

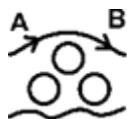
Plasmonic sensing to follow the reactivity on Pt NPs and clusters

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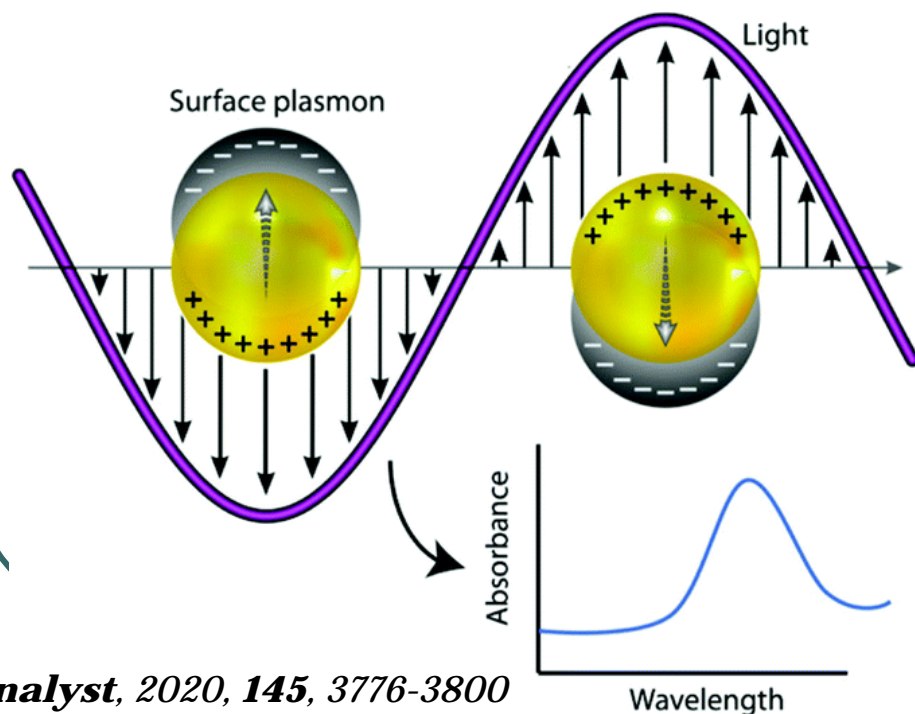
Nanosensors based on the LSPR (*Localized Surface Plasmon Resonance*)

Understanding how gas molecules interact with NPs :

→ essential challenge in atmospheric chemistry and catalysis

Extraordinary optical properties of noble-metal nanoparticles :

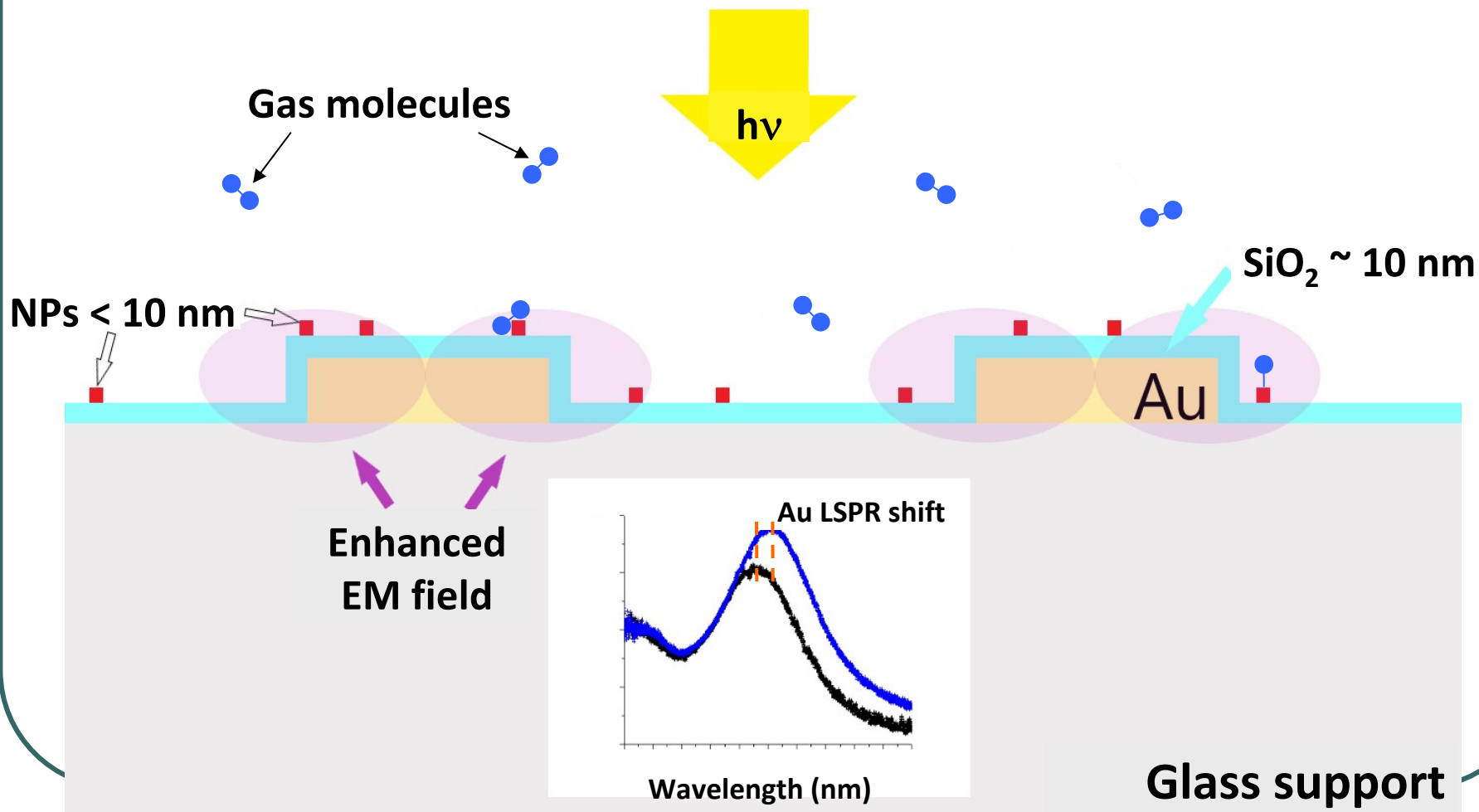
→ development of (chemical, biological, ...) sensitive nanosensors



LSPR extinction peak :
collective oscillation of electrons
of an illuminated metal
nanoparticle

The minimum of reflected light
corresponds to a maximum of
absorbance

Indirect nanoplasmonic sensing: INPS



CO and O₂ Adsorption and CO Oxidation on Pt Nanoparticles by Indirect Nanoplasmonic Sensing

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Metrics & More

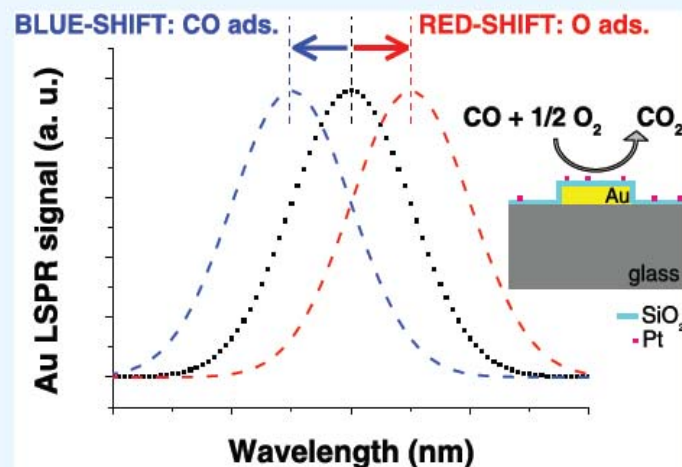


Article Recommendations

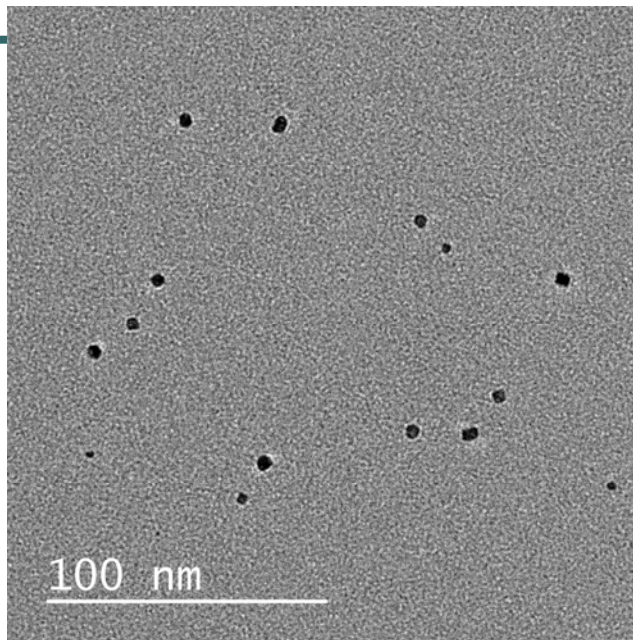
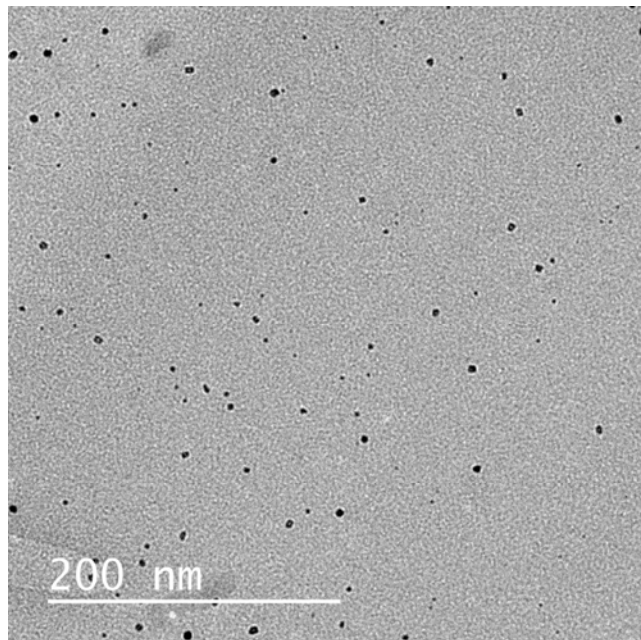


Supporting Information

ABSTRACT: We used indirect nanoplasmonic sensing (INPS) coupled with mass spectrometry to study CO and oxygen adsorption as well as CO oxidation, on Pt nanoparticles, in the Torr pressure range. Due to an optimization of the physical parameters of our plasmonic sample, we obtain a highly sensitive probe that can detect gas adsorption of a few hundredths of a monolayer, even with a very low number density of Pt particles. Moreover and for the first time, a similarity is observed between the sign and the evolution of the localized surface plasmon resonance (LSPR) peak shift and the work function measurements for CO and oxygen chemisorption. Controlling the size, shape, and surface density of Pt particles, the turnover frequency (TOF) has also been accurately determined. For similar experimental conditions, the TOF is close to those measured on Pt/oxide powder catalysts and Pt(100) single crystals.



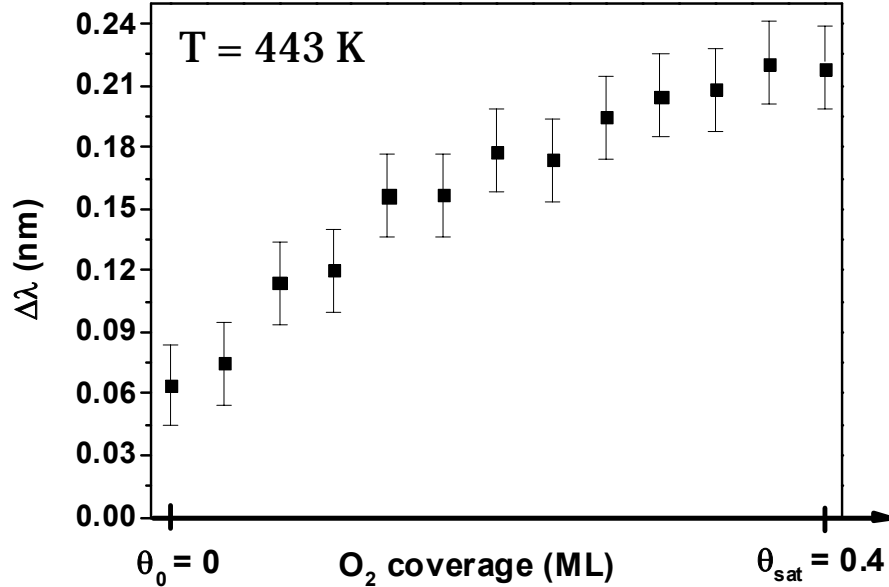
Pt NP's fabrication



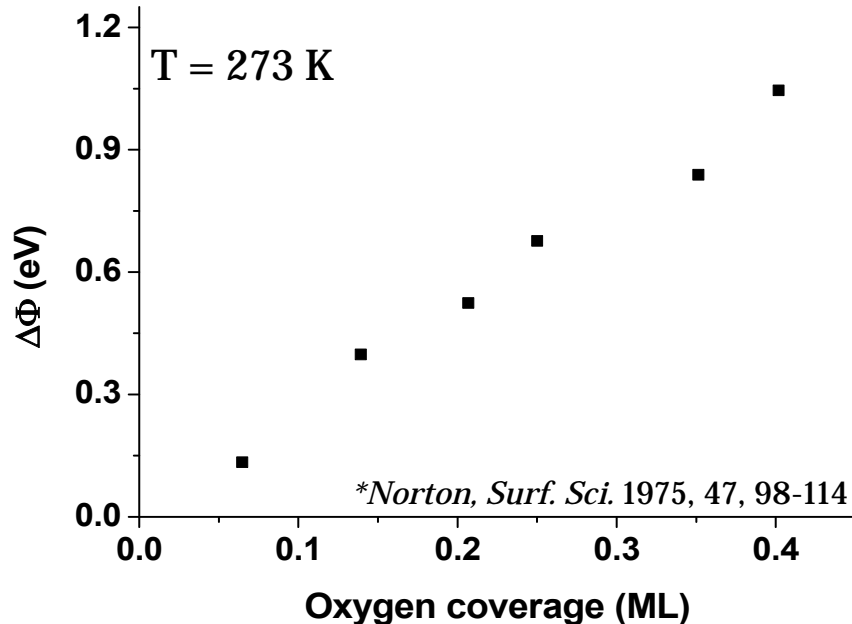
*TEM pictures
JEOL JEM 2010*

- Chemical synthesis (plasmonic sample immersed in Pt(acac)₂ + chloroform)
- Reduction (CO, H₂) + heating treatment (200 °C) → transfer HV reactor
- Pt NPs cubic shape
 - $d = 3.0 \pm 1$ nm
 - $a_s = n_s d^2 = 0.52$ % (very low !)

Oxygen adsorption: INPS vs $\Delta\Phi$



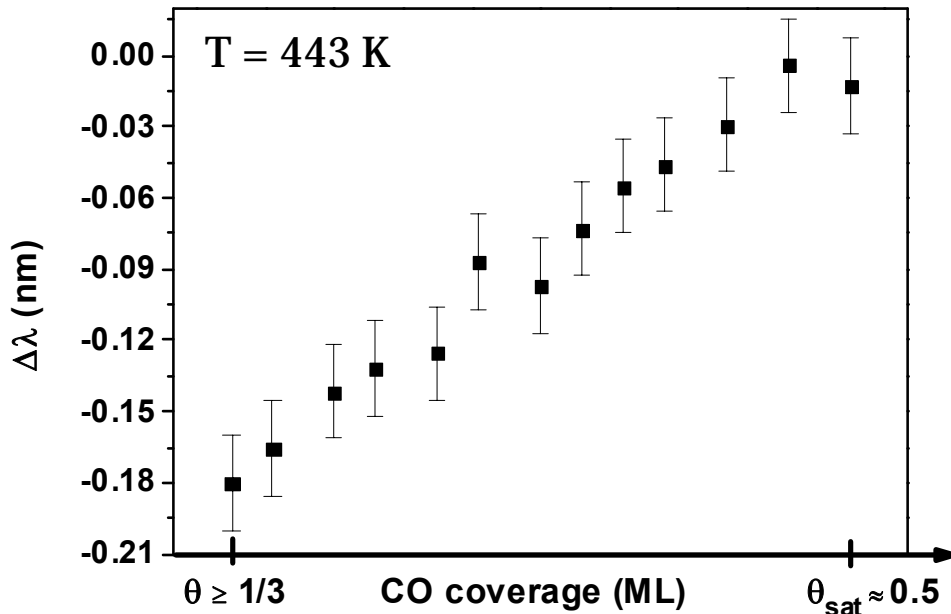
- INPS on our sample:
 $\Delta\lambda > 0$ and increases with oxygen coverage
Error bars =
lower limit of detection = 0.04 ML !!!



- Literature \rightarrow work function measurements on polycrystalline Pt*
 $\Delta\Phi > 0$ and increases with oxygen coverage

\rightarrow oxygen is irreversibly adsorbed on Pt NPs until the saturation coverage $\Theta \sim 0.4$ ML

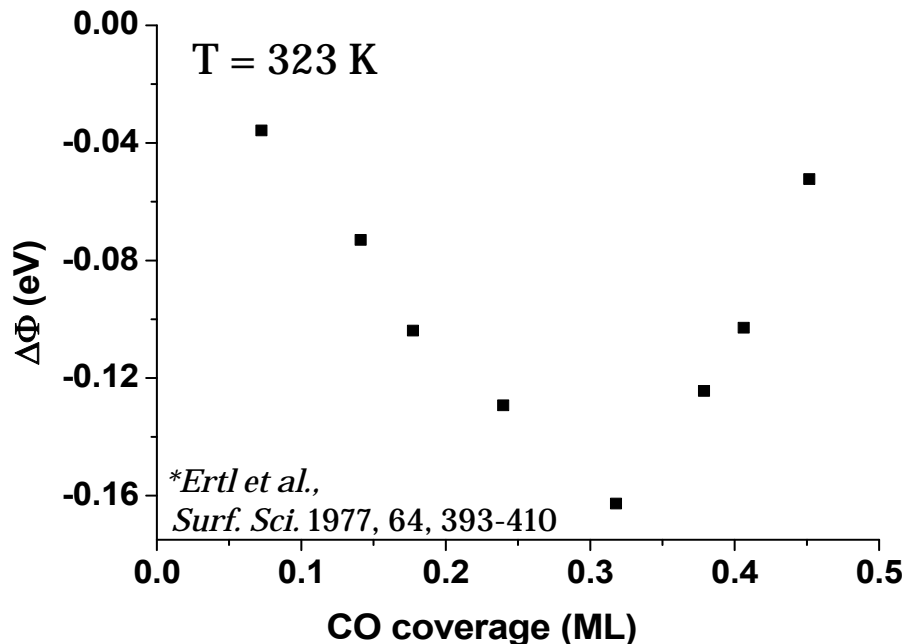
CO adsorption: INPS vs $\Delta\Phi$



- INPS on our sample:
 $\Delta\lambda < 0$ and increases when $0.3 < \Theta < 0.5$ ML

Error bars =

lower limit of detection = 0.04 ML !!!

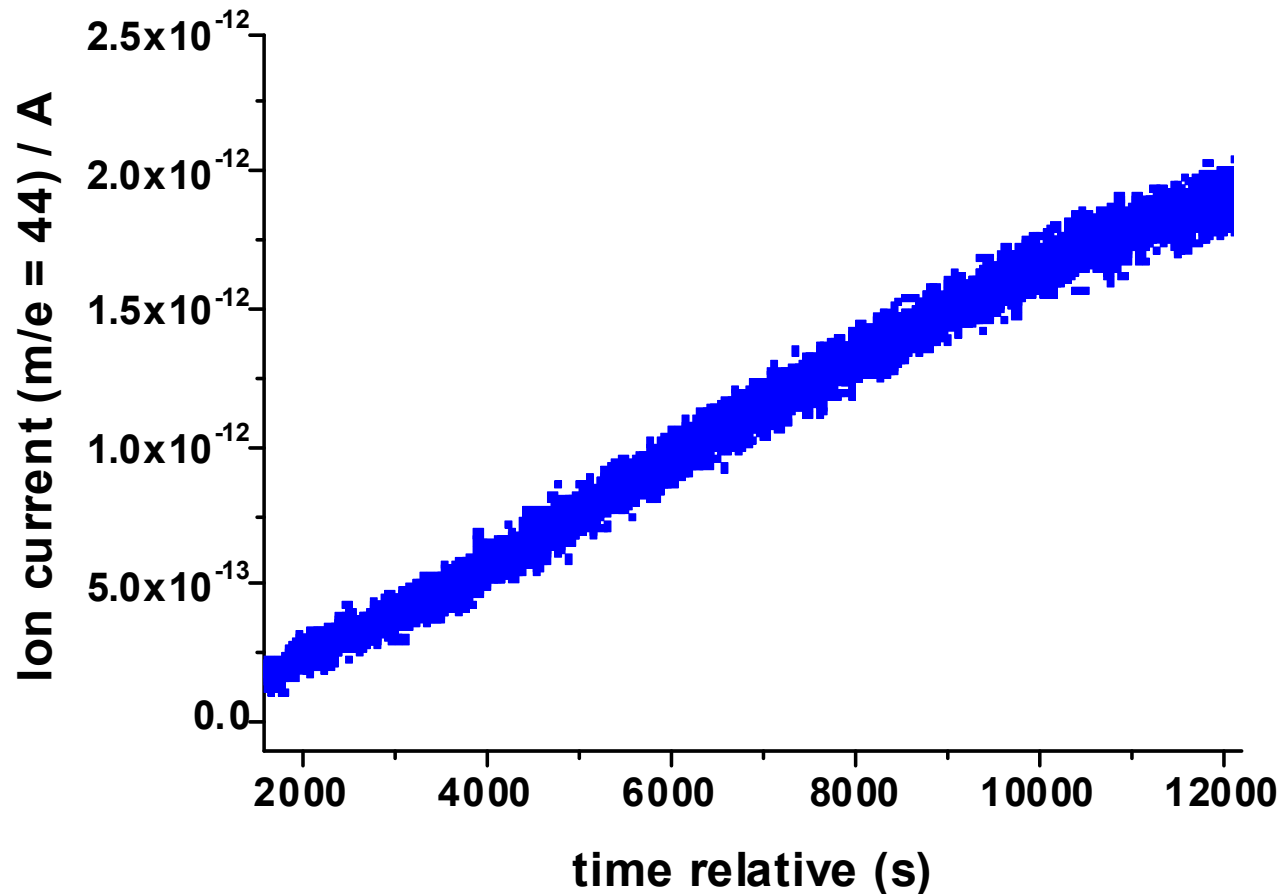


- Literature \rightarrow work function measurements on Pt(111)*:

$\Delta\Phi < 0$ and increases when $0.3 < \Theta < 0.5$ ML

\rightarrow CO is reversibly adsorbed on Pt NPs until the saturation coverage $\Theta \sim 0.5$ ML

QMS coupling: quantitative measurements



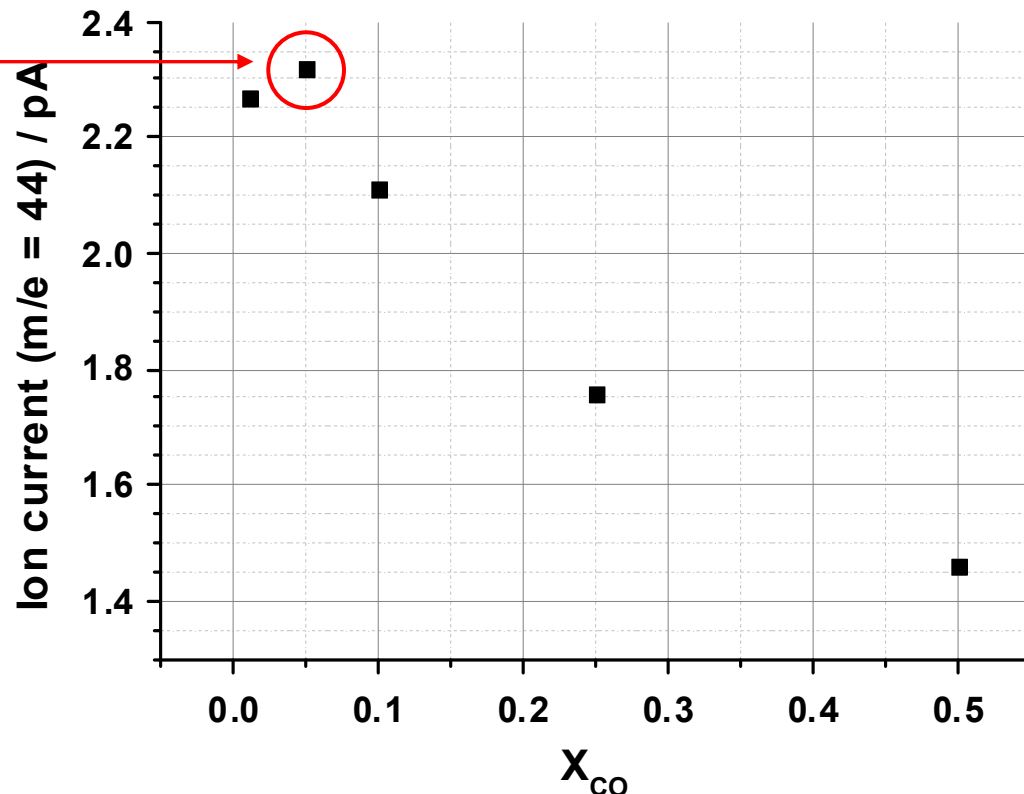
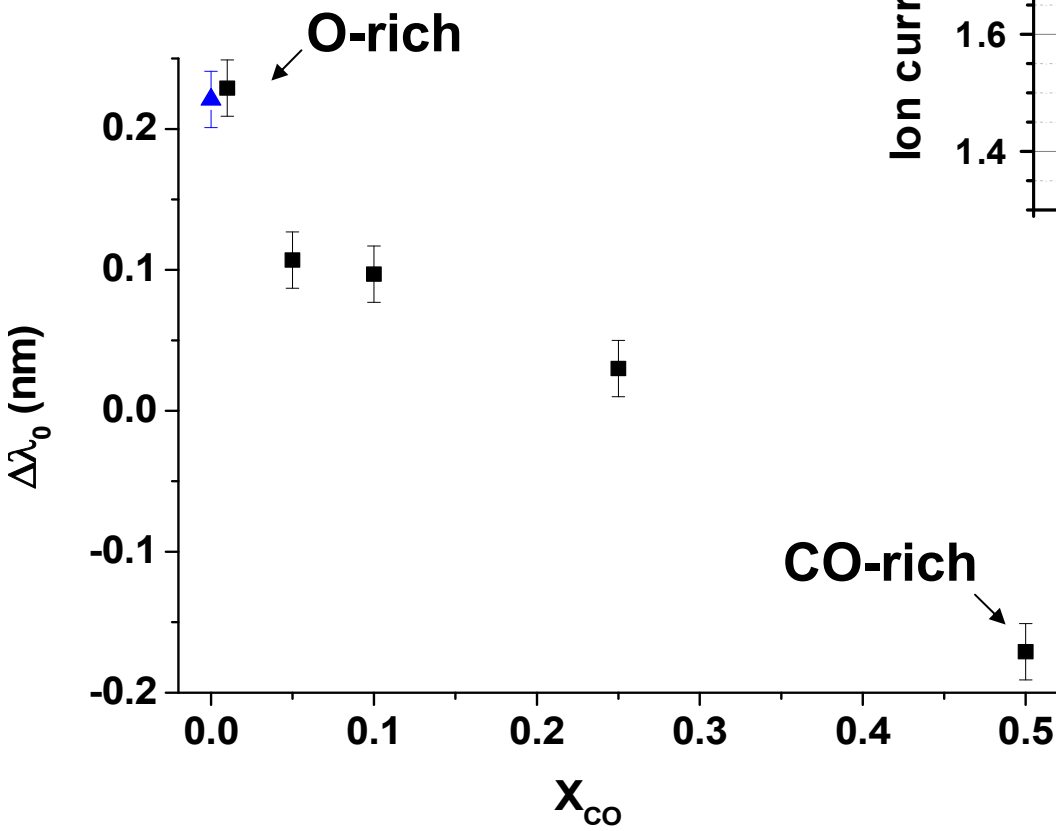
- QMS → monitoring the CO₂ production during CO oxidation on Pt NPs
T = 443 K, $\mathbf{X}_{\text{CO}} = \mathbf{P}_{\text{CO}} / (\mathbf{P}_{\text{CO}} + \mathbf{P}_{\text{O}_2}) = 0.25$
- CO₂ production by the plasmonic sample itself (contribution from the bare HV reactor has been subtracted)

QMS / INPS to follow the CO oxidation

QMS:

At $X_{CO} = 0.05$ maximum of CO_2 production

in agreement with the work of Langhammer et al. (ACS Nano 2019) on large (70 nm) single Pt particles at 473 K



INPS:

$\Delta\lambda_0$ increases when X_{CO} decreases from 0.5 to 0.01

in agreement with the work of Langhammer

To go further...

0.5% of the sensor surface is covered by Pt nanocubes

- detection of a few hundredths of a monolayer

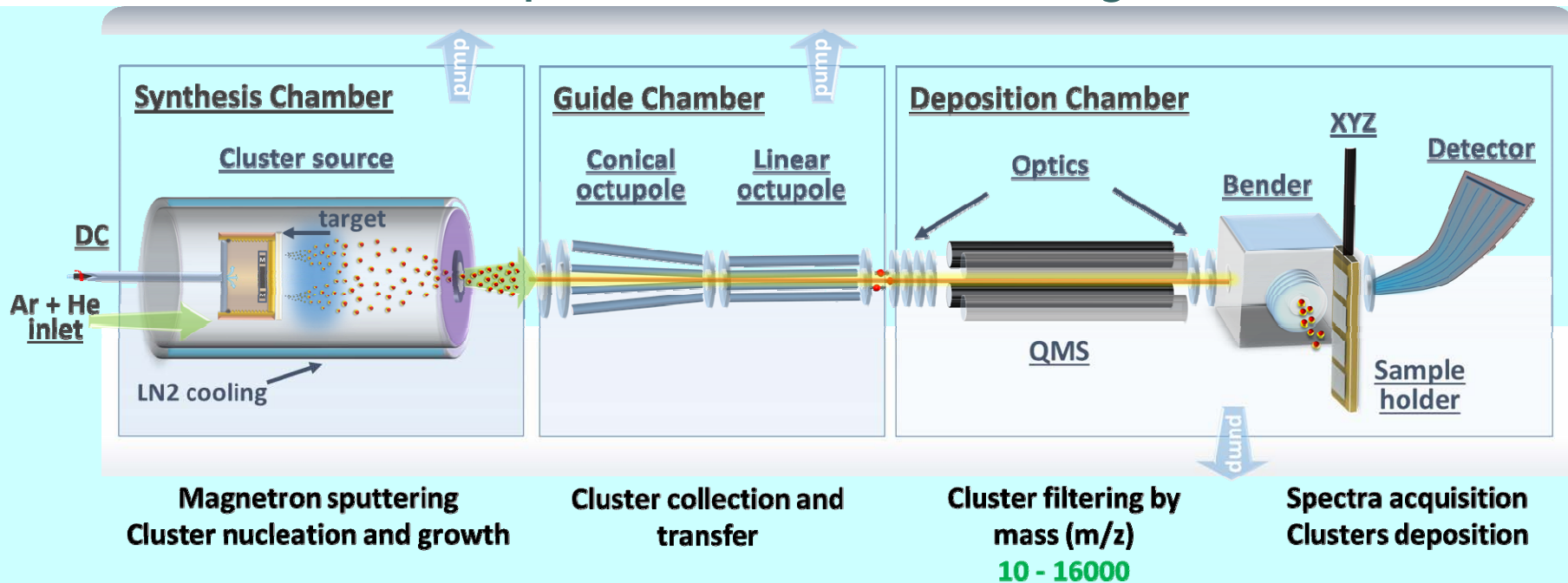
Work on size-sorted Pt clusters (10 to 20 atoms)

- Decrease the amount of Pt (rare and expensive)
- INPS measurable ?
- Sensitivity vs the Pt cluster size ?

Collaboration with



Synthesis of atomically precise Pt catalysts

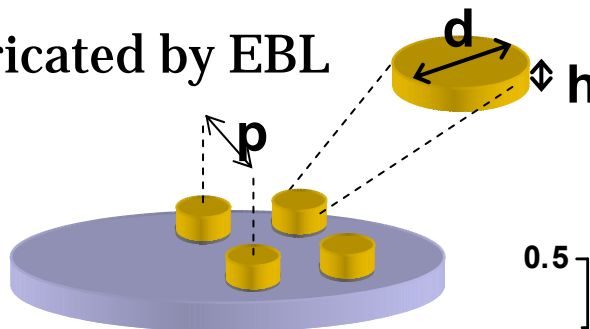


Combination of the condensation of metal atoms from the gas phase by means of Gas Aggregation Cluster Source and Quadrupole Mass Selection

- **Pt 10 deposited directly onto the INPS sensor**
10 % at. ML eq.

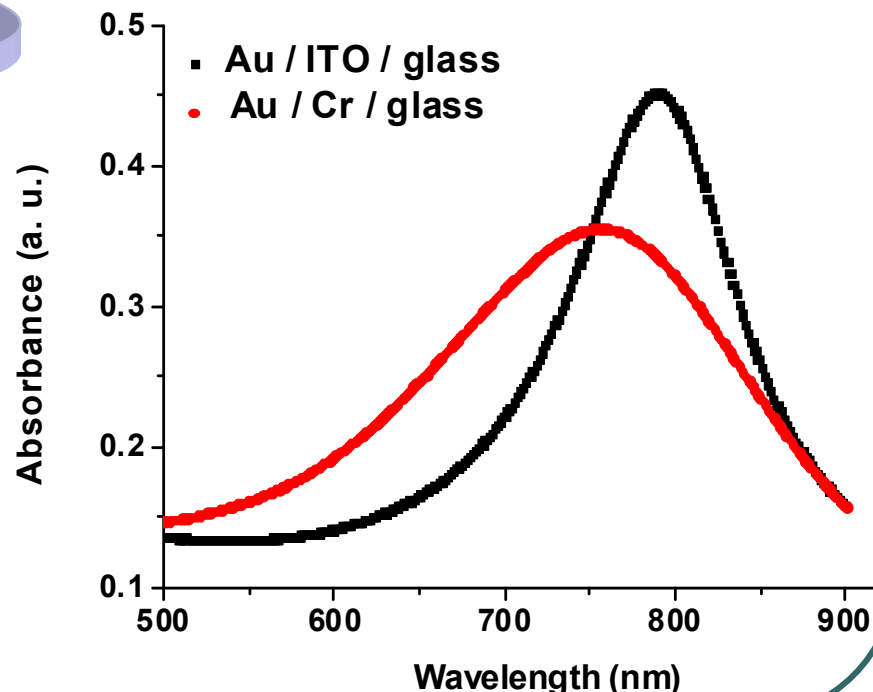
New INPS nanosensors

- Au nanodisks fabricated by EBL *as previously*



- Substrate: **Glass** → **ITO/glass**
- ITO conductive for Pt cluster deposition
- no Cr adhesion layer

signals more intense and sharper
→ better nanosensors sensitivity



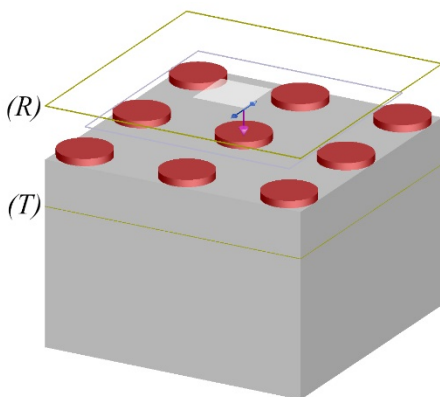
Pt10 deposit → LSPR red-shift

Experiments:

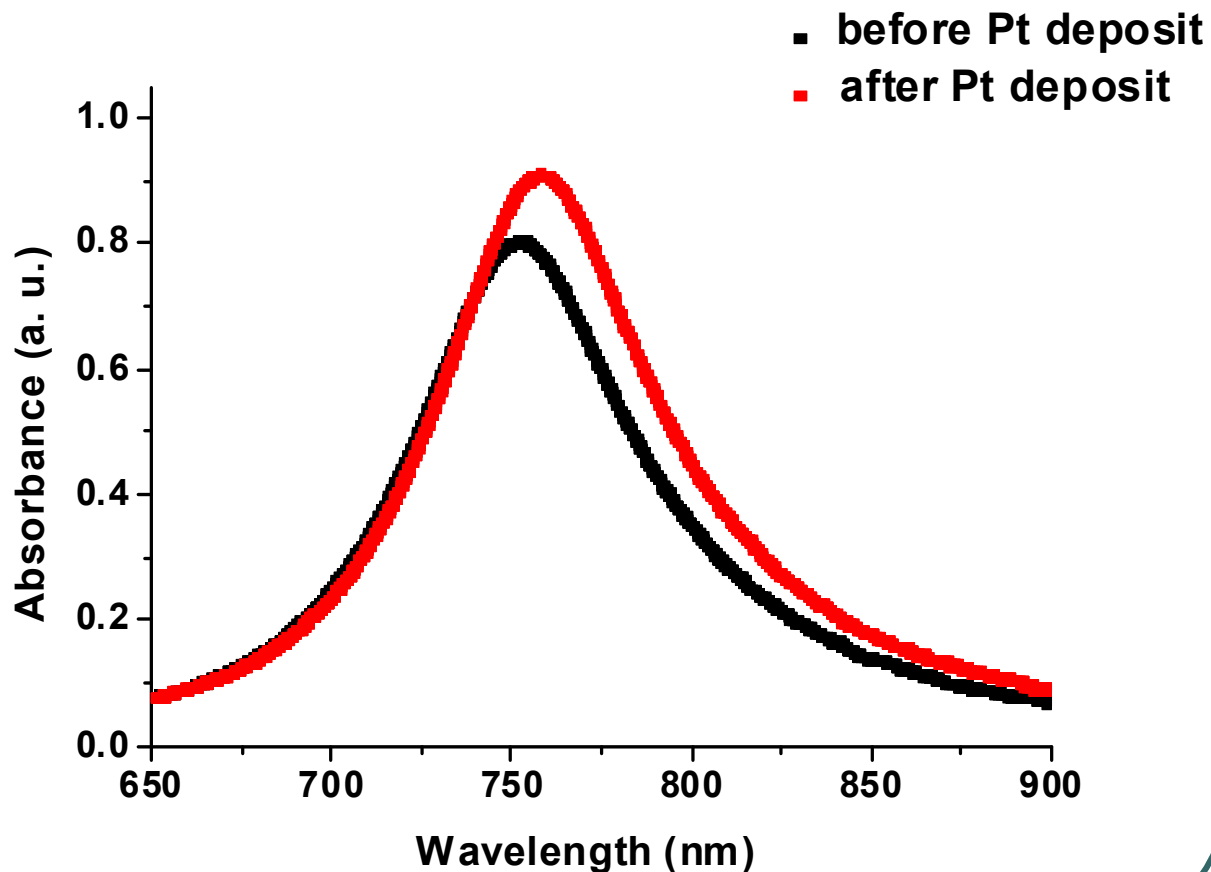
$$\Delta\lambda = + 6.1 \text{ nm}$$

FDTD

calculations:



$$\Delta\lambda = + 2.8 \text{ nm}$$



CO adsorption on Pt10 clusters

T = 418 K

Blue-shift:

$\Delta\lambda \sim -0.1 \text{ nm}$

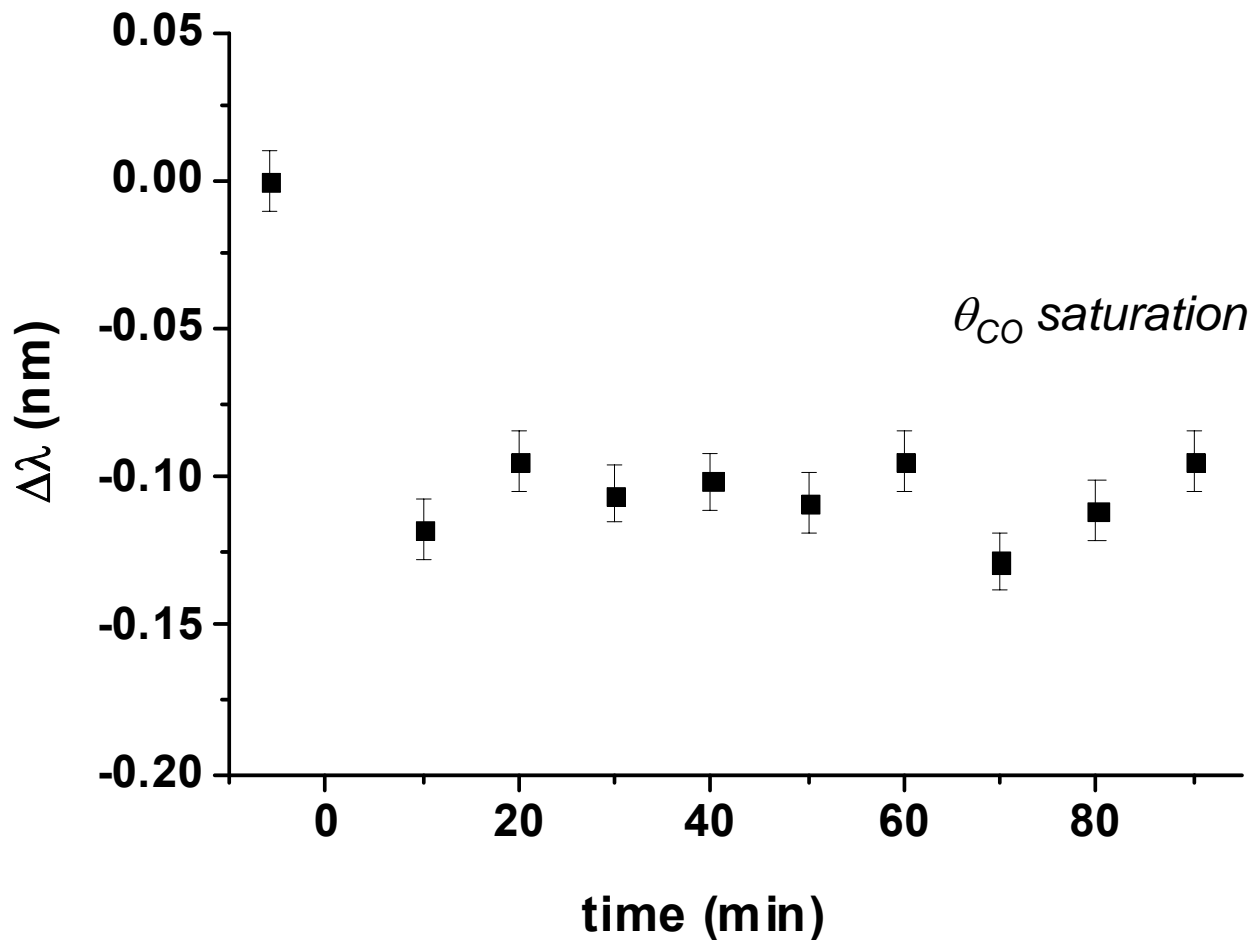
for $P_{\text{CO}} \leq 0.34 \text{ torr}$

For NP's cubes

Blue-shift:

$\Delta\lambda \sim -0.2 \text{ nm}$

But with ~ 2 x more Pt surface atoms



Conclusions and outlooks

- **INPS = non destructive probe on large (P, T) domains**
- **With cubic Pt NP's: quantitative + very sensitive probe**
- **With Pt10 clusters: first results on CO adsorption ...**

Outlooks :

- **Pt10 at lower P_{CO} , O_2 , and CO oxidation + Mass Spectrom.**
- **Increase the Pt cluster size**
- **Measure the isosteric heat of adsorption**