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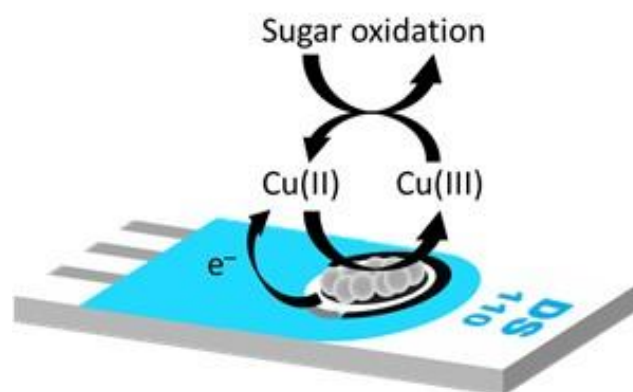
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GRAPHICAL ABSTRACT



Highlights

- Copper was electrodeposited by galvanostatic method on screen-printed electrodes.
- Copper oxide nanospheres were generated on the electrode surface.
- Electrodes showed a great electrocatalytic effect towards sugars oxidation.
- Low μM concentrations of reducing sugars were easily detected.

**Galvanostatic electrodeposition of copper nanoparticles on screen-printed carbon
electrodes and their application for reducing sugars determination**

Beatriz Pérez-Fernández, Daniel Martín-Yerga and Agustín Costa-García*

Nano-bioanalysis Group

Department of Physical and Analytical Chemistry

University of Oviedo

* Corresponding author: Prof. Dr. Agustín Costa-García

Departamento de Química Física y Analítica

Universidad de Oviedo

Julián Clavería 8, Oviedo 33006 (Spain)

E-mail: costa@uniovi.es

Telephone: (+34) 985103488

Abstract

In this work, a novel method for the galvanostatic electrodeposition of copper nanoparticles on screen-printed carbon electrodes was developed. Nanoparticles of spherical morphology with sizes between 60 and 280 nm were obtained. The electrocatalytic effect of these copper nanospheres towards the oxidation of different sugars was studied. Excellent analytical performance was obtained with the nanostructured sensor: low detection limits and wide linear ranges (1-10000 μM) were achieving for the different reducing sugars evaluated (glucose, fructose, arabinose, galactose, mannose, xylose) with very similar calibration slopes, which demonstrates the possibility of total sugar detection. The reproducibility of these sensors was 4.4% (intra-electrode) and 7.2% (inter-electrode). The stability of the nanostructured electrodes was at least 30 days, even using the same device on different days. Several real samples (honey, orange juice and normal and sugar-free soft drinks) were evaluated to study the reliability of the nanostructured sensor.

Keywords

Screen-printed carbon electrodes, non-enzymatic sensor, copper nanospheres, carbohydrates, galvanostatic electrodeposition.

1. Introduction

The development of non-enzymatic sensors for determination of sugars is a constant concern as they could simplify the current analytical methods and decrease the analysis cost. Metals, alloys or metal oxides, which acts as catalysts for the oxidation of carbohydrates are widely employed in these non-enzymatic sensors. It has been shown that copper oxide nanomaterials have a high electrocatalytic response for carbohydrates oxidation due to their p-type semiconducting properties, since it increases the electron transfer between the solution and the electrode surface [1–3]. The most used methods for manufacturing copper nanoparticles are chemical and thermal treatments [4–8], where the process is carried out in solution. A disadvantage of the *ex situ* preparation of the nanoparticles is the more laborious electrode modification [9,10]. An example of this method was described by Wenzhao Jia et al., [11] who developed the synthesis of copper nanospheres by a thermal method, and then, these copper nanospheres were immobilized on a carbon electrode with nafion (CuO/Nafion/GC). Electrodeposition methods present some advantages as the nanostructures are generated *in situ* and the experimental conditions can be modified easily to generate surfaces with different geometries, sizes or distribution. Jing Yang et al. [1] employed two-steps electrodeposition of CuO nanoparticles onto vertically well-aligned array of multi-walled CNTs (MWCNTs) on Ta substrate for developing a blood glucose biosensor. The Cu nanoparticles were electrochemically deposited onto MWCNTs arrays applying a constant-potential film-plating technique (first step) and oxidized *in situ* into CuO nanoparticles (second step) by the cyclic potential sweep technique. Hajar Shekarchizadeh et al., [12] developed a glassy carbon electrode modified with CuO nanoparticles and multiwalled carbon nanotubes (MWCNTs) to improve its electroactivity and selectivity for nonenzymatic detection of some carbohydrates (glucose and fructose). In addition, Cu nanostructures were synthesized by Y. Zhao et al., [13] via chemical reduction of CuO nanoleaves at room temperature. Two different novel morphologies with flower and octahedral cage shapes were proposed by controlling the dosage of reducing agent. The as-prepared Cu nanostructures were used to construct nonenzymatic glucose sensors. The detecting results showed that the designed sensors had well-defined, stable and fast amperometric responses to glucose, and Cu flower modified electrode had higher sensitivity than octahedral cage modified one.

However, as far as we are aware, the galvanostatic electrodeposition of copper on electrodes was not still reported for the non-enzymatic determination of sugars.

Screen-printed carbon electrodes (SPCEs) [14] are widely used due to their low cost, small size, disposability, and good electrochemical performance. One disadvantage of SPCEs is the solid quasi-reference electrode, which could have a lower stability specially in rough conditions such as high chloride concentration or acidic media, where the silver surface could be oxidized. As the geometry, size and density of the electrodeposited nanoparticles are very important parameters for electrocatalytic applications, small changes in the electrodeposition potential could lead to low precise results. However, this issue could be avoided using galvanostatic electrodeposition. In this case, a constant current is employed to carry out the electrodeposition and, therefore, the effect of potential variations would be minimized. For this reason, the modification of SPCEs with copper by galvanostatic electrodeposition could be an interesting technique for electrocatalytic applications. However, as far as we are aware, no reports on the galvanostatic copper electrodeposition on SPCEs has been described. Based on previous studies, where the galvanostatic electrodeposition has been applied for gold [15], nickel [16] or graphene oxide [17], we report for the first time, the galvanostatic electrodeposition of copper nanospheres on screen-printed carbon electrodes (CuNS-SPCE). These electrodes have shown an excellent electrocatalytic effect towards the oxidation of reducing sugars.

2. Methods and materials.

Instrumentation, electrodes, reagents and solutions used in this work are described in the Supporting Information.

2.1 Galvanostatic electrodeposition of copper nanospheres

Copper nanospheres were electrodeposited by dropping 40 μL of the 10 mM Cu(II) solution on the electrode and applying a current of -225 μA for 60 s. In this process, Cu (II) is reduced to Cu (0). Then, spontaneous oxidation of copper by contact with oxygen from air could take place forming surface

oxides. In order to stabilize the electrode surface, a cyclic voltammetry activation was performed by applying 20 cyclic sweeps between 0V to +1 V at a scanning rate of 100 mV/s in 0.1 M NaOH.

2.2 Chronoamperometric measurements

The determination of sugars were performed by chronoamperometric measurements at a potential of +0.65 V for 100 s. The analytic signal was the intensity obtained at 100 s.

2.3 Samples preparation

For orange juice, 1.5 μ L of the sample were taken and diluted with 1 mL of 0.1 M NaOH. In the case of honey samples, 1.0003 ± 0.0001 g of honey was weighed and dissolved in 50 mL of ultrapure water. Then, 38 μ L were taken, and a 1:40 dilution in 0.1 M NaOH was prepared. For samples of sugar-free and normal soft drinks, 100 and 160 μ L were taken and diluted up to 1 and 1.6 mL with 0.1 M NaOH, respectively. In the case of the drink with sugar, another 1:5 dilution was performed to bring the concentration into the lineal range. In all cases, solutions with known increasing concentrations of glucose were prepared for the determination of total sugars by the standard additions method.

3. Results and discussion

3.1 Characterization of screen-printed electrodes modified with copper nanospheres

Electrodeposition of copper on SPCEs was studied by cyclic voltammetry (CV) for various concentrations of Cu (II) (0, 10, 25 mM) in 0.1 M H₂SO₄, as can be seen in **Figure 1A**. A cathodic process that increased with Cu(II) concentration appeared around -0.65 V, which is attributed to the reduction of Cu(II) to Cu(0). The stripping of Cu(0) could also be observed in the reverse sweep at a potential near +0.2 V. Another cathodic process is observed, specially, in the blank solution, which is assigned to the oxygen reduction reaction (ORR) as has been observed previously at SPCEs [18]. It is also interesting to note that the copper electrodeposition is able to catalyze the hydrogen evolution reaction (HER) as revealed by the increasing current at the more negative potentials in comparison to the blank solution. As noticed in this voltammetric experiment, the copper electrodeposition could be

carried out on SPCEs satisfactorily at potentials more positive than the cathodic potential window, and even more positive than the ORR.

Then, the galvanostatic electrodeposition of copper was studied as this technique could be more appropriate for electrode systems with quasi-reference electrodes as described in the introduction. A reduction current of -225 μA was applied for 60 s using a solution of 10 mM of Cu(II) in 0.1 M H_2SO_4 , and the chronopotentiogram recorded is shown in the **Figure 1B**. At least, three different potential steps were observed during the experiment. Initially, a potential about -0.55 V is acquired where the reduction of Cu(II) to Cu(0) takes place. Then, the potential decreased continuously while Cu(II) was being consumed until reaching a new plateau at -0.75 V due to the ORR, which is also consumed quickly at this cathodic current. Starting from 8 s upwards, the potential remains practically constant at -1.10 V, where the HER happened for the rest of the experiment (generation of a few bubbles was also observed during this time).

[FIGURE 1]

The influence of the copper modification on the electroactive area of the electrode was studied by estimating this area with a cyclic voltammetry experiment at different scan rates. $[\text{Ru}(\text{NH}_3)_6]^{3+}$ was employed as model species as the electron transfer process is usually fast and follows an outer-sphere mechanism [19]. **Figure S1** shows the cyclic voltammograms at different scan rates for both SPCEs and SPCEs modified with copper by galvanostatic electrodeposition. Under these conditions an irreversible process was obtained (ΔE_p increased with scan rate) and then, the Randles-Sevcik equation (**Eq. 1**) modified for these systems was applied:

$$i_p = (2.99 \times 10^5) \alpha n^{3/2} A C D^{1/2} v^{1/2} \quad (1)$$

where i_p is the peak current intensity (A), n the number of electrons involved in the reaction, A the area of the electrode (cm^2), C the concentration of the species (mol/cm^3), D the diffusion coefficient ($5.17 \times 10^{-6} \text{ cm}^2/\text{s}$ in 0.1 M K_2SO_4) [20], α is the transfer coefficient (0.5) and v the scan rate (V/s). The electroactive area of the bare electrode was estimated to be $7.46 \pm 0.05 \text{ mm}^2$. For the electrode modified

with copper, an area of $7.9 \pm 0.3 \text{ mm}^2$ was estimated. Thus, a slight increment of the electroactive area was found for the copper-modified electrodes.

Differential pulse voltammetry (DPV) was used to estimate the amount of Cu deposited on the electrode by using the Faraday law (described in the Supporting Information). **Figure S2** shows the voltammograms obtained. An amount of 4.8×10^{-10} moles of copper was estimated to be deposited. Considering the geometric area of the electrode (0.012 cm^2), a surface density of 4×10^{-8} moles/ cm^2 was estimated, indicating the high density of copper on the surface as also can be observed in the SEM images (below).

The morphology of the electrode surface after the galvanostatic electrodeposition was studied by recording SEM images. **Figure 1C** shows an image of the electrode surface after the modification, and the EDX spectrum (**Figure S3A**) confirms the presence of copper (besides Cl, O and C from the electrode ink). Numerous spherical nanoparticles well-distributed across all the electrode surface are observed. Agglomerates of several nanoparticles forming bigger particles are also observed. A histogram representing the nanoparticles size is shown in **Figure S3B**. These data, and as visually observed in the SEM images, indicate that a good fraction of the nanoparticles is around 40-50 nm, but with a good fraction also of bigger particles up to 250 nm approximately (average size of 115 nm). This quite heterogeneous size distribution suggests that the process follows a progressive nucleation mechanism, expected for particles that nucleate (and grow) at different times during the electrodeposition.

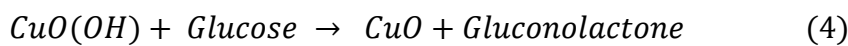
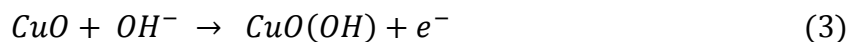
The oxidation state of the copper nanospheres deposited on the electrode surface was studied by XPS. **Figure 2** shows the spectra for Cu2p and O1s. The first peak of Cu $2p_{3/2}$ is due to Cu (II) at a binding energy of 933.27 eV corresponding to the CuO species [21–23]. At 941.74 eV the satellite peak at a peak difference of 8.47 eV could be assigned. At a distance of approximately of 20 eV, the characteristic peak Cu $2p_{1/2}$ of CuO at an energy of 952.83 eV with its satellite peak to 960.78 eV with a difference of 7.95 eV can be tentatively assigned. In the spectrum of O1s, a peak at 529.40 eV that could be assigned to O^{2-} , and would confirm the solely presence of CuO species [8]. Therefore, it seems that the surface of

the copper nanospheres present on the electrode is composed of CuO, which also confirms the spontaneous oxidation by contact with the O₂ from the atmosphere.

[FIGURE 2]

3.2 Electrocatalytic oxidation of sugars with CuNS-modified electrodes

The catalytic effect of the CuNS-SPCE towards the oxidation of sugars was studied. Cyclic voltammograms of different sugars were recorded at a concentration of 2 mM and for a blank solution of 0.1 M NaOH. **Figure 3A** shows the results obtained for glucose and fructose (the voltammograms for other sugars are shown in **Figure S4**). An increased current evolved in presence of sugars demonstrating the good electrocatalytic behavior of CuNS electrodes. This catalytic effect is due to the following reactions (in the case of glucose) [24–25]:



The oxidation of the sugar is catalyzed by the electrogenerated Cu(III) species, which acts as a mediator and Cu(II) is again generated. The catalysis also occurs with other sugars like arabinose, galactose, mannose and xylose giving a signal similar to glucose and fructose, because the oxidation is produced by a dehydrogenation of the hemiacetal group of sugars [12,26,27]. All these sugars have a very similar structure so they respond equivalently to the catalysis produced by Cu (III). In order to have more information on the electrocatalytic process, a voltammetric study for a solution of 800 µM of glucose at different scan rates (10-500 mV/s) was performed. **Figure 3B** shows the linear relationship between the peak current and the square root of the scan rate, which indicates that the limiting step of the reaction is the diffusion of glucose or hydroxide ions to the electrode surface (as both species are involved in the reaction).

[FIGURE 3]

As previously mentioned in the introduction, a possible issue with systems with quasi-reference electrodes is the variation of the applied potential if the surface of quasi-reference electrode were not totally stable. In order to highlight the advantage of using the galvanostatic electrodeposition, a comparison was performed with the potentiostatic electrodeposition. **Table S1** shows the response for chronoamperometric measurements (at +0.65 V) for blank and 1 mM glucose solutions using electrodes modified with copper by using both electrodeposition methods. Although, no differences in the response of the sugar was obtained, a lower precision was found with the blank solution using the electrodes modified by the potentiostatic method (48% vs 12% RSD, respectively). This fact is important in order to achieve a low limit of detection as the signal/noise ratio would be higher for the galvanostatic method and it is presumed that the limit of detection would be lower.

3.3 Analytical performance of CuNS-SPCEs for sugars determination

Different parameters affecting the analytical signal were optimized. Chronoamperometry was employed for evaluating the response of the blank solution and a solution of 200 μM of glucose. First, the parameters related to the electrodeposition of Cu (II) were optimized, such as: deposition current (-100 to -500 μA), Cu(II) concentration (1 to 50 mM) and deposition time (5 to 300 s). By selecting the highest signal-to-blank ratio, a current of -225 μA , a time of 60 s and a Cu (II) concentration of 10 mM were chosen. Then, in order to increase the homogeneity of the copper surface, an activation step was performed by cyclic voltammetry between 0 and +1 V in 0.1 M NaOH. The higher signal/noise ratio was obtained after 20 cycles of this activation. No significant differences were found for the geometry or size of the copper nanospheres generated on the electrode surface (**Figure S5**), suggesting that this process only influences the copper surface features. Finally, the measurement potential was optimized using (between +0.5V to +0.75 V), selecting +0.65 V as the most appropriate potential.

Figure 4 shows the chronoamperograms for different glucose concentrations and the calibration plots for glucose, fructose and arabinose (the remaining calibration plots for other sugars are shown in the **Figure S6**). The chronoamperometric responses for each sugar are shown in **Figure S7** and the data values in **Table S2**. **Table 1** displays the analytical characteristics obtained for all the sugars: similar

linear range between 1 μM to 10 mM, similar calibration slopes (sensitivity around 0.030 $\mu\text{A}/\mu\text{M}$) and low limits of detection were obtained in all cases. The reproducibility of the calibration slopes was less than 7% (RSD, n=3). The limit of detection has been estimated as the concentration given by the blank signal plus three times the standard deviation of the blank and the quantification limit as ten times this value. Lower detection limits could be estimated by other methods such as using the standard deviation of the blank solution. **Table 2** shows a comparison of our work with others previously published. The CuNS electrodeposited by a galvanostatic method have shown a great electrocatalytic activity towards sugars as can be seen by comparing these analytical characteristics our sensor has very good analytical characteristics with respect to the others shown.

[FIGURE 4]

[TABLE 1]

[TABLE 2]

3.4 Stability and precision studies

A study of the reproducibility and stability of the sensor was carried out. For this, several measurements of a solution of 500 μM of glucose were performed on the same electrode, obtaining 4.4% of RSD (n = 10). In the case of the inter-electrode study, a RSD of 7.2% was obtained (n = 3). Although both values were good, showing the good reproducibility of the sensor, a better precision was obtained when the same electrode was used for all measurements. This could be very important in industrial setups to reduce the analysis cost.

Stability was studied for different electrodes and for the same electrode in different days. The deposition is performed and the electrode is stored at room temperature. The activation of the surface is carried out the same day of the measurement (20 voltammetric cycles). In the case of the intra-electrode stability study, the activation was only made for the first day. As can be seen in **Figure S8**, the sensor is stable at least for 30 days. Although more precise results were found when the activation takes place the day of

the measurement, these results also show the good stability of the sensor if it is repeatedly used during a period of time.

3.5 Selectivity study

The selectivity of our sensor was studied for different species that may be interfering with sugars in foods, such as glycerol, ethanol, lactic, ascorbic and citric acid, because they have a near oxidation potential or could be influence the electrode surface. These species are found in low concentrations compared with sugars. Solutions of 1 mM glucose were prepared with different concentrations of interfering species (0.1, 0.5, 1, 5, 10 mM), and they were measured by chronoamperometry under the optimum conditions of our sensor. In the **Table S3**, the lowest concentration of the interfering species affecting to the sensor signal is shown together with the variation of signal. As illustrated in the table, the higher influence comes from a solution 1:2 of glucose/ascorbic acid, but this ratio is significantly higher than those found in most food samples (for instance, the ratio between sugars/ascorbic acid in orange juice is at least 100:1). At least an equimolar concentration of glycerol or ethanol and a 5:1 solution for lactic acid is necessary to influence the signal obtained for glucose. No interfering effect was found for citric acid, at least in a 10:1 solution.

3.6 Real samples

To study the performance of the sensor in real food samples, measurements were carried out using the standard addition method (final glucose concentration: 50, 100, 500 and 1000 μM). These samples were orange juice, honey, soft drinks without and with sugars. The estimated sugar concentration in orange juice was 0.99 ± 0.06 g/L (nutritional value specified of 0.94 g/L), honey was 8.4 ± 0.5 g/kg (nutritional value of 7.8 g/kg and in previous publications of the group 6.8 ± 0.9 g/kg with a nickel nanoflowers sensor [16] and for enzymatic fructose and glucose sensors, 6.3 ± 0.1 g/kg [28,29]). For soft drink samples, concentrations of 0.0030 ± 0.0002 g/L (without sugar) and 1.13 ± 0.08 g/L (with sugar) were estimated (nutritional values of < 0.01 g/L and 1.06 g/L respectively). These results demonstrate that the CuNS-SPCE sensor is useful for the determination of total reducing sugars in real samples.

4. Conclusions

In this work, for the first time, it has been shown the possibility of generating *in situ* copper nanospheres on screen-printed carbon electrodes by a galvanostatic electrodeposition method. These nanoparticles have shown an excellent catalytic effect towards the oxidation of reducing sugars, with wide linear range, and low detection limits. The short analysis time, small sample volume together to the excellent stability and precision of the non-enzymatic sensor are interesting features to be applied in the food industry, as demonstrated here with different food samples. Interestingly, the possibility of using the same sensor for several times with high precision makes the cost of analysis especially low. This work proves the excellent characteristics of the galvanostatic deposition of nanomaterials on electrode systems and open the door to be explored with other nanomaterials in future works.

Acknowledgements

This work has been supported by the FC-15-GRUPIN-021 project from the Asturias Regional Government and the MINECO-15-CTQ2014-58826-R project from the Spanish Ministry Economy and Competitiveness (MEC). Authors thank the Spectroscopy Unit of the Scientific and Technical Services of the University of Oviedo for the help with the XPS measurements.

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TABLES AND FIGURES

Table 1. Analytical characteristics of the different sugars evaluated with the CuNS electrodes.

Sugar	Lineal range (μM)	Calibration	R^2	LOD (μM)
Glucose	1 – 10.000	$0.029x + 0.06$	0.9994	0.57
Fructose	1 – 10.000	$0.027x + 0.11$	0.9999	0.61
Arabinose	1 – 10.000	$0.029x + 0.09$	0.9999	1.0
Galactose	1 – 10.000	$0.031x + 0.03$	0.9992	0.89
Mannose	1 – 10.000	$0.029x + 0.42$	0.9998	1.3
Xylose	1 – 10.000	$0.028x + 0.16$	0.9995	1.04

Table 2. Analytical characteristics of different copper electrodes used for determination of glucose.

Electrode modified	Lineal Range (μM)	Detection Limit (μM)	Reference
Cu nanospheres	1 – 10000	0.57	This work
NiCu nanowires	50 – 1000	80	[30]
5% Copper (II) oxide	50 – 1200	4	[31]
Cu nanobelt	10 – 1130	10	[32]
Cu foam	180 – 3470	12.75	[25]
CuO nanowires	0 – 500	10	[33]
CuTiPNPs	25 - 2000	7	[34]
Cu/Graphene	0.12 - 500	0.03	[35]
Cu ₂ O/Graphene	10 - 3000	0.36	[36]

*CuTiPNPs: copper-modified titanium phosphate nanoparticles

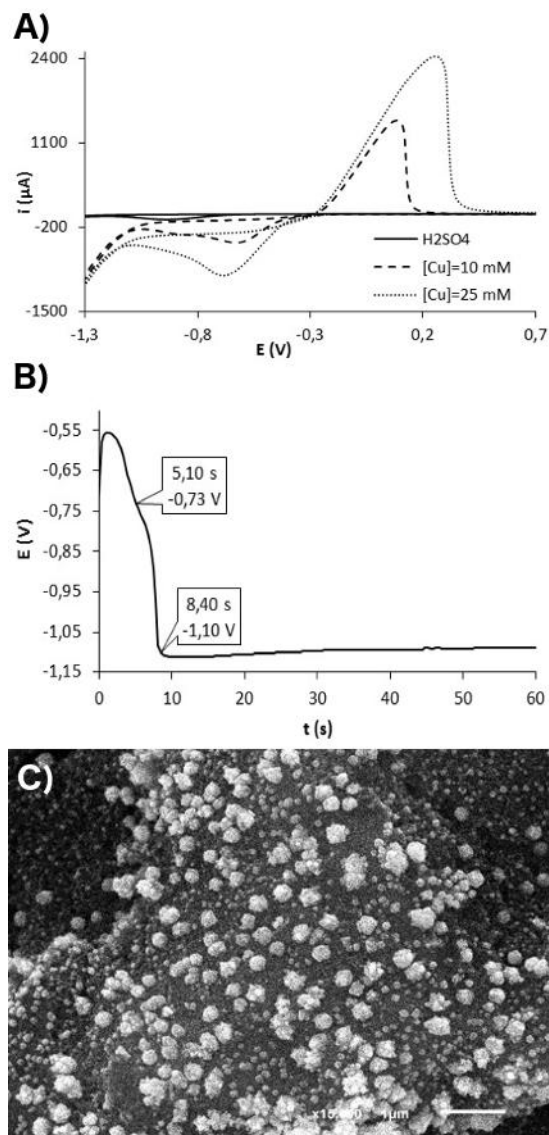


Figure 1. **A)** Cyclic Voltammograms of 10 mM, 25 mM of Cu(II) and blank solutions in a 0.1 M H_2SO_4 at 100 mV/s (potential window: +0.7 to -1.3 V). **B)** Chronopotenciogram for the galvanostatic electrodeposition of 10 mM Cu(II) in 0.1 M H_2SO_4 by applying -225 μA during 60 s. **C)** SEM image of the electrode surface after the galvanostatic electrodeposition.

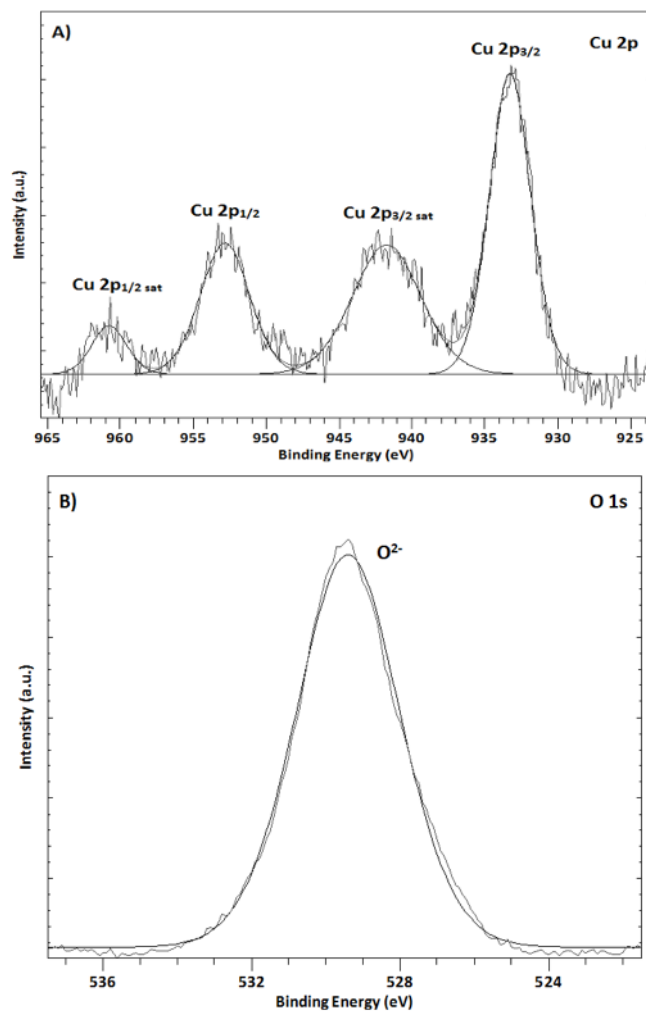


Figure 2. XPS spectrum of **A)** Cu2p and **B)** O1s for the copper nanospheres electrodeposited with galvanostatic method.

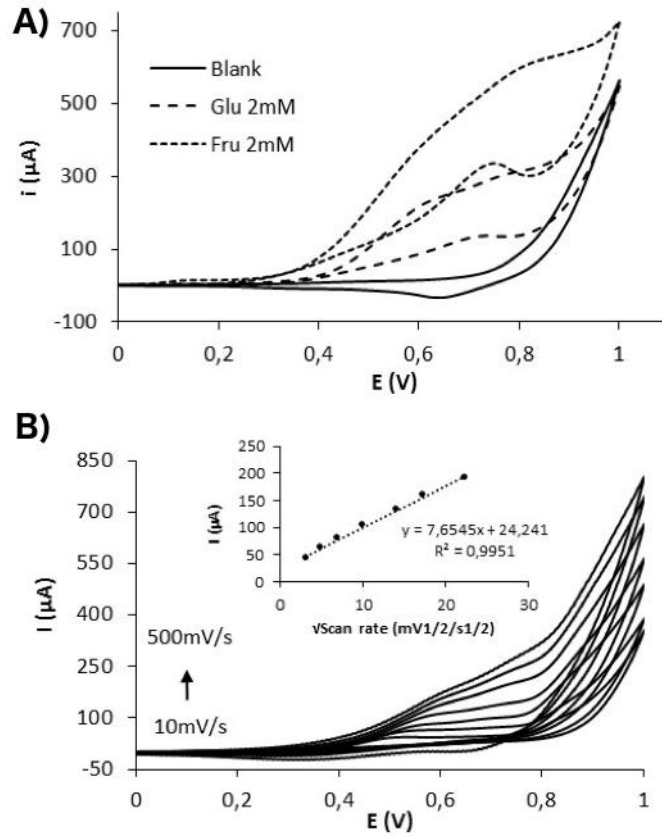


Figure 3. A) Cyclic voltammograms of the CuNS-SPCE sensor in presence of 2 mM of glucose (dashed line), 2 mM of fructose (dotted line) and blank (solid line) at 100 mV/s (window potential: 0V to +1 V).

B) Cyclic voltammograms of 800 μ M Glucose at several scan rates (10, 25, 50, 100, 200, 300, 500 mV/s) (window potential: 0V to +1 V). The inset shows the representation of intensity vs square root of the scan rate.

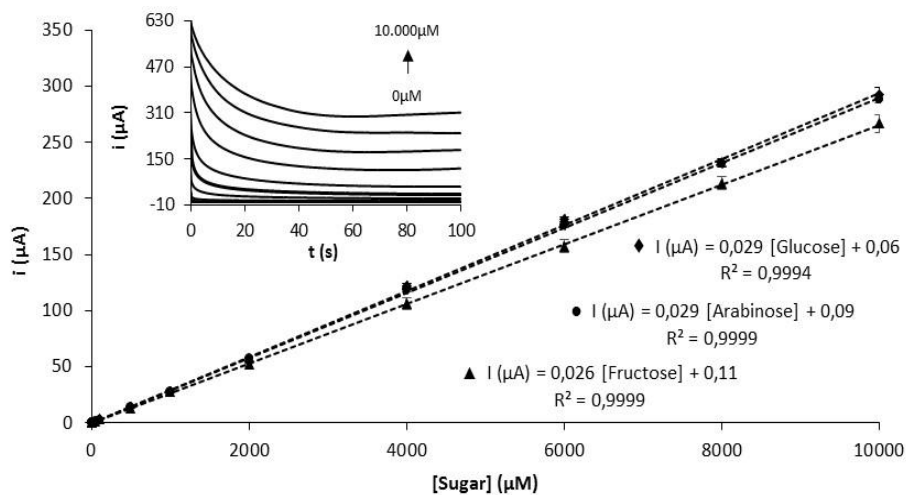


Figure 4. Calibration plots for glucose, fructose and arabinose. (Error bars indicate standard deviation of five measurements). Internal graph represents chronoamperograms for concentration of glucose measured at +0.65 V for 100 s.

Supporting Information

Galvanostatic electrodeposition of copper nanoparticles on screen-printed carbon electrodes and their application for reducing sugars determination

Beatriz Pérez-Fernández, Daniel Martín-Yerga and Agustín Costa-García*

Nano-bioanalysis Group

Department of Physical and Analytical Chemistry

University of Oviedo

*E-mail: costa@uniovi.es

METHODS AND MATERIALS

Instruments and electrodes

A potentiostat/galvanostat μ Autolab Type II controlled by GPES 4.9 software was used to carry out the electrochemical measurements and for the preparation of the electrodes. Screen-printed carbon electrodes (ref. DRP-110) were used. Each device consisted of an electrochemical cell with a three electrodes configuration (working and counter electrodes are made of carbon ink and the quasireference electrode is made of silver ink). The device has silver electrical contacts for connecting to the potentiostat through the a DRP-DSC connector from Dropsens (Spain). The working electrode was a 4 mm-diameter circular electrode. A JEOL 6610LV scanning electron microscope was used to characterize the sensor surface. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Phoibos 150/MCD-5 SPCEs spectrometer, using a monochromatic Al K α excitation source with an energy of 1486.74 eV. High resolution and general spectra were collected to 30 eV and 90 eV of energy pass and 0.1 and 1 eV of energy jump, respectively.

Reagents and solutions

Glucose, absolute ethanol, sodium hydroxide, sulfuric acid and glacial acetic acid were purchased by Merck (Spain). Orthophosphoric acid was purchased from Panreac (Spain). Boric acid, fructose, arabinose, galactose, mannose, xylose, glycerol, ascorbic acid, citric acid, lactic acid were provided by Sigma-Aldrich (Spain). Copper sulfate (II) was purchased from Probus. The ultrapure water used during all the work was obtained with a Millipore Direct-Q5 purification system from Millipore Ibérica (Spain). The working copper solutions were prepared in 0.1 M H₂SO₄. The working solutions of sugar and interfering species were prepared in 0.1M NaOH. All other reagents were of analytical grade.

TABLES AND FIGURES

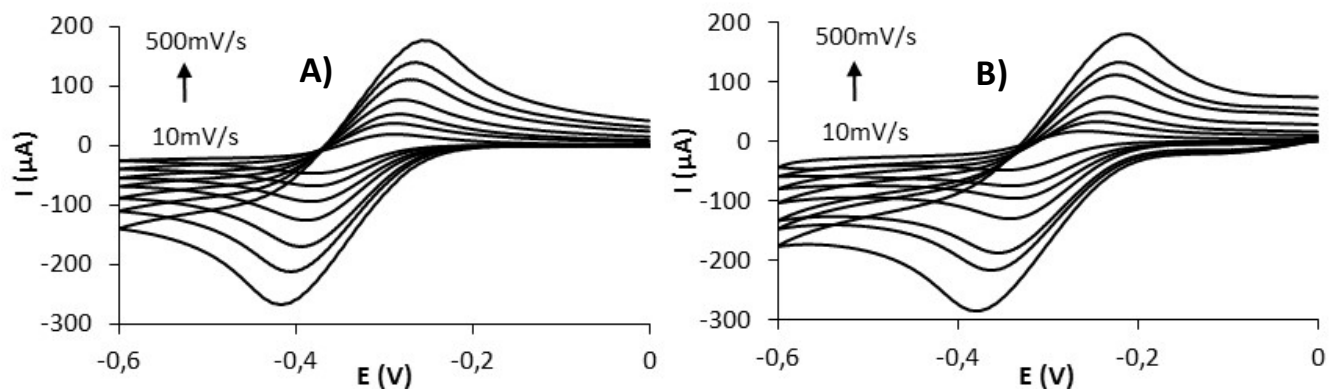


Figure S1. Cyclic voltammograms of 5 mM $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ in 0.1 M Na_2SO_4 for bare SPCE (A) and Cu-SPCE (B) for different scan rates (window potential: +0V to -0.6V)

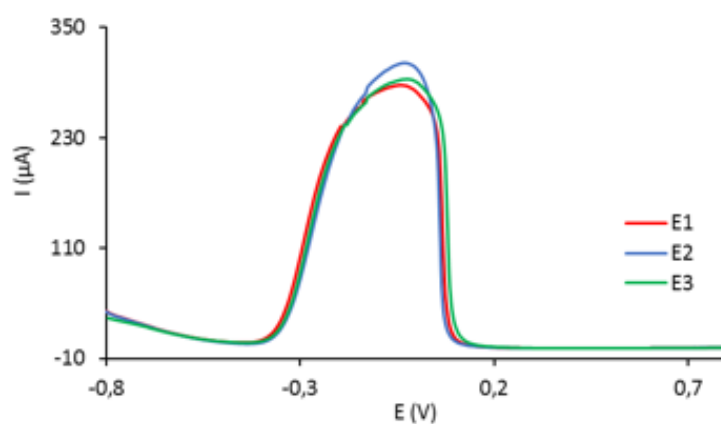


Figure S2. Differential-pulse voltammograms of the copper-modified screen-printed electrodes in 0.1 M H_2SO_4 . Applying a potential scan between -0.8 V to +0.8 V, a peak for the stripping of copper was obtained. The charge of this peak can be related to the amount of deposited copper. Faraday law illustrated by **Eq. 2**, where Q is the charge transfer (C), n the number of exchanged electrons, F constant of Faraday (96480 C/mol), m the deposited mass of Cu and M the molecular mass of Cu (63.546 g/mol), was used to estimate this value. An amount of 4.8×10^{-10} moles of copper was estimated to be deposited. Considering the geometric area of the electrode (0.012 cm^2), a surface density of $4 \times 10^{-8} \text{ moles/cm}^2$ was calculated, indicating the high density of copper on the surface as also can be observed in the SEM images (below).

$$\frac{m}{M} = \frac{Q}{nF} \quad (2)$$

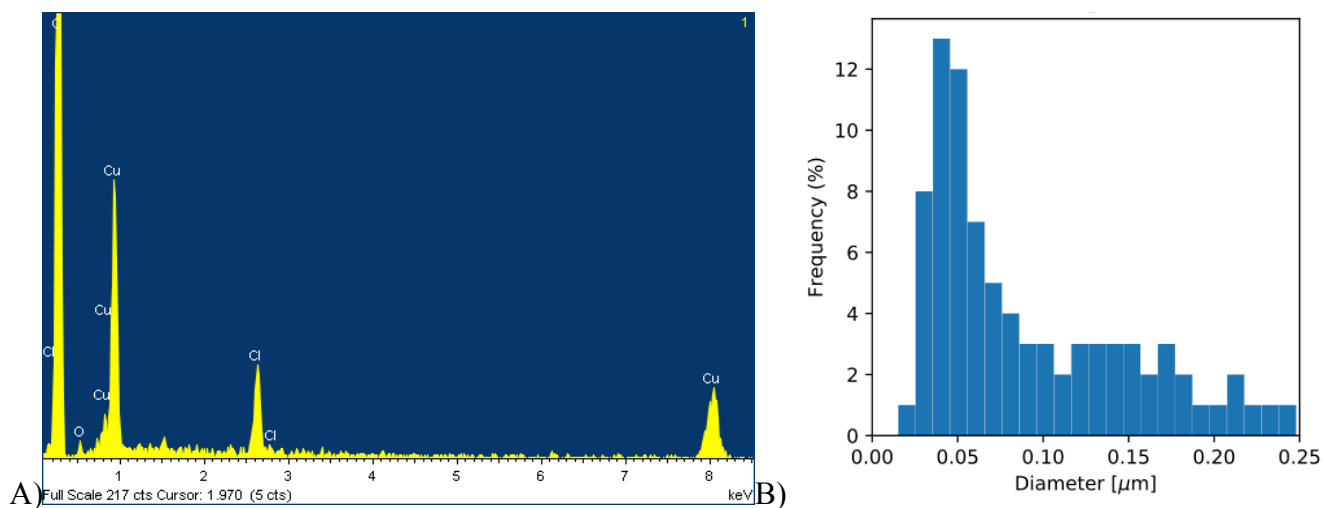


Figure S3. A) EDX spectrum of the electrode surface after the galvanostatic electrodeposition of copper nanospheres. B) Histogram plot illustration the size distribution of the copper nanospheres.

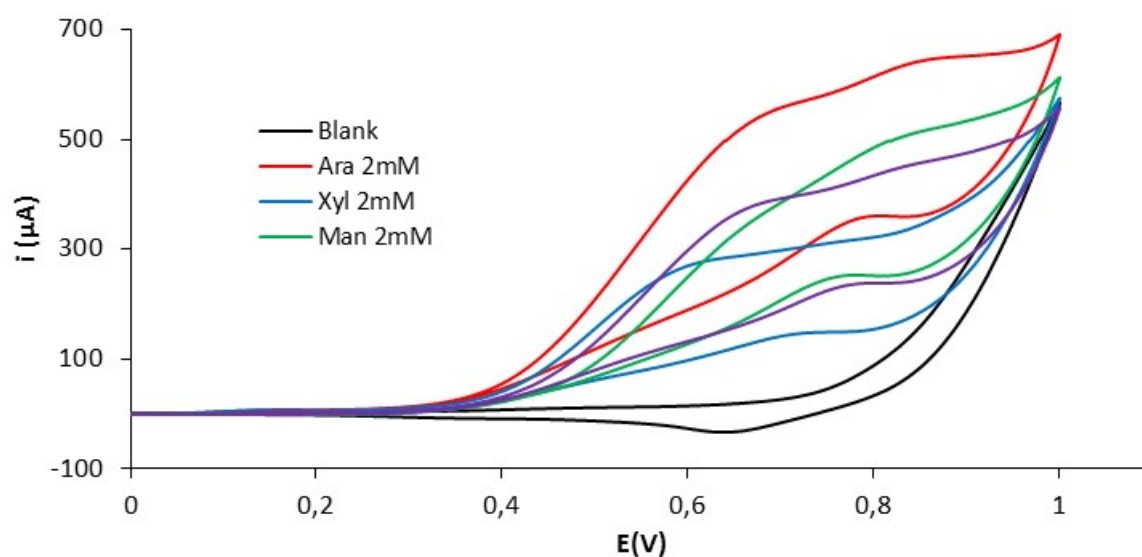


Figure S4. Cyclic voltammetry of 2mM of Arabinose, Galactose, Mannose, Xylose, and 0.1M NaOH obtained by copper nanospheres modified screen-printed-electrodes.

Table S1. Comparison between potentiostatic and galvanostatic electrodeposition methods.

	Blank response (μA)	RSD	1 mM glucose response (μA)	RSD	S/B
Potentiostatic	0.15 ± 0.07	48.7%	29.5 ± 1.4	4.7%	196.7
Galvanostatic	0.096 ± 0.012	12.1%	27.9 ± 1.7	6.1%	290.6

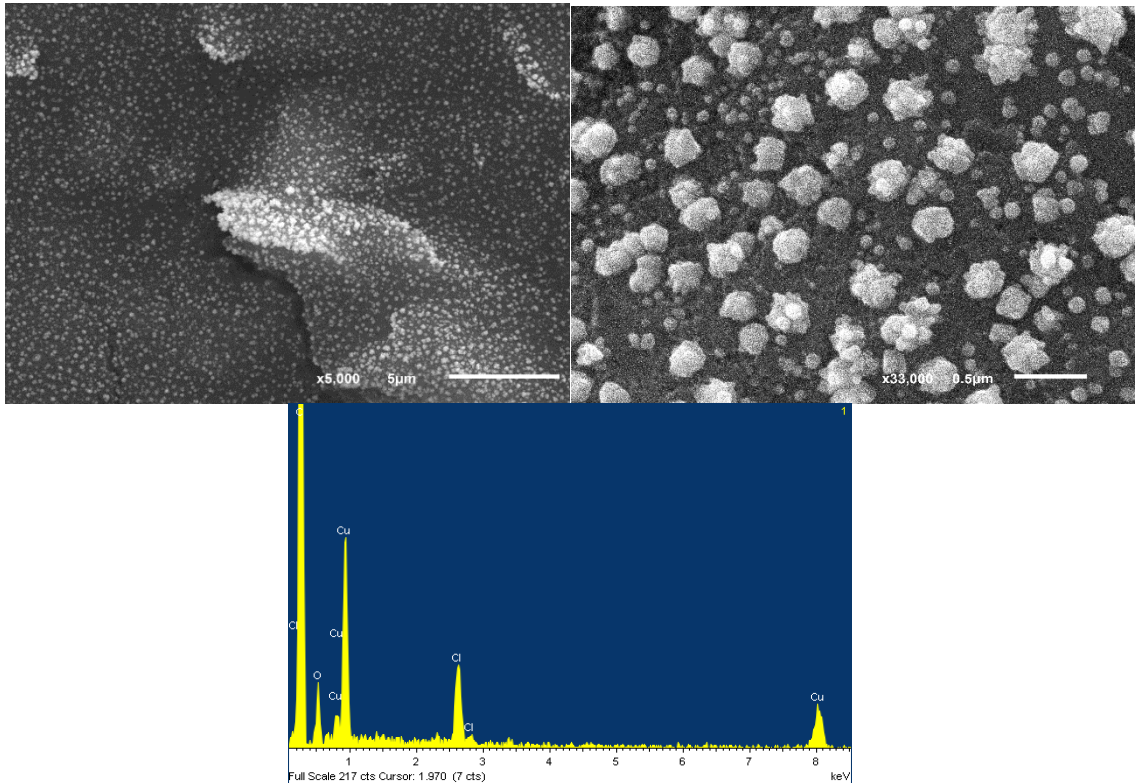


Figure S5. SEM images and EDX of the electrode surface after the voltammetric activation step.

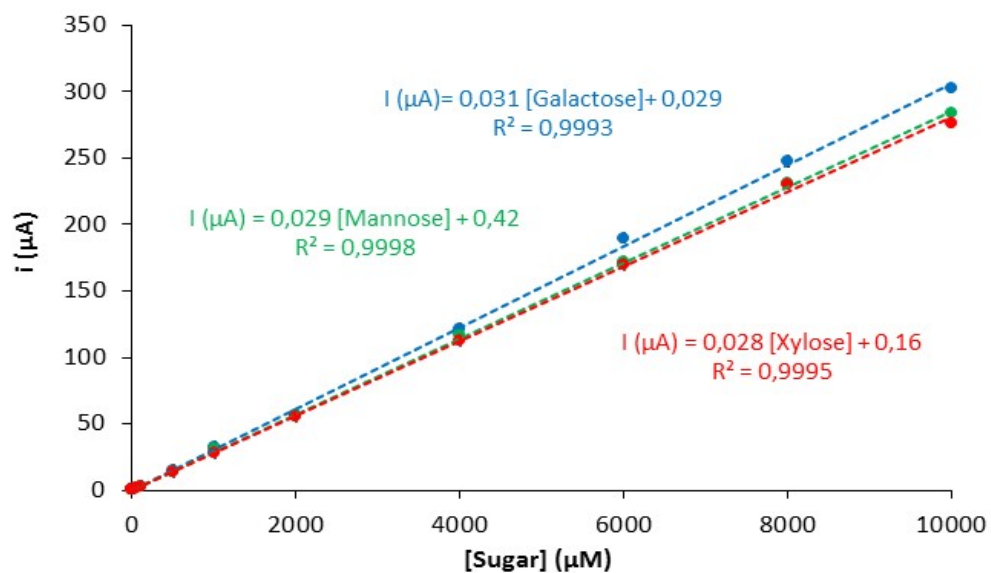


Figure S6. Calibration plots for Galactose, Mannose and Xylose.

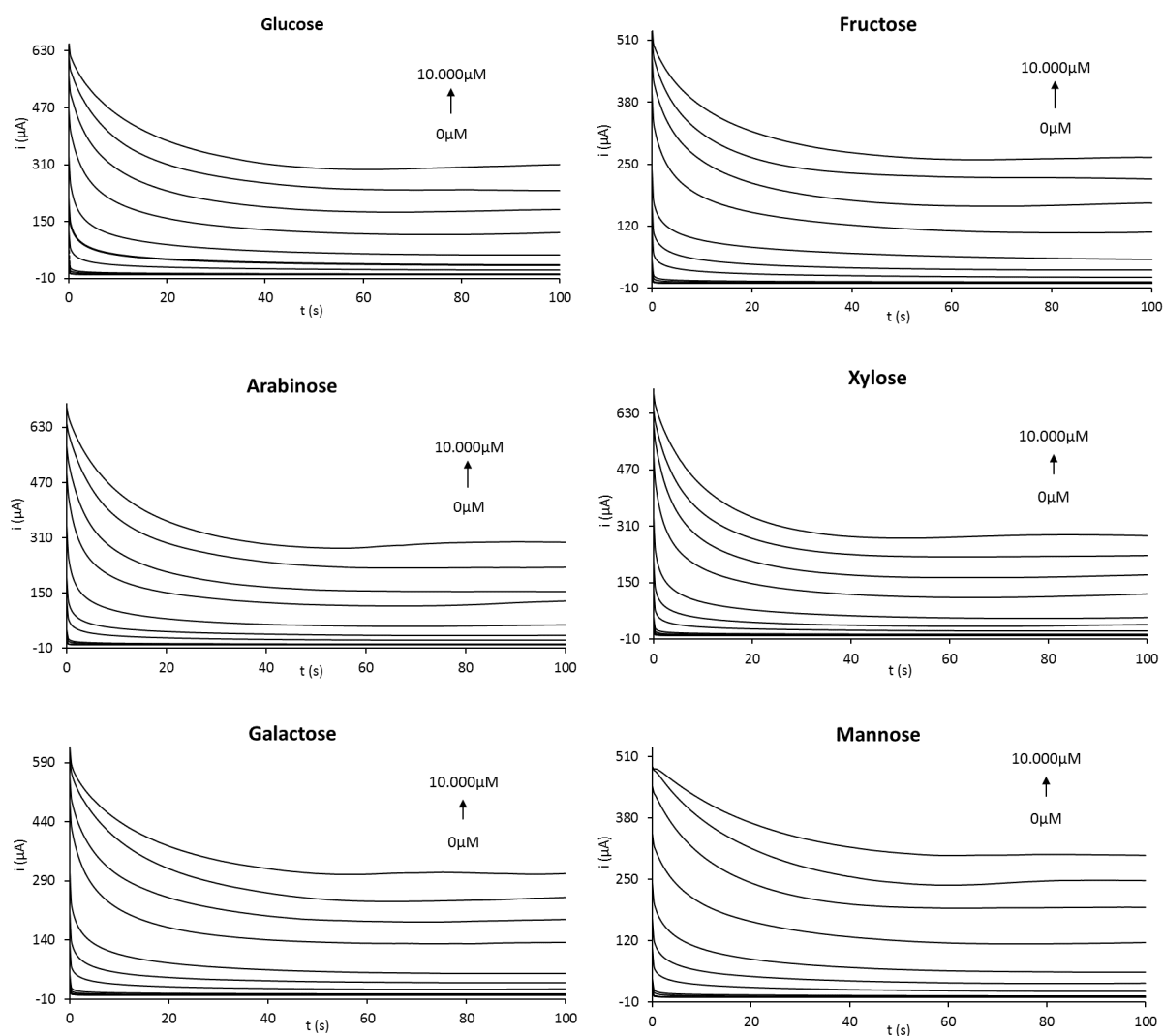


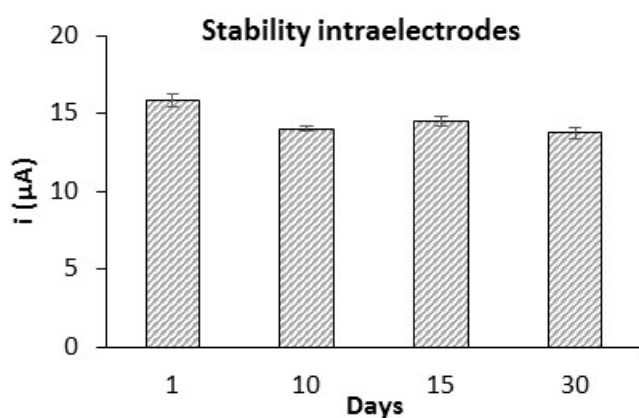
Figure S7. Typical chronoamperometric responses for increasing concentrations of each sugar (glucose, fructose, arabinose, xylose, galactose, mannose).

Table S2. Values obtained for increasing concentrations of each sugar during the chronoamperometric experiments performed to record the calibration plots. Standard deviation and relative standard deviation are also shown.

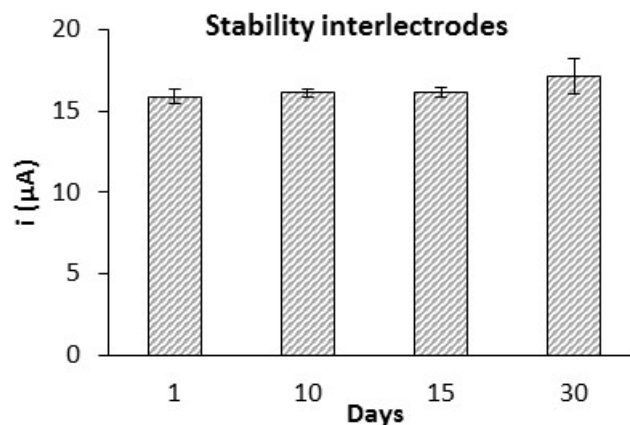
[Glu] (μM)	Signal (μA)	SD	RSD	[Fru] (μM)	Signal (μA)	SD	RSD
0	0,1026	0,0078	8%	0	0,0780	0,0128	16%
1	0,3249	0,0504	16%	1	0,2693	0,1107	41%
5	0,4902	0,0565	12%	5	0,4093	0,0995	24%
10	0,6206	0,0507	8%	10	0,5211	0,1247	24%
50	1,719	0,083	5%	50	1,677	0,172	10%
100	3,011	0,122	4%	100	3,026	0,209	7%
500	14,43	0,09	1%	500	13,45	0,73	5%
1000	27,96	0,98	4%	1000	28,02	1,33	5%
2000	54,80	0,44	1%	2000	51,86	1,57	3%
4000	122,02	1,91	2%	4000	105,98	5,39	5%
6000	181,30	2,45	1%	6000	157,52	6,13	4%
8000	231,76	3,46	1%	8000	213,73	5,95	3%
10000	293,07	5,52	2%	10000	266,89	8,18	3%

[Ara] (μM)	Signal (μA)	SD	RSD	[Gal] (μM)	Signal (μA)	SD	RSD
0	0,1365	0,0043	3%	0	0,1794	0,0073	4%
1	0,1695	0,0051	3%	1	0,2317	0,0131	6%
5	0,2756	0,0037	1%	5	0,3394	0,0083	2%
10	0,4303	0,0041	1%	10	0,5130	0,0146	3%
50	1,578	0,028	2%	50	1,871	0,013	1%
100	2,911	0,018	1%	100	2,998	0,137	5%
500	13,82	0,08	1%	500	15,18	0,49	3%
1000	28,15	0,27	1%	1000	32,22	0,25	1%
2000	57,16	0,21	0%	2000	56,14	1,30	2%
4000	118,65	2,00	2%	4000	121,38	1,06	1%
6000	175,88	1,42	1%	6000	189,95	1,08	1%
8000	231,43	2,36	1%	8000	247,64	3,43	1%
10000	288,62	3,11	1%	10000	302,56	2,60	1%

[Man] (μM)	Signal (μA)	SD	RSD	[Xyl] (μM)	Signal (μA)	SD	RSD
0	0,1188	0,0041	3%	0	0,1192	0,0116	10%
1	0,1477	0,0029	2%	1	0,2001	0,0021	1%
5	0,2497	0,0054	2%	5	0,2494	0,0034	1%
10	0,4058	0,0172	4%	10	0,4458	0,0037	1%
50	1,565	0,017	1%	50	1,536	0,017	1%
100	2,842	0,052	2%	100	2,855	0,136	5%
500	14,31	0,34	2%	500	13,38	0,10	1%
1000	30,88	0,13	0%	1000	28,27	0,71	3%
2000	56,15	0,12	0%	2000	55,76	1,18	2%
4000	116,99	0,40	0%	4000	112,27	0,52	0%
6000	171,65	4,47	3%	6000	169,97	1,54	1%
8000	230,75	1,65	1%	8000	230,38	3,71	2%
10000	283,91	2,24	1%	10000	276,20	3,02	1%



A)



B)

Figure S8. Electrochemical response of CuNS-SPCE in different days, using the same device (a) and different device (b). (Error bars indicate standard deviation of five measurements).

Table S3. Lower concentration of interfering species that influences the analytical signal for 1 mM of glucose and the percentage variation of the analytical signal produced.

Interfering species	Concentration	Variation (%)
Glicerol	1 mM	127%
Ethanol	1 mM	86%
Lactic acid	5 mM	77%
Ascorbic acid	0.5 mM	123%
Citric acid	-	-