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Benjamin Demirdjian, Igor Ozerov, Frédéric Bedu, Alain Ranguis, Claude R Henry

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# Nanoplasmonic sensing for efficient gas sensing and detection

B. Demirdjian, I. Ozerov, F. Bedu, A. Ranguis, C. R. Henry

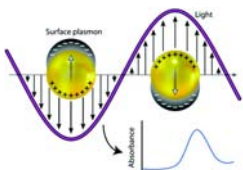
Aix-Marseille University, CNRS, CINaM UMR 7325, 13288 Marseille, France



## NANOSENSORS BASED ON LSPR

Extraordinary optical properties of noble-metal nanoparticles :

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

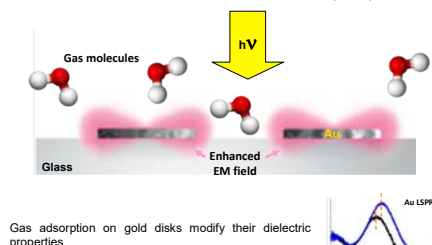


Localized surface plasmon resonance (LSPR) extinction peak : collective oscillation of electrons of an illuminated metal nanoparticle (NP)

The minimum of reflected light corresponds to a maximum of absorbance

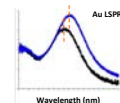
Analyst, 2020, 145, 3776-3800

## DIRECT NANOPLASMONIC SENSING (DNPS)

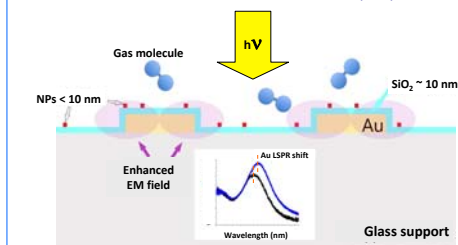


Gas adsorption on gold disks modify their dielectric properties

→ a wavelength shift of the LSPR response of the gold disk sensor



## INDIRECT NANOPLASMONIC SENSING (INPS)



NPs react with gas molecules → modification of the dielectric properties at the NP surface  
→ LSPR shift of the underlying Au detector.

## FDTD AND OPTIMISATION OF GOLD NANODISKS PARAMETERS

FDTD Simulations (Ansys Lumerical) :

→ Parameters (p, h, d) giving the best theoretical S/N (time saving for nanofabrication)

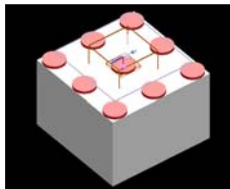
→ Interpreting LSPR spectra

Au disks sensors / borosilicate glass window (750 x 750 x 750 nm<sup>3</sup>)

Computational domain :  
ΔX = ΔY = 300 nm, ΔZ = 400 nm.

Periodic boundary conditions in X and Y  
Perfectly Matched Layers in Z direction to avoid unwanted reflections.

Optical source = incident plane wave perpendicular to the surface of the structure (XY plane) propagating in the negative sense of the Z direction



<p> = 300 nm  
<h> = 25 nm  
<d> = 150 nm

## GOLD NANODISKS FABRICATION: EBL PROCESS (PLANETE)

Sample holder = borosilicate glass window, e = 1 mm, Ø = 25 mm  
Cleaning: acetone + US, then Isopropanol + US, EDI rinsing, oxygen plasma oven at 150°C (300 W during 10 min)

PMMA spin-coating (resin 950 K at 4%, speed : 4000 rpm, e = 270 nm annealing 10 min at 170°C)

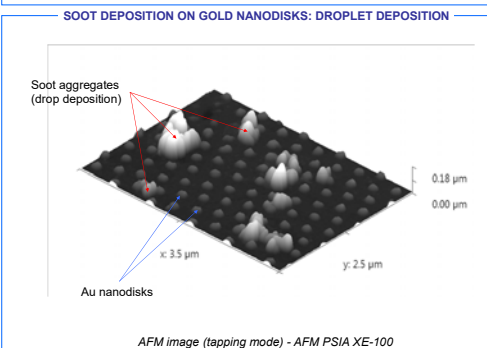
Gold layer deposition (5 nm) to remove the charges (Edwards 306)

Gold film irradiated with an electron beam (Raith PIONEER)

Revelation in acetone (Au is removed) then with MIBK/IPA 1 : 3 during 45 s  
Then with IPA during 45 s (→ holes in the resin)

Cr and Au evaporation within the PMMA resin (Edwards 306)  
e<sub>Cr</sub> = 2 nm, e<sub>Au</sub> = 20 nm  
Lift-off of the resin (acetone + US)

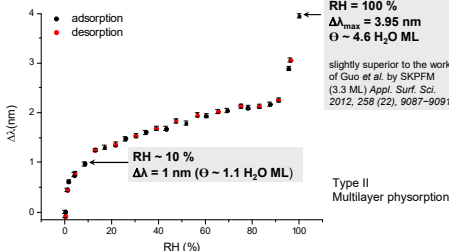
→ Precise control of the shape, the size and the pitch of gold nanodisks



AFM image (tapping mode) - AFM PSIA XE-100

## DNPS: WATER ADSORPTION ISOTHERM ON BARE GOLD NANODISKS

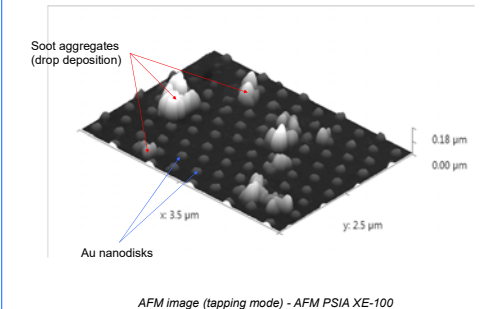
Langmuir 34 (2018) 5381-5385



Type II Multilayer physisorption

High sensitivity: error bars on Δλ ~0.04 nm ~ 4/100 H<sub>2</sub>O ML ! (equation (1))  
Reversibility: no chemisorption of water on gold (good agreement with Heras et al., Z. Phys. Chem. 129, 11-20 1982)

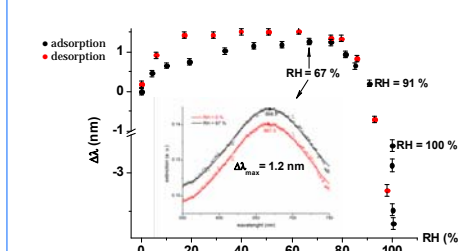
## SOOT DEPOSITION ON GOLD NANODISKS: DROPLET DEPOSITION



AFM image (tapping mode) - AFM PSIA XE-100

## INPS: WATER ADSORPTION ON HYDROPHILIC SOOT PARTICLES

The Journal of Physical Chemistry Letters 6 (2015) 4148-4152

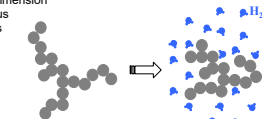


Highly sensitive sensor → detection of about 2/100 of a water ML !  
At RH > 70 % → peculiar blue shift ! (Δλ<sub>min</sub> = -3.7 nm)  
Desorption: small hysteresis → porosity

## BLUE SHIFT ? → MODELLISATION (A. KARAPETYAN)

RH → hydrophilic soot aggregates collapse into + dense structures (Mikhailov et al., J Geophys. Res. 2006, 111, D07209)

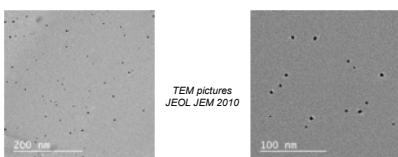
→ RH = 100 % soot aggregates are more compact:  
• higher mass fractal dimension  
• smaller gyration radius  
• higher n and k values



Simulations: analytical Born and Wolf equations → absorbance of the thin multilayers system C/SiO<sub>2</sub>/gold/glass

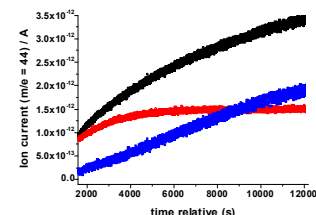
With a thinner C layer (-10 nm) and a higher n value (+0.1):  
→ Δλ = -4 nm (- exp. value)

## PT NPS FABRICATION AND TEM OBSERVATIONS (A. ALTIE, D. CHAUDANSON)

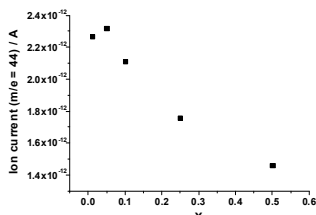


- Chemical synthesis (plasmonic sample immersed in Pt(acac)<sub>3</sub> + chloroform)  
- Reduction (CO, H<sub>2</sub>) + heating treatment (200 °C) → transfer HV reactor  
- Pt NPs cubic shape  
• d = 3.0 ± 1 nm  
• θ<sub>s</sub> = n<sub>s</sub> d<sup>2</sup> = 0.52 % (very low !)

## QMS TO FOLLOW CO OXIDATION - QUANTITATIVE MEASUREMENTS



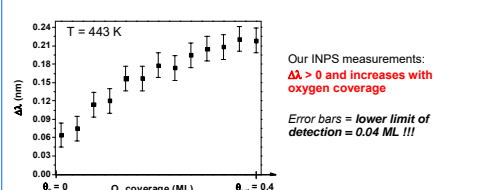
QMS → monitoring the CO<sub>2</sub> production during CO oxidation on Pt NPs (T = 443 K, X<sub>CO</sub> = P<sub>CO</sub> / (P<sub>CO</sub> + P<sub>CO<sub>2</sub>)) = 0.25)  
CO<sub>2</sub> production by the plasmonic sample itself (blue) since the contribution from the bare HV reactor (red) has been subtracted.</sub>



→ the maximum of the steady state CO<sub>2</sub> production is obtained for X<sub>CO</sub> = 0.05 in agreement with the work of Langhammer et al. (ACS Nano 2019, 13, 6090-6100) on large (70 nm) single Pt particles at 473 K

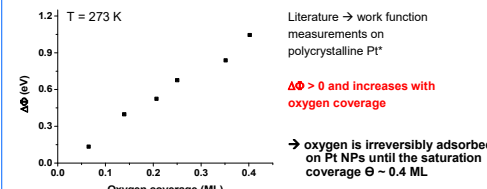
## INPS: OXYGEN AND CO ADSORPTION : ANALOGY Δλ/Δθ

ACS Omega 6 (2021) 13398-13405



Our INPS measurements:  
Δλ > 0 and increases with oxygen coverage

Error bars = lower limit of detection = 0.04 ML !!!

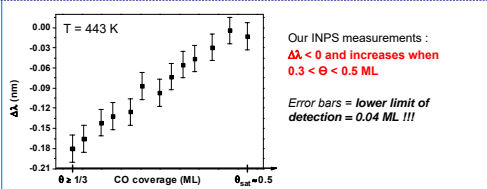


Literature → work function measurements on polycrystalline Pt\*

Δθ > 0 and increases with oxygen coverage

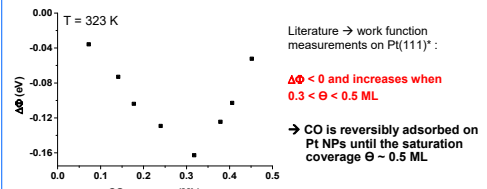
→ oxygen is irreversibly adsorbed on Pt NPs until the saturation coverage θ ~ 0.4 ML

\*Norton, Surf. Sci. 1975, 47, 98-114



Our INPS measurements :  
Δλ < 0 and increases when 0.3 < θ < 0.5 ML

Error bars = lower limit of detection = 0.04 ML !!!



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

Δθ < 0 and increases when 0.3 < θ < 0.5 ML

→ CO is reversibly adsorbed on Pt NPs until the saturation coverage θ ~ 0.5 ML

\*Ertl et al. Surf. Sci. 1977, 64, 393-410

## CONCLUSIONS AND OUTLOOKS

### Nanoplasmonic sensing :

Quantitative + very sensitive probe: a few hundredths of a ML of adsorbed gas !

Large (P, T) domains for gas sensing, adsorption, reactivity, catalysis ...

Non destructive probe (compare to other probes)

### Outlooks :

Improve the LSPR signal (morphology, coupling ...) - FDTD calculations

Increase the density of NP's for INPS (e-beam UHV evaporation)

Theoretical investigation of analogy Δλ/Δθ (shown for the 1st time)

