Glyphosate IR spectroscopy with an optical transducer based on functionalized semiconductor plasmonic nanoantennas

A. Taleb Bendiab[1], C. Pohar[1], M. Mortamais[2], N. Marchi[4], J. Perroy[4], A. Baghdadli[3], T. Taliercio[1], F. Gonzalez-Posada Flores[1]

[1] IES, Univ. Montpellier, CNRS, Montpellier, France
[2] INM, Univ. Montpellier, INSERM, Centre d'Excellence sur l'Autisme et les Troubles Neuro-developpementaux (CeAND), Montpellier, France.
[3] Univ. Paris-Saclay, UVSQ, Inserm, CESP, CeAND, Fac. Medecine, Univ. Montpellier, France.
[4] IGF, CNRS UMR 5203, Inserm U1191, Univ. Montpellier, France.
Presenting author's email: fernando.gonzalez-posada-flores@umontpellier.fr

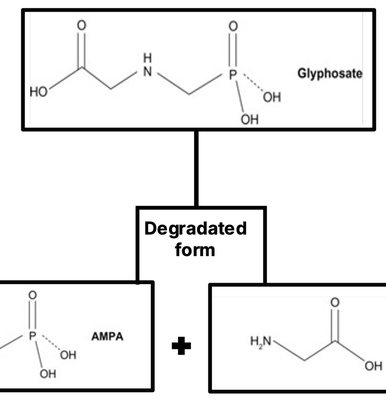
Context

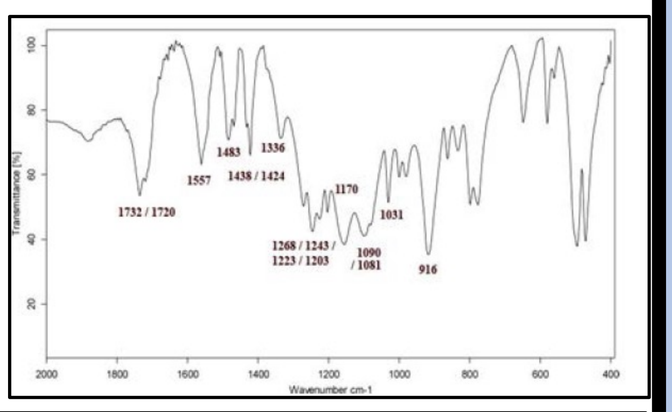
- Glyphosate is the most common non-selective herbicide used in the agricultural field and represents a significant public health concern [1] .
- Based on epidemiological studies, this pesticide input is considered as toxicologically harmful; potentially linked with brain diseases such as the autism spectrum disorders (ASD) [2].
- The challenge to confirm such a causality requires a quick and precise device to detect and quantify these molecules for enviromental control.
- Biosensors based on III-V semiconductors such as InAsSb plasmonic nanoantennas address these challenges [3].

[1] A.L.Valle et al, Environmental Chemistry Letters (2019)17:291
[2] J.R. Roberts, et al. Pediatric Research (2019)85:234
[3] F. Barho et al. Nanophotonics (2018)7:507

Molecule description

- Glyphosate molecules can be observed in different chemical structures:
  - A complete molecular strucutre (N[phosphonomethyl]-glycine)
  - In degradated form : AMPA (Acideaminomethylphosphonic) + Glycine
- Glyphosate MIR absorption fingerprint: 1500cm^{-1} to 500cm^{-1}
- Phosporus group absorption lines Detection ➤ Sélectivity

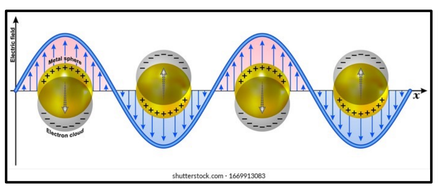


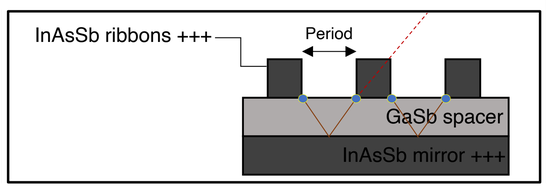


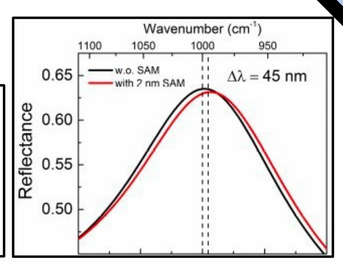
Specific absorption lines related to the Phosphorus group:

- P-OH: 1170, 1223 cm-1
- P-O : 830 (deformation), 1000 cm-1
- PO3H-: 798 cm-1, , 1268 cm-1

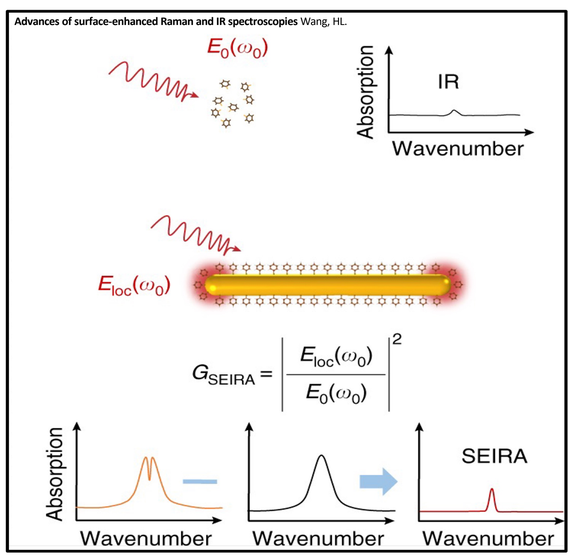
Sensor concept





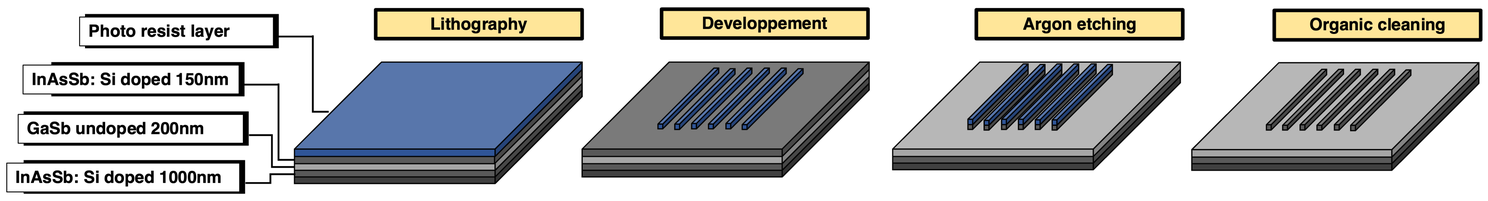


- Based on SPR (Surface Plasmon Resonance).
- External environnement refractive index changes
  ☞ Plasmonic peak red shifts
- SEIRA effect (Surface Enhanced InfraRed Absorption) Molecular adlayer vibrational bands enhanced by the nanoantennas electromagnetic field.

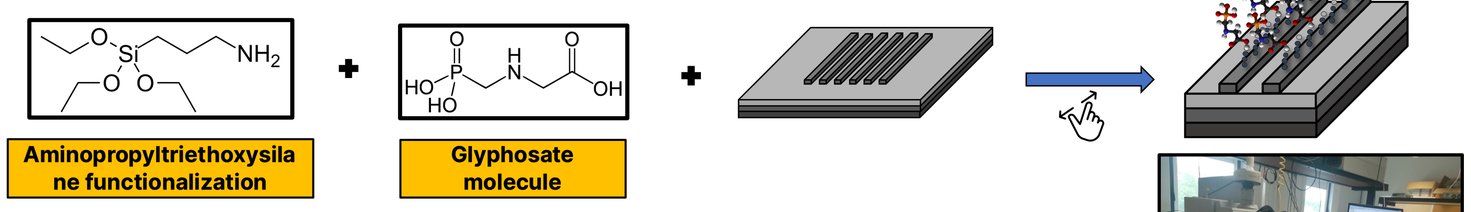


Materials & method

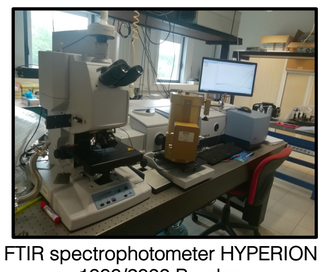
Nanoantennas fabrication process :



Functionnalization and optical characterization :

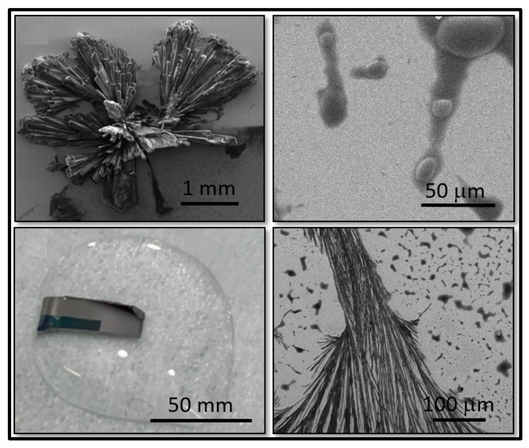


- HEPES buffer (EDC/NHS) to activate carbonyl groups on glyphosate ➤ Chemical bonding
- Nanoantennas optical characterization by FTIR spectroscopy.

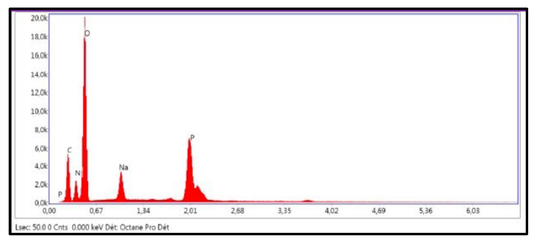


FTIR spectrophotometer HYPERION 1000/2000 Brucker

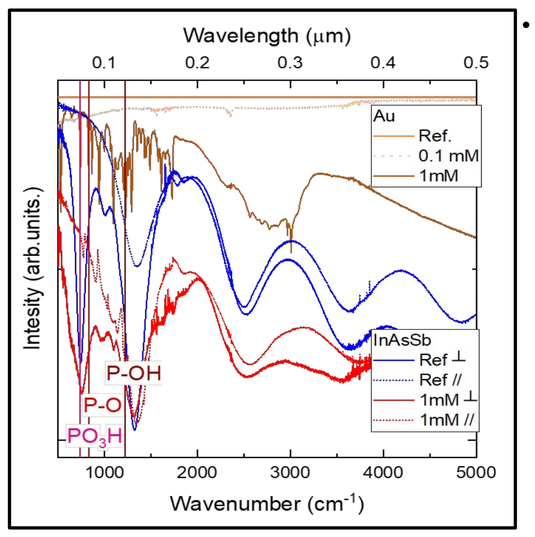
Results



- The molecule is well detected by Energie Dispersion Spectroscopy method as shown on the figure the Phosphorus (P) atom is highly present in the acquisition made



- Glyphosate forms a crystal structure that can be observed on scanning electron microscopy and helps to describe the cinetic behaviour of the molecule on a surface ;



- The FTIR measurements show the main absorption lines, on both the photonic and plasmonic peaks, related to phosphorus group present in the glyphosate molecular chain for both concentrations of 0.1mM and 1mM .

Conclusion & perspectives

- The surface functionalization chemistry showed the atempted behaviour on the plasmonic response.
- Optical properities of semi-conductors in plasmonic were characterized for a InAsSb ribbons design.
- The optimized ribbons design is yet to be reached for a better glyphosate fingerprint detection.
- The detection limit has to be determined for lower concentrations than 0.1 mM.