# Study of nanoparticles in electrochemical sensor for environmental applications.

## The experience in Costa Rica

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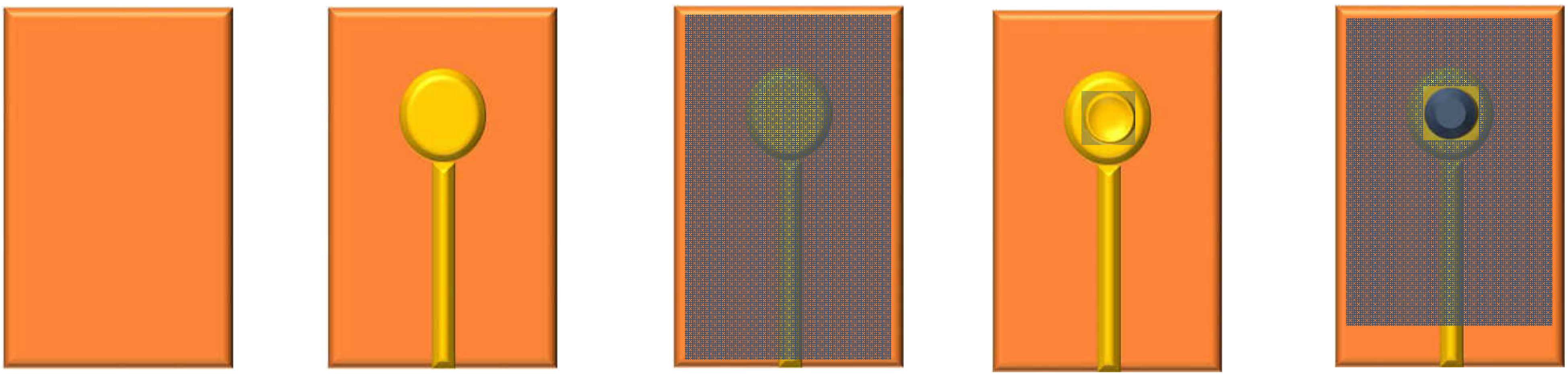
# Electrode fabrication



*1. Flexibel film Kapton®*

*2. Gold deposition by sputtering (45 nm) on the flexible film using a shadow mask*

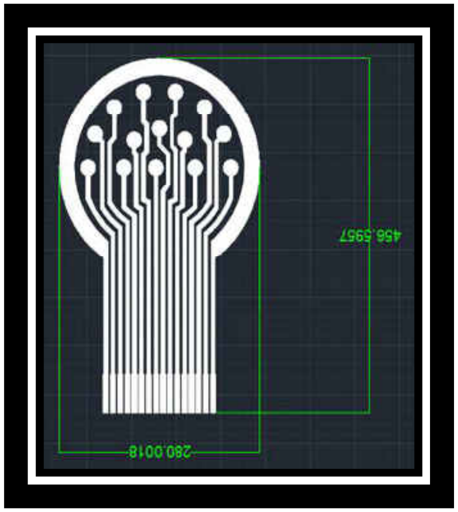
*3. Passivation by photolithography*

*4. Electrode with specify area are prepared*

*5. Chemical modification of the electrode.*

# Electrode fabrication

- Metal deposition mask



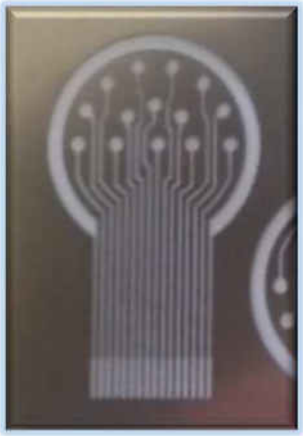



**Fig. 5:** Mask for flexible electrodes. Designed by Hayden Phillips

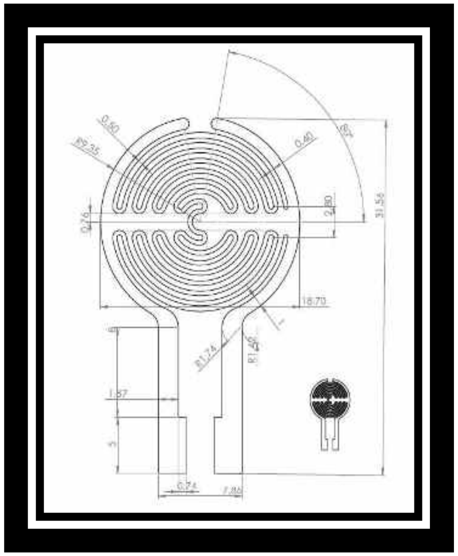


**Fig. 6:** Impedance interdigitated flexible electrodes. Designed by Jorge Sandoval

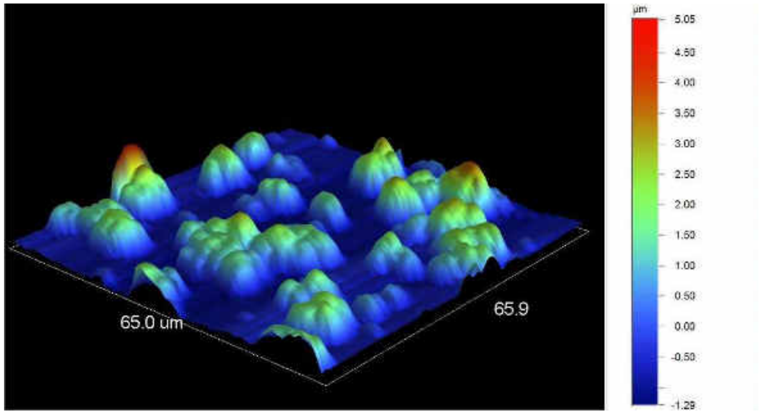
# Electrode fabrication

**Fig. 7:** (A) Home-made gold electrodes (CICIMA-UCR); (B) Chemical modified gold electrode by PEDOT

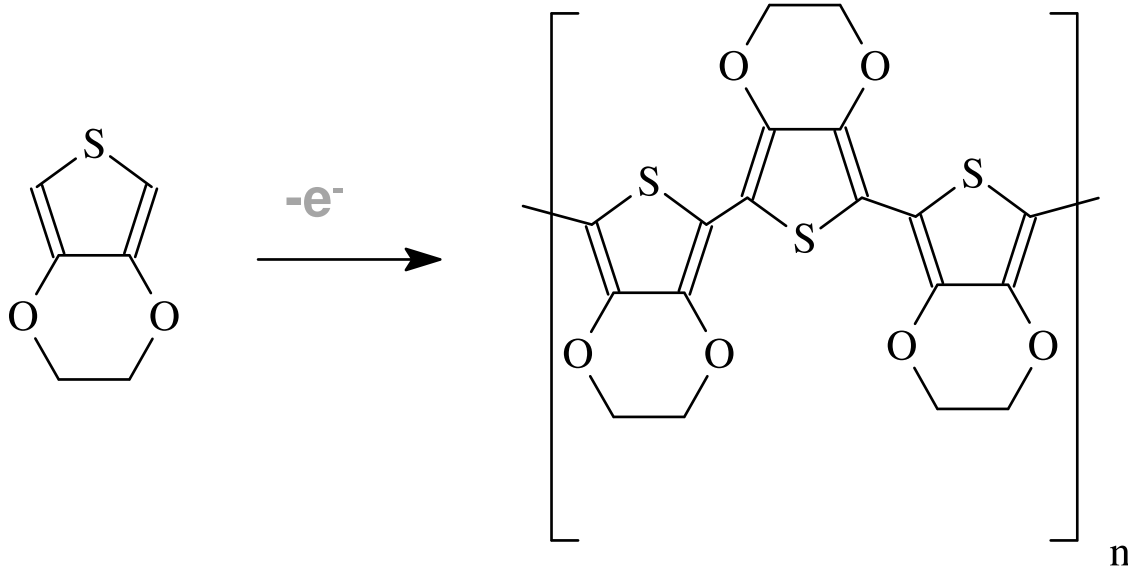
# Chemical Modification

# Conductive Polymer properties

- Electrochemically stability
- Biocompatibility
- Low electrode impedance
- High charge injection capability
- High corrosion resistance
- Can be structured at micro and nanoscale
- Provides a dispersion system for further formulation



# Polymerization




$$Q = n_e F N$$

**Q:** charge
**$n_e$:** number of electrons
**N:** moles
**F:** Faraday constant (96500 C/mol).

**Fig. 1**: EDOT polymerization: oxidation of the 3,4-ethylenedioxythiophene monomer

# Conductive Polymer: interface

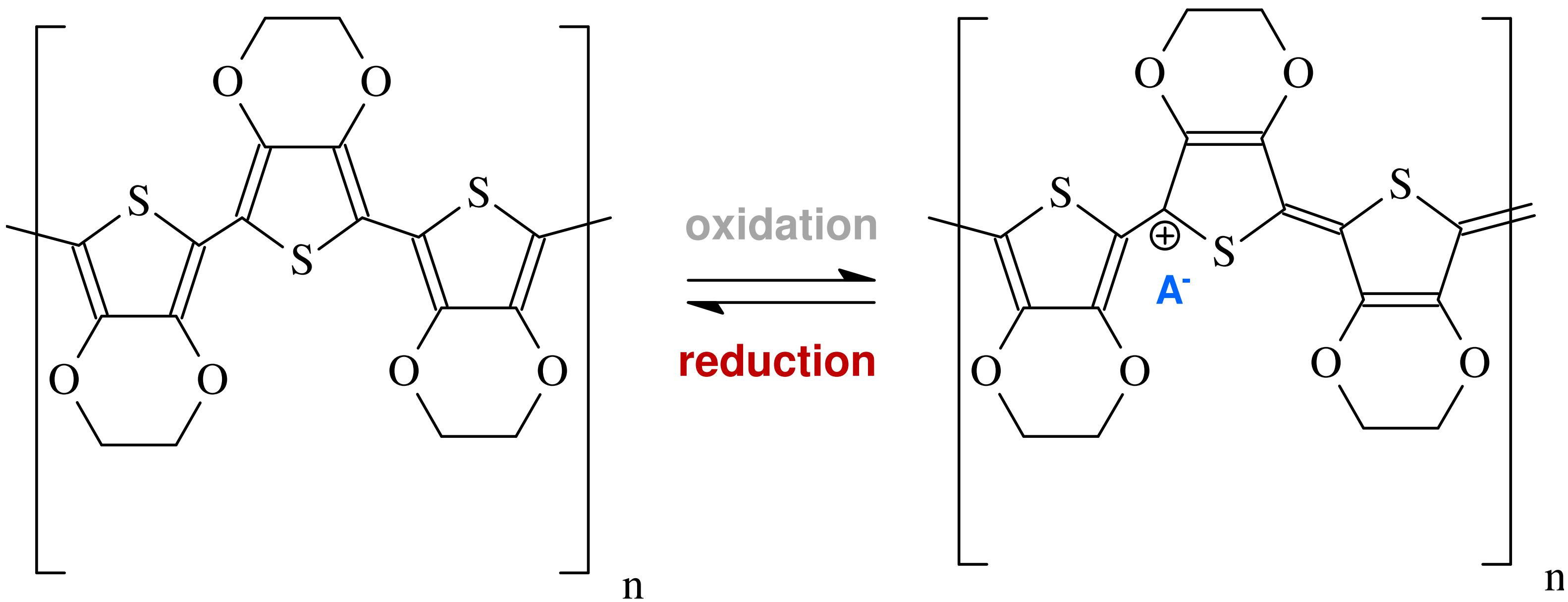



**Fig. 2**: PEDOT REDOX mechanism

# Electrode Interface: Double layer mechanism

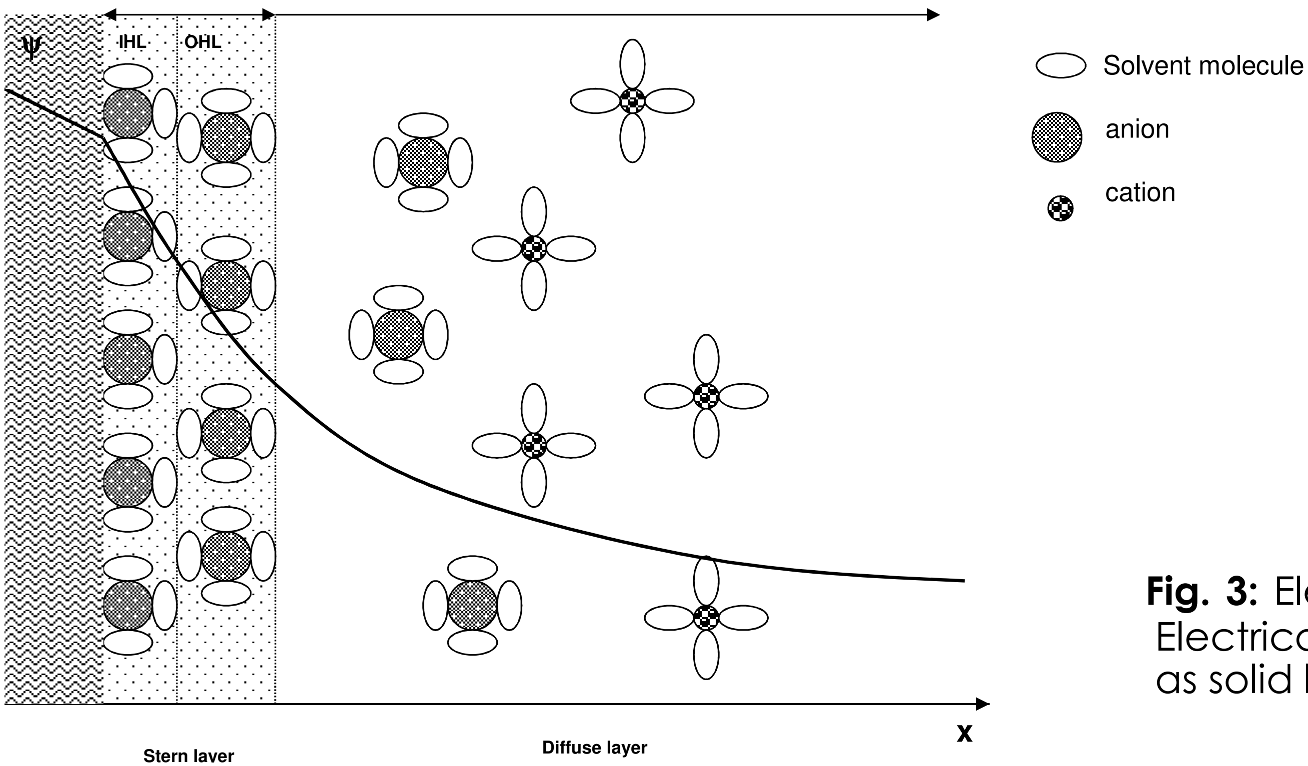



**Fig. 3:** Electric double layer structure. Electrical potential profile (ψ) shows as solid line.

# Conductive Polymer: Electrode Interface

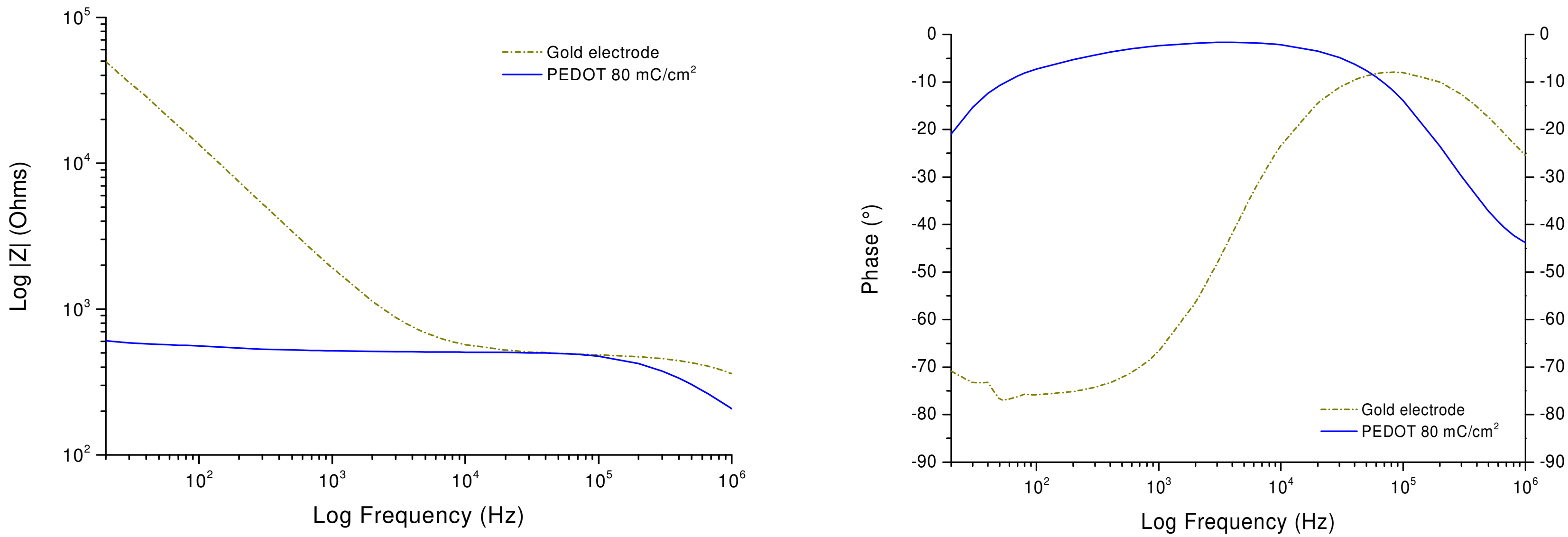
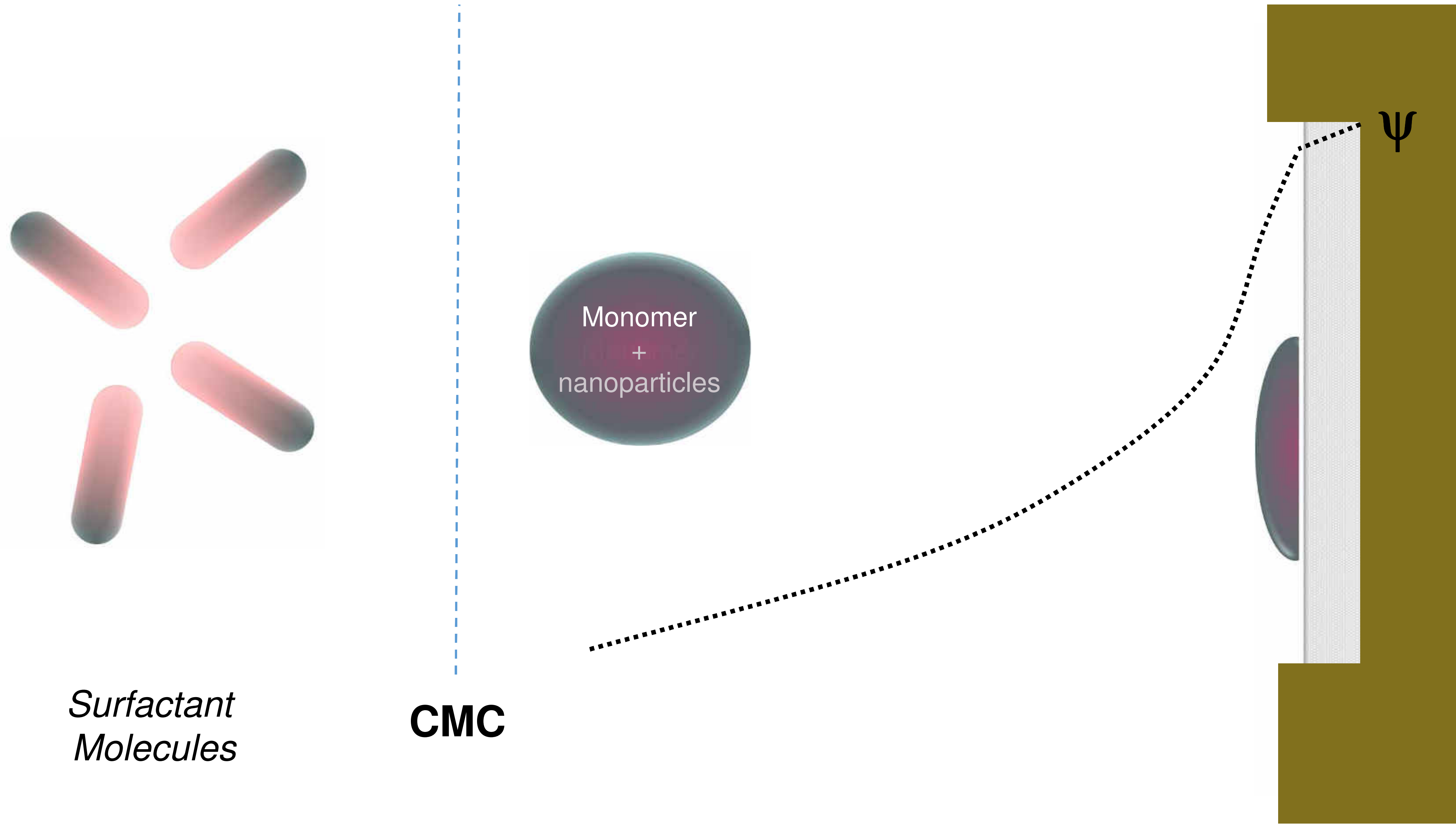
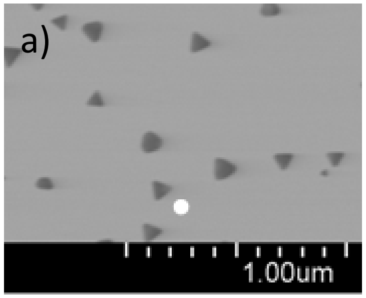
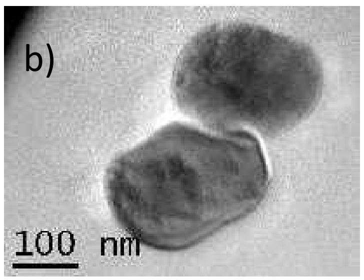



**Fig. 4**: Comparative impedance spectroscopy (left) and phase measurements (right) of a 1 $mm^2$ gold electrode and the same electrode cover with PEDOT (80 $mC/cm^2$ charge density).


Monomer
+
nanoparticles
Ψ
Surfactant
Molecules
CMC




Rojas, Oscar, et al., 2009, Journal of colloid and interface science **333.2**, 782-790.




Starbird-Pérez, Ricardo, et al. 2015, *Revista Tecnología en Marcha* 28.3 (2015): 45-54.

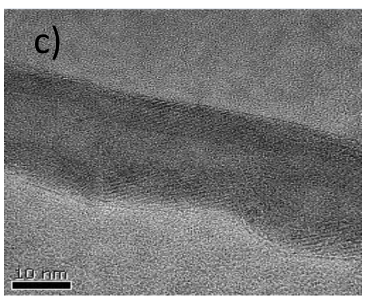



**Fig. 8:** TEM nanoparticles images (a) gold (b) iron oxide and (c) commercial CNT

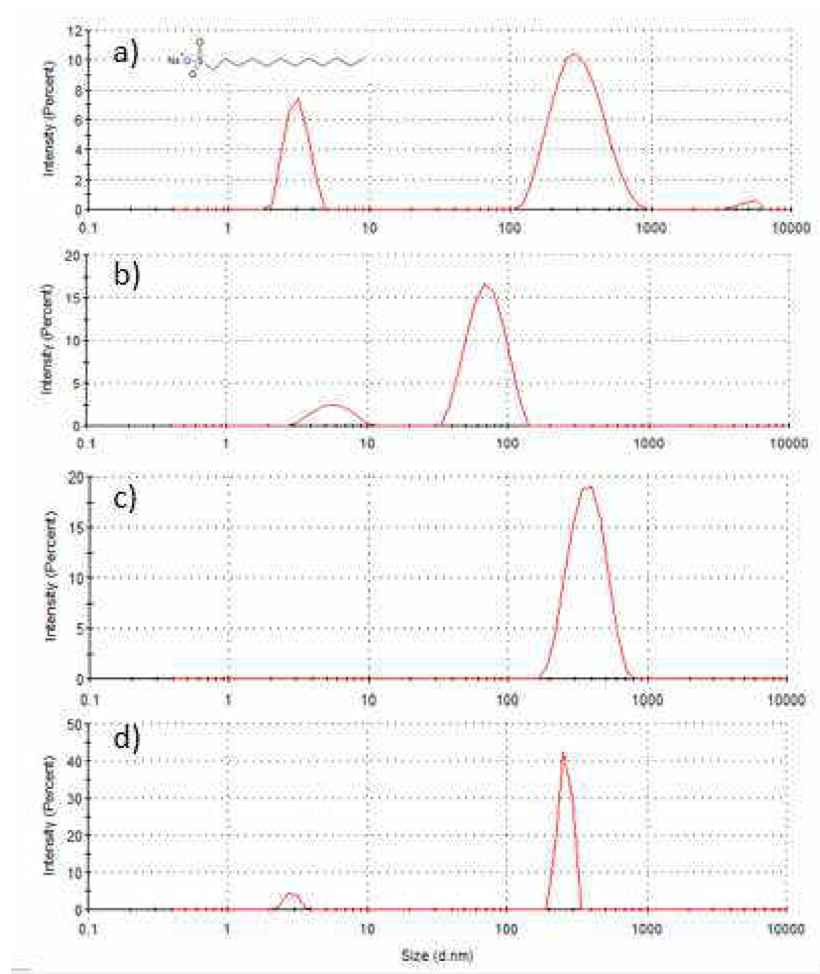



**Fig. 9:** Dynamic light scattering analysis of (a) gold-EDOT micelle (b) iron-EDOT micelle and (c) commercial CNT-EDOT micelle in a Sodium dodecyl sulfate (8,2 mM)

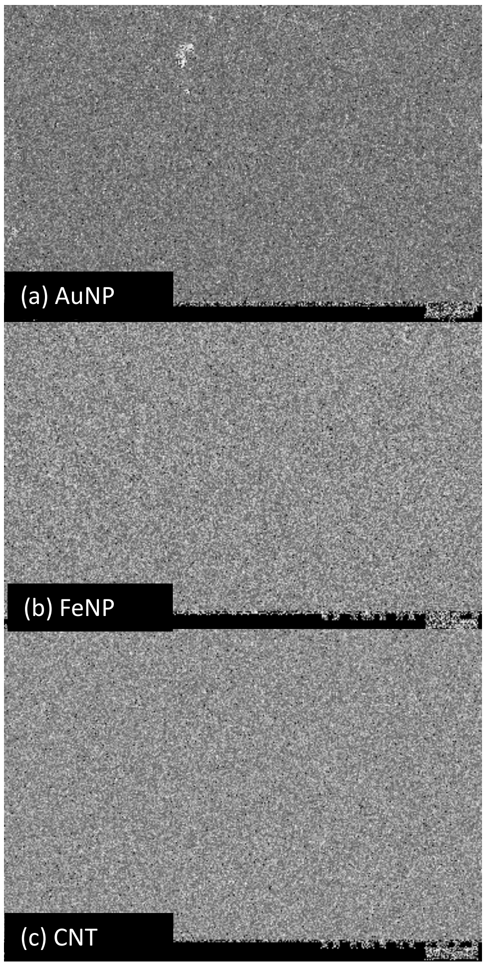



**Fig. 10:** SEM images of (a) AuNP-PEDOT (b) FeNP-PEDOT and (c) commercial CNT-PEDOT electrodeposited samples.

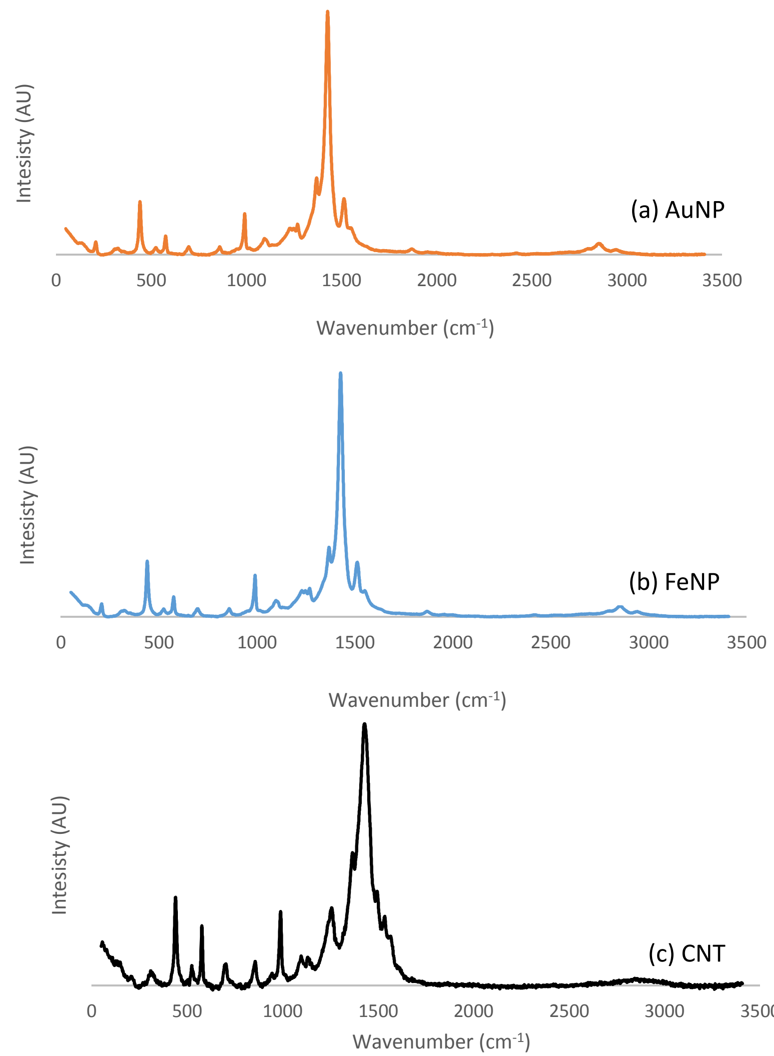



**Fig. 11:** Raman spectra of (a) AuNP-PEDOT (b) FeNP-PEDOT and (c) commercial CNT-PEDOT samples.

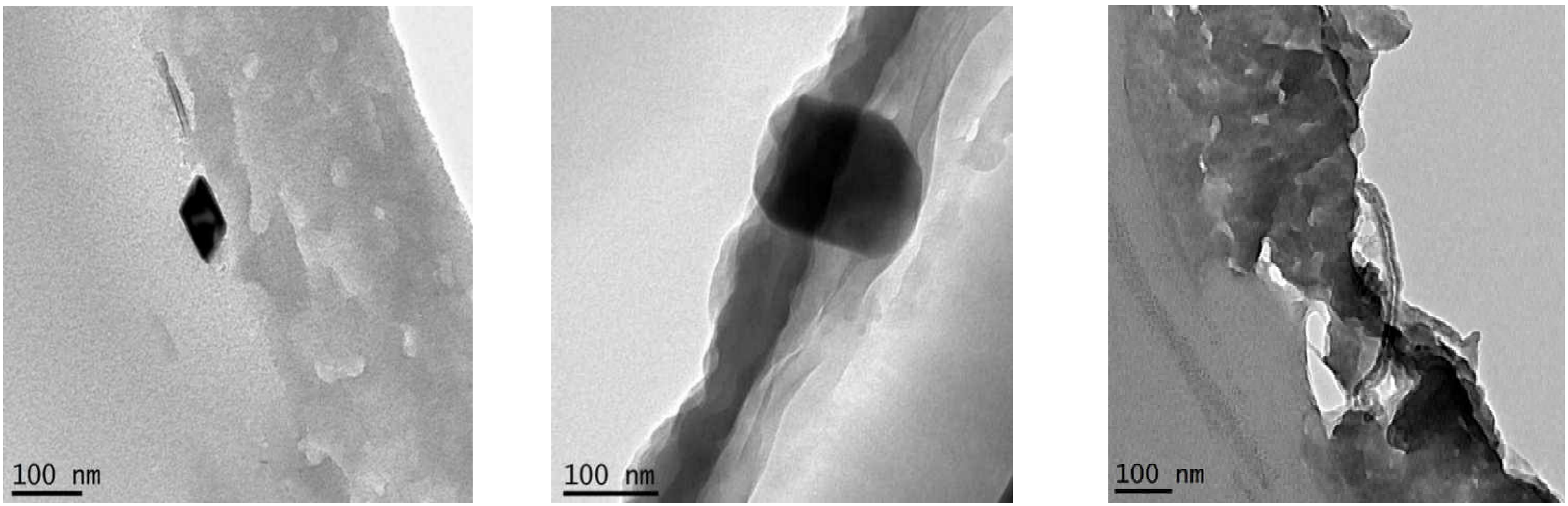



**Fig. 12:** TEM images of (a) AuNP-PEDOT (b) FeNP-PEDOT and (c) commercial CNT-PEDOT electrodeposited samples.

# Electrochemical Characterization

The $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$ couple is used as reversible redox system in order to study the chemical response of the electrode surface.

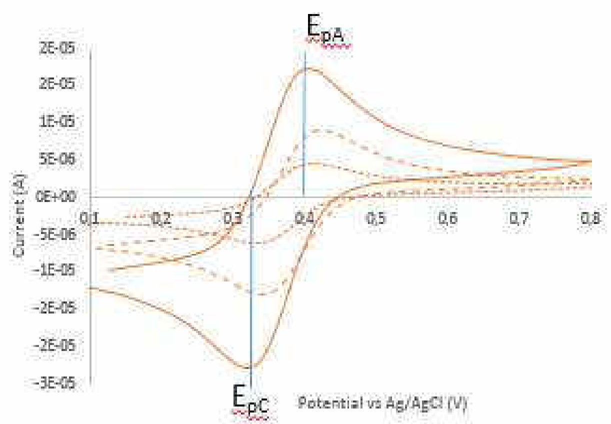



**Fig. 13:** Cyclic voltagramm of (a) effect of $Fe^{3+}/Fe^{2+}$ concentration (2 mM dotted line, 5 mM dashed line, 10 mM solid line) on a gold electrode in 1M KCl. Scan rate: 100 mV/s. Initial scan direction: positive.

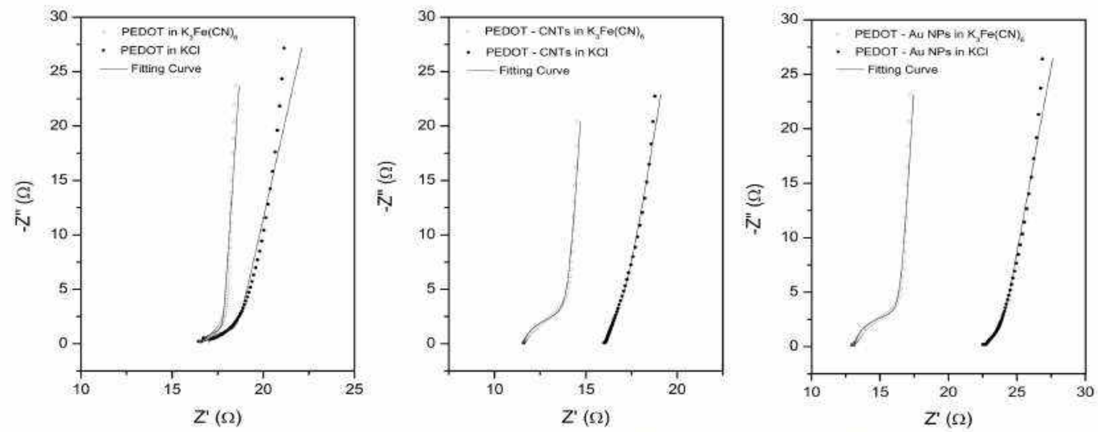
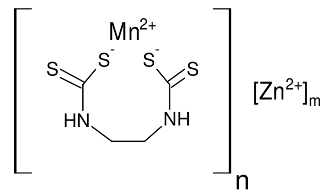



**Fig. 3.** Nyquist graph with fitting curve of a) PEDOT b) PEDOT/CNTs and c) PEDOT/AuNP electrodes

# Applications  Electrochemical sensors

# Mancozeb




- It is used as a fungicide in fruits, vegetables, rice and ornamental plants.
- Health effects included metal overload in human colon cells, thyroid hormone disruption in rats, toxic effects on mammalian granulosa cells, and more importantly, tumor-initiating activity in mouse skin.
- In Costa Rica, residues for MCZ were detected in the urine samples of children living close to agricultural plantations.

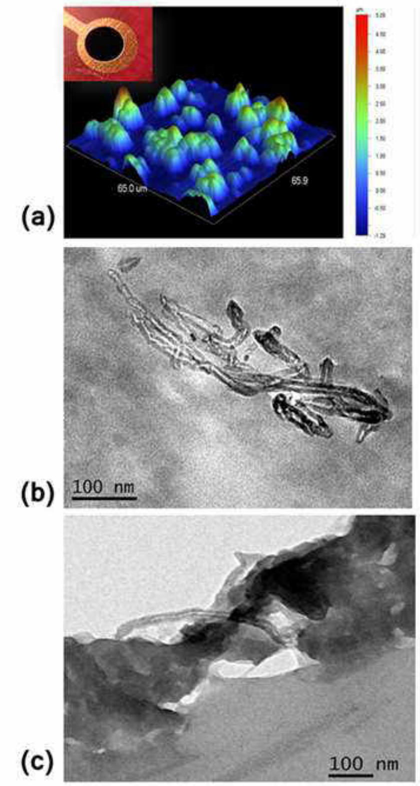



**Figure 3.** Coated electrode imagens: a) electrode surface roughness (inset: PEDOT/MWCNT coated electrode), b) MWCNT aggregates inside the PEDOT layer and c) MWCNT anchored to the PEDOT layer.

**Ricardo Starbird et. al.** Development of Poly(3,4-ethylenedioxythiophene(PEDOT)/carbon Nanotube Electrodes for Electrochemical Detection of Mancozeb in Water. *Int. J. Electrochem. Sci.*, 13(2018)1931-1944 ,doi: 10.20964/2018.02.20

# Mancozeb

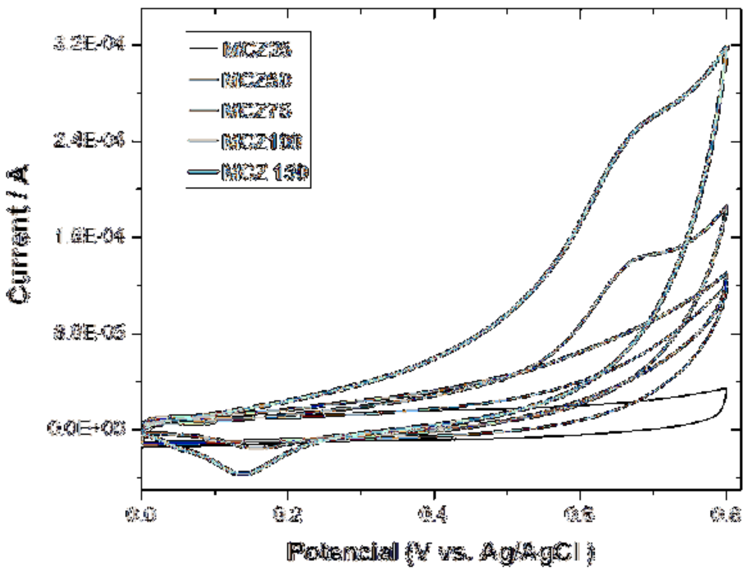



**Figure 4.** Voltammograms obtained for different MCZ concentrations of 0, 25, 50, 75, 100, 150, 200 and 250 µmol/L in BRBS at pH 7 using PEDOT/MWCNT electrode.

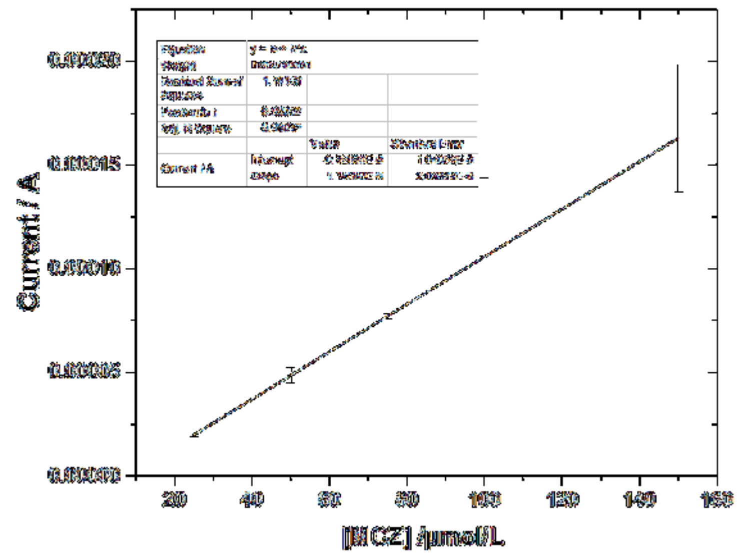
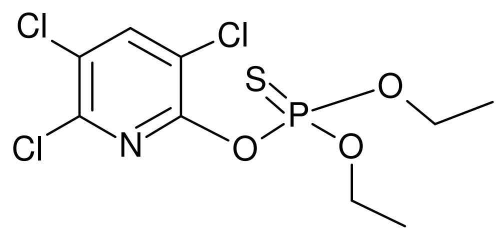
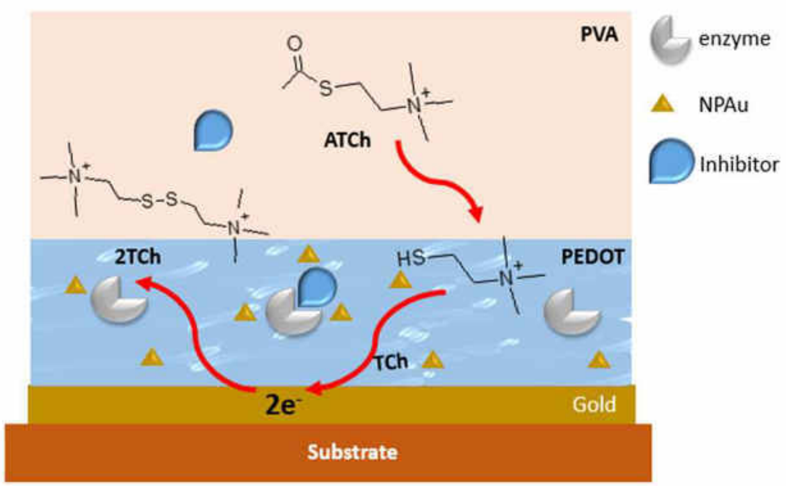



**Figure 5.** Calibration curve MCZ (25, 50, 75, 100 and 150 µmol/L) in BRBS at pH 7 using PEDOT/MWCNT electrode.

# Chlorpyrifos




- Chlorpyrifos (CPF) is an organophosphate insecticide.
- It can cause cholinesterase inhibition in humans leading to an overstimulated nervous system and death at very high exposures.
- A biosensor may be produce if an enzyme is fixed to a sensor and its activity is reduce in a 70% by the presence of the CPF.



# Biosensor: enzyme immobilization

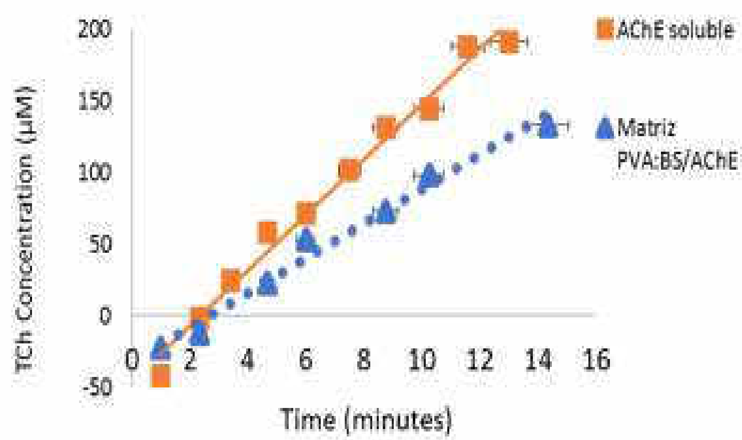



**Fig. 14:** Enzymatic activity curve (a) AChE soluble (b) AChE fixed in a polymeric Matrix

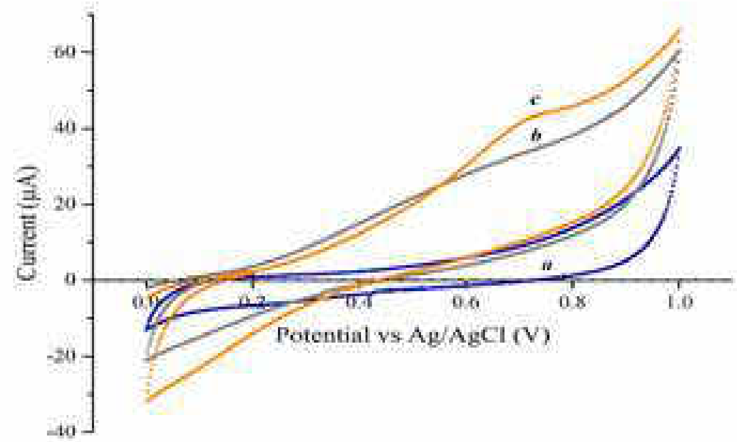



Fig. 2. Measurements of the ATCh (1500 μM) by cyclic voltammetry without inhibitor at a) 0 min of reaction, b) 1.5 min of reaction and c) 10 min of reaction.

# Biosensor

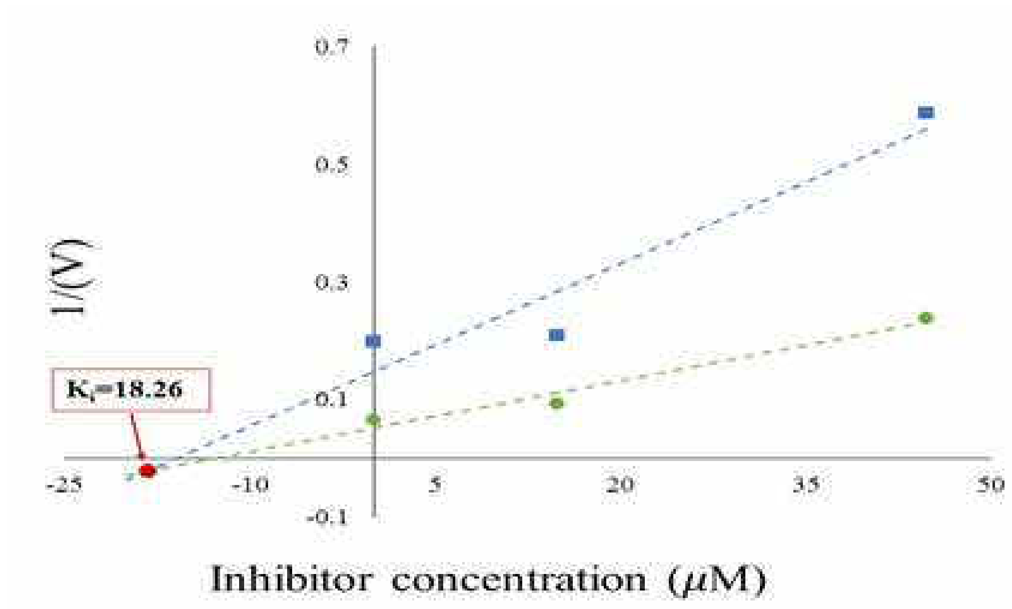



**Fig. 4.** Determination of Inhibition constant (Ki) according to inhibitor concentration and reaction velocity (■) 500 µM (●) 375 µM ATCh.

# Microfluidic cells

Fig 1. Microfluidic cell (Fabricated by Jorge Sandoval, ITCR)

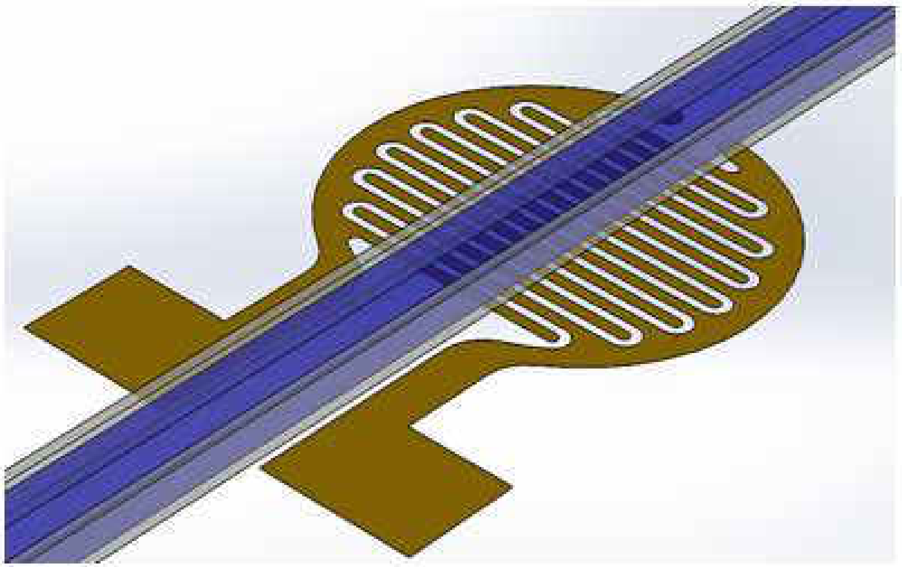


Fig 2. Electrochemical sensor in a microcavity

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