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Nanoplasmonic sensing for probing gas/particle interactions

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

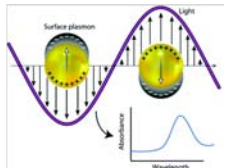
Aix-Marseille University, CNRS, CINaM UMR 7325, 13288 Marseille, France



NANOSENSORS BASED ON LSPR

Extraordinary optical properties of noble-metal nanoparticles :

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

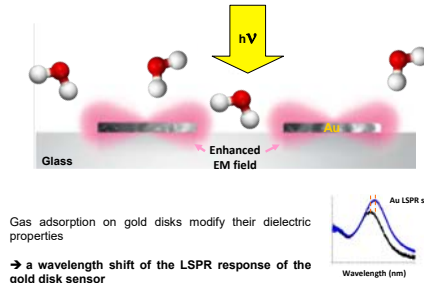


Localized surface plasmon resonance (LSPR) extinction peak : collective oscillation of electrons of an illuminated metal nanoparticle (NP)

The minimum of reflected light corresponds to a maximum of absorbance

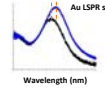
Analyst, 2020, 145, 3776-3800

DIRECT NANOPLASMONIC SENSING (DNPS)

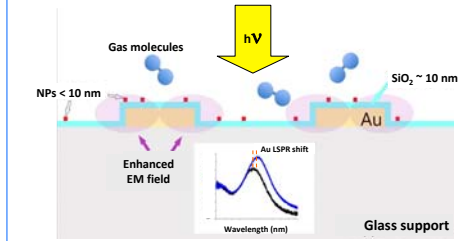


Gas adsorption on gold disks modify their dielectric properties

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



INDIRECT NANOPLASMONIC SENSING (INPS)

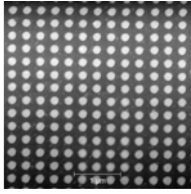


NPs react with gas molecules → modification of the dielectric properties at the NP surface
→ LSPR shift of the underlying Au detector.

OPTIMISATION OF GOLD NANODISKS PARAMETERS

FDTD Simulations
→ parameters (p, h, d) giving the best theoretical S/N

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



Tapping mode topographical AFM image of Au nanodisks on borosilicate glass (covered by a SiO₂ layer) PSIA apparatus (XE-100)

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)

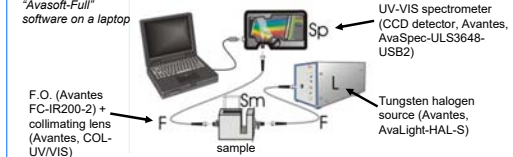
The gold film is irradiated with an electron beam (Raith PIONEER) Area of 1 x 1 mm²

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 THE LSPR NANOSENSORS

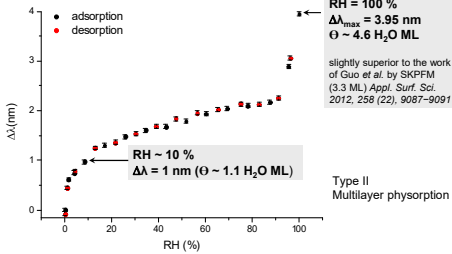
The response of LSPR nanosensors follows a simple model described by the group of Campbell (Langmuir 1998, 14, 5636-5648)

$$\Delta\lambda = m (n_2 - n_1) [1 - \exp(-2d/l_0)] \quad (1)$$

$\Delta\lambda$: wavelength shift
 m : sensitivity of the refractive index (RI)
 n_2 and n_1 : RI of different surrounding media
 d : effective thickness of the adsorbate layer
 l_0 : characteristic decay length of the evanescent electromagnetic field.

DNPS: WATER ADSORPTION ISOTHERM ON BARE GOLD NANODISKS

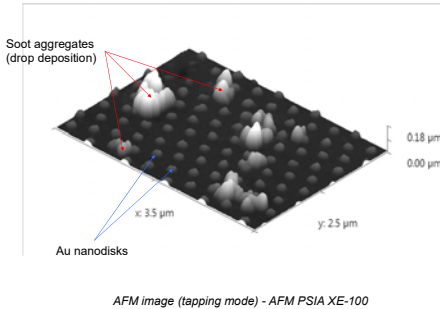
Langmuir 34 (2018) 5381-5385



Type II Multilayer physisorption

High sensitivity: error bars on $\Delta\lambda$ ~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)

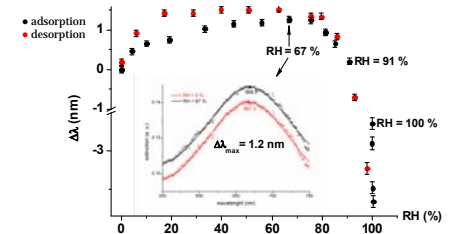
SOOT DEPOSITION ON GOLD NANODISKS: DROPLET DEPOSITION



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

INPS: WATER ADSORPTION ON HYDROPHILIC SOOT PARTICLES

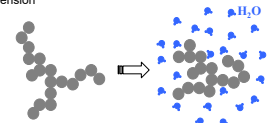
The Journal of Physical Chemistry Letters 6 (2015) 4148-4152



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

BLUE SHIFT ? → MODELLISATION (A. KARAPETYAN)

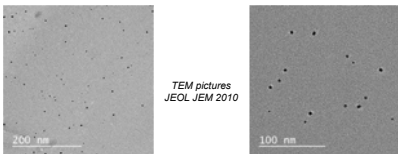
RH → hydrophilic soot aggregates collapse into + dense structures (Mikhailov et al., J Geophys. Res. 2006, 111, D07209)
→ RH = 100 % soot aggregates are more compact:
• higher mass fractal dimension
• smaller gyration radius
• higher n and k values



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

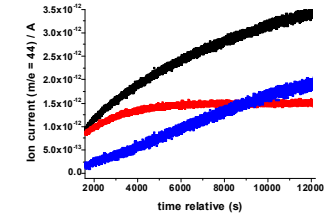
With a thinner C layer (-10 nm) and a higher n value (+0.1):
→ $\Delta\lambda = -4$ nm (- exp. value)

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

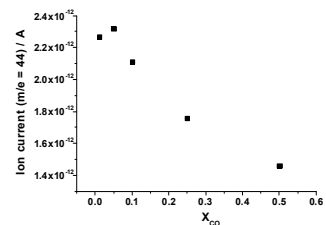


- Chemical synthesis (plasmonic sample immersed in Pt(acac)₃ + chloroform)
- Reduction (CO, H₂) + heating treatment (200 °C) → transfer HV reactor
- Pt NPs cubic shape
• d = 3.0 ± 1 nm
• $\theta_p = n_p d^2 = 0.52$ % (very low !)

QMS TO FOLLOW CO OXIDATION AND FOR QUANTITATIVE MEASUREMENTS



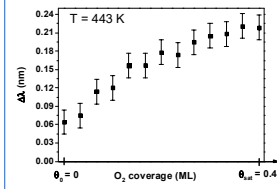
QMS → monitoring the CO₂ production during CO oxidation on Pt NPs (T = 443 K, X_{CO} = P_{CO} / (P_{CO} + P_{CO2}) = 0.25)
• CO₂ production by the plasmonic sample itself (blue) since the contribution from the bare HV reactor (red) has been subtracted.



→ 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

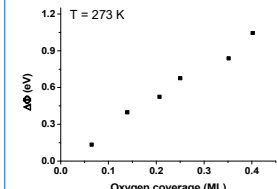
INPS: OXYGEN AND CO ADSORPTION : ANALOGY Δλ/ΔΦ

ACS Omega 6 (2021) 13398-13405



Our INPS measurements:
 $\Delta\lambda > 0$ and increases with oxygen coverage

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

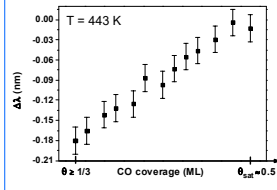


Literature → work function measurements on polycrystalline Pt*

$\Delta\Phi > 0$ and increases with oxygen coverage

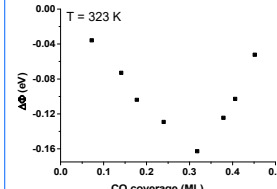
→ oxygen is irreversibly adsorbed on Pt NPs until the saturation coverage $\Theta \sim 0.4$ ML

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



Our INPS measurements :
 $\Delta\lambda < 0$ and increases when $0.3 < \Theta < 0.5$ ML

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



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

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

→ CO is reversibly adsorbed on Pt NPs until the saturation coverage $\Theta \sim 0.5$ 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 adsorption, reactivity, catalysis ...

Non destructive probe (compare to other probes)

Outlooks :

Enhanced the detector EM field (morphology, coupling ...)

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

Theoretical investigation of analogy $\Delta\lambda/\Delta\Phi$ (shown for the 1st time)

