Graphene oxide nanostructures in analysis of traces of lead

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Outline

Introduction

Analysis of traces of lead in running water

Graphene oxide role as the sorbent and the electrode material

Methods

Results and discussion

Electrochemical detection of lead on screen printed electrodes

AFM of nano-structures at glass substrate

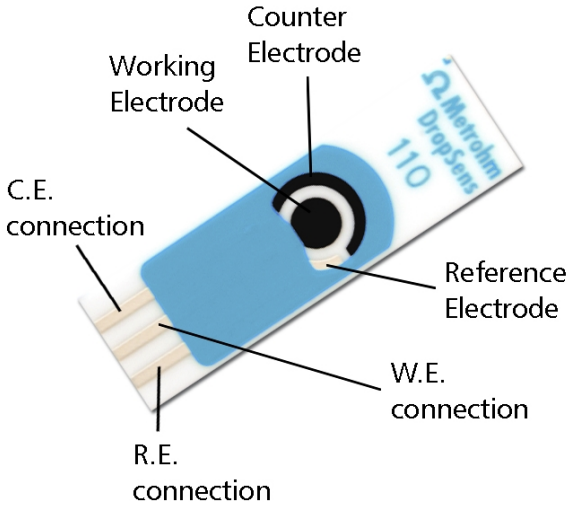
Introduction

Heavy metal contamination of surface water, [1,2] and most importantly the drinking water, states a serious problem both in developing countries, [3] facing starvation and shortage of potable water, [4] but also in already developed countries. [5] The interaction of running line water conditioners and disinfectants (such as chlorine, monochloramine) [6,7] with elements of hydraulic installations (not only made from metal but also from recycled plastics)[8–10] might produce elevated levels of heavy metals.

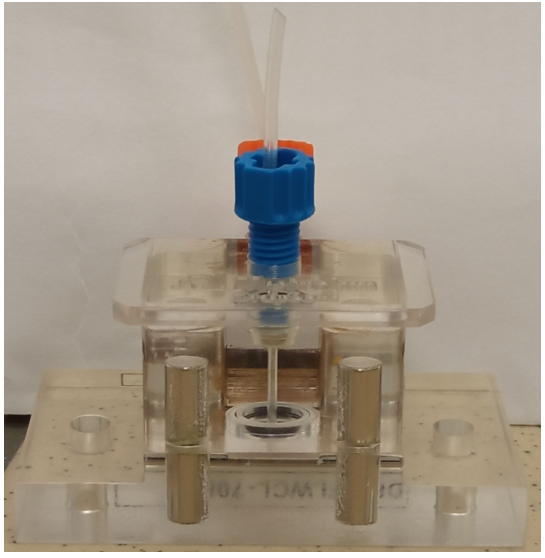
1 B. Sarkar, *Heavy metals in the environment*, CRC press, **2002**.
2 M. I. Ahamed, E. Lichtfouse et al., *Water pollution and remediation: Heavy metals*, Springer, **2020**.
3 G. E. Zaikov, L. I. Weisfeld, E. M. Lisitsyn and S. A. Bekuzarova, *Heavy metals and other pollutants in the environment: biological aspects*, CRC Press, **2017**.
4 S. K. Sharma, *Heavy metals in water : presence, removal and safety*, Royal Society of Chemistry, Gld edn, **2014**.
5 P. S. Rawat, S. Singh, A. A. Mahdi and S. Mehrotra, Journal of Trace Elements in Medicine and Biology, **2022**, 126981.
6 V. V. Rajasekharan, B. N. Clark, S. Boonsalee and J. A. Switzer, Environmental Science and Technology, **2007**, 41, 4252–4257.
7 J. A. Switzer, V. V. Rajasekharan, S. Boonsalee, E. A. Kulp and E. W. Bohannan, Environmental Science and Technology, **2006**, 40, 3384–3387.
8 A. Turner and M. Filella, Journal of Hazardous Materials, **2021**, 404, 124131.
9 B. P. Lanphear, PLOS Biology, **2017**, 15, e2003066.
10 A. Turner, Environment International, 2018, 117, 308–318.

Goal of the study

Improve detection limit of screen-printed electrodes (SPE) in Pb^{2+} detection



Typical SPE (DropSens)



Typical flow cell (DropSens)

Methods

Materials: Graphene oxides (Hummer's, Brodie's, Sigma Aldrich)

Modification of SPE with: A) drop casting and B) electro-polymerization with use of GO/metal ion precursor (Cu, Cd, Pb)

Square Wave Voltammetry in flow system with deposition step, where the lead concentration is 1 ppm

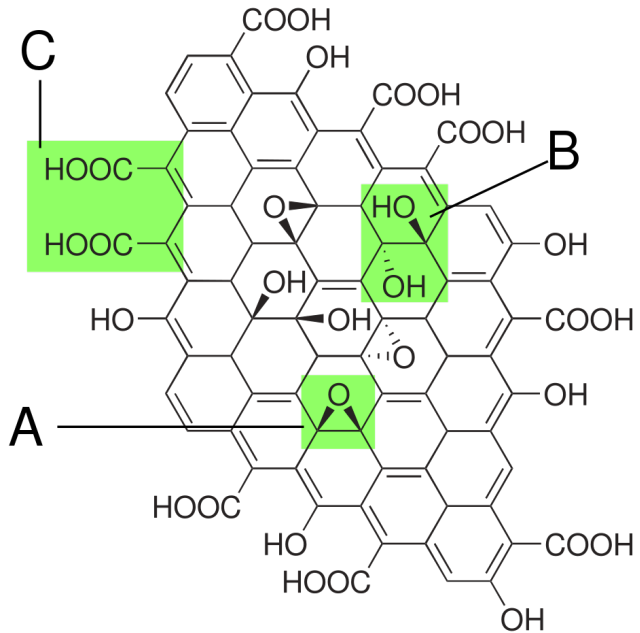
Atomic Force Microscopy for the selected graphene oxide/metal ions assemblages on glass surface

Methods

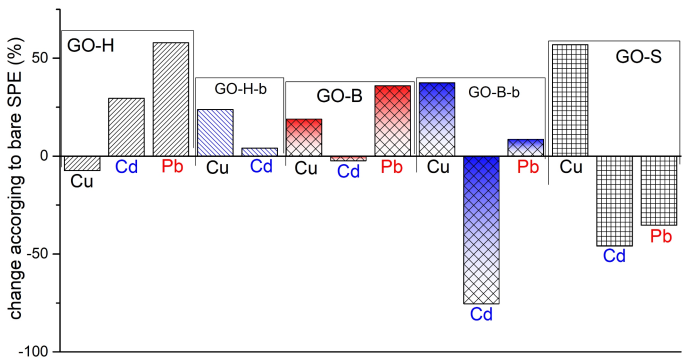
Screen printed electrodes modification:

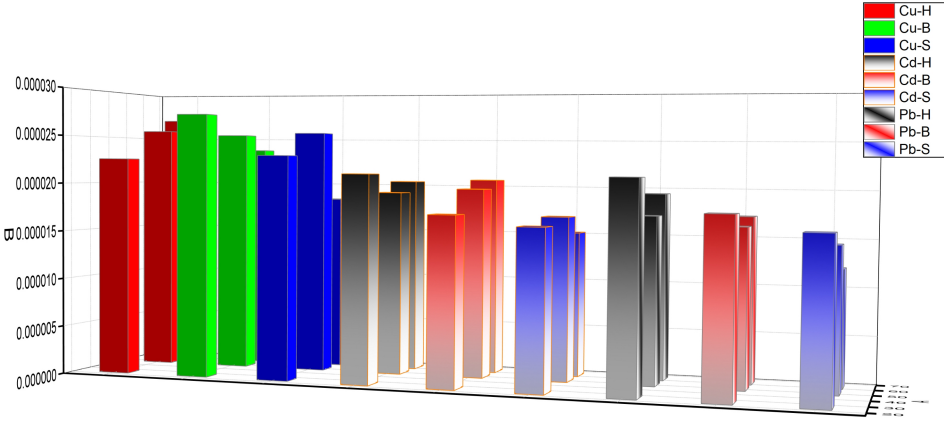
DRP-C110 + precursor solution, drop casting&aging at 100 °C for 10-20 min

Measurement: SWV with preconditioning in flow cell with 0.33 mL/min flow velocity of electrolyte with 1 ppm Pb^{2+}



Results - overview

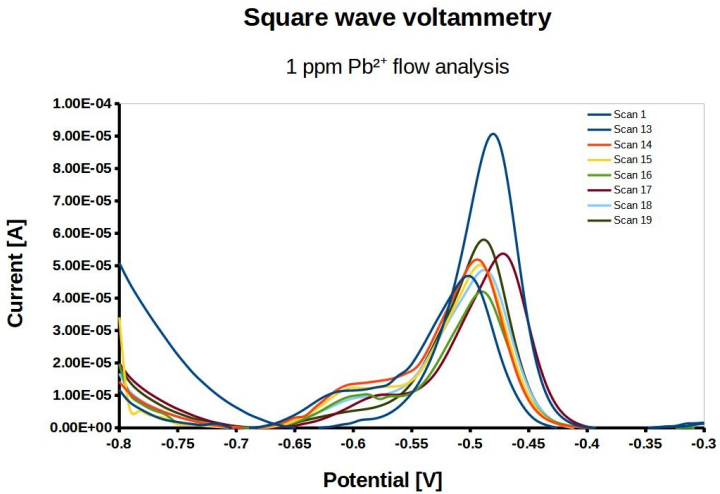




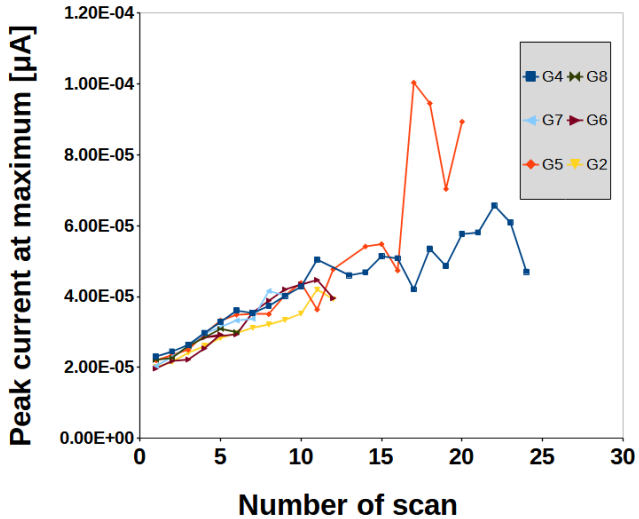
Peak currents of lead oxidation at -0.6V in series of sensors prepared from three types of graphene oxides (H - Hummer's, B – Brodie's, S - commercial, b - filtrated) Room temperature, lead concentration 1 ppm, electrolyte concentration 0.1 M potassium chloride, pH=1.5 acidified with nitric acid. Flow speed 0.33 mL/min.

The peak currents (axis B) vs. scan number (axis A) in subsequent scans in determination of lead by square wave voltammetry in a flow system.

Results – multiscan mode

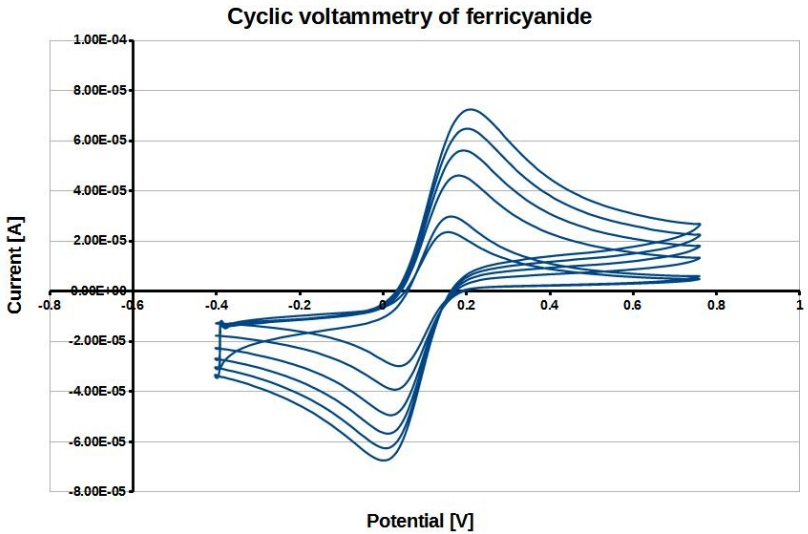


The multiscan SWV experiment at the electrode modified with cadmium (sedimentated Hummer's, Cd^{2+}, 75 pmoles per 15 µL aliquot). Acidified to pH=1.5 with nitric acid. Room temperature, flow velocity within the cell 0.33 mL/min.

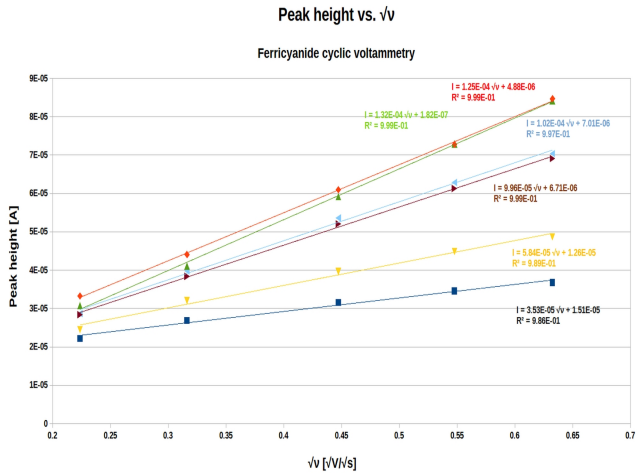


The peak current of lead oxidation peak at the graphene oxide modified electrodes. Room temperature, lead concentration 1 ppm. Flow velocity 0.33 mL/min. Legend: G2: GO-H-Cd^{2+}~38 (pmole in 15 uL aliquot),G4: GO-H-Cd^{2+}~63 ,G5: GO-H-Cd^{2+}~75,G6: GO-H-Cd^{2+}~88,G7: GO-H-Cd^{2+}~100,G8: GO-H-Cd^{2+}~113.

Randles-Sevcik relation



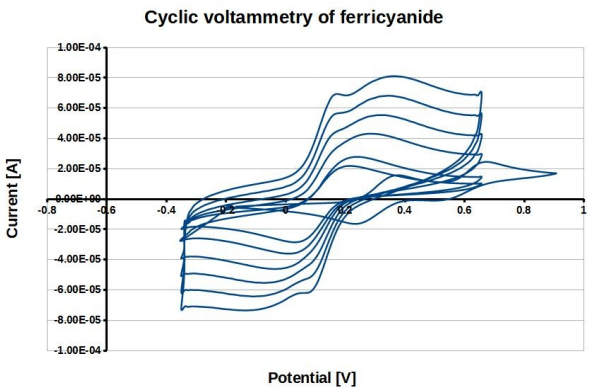
Potentiostatic cyclic voltammetry done in 50 microliter aliquots of elelctrolyte solution containing 0.9 mM potassium ferricyanide. The sweep rates of 50, 100, 200, 300, 400 and 500 mV/s correspond to increasing peak currents. The B-Cu SPE electrode was used (13 pmoles per 15 microL deposited on the working surface). Room temperature, 0.1 M potassium chloride.



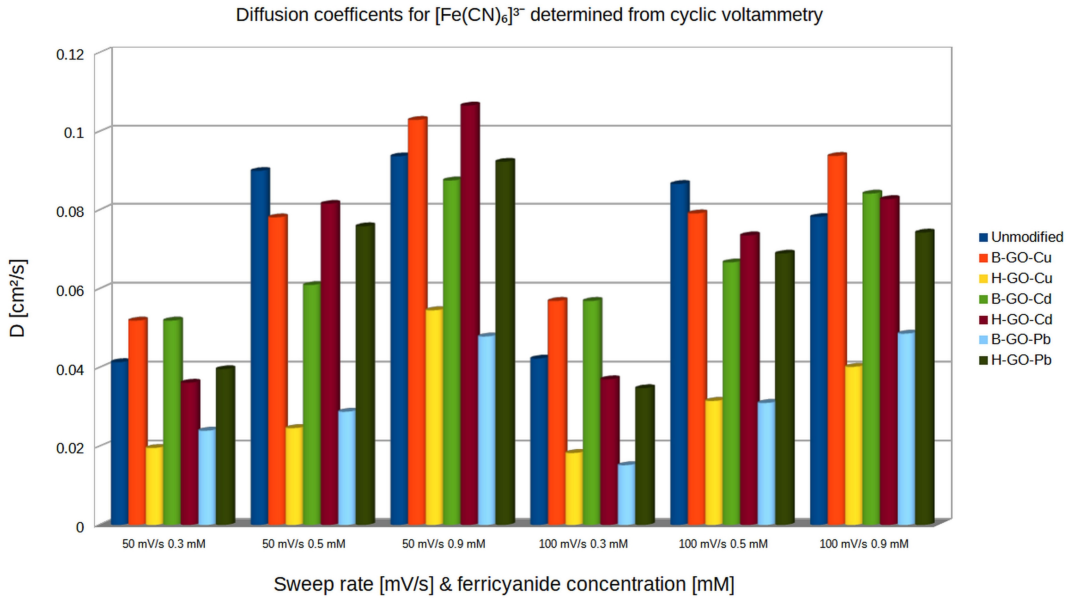
The Randles–Sevcik relation validation for the potentiostatic cyclic voltammetry of potassium ferricyanide at modified SPE. The series of SPE electrodes modified with graphene oxides and metal ions (13 pmoles per 15 microL deposited on the working surface): H-Cu (blue), H-Cd (red), H-Pb (yellow), B-Cu (green), B-Cd (brown), B-Pb (light blue). Room temperature. Working electrode surface radius 4 mm.

$[Fe(CN)_6]^{3-/2-}$ sonde ion, diffusion coefficient D

$$D = \frac{I_p^2 \cdot R \cdot T}{0.1991 \cdot n \cdot F^3 \cdot v \cdot A^2 \cdot c^2} \left[\frac{cm^2}{s}\right]$$

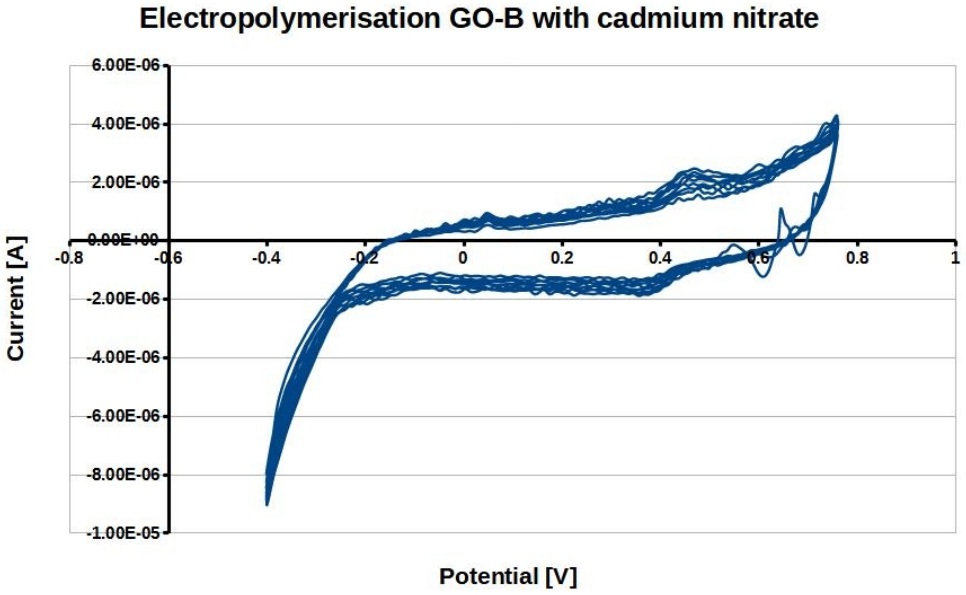


Diffusion coefficient: the quantity of a substance that in diffusing from one region to another passes through each unit of cross section per unit of time when the volume-concentration gradient is unity.

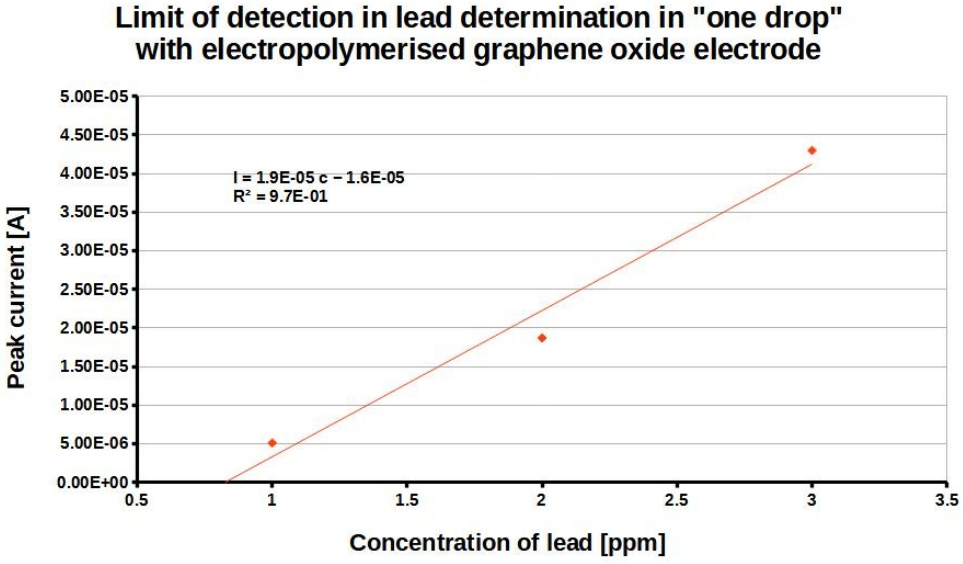


The diffusion coefficients of ferricyanide ion for the series of SPE electrodes. The potentiostatic cyclic voltammetry measurements were done in 50 uL solution aliquots containing 0.1M aqueous potassium chloride and 0.3, 0.5 and 0.9 mM concentration of potassium ferricyanide. Room temperature. Working electrode surface radius 4 mm.

Electropolymerisation of GO/Cd^{2+}

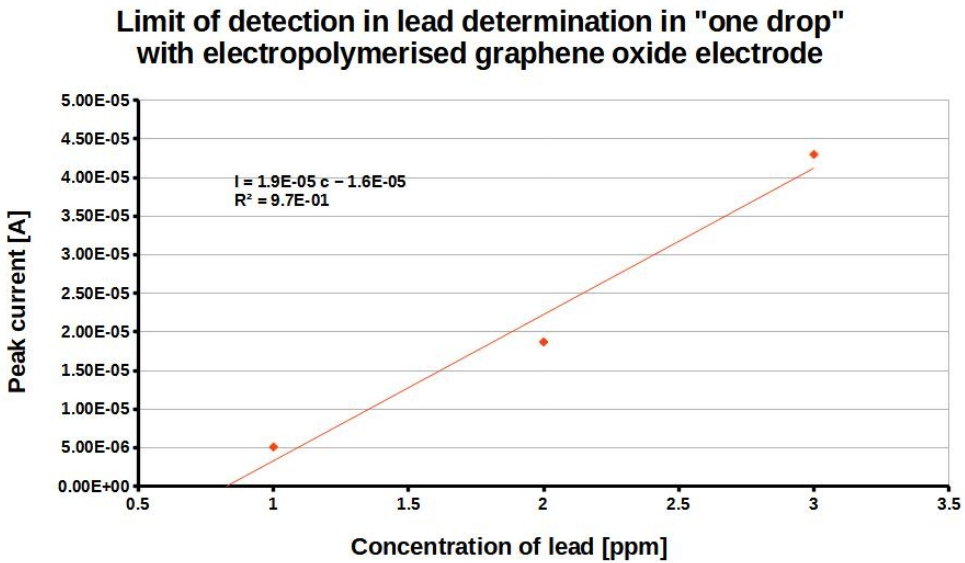


The electropolymerisation experiment in one drop experiment, in an aliquot containing 50 µL of 0.1M potassium chloride at pH=1.5, 10 µL of 0.001 M solution of cadmium ions and 25 µL of filtrated graphene oxide suspension.

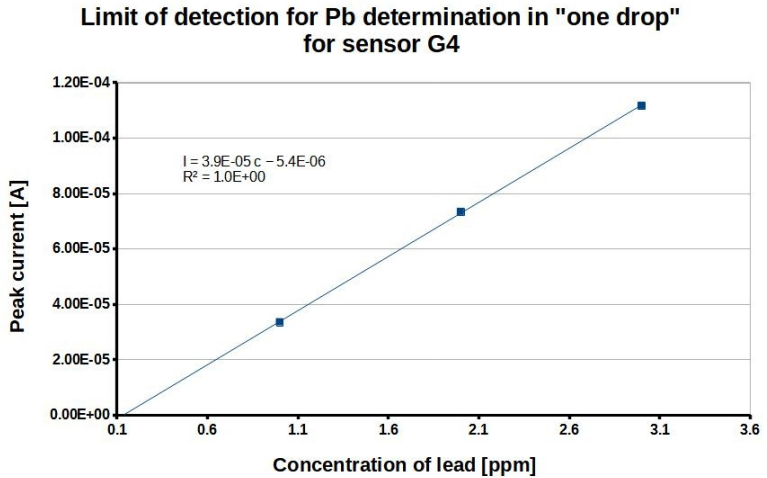


The peak current vs. lead concentration regression for electropolymerised electrode. Room temperature.

Limits of detection for electropolymerised and drop casted sensors

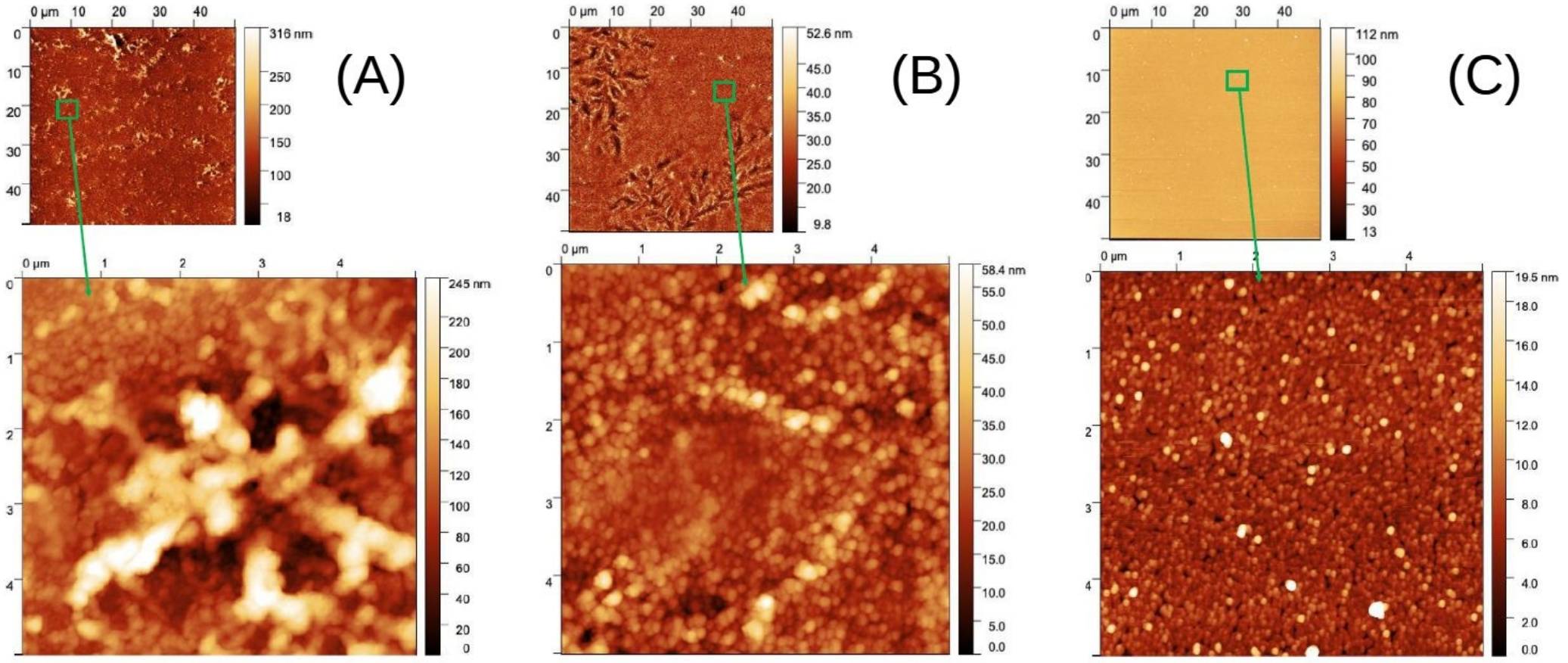


The peak current vs. lead concentration regression for electropolymerised electrode. Room temperature.

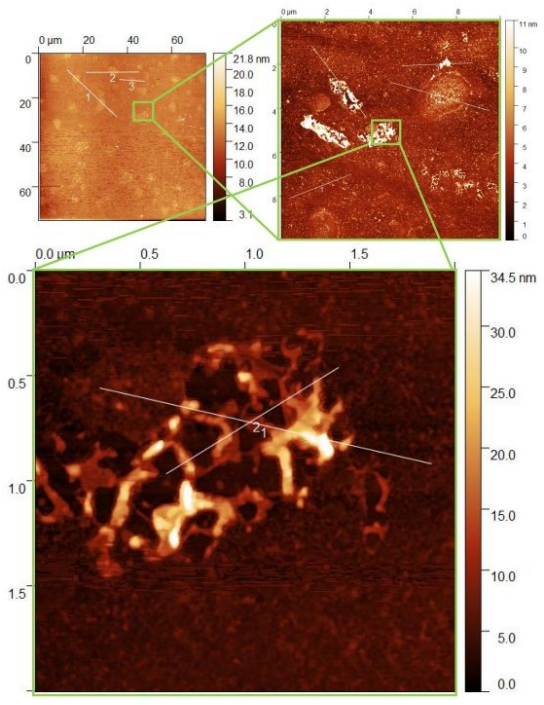


The peak current vs. lead concentration regression for drop casted electrode. Deposition potential -1.0 V applied for 60 s prior to registration of EI curve with a voltage step 0.008 V, modulation amplitude 0.02 V and frequency 25 Hz. Room temperature, lead concentration 1 ppm, electrolyte concentration 0.1 M potassium chloride, pH=1.5 acidified with nitric acid. Room temperature.

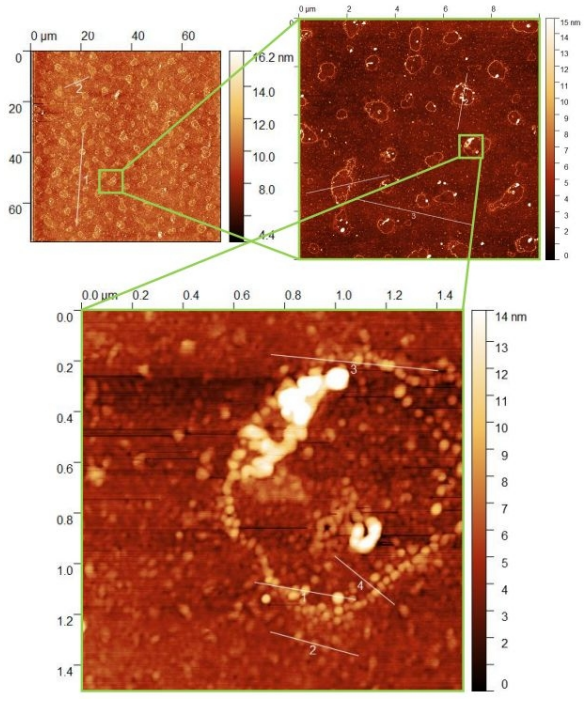
AFM topographies of sedimentated Aldrich (A), Brodie's (B) and Hummer's (C) GO



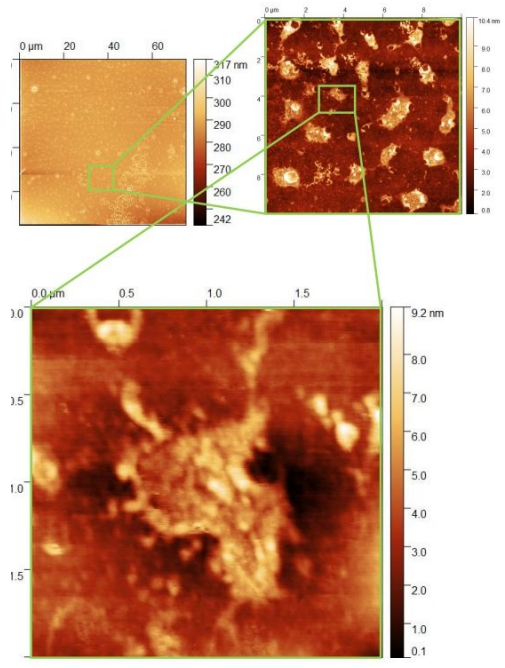
Im”Imprinted-like” AFM topographies at glass substrate of GO in presence of Cu^{2+}, Cd^{2+} and Pb^{2+}



Cu^{2+}

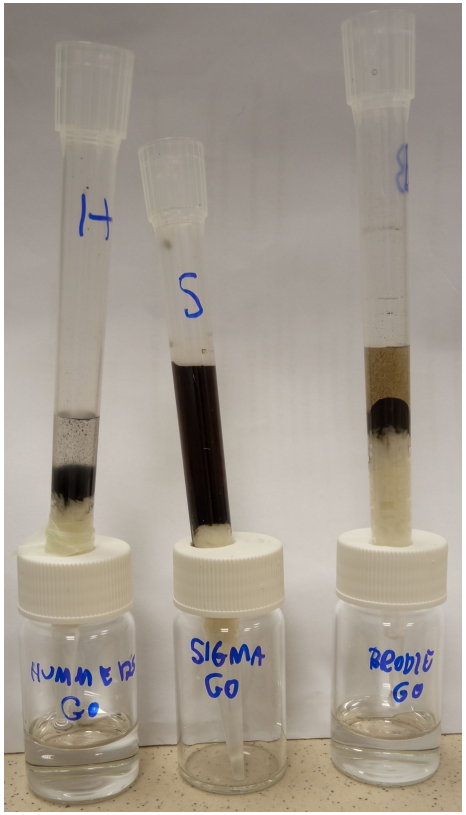


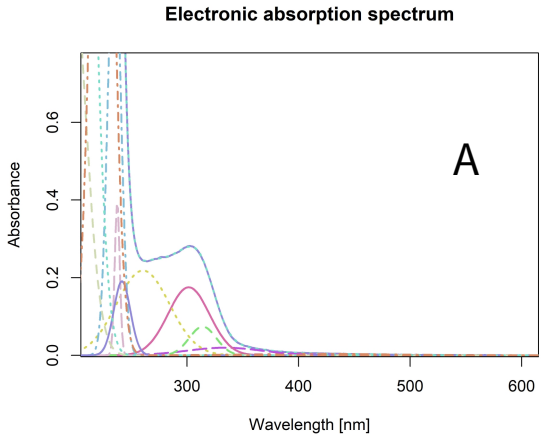
Cd^{2+}

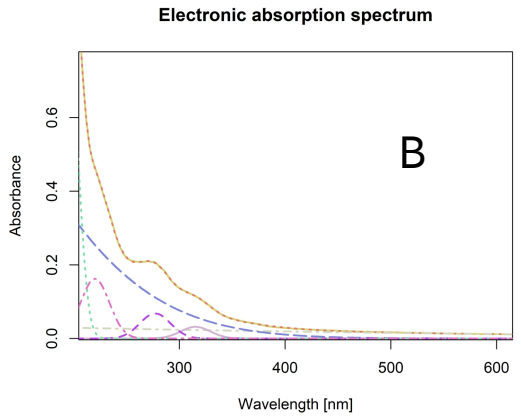


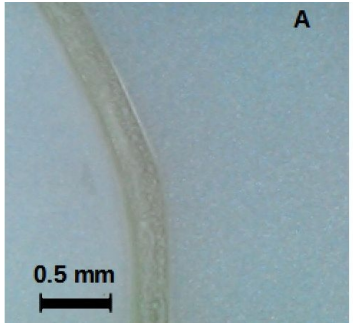
Pb^{2+}

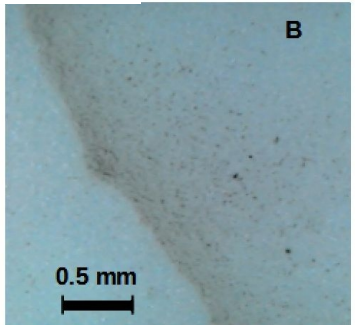
Gravitational filtration of GOs, absorption spectra of filtrates

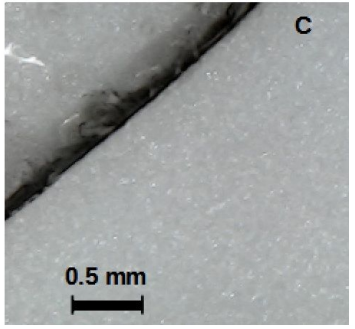




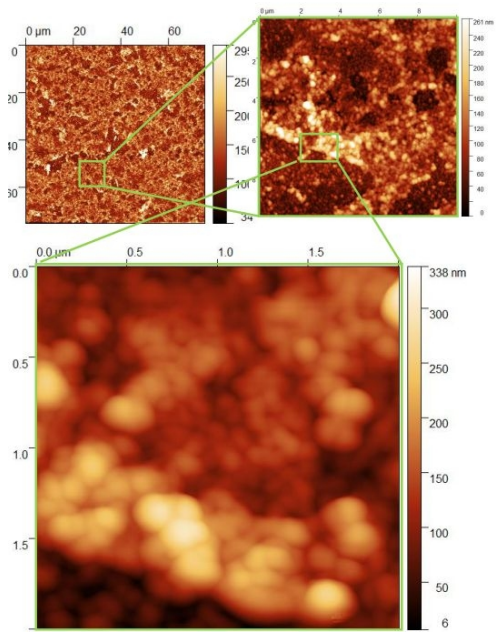




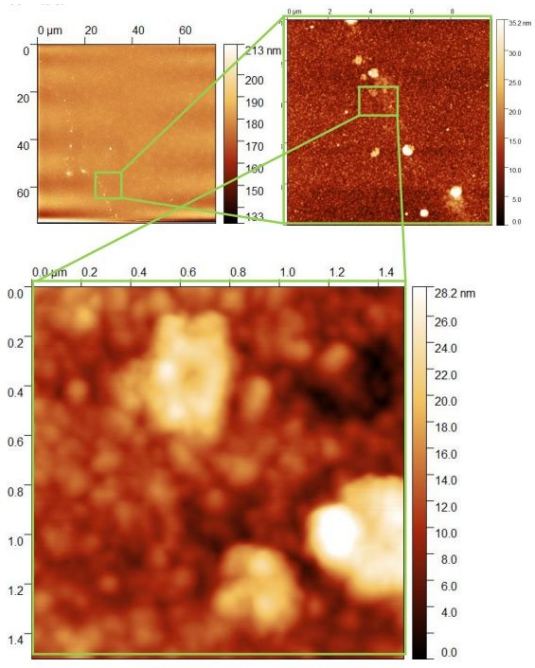




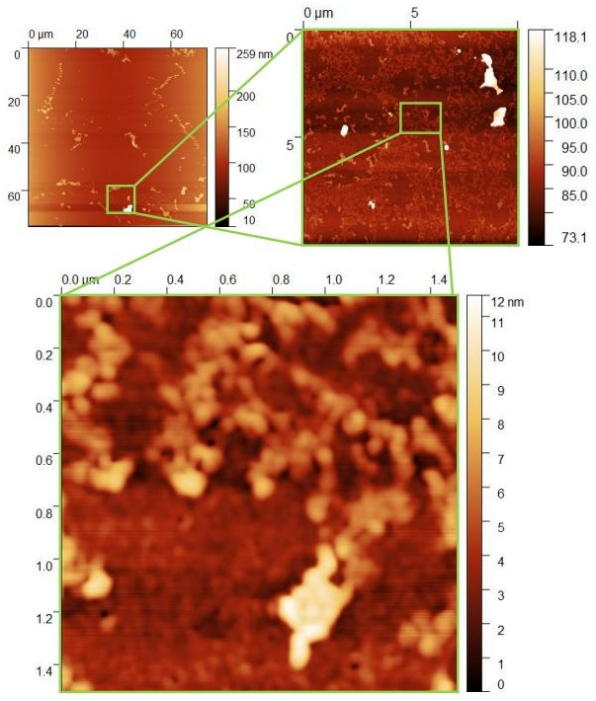
AFM topographies at glass substrate of filtered: Aldrich (A), Brodie's (B) and Hummer's (C) GO



A)



B)



C)

Conclusions

By varying the metal ion concentration the improved sensitivity ~2 times has been achieved in peak sensitivity towards Pb

Short analysis times at 1 ppm level of concentration of Pb have been achieved

The “imprinted” structures may facilitate formation of nano-alloy particles

Thank you



Tomas Bata University in Zlín