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From Nanomaterial to Laser engraving: Carbon based Electrochemical Sensor Engineering for Metal Contaminants monitoring in Water

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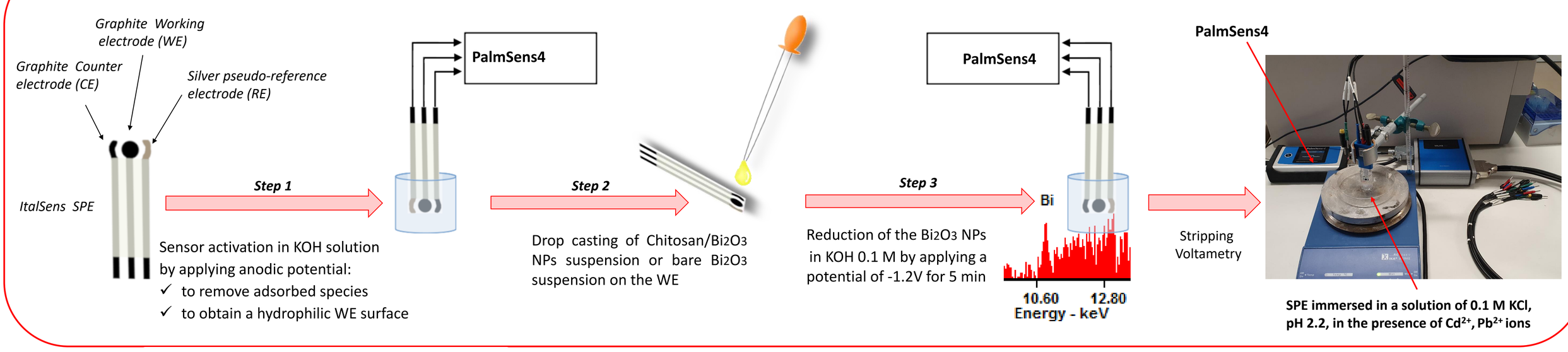
Summary

Heavy metal contaminants in water represent an environmental and health issue, therefore it is important to monitor and quantify their concentration even when in traces.
Among various detection techniques, the stripping voltammetry one is widely used for its sensitivity and accuracy. Commonly exploited mercury-based electrodes show potential high toxicity if they are not used properly, while bismuth-based sensors are an environmental friendly alternative [1,2].
The growing demand for cheap and reliable systems addresses towards miniaturized and nanostructured sensors, which exhibit attractive properties compared to traditional bulk electrodes.
In this context, first, a method for modifying commercial screen-printed graphite electrodes (SPE) with bismuth is proposed. Anodic stripping square wave voltammetric measurements were carried out by PalmSens4 analyzer with PSTrace 5 software, and, compared to the bare graphite sensor, better results are obtained in the simultaneous detection of cadmium and lead with the bismuth engineered working electrode (WE). The modified WE allows to achieve a detection limit of 3 µg/L for Cd/Pb. A linear behavior from 3 to 15 µg/L for Cd and from 3 to 20 µg/L for Pb was observed. Furthermore, Bi_2O_3 NPs stabilized in water in the presence of LMW chitosan are successfully exploited to modify the WE surface in order to improve metal ions absorption.

Besides the benefits brought by graphite surface modification with nanomaterials/polymeric films, the fabrication of Laser-Induced Graphene (LIG) electrodes by means of direct laser writing technique is an emerging research field, as it allows a time and cost-effective fabrication of two-dimensional carbon based electronic materials with applications in microelectronics [3]. Many types of carbon-containing raw materials can be converted into conductive material by laser engraving in a single step, without chemical synthesis routines, using a variety of lasers [4].
The second approach we aim to present exploits the LIG technique, for the fabrication of a three-electrode system. The precursor material is a *Kapton* tape applied on a PVC substrate. Through the carbonization process operated by a blue laser system (EleksMaker A3 Pro, 445 nm, 2.5 W) controlled by EleksCAM software in a nitrogen conditioned atmosphere, the polyimmide film is converted into a conductive material.

Modification steps of SPE with Bismuth only or Chitosan/Bismuth



Modified SPE with bismuth: results

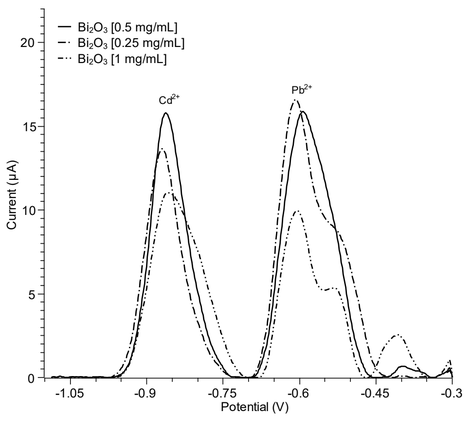


Fig. 1. Detection of 20 µg/L of Cd^{2+} and Pb^{2+}: variation of SPE response as a function of bismuth oxide concentration

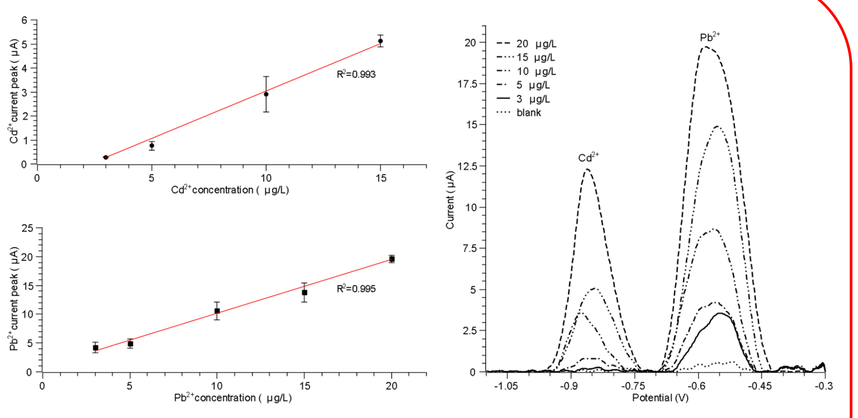


Fig. 2. SPE response in the detection of 3,5,10,15,20 µg/L of Cd^{2+} and Pb^{2+} in KCl 0.1M pH 2.2

Modified SPE with chitosan/bismuth: results

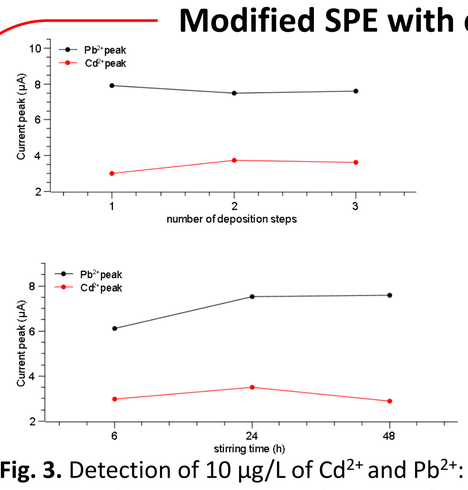


Fig. 3. Detection of 10 µg/L of Cd^{2+} and Pb^{2+}: variation of SPE response as a function of the number of deposition steps and stirring time during NPs synthesis.

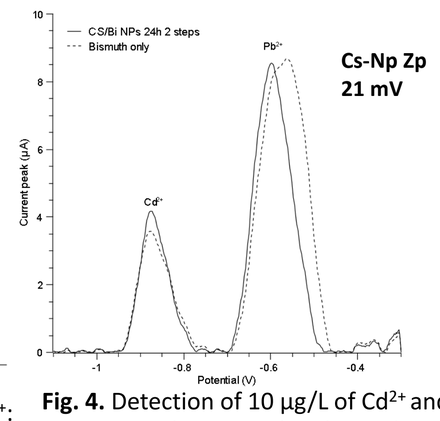


Fig. 4. Detection of 10 µg/L of Cd^{2+} and Pb^{2+}: comparison between the electrode modified with Chitosan-bismuth NPs and the electrode modified with bismuth NPs

LIG: technique & parameters

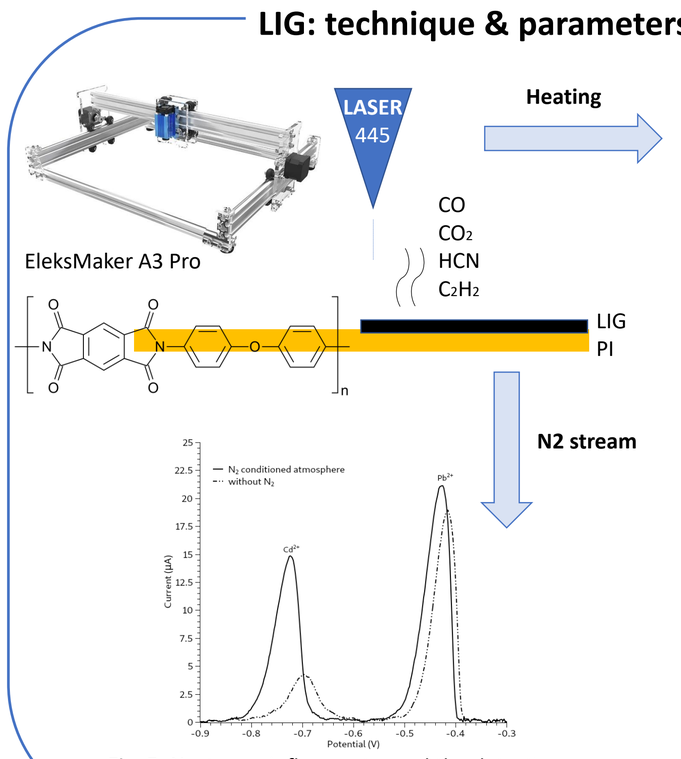


Fig. 5. N_2 stream influence toward the detection of a mix of 250 µg/L of Cd^{2+} and Pb^{2+}.

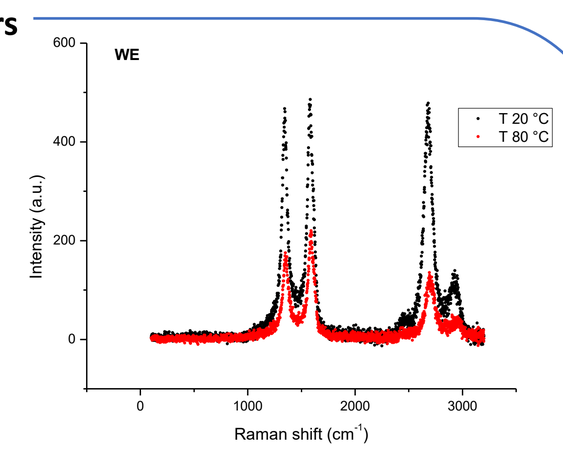
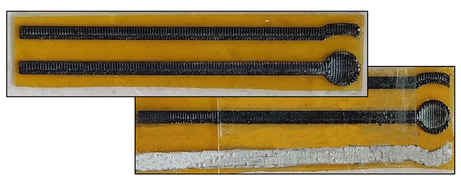


Fig.6. Different peak intensity are an indication of a different structuring.



On the top: home made 2-electrode system.
On the bottom: home made 3-electrode system, with RE obtained through Ag NWs deposition.

LIG SENSOR performance & NPs-WE modification

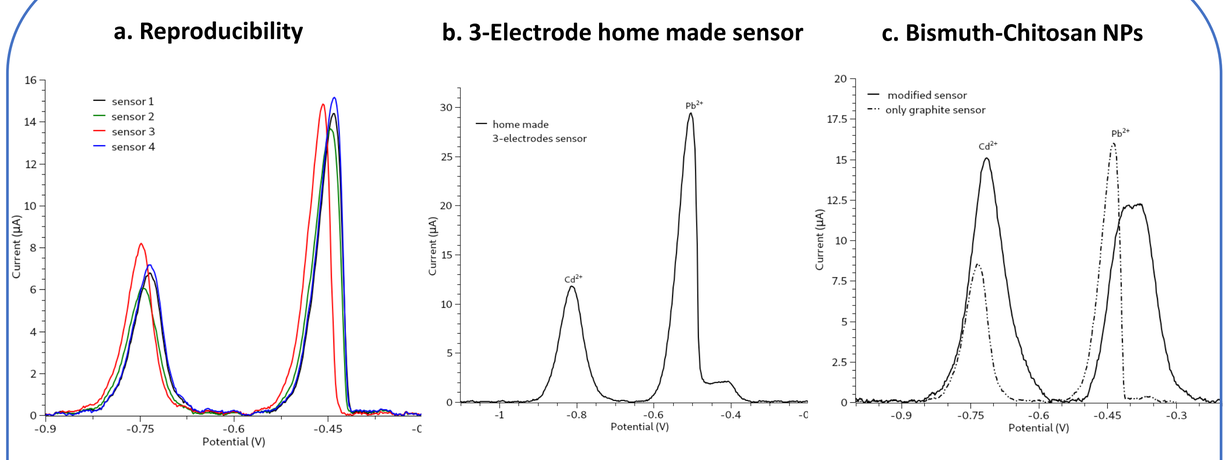


Fig. 7. a: Response to 100 µg/L of Cd^{2+} and Pb^{2+} of 4sensors manifactured at room T, with external RE.
b: Response to detection of 100 µg/L of Cd^{2+} and Pb^{2+} a sensor (manifactured at room T), with homemade RE.
c: Comparison between the performance of pristine-graphite sensor vs bismuth-Cs NPs modified sensor.

Conclusions

In order to verify the performance of these low cost, flexible and disposable miniaturized sensor, the same protocol optimized on the commercial graphite SPE is successfully applied. Taking advantage of Electronics, Micro and Nanosystems for Agri-Food and environmental sustainability, physical characterization and electrochemical measurements were focused to highlight elemental and structural differences relation with diverse sensors performance, for appropriate and promising application in water contaminants monitoring - on site.

- **The bismuth - modified graphite SPE allows to achieve a LOD of 3 µg/L for Cd/Pb.**
- **Preliminary results, obtained with the chitosan coated-bismuth oxide NPs, show an improvement in the detection of Cd.**
- **Direct laser writing on polyimide substrate has been successfully used for home-made carbon based - flexible sensors. They show an accurate response in the range of 100 µg/L. Studies are in progress with respect to promising Chitosan Bismuth NPs - modified LIG sensor.**

[1] N. Serrano et al., Coating methods, modifiers and applications of bismuth screen-printed electrodes. Trends in Analytical Chemistry, Vol. 46, 2013.
[2] X. Niu et al., Review: Electrochemical Stripping Analysis of Trace Heavy Metals Using Screen-Printed Electrodes. Analytical Letters, 46:16 2479–2502, 2013.
[3] R. Ye, D. K. James, and J. M. Tour, Laser-Induced Graphene: From Discovery to Translation, Adv. Mater. 2019, 31, 1803621;
[4] G. Li, Direct laser writing of graphene electrodes, J. Appl. Phys. 127, 010901 (2020).

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