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In situ electrochemical generation of gold nanostructured screen-printed carbon electrodes. Application to the detection of lead underpotential deposition

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ABSTRACT

In the present work, an electrochemical method for the reproducible and stable generation of gold nanostructures on the surface of screen-printed carbon electrodes was developed. This technique is based on the application of a constant current over an appropriate time interval. Gold nanostructured screenprinted carbon electrodes were characterized using both SEM and electrochemical methods. The mean diameter and the dispersion of gold nanoparticles that were generated electrochemically depended on the gold concentration, the time deposition and the current intensity. Smaller diameters and better distribution of nanoparticles were obtained when a shift of potential to -0.70 V occurred during the gold electrodeposition process. Moreover, the underpotential deposition (UPD) of lead on these nanostructured surfaces was studied, as was their behavior as array electrodes. The best results, using UPD combined with square wave stripping voltammetry, were obtained for gold nanostructured surfaces with a mean diameter of 78 ± 24 nm and a density of 4.4×10^7 nanoparticles/mm². These gold nanostructured screenprinted carbon electrodes were obtained by applying a current intensity of $-100 \ \mu A$ for 300 s using a gold concentration of 0.5 mM. The reproducibility and limit of detection obtained using these nanostructured electrodic surfaces were 2.4% (in terms of RSD) and 0.8 ng/mL, respectively.

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1. Introduction

Nanosized particles of noble metals, especially gold nanoparticles, have received interest due to their attractive electronic, optical and thermal properties as well as their catalytic properties and potential applications in the fields of physics, chemistry, biology, medicine and material science as well as their interdisciplinary fields [1,2]. For the electroanalytical chemist, more attention has been paid to gold nanoparticles because of their good biocompatibility, excellent conducting capability and high surface-to-volume ratio. The introduction of gold nanoparticles onto electrochemical interfaces has infused new vigor into electrochemistry [3–11]. There are numerous approaches to the fabrication of gold nanostructures on electrode surfaces, including the use of gold nanoparticle-modified composite materials [12-16], the adsorption or electro-adsorption of gold nanoparticles onto electrode surfaces [17-19], covalent binding using organic molecules (such as thiols and polymers) between the electrode and gold nanoparticles [20-22], attachment via a polymer film [23], sol-gel techniques [24] and electrochemical deposition [25-34]. Electrochemical deposition is a convenient and fast method for the preparation of gold nanoparticles on large areas of conductive substrates because the mechanism of electrodeposition is very similar to crystallisation and allows for the electrodeposition of crystals with nanometer scale dimensions under an adequate deposition time. The fundamental principles and simulations for the growth of gold nanoparticles on graphite electrode surfaces have been investigated in detail [35–39].

Although different kind of electrodes have been used as substrates for the fabrication of gold nanostructures, it is necessary to develop cost-effective, disposable and reproducible devices. Screen-printing technology has the strong advantage of creating a large number of near-identical electrodes that can be used in a single shot context at a low cost. The establishment of a simple and quick method for fabricating gold nanoparticles onto a screenprinted electrode surface would contribute to the generation of a new transducer for biosensor applications. In this work, an electrochemical method based on the application of a constant current for the fabrication of stable and reproducible gold nanostructured screen-printed carbon electrodes (SPCnAuEs) has been developed. SEM was used to characterize the gold-modified electrodes.

Additionally, these gold nanostructured electrodes were used as transducers for the detection of lead based on the lead underpotential deposition (UPD) process. Metal UPD on different substrates has been extensively studied in recent years and offers advantages

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over the use of bulk metal deposition [40], including better sensitivity and good repeatability of the analytical response. Lead UPD has been extensively investigated on gold electrodes [41-45] and very different UPD processes have been observed, depending upon the nature of the substrate (poly or single-crystalline gold surface structure). Here, the lead UPD on these gold nanostructured screenprinted carbon electrodes exhibits two pairs of peaks, as it also occurs on polycrystalline gold electrodes [43].

2. Experimental

2.1. Reagents

Standard gold (III) tetrachloro complex $(1.000 \pm 0.0001 \text{ g} \text{ of} \text{ tetrachloroaurate}$ (III) in 500 mL of 1 M HCl), Pb(NO₃)₂ and hydrochloric acid (37%) were purchased from Merck. Dilutions from the standard gold solution and Pb(NO₃)₂ solutions were prepared in 0.1 M HCl.

Water was obtained from an ultrapure Millipore Milli-Q water system.

2.2. Apparatus and electrodes

Voltammetric measurements were performed with an ECO CHEMIE μ Autolab Type II potentiostat/galvanostat coupled with a computer and controlled by Autolab GPES software version 4.9 for Windows. All measurements were carried out at room temperature.

Screen-printed carbon electrodes (SPCEs) and screen-printed gold electrodes (SPGEs), together with an edge connector, were purchased from DropSens (Oviedo, Spain). The DropSens electrodes incorporate a conventional three-electrode configuration, printed on ceramic substrates ($3.4 \, \mathrm{cm} \times 1.0 \, \mathrm{cm}$). In the case of screen-printed carbon electrodes (SPCEs), both the working (disk-shaped 4 mm diameter) and counter electrodes are made of carbon inks, whereas the pseudo-reference electrode and electric contacts are made of silver. In the case of screen-printed gold electrodes, the working and counter electrodes are made of gold ink. An insulating layer was printed over the electrode system, leaving uncovered the electric contacts and a working area, which constitutes the reservoir of the electrochemical cell, with a volume of 50 μ L.

SEM images of the working electrode surfaces were obtained with a JEOL JSM-6100 scanning electron microscope (20 kV, Japan).

Leica QWIN software was used to digitally process the SEM images.

2.3. Analytical procedures

2.3.1. Electrochemical generation of gold nanostructures on the electrode surface

To obtain the gold nanoparticles on the electrode surface, an aliquot of 40 μ L of a solution of 0.1, 0.5 or 1.0 mM AuCl₄⁻ in 0.1 M HCl was dropped onto the SPCEs and a constant current was applied for a fixed time. Different current intensities and deposition times were tested. A chronopotentiogram was recorded during the electrodeposition of gold in all cases. After the electrodeposition of gold, the SPCnAuEs were generously rinsed with water.

2.3.2. Characterization of the gold nanostructured SPCEs (SPCnAuEs)

Gold nanostructures were characterized via SEM and chronoamperometry. For each gold nanostructuration procedure, SEM images were obtained for three electrodes and the mean diameter of the gold nanoparticles was measured. Chronoamperometry measurements were performed to determine the amount of gold deposited over the SPCEs. After the generation of the gold nanostructured SPCEs, an aliquot of $40 \,\mu$ L of 0.1 M HCl was dropped onto the electrode and the oxidation of gold was carried out by holding the electrode at a potential of +0.85 V, recording the current intensity vs. time. Three electrodes were measured for each gold concentration, current intensity and deposition time assayed. The area under the curve (charge) was used to calculate the mass of gold involved in the process using the Faraday equation.

2.3.3. Anodic stripping voltammetry of lead on SPCnAuEs and SPGEs

An aliquot of 40 μ L of a solution of Pb(NO₃)₂ in 0.1 M HCl was dropped onto the different SPCnAuEs and SPGEs, and a potential of -0.5 V was applied for 90 s. Then, a square wave anodic stripping was carried out from the electrodeposition potential to +0.1 V, using a square wave amplitude of 25 mV, a frequency of 50 Hz and a step potential of 2 mV. Calibration plots of lead were obtained for SPGEs and different SPCnAuEs.

3. Results and discussion

3.1. Gold nanostructured screen-printed carbon electrodes (SPCnAuEs)

In the constant current electrolytic process, gold (III) was reduced and deposited onto the surface of SPCEs. Moreover, by applying a constant current, the amount of charge that passed through the electrode surface was kept constant during the electrodeposition process. The amount of gold deposited onto the electrode surface was calculated for different gold concentrations, current intensities and deposition times, using the procedure explained in Section 2.3.2 and Faraday's Law. Although some authors assert that the complete reoxidation of the electrodeposited gold is not possible because it is a chemically irreversible process [36], when a second chronoamperometry measurement was carried out in the same electrode with a fresh drop of 0.1 M HCl, no reoxidation of gold was observed.

Fig. 1 shows the variation of the amount of gold deposited on the electrode surface with current intensity for 120s of deposition time (Fig. 1A) and with deposition time for -5 and $-50 \,\mu\text{A}$ of current intensity (Fig. 1B). For small negative current intensities, the amount of gold deposited on the electrode surface increased when a more negative current intensity was applied, reaching a plateau for all the gold concentrations assayed. The amount of gold deposited on the electrode surface was higher as the gold concentration became higher. The value of current intensity at the plateau was -1, -10 and $-25 \,\mu$ A for 0.1, 0.5 and 1 mM gold, respectively. Moreover, the amount of gold deposited on the electrode surface increased with deposition time (Fig. 1B) for the same current intensity. For a gold concentration of 0.1 mM, the increase of the gold amount deposited on the electrode surface obtained for -5 and $-50 \,\mu$ A was similar for deposition times between 60 and 200 s. However, for longer deposition times, the amount of gold deposited on the electrode surface was higher at $-5 \,\mu$ A than was obtained at $-50 \,\mu$ A. This behavior could be due to the different potential changes observed during the electrodeposition process at these current intensities for this gold concentration, because for $-50 \,\mu$ A, the potential shifted rapidly towards $-0.70 \,\text{V}$, whilst for $-5 \,\mu$ A, the potential remained at 0.0 V for the first 200 s and then shifted towards -0.7 V.

To study the morphology of the gold deposited on the electrode surfaces, SEM images were obtained for each gold concentration and for different current intensities and deposition times. Fig. 2 shows some of these SEM micrographs. In all cases, the formation of gold nanoparticles on the electrode surface with different mean diameters and distributions can be observed. Additionally,



Fig. 1. Effect of current intensity (A) and deposition time (B) on the amount of gold deposited on the electrode surface for (♦) 0.1 mM, (▲) 0.5 mM and (●) 1.0 mM of AuCl₄⁻. In (A), deposition time: 120 s; in (B), -5 µA (dotted lines) and -50 µA (dashed lines). The small graphic beside (B) is the amplification of the graphic corresponding to the data for 0.1 mM of gold concentration.



Fig. 2. SEM images of the surfaces of gold nanostructured screen-printed carbon electrodes obtained for different experimental conditions. a' and b' are amplified SEM images of a and b SEM images.

Table 1

Mean diameter and standard deviation of the gold nanoparticles obtained for different gold concentrations, current intensities and deposition times.

$[AuCl_4^-](mM)$	Deposition time (s)	Current intensity (µA)				Potential changes	
		-5	-10	-50	-100		
0.1	120	$77\pm8nm$	$85\pm19nm$	$105\pm12nm$	$80\pm20nm$	-5μ A, +0.40 to +0.00 V and it remains at this potential for	
		$120 \pm 15\text{nm}$	$\textbf{41} \pm 13 \text{ nm}$	$\textbf{68} \pm \textbf{10}\text{nm}^{\text{a}}$		to -0.70 V	
	300		$70 \pm 13 \text{nm}$	$76 \pm 17 \text{nm}$	$73\pm20nm$	-10μ A, +0.40 to -0.1 V an maintained at this potential for 80 s. Then the potential shifts to -0.70 V	
		$\textbf{72} \pm \textbf{15}\text{nm}^{\text{a}}$				-50 and -100μ A, the potential shifts to $-0.70V$	
	120	$638\pm9nm$	$231\pm28nm$	$164\pm35nm$	$70\pm20nm$	–5 μA, the potential remains at +0.40 V	
0.5		$\textbf{75} \pm \textbf{14}\text{nm}^{\text{a}}$	$123\pm41\text{nm}^{\text{a}}$	$72 \pm 22 \text{nm}^{\text{a}}$		– 10 μA, +0.40 to +0.00 V for 50 s and then the potential remains at this potential	
	300	$890\pm 66nm$	$202\pm79nm$	$84\pm26nm$	$78\pm24nm$	-50μ A, +0.40 to $-0.30 V$ and it remains at this potential for 50 s. Then the potential shifts to $-0.70 V$	
		$\textbf{78} \pm \textbf{25} nm^a$	$89\pm14nm^a$			-100μ A, the potential shifts to -0.70V	
	120	$799\pm90nm$	770 ± 90	$200\pm29nm$	$73\pm22nm$	–5 and –10 μA, the potential remains at +0.40 V	
1.0	300	$129 \pm 41 \text{ nm}$ 1108 ± 206	$\begin{array}{l} \textbf{74} \pm \textbf{24} \texttt{nm} \\ \textbf{536} \pm \textbf{98} \texttt{nm} \end{array}$	$\begin{array}{l} \textbf{78} \pm \textbf{22}\text{nm} \\ 201\pm58\text{nm} \end{array}$	$130\pm48nm$	-50 and -100μ A, the potential shifts to -0.70 V	
		$\textbf{234} \pm \textbf{40}\text{nm}^{\text{a}}$	$\textbf{192} \pm \textbf{55} nm^a$	$\textbf{97} \pm \textbf{21} nm^a$			

The value of mean diameter written with bold letters corresponds to the group with greater number of nanoparticles.

^a In these cases, the electrode surface was covered with two groups of gold nanoparticles with two mean diameters.

the mean and standard deviation of the diameters of gold nanoparticles formed on the working electrode of SPCEs were obtained from SEM images. Their values are listed in Table 1. Moreover, in the last column of Table 1, changes in the potential observed during the electrodeposition of gold at constant current are shown. In most cases, two groups of nanoparticles with two mean diameters covered the electrode surfaces. It can be observed from Fig. 2 and the data given in Table 1 that when a more negative constant current intensity was applied during gold electrodeposition for the same gold concentration and the same deposition time, the mean diameters of the nanoparticles decreased or remained constant. Moreover, the quantity of larger nanoparticles decreased whereas the number of the smaller nanoparticles increased to create a situation where monodisperse nanoparticles were obtained in all cases with a mean diameter around 75 nm (except for the case of a gold concentration of 1 mM and 300 s of deposition time). This was noted when a shift towards more negative potentials (-0.70 V) was recorded during the gold electrodeposition. This shift in potential occurred at different values of current intensities, depending on the gold concentration and deposition time. For example, in Fig. 3, it can be observed that for a gold concentration of 0.1 mM, the potential observed during the gold electrodeposition for $-5 \,\mu$ A (thick black chronopotentiogram) changed from +0.40 to 0.00 V, remained at this potential for the first 200 s, and then shifted towards -0.70 V. However, when the current intensity applied was $-100 \,\mu\text{A}$ (thin black chronopotentiogram), the potential shifted rapidly towards -0.70 V and remained at this value during 300 s. For a 1.0 mM gold concentration and a current intensity of $-5 \,\mu$ A, the potential recorded remained constant at +0.40 V during the gold electrodeposition process (grey chronopotentiogram). In the acid medium, the generation of hydrogen occurred at this potential (-0.70 V); this improved the nucleation of gold on the electrode surface in a detriment of growth of nanoparticles. Therefore, more gold nuclei were formed. Moreover, the rate of growth was similar for each individual metal nanoparticle and strongly favored narrowing of the distribution. When the potential remained at positive values (or small negative potentials), the generation of hydrogen did not occur and the individual metal nanoparticles grew independently from each other and the particle size dispersion produced via nucleation in two groups of nanoparticles was preserved during particle growth.

In general, gold monodispersed nanostructured surfaces were formed at a current intensity of $-100 \,\mu$ A. For values of current intensity less negative than $-100 \,\mu$ A, the general trend was toward the formation of two groups of nanoparticles, though this trend depends on the gold concentration and deposition time. At this current intensity value ($-100 \,\mu$ A), the density of nanoparticles increased with the gold concentration and deposition time, except when the mean diameter of gold nanoparticles increased (Table 1,



Fig. 3. Chronopotentiograms obtained during the gold electrodeposition for a gold concentration of 0.1 mM and current intensities of $-5 \,\mu$ A (thick black curve) and $-100 \,\mu$ A (thin black curve) and for a gold concentration of 1.0 mM and a current intensity of $-5 \,\mu$ A (grey curve).

1 mM gold concentration and 300 s of deposition time). Although the selection of the appropriate gold nanostructured electrode surface will depend on the application, better reproducibility and distribution of the gold nanostructured surfaces is obtained by applying a current intensity of $-100 \,\mu$ A during 300 s for gold concentrations of 0.1 or 0.5 mM.

3.2. Electrochemical behavior of lead on SPCnAuEs

Fig. 4 shows three cyclic voltammograms for a lead concentration of $200 \,\mu\text{g/mL}$, obtained using a SPCE (A), a SPGE (B) and a gold nanostructured SPCE (C), characterized by SEM in the previous section. A cathodic process (C_1) was observed at a potential of -0.625 V, corresponding to the bulk deposition of lead on SPCE as well as the anodic stripping of lead (A_1) at a potential of -0.37 V. In the cases of SPGE and SPCnAuE, small peaks were observed at potentials more positive than the bulk lead deposition and stripping processes. With SPGE, a single cathodic process was observed at $-0.324 V(C_n)$ and an anodic process was observed at $-0.43 V(A_3)$. In the case of SPCnAuE, two cathodic peaks were observed at -0.26 and -0.45 V (C₂ and C₃ in Fig. 4C); an anodic stripping peak was also observed at -0.13 V (A₂). These two cathodic peaks, observed in the presence of gold on the electrode surface, correspond to the formation of a lead monolayer on the gold substrate at potentials more positive than the reversible Nernst potential for bulk metal formation, referred to as underpotential deposition (UPD) [40-45]. The processes observed here are consistent with previous reports of lead UPD on a polycrystalline gold rotating ring-disk electrode, where two pairs of peaks were observed [41,43]. The process labeled C_n in Fig. 4B corresponds to the two peaks of lead UPD that overlapped in a single process, whereas on the SPCnAuE, these peaks were observed to be separate. However, the anodic stripping process corresponding to the second lead UPD (A₃) was not observed on SPCnAuE because it was overlapped by the anodic stripping peak of the lead bulk deposition (A_1) .

Fig. 5A displays four cyclic voltammograms obtained for a lead concentration of 500 ng/mL on SPCE (a), SPGE (b) and two SPCnAuEs (c and d). Lead was previously deposited at -0.8 V over 90 s on the electrode surface and then an anodic stripping scan was carried out. Whereas on the SPCE lead bulk deposition was observed, in the cases of gold electrodes only the first lead UPD was observed under these experimental conditions. In accord with the results of other studies [43], the second UPD peak did not appear until the first UPD had reached its maximal charge. Moreover, lead bulk deposition only appeared when the first and second peaks of lead UPD reached their maximal charge. This behavior can be seen in Fig. 5B, where lead was deposited during different deposition times at -0.8 V on a SPCnAuE. The first peak of lead UPD increased with the deposition time reaching a plateau at 300 s, where the second peak of lead UPD appeared. This behavior was also observed when lead concentration was increased (data not shown). In the case of SPGE, the saturation of the first UPD occurred at higher deposition times and lead concentrations due to the greater electrode area. Both the cathodic and corresponding anodic stripping peaks of the first lead UPD were linear with scan rate, according to the following equations:

Cathodic peak : i_p (μ A) = 0.031 ν (mV/s) + 3.33, r^2 = 0.9979

Anodic stripping peak :

$$i_p$$
 (µA) = 0.049 ν (mV/s) + 4.24, $r^2 = 0.9951$

This behavior allowed for the conclusion that the UPD process on the SPCnAuE is an adsorption-controlled process. A similar behavior was obtained on SPGE and other gold electrodes [43,45].



Fig. 4. Cyclic voltammograms obtained for a lead concentration of 200 μ g/mL using a SPCE (A), a SPGE (B) and a SPCnAuE (C). Potential scans were carried out from 0.00 to -1.2 V (A), -0.7 V (B) and -0.9 V (C) at 100 mV/s. SPCnAuE was obtained by gold electrodeposition at -100 μ A for 300 s; gold concentration: 1.0 mM.

On the other hand, the cathodic and anodic peak currents of the lead UPD, when SPCnAuEs were used as working electrodes, were higher when the mean diameter of gold nanoparticles formed on the electrode surface increased (compare cyclic voltammogram c with d in Fig. 5A and see Table 1). According to other authors [33], this occurs because the gold nanoparticles (electrochemically generated on the electrode surface) have more active surface gold



Fig. 5. (A) Cyclic voltammograms obtained for a lead concentration of 500 ng/mL using a SPCE (a), a SPGE (b) and two SPCnAuEs (c and d). Lead was deposited onto the electrode at -0.8 V for 90 s, then, a potential scans were carried out from -0.8 V to +0.3 V at 0.5 V/s. SPCnAuEs was obtained by gold electrodeposition at $-100 \,\mu$ A for 300 s; gold concentration: 0.1 mM (c) and 1.0 mM (d). (B) Cyclic voltammograms obtained for the same lead concentration at different deposition times: (a) 45 s, (b) 60 s, (c) 90 s, (d) 180 s, (e) 300 s and (f) 600 s using a SPCnAuE fabricated as in Fig. 4.

atoms, which results in a higher reduction current than that of the bulk gold. Moreover, it was observed that peak separations (ΔE_p) of the redox signals at the SPCE, SPGE and SPCnAuEs were 330, 130, and 10 mV, respectively. This significant improvement in the electrochemical performance is attributed to the metal modification of the electrode surface. Moreover, according to other authors [46], the gold nanostructured screen-printed carbon electrode can be considered as a nanodisc array-type electrode, at which the diffusion layers of individual metal nanoparticles overlap with each other to form a linearly expanding diffusion region, whereas the capacitive



Fig. 6. Square wave voltammogram obtained for a concentration of lead of 50 ng/mL, using a SPCnAuE fabricated as in Fig. 5A. Amplitude: 25 mV; frequency: 50 Hz; step potential: 2 mV. Lead potential deposition: -0.50 V; lead deposition time: 90 s.

layers of each individual nanoparticle do not overlap. Thus, the ratio between the faradaic and capacitive currents is higher.

Using this lead UPD process combined with anodic stripping square wave voltammetry, calibration plots for lead using different gold nanostructured screen-printed carbon electrodes were obtained. A calibration plot for lead using screen-printed gold electrodes was also obtained. Fig. 6 shows a square wave voltammogram for 50 ng/mL of lead obtained for SPCnAuE, which was fabricated by electrodepositing gold from a solution of 0.1 mM of AuCl₄⁻ in 0.1 M HCl at -100μ A for 300 s. Lead was previously deposited at -0.5 V for 90 s. An anodic stripping peak for lead was observed at -0.25 V. In Table 2, nanoparticle densities, slopes and linear ranges of the calibration plots obtained as well as limits of detection and interelectrodic reproducibilities are listed. Wider linear ranges and more sensitive calibration plots were obtained for SPCnAuEs that are covered with monodisperse nanoparticles due to higher surface-to-volume ratios. For these monodispersed nanostructured surfaces, the best limit of detection and interelectrodic reproducibility were obtained with SPCnAuEs with a higher nanoparticles density $(4.4 \times 10^7 \text{ nanoparticles/mm}^2)$ because of a higher mass transport rate. This density value was obtained by applying a current intensity of $-100 \,\mu$ A during 300 s for a gold concentration of 0.5 mM. Moreover the sensitivity (in terms of slope of calibration plot) obtained with SPGEs was less than or equal to those obtained with SPCnAuEs, and the interelectrodic reproducibility obtained for screen-printed gold electrodes was worse than those obtained for SPCnAuEs. Comparing the results to those obtained in other works where different gold modified screen-printed electrodes were used, the limits of detection obtained here are similar to those obtained in other works, although the linear ranges are

Table 2

Lead calibration plots obtained with different gold nanostructured screen-printed carbon electrodes and screen-printed gold electrodes.

Electrode	Gold deposition		Density (nanoparticles number/mm ²)	Linear range (ng/mL)	Slope (µA mL/ng)	R^2	DL (ng/mL)	RSD%
	$[AuCl_4^-](mM)$	Current intensity $(\mu A)^b$						
SPCnAuE	0.1	-10	$1.8 imes 10^7$	2.5-150	0.056	0.9981	2.0	3.6
		-100	$3.0 imes 10^7$	2.5-100	0.081	0.9995	1.5	2.4
	0.5	-10	$4.2 imes 10^{6}$ c	1-250	0.065	0.9964	0.7	2.4
		-100	$4.4 imes 10^7$	1-1000	0.089	0.9978	0.8	2.4
	1.0	-10	1.2×10^{6} c	2.5-150	0.054	0.9976	1.0	4.0
		-100	$9.1 imes 10^6$	2.5-1000	0.118	0.9992	2.0	4.0
SPGE				15-1000	0.050	0.9975	10	13.0

^a Reproducibility obtained for four electrodes.

^b Deposition time of gold = 300 s.

^c Total nanoparticles number/mm² of the two mean diameters.



Fig. 7. Stability of the lead sensor for a month. Lead concentration: 25 ng/mL.

wider. Gold-coated carbon screen-printed electrodes obtained by electrochemically preplating a gold film from a gold solution have been used to measure lead and the limits of detection obtained in this case were 0.1 and 0.6 ng/mL for 20 and 4 min of lead deposition times, respectively [27]. In addition, gold-sputtered [47] and gold-based screen-printed electrodes [48] have been used as lead sensors and in these cases the limits of detection were 0.8 and 0.5 ng/mL for 120 s of lead deposition time.

In comparison to other works, where screen-printed carbon electrodes modified with calixarenes [49] or -(2-pyridylazo)-2-naphthol (PAN) [50] were used to detect lead, the limits of detection were higher (5 ng/mL for 10 min deposition time, and 15 ng/mL for 5 min deposition time, respectively) than those obtained with these gold nanostructured screen-printed carbon electrodes.

The detection of lead has also been carried out using electrodes such as Hg [51] or Bi [52] coated electrodes. Despite the fact that Hg-coated electrodes have offered better results for the analysis of heavy metals, they have been progressively substituted by nontoxic, environmental-friendly materials, including gold or bismuth. A similar linear range was obtained when Bi-coated electrodes [52] were used as detectors because lead only gives rise to a bulk deposition process over this kind of electrode, as also occurs with SPCEs, and the bulk deposition occurs for higher concentrations of metal. However, gold is also a biocompatible and non-toxic material. As in the case of Hg, lead gives UPD processes on gold, which facilitates the measurement of lower concentrations of lead, because these processes only involve a few atoms of lead, giving rise to lower detection limits that permit the detection of lead in water inside the legal limits.

Finally, with respect to the stability of the gold nanostructured screen-printed carbon electrodes, several SPCnAuEs were prepared and stored at room temperature. These sensors were tested daily with a lead concentration of 25 ng/mL. After 7 days of preparation, the analytical signal had reached a stable value, then, the analytical signal remained constant for one month (Fig. 7).

4. Conclusions

Gold nanostructured screen-printed carbon electrodes can be formed by the electrodeposition of gold at a constant current. The size and density of the gold nanoparticles formed depend on the current intensity, deposition time and gold concentration. In general, when a value of current intensity of $-100 \,\mu\text{A}$ is applied, the electrode surface is covered with monodisperse nanoparticles with a mean diameter around 75 nm, and the nanoparticle density increases with gold concentration and deposition time, except for the case of 1.0 M gold concentration and 300 s of deposition time, where a larger mean diameter is obtained (130 nm). This is due to the generation of hydrogen during the deposition of gold, which facilitates the nucleation of gold on the electrode surface and, consequently, a better dispersion of the nanoparticles is obtained. Compared to screen-printed carbon electrodes, these screen-printed gold electrodes and gold nanostructured screenprinted carbon electrodes show a lead UPD process at more positive values than seen for lead bulk deposition. This UPD process, combined with square wave anodic stripping voltammetry, allows one to obtain higher sensitivity in detecting lead, according to the literature. However, the gold nanostructuring of the electrode surface allows one to obtain higher cathodic and anodic stripping peaks. Therefore, an enhancement of the sensitivity is produced because these electrodes act as a nanodisc array-type electrode, with a higher ratio between the faradaic and capacitive currents. The sensitivity in terms of slope of the lead calibration plot is higher for those gold nanostructured screen-printed carbon electrodes with higher nanoparticle density due to a higher surface-to-volume ratio and a higher mass transport rate.

Moreover, the methodology described in this work allows for reproducible and stable gold nanostructured screen-printed carbon electrodes that can be excellent platforms for the design of different sensors (enzymatic, immuno- or genosensors) because of their good biological compatibility, excellent conducting capability and high surface-to-volume ratio.

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