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Nanoplasmonic sensing for efficient gas sensing and detection

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

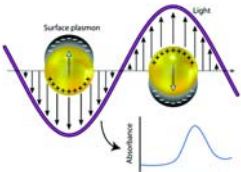
Aix-Marseille University, CNRS, CINaM UMR 7325, 13288 Marseille, France



NANOSENSORS BASED ON LSPR

Extraordinary optical properties of noble-metal nanoparticles :

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

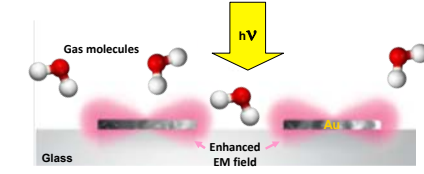


Localized surface plasmon resonance (LSPR) extinction peak : collective oscillation of electrons of an illuminated metal nanoparticle (NP)

The minimum of reflected light corresponds to a maximum of absorbance

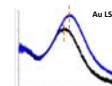
Analyst, 2020, 145, 3776-3800

DIRECT NANOPLASMONIC SENSING (DNPS)

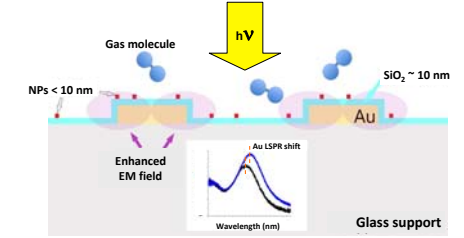


Gas adsorption on gold disks modify their dielectric properties

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



INDIRECT NANOPLASMONIC SENSING (INPS)



NPs react with gas molecules → modification 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)

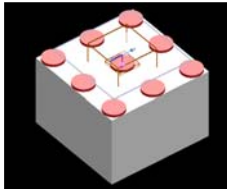
→ Interpreting LSPR spectra

Au disks sensors / borosilicate glass window (750 x 750 x 750 nm³)

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)

Area of 1 x 1 mm²

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)

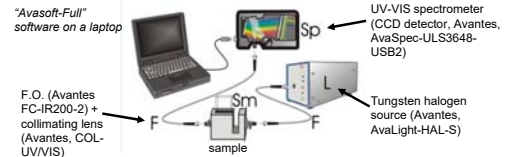
Cr and Au evaporation within the PMMA resin (Edwards 306)

e_{Cr} = 2 nm, e_{Au} = 20 nm

Lift-off of the resin (acetone + US)

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

LSPR MEASUREMENTS: EXPERIMENTAL SET-UP



RESPONSE OF DNPS SENSORS

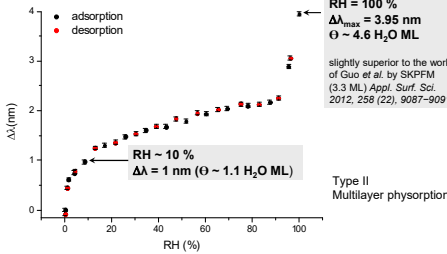
The response of LSPR nanosensors follows a simple model described by the group of Campbell (Langmuir 1998, 14, 5636-5648)

$$\Delta\lambda = m (n_2 - n_1) [1 - \exp(-2d / l_d)] \quad (1)$$

Δλ: wavelength shift
m: sensitivity of the refractive index (RI)
n₂ and n₁: RIs of different surrounding media
d: effective thickness of the adsorbate layer
l_d: characteristic decay length of the evanescent electromagnetic field.

DNPS: WATER ADSORPTION ISOTHERM ON BARE GOLD NANODISKS

Langmuir 34 (2018) 5381-5385



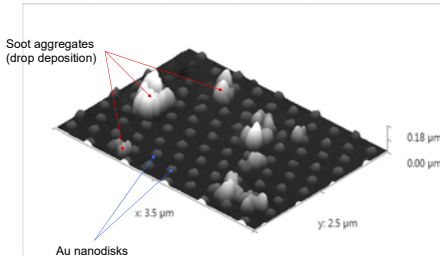
RH = 100 %
Δλ_{max} = 3.95 nm
Θ ~ 4.6 H₂O ML

slightly superior to the work of Guo et al. by SKPFM (0.3 ML) Appl. Surf. Sci. 2012, 258 (22), 9087-9091

Type II
Multilayer physisorption

High sensitivity: error bars on Δλ ~ 0.04 nm ~ 4/100 H₂O ML ! (equation (1))
Reversibility: no chemisorption of water on gold (good agreement with Heras et al., Z. Phys. Chem. 129, 11-20 1982)

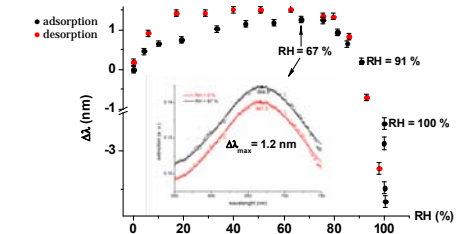
SOOT DEPOSITION ON GOLD NANODISKS: DROPLET DEPOSITION



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

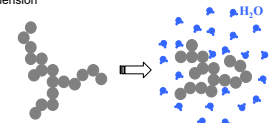


Highly sensitive sensor → detection of about 2/100 of a water ML !
At RH > 70 % → peculiar blue shift ! (Δλ_{min} = -3.7 nm)
Desorption: small hysteresis → porosity

BLUE SHIFT ? → MODELLISATION (A. KARAPETYAN)

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

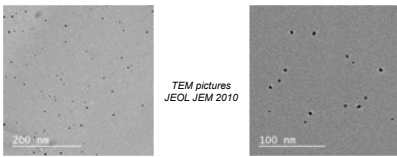
→ RH = 100 % soot aggregates are more compact:
• higher mass fractal dimension
• smaller gyration radius
• higher n and k values



Simulations: analytical Born and Wolf equations → absorbance of the thin multilayers system C/SiO₂/gold/glass

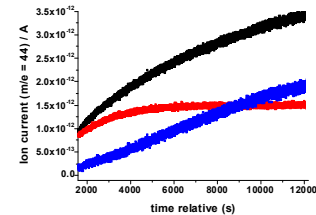
With a thinner C layer (-10 nm) and a higher n value (+0.1):
→ Δλ = -4 nm (- exp. value)

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



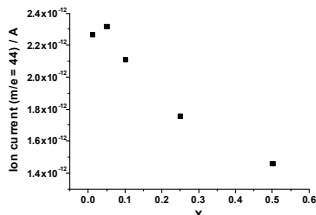
- Chemical synthesis (plasmonic sample immersed in Pt(acac)₃ + chloroform)
- Reduction (CO, H₂) + heating treatment (200 °C) → transfer HV reactor
- Pt NPs cubic shape
• d = 3.0 ± 1 nm
• θ_s = n_s d² = 0.52 % (very low !)

QMS TO FOLLOW CO OXIDATION - QUANTITATIVE MEASUREMENTS



QMS → monitoring the CO₂ production during CO oxidation on Pt NPs (T = 443 K, X_{CO} = P_{CO} / (P_{CO} + P_{CO₂)) = 0.25)}

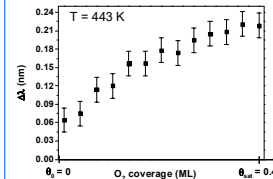
CO₂ production by the plasmonic sample itself (blue) since the contribution from the bare HV reactor (red) has been subtracted.



→ the maximum of the steady state CO₂ production is obtained for X_{CO} = 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

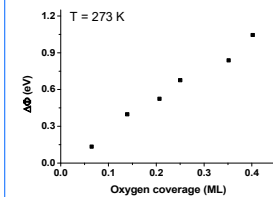
INPS: OXYGEN AND CO ADSORPTION : ANALOGY Δλ/Δθ

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 !!!

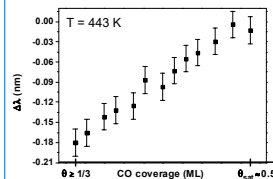


Literature → work function measurements on polycrystalline Pt*

Δθ > 0 and increases with oxygen coverage

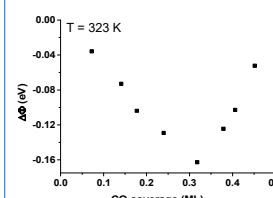
→ oxygen is irreversibly adsorbed on Pt NPs until the saturation coverage Θ ~ 0.4 ML

*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)

