# Tunable Electrochemical sensors based on carbon nanocomposite materials towards enhanced determination of cadmium, lead and copper in water

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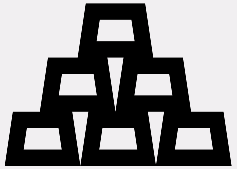
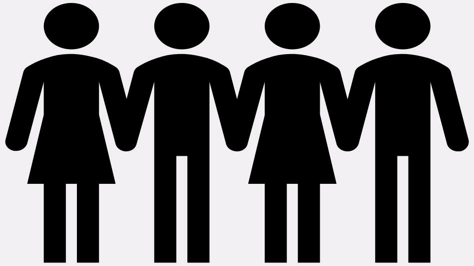
# Introduction





- AAS
- ICP-AES
- ICP-MS
- Spectrophotometry
- HPLC

→ extensive sample preparation
expensive equipment
specialized technicians
non-portable

- Electrochemical techniques

→ relatively short time of analysis
low-cost equipment
specialized personnel is not required
portable

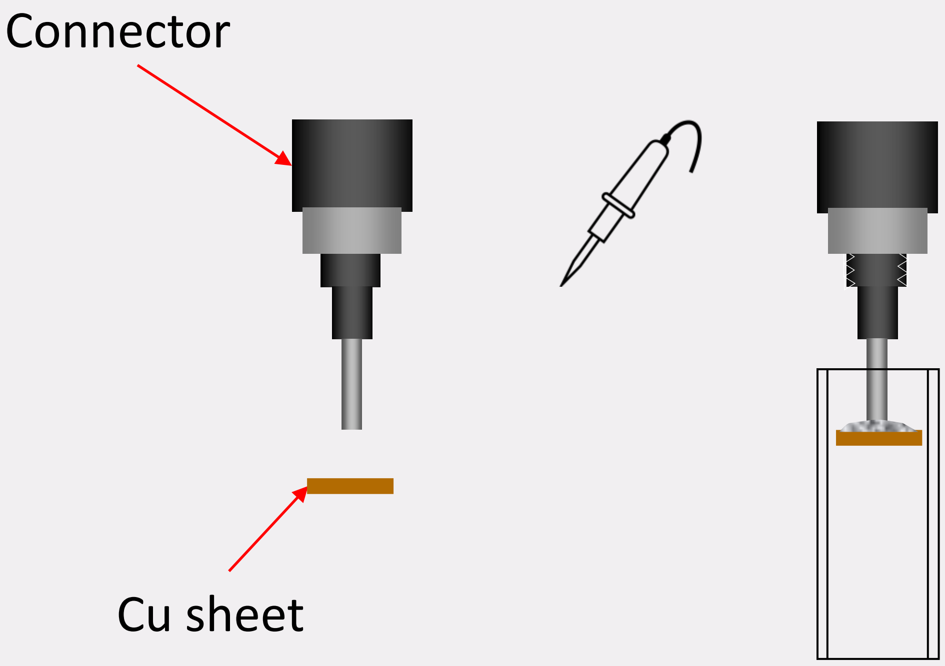
# **Introduction:** Composite Materials

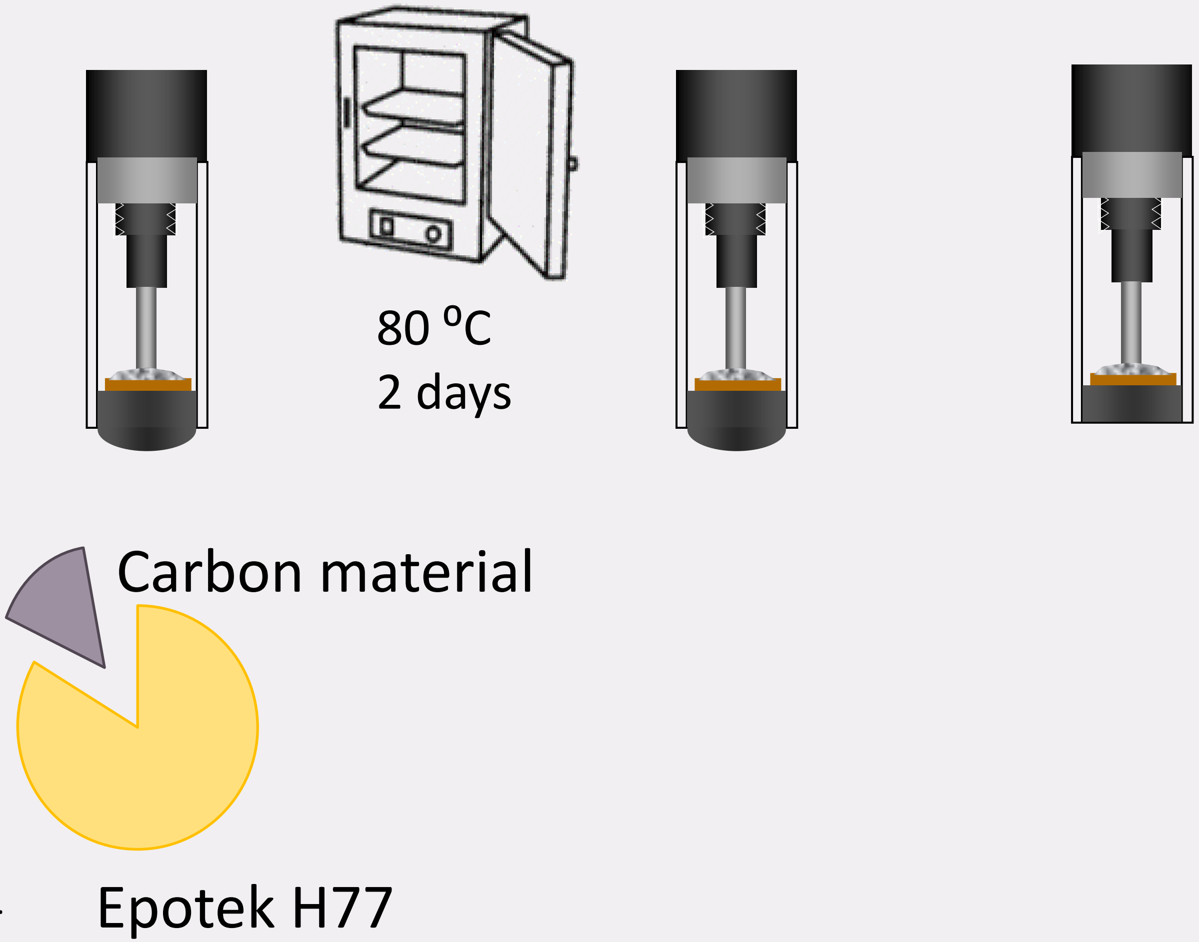
**Composite material** = material 1 + material 2 + material n

Requirement: the materials must not react with each other.

The composite material is a new material with new physical, chemical and mechanical properties.

# Introduction: Electrode Construction



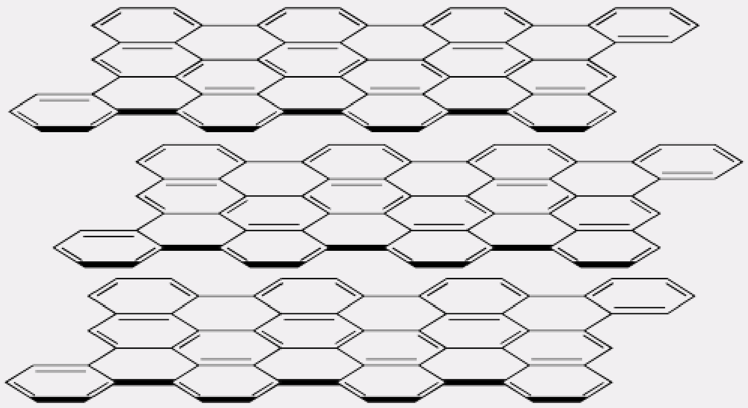

R. Montes, J. Bartrolí, F. Céspedes, and M. Baeza, "Towards to the improvement of the analytical response in voltammetric sensors based on rigid composites," *J. Electroanal. Chem.*, vol. 733, pp. 69–76, 2014.

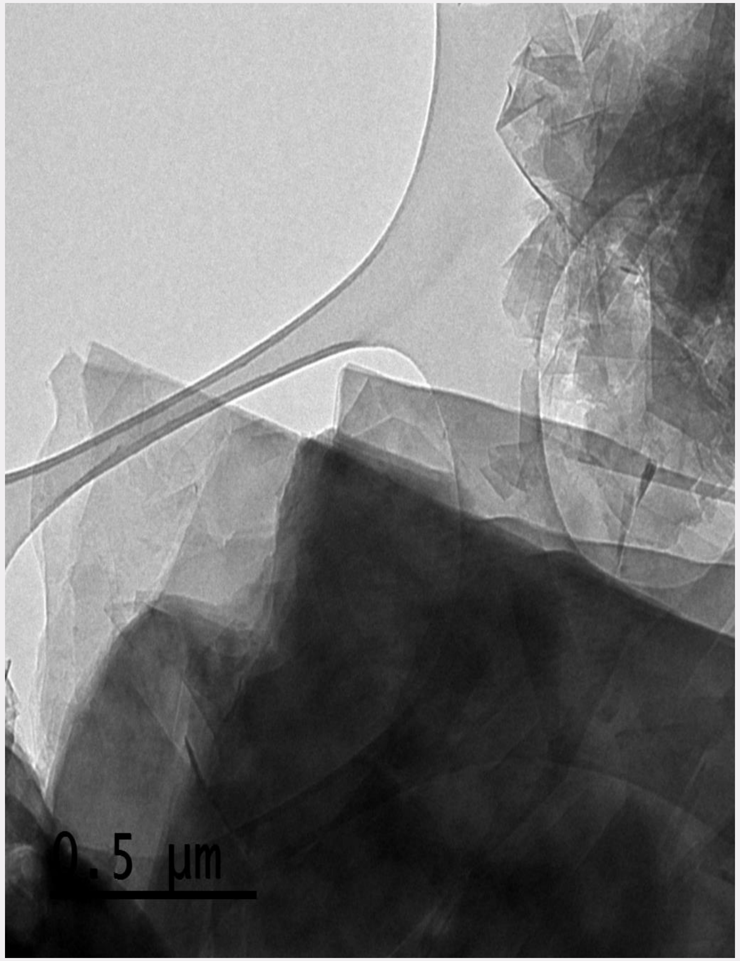
# Introduction: Carbon Materials

## Carbon Materials

- ✓ Graphite
- X rGO
- ✓ MWCNTs

Graphite



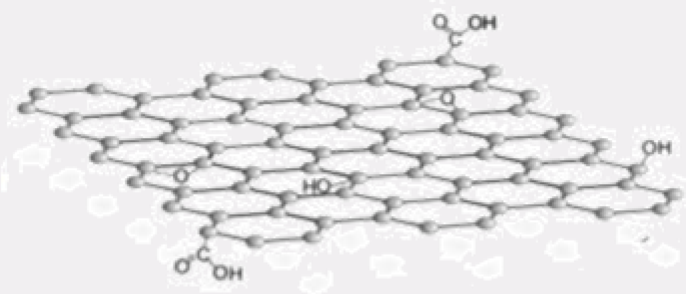


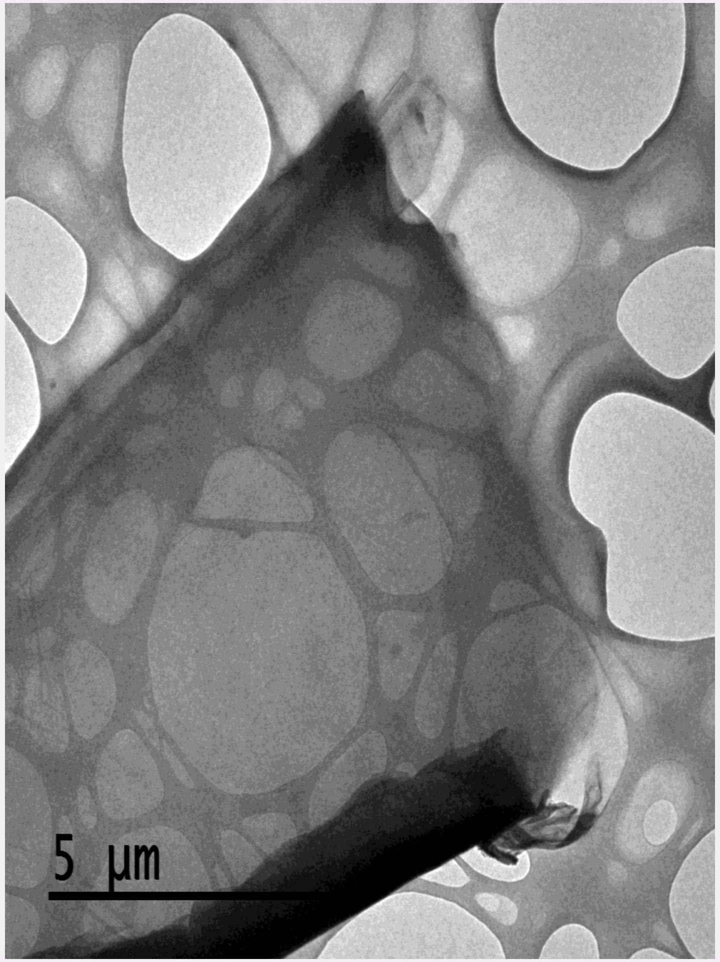
# Introduction: Carbon Materials

**Carbon Materials**

- ✓ Graphite
- X rGO
- ✓ MWCNTs

rGO



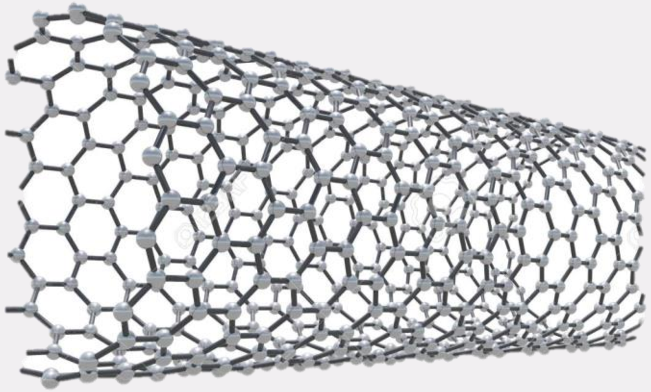



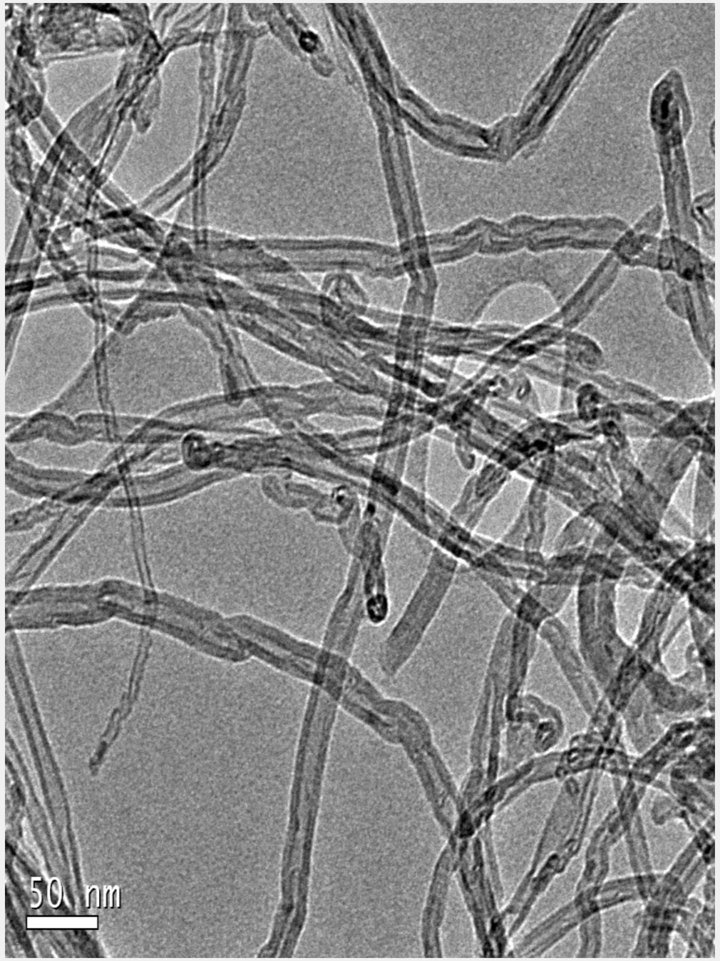
# Introduction: Carbon Materials

**Carbon Materials**

- ✓ Graphite
- X rGO
- ✓ MWCNTs

MWCNTs

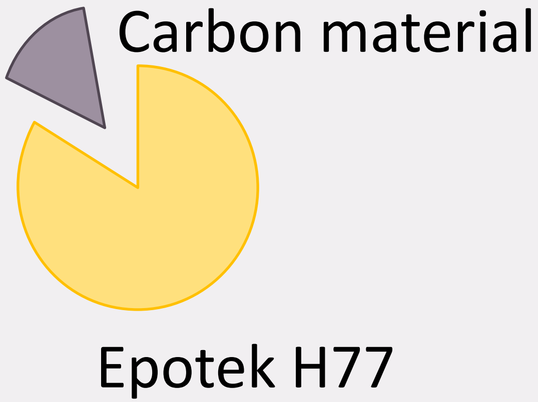




# Introduction: Carbon Materials

**Carbon Materials**

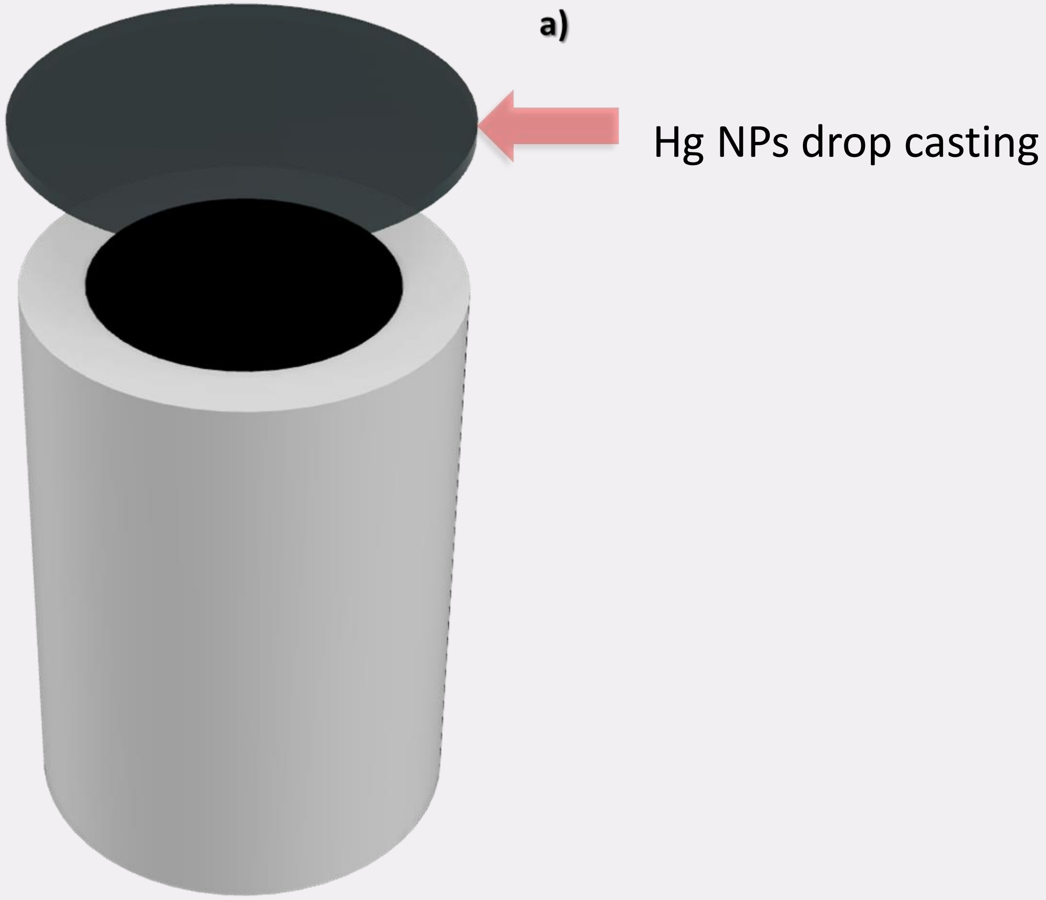
- ✓ Graphite
- X rGO
- ✓ MWCNTs




Composites tested:

| | |
|---|---|
| Graphite (15 %, 20 %) | Epotek H-77 |
| rGO (15 %) | Epotek H-77 |
| MWCNTs (10 %) | Epotek H-77 |

# Introduction: Electrode Modification



# Introduction: Electrochemical Techniques



**Characterization techniques**

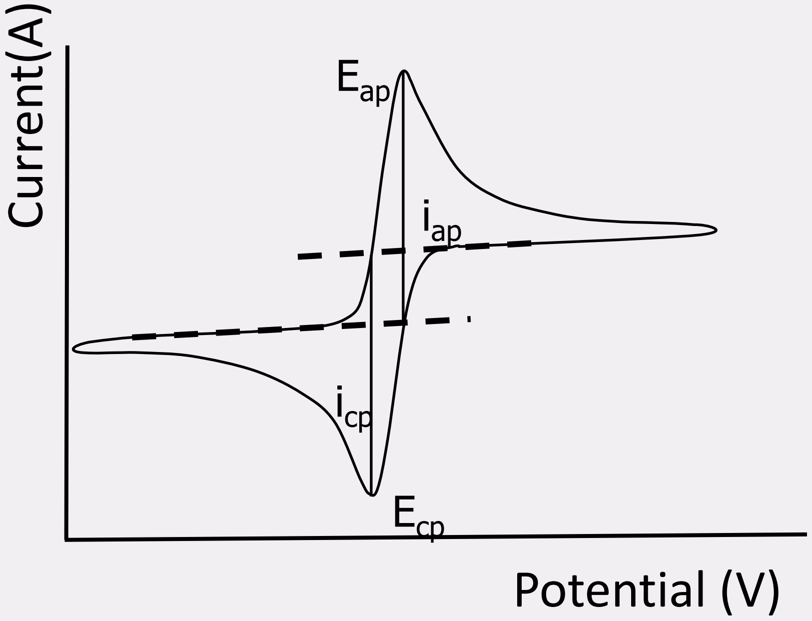
- Cyclic Voltammetry (CV)
- Electrochemical Impedance Spectroscopy (EIS)

**Measurement techniques**

- Square-Wave Anodic Stripping Voltammetry (SWASV)

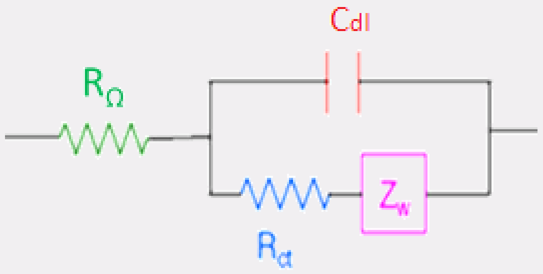
# Introduction: Cyclic Voltammetry (CV)

CV is the measurement of the current that flows through an electrode as a triangular variation of potential is applied. Peaks correspond to an electronic transfer between the electrode and a dissolved species.

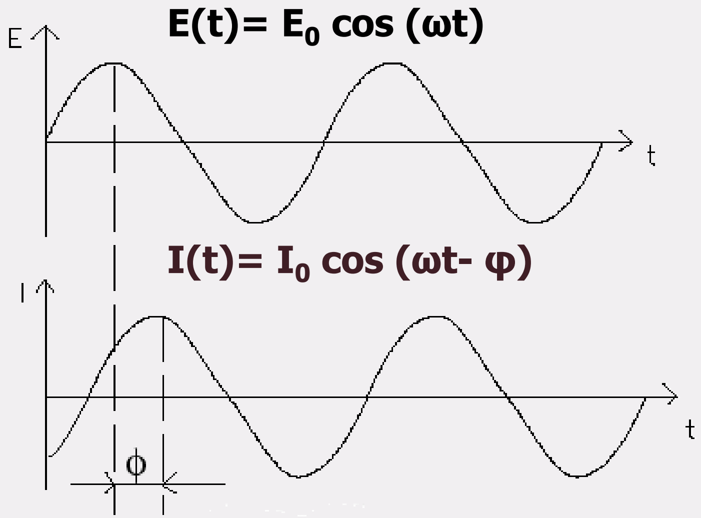


# Introduction: Electrochemical Impedance Spectroscopy (EIS)

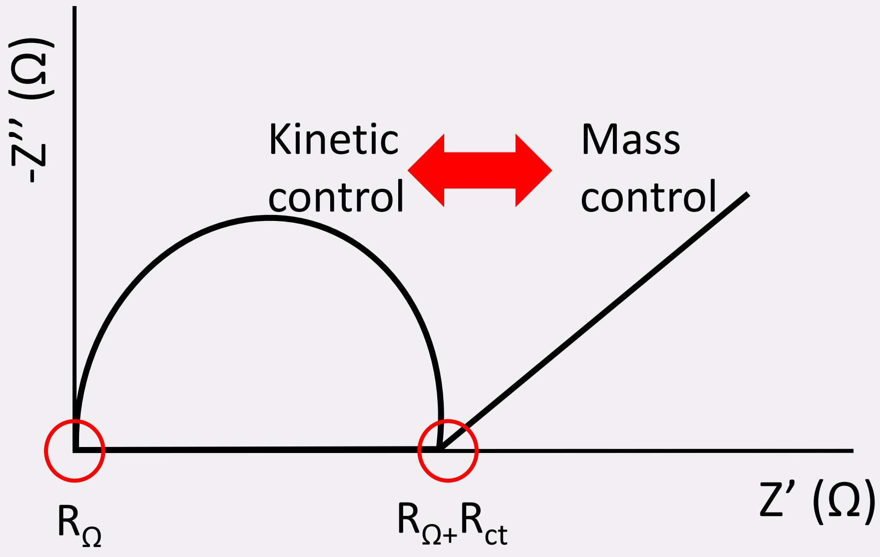
EIS is a perturbative characterization of the dynamics of an electrochemical process. It is based on the application of an alternating current and measure the resistance of the current to go through the material .




Randles Circuit

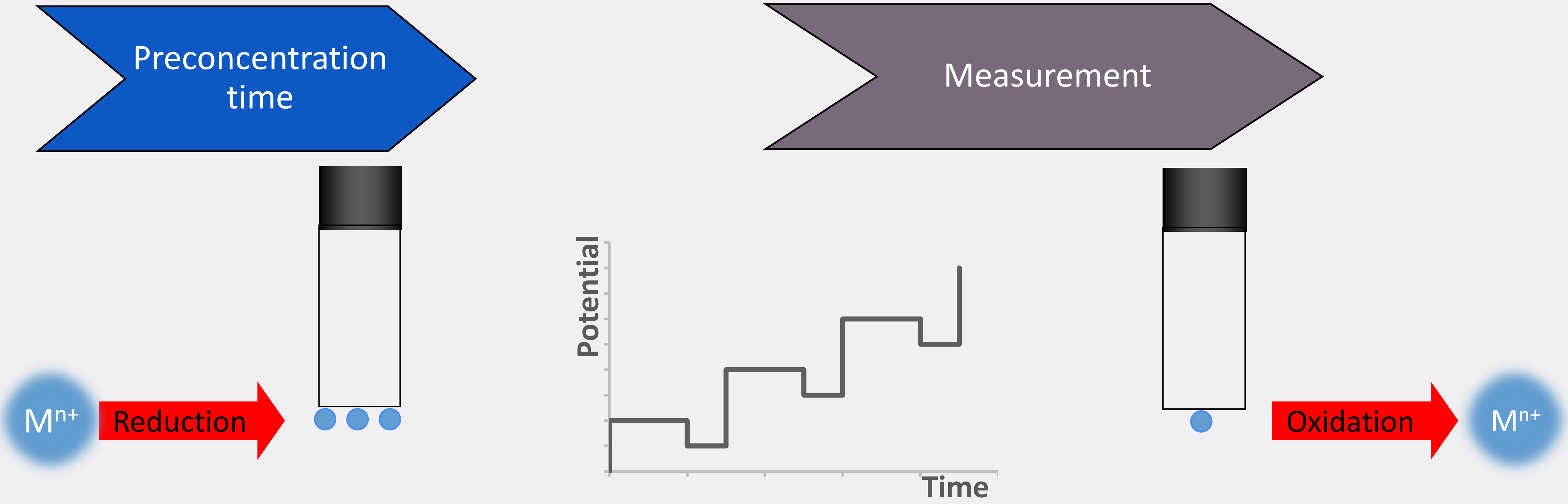



$$Z = \frac{E(t)}{I(t)}$$




Nyquist plot

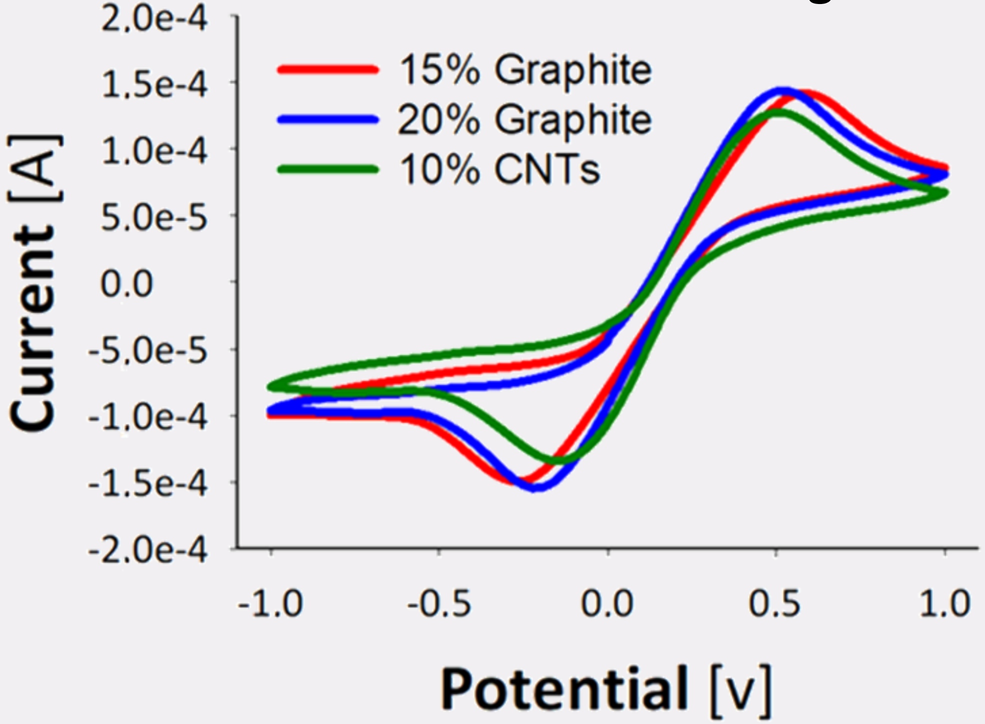
# Introduction: Square Wave-Anodic Stripping Voltammetry (SWASV)

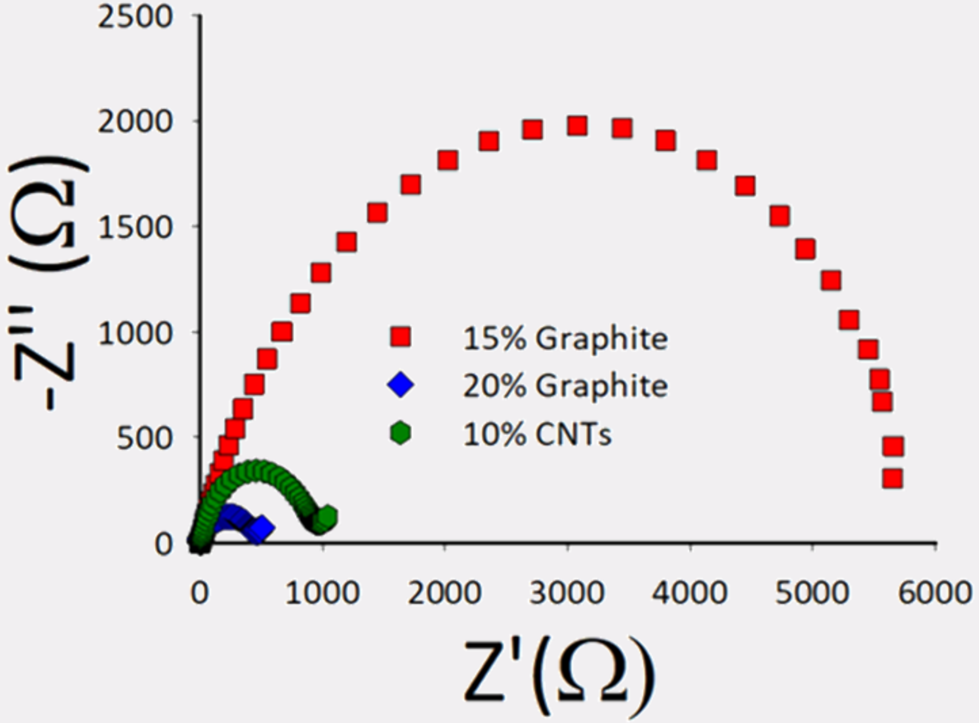



B. K. Bansod, T. Kumar, R. Thakur, S. Rana, and I. Singh, “A review on various electrochemical techniques for heavy metal ions detection with different sensing platforms,” Biosens. Bioelectron., vol. 94, no. March, pp. 443–455, 2017

# Results: Carbon Material

**Electrode characterization before using:**



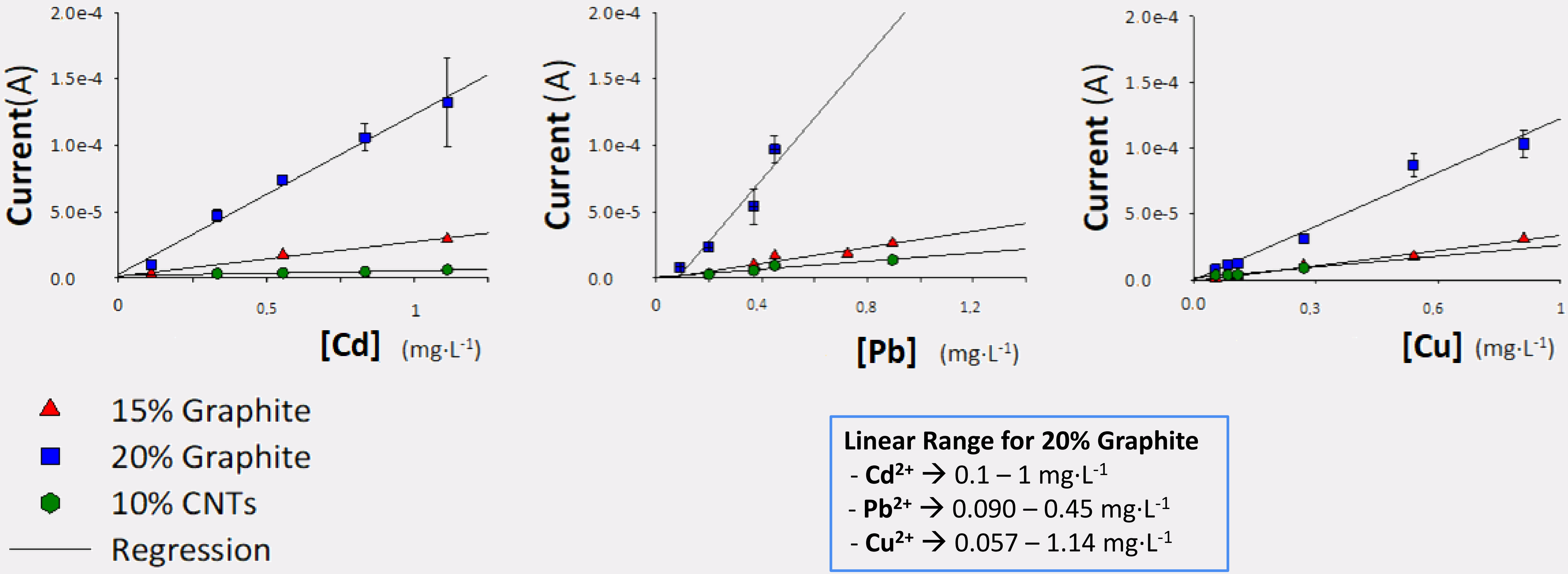




**Experimental conditions:**

$Fe(CN_6)^{4+}$ 0.01M
$Fe(CN_6)^{3+}$ 0.01M
KCl 0.1M
Scan rate: 10 mV/seg

**WE:** composite electrode
**RE:** Ag/AgCl
**CE:** Pt

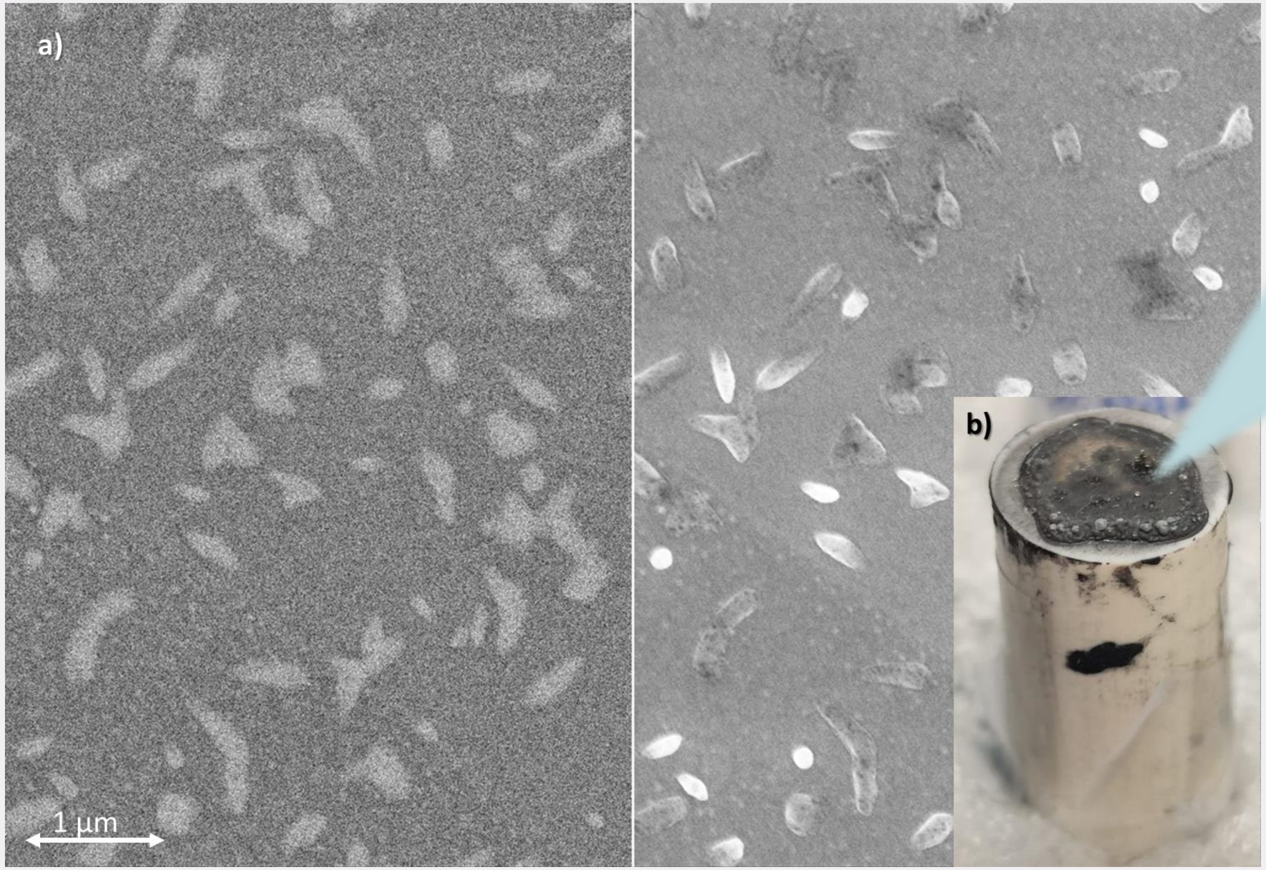
# **Results:** Carbon Material

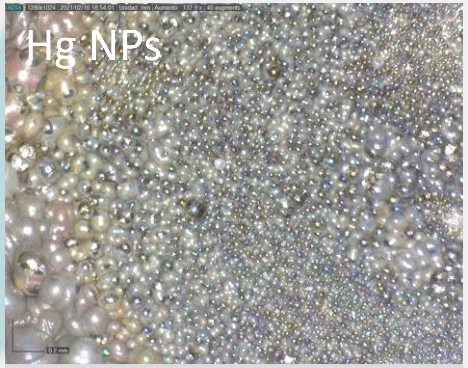



**Linear Range for 20% Graphite**

- **$Cd^{2+}$** → 0.1 – 1 $mg{\cdot}L^{-1}$
- **$Pb^{2+}$** → 0.090 – 0.45 $mg{\cdot}L^{-1}$
- **$Cu^{2+}$** → 0.057 – 1.14 $mg{\cdot}L^{-1}$

# **Results:** Mercury Nanoparticles



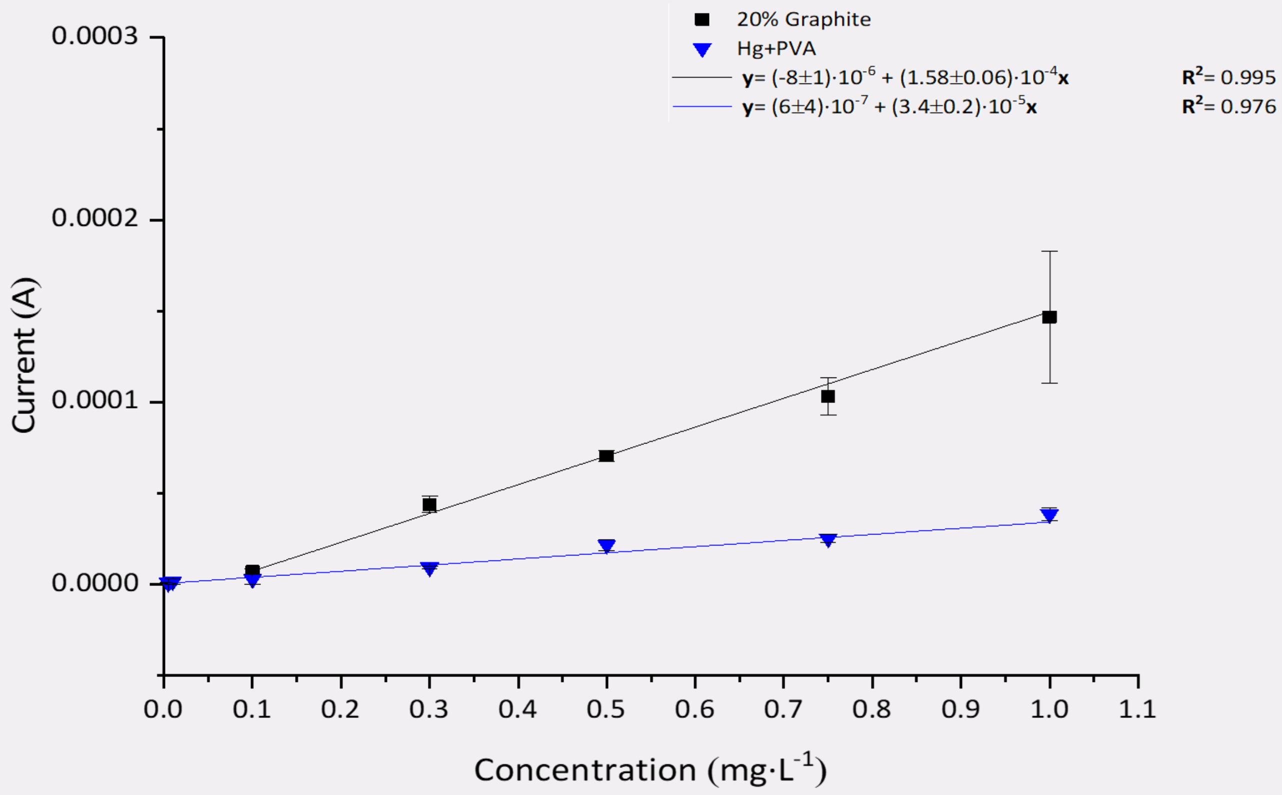

DinoLite images of the electrodes' surface

a) Retrodispersive (left) and secondary electron (right) SEM images. b) 20% graphite electrode drop casted with HgNPs image.

G. V. Ramesh, M. D. Prasad, and T. P. Radhakrishnan, "Mercury nanodrops and nanocrystals," *Chem. Mater.*, vol. 23, no. 23, pp. 5231–5236, 2011

# Results: Mercury Nanoparticles

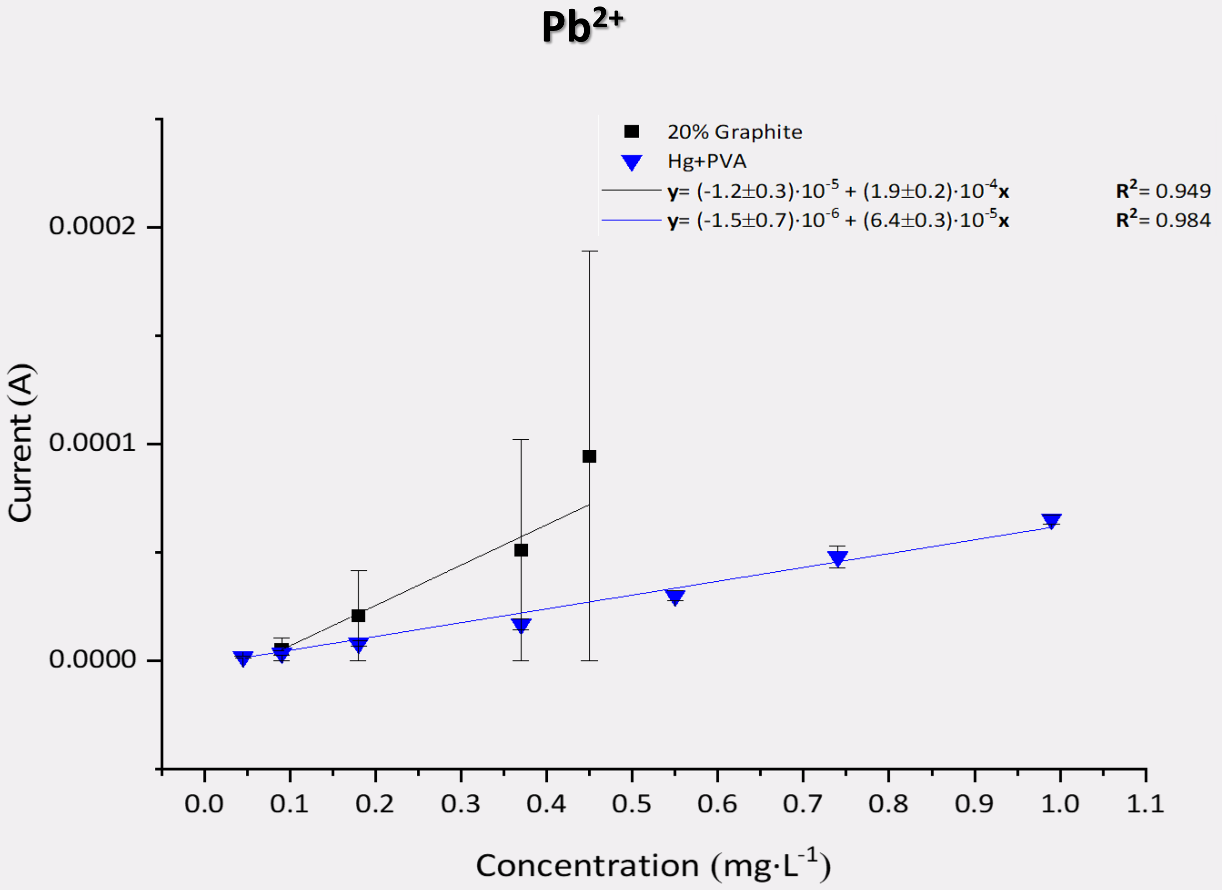
**$Cd^{2+}$**




**Linear Range for 20% Graphite**
- **$Cd^{2+}$** → $0.1 – 1\ mg \cdot L^{-1}$

**Linear Range for Hg NPs**
- **$Cd^{2+}$** → $0.005\text{-}1\ mg \cdot L^{-1}$

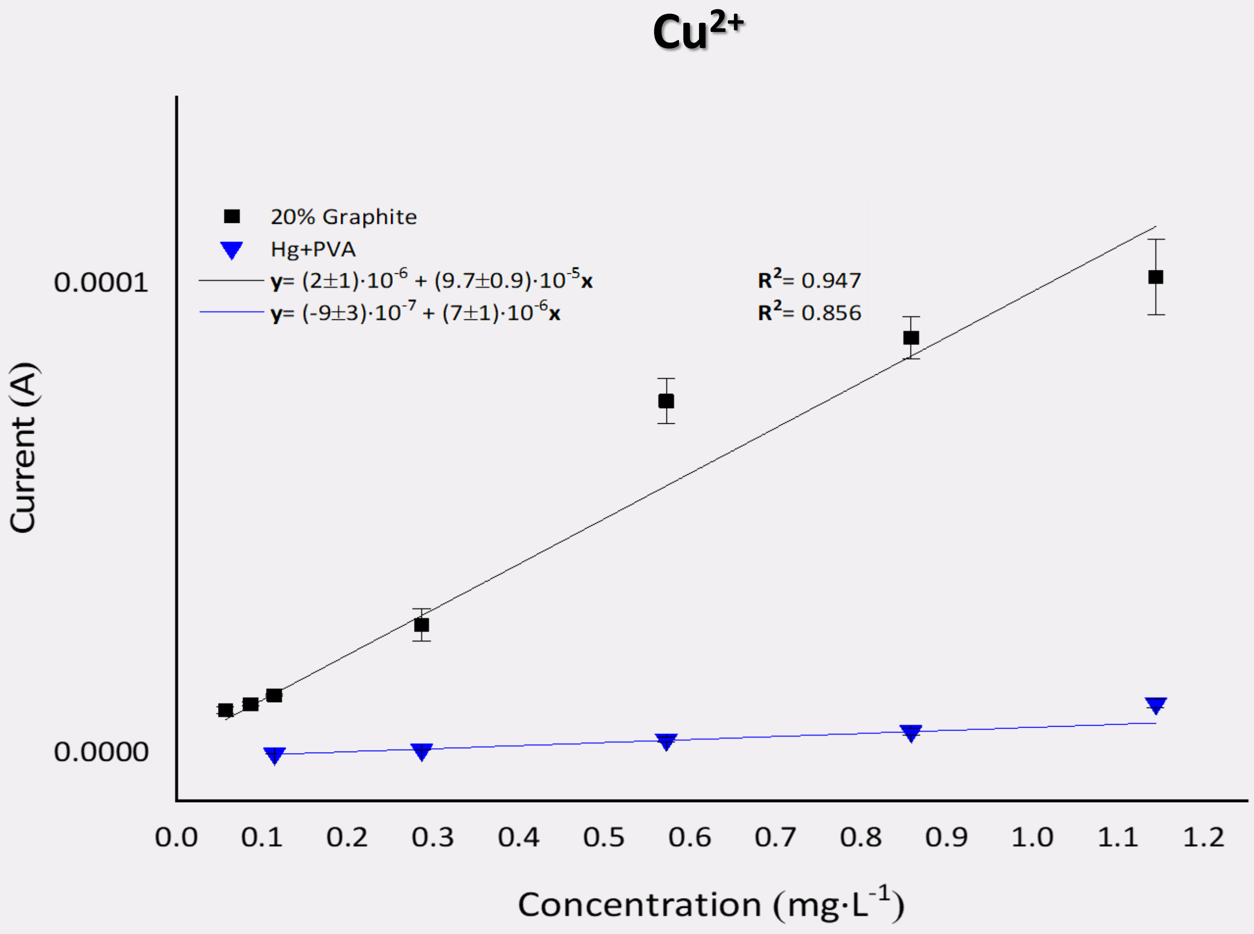
# **Results:** Mercury Nanoparticles




**Linear Range for 20% Graphite**
- **$Pb^{2+}$** → 0.090 – 0.45 mg·$L^{-1}$

**Linear Range for Hg NPs**
- **$Pb^{2+}$** → 0.045-1 mg·$L^{-1}$

# Results: Mercury Nanoparticles




**Linear Range for 20% Graphite**
- **$Cu^{2+}$** → 0.057 – 1.14 mg·$L^{-1}$

**Linear Range for Hg NPs**
- **$Cu^{2+}$** → 0.1-1.14 mg·$L^{-1}$

# Conclusions

- The most suitable option of the non-modified electrode to determine $Cd^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ using SWASV is the composite electrode with 20% graphite.
- Hg nanoparticles are good option to modify composite electrodes to determinate those metals.
  - Lower concentrations can be determined.
  - For $Cd^{2+}$ and $Pb^{2+}$a wider linear range can be achieved

# TUNABLE ELECTROCHEMICAL SENSORS BASED ON CARBON NANOCOMPOSITE MATERIALS TOWARDS ENHANCED DETERMINATION OF CADMIUM, LEAD AND COPPER IN WATER

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