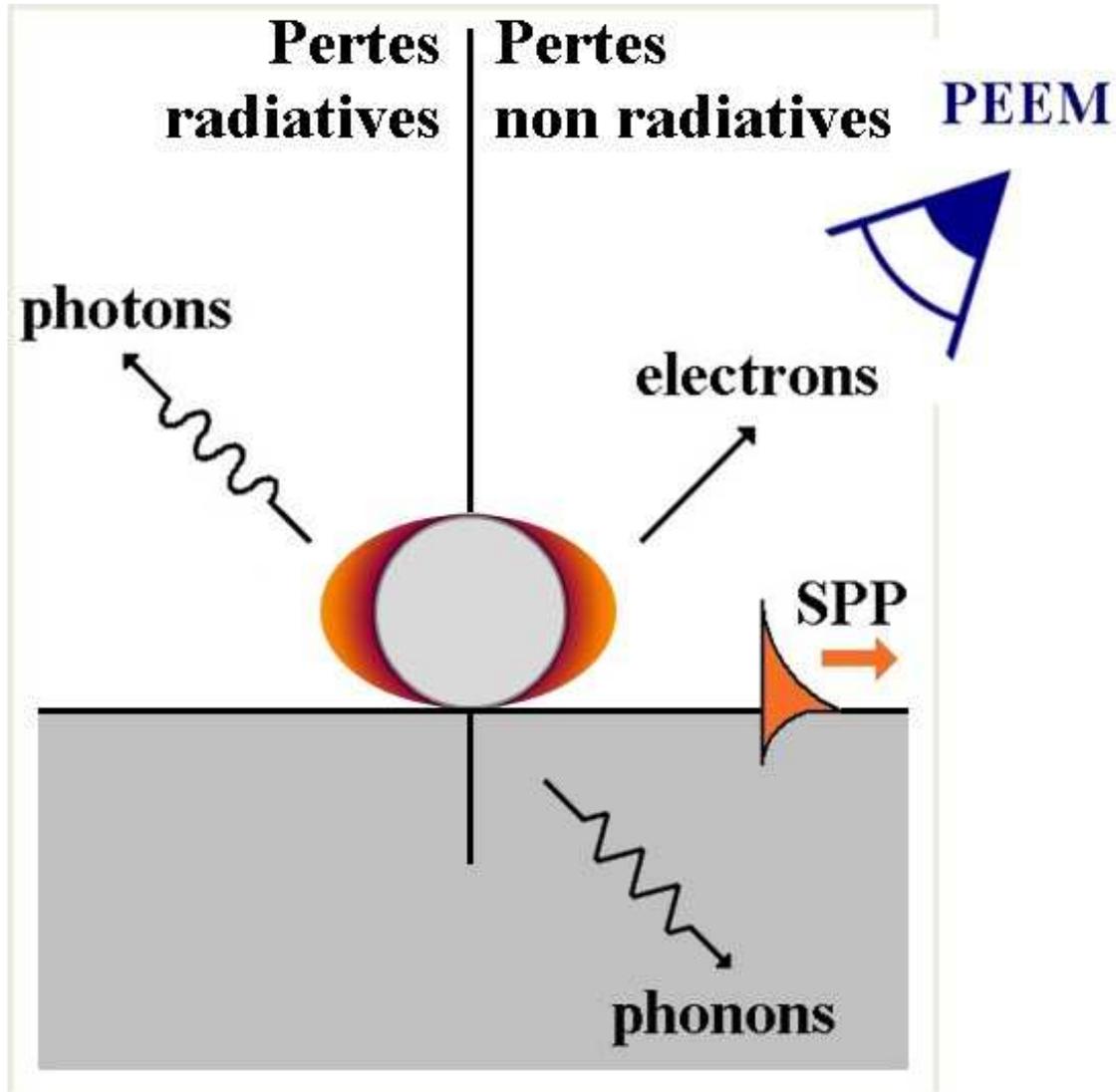


# Mapping the evanescent field at the nanometre

## Near field microscopies



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## What is plasmonics ?

➤ “A way to confine electromagnetic fields over dimensions on the order or smaller than the wavelength  $\lambda_{hv}$ ”

*S. Maier in Plasmonics: Fundamentals and Applications (2007) Springer*

➤ Interaction processes between electromagnetic radiation and conduction electrons at metallic interfaces = **coherent collective charge oscillations**

➤ **Basic ingredients**

(i) *Surface plasmons-polaritons* SPP - Metal / dielectric interface - Hybrid wave between a photon and a plasma oscillation - Propagative mode along the interface, evanescent in perpendicular direction

(ii) *Localised surface plasmons* LSP - Sub wavelength object - Non propagative mode



## The promise of Plasmonics

➤ A way to bridge the size gap between nanoelectronics and photonics

	Working frequency	Spatial scale
Photonics	High working frequency Optical frequency 500 THz (600 nm) = $5 \cdot 10^{14}$ Hz 500 THz = 500 000 GHz	Low spatial integration $\sim \lambda_{hv}$ Light wavelength $\sim 600$ nm in visible spectrum
Plasmonics	High working frequency Optical frequency 500 THz (600 nm) = $5 \cdot 10^{14}$ Hz 500 THz = 500 000 GHz	Moderate - High spatial integration $\lambda_{hv} / 10 \sim 60$ nm (visible)
Electronics	Low working frequency $\sim 1$ GHz = $1 \cdot 10^9$ Hz	High spatial integration Int. Tech. Roadmap for Semicond. → 7 nm node in 2018



## Plasmonic near field – Experimental relevant scales

- Investigation of the full plasmonic picture requires adequate experimental resolutions in

.space

.time

.energy

- Additional degrees of freedom are

.light polarisation

.light angular momentum

.electron momentum distribution



## Plasmonics - Physical orders of magnitude - Spatial scale

### Relevant length scales of a plasmonic field

- Near field phenomena imply field spatial distribution scale  $\ll$  Light wavelength  $\lambda_0$
- Localized surface plasmon
  - Collective coherent electron oscillation
  - Electrons perceive a static electric field amplitude (quasi static QS approximation)
  - Object dimension  $L \ll$  Light wavelength  $\lambda_0$
- Thomas Fermi screening length  $\approx 0.1$  nm  $\ll$  Coherent charge fluctuation period
- Propagation length of a surface plasmon polariton  $L_{prop.} = 1/e$  plasmonic field decay length

$$L_{prop} = \frac{1}{k_x''} \quad k_x'' = \text{Im} \left\{ \frac{\omega}{c} \sqrt{\frac{\epsilon_{Dielec} \epsilon_{Metal}}{\epsilon_{Dielec} + \epsilon_{Metal}}} \right\}$$

N.A. Au/vacuum interface @ 800 nm wavelength excitation  $L_{prop.} = 88 \mu\text{m}$

**A few tenths of a nanometer  $\sim 0.1$  nm =  $1 \times 10^{-10}$  m**

<

**Plasmonic Spatial scale**

<

**A few tens of micrometers  $\sim 10 \mu\text{m} = 1 \cdot 10^{-5}$  m**



## Plasmonics – Physical orders of magnitude – Time scale

### Dynamics of the plasmonic near field

#### ➤ Characteristic times of plasmonic physics

- .Photon absorption time = Half-period of a Rabi oscillation  $\sim 1.10^{-16}$  s
- .Photon field oscillation  $\sim 1 / 500$  THz  $\approx 1.10^{-15}$  s
- .Plasmonic field oscillation  $\sim 1 / 500$  THz  $\approx 1.10^{-15}$  s
- .Plasmon coherence lifetime  $\sim 10$  fs =  $1.10^{-14}$  s
- .Thermalisation time of a hot  $e^-$  gas  $\sim 100$  fs =  $1.10^{-13}$  s
- .Thermalisation time of a hot  $e^-$  gas coupled to a phonon bath  $\sim 1$  ps =  $1.10^{-12}$  s

**A few tenths of a femtosecond  $\sim 0.1$  fs =  $1 \times 10^{-16}$  s**

<

**Plasmonic Time scale**

<

**One picosecond 1 ps =  $1.10^{-12}$  s**



## Plasmonics – Physical orders of magnitude – Energy scale

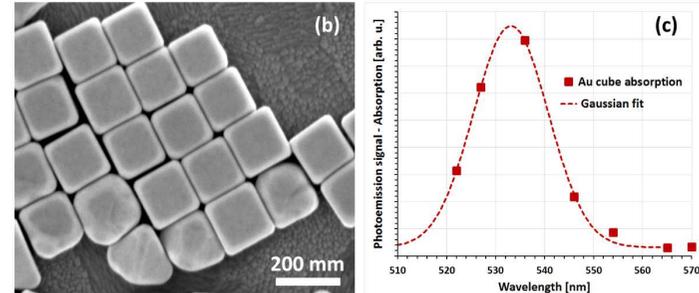
Energy of a localised surface plasmon, surface plasmon polariton

- Localised plasmon resonance energy - Full Width at Half Maximum FWHM

$$\text{FWHM} = \frac{2\hbar}{\text{Plasmon coherence time } T}$$

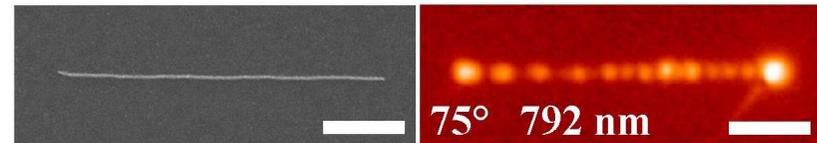
N.A. Plasmon coherence time  $T \approx 10 \text{ fs} = 1 \cdot 10^{-14} \text{ s}$

FWHM  $\approx 100 \text{ meV} \Leftrightarrow 23 \text{ nm}@530 \text{ nm}$



- Energy of a plasmon propagating along an infinite cylinder of sectional radius  $R$

$$\lambda_{SR-SPP} = 2\pi R \left( a_1 + a_2 \frac{\lambda_0}{\lambda_{Au \text{ plasma}}} \right)$$



N.A.  $R = 20 \text{ nm}$ ,  $\lambda_{0 \text{ vacuum}} = 792 \text{ nm}$ ,  $\lambda_{Au \text{ plasma}} = 138 \text{ nm}$ ,  $(a_1, a_2) = f(\epsilon_{Au})$

$\lambda_{SR-SPP} = 335 \text{ nm} \Leftrightarrow E_{SR-SPP} = 3.7 \text{ eV}$ , so in the range 1 – 10 eV

**A few tens of meV ~ 10 meV = 0.01 eV**

<

**Plasmonic Energy scale**

<

**Several eV ~ 10 eV**



## Plasmonic near fields – Physical orders of magnitude

**A few tenths of a nanometer  $\sim 0.1 \text{ nm} = 1 \times 10^{-10} \text{ m}$**

<

**Plasmonic Spatial Scale**

<

**A few tens of micrometers  $\sim 10 \text{ }\mu\text{m} = 1 \cdot 10^{-5} \text{ m}$**

**A few tenths of a femtosecond  $\sim 0.1 \text{ fs} = 1 \times 10^{-16} \text{ s}$**

<

**Plasmonic Time Scale**

<

**One picosecond  $1 \text{ ps} = 1 \cdot 10^{-12} \text{ s}$**

**A few tens of meV  $\sim 10 \text{ meV} = 0.01 \text{ eV}$**

<

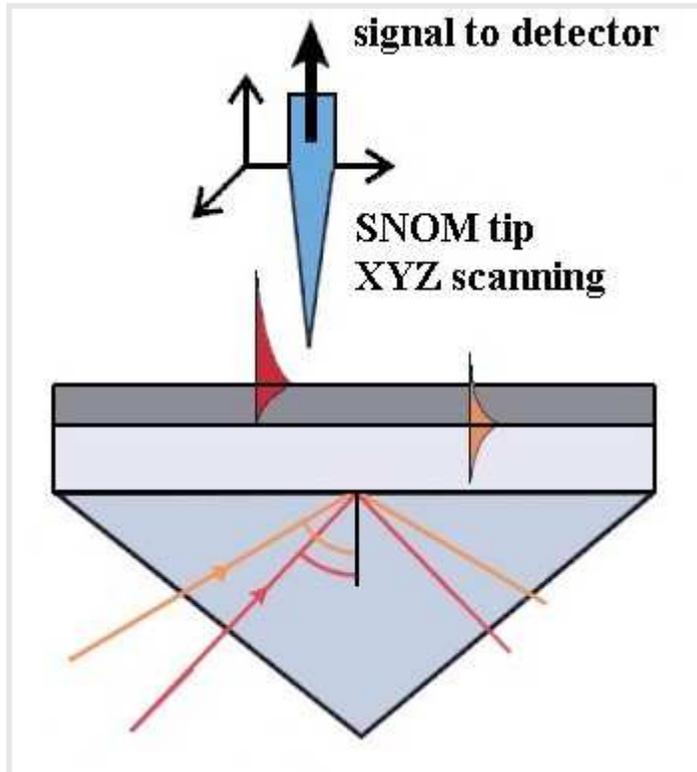
**Plasmonic Energy Scale**

<

**Several eV  $\sim 10 \text{ eV}$**

# Mapping the evanescent field at the nanometre

SNOM/NSOM - *scanning near-field optical microscopy* (1984...)



## ➤ Basic principle

.scanning probe microscopy SPM. Closely related to scanning tunnelling microscopy STM

.introduction of a tip (glass fiber, metal...) in the near field of the object to be studied – **intrusive technique**

.routine resolution 50 - 100 nm

.many variants (illumination and collection modes)

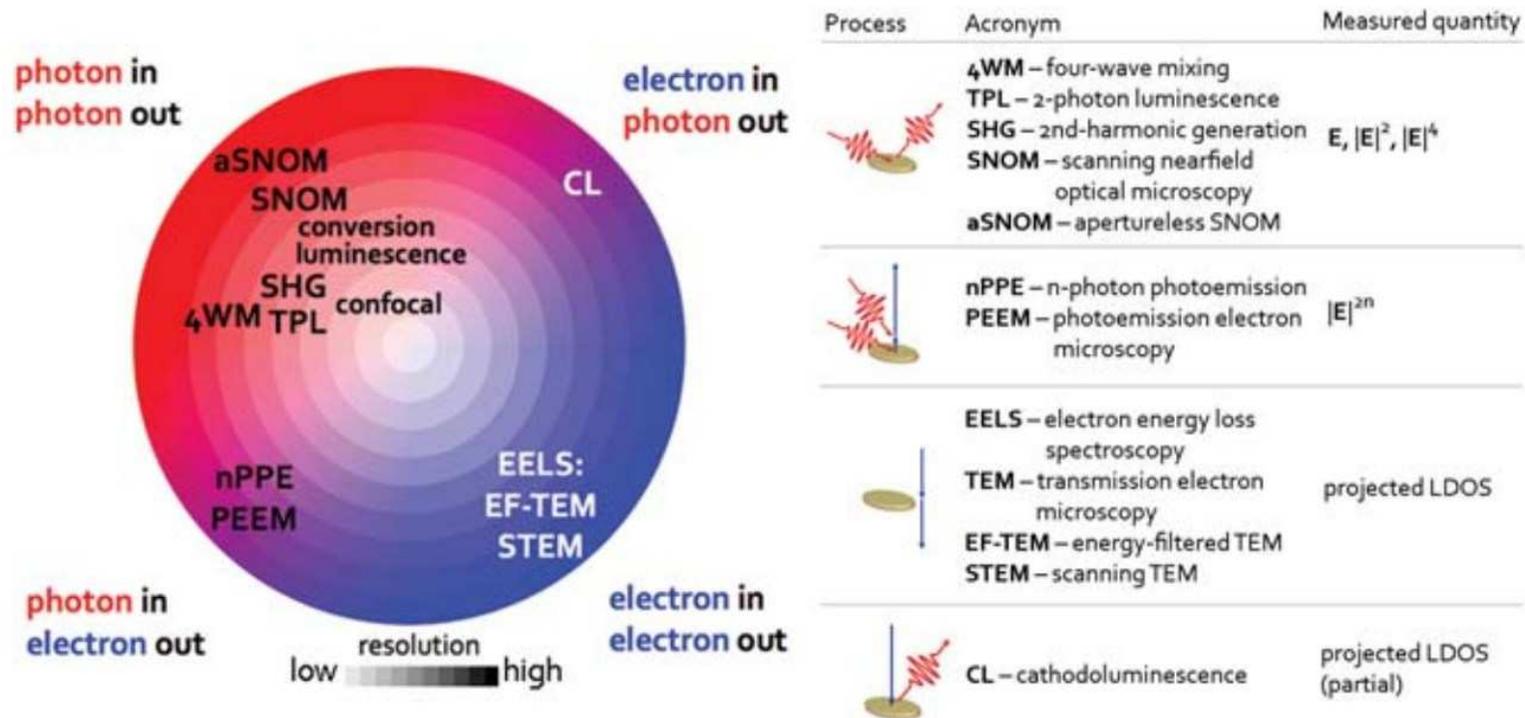
## ➤ Drawbacks

.low reproducibility of tips

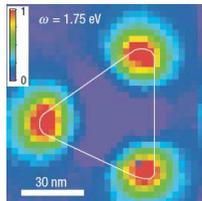
.possible perturbation of the evanescent field due to LSP excitation and lightning-rod geometric effect at the tip-surface junction

# Mapping the evanescent field at the nanometre

## Alternative non intrusive methods (2012)

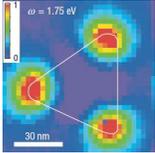


- STEM EELS *scanning transmission microscopy in electron energy loss spectro. mode* (electron in, electron out) = Mapping of an electron energy loss signature
- CL *cathodoluminescence* (electron in, photon out) related to EELS
- PEEM *photoemission electron microscopy* (photon in, electron out), other acronym = n-PPE *n photon photoemission*



# Electron Energy Loss Spectrometry EELS

## A tool for plasmonics



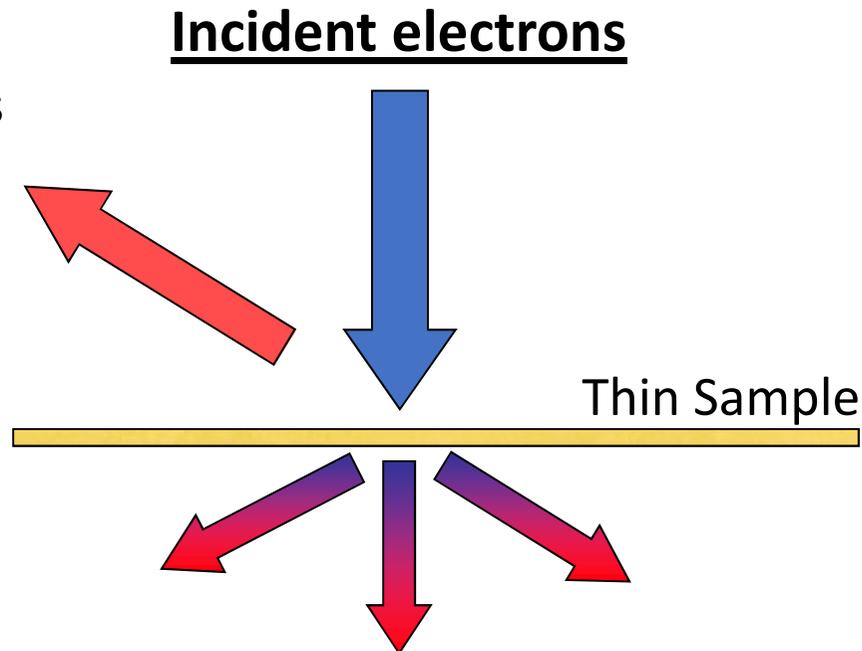
# Electron energy loss spectrometry, a tool for plasmonics

Basic principle – Electron energy loss mapping

➤ To probe locally a sample (surface, thin film, particle) with a focused electron beam and investigate its excitations using the inelastically diffracted / scattered electrons

Secondary electrons  
Backscattered electrons  
Auger electrons

**SEM, AES**



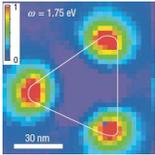
Inelastically diffracted and scattered electrons  
♦ Individual excitations  
♦ Collective excitations

**EELS Spectrometry**

Transmitted electrons  
**TEM Bright Field Imaging**

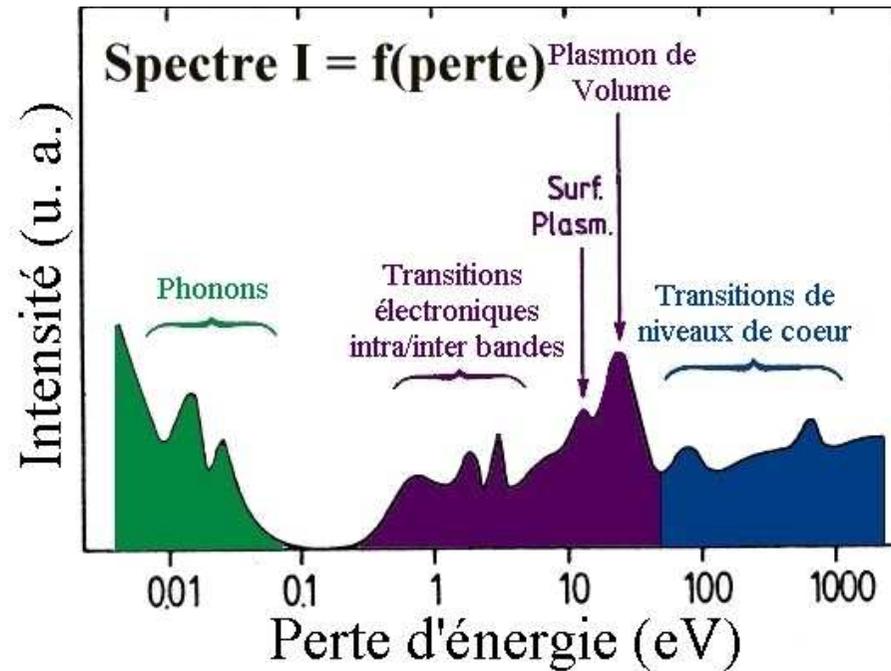
Elastically scattered and diffracted electrons

**HR Diffraction (HA)ADF  
Holography**



# Electron energy loss spectrometry, a tool for plasmonics

Basic principle – Electron energy loss spectrum



**Zero loss region – Low primary energies, high energetic resolution**

$$1 \text{ meV} < \Delta E < 100 \text{ meV}$$

→ High Resolution Electron Energy Loss Spectrometry HREELS

**Low loss region**

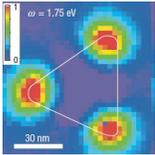
$$100 \text{ meV} < \Delta E < 50 \text{ eV}$$

→ Electron Energy Loss Spectrometry EELS

**High loss region – High primary energies**

$$\Delta E > 50 \text{ eV}$$

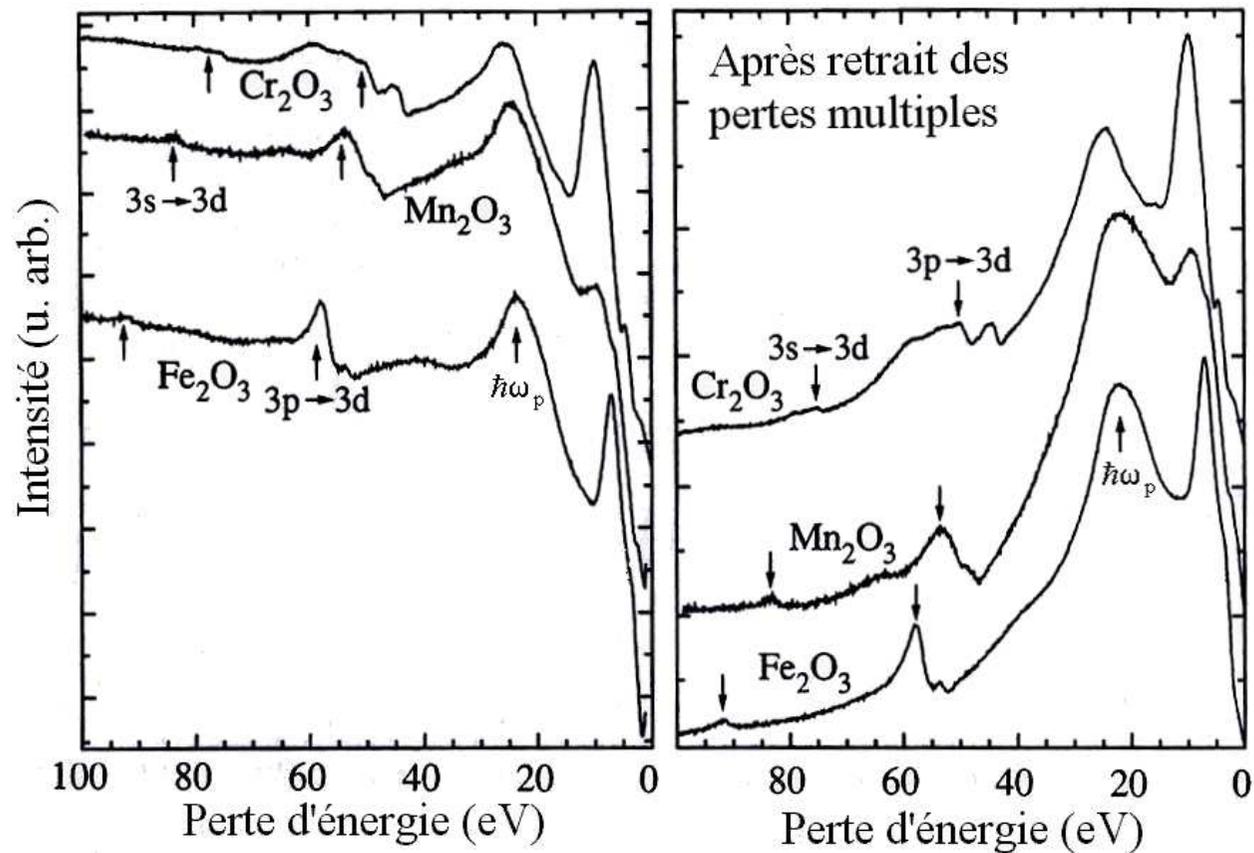
→ EXTENDED Electron energy Loss Fine Structures EXELFS



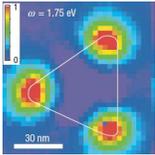
## Electron energy loss spectrometry, a tool for plasmonics

Basic principle – EELS, loss region  $100 \text{ meV} < \Delta E < 50 \text{ eV}$

- Excitation mechanism n°1
  - Individual excitations
  - Electronic intra-, resp. interband transitions



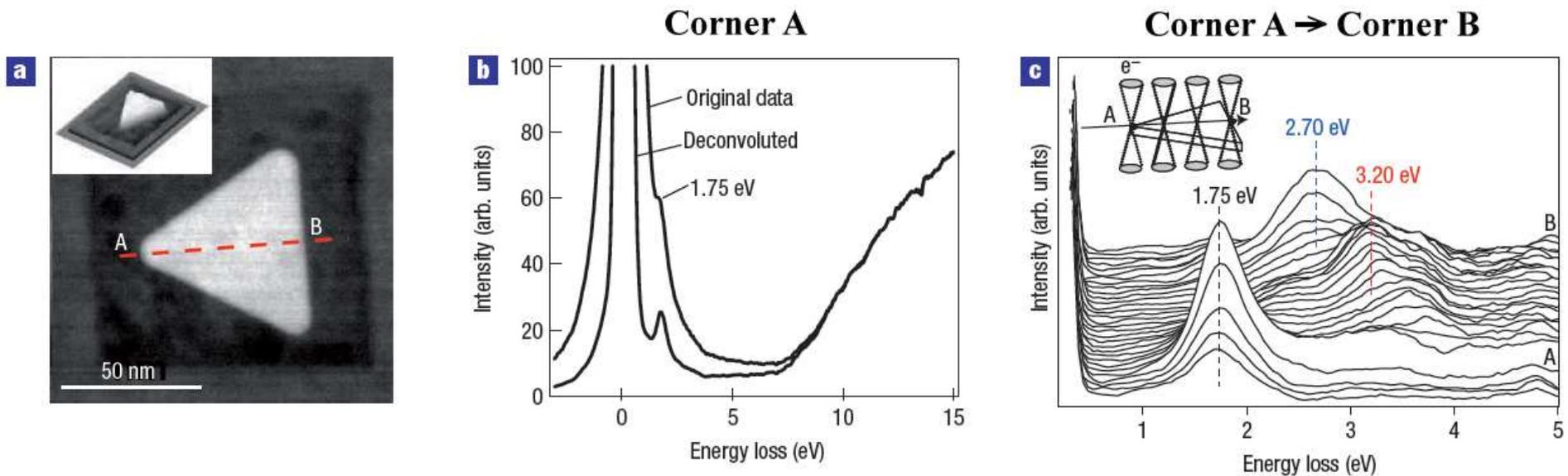
Electron energy loss spectra of transition metal oxides R. Zimmerman PhD (1996)



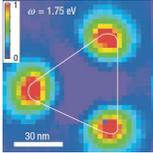
# Electron energy loss spectrometry, a tool for plasmonics

Basic principle – EELS, loss region  $100 \text{ meV} < \Delta E < 50 \text{ eV}$

- Excitation mechanism n°2
- Collective excitations
- Surface and bulk plasmons**



- (a) Regular Au nanoprism particle. HAADF-STEM imaging
- (b) EELS spectra acquired at corner A. One plasmon loss peaks at 1.75 eV
- (c) A series of 32 successive low loss STEM EELS spectra acquired along the line A - B of the nanoprism. Three plasmon resonances are detected 1.75, 2.70 and 3.20 eV



## Electron energy loss spectrometry, a tool for plasmonics

Basic principle – EELS probability for a small sphere  $a \ll \lambda$

➤ The transient electric field associated to the e-beam is similar to a plane wave pulse of white light. The nanoparticle (NP) sees a pulse containing a large spectrum of frequencies.

(e, e) Coulombian coupling in nature

➤ All the energy absorbed or scattered by a plasmonic particle has to be provided by the incident electrons. So, full electron losses are proportional to the particle extinction cross section

$$\Gamma_{\text{loss}} = \Gamma_{\text{EELS}} + \Gamma_{\text{Rad. CL}}$$

$$\Gamma_{\text{EELS}}^{\text{sphere}}(R_{\perp}, \omega) = \frac{4e^2 a}{\pi \hbar v^2} \sum_{l=1}^{\infty} \sum_{m=-l}^l \frac{(a\omega/v)^{2l} (2 - \delta_{0,m})}{(l+m)!(l-m)!} K_m^2 \left( \frac{\omega R_{\perp}}{v} \right) \Im \{ \alpha_l(\omega) \}$$

$a$  Sphere diameter

$R_{\perp} = (x, y)$  Impact parameter of the electrons traveling along the  $z$  direction at speed  $v$ ,

$\hbar\omega$  Loss energy,  $\omega$  pulsation =  $2\pi \cdot \text{frequency}$

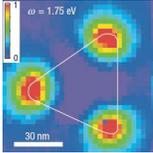
$K_m$  Modified Bessel function of the second kind

$\Im$  Imaginary part

$\alpha_l$  Sphere polarizability for mode  $l$

Non relativistic electrons. For relativistic electrons the Lorentz factor  $\gamma = 1/\sqrt{1 - v^2/c^2}$  has to be considered

➤ EELS depends on all resonance modes  $l$  of the NP



## Electron energy loss spectrometry, a tool for plasmonics

Basic principle – EELS probability for a small sphere  $a \ll \lambda$

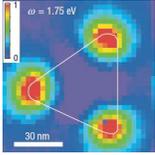
- The e-beam electric field is similar to a plane wave pulse of white light. The NP sees a pulse containing a large spectrum of frequencies
- In the quasi-static QS approximation, the exciting field is static, i.e. presents no spatial variation over the particle. Thus, it couples only to the  $l=1$  dipolar mode

$$\Gamma_{EELS}^{sphere}(\omega, R_{\perp}) \propto \left(\frac{\omega}{\gamma v^2}\right)^2 \Im(\alpha_{l=1}(\omega)) \left( K_1^2\left(\frac{\omega R_{\perp}}{\gamma v}\right) + \frac{1}{\gamma^2} K_0^2\left(\frac{\omega R_{\perp}}{\gamma v}\right) \right)$$

$$\Gamma_{EELS}^{sphere}(\omega, R_{\perp}) \propto \Im(\alpha_{l=1}(\omega)) \cdot \exp\left(-\frac{R_{\perp}}{\gamma v/\omega}\right)$$

$$\sigma_{ext.} \cong \sigma_{abs.} \propto \Im(\alpha_{l=1}(\omega))$$

- EELS probability of a small sphere is proportional to its absorption cross-section as measured in far field optics,  $\sigma_{ext.} \cong \sigma_{abs.} \propto \Im(\alpha_{l=1}(\omega)) \propto a^3$
- EELS probability is position-dependent with a quasi-exponential decay with e-beam to sphere distance  $R_{\perp}$ , attenuation length =  $\gamma v/\omega \sim 10 - 100$  nm



# Electron energy loss spectrometry, a tool for plasmonics

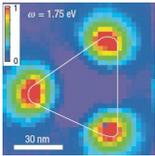
## Basic principle – EELS probability vs EMLDOS

In quasi-static approximation

$$\Gamma_{EELS}^{sphere}(\omega, \vec{R}_{\perp}) = \frac{e^2}{\pi \hbar \omega^2} \sum_i \Im(f_i(\omega)) \left| TF_z(\vec{E}_i^z(\vec{R}_{\perp}, \frac{\omega}{v})) \right|^2$$

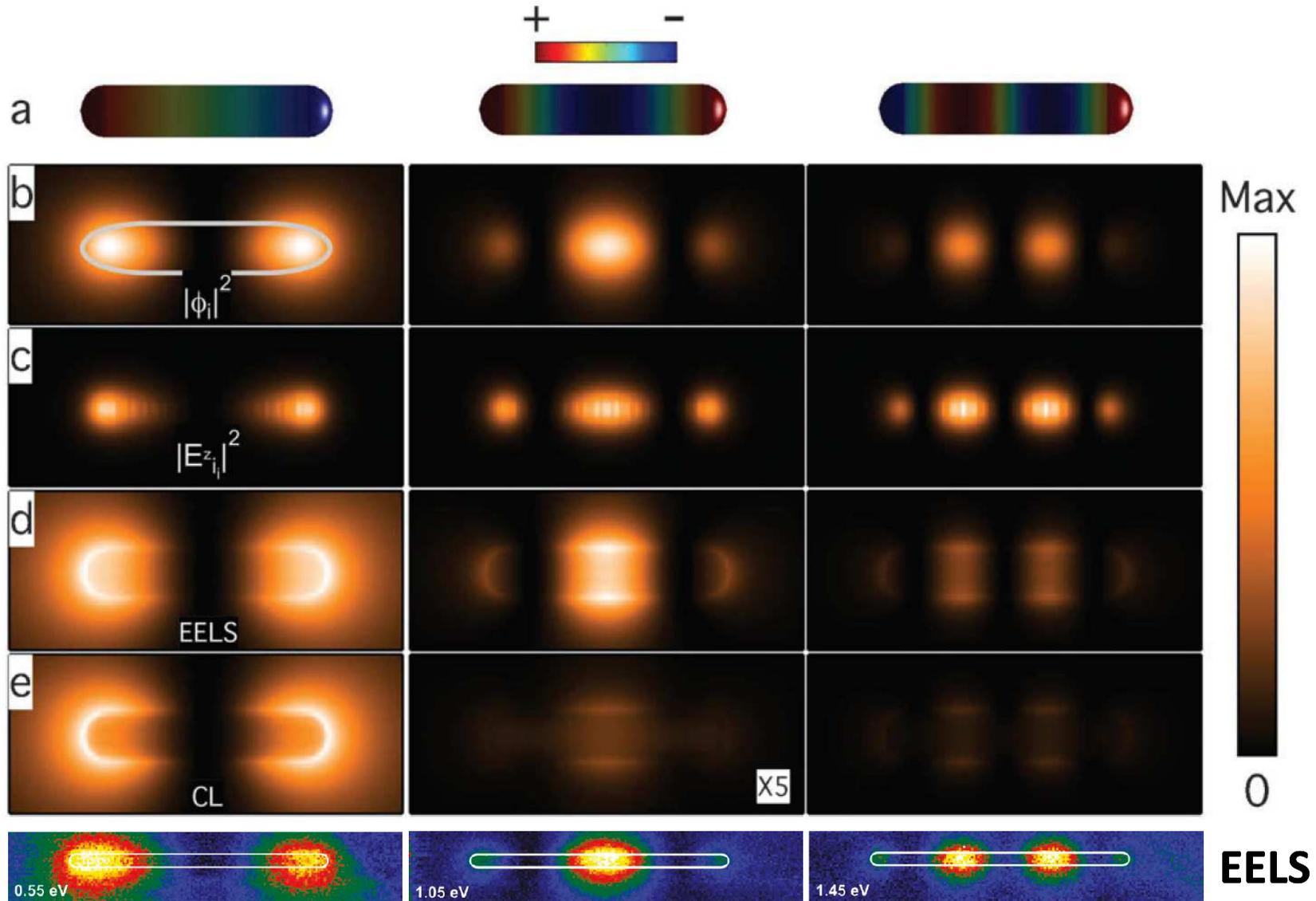
$f_i$  generalized polarizability, i.e. the spectral dependence of the plasmon (plasmon energies =  $f_i$  poles);  $TF_z$  is a Fourier transform along the e-beam direction at point  $\vec{R}_{\perp} = (x, y)$  in real space and momentum  $q_z = \omega / v$  in reciprocal space of the electron induced nearfield electric field

- Within a  $TF_z$ , EELS maps spectrally and spatially the zEMLDOS, i.e. the electromagnetic density of states in the direction along the e-beam axis
- EELS = Out-of-plane EMLDOS ( $\vec{v}_e \cdot \vec{E}_{ind} = \vec{v}_{e,z} \cdot \vec{E}_{ind,z}$ )
- Electron selection rules  $\neq$  photon selection rules  $\rightarrow$  Dark modes accessible
- Not a true optical process, so no direct control over the near field polarization



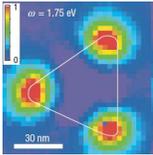
# Electron energy loss spectrometry, a tool for plasmonics

Basic principle – EELS probability



D. Rossouw *et al.* *Nano Lett.* **11** (2011) 1499

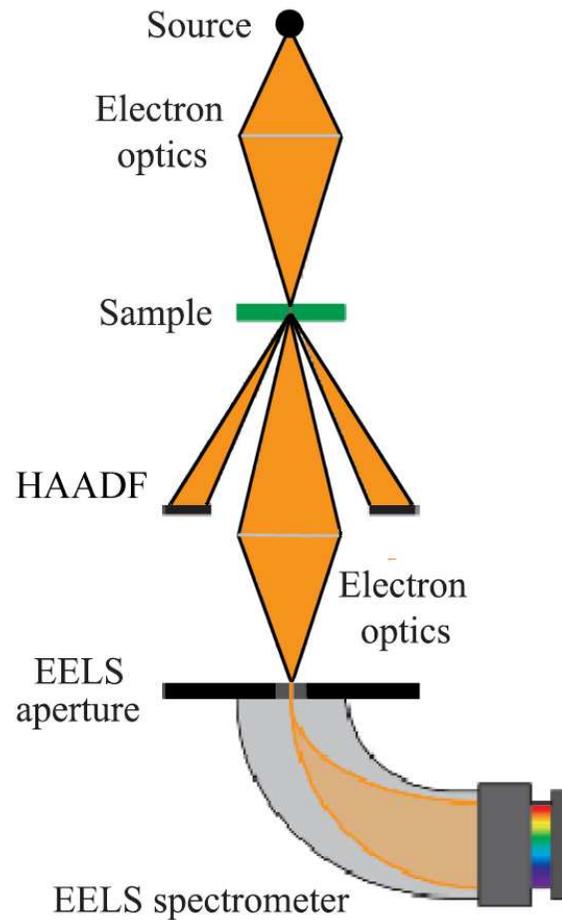
M. Kociak & O. Stéphan *Chem. Soc. Rev.* **43** (2014) 3865



# Electron energy loss spectrometry, a tool for plasmonics

Instrumentation – STEM EELS mode

## STEM - EELS



➤ Scanning transmission electron microscope in electron energy loss mode - (electron in, electron out) process

Electron source (electron field gun)

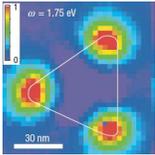
Electron optics

Energy = Hundreds of keV (TEM)

The electron beam is focused and raster scanned on the sample. Beam diameter  $\varnothing \leq 1$  nm

EELS spectrometer for the extraction of the EELS spectrum at precise (x, y) position – Serial recording

➤ Near field imaging through the mapping of a particular electron energy loss (plasmon energy). Spatial resolution  $\approx$  beam diameter

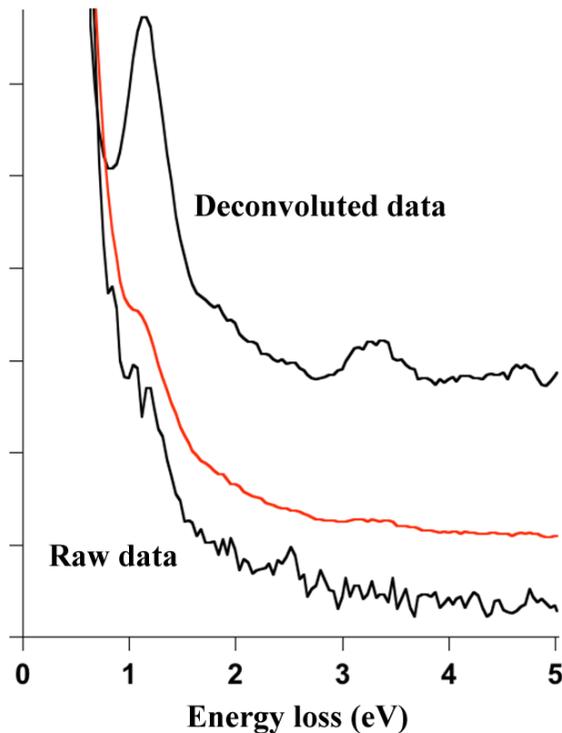


# Electron energy loss spectrometry, a tool for plasmonics

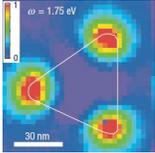
## Instrumentation – STEM EELS Difficulties & Limitations

### ➤ How to get rid of the Zero Loss Peak ZLP

- ◆ The major experimental issue is to get at the same time both high energy- ( $\delta E = 100$  meV) and high spatial- ( $\delta R = 0.1$  nm) resolutions
- ◆ Thank to high brightness electron gun developments, beam monochromatisation ( $\delta E$ ) is possible without too large drops of brightness ( $\delta R$ )
- ◆ Numerical treatments for better spectral deconvolution are now available. PSF deconvolution, Richardson-Lucy Deconvolution Gloter *et al.* Ultramicroscopy **96** (2003) 385
- ◆ Less noisy and faster CCD detectors are available



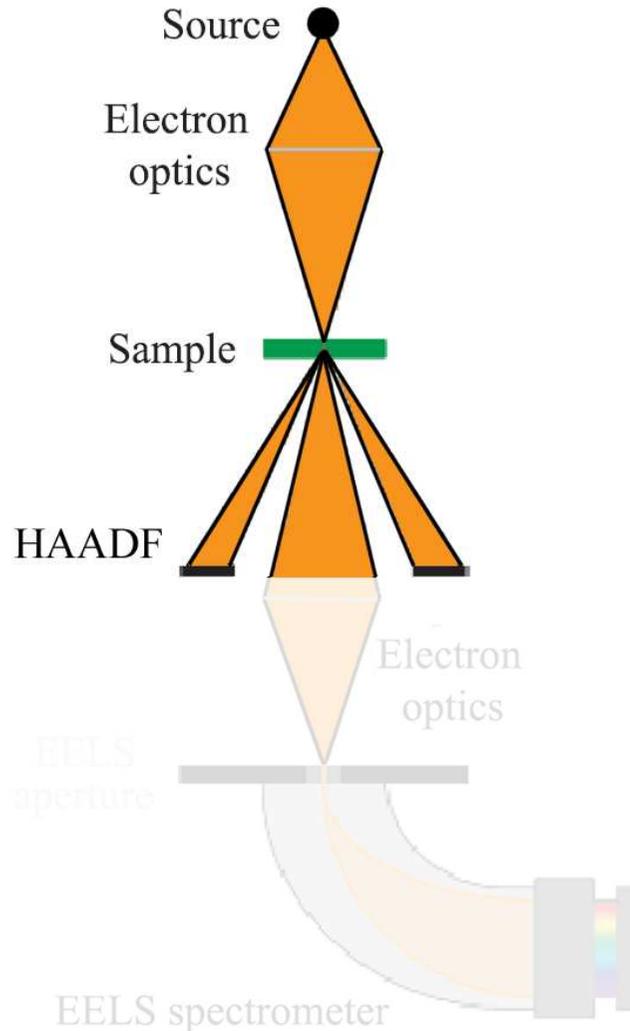
### ➤ Electron monochromator resolution is now down to 10 meV = 0.01 eV (2019)



# Electron energy loss spectrometry, a tool for plasmonics

Instrumentation – STEM Bright Field Imaging mode

## STEM - EELS



➤ Electron imaging

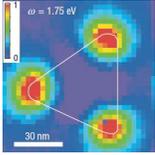
Electron source (electron field gun)

Electron optics

The electron beam is focused and raster scanned on the sample. Beam diameter  $\varnothing \leq 1 \text{ nm}$

➤ SEM Imaging. Image is build on backscattered, secondary and/or Auger electrons

➤ TEM Imaging. Image is build on transmitted electrons

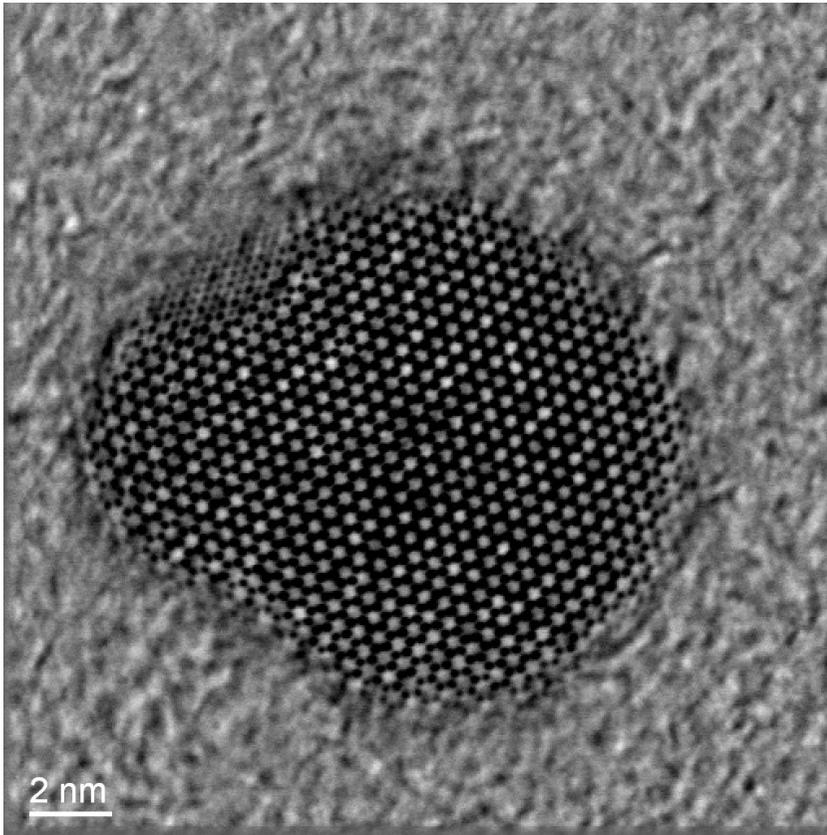


# Electron energy loss spectrometry, a tool for plasmonics

Instrumentation – STEM Imaging mode

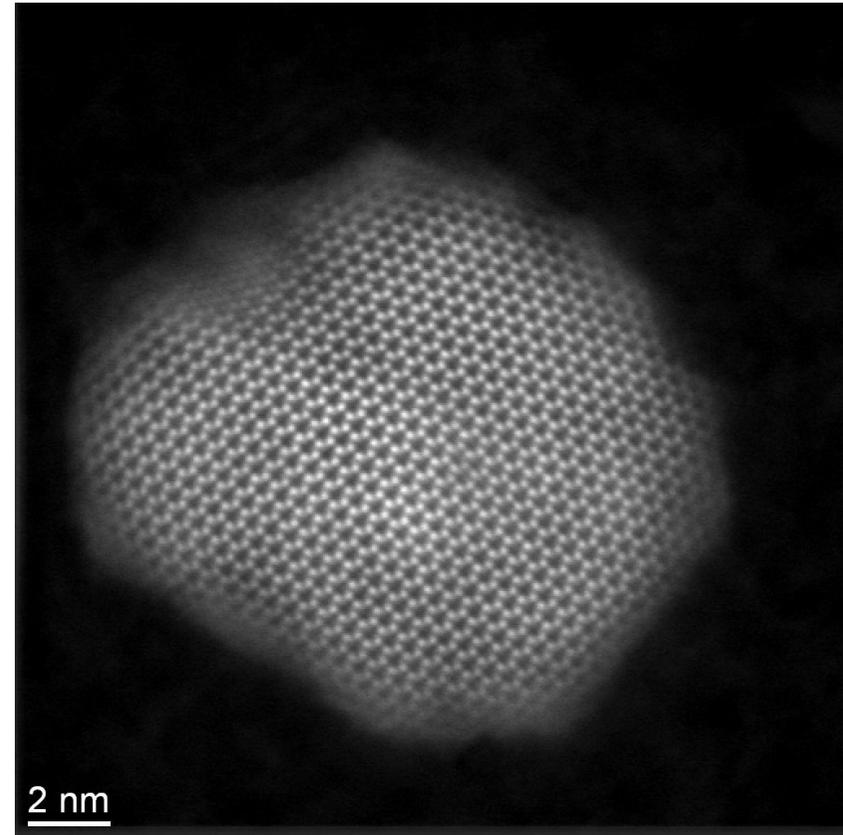
## Bright field imaging mode

CdSe Platelets, courtesy B. Dubertret

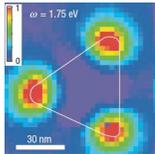


## Dark Field imaging mode

CdSe Platelets, courtesy B. Dubertret

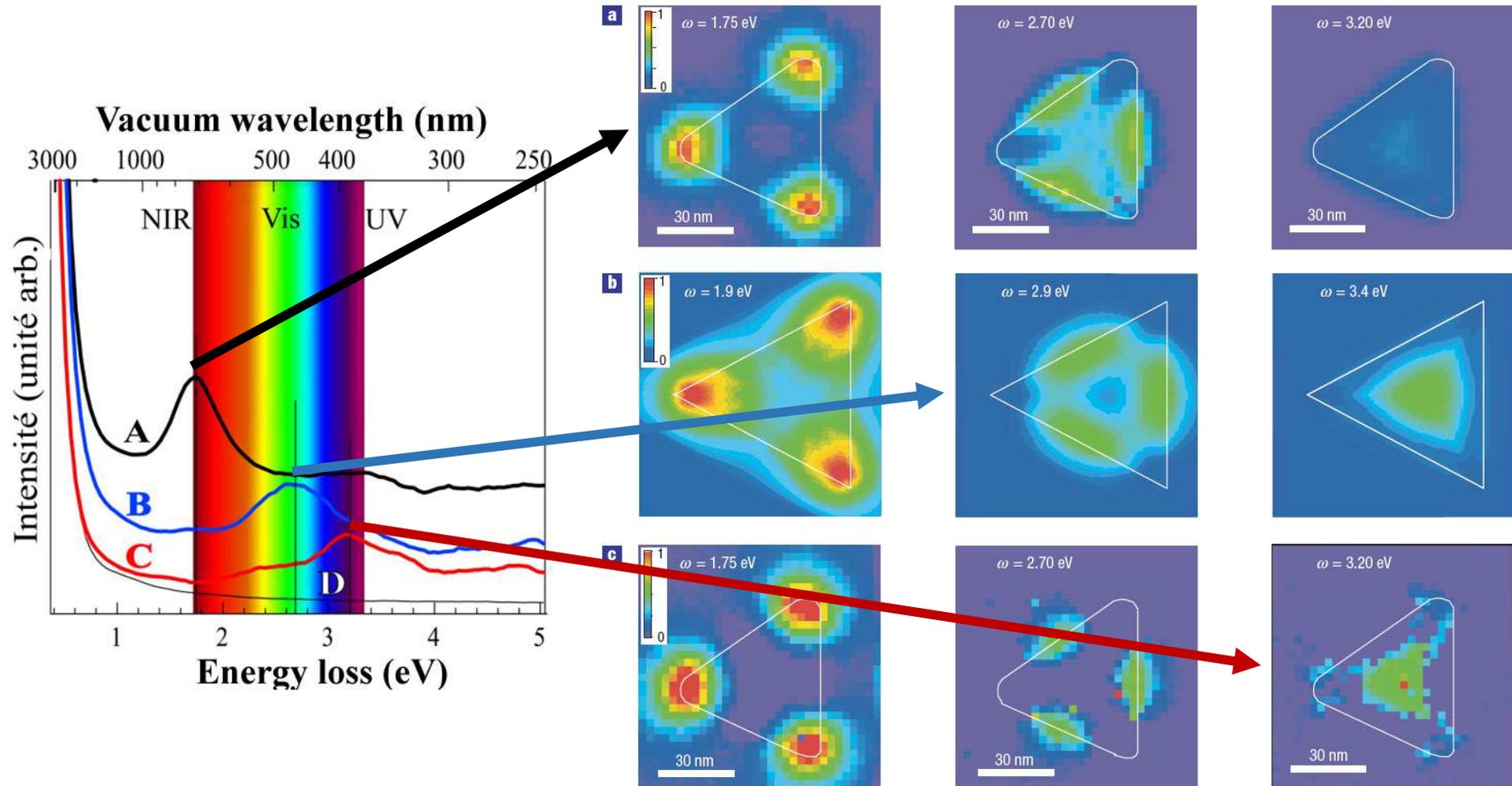


- Fast electron probes can be made much smaller than the typical visible light wavelength. Atomic resolution  $\approx 0.1$  nm possible

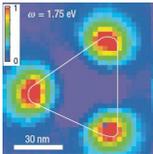


# Plasmonics of 2D objects - NanoPrism $D_{3h}$ - STEM EELS

EELS near field imaging

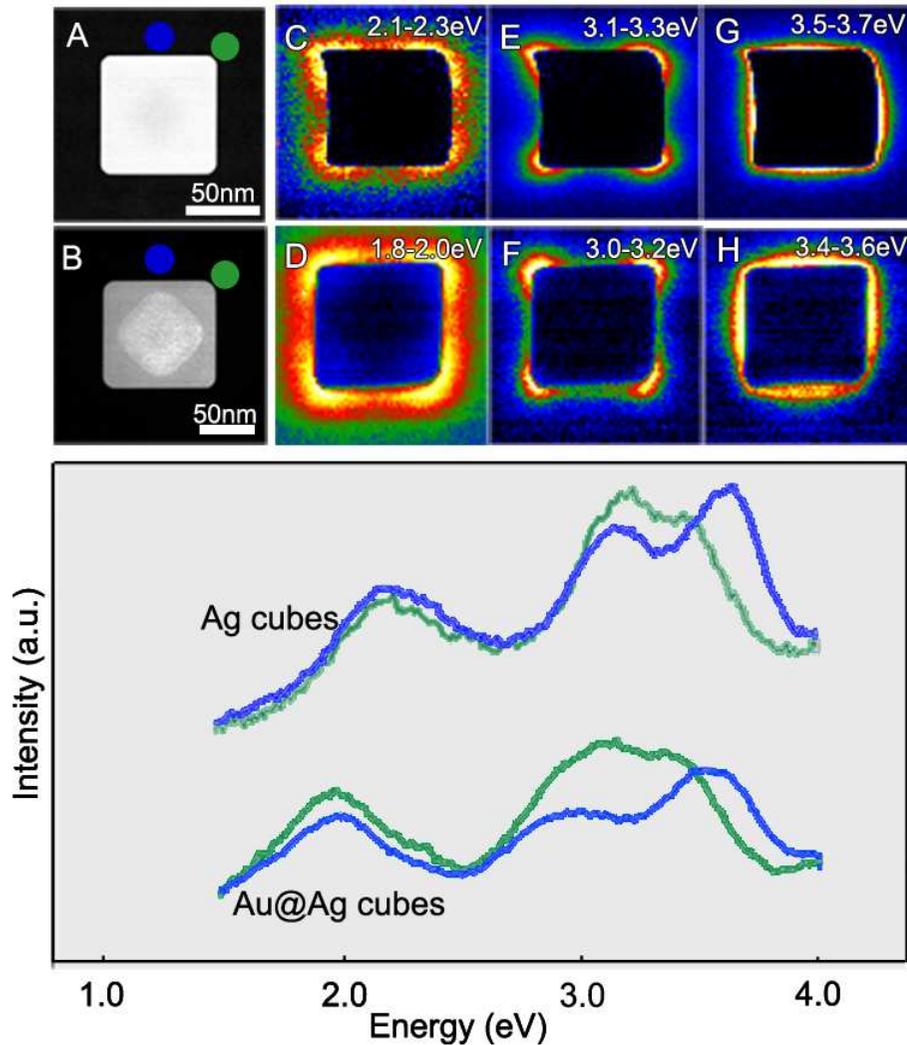


Regular nanoprism 78 nm. Near field Imaging. Resonance modes,  $m = \{1, 2, 3\}$  – STEM EELS  
 (a) Raw exp data – ZLP, (b) FDTD simulation , (c) Gaussian fitting of the exp. data



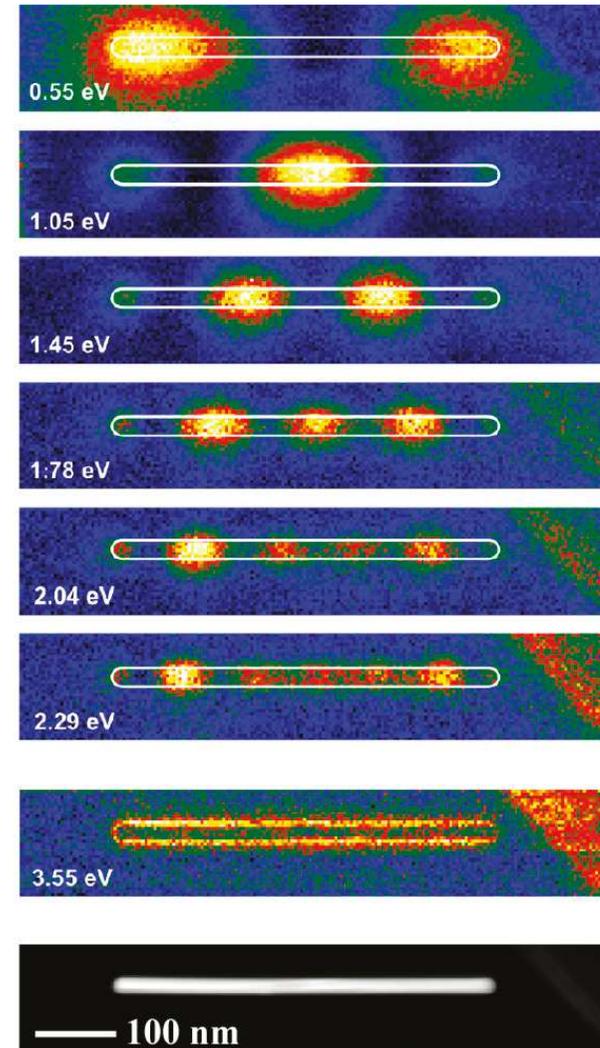
# Plasmonics of Nanoobjects – Cubes & Rods - STEM EELS

EELS near field imaging



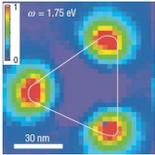
Ag and Au@Ag NanoCubes 70 nm

B. Goris *et al.* *J. Phys. Chem. C* **118** (2014) 15356



Ag NanoRods, 14 nm in diameter

D. Rossouw *et al.* *Nano Lett.* **11** (2011) 1499



# Electron energy loss spectrometry, a tool for plasmonics

## EELS near field imaging - Variants & Advances

- ◆ EELS 3D tomography

- 3D mapping of plasmon resonances O. Nicoletti *et al. Nature* **502** (2013) 80; A. Hörl *et al. Phys. Rev. Lett.* **111** (2013) 076801

- ◆ Time-resolved EELS measurements in the fs time range

- Use of a pulsed optical excitation combined with a pulsed electron probe F. Carbone *et al. Science* **325** (2009) 181

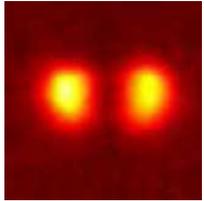
- ◆ Vortex EELS measurements

- Use of an electron beam that carries an angular orbital momentum (diffractive phase plate, magnetic lens aberrations)

Applications = Measurement of magnetic phenomena at the nanoscale

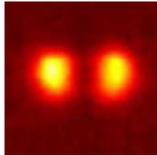
Magnetic plasmon mapping Z. Mohammadi *et al. Opt. Express* **20** (2012) 15024

Magnetic dichroism measurements in plasmonic structures X. Zambrana-Puyalto *et al. Nat. Commun.* **5** (2014) 4922



# **Cathodoluminescence CL**

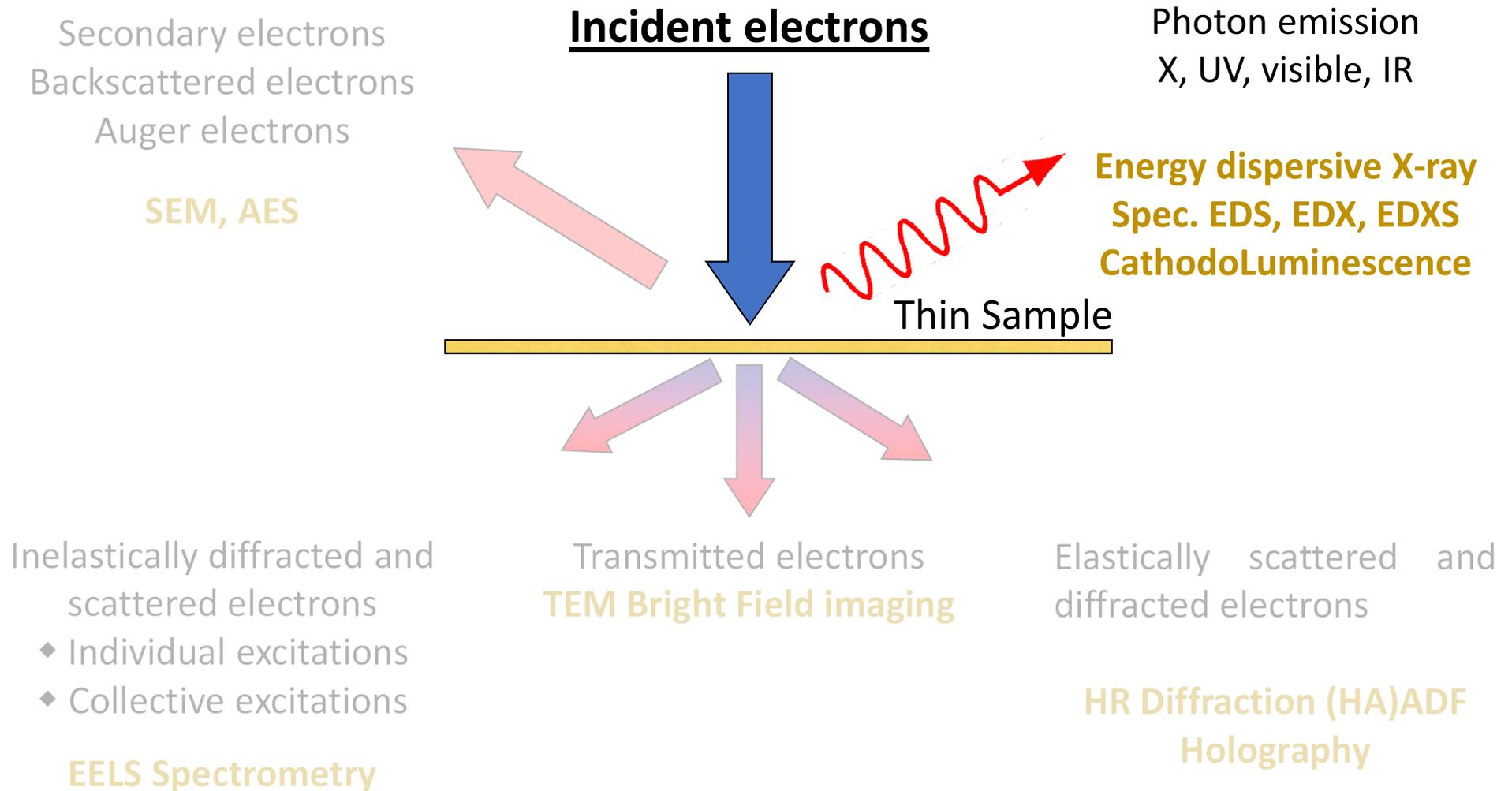
## **A tool for plasmonics**

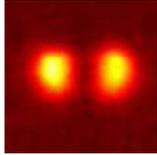


## Cathodoluminescence, a tool for plasmonics

Basic principle – Cathodoluminescence near field imaging

- To probe locally a sample (surface, thin film, object) with a focused electron beam and investigate its excitations by collecting the emitted light (vis. spectrum)





## Cathodoluminescence, a tool for plasmonics

### Basic principle – Coherent CL probability

- The transient electric field associated to the e-beam is similar to a plane wave pulse of white light. The NP sees an EM pulse containing a large spectrum of frequencies
- In the QS approximation, the exciting field is static, i.e. presents no spatial variation over the particle size. Thus, it couples only to the  $l=1$  dipolar mode

$$\Gamma_{CL}^{sphere}(\omega, R_{\perp}) \propto \omega^3 \left(\frac{\omega}{\gamma v^2}\right)^2 |\alpha_{l=1}(\omega)|^2 \left( K_1^2\left(\frac{\omega R_{\perp}}{\gamma v}\right) + \frac{1}{\gamma^2} K_0^2\left(\frac{\omega R_{\perp}}{\gamma v}\right) \right)$$

$$\Gamma_{CL}^{sphere}(\omega, R_{\perp}) \propto |\alpha_{l=1}(\omega)|^2 \exp\left(-\frac{R_{\perp}}{\gamma v/\omega}\right)$$

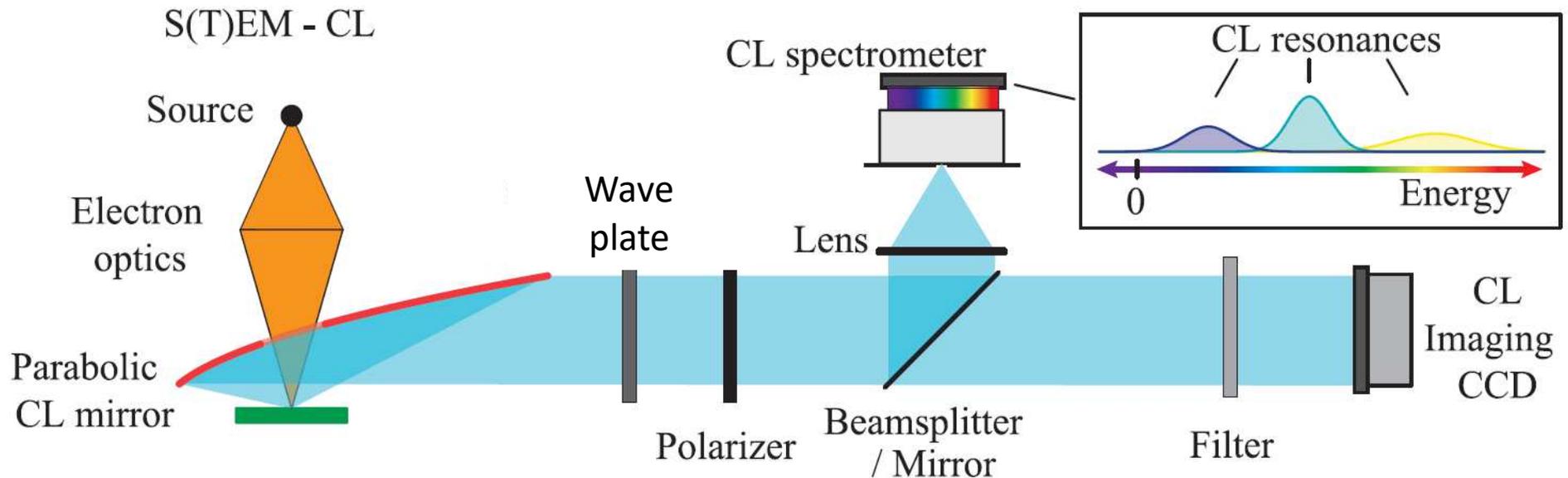
a Sphere diameter;  $R_{\perp} = (x, y)$  Impact parameter of the electrons traveling along the z direction at speed  $v$ ;  $\hbar\omega$  Energy of the emitted photon;  $K_m$  Modified Bessel function of the second kind;  $\alpha_l$  Sphere polarizability for mode  $l$

- CL probability of a small sphere is proportional to its scattering cross section as measured in far field optics,  $\sigma_{sca.} \propto |\alpha_{l=1}(\omega)|^2 \propto a^6$
- CL probability is position-dependent with a quasi-exponential decay with e-beam to sphere distance  $R_{\perp}$ , attenuation length  $\gamma v/\omega \sim 10 - 100$  nm
- Radiative bright field modes accessible



## Cathodoluminescence, a tool for plasmonics

Instrumentation – SEM CL (a few 10 kV) , STEM CL (a few 100 kV)



➤ Scanning (transmission) electron microscope in cathodoluminescence mode - (electron in, photon out) process

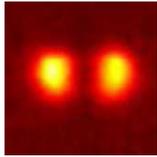
.Electron source (electron field gun)

.Electron optics, Electron energy = Tens of keV for a SEM, hundreds of keV for a TEM

.The electron beam is focused and raster scanned on the sample. Beam diam.  $\varnothing \approx 10$  nm

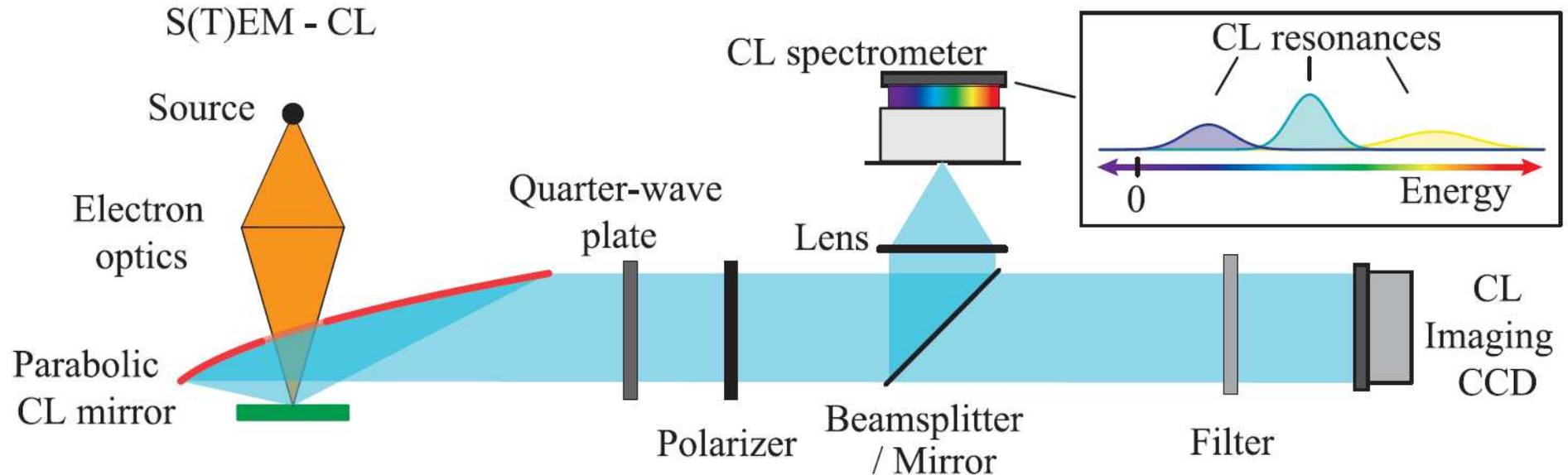
.The optical luminescence spectrum is collected using a parabolic mirror at each beam position (x, y)

➤ Near field imaging through the mapping of a cathodoluminescence signal



## Cathodoluminescence, a tool for plasmonics

Instrumentation – SEM CL (a few 10 kV) , STEM CL (a few 100 kV)

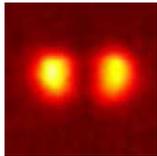


### ➤ Scanning (transmission) electron microscope in cathodoluminescence mode

- ◆ CL imaging mode. Acquisition of the spatially resolved cathodoluminescence signal at a particular optical wavelength  $\lambda$ . Spatial resolution  $\delta R \approx$  electron beam diameter  $\approx 10$  nm.

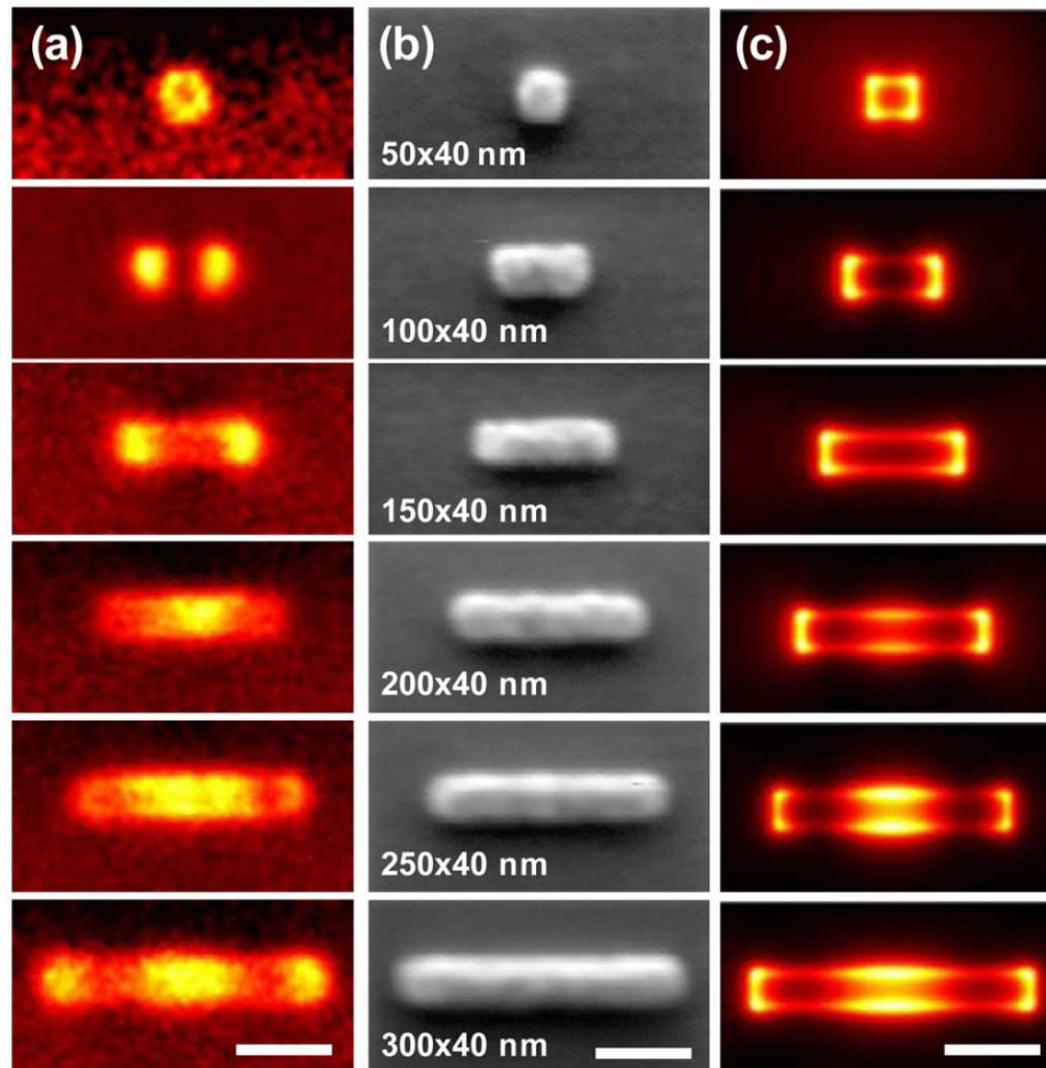
- ◆ CL spectrometry. Acquisition of a CL spectrum  $I_{CL} = f(\lambda)$  at a fixed position  $(x, y)$   
CL signal spectral resolution 1 - 10 meV  $\Leftrightarrow$  0.3 – 3 nm @ 600 nm  
Significant broad luminescence background (post treatment analysis required)

- ◆ Optical signal = Additional information available like the polarization of the emitted light

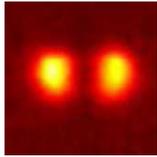


## Plasmonics of Nanoobjects - NanoRods

Cathodoluminescence near field imaging – STEM CL (x,y) mode

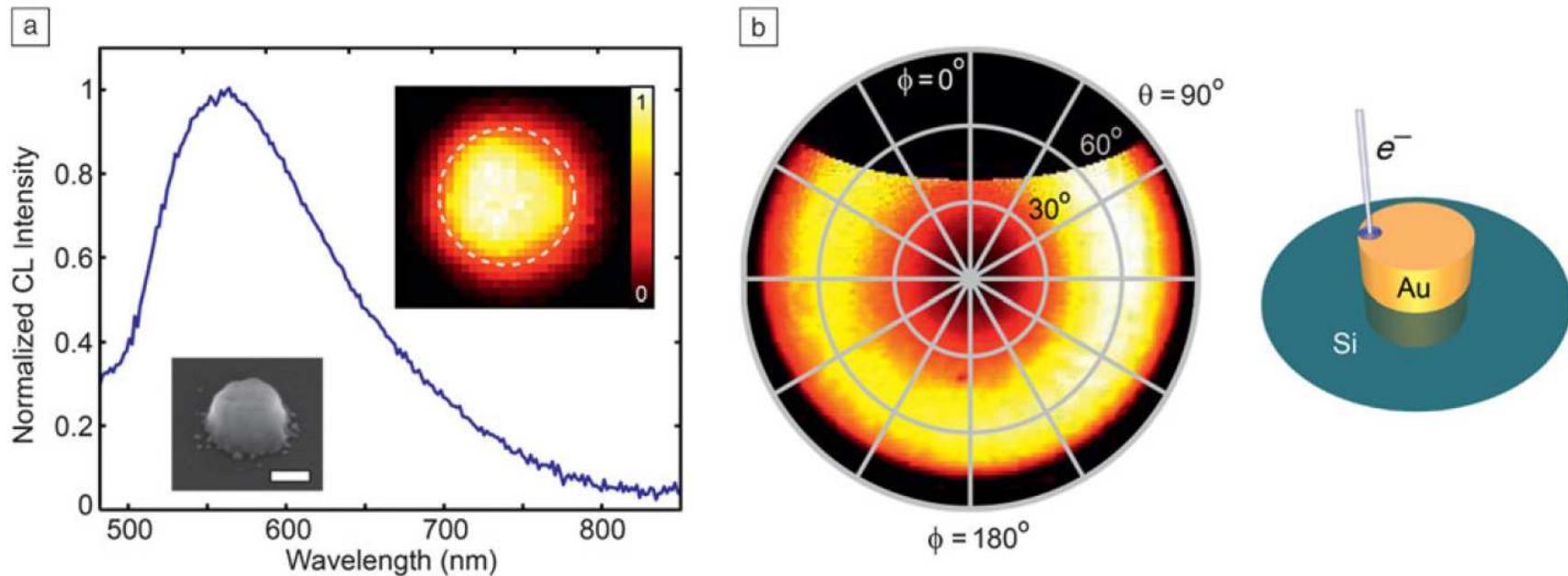


Al nanorods (a) CL near field imaging for energy range 2.5 – 3.0 eV  
(b) SEM images (c) Calculated electromagnetic field distribution (FDTD)



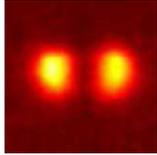
## Cathodoluminescence, a tool for plasmonics

Cathodoluminescence near field spectro. – STEM CL ( $\lambda$ ) mode



Au nanoparticle 100 nm in diameter and 80 nm in height on Si

- CL Spectrometry. (a) CL spectrum spatially averaged over the particle with a 5 nm resolution. A clear resonant spectrum is observed, which reflects the CL radiation of a vertically-oriented dipolar plasmon resonance in the Au NP peaking at  $\lambda = 560$  nm
- Angle resolved CL imaging. (b) Angular distribution of the CL radiation emitted by the Au NP. Off center  $e^-$  beam excitation translates into an asymmetric intensity profile ( $\perp$  &  $//$  dipoles)



# Cathodoluminescence, a tool for plasmonics

## CL near field mapping - Advances & Variants

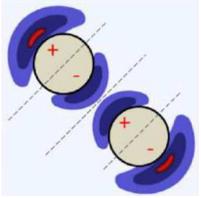
- ◆ CL 3D tomography

- Reconstruction of 3D CL intensity maps *A. C. Atre et al. Nat. Nanotechnol.* **10** (2015) 429

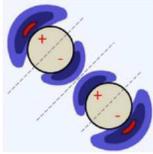
- ◆ Angle resolved CL imaging polarimetry

- Ability to characterize both directionality and polarisation characteristics of CL emission in the hemisphere above a plasmonic structure *B. J. M. Brenny et al. Appl. Phys. Lett.* **107** (2015) 201110; *C. I. Osorio et al. ACS Photonics* **3** (2016) 147

- ◆ Time resolved CL experiment, but in the ps time range (2019), not so relevant for plasmonics (1 - 10 fs time range)



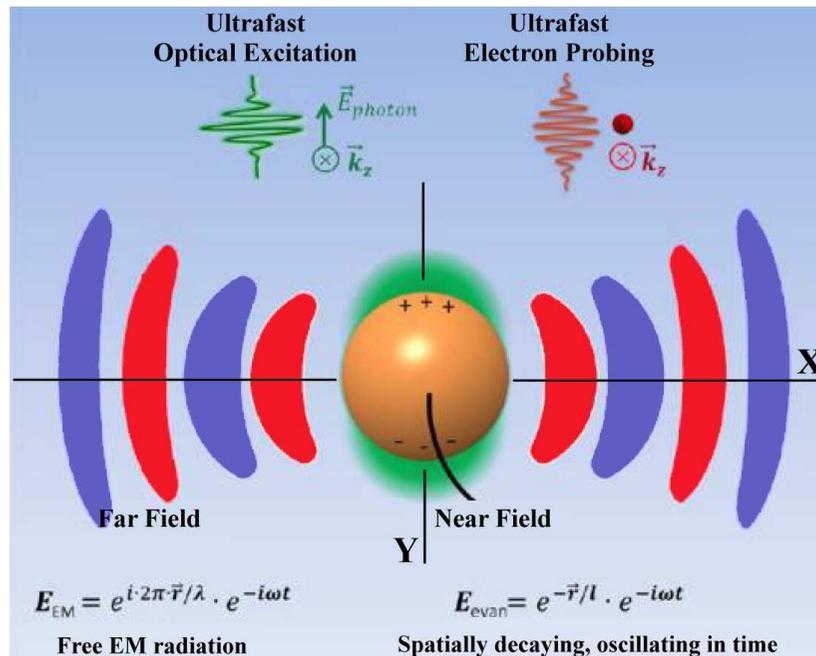
# **Photon-Induced Near-Field Electron Microscopy PINEM, A tool for plasmonics**



# Photon-Induced Near-Field Electron Micros., a tool for plasmonics

Basic principle – PINEM near field imaging

➤ In PINEM, the plasmonic sample is excited with a photon pulse of femtosecond duration and, simultaneously, an ultrashort electron pulse images the near field induced using the optical excitation ⇒ **Three body interaction ( $\hbar\omega$ , plasmon, e-)**



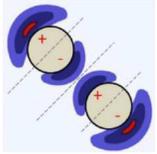
## ➤ Three body interaction

In free space, photons and electrons interact weakly because of a large momentum mismatch

$$e^- \text{ viewpt} \quad \Delta p(e^- + n \cdot \hbar\omega) = n \cdot \hbar\omega / v_e$$

$$\hbar\omega \text{ viewpt} \quad \Delta p(e^- + n \cdot \hbar\omega) = n \cdot \hbar\omega / c, \quad c > v_e$$

In solids, possible interaction between electrons and photons through a plasmon exchange, an additional source of energy and momentum - **Evanescent wave**,  $\Delta z \cdot \Delta p \sim \hbar/2$

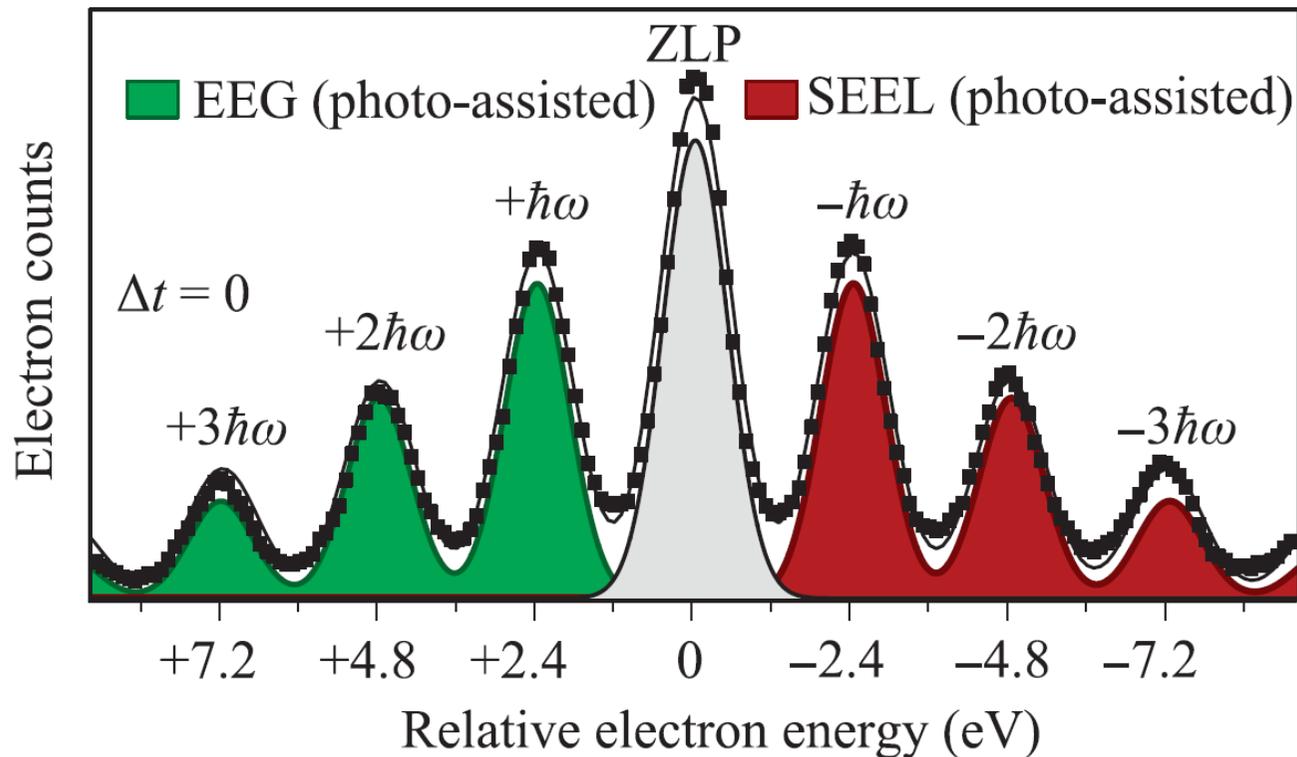


# Photon-Induced Near-Field Electron Micros., a tool for plasmonics

Basic principle – PINEM near field imaging

## ➤ Energy Electron Gain Spectrometry EEGS

In this three body interaction scheme, the electron packets **lose** and/or **gain energy** in discrete quanta of the photon energy  $\hbar\omega$ , because of the presence of a time oscillating electric field, the evanescent field associated with the resonant plasmon of the particle



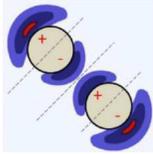
Carbon nanotubes, electrons of 200 keV, fs lifetime

photons of 2.4 eV, fs lifetime

Full temporal overlap  $\Delta t(\hbar\omega, e^-) = 0$  s

B. Barwick, D. Flannigan, A. Zewail *Nature* **462** (2009) 902

A. Yurtsever, A. Zewail *Nanoletter* **12** (2012) 3334



## Photon-Induced Near-Field Electron Micros., a tool for plasmonics

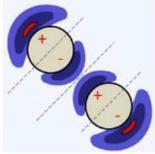
Basic principle – PINEM probability for a small sphere

$$\Gamma_{EEGS}^{sphere}(\omega, R_{\perp}) \propto \left(\frac{\omega}{\gamma v^2}\right)^2 I_0 |\alpha_{l=1}(\omega)|^2 K_1^2\left(\frac{\omega R_{\perp}}{\gamma v}\right) \delta(\omega - \omega_{ph.})$$

$$\Gamma_{EEGS}^{sphere}(\omega, R_{\perp}) \propto \left(\frac{\omega}{\gamma v^2}\right)^2 I_0 |\alpha_{l=1}(\omega)|^2 \delta(\omega - \omega_{ph.}) \exp\left(-\frac{R_{\perp}}{\gamma v/\omega}\right)$$

$I_0$  Intensity of the excitation laser;  $R_{\perp} = (x, y)$  Impact parameter of the electrons traveling along the  $z$  direction at speed  $v$ ;  $\hbar\omega$  Loss energy;  $\hbar\omega_{ph.}$  photon energy;  $\gamma$  Lorentz factor  $\gamma = 1/\sqrt{1 - v^2/c^2}$  (relativistic electrons);  $K_m$  Modified Bessel function of the second kind;  $\alpha_l$  Sphere polarizability for mode  $l = 1$

- PINEM probability of a small sphere is proportional to its scattering cross section as measured in far field optics,  $\sigma_{sca.} \propto |\alpha_{l=1}(\omega)|^2 \propto a^6$
- PINEM probability is position-dependent with a quasi-exponential decay with e-beam to sphere distance  $R_{\perp}$ , attenuation length  $\gamma v/\omega \sim 10 - 100$  nm



# Photon-Induced Near-Field Electron Micros., a tool for plasmonics

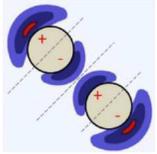
## Basic principle – PINEM vs EMLDOS

- By energy-filtering only those electrons resulting from **one specific photon absorption**, it is possible to :
  - image directly in space the nearfield electric field distribution
  - obtain the temporal behavior of the field on the femtosecond timescale
  - map its spatial polarization dependence – **Polarisation control (bright modes)**
- Similar to CL, and EELS, within a Fourier transform PINEM detects the nearfield electric field component along the direction of the electron beam

$$I_{\text{PINEM}}(x, y, \Delta t) = \left| \int_{+\infty}^{-\infty} E_z^{\text{photon}}(x, y, z, \Delta t) e^{-i\left(\frac{\omega}{v}\right)z} dz \right|^2$$

$E_z^{\text{photon}}$  photon induced nearfield electric field

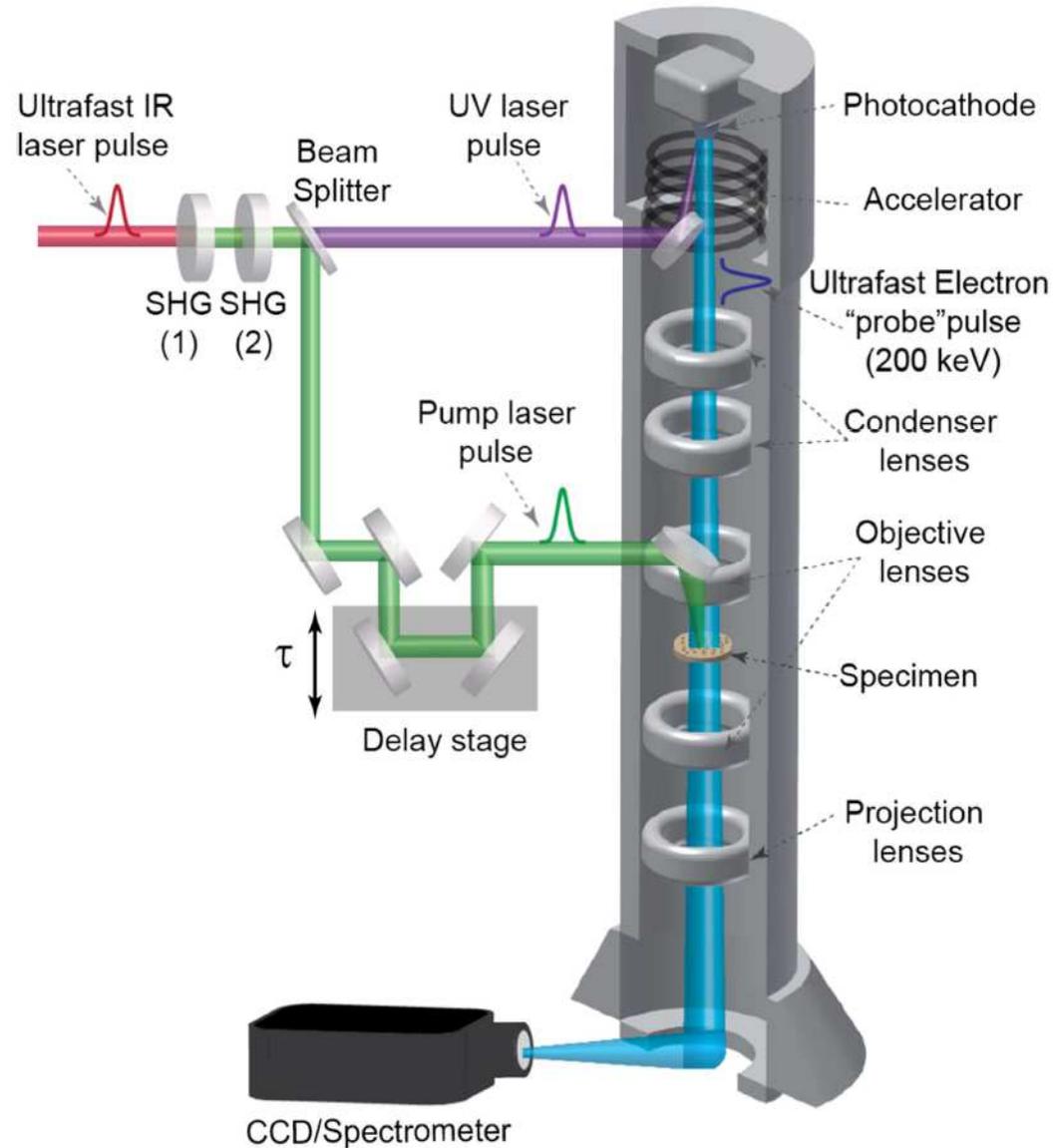
Fourier transform along the e-beam direction at point  $\vec{R}_{\perp} = (x, y)$  in real space, momentum value  $q_z = \omega / v$  in reciprocal space and time delay  $\Delta t$  between electron and photon pulses (power spectrum)

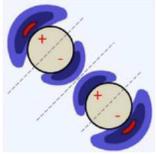


# Photon-Induced Near-Field Electron Micros., a tool for plasmonics

Instrumentation – Ultrafast Electron microscope UEM

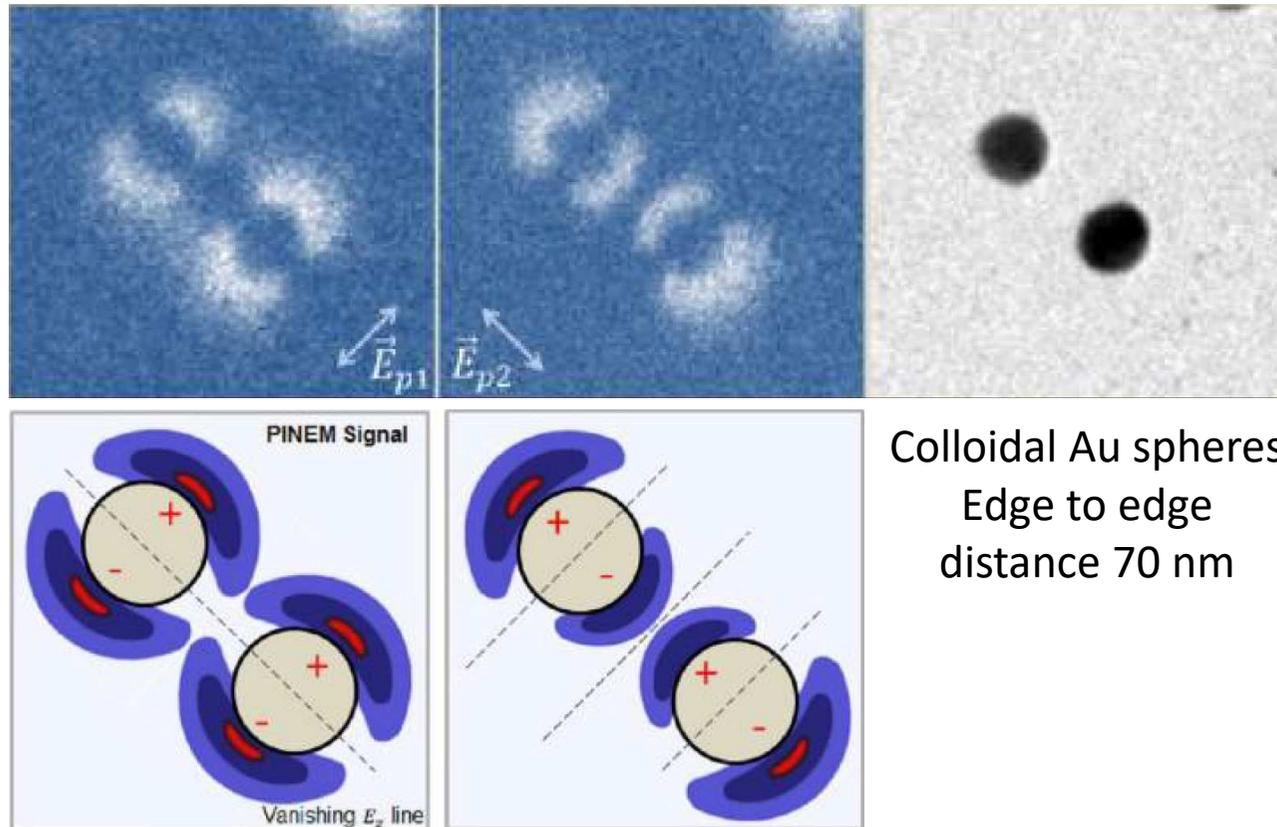
(photon in,  
electron in,  
electron out)  
process



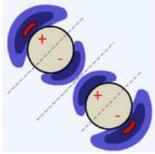


## PINEM near field imaging

Plasmonics of 0D objects - Au NanoSpheres

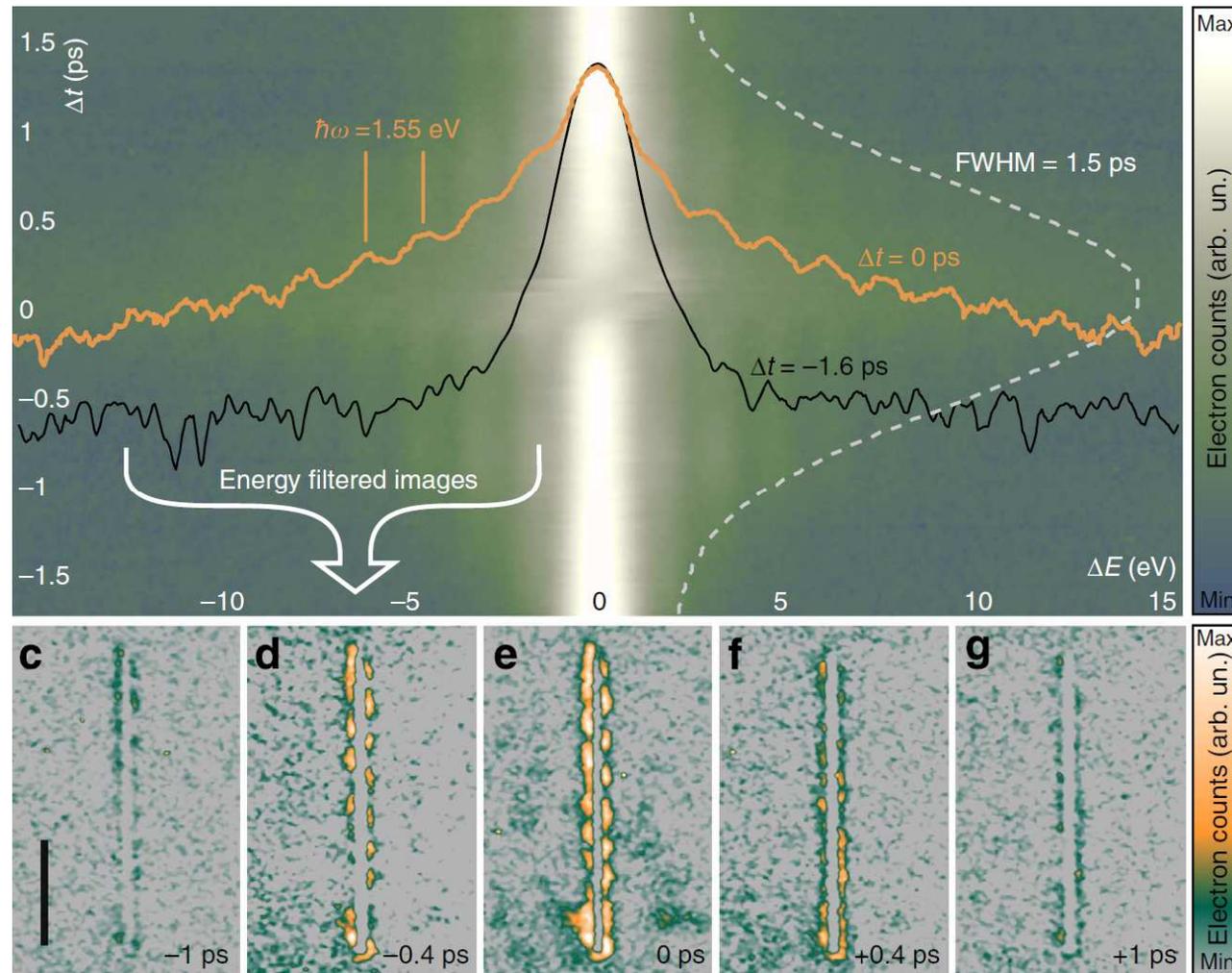


- Near field electric field mapping along the direction of the electron beam  $E_z$
- Spatial polarization dependence – **Optical Polarisation Control**

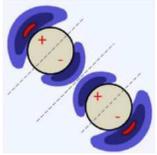


## PINEM near field imaging

Plasmonics of 1D objects – Ag Nanowires  $5.7 \mu\text{m} \times 0.134 \mu\text{m}$

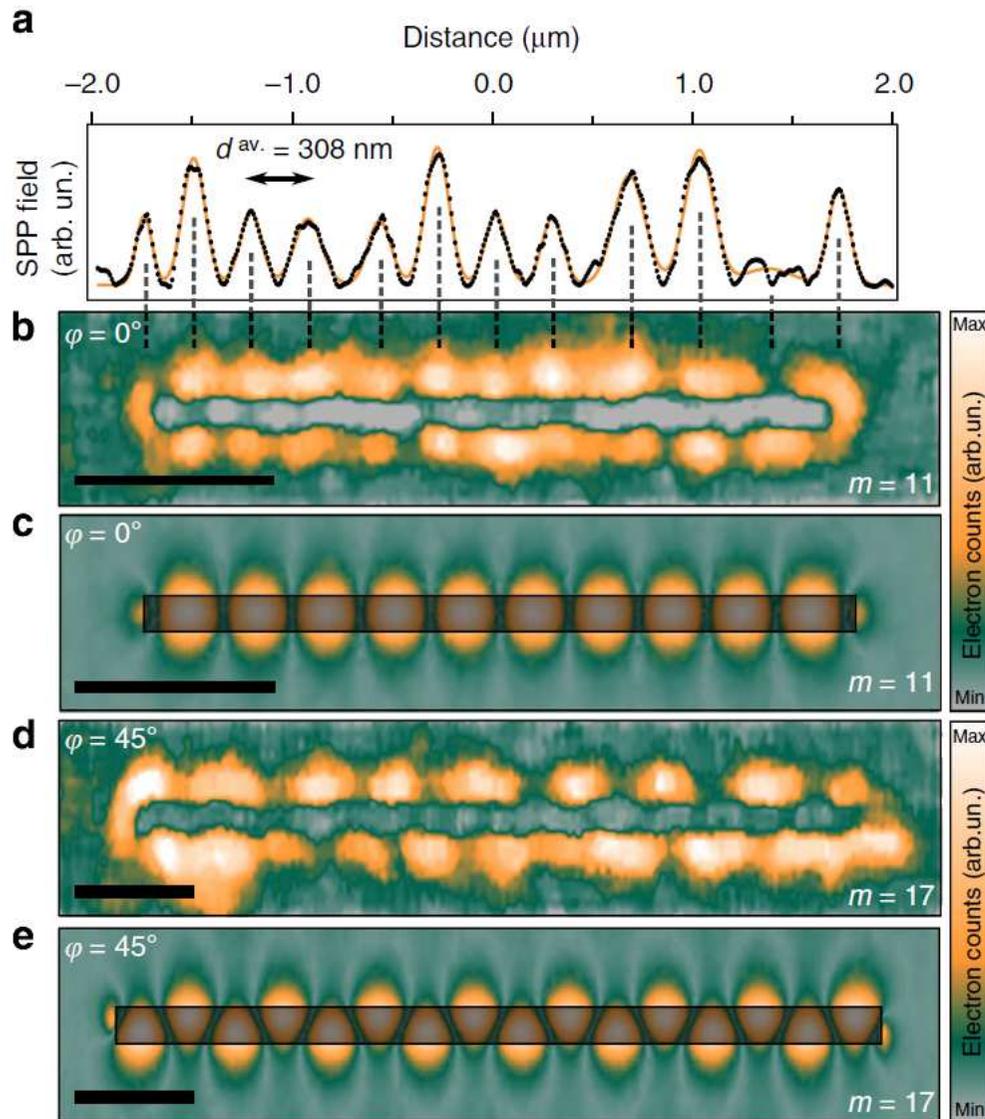


➤ Electron intensity map vs the time delay  $\Delta t$  between the optical pump and electron probe pulses. Wavelength 800 nm, polarization angle  $45^\circ$ . (c – g) Pictures of a single Ag nanowire at different  $\Delta t$  obtained using EEG electrons (white arrow). Scale bar  $2 \mu\text{m}$ .

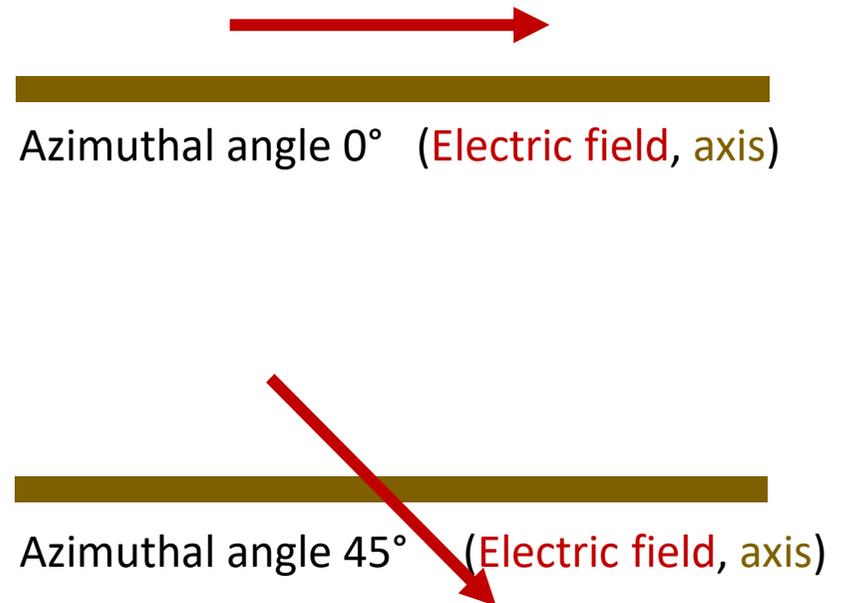


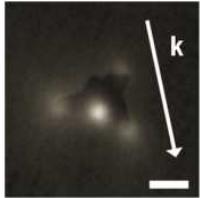
# PINEM Near field imaging

Plasmonics of 1D objects - Nanowires, polarization dependence



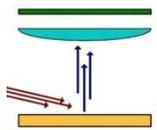
Ag Nanowire 3.4  $\mu\text{m}$  in length, 90 nm in diameter. **800 nm excitation wavelength**. EEG electrons at time delay  $\Delta t = 0 \text{ ps}$ . Scale bar 1  $\mu\text{m}$ .





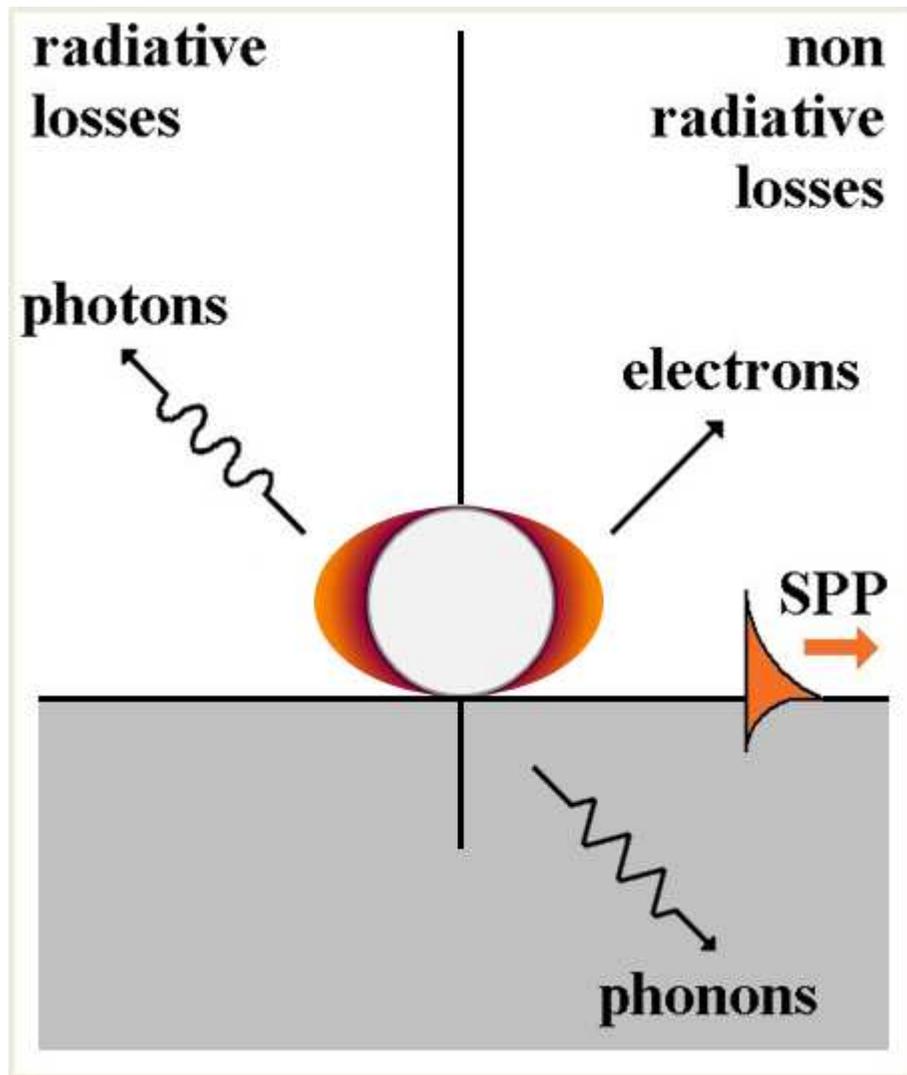
# Photoemission electron microscopy PEEM

## A tool for plasmonics



# Photoemission electron microscopy, a tool for plasmonics

Basic principle – Plasmon decay channels



## ➤ Plasmon decay channels

### .free-space radiative losses

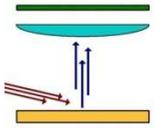
scattering  
luminescence

### .non radiative losses

ohmic losses (phonons)  
secondary SPP excitation  
**electron emission**

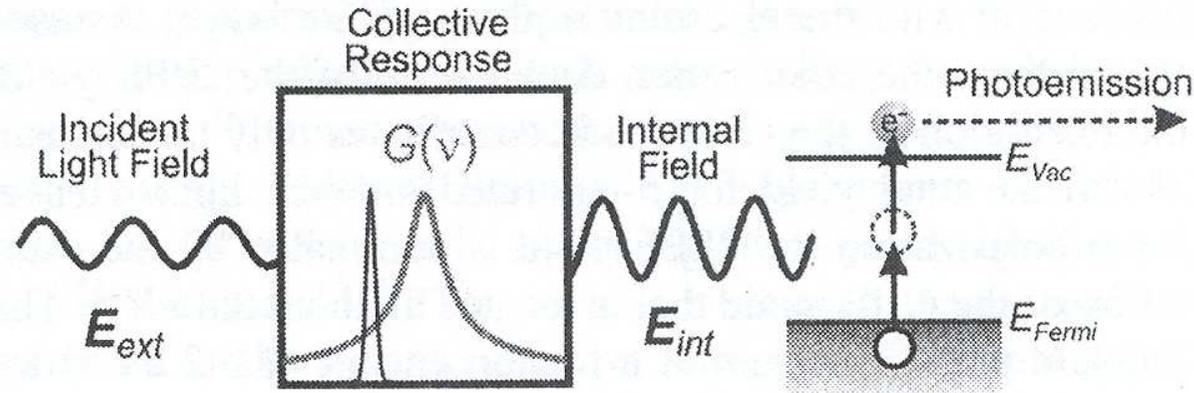
...

## ➤ Mapping the near field at the nanoscale through electron emission - Photoelectric effect



# Photoemission electron microscopy, a tool for plasmonics

## Physical principle



(i) Plasmon excitation  $\Leftrightarrow$  Exalted photoelectric effect in plasmonic field

(ii) Non linear photoemission process

Plasmon res.  $E_{\text{plasmon}} \approx 1,55 \text{ eV}$  (IR 800 nm)

Metal work function  $\Phi_{\text{metal}} \approx 4,5 \text{ eV}$

$$E_{\text{int.}}(\nu) = G(\nu) \cdot E_{\text{ext.}}(\nu), \quad G_{\text{Sphere}} = \frac{3\epsilon_m}{\epsilon + 2\epsilon_m}$$

$$n \cdot h\nu > \Phi_{\text{Metal}}$$

$E_{\text{int.}}$  Internal electric field [V/m]

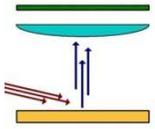
G Response function of the many electron system

$E_{\text{ext.}}$  Incident electric field [V/m]

n order of non linearity,

$h\nu$  photon energy [eV],

$\Phi_{\text{metal}}$  metal work function [eV]



## Photoemission electron microscopy, a tool for plasmonics

### Basic principle

- The non linear photoemission process is proportional to the  $2n^{\text{th}}$  power of the surface electric field  $E_{\text{int.}}$  (electron reservoir, surface photoemission process)
- Multiphotonic cascade absorption and/or coherent absorption from a hot electron gas

$$I_{e^-} \propto (\vec{p} \cdot \vec{E}_{\text{int.}})^{2n} \propto (\vec{p} \cdot G \vec{E}_{\text{ext.}})^{2n}$$

$p$  electron momentum [kg.m/s]

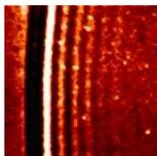
$E_{\text{int.}}$  internal electric field [V/m]

$n$  non linearity order

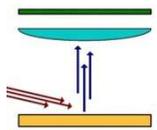
$E_{\text{ext.}}$  incident electric field [V/m]

- Bright field modes accessible (**photon in**)

For large objects  $\geq \lambda_{\text{hv}}$ , the internal electric field of the plasmon excitation  $\vec{E}_{\text{int.}}^{\text{SPP}}(r, t)$  (group velocity  $v_{\text{SPP}} < c$ ) interferes with a  $2^{\text{nd}}$  component linked to the incident field  $\vec{E}_{\text{int.}}^{\text{hv}}(r, t)$  (group velocity  $c$  / refractive index).

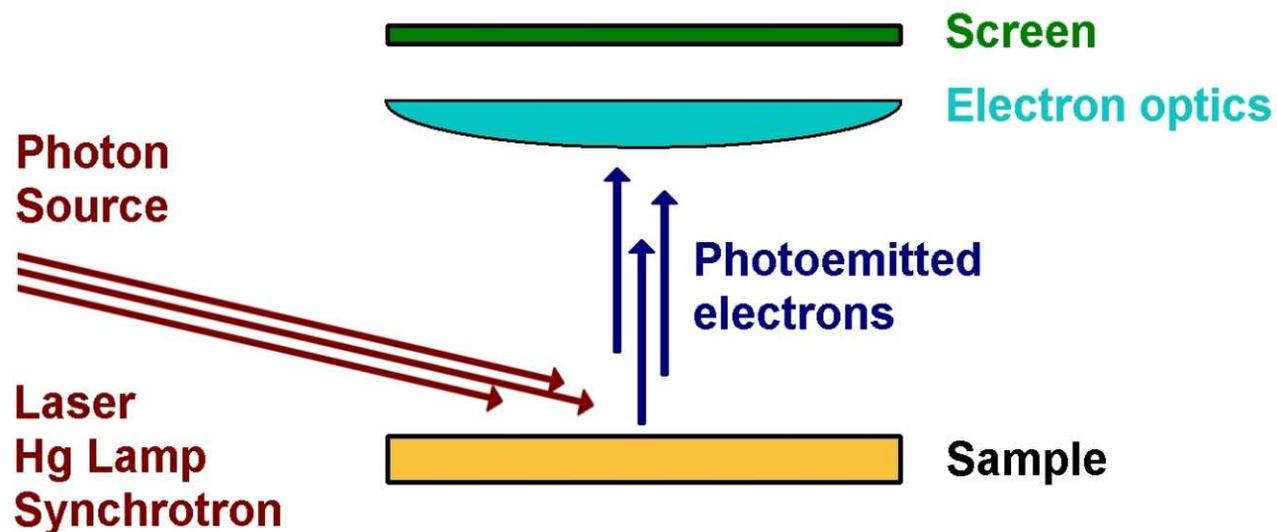


- For large objects  $\geq \lambda_{\text{hv}}$ , observation of beating interference patterns between  $(\vec{E}_{\text{int.}}^{\text{SPP}}(r, t), \vec{E}_{\text{int.}}^{\text{hv}}(r, t))$



## PEEM – photoemission electron microscopy (1933)

### Instrumentation



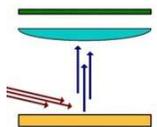
➤ **Basic principle. Mapping of the photoemitted electron distribution in two dimensions (photon in, electron out)**

- .standard electron optics (electrostatic, magnetic lenses)
- .full field microscopy, no scanning probe
- .non intrusive technique, no physical tip in the vicinity of the measuring volume ( $\neq$  SNOM)

.image contrast: work function  $\Phi$  (small photon  $h\nu$ ), photoemission lines (large photon  $h\nu$ )

.surface sensitivity  $\sim$  electron inelastic mean free path  $\lambda_{\text{electron}}$

.lateral resolution (16 / 84 criteria)  $\approx$  **20 nm, resp.  $\leq$  5 nm on AC instrument**

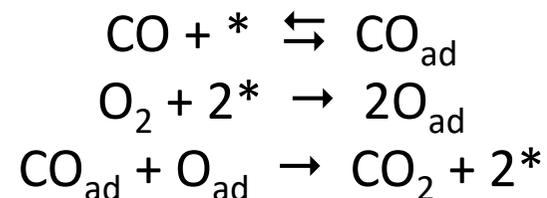


## PEEM – photoemission electron microscopy (1933)

### Oxidation of carbon monoxide on Pt(110)



- Oxidation reaction ( $445 \times 445 \mu\text{m}^2$ )



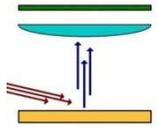
\* = Free Pt(110) site

Carbon monoxide “Bright”  $\Phi = 5.8 \text{ eV}$

Oxygen “Dark”  $\Phi = 6.5 \text{ eV}$

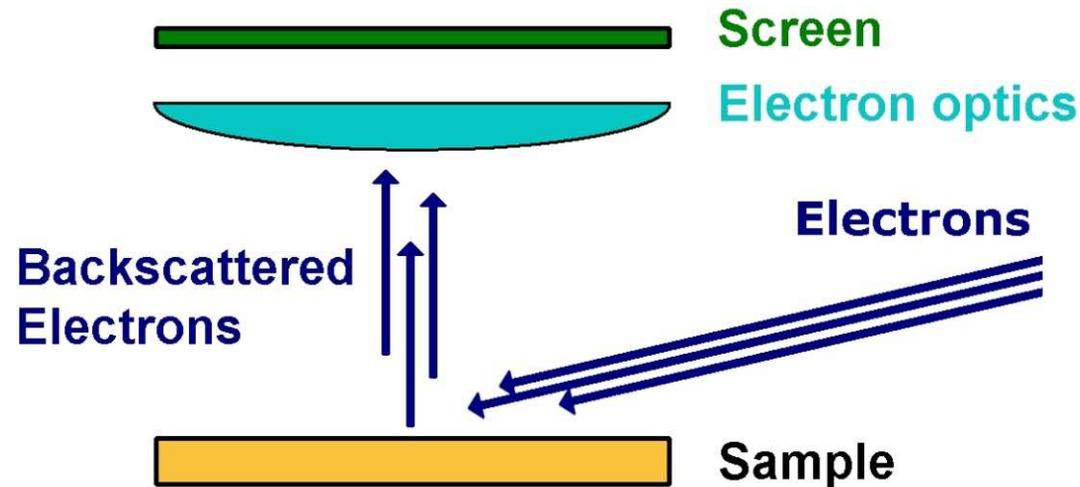
Freedom degrees  $P_{\text{CO}} = 4.3 \cdot 10^{-5} \text{ mb}$ ,  $P_{\text{O}_2} = 4 \cdot 10^{-4} \text{ mb}$ ,  $T = 448 \text{ K}$

- Spatio-temporel pattern of the surface reaction (spiral diffusion fronts)

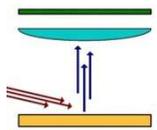


## LEEM – low energy electron microscopy

### Instrumentation

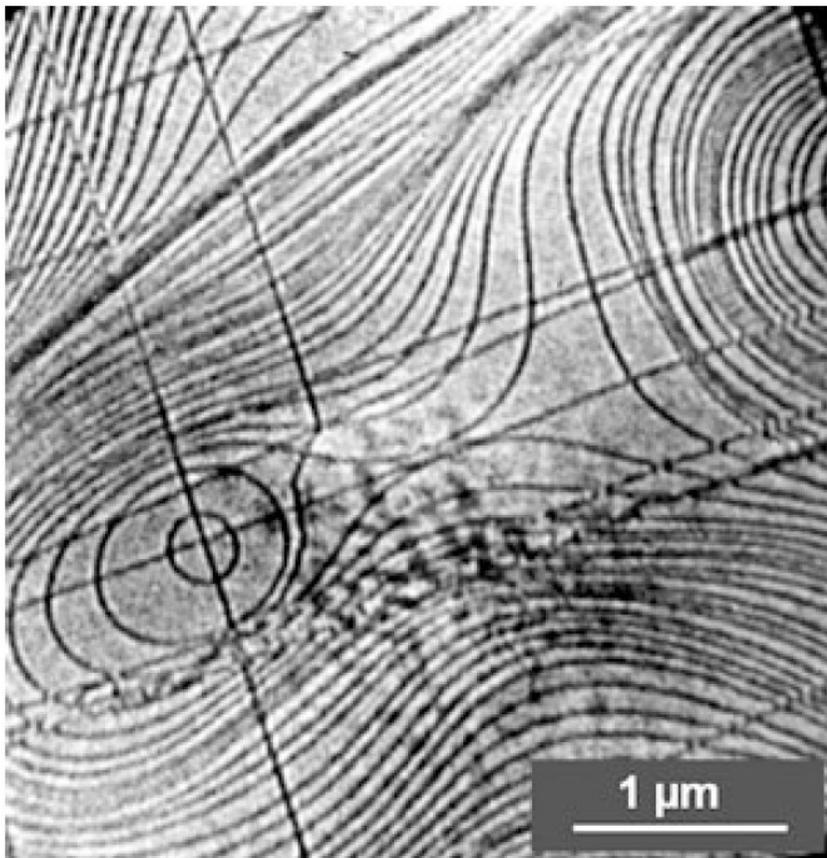


- **Basic principle. Mapping of the 2D backscattered electron distribution (electron in, electron out)** - Topographic imaging LEEM = TF(LEED + phase)
  - .standard electron optics (electrostatic & magnetic lenses)
  - .full field microscopy, no scanning probe
  - .non intrusive technique, no physical tip in the vicinity of the measuring volume
  
  - .contrast = diffraction, interferences between optical electron paths...
  - .vertical resolution = atomic step
  - .lateral resolution (16/84 criteria)  $\approx$  **10 nm, resp.  $\leq$  2 nm on AC instrument**

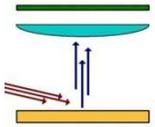


## LEEM – low energy electron microscopy (1962)

Mo(100) Surface

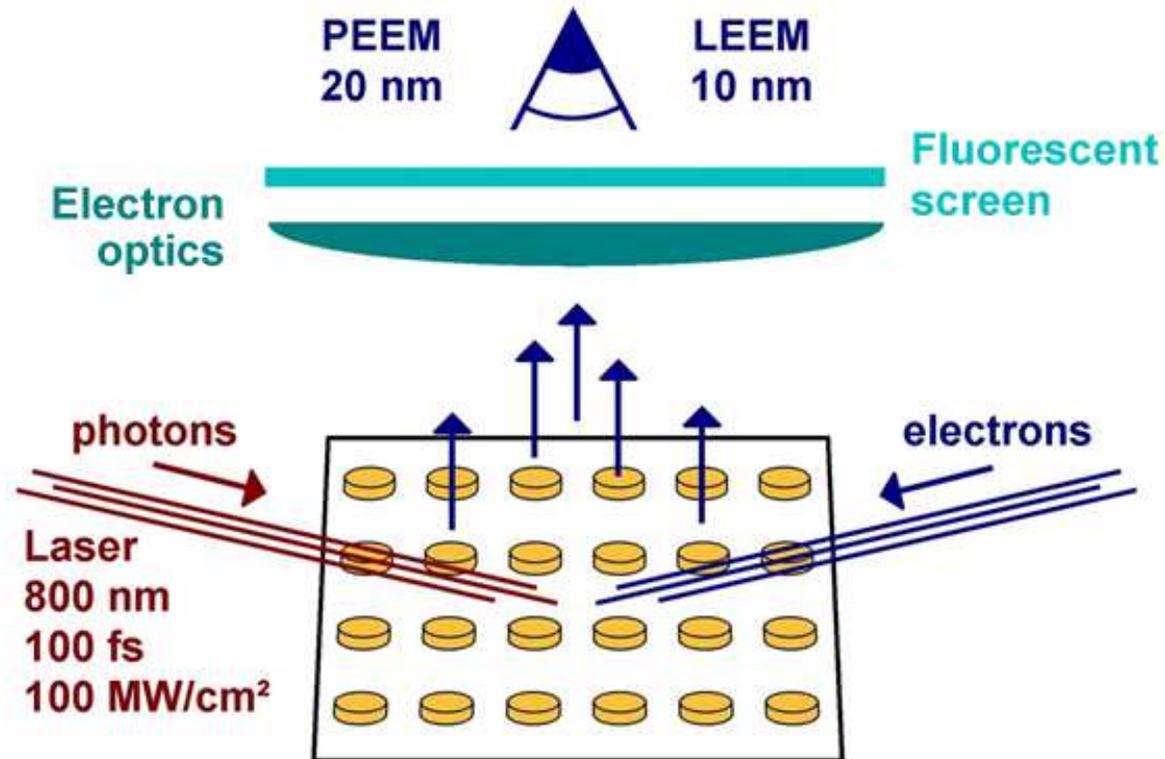


- Mo(110) Surface  
LEEM  
Electron kinetic energy 14 eV  
Monoatomic step contrast

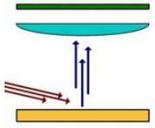


# Mapping the evanescent field at the nanometre

LEEM/PEEM instrument (CEA IRAMIS Saclay)

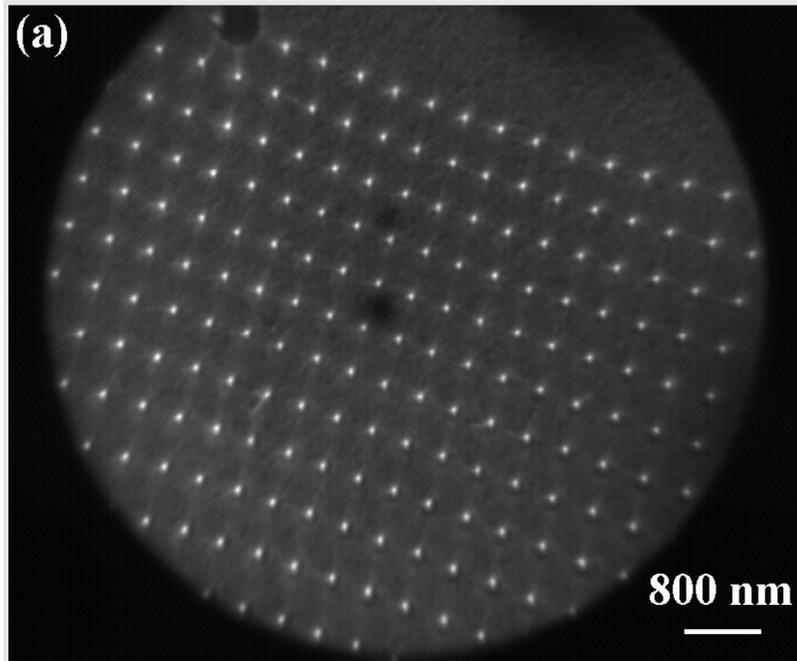


- Conductive sample (no charging effect) of low roughness
- LASER source Ti:Al<sub>2</sub>O<sub>3</sub>, 130 fs, wavelength [690 nm, 1100 nm] (IR) + OPO wavelength [525 nm, 680 nm], incidence angles {-90°, -45°, +3°, +15°, +90°} / sample surface plane
- LEEM / PEEM III equipped with an electron energy analyser [www.elmitec-gmbh.com](http://www.elmitec-gmbh.com)
  - PEEM field of view 1.5 - 120 μm, 16/84 lateral resolution **20 nm** (≤ 5 nm AC)
  - LEEM field of view 1.5 - 80 μm, 16/84 lateral resolution **10 nm** (≤ 2 nm AC)



# Mapping the evanescent field at the nanometre - PEEM

## Nanoparticle assemblies - LSP

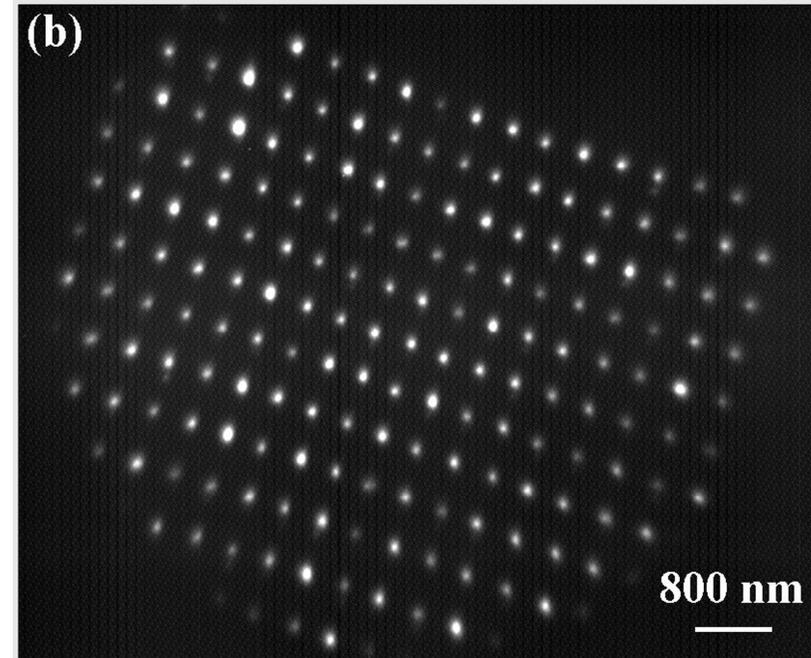


Au disks / ITO -  $\varnothing$ 120 nm, lattice spacing 400 nm  
Source UT Troyes

➤ **LEEM picture (topographic imaging mode)**

Excitation = electrons (LASER off)

Signal = backscattered electrons



Au disks / ITO - Grazing incidence p pol. 150 MW/cm<sup>2</sup>

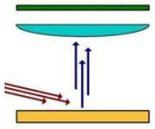
➤ **PEEM picture under LASER illumination**

Excitation = 766 nm photons

$h\nu$  (1.62 eV) <  $\Phi_{\text{Au}}$  (4.6 - 5.1 eV)

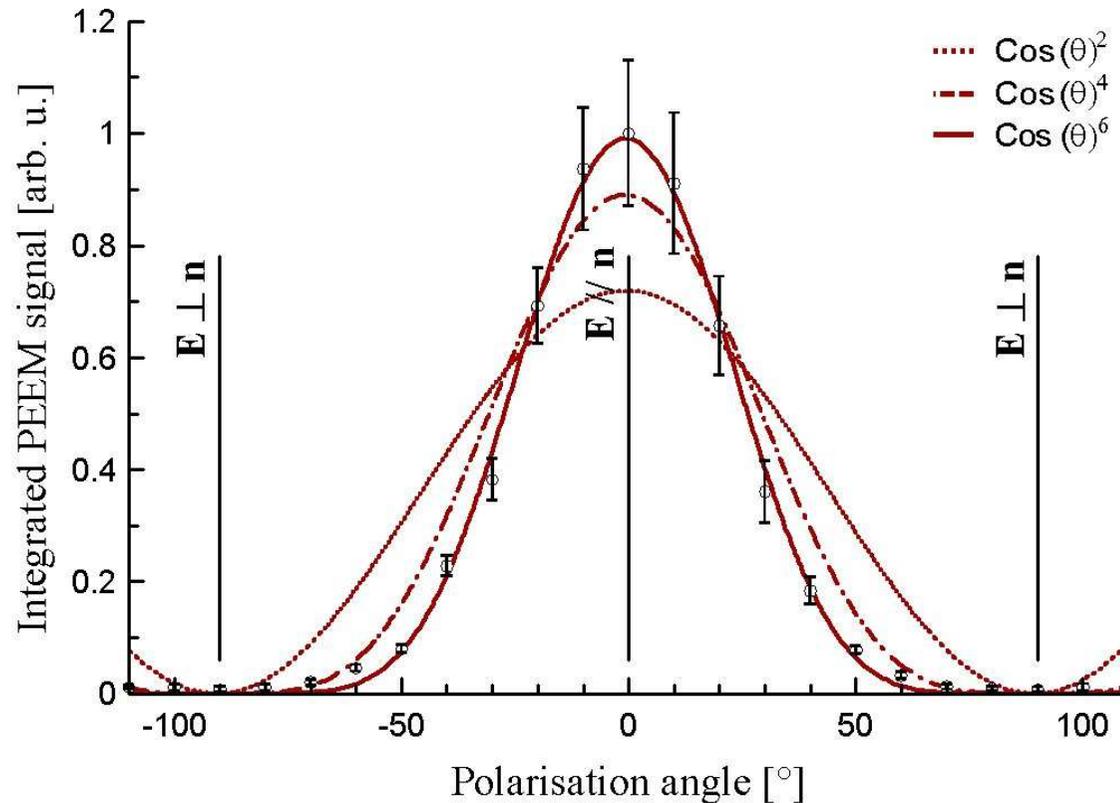
Signal = photoelectrons ! (3  $h\nu$  /  $e^-$ )

High signal to noise ratio



## Non linear photoemission – PEEM

Nano-particle assemblies – Off plane polarisation dependence



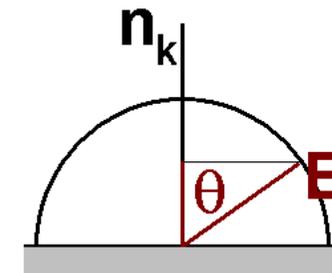
**Au disks / ITO**  $\varnothing$ 120 nm

grazing incidence  $17^\circ$

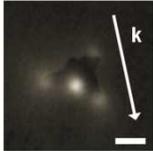
photon 880 nm (1.41 eV)

power dens. 140 MW/cm<sup>2</sup>

Keldysh factor 36  $\gg$  1

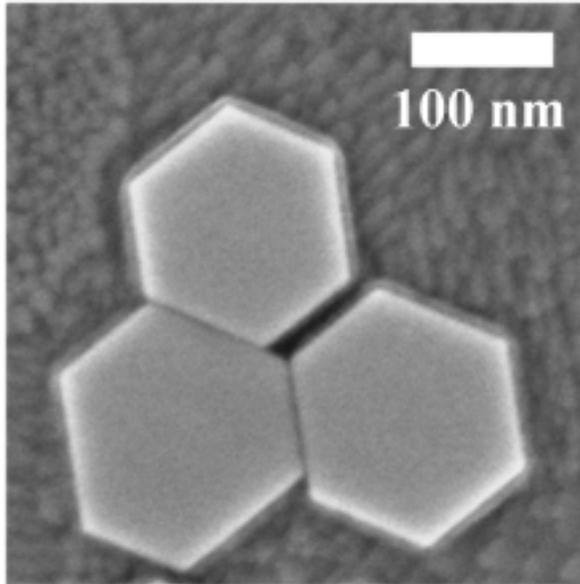


- Dependence of the photoemission yield with the polarisation angle  $\theta$  at grazing incidence  $\Leftrightarrow$  PEEM integrated signal scales as  $\cos(\theta)^6$
- **3 photon photoemission process** ( $3 \times 1.41 \text{ eV} = 4.23 \text{ eV}$ ,  $\Phi_{\text{Au}} \approx 4.6 - 5.1 \text{ eV}$ ). Probable electronic temperature assisted 3-PPE mechanism.



# Plasmonics of 2D objects - Nanohexagon $D_{6h}$ - PEEM

Near field mapping - Linear polarisation

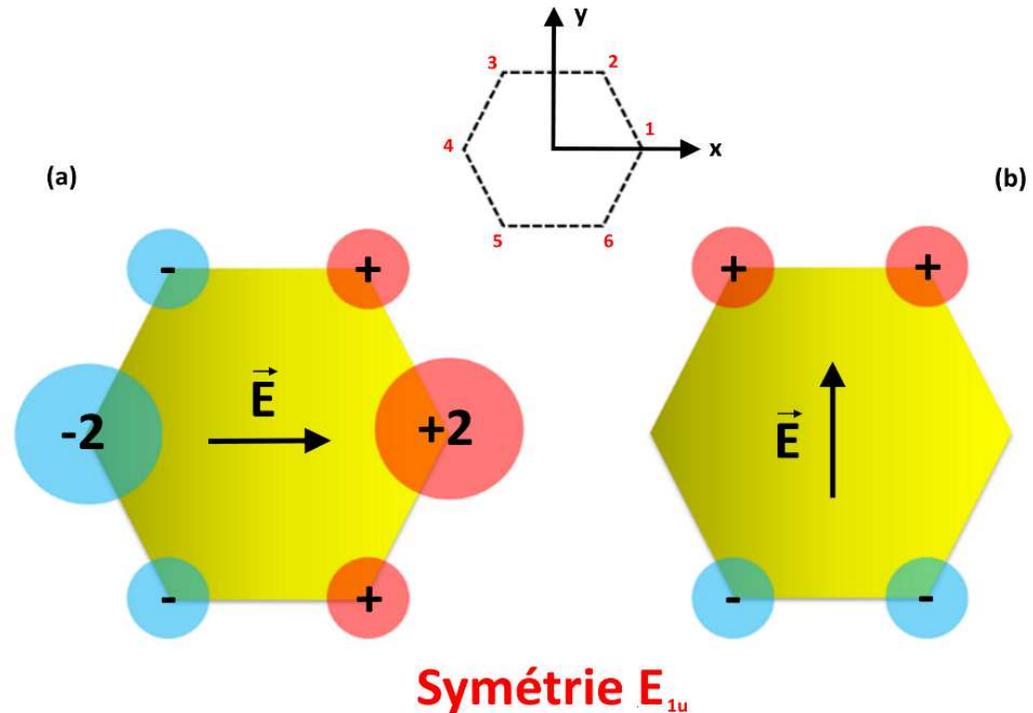


## Au Hexagon - SEM

$L = 150 - 200 \text{ nm}$

Thickness  $\approx 15 \text{ nm}$

(Colloïdal synthesis, CEA S. Marguet)



## ➤ Group Theory

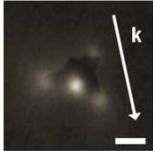
Hexagon = Object of  $D_{6h}$  symmetry

Eigenstates of the dipolar plasmon resonance  
for a linear polarisation excitation

S. Mitiche PhD (2018)

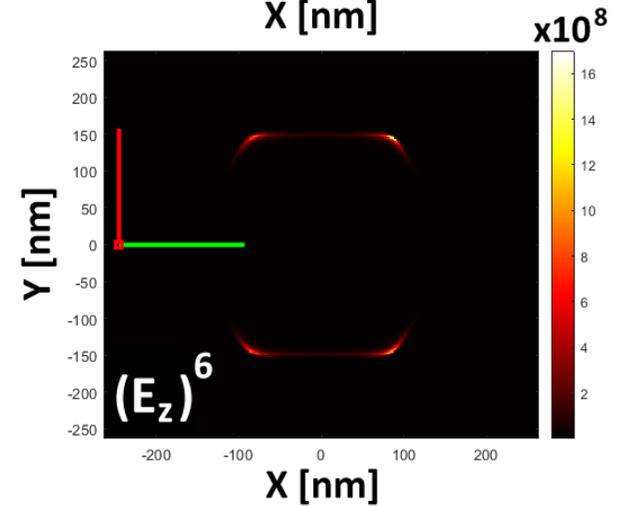
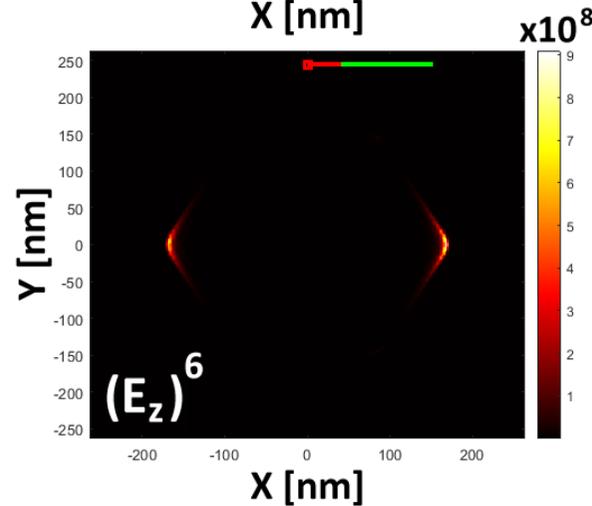
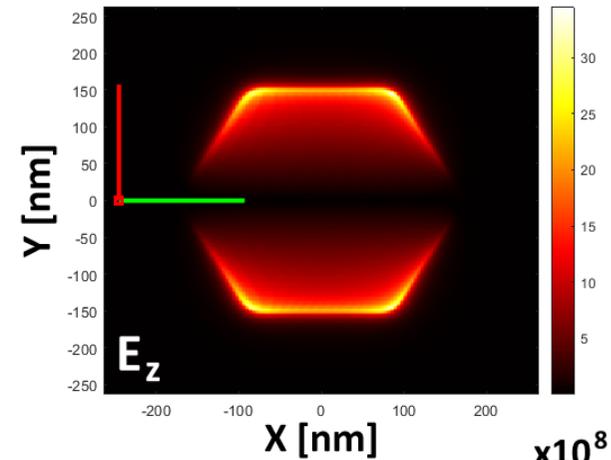
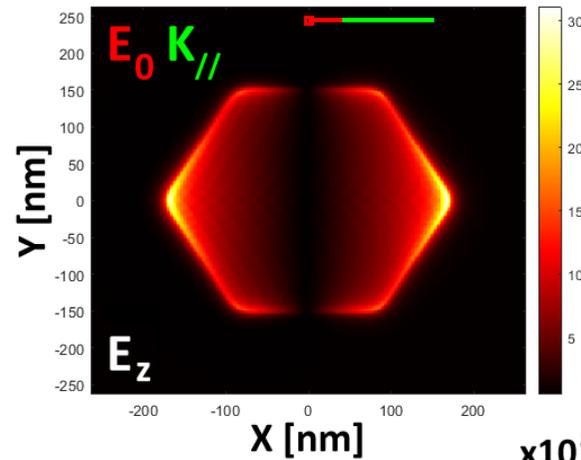
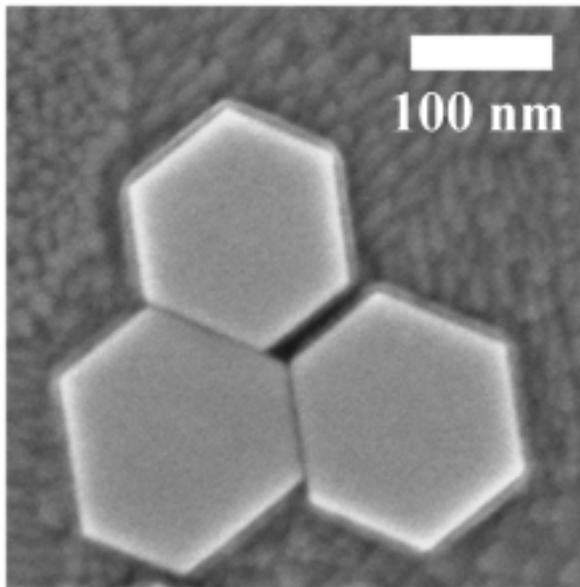
S. Mitiche, *et al. J. Phys. Chem. C* **121** (2017) 4517

C. Awada, T. Popescu *et al. J. Phys. Chem. C* **116** (2012) 14591



# Plasmonics of 2D objects - Nanohexagon $D_{6h}$ - PEEM

Near field mapping - Linear polarisation



## Au Hexagon - SEM

$L = 150 - 200 \text{ nm}$

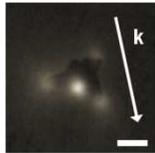
Thickness  $\approx 15 \text{ nm}$

(Colloidal synthesis, CEA S. Marguet)

## ➤ *Boundary Element Method (BEM) Simulation*

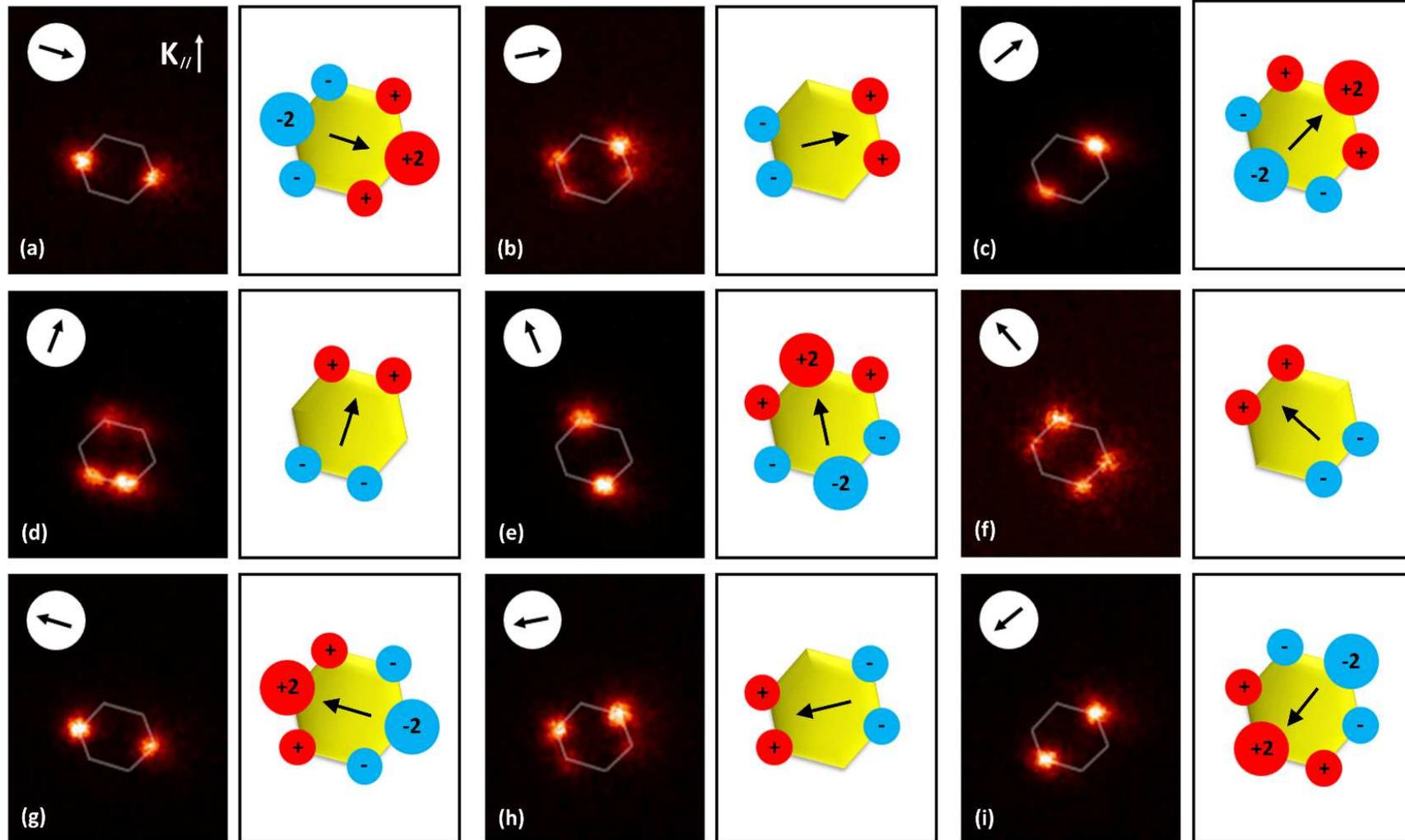
Au Hexagon

Electric field maps, z components  $|E_z|$  &  $|E_z|^6 = 2 \times 3$

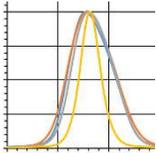


# Plasmonics of 2D objects - Nanohexagon $D_{6h}$ - PEEM

Near field mapping - Linear polarisation

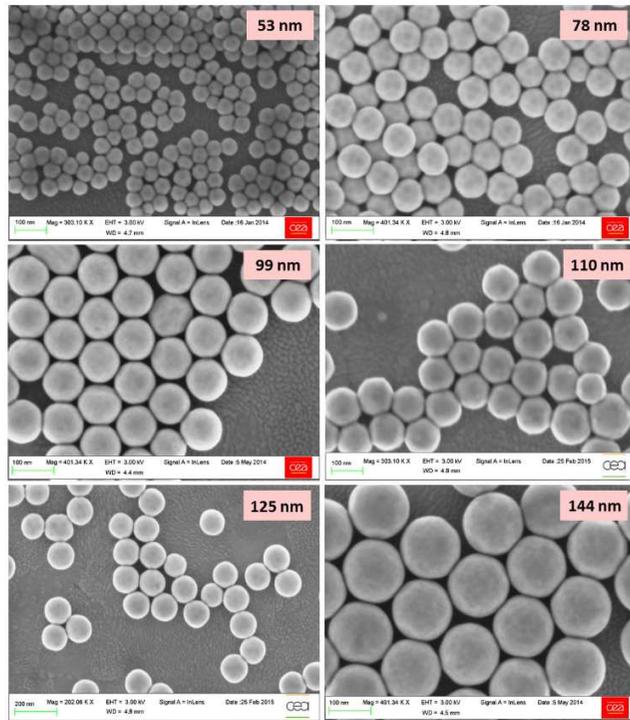


- 150 nm Au Hexagon – Dipolar resonance ( $\lambda = 850$  nm) under linear pol. exc.  
PEEM Imaging & Group Theory Interpretation (S. Mitiche PhD 2018)

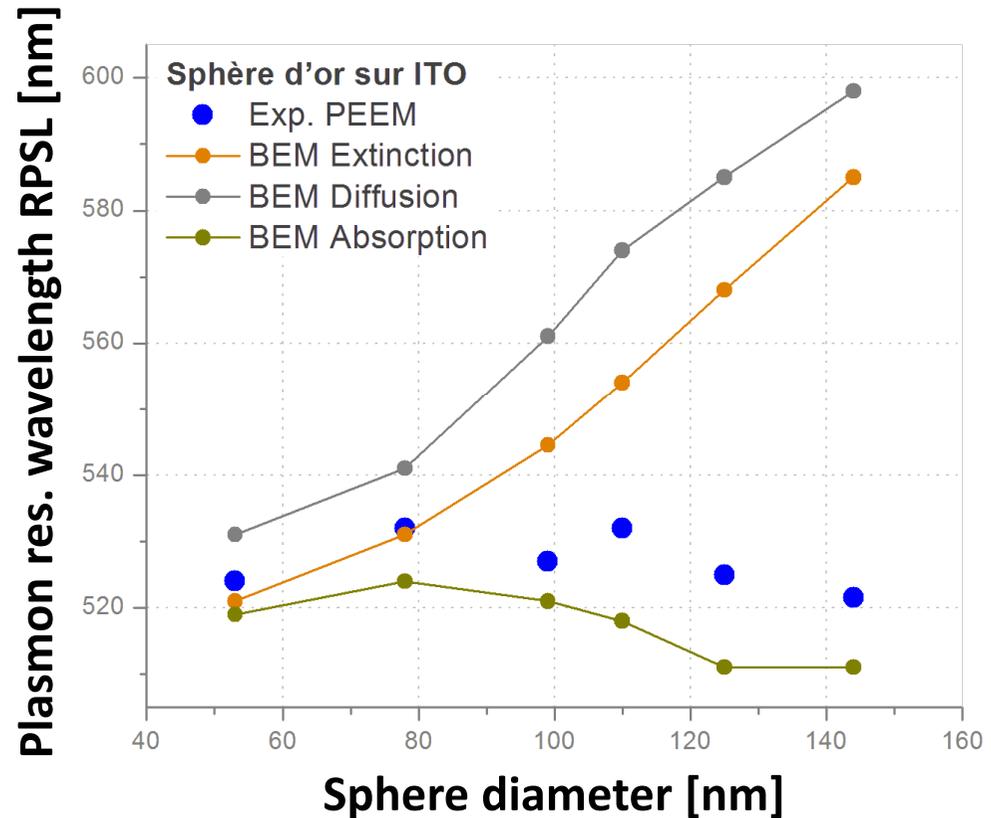


# Non linear photoemission - PEEM – Absorption spectrum

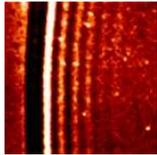
## Spheres - Absorption resonance = $f(\text{diameter } 2R)$



**Au colloïdal spheres**  
(S. Marguet CEA, NIMBE)

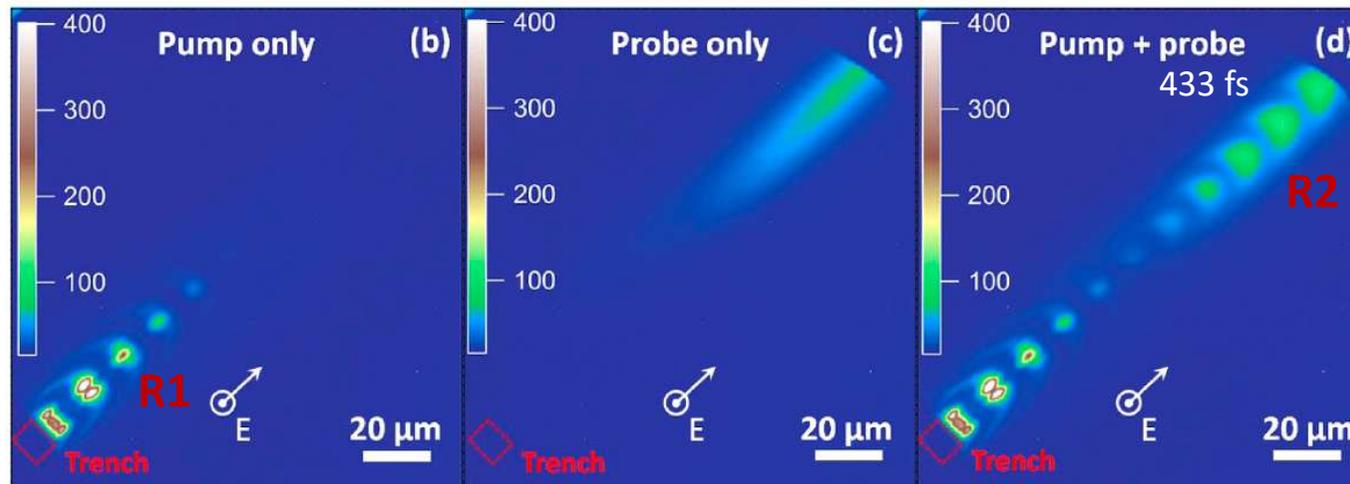
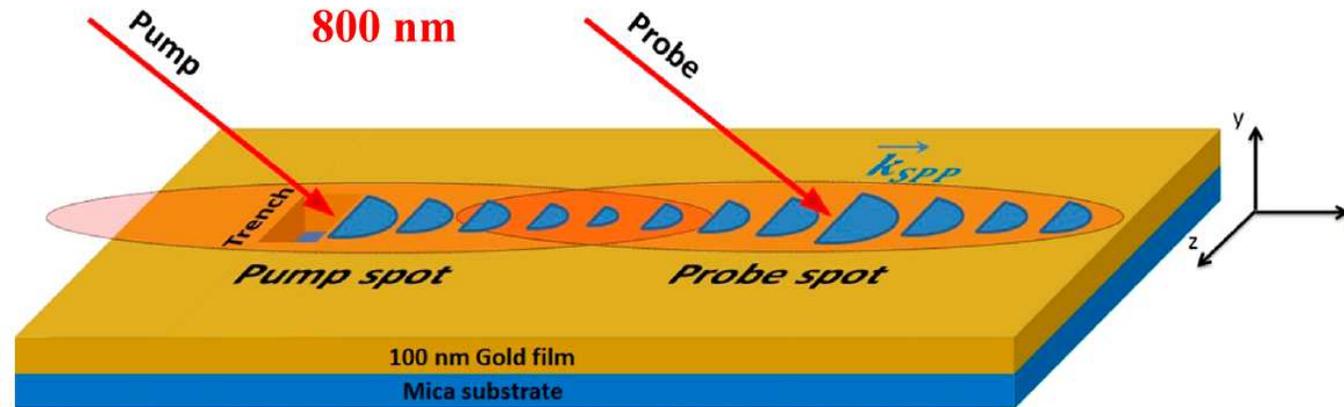


- Plasmon resonance maxima vs sphere diameter  $2R$
- Absorption spectrum on individual object,  $I_{\text{photoemission}} = f(\text{incident wavelength})$
- Spectral resolution  $\approx 1 \text{ nm}$  (130 fs, 2.5 meV)



# Propagation of plasmons-polaritons (nm, fs) – PEEM

2D Symmetry – Pump-probe experiment - Au / mica interface

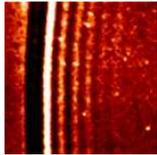


## ➤ Plasmon propagation from a trench in a Au film ( $\vec{k}$ conservation)

Pump-probe experiment. Time resolution = 0,2 fs, spatial resolution = 20 nm

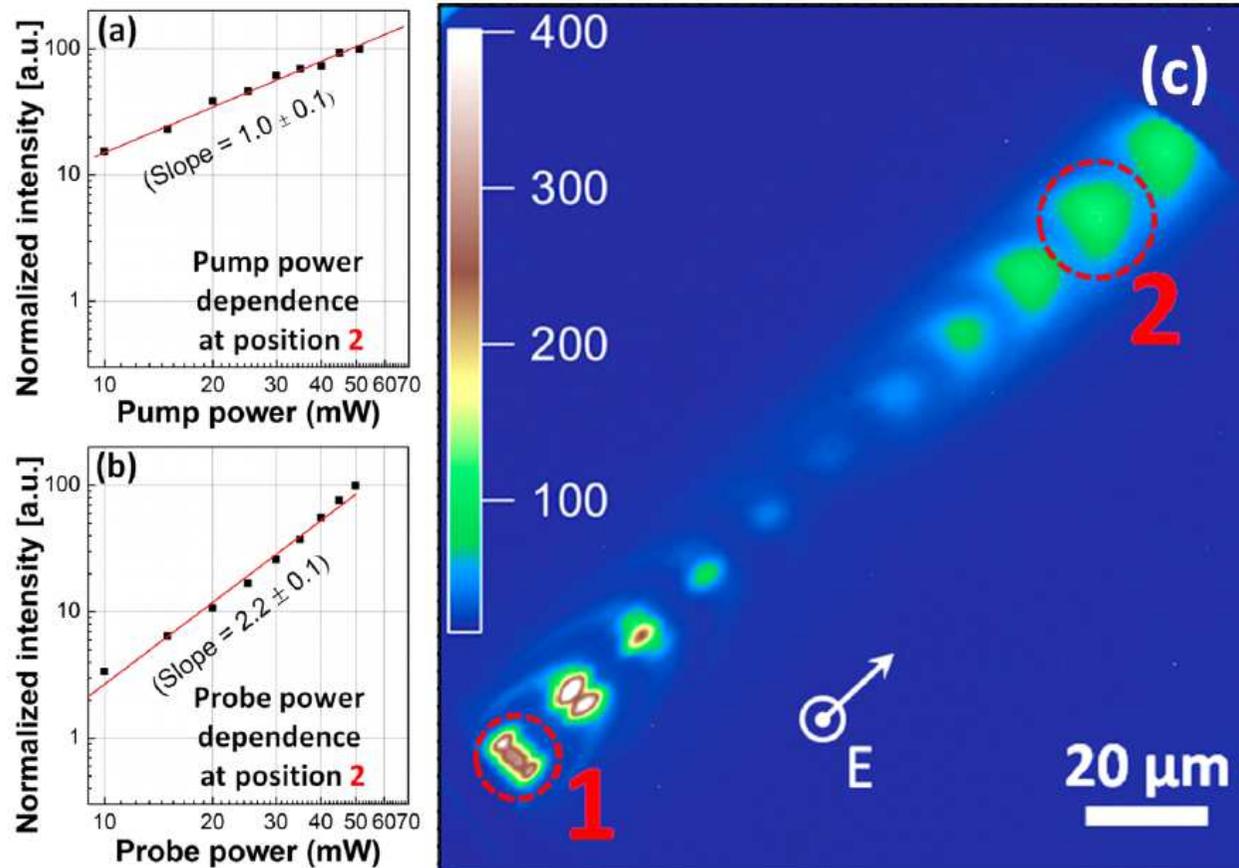
Field propagation length  $\delta(\text{Au}, 800 \text{ nm}) = 88 \mu\text{m}$  (92  $\mu\text{m}$  JC72, 89  $\mu\text{m}$  Ordal87)

Group velocity SPP = 0,95c

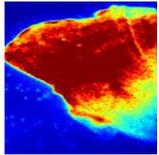


# Propagation of plasmons-polaritons (nm, fs) – PEEM

2D Symmetry – Pump-probe experiment - Au / vide interface

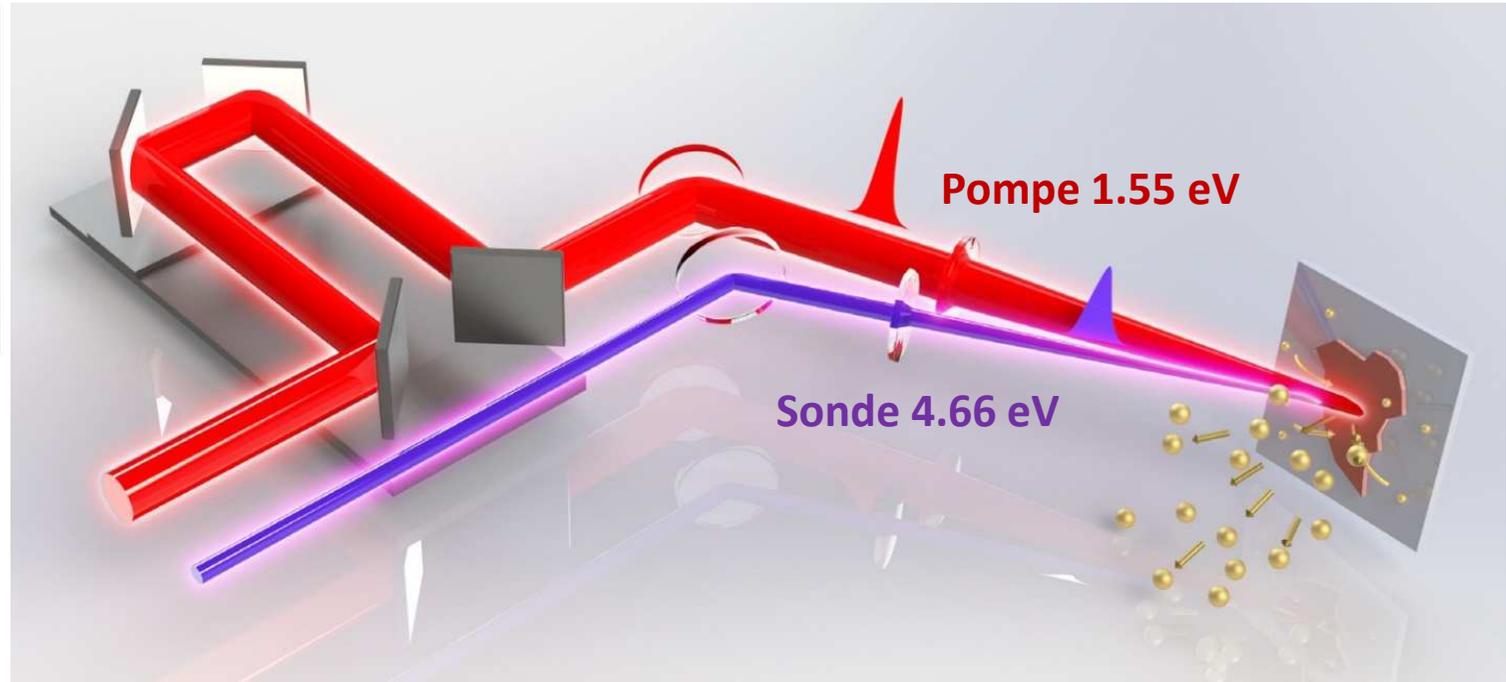
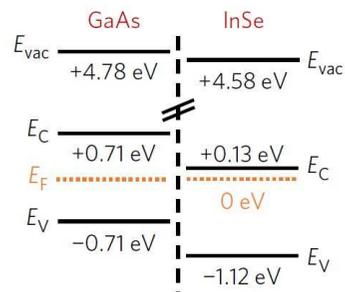
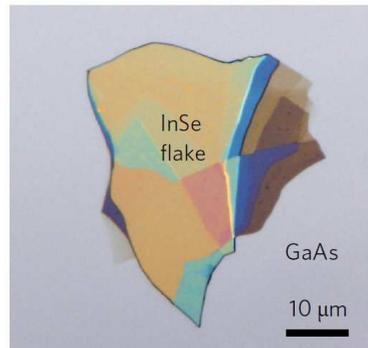


- **PEEM Region 1.** SPP signal close to the geometric launcher  $I_{\text{PEEM}} \propto (E_{\text{pump}})^6$
  - **PEEM Region 2.** SPP signal far away from the launcher  $I_{\text{PEEM}} \propto (E_{\text{pump}})^2 \cdot (E_{\text{probe}})^4$
- Sequential coherent photoemission process. Attenuation  $\delta(\text{Au}, 800 \text{ nm}) = 88 \mu\text{m}$



## Electron dynamics in a solid - PEEM

Time-resolved PEEM variant – (space, time, energy) = (nm, fs, eV)



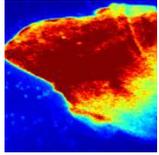
- Investigation of the electron dynamics (space, time, energy) in an elementary (p, n) junction (InSe, AsGa) = InSe flake on a AsGa substrate

Two colors Pump Probe experiment:

**pump laser NIR 800 nm 1.55 eV**

**probe laser UV 266 nm 4.66 eV**

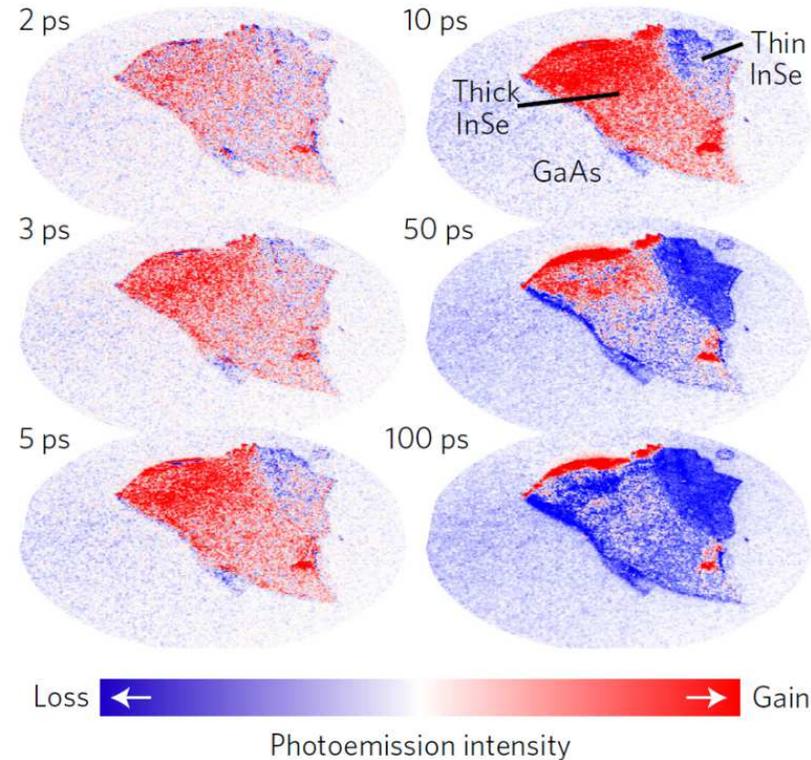
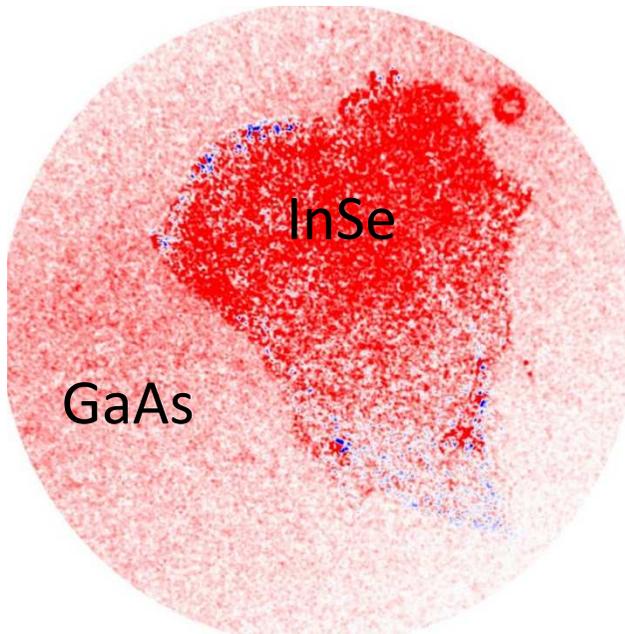
LEEM - PEEM III Microscope



## Electron dynamics in a solid - PEEM

Time-resolved PEEM variant – (space, time, energy) = (nm, fs, eV)

0 ps



### ➤ PEEM Image in energy-integrated mode @ $\Delta t = 0$ ps

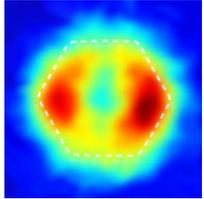
Non-equilibrium distribution of charges with high-energy electrons localized in GaAs and in available states in InSe due to a lower conduction band minimum

Electron temperature  $\approx 1700$  K

### ➤ Electron transport over time in 2 steps

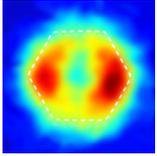
(i)  $e^-$  accumulate in all parts of InSe at early time delays due to electron transfer from high-energy GaAs states

(ii) the initial rapid accumulation of charge in various parts of InSe slows down (electric field), followed by eventual recombinations



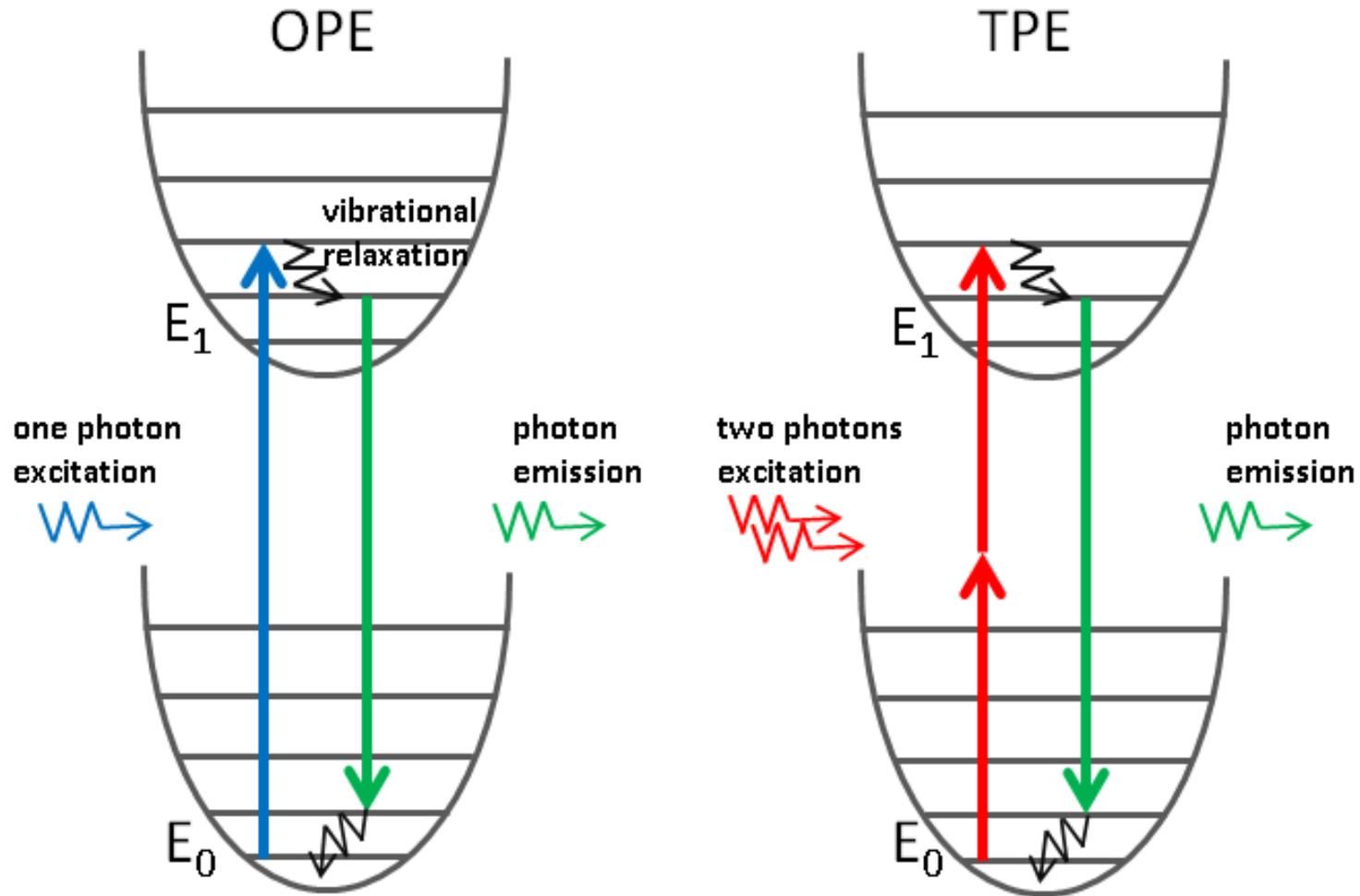
## **Two photon luminescence TPL**

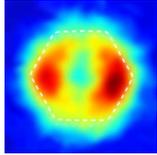
### **A tool for plasmonics**



## Two photon luminescence TPL, a tool for plasmonics

Two photon excitation principle (2 x photon in, 1 x photon out)





## Two photon luminescence TPL, a tool for plasmonics

Two photon excitation signal intensity

$$I_{TPL}(\omega, \vec{R}_0) \propto \int_V |E_0(R_0, r, \omega)|^4 EMLDOS_{\parallel}^2(r, \omega) dr$$

$\hbar\omega$  energy of the incident photon

$I_{TPL}$  two photon luminescence signal intensity

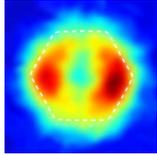
$r(x, y, z)$  arbitrary position within the metallic particle volume  $V$

$R_0(x_0, y_0, z_0)$  light beam waist center, i.e. focal point position

$E_0$  incident electric field

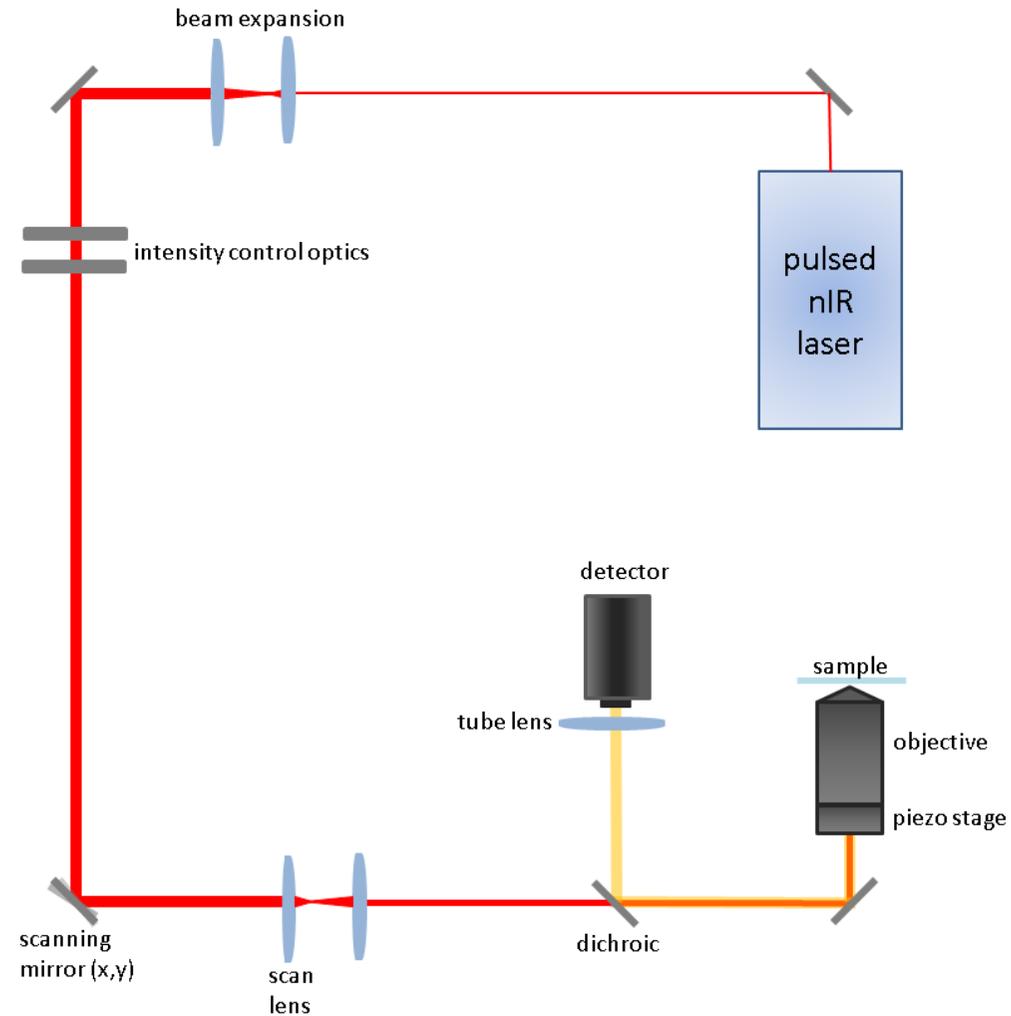
$EMLDOS_{\parallel}(r, \omega)$  in-plane electromagnetic density of states

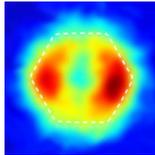
- TPL is proportional to the (i) squared projection of the in-plane electromagnetic density of states along the polarization direction for a linear polarization, and (ii) the squared of the in-plane electromagnetic density of states for a circular polarization



# Two photon luminescence TPL, a tool for plasmonics

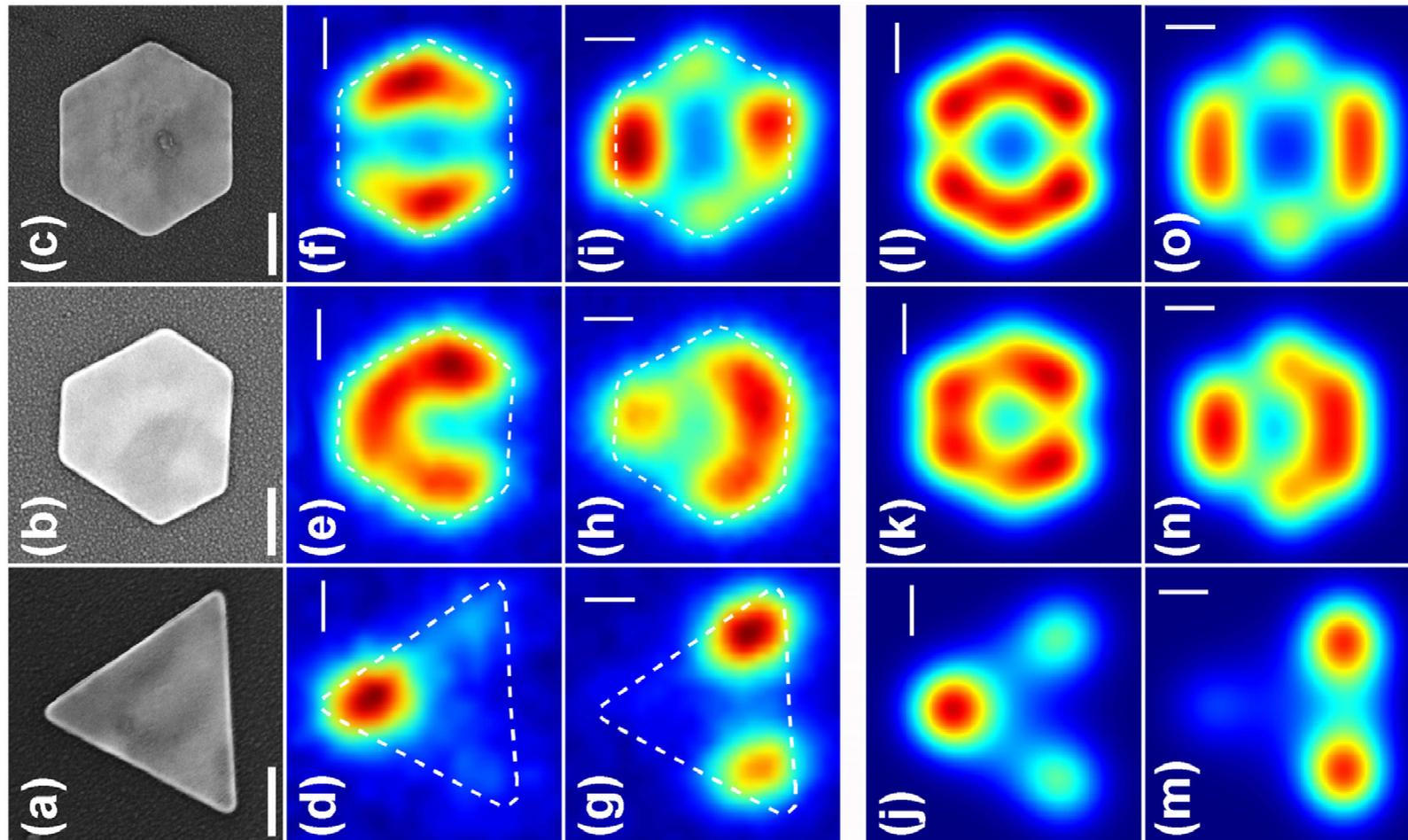
## Instrumentation





## Two photon luminescence TPL, a tool for plasmonics

TPL near field imaging - Au nanoplatelets



(a, b, c) SEM images of triangular, truncated triangular, and hexagonal Au nanoplatelets  
(d) - (i) TPL maps acquired with  $\lambda = 700$  nm and linear polarization of  $0^\circ$  (d, e, f) and  $90^\circ$  (g, h, i), white bars in the upper right corners. (j, k, l, m, n, o) Simulated maps. Scale bars 200 nm.

➤ Reference Reviews

A. Losquin, T. A. Lommen **Electron microscopy methods for space-, energy-, and time-resolved plasmonics** *Front. Phys.* **12** (2017) 127301, DOI 10.1007/s11467-016-0605-2

A. Merlen, F. Lagugné-Labarthe **Imaging the Optical Near Field in Plasmonic Nanostructures** *Applied Spectroscopy* **68** (2014) 1307-1326, DOI 10.1366/14-07699

M. Kociak, O. Stéphan **Mapping plasmons at the nanometer scale in an electron microscope** *Chem. Soc. Rev.* **43** (2014) 3865, DOI 10.1039/C3CS60478K

T. Coenen *et al.* **Cathodoluminescence microscopy: Optical imaging and spectroscopy with deep-subwavelength resolution** *MRS Bulletin* **40** (April 2015) 359, DOI 10.1557/mrs.2015.64

L. Douillard, C. Charra **High-resolution mapping of plasmonic modes: photoemission and scanning tunnelling luminescence microscopies** *J. Phys. D: Appl. Phys.* **44** (2011) 464002, DOI [10.1088/0022-3727/44/46/464002](https://doi.org/10.1088/0022-3727/44/46/464002)