Controlling intrinsic optical properties by film thickness

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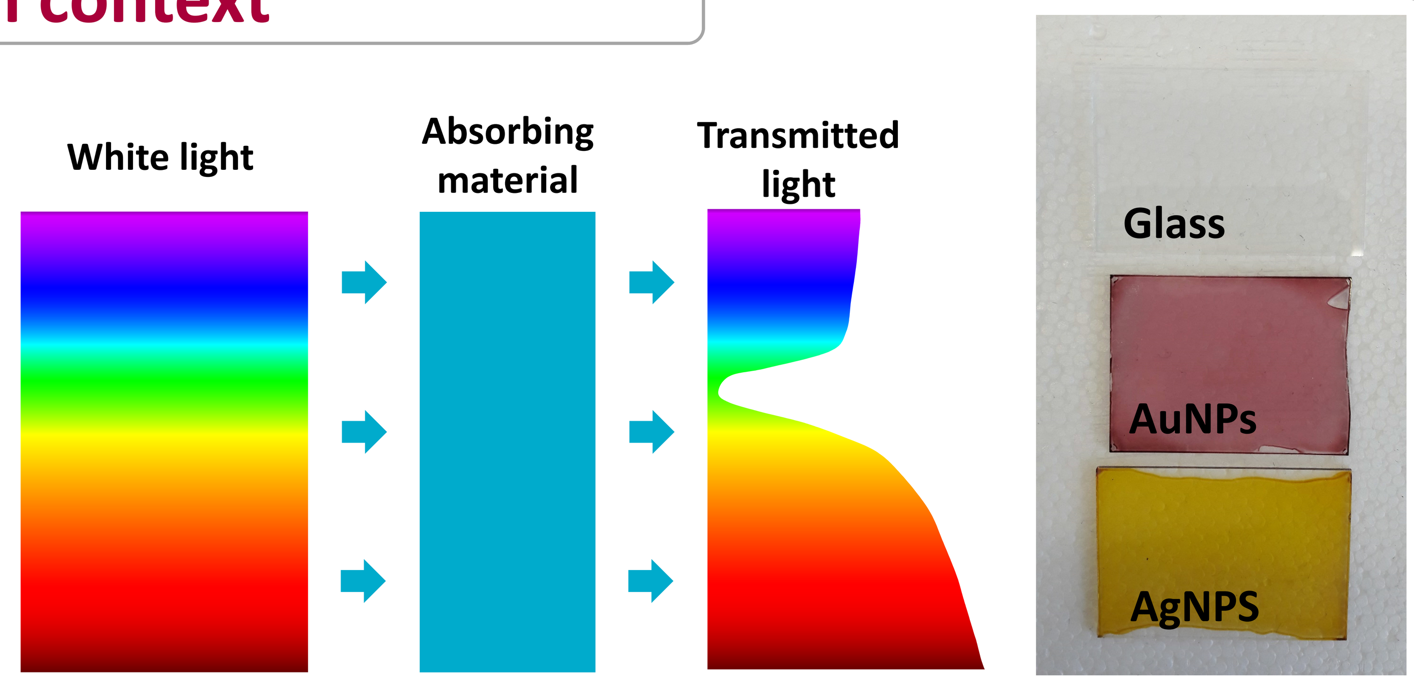
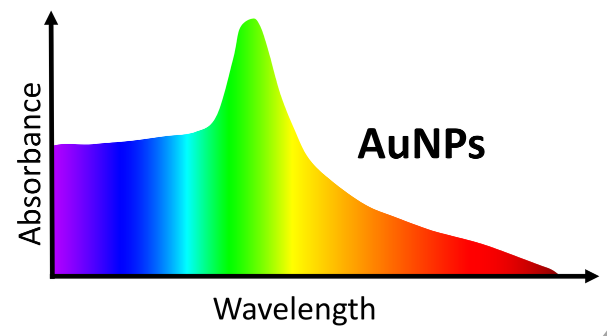
Introduction and research context

Research context and motivation :

- **Optical properties** of metal nanoparticles (NPs) determined by a collective oscillation of the conduction electrons : **Localized Surface Plasmon Resonance (LSPR)**
- **Model system** : $HAuCl_4$ or $AgNO_3$ mixed with poly(vinyl alcohol) (PVA) and chemical reduction of the metal salt by **thermal annealing** of the spin-coated film to obtain Au^0 or Ag^0 NPs in PVA matrix ($\lambda_{Au} \approx 540\ nm$ and $\lambda_{Ag} \approx 420\ nm$)
- ***In situ* route for synthesis :** spontaneous encapsulation in a matrix during synthesis but less control on the shape/size of the NPs
- **Advantages : High concentration** of NPs in the film and *in situ* synthesis is **simpler** and **faster** than the conventional bottom up approach

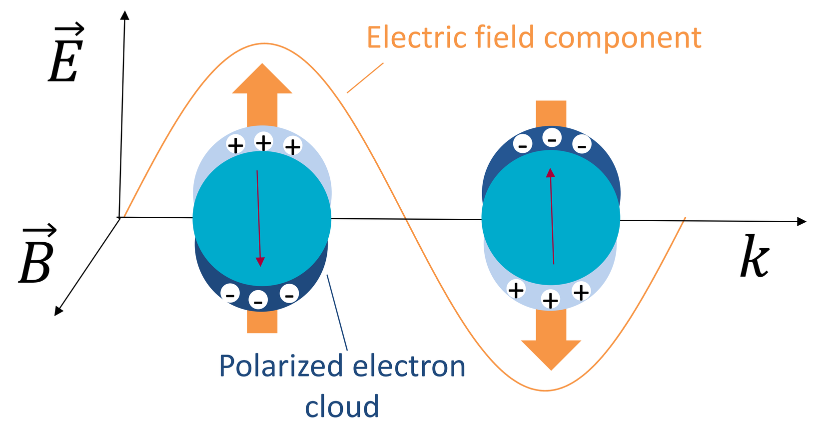


$$A(\lambda) = -\log \frac{I_s}{I_0}$$



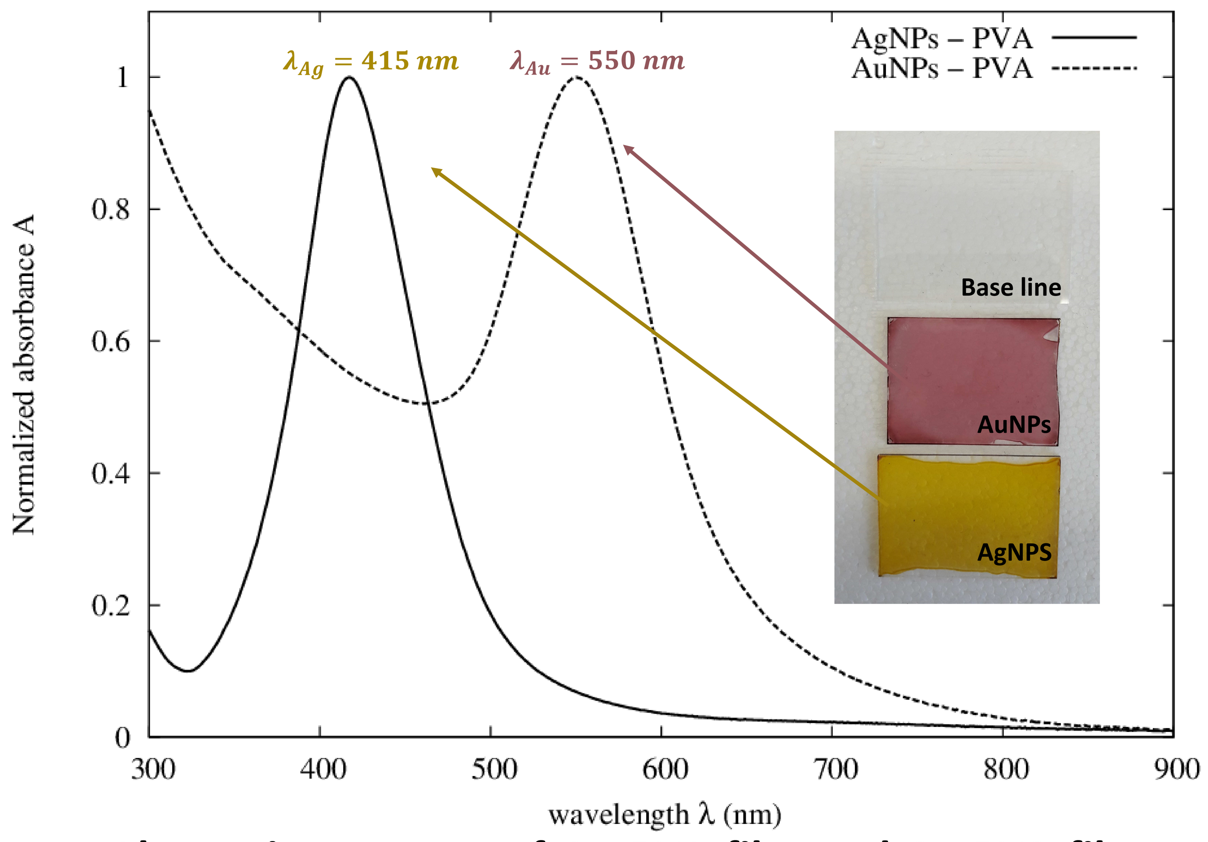
Optical characterization :

- Spectrophotometer UV-Vis. Genesys™ 10S with a measuring range from 190 nm to 1100 nm



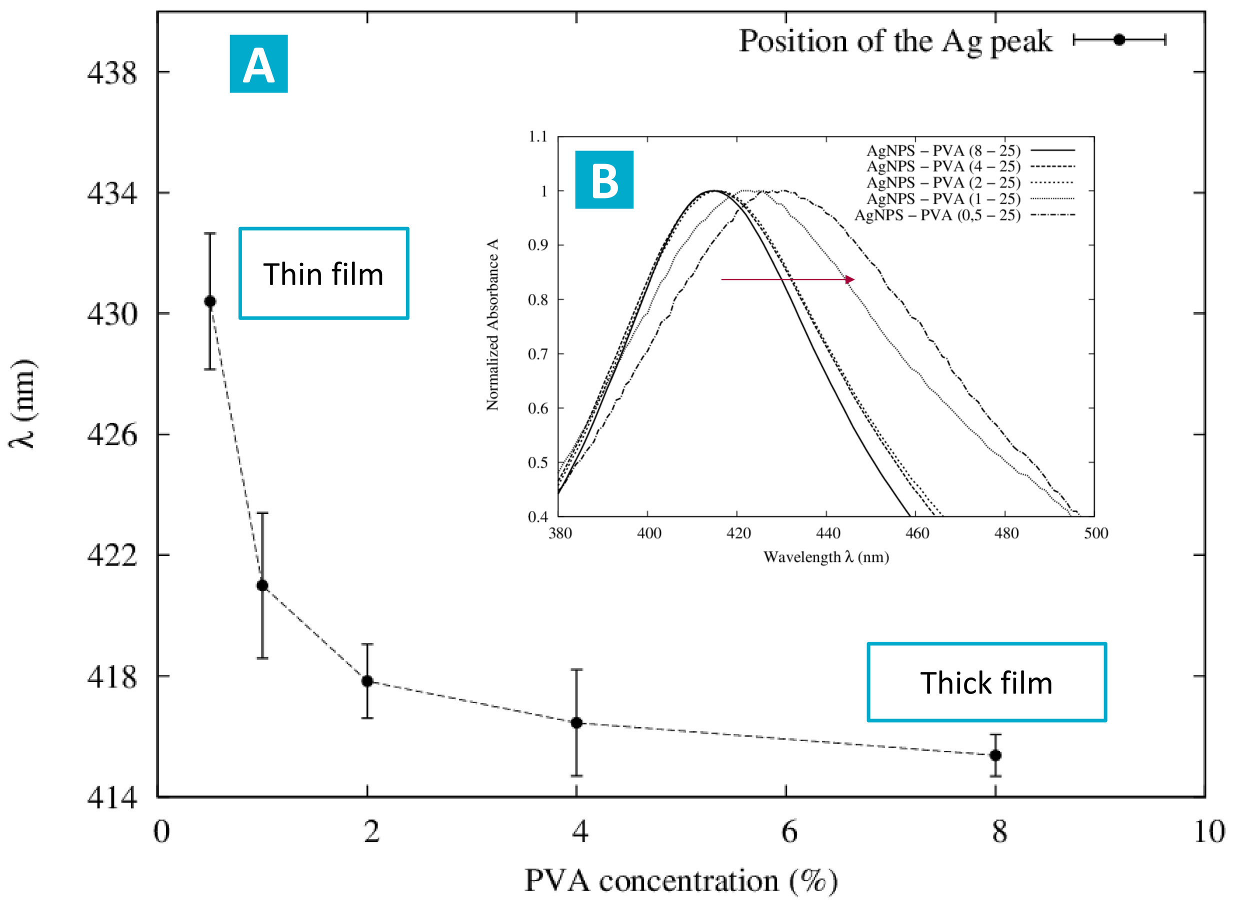
Experimental results

Absorption spectra of Ag NPs & Au NPs



Absorption spectra of Au-PVA film and Ag-PVA film on glass (plain line Ag – PVA; dashed line Au – PVA)
$\lambda_{Ag} \approx 415\ nm$ & $\lambda_{Au} \approx 550\ nm$

Shift of the resonance peak = variation of the size of the NPs

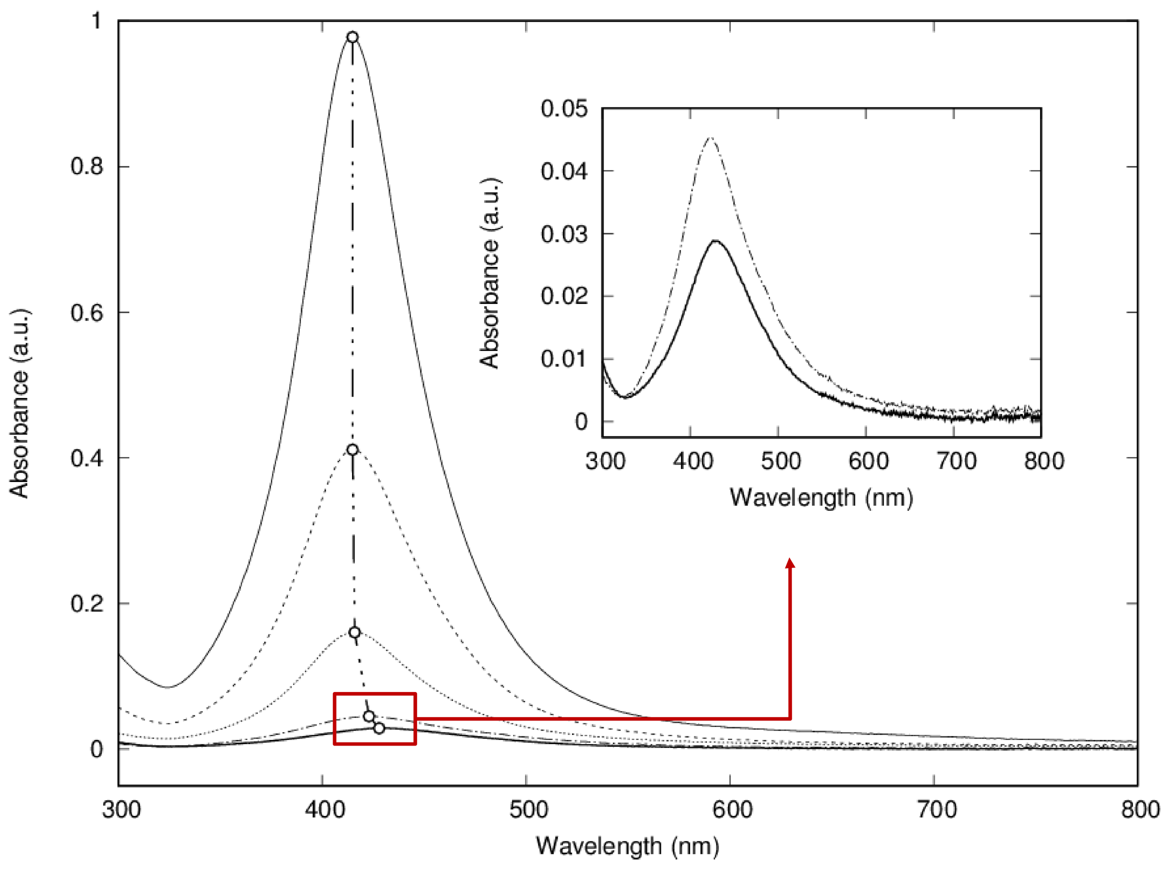


A Position of the absorption band in function of the polymer concentration (i.e. the thickness of the film)

B Normalized absorption spectra of the Ag – PVA film for different thicknesses of the film. Evident shift of the position of the resonance peak

Thin film : shift of the position of the resonance peak to a higher wavelength correspond to bigger NPs inside the nanocomposite

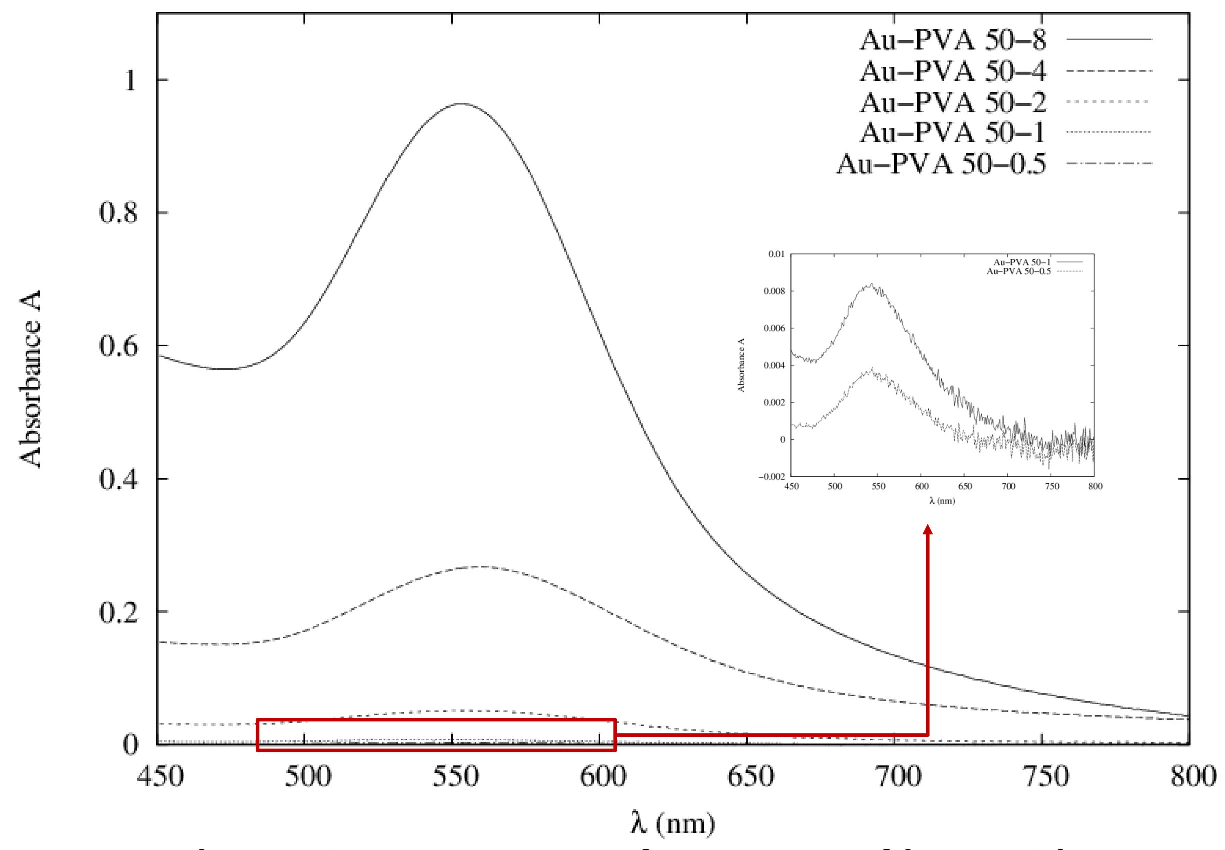
Absorption spectra of Ag-PVA films



Absorption spectra of Ag-PVA film with a decreasing thickness at the same mass ration Ag/PVA [25% w:w]

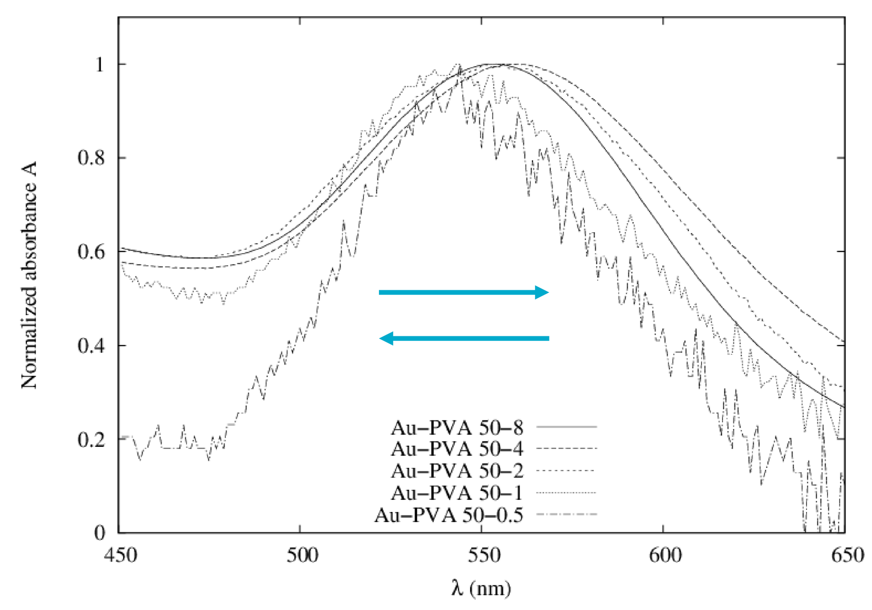
Shift of the resonance peak

Absorption spectra of Au-PVA films



Absorption spectra of Au-PVA film with a decreasing thickness at the same mass ration Au/PVA [50% w:w]

Small shift of the position of the resonance peak



The evolution of the position of the absorption band is more complex in the case of Au – PVA films : more experiments are needed

Both Au & Ag NPs seems to growth differently with the thickness of the film : change in the optical properties of the nanocomposites (size of the NPs)

Conclusions and acknowledgements

- **Easy** and **fast procedure** to generate plasmonic nanocomposite with a **high concentration of NPs**
- Reducing the thickness of the film **change the formation of the NPs** inside the polymer matrix with the same mass ratio polymer/metal : modification of the size of the NPs ➡ Bigger NPs in thin film for Ag-PVA films (Au-PVA films more complex)

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