



# Synthesis of CuNP-modified carbon electrodes obtained by pyrolysis of paper



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## ARTICLE INFO

### Article history:

Received 4 November 2015

Received in revised form

10 December 2015

Accepted 28 December 2015

Available online 2 January 2016

### Keywords:

Copper nanoparticles

Carbon electrodes

Non-enzymatic glucose sensor

Electrochemical sensors

## ABSTRACT

A one-step approach for the synthesis and integration of copper nanoparticles (CuNPs) onto paper-based carbon electrodes is herein reported. The method is based on the pyrolysis (1000 °C under a mixture of 95% Ar/5% H<sub>2</sub> for 1 h) of paper strips modified with a saturated solution of CuSO<sub>4</sub> and yields to the formation of abundant CuNPs on the surface of carbonized cellulose fibers. The resulting substrates were characterized by a combination of scanning electron microscopy, EDX, Raman spectroscopy as well as electrical and electrochemical techniques. Their potential application, as working electrodes for non-enzymatic amperometric determination of glucose, was then demonstrated (linear response up to 3 mM and a sensitivity of 460 ± 8 μA cm<sup>-2</sup> mM<sup>-1</sup>). Besides being a simple and inexpensive process for the development of electrochemically-active substrates, this approach opens new possibilities for the *in-situ* synthesis of metallic nanoparticles without the traditional requirements of solutions and adjuvants.

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## 1. Introduction

One of the most active areas in current analytical chemistry is the synthesis and application of metallic nanoparticles (NPs). This interest is driven by the unique structure, high surface area, good mechanical [1] and thermal stability, and unusual optical, chemical, magnetic, and catalytic properties of these nanostructures [2]. The great diversity of composition, shape, and size of metallic NPs [3,4] have also allowed researchers exploring their applications in related fields, such as catalysis [5], optical devices [6], and electronic components [7]. Following these developments, the modification of surfaces with metallic nanomaterials is one of the most important strategies to improve the performance of electrochemical sensors [8–11]. In this way, a variety of electrodes modified with metallic nanomaterials (with different compositions and morphologies) such as platinum [12], palladium [13], silver [14], gold [15], or nickel [16] have been recently reported. Although improved performance is commonly reported, the high cost and the limited availability of some of these materials can impose restrictions to the development of sensors for low-income communities. Aiming to address these limitations, other metallic nanomaterials such as copper nanopar-

ticles (CuNPs) have emerged as alternative materials with potential applications in catalysis [17,18], electronics [19,20], optics [21], and medicine [22,23]. Despite their potential toxicity [24], CuNPs are relatively inexpensive and provide access to a number of chemical routes for their derivatization. Their reactivity [25] and molecular recognition capabilities [26] have also sparked their use in electrochemical sensors for dopamine [27], glucose [28–30], amino acids [31], and ascorbic acid [32].

Obtaining CuNPs is relatively straightforward and a number of methods have been reported for their synthesis [25] including electrodeposition [28,29], reduction of Cu salts [27] or organometallic precursors [33], thermal decomposition [34], laser ablation [35], or photochemical reactions [36]. Among these methods, the chemical reduction of copper ions in aqueous solution is probably the most popular route. Moreover, due to the low reduction potential for Cu<sup>+2</sup> [33], a number of materials (even tea [37]) can lead to the formation of CuNPs with different shapes, sizes, and properties. One common limitation affecting all these synthetic routes is the tendency of CuNPs to form larger aggregates with different (typically much lower) activity [29,33,38]. While the as-formed clusters and NPs can be stabilized by surfactants and other protective molecules, these additives can also hinder their compatibility with other elements of a sensor, especially if traces of surfactants or reducing agents are bound to the surface of the NPs. Without a question,

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more efficient methods to synthesize, disperse, and apply CuNPs are required.

To address this need and develop more efficient catalytic surfaces, we report a one-step method for the synthesis of paper-based carbon electrodes modified with CuNPs. The methodology is based on the pyrolysis (under reductive conditions) of paper strips pretreated with a  $\text{CuSO}_4$  solution. This process, one of the simplest reported to date, yields abundant CuNPs distributed on the surface of the carbonized cellulose fibers. The resulting electrodes were characterized by scanning electron microscopy, EDX, Raman spectroscopy, and electrical/electrochemical techniques. Their potential application as working electrodes for non-enzymatic determination of glucose in alkaline media was also demonstrated.

## 2. Material and methods

### 2.1. Reagents

All aqueous solutions were prepared using 18 M $\Omega$  cm water (NANOpure Diamond, Barnstead; Dubuque, IA, USA) and analytical grade reagents. Copper(II) sulfate was purchased from Fisher Scientific (Fair Lawn, NJ, USA). D-Glucose was acquired from Aldrich Chemical Company, Inc., (Milwaukee, WI, USA). Uric acid and dopamine hydrochloride were obtained from Alfa Aesar (Ward Hill, MA, USA). Acetylsalicylic acid, diclofenac sodium salt, and L-ascorbic acid were purchased from Sigma Aldrich (St. Louis, MO, USA). D-Fructose was acquired from Lancaster Synthesis, Inc. (Pelham, NH, USA). All reagents were used without further treatment. Unless specifically stated, the electrochemical measurements were performed in 100 mM NaOH solution (pH 13.0). The D-glucose stock solutions were prepared dissolving the corresponding amount of solid in 100 mM NaOH solution and stored in the fridge after use. Standard solutions of L-ascorbic acid (AA), uric acid (UA), dopamine hydrochloride (DA), D-fructose, and diclofenac sodium salt were freshly prepared also in 100 mM NaOH solution before each experiment. Soft drinks used as real samples were obtained from a local market.

### 2.2. Fabrication of CuNPs-modified carbon electrodes (CuNPs@CE)

As a modification from a recent publication from our group [39], CuNPs@CEs were obtained by pyrolysis of paper strips (JP40 filter paper, 80 g m<sup>-2</sup>, Quanty; J-Prolab, Brazil) of 1.5 cm × 3.5 cm modified with a solution containing  $\text{CuSO}_4$ . The advantages and limitations of this method (rendering bare carbon electrodes) were described in the aforementioned report. Upon immersion in the solution, the paper strips were placed between two silicon wafers, dried in a convection oven (at 100 °C for 2 h), and then transferred to a tube furnace (Type F21100, Barnstead–Thermolyne; Dubuque, IA, USA). The quartz tube was flushed with forming gas (5%  $\text{H}_2$ /95% Ar, 1 L min<sup>-1</sup>) for 5 min (to remove the  $\text{O}_2$  and avoid oxidation reactions) and then allowed to reach a temperature of 1000 °C, at a rate of 20 °C min<sup>-1</sup>. After 1 h, the tube furnace was turned off and allowed to cool-down to room temperature while maintaining the flow of forming gas. Finally, the pyrolyzed samples were removed from the furnace and stored in a Petri dish until use. In order to obtain electrodes with uniform dimensions, CuNPs@CE were patterned using a commercial  $\text{CO}_2$  laser engraver (Mini24, Epilog Laser Systems; Golden, CO, USA) and then fixed to a Plexiglas substrate using double-sided tape. The process defined electrodes with a geometric area of 0.385 cm<sup>2</sup>. In order to prevent water from wicking up the stem of the electrode (and therefore increasing the elec-

trode area), paraffin paper was melted and deposited on base of the stem, between the circular pad and the contact area. Finally, silver paint (SPI Supplies; West Chester, PA, USA) was applied at the upper end of the stem to define a contact area for the potentiostat. Plain carbon electrodes (without CuNPs) were also prepared using the conditions described above (but soaking the paper strips in DI water) and used as control. As a summary, a scheme describing the fabrication procedure is provided as Supplementary Information.

### 2.3. Instruments

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were employed to investigate the electrochemical performance of the electrodes produced. The experiments were performed using 100 mM KCl, as supporting electrolyte, containing 1.0 mM  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ , as the redox couple. In all cases, a standard three-electrode cell comprised of the paper-derived electrodes, a silver/silver chloride ( $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ ), and a platinum wire were used as working, reference, and counter electrode, respectively. CV experiments were carried out using a CHI812 Electrochemical Analyzer (CH Instruments, Inc.; Austin, TX). EIS data were obtained using a PC-controlled CHI 660A potentiostat by scanning from 10<sup>-4</sup> Hz to 10<sup>5</sup> Hz at a 5 mV amplitude, with 10 data points per frequency decade. To avoid the electrochemical oxidation of the CuNPs, experiments were performed at the open-circuit potential of the electrodes. The impedance spectra were then analyzed with the simulation software Zview-Impedance® (version 2.4a) by fitting the spectra with a Randles-type equivalent circuit.

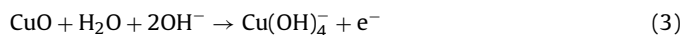
Micrographs of bare pyrolyzed paper samples and CuNPs-modified carbonized paper were obtained using a scanning electron microscope (Hitachi STEM-5500) equipped with a solid-state Bruker detector used to acquire the spatially-resolved chemical analysis by X-ray emission spectroscopy. A confocal Raman automated imaging spectrometer (iHR320, Horiba Jobin Yvon) was used to study the carbon structure of the electrodes obtained from pyrolyzed paper. The Raman spectrometer was equipped with an excitation laser of 488 nm wavelength and a Synapse CCD detector. The Raman spectra were collected in the 1100–2000 cm<sup>-1</sup> range, with an exposure time of 2 s, an accumulation factor of 2, and a 100X objective.

### 2.4. Electrocatalytic mechanism of metallic copper towards glucose

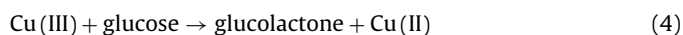
Considering the catalytic properties of CuNPs, the potential analytical applications of CuNPs@CEs were demonstrated by developing a non-enzymatic electrochemical sensor for glucose. Although the oxidation of glucose in alkaline media by metallic copper has not been definitively elucidated, previous reports have described a critical role of Cu(III) compounds ( $\text{CuOOH}$  and/or  $\text{Cu}(\text{OH})_4^-$ ) formed on the electrode surface [40–42]. In general, the most commonly reported electrochemical process involves the oxidation of Cu to CuO in presence of  $\text{OH}^-$  ions (Eq. (1)).

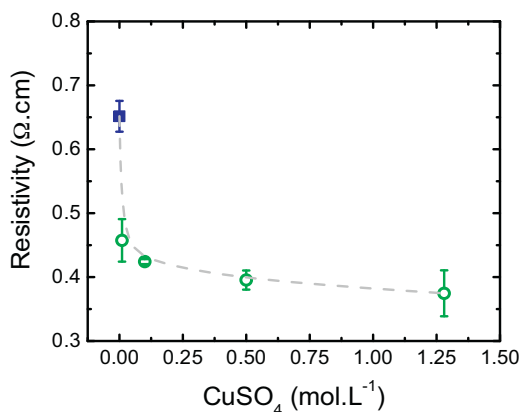


As described by Eq. (2) and/or Eq. (3), CuO is then electrochemically converted to Cu(III) species that have a strong oxidizing power.



Finally, the Cu(III) compounds are able to oxidize glucose to gluconolactone (Eq. (4)), which then generates gluconic acid by hydrolysis (Eq. (5)):





**Fig. 1.** Resistivity of the pyrolyzed paper without CuNPs (solid square) and the CuNPs-modified carbonized paper (open circles). Line included to guide the eye.



### 3. Results and discussion

#### 3.1. Resistivity of CuNPs-modified pyrolyzed paper

To study the effect of the synthesized CuNPs on the resistivity of the pyrolyzed samples, different CuNPs-modified pyrolyzed papers were prepared by using paper strip soaked in solutions containing increasing concentrations of  $\text{CuSO}_4$  (0.01, 0.10, 0.50, and 1.3 M). The resistivity of the carbonized samples was calculated using the resistance values measured using a standard digital multimeter (2216–20 TRMS, Milwaukee Electric Tool Corp.; Brookfield, WI) and the procedure previously described [39]. In order to improve the electrical contact with the multimeter connectors, silver paint was applied on the CuNPs-modified pyrolyzed samples by displaying silver contacts with a gap of 1 cm. The experimental results obtained are summarized in Fig. 1.

As it can be observed, the resistivity of the carbon electrodes showed an exponential decay (from  $0.65 \pm 0.02 \, \Omega \text{ cm}$  for the bare substrate [39]) as the  $\text{CuSO}_4$  concentration was increased in the solution used to soak the paper. The lowest resistivity ( $0.37 \pm 0.03 \, \Omega \text{ cm}$ ) was obtained when a saturated solution of  $\text{CuSO}_4$  was used to fabricate the CuNPs@CE. In this case, amount of copper deposited in the pyrolyzed paper strip was estimated to be  $57 \, \mu\text{mol cm}^{-2}$  (geometric area). The trend described in Fig. 1 was attributed to the fact that the higher the  $\text{CuSO}_4$  concentration, the higher the  $\text{Cu}^{2+}$  available for the reduction reaction, and consequently the larger the amount of CuNPs deposited on the carbon fibers. These experimental results suggest that CuNPs could bridge clusters of conductive graphitic carbon formed during the pyrolysis. Considering these results, all subsequent CuNPs@CEs were obtained from paper strips soaked in a saturated solution (containing 1.3 M) of  $\text{CuSO}_4$ .

#### 3.2. Electrochemical impedance spectroscopy

To obtain quantitative information about the electrical behavior of the resulting carbon electrodes, electrochemical impedance spectroscopy (EIS) was performed using  $1.0 \text{ mM Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$  as the redox couple and  $100 \text{ mM KCl}$  as supporting electrolyte. EIS experiments were carried out using either bare CE or CuNPs@CE and the corresponding spectra fitted with a Randles-type equivalent electrical circuit. The latter was assembled taking into account the bulk-solution resistance ( $R_{\text{sol}}$ ), the electri-

**Table 1**

Fitting parameters obtained for each element in the proposed electric circuit.

	Bare CE	CuNPs@CE
$R_{\text{sol}} \, (\Omega)$	$83.0 \pm 0.8$	$49.6 \pm 0.3$
$C_{\text{film}} \, (\text{mF})$	$0.046 \pm 0.002$	$0.5 \pm 0.1$
$R_{\text{film}} \, (\Omega)$	$58 \pm 2$	$2.1 \pm 0.3$
$\text{CPE}_{\text{dl}} \, (\text{mF})$	$1.6 \pm 0.1$	$2.7 \pm 0.7$
$\alpha_{\text{CPEdl}}$	0.43	0.38
$R_{\text{ct}} \, (\Omega)$	$800 \pm 200$	$20 \pm 3$
$Z_{\text{W-R}}$	$5800 \pm 1700$	$700 \pm 100$

cal properties of the pyrolyzed samples (such as the capacitance compartment,  $C_{\text{film}}$ , and the internal resistance,  $R_{\text{film}}$ , of the electrode), and the electrode interfacial behavior (represented by a constant-phase element that accounts for the capacitance of the double layer,  $\text{CPE}_{\text{dl}}$ , and the charge-transfer resistance,  $R_{\text{ct}}$  at the interface) [43–46]. Furthermore, a Warburg impedance ( $Z_{\text{W}}$ ) was included to consider the diffusion of electroactive species involved in the redox reaction. As a summary, Table 1 shows representative results of the fitting process.

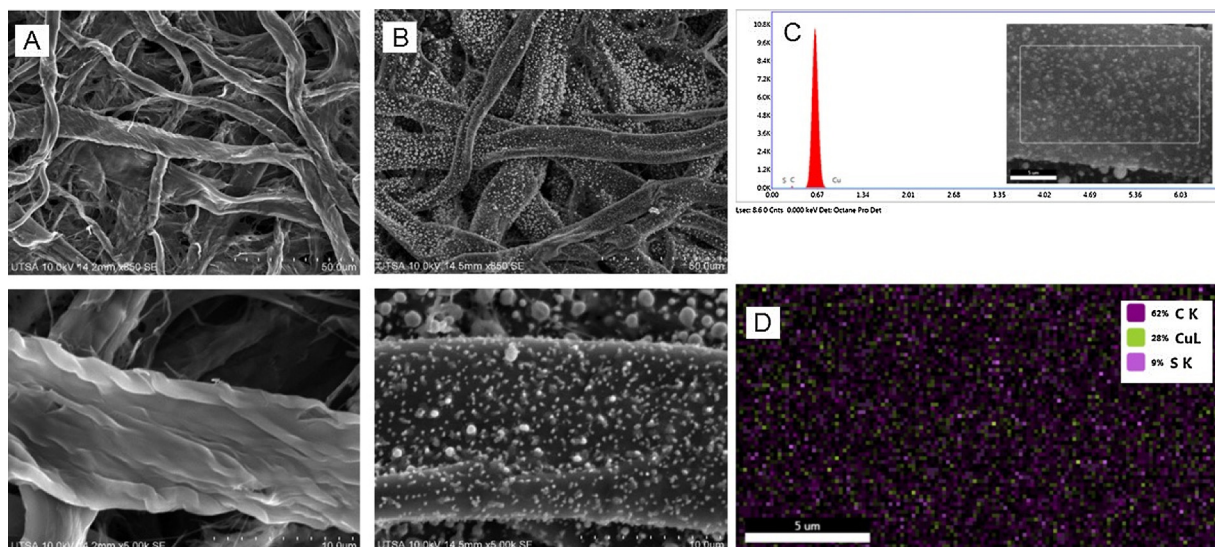
These results demonstrate that the addition of CuNPs provides significant enhancements in the electrochemical activity of the resulting carbon electrodes. It is important to note that the  $R_{\text{film}}$  decreased around a 96% respect to the resistance value displayed by the blank (bare CE), in agreement with the hypothesis that the conductivity is favored by the metallic properties of the nanoparticles. It was also observed that the electric double-layer capacitance (fitted using a  $\text{CPE}_{\text{dl}}$  to represent the deviation from the ideal compartment) showed a slight increase with respect to the bare electrodes, observation that can be attributed to heterogeneities and roughness in the electrode surface [47–49] and that correlate well to the presence of CuNPs on the surface of the carbon fibers. In agreement with features observed in the SEM micrograph (Fig. 2), the lower exponent values obtained for both substrates ( $\alpha_{\text{CPEdl}} < 0.5$ ) [45] suggest that they behave as porous electrodes. On the other hand, the significant decrease on the  $R_{\text{ct}}$  calculated for the CuNPs@CE ( $\sim 2\%$  of the bare CE value) was related to the greater amount of electroactive sites exposed toward the bulk solution.

#### 3.3. Surface topography of pyrolyzed samples

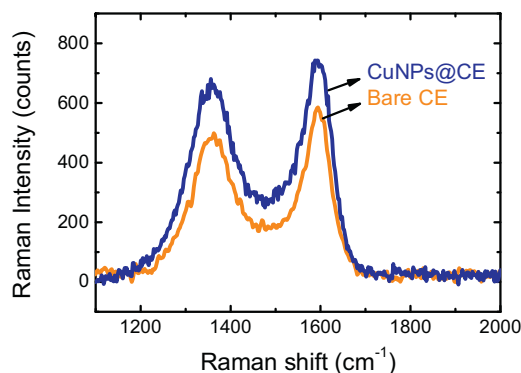
The morphology and microstructure of the carbonized paper and the CuNPs@CE were also examined by scanning electron microscopy (SEM). The SEM micrographs evidence the structure of the bare carbonized paper fibers (Fig. 2A) and the fibers with CuNPs (Fig. 2B). As it can be also observed, a large number of CuNPs (varying in size and shape) was obtained on the surface of the carbonized cellulose fibers. Although not evident in the micrograph, larger NPs appear to be formed by aggregates of smaller NPs, phenomenon that can be attributed to the absence of stabilizing polymers or ligands during the synthesis as well as the high concentration of  $\text{Cu}^{2+}$ . In general, CuNPs with diameters in the 20–70 nm range were observed decorating the surface of carbonized paper fibers. The presence of CuNPs was also confirmed by energy-dispersive X-ray spectroscopy (EDX), which displayed a high intensity peak (28% of total intensity, Fig. 2C). Carbon (62%) and sulfur (9%) were additionally identified by the elemental composition analysis (Fig. 2D).

Although the EDX data only provides evidence about the presence of elemental Cu, the obtained trend in resistivity (Fig. 1) and the cyclic voltammograms (*vide infra*, Fig. 4) are compatible with the presence of metallic Cu; expected on the electrode as a result of the reductive conditions used during the pyrolysis and in agreement with data reported by other groups [50]. Based on the distribution of Cu obtained from the EDX analysis, it is reasonable to consider the possibility of having Cu not only in the form of





**Fig. 2.** SEM micrographs of pyrolyzed paper fibers in absence (A) and presence (B) of CuNPs. EDX spectrum (C), and EDX elemental mapping (D) of CuNPs-modified carbon paper.



**Fig. 3.** Raman spectra obtained from pyrolyzed paper and CuNPs-modified pyrolyzed paper.

nanoparticles but also as a film on the surface of the carbon fibers. Because  $\text{CuSO}_4$  decomposes at approximately  $850^\circ\text{C}$  [51] ( $\sim 150^\circ\text{C}$  lower than the pyrolysis temperature), the presence of the S peak could be attributed to the formation of secondary sulfur compounds that remain within the structure of the pyrolyzed cellulose.

### 3.4. Microstructure of pyrolyzed samples

It is well known that carbon has several allotropes, which can be formed during the pyrolysis step [52,53]. To obtain structural information related to the carbon material in the samples with and without CuNPs, Raman spectroscopy was used. Fig. 3 shows representative Raman spectra of the analyzed samples.

As it can be observed, very similar spectra were obtained with both samples. In both cases, two clear peaks were observed around  $1590\text{ cm}^{-1}$  and  $1362\text{ cm}^{-1}$ . These features were attributed to the traditional G and D bands that correspond to the breathing of C–C bonds in graphite-like carbon ( $\text{sp}^2$ ) and the breakdown of such symmetry, respectively. The relative intensity ratio between the D and G bands was used to obtain information about the defect and edge sites of carbon. As a result, the D/G ratio did not show significant differences between both carbonized paper samples. In agreement with previous reports [39], the ratio of the peak's intensity was  $1.5 \pm 0.1$ , suggesting that the addition of CuNPs does not affect the resulting structure of the carbon. It is also important to highlight

that this result is in line with the experimental data obtained in Section 3.1 (*vide supra*). In other words, the low resistivity observed in the CuNPs@CE (with respect to the pyrolyzed paper without CuNPs) can be attributed to the presence of CuNPs bridging clusters of conductive carbon.

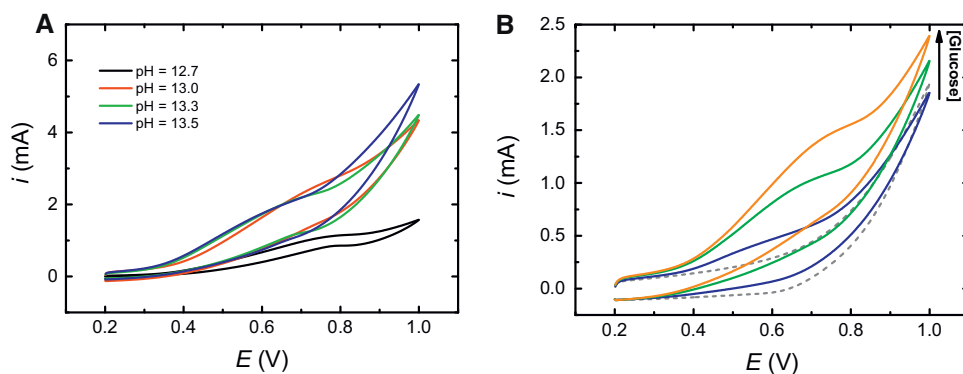
### 3.5. Electrochemical behavior of glucose at CuNPs@CE

As it was previously reported [54], the catalytic oxidation of glucose (and other carbohydrates) by metallic surfaces can be affected by the pH of the solution. For this reason, the effect of the concentration of  $\text{OH}^-$  ions on the oxidation of glucose was investigated by cyclic voltammetry. As shown Fig. 4A, the electrocatalytic response of the CuNPs@CE towards glucose showed a significant improvement when the solution pH was increased from 12.7 to 13.0 (a change in the NaOH concentration from 50 to 100 mM). However, subsequent additions of NaOH did not yield significant differences in electrochemical response, obtained within the potential window between +0.5 V and +0.7 V. As a result, all remaining electrochemical experiments were carried out using 100 mM NaOH as the background electrolyte.

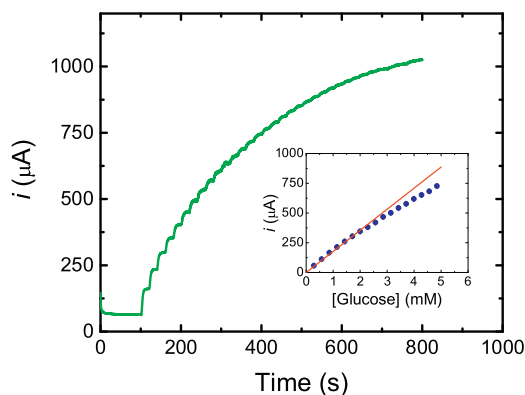
The electrocatalytic behavior of CuNPs@CE towards glucose was investigated by performing successive additions of glucose and recording the corresponding cyclic voltammograms. The results are summarized in Fig. 4B. As it can be observed, a broad anodic peak was obtained in the potential range of +0.4 V and +0.8 V. Upon sequential additions of glucose, increments in the anodic current as well as a shift in the peak potential were obtained. Similar results have been previously obtained with other electrodes containing copper structures [42,55,56]. Considering these results, a potential of +0.65 V (versus  $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ ) was selected to perform the amperometric detection of glucose. This value provides an adequate balance between sensitivity and selectivity.

### 3.6. Amperometric detection of glucose

To demonstrate the potential use of the proposed methodology, the electrochemical response of CuNPs@CE towards glucose was investigated by amperometry. A typical anodic chronoamperogram of CuNPs@CE obtained by successive additions of glucose is shown in Fig. 5. As it can be observed, under the selected experimental



**Fig. 4.** A Cyclic voltammetry of CuNPs@CE in NaOH solution at different concentrations containing 10 mM of glucose. Scan rate =  $50 \text{ mV s}^{-1}$ . (B) Cyclic voltammetry of CuNPs@CE in absence (dash grey line) and presence of glucose at concentrations 1, 3, and 5 mM. Conditions: scan rate =  $50 \text{ mV s}^{-1}$ , 100 mM NaOH.

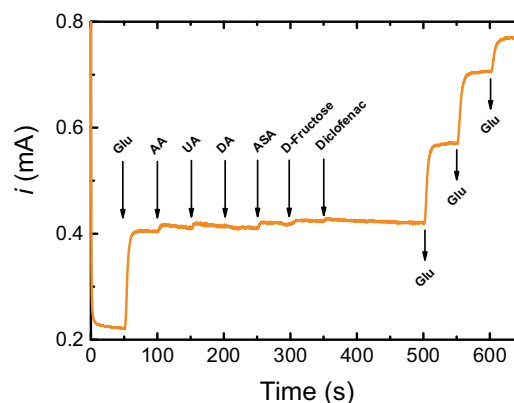


**Fig. 5.** Chronoamperometric response of CuNPs@CE carried out at +0.65 V (versus Ag/AgCl|KCl<sub>sat</sub>) by adding known amounts of glucose into 100 mM NaOH solution under continuous stirring. Insert: Calibration curve of glucose performed by the CuNPs@CE. Data points and error bars (contained within the data points) represent the average and standard deviation calculated by using four different electrodes.

conditions (100 mM NaOH, +0.65 V, CuNPs@CE), about 100 s were required to stabilize the sensor's baseline.

After each glucose addition, a fast increase in the current was obtained (10 s to reach 95% steady-state current). The repeatability of the measurement was evaluated by performing successive calibration curves of glucose (using the same electrode) and demonstrated a relative variation of only 2.5% within a 3-h period. The repeatability of the electrode preparation was evaluated by performing calibration curves using four different electrodes and identical experimental conditions. In this case, an agreement within 5% on the slope was obtained, providing further evidence about the robustness of the proposed methodology. As also shown in Fig. 5 (see insert), the relationship between current and glucose concentration can be described with a linear equation up to 3 mM glucose ( $i = 460 \pm 8 [\text{glucose}] \mu\text{A cm}^{-2} \text{ mM}^{-1}$ ,  $R^2 = 0.998$ ). Thereafter, non-linear increases in current were obtained with subsequent additions of glucose. This behavior (first-order dependence and subsequent decrease in the sensitivity obtained at higher concentrations) has been previously reported for a number of electrodes containing copper [50,57–59] and attributed to the saturation of the surface sites involved in the reaction [50]. The limit of detection (defined as the signal corresponding to 3 times the standard deviation of the blank) and the limit of quantification (defined as the signal corresponding to 10 times the standard deviation of the blank), were calculated to be  $5 \mu\text{M}$  and  $17 \mu\text{M}$ , respectively.

As expected, the control experiment carried out with a bare carbon electrode showed no current changes upon successive additions of glucose (data not shown) and demonstrated that the



**Fig. 6.** Amperometric response of CuNPs@CE at +0.65 V upon addition of 1 mM Glu and selected interfering species as indicated. As control, two additions of 1 mM Glu and one addition of 0.5 mM Glu were performed under continuous stirring.

integration of CuNPs to carbon electrodes plays a critical role in the electrocatalysis of glucose. In order to evaluate the effect of common interfering compounds on the electrochemical signal of glucose at +0.65 V, the response of ascorbic acid (AA), uric acid (UA), dopamine (DA), acetylsalicylic acid (ASA), D-fructose, and diclofenac were investigated. After an initial addition of glucose (1 mM), the selected interfering agents were added at intervals of 50 s, to a final concentration of 0.05 mM (Fig. 6). In order to show that the response of the electrode towards glucose was not affected, three additional injections of glucose were performed.

As it can be observed in Fig. 6, the addition of the selected interfering agents only produced marginal changes (<4%) in the electrochemical response of the sensor. In line with previous reports [41], these experimental results suggest a high selectivity of the CuNPs@CEs towards glucose.

### 3.7. Assay for glucose in beverage samples

To demonstrate the applicability of the CuNPs@CE to real samples, the content of glucose in commercial soft beverages was measured using the standard addition method.

As shown in Table 2, the glucose levels obtained by the proposed method were in good agreement (difference <5%) with respect to those declared by the manufacturer. Additionally, the experimental results obtained with the samples declared as free glucose beverage suggest that the presented method may be successfully used for glucose detection in beverage samples without any pretreatment step. In other words, the CuNPs@CEs showed no response

**Table 2**

Analysis of glucose in different soft beverages using CuNPs@CE.

Sample	Concentration reported (mM)	Concentration measured (mM)	Agreement (%)
1	610.6	643.9	94.8
2	676.2	686.2	98.5
3	0.0	0.0	100
4	0.0	0.0	100

towards other compounds (dyes, conservatives, etc.) present in the beverages.

### 3.8. Critical assessment of the electrode's performance

Although better sensitivity values have been reported for electrodes prepared with CuO nanoparticles ( $1397 \mu\text{A cm}^{-2} \text{mM}^{-1}$ , LOD =  $5 \mu\text{M}$  [60,61],  $1620 \mu\text{A cm}^{-2} \text{mM}^{-1}$ , LOD =  $49 \mu\text{M}$  [62]); the sensitivity obtained with the proposed CuNPs@CE is comparable to that obtained with Cu nanowires ( $420 \mu\text{A cm}^{-2} \text{mM}^{-1}$ , LOD =  $35 \text{ nM}$  [50]), nanofibers decorated with CuNPs ( $415 \mu\text{A cm}^{-2} \text{mM}^{-1}$ , LOD =  $0.2 \mu\text{M}$  [63]) and better than the ones obtained with CuNPs deposited on multiwalled carbon nanotubes ( $272 \mu\text{A cm}^{-2} \text{mM}^{-1}$ , LOD =  $0.5 \mu\text{M}$  [64]), CuNP deposited on carbon nanotubes ( $253 \mu\text{A cm}^{-2} \text{mM}^{-1}$ , LOD =  $0.21 \mu\text{M}$  [65]), or CuNPs deposited on graphene sheets ( $157 \mu\text{A cm}^{-2} \text{mM}^{-1}$ , LOD =  $0.5 \mu\text{M}$  [41]). While, in comparison to the aforementioned reports, the LOD obtained with the CuNPs@CE is rather high ( $5 \mu\text{M}$ ), this simple and straightforward method to produce CuNPs on the surface of carbon electrodes offers competitive advantages with respect to previously reported systems based on combinations of nanoparticles and carbon-based nanomaterials (which are probably justified for samples containing glucose at nM levels). Although outside the scope of the present report, further improvements in the analytical performance of the proposed electrodes could be obtained combining the selectivity of enzymes (oxidases) with the catalytic activity of CuNP towards  $\text{H}_2\text{O}_2$  [57,66–68]. In this regard, an additional advantage of this methodology is that the surface of CuNPs@CE does not contain dispersion agents, which are typically required to avoid agglomeration of the CuNPs and that could affect the structure of the biorecognition element.

## 4. Conclusions

This article describes a simple approach for the development and fabrication of CuNPs@CE. The procedure is based on the *in-situ* synthesis of CuNPs by pyrolysis of filter paper modified with  $\text{CuSO}_4$ . The material was characterized by a combination of techniques (resistivity, microscopy, Raman spectroscopy, cyclic voltammetry, and electrochemical impedance) and applied for the analysis of glucose in beverages. The proposed methodology offers a convenient route for the development of electrochemically-active surfaces and could enable their integration with other low-cost platforms such as paper-based microfluidic devices [69]. Although the present report was focused on the development and use of CuNPs@CE using the concentration of  $\text{CuSO}_4$  as the main variable, it is expected that a careful selection of the pyrolysis conditions (precursor, temperature,  $\text{H}_2$  pressure, and time) may yield to a more uniform distribution of CuNPs. Overall, the results highlight the advantages of pyrolysis as a competitive route for the development of conductive materials modified with metallic nanoparticles.

## Acknowledgments

This work was supported in part by the NIH-Research Centers at Minority Institutions (G12MD007591), the CTQ2013-48411-P

(MINECO of Spain) and the PEIC-2014-001-P (JCCM). Gema M. Duran also thanks MINECO of Spain for the pre-doctoral (BES-2011-045438) and stay (EEBB-I-14-08461) grants. Jason G. Giuliani thanks the financial support provided by the MBRS-RICE Program (GM060655).

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2015.12.093>.

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