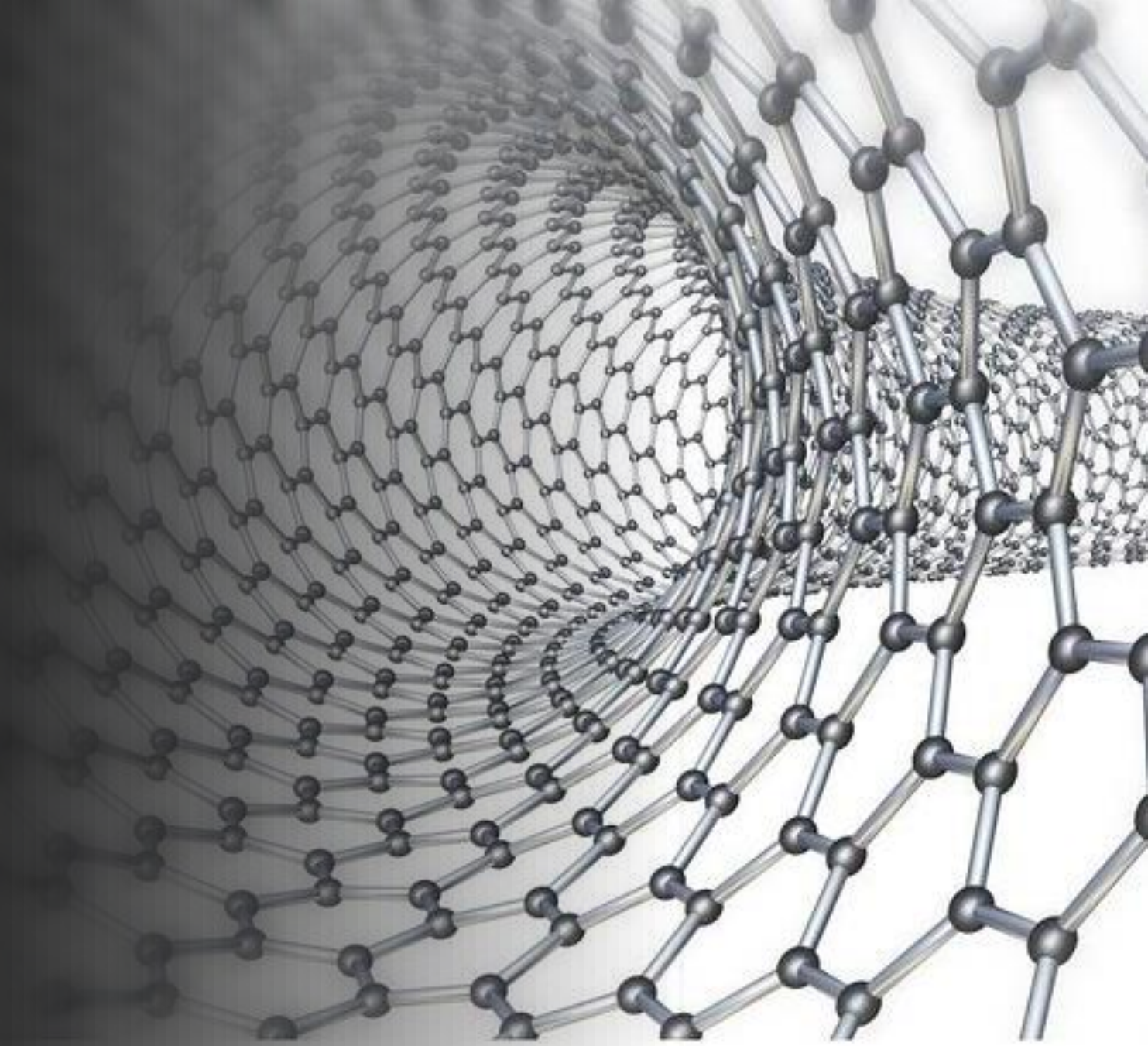
CARBON NANOSTRUCTURE FOR SENSOR DEVICES



Lesson 30/11/2023

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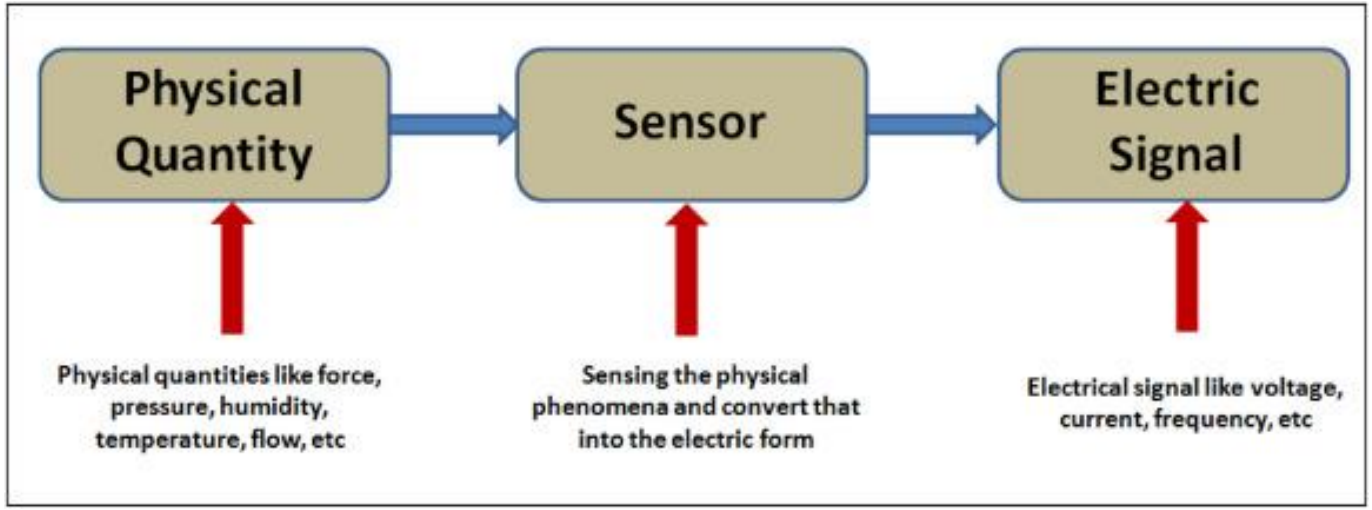
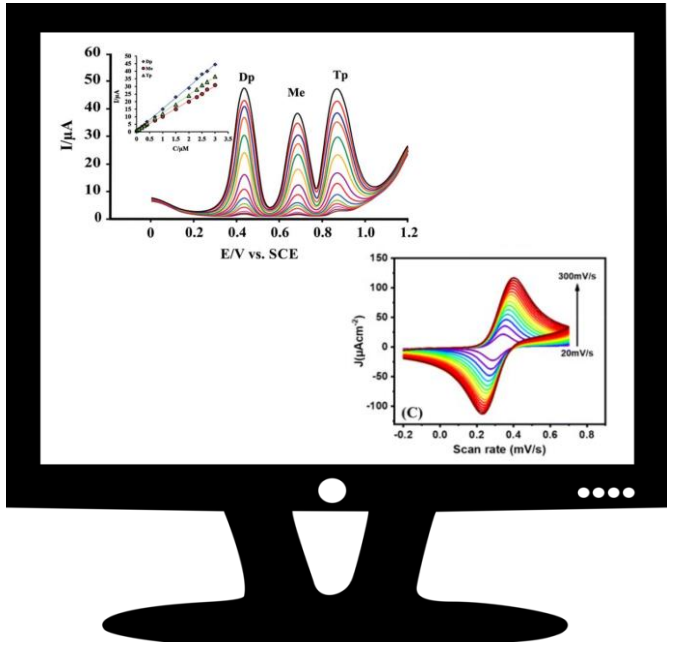
What is a sensor

It is an object that **detects signals** from **its sorrounding environment** and converts it to **quantifiable information**. A sensor should translate a reaction process (physical or chemical) into quantitative signal for data analysis.

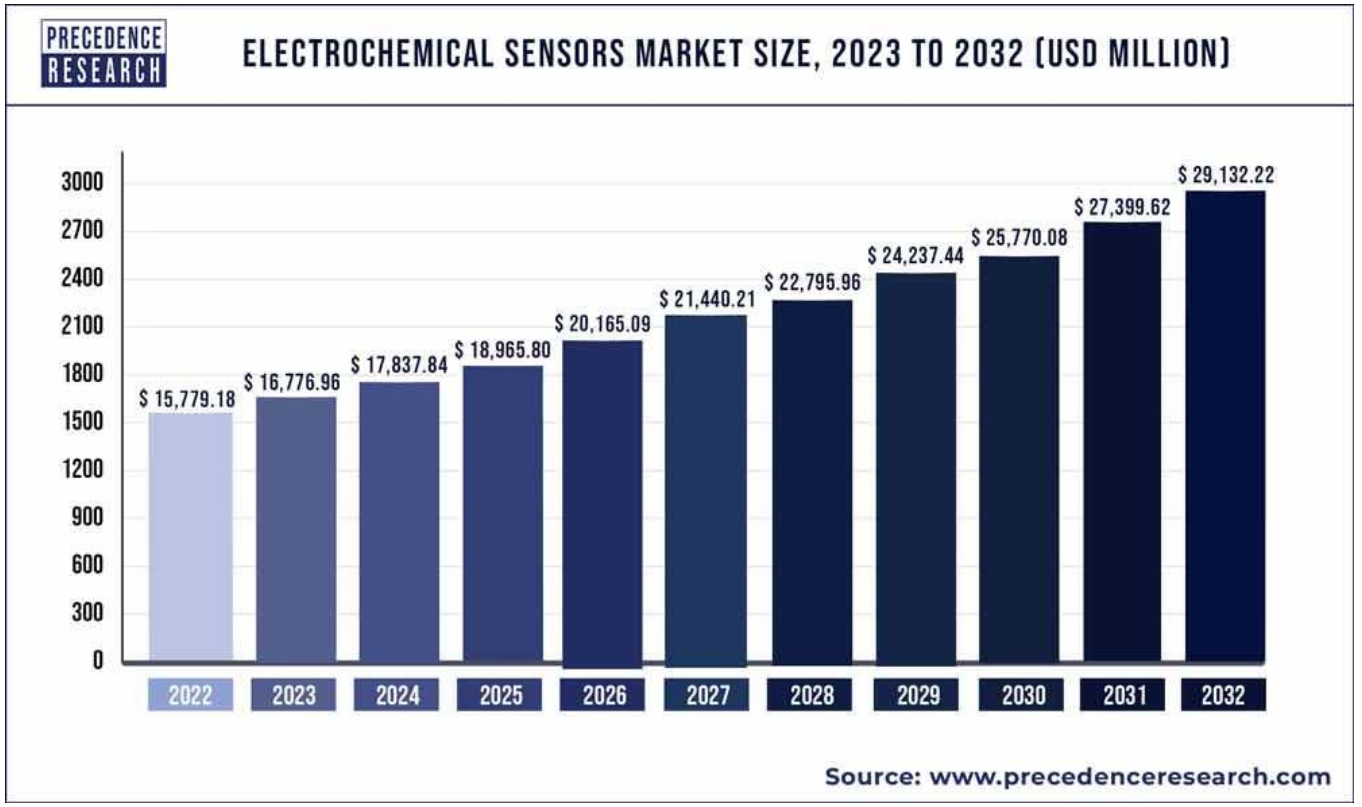




What is a sensor

Many type of sensor are actually present on the market and it is expected to grow up in the next years:

- Monitor of structural stability
- Gas monitoring
- Blood analysis
- Acustic pollution
- Water pollutant



Type of sensors

- **Physical (magnetic, electric, mechanical) sensors**

- **Chemical sensors**

- **Light driven sensors**

- **Electrochemical sensors**

Electrochemical sensor

The electrochemical sensors make use of the **chemical interaction** among the **analyte** (**sample**) and the **substrate (transducer)** of the sensor to convert the reaction into a measurable electrical signal.

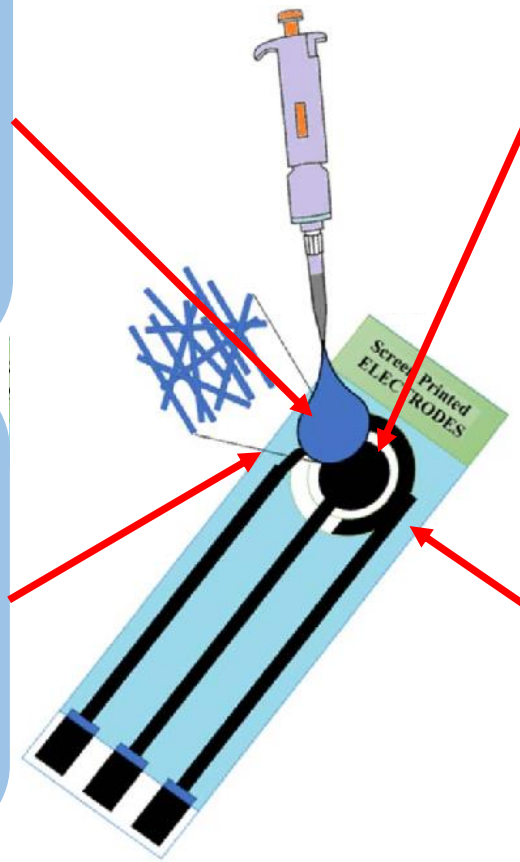
The substrate will either **oxidize** or **reduce** the analyte of interest, resulting in measurable current proportional to the sample concentration.

The reaction can be **catalyzed** directly from the **substrate** or through **specific catalyzer** (metals, metal oxides or biomolecules).

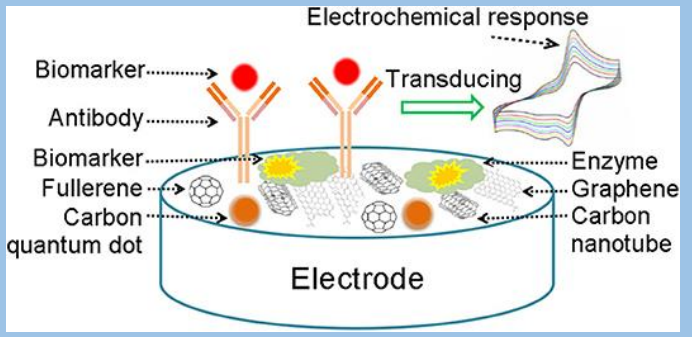
Electrochemical sensor

ANALYTE: solution containing the chemical species or molecules to be detected

COUNTER ELECTRODE: electrode used to collect the current



SUBSTRATE (WORKING ELECTRODE): the modified active material of the sensor



REFERENCE ELECTRODE: electrode used to measure the stable potential (usually Ag or Ag/AgCl)

Electrochemical sensor

TYPE OF MEASUREMENT:

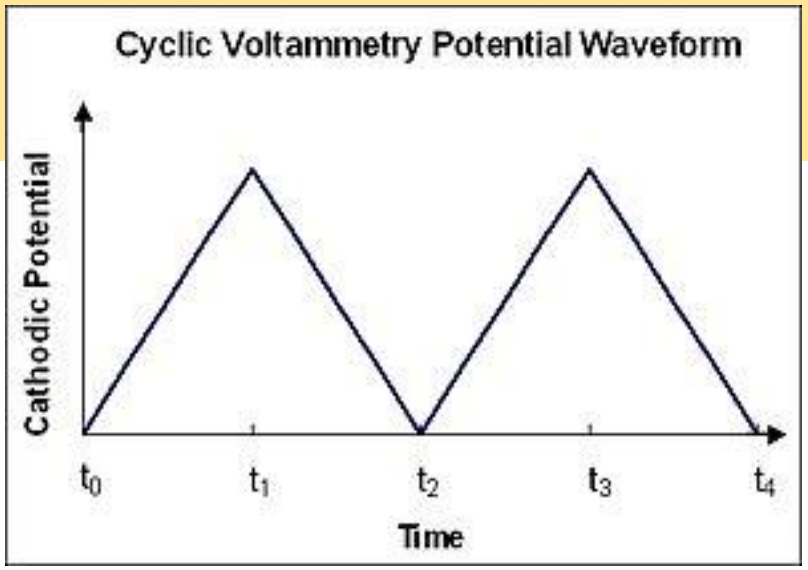
CYCLIC VOLTAMMETRY

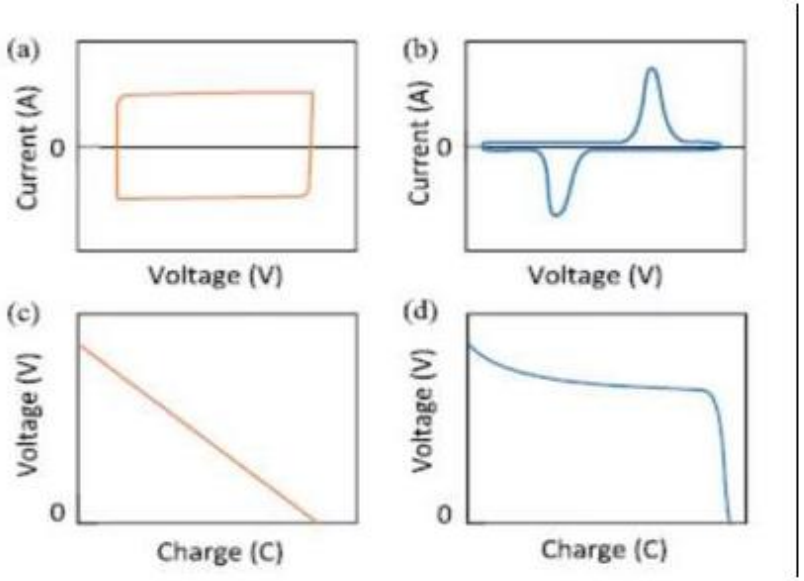
The applied potential is **increased and decreased** in **steps (mV/s)** in a specific voltage window.

$$C = \frac{I}{dV/dt} = \frac{1}{\Delta V\left(\frac{dV}{dt}\right)}\int IdV$$

$$E = \frac{1}{2}C\Delta V^2$$

In presence of **redox peak**, an extra contribution to the current come from redox reaction (peaks)





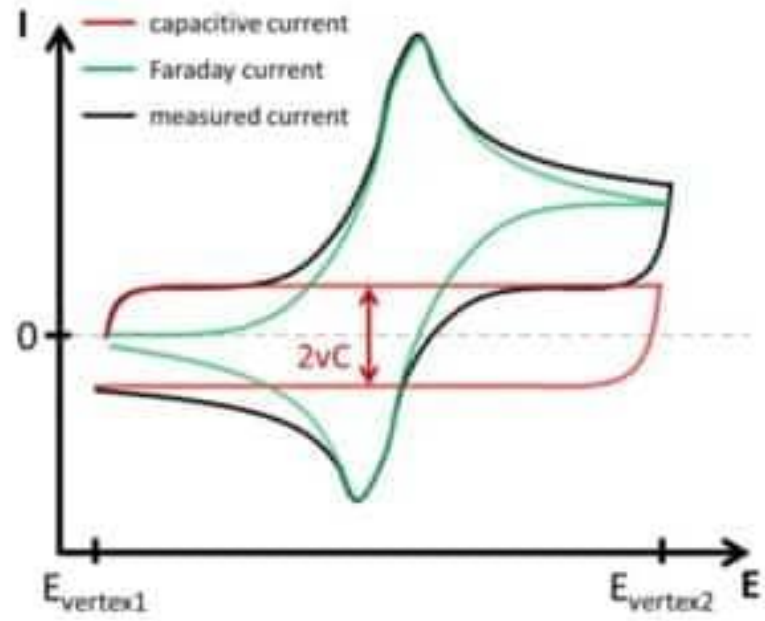
Electrochemical sensor

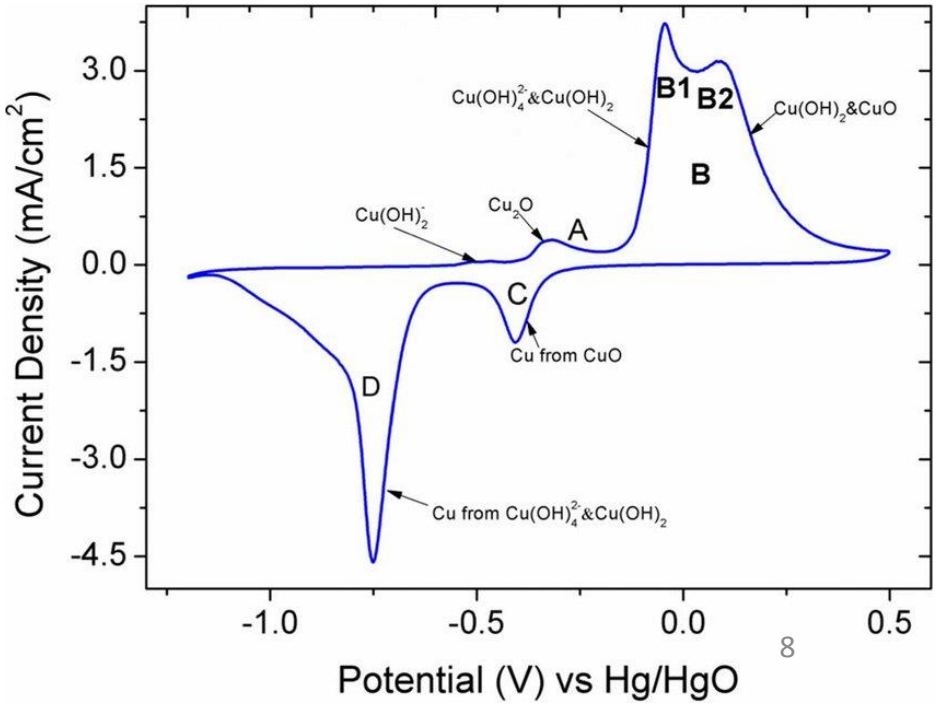
TYPE OF MEASUREMENT:

CYCLIC VOLTAMMETRY

Usually CV in presence of redox species, presents a mix response between capacitive and faradaic behaviour.

CV is commonly used to characterize the sensor electrodes, in order to detect the response of extra species or atoms added to increase the response (molecules, metals, metal oxides …)





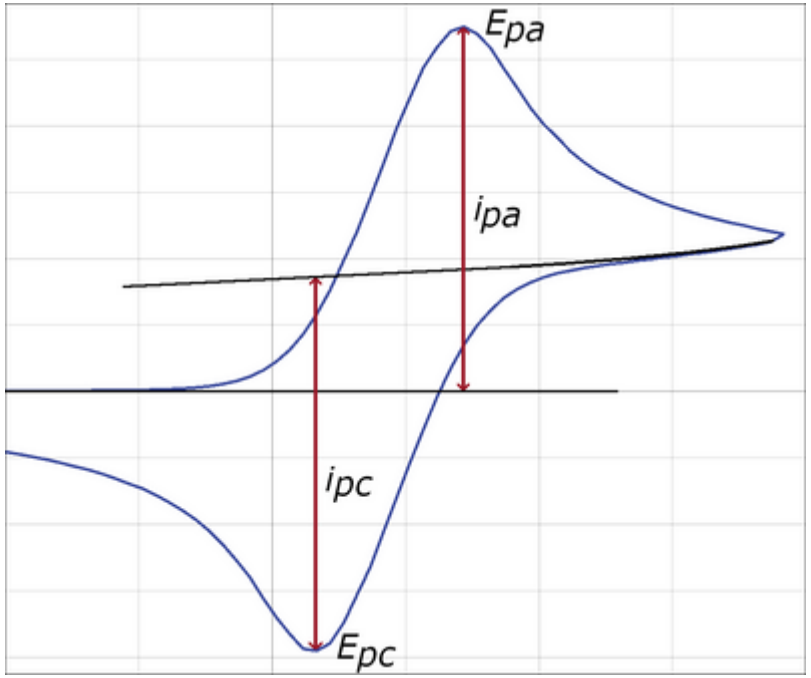
Electrochemical sensor

TYPE OF MEASUREMENT:

CYCLIC VOLTAMMETRY

In a reversible system, an oxidation peak (**anodic**) is observed **increasing** the potential. The reduction peak (**cathodic**) is observed **decreasing** the potential.

If the reaction is reversible $\frac{i_A}{i_C} = 1$



Electrochemical sensor

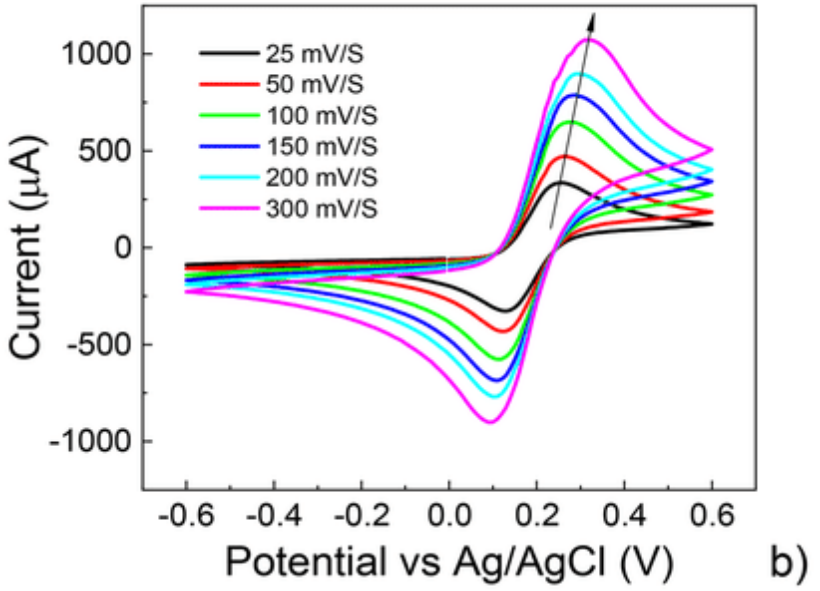
ELECTRODE CHARACTERISATION

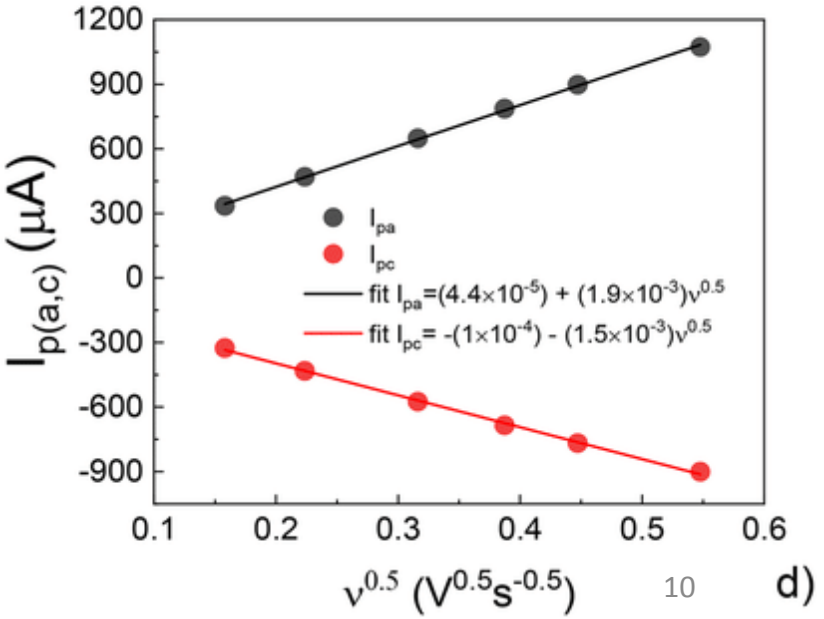
The electrodes are usually tested in presence of ferricyanide (reversible reaction)

$$Fe[(CN)_6]^{4-} \rightleftharpoons Fe[CN)_6]^{3-} + e^-$$

The effect of scan rate on the peak current is described by Randles-Sevcik equation

$$i_p = 0.4463\, nFAC \left(\frac{nFvD}{RT}\right)^{1/2}$$



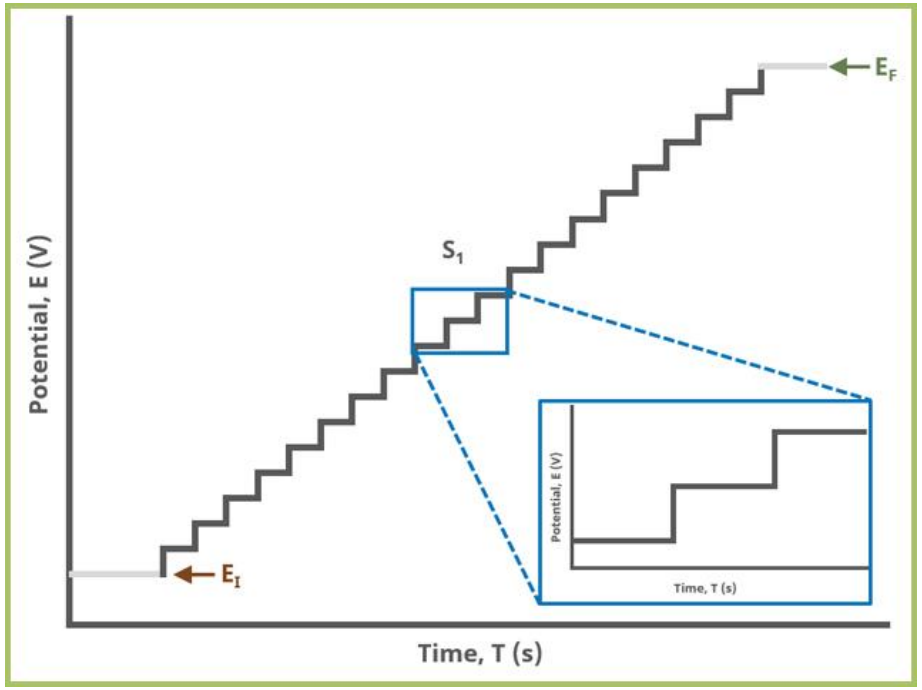


Electrochemical sensor

TYPE OF MEASUREMENT:

VOLTAMMETRY

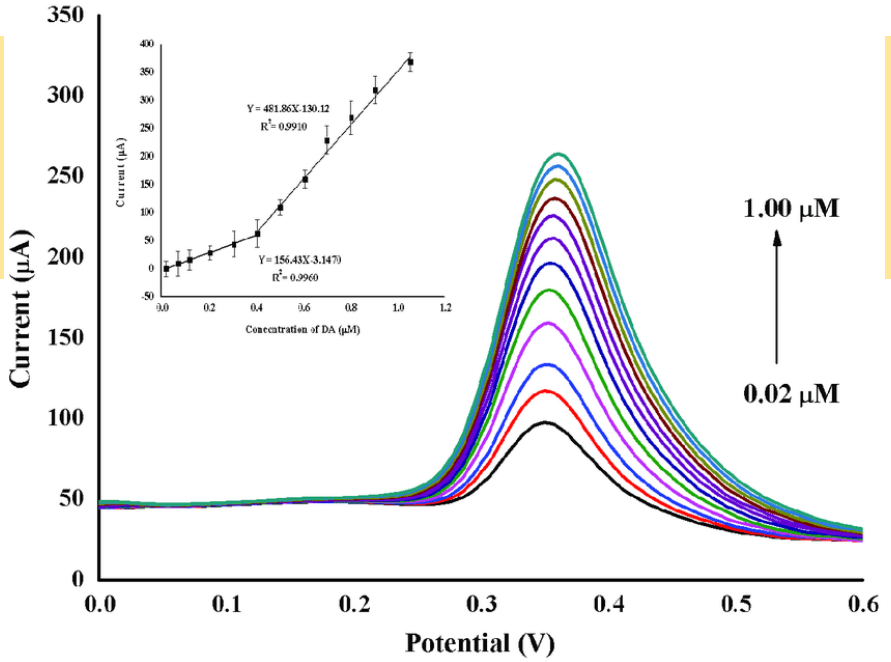
The ***potential is increased in steps*** only in one direction (semicycle). It is important the moment in which the current is measured (usually after a diley time).

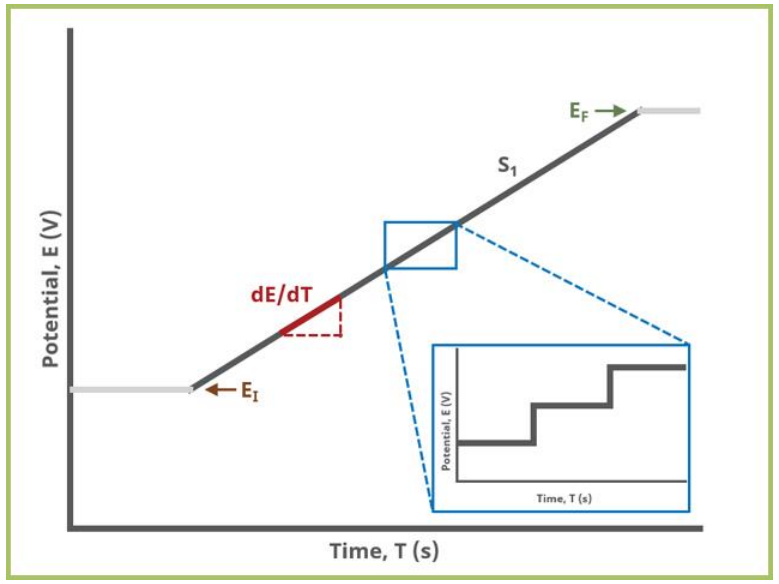


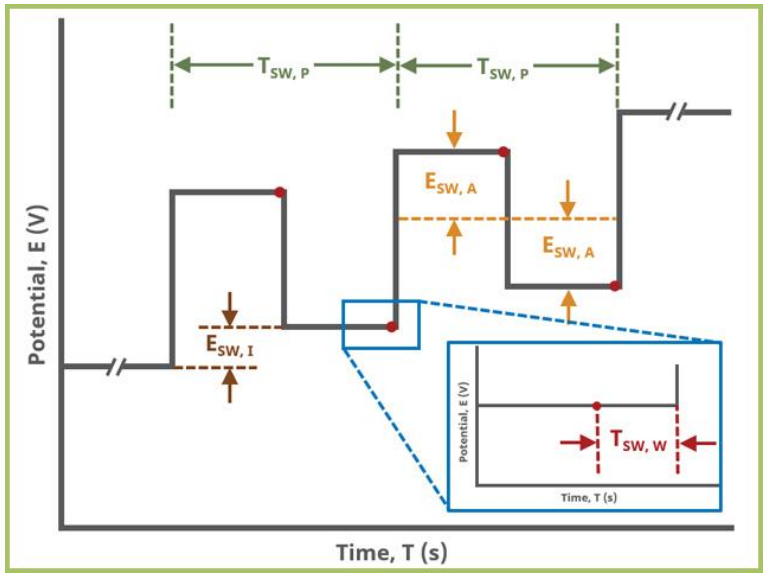
Useful to detect oxidation redox peaks**, reducing the capacitive** contribution. Many voltammetry technique as been developed.

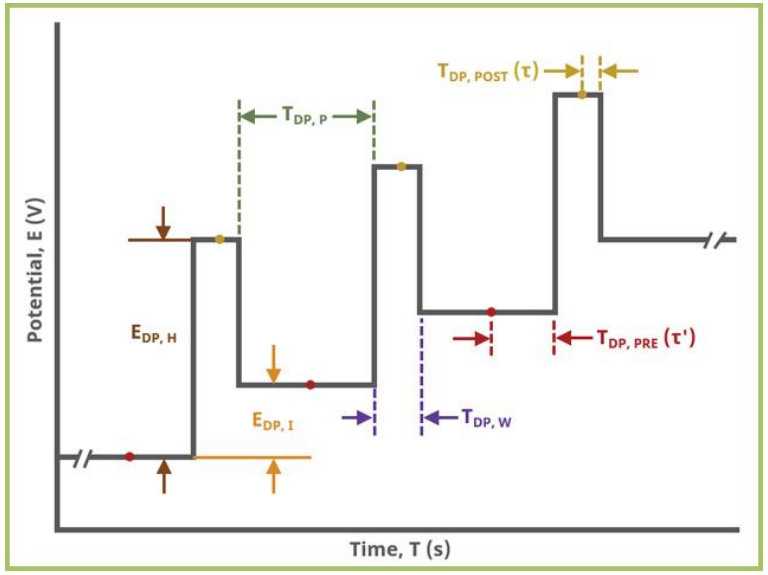
VOLTAMMETRY

- Linear Sweep Voltammetry
- SquareWave Voltammetry
- Differential Pulse Voltammetry







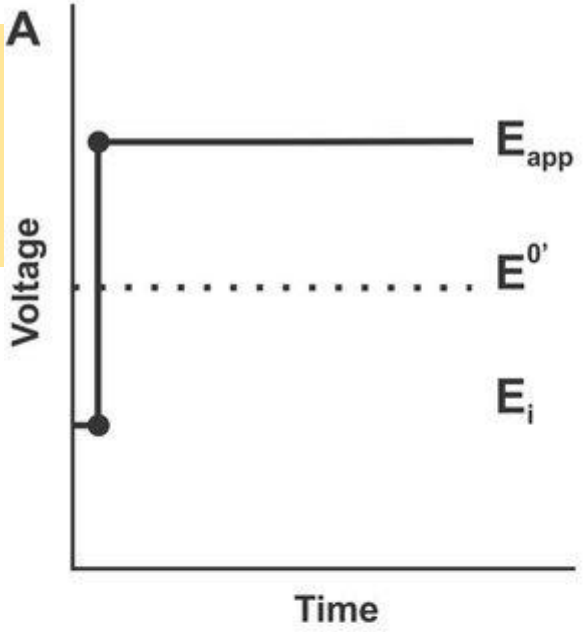


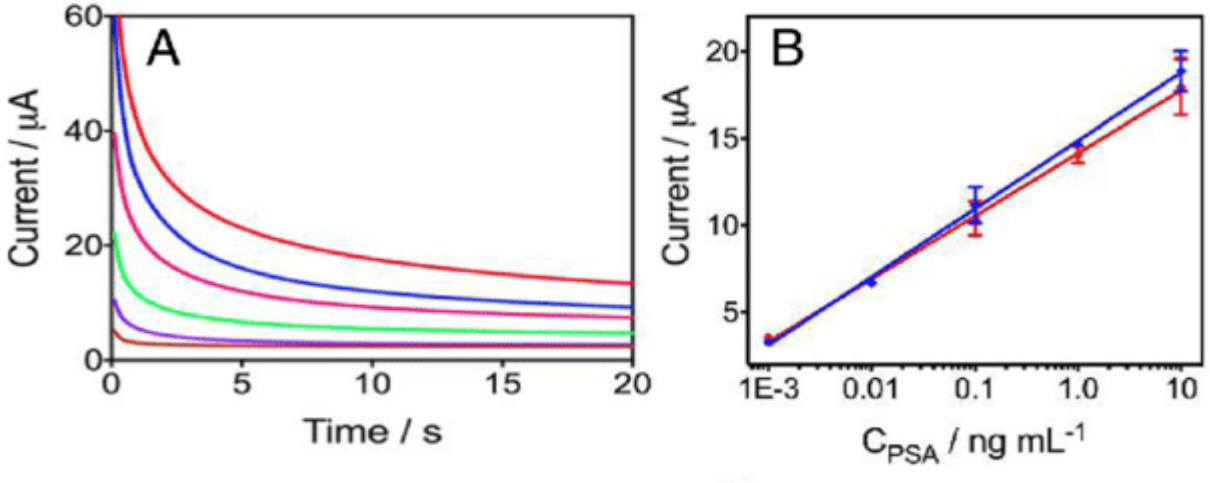
Electrochemical sensor

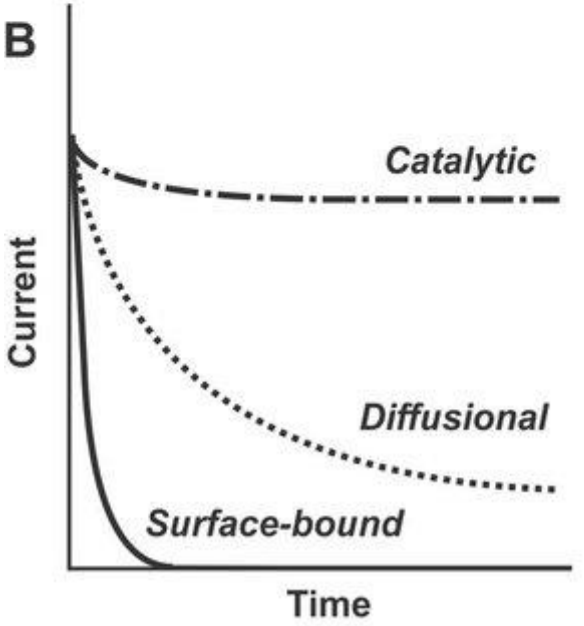
TYPE OF MEASUREMENT:

CHRONOAMPEROMETRY

The ***applied potential*** is ***constant in time*** and the current is registered. In case of catalytic activity of the sensor the current does not drop to zero but to a ***constant value proportional*** to the ***eletrochemical active specie*** in solution.



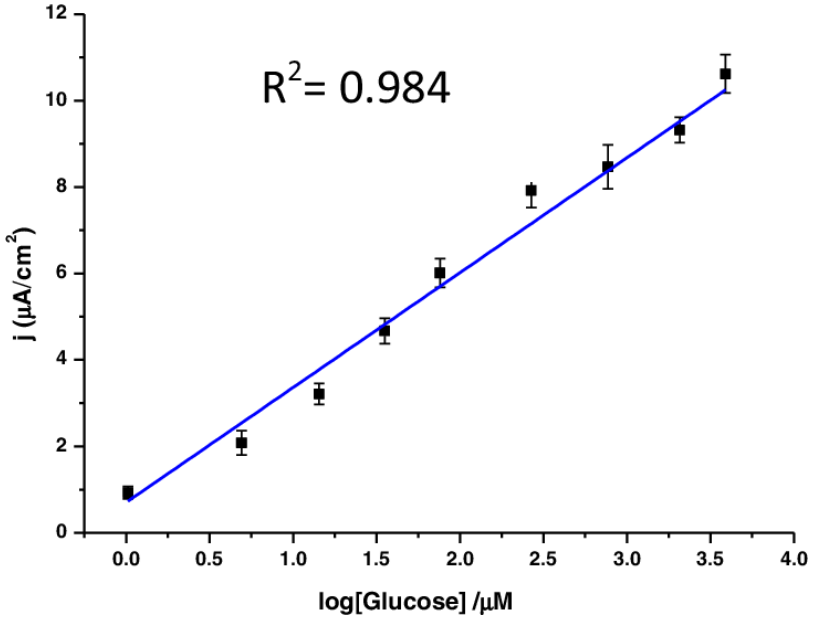




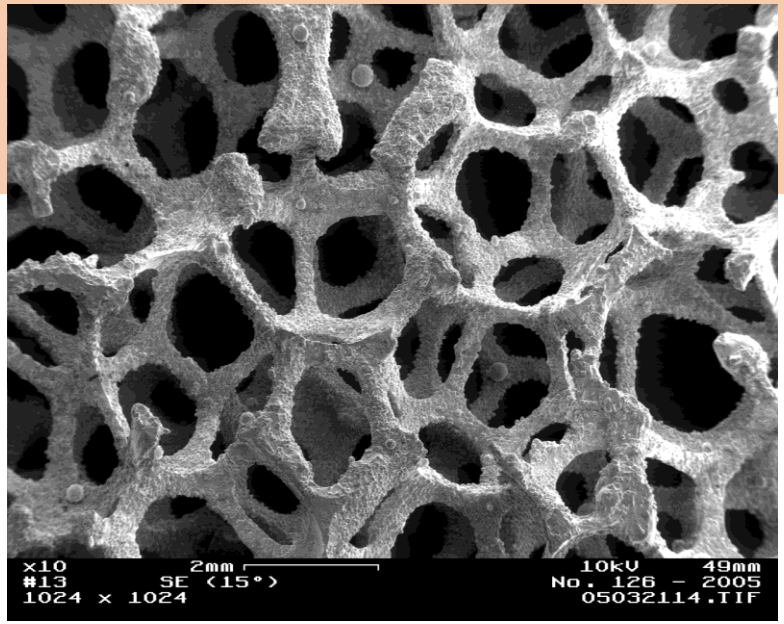
Electrochemical sensor

IMPORTANT PARAMETERS

1) **SENSITIVITY:** coefficient of the calibration curve $\left[\frac{\mu A}{mmol*cm^2}\right]$
2) **LINEAR RANGE**
3) **Limit Of Detection (LOD)**: minimum quantity of analyte detectable (nM, uM, mM …) $\mathrm{LOD} = \frac{3\sigma}{S}$
4) **SELECTIVITY**

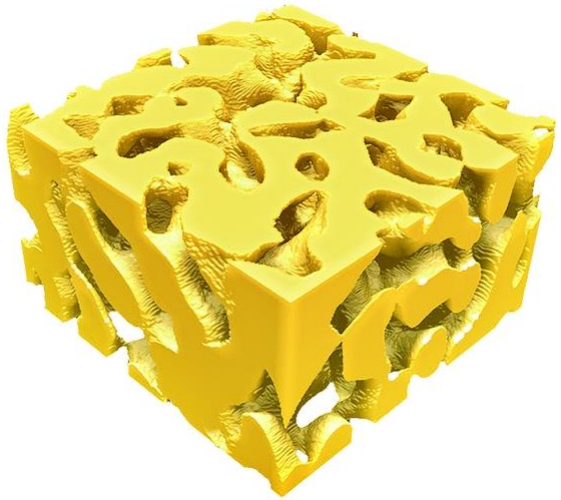


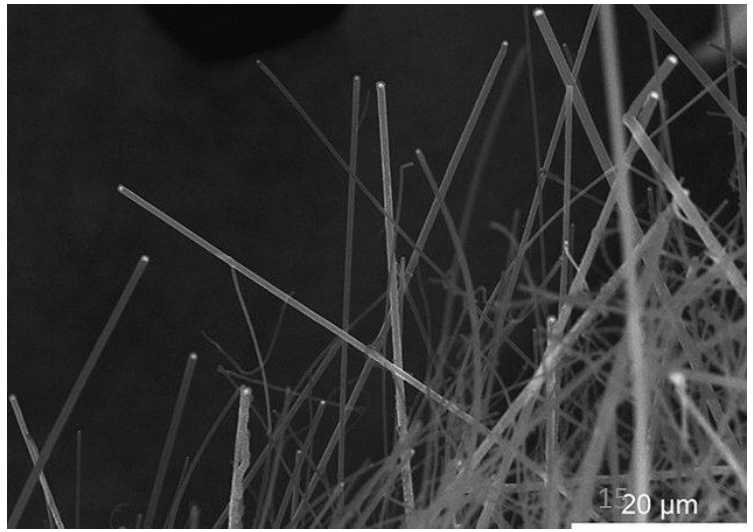
Electrochemical sensor



<u>MATERIAL FOR ELECTROCHEMICAL SENSORS</u>:

- High ***<u>electrical conductivity</u>*** (metals or conductive carbon)
- ***<u>Easy to modify</u>*** with external species or molecules (-COOH, -COH …)
- ***<u>Large surface area</u>***
- Mechanical strenght
- Reproducibility
- Cheap





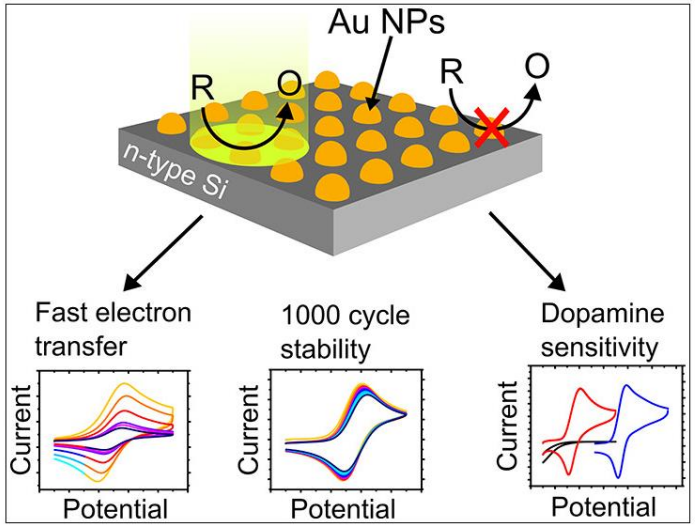
Electrochemical sensor

- The **signal** is extracted from **reaction of inorganic materials** with the analyte.

- Usually the **reaction** involves the **oxidation** of the analyte by the substrate at specific potential.

-Extra species, such as **metals**, **metal oxides** and other **molecules** who display a **catalytic activity** in analyte detenction.

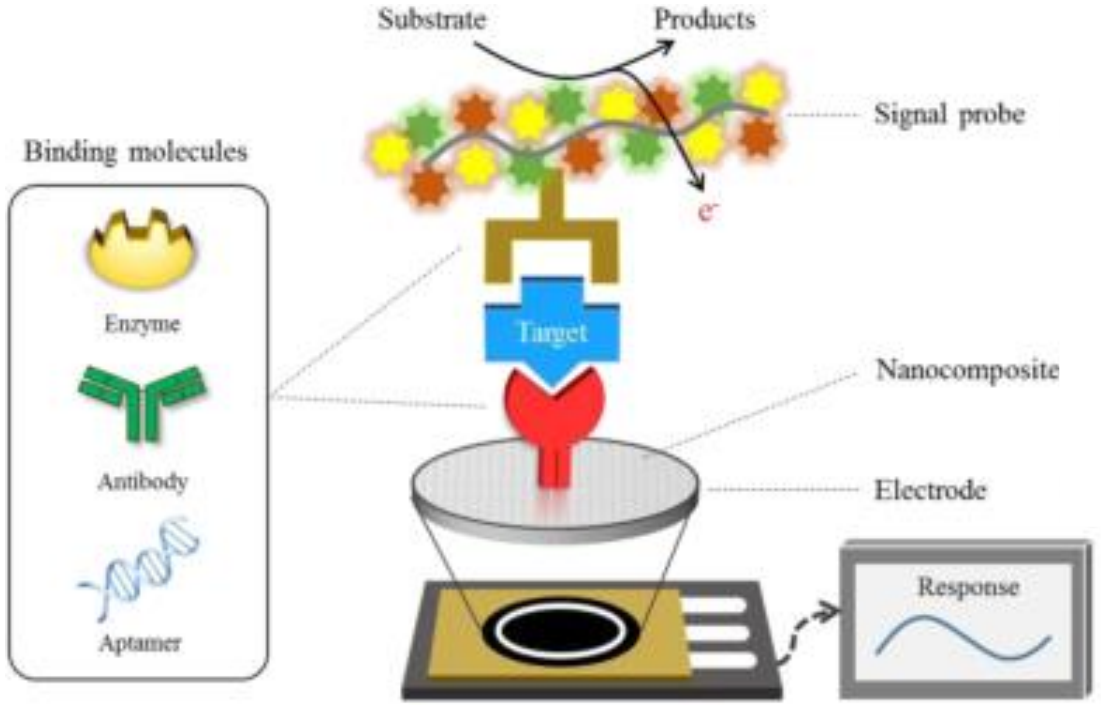
$$X + Mt \rightarrow X^{+} + Mt + e^{-}$$



Electrochemical Biosensor

The modified electrodes make use of **enzymes or antybodies** or **other biological molecules** anchored to the substrates.

The diffusion of the analyte on the modified surface allows the **interaction between the enzyme and the molecule**. The **wasting product** can be **detected** with a specific **transducer**.



Advantage and Disadvantage

Biosensor:

- ✓ High selectivity
- ✓ Reproducibility
- ✓ Working pH=7

- × Low stability for long time
- × High costs
- × Non conductive
- × Degradation at high Temperature
- × Difficult to anchor

Non-Enzymatic Sensor:

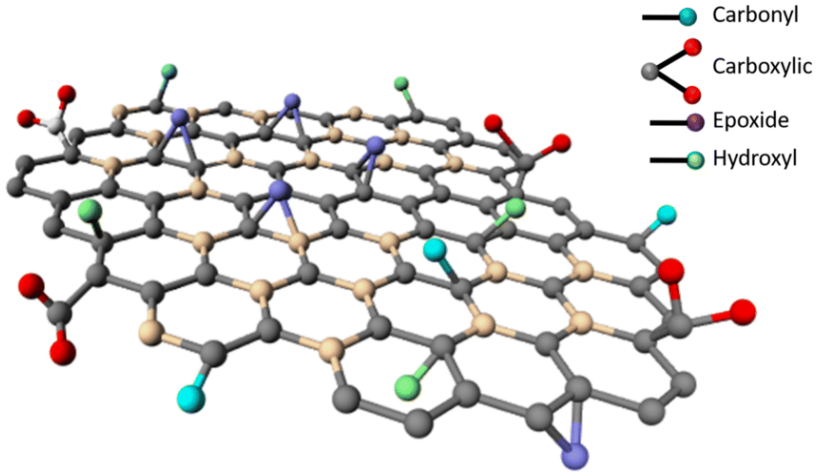
- ✓ High stability in time
- ✓ High stability in temperature
- ✓ Cheap
- ✓ Easy to scale up

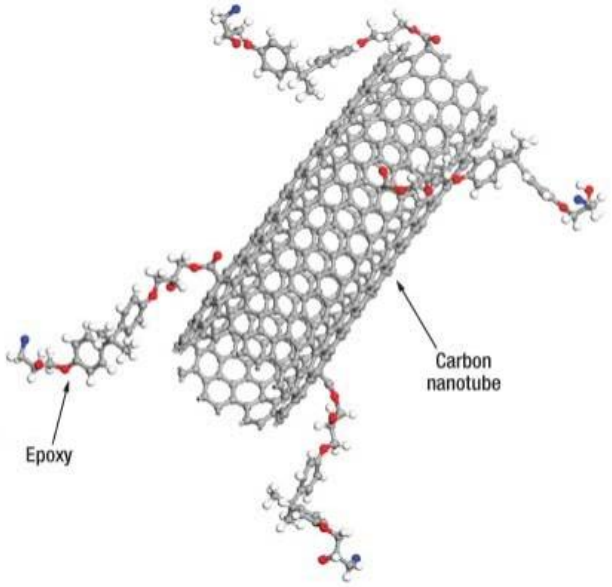
- × Low selectivity
- × Working pH different from 7

Carbon nanostructure for electrochemical sensing devices

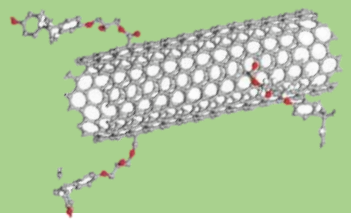
The best candidate for electrochemical sensing devices are carbon nanostrutures:

- ***Carbon Nanotubes*** (SWCNs and MWCNs)
  - Surface area (from 800 to 100 m2/g)
  - Conductivity (from 0.15 to 50 S/cm)
  - Functionalisation
- ***Graphene***
  - Surface area (from 300 to 2640 m2/g)
  - Conductivity (from 2700 to 6 S/cm)
  - Functionalisation
- ***Porous Carbon***
  - Surface area (up to 3000 m2/g)
  - Conductivtiy (up tp 30 S/cm)





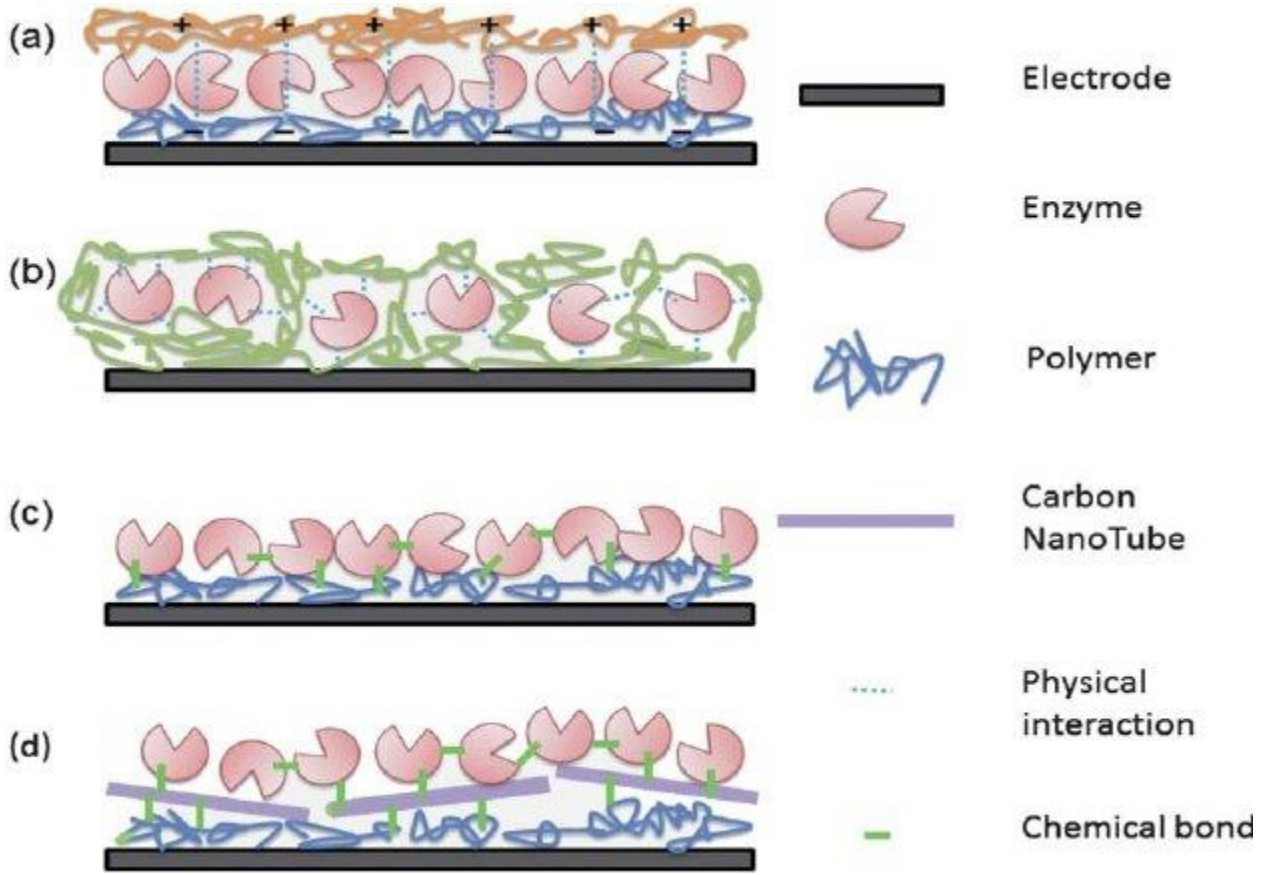
Application of **Nanotubes**



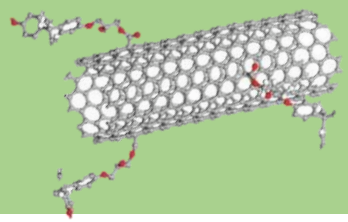
Biosensors

Enzymes and biological molecules can be easely ***anchored*** on CNTs.

- **Adsorption:** weak interaction among enzymes and CNTs
- **Covalent bond**: the carboxilic group can be used as covalent bridge for FAD immobilisation
- **Encapsulation:** the Enzymes can be incapsulated in polymer matrix (Nafion, Chitosan …)

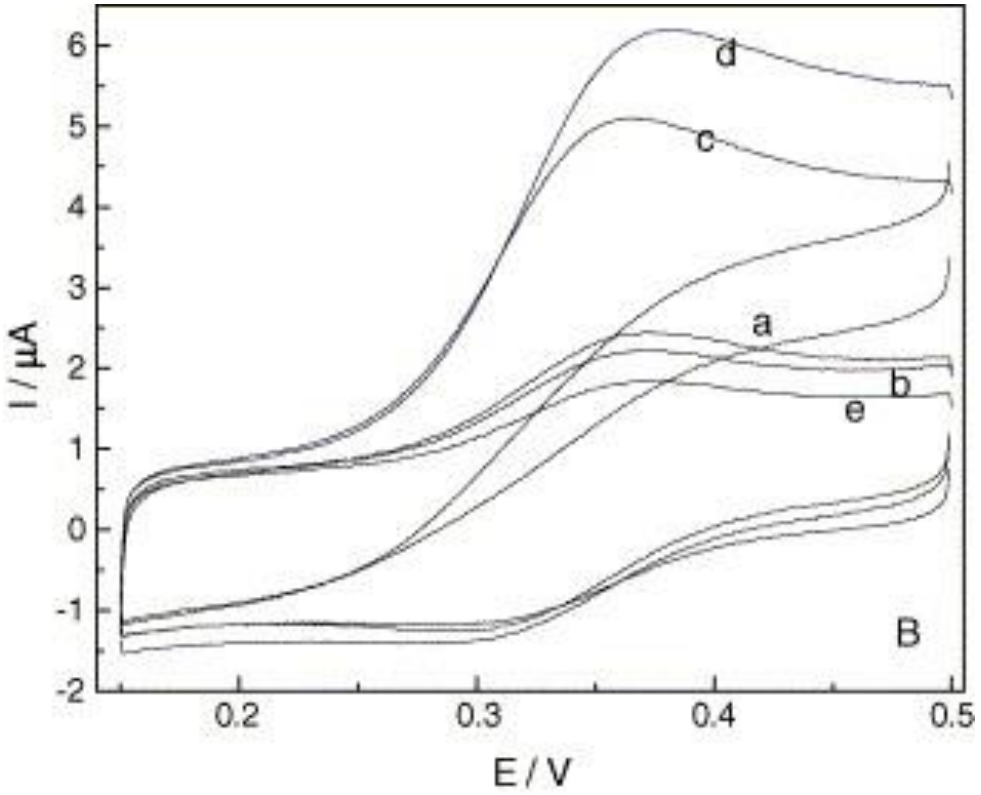


Application of Nanotubes



Biosensors: GLUCOSE BIOSENSOR

PREPARATION: CNTs are mixed in a solution of chitosan (polymer) with Glucose Oxidase (GOD) and The ferrocene monocarboxilic acid (FMCA). Finally, deposited on glassy carbon electrodes.



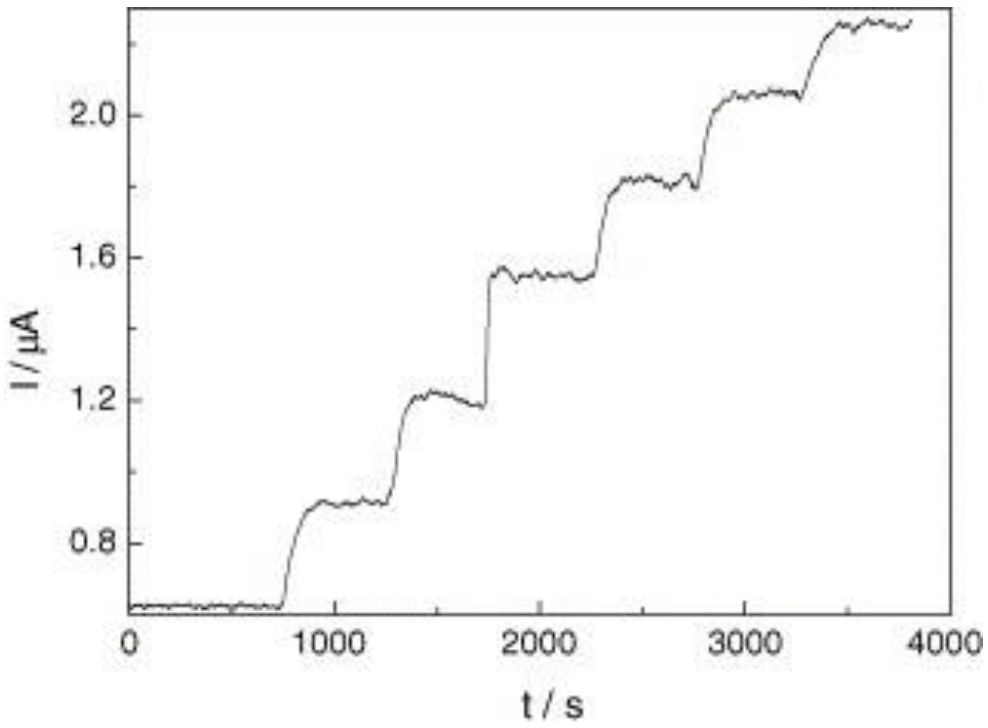
REACTION MECHANISM

The ferrocene monocarboxilic acid (FMCA) has been used as transducer:

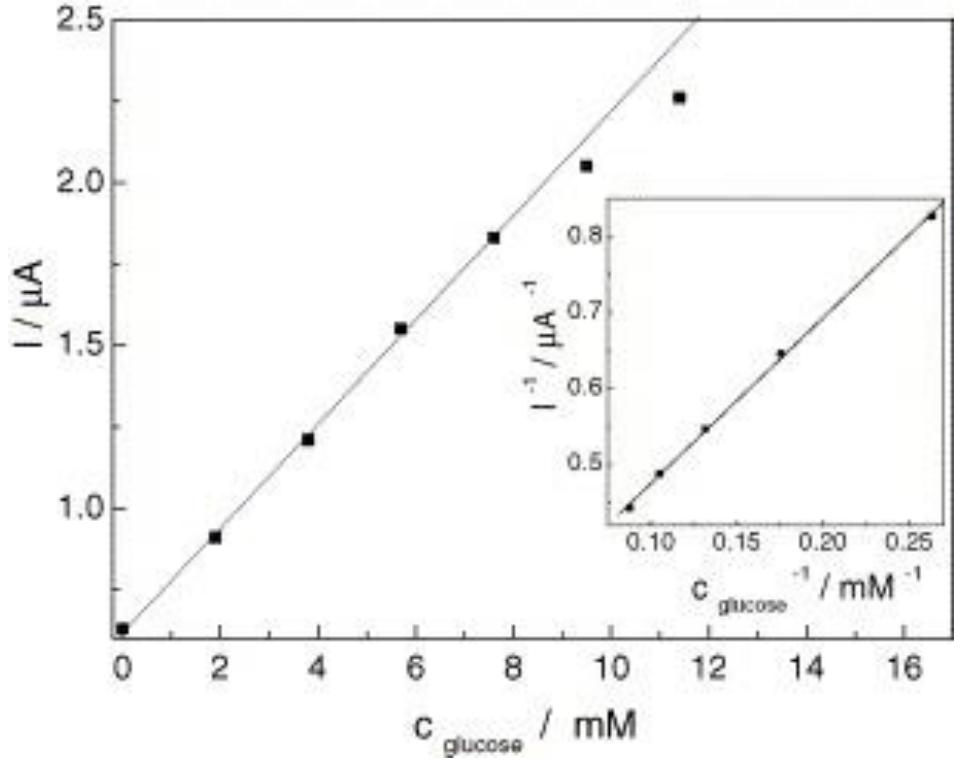
$$\text{glucose} + GOD_{OX} \rightarrow gluconolactone + GOD_{red}$$

$$GOD_{red} + 2FMCA^{+} \rightarrow GOD_{OX} + 2FMCA + 2H^{+}$$

CHRONOAMPEROMETRY



CALIBRATION CURVE

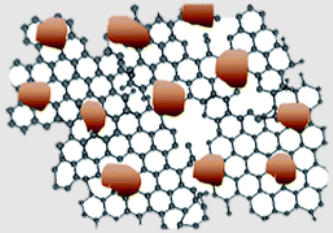


Sensitivity = 0.52 µA/mmol

LOD = 0.01 mmol

[1] Y. Liu, M. Wang, F. Zhao, Z. Xu, S. Dong, “The direct electron transfer of glucose oxidase and glucose biosensor based on carbon nanotubes/chitosan matrix”, Biosensors and Bioelectronics, Volume 21, Issue 6,2005, Pages 984-988,https://doi.org/10.1016/j.bios.2005.03.003.

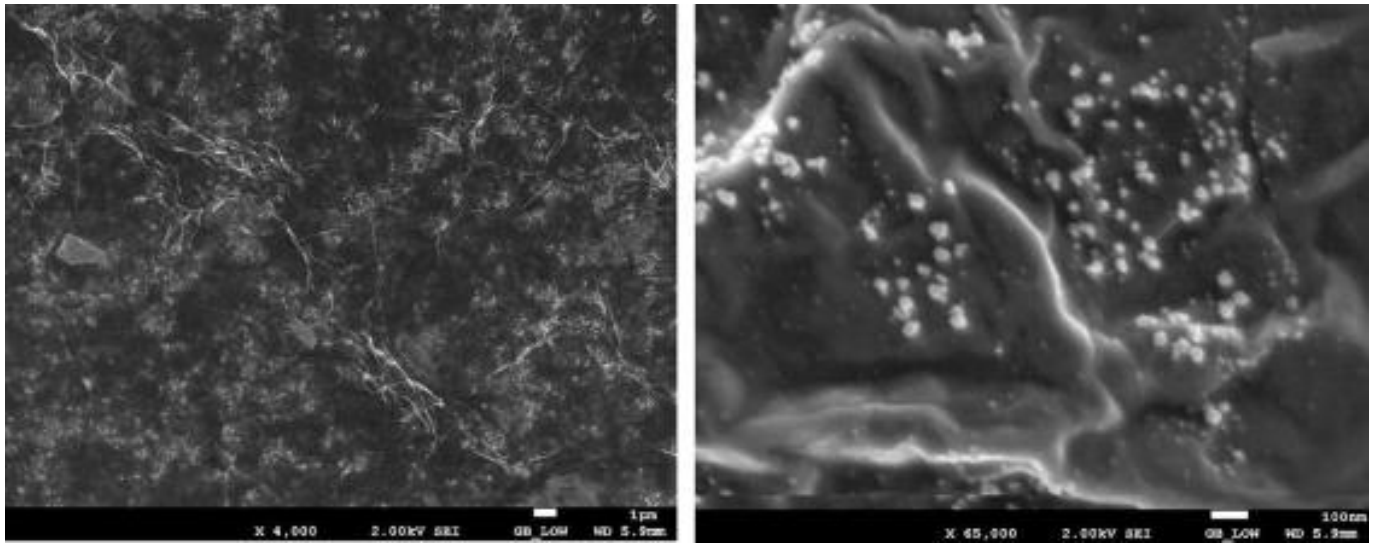
Application of graphene



Sensor for ELECTROCHEMICAL DETENCTION OF HEAVY METALS

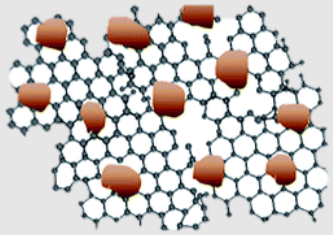
PREPARATION: graphene obtained from the reduction of Graphene Oxide was decorated with Sn NPs.

A mixture of GO and $SnCl_2$ is prepared, and deposited on glassy carbon electrodes. After drying, it is immerse in NaCl solution, and reduced applying a constant potential of -1 V for 15 min.

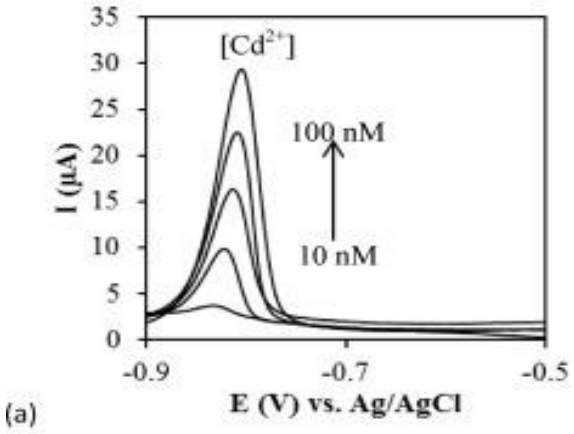


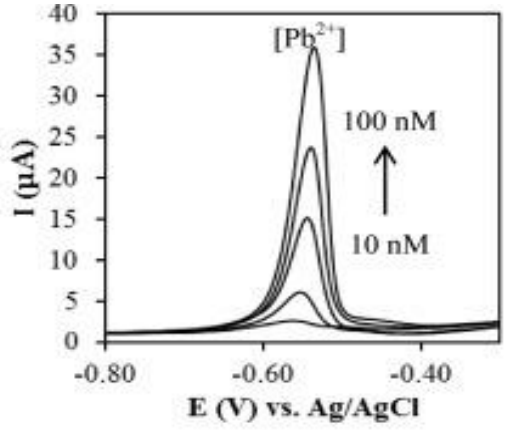
[2] P. M. Lee, Z. Chen, L. Li, E. Liu, "Reduced graphene oxide decorated with tin nanoparticles through electrodeposition for simultaneous determination of trace heavy metals", Electrochimica Acta, Volume 174, 2015, Pages 207-214, https://doi.org/10.1016/j.electacta.2015.05.092.

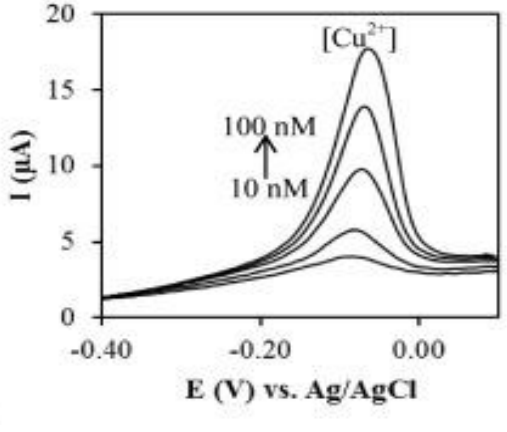
Application of graphene

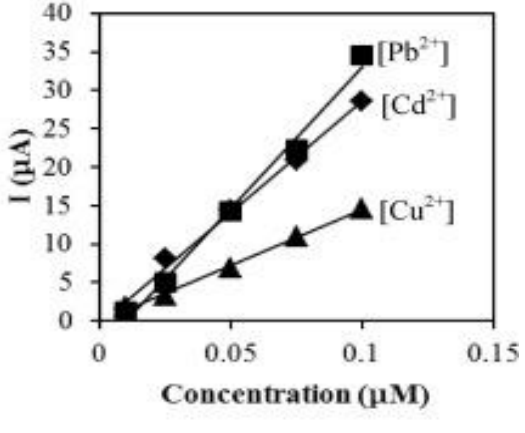


Sensor for Electrochemical detenction of heavy metals

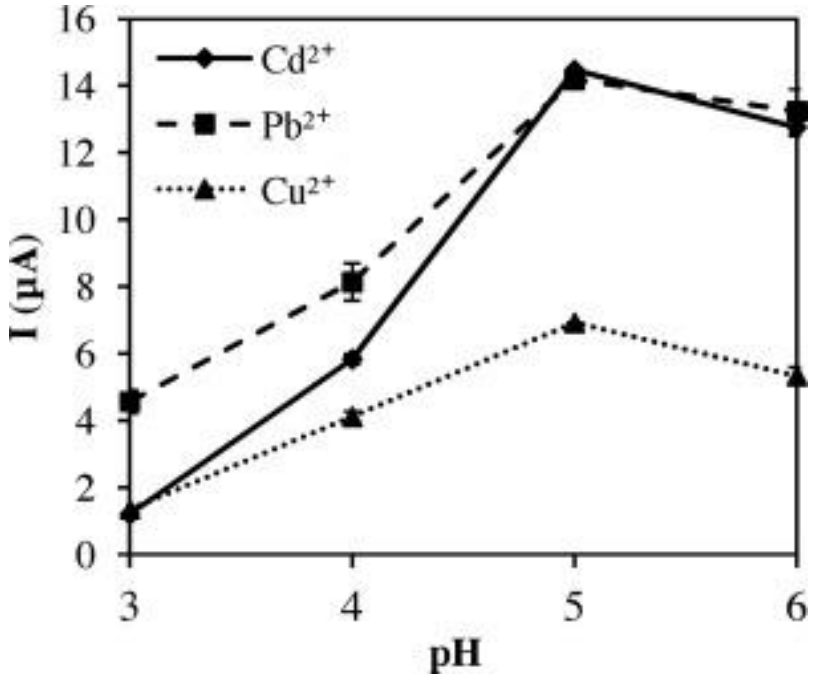




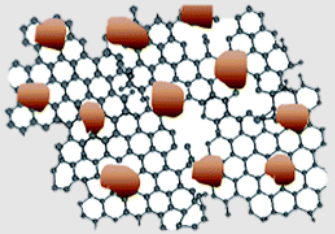




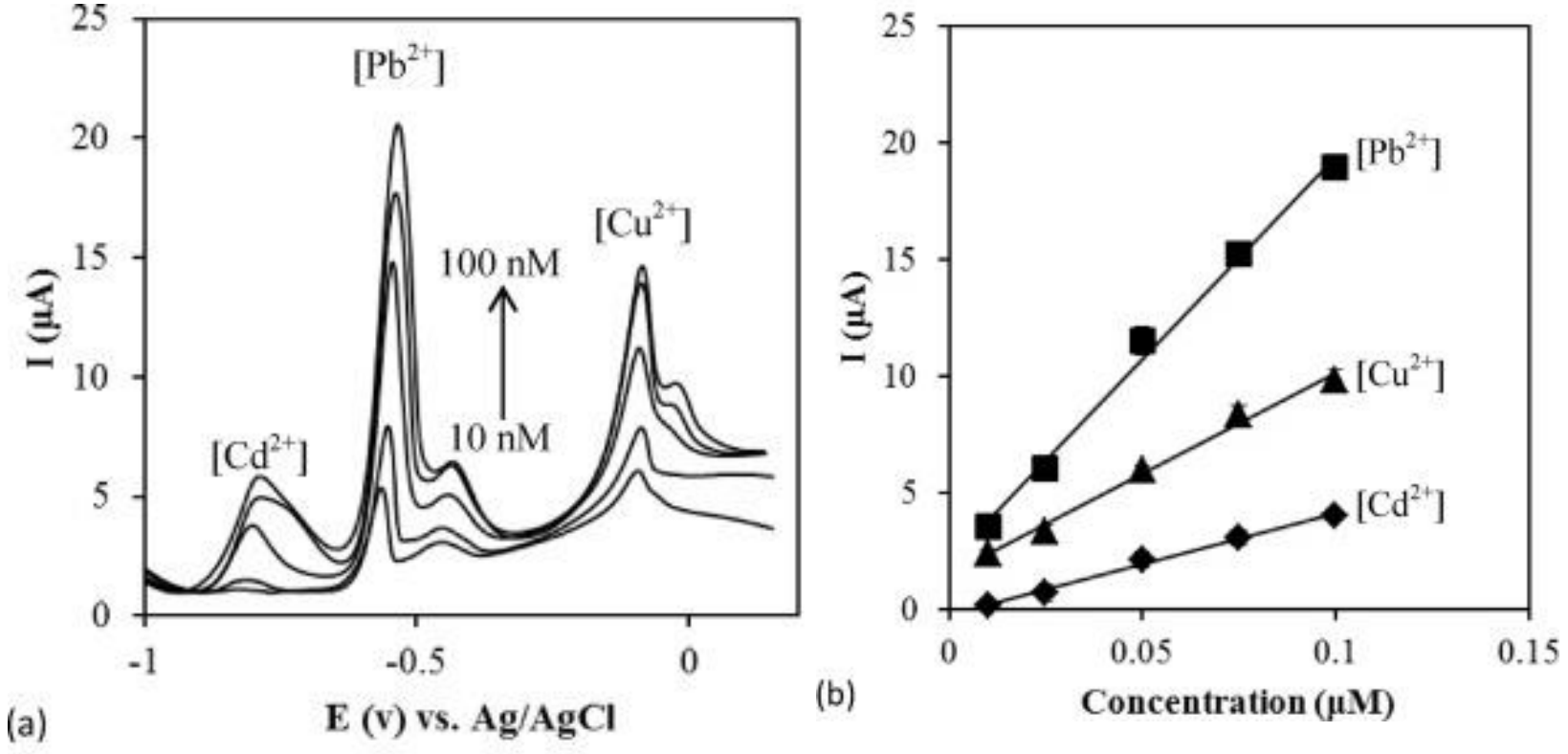
The electrodes were tested in presence of dissolved heavy metal ions: $\boldsymbol{Pb^{2+}}, \boldsymbol{Cd^{2+}}, \boldsymbol{Cu^{2+}}$, in solution.



Application of graphene



Sensor for Electrochemical detenction of heavy metals



LOD(Pb) = 0.63 nM

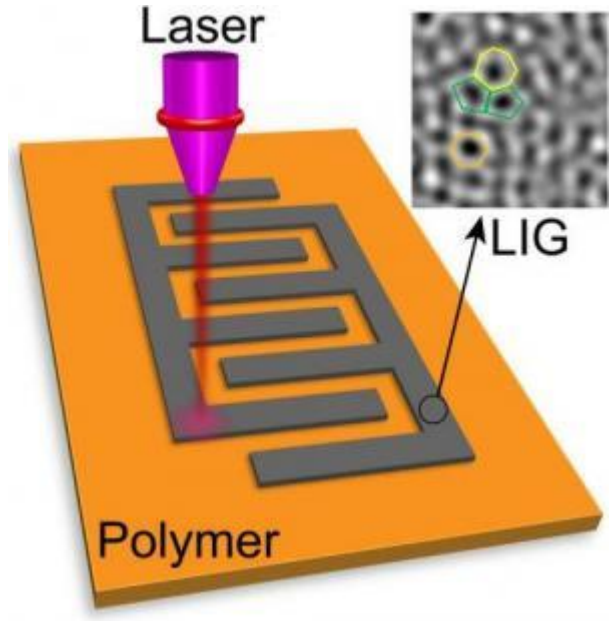
LOD(Cd) = 0.60 nM

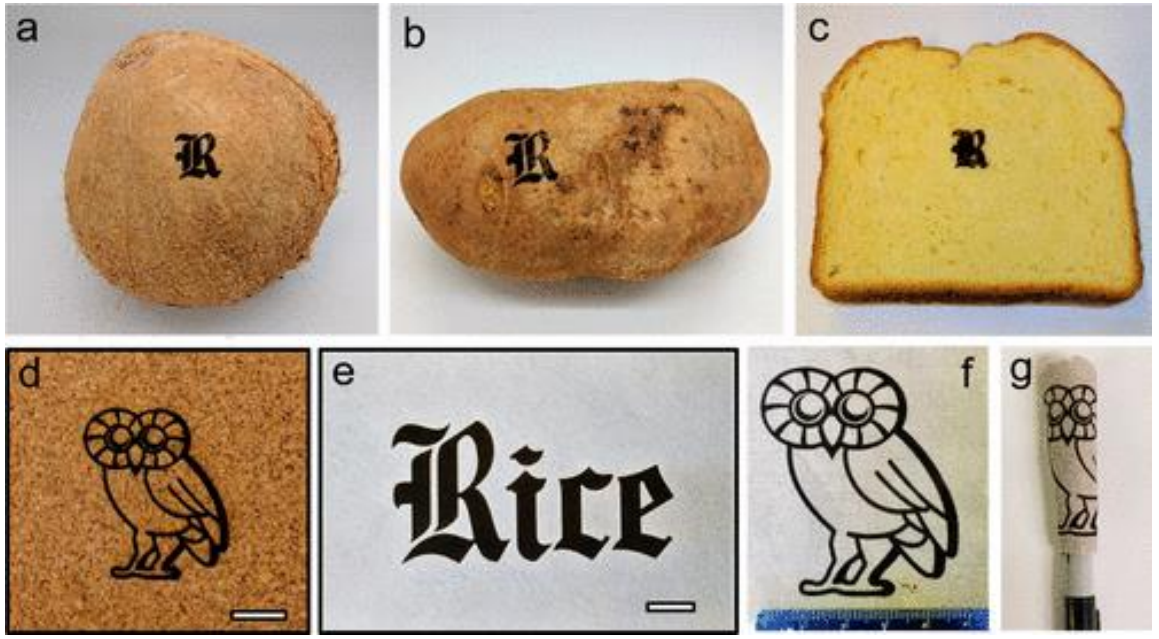
LOD(Cu) = 0.52 nM

[2] P. M. Lee, Z. Chen, L. Li, E. Liu, "Reduced graphene oxide decorated with tin nanoparticles through electrodeposition for simultaneous determination of trace heavy metals", Electrochimica Acta, Volume 174, 2015, Pages 207-214, https://doi.org/10.1016/j.electacta.2015.05.092.

LASER INDUCED GRAPHENE

Recently a **novel method** of graphene synthesis has been discovered. The **direct irradiation** by a **laser source** of a polymeric substrate **result in a few layer graphene** material called **LIG** (Laser Induced Graphene)

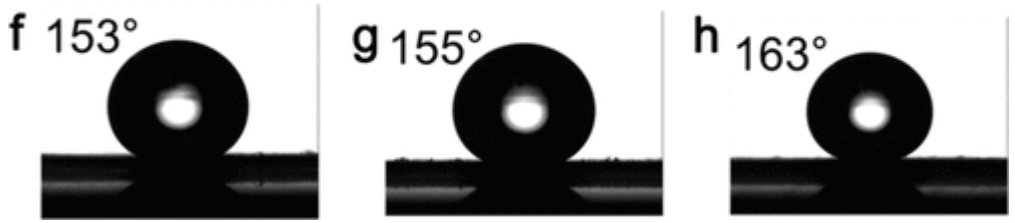


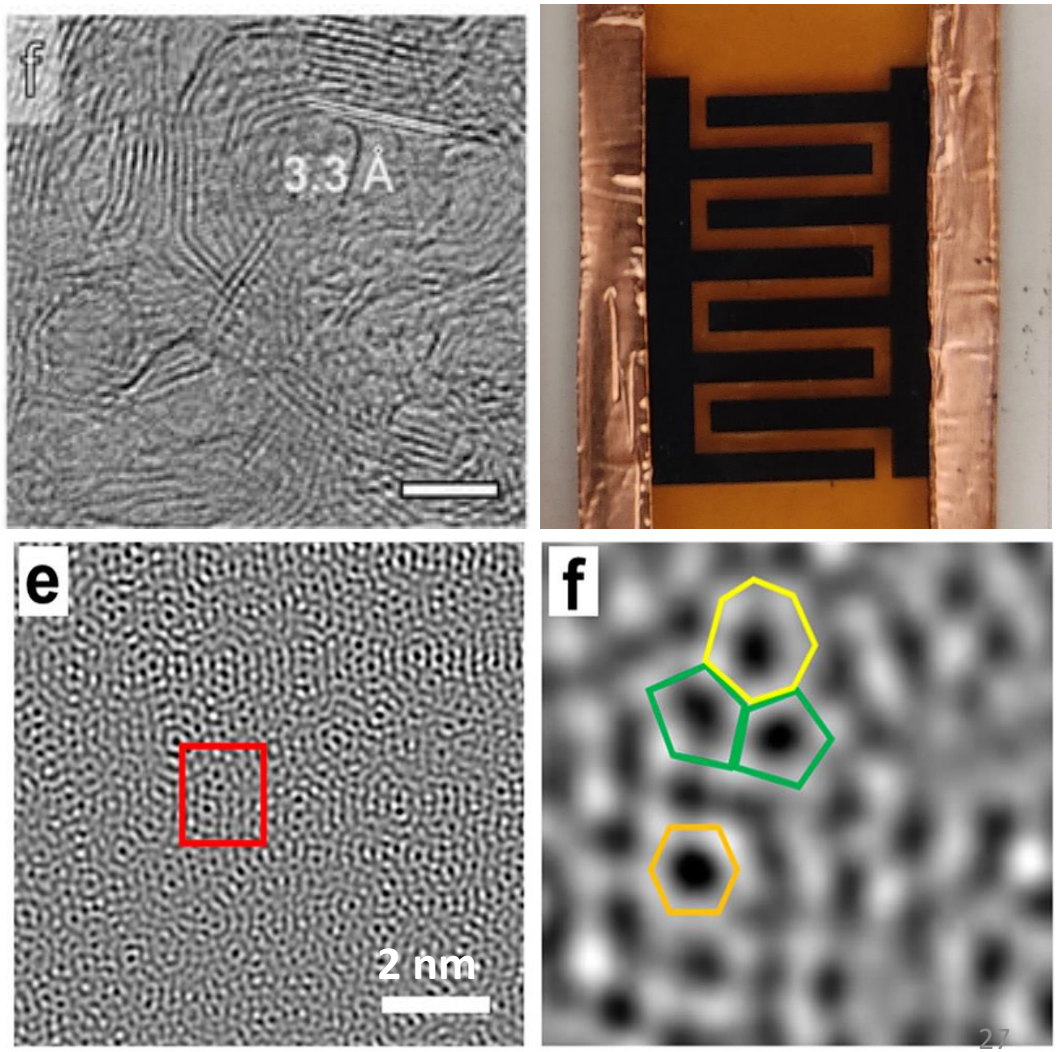


LASER INDUCED GRAPHENE

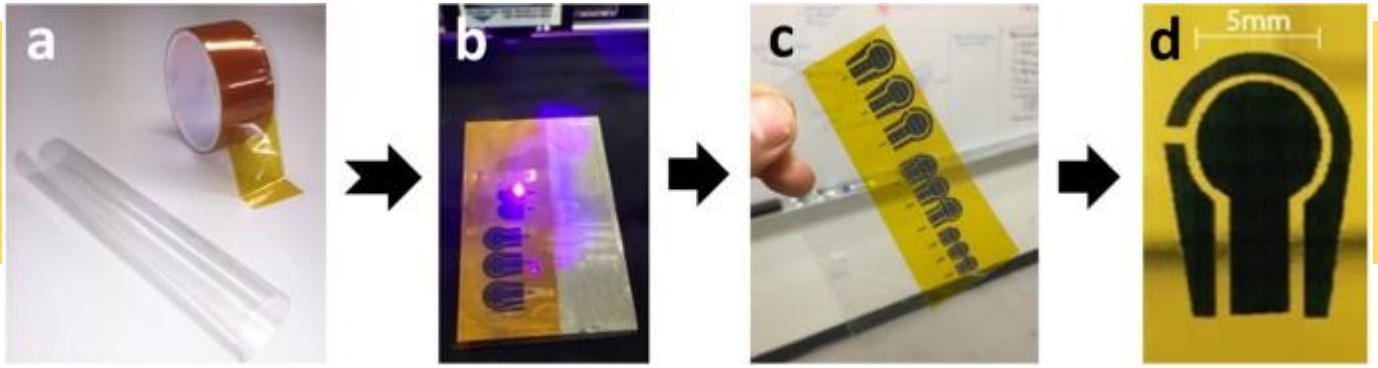
PHYSICAL AND CHEMICAL PROPERTIES

- High conductivity ***(25 S cm^{-1})***
- High porosity ***(340 m^2/g)***
- ***Kinetic Graphene***: lattice made of hexagon and ***pentagon-heptagon*** rings
- Flexibility
- Fast production
- Cheap





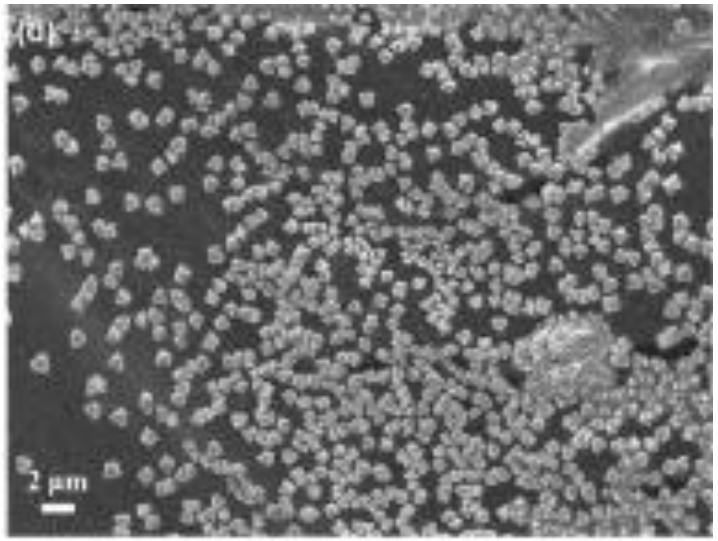
Application of LIG

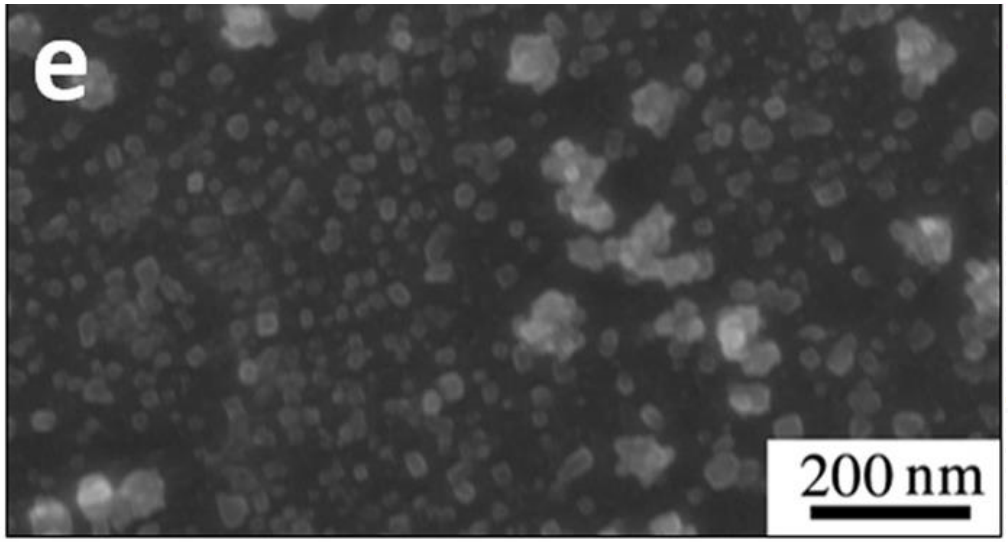


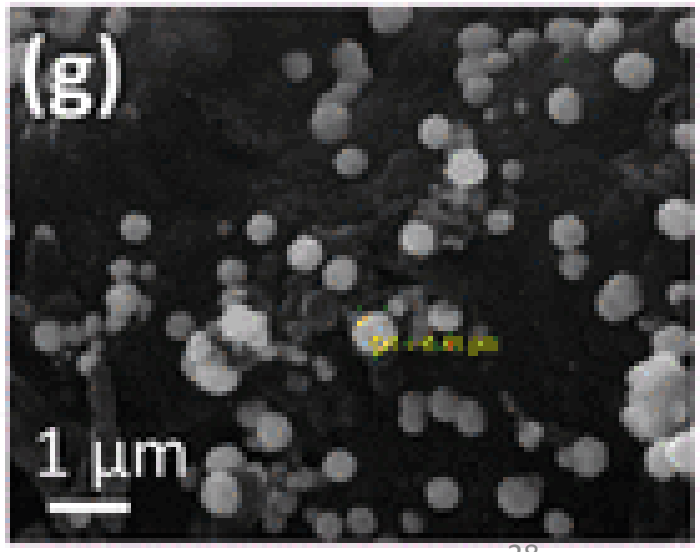
ENZYME-FREE GLUCOSE SENSOR

LIG can be decorated with metallic nanoparticles to increase the catalytic activity through glucose oxidation.

COPPER (Cu)

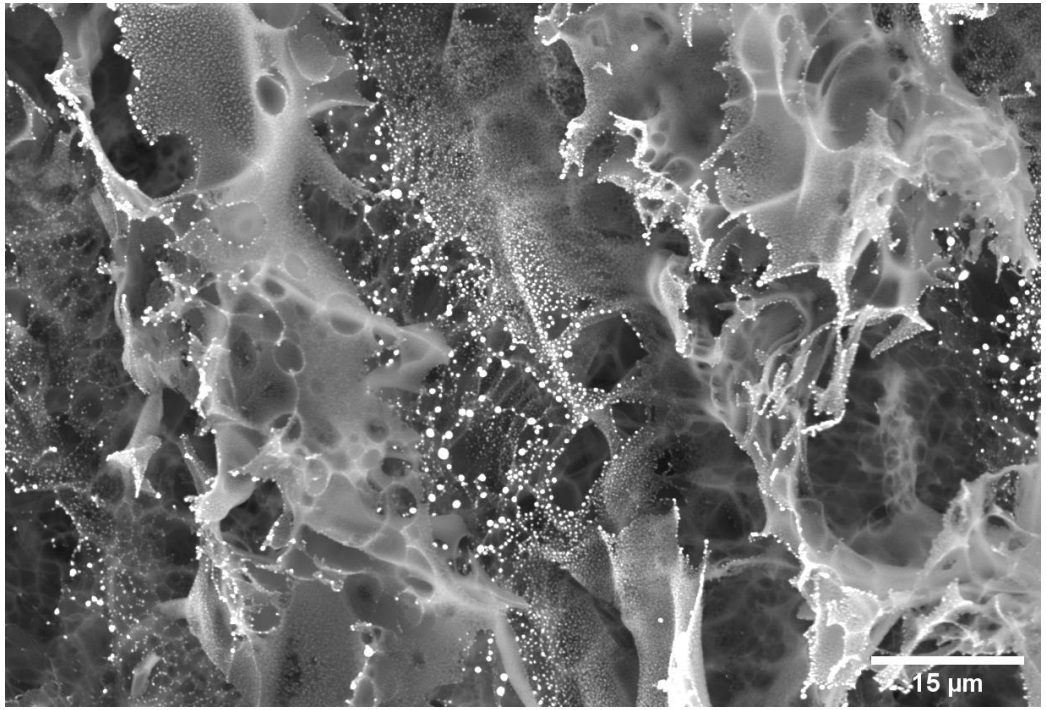


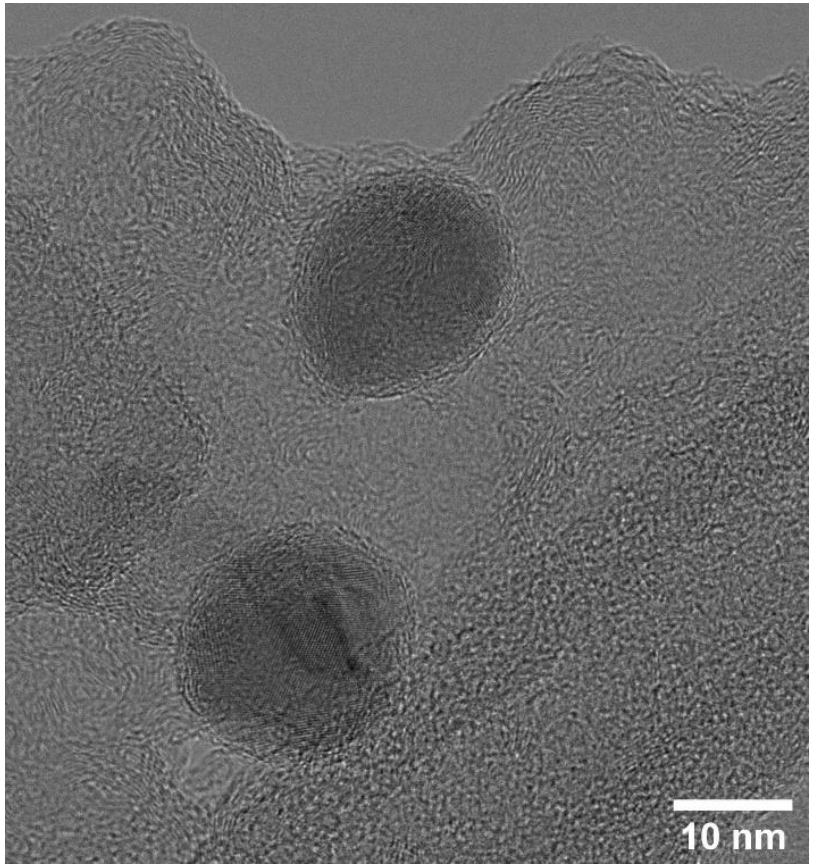




Application of LIG

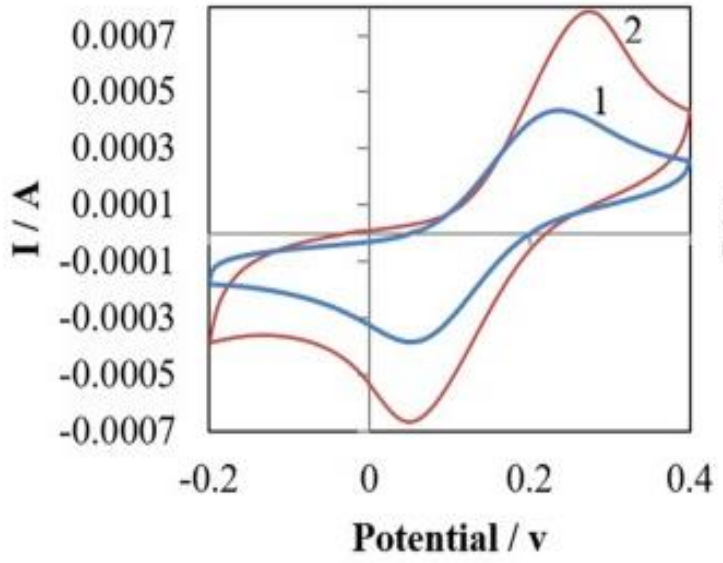
ENZYME-FREE GLUCOSE SENSOR

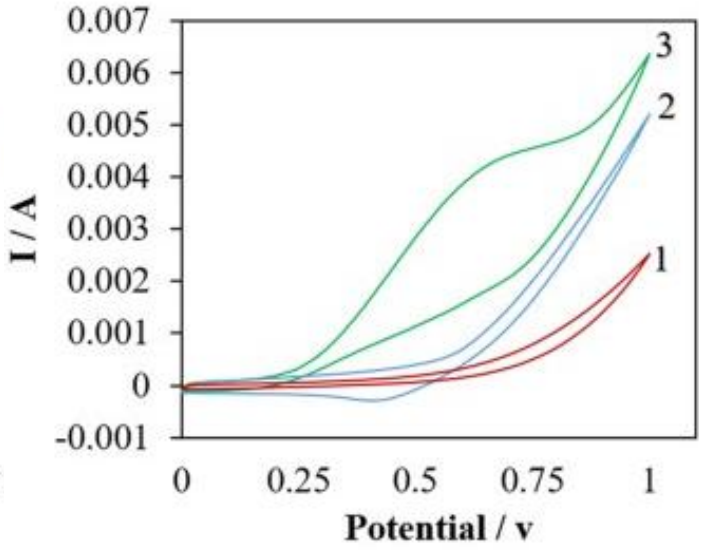


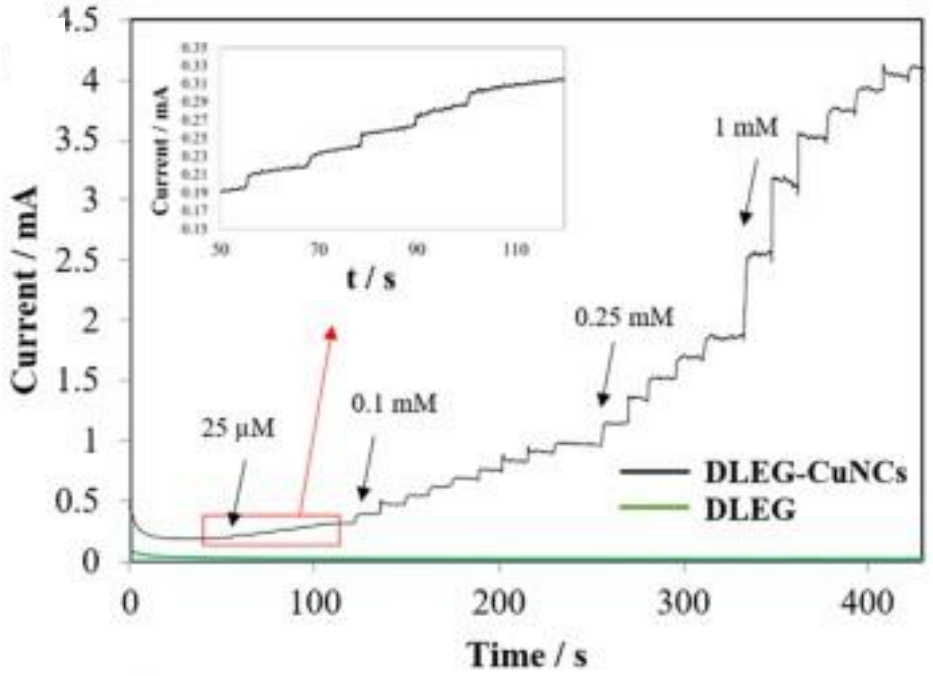


CHARACTERISATION

1) **CV** with $Fe[(CN)_6]^{4-}$ to determine the **active area** and the **kinetic** at the interface of the electrode.
2) **CV** in presence of **glucose** (detect the potential of oxidation).
3) **CHRONOAMPEROMETRY** for calibration.





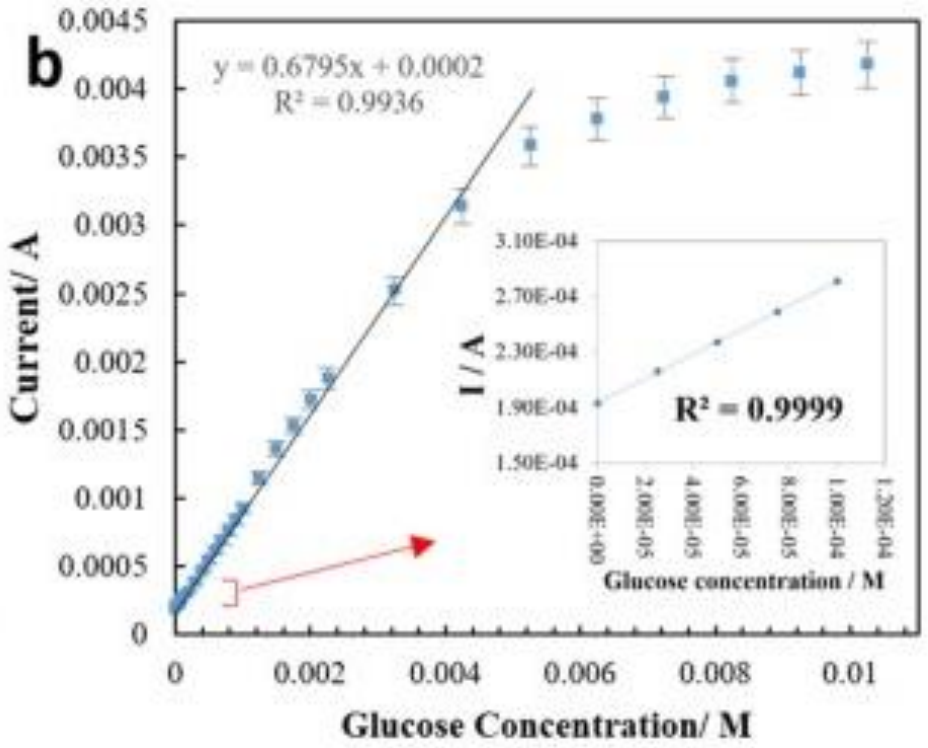


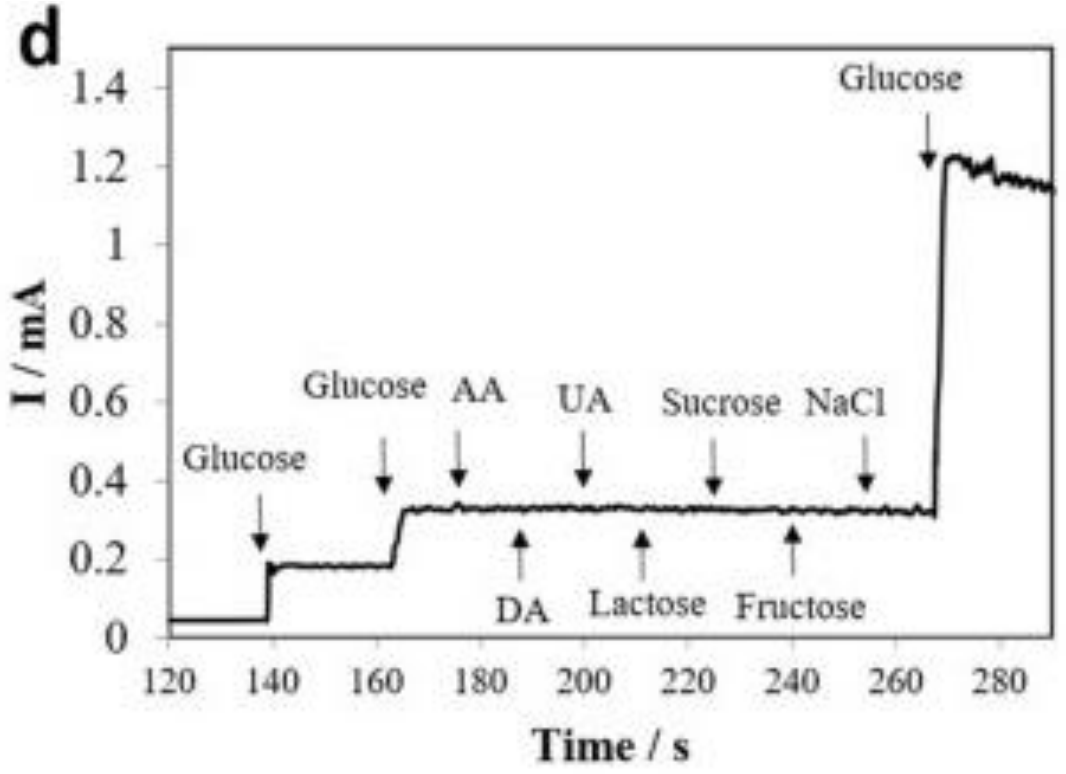
[3] Tehrani, Farshad, Bavarian, Behzad, 2016, 2016/06/16TI, "Facile and scalable disposable sensor based on laser engraved graphene for electrochemical detection of glucose", Scientific Reports, 27975, 6I 1AB, 2045-2322, https://doi.org/10.1038/srep27975

CHARACTERISATION

4) **PLOT** of the calibration curve (**sensitivity** and **LOD**).

5) **SELECTIVITY** among other analytes.





[3] Tehrani, Farshad, Bavarian, Behzad, 2016, 2016/06/16TI, "Facile and scalable disposable sensor based on laser engraved graphene for electrochemical detection of glucose", Scientific Reports, 27975, 6I 1AB, 2045-2322, https://doi.org/10.1038/srep27975

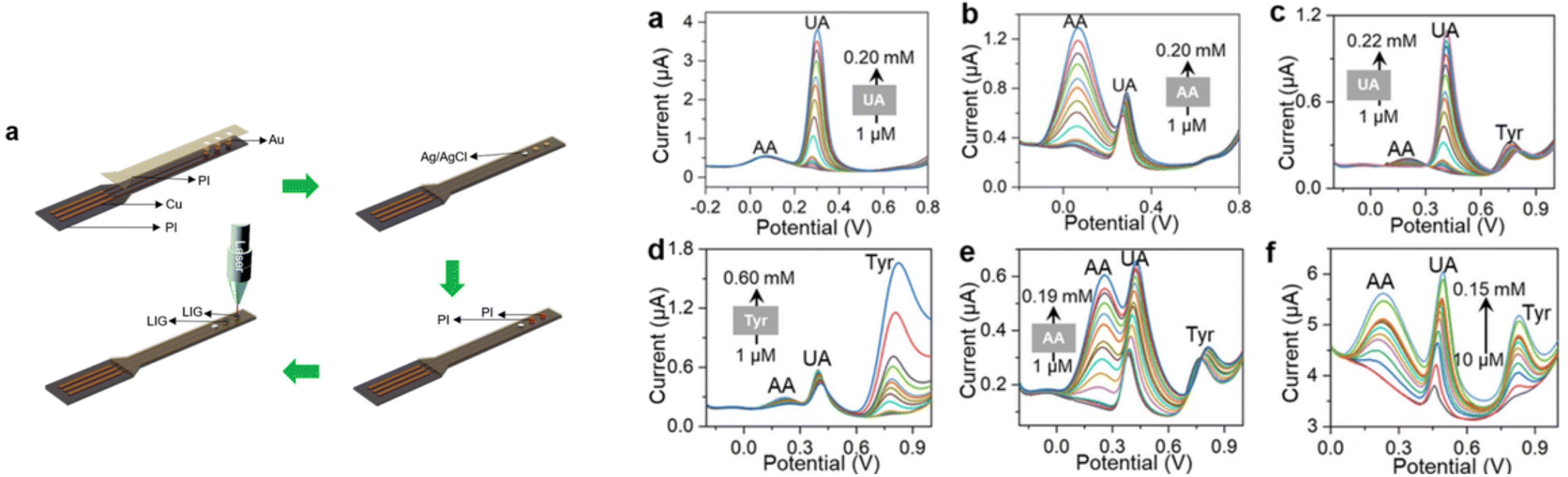
Comparison

Materials	Functionalization Technique	Characteristics	Analysis Method
Graphene, copper nanocubes, Polyimide	Electroplating	Avg. resistance value: 15.6 Ω/cm Sensitivity: 1643.31 μA/mm·cm^2 Linear range: 0.05 mm–1 m Limit of detection: 0.05 mm	Cyclic voltammetry
Graphene, copper nanocubes, polyvinyl chloride	Electrodeposition	Sensitivity: 1643.31 μA/mm·cm^2 Linear range: 25 μm–4 mm Limit of detection: 250 nm Reproducibility: 96.8% Stability: 97.4%	Cyclic voltammetry
Graphene, copper nanoparticles, Polyimide	Chrono-potentiometry	Sensitivity: 1438.8 μA/mm·cm^2 Limit of detection: 124 nm	Cyclic voltammetry
Graphene, copper nanoparticles, Zinc foil, polyethylene terephthalate (PET)	Substrate-assisted electroless deposition	Sensitivity: 495 μA/mm·cm^2 Limit of detection: 0.39 μm Response time: <0.5 s	Cyclic voltammetry
Graphene, copper oxide nanoparticles, commercial scotch brand tape	3D patterning	Linear range: 1 μm–5 μm Limit of detection: 0.1 μm Response time: <0.2 s	Cyclic voltammetry
Graphene, copper oxide,	Electrodeposition	Sensitivity: 1321.54 μAL/mmol·cm^2 Reproducibility: 5.47%	Cyclic voltammetry

Application of LIG

ENZYME-FREE TYROSINE, URIC ACID, ASCORBIC ACID SENSOR

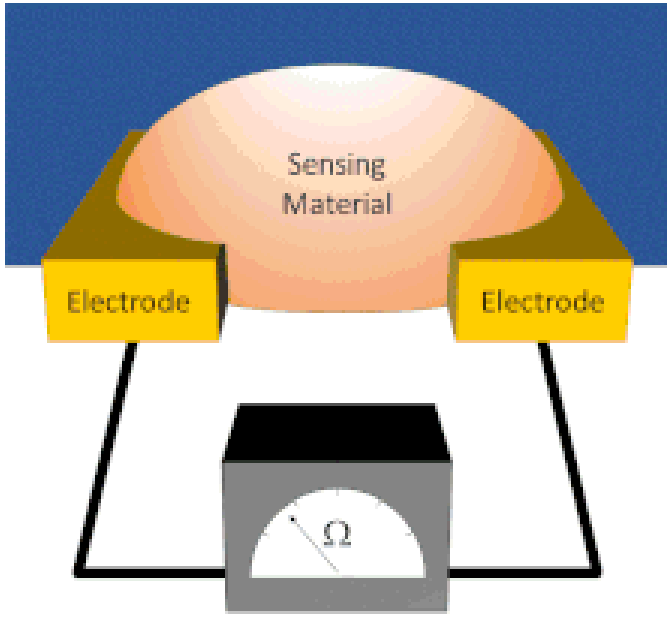
LIG can be directly used as electrodes for Tyrosine, Uric Acid and Ascorbic Acid detenction in sweat. Those species oxidise at different potentials



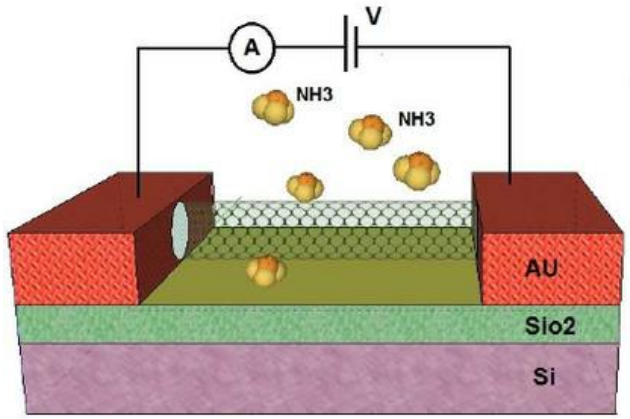
[4] S.Chen, Z. Cao, K. Zhou, S. Li, H. Li, K. Xu, H. Tang, H. Deng, Q. Zhou, J. Pan, F. Xia, "Screen printing and laser-induced flexible sensors for the simultaneoussensitive detection of uric acid, tyrosine, and ascorbic acid in sweat", *Analyst*, 2023, **148**, 2965-2974, DOI: 10.1039/D3AN00591G

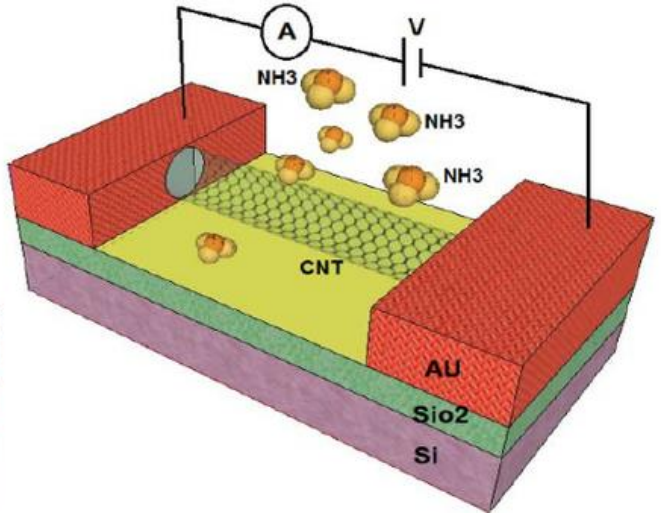
CHEMIRESISTOR (GAS SENSOR)

Gas sensors can be projected in different way. The most diffused is **chemiresistor system**. The **resistance** between two conductive electrodes is measured at **different concentration of specific gases**.



Electrical Resistivity Measurement





CHEMIRESISTOR (GAS SENSOR)

The key parameter is the **change of resistance**

$$\frac{\Delta R}{R} = \frac{R_a - R_g}{R_a} \times 100$$

The channel resistance changes in presence of specific gas molecules:

1. Change of **thermal conductivity** $\boldsymbol{\kappa}\ \left[\frac{\boldsymbol{mW}}{\boldsymbol{mK}}\right]$
2. **Chemical interaction** (loss or gain of electrons/holes)

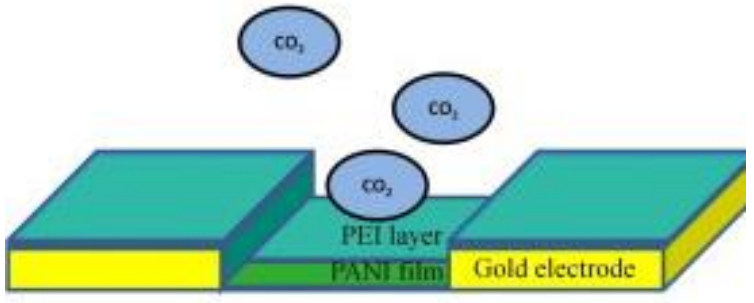
CHEMIRESISTOR (GAS SENSOR)

1) Change of Thermal conductivity

The current flowing through the channel is origin of **Joule effect** ($Q = P \cdot t = I^2 R \cdot t$)

Since the channel resistance **depend on the temperature**, it depends on the current flowing, due to the Joule effect, but also on the **dissipation of heat** thanks to the gas around the filament.

Each gas has his **specific thermal conductivity (κ)**, so the heat dispersion will be different, consequently the local temperature and the resistance.

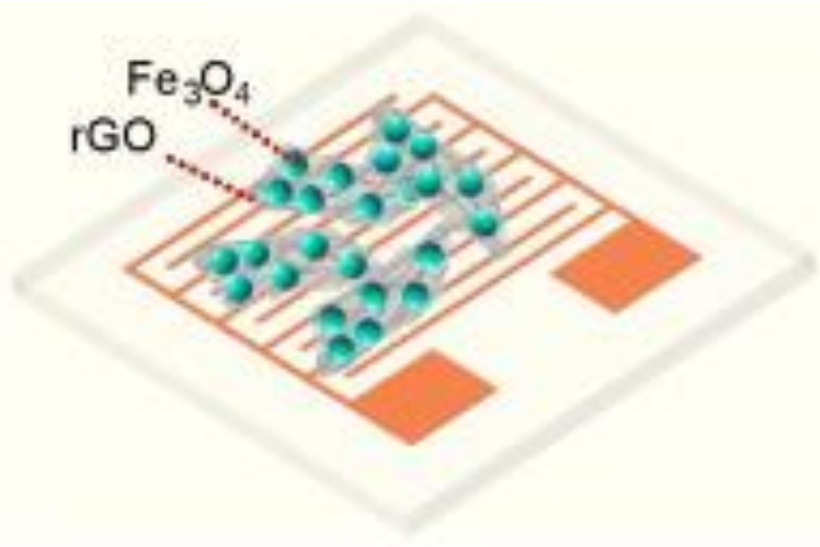


CHEMIRESISTOR (GAS SENSOR)

2) Chemical interaction

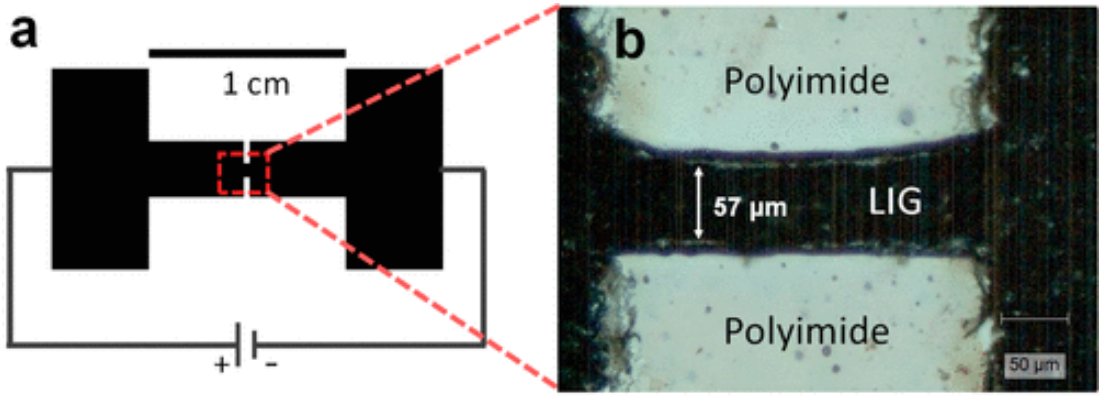
Changing in relative resistance can be caused by the **releasing of electrons** through the **chemical interaction** between the channel and the gas.

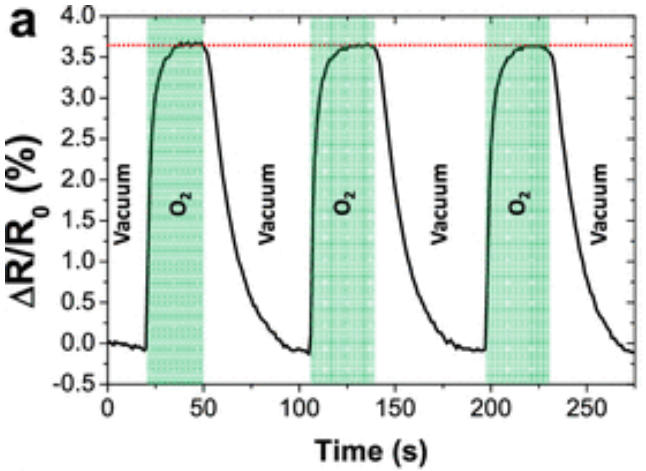
For those application, the **channel can be decorated** with extra species or molecules able to react with the enviromental gas

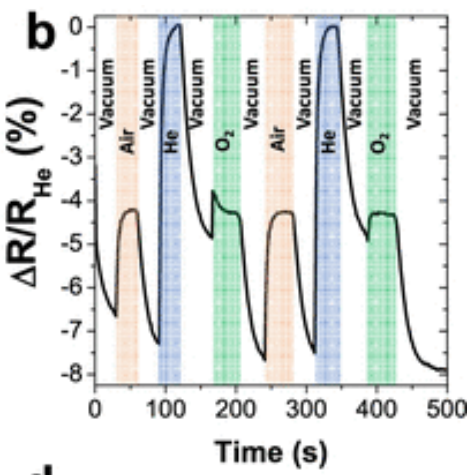


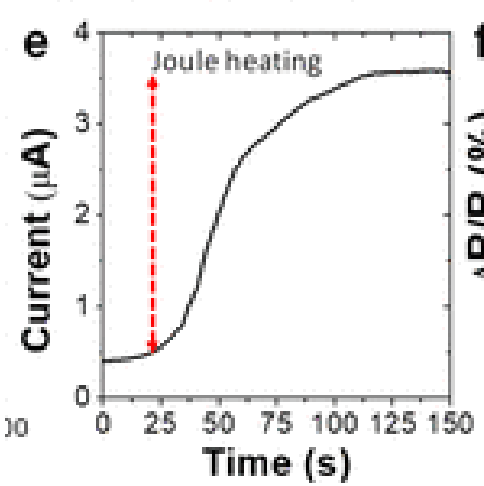
LIG FOR GAS SENSOR

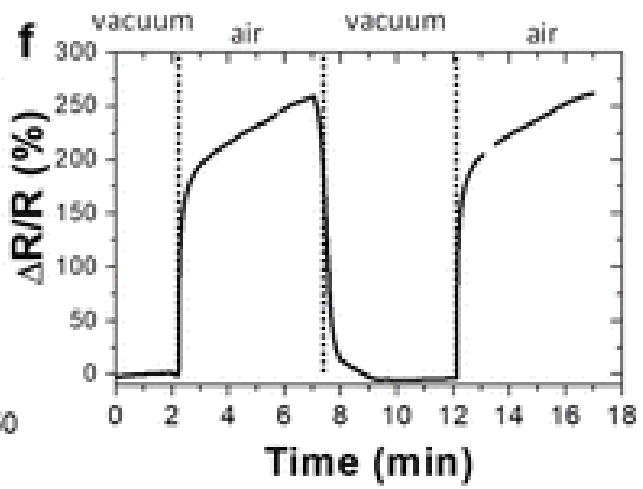
He, N2, O2 and CO2 gas sensor

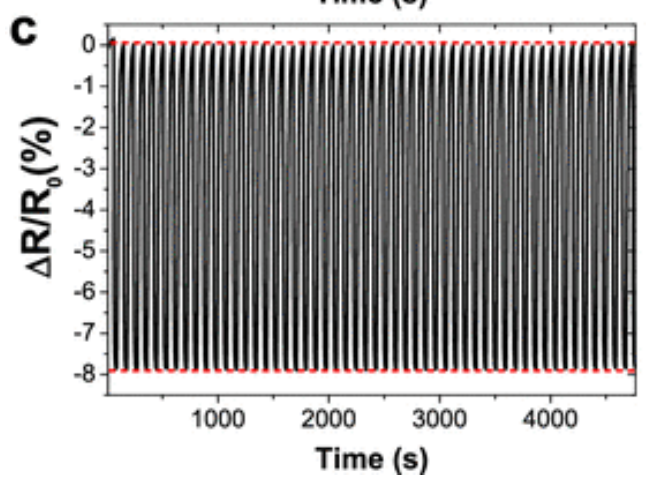


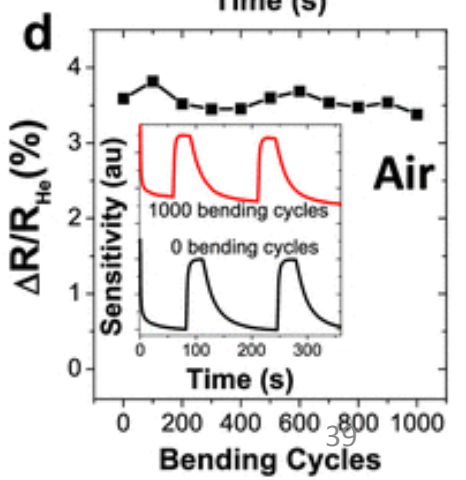








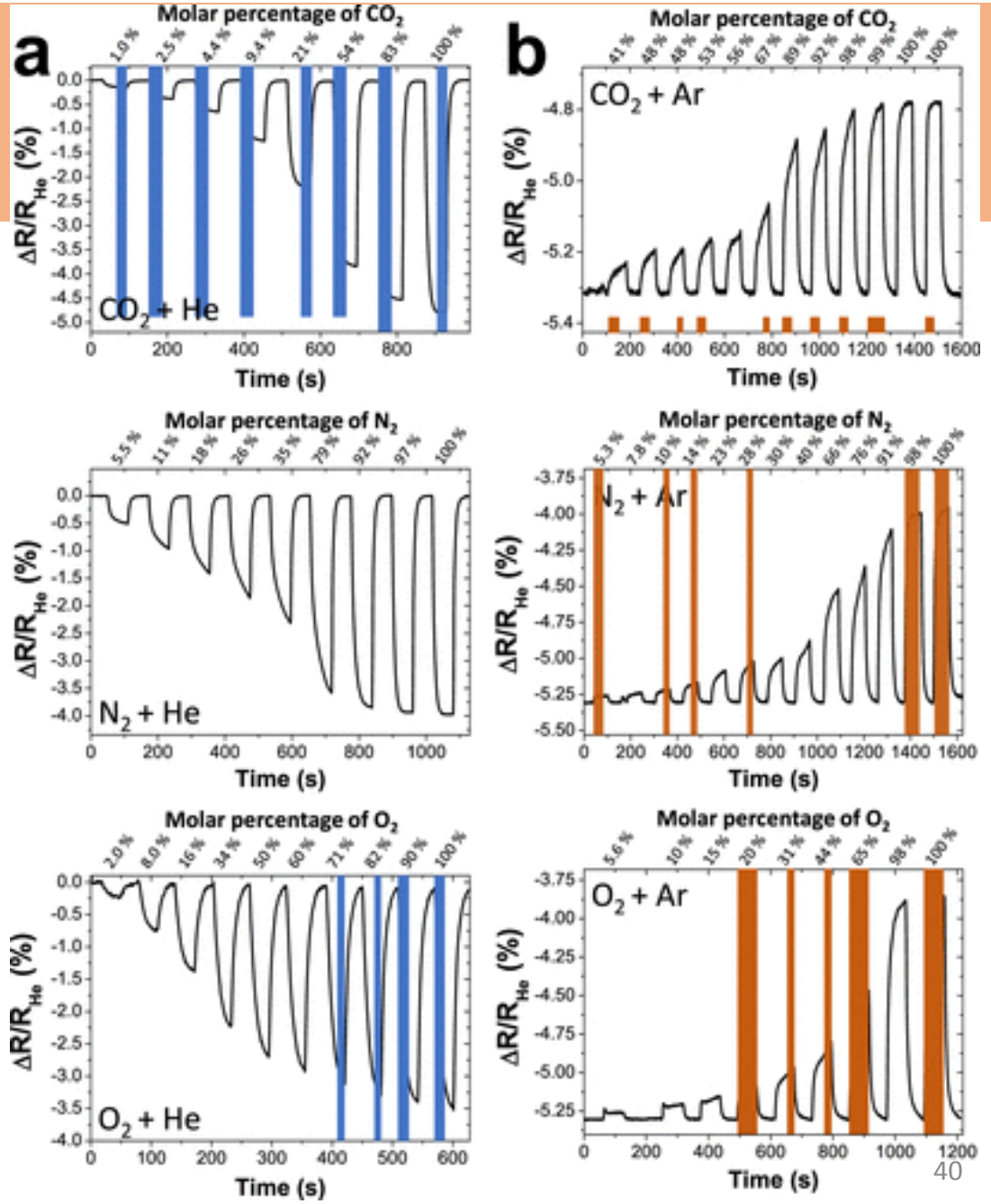




LIG FOR GAS SENSOR

He, N2, O2 and CO2 gas sensor

It is possible to understand the relative percentage of gases with opportunity post processes calculation taking into account of thermal conductivtiy of each gas.

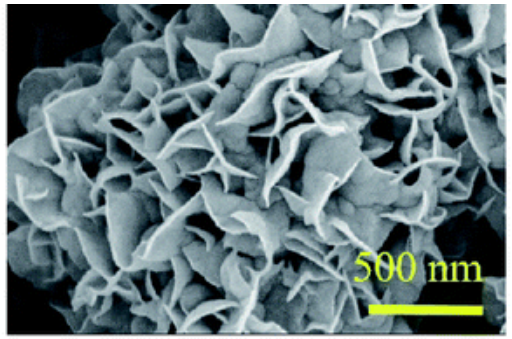


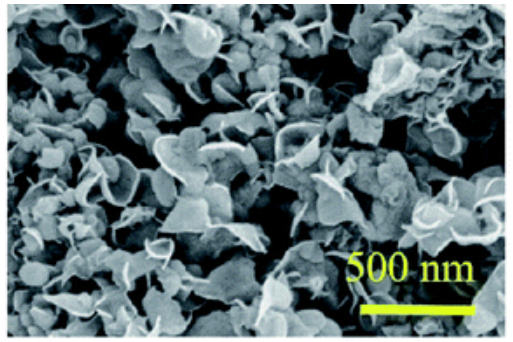
[5] " Laser-Induced Graphene for Flexible and Embeddable Gas Sensors", Michael, Yang, Kaichun, Chyan, Yieu, Kittrell, Carter, Tour James M., 2019, 3474-3482, 13,American Chemical Society, doi: 10.1021/acsnano.8b09622

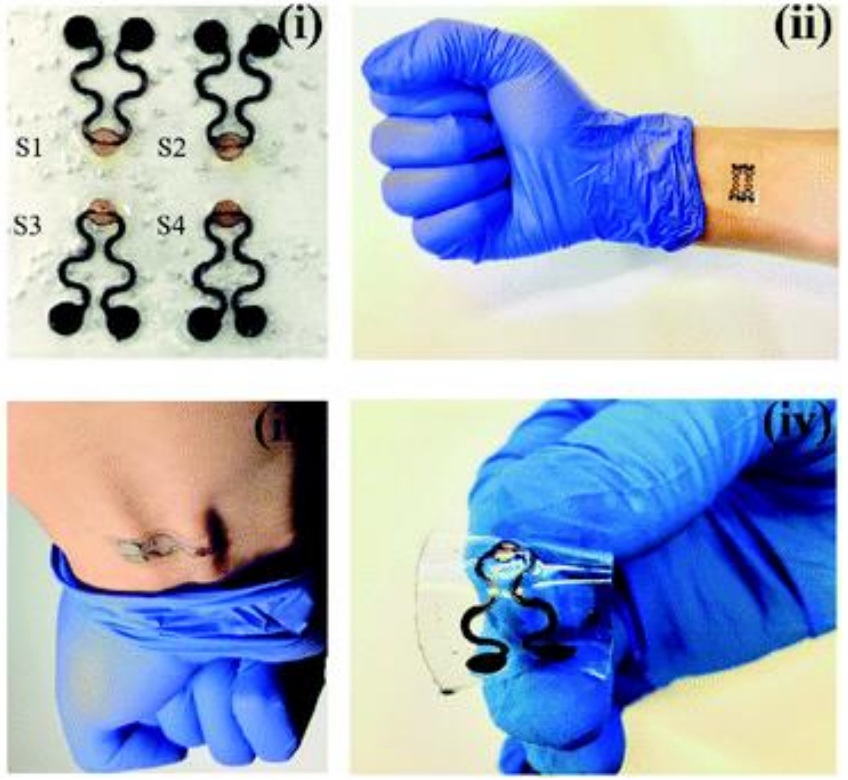
LIG FOR GAS SENSOR

NO_2 gas sensor

In this case an extra compound is added at the channel (MoS_2), in order to be selective on NO_2 gas detection



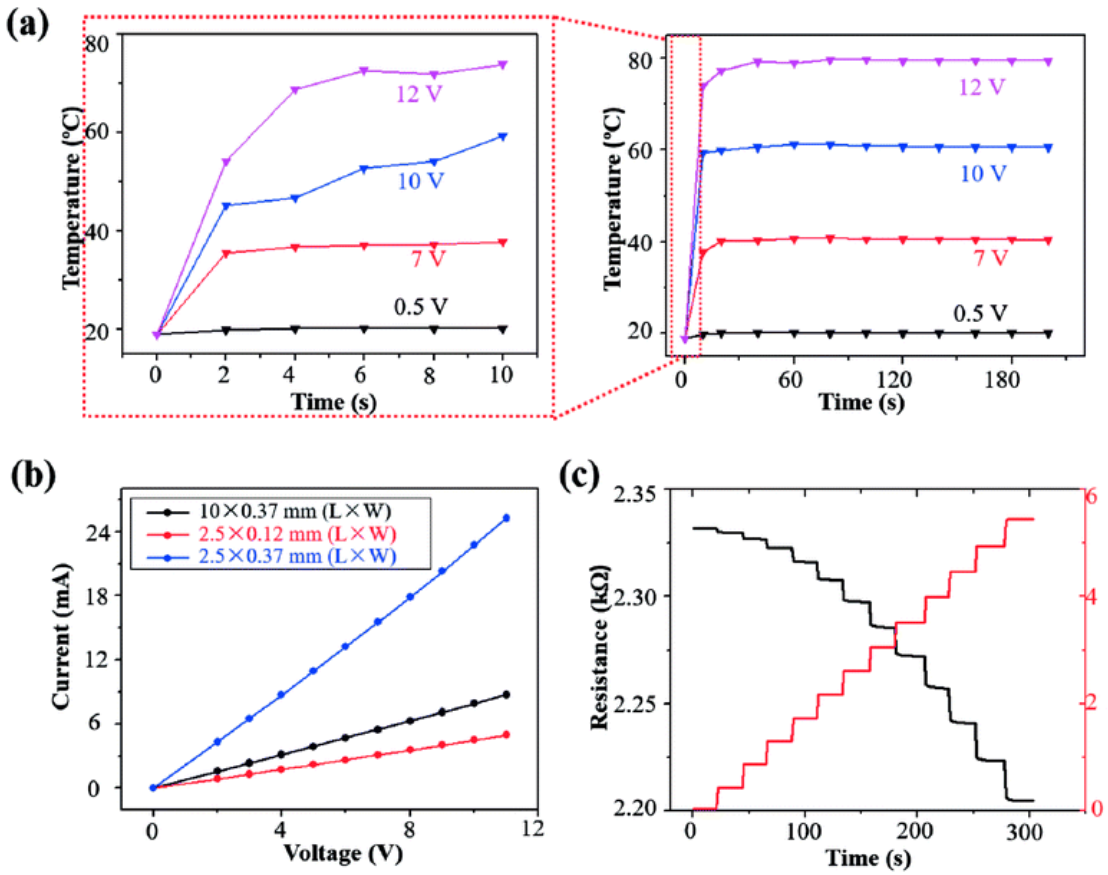


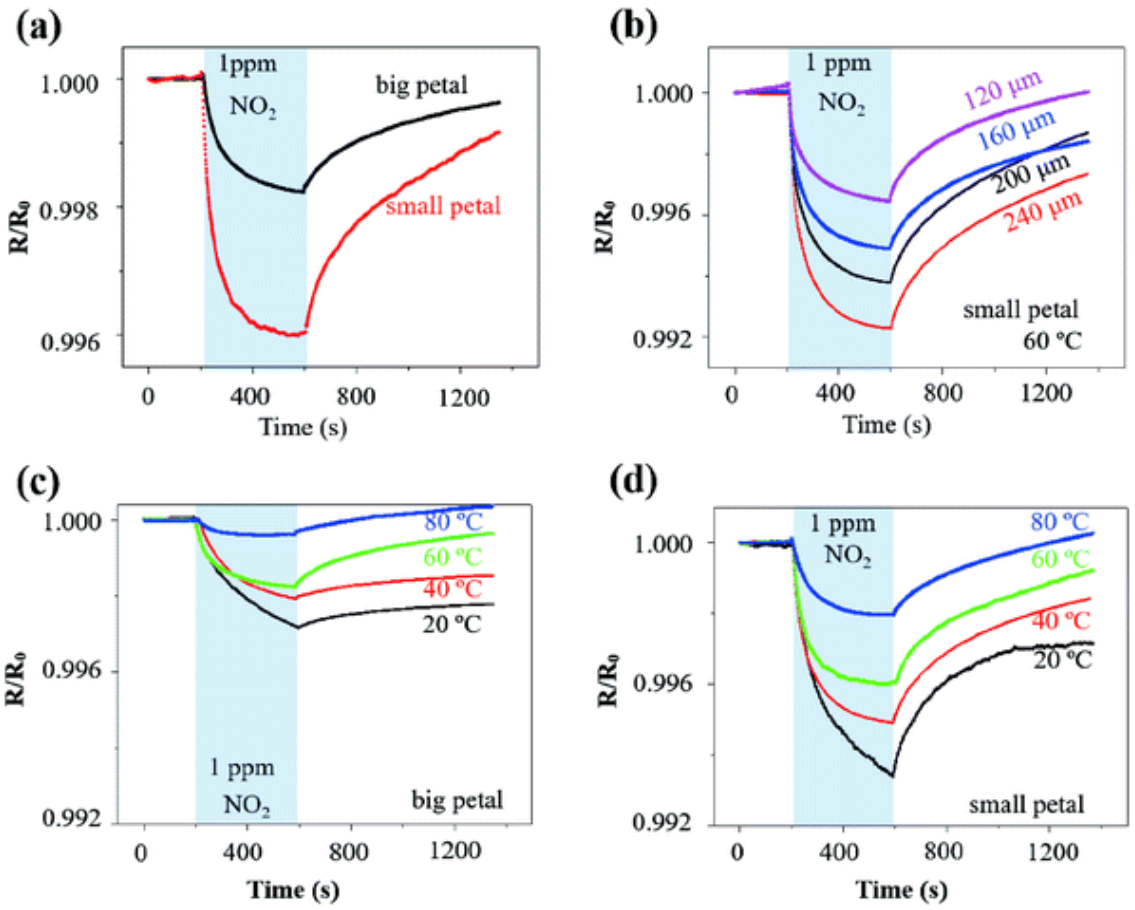


[6] L.Yang, N. Yi, J. Zhu, Z. Cheng, X. Yin, X. Zhang, H. Zhu and H. Cheng, "Novel gas sensing platform based on a stretchable laser-induced graphene pattern with self-heating capabilities ", *J. Mater. Chem. A*, 2020, 8, 6487-6500, DOI: 10.1039/C9TA07855J

LIG FOR GAS SENSOR

NO_2 gas sensor



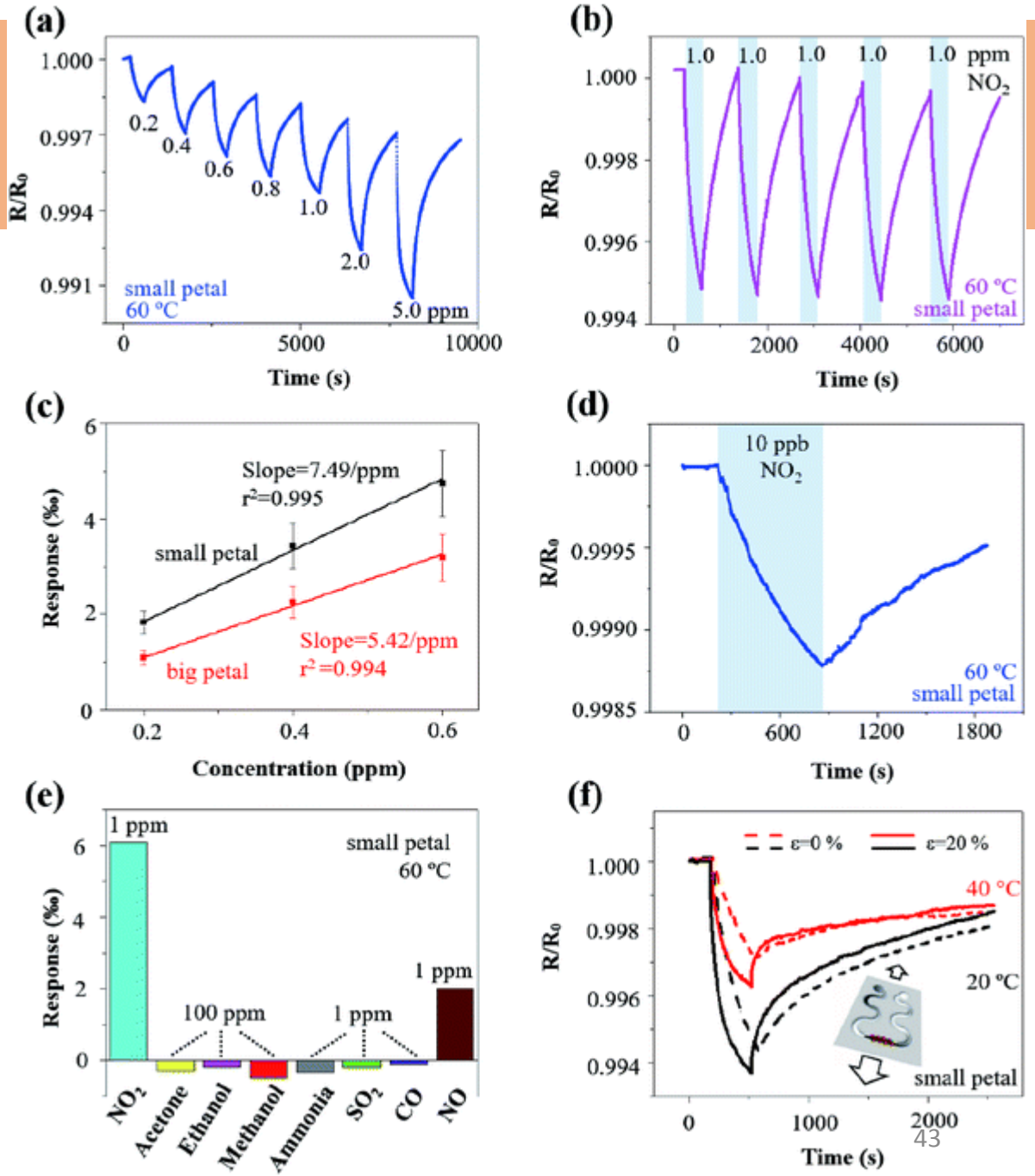


LIG FOR GAS SENSOR

NO₂ gas sensor mechanism promoted by MoS₂

$$NO_2(gas) + e^- \rightarrow NO_2^-(ads)$$

$$NO_2(gas) + O^- + e^- \rightarrow NO(ads) + 2O^-$$



[6] L.Yang, N. Yi, J. Zhu, Z. Cheng, X. Yin, X. Zhang, H. Zhu and H. Cheng, "Novel gas sensing platform based on a stretchable laser-induced graphene pattern with self-heating capabilities
", J. Mater. Chem. A, 2020, 8, 6487-6500, DOI: 10.1039/C9TA07855J