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Tunable Electrochemical Sensors Based on Carbon Nanocomposite Materials towards Enhanced Determination of Cadmium, Lead and Copper in Water †

Laia L. Fernández [1,2], Julio Bastos-Arrieta [3], Cristina Palet [1] and Mireia Baeza [2,*]

[1] Grup de Tècniques de Separació en Química (GTS), Departament de Química, Universitat Autònoma de Barcelona, Carrer dels Til·lers, 08193 Bellaterra, Catalunya, Spain; Laia.Lopez@uab.cat (L.L.F.); cristina.palet@uab.cat (C.P.)
[2] Group of Biological Treatment and of Liquid and Gaseous Effluents, Nutrient Removal, and Odors and Volatile Organic Compounds (GENOCOV), Departament Química, Universitat Autònoma de Barcelona, Carrer dels Til·lers, 08193 Bellaterra, Catalunya, Spain
[3] Grup de Biotecnologia Molecular i Industrial, Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, Rambla Sant Nebridi, 22, 08222 Terrassa, Catalunya, Spain; julio.bastos@upc.edu
* Correspondence: mariadelmar.baeza@uab.cat
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Abstract: Many carbon materials are well-known conductive materials, widely used in the fabrication of composite electrodes. In this work, diverse allotropic forms of carbon such as graphite, MWCNTs and rGO were tested. Furthermore, these materials allow the construction of cheaper, smaller, portable, reliable and easy-to-use devices, which can be easily modified. The above-mentioned composite electrodes were developed for metal analysis in water such as Cu, Cd and Pb that, at a high concentration, can have consequences on human health. SWASV is the selected technique. It would be ideal to exploit the potential properties of mercury for metal detection by tuning the electrode's surface. Due to mercury's hazardous properties and to reduce the amount of this substance used in polarography, the use of nanoparticles is a good option due to their properties. Mercury nanoparticles were used to modify the surface of the composite electrodes to improve electroanalytical sensor response. For this reason, using these modified composite electrodes can lower detection limits and widen the linear range that can be achieved for Cd (0.05–1 mg·L^{-1}) and Pb (0.045–1 mg·L^{-1}). However, for Cu (0.114–1.14 mg·L^{-1}), meaningful variations were not observed compared to the bare electrode.

Keywords: electrochemistry; Hg nanoparticles; graphite; composite electrodes; metal analysis; SWASV

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1. Introduction

Water is fundamental for all Earth's living forms, and a key issue for social and economic development. Currently, water analysis is a vital topic, for because monitoring some parameters is important to prevent some health problems. One of the parameters that has become important involves determining the concentration of heavy metals in water. To do this, several analysis techniques are used, such as atomic absorption spectroscopy (AAS) [1], inductively coupled plasma (ICP) [2], high-performance liquid chromatography (HPLC) [3], etc. Some of the metals that can be found in water are Cu, Cd and Pb and, at high concentrations, can have consequences on human health [4–6].

In this work, a voltametric technique has been chosen, known as square-wave anodic stripping voltammetry (SWASV) [7,8]. SWASV consists of two steps: first, applying a potential to preconcentrate the analyte on the surface of the electrode; second, taking a measurement by applying staircase potential to record the current generated.

To use this technique, composite electrodes were construct using different carbon materials and a non-conductor epoxy. The behavior of graphite, reduced graphene oxide (rGO) and carbon nanotubes (CNTs) were tested in the detection of Cd, Pb and Cu. However, we work with the bare electrode; the modification of their surface with mercury nanoparticles (Hg-NPs) was also tested [9]. Mercury was used, a long time ago, in polarography, and it is well-known for its ability to form amalgams with some metals, reducing the potential where they appear [10,11]. Hence, taking advantage of these properties, the aim of this work is to reduce the amount of mercury used in polarography for the determination of Cd, Pb, and Cu.

2. Composite Electrodes Construction, Characterization, and Modification

2.1. Composite Electrode Construction

Composites were constructed using three different carbon materials: graphite, CNTs and rGO. The first step is to weld a copper sheet to a commercial connector; after that, it is placed in a PVC tube. A mixture of one of the carbon materials and Epotek H77 is prepared, and the PVC tube (2.1 cm, ∅6 mm) is filled with this mixture. Then, it is cured for 2 days at 80 °C. Then, the surface must be polished.

The percentages tested of carbon materials are shown in Table 1. These percentages were optimized previously, and they are related to their respective improvement in the electroanalytical properties of developed sensors, in terms of detection limit and sensitivity [12].

Table 1. Percentages used in the construction of each electrode.

Material	% Carbon Material	% Epotek H77
Graphite	15	85
	20	80
CNTs	10	90
rGO	15	85

2.2. Composite Electrode Chacaterization

Electrodes were characterized using Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) using a computer-controlled Multi-AUTOLAB M101 (Eco Chemie, Utrecht, The Netherlands) with a three-electrode cell: a platinum-based electrode 53–671 (Crison Instruments, Alella, Barcelona, Spain) as a counter electrode, an Ag/AgCl handmade electrode as a reference electrode and the constructed composite electrodes as working electrodes. The characterization was performed in solution composed of 0.01 M $K_4Fe(CN_6)$, 0.01 M $K_3Fe(CN_6)$ and 0.1 M KCl. For CV, the scan rate was 10 $mV \cdot s^{-1}$ and the rate of frequencies used in EIS was 0.01 to 10^4 Hz.

The behavior of the 15% rGO electrode was unusual, possibly related to the orientation of the layers in the Epotek H77 matrix, and its characterization using CV and EIS was not successful. In Figure 1, the characterization of the rest of the carbon electrodes, with graphite or CNTs, can be observed. The most notable difference is showed in EIS, where the 20% graphite presents the lower charge transference resistance. Thus, a highly conductive surface is then available for the preconcentration of cationic metals.

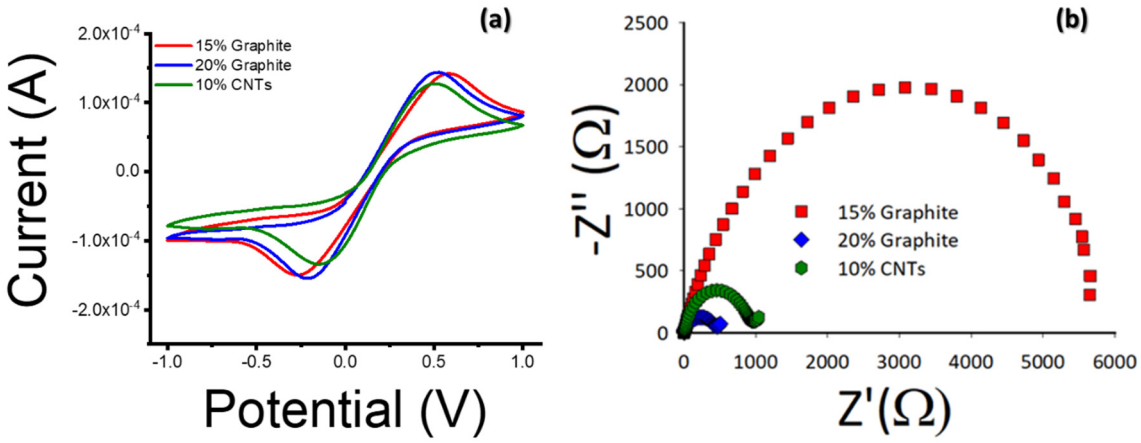

Figure 1. CV (**a**) and EIS (**b**) characterization of the different electrodes.

2.3. Composite Electrode Modification with Hg-Nps

After electrode characterization, the surface of the electrode is modified with mercury nanoparticles (Hg-NPs) following the synthesis from [9]. In the synthesis, 78 mg $Hg_2(NO_3)_2{\cdot}2H_2O$ is used, 1 mL 1 M HNO_3 is added and then 0.5 mL of a solution of 3.5 g of PVA (Polyvinyl Alcohol) added to 16 mL of Milli-Q water. All the steps of the synthesis were performed at 25 °C and under stirring conditions.

A total of 20 µL of the nanoparticle solution is drop casted on the electrode surface and dried in the oven at 80 °C for 2 h. The modified electrodes were characterized using scanning electron microscopy (SEM) (MerlinFe-SEM, Carl Zeiss, Germany) and the Hg-NPs were characterized using transmission electron microscopy (TEM) (JEM-2011 200 kV, Jeol, Peabody, MA, USA) (see Figure 2).

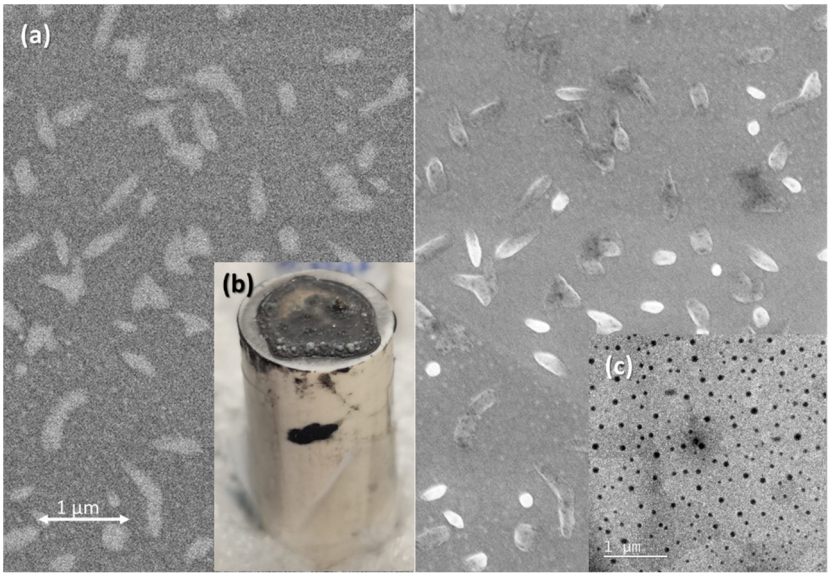

Figure 2. (**a**) Retrodispersive (**left**) and secondary electron (**right**) SEM images; (**b**) 20% graphite electrode drop casted with Hg-NPs image; (**c**) TEM image of the Hg-NPs.

2.4. Metal Solution Preparation and Determination

The metal solutions were prepared using certified stock standards of 37 $mg{\cdot}L^{-1}$ $Pb(NO_3)_2$ (≥99%, supplied from Sigma-Aldrich), 11,438 $mg{\cdot}L^{-1}$ $Cu(NO_3)_2$ (99.5 %, purchased from Merck) and 1000 $mg{\cdot}L^{-1}$ $Cd(NO_3)_2$ (99 %, obtained from Panreac). They were added to a 0.1 M acetic acid (CH_3COOH, 99.9% acquired from J.T.Baker, HPLC

reagent)/0.1 M Ammonium acetate (NH_4CH_3COO, 97 % purchased from Panreac) buffer with Milli-Q water at pH 4.6 [13].

2.5. Bare Composite Electrodes

For metal determination, the technique chosen was SWASV. This consists of applying a potential (−1.4 V) for 7 min that reduces the metal ions on the electrode surface; then, staircase potential is applied and the current generated is recorded. This process is performed under N_2 bubbling. Moreover, a modification in the electrochemical cell is used. Instead of using a handmade reference electrode, the one used for the measurements is Orion 900 electrode (Thermo Scientific, Beverly, MA, USA).

Firstly, the bare electrodes were used for the electrochemical detection of Cd, Pb and Cu. The results for all electrodes studied are shown in Figure 3.

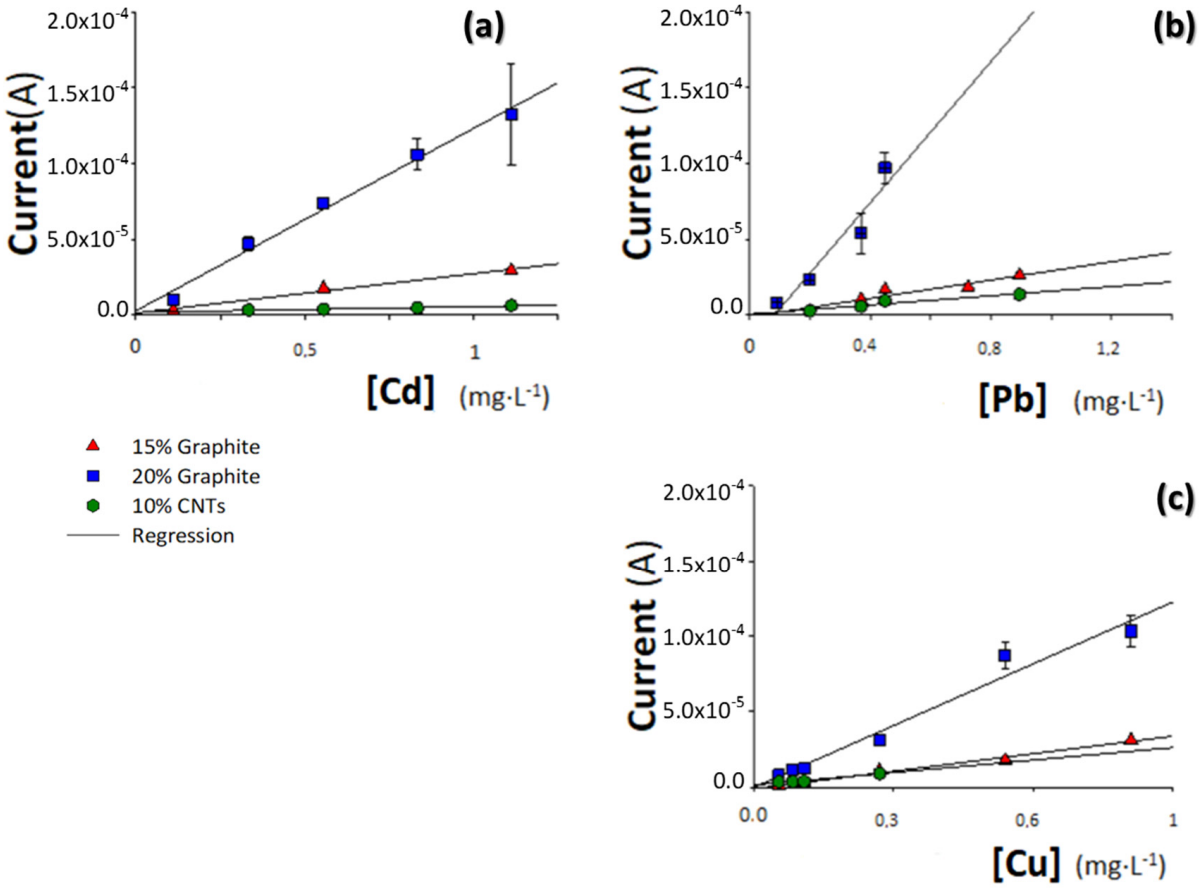

Figure 3. Calibration curves for Cd (**a**), Pb (**b**) and Cu (**c**) for each raw material.

As can be seen, 20% graphite electrodes showed the best response, as it has a better sensitivity compared with 15% graphite and 10% CNTs composite electrodes for three metal cations analyzed.

2.6. Hg-NPs Drop Casted Electrodes

The next step is to modify the surface of the 20% graphite electrode with Hg-NPs, as mentioned above. Once the surface is modified, the electrode is tested for Cd, Pb and Cu determination using SWASV. The corresponding results are shown in Figure 4.

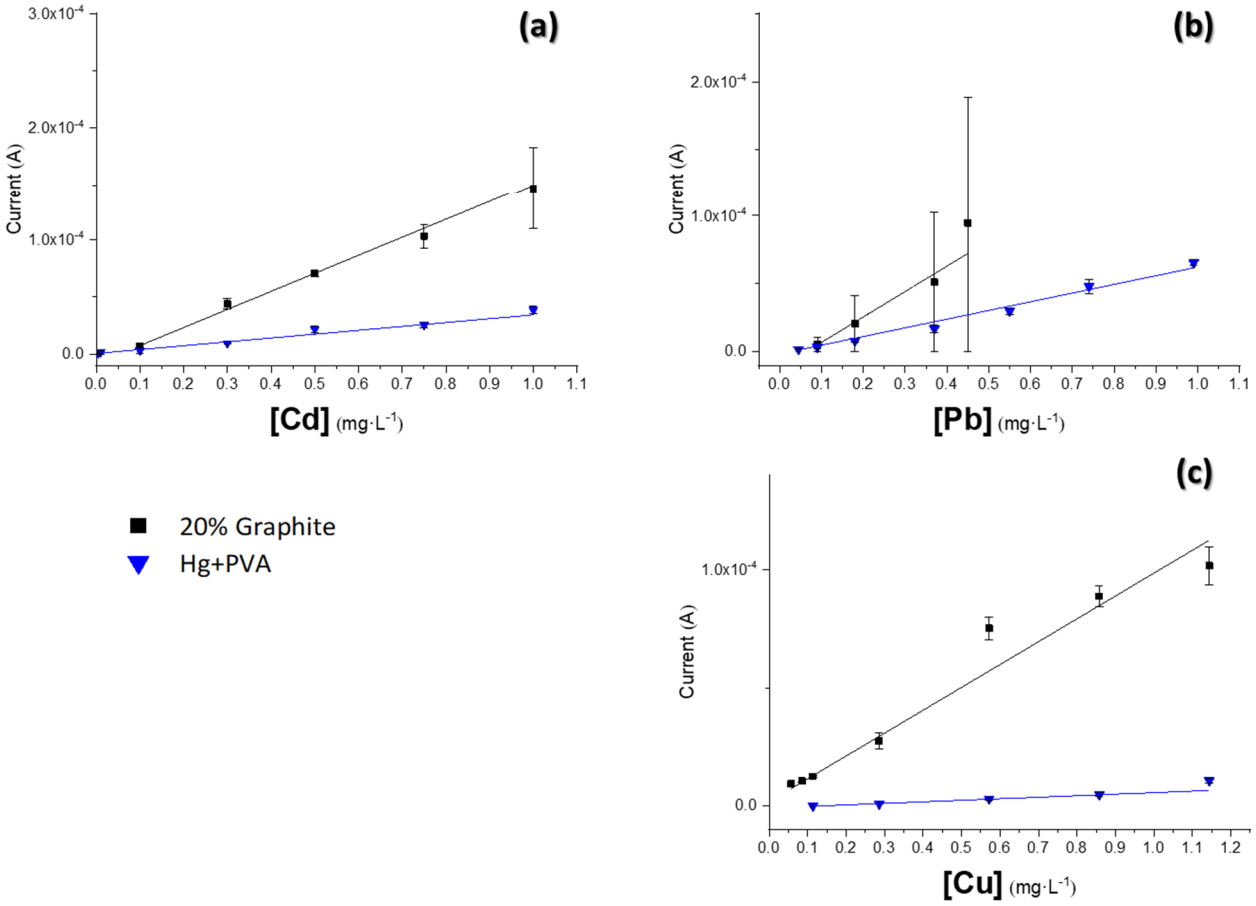

Figure 4. Calibration curves for Cd (**a**), Pb (**b**) and Cu (**c**) for 20% graphite (black) and 20% graphite plus Hg-NPs (blue).

With this modified 20% graphite electrode, lower quantification limits can be achieved. In Table 2, all the parameters of the calibration curves are summarized.

Table 2. Feature parameters: sensitivity, r^2 and linear range of each cationic metal detected separately.

[Cd^{2+}]			
Electrode (20% graphite)	**Sensitivity** [A·(mg·L^{-1})$^{-1}$]	**r^2 (n)**	**Linear Range** (mg·L^{-1})
Bare	$(1.6 \pm 0.1) \times 10^{-4}$	0.995 (n = 5)	0.1–1
plus Hg-NPs	$(3.4 \pm 0.2) \times 10^{-5}$	0.98 (n = 6)	0.05–1
[Pb^{2+}]			
Electrode (20% graphite)	**Sensitivity** [A·(mg·L^{-1})$^{-1}$]	**r^2 (n)**	**Linear Range** (mg·L^{-1})
Bare	$(1.9 \pm 0.2) \times 10^{-4}$	0.95 (n = 4)	0.09–0.45
plus Hg-NPs	$(6.4 \pm 0.3) \times 10^{-5}$	0.98 (n = 7)	0.045–1
[Cu^{2+}]			
Electrode (20% graphite)	**Sensitivity** [A·(mg·L^{-1})$^{-1}$]	**r^2 (n)**	**Linear Range** (mg·L^{-1})
Bare	$(9.7 \pm 0.9) \times 10^{-5}$	0.95 (n = 7)	0.057–1.14
plus Hg-NPs	$(7 \pm 1) \times 10^{-6}$	0.90 (n = 5)	0.114–1.14

3. Conclusions

Carbon composite electrodes are very versatile, robust, and reliable electrodes to work with for Cd, Pb and Cu detection. The well-known properties of mercury to form an

amalgam with other metals can be taken advantage of to modify the surface of the carbon composite electrode in order to decrease the limit detection of the bare electrode. To emulate the polarography, the use of Hg-NPs reduces the amount of mercury used without losing its properties. In this case, Cd and Pb form an amalgam with Hg, reducing the detection limit (Cd = 0.05 mg·L^{-1}; Pb = 0.045 mg·L^{-1}) in comparison with the bare electrode. The Cu metallic cation does not exhibit this behavior. Although the bare electrode has higher sensitivity because its electroactive area is not modified, when the electrode was modified with Hg-NPs, its electroactive area decreases. We added a polymer (from the synthesis of the NPs) over the electrode's surface that is not as good as a conductor as graphite. On the other hand, we improved the detection limit due to the specific interaction of mercury with metals cations.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/CSAC2021-10456/s1.

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Conflicts of Interest: The authors declare no conflict of interest.

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