Biological Systems: Open Access

Smaini et al., Biol Syst Open Access 2017, 6:1
DOI: 10.4172/2329-6577.1000173

Research Article OMICS International

Electrochemical Detection and Removal of Mercury (II) at DNA Modified Carbon Paste Electrode

MA Smaini, R Maallah, S Touzara, C Laghlimi, S El Qouatli and A Chtaini*

Molecular Electrochemistry and Inorganic Materials Team, Beni Mellal Faculty of Science and Technology, Sultan Moulay Slimane University, Marocco

***Corresponding author:** Chtaini A, Molecular Electrochemistry and Inorganic Materials Team, Beni Mellal Faculty of Science and Technology, Sultan Moulay Slimane University, Marocco, Tel: 0021265129257; E-mail: a.chtaini@usms.ma

Received date: January 04, 2017; **Accepted date:** January 24, 2017; **Published date:** February 01, 2017

Abstract

Herein, we report a simple and inexpensive way for the fabrication of a microelectrode, DNA modified carbon paste electrode (DNA-CPE). DNA is deposited onto carbon paste electrode surface by self-assembled monolayers. The electrochemical behaviour of DNA-CPE's was studied by cyclic voltammetry (SWV) tests. The recorded CV's showed two redox peacks simultaneously at E oxidation=0.3 V and E reduction=0.2 V. The recorded SWV curves at DNA-CPE have shown great efficiency in the analysis of mercury (II) at different concentrations.

Keywords: DNA; Modified electrodes; Mercury; SWV; Cyclic voltammetry

Introduction

Mercury is the only metal that can be found in the liquid state at room temperature; it enters the environment through not only coal burning but also through mining or industrial wastes. Mercury has the power to form amalgams with several metals, such as silver, it has been widely used in dentistry, but the new legislation prohibited its use because of its toxic effects [1,2]. The most commonly used methods are atomic absorption [3], inductively coupled plasma mass spectrometry [4] and cold vapor atomic fluorescence spectrometry [5]. The electrochemical methods have proved highly effective in detecting mercury, with many advantages, such as, simplicity of implementation and inexpensive. The use of mixed assembled mono layers of DNA has received an increasing attention for the determination of metal ions [6]. In this study, we have prepared a carbon paste electrode on which we have deposited by self-assembly a DNA film. This prepared electrode was used, in conjunction with electrochemical methods, as CV's and SWV, for the removal and the detection of mercury (II). The DNA-CPE is successively exploited the favorable mechanical and electrochemical properties of carbon paste electrode, and the high flexibility of DNA structure to chelate mercury.

Experimental

Reagents and chemicals

All the chemicals used in this work, are of high quality. The carbon graphite was purchased from Aldrich, and was used in its state without modification. $HgCl_2$ was obtained from Merck chemicals. Deionised water was used to prepare all solution. The DNA used in this work is taken from quail blood, according to the protocol below:

- 5 l of blood taken from the axillary vein is poured into an Eppendorf containing 500 µl of danazol,
- The solution is stirred for 5 min by vortexing and centrifuged at 6000 rpm/5 min,
- The supernatant is removed and then 400 µl of isopropanol is added to the residue remaining in the Eppendorf,
- The mixture was vortexed and centrifuged at 6000 rpm/5 min,
- The supernatant was removed and 500 µl of pure water was added to suspend the DNA.

Apparatus

The electrochemical studies were performed with a potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by a general purpose electrochemical systems data processing software (voltalab master 4 software). The three electrode system consisted of a modified paste electrode as the working electrode, a saturated calomel electrode (SCE) serving as reference electrode, and platinum as an auxiliary electrode.

Electrode preparation

The DNA-modified carbon paste electrode was prepared by thoroughly hand-mixing of high purity graphite powder (CP), then a portion of the resulting paste was grounded and squeezed into a home-made PTFE cylindrical tube (geometric area 0.1256 cm^2) electrode. Inside the tube, the mass was in contact with a bar of carbon, which was in turn connected to an electric wire to complete the measurement circuit. DNA-CPE's were prepared by immobilizing the DNA system by soaking the preformed carbon paste electrode in a solution containing the DNA solution.

Results and Discussion

A carbon paste electrode modified with DNA was carefully washed with distilled water, heated at room temperature and transferred to electrochemical cell containing 0.1 M NaCl electrolyte. Mercury was accumulated at DNE-CPE for 15 min [6]. CV scanning was performed from -2 to 2 V at a scan rate of 100 mV/s.

Figure 1 show the voltammograms recorded, respectively at CPE and DNA-CPE, in 0.1 M NaCl. Two reduction peaks were observed at DNA-CPE towards the negative sweep direction, the first one around

-0.12 V and the second approximately 0.1 V versus SCE; these peaks can correspond to internal reductions of the macro-DNA molecule.

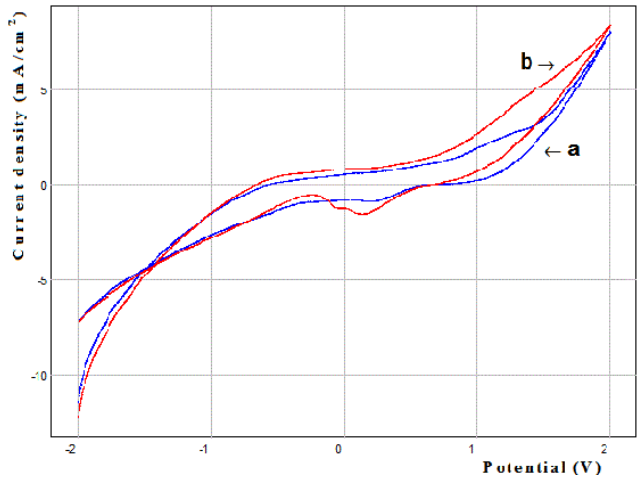

Figure 1: CV's recorded, in electrolytic solution, at CPE (curve a) and DNA-CPE (curve b), scan rate 100 mV/s.

Electrochemical impedance spectroscopy (EIS) corresponding to CPE and DNA-CPE can be seen in Figure 2. We can notice that the two electrodes exhibit a large ohmic drop, i.e., a high electrolyte resistance, which masks the part of the high-frequency diagram. However, we can see a drop in total impedance at low frequencies in the case of DNA-CPE; this is probably due to the appearance of an additional capacitance relative to the DNA film.

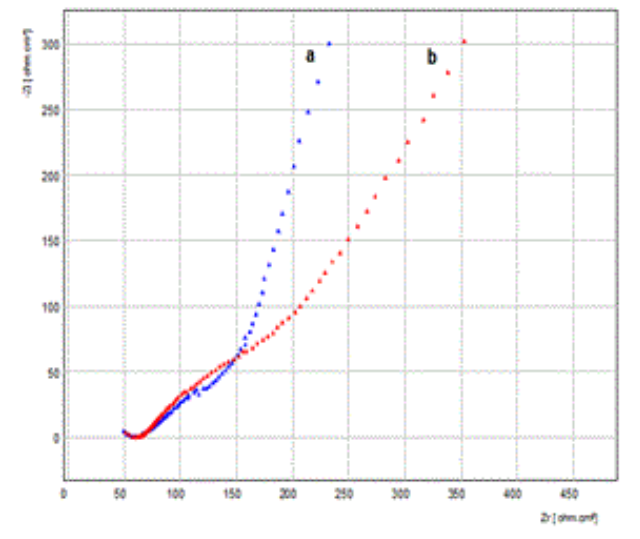

Figure 2: EIS spectra of CPE (curve a) and DNA-CPE (curve b), the frequency range was set on 1 Hz up to 1 MHz.

Mercury (II) was pre-concentrated from the solution into the DNA-modified CPE at open circuit potential, then the CV's was used to reduce Hg^{2+} (Figure 3-P1), According to the following reaction:

$$[Hg^{2+}....DNA\text{-}CPE]_{ads} + 2e^{-} \rightarrow [Hg^{0}....DNA\text{-}CPE]_{ads}$$

The peak P2 corresponds to the phenomenon of oxidation of Hg and of salting out of Hg2+, by following the mechanism below:

$$[Hg^{0}....DNA\text{-}CPE]_{ads} \rightarrow Hg^{2+} + 2e^{-} + DNA\text{-}CPE$$

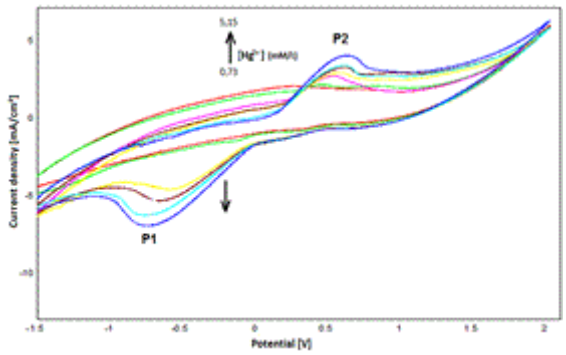

Figure 3: Cyclic voltammograms of different concentrations of Hg(II) at DNA-CPE in 0.1 M NaCl, scan rate 100 mV/s.

Figure 4 shows some of typical square-wave voltammetry (SWV) curves recorded at DNA-CPE after being in contact with different mercury (II) concentrations for 15 min of accumulation time, then, we established a calibration curve based on the current density of the observed peak. As can be seen, the current density of the peak depends linearly on the mercury concentration. The resulting equation of the linear regression analysis is as follows (Figure 5).

$$iP1=-0.029 \times [Hg^{2+}]-0.373 \; R^2=0.966$$

and

$$iP2=0.019 \times [Hg^{2+}]+0.268 \; R^2=0.991$$

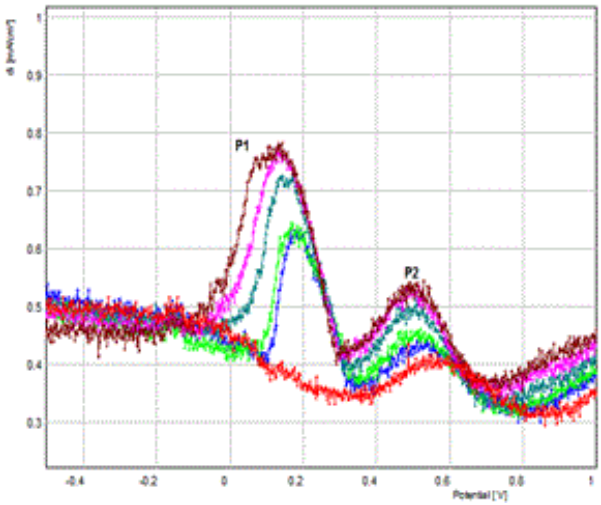

Figure 4: Square wave voltammograms in 0.1 M NaCl, preconcentration time 15 min of mercury (II) at different concentrations.

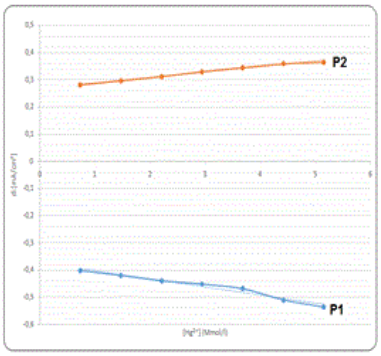

Figure 5: Calibration curves of Hg^{2+} in 0.1 M NaCl.

The effect of the scanning rate has been studied, and we find that the anodic and cathode peak current increase linearly for scanning rate value variant between 40 and 140 mV/s (Figures 6 and 7), suggesting that the electrons transfers for mercury at the DNA-CPE is adsorption controlled reaction [7].

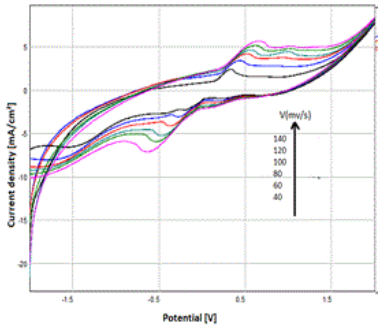

Figure 6: Cv's recorded at DNA-CPE preconcentrated in mercury solution, in 0.1 M NaCl, Effect of the scan rate.

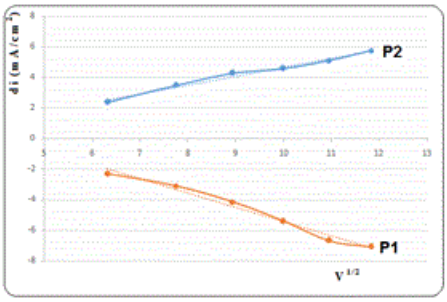

Figure 7: Dependence of the current densities of the peaks (P1 and P2) with the scanning rate.

The morphology of the prepared electrode surfaces, CPE (a), DNA-CPE (b) and DNA-CPE after accumulating in mercury solution (c), was studied by optical microscopy, (Figure 8). We can see that the DNA film forms a thin layer that covers the all carbon surfaces. Mercury adsorbed into DNA film forms a porous structure [8].

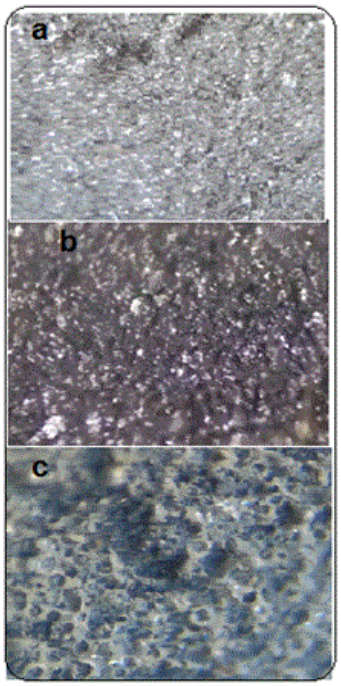

Figure 8: Images taken by optical microscopy for: a- CPE, b- DNA-CPE and DNA-CPE after preconcentration in Hg^{2+} solution.

Conclusion

This work demonstrated that DNA-CPE is a feasible alternative for the analytical determination of mercury (II). Analytical results show that the proposed electrode was able to detect very low concentrations with good sensitivity and reproducibility.

References

1. Yarto MA, Gavilan J, Castro (2004) Mercury pollution in Mexico ecological gazette. Mexico 72: 21-34.
2. Global Evaluation on Mercury (2002) United Nations Environment Program, Geneva Switzerland.
3. Evans EH, Day JA, Palmer CD, Price WJ, Smith CMM, Tyson JF (2008) Atomic spectrometry update. Advances in atomic emission, absorption and fluorescence spectrometry, and related techniques. Spectrom J Anal At 23: 889-819
4. Montes MB, DeNicola K, Caruso JA (2003) Liquid chromatography-inductively coupled plasma mass spectrometry. J Chromatogr 1000: 457-476.
5. Zhang Y, Adeloju SB (2015) Coupling of non-selective adsorption with selective elution for novel in-line separation and detection of cadmium by vapour generation atomic absorption spectrometry. Talanta 137: 148-155.
6. Touzara S, Najih R, Chtaini A (2015) Electrochemical Chelation of Lead by NDA Modified Carbon Paste Electrode. J Biosens Bioelectron 6: 3.
7. Elouafi T, Chtaini A, Oulfajrite H, Najih R (2015) Electrochemical detection of p-chloroaniline at clay modified carbon paste electrode: Application in tap water. J Drug Metab 5: 6
8. Mirsaleh NL, Sauche L, Bass AD (2011) Effect of morphology of thin DNA films on the electron stimulated desorption of anions. J Chem Phys 134: 7.