Nanoplasmonics for efficient gas sensing and detection

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Nanoplasmonic sensing for efficient gas sensing and detection

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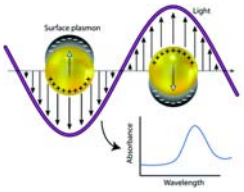
NANOSENSORS BASED ON LSPR

Extraordinary optical properties of noble-metal nanoparticles :

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

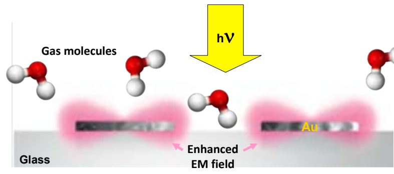


Localized surface plasmon resonance (LSPR) extinction peak : collective oscillation of electrons of an illuminated metal nanoparticle (NP)

The minimum of reflected light corresponds to a maximum of absorbance

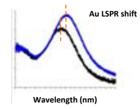
Analyst, 2020, 145, 3776-3800

DIRECT NANOPLASMONIC SENSING (DNPS)

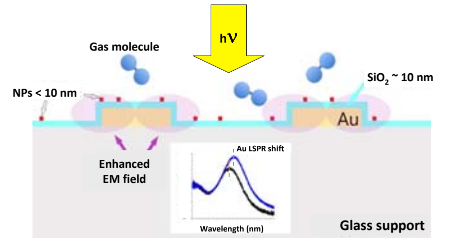


Gas adsorption on gold disks modify their dielectric properties

→ 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)

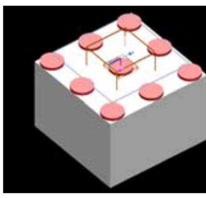
→ Interpreting LSPR spectra

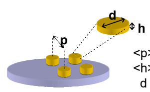
Au disks sensors / borosilicate glass window (750 x 750 x 750 nm^3)

Computational domain :
$\Delta X = \Delta Y = 300$ nm, $\Delta Z = 400$ 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



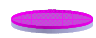


<p> = 300 nm
<h> = 25 nm
d = 150 nm

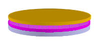
GOLD NANODISKS FABRICATION: EBL PROCESS (PLANETE)

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)

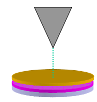
PMMA spin-coating (resin 950 K at 4 %, speed : 4000 rpm, e = 270 nm annealing 10 min at 170°C)



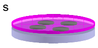
Gold layer deposition (5 nm) to remove the charges (Edwards 306)



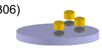
Gold film irradiated with an electron beam (Raith PIONNEER) Area of 1 x 1 mm2



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

"Avasoft-Full" software on a laptop

UV-VIS spectrometer (CCD detector, Avantes, AvaSpec-ULS3648-USB2)

F.O. (Avantes FC-IR200-2) + collimating lens (Avantes, COL-UV/VIS)

Tungsten halogen source (Avantes, AvaLight-HAL-S)

RESPONSE OF DNPS SENSORS

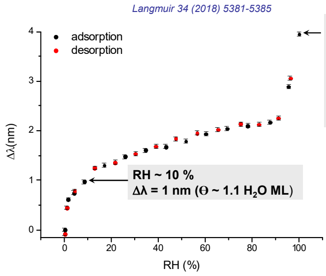
The response of LSPR nanosensors follows a simple model described by the group of Campbell *(Langmuir 1998, 14, 5636−5648)*

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

$\Delta\lambda$: wavelength shift
m: sensitivity of the refractive index (RI)
n_2 and n_1: 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



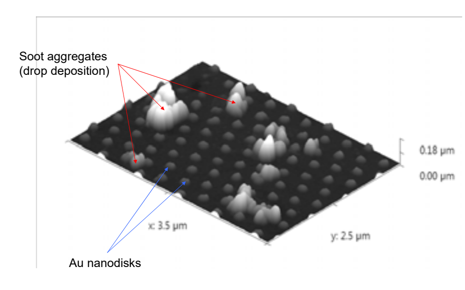
RH = 100 %
$\Delta\lambda_{max}$ = 3.95 nm
Θ ~ 4.6 H_2O ML

slightly superior to the work of Guo *et al.* by SKPFM (3.3 ML) *Appl. Surf. Sci. 2012, 258 (22), 9087−9091*

Type II
Multilayer physorption

High sensitivity: error bars on Δλ ~0.04 nm ~ 4/100 H_2O ML ! *(equation (1))*
Reversibility: no chemisorption of water on gold (good agreement with Heras *et al., Z. Phys. Chem. 129, 11−20 1982*)

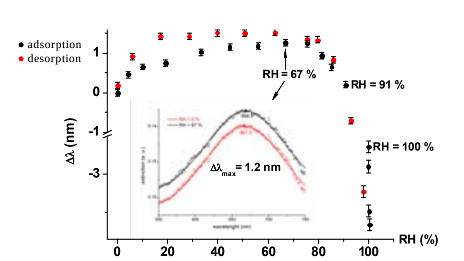
SOOT DEPOSITION ON GOLD NANODISKS: DROPLET DEPOSITION



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

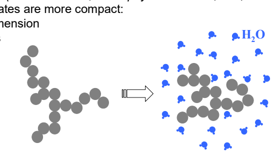


- **Highly sensitive sensor → detection of about 2/100 of a water ML !**
- At RH > 70 % → **peculiar blue shift !** ($\Delta\lambda_{min}$ = -3.7 nm)
- Desorption: small hysteresis → porosity

BLUE SHIFT ? → MODELISATION (A. KARAPETYAN)

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

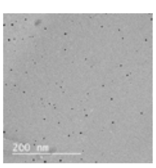
→ RH = 100 % soot aggregates are more compact:
- higher mass fractal dimension
- smaller gyration radius
- higher n and k values



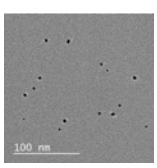
Simulations: analytical Born and Wolf equations → absorbance of the thin multilayers system C/SiO2/gold/glass

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)

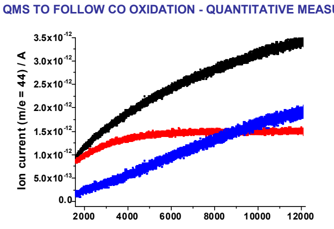


TEM pictures JEOL JEM 2010

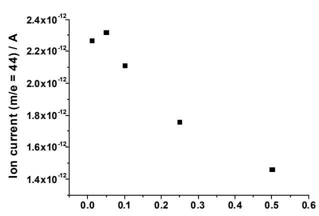


- Chemical synthesis (plasmonic sample immersed in $Pt(acac)_2$ + chloroform)
- Reduction (CO, H_2) + heating treatment (200 °C) → transfer HV reactor
- Pt NPs cubic shape
  - *d* = **3.0** ± 1 nm
  - $a_s = n_s\, d^2$ = **0.52 % (very low !)**

QMS TO FOLLOW CO OXIDATION - QUANTITATIVE MEASUREMENTS



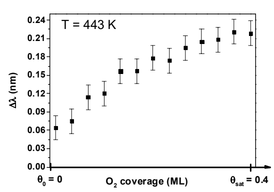
- QMS → **monitoring the CO_2 production during CO oxidation on Pt NPs**
  (T = 443 K, $X_{CO} = P_{CO} / (P_{CO} + P_{CO2})$ = 0.25)
- CO_2 production by the plasmonic sample itself (blue) since the contribution from the bare HV reactor (red) has been subtracted.



→ **the maximum of the steady state CO_2 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

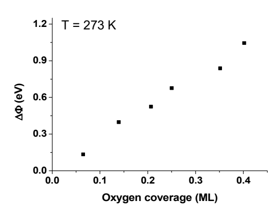
INPS: OXYGEN AND CO ADSORPTION : ANALOGY Δλ / ΔΦ

ACS Omega 6 (2021) 13398-13405



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

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

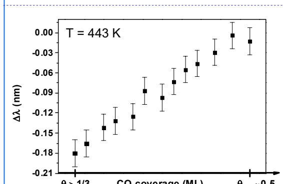


Literature → work function measurements on polycrystalline Pt*

ΔΦ > 0 and increases with oxygen coverage

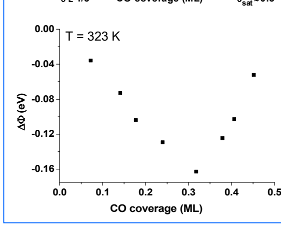
→ oxygen is irreversibly adsorbed on Pt NPs until the saturation coverage Θ ~ 0.4 ML

**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)* :

ΔΦ < 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*

CONLUSIONS 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 calulations

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

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