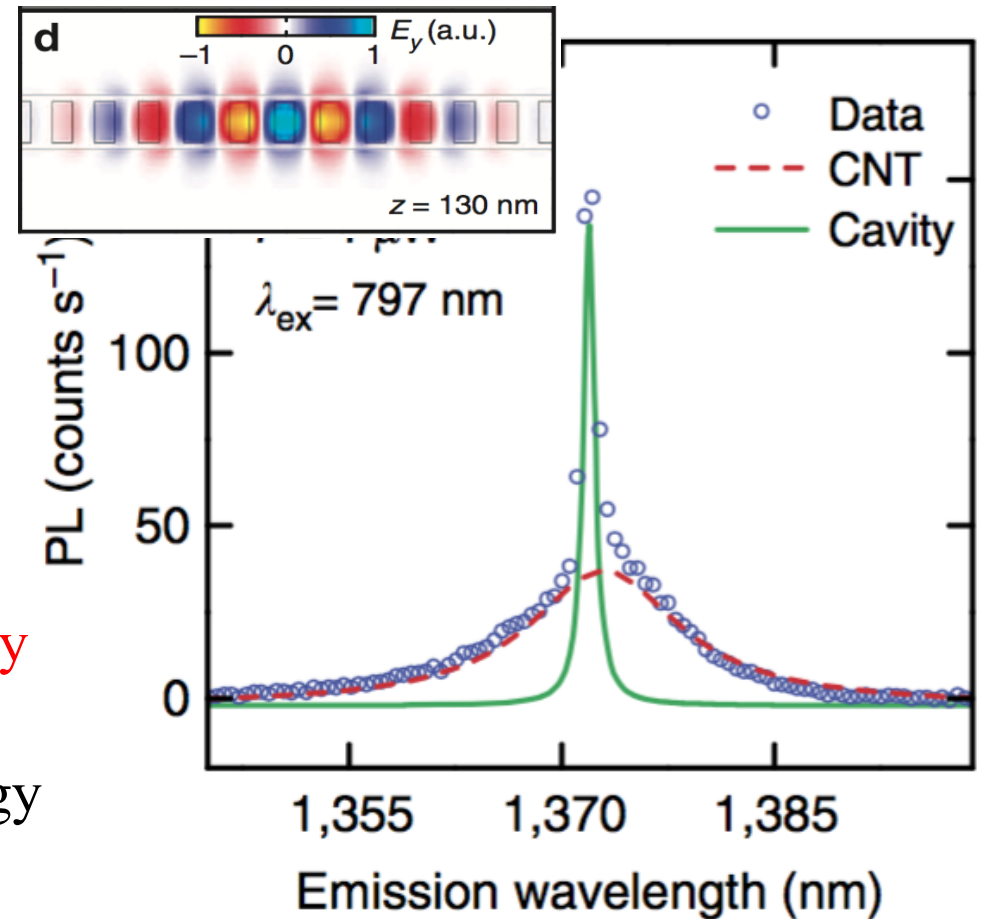
$$\Gamma = \frac{2\pi}{\hbar^2} | \langle 0 | - \vec{d} \cdot \vec{E} | 1 \rangle |^2 \rho(\vec{r}, \omega)$$

→ increased density of elect. states

$$\Gamma \propto \frac{Q}{V_m} \quad \text{Dielectric strategy}$$

$$\Gamma \propto \rho(\vec{r}, \omega) \quad \text{Plasmonic strategy}$$

$$\Gamma \propto |\vec{E}(\vec{r}, t)|^2 \quad \text{Hotspots strategy}$$



R. Miura et al.

Nature communications 6580 (2014)

Carbon nanotubes + metallic rough surface

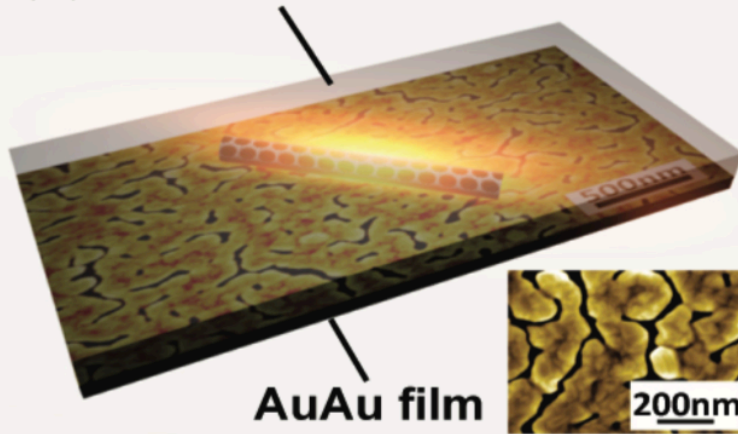
Hotspots strategy

Metal-Enhanced Fluorescence of Carbon Nanotubes

Hong et al.

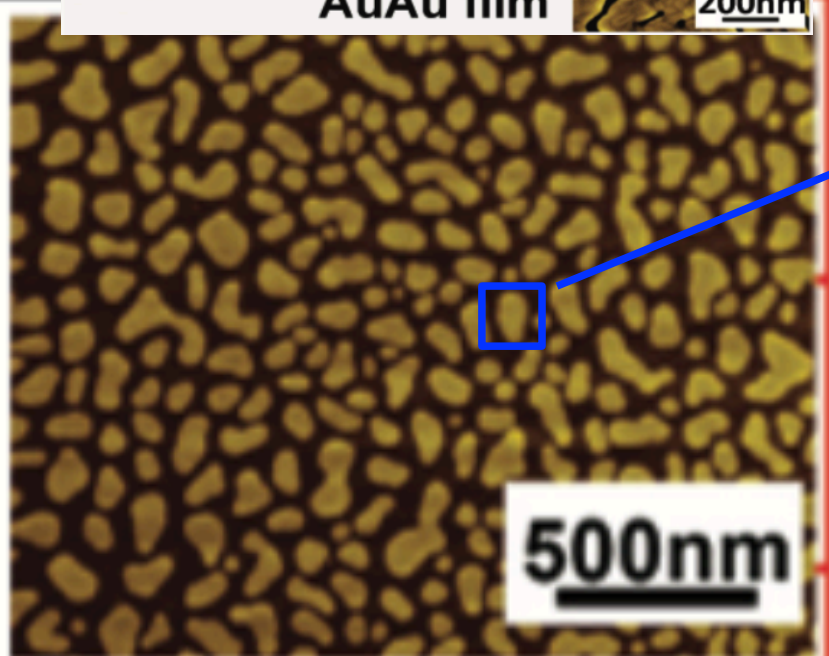
Journal of the American Chemical Society
(2010), 132 15920-15923

(b) SWNT in polymer film



AuAu film

200nm



Elementary cell:
Gold island (random shape)

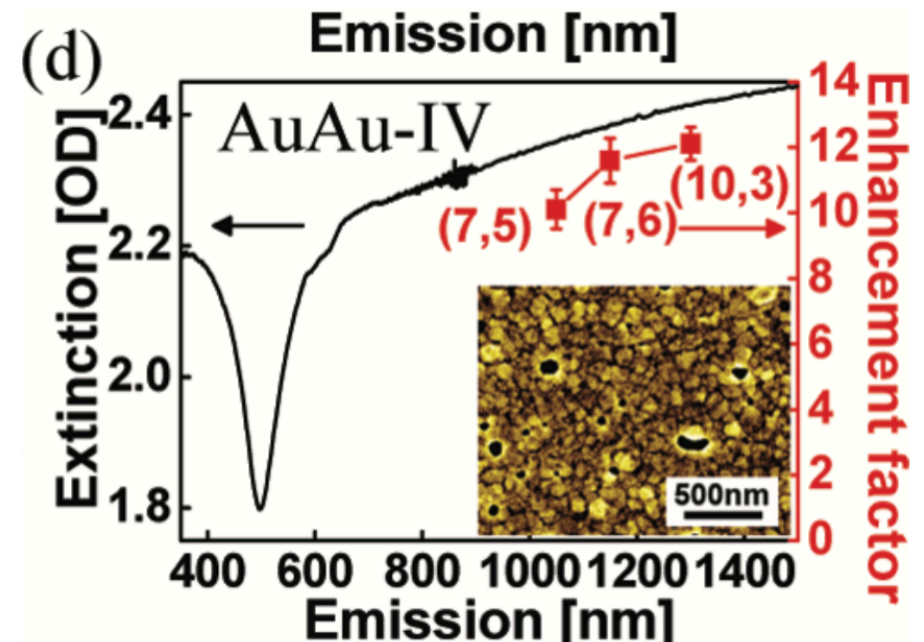
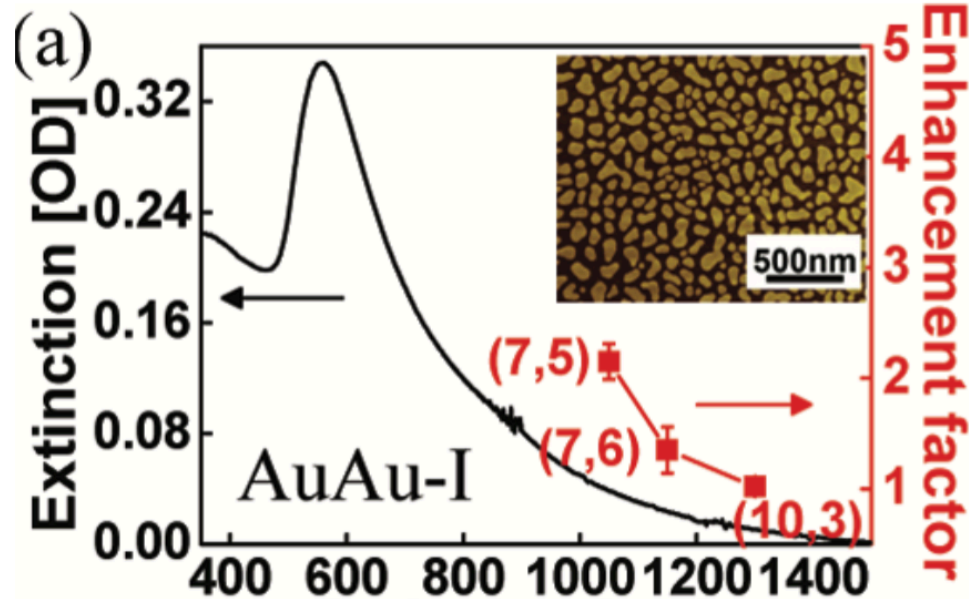
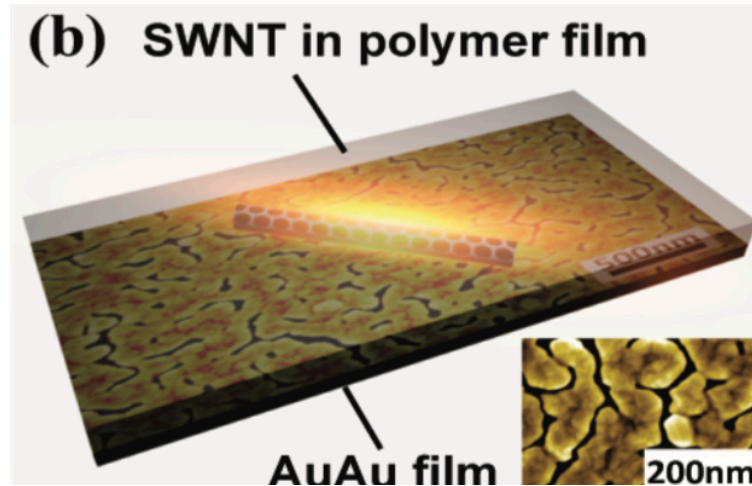
Carbon nanotubes + metallic rough surface

Hotspots strategy

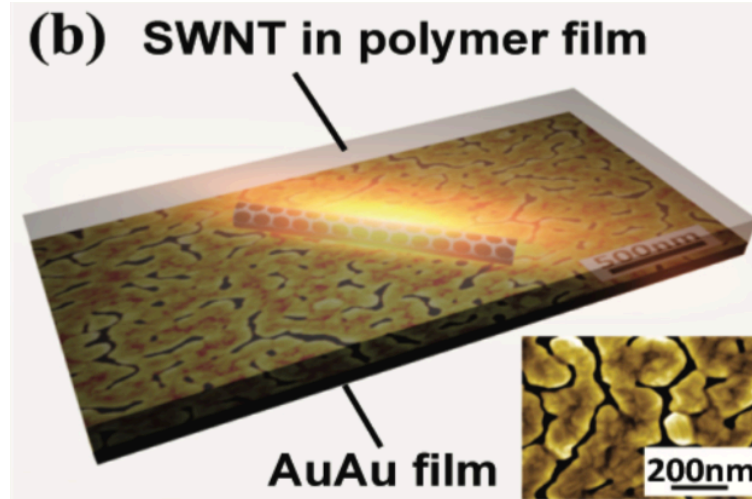
Metal-Enhanced Fluorescence of Carbon Nanotubes

Hong et al.

Journal of the American Chemical Society
(2010), 132 15920-15923



Carbon nanotubes + metallic rough surface



Metal-Enhanced Fluorescence of Carbon Nanotubes
 Hong et al.
 Journal of the American Chemical Society
 (2010), 132 15920-15923

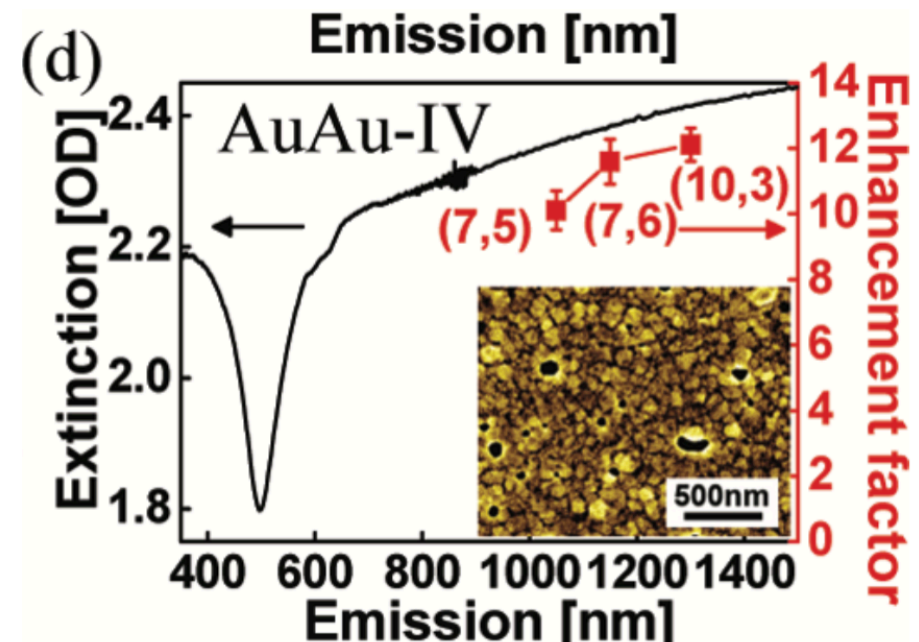
Larger enhancement:

~ 10-fold

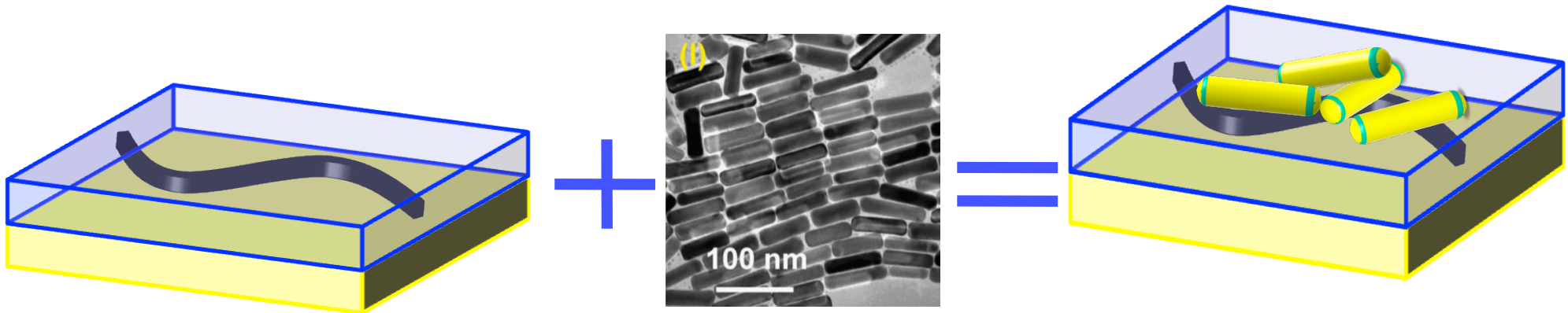
More dense rough surface

No spacer

No modifications of CNT spectrum



Carbon nanotubes + plasmonic antennas



Few carbon nanotubes
(1 single)
Quantum emitter

Collection of
gold nanorods

Luminescence
Enhancement?

Field of plasmonics (optics of metals)

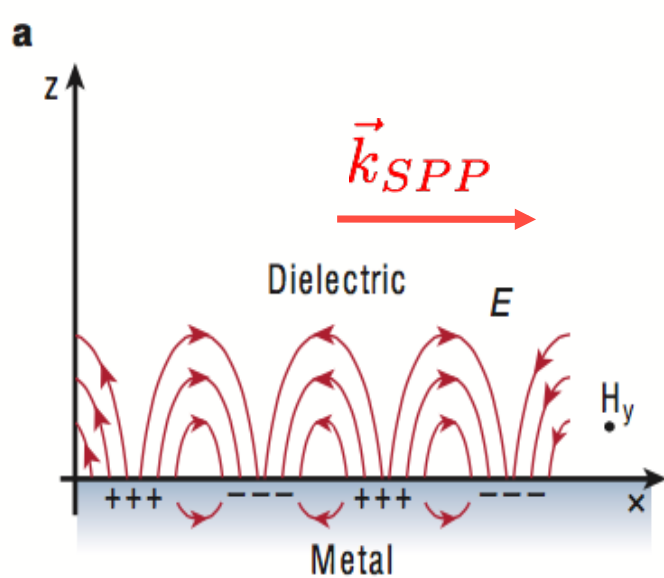
Purcell effect : how environment modify quantum emitter luminescence

Hotspots + plasmonics strategies?

Broad-band enhancement: for the 5 chiralities

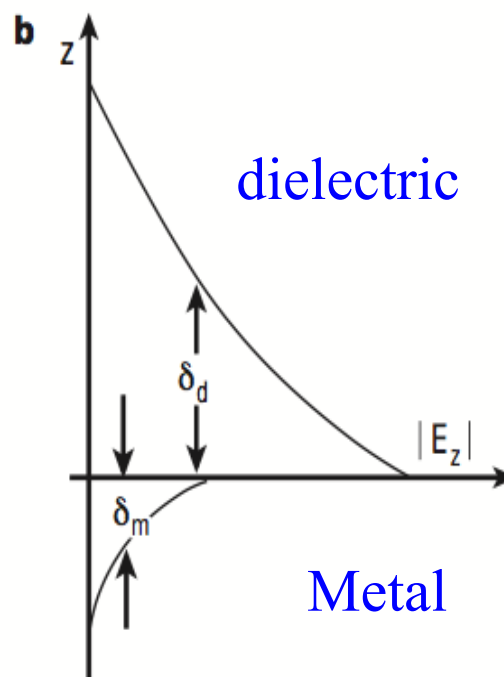
Plasmonics and plasmonics antennas

Surface Plasmon Resonance = high density of e.m. states



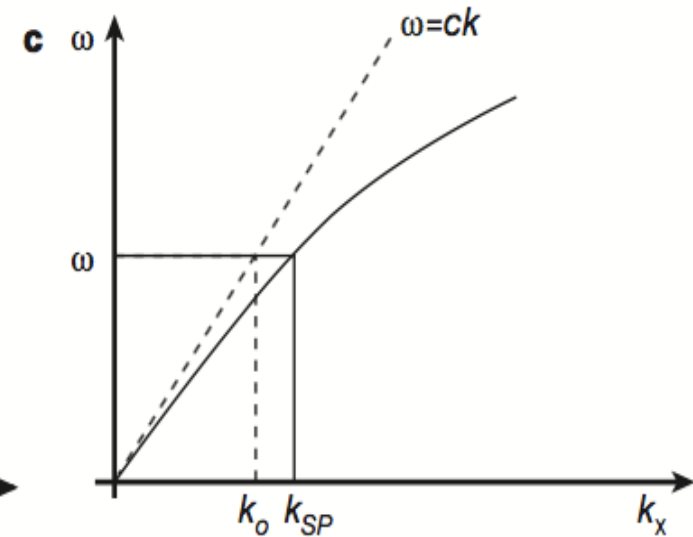
Charge density :

E perpendicular component
Surface wave: resonant mode
Propagation along the metallic plane



Evanescent field :

Exponential decrease
from the metallic interface
Field confinement

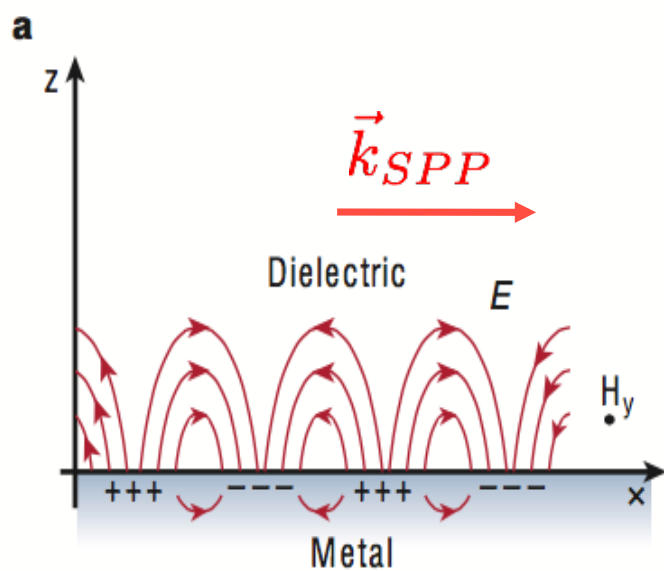


Dispersion relation :

Below light cone
Non-radiating mode

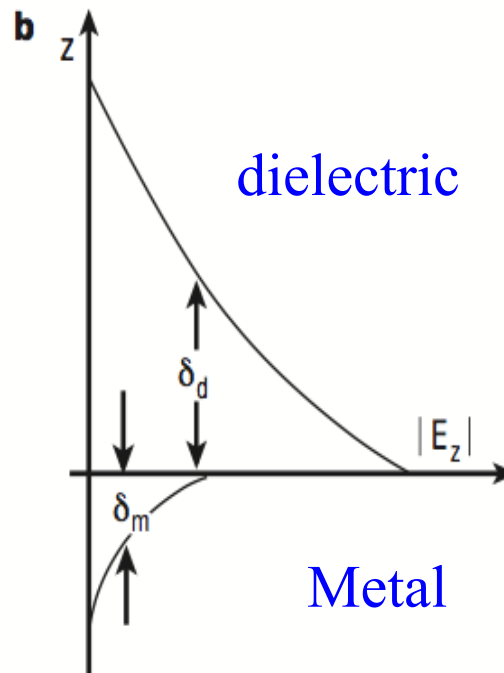
Plasmonics and plasmonics antennas

Surface Plasmon Resonance = high density of e.m. states



Propagating waves :

Typical modal volume $\sim \lambda^3$

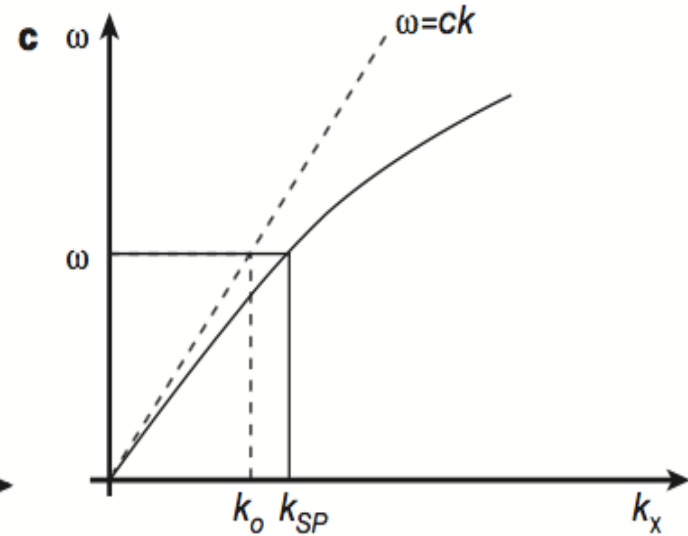


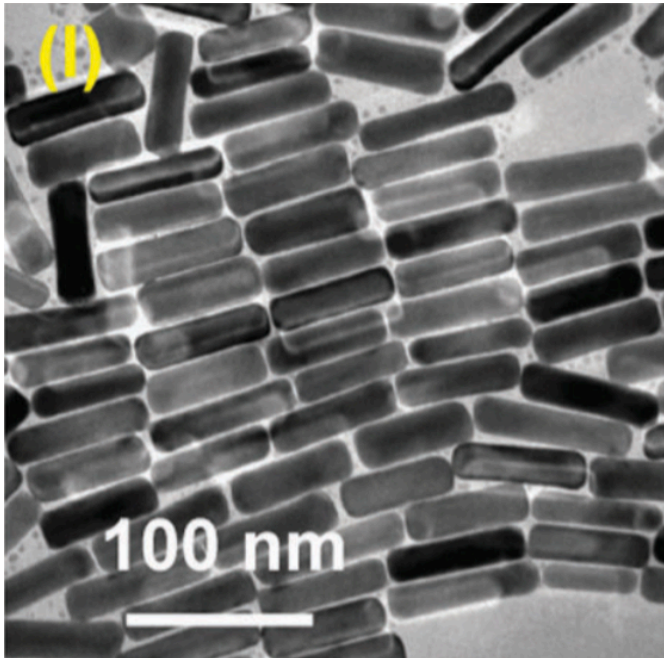
Evanescent field :

Typical modal volume: Not limited by diffraction
=> Large density of e.m. states

Given by the geometry

Can be very small $\sim (10 \text{ nm})^3$





Metallic nanoparticles

Diffraction => Localized plasmon resonance

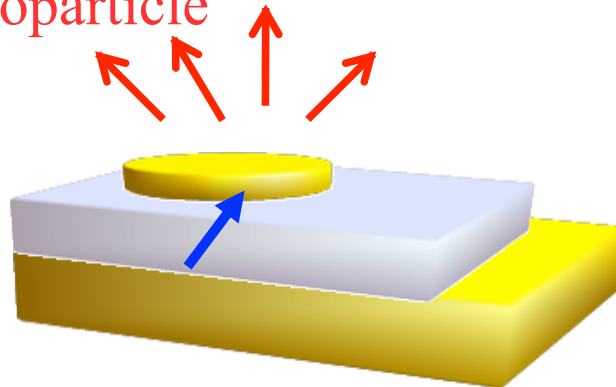
Can act as antennas in the visible regime :

-modify radiative pattern (directivity)

- modify luminescence intensity
(energy extraction, Purcell effect)

The plasmonic strategy: The patch antenna

metallic nanoparticle



Dielectric

metallic mirror

Bottom metallic mirror:

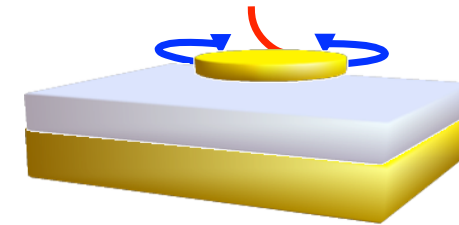
- Light emits in one direction
- Increase electric field confinement

Finite size metallic nanoparticle:

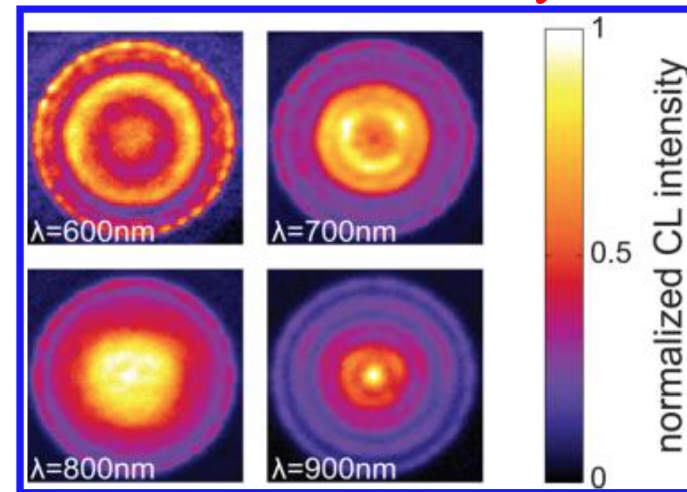
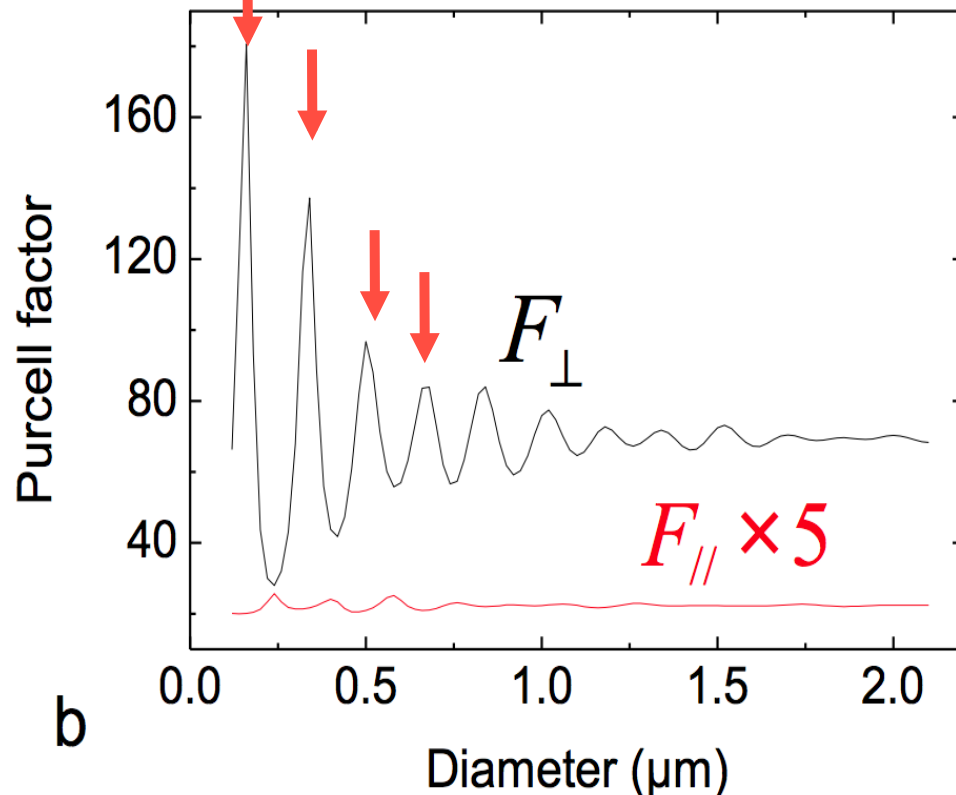
- scatter the near-field
- Can increase of the power radiates by the emitter

The plasmonic strategy: plasmonic cavity

modes



Resonances due to cavity modes

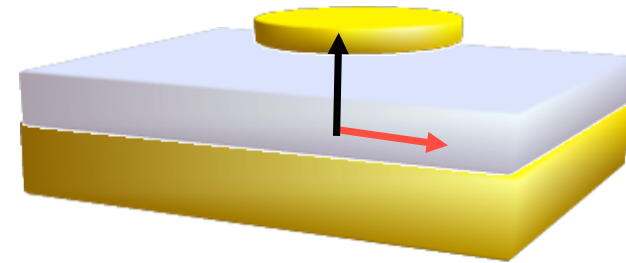
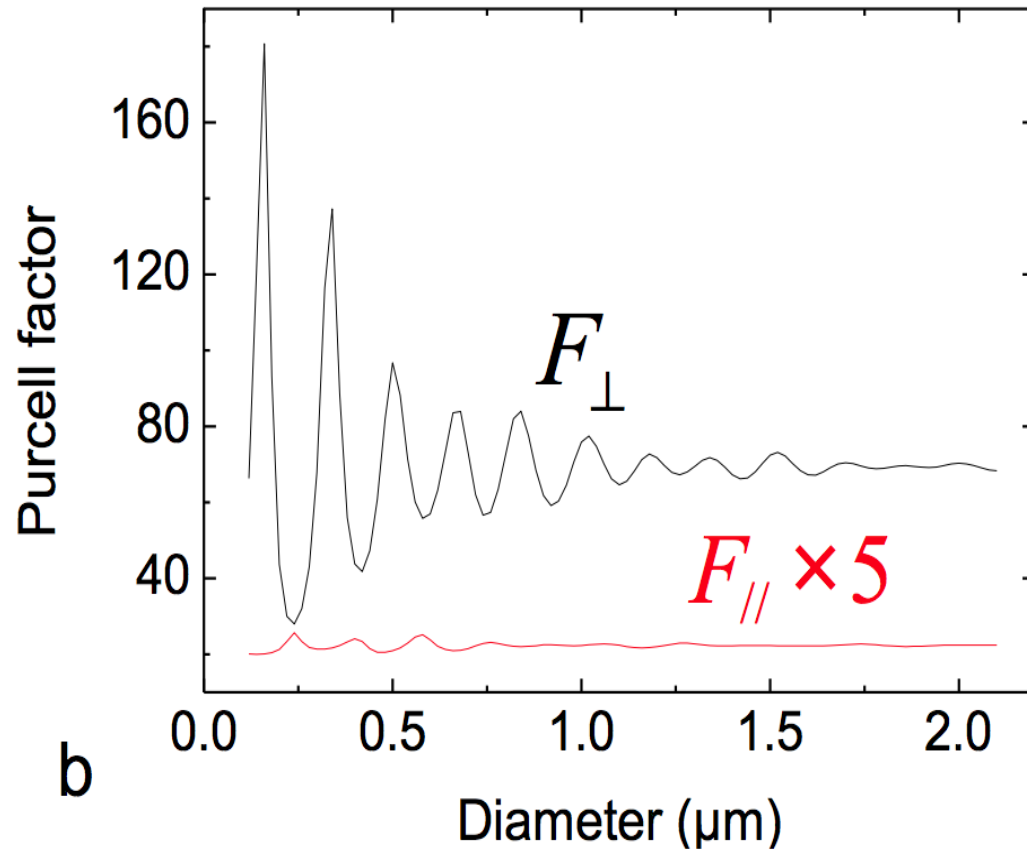


Mohtashami *et al.* ACS Photonics (2014) 1, 1134–1143

Cavity (plasmonic) modes : cavity geometry defines resonant modes
Large cavity ($\sim 1\mu\text{m}$) many cavity modes (kind of continuum)

Smaller nanoparticles = higher enhancement + lower losses

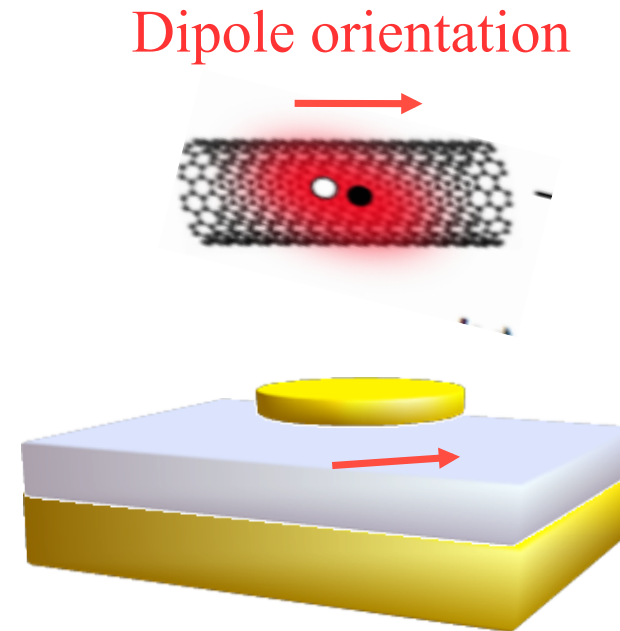
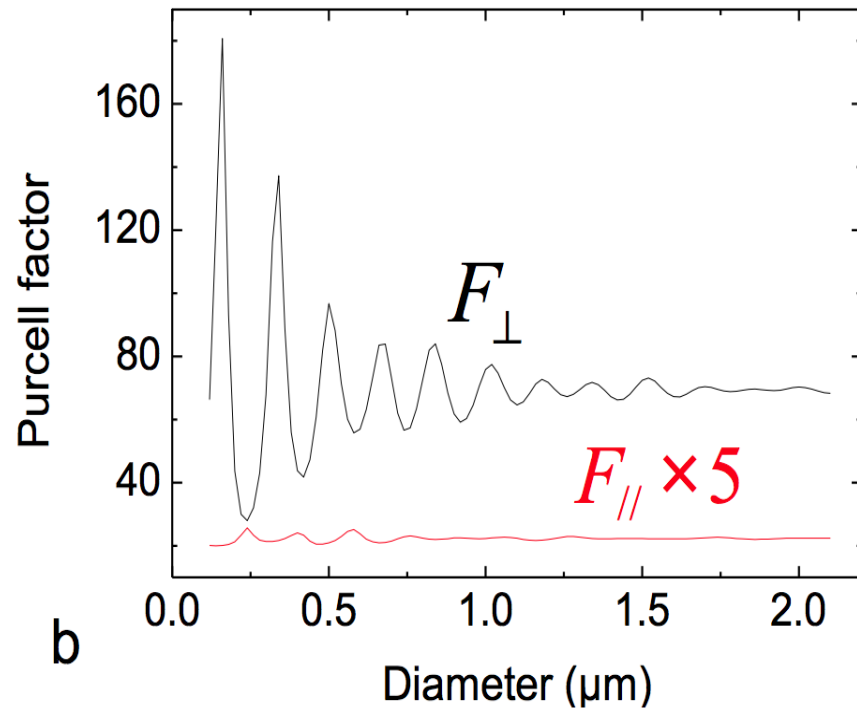
The patch antenna: dipole orientation



Belacel *et al.* **Nano Lett.**, 2013, 13 (4), pp 1516–1521

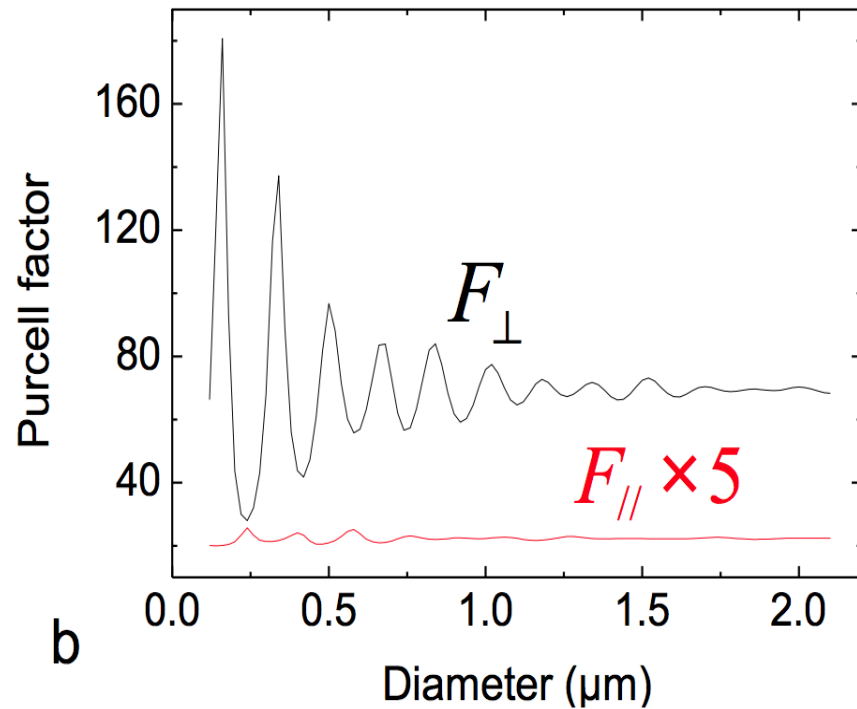
The purcell factor depends drastically on the dipole orientation

The patch antenna: dipole orientation

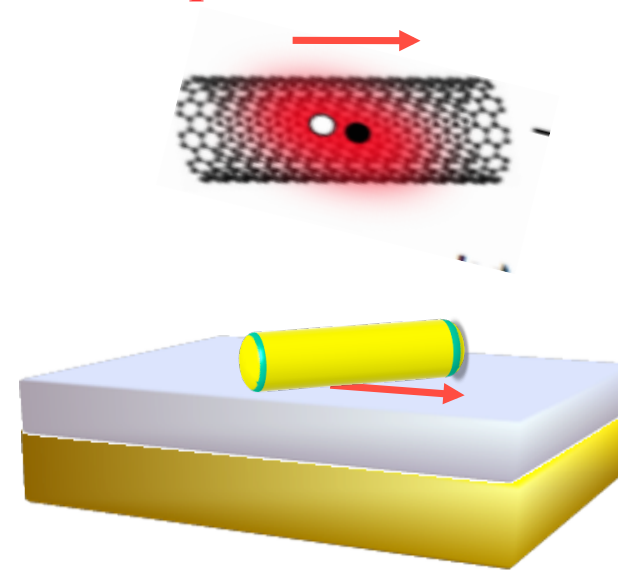


Unfortunately not favorable for CNT !!

The nanorod antenna: dipole orientation



Dipole orientation



Nanorod patch antenna...

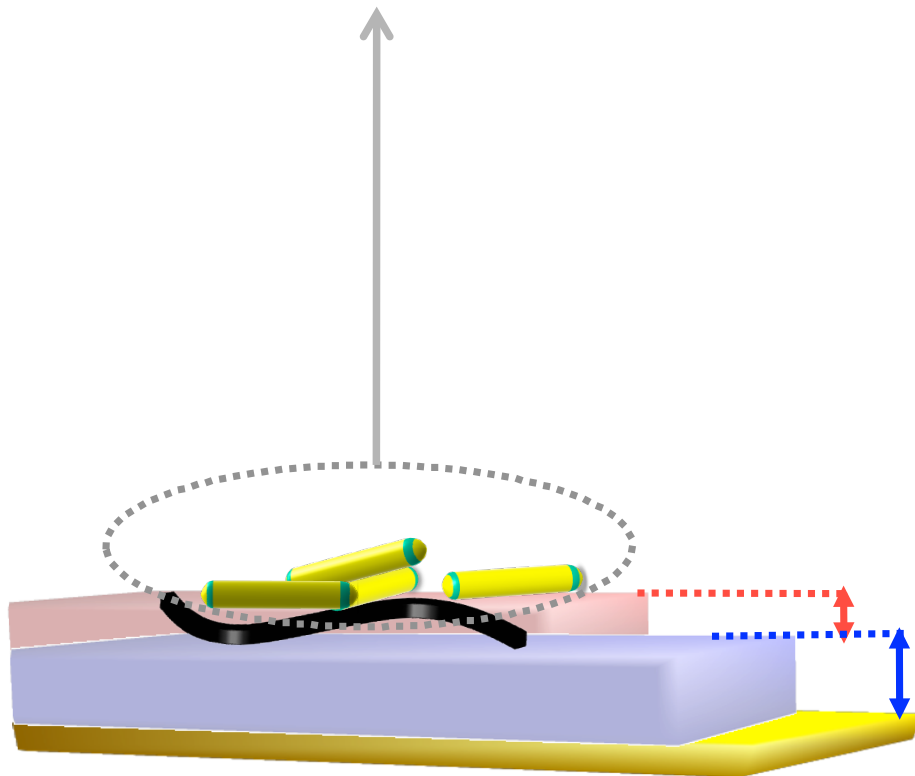
Helicoidal plasmon mode along cylinder axis

Cluster of plasmonics nanoparticles: The hotspots strategy:

Collection of nanorods:

Breaking of the planar geometry

Dipolar resonance in the wavelength range of interest



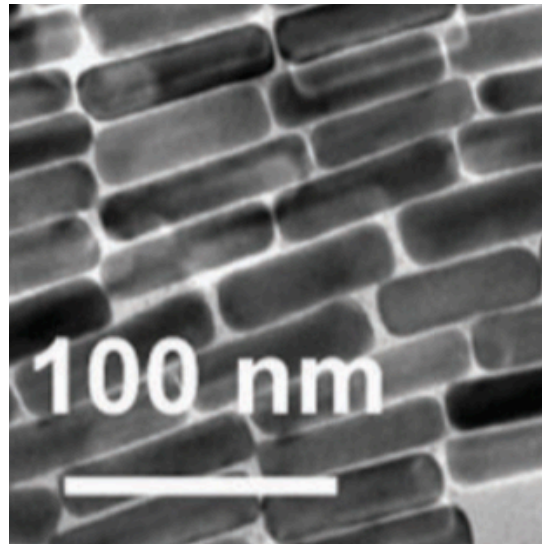
Dipolar resonance → Large Purcell factor/ low losses

Random distribution of plasmonic nanoparticles & nanorods
→ electromagnetic hotspots

Carbon Nanotubes layer : 5 nm

Dielectric spacer : 5 nm

The sample : the plasmonic nanoparticles

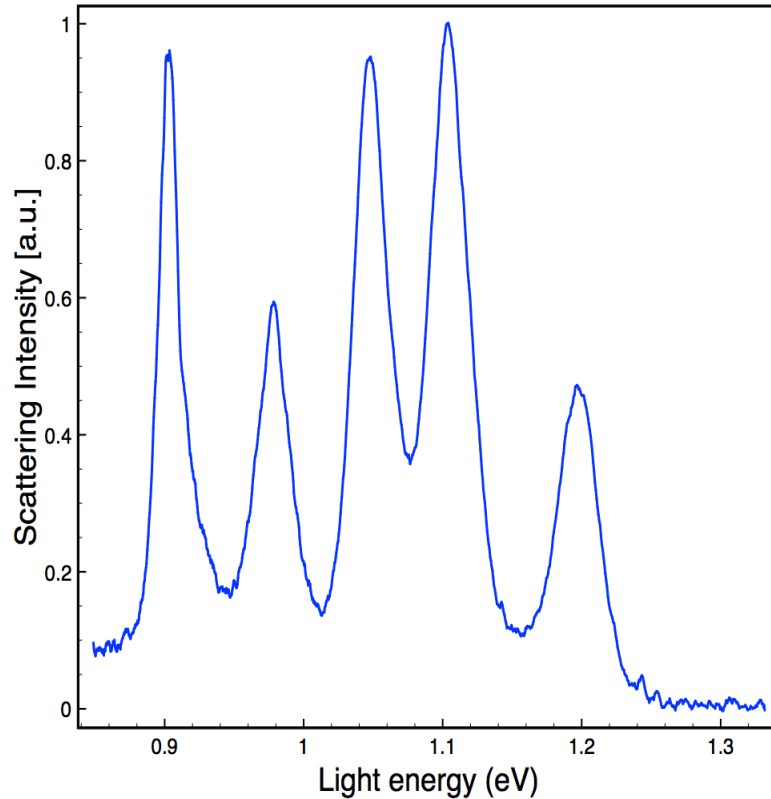


Colloidal nanorods made on gold => good surface state, low losses

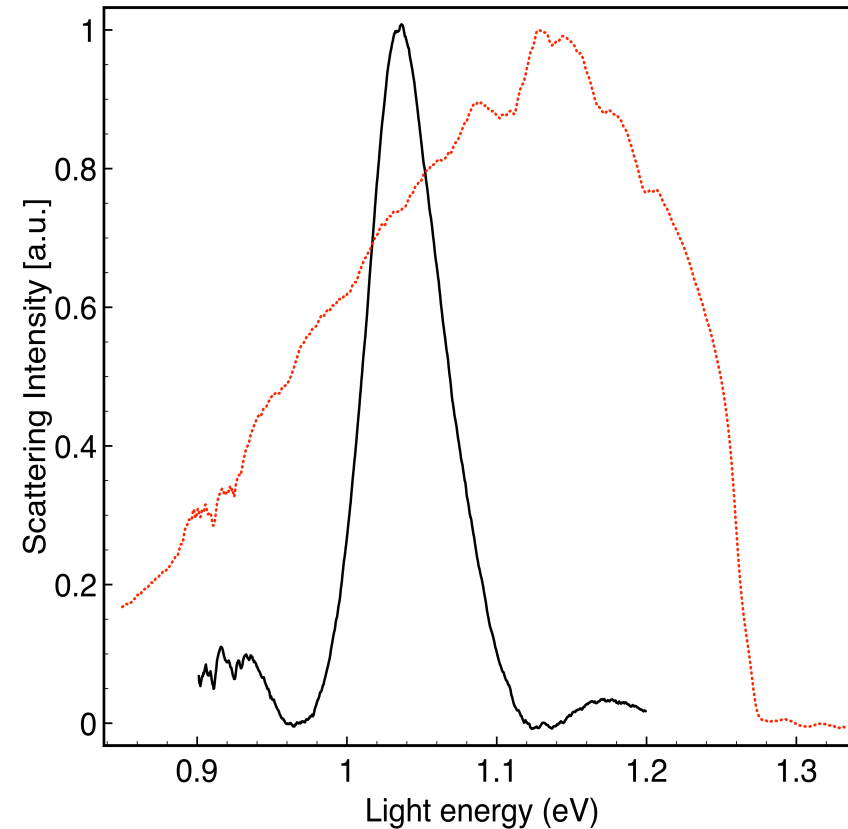
Resonant @ 1200 nm
with broad size dispersion

The sample : the plasmonic nanoparticles

CNT luminescence spectrum



Nanorods scattering spectrum



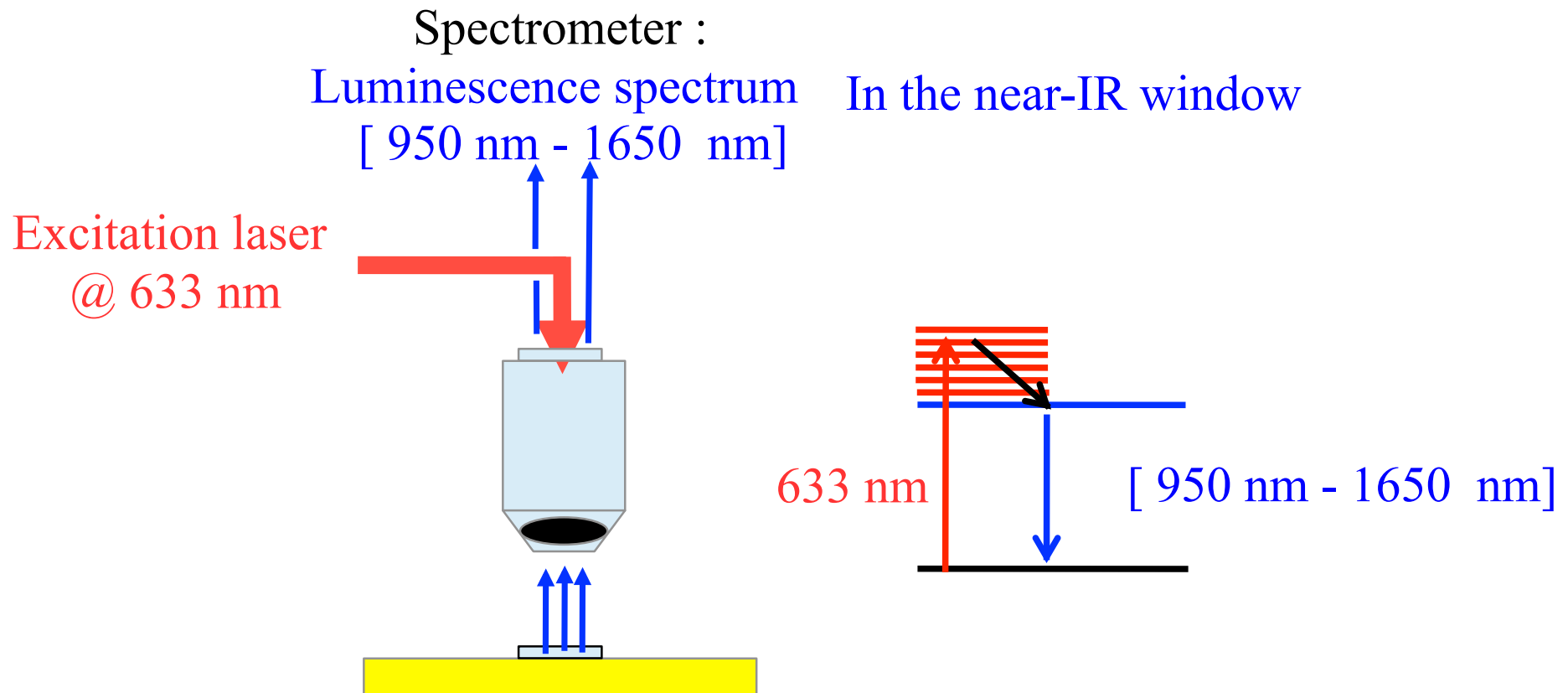
broad size dispersion:

=> broad “resonance” peak (inhomogeneous broadening)

=> broad-band enhancement

The experimental setup:

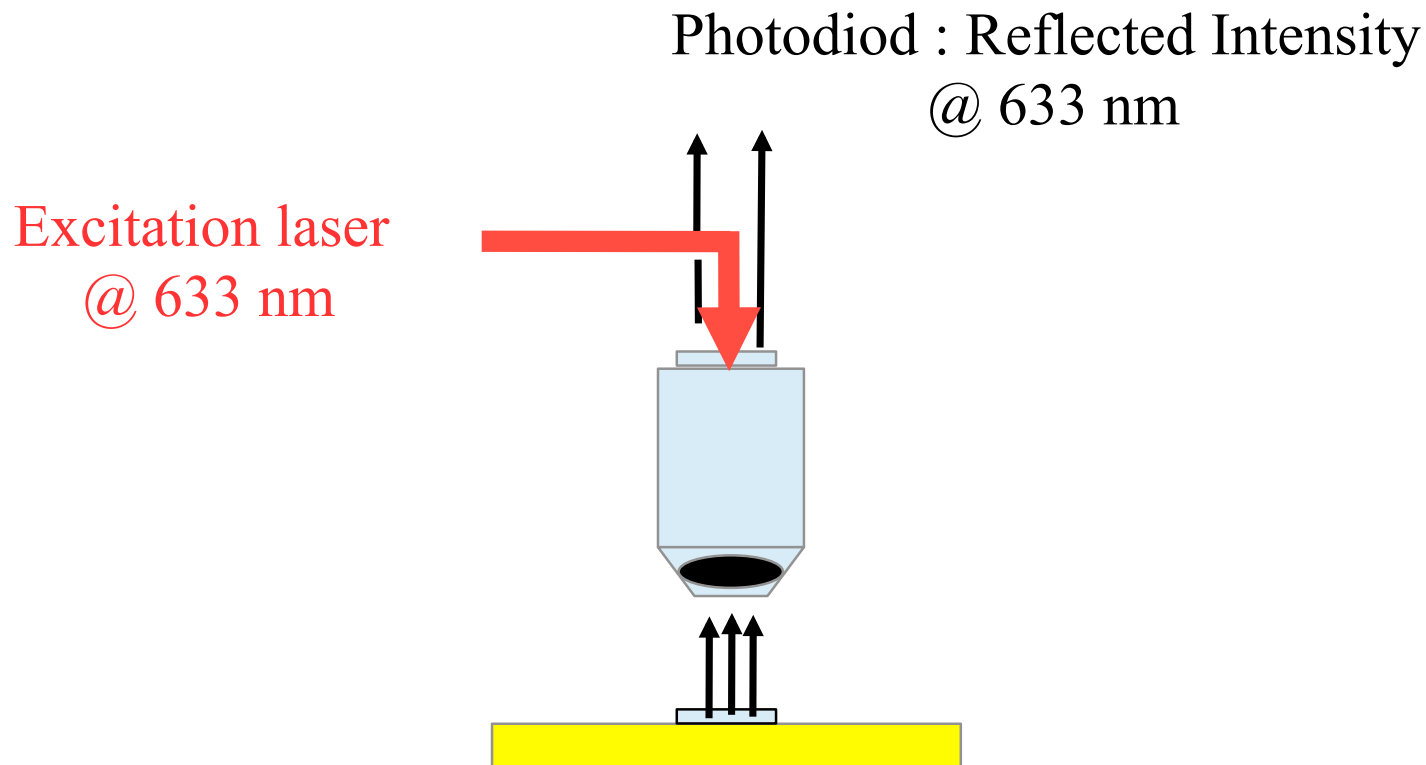
Luminescence spectrum



Cartography of the sample luminescence (XY-map)
From room temperature to 4 K

The experimental setup:

Reflectivity

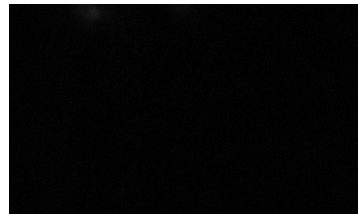


Cartography of reflectivity of the sample surface (XY-map)

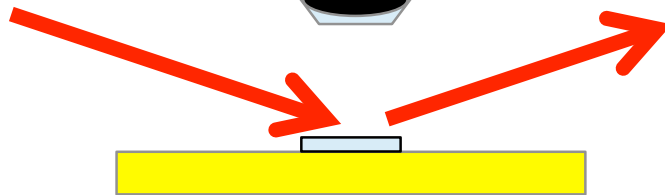
The experimental setup:

Dark field measurement
Scattering spectroscopy

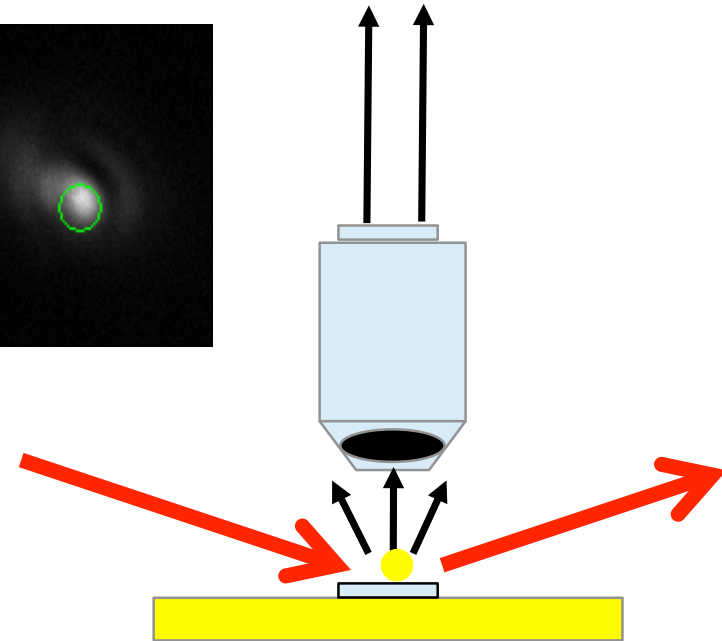
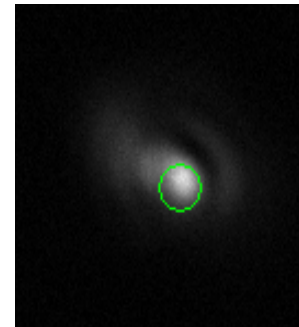
Spectrometer :
[950 nm - 1650 nm]



Incident light
White source



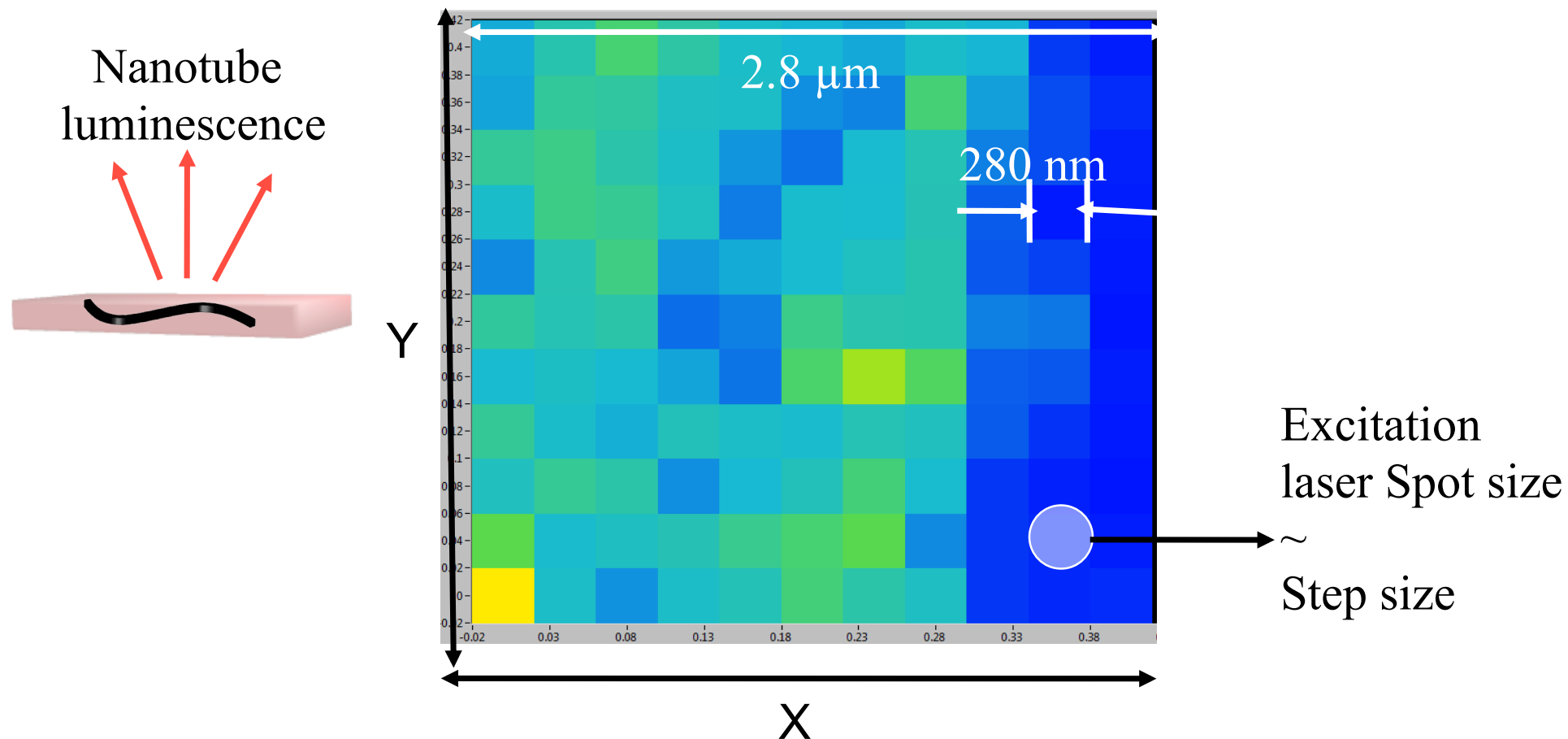
Spectrometer :
[950 nm - 1650 nm]



Cartography of scattering of the sample surface (XY-map)

Map of the sample luminescence

XY-Map of the Total Intensity – Without particles



Color scale :

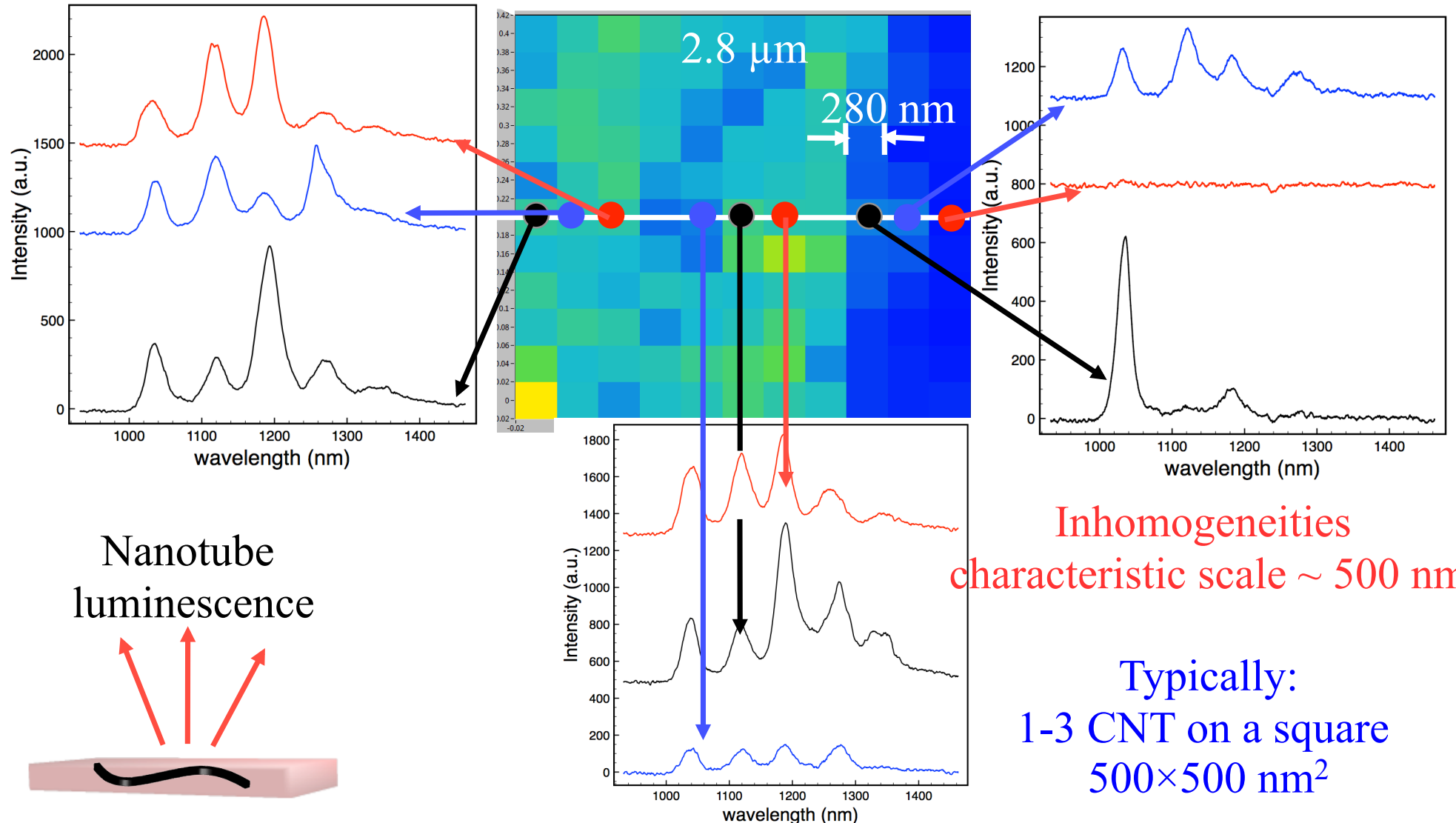
blue \rightarrow low intensity

orange \rightarrow moderate intensity

red \rightarrow high intensity

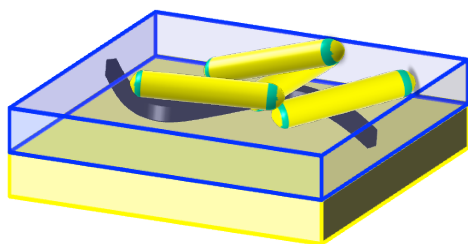
Map of the sample luminescence

XY-Map of the Total Intensity

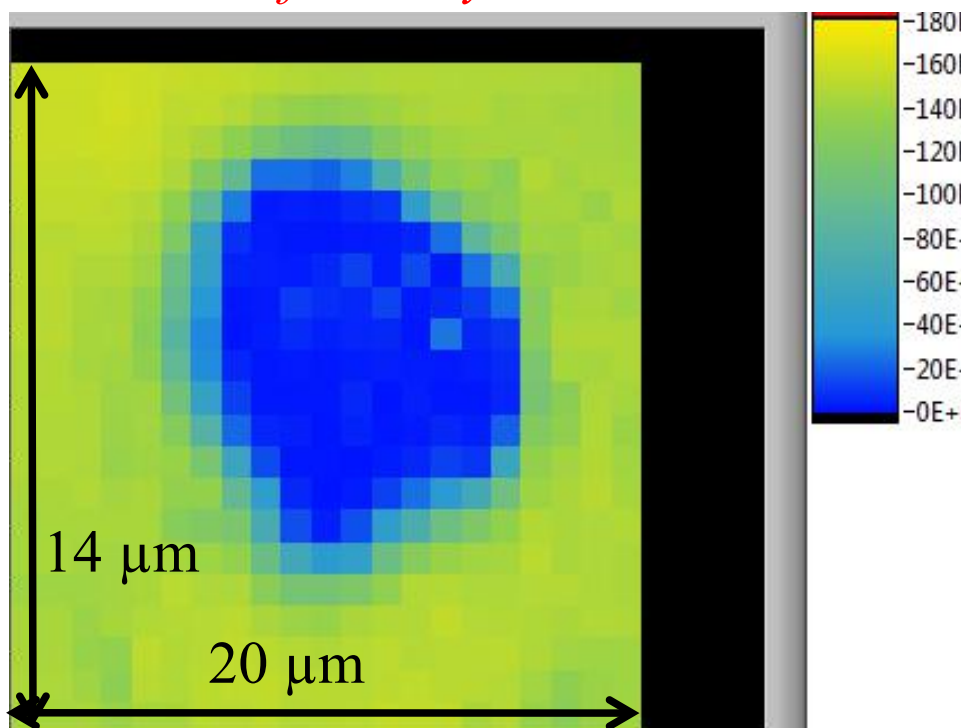


CNT coupled with nanoparticles

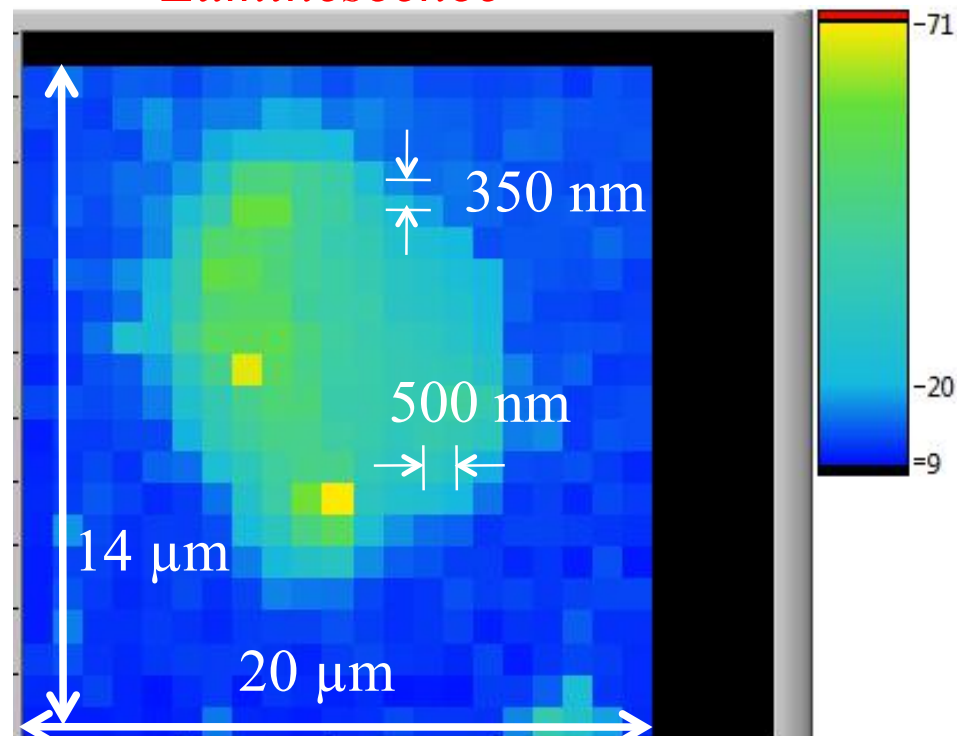
Reflectivity and Luminescence cartography



Reflectivity



Luminescence

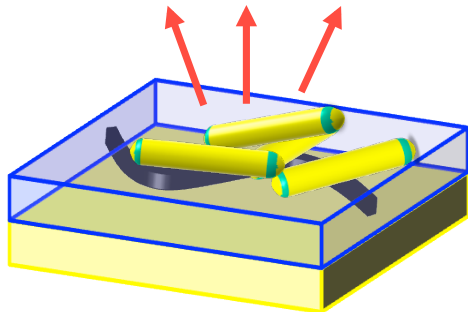


CNT coupled with nanoparticles

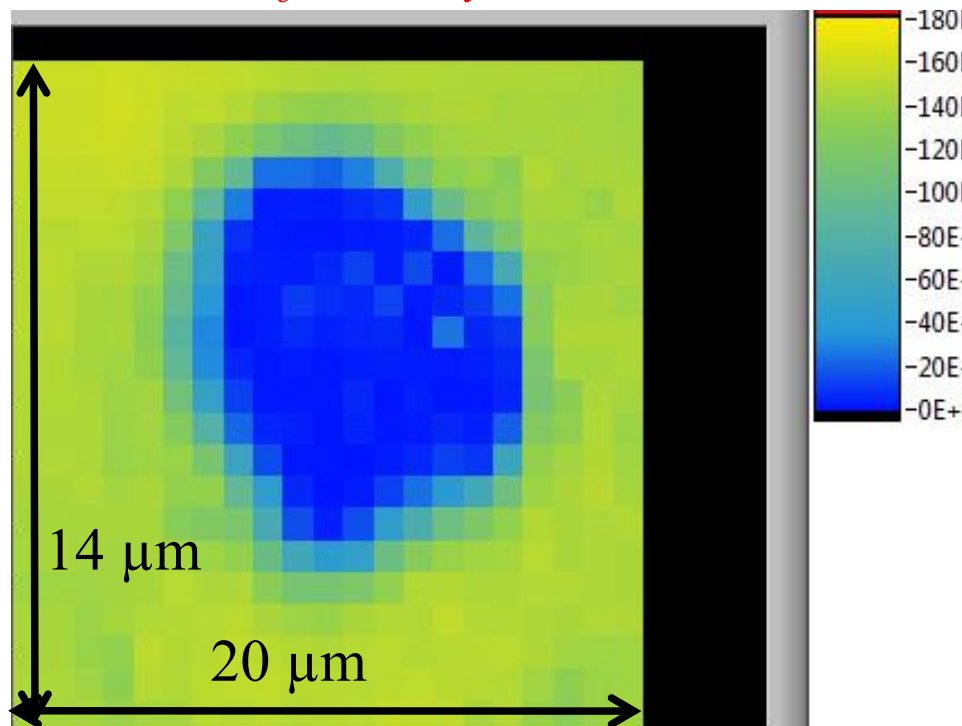
Reflectivity and Luminescence cartography

Perfect match between reflectivity/luminescence

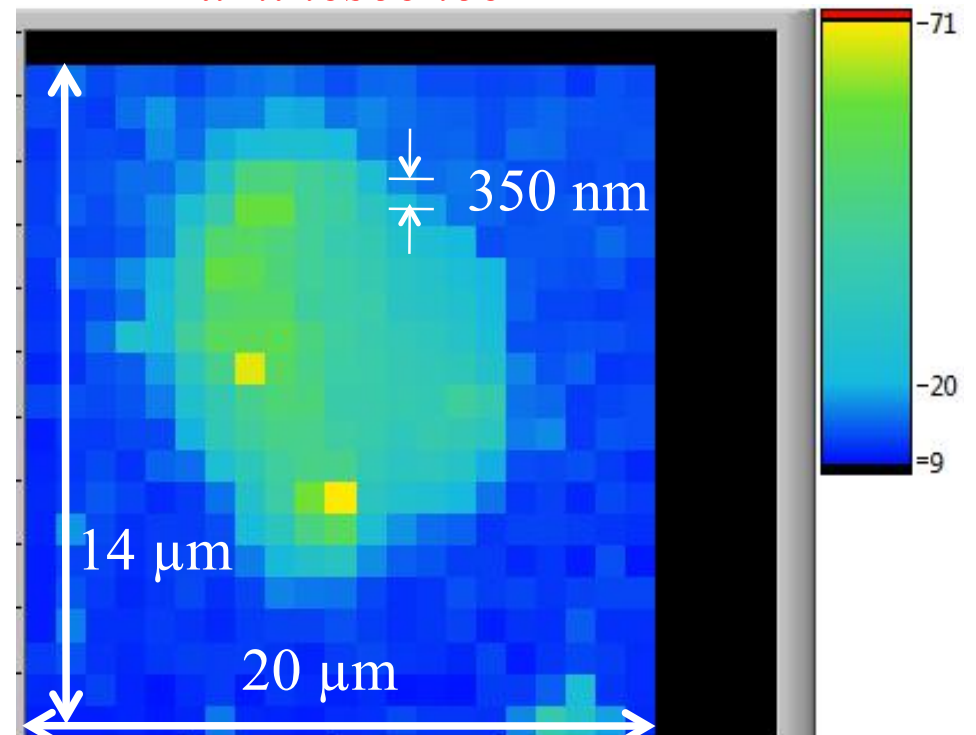
=> Enhancement due to gold nanorods



Reflectivity

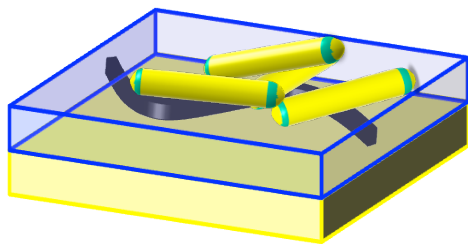


Luminescence



CNT coupled with nanoparticles

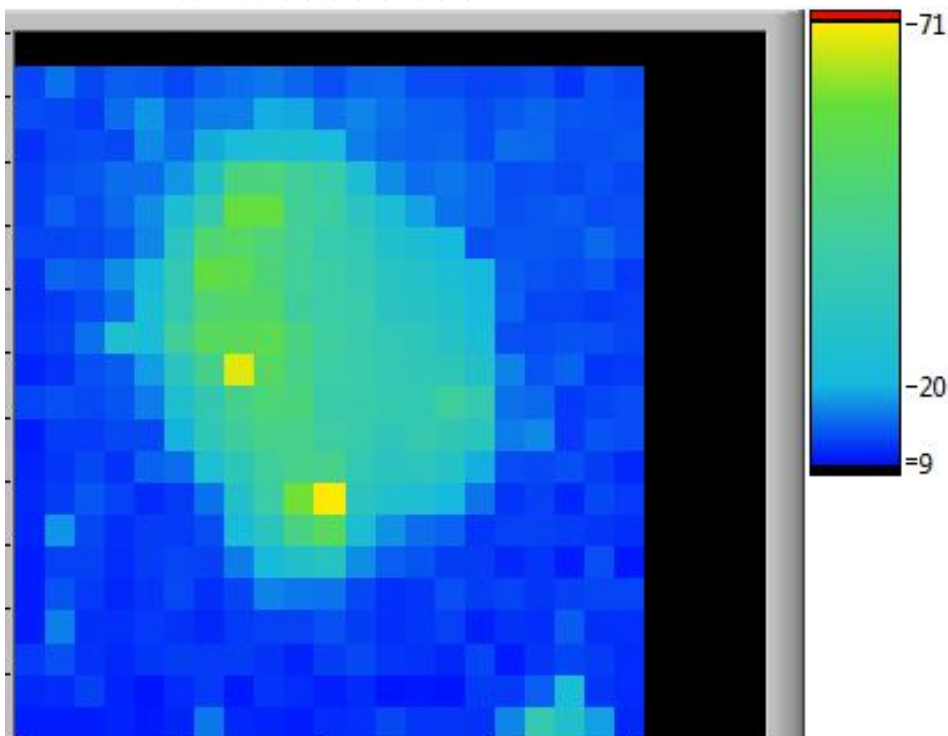
Reflectivity and Luminescence cartography



Perfect match between reflectivity/luminescence

=> Enhancement due to gold nanorods

Luminescence



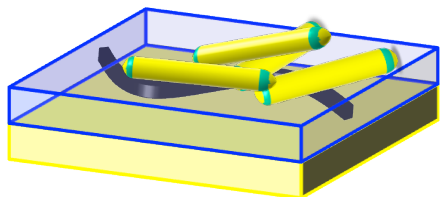
*Enhancement:
(compared to CNT on gold plane)*

=> *Typically 3-5 fold on the cluster*

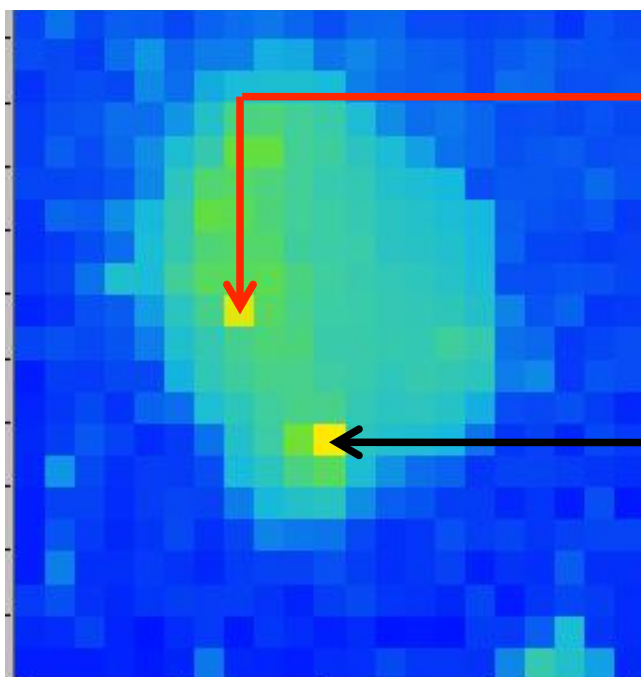
=> *hotspots: 20-40 fold*

=> *modification of the CNT spectrum*

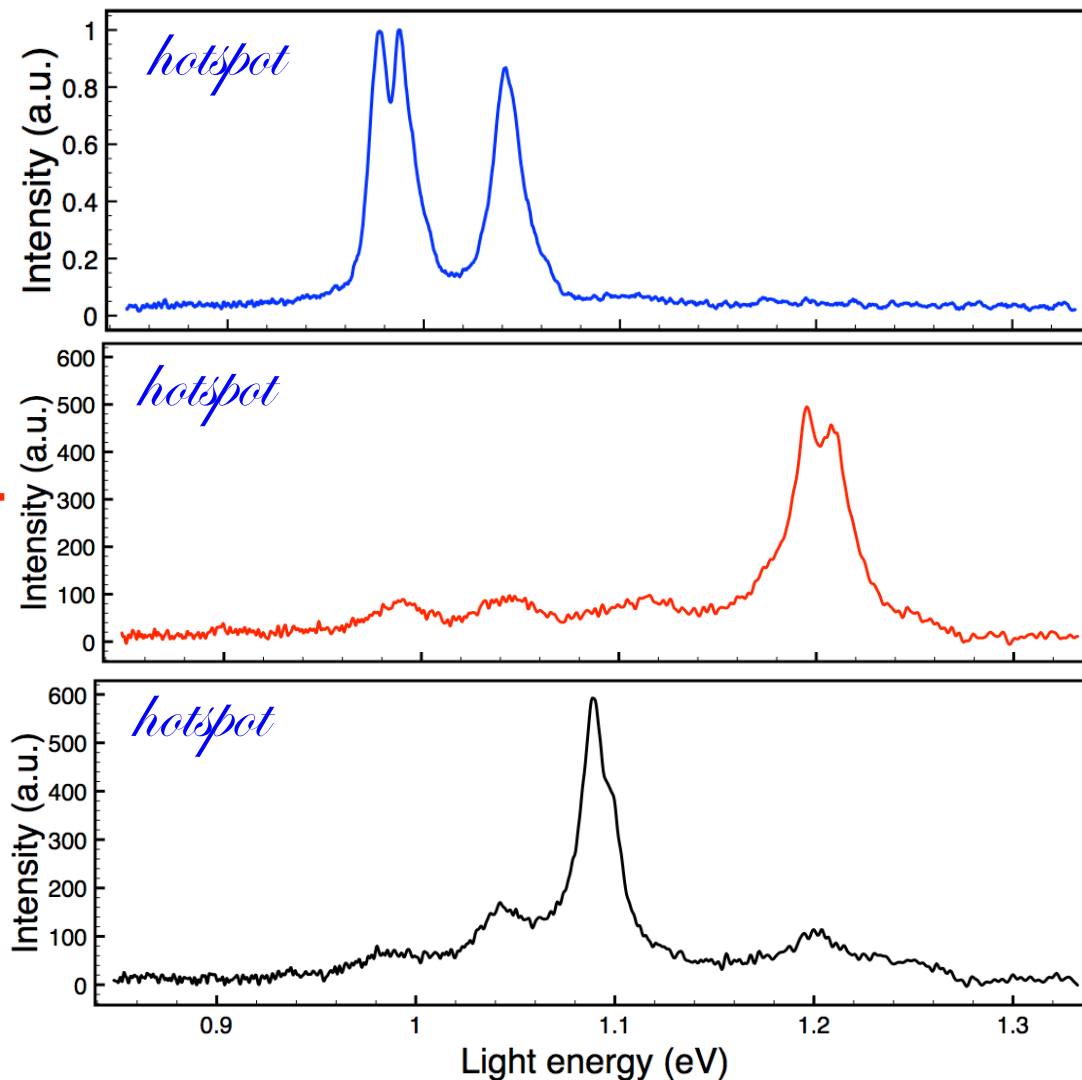
CNT coupled with nanoparticles



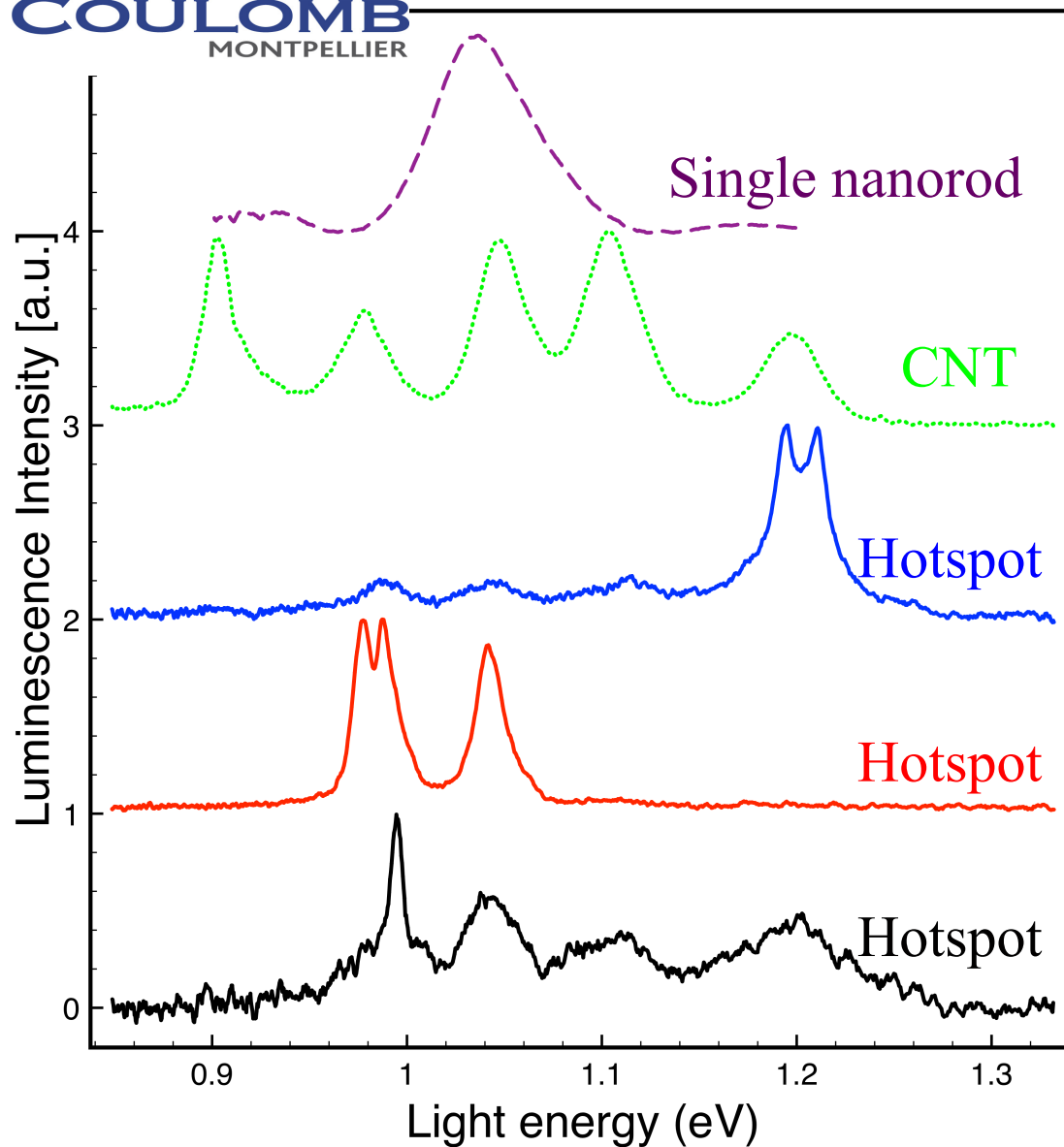
Luminescence



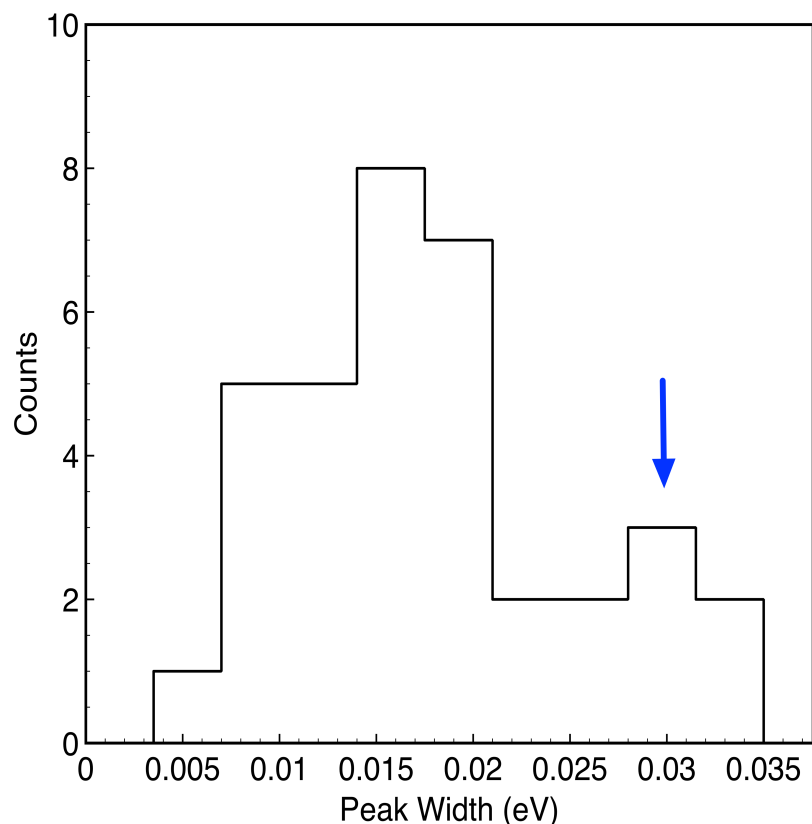
Spectrum modifications



Luminescence enhancement



Peaks-width histograms and Q-factors

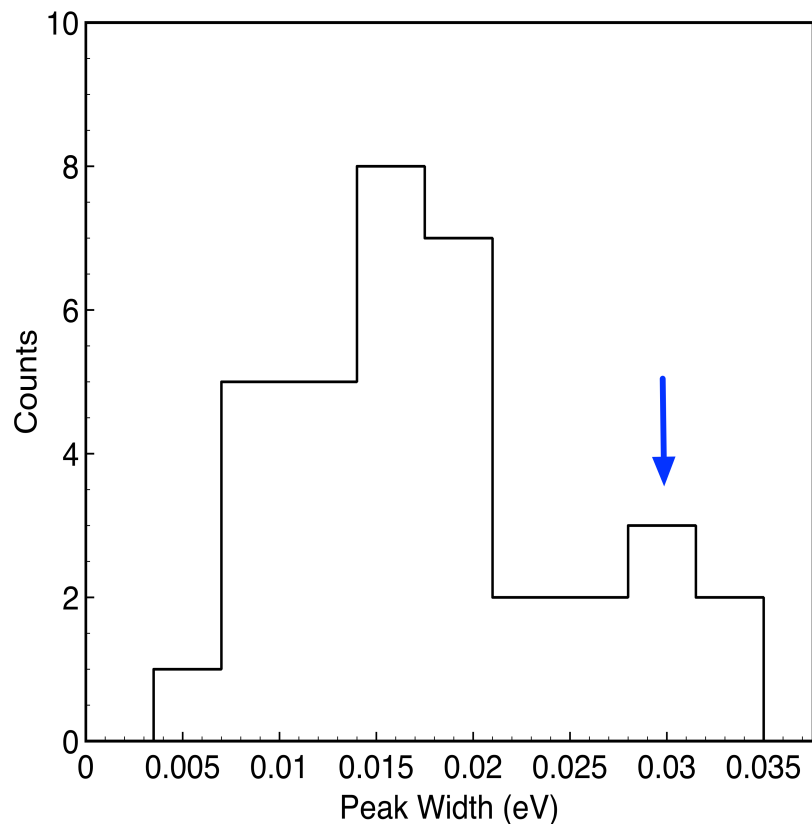


CNT Q-factor $\sim 30-50$

Nanorod Q-factor $\sim 10-15$

HotSpot Q-factor $\sim 70-80$ (up to 200)

high Q-factors mode origin?



Symmetric mode
E-field localized in the gap
High-Q factor



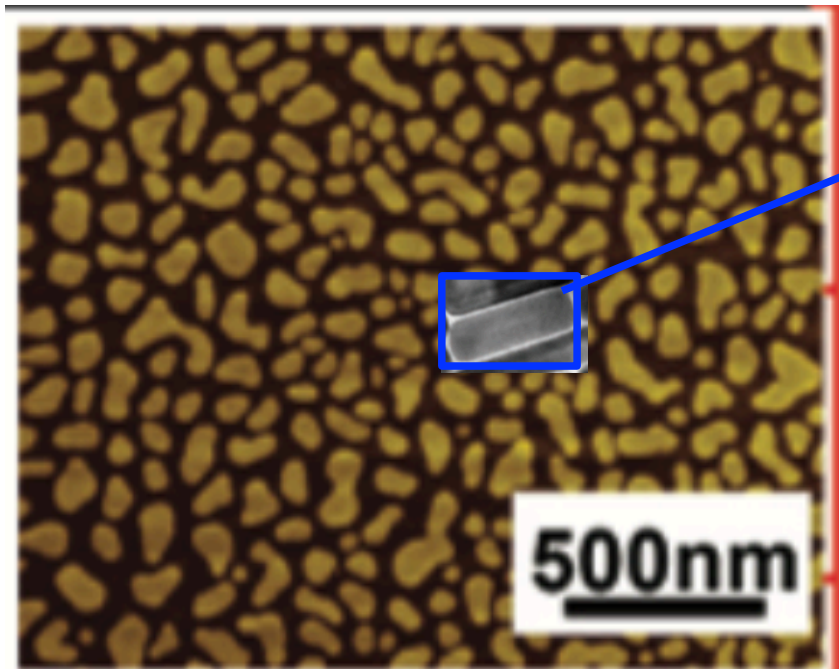
Antisymmetric mode
E-field localized in the metal
Low-Q factor

Because of randomness?

Conclusion:

Because of the emitter dipole orientation:

Hotspots + plasmonics strategy to enhance the CNT luminescence



Rough surface

Well-controlled elementary cell

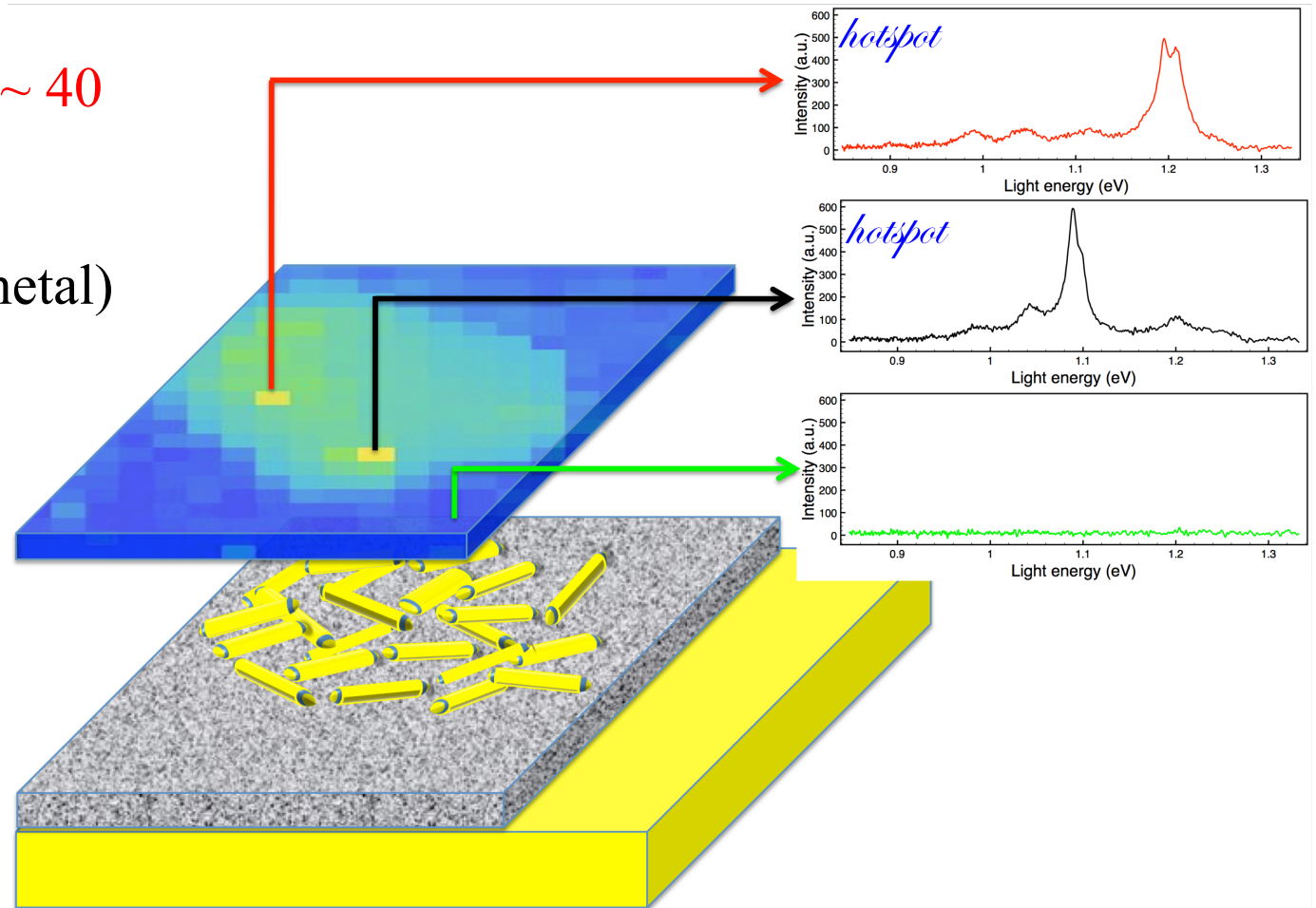
Dipolar resonance in the frequency range of interest
=> High Purcell factor

Conclusion

Radiative enhancement ~ 40

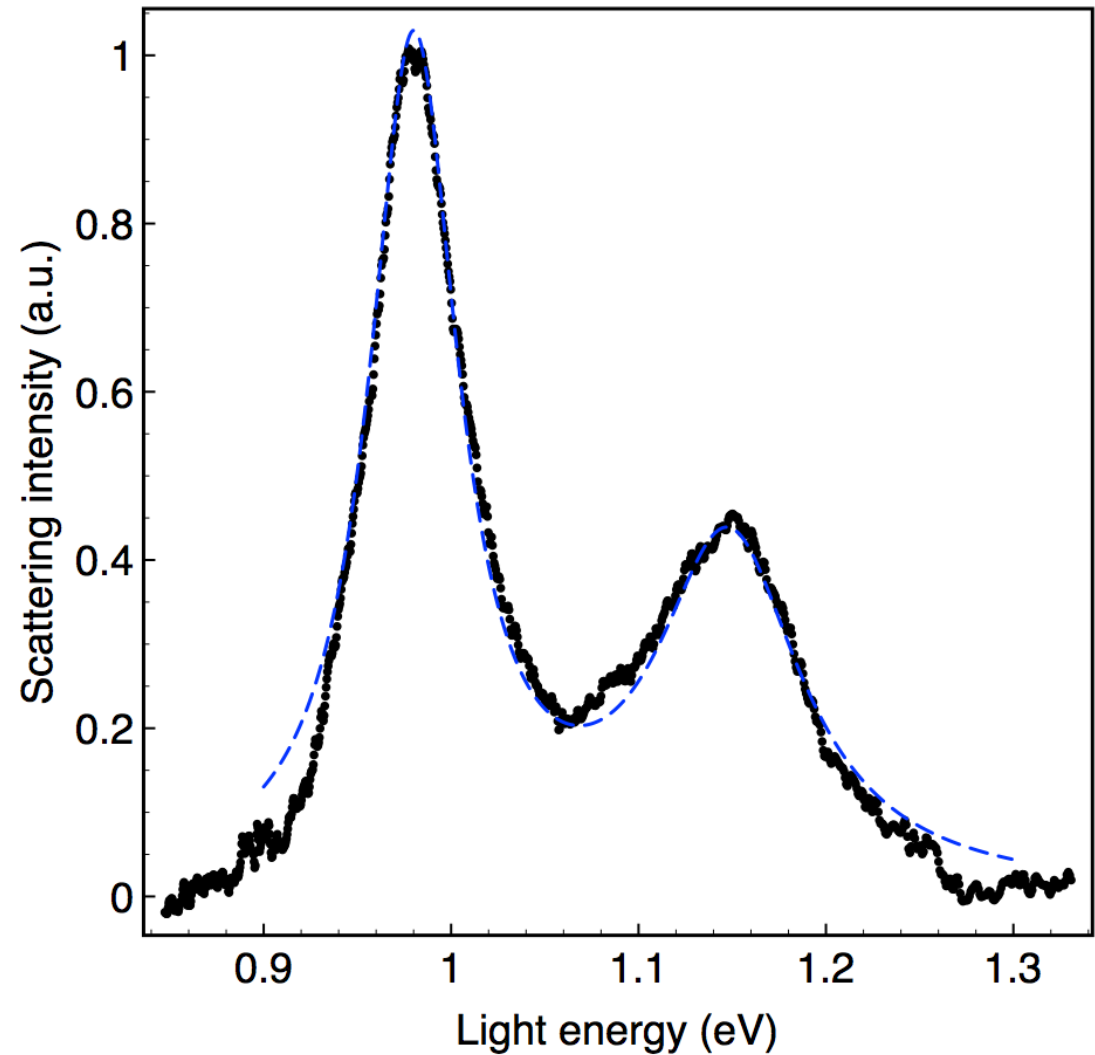
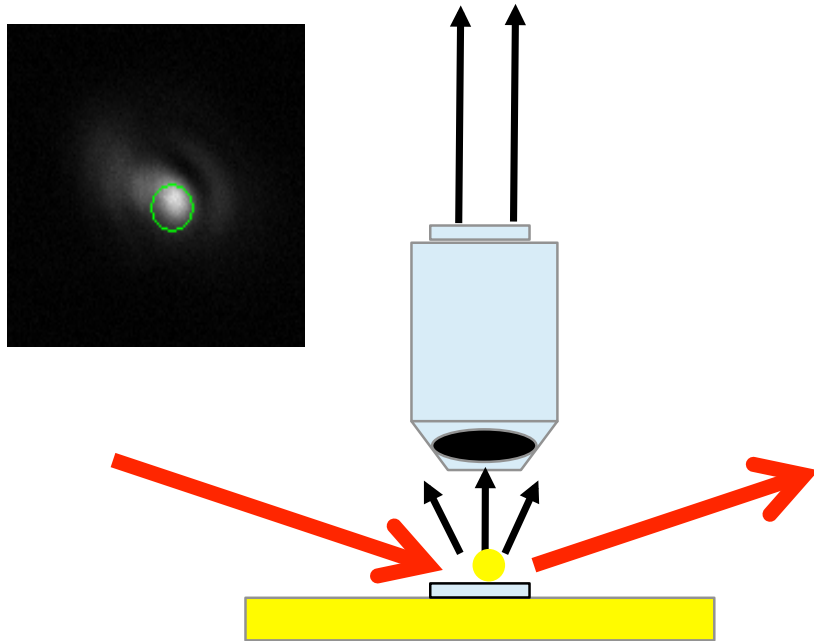
Typically ~ 20
(compared to CNT on metal)

Resonant hotspots
With *high* Q-factor



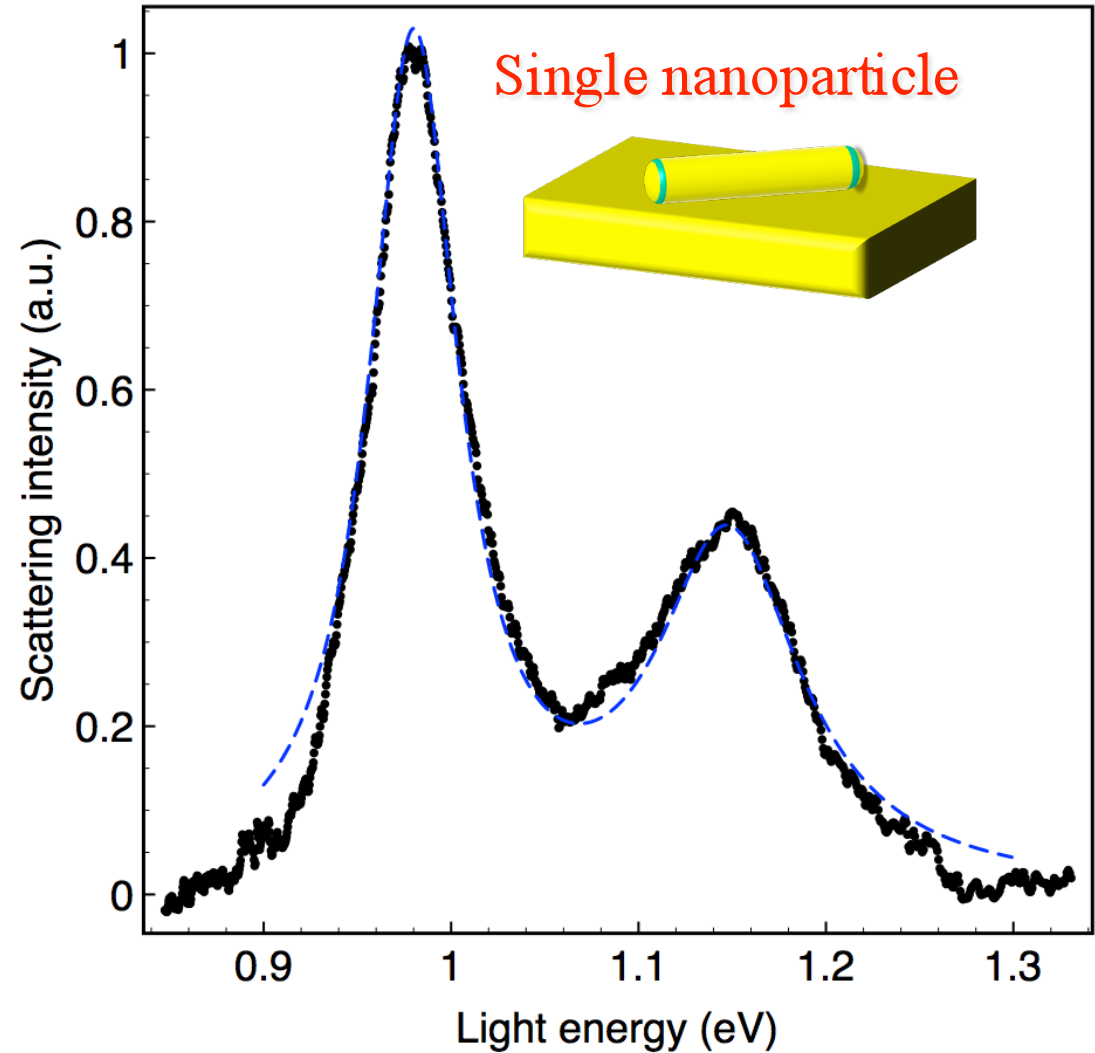
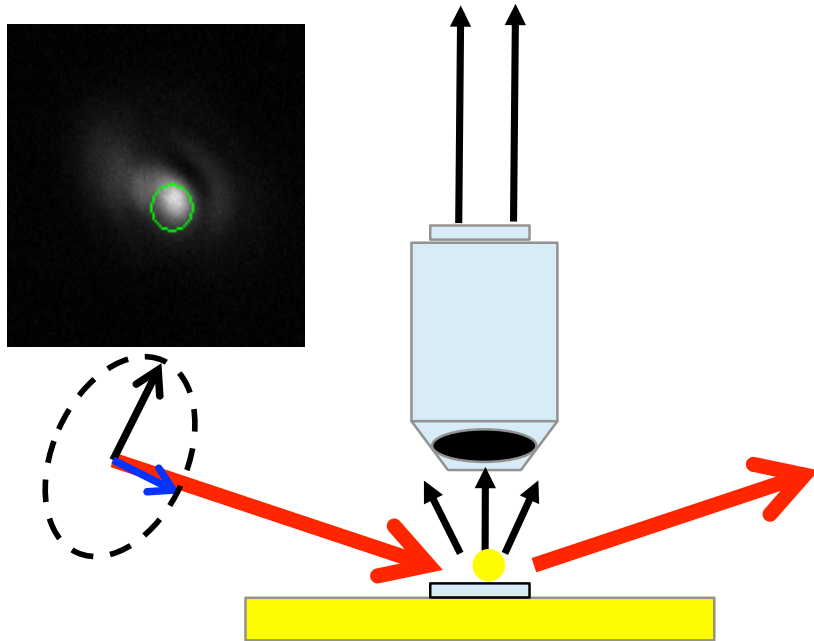
Dark field measurement: Scattering spectroscopy

Spectrometer :
[950 nm - 1650 nm]



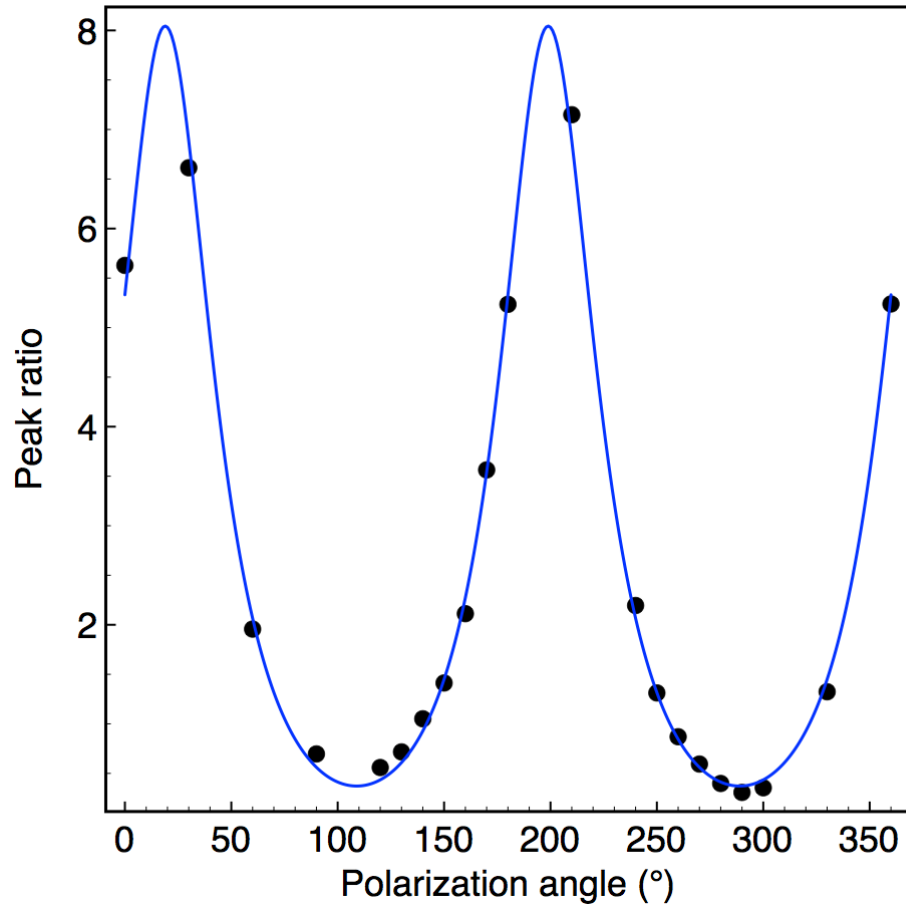
Dark field measurement: Scattering spectroscopy

Spectrometer :
[950 nm - 1650 nm]

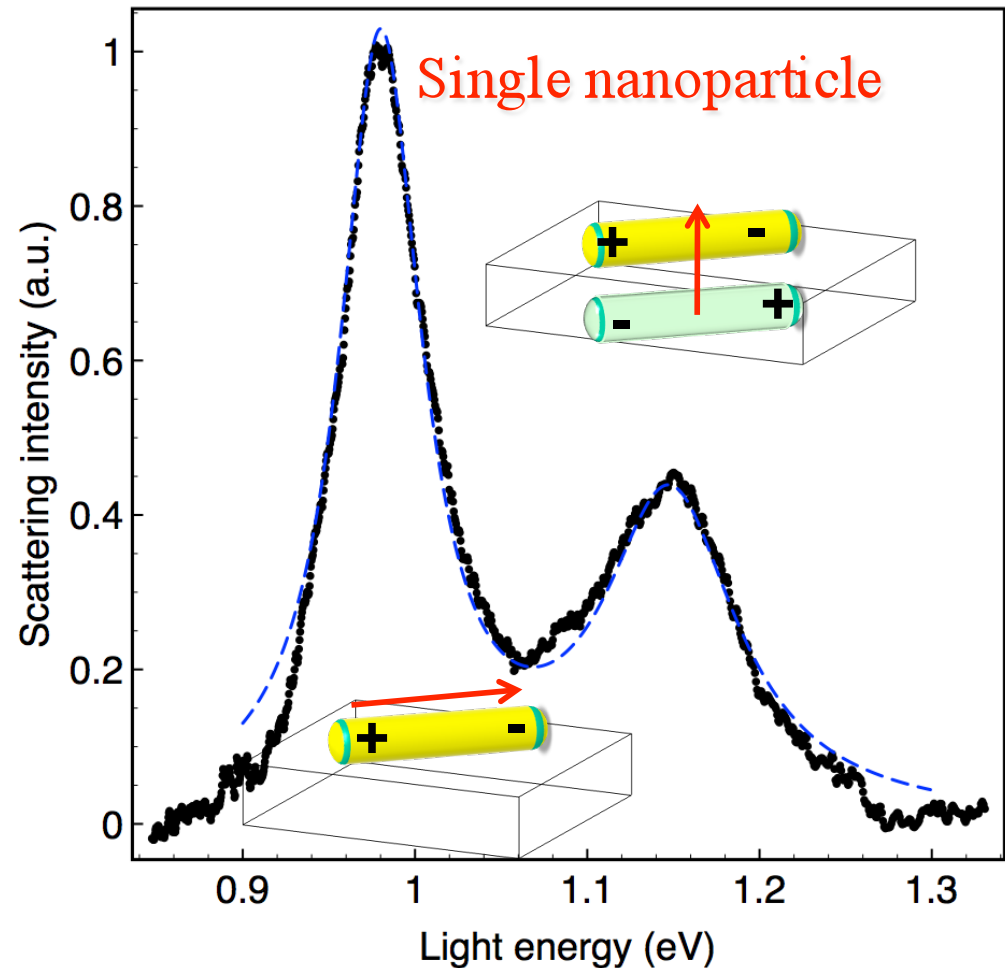


Dark field measurement:

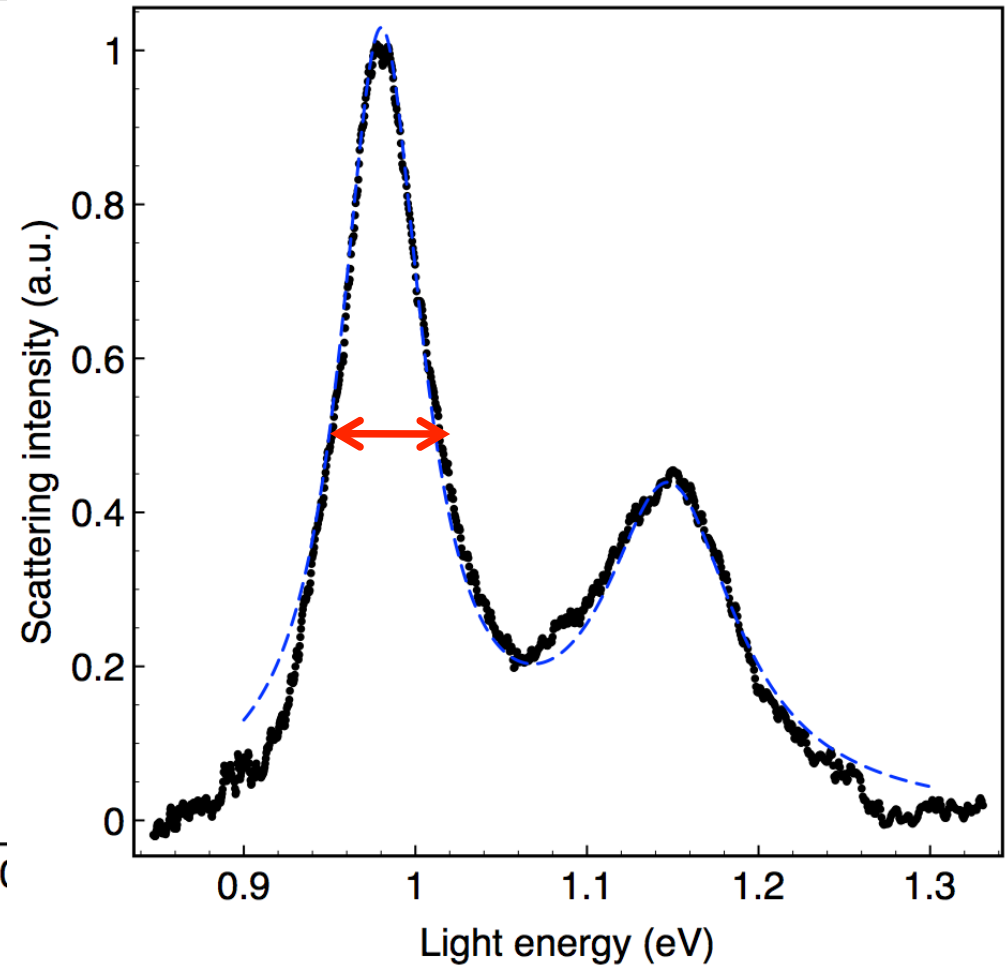
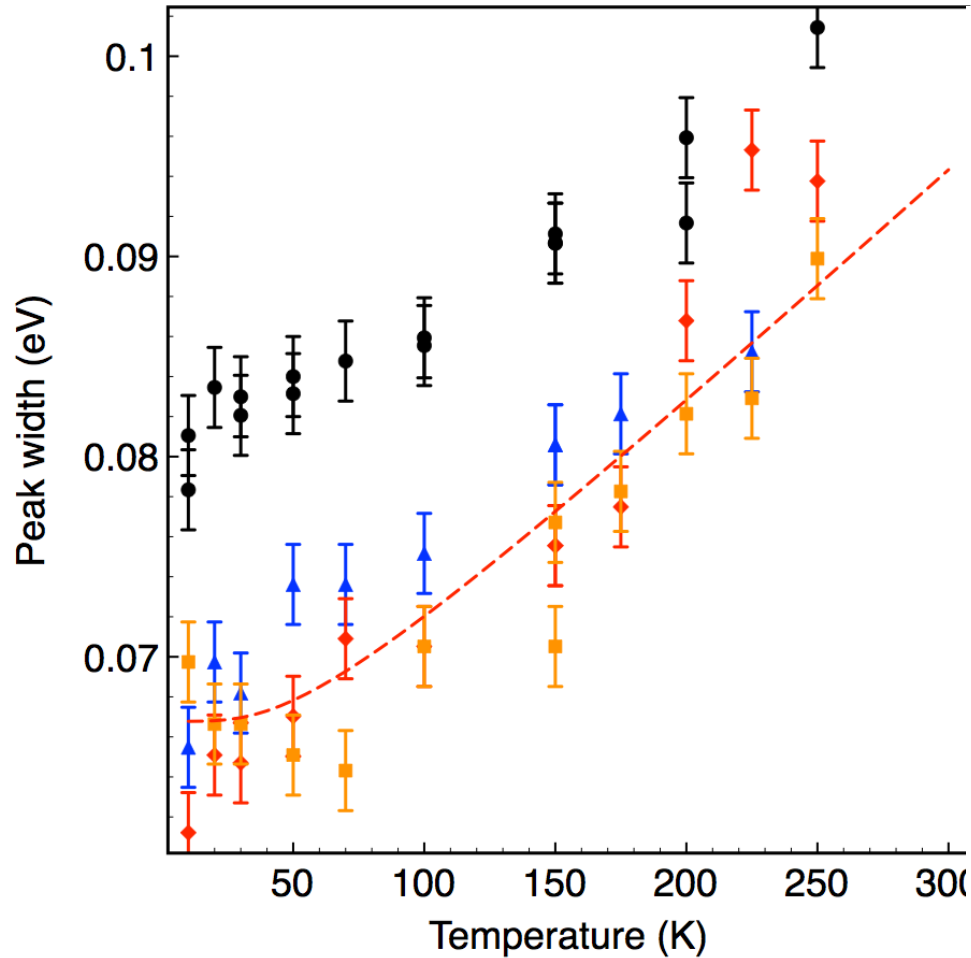
Scattering spectroscopy with light polarization



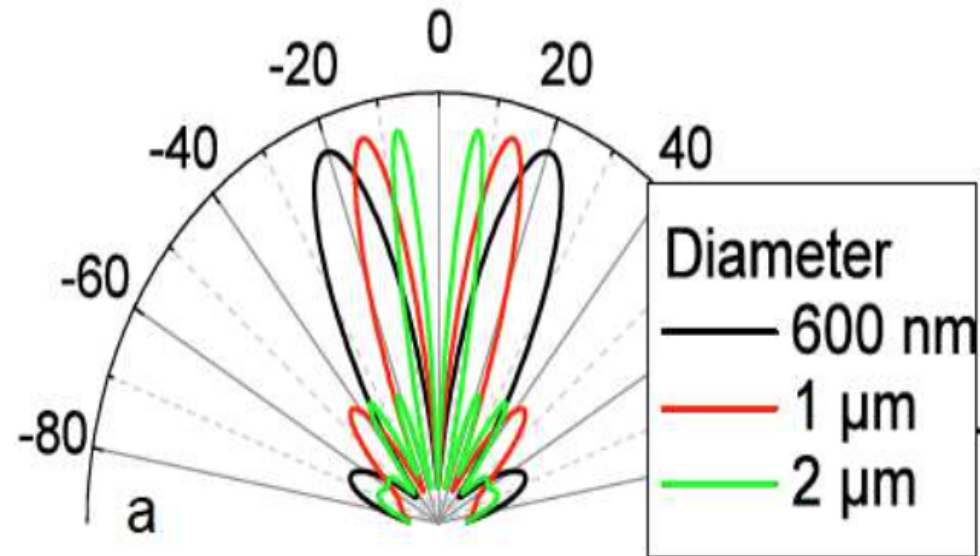
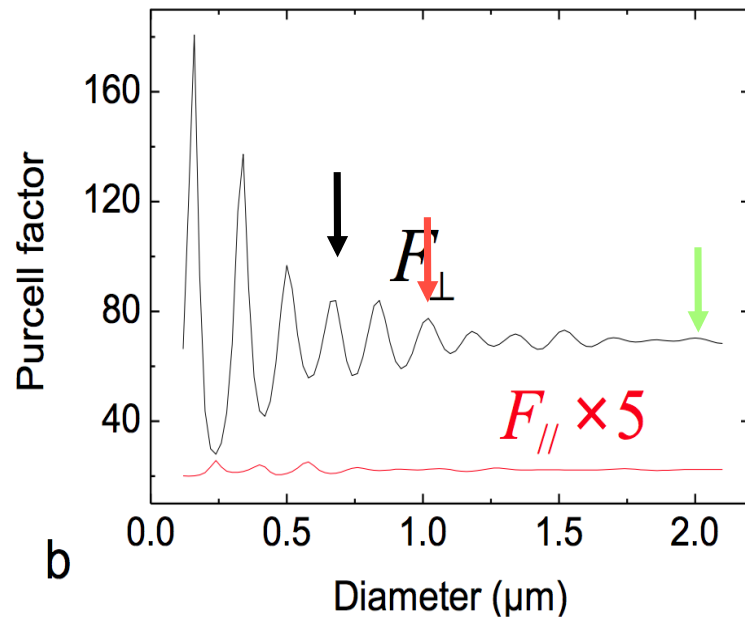
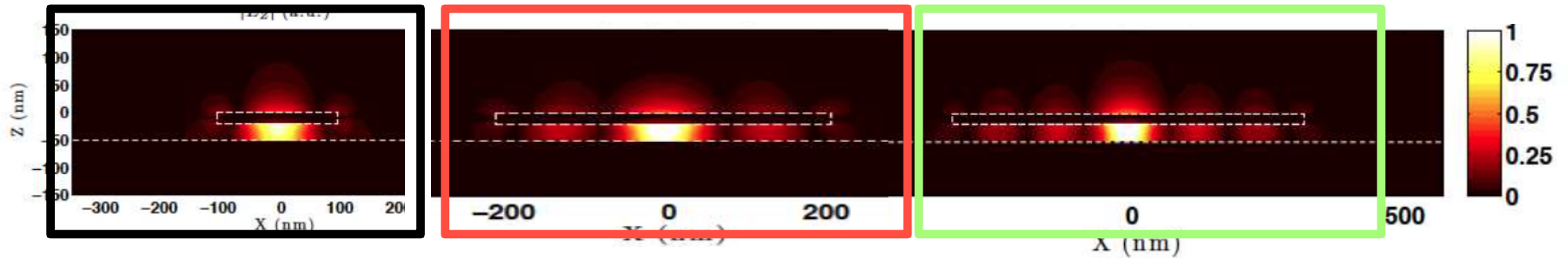
$$I_{long}(\theta) = I_0 \cos^2(\theta + \phi) + I_1$$



Dark field measurement: Scattering spectroscopy with temperature



The patch antenna: radiation pattern



Large antennas = better directivity