



Plasmonic hydrogel nanocomposites with combined optical and mechanical properties for biochemical sensing

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Outline

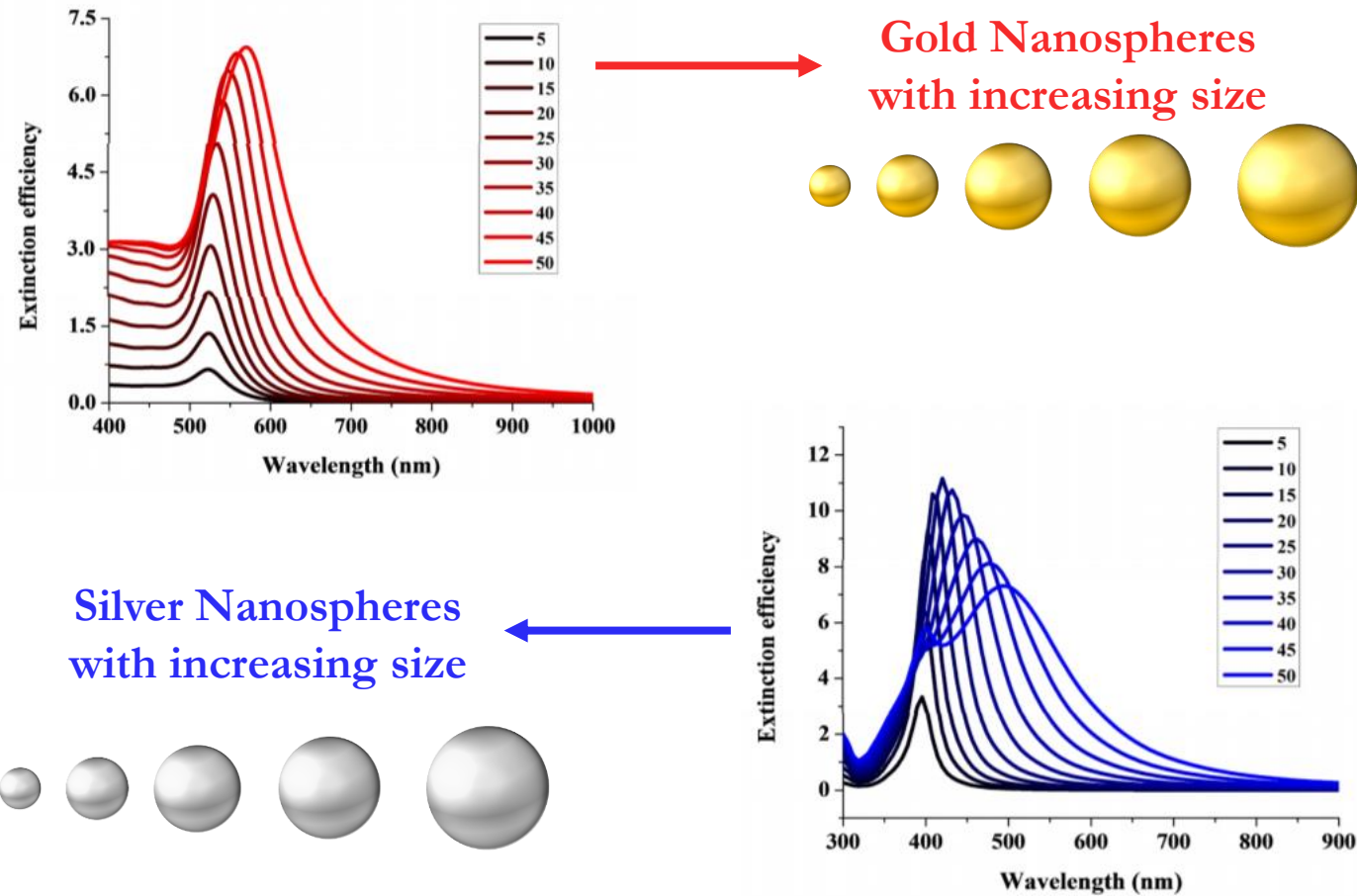
- Localized Surface Plasmon Resonance and Metal-Enhanced Fluorescence
- Plasmonic Hydrogels: Design and Optical Characterization
- Dual-Sensing of Streptavidin in PEGDA 10kDa as a Proof of Concept
- Conclusions and Future Perspectives

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Introduction: LSP Resonance

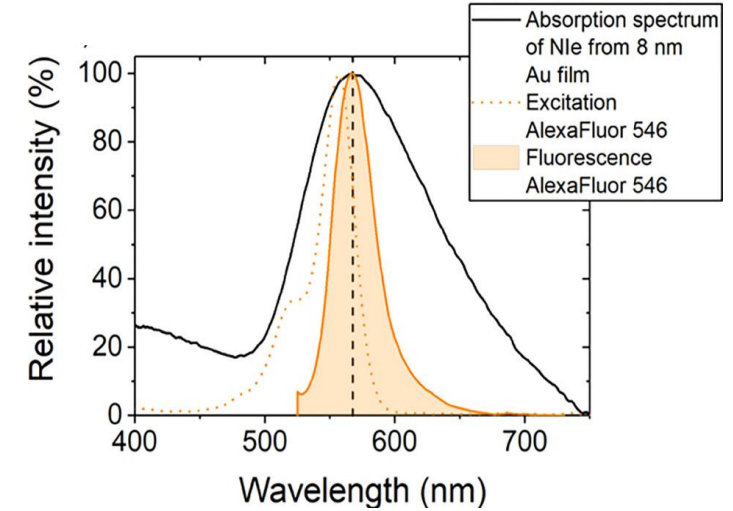
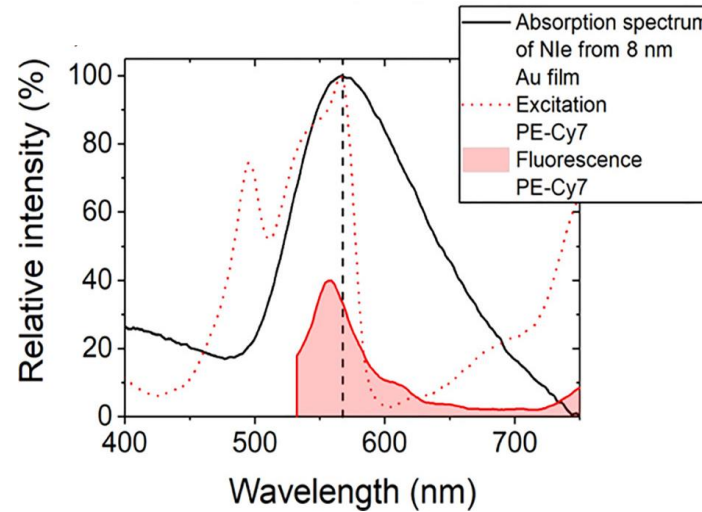
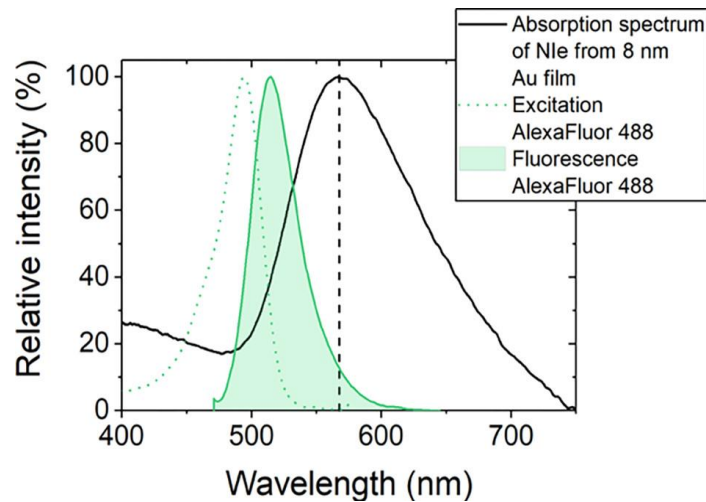
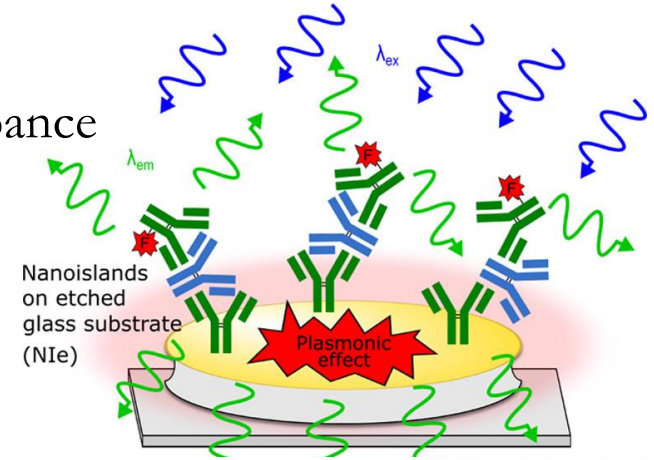
- *Plasmon*: oscillation of electron density with respect to the fixed positive ions in a metal.
- **Localized surface plasmon resonance (LSPR)**: a size and shape-dependent coherent oscillation of the conduction electrons of a noble metal nanoparticle ($d \ll \lambda$).
- LSPRs exhibit strong field enhancement in the surroundings of the nanoparticles, which makes their resonance locally sensitive to refractive index variations.



S.Maier, Plasmonics: Fundamentals and Application. Springer, 2007;
B. Sepùlveda *et al.*, Nano Today, 2009
Farooq, S. and de Araujo, R.E, Open Journal of Applied Sciences, 2018.

Introduction: Metal-Enhanced Fluorescence

- *Metal-Enhanced Fluorescence* is a phenomenon dependent on:
 - the spectral overlap between a fluorescent dye and the plasmon absorbance
 - the fluorophore-nanostructure distance z .
- Förster resonance energy transfer (FRET) mechanism
- Purcell effect mechanism
- Dual-mechanism



B. Miranda *et al.*, ACS Applied Nano Materials, 2020

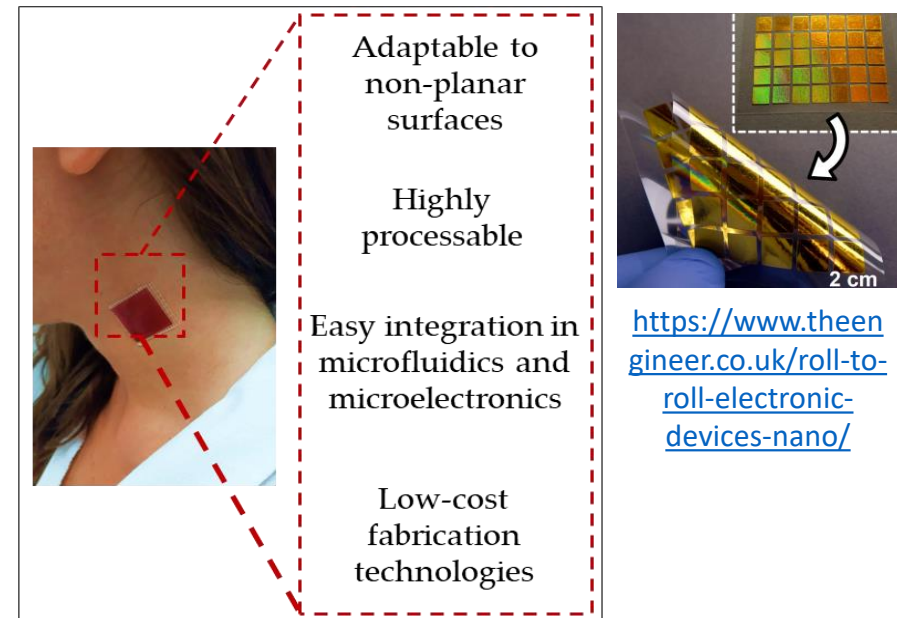
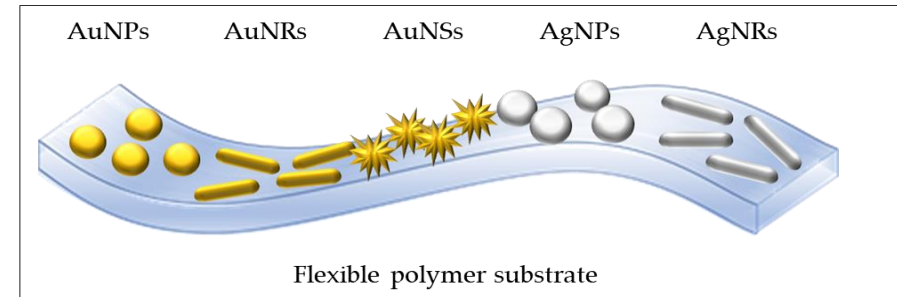
A. Minopoli *et al.*, Nature Communications, 2021

Introduction: Flexible Plasmonic Nanocomposites

“Flexible Plasmonic Nanocomposites”: plasmonic nanoparticles impregnated over/in flexible solid substrates.

Advantages:

- ✓ Cost-Effectiveness
- ✓ High Processability
- ✓ Adaptable to non-planar substrates
- ✓ *In-situ/In-vivo* collection of the samples
- ✓ Easy integration into more complex systems



Polavarapu *et al.*, Physical Chemistry Chemical Physics, 2013
B. Miranda *et al.*, Biosensors, *under review*, 2021

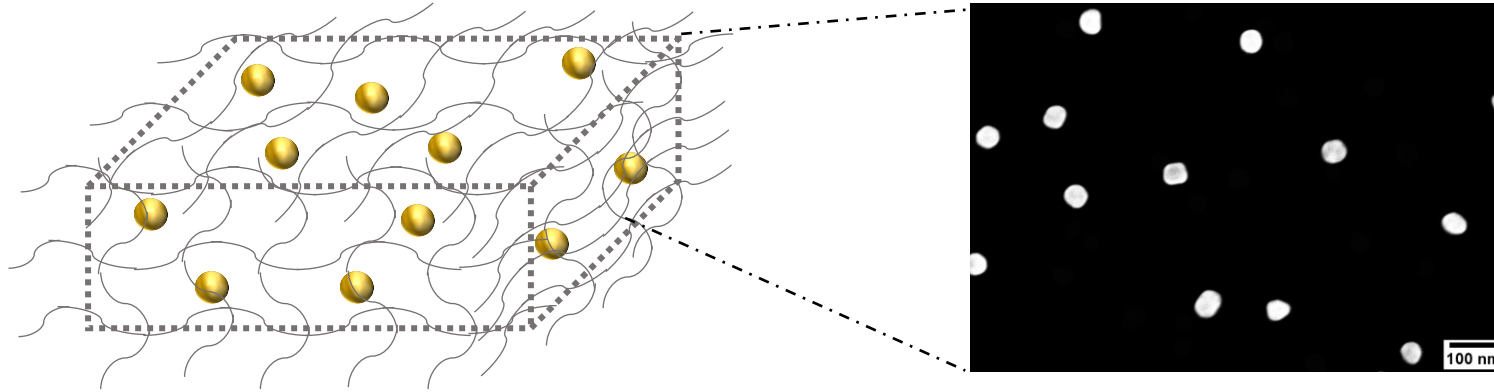
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Plasmonic Hydrogels: Fabrication

Hydrogels for miniaturized 3D biosensors

- ✓ Biorecognition elements are adhered onto a 3D architecture



Polyethylene glycol diacrylate (PEGDA)

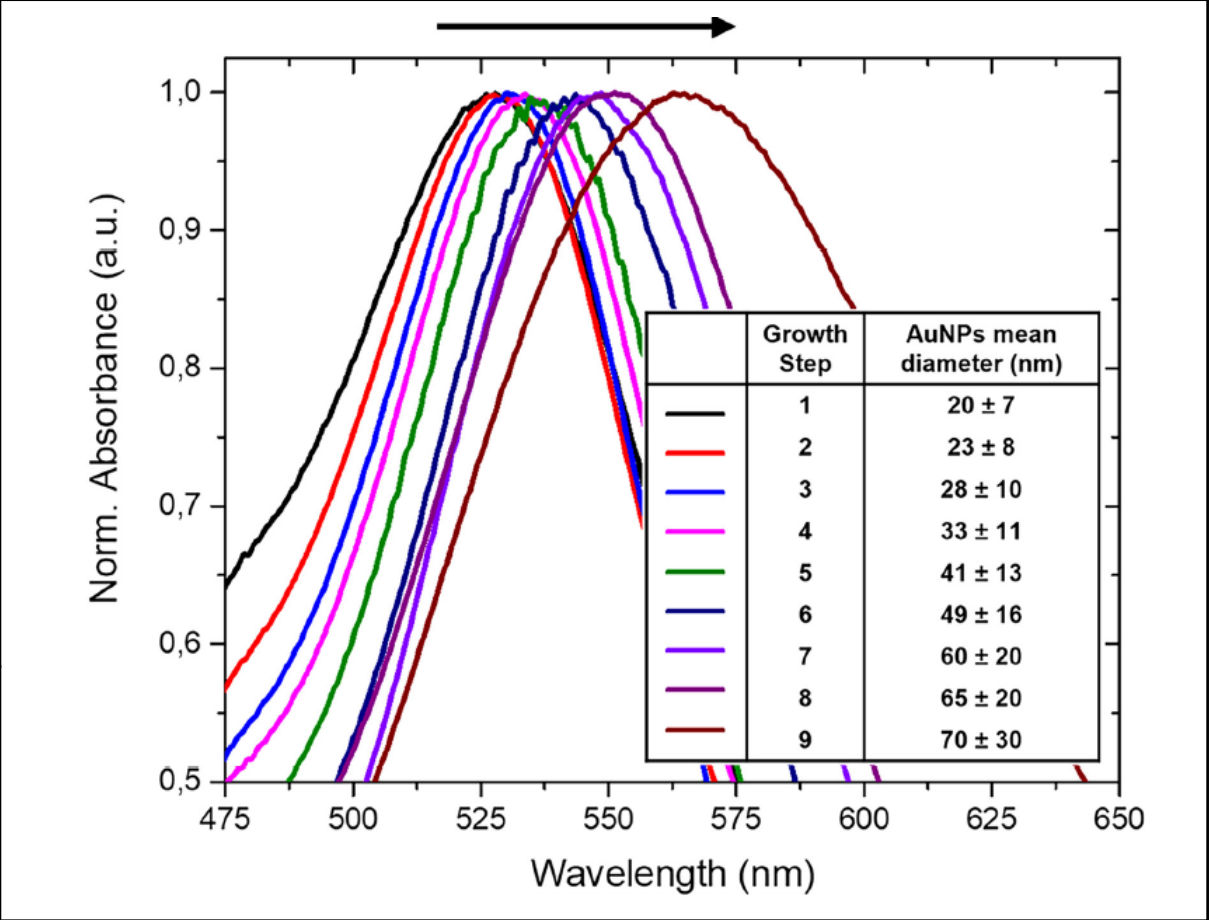
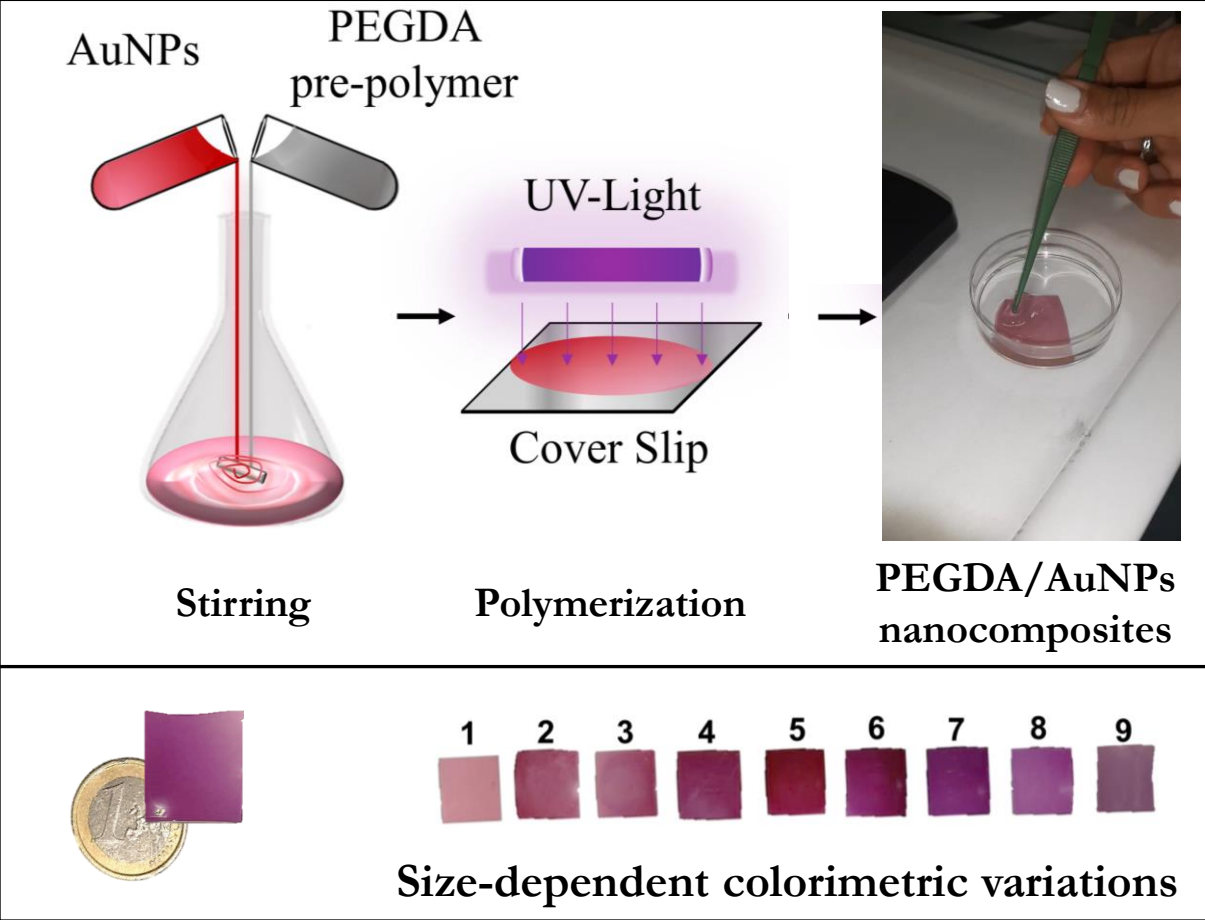
- ✓ Excellent matrices for the entrapment of biomolecules
- ✓ Non-fouling material (useful for complex solutions)
- ✓ Tunable micropatterning with photolithographic techniques.
- ✓ Tunable network in terms of mesh size and crosslinking

Colloidal citrate gold nanoparticles (Au-NPs)

- ✓ Tunable in size and shape
- ✓ Many surface chemistry protocols have been optimized

Pedrosa et al., *Electroanalysis*, 2011; Love et al., *Chemical Reviews*, 2005;
Rebelo et al., *Biosensors and Bioelectronics*, 2019;
B. Miranda *et al.*, *Journal of Applied Physics*, 2021.

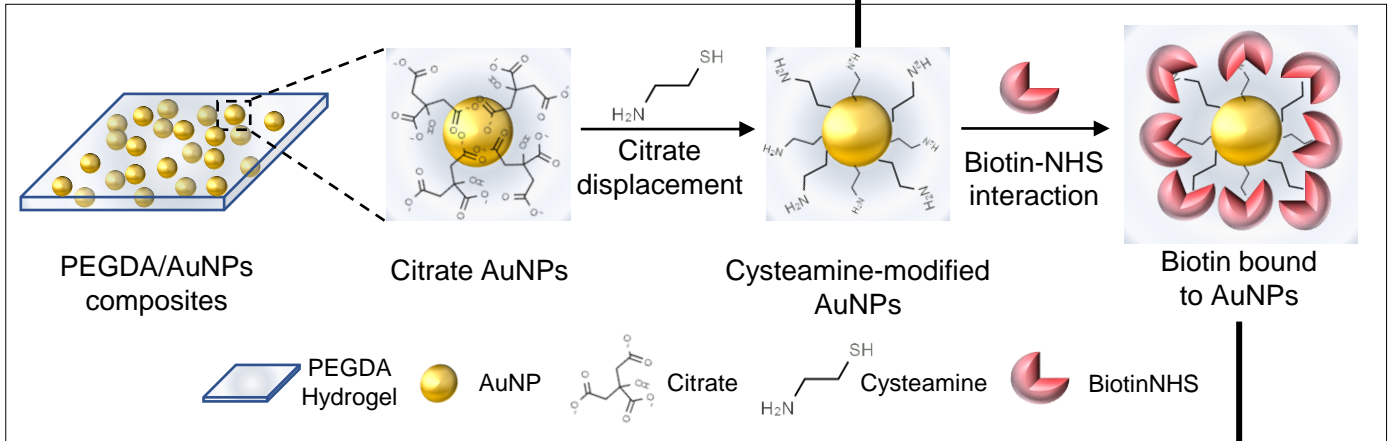
Plasmonic hydrogels: Fabrication and Characterization



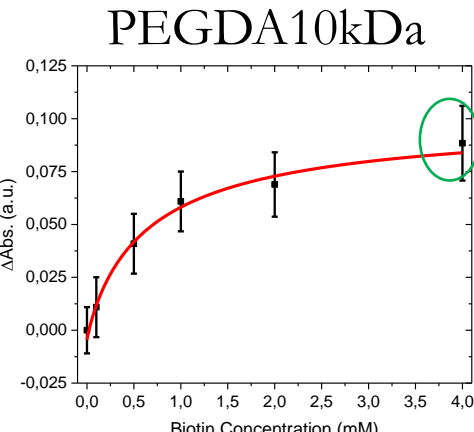
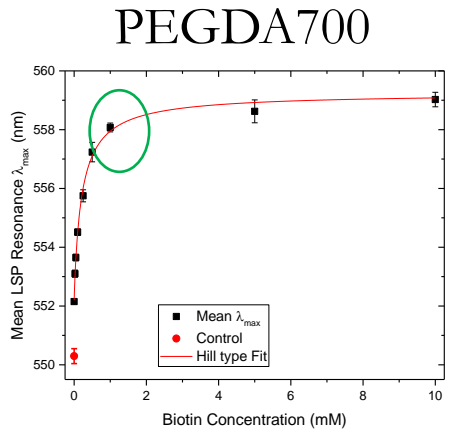
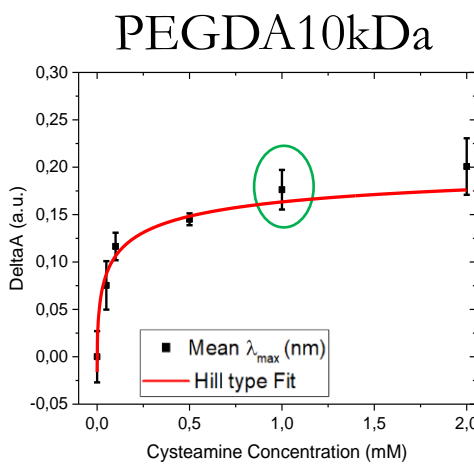
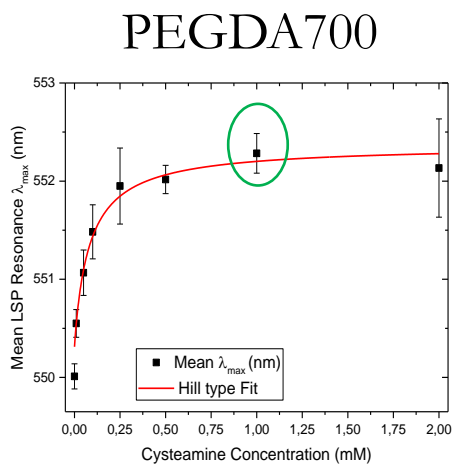
B. Miranda *et al.*, 2020 Italian Conference on Optics and Photonics (ICOP), Parma, Italy, IEEE Xplore, 2020
 B. Miranda *et al.*, Journal of Applied Physics, 2021

Plasmonic Hydrogels: Functionalization

LSPR measurements are used to monitor the functionalization steps.



A Bio-responsive hydrogel is obtained by functionalizing gold nanoparticles within the hydrogel with a biorecognition element.

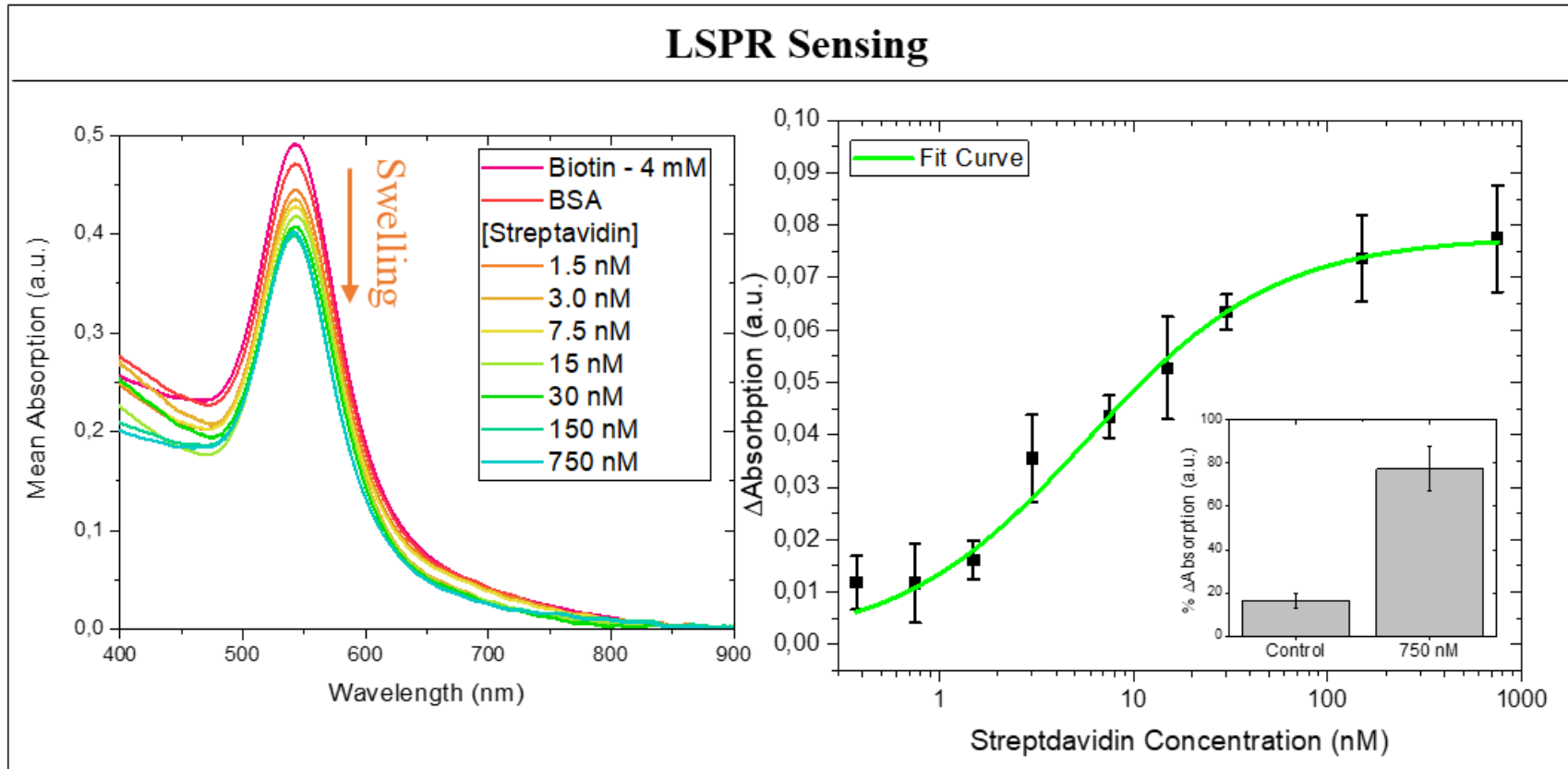


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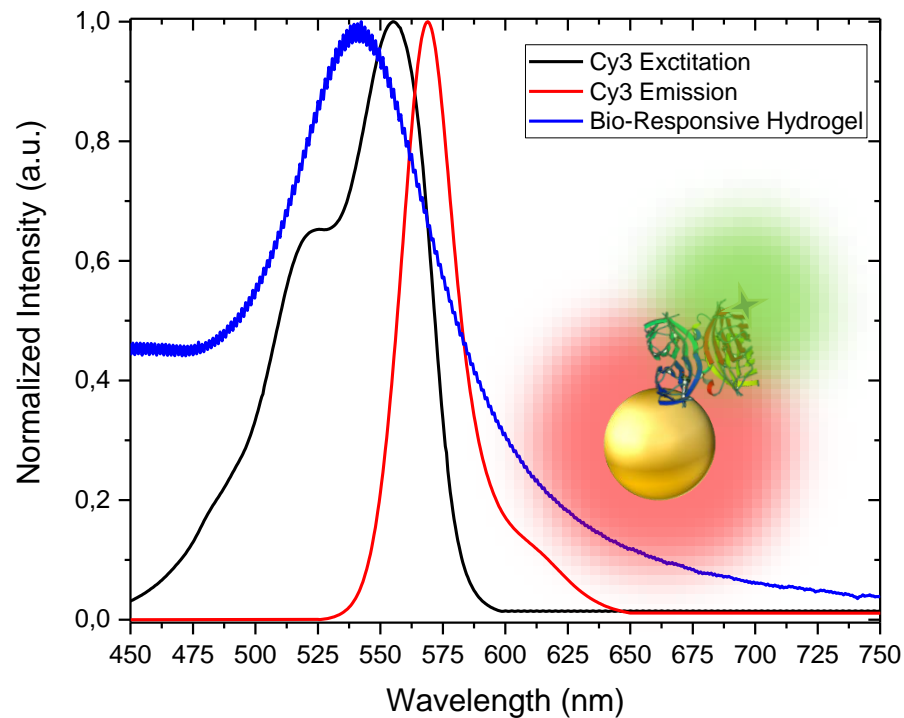
LSPR sensing of Streptavidin

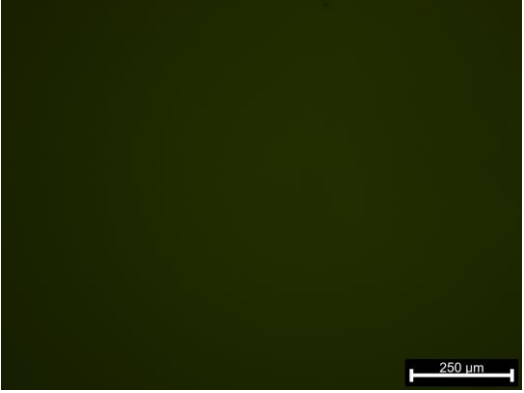

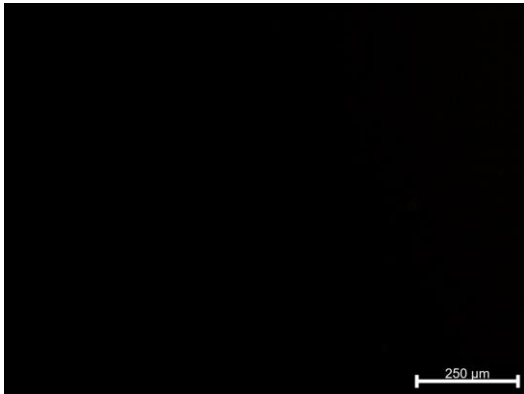

Streptavidin was incubated in PEGDA/AuNPs nanocomposites in the same conditions to evaluate plasmon decoupling as a function of the target concentration.



Fluorescence-Enhancement Evaluation

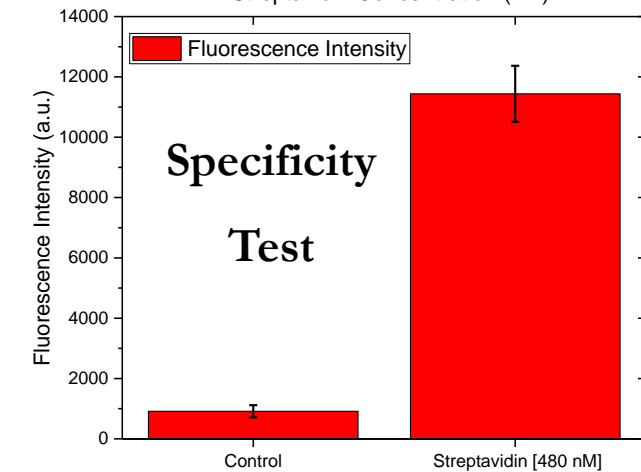
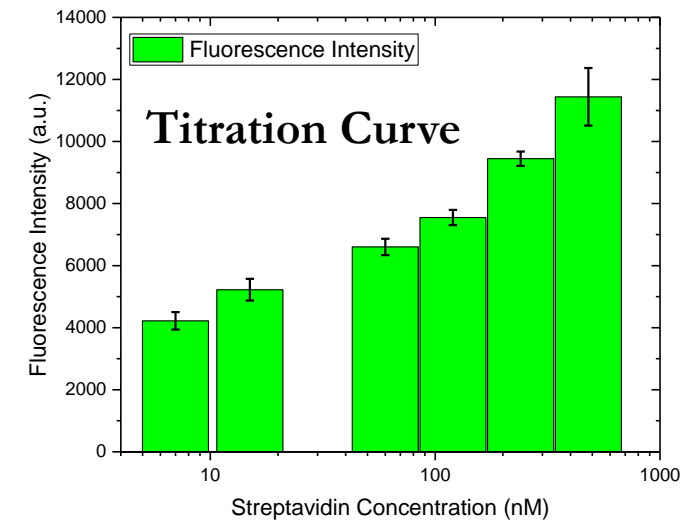
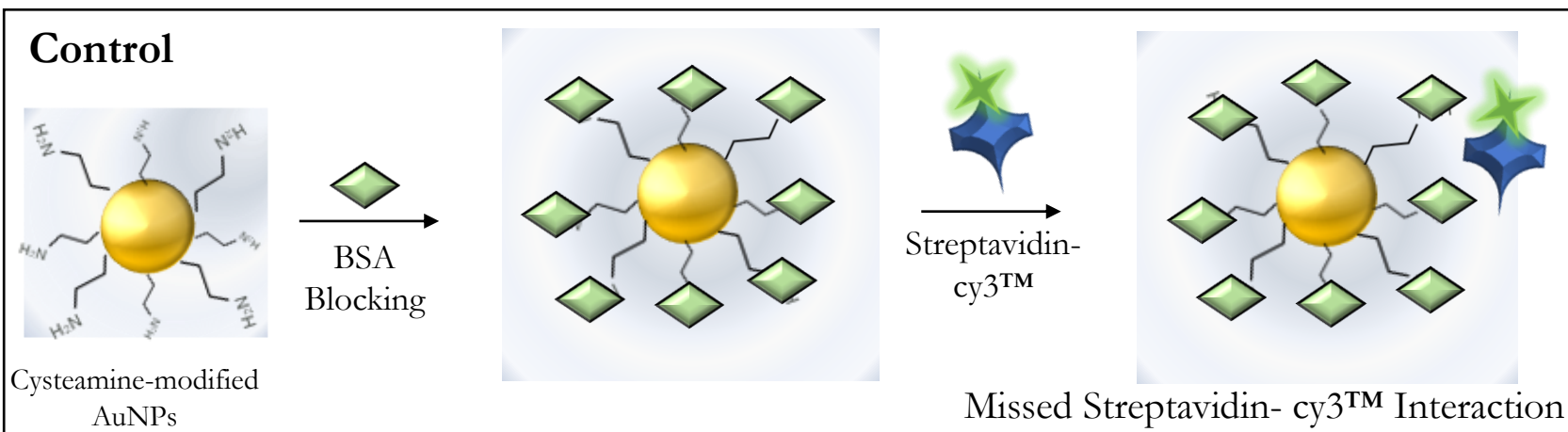
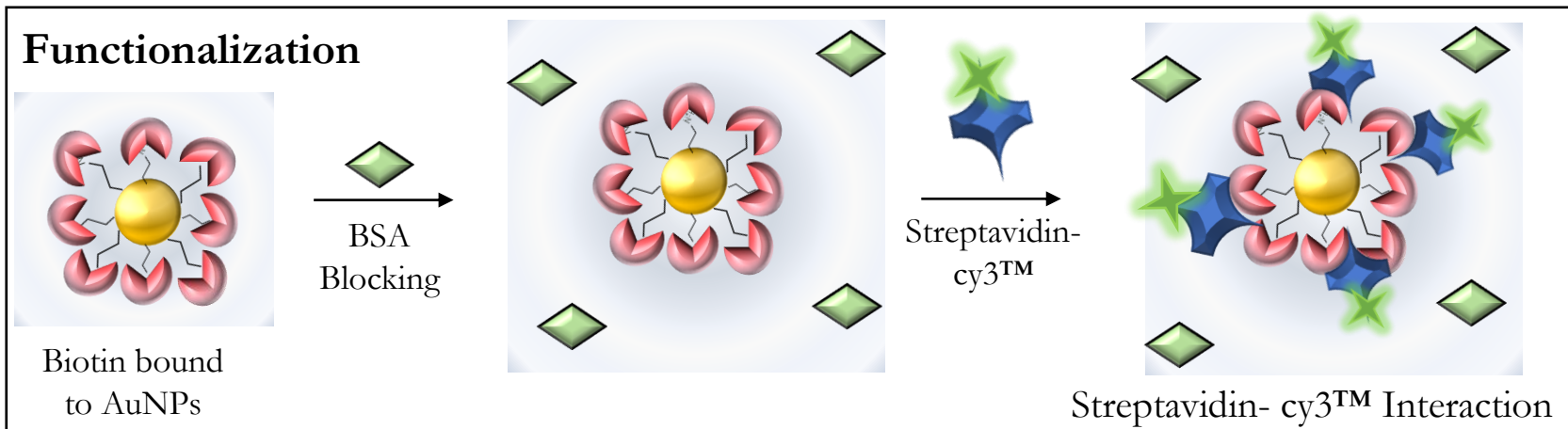
Fluorescent Streptavidin–cy3TM (100 nM) was incubated in PEGDA hydrogels and PEGDA/AuNPs nanocomposites in the same conditions to allow the computation of the Fluorescence Enhancement (FE).



PEGDA – Streptavidin–cy3 TM	PEGDA/AuNPs – Streptavidin–cy3 TM
	
PEGDA – Background	PEGDA/AuNPs – Background
	

3D MEF Biosensor: Streptavidin Sensing

Bio-responsive PEGDA/AuNPs nanocomposites functionalized with Biotin with Streptavidin- cy3TM.



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Conclusions and Future Perspectives

Achievements



✓ Evaluation of Fluorescence enhancement by MEF - dual mechanism in 3D-bioresponsive hydrogels.

- ✓ Optimization of the functionalization scheme.
- ✓ Chemical modification of the AuNPs surfaces within the hydrogel and sensing of the fluorescent streptavidin.

To Do List

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- 1.
- 2.
- 3.

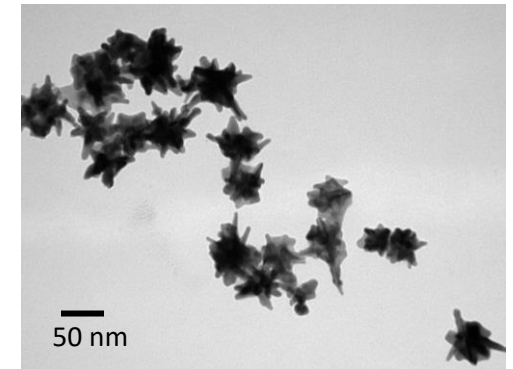


! Study of the swelling effect on the re-arrangement of nanoparticles within the 3D network.

Work in Progress



- Combination of the designed 3D bio-responsive hydrogels with miniaturized LED and spectrometer as portable device (POCT).
- Fabrication of nanocomposites embedding differently shaped nanoparticles (gold nanostars).



**Thank you for your
kind attention**

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Dr. Principia Dardano, Researcher
Dr. Ilaria Rea, Researcher
Dr. Mario Battisti, Researcher
Dr. Selene De Martino, Researcher
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