Artigo

Carbon Graphite Obtained of Zinc-Carbon Exhausted Batteries Applied as Electrode in Electrochemical Sensors

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Rev. Virtual Quim., 2018, 11 (1), 275-296. Data de publicação na Web: 8 de fevereiro de 2019

<http://rvq.sbq.org.br>

Carbono Grafite Obtido de Baterias de Zinco-Carbono Exauridas Aplicadas como Eletrodo em Sensores Eletroquímicos

Resumo: Este artigo descreve a construção de um eletrodo de baixo custo e reutilizável, utilizando eletrodo de carbono grafite (CG) obtido de baterias de zinco-carbono exauridas, modificados com micropartículas de ouro. O eletrodo de CG foi modificado pela eletrodeposição potencioestática de micropartículas de ouro e aplicado como sensor eletroquímico para detecção simultânea de dopamina (DA) e ácido úrico (AU). Os efeitos do tempo de deposição, potencial e concentração do precursor tetracloroaurato(III) de hidrogênio ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) na formação das micropartículas de ouro foram sistematicamente estudados, utilizando microscopia eletrônica de varredura (FEG-SEM), difração de raios X (XRD) e métodos eletroquímicos incluindo voltametria cíclica e cronoamperometria. Os resultados confirmaram que as partículas de ouro possuem boa atividade eletrocatalítica para a detecção eletroquímica simultânea de dopamina e ácido úrico na faixa de 9,9 a 90,0 $\mu\text{mol L}^{-1}$ para DA e na faixa de 0,13 a 0,51 mmol L^{-1} para AU com limites de detecção de 2,6 $\mu\text{mol L}^{-1}$ e 58,9 $\mu\text{mol L}^{-1}$, respectivamente. Esses resultados indicaram que o eletrodo CG reutilizado de baterias exauridas, tem potencial aplicação como sensor eletroquímico, além de benéfico ao meio ambiente e de baixo custo.

Palavras-chave: Eletrodo de grafite de carbono; ouro; eletrodeposição potencioestática; sensor eletroquímico; baterias exauridas.

Abstract

This paper describes the construction of a facile, low cost and reusable electrode using carbon graphite (CG) of zinc-carbon exhausted batteries modified with gold microparticles. CG electrode was modified by potentiostatic electrodeposition of gold microparticles and applied as electrochemical sensor for simultaneous detection of dopamine (DA) and uric acid (UA). The effects of the deposition time, potential and concentration of precursor hydrogen tetrachloroaurate(III) ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) for the gold microparticles formation were systematically investigated using field emission gun scanning electron microscopy (FEG-SEM), X-ray diffraction (XRD) and electrochemical methods including cyclic voltammetry and chronoamperometry. The results confirmed that gold particles have good electrocatalytic activity for the simultaneous electrochemical detection of dopamine and uric acid in the range from 9.9 to 90.0 $\mu\text{mol L}^{-1}$ for DA and in the range from 0.13 to 0.51 mmol L^{-1} for UA with detection limits of 2.6 $\mu\text{mol L}^{-1}$ and 58.9 $\mu\text{mol L}^{-1}$, respectively. These results indicated that CG electrodes reused of exhausted batteries have potential application as electrochemical sensors besides advantages such as environmentally friendly and low cost.

Keywords: Carbon graphite electrode; gold; potentiostatic electrodeposition; electrochemical sensor; spent batteries.

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DOI: [10.21577/1984-6835.20190020](https://doi.org/10.21577/1984-6835.20190020)

Carbon Graphite Obtained of Zinc-Carbon Exhausted Batteries Applied as Electrode in Electrochemical Sensors

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Recebido em 3 de agosto de 2018. Aceito para publicação em 20 de novembro de 2018

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1. Introduction

Due to the increased production of portable electronic equipment, the use of batteries has expanded, mainly the use of non-rechargeable (zinc/carbon) batteries, because of their low cost. However, the useful life of these batteries is small, therefore, it is

necessary to constantly replace them.¹ The zinc/carbon batteries are constituted of zinc coating as anode and carbon graphite (CG) as cathode. Nowadays, some processes have been developed to recycle the metals of these batteries,^{2,3} however the reuse of CG electrodes present in these batteries is also of great importance. Carbonaceous materials can be applied in the development of the electrochemical sensors due to its

electrochemical properties, besides its low cost, good mechanical rigidity and environmentally friendly. Additionally, CG electrodes can be easily modified with different species in order to improve their electrocatalytical properties.^{4,5} The conductive properties of CG electrode can be enhanced by modifying it with nanoparticles or metallic microstructures, such as: Pt, Ni and Au,⁶⁻⁹ which leads to a wide variety of applications, such as electrode materials for supercapacitors,¹⁰ fuel cells,¹¹ and electrochemical sensors.¹² Microstructures of noble metals, especially gold, have received great interest due to their large electroactive area and electrocatalytic activities.^{8,13,14} Compared with other methods of obtaining gold nano/microstructures, the potentiostatic electrodeposition technique is often utilized, because it enables the control of the size and morphology of electrodeposited structures by adjusting the deposition conditions, such as precursor concentration, applied potential and electrodeposition time.¹⁵ Recently, several works have reported the modification of glassy carbon electrodes,^{11,12} and carbon graphite,^{8,9,16} with gold nano/microstructures, due to physicochemical properties such as good electrical conductivity, large surface area and biocompatibility which have been applied as electrochemical sensors in the detection of glucose, ibuprofen, nitrate, azathioprine and dopamine.¹⁶⁻¹⁹ Dopamine (DA) is a neurotransmitter present in the mammalian central nervous system and assists the neurophysiological control of attention, perception, motivation, and emotion. Changes in the concentration of dopamine on the dopaminergic system may cause several neurobehavioral disorders, such as Parkinson's disease, schizophrenia and depression.²⁰ However, the electrochemical detection of DA in biological fluids is hampered due to the presence of interfering, such as uric acid (UA) due to the overlap of the potential peaks.¹⁹ Therefore, this study consists in the use of carbon graphite electrodes obtained from spent batteries as a current collector modified with gold microstructures, as an electrochemical sensor

for the simultaneous detection of dopamine and uric acid.

2. Materials and Methods

2.1. Reagents and apparatus

Dopamine, uric acid, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Na_2HPO_4 , NaH_2PO_4 , NaCl , KCl were purchased from Sigma-Aldrich. Phosphate buffered solution (PBS) were prepared with 0.1 mol L^{-1} NaH_2PO_4 , 0.1 mol L^{-1} Na_2HPO_4 , and 0.1 mol L^{-1} NaCl , and the pH was adjusted to 7.0 by adding NaOH . All reagents were of analytical grade and were used as received without further purification. The zinc-carbon batteries of 1.5 V were collected in batteries disposal sites.

2.2. Characterization of CG electrode

The morphology of the surface CG was analyzed using scanning electron microscopy (SEM) MIRA-TESCAN. Images were recorded with an accelerating voltage of 20 kV. The structure of the CG was analyzed using Raman and FTIR spectroscopy. The spectrometers used were BRUKER Senterra at 632.8 nm, in the range from 100 to 2500 cm^{-1} and SHIMADZU FTIR-8400 in the range from 500 to 3500 cm^{-1} , respectively. The XRD measurements were obtained with a diffractometer Rigaku, modelo IV, $\text{Cu K}\alpha$ ($K = 1.54 \text{ \AA}$). The XRD patterns were collected in continuous-scanning mode with interval from 10 to 80° .

2.3. Electrochemical measurements

The CG electrodes (0.4 cm diameter) were removed of zinc-carbon spent batteries and were cleaned using the

following procedures a) mechanical polishing of the electrode surface with sandpaper (grit 1300); b) washing with chloroform, isopropyl alcohol and finally with distilled water. After, the surface of CG was isolated using epoxy resin. In Fig S1 is showed the image of the electrode after being removed from the battery. The residues of batteries were stored for further treatment, because the Zn and Mn can be recovered and recycled for manufacturing of new batteries and they can also be used in the synthesis of ferrites.^{21,22} The CG electrode was used as working electrode. For all electrochemical measurements a conventional three electrode compartment with an

electrochemical cell with volume of 10.0 mL was employed using a Pt wire (1.0 cm² geometric area) as auxiliary electrode and Ag|AgCl in 3.0 mol L⁻¹ KCl as reference electrode. The cyclic voltammetry measurements were performed in presence of 5.0 mmol L⁻¹ [Fe(CN)₆]^{3-/4-} in 0.1 mol L⁻¹ PBS, pH 7.0, in the potential range from -0.2 to 0.7 V and scan rate of 50.0 mV s⁻¹.

The electroactive area of the modified and unmodified electrode was determined by Randles-Sevcik equation (Eq. 1) using cyclic voltammetric method in presence of the 5.0 mmol L⁻¹ K₃Fe(CN)₆ in KCl 0.5 mol L⁻¹.

$$I_{pa} = k \cdot n^{3/2} \cdot A \cdot D^{1/2} \cdot C \cdot v^{1/2} \quad \text{Eq. 1}$$

In this equation, *I_{pa}* is the peak current, *k* is a constant of 2.69 x 10⁵ C mol⁻¹, *n* is the number of electrons, *A* is the electrode area (cm²), *C* is the concentration of K₃Fe(CN)₆ in mol cm⁻³, *D* is the diffusion coefficient (7.6 x 10⁻⁶ cm² s⁻¹) of K₃Fe(CN)₆ and *v* is the scan rate in V s⁻¹.^{23,24} Electrochemical impedance spectroscopy (EIS) measurements were carried out performed in presence of 5.0 mmol L⁻¹ [Fe(CN)₆]^{3-/4-}, in 0.1 mol L⁻¹ PBS (pH 7.0), applying a sine wave with amplitude of 10 mV on the open-circuit potential (OCP) in the frequency range of 10 kHz to 0.1 Hz. Electrochemical experiments were performed using a PGSTAT100 Autolab electrochemical system and GPES/FRA softwares. To obtain the charge transfer resistance (*R_{CT}*) values from the EIS results, the Randles equivalent circuit was applied using Zview software.

2.4. CG electrode modification with gold

Direct electrodeposition of the gold microstructures in the CG electrode

surface was carried out via potentiostatic method. The variables involved in the electrodeposition process, such as the deposition time, deposition potential and the concentration of precursor solution were investigated. The influence of the applied potential was evaluated from -0.6 at +0.6 V. After determining the optimal potential, the concentration of precursor (HAuCl₄·3H₂O) solution was investigated in the range from 1.0 mmol to 100.0 mmol L⁻¹ in Na₂HPO₄ 0.1 mol L⁻¹. Finally, the electrodeposition time was evaluated in the range from 200 to 1200 s. These optimizations were evaluated in presence of the probe molecule [Fe(CN)₆]^{3-/4-}. The modified electrodes were characterized by scanning electron microscopy (FEG-SEM) using a MIRA-TESCAN equipment with accelerating voltages of 20 kV and with different magnifications. The images were analyzed using ImageJ software for average diameter measurements of the electrodeposited gold particles. The X-ray diffractograms were obtained as described in item 2.1.

The CG/Au electrode obtained under the optimal electrodeposition conditions

was selected to investigate the catalytic properties for electrochemical detection of the DA and UA.

2.5. Electrochemical detection of DA and UA

The simultaneous determination of DA and UA was evaluated using square wave voltammetry (SWV) with the following optimized conditions: $f = 40$ Hz, $a = 70$ mV and $\Delta E_s = 1.0$ mV, in a potential range from 0.0 to 0.75 V. For the analytical curve, the concentration of DA ranged from 9.9 to 90.0 $\mu\text{mol L}^{-1}$ keeping the concentration of UA fixed in 100.0 $\mu\text{mol L}^{-1}$. For the UA analytical curve, the concentration range

was from 134.0 to 517.0 $\mu\text{mol L}^{-1}$, with a fixed DA concentration of 90.0 $\mu\text{mol L}^{-1}$. All experiments were performed at room temperature (296.15 K).

3. Results

3.1. Characterizations of CG

Firstly, the CG obtained from spent batteries was characterized. As presented in Fig. 1, the SEM images show the surface of the CG before and after polishing process.

Figure 1. SEM images of CG surface (a) before and (b) after the polishing process

Comparing the images of CG surface, it is verified that the roughness of the surface significantly reduced and a homogeneous pattern was obtained after polishing. The homogeneity of the surface is important to ensure the reproducibility of subsequent modification. Therefore, before use, the electrodes were submitted to the procedure of cleaning and polishing. The results of elementary composition of

the CG electrodes obtained with SEM-EDS are showed in the Table 1.

The result of this analysis showed that 99.75 % of the atomic composition of the CG electrodes is carbon. However, the possible influence of low percentages of impurities in the voltammetric profile of the GC electrode was evaluated by voltammetric studies.

Table 1. Elemental composition of CG electrode obtained with SEM-EDS

Element	% atomic
Carbon	99.75 ± 0.12
Iron	0.08 ± 0.04
Sulphur	0.14 ± 0.04
Calcium	0.03 ± 0.02

Graphitic materials are constituted by a series of layers of carbon atoms, which form a hexagonal network of graphene layers. These layers can be stacked in the ABAB sequence leading to the hexagonal structure or in the ABCABC arrangement characteristic of rhombohedral

structures.²⁵ Highly ordered graphite structures show hexagonal structure but even high quality samples can contain a fraction of the rhombohedral phase.²⁶ Therefore, X-ray diffraction (XRD) technique was used (Fig. 2) to investigate the structure of the CG electrodes.

Figure 2. XRD patterns of carbon graphite electrodes

According to the literature,^{25,26} the peaks in 26.5°, 54.4° and 77.2° are due to (0 0 2), (0 0 4) and (1 1 0) reflections related to hexagonal structure. However, the peak in 43.8° is due to (1 0 1) which correspond to the rhombohedral structures. This phase normally coexists with common hexagonal phase.²³ From XRD pattern and using Bragg equation,^{27,28} the interlayer spacing was determined as 3.4 Å.

According to the literature, the spacing between two perfectly oriented graphitic layers is 3.3 Å.²⁶

The Raman and FTIR spectroscopy were employed to investigate the presence of possible functional groups and defects in the structure of the CG electrodes. The results are showed in the Fig. 3.

Figure 3. (a) FTIR (b) Raman spectra of carbon graphite electrodes

The FTIR band at 3245 cm^{-1} can be attributed to -OH stretching. The bands at 2905 and 2847 cm^{-1} are due to vibrational stretching of the C-H group with hybridization sp^3 and sp^2 .^{4,29,30} The bands observed in 1690 and 1413 cm^{-1} can be attributed to stretching of the C=C and ester groups, respectively.³¹ These results indicate the presence of functional groups and defects in the structure of CG electrode. The Raman spectra of the CG electrodes revealed two bands at 1337 and 1573 cm^{-1} attributed to the D and G bands, respectively.³²⁻³⁴ The G band is related to the aromatic carbon stretching in the plane,²⁷ and D band reflects the presence of disorders or defects in the graphitic structure, such as the presence of functional groups and carbon with sp^3 hybridization.³⁴

The intensity ratio of G and D bands (I_D/I_G) has been used to evaluate the degree of disorder in carbon graphite.³⁵ Analyzing the intensities of D and G bands, it was possible to estimate the ratio between them and the value found was 0.84 . According to the literature,^{35,36} the I_D/I_G estimated for carbon nanotubes is 0.81 . After oxidative treatment

the ratio between these bands increased to 1.01 , indicating the functionalization and the presence of defects in the structure. Therefore, analyzing the spectra and the ratio between the intensities of the bands D and G, it is evident the presence of defects and heteroatoms in the structure of the CG electrodes.

The reproducibility of five CG electrodes was evaluated electrochemically by cyclic voltammetry technique in the presence of the probe $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (Fig. S1). The results showed that the CG electrodes exhibited potential anodic peak constant $E_{pa} = 0.34 \pm 0.06\text{ V}$ and $I_{pa} = 0.70 \pm 0.06\text{ mA.cm}^{-2}$. Therefore, the electrodes showed a good reproducibility with a small relative standard deviation.

3.2. Gold electrodeposition on CG

The potential of the reduction of $[\text{AuCl}_4]^-$ on the surface of the CG electrode was evaluated by cyclic voltammetry and the voltammetric profile is shown in Fig. 4.

Figure 4. Cyclic voltammograms recorded during gold electroreduction at a CG electrode in a $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{HPO}_4$ deaerated solution containing HAuCl_4 10.0 mmol L^{-1} : first (solid line) and second (dashed line) consecutive scans, $\nu = 50 \text{ mV s}^{-1}$

The first scan exhibits the reduction of Au(III) to Au(0) with a cathodic peak at 0.50 V . This peak is assigned the deposition of gold onto the CG electrode surface. On the backward scan, a current crossover occurred at 0.62 V , which is an indicate of nucleation process. However, this behavior was not observed in the following scans, due to the growth of Au nanoparticles on the nuclei formed during the first scan.^{13,17}

It is observed in the first and fifth scans (dashed lines), the reduction peak of Au (III) was shifted from 0.50 to 0.69 V . This displacement in the potential of Au deposition occurred due to fact that thermodynamically the growth of new particles on previously formed particles is easier than the nucleation of new particles on CG electrode, therefore the energy necessary for deposition of gold on gold is lower than on CG.^{17,37} For this reason, the voltammetric peak tends to shift in the direction to the standard reduction

potential of the $\text{AuCl}_4^-/\text{Au}$ redox pair, which is 0.99 V vs the standard hydrogen electrode (SHE).³⁸

The deposition of gold may be performed using a cyclic voltammetry technique. However, the potentiostatic method allows varying the potential and deposition time, thereby controlling the size and morphology of the electrodeposited particles.

3.3. The influence of the electrodeposition potential

Among the parameters involved in the electrodeposition technique, the applied potential is an important parameter for the control of the morphologies of gold microstructures. Therefore, the influence of the applied potential was evaluated and the results of these characterizations are showed in the Fig. 5.

Figure 5. SEM images of Au particles electrodeposited in 0.1 mol L⁻¹ Na₂HPO₄ solution containing 10.0 mmol L⁻¹ HAuCl₄ for 700 s at potentials of (a) $E = +0.6$ V, (b) $E = +0.3$ V, (c) $E = -0.3$ V, and (d) $E = -0.6$ V. The scale bars for all images is 2 μ m

Under a potential of deposition of +0.6 V (Fig. 5a), the image reveals gold microstructures dispersed with flower-like shapes with diameter of approximately 1.8 μ m, however their distribution of microstructures on the electrode surface is not homogeneous. Similar results were reported by Guo *et al.*³⁹ studied the influence of the electrodeposition potential in the morphology of the gold structures. The microstructures obtained at potentials of 0.5 and 0.7 V exhibited flower-like structures with average diameter of 2 μ m. When the applied potential was +0.3 V (Fig. 5b), it was verified a homogenous coating by gold particles with spherical shapes. These particles showed an average diameter of

420 nm. Decreasing the electrodeposition potential for -0.3 V resulted in some dendrite-like gold microstructures on the surface (Fig. 5c), and when applying -0.6 V it was observed particles with morphology of rods as shown in Fig. 5d. In this potential of -0.6 V, it was observed air bubbles on the surface of the CG electrode hindering the growth of the Au microstructures. Moreover, the gold particles easily detached from the surface of CG electrode. Similar results were reported by Shu *et al.*¹⁴ which reported the study of electrodeposition of gold microstructures on glassy carbon electrode using different potentials. It was observed that at potentials of -0.5 and -0.7 V, a large amount of air bubbles on the surface of the GC electrode were formed, preventing the

growth of gold structures on the surface of the substrate.

The change in the morphology of particles due to the change of overpotential is related to the process of nucleation and grain growth.^{13,40} The process of nucleation/growth

for gold particles can be described according to the model proposed by Scharifker and Hills.⁴¹ According to this model, the mechanism can be instantaneous or progressive, which are described by the following equations:

$$(i/i_{\max})_{\text{pro}}^2 = 1.2254(t_{\max}/t)\{1 - \exp[-2.336(t/t_{\max})^2]\}^2 \text{ Eq. 2}$$

$$(i/i_{\max})_{\text{inst}}^2 = 1.9542(t_{\max}/t)\{1 - \exp[-1.2564(t/t_{\max})^2]\}^2 \text{ Eq. 3}$$

The mechanism of gold nucleation on CG electrodes was investigated by potentiostatic transient measurements obtained at different potentials in the range +0.6 at -0.6 V (Fig. S 2). Comparing the experimental data with theoretical curves given by Eqs. (2) and (3) it is verified that there is a transition between the progressive and instantaneous mechanisms due to applied potential. For the deposition in potentials of -0.6 and -0.3 V, the nucleation resembles more to instantaneous growth than progressive. In potentials positive (+0.3 and +0.6 V) the profile of the experimental curves can be

described by the progressive mechanism. These results are in agreement with data reported in the literature which report that high overpotentials favors instantaneous nucleation and low potential favors progressive nucleation.^{13,42}

The electrochemical behavior of CG modified electrodes with gold microstructures obtained with different applied potentials were investigated by cyclic voltammetry, in presence of $[\text{Fe}(\text{CN})_6]^{3-/4-}$. The results are shown in Fig. 6.

Figure 6. Cyclic voltammograms obtained for the CG electrodes modified with microstructures of gold obtained with different electrodeposition potentials, $[\text{HAuCl}_4]$ 10.0 mmol L⁻¹ and electrodeposition time of 700 s) in presence of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ 5.0 mmol L⁻¹ in 0.1 mol L⁻¹ KCl, $\nu = 50 \text{ mV s}^{-1}$

The cyclic voltammograms of the CG electrodes modified with gold particles (CG/Au) obtained with potential of the -0.6 V showed the peak potential separation ($\Delta E_p = 162$ mV) and the lowest peak current anodic density ($I_{pa} = 1.07$ mA cm⁻²). This result is in agreement with SEM images (Fig. 5d), which showed that in this potential the growth of the Au microstructures on the surface of the CG electrode is hampered and the surface coating is not homogeneous. The electroactive area calculated by the Eq. 1 was of 0.16 cm². When the overpotential was reduced for -0.3 V, it was verified the presence of dendrite-like gold microstructures which have improved the electrochemical response of the probe molecule. In this case, ΔE_p decrease from 162 mV to 122 mV and peak current anodic density increase from 1.07 mA cm⁻² to 1.52 mA cm⁻², in comparison to CG/Au obtained at -0.6 V. This reduction in the ΔE_p and increase of peak current anodic density is probably associated with the increase of the electroactive area, which was estimated as 0.21 cm². The CG/Au obtained in +0.3 V showed the lower ΔE_p ($\Delta E_p = 90$ mV) and the highest peak anodic current density (1.68 mA cm⁻²). This increase in the current density occurred due to homogeneous coverage of the

surface with gold particles and increasing the electroactive area (0.25 cm²). However, in potential of the +0.6 V the current density decreased for 1.26 mA cm⁻² with $\Delta E_p = 120$ mV, which is associated to the decrease in the electroactive area (0.18 cm²). As the current densities of the modified electrodes with the Au microstructures obtained in -0.3 and +0.3 V were similar, repeatability of measurements was performed. The average current densities for the modified electrodes in the potentials of +0.3 V and -0.3 V were 1.69 mA cm⁻² $\pm$ 0.05 mA cm⁻² and 1.73 mA cm⁻² $\pm$ 0.37 mA cm⁻², respectively. This increase of standard deviation observed for the previous one is a probably a consequence of the low reproducibility of dendritic structures. Therefore, the potential of +0.3 V was maintained for other experiments.

3.4. Effect of precursor concentration

The concentration of HAuCl₄ was also investigated in the electrochemical Au deposition process on CG electrode surface. Fig. 7 shows the SEM-FEG for the CG/Au electrodes prepared with different precursor concentrations.

Figure 7. FEG-SEM images with a magnification of 15000X of CG/Au electrodes prepared at different concentrations of HAuCl₄ (a) 1.0 mmol L⁻¹, b) 10.0 mmol L⁻¹ and (c) 100.0 mmol L⁻¹, in 0.1 mol L⁻¹ Na₂HPO₄ solution, with $E = +0.3$ V vs Ag|AgCl and electrodeposition time of the 700 s. The scale bars for all images is 2 μ m

The results from SEM images indicate that the gold particles electrodeposited are considerably affected by the precursor concentration. As can be seen in Fig. 7a using the initial concentration of 1.0 mmol L^{-1} the covering of the CG electrode surface was not homogeneous and the particles showed an average size of 230 nm. When the precursor concentration is increased to 10.0 mmol L^{-1} , it was obtained particles with spherical shape and an average size of

the 420 nm, which were uniformly distributed over the surface of the CG electrode. Increasing the precursor concentration for $100.0 \text{ mmol L}^{-1}$, resulted in increase of average size to $2.4 \text{ }\mu\text{m}$ due to the aggregation of the Au particles. The effect of the precursor concentration on the deposition of particles was also evaluated electrochemically. The results are summarized in the Table 2.

Table 2. Gold particles electrodeposited onto CG electrodes at different concentrations of HAuCl_4 , applying potential of $E = +0.3 \text{ V}$ and electrodeposition time of 700 s

[HAuCl_4] (mmol L^{-1})	ΔE_p (V)	I_{pa} (mA cm^{-2})	I_{pc} (mA cm^{-2})	Area (cm^2)	I_{pc} (mA cm^{-2})
1.0	0.11	1.28	1.22	0.18	1.22
10.0	0.09	1.73	1.80	0.25	1.80
100.0	0.10	1.67	1.74	0.22	1.74

The electrode modified with 1.0 mmol L^{-1} of the HAuCl_4 showed the lower anodic current density, which is in agreement with the lower electroactive area ($A = 0.18 \text{ cm}^2$), when compared to CG/Au electrode prepared with a concentration of 10.0 mmol L^{-1} ($A = 0.25 \text{ cm}^2$). However, when the concentration was increased for $100.0 \text{ mmol L}^{-1}$ resulted in an increase of the average size and reduction of the electroactive area for 0.22 cm^2 . Therefore, the concentration of 10.0 mmol L^{-1} was maintained for others optimizations.

3.5. Effect of electrodeposition time

The study of the potential showed that the nucleation process can transit between progressive and instantaneous. Independent of nucleation process, the nucleus gradually grows as a function of deposition time. Therefore, the influence

of deposition time can change the roughness, due to coalescence of the grains and consequently promotes the decrease of the contact area.^{8,14} Therefore, the influence of the deposition time in morphology were evaluated and characterized by FEG-SEM (Fig S 3). The micrographs of the CG/Au electrode modified with electrodeposition time of the 200 s (Fig. S 3a) showed a surface with many defects. When the electrodeposition time was increased to 700 s, spherical shape particles uniformly distributed over the surface of the CG electrode were obtained. However, increasing the electrolysis duration for 1200 s (Fig. S 3c), it is verified the presence of a compact structure, due to growth and coalescence of the Au particles. The electrodes CG/Au modified with different electrodeposition times also were electrochemically characterized. The results of this characterization are summarized in the Table 3.

Table 3. Gold particles electrodeposited onto CG electrodes with different electrodeposition times by applying potential step electrolysis of the $E = +0.3$ V and $[\text{HAuCl}_4] 10.0 \text{ mmol L}^{-1}$

Time of deposition	ΔE_p (V)	I_{pa} (mA cm^{-2})	I_{pc} (mA cm^{-2})	Area (cm^2)
200 s	0.10	1.39	1.45	0.20
700 s	0.09	1.69	1.73	0.25
1200 s	0.12	1.51	1.49	0.21

The current density for $[\text{FeCN}_6]^{3-/4-}$ increased with the increase of the deposition time from 200 s at 700 s. However, further increasing the deposition time for 1200 s resulted in the decrease in the anodic current density. These electrochemical results are in agreement with the morphological studies, which showed that in the deposition time of 700 s the CG electrode is almost completely covered by gold

particles (Fig. S 3b), promoting an increase of electroactive area. Therefore, after optimizing all the variables, the better deposition conditions were, 10.0 mmol L^{-1} of $[\text{AuCl}_4]^-$, deposition time of 700 s and deposition potential of +0.3 V. After the process of electrodeposition onto CG surface was optimized, the structure of the gold particles was characterized by XDR (Fig. 8).

Figure 8. XRD patterns of CG/Au electrode (electrodeposition conditions: $[\text{HAuCl}_4] 10.0 \text{ mmol L}^{-1}$, time of 700 s at +0.3 V

The XRD patterns showed three diffraction peaks at the 2θ angles of 38° , 44° and 64° which can be attributed to (1 1 1), (2 0 0) and (2 2 0) reflections of the face-centered cubic structure of metallic gold particles.⁴³ The peaks located at 77° correspond to planes (1 1 0) of the carbon graphite substrate.²⁵

The electrochemical performance of the unmodified CG electrodes and Au was compared to the modified electrode CG/Au obtained in the optimized conditions. The voltammetric results are shown in Fig. 9.

Figure 9. (a) Cyclic voltammograms (b) Nyquist plots of impedance spectra of the bare gold electrode, bare CG electrode and CG/Au electrodes in KCl 0.1 mol L⁻¹ containing 5.0 mmol L⁻¹ [FeCN₆]^{3-/4-}, $\nu = 50$ mV s⁻¹

The voltammetric results demonstrated that the CG/Au electrode showed higher oxidation currents for [FeCN₆]^{3-/4-} ($I_{pa} = 1.70$ mA cm⁻²) compared with Au ($I_{pa} = 0.58$ mA cm⁻²) and CG ($I_{pa} = 0.75$ mA cm⁻²) electrodes. This increase in the anodic peak current intensities occurred due to the increase of electroactive area, because the CG/Au showed electroactive of 0.25 cm², CG and Au showed 0.12 and 0.02 cm², respectively.

Using the methodology of equivalent circuits (inset in Fig. 9b), the electrochemical impedance spectroscopy (EIS) data were adjusted. According to this model, the proposed equivalent circuit for CG/Au consists of a resistor (R_1) representing the series resistance (resistance from solution, electrode materials and contacts contribution), an element (R_2) corresponds to the charge transfer resistance (R_{CT}) caused by the faradaic processes in the electrode/solution interface, a constant phase element (CPE) representing the

capacitance of the electric double layer and element (W_1) which is semi-finite diffusion.⁴⁴ The EIS measurements (Fig. 9b) show that CG electrode has higher charge transfer resistance ($R_{CT} = 7.22$ Ω cm²), compared to Au and CG/Au electrodes. However, the CG/Au showed lower R_{CT} ($R_{CT} = 1.83$ Ω cm²) than the Au electrode ($R_{CT} = 3.05$ Ω cm²). This decrease in the R_{CT} can be attributed to the good electronic conductivity of Au and the increase of electroactive area provided by the gold particles electrodeposited, which facilitate the electronic transfer process in the electrode/solution interface.⁴⁴⁻⁴⁷

3.6. Electrochemical detection of Dopamine and Uric Acid

The electrocatalytic performance of CG, Au and CG/Au electrodes was evaluated using cyclic voltammetry analysis in presence of dopamine (DA) as shown in Fig. 10.

Figure 10. Cyclic voltammograms of CG, Au and CG/Au electrodes in 0.1 mol L⁻¹ PBS (pH 7.0) containing 1.0 mmol L⁻¹ of DA, $\nu = 50 \text{ mV s}^{-1}$

The CG/Au, CG and Au showed the following anodic peak current intensities in presence of DA, $I_{pa} = 27.2 \text{ } \mu\text{A cm}^{-2}$, $I_{pa} = 18.0 \text{ } \mu\text{A cm}^{-2}$ and $I_{pa} = 12.6 \text{ } \mu\text{A cm}^{-2}$, respectively. The CG/Au electrode presented the highest peak current intensity and also showed the lowest peak potential separation ($\Delta E_p = 0.06 \text{ V}$) when compared to CG ($\Delta E_p = 0.11 \text{ V}$) and Au ($\Delta E_p = 0.10 \text{ V}$) electrodes. This significant increase in the peak current intensity and lower ΔE_p occurred due to large surface area and electrocatalytic activity of the gold particles electrodeposited.^{8,13} The effect of scan rate on the oxidation of DA at CG/Au was evaluated and the result is showed in Fig. 11.

Plotting the $j \text{ (} \mu\text{A cm}^{-2} \text{)}$ vs $\nu^{1/2} \text{ (mV s}^{-1} \text{)}$, a linear correlation was obtained with $R = 0.9984$ (Fig. 11b), indicating that the DA oxidation process is controlled by species diffusion to the electrode surface.⁴⁸ In order to confirm that the process is controlled by diffusion, the relationship of $\log (j / \mu\text{A cm}^{-2})$ vs $\log (\nu / \text{mV s}^{-1})$ was evaluated (Fig. 11c). In this case, a slope of 0.5 was obtained, confirming that the

oxidation process controlled by diffusion of the species.^{49,50}

The performance of CG/Au electrode was evaluated in the simultaneous detection of DA and UA (Fig. 12).

As can be seen in Fig 12, CG/Au electrode showed a pair of redox peaks at +0.25 and +0.15 V attributed to the oxidation and reduction of DA, and other irreversible peak of oxidation in +0.57 V due to urate oxidation ($pK_a = 4.8$).⁵¹ The CG/Au electrode simultaneously detected both species, similar to other unmodified electrodes. However, the CG/Au electrode showed for DA, the higher anodic peak current density ($27.4 \text{ } \mu\text{A.cm}^{-2}$) compared to the CG ($17.7 \text{ } \mu\text{A.cm}^{-2}$) and Au ($11.35 \text{ } \mu\text{A.cm}^{-2}$) electrodes. Beside this, the CG/Au showed the higher separation potential peak (320 mV) compared to the CG (180 mV) and Au (290 mV) electrodes. Therefore, the CG/Au was applied in simultaneous electrochemical detection of these species and the performance of the electrode was evaluated using the square wave voltammetry (SWV).

Figure 11. (a) CVs of the CG/Au obtained in the presence of 10 mmol L⁻¹ DA with different scan rates in the range from 10 to 100 mV s⁻¹. CVs were obtained in 0.1 mol L⁻¹ PBS (pH 7.0). (b) Relationship between the j ($\mu\text{A cm}^{-2}$) vs $\nu^{1/2}$ (mV s⁻¹) and $\log(j/\mu\text{A cm}^{-2})$ vs $\log(\nu/\text{mV s}^{-1})$

Figure 12. Cyclic voltammograms of Au, CG and CG/Au in PBS 0.1 mol L⁻¹ (pH 7.0), $\nu = 50 \text{ mV s}^{-1}$, in presence of 1.0 mmol L⁻¹ DA and UA 1.0 mmol L⁻¹

3.7. Simultaneous Electrochemical detection of DA and UA at CG/Au

The SWV technique is often used in electrochemical analysis, because it has a better resolution than cyclic voltammetry and higher sensitivity.⁴⁸ However, the

important parameters of the SWV technique such as frequency (f), step potential (ΔE_s) and amplitude (a) should be optimized.⁵² Therefore, the optimized parameters were $f = 70$ Hz, $a = 70$ mV, and

$\Delta E_s = 1$ mV. Fig. 13 shows SWV obtained for different concentrations of DA in presence of UA and different concentrations of UA in the presence of DA at CG/Au.

Figure 13. (a) SWV of CG/Au in 0.1 mol L^{-1} PBS (pH 7.0) containing UA 100.0 $\mu\text{mol L}^{-1}$ and different concentrations of DA from 9.9 to 90.0 $\mu\text{mol L}^{-1}$ (b) Analytical curve for DA in presence of $[\text{UA}] = 100.0 \mu\text{mol L}^{-1}$ (c) SWV of CG/Au containing DA 90.0 $\mu\text{mol L}^{-1}$ and different concentrations of UA from 134.0 to 517.0 $\mu\text{mol L}^{-1}$. (d) Analytical curve for UA in presence of $[\text{DA}] = 90.0 \mu\text{mol L}^{-1}$. The error bars represent standard deviations for three measurements

Fig. 13a shows oxidation peaks at 0.20 V for DA and 0.57 V for UA with peak separation of the $\Delta E_p = 370$ mV. Keeping constant the concentration of UA in 100 $\mu\text{mol L}^{-1}$, it was found that oxidation peak current of DA linearly increased with the concentration in the range from 9.9 to 90.0 $\mu\text{mol L}^{-1}$ according to the equation: $j \mu\text{A cm}^{-2} = 0.992 + 9.9917C_{\text{DA}}$ with linear relative coefficients $R = 0.999$. In Fig. 13c, the concentration of DA was fixed in 90 $\mu\text{mol L}^{-1}$ and anodic peak current of UA increased linearly in the range from 134.0

to 517.0 $\mu\text{mol L}^{-1}$ according to the equation: $j \mu\text{A cm}^{-2} = 24.847 + 261.706C_{\text{UA}}$ and $R = 0.999$, without significantly influence on the response peak of DA. From analysis of these data, the detection limit (LOD) was estimated by IUPAC method, based on standard deviation for the blank signals. The detection limit for DA was $\text{LOD} = 2.6 \mu\text{mol L}^{-1}$ and for UA $\text{LOD} = 58.9 \mu\text{mol L}^{-1}$. The detection limits of CG/Au for DA and UA was compared with other sensors described in the literature, as shown in Table 4.

Table 4. Comparison of some modified electrodes applied for the determination of DA and UA describe in the literature

Electrodes	Linear range ($\mu\text{mol L}^{-1}$) ¹⁾		LOD ($\mu\text{mol L}^{-1}$)		ΔE p mV	Reference
	DA	UA	DA	UA		
CPE/PAYR ^a	83.6 – 488.1	381.6 – 111.0	0.1	9.5	130	[49]
CGE/Au-PtNP ^b	103.0 – 165.0	21.0 – 336.0	24.0	21.0	170	[53]
ITO/SiPy ⁺ Cl ⁻ /NiTsPc ^c	10.0 – 99.0	100.0 – 900.0	2.3	5.2	460	[54]
GCE/PPy/AgNP ^d	0.5 – 155.0	2.0 – 100.0	0.1	0.5	170	[55]
CGE/RGO/PAMAM/MWCNT/AuNP ^e	10.0 – 320.0	1.0 – 114.0	3.3	0.3	130	[56]
CG/Au	9.9 – 90.0	134.0 – 517.0	2.6	58.9	370	This work

^apoly(alizarin yellow R)-modified carbon paste electrode. ^bAu and Pt nanoparticles-modified glassy carbon electrode. ^c3-n-propylpyridinium silsesquioxane and nickel(II) tetrasulfophthalocyanine film-modified indium tin oxide coated glass electrode. ^dPPy/AgNP nanoparticles modified polypyrrole nanofibers-modified glassy carbon electrode. ^egraphene oxide functionalized by poly(amido-amine), multi-walled carbon nanotubes and Au nanoparticles-modified glassy carbon electrode

As can be seen in Table 4, the LOD and LOQ presented by GC/Au electrode were similar to other electrochemical sensors described in the literature, however, besides being environmental friendly,

the electrode proposed is, low cost and the substrate can be regenerated.

4. Conclusion

The CG electrodes obtained from spent batteries were successfully employed as electrode material, showing a promising alternative for the development of electrochemical sensors, due to advantages such as low cost, high electrochemical reactivity, robustness and easy of modification. Moreover, the surface can be renewed after the polishing procedure. The

electrodeposition technique is a powerful tool to deposit metallic particles, due to control of deposition conditions such as electrodeposition time, overpotential and concentration of the precursor. Depending on these conditions, the size and morphology of the Au microstructure can significantly change, which may influence in the electrode reactivity. The electrodeposition of gold particles on the CG electrodes increased its electroactive area and promoted electrocatalysis towards the dopamine oxidation, allowing the simultaneous detection of this catecholamine and uric acid with detection limits similar or lower than other electrodes reported in the literature. These results confirm that the CG electrodes combined with the electrodeposition technique is an excellent strategy for the development of electrochemical sensors. In addition, reused CG can be used as an

alternative material to obtain modified electrodes.

Acknowledgements

We would like to thank Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação Araucária (Brazil) for financial support. The authors are also grateful for the Institutional Laboratory C-LABMU (UEPG).

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