

**Please cite the Published Version**

Camargo, Jéssica R , Cleto, Sabrina, Neumann, Amanda, Azzi, Déborah C, Crapnell, Robert D , Banks, Craig E  and Janegitz, Bruno C (2024) Edible gold leaf as a viable modification method for screen-printed sensors. *Electrochimica Acta*, 478. 143825 ISSN 0013-4686

**DOI:** <https://doi.org/10.1016/j.electacta.2024.143825>

**Publisher:** Elsevier BV

**Version:** Accepted Version

**Downloaded from:** <https://e-space.mmu.ac.uk/633922/>

**Usage rights:**  [Creative Commons: Attribution-Noncommercial-No Derivative Works 4.0](https://creativecommons.org/licenses/by-nc-nd/4.0/)

**Additional Information:** © 2024. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <https://creativecommons.org/licenses/by-nc-nd/4.0/> ([opens in new tab/window](#))

**Data Access Statement:** Data will be made available on request.

**Enquiries:**

If you have questions about this document, contact [openresearch@mmu.ac.uk](mailto:openresearch@mmu.ac.uk). Please include the URL of the record in e-space. If you believe that your, or a third party's rights have been compromised through this document please see our Take Down policy (available from <https://www.mmu.ac.uk/library/using-the-library/policies-and-guidelines>)

# Edible gold leaf as a viable modification method for screen-printed sensors

Jéssica R. Camargo<sup>a,b,d,\*</sup>, Sabrina Cleto<sup>a</sup>, Amanda Neumann<sup>a</sup>, Déborah C. Azzi<sup>c</sup>, Robert D. Crapnell<sup>d</sup>, Craig E. Banks<sup>d</sup>, Bruno C. Janegitz<sup>a,\*</sup>

<sup>a</sup> *Laboratory of Sensors, Nanomedicine and Nanostructured Materials, Federal University of São Carlos, Araras, 13600-970, Brazil*

<sup>b</sup> *Department of Physics, Chemistry, and Mathematics, Federal University of São Carlos, Sorocaba, São Paulo, Brazil, 18052-780*

<sup>c</sup> *ADB Pesquisa e Desenvolvimento, Araras 13600-140, SP, Brazil*

<sup>d</sup> *Faculty of Science & Engineering, Manchester Metropolitan University, John Dalton Building, Chester Street, Manchester M1 5GD, UK*

---

## A B S T R A C T

The demand for low-cost, efficient, selective, and sensitive analytical methods is increasing globally, making electroanalysis combined with screen-printed electrodes an appealing option. Gold, known for its excellent electrical conductivity and biocompatibility, improves the electrocatalytic activity of the sensors and reduces interference with other substances. Here, we propose the modification of disposable sensors with edible gold leaf, which is a cost-effective alternative to sputtering. The gold leaf was immobilized on the screen-printed electrode surface with chitosan. L-tyrosine, an amino acid, and an important biomarker for the diagnosis of various diseases was detected as a proof-of-concept. Using square-wave voltammetry for the determination of L-tyrosine, the disposable sensor modified with gold leaf showed a linear response in the range between 0.10 to 70  $\mu\text{mol L}^{-1}$  with a limit of detection of 0.09  $\mu\text{mol L}^{-1}$ . Overall, the use of gold leaf to modify disposable electrochemical sensors for L-tyrosine detection represents a promising approach for electrochemical sensing.

---

## 1. Introduction

Currently, the search for analytical methods that pollute less, produce easily, and are more accurate is growing at the same pace as scientific progress [1]. In this context, electrochemical sensors have emerged as indispensable instruments for everyday living, performing analysis in various industrial fields with greater efficiency [2,3]. In recent years, the use of many classical bulky electrodes has been abandoned, making way for small and inexpensive electrodes with enhanced flexibility and easy-to-use systems [4–6]. This makes disposable electrodes an attractive alternative, as their single-use nature overcomes problems with poisoning or adsorption on the electrode surface [7,8].

Gold is an exceptional electrical conductor and has excellent biocompatibility. Its use as a surface coating on electrochemical sensors can improve the electrocatalytic activity of the electrode and reduce interference from other substances [9–11]. The gold surface can also prevent the oxidation of the conductive graphite ink, which can affect the performance of the sensor [12,13]. Modification of disposable electrochemical sensors with gold involves applying a thin layer of gold to the surface of the sensor [14] which can be achieved using a sputtering technique, in which gold atoms are ionized and deposited on the

sensor surface using an electric field [15,16]. However, this modification has a high cost due to the need for the metallizer. Gold leaf is a thin layer of gold that is commonly used for decorative and food purposes [17], which can also be used as a method to modify disposable electrochemical sensors [14]. In the literature, there are some works proposed using gold leaves, such as Li et al. [18] and Zhang et al. [19] that developed glassy carbon electrodes modified with these materials.

L-tyrosine is an amino acid used as a nutritional supplement [20] and it can be found in many proteins, and its detection is important for the diagnosis of various diseases [21]. In the body, it has a primary function in the brain as it is involved in the synthesis of dopamine, which is responsible for mood, sleep, and attention [22]. Typically, the concentration of Tyr in healthy individuals is in the range of 30 to 120  $\mu\text{mol L}^{-1}$ ; however, in the biological fluids of patients with tyrosine metabolism disorders, it may surpass 200  $\mu\text{mol L}^{-1}$ . In urine, the acceptable level is 11 to 135  $\mu\text{mol}$  per gram of creatinine [23]. In this context, the use of disposable electrochemical sensors allows the easy and rapid detection of L-tyrosine, which may be important in the clinical setting. Also, the use of gold leaf as a method to modify disposable electrochemical sensors for L-tyrosine detection offers a promising approach for the diagnosis of various diseases. Thus, the focus of this work is to

---

\* Corresponding authors.

E-mail addresses: [jessica.10.camargo@gmail.com](mailto:jessica.10.camargo@gmail.com) (J.R. Camargo), [brunocj@ufscar.br](mailto:brunocj@ufscar.br) (B.C. Janegitz).

demonstrate the simplicity and functionality of the preparation of the edible gold leaf-modified screen-printed electrodes and the application of this system in the electrochemical detection of L-tyrosine.

## 2. Experimental

### 2.1. Reagents and solutions

All reagents utilized in this work were of analytical grade, from Sigma- Aldrich®, USA, Synth, or Dinamica Química. Ultrapure water (Milli Q, USA) with a resistivity  $<18 \text{ M}\Omega \text{ cm}$  was employed to prepare all aqueous solutions. The electrochemical characterization of the electrodes was conducted using a solution containing  $1.0 \text{ mmol L}^{-1}$  Ferrocenemethanol ( $\geq 97\% \text{ w/w}$ ) and  $0.1 \text{ mol L}^{-1}$  KCl. Phosphate buffered saline (PBS) with a pH of 7.0 was used as the supporting electrolyte for L-tyrosine detection. Synthetic urine was prepared according to the literature with adaptations [24], which consisted of the following components:  $90.0 \text{ mmol L}^{-1}$  sodium chloride (99% w/w) from Synth,  $170.0 \text{ mmol L}^{-1}$  urea (99% w/w),  $2.5 \text{ mmol L}^{-1}$  calcium chloride dihydrate ( $\geq 99\% \text{ w/w}$ ),  $10.0 \text{ mmol L}^{-1}$  anhydrous sodium sulfate (99% w/w),  $0.4 \text{ mmol L}^{-1}$  uric acid (99% w/w), and  $7.0 \text{ mmol L}^{-1}$  creatinine ( $\geq 98.5\% \text{ w/w}$ ) from Sigma-Aldrich®, USA, and  $2.0 \text{ mmol L}^{-1}$  citric acid (99.5% w/w) and  $25.0 \text{ mmol L}^{-1}$  ammonium chloride (99.5% w/w) from Dinamica Química (Indaiatuba, Brazil). (Diadema, Brazil). The determination of L-tyrosine was performed in the tap water of Araras City (São Paulo State) (−22.315206, −47.380840).

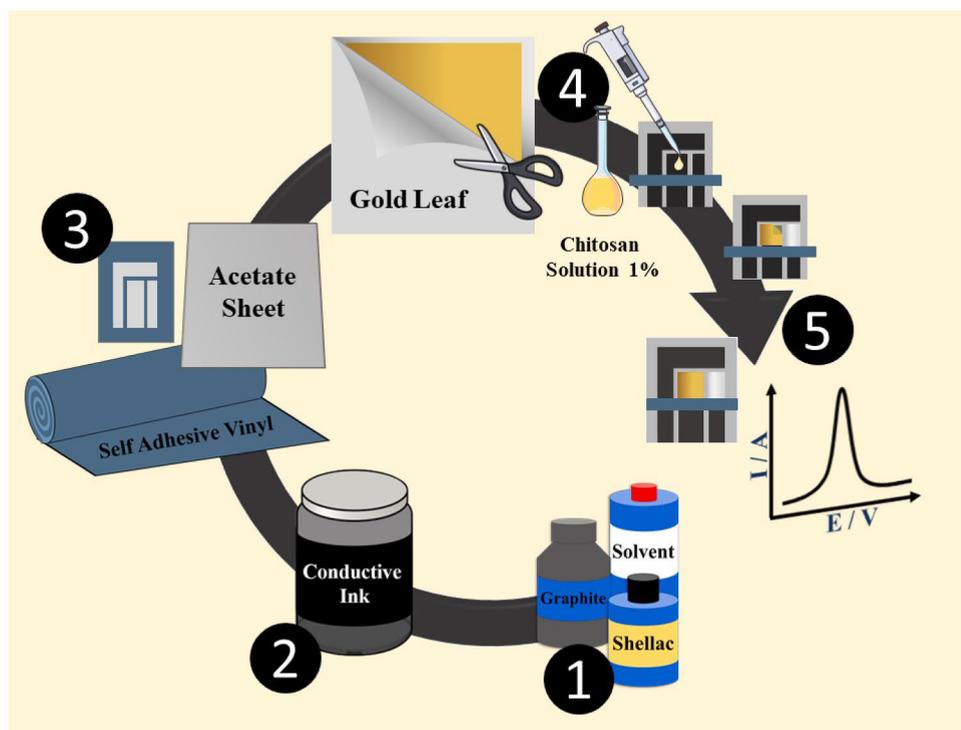
### 2.3. Apparatus and electrochemical measurements

The sensor surface was characterized by scanning electron microscopy (SEM) using a Thermo Fisher Scientific Prisma. The conductive ink was blended using a SpeedMixer™ Dac 150.1 FVZ-K (FlackTec Inc., Landrum, USA), which is a double asymmetric centrifuge. All

electrochemical measurements were performed with an AutoLab PGSTAT204 potentiostat/galvanostat managed by NOVA 2.1.5 software (Metrohm, Netherlands). Cyclic voltammetry (CV) measurements were performed from  $-0.2$  to  $+1.2 \text{ V}$ , at a scan rate of  $50 \text{ mV s}^{-1}$  and square wave voltammograms (SWV) measurements (modulation amplitude  $60 \text{ mV}$ ; Frequency  $35 \text{ Hz}$ ; step potential:  $5.0 \text{ mV}$ ) were used for L-tyrosine quantification. To evaluate the optimization parameters for SWV (Square Wave Voltammetry), a DoE (Design of Experiment) approach was used with Statistica 64 software from Statsoft (Dell, Tulsa, USA). The DoE aimed to identify the factors influencing the electrochemical measurement and to determine the optimal values of these factors that would give the desired result within the given parameters.

### 2.4. Manufacture of the disposable electrodes modified with gold leaf

The conductive ink was prepared according to the literature [25] by combining shellac (SH, 2.0 g), solvent for polyurethane (4.0 g), and graphite (GP, 2.0 g) as shown in step 1 (Fig. 1). To ensure complete mixing, the reagents were mixed using the SpeedMixer™. The mixing procedure comprised three cycles, each running at 3500 rpm for 180 seconds (step 2). Self-adhesive vinyl was cut out with a precision printer to produce the masks. The design of these masks was created using Silhouette Studio software. Acetate sheets (AS) were used as the backing and sanded in one direction with 220 grit sandpaper (3M) to improve ink application. The sheet was then cleaned with 70% alcohol to remove all residue and the masks were glued on. A sufficient amount of ink was applied to the masks with the aid of a spatula. Immediately after the ink was applied the masks were quickly removed before the ink dried (step 3). The ink was allowed to dry for 120 minutes, after which the devices were cut out individually. Using a nail dotting pen, the silver ink (Electron Microscopy Sciences) was applied to the pseudo reference electrode, creating a system with working ( $0.25 \text{ cm}^2$ ), auxiliary, and reference electrodes. A gold leaf (Au) was cut into a square  $5 \times 5 \text{ mm}$



**Fig. 1.** Illustration of the manufacturing process of the gold leaf SPE electrodes. The ink was prepared using a mixture of shellac, solvent for PU, and graphite (step 1). The SpeedMixer® was used to make the conductive ink (step 2). The acetate sheet was sanded and washed, and a self-adhesive vinyl cut with the Silhouette machine adhered to the surface. The ink was spread on the surface with a spatula and allowed to dry at room temperature for 2 hours (Step 3). The edible gold leaves were cut into  $5 \text{ mm}^2$  and glued to the surface of the working electrode with 1% chitosan solution (w/v) (step 4). The electrodes were dried at  $50^\circ\text{C}$  for at least 2 hours until the chitosan solution was completely dry and the electrodes Au-SH-GP/AS were ready for use (step 5).

using scissors. A 1% chitosan solution was prepared using a 2% acetic acid solution. An amount of 10  $\mu\text{L}$  of this solution was used to glue the edible gold leaves into the surface of the working electrode, named Au-SH-GP/AS. The electrodes were dried at 50°C for at least 2 hours until the chitosan solution was completely dry and the electrodes were ready for use (step 5). The entire process was carried out at room temperature (25°C).

### 3. Results and discussion

#### 3.1. Morphological characterization of the Au-SH-GP/AS

Fig. 2a shows the image of the electrode Au-SH-GP/AS with a total area of 2 cm  $\times$  1.5 cm and an area of 0.25 cm<sup>2</sup> for the working electrode. Fig. 2b shows the electrode connected to the potentiostat, onto the surface of which an amount of 150  $\mu\text{L}$  of the sample was dropped. The SEM images of Au-SH-GP /AS show the area of the working electrode modified with the gold leaf (in red) and the carbon ink (surface of the counter electrode, in blue). The image (Fig. 2c) shows the graphite ink distributed over the entire surface with parallel layers [26], while Fig. 2d shows the surface modified with the gold sheet, at 2000x magnification.

#### 3.2. Electrochemical characterization of the Au-SH-GP/AS

The Au-SH-GP/AS electrode and SH-GP/AS were compared by cyclic voltammetric analysis in the presence of 1.0 mmol L<sup>-1</sup> ferrocenemethanol / 0.1 mol L<sup>-1</sup> KCl. Cyclic voltammograms (Fig. 3) were obtained at a scan rate of 50 mV s<sup>-1</sup> and showed anodic and cathodic peaks at +20.0 and +0.09 mV for Au-SH-GP/AS and +26.0 and +19.6 mV for SH-GP/AS, respectively (vs. a silver ink reference electrode). The proposed sensor modified with the gold leaf showed a  $\Delta E_p$  of about 102 mV and anodic and cathodic peaks with current at 49.1  $\mu\text{A}$  and -41.7  $\mu\text{A}$ ,

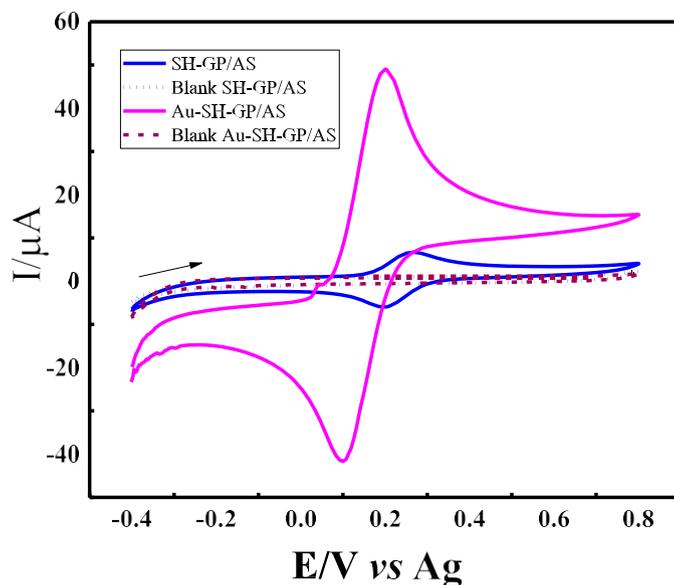


Fig. 3. Cyclic voltammograms obtained with Au-SH-GP/AS (pink line) and SH-GP/AS (blue line) electrodes in 0.1 mol L<sup>-1</sup> KCl in the presence of 1.0 mmol L<sup>-1</sup> ferrocenemethanol. Scan rate = 50 mV s<sup>-1</sup>.

respectively. The unmodified sensor shows anodic and cathodic current at 6.7  $\mu\text{A}$  and -6.0  $\mu\text{A}$ , with a  $\Delta E_p$  of about 70 mV. This confirms that the modification of the gold increased the current by about 12 times.

Cyclic voltammetry measurements were performed with an electrochemical probe at various scan rates from 20 to 150 mV s<sup>-1</sup> (20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140 and 150 mV s<sup>-1</sup>, see Fig. 4a)

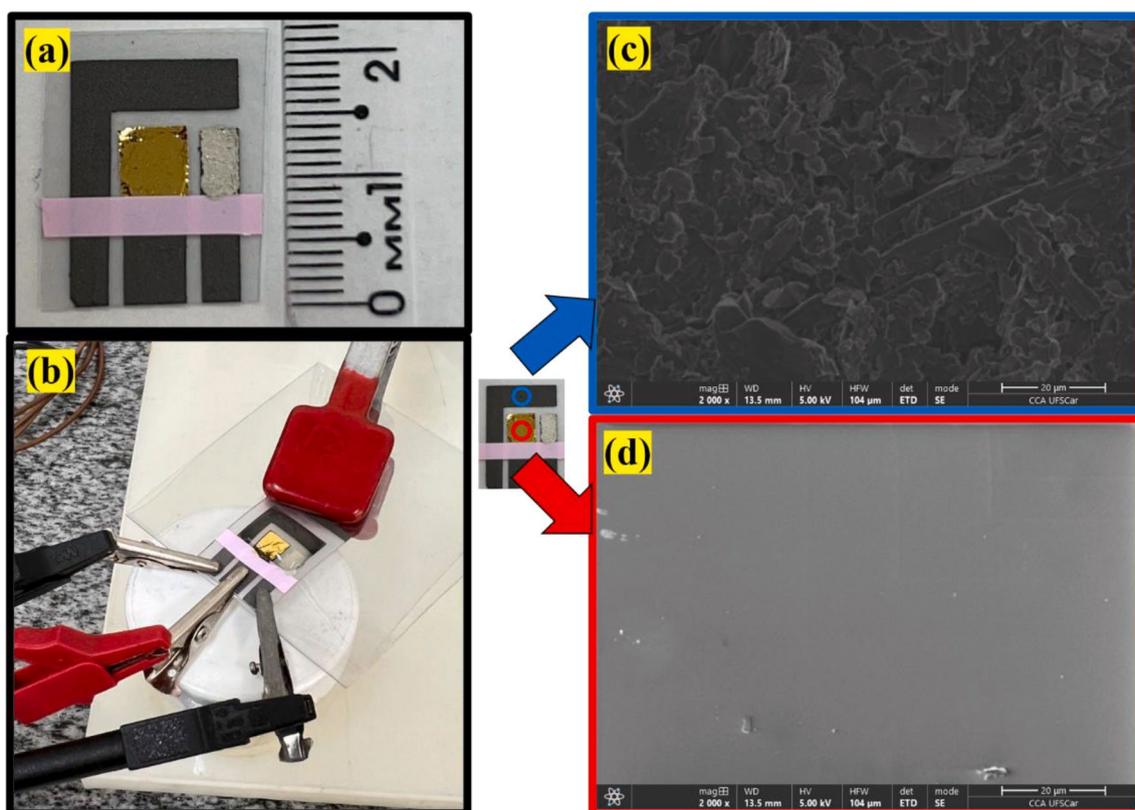
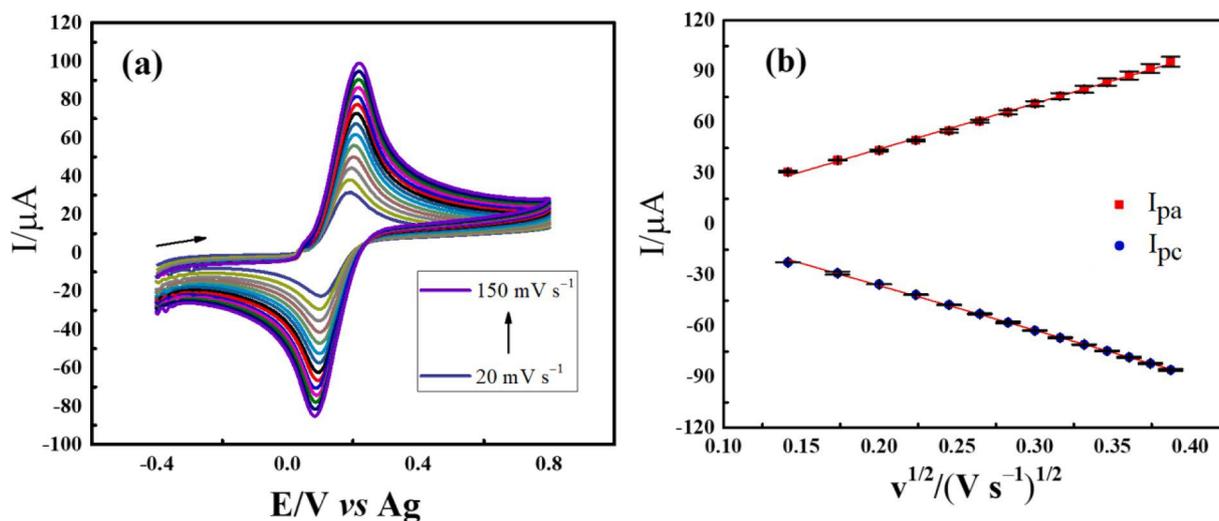


Fig. 2. (a) Photograph of the Au-SH-GP/AS electrode; (b) the proposed electrode connected to the potentiostat with sample dropped on the surface; SEM images obtained for Au-NP-GP/AS at 2000x magnification of (c) the carbon ink (counter electrode region surface) and (d) gold leaf (working electrode region surface).



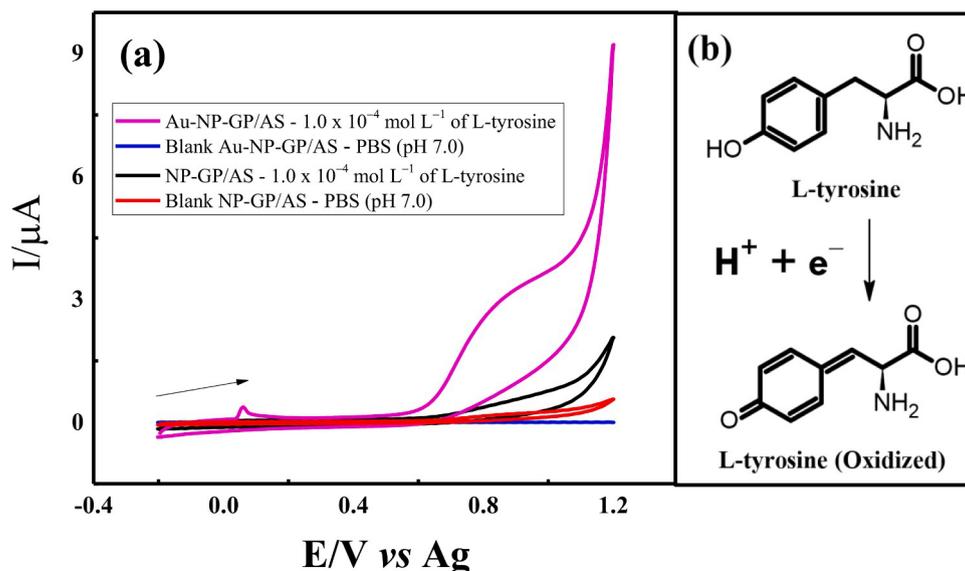
**Fig. 4.** (a) Cyclic voltammograms obtained in the presence of equimolar  $1.0 \text{ mmol L}^{-1}$  Ferrocenemethanol in  $0.1 \text{ mol L}^{-1}$  KCl solution, varying the scan rate from 20 to  $150 \text{ mV s}^{-1}$  (20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140 and  $150 \text{ mV s}^{-1}$ ). (b) The plot of current response vs.  $v^{1/2}$ .

to evaluate the electron transfer behavior in the proposed electrode. As observed in Fig. 4b, we observe an increase in both anodic peak current ( $I_{pa}$ ) ( $R^2 = 0.9977$ ) and cathodic peak current ( $I_{pc}$ ) showing a linear correlation ( $R^2 = 0.9990$ ) with the square root of the scan rate ( $v^{1/2}$ ), indicating a diffusion-controlled transport process. Furthermore, the Randles-Sevcik equation (1) [27] was used to determine the electroactive area of the Au-SH-GP/AS electrode and SH-GP/AS electrode. The result was a value of  $0.36 \text{ cm}^2$  and  $0.07 \text{ cm}^2$ , in this way, the modified electrode obtained about 5 times an increase of electroactive area after modification of gold. Using the equation ( $\%Real = (A_{real}/A_{geo}) \times 100$ ) [28], the real area of the Au-SH-GP/AS electrode was found to be  $\%Real = 144\%$  or 1.44 times the geometric area. The durability of the sensor was tested by CV using Au-SH-GP/AS prepared on the same day and 1 year ago in  $0.1 \text{ mol L}^{-1}$  KCl in the presence of  $1.0 \text{ mmol L}^{-1}$  ferrocenemethanol at a scan rate of  $50 \text{ mV s}^{-1}$ . The  $\Delta E$  was  $133.7 \text{ mV}$  for the sensor prepared on the same day and  $158.3 \text{ mV}$  for the sensor prepared 1 year ago, resulting in an increase of 18 % between measurements. The anodic current was  $47.4 \text{ mV}$  and the cathodic current was  $-39.0 \text{ mV}$  for the sensor manufactured on the same day. An anodic current of  $51.3 \text{ mV}$

and a cathodic current of  $-45.3 \text{ mV}$  were determined for the sensor manufactured 1 year ago, which represents an increase of 7.61 % for the anodic current and 13.9 % for the cathodic current after 1 year. The voltammograms of this study are shown in Figure S1. Also, 50 measurements using a unique sensor were performed in the same conditions as the aforementioned study. It has been observed that the analytical signal is still maintained without a noticeable change. This indicates the robustness of the system, allowing for multiple measurements to be performed in the same drop without compromising the signal quality is detailed in the supporting information in Figure S2.

### 3.3. Determination of L-tyrosine

Cyclic voltammetric measurements in the absence and presence of  $100 \text{ } \mu\text{mol L}^{-1}$  L-tyrosine from  $-0.2$  and  $1.2 \text{ V}$ , with a scan rate of  $50 \text{ mV s}^{-1}$  were obtained in  $0.10 \text{ mol L}^{-1}$  phosphate buffer solution (pH 7.0) (Fig. 5a). The Au-SH-GP/AS electrode showed an irreversible redox process, with an oxidation peak at  $0.87 \text{ V}$ , attributed to the oxidation of L-tyrosine to oxidized L-tyrosine [29]. To compare, the SH-GP/AS



**Fig. 5.** Cyclic voltammograms obtained with Au-NP-GP/AS and NP-GP/AS electrodes in  $0.1 \text{ mol L}^{-1}$  PBS (pH 7.0) without and in the presence of  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  L-tyrosine. Scan rate =  $50 \text{ mV s}^{-1}$ ; (b) the electrochemical mechanism of L-tyrosine oxidation.

electrode was used without modification for the L-tyrosine detection. We can observe that the sensor modified with gold leaf increases the performance of the system. The oxidation of L-tyrosine [30] is also reported in the literature, with a one-electron and one-proton process as shown in Fig. 5b.

Square wave voltammetry (SWV) was used for L-tyrosine detection. In this sense, the optimization of SWV parameters (modulation amplitude and frequency) was performed to ensure the best electrochemical response by using the design of experiments. The pH study was conducted using PBS at different pH values of 6.0; 7.0; 8.0; 9.0 and 10.0 with 70  $\mu\text{mol L}^{-1}$  L-tyrosine, with pH 7 performing best. This study can be found in Figure S3. For this purpose, a response curve was established to determine the optimal values of the tested factors. This study was

performed with a solution containing 50  $\mu\text{mol L}^{-1}$  tyrosine. The experimental design used can be found in Table S1. Figures S4a and S4b show higher current values are observed in the violet region, among the

evaluated values that were performed, the higher ones were obtained at 60 mV and 35 Hz modulation amplitude and frequency values, respectively. Such values were selected as the optimal conditions for further studies. The step was maintained at 5 mV in all analyses.

A calibration plot was obtained under optimized conditions to assess different concentrations of L-tyrosine (Fig. 6a), ranging from 0.10 to 70  $\mu\text{mol L}^{-1}$  (0.1, 5.0, 8.0, 20, 30, 50, and 70  $\mu\text{mol L}^{-1}$ ), and a linear correlation between concentration and peak current was observed (Fig. 6b).

The obtained equation was:  $I_p (\mu\text{A}) = -2.163 \times 10^{-8} + 0.008 C_{\text{L-tyrosine}}$

( $\mu\text{mol L}^{-1}$ ), with an  $R^2$  value of 0.990. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated by three and ten times the standard deviation of the intercept divided by the slope of the calibration plot, respectively [31]. The LOD value was found to be 0.013  $\mu\text{mol L}^{-1}$  and the LOQ value was found to be 0.044  $\mu\text{mol L}^{-1}$ .

To evaluate the accuracy of the sensor, repeatability (n=5) and reproducibility (n=5) tests were performed (Figure S5), which yielded

RSD values of 0.52 % and 3.64 %, respectively, which highlights the excellent performance of the gold leaf-modified electrodes. The feasibility of using the Au-NP-GP/AS electrodes as an L-tyrosine sensor was investigated using synthetic urine and tap water samples. After enriching the samples with four different L-tyrosine concentrations (5.0, 7.0, 20, and 30  $\mu\text{mol L}^{-1}$ ), recovery tests were performed, and the results are shown in Table 1. To investigate interferences, SWV measurements were performed at a concentration of 20  $\mu\text{mol L}^{-1}$  in the presence of competing species, such as ascorbic acid, urea, and uric acid at the same concentration. As shown in Figure S6, the investigated species showed a higher signal deviation of 2.3 %, indicating that these species do not cause significant interference.

The analytical performance of Au-NP-GP/AS electrodes was compared with other electrochemical techniques commonly used for L-tyrosine detection (see Table 2). For example, Zribi et al [32] developed

**Table 1**

Recovery values (n = 3) for L-tyrosine additions in urine and tap water samples.

Sample (n=3)	Added ( $\mu\text{mol L}^{-1}$ )	Found ( $\mu\text{mol L}^{-1}$ )	Recovery (%)
Tap Water	5.0	5.62 $\pm$ 0.07	112.4 $\pm$ 7.06
	7.0	6.75 $\pm$ 0.22	96.5 $\pm$ 2.79
Synthetic urine	5.0	5.33 $\pm$ 0.06	106.7 $\pm$ 5.56
	30.0	28.8 $\pm$ 0.04	95.9 $\pm$ 2.58
	20.0	19.2 $\pm$ 0.11	96.2 $\pm$ 4.00

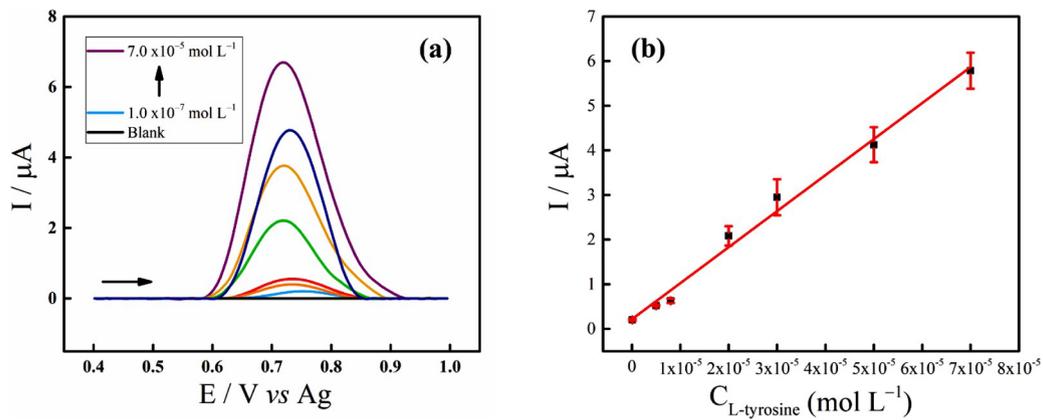
**Table 2**

Analytical performance of Au-NP-GP/AS sensor for L-tyrosine determination compared with the literature

Electrode	Technique	LDR ( $\mu\text{mol L}^{-1}$ )	LOD ( $\mu\text{mol L}^{-1}$ )	Sample Application	Refs.
2D-MoS <sub>2</sub> -AuBSPE	CV	10 to 500	0.5	Commercial food integrator	[32]
AuNPs/MWCNT/GCE	DPV	0.4 to 80.0	0.21	Blood serum and pharmaceutical	[33]
MWCNTs-Nafion/GCE	DPV	2 to 120	0.8	Human serum	[34]
B.P.Tyr/M/SN-MPTS/SPE	DPV	0.05 to 600	0.02	Human plasma	[35]
$\beta$ -CD modified gold electrode	DPV	36 to 240	12	Pharmaceutical formulations	[37]
MIP-polypyrrole modified gold electrode	SWV	0.005 to 0.025	0.0025	Human plasma	[36]
<b>Au-NP-GP/AS</b>	<b>SWV</b>	<b>0.1 to 70</b>	<b>0.09</b>	<b>Tap water and synthetic urine</b>	<b>This Work</b>

**LDR:** Linear dynamic range; **2D-MoS<sub>2</sub>-AuBSPE:** Exfoliated 2D-MoS<sub>2</sub> nanosheets on carbon and gold screen printed electrodes; **Pt-ZnO/CNTs/GCE:** Glassy Carbon Electrode Amplified with a nanocomposite of zinc oxide-Platinum/carbon nanotubes; **AuNPs/MWCNT/GCE:** gold nanoparticles/multiwalled carbon nanotube nanocomposite modified glassy carbon electrode; **MWCNTs-Nafion/GCE:** processed MWCNTs and Nafion on a glassy carbon electrode; **B.P. Tyr/M/SN-MPTS/SPE:** graphite screen printed electrode modified with a paper disc doped with 3-mercaptopropyl trimethoxy silane-functionalized silica nanoparticles and banana peel tissue;  **$\beta$ -CD modified gold electrode:**  $\beta$ -cyclodextrins on a gold electrode; **MIP-polypyrrole modified gold electrode:** molecularly imprinted polypyrrole modified gold electrode;

a system based on the enhanced catalytic activity of two-dimensional molybdenum disulfide nanosheets (2D-MoS<sub>2</sub>) over SPE gold electrodes. The authors obtained a wide linear range from 10 to 500  $\mu\text{mol}$



**Fig. 6.** (a) SWV voltammograms recorded at different L-tyrosine concentrations 0.1, 5.0, 8.0, 20, 30, 50, and 70  $\mu\text{mol L}^{-1}$  in 0.1  $\text{mol L}^{-1}$  PBS (pH 7.0); step = 5 mV modulation amplitude: 60 mV and frequency: 35 Hz; (b) Calibration plot for L-tyrosine ( $I_p$  vs.  $C_{\text{L-tyrosine}}$ ).

L<sup>-1</sup>, with an extensive synthesis process that requires many reagents and at least 45 min to prepare only the 2D-MoS<sub>2</sub>. Madrakian et al. [33] and Li et al. [34] used GCE and multi-walled carbon nanotubes to develop sensors for tyrosine, and this kind of system always requires some steps such as polishing with alumina and activation in acid besides modification with carbon. This makes the sensor fabrication process more time-consuming and expensive. Rahimi-Mohseni et al. [35] develop a nano-biosensor using the co-catalytic action of tyrosinase from banana peel tissue to detect L-tyrosine. This work demonstrates a high-performance enzymatic biosensor with a linear range of 0.05 to 600 μmol L<sup>-1</sup> and a low LOD of 0.02 μmol L<sup>-1</sup>. However, more than five steps are required to construct the electrode and the SPE used is a commercial one, which makes the fabrication of the sensor more expensive. About the gold electrodes employed in the detection of L-tyrosine, the device developed by Ermis, et al. [36] is a molecularly imprinted polypyrrole-modified gold electrode for the determination of tyrosine in plasma samples. Quintana et al. [37] develop nanostructures on gold electrodes based on host-guest supramolecular interactions to detect L-tyrosine in pharmaceutical formulations. Indeed, our proposed sensor, which is fabricated in the laboratory with a simple modification that does not require chemical treatments or multiple surface modification steps, provides efficient detection of L-tyrosine being inexpensive and easy to fabricate.

#### 4. Conclusion

In summary, the demand for cleaner, more efficient, and more accurate analytical methods for analysis has driven scientific progress and led to the development of alternative electrode materials. The move toward small, inexpensive, and flexible electrodes has solved the problems of surface adsorption and poisoning and made them a viable option. Edible gold leaves, with their excellent electrical conductivity and biocompatibility, have emerged as a beneficial material that enhances electrocatalytic activity and minimizes interference with other substances. The modification of disposable sensors with gold leaf, which is cost-effective compared to sputtering, offers a promising solution. The application of square-wave voltammetry to disposable sensors modified with gold leaf has shown a linear response in the range of 0.10 to 70 μmol L<sup>-1</sup> with a remarkably low detection limit of 0.09 μmol L<sup>-1</sup>. This approach shows great potential for accurate detection of L-tyrosine and paves the way for improved diagnosis of various diseases.

#### CRediT authorship contribution statement

**Je´ssica R. Camargo:** Conceptualization, Data curation, Investigation, Methodology, Resources, Validation, Writing – original draft, Writing – review & editing. **Sabrina Cleto:** Data curation, Investigation, Validation, Writing – original draft. **Amanda Neumann:** Conceptualization, Data curation, Investigation, Validation, Writing – original draft, Writing – review & editing. **De´borah C. Azzi:** Conceptualization, Data curation, Resources, Validation, Writing – review & editing. **Robert D. Crapnell:** Conceptualization, Data curation, Resources, Validation, Writing – review & editing. **Craig E. Banks:** Conceptualization, Data curation, Resources, Validation, Writing – review & editing. **Bruno C. Janegitz:** Conceptualization, Funding acquisition, Project administration, Supervision, Visualization, Writing – review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

#### Acknowledgments

This study was financed in part by the CNPq-Brazil, Coordenaça˜o de Aperfeiçoamento de Pessoal de Nível Superior - Brazil (CAPES-Brazil) - Finance Code 001 and 88887.504861/2020-00. Fundaç˜ao de Amparo a Pesquisa do Estado de Sa˜o Paulo, FAPESP-Brazil (grant# 2017/21097-3 2019/23177-0, grant# 2023/00321-3) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) (Grant Numbers: 301796/2022-0)

#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.electacta.2024.143825](https://doi.org/10.1016/j.electacta.2024.143825).

#### References

- [1] J.J.A.o.c.r. Wang, Real-time electrochemical monitoring: toward green analytical chemistry, 35 (2002) 811–816.
- [2] M. Javaid, A. Haleem, R.P. Singh, S. Rab, R. Suman, Significance of sensors for industry 4.0: Roles, capabilities, and applications, *Sensors International* 2 (2021) 100110.
- [3] S.S. Shah, M.N. Shaikh, M.Y. Khan, M.A. Alfassane, M.M. Rahman, M.A.J.T.C.R. Aziz, Present status and future prospects of jute in nanotechnology: A review, 21 (2021) 1631–1665.
- [4] L.A. Pradela-Filho, I.A. Andreotti, J.H. Carvalho, D.A. Araujo, L.O. Orzari, A. Gatti, R.M. Takeuchi, A.L. Santos, B.C.J.S. Janegitz, A.B. Chemical, Glass varnish-based carbon conductive ink: A new way to produce disposable electrochemical sensors, 305 (2020) 127433.
- [5] R.R. Suresh, M. Lakshmanakumar, J.B.B. Arockia Jayalatha, K.S. Rajan, S. Sethuraman, U.M. Krishnan, J.B.B. Rayappan, Fabrication of screen-printed electrodes: opportunities and challenges, *Journal of Materials Science* 56 (2021) 8951–9006.
- [6] S. Singh, J. Wang, S. Cinti, An overview on recent progress in screen-printed electroanalytical (bio) sensors, *ECS Sensors Plus* (2022).
- [7] J.R. Camargo, I.A. Andreotti, C. Kalinke, J.M. Henrique, J.A. Bonacin, B.C.J.T. Janegitz, Waterproof paper as a new substrate to construct a disposable sensor for the electrochemical determination of paracetamol and melatonin, 208 (2020) 120458.
- [8] A. Barhoum, S. Hamimed, H. Slimi, A. Othmani, F.M. Abdel-Haleem, M. Bechelany, Modern designs of electrochemical sensor platforms for environmental analyses: Principles, nanofabrication opportunities, and challenges, *Trends in Environmental Analytical Chemistry* (2023) e01199.
- [9] L. Fu, A. Wang, K. Xie, J. Zhu, F. Chen, H. Wang, H. Zhang, W. Su, Z. Wang, C. Zhou, Electrochemical detection of silver ions by using sulfur quantum dots modified gold electrode, *Sensors and Actuators B: Chemical* 304 (2020) 127390.
- [10] S. Sharma, N. Singh, V. Tomar, R. Chandra, A review on electrochemical detection of serotonin based on surface modified electrodes, *Biosensors and Bioelectronics* 107 (2018) 76–93.
- [11] Z. Han, X. Zhang, H. Yuan, Z. Li, G. Li, H. Zhang, Y. Tan, Graphene oxide/gold nanoparticle/graphite fiber microelectrodes for directing electron transfer of glucose oxidase and glucose detection, *Journal of Power Sources* 521 (2022) 230956.
- [12] J.R. Camargo, L.O. Orzari, D.A.G. Araujo, P.R. de Oliveira, C. Kalinke, D.P. Rocha, A.L. dos Santos, R.M. Takeuchi, R.A.A. Munoz, J.A. Bonacin, Development of conductive inks for electrochemical sensors and biosensors, *Microchemical Journal* 164 (2021) 105998.
- [13] Y.Z.N. Htwe, M. Mariatti, Printed graphene and hybrid conductive inks for flexible, stretchable, and wearable electronics: Progress, opportunities, and challenges, *Journal of Science: Advanced Materials and Devices* (2022) 100435.
- [14] P. Prasertying, N. Jantawong, T. Sonsa-Ard, T. Wongpakdee, N. Khoonrueng, S. Buking, D. Nacapricha, Gold leaf electrochemical sensors: applications and nanostructure modification, *Analyst* 146 (2021) 1579–1589.
- [15] F.H. Alsultany, B.S. Abdalrhadi, G.H. Seood, Preparation of a highly-reflective gold thin film by a sputtering technique using ionic coating system, in: *Materials Today: Proceedings* 61, 2022, pp. 627–631.
- [16] Y.S. Kornbluth, L. Parameswaran, R. Mathews, L.M. Racz, L.F. Vel´asquez-García, Fully 3D-Printed, Ultrathin Capacitors via Multi-Material Microsputtering, *Advanced Materials Technologies* 7 (2022) 2200097.
- [17] K. Kato, A. Motomura, K. Ikematsu, H. Nakamura, Y. Igarashi, Demonstrating FoodSkin: A Method for Creating Electronic Circuits on Food Surfaces by Using Edible Gold Leaf for Enhancement of Eating Experience, pp. 1–4.
- [18] N. Li, C. Nan, X. Mei, Y. Sun, H. Feng, Y. Li, Electrochemical sensor based on dual-template molecularly imprinted polymer and nanoporous gold leaf modified electrode for simultaneous determination of dopamine and uric acid, *Microchimica Acta* 187 (2020) 496.
- [19] R. Zhang, Y. Zhang, X. Deng, S. Sun, Y. Li, A novel dual-signal electrochemical sensor for bisphenol A determination by coupling nanoporous gold leaf and self-assembled cyclodextrin, *Electrochimica Acta* 271 (2018) 417–424.

- [20] T. Lütke-Eversloh, C.N.S. Santos, G. Stephanopoulos, Perspectives of biotechnological production of L-tyrosine and its applications, *Applied microbiology and biotechnology* 77 (2007) 751–762.
- [21] M.E.J.M.E. Ayhan, CVD graphene-based flexible and transparent SERS substrate towards L-tyrosine detection, 241 (2021) 111546.
- [22] R. Meeusen, P. Watson, H. Hasegawa, B. Roelands, M.F. Piacentini, Brain neurotransmitters in fatigue and overtraining, *Applied Physiology, Nutrition, and Metabolism* 32 (2007) 857–864.
- [23] K. Nakamura, S. Matsumoto, H. Mitsubuchi, F. Endo, Diagnosis and treatment of hereditary tyrosinemia in Japan, *Pediatrics International* 57 (2015) 37–40.
- [24] T. Brooks, C.J.L.i.a.m. Keevil, A simple artificial urine for the growth of urinary pathogens 24 (1997) 203–206.
- [25] J. Melo Henrique, J. Rocha Camargo, G. Gabriel de Oliveira, J. Santos Stefano, B. Campos Janegitz, Disposable electrochemical sensor based on shellac and graphite for sulfamethoxazole detection, *Microchemical Journal* 170 (2021) 106701.
- [26] R. Sengupta, M. Bhattacharya, S. Bandyopadhyay, A.K. Bhowmick, A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites, *Progress in polymer science* 36 (2011) 638–670.
- [27] A.J. Bard, L.R. Faulkner *electrochemical methods*, Wiley, New York, 1980.
- [28] A. García-Miranda Ferrari, C.W. Foster, P.J. Kelly, D.A.C. Brownson, C.E. Banks, Determination of the Electrochemical Area of Screen-Printed Electrochemical Sensing Platforms, *Biosensors* (2018).
- [29] Q. Xu, S.-F. Wang, Electrocatalytic Oxidation and Direct Determination of L-Tyrosine by Square Wave Voltammetry at Multi-wall Carbon Nanotubes Modified Glassy Carbon Electrodes, *Microchimica Acta* 151 (2005) 47–52.
- [30] N. Baig, A.-N. Kawde, A novel, fast and cost effective graphene-modified graphite pencil electrode for trace quantification of l-tyrosine, *Analytical Methods* 7 (2015) 9535–9541.
- [31] A. Shrivastava, V.B. Gupta, Methods for the determination of limit of detection and limit of quantitation of the analytical methods, *Chron. Young Sci* 2 (2011) 21–25.
- [32] R. Zribi, R. Maalej, E. Messina, R. Gillibert, M.G. Donato, O.M. Marago', P. G. Gucciardi, S.G. Leonardi, G. Neri, Exfoliated 2D-MoS<sub>2</sub> nanosheets on carbon and gold screen printed electrodes for enzyme-free electrochemical sensing of tyrosine, *Sensors and Actuators B: Chemical* 303 (2020) 127229.
- [33] T. Madrakian, E. Haghshenas, A. Afkhami, Simultaneous determination of tyrosine, acetaminophen and ascorbic acid using gold nanoparticles/multiwalled carbon nanotube/glassy carbon electrode by differential pulse voltammetric method, *Sensors and Actuators B: Chemical* 193 (2014) 451–460.
- [34] Z.-Y. Li, D.-Y. Gao, Z.-Y. Wu, S. Zhao, Simultaneous electrochemical detection of levodopa, paracetamol and l-tyrosine based on multi-walled carbon nanotubes, *RSC advances* 10 (2020) 14218–14224.
- [35] M. Rahimi-Mohseni, J.B. Raoof, R. Ojani, T.A. Aghajanzadeh, A. Bagheri Hashkavayi, Development of a new paper based nano-biosensor using the co-catalytic effect of tyrosinase from banana peel tissue (*Musa Cavendish*) and functionalized silica nanoparticles for voltammetric determination of l-tyrosine, *International Journal of Biological Macromolecules* 113 (2018) 648–654.
- [36] N. Ermis, N. Tmkılıç, Preparation of Molecularly Imprinted Polypyrrole Modified Gold Electrode for Determination of Tyrosine in Biological Samples, *International Journal of Electrochemical Science* 13 (2018) 2286–2298.
- [37] C. Quintana, S. Suárez, L. Hernández, Nanostructures on gold electrodes for the development of an l-tyrosine electrochemical sensor based on host–guest supramolecular interactions, *Sensors and Actuators B: Chemical* 149 (2010) 129–135.