GRAPHENE AND 2DM VIRTUAL CONFERENCE & EXPO

10 ANNIVERSARY

Graphene online 2020 October 19-23

Graphene based sensors for heavy metals or organic micropollutants electrochemical detection

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Since its exfoliation in 2004, graphene attracted an huge interest in scientific and in industrial communities due to its physical and chemical properties. The graphene strong interaction with its environment properties can be used for sensing application, in mechanical, biological and chemical fields. Indeed one of the main challenge of our modern society, is the evaluation and the control of pollution in the environment, especially for the air and water quality. For water, the European Union has edicted the water frameworks directive in 2000. The revision of this directive (2013) defines new thresholds of detection and new settings for the analysis of 45 priority micropollutants in aqueous media, as heavy ions, organic molecules, pesticides or Polycyclic Aromatic Hydrocarbons (PAH). This chemical diversity involves the development of selective and sensitive sensors for their detection. In the laboratory ICMN, we develop electrochemical sensors dedicated to the detection of micropollutants in aqueous media.

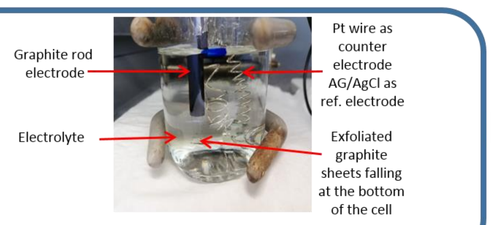
In this way, for performing the detection of heavy metals, or Polycyclic Aromatic Hydrocarbons (PAH), we used graphene as an electrochemical platform, for grafting of diazonium salt for the detection of targeted heavy metals, or performing electropolymerization of the Molecular Imprinted Polymer (MIP) for the detection of PAH. After this step of graphene modification, the functionalized graphene sensors were used for the detection of targeted molecules.

We will present here, 100% graphene based sensors. One dedicated to the detection of copper based on electrochemical exfoliated graphene electrodes modified by diazonium salt grafting. The second one dedicated to the detection of Anthracene or isoproturon based on CVD graphene electrodes modified by an electropolymerized MIP. For these three micropollutants concentrations at ppb level have been obtained.

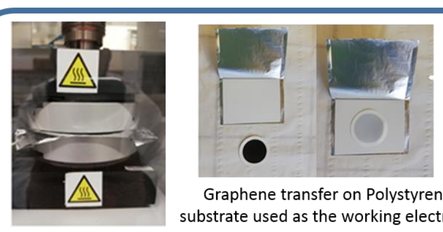
We gratefully acknowledge the financial support provided to the PIVOTS project by the Region Centre-Val de Loire (ARD 2020 program and CPER 2015-2020) and the French Ministry of Higher Education and Research (CPER 2015-2020 and public service subsidy to CNRS and Université d'Orléans).

100% Gaphene electrodes Production and Design

Electrochemical Exfoliated Electrodes

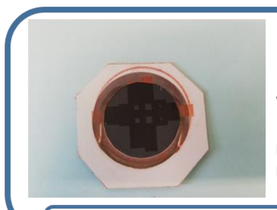


Electrochemical Exfoliation



Graphene transfer on Polystyrene substrate used as the working electrode

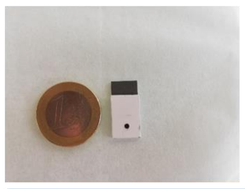
Graphene transfer using pressure and temperature



Definition of the working area surface

Working areas :
10 mm^2,5 mm^2, 1 mm^2, 500 μm^2, 250 μm^2, 100 μm^2, 10 μm^2

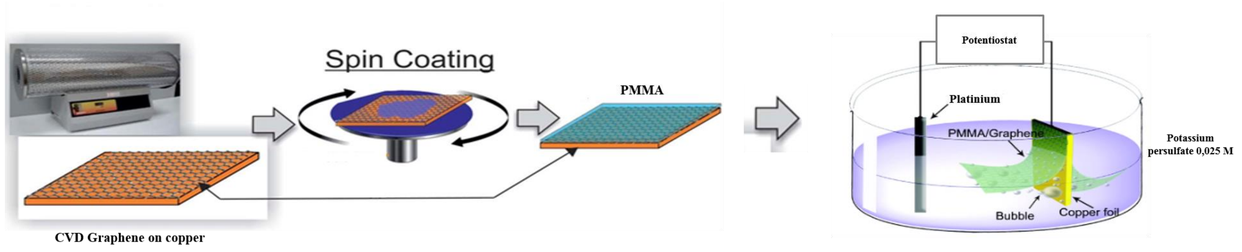
Photolithography of graphene

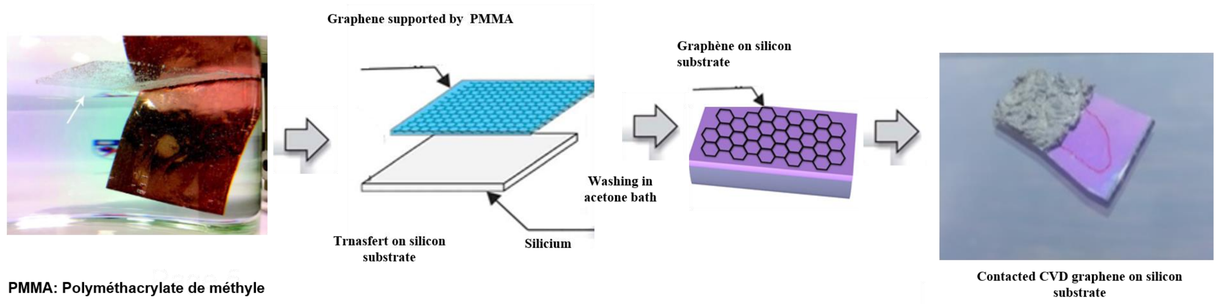


Final electrode used as based for sensors

100% graphene electrodes with define surface area

CVD Graphene electrodes





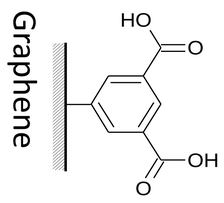
PMMA: Polyméthacrylate de méthyle

Two strategies for Development of graphene sensors dedicated to the detection of targeted pollutant

Electrochemical grafting of diazonium salt

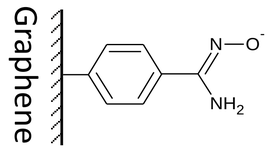
Example Electrochemical grafting of diazonium salts by cyclo-voltametry

3,5-dicarboxylphenyl diazonium

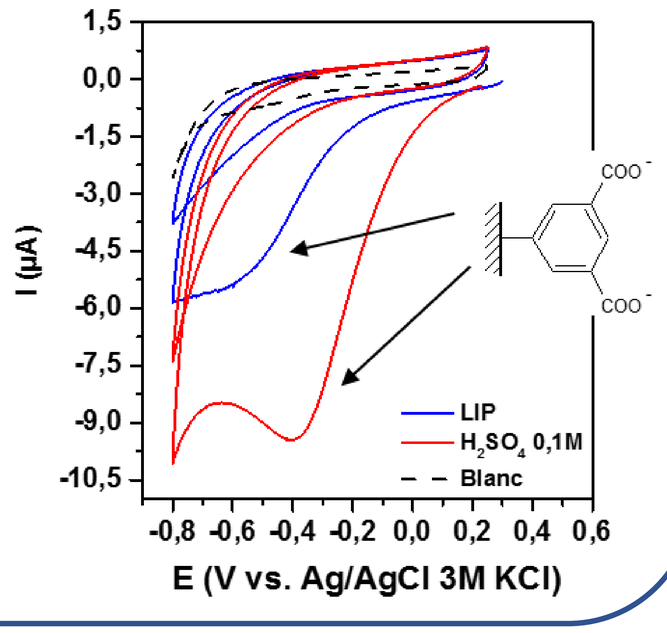


Lead detection (Pb^{2+})

4-Nitrobenzene diazonium

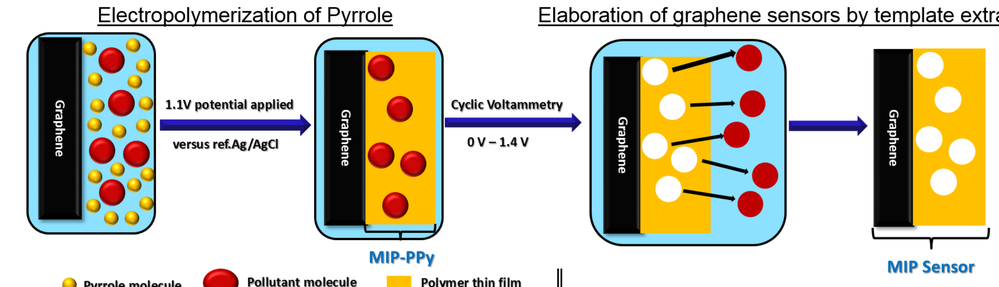


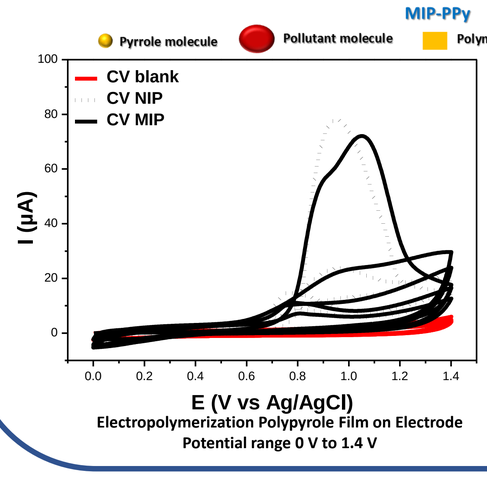
Nickel detection (Ni^{2+})



Detection Steps:
1- Adsorption of the target pollutant on the grafting electrode
2- Electrodeposition of the targeted pollutant on the grafting electrode
3- Electrochemical detection
4- Sensors regeneration

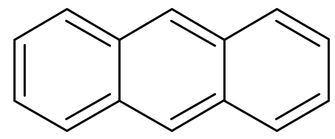
Electropolymerization of Pyrrole



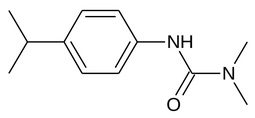


Targeted pollutants:

Anthracene

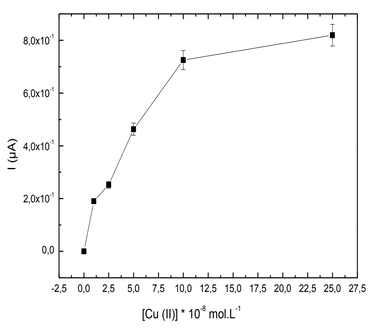


Isoproturon



Detection Steps:
1- Adsorption of the target pollutant on the grafting electrode
2- Electrochemical detection
3- Sensors regeneration

Electrochemical detection of heavy ions



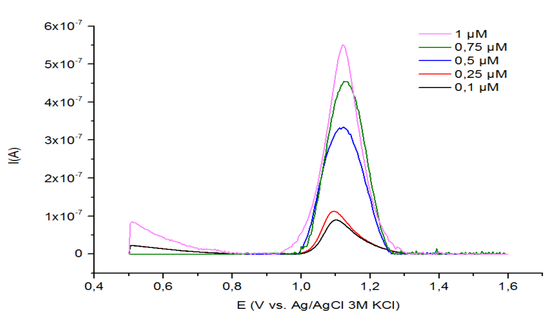
On electrochemical exfoliated Graphene electrodes

Lowest concentration peak detection experimental detection :

$$Cu^{2+} = 10^{-8}\ M$$

$$LOD = 2 \times 10^{-9} M$$
$$LOQ = 6.6 \times 10^{-9} M$$

Electrochemical detection of Molecules



On CVD-MIP Graphene electrodes

Lowest concentration peak detection:

Experimental Limit Of Detection

$$C_{Anthracene} = 7.5 \times 10^{-8}\ mol.L^{-1}$$

In pure Water

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