RESPONSE TO REVIEWERS' COMMENTS

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Title: Paper-based electrochemical transducer modified with nanomaterials for mercury determination in environmental waters

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We would like to thank the editor and reviewers for their constructive comments on our manuscript. The following changes have been made.

REVIEWER #1:

1. When referring to metals (including Hg (II)) please use the cationic form (i.e Cd(II), Pb(II), Cu(II), Zn(II) instead of cadmium, lead, copper and zinc) throughout the text

The manuscript was modified to referring all the metals mentioned as the cationic form.

2. The proposed transducers are obviously for single use. The life-time of the underlying ceramic SPE (in terms of number of analyses it can sustain) should be also reported

We have included the average use of the underlying ceramic SPE in the paragraph 2.2 of page lines 122-124. It can be higher for skilled operators:

"The SPE can be reused for an average of 7-8 measurements with no effect on ̶the structure of the platform"

3. The procedure for placing the sample on the WE is not specified. If a sample drop is applied on the electrode surface, its volume should be reported.

The following sentence has been added (line 167): 40 mL of sample solution were deposited on the electrochemical cell. Figure 1 was also modified to include the volumes of sample aliquots and nanomaterial suspension added on the electrode surface

4. Page 10, 2nd paragraph: "Increasing concentrations of KCl resulted on voltammograms with lower capacitance and better defined and more intense peaks (Figure 3)". However, Figure 3 compares the CVs with different modifiers and not the KCl concentration. Please correct. Also, no discussion on the findings of Fig. 3 can be found.

We have corrected the mistake by referring the Figure 2 instead of Figure 3 (line 206, page 7) to explain the influence of the KCl concentration. Figure 3 was used as reference at the discussion of the assignation of electrochemical peaks at page 7, lines 189-198. Discussion has been completed at lines 211-215.

5. Figure 4: the concentration ranges in the 2 types of electrodes are different. Is there a reason for this?

Firstly, both types of electrodes were used to study the same concentration range. However, the sensitivity of rGO/AuNPs paper-based electrode is lower, so the lowest concentration could not be determined. The different linear concentration ranges, according the sensibility of each modified electrode are shown at Figure 4.

6. Figure 12: a caption for Fig. 6 appears. However, no Figure 6 exists.

The caption referred to Figure 5. We have corrected the mistake.

7. Figure 12: it is stated that "Figure 5 shows the results of this interference study" but these are shown in Table 1.

We have corrected the mistake. Figure 5 showed matrix effect.

8. Figure 5: the standard addition straight line should be extrapolated to the point where it intersects with the x axis to show the concentration determined by the analysis. How was the recovery value derived?

Figure 5 was modified to include the extrapolations, showing how the concentration of the sample was calculated. Recovery values were the percentage of concentration found (with the calibration line) related to the known spiked concentration on river water.

9. Table 1 is not necessary and can be deleted

Table 1 has been deleted. The absence of interference from Pb (II), Cd (II), Zn (II) and Cu (II) was reported (lines 296-302).

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4 **Paper-based electrochemical transducer modified with nanomaterials**
5 **for mercury determination in environmental waters**

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Abstract

A sensor for Hg (II) determination in water was developed by using paper working electrodes modified with nanomaterials. The cellulose matrix was modified with hybrids of carbon nanofibers (CNFs) or reduced graphene oxide (rGO) and gold nanoparticles (AuNPs), in order to increase the selectivity and sensitivity. The AuNPs helped the electrodeposition of Hg (II) at more positive potentials, due to their affinity for mercury. The determination was possible up to 1.2 µM with no interference of other heavy metals such as Cd (II), Pb (II), Cu (II) and Zn (II). The CNFs/AuNPs modified paper-based electrode was the most sensitive option with a detection limit of 30 nM. River water samples were evaluated by the standard addition method.

1. Introduction

Heavy metals are becoming a high concern in terms of human health and environment. Excessive concentration in drinking water may result in chronic diseases or even mortality [1–3]. One of the most hazardous is Hg (II). This element can be present in organic and inorganic forms, being both dangerous because of their toxicity and bio-accumulation in many species [4–6].

Organizations like World Health Organization (WHO) have established 30 nM as the top limit value for drinking water [7]. This has carried along the need for determination methods with high sensitivity. Some of the available methods include spectroscopic techniques such as Cold Vapour Atomic Absorption Spectroscopy (CVAAS) [8] or Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [9], but these procedures are not suitable for *in situ* analysis because they require expensive instruments and qualified people. Electroanalytical methods, in contrast, allow simultaneous determination of several heavy metals at low cost, with minimum volume of sample and easy-to-use instruments [10]. Most of the heavy metals, like Hg (II) or Pb (II) can be determined by Anodic Stripping Voltammetry (ASV) [11,12]. Electrodes can be modified with conductive materials like polymers or with biological compounds to increase their conductivity and improve the sensitivity and selectivity of the sensors [13–16].

For the purpose of Hg (II) determination, gold is often the preferred electrodic material, because of its strong affinity for Hg. This can be used to enhance the preconcentration effect during the accumulation step [17,18]. It has been used as a bulk electrode or in the form of microdisks, but as gold nanoparticles (AuNPs), their high surface area-to-volume ratio results in both sensitivity and selectivity improvements [19–22]. AuNPs can be synthesized *in situ* by electrodeposition [23–25].

Sensitive Hg (II) determinations in water were achieved with glassy carbon [26,27], or screen-printed carbon electrodes (SPCEs) [28] modified with AuNPs and/or nanohybrids. SPCEs have advantages such as low cost and little amount of sample and reagents required. However, most of the ceramic SPCEs designed are usually discarded after one measurement because of the fouling of the surface. In recent years, efforts have been made to develop low-cost alternatives more feasible for developing countries such as transparency films [29] or paper [30–33].

Paper is mainly composed of cellulose fibres which can be modified by the addition of hydrophobic materials such as wax, with the aim to form barriers that define the electrochemical cell. Cellulose can be modified with conductive ink to allow the study of electrochemical probes [34,35]. It can also be modified with nanoparticles increasing the conductivity and selectivity of the method [36], it is inexpensive and easy to destroy after use.

Here, we have studied the utility of a nanostructured paper-based electrode as the working electrode of a simple and low-cost platform for Hg (II) in water. The paper substrate was modified with carbon materials such as graphene-oxide (GO) or carbon

nanofibers (CNF) and with gold nanoparticles (AuNPs) to obtain a new and "*easy-to-make*" working electrode. It was connected to the auxiliary and reference electrodes of a screen-printed card having its own working electrode isolated from the sample. This ensures its use without any interference, and the stability required in order to apply electrochemical treatments.

2. Experimental
2.1. Materials and Methods

Potassium chloride, Cd (II) standard, Zn (II) standard and HCl were purchased from Merck KGaA (Germany). Potassium hexacyanoferrate (II), trihydrate potassium hexacyanoferrate (III), tris (hydroxymethyl)aminomethane, Pb (II) standard, Cu (II) nitrate trihydrate and Hg (II) acetate were purchased from Sigma-Aldrich (USA). Water used was obtained from a Millipore Milli-Q purification system (Millipore Direct-Q® 3 U) from Millipore Ibérica S.A (Madrid, Spain).

Graphene oxides (GOs) were obtained from Instituto Nacional del Carbón (INCAR, CSIC, Spain). Graphite was obtained following a heat treatment at 2800ºC. Then, a modified Hummers method was used to transform it into GO [37]. A 1 mg/L solution on ultrapure water is the final product. Nanofibers were obtained from Grupo Antolin (Spain). Carbon paste (ref. C10903P14) was acquired from Gwent group (United Kingdom).

Screen-printed electrode cards were obtained from Dropsens S.L. (SPCEs, ref. DRP-110, Spain). Working and auxiliary electrodes are made of carbon ink, with a pseudoreference electrode made of silver. A DSC connector (ref DRP-DSC) from the same company was used to connect them with the potentiostat.

A wax printer (Xerox Colorqube 8570) was used to print the paper. Wax was melted using a thermostat model (Nabertherm d-2804). The spray adhesive 3M Spray Mount^{TM} was acquired from local stores.

Electrochemical measurements were carried out with a potentiostat (Autolab, PGSTAT 10) controlled by the Autolab GPES software. Cyclic voltammetry was used to study the influence of gold nanoparticles (AuNPs) and chloride ions on the electrochemical process of mercury (E_i = -0.35 V, E_f = +0.60 V, E_s = 2 mV and v = 50 mV/s).

2.2. Design of paper-based electrodes

Whatman Grade 1 chromatographic paper was chosen as a cellulose substrate. A wax printer was used to print hydrophobic wax patterns on the paper. Paper patterns designs were made using Inkscape software. After melting the wax at 80ºC and cooling at room temperature, the paper was modified by addition of 2 µL of carbon ink solution by drop casting on one of the sides. In this way, a side was covered by ink (bottom side) and the other side was used to add nanomaterial and sample solutions (upper side). The carbon ink used to modify the cellulose paper was made by dispersion of the

commercial carbon paste in anhydrous N,N-dimethylformamide (DMF) (concentration
of 30 % (w/w)) in an ultrasound bath for one hour.

Following a procedure previously developed in our group [34,38], the working
electrode (WE) of the screen-printed platform as well as the ceramic surface that is
located between the WE and auxiliary (AE) and reference (RE) electrodes, were
covered by the cellulosic electrode. Every paper electrode was cut to obtain a circle with
an area of 4 mm^2 as shown in Figure 1. The carbon ink of the paper working electrode
was covered by a protector. Then, an adhesive was sprayed and after removing the
cover, the cellulosic electrode was placed over the WE of a screen-printed electrode
card (SPE), in such a way that the carbon ink of the paper electrode contacted the WE of
the SPE, as shown in Figure 1 B. With this methodology, there was no any interference
from the adhesive spray. Before measurements were made, full overlap was verified.
The solution was added on the upper side of the paper electrode that was not contacting
the WE of the SPE, making sure there were no interferences from previous
measurements. Then, the WE of the SPE remained unmodified, acting only as
connection [34–36, 38]. The SPE can be reused for an average of 7-8 measurements
with no effect on the structure of the platform.

2.3.   Modification with carbon nanomaterials and gold nanoparticles

Paper electrodes with carbon ink were modified with a combination of carbon
nanomaterials followed by a generation of gold nanoparticles (AuNPs). Both procedures
are shown in Figure 1 (C1 and C2). Carbon nanomaterials were added before placing
the paper electrode over the screen-printed card, whereas gold nanoparticles were
generated afterwards. Graphene oxide added was also electrochemically reduced before
the generation of gold nanoparticles. Hybrids of carbon nanomaterials with AuNPs were
investigated to optimize the detection.

2.3.1. Modification with carbon nanofibers (CNFs)

Suspensions of CNFs were prepared in ultrapure water by solving an amount of
CNFs in an ultrasonic bath for 1 hour. An aliquot of 2 μL of a 1 mg/mL nanofiber
suspension was deposited onto the upper part of the paper and left to dry at room
temperature before placing it on the screen-printed electrode card.

2.3.2. Modification with graphene oxide (GO)

Aliquots of 6 μL of GO (100 mg/L) were added to the upper part of the paper
and left to dry at room temperature. Graphene oxide needs to be reduced in order to
remove oxide and hydroxide groups. Therefore, after placing it over the screen-printed
electrode card, a constant cathodic current of -100 μA was applied and the reduction
process was followed chronopotentiometrically in 0.1 M NaOH, according to a
procedure developed in our research group to generate reduced graphene oxide (rGO)
[37].

2.3.3. Modification with gold nanoparticles (AuNPs)

148   AuNPs were synthesized in situ by a method previously developed in our
149 research group for screen-printed carbon electrodes [36] and successfully tested in
150 paper-based electrodes [34,36]. AuNPs were electrogenerated after deposition of 40 μL
151 of 1 mM $AuCl_4^-$ on a cellulose disk overlaying the surface of the working electrode, at
152 the screen-printed card. A current of −100 μA was applied and the corresponding
153 chronopotentiogram was recorded.

154   **INSERT FIGURE 1**

155 **Fig. 1** Schematic diagram showing the preparation of the paper electrodes used. (A) Modification of
156 cellulose substrate by addition of carbon ink on one side. As result, the platform has two visually different
157 sides. Solution is added with a micropipette through the upper side. (B) Overlapping process of the
158 bottom (ink) side of the paper electrode, on the screen-printed card. (C) Modification of the paper
159 electrode with 1) CNFs and AuNPs, and 2) rGO and AuNPs.

160   **2.4.   River water analysis**

161   Water from river Nora (Asturias, Spain) was collected for mercury
162 determination. The sample was spiked with 1 μM of mercury (II) acetate. For the
163 determination, standard additions were made by adding 100, 200 and 400 μL of 20 μM
164 Hg (II) standard (in 0.1 M HCl + 0.9 M KCl, i.e. 1 M Cl^- background electrolyte) to 300
165 μL of the spiked sample and making up to 1 mL with 1 M Cl^- background electrolyte.

166   Real sample measurements and calibration plots were made by linear sweep
167 voltammetry. 40 μL of sample solution were deposited on the electrochemical cell. Hg
168 (II) in the samples was preconcentrated by applying a potential of +0.2 V for 600 s.
169 Then, the reduced mercury was stripped from the electrode surface by scanning the
170 potential in the anodic direction (E_i = +0.2 V, E_f = +0.6 V, E_s = 2 mV and v = 50 mV/s).

171   **3. Results and discussions**
172
173   **3.1.   Electrochemical behaviour of Hg (II) at carbon nanomaterials-AuNPs**
174   **modified paper-based electrodes**

175   The electrochemical processes of mercury on paper-based electrodes modified
176 with both carbon nanomaterials and gold nanoparticles were studied by cyclic
177 voltammetry using a 10^{-4} M Hg (II) acetate solution in 0.1 M HCl. This analyte was
178 preconcentrated by applying a reduction potential of -0.35 V for 480 s, and then the
179 potential was scanned in the positive sense. Figure 2 shows the voltammograms
180 obtained in CNFs/AuNPs paper-based electrodes. Different amounts of KCl were added
181 to improve the conductivity without increasing the acidity of the solution. This could
182 remove the adhesive and release the paper substrate from the screen-printed card. The
183 three anodic peaks observed (in 0.1 M HCl + 0.9 M KCl) at +41 (A3), +235 (A2) and
184 +426 (A1) mV seem to form a redox pair with the three corresponding cathodic peaks at
185 −14.8 (C3), +230 (C2) and +400 (C1) mV. The voltammogram is similar to that
186 obtained by using AuNPs-SPCEs [37]. As it was described there, the redox pairs A1/C1
187 and A2/C2 correspond to the adsorption of Hg (II) ions on the surface of AuNPs,
188 making an amalgam in a process called underpotential deposition (UPD), only observed

189 at electrodes modified with AuNPs, as shown in Figure 3 for these paper electrodes.
190 The UPD corresponds to an electrochemical process that takes place at a more positive
191 potential than the reversible Nernst potential for the formation of bulk metal. The first
192 UPD process (A1/C1) occurs at +413 mV ($E_{pa} + E_{pc}/2$), and a second UPD (A2/C2) at
193 +230 mV is normally observed when all AuNPs are saturated of mercury atoms, having
194 hence a weaker influence. The anodic peak A3 at +41 mV was also observed at
195 unmodified paper electrodes, and therefore it was assigned to the bulk deposition of Hg
196 at the carbon ink [39]. It was also present in paper modified with CNF and rGO (Figure
197 3). The other anodic peak, that appears at a lower potential, could be related to the
198 presence of chloride ions in the medium [40].

199

200   **INSERT FIGURE 2**

201 **Fig. 2** Cyclic voltammograms obtained at CNFs/AuNPs electrodes in a 10^{-4} M Hg (II) acetate solution in
202 (A) 0.1 M HCl, (B) 0.1 M HCl + 0.9 M KCl and (C) 0.1 M HCl + 1.9 M KCl solutions. (D) Background
203 voltammogram recorded in a 0.1 M HCl +0.9 M KCl solution.

204

205   Increasing concentrations of KCl resulted on voltammograms with lower
206 capacitance and better defined and more intense peaks (Figure 2). The potential of the
207 processes decreases slightly using more concentrated electrolyte, indicating that the
208 oxidation processes result favoured. The best results were obtained with a 1 M
209 concentration of chloride ion. Higher concentrations did not make any improvement.
210 Then, a 1 M of chloride ion (i.e., 0.1 M HCl + 0.9 M KCl) solution was employed as
211 background electrolyte for the remainder of the work. UPDs peaks were better defined
212 for CNFs/AuNPs paper-based electrodes in comparison with those modified with
213 rGO/AuNPs. This could be due to the higher capacitance of the cellulose matrix
214 modified with reduced graphene oxide. The effect of the carbon nanomaterials on the
215 capacitive currents in absence of AuNPs can also be observed in Figure 3.

216   The UPDs at AuNPs nanostructured electrodes are advantageous for sensitive
217 and selective determination of low concentrations of Hg. Bulk deposition was only
218 observed at higher concentrations. Bulk deposition at CNFs and rGO paper electrodes
219 has low reproducibility and less selectivity in comparison with paper electrodes
220 modified also with AuNPs, so they were not considered. On the other hand, the
221 modification with carbon nanomaterials increases the reproducibility of the
222 electrodeposition of gold nanoparticles. For this reason, the use of AuNPs paper
223 electrodes with no carbon nanomaterials was discarded. In conclusion, a hybrid
224 nanostructuration resulted then more convenient. The first UPD (A1/C1) was chosen for
225 the development of the sensor for the determination of mercury (II) ions by anodic
226 stripping voltammetry. Then, mercury was preconcentrated (reduction of Hg (II) to Hg
227 (0)) at a potential more negative than C1. Then, a anodic potential sweep was applied
228 for Hg redissolution (from Hg (0) to Hg (II)). The analytical signal measured was the
229 intensity of the A1 peak current.

231   **INSERT FIGURE 3**

Fig.3 Cyclic voltammograms for a 10^{-4} M Hg (II) acetate solution at A) CNFs/AuNPs, (B) CNFs, (C) rGO/AuNPs and (D) rGO modified electrodes. Background electrolyte: 0.1 M HCl + 0.9 M KCl solution.

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3.2. Study of the determination of Hg (II) at carbon nanomaterials / AuNPs paper-based electrodes

We have optimized the electrogeneration of AuNPs in paper electrodes modified with carbon nanofibers (CNFs) or reduced graphene oxide (rGO) by chronopotenciometry. Current intensity of −100 μA was applied at different time intervals. A value of 360 s resulted on the highest oxidation peak for mercury, around +380 mV. (E_{pa} for the A1 process). The difference on the potential value with respect to the anodic peak A1 could be due to the influence of the ion chloride Cl$^-$ on the pseudoreference electrode of Ag at the screen-printed card. It could partially form AgCl, changing the redox potential of mercury ions, therefore. Hg (II) was then determined by anodic stripping voltammetry, measuring the current intensity of the anodic peak around +380 mV. A potential of +200 mV was chosen for studying the influence of different electrodeposition times for both procedures (CNFs/AuNPs and rGO/AuNPs). Square wave voltammetry (SWV), differential pulse voltammetry (DPV) and linear sweep voltammetry (LSV) were evaluated. The most reproducible results were obtained with linear sweep voltammetry, by applying a potential of +200 mV for 600 s (480 s for graphene oxide) as a preconcentrating step, followed by an anodic potential scan from +0.2 to +0.6 V.

To compare carbon nanomaterials and study the sensitivity of the analytical methodologies, both types of modified paper electrodes (CNFs/AuNPs and rGO/AuNPs) were tested for different concentrations of mercury (II) acetate. Figure 4 shows two calibration plots for the hybrid structures CNFs/AuNPs and rGO/AuNPs. The best fit corresponded to the former, with CNFs/AuNPs (calibration line: I_{pa} (μA)= 0.4461 [Hg(II)] − 0.0305, R^2 = 0.9969). The linear range was comprised between 0.1 and 1.2 μM. The limit of detection (LOD) for the hybrid nanostructuration with CNFs/AuNPs was calculated as 30 nM by the formula $3S_a/m$, where S_a is the standard deviation of the blank and m is the slope of the calibration line, using the lower range concentration values. The capacitive current was lower for CNFs/AuNPs paper-based electrodes. In conclusion, this was the system chosen to analyse the river water samples.

264

265   **INSERT FIGURE 4**

Fig. 4 (A) Calibration plots for mercury (II) acetate in CNF/AuNPs and rGO/AuNPs paper-based electrodes. (B) Linear sweep voltammograms in CNF/AuNPs paper-based electrodes at increasing concentrations of mercury (II) acetate in a 0.1 M HCl + 0.9 M KCl solution.

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Water samples were taken from river Nora (Asturias, Spain). Mercury was not detected. Then, aliquots for mercury determination at the CNFs/AuNPs and rGO/AuNPs paper-based electrodes were prepared by spiking 1 µM of mercury (II) acetate. Solutions were analysed by the anodic stripping voltammetry method developed (Section 2.4). For the determination, standard additions were made to aliquots of 300 µL of the spiked sample. Then, different volumes of Hg (II) standard in 1M Cl$^-$ background electrolyte were added. The comparison of the standard addition line of the spiked samples with the calibration plot line indicated matrix effects (Figure 5). This can be explained because of the different compounds from the matrix river which can alter the background of the solution and its conductivity. However, the method is based on the UPD electrodeposition of mercury (II) ions at the AuNPs surface, and subsequent anodic redisolution. The interference study at next section shows that the determination is quite selective nevertheless. Moreover, matrix effects could be corrected by using the standard addition method. Results indicated that 91% of the spiked concentration was recovered, being still a suitable alternative to study real samples. Samples were also analysed by the method previously developed at AuNPs and SPCEs [39]. The results obtained at the SPCEs (97%) were consistent with those obtained at paper-based electrodes developed in this study.

INSERT FIGURE 5

Fig.5 (A) Calibration plots for Hg (II) acetate solutions (1 M in Cl$^-$) at CNF/AuNPs electrodes. (B) Standard additions line for Hg (II) acetate additions to river water at CNFs/AuNPs electrodes. Values shown are the average of 3 measurements at independent electrodes.

3.3 Interference study

Solutions of 1 µM Hg (II) acetate with 100 µM of Pb (II), Cd (II), Zn (II) and Cu (II) were prepared to study the interference made by each one in comparison with a 1 µM mercury (II) acetate solution. CNF-AuNPs paper electrodes were used for Hg (II) quantification by the optimized procedure for the 1st UPD described in section 3.2. No variation of the oxidation peak intensity was observed, showing no signs of interference for these metals and confirming the selectivity of the method. All combinations were studied by triplicate.

The analytical characteristics reported in the literature for mercury ions determination by using paper devices are shown in Table 1. Most of mercury sensors in published paper-based devices are based on a colour change response due to the binding with specific ligands. These need normally higher quantity of reagents and more expensive detectors, limiting the portability. Electrochemical paper devices are more selective and the affinity with gold nanoparticles improves their sensitivity, but their

uses are still scarce. The sensor developed in this work has the advantages of using a fast and low-cost modification procedure. The electrodeposition of gold nanoparticles with the high conductivity of carbon nanomaterials allows reaching a limit of detection of 30 nM, suitable for safety control in waters. As an additional advantage, mercury stays in the cellulose fibers of the working paper electrode, and therefore the screen-printed platform can be reused without any contamination, reducing the analysis cost. In regard to waste management, the single-use paper electrode can be easily disposed, because of its small size.

INSERT TABLE 1

Table 1: Analytical characteristics of other paper devices described at the literature.

4. Conclusion

We tested the efficacy of an *easy-to-prepare* paper-based working electrode as a sensor for Hg (II) ions in river water, overlapping a screen-printed electrode as a connection system. The bare screen-printed electrode used remained free of mercury after the measurement. CNFs and rGO improve the conductivity of the electrode whereas electrodeposited AuNPs allow the sensitive and selective determination of Hg (II). By using the underpotential deposition of mercury on AuNPs, a limit of detection of 30 nM was obtained when both nanomaterials (CNFs and AuNPs) were used to modify the cellulose substrate. The determination was not affected by the presence of Zn (II), Cd (II), Pb (II) and Cu (II) ions. Mercury could be determined in spiked river samples (91% recovery and 6.2% RSD). The nanostructured paper-based electrode developed in this work could be the basis for a low-cost mercury sensor by electrochemical devices in paper platforms.

5. References

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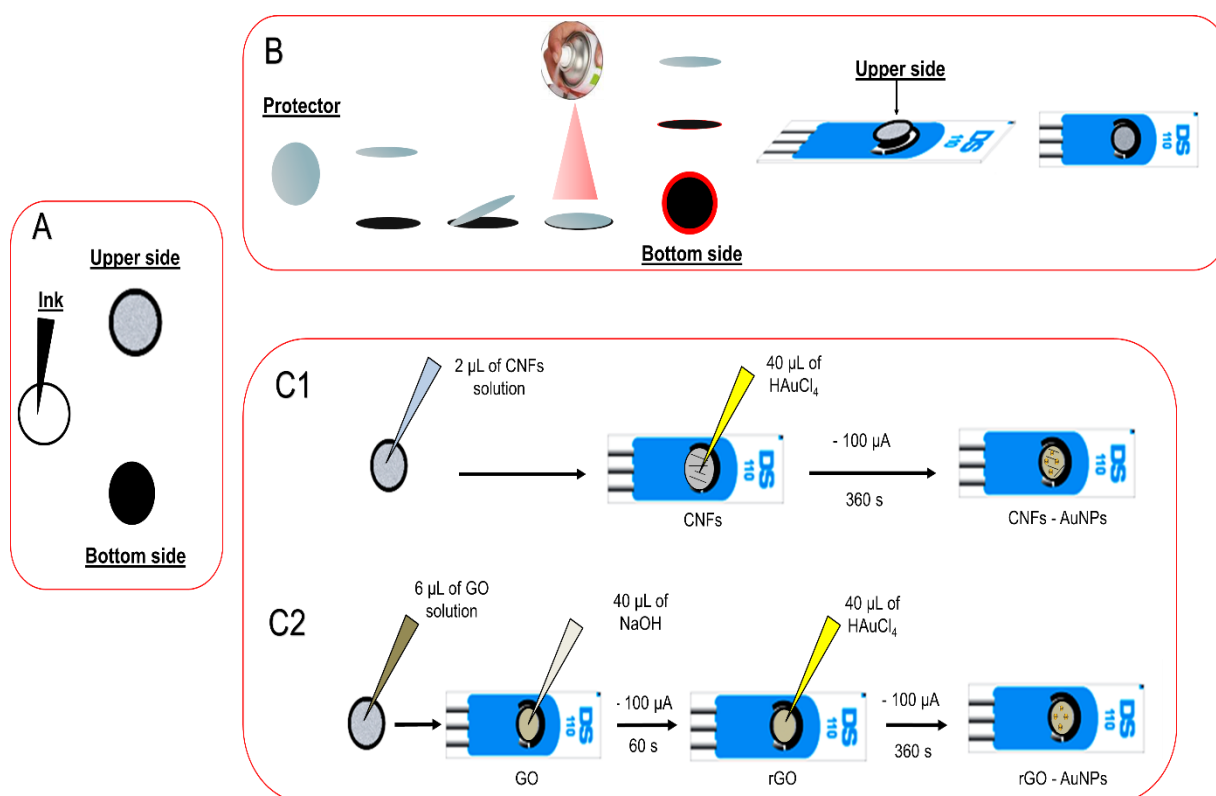509   doi:10.1021/ac5008688.

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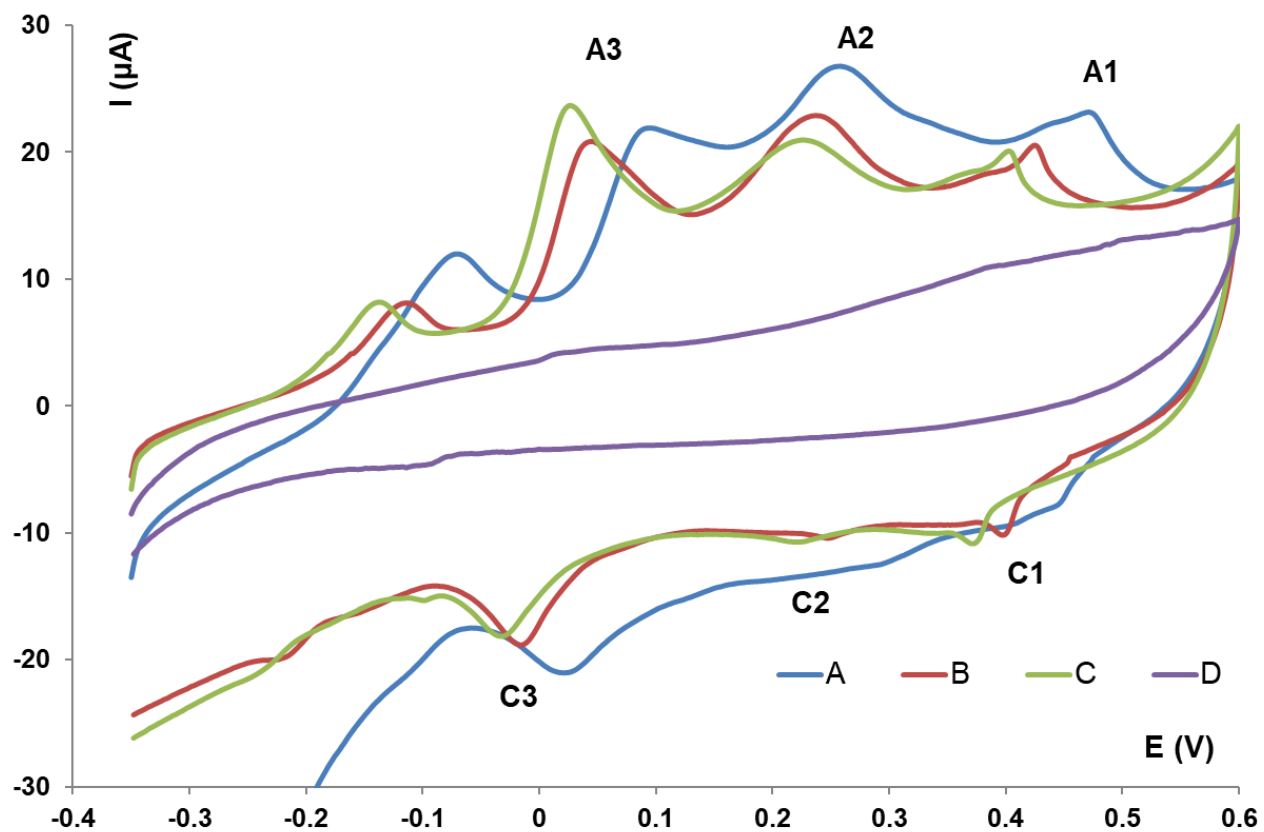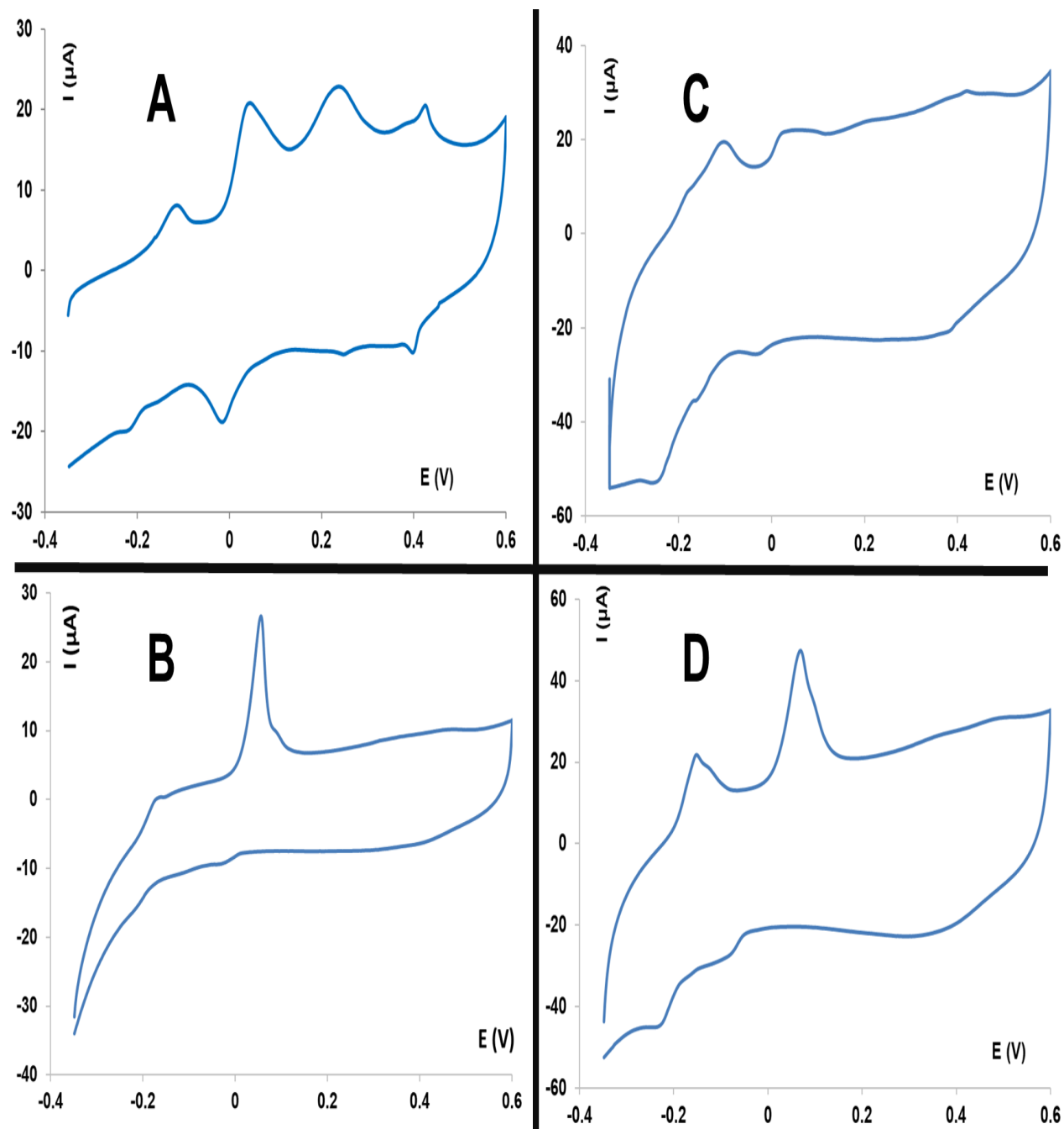513   doi:10.1039/C5AN00802F.

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Fig. 1 Schematic diagram showing the preparation of the paper electrodes used. (A) Modification of cellulose substrate by addition of carbon ink on one side, having the platform two visually different sides. Solution is added with a micropipette through the upper side. (B) Overlapping process of the bottom (ink) side of the paper electrode on the screen-printed card. (C) Modification of the paper electrode with 1) CNFs and AuNPs, and 2) rGO and AuNPs.
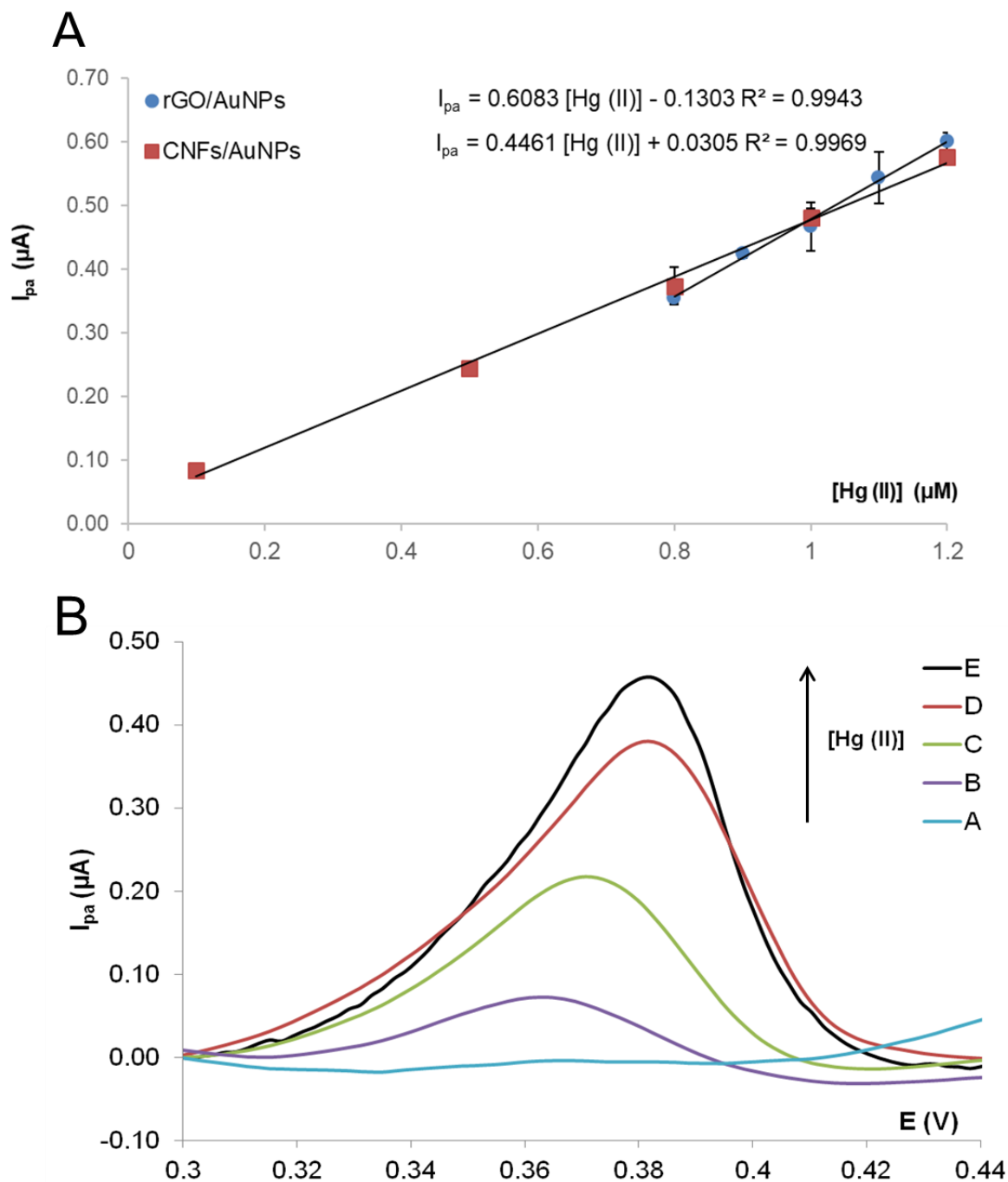
Fig. 2 Cyclic voltammograms obtained at CNFs/AuNPs electrodes in a 10^{-4} M Hg (II) acetate solution in (A) 0.1 M HCl, (B) 0.1 M HCl + 0.9 M KCl and (C) 0.1 M HCl + 1.9 M KCl solutions. (D) Background voltammogram recorded in a 0.1 M HCl +0.9 M KCl solution.
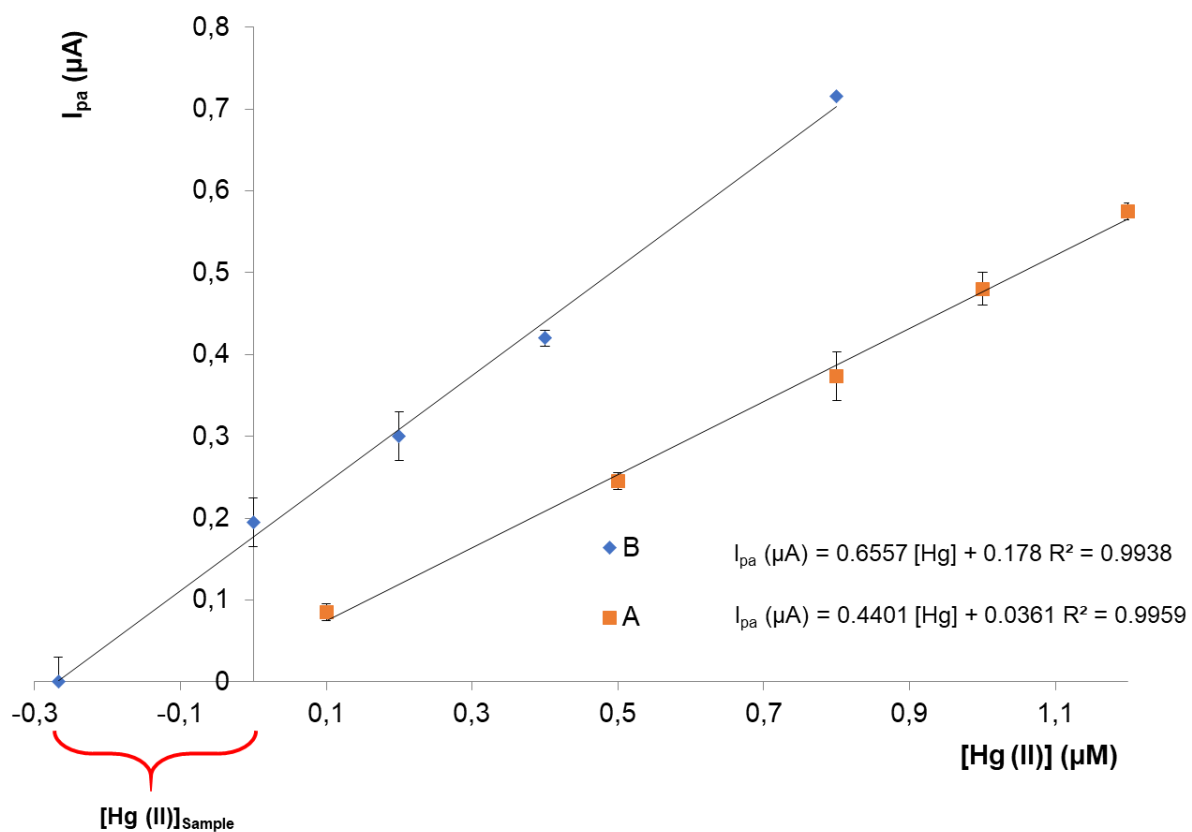
Fig. 3 Cyclic voltammograms for a 10^{-4} M Hg (II) acetate solution at A) CNFs/AuNPs, (B) CNFs, (C) rGO/AuNPs and (D) rGO modified electrodes. Background electrolyte: 0.1 M HCl + 0.9 M KCl solution.

Fig. 4 (A) Calibration plots for Hg (II) acetate in CNF/AuNPs and rGO/AuNPs paper-based electrodes. (B) Linear sweep voltammograms in CNF/AuNPs paper-based electrodes at different concentrations of mercury (II) acetate in a 0.1 M HCl + 0.9 M KCl solution.

I_{pa} (μA) = 0.6557 [Hg] + 0.178 R² = 0.9938

I_{pa} (μA) = 0.4401 [Hg] + 0.0361 R² = 0.9959

Table(s)

Analytical characteristics of other paper devices described at the literature for Hg (II) determination.

Sensor	Analytical signal	Range (µM)	LOD (µM)
Array for multi-heavy metal ions [42]	Colour change	10-50	10
Gold nanoparticles paper-based device [43]	Colour change	0.025-0.75	0.05
Terbium/gold nanocluster [44]	Fluorescence	0.005-7	0.01
Dual detection of nitrate and mercury with AuNPs [30]	Electrochemical (DPV)	0.07-17.5	0.005
CNFs /AuNPs (this work)	Electrochemical (LSV)	0.1-1.2	0.03