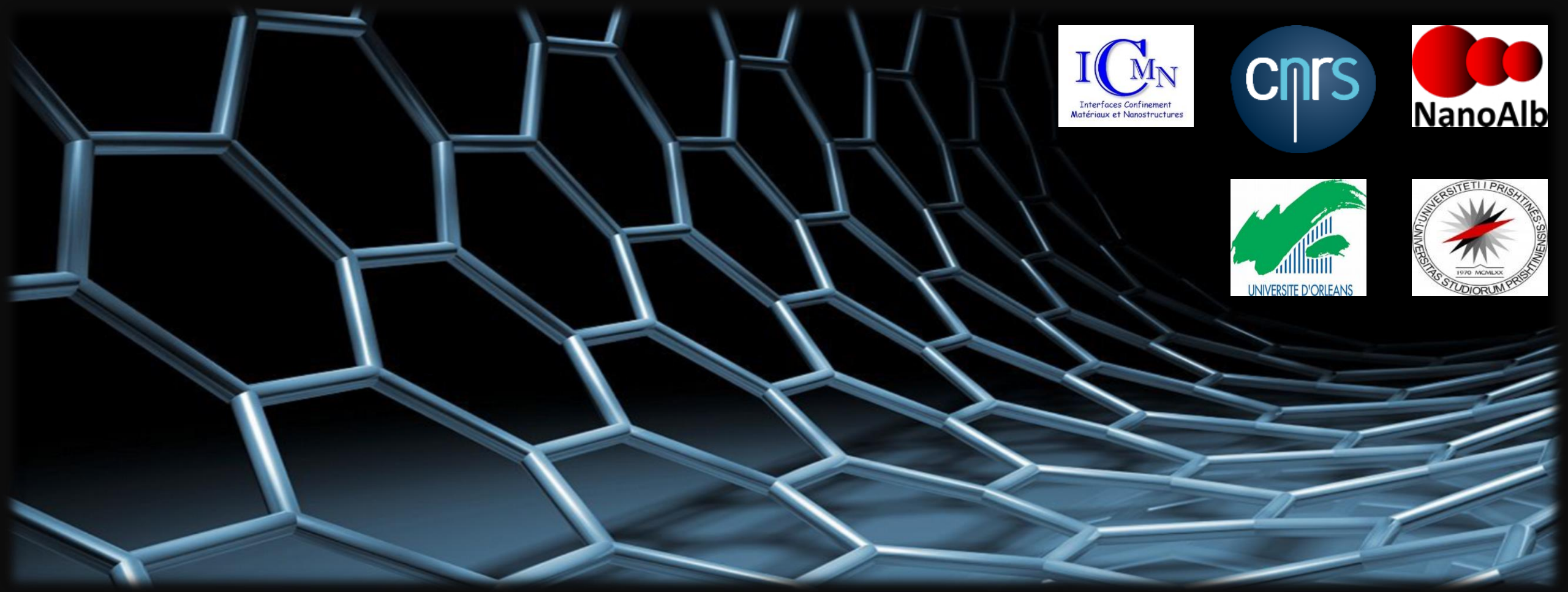


Molecularly imprinted polymer onto glassy carbon and onto graphene electrodes for electrochemical determination of pesticides

Imer SADRIU., PhD

Summer School

22nd – 24th March, Tirana, Albania

Plan

1. Elaboration of pure graphene electrodes for sensing application

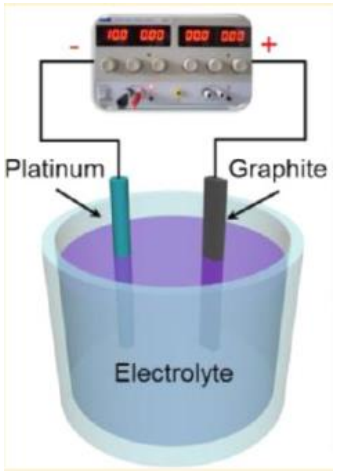
2. Characterization of elaborated graphene electrodes

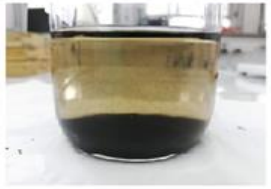
3. Electropolymerization of molecularly imprinted polymer (MIP) film onto pure graphene electrodes for isoproturon detection

4. Conclusions and future perspectives

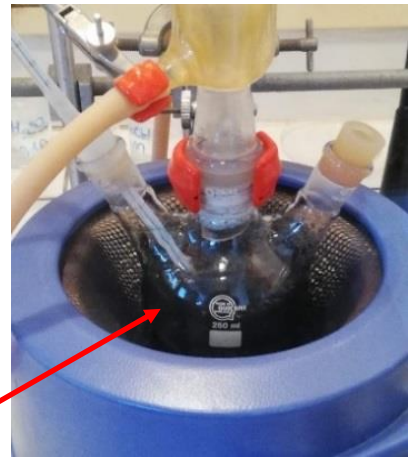
Elaboration of pure graphene electrodes for sensing application

The electrochemical exfoliation in aqueous solvent media: **anodic exfoliation**

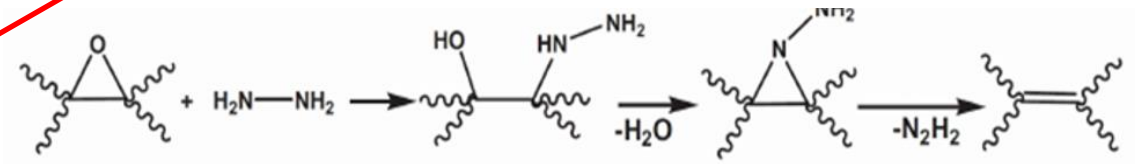




-electrolyte: **0.1M $(NH_4)_2SO_4$** dissolved in **water**
-exfoliation time **12h**



Chemical reduction with ***hydrazine*** at high temperature (100 ˚C)



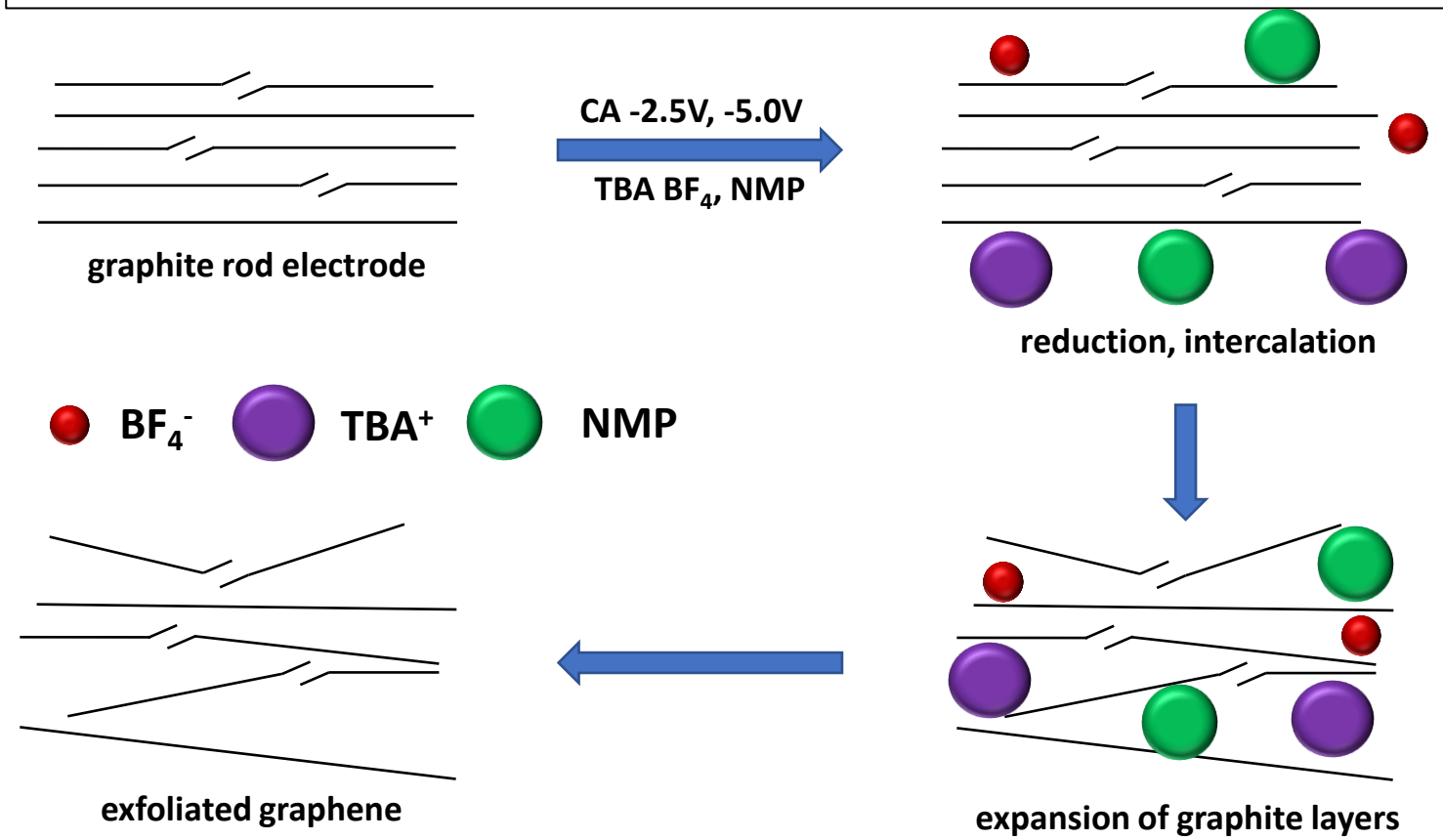
The mechanism of the chemical reduction of GOx into rGOx with hydrazine hydrate

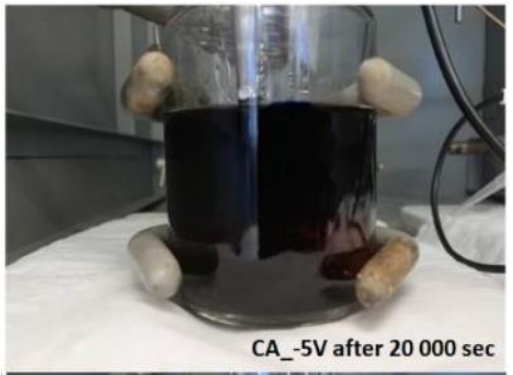
-reduction time **24h**

K. Parvez *et al.*, "Exfoliation of Graphite into Graphene in Aqueous Solutions of Inorganic Salts," *J. Am. Chem. Soc.*, vol. 136, no. 16, pp. 6083–6091, Apr. 2014, doi: 10.1021/ja5017156.

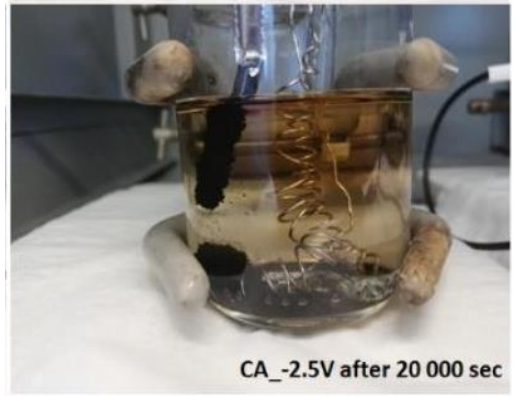
Elaboration of pure graphene electrodes for sensing application

The electrochemical exfoliation in organic solvent media: **cathodic exfoliation**





by **CA** at **-5.0 V**

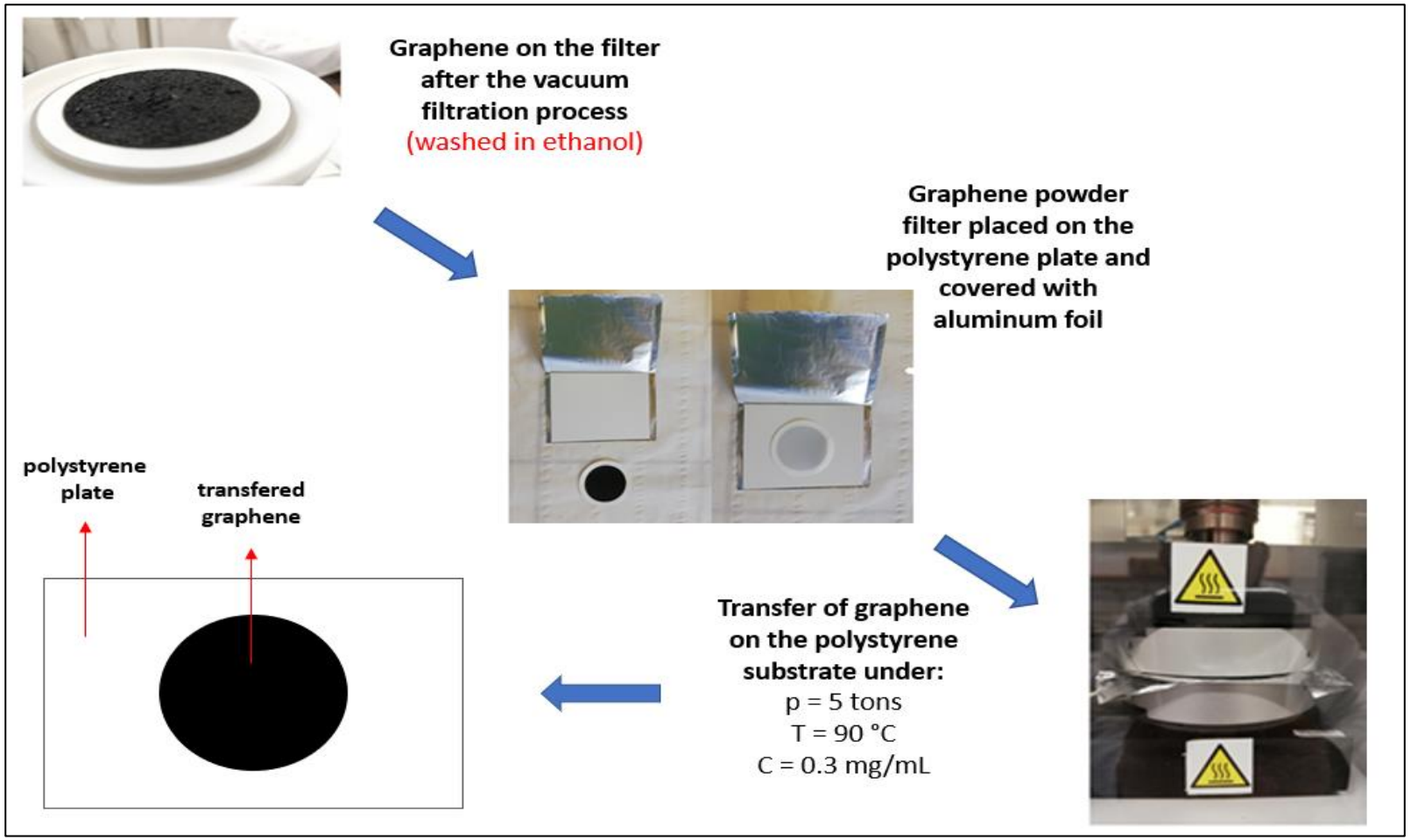


by **CA** at **-2.5 V**

Electrochemical exfoliation of graphite rod electrode at different times of exfoliation
-electrolyte: **0.1M TBA BF_4** dissolved in **NMP (1-methyl-2-pyrrolidinone)**
-exfoliation time: **6h**

A. J. Cooper, N. R. Wilson, I. A. Kinloch, and R. A. W. Dryfe, "Single stage electrochemical exfoliation method for the production of few-layer graphene via intercalation of tetraalkylammonium cations," *Carbon*, vol. 66, pp. 340–350, Jan. 2014, doi: 10.1016/j.carbon.2013.09.009.

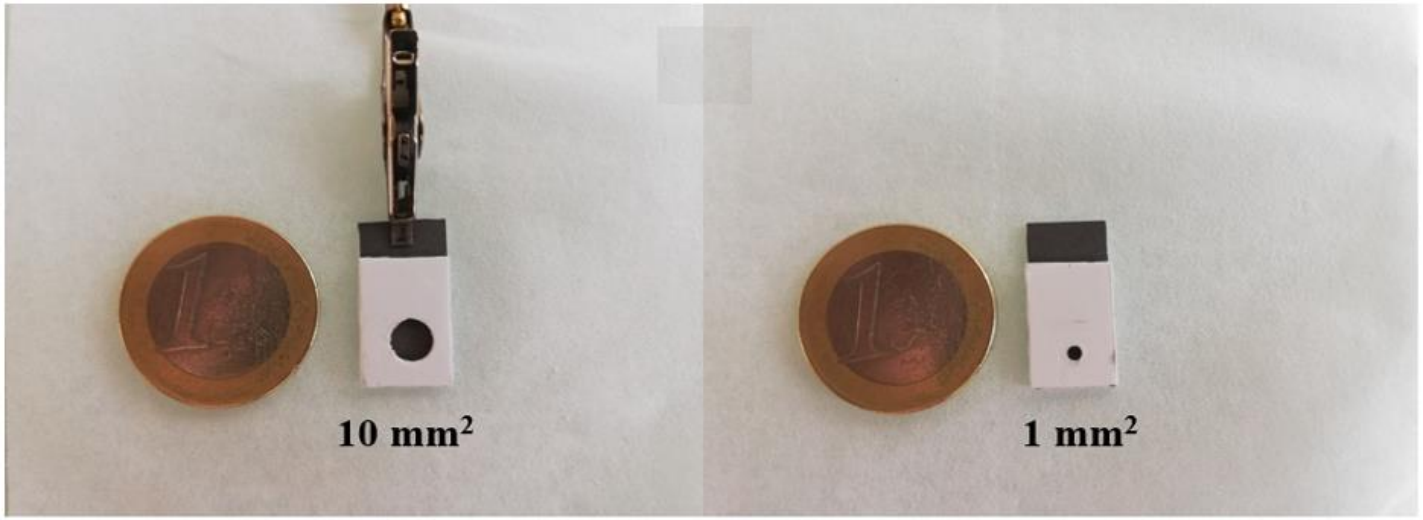
The transfer process of graphene powder onto polystyrene substrate: **graphene/PS electrode fabrication**



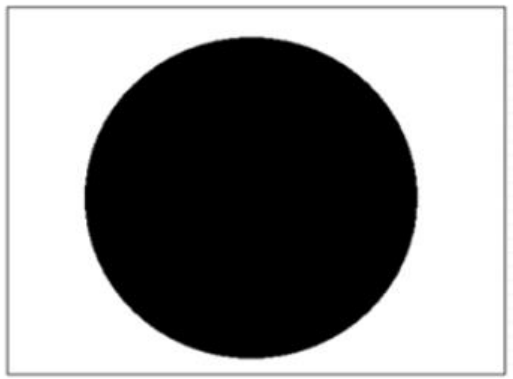
➢ **NO optimization of the parameters for this procedure**

Elaboration of pure graphene electrodes for sensing application

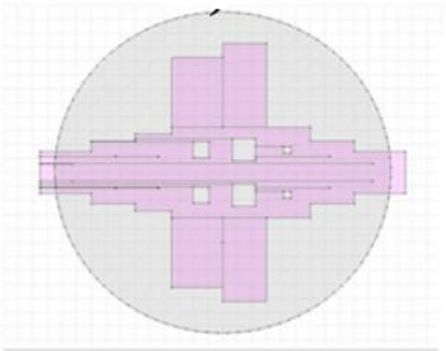
The choice of the design: **methods used for the precision of graphene working electrode surface area**



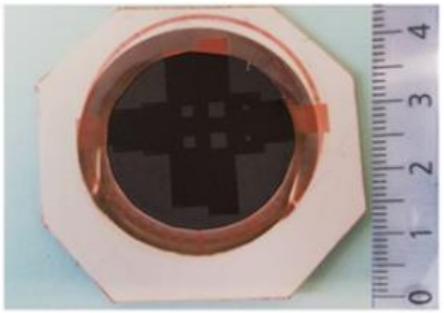
→ **Classical method** developed in our laboratory



Graphene/PS



Mask for photolithography



Graphene/PS lithography electrodes

→ **Photolithography method** performed in clean room

A = 500 µm²
A = 1 mm²
A = 5 mm²
A = 10 mm²

Characterization of graphene electrodes

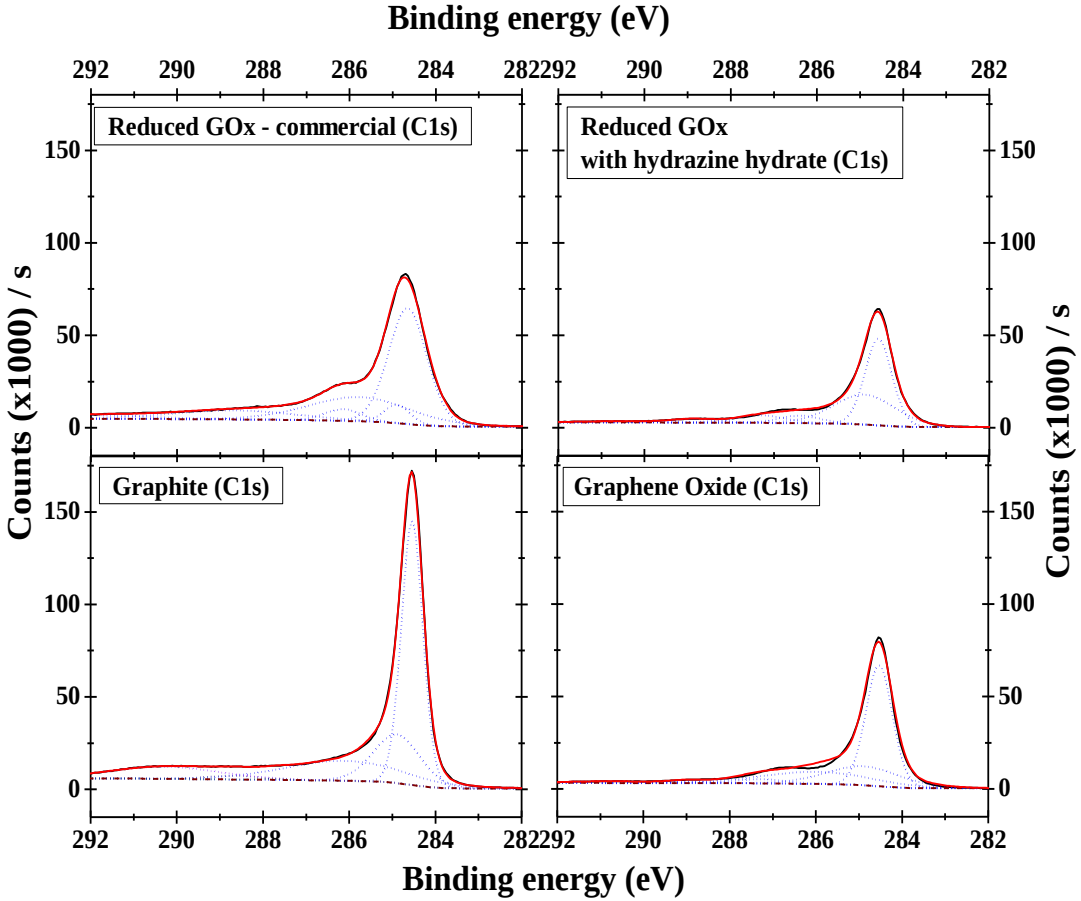
The characterization of chemical structure of graphene electrodes:

-XPS characterization
-Raman characterization
-FT-IR characterization

The characterization of electrochemical behavior of graphene electrodes:

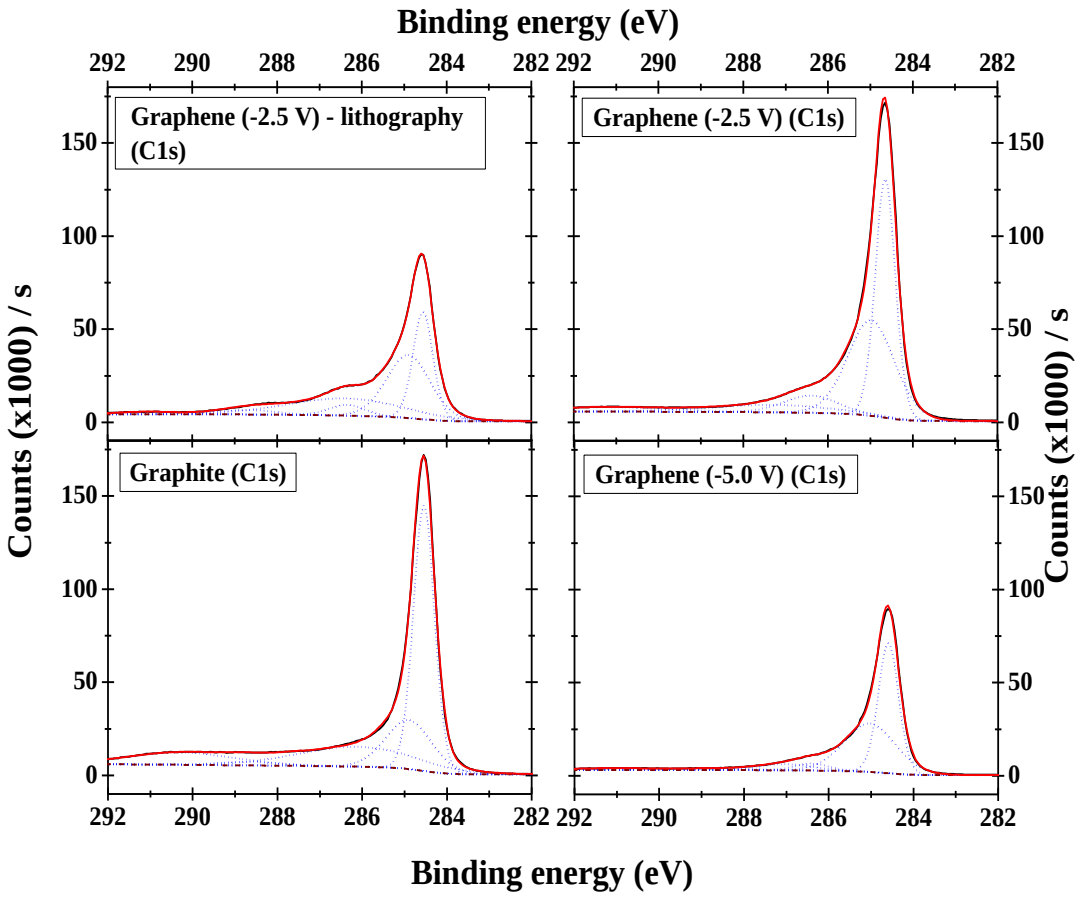
-electrochemical behavior in presence of redox probes
-evolution of electrochemical active area
-using electrochemical window range

XPS characterization of graphene electrodes



C1s XPS spectra

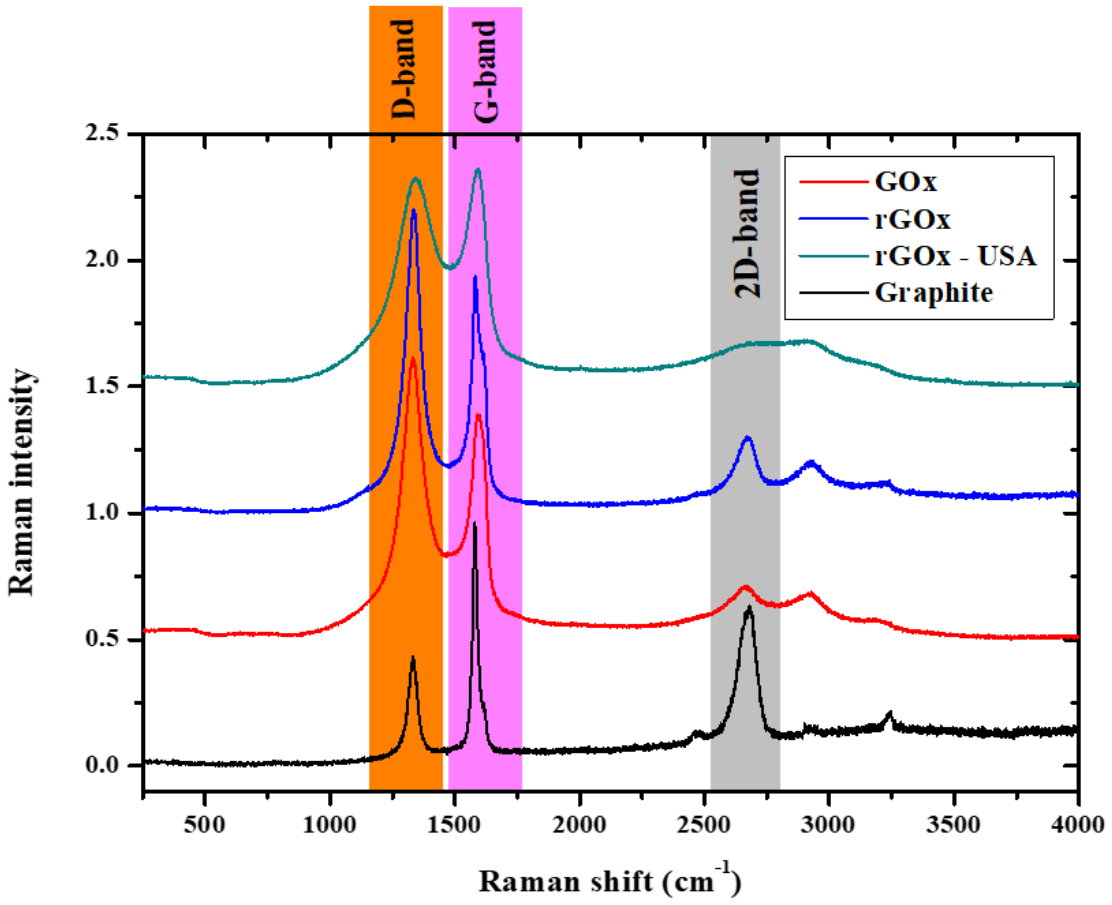
-graphene exfoliated in aqueous solvent media



C1s XPS spectra

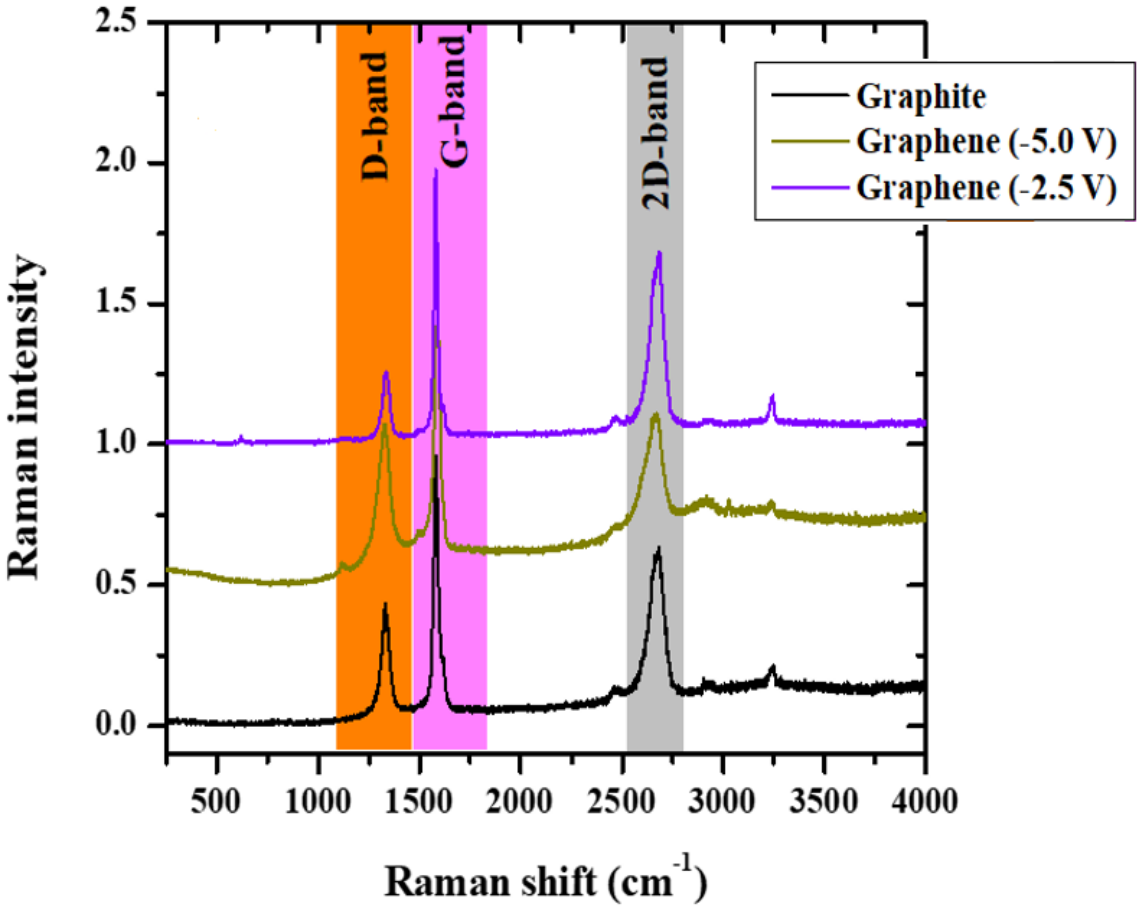
-graphene exfoliated in organic solvent media

Raman characterization of graphene electrodes



Raman spectra

-graphene exfoliated in aqueous solvent media

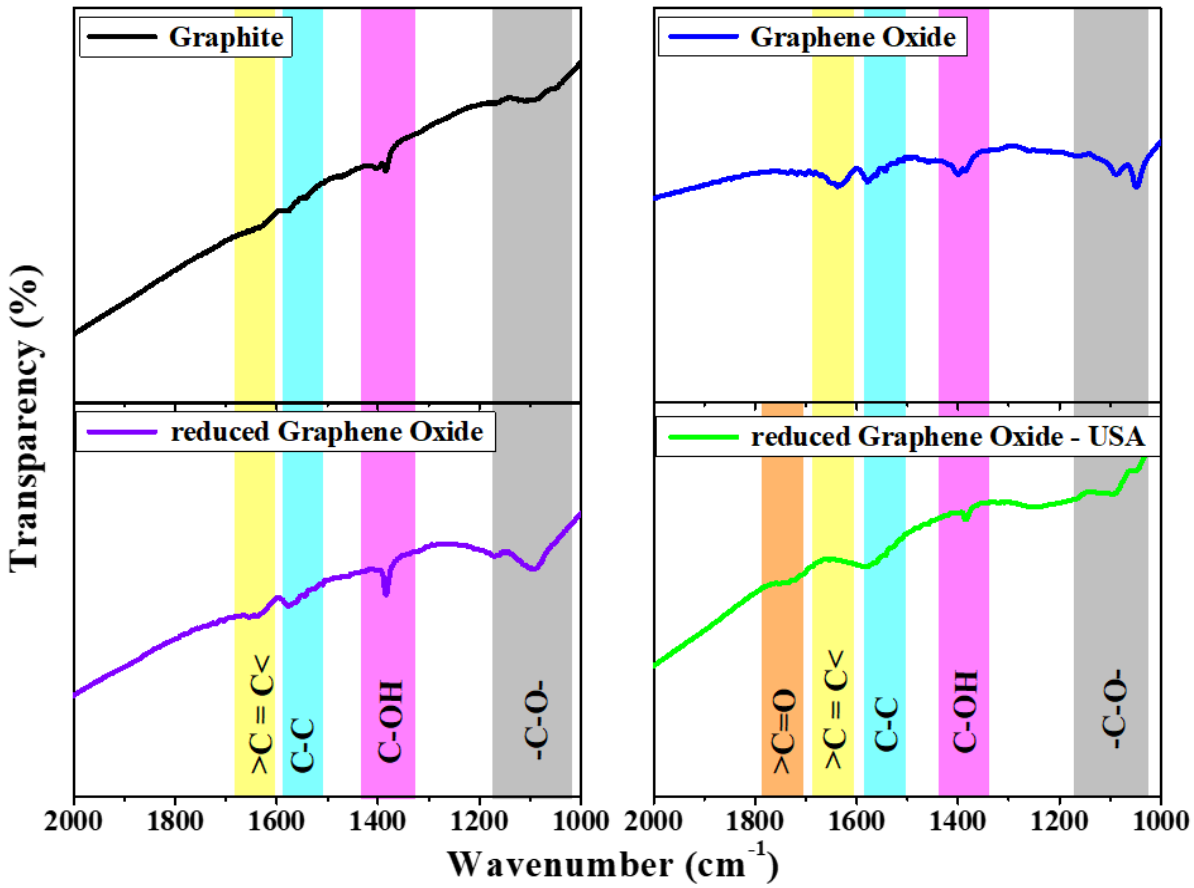


Raman spectra

-graphene exfoliated in organic solvent media

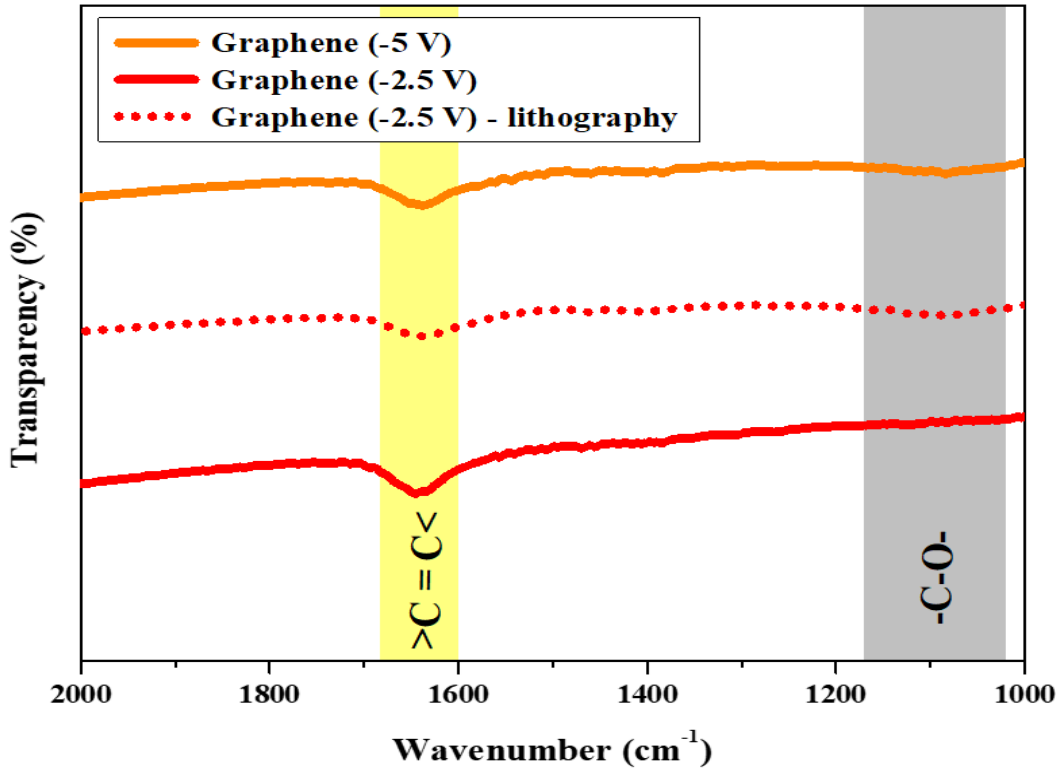
Characterization of elaborated graphene electrodes

FT-IR characterization of graphene electrodes



IR spectra

-graphene exfoliated in aqueous solvent media



IR spectra

-graphene exfoliated in organic solvent media

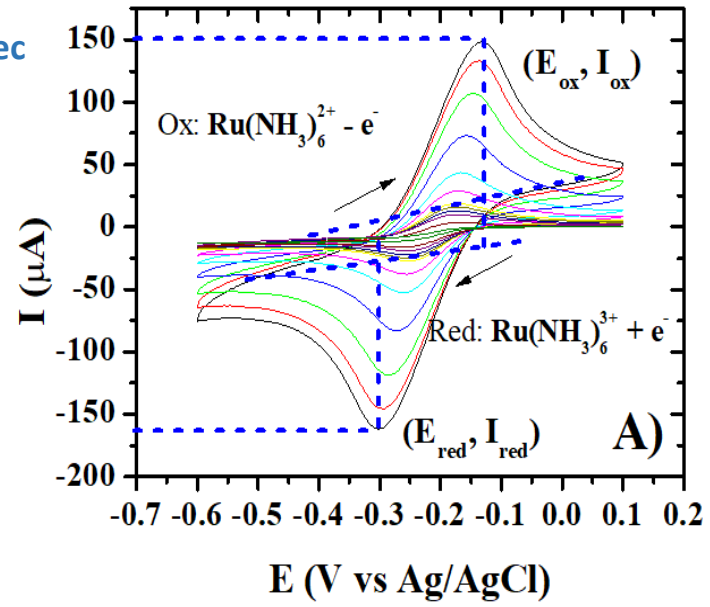
Ref: G. Venugopal, K. Krishnamoorthy, R. Mohan, and S.-J. Kim, *Mater. Chem. Phys.*, vol. 132, no. 1, pp. 29–33, Jan. 2012, doi: 10.1016/j.matchemphys.2011.10.040.

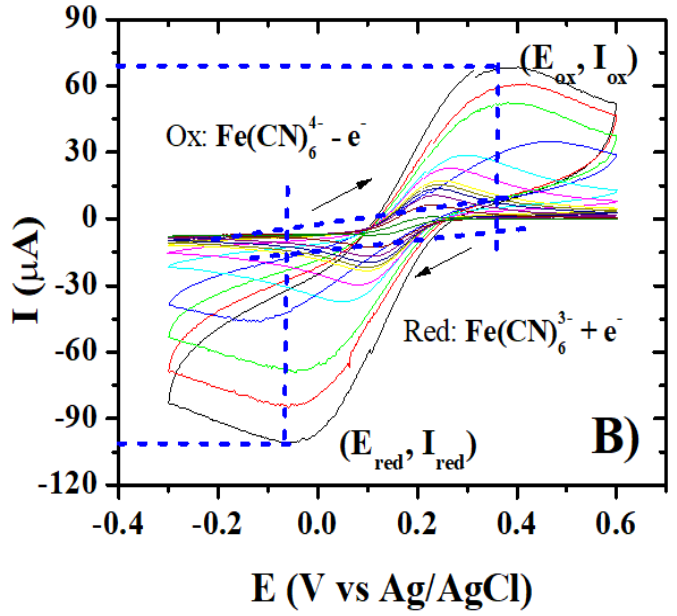
Characterization of elaborated graphene electrodes

Electrochemical characterization – **evolution of electrochemical active surface area**

1000 mV/sec

1 mV/sec





Two different redox probes:

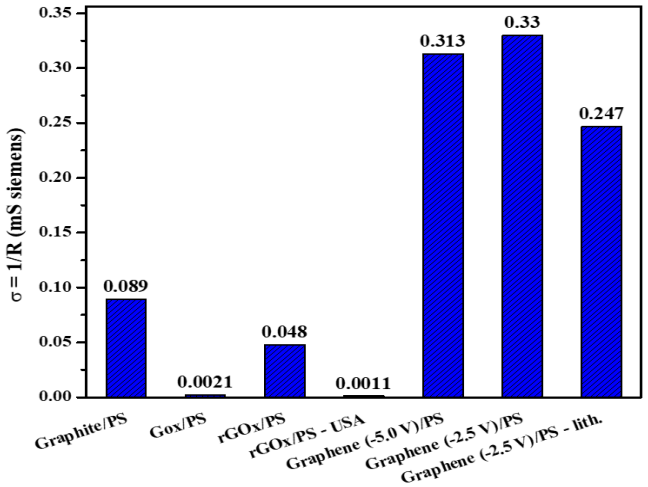
Hexaammineruthenium (III)

$Ru(NH_3)_6^{3+} + e^- \leftrightarrow Ru(NH_3)_6^{2+}$

Ferrocyanure

$Fe(CN)_6^{3-} + e^- \leftrightarrow Fe(CN)_6^{4-}$

Four-point probe electrical conductivity measurements of different samples transferred on polystyrene substrate



Why isoproturon?

WFD

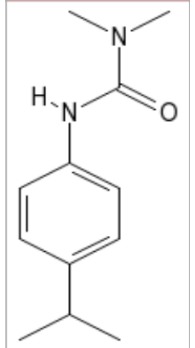
WHO

- the maximum allowed concentration at **0.3 µg.L^{-1} (1.45 x 10^{-9}M)**
- attempts for finding the simplest way how to **determine** micropollutants

In 2013, list of **45 Priority Substances** in the Field of Water Policy

Hexachlorobutadiene	X
Hexachlorocyclohexane	X
Isoproturon	
Lead and its compounds	
Mercury and its compounds	X
Naphthalene	

Isoproturon



Formula

$C_{12}H_{18}N_2O$

ISO (3-(4-isopropylphenyl)-1,1-dimethylurea or 3-p-cumenyl-1,1-dimethylurea)

a phenyl herbicide urea

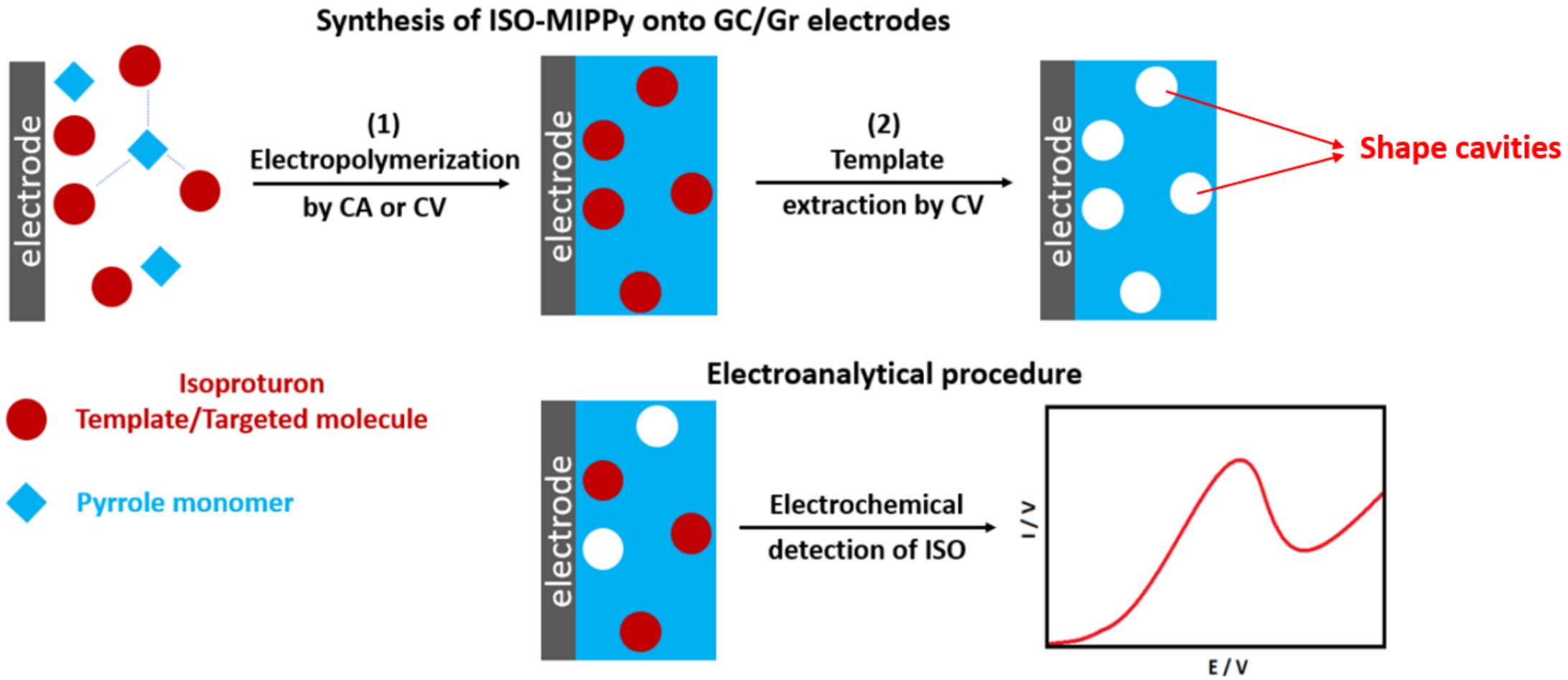
kill weeds in agricultural soils

the EU banned its use in 2016

"Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policyText with EEA relevance," p. 17.

Electropolymerization of molecularly imprinted polymer (MIP) film onto pure graphene electrodes for isoproturon detection

Experimental strategy for the preparation of the MIPPy thin films on GC/Gr electrodes

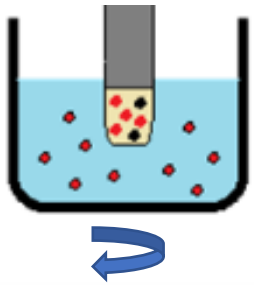


Schematic representation of the procedure used for the preparation of ISO-MIPPy films onto GC and Gr electrodes, including two steps: 1) electropolymerization of MIPs by CA and/or CV, and 2) the CV extraction of ISO molecules. Both electrodes were tested for electrochemical detection of ISO.

Electropolymerization of molecularly imprinted polymer (MIP) film onto pure graphene electrodes for isoproturon detection

Electrochemical preparation of MIP/Graphene (-2.5 V) electrodes for the detection of isoproturon in water

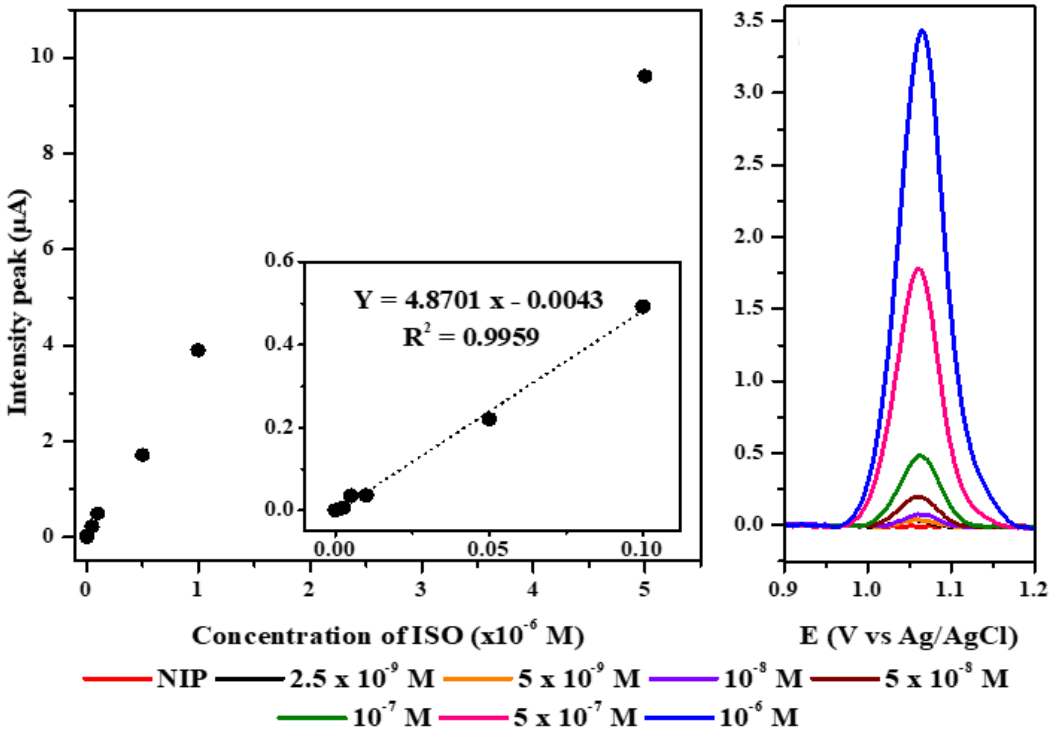
Adding isoproturon in milli-Q water for analysis

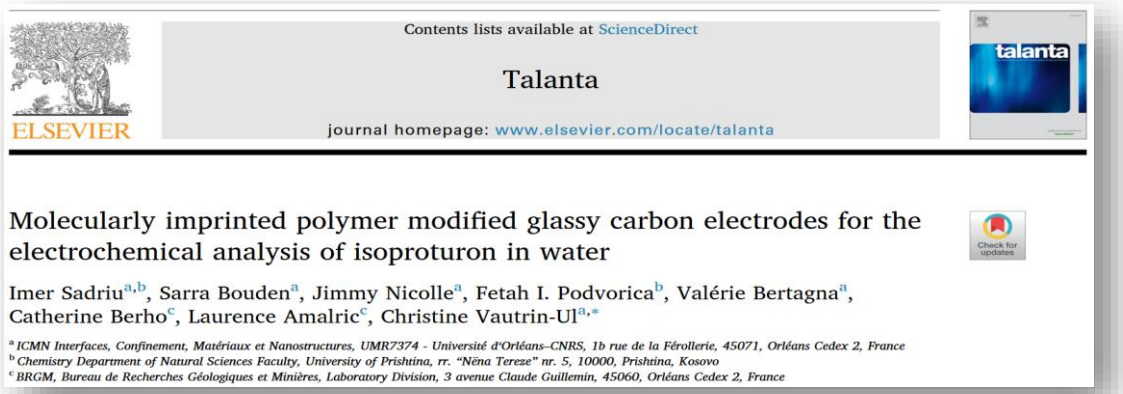


-five detections at each value of conc.

-inside a clean room for trace analysis

Calibration plots obtained during the **SWV** determination of low concentrations of isoproturon milli-Q water samples





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Molecularly imprinted polymer modified glassy carbon electrodes for the electrochemical analysis of isoproturon in water

Imer Sadriu[a,b], Sarra Bouden[a], Jimmy Nicolle[a], Fetah I. Podvorica[b], Valérie Bertagna[a], Catherine Berho[c], Laurence Amalric[c], Christine Vautrin-Ul[a,*]

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[b] Chemistry Department of Natural Sciences Faculty, University of Prishtina, rr. "Nëna Tereze" nr. 5, 10000, Prishtina, Kosovo
[c] BRGM, Bureau de Recherches Géologiques et Minières, Laboratory Division, 3 avenue Claude Guillemin, 45060, Orléans Cedex 2, France

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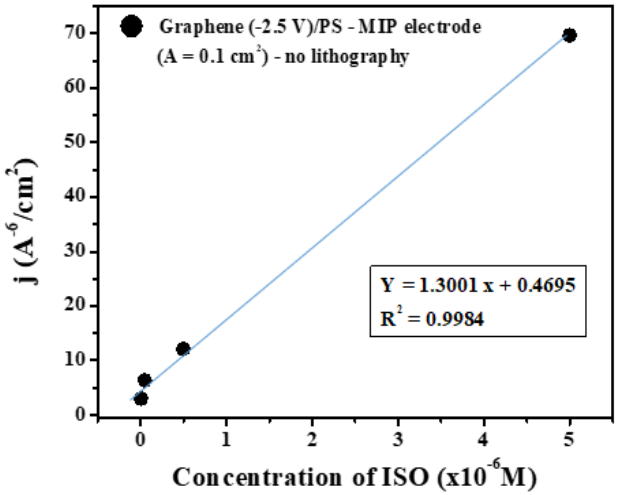
Sadriu et al. 2020, Talanta, Elsevier DOI: 10.1016/j.talanta.2019.120222

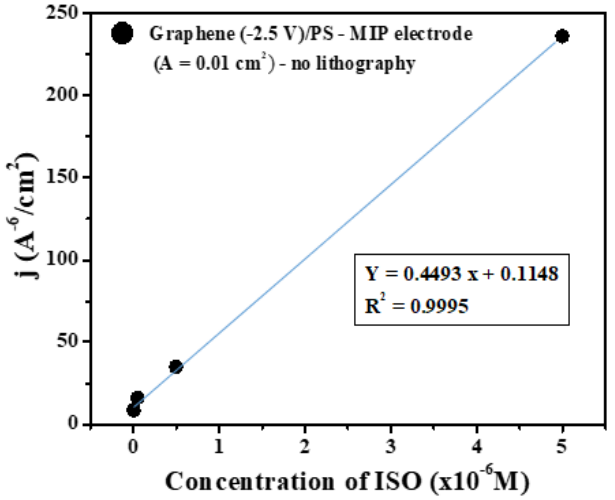
(LOD) = **2.76 x 10^{-9} M (0.5 µg L^{-1})**

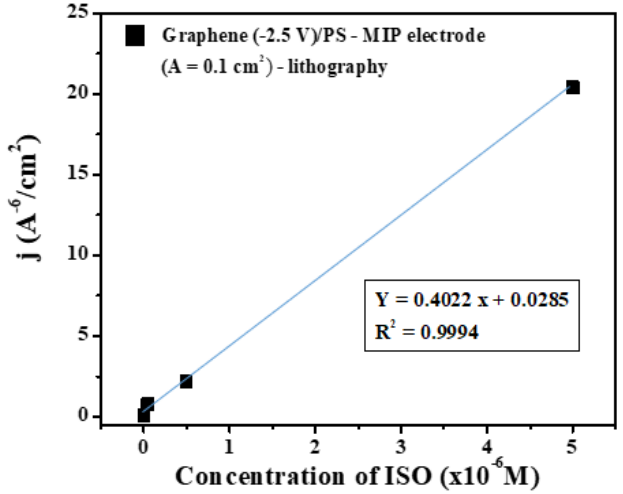
(LOQ) = **9.2 x 10^{-9} M (1.9 µg L^{-1})**

Electropolymerization of molecularly imprinted polymer (MIP) film onto pure graphene electrodes for isoproturon detection

Electrochemical preparation of MIP/Graphene (-2.5 V) electrodes for the detection of isoproturon in water







Calibration plots obtained during the **SWV** determination of low concentrations of isoproturon milli-Q water samples

Electrode	Straight line equation	LOD	RSD
Graphene (-2.5 V)/PS - no lithography A = 10 mm²	I (µA) = 1.3 [Isoproturon] + 0.46 (R^2 = 0.99)	6.9 x 10^{-8} M (14.2 µg/L)	13.1 %
Graphene (-2.5 V)/PS - no lithography A = 1 mm²	I (µA) = 0.45 [Isoproturon] + 0.11 (R^2 = 0.99)	6.6 x 10^{-8} M (13.6 µg/L)	9.5 %
Graphene (-2.5 V)/PS - lithography A = 10 mm²	I (µA) = 0.4 [Isoproturon] + 0.02 (R^2 = 0.99)	8.9 x 10^{-8} M (18.4 µg/L)	17.2 %
Glassy carbon electrode A = 1 mm²	I (µA) = 4.87 [Isoproturon] - 0.004 (R^2 = 0.99)	2.76 × 10^{-9} M (0.5 µg/L)	7.6 %

-four detections at each value of conc.

-by SWV in an ethanol/water solution (70:30 v/v) of H_2SO_4 0.1 M

Conclusions and future perspectives

- The elaboration of pure graphene electrode and use them for the preparation of MIP sensors for ISO detection

An original method for elaboration of 100% graphene electrodes by performing exfoliation of graphite

Graphene was transferred onto polystyrene substrate for graphene/PS electrodes

Characterization results showed higher quality for graphene made by CA (-2.5V) in organic media

Electropolymerization of MIPs on graphene for isoproturon detection

- Electrochemical exfoliation of graphite in organic solvent media is to replace the NMP (1-methyl-2-pyrrolidinone) as solvent with another solvent which is more friendly for the environment
- To improve the sensitivity of the electrochemical detection of ISO by using 100% graphene electrodes will involve the optimization of the design and the parameters procedure
- Further improvement of the properties such as sensitivity, robustness, reliability, adaptability will also help in the increasing of the performance of this technique for environmental applications

Thank you for your kind attention!