

Indirect nanoplasmonic sensing: a very sensitive and promising probe

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Nanosensors based on the LSPR

Extraordinary optical properties of noble-metal nanoparticles :

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



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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

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Indirect Nanoplasmonic Sensing to Probe with a High Sensitivity the Interaction of Water Vapor with Soot Aerosols

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Supporting Information

ABSTRACT: We demonstrate in this work that the indirect nanoplasmonic sensing lets us follow the adsorption/desorption of water molecules on soot particles that are a major contributor of the global warming. Increasing the relative humidity of the surrounding medium we measure a shift in wavelength of the localized surface plasmon resonance response of gold nanodisks on which soot particles are deposited. We show a singular and reversible blue shift with hydrophilic aircraft soot particles interpreted from a basic model as a reversible morphological change of the soot aggregates. This new method is highly sensitive and interesting to follow the change of optical properties of aerosols during their aging in the atmosphere, where they can adsorb and react with different gas molecules.



INPS on soot NPs / Au disks



INPS probes the water/soot interaction



Highly sensitive sensor → detection of about 2/100 of a water ML !

- At RH > 70 % \rightarrow peculiar blue shift ! ($\Delta\lambda_{\min} = -3.7 \text{ nm}$)
- Desorption: small hysteresis → porosity

Why a peculiar blue-shift ???

 $RH \nearrow \rightarrow hydrophilic soot aggregates collapse into + dense structures$

(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 \rightarrow absorbance of the thin multilayers system C/SiO2/gold/glass

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



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Pt NP's fabrication

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TEM pictures JEOL JEM 2010

- Chemical synthesis (plasmonic sample immersed in Pt(acac)2 + chloroform)
- Reduction (CO, H₂) + heating treatment (200 °C) \rightarrow transfer HV reactor
- Pt NPs cubic shape

- *d* = **3.0** ± 1 nm
- $a_s = n_s d^2 = 0.52$ % (very low !)

Oxygen adsorption : INPS $vs \Delta \Phi$



- INPS on our sample:
 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

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 → 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



QMS coupling: quantitative measurements



• QMS \rightarrow 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.

QMS to follow the CO oxidation



→ 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 :

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Quantitative + very sensitive probe (a few hundredths of a ML of adsorbed gas) even with a low NP's surface coverage

- Large (P, T) domains of studies
- > Non destructive probe (compare to other probes)

<u>Outlooks :</u>

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

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