Surface-Enhanced Raman Scattering on gold nanowire arrays

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SERS objectives:

- To study relation between Localized Surface Plasmon (LSP) Resonance and SERS
- To highlight multipolar orders of LSP efficiency in SERS
- Better understanding of the SERS process
Nanoparticle arrays

The nanostructures of desired shape, size and arrangement are designed on glass substrates through Electron Beam Lithography (EBL) and Lift-off techniques.

- This technique provides homogenous array covers an area of 80 per 80 micrometer

- $L = $ from 50 nm to 1000 nm, $l = $ 60 nm, height $=50$ nm.

- $PPX = PPY = 200$ nm

- Molecular probe: trans-1, 2 bis(4-pyridyl)ethylene (BPE),

Control of the nanowire and the array parameters

SERS and LSPR: setup

- **Device:** Jobin -Yvon micro-Raman spectrophotometer (Labram).

- **Extinction:** normal incidence with a collimated white light polarized along the nanowires length.

- **Raman:** x100 magnification objective (NA: 0.90) in back scattering geometry with the 633 nm line of He-Ne laser polarized along the length of nanowires.
Gold Nanowire: SERS

- Strong dependence of the Raman intensity on the length

![Graph showing Raman enhancement as a function of nanowire length]

Raman enhancement maximum for optimum length: \((L = 670 \text{ nm and } L = 900 \text{ nm})\).

*L. Billot and al, CPL, 422, p.303 (2006)*
Gold Nanowire: Origin of SERS Signal

FDTD calculation shows that the Raman enhancement essentially comes from the field enhancement at the end of the nanowires.

when the nanowires are longer, the signal is more confined at the apex.

Gold Nanowire : LSPR

- Observation of odd multipolar LSP whose position are red shifted when increase the nanowire length

\[ (G. \text{ Schider et al., PRB 68, 155427, 2003}) \]
Some multipolar LSPR have better enhancement than dipolar LSPR

Best enhancement for LSPR close to 675 nm ($\lambda_R$)
Gold Nanowire : 676 nm

New wavelength : $\lambda_{\text{exc}} = 676\text{nm}$ and $\lambda_R = 736\text{nm}$

- Raman enhancement depends on the nanowire length and laser excitation.
Gold Nanowire : 676 nm

- Best enhancement for LSPR close to 730 nm ($\lambda_R$)
- Same conclusions than 633 nm wavelength
Gold Nanowire

N. Calander et al., JAP 92, 4878, 2002

- **Model**: Solving Maxwell equation in spheroidal coordinates
  - $\lambda_{\text{exc}} = 633\text{nm}$
  - silver particle
  - dephasing effect

- **Enhancement at the extremity of the particle**

> **Gold and silver**: close behaviour

\[ \varepsilon_{\text{Au}} = -10.7 + 1.34.i \quad \text{and} \quad \varepsilon_{\text{Ag}} = -15.90 + 1.04.i \]
Calander’s results

⇒ There are maximum intensity for lengths close to 600 and 900 nm.
Gold Nanowire: width

Different behaviours for different nanowire widths
Gold Nanowire: width

\[ \rightarrow \text{LSPR is red shifted when the length increases.} \]
Gold Nanowire: $\lambda_{\text{LSPR}}$ VS shape - First results

Mapping of $\lambda_{\text{LSPR}}$ versus the length (L) and the ratio (R = length / width) of nanowires with MathLab software.
Gold Nanowire: \( I_{\text{SERS}} \) VS shape – First results

Mapping of SERS signal versus the length (L) and the ratio (R) (length on width) of nanowires with MathLab software.

We have got a efficiency SERS maxima for zones where LSPR is positioned enter 650 nm and 700nm.

In progress…
Conclusions

- Key role of the choice of the size and the shape of the nanostructures for LSPR position
- SERS efficiency is correlated to LSPR position
- Multipolar order of LSPR explain SERS maxima

Final goal: optimisation of SERS substrate
Gold Nanowire: 
$\lambda_{\text{LSPR}}$ VS shape - First results

Mapping of $\lambda_{\text{LSPR}}$ versus the length (L) and the ratio (R= length /width) of nanowires with MathLab software.