

# **Electrochemical Reduction of Oxygen on Gold Nanoparticle-Electrodeposited Glassy Carbon Electrodes**

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The electrochemical reduction of oxygen ( $O_2$ ) on Au nanoparticle-electrodeposited glassy carbon electrodes (GCEs) has been performed in 0.1 M phosphate buffer solution (pH 7.2). Two well-separated electrochemical reduction peaks for  $O_2$  on GCE were observed at about -750 and -2000 mV vs. Ag/AgCl/KCl (sat.) *i.e.*, a peak separation of *ca.* 1250 mV. Those two peaks were attributed to the two-step four-electron reduction of  $O_2$  to  $H_2O$  through  $H_2O_2$ . A remarkable decrease of the separation of the two peaks (down to 550 mV) along with a significant positive shift of the two reduction peaks of  $O_2$  to -350 and -9880 mV, respectively, were observed upon loading of a very minute amount of Au nanoparticles onto the GCE (typically  $2.78 \times 10^{-7}$  g cm<sup>-2</sup>). Further positive potential shift of the two peaks along with a concurrent decrease of the peaks separation could be achieved by controlling the extent of Au loading on the GCE. Au-electrodeposited GCE with an equivalent Au film thickness of 10 nm showed almost the same behavior toward the  $O_2$  reduction as the bulk Au electrode. These observations were interpreted in view of the increase of the effective (real) surface area of the Au film by the increase of its thickness, as indicated by scanning electron micrographs in addition to the characteristic cyclic voltammogram for Au nanoparticle-electrodeposited GCEs in N<sub>2</sub>-saturated 0.05 M H<sub>2</sub>SO<sub>4</sub>.

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The electrocatalytic reduction of molecular oxygen (O<sub>2</sub>) to either hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) or to water (H<sub>2</sub>O) is a reaction of prime importance in many industrial, environmental,<sup>1-3</sup> and electrochemical applications like fuel cells.<sup>4-7</sup> This reaction has been extensively studied at various electrode materials in different media.<sup>8-12</sup> The reaction pathway depends markedly on the electrode material as well as the electrolyte pH. A desirable cathode for such applications should satisfy several advantages, *e.g.*, low overpotential, high current density (*i.e.*, high reaction rate), long lifetime of operation, as well as low cost.

Glassy carbon electrodes (GCEs) are characterized by their high chemical inertness as well as low oxidation rate in addition to small gas and liquid permeability.<sup>13</sup> These properties render GCEs a suitable base for the loading of various metals and polymer thin films aiming to improve its electrocatalytic activity toward several electrochemical applications<sup>14-16</sup> rather than use as a bulk electrode. For instance, Au thin-film-coated GCEs have been used as cathodes for  $\mathrm{O}_2$  reduction in acidic and in alkaline media.  $^{16,17}$  The electrocatalytic activity of such electrodes toward the O<sub>2</sub> reduction in acidic medium was independent of film thickness and was similar to that of the bulk Au electrode, which supports mainly the two-electron reduction mechanism of  $O_2$  to  $H_2O_2$ .<sup>16</sup> While in alkaline medium<sup>17</sup> the Au thin-film-coated GCE produces HO<sub>2</sub><sup>-</sup> as a major reduction product at relatively positive overpotentials, and at higher cathodic overpotentials the formation of OH<sup>-</sup> predominates (i.e., two-step four-electron pathway). This behavior is also similar to that of bulk Au in alkaline medium.<sup>12</sup> In both cases the Au films were deposited onto the GCE via the evaporation technique.

Recently, the use of nanoparticle-based electrodes have shown superior advantageous electrocatalytic properties over bulk electrodes for many vital electrochemical reactions, *e.g.*, CO oxidation,  $O_2$  reduction, and for catalytic hydrogenation of unsaturated alcohols and aldehydes.<sup>8,18,19</sup>

In this study, the electrochemical deposition of Au nanoparticles onto GCE has been performed under different conditions of electrolyte concentration and deposition time. These Au nanoparticleelectrodeposited GCEs are used as cathodes for the electrochemical reduction of  $O_2$  in 0.1 M phosphate buffer (pH 7.2). A significant and regular positive shift in the overpotential of  $O_2$  reduction was achieved upon loading the Au nanoparticles onto the GCE. The electrocatalytic activity of such electrodes was compared with that of the bare GCE and bulk Au electrode in the same electrolyte.

#### Experimental

The working electrodes were bare glassy carbon (GC) and Au nanoparticle-electrodeposited GC electrodes ( $\phi = 3 \text{ mm}$ ), and bulk Au electrodes ( $\phi = 1.6$  and 2.0 mm) were used for the cyclic voltammetric (CV) and the rotating disc electrode (RDE) voltammetric experiments. A spiral Pt wire and an Ag/AgCl/KCl (sat.) were the counter and the reference electrodes, respectively. Prior to the electrodeposition of Au nanoparticles, the GCEs were polished first with no. 2000 emery paper, then with aqueous slurries of successively finer alumina powder (particle size down to 0.06 µm) with the help of a polishing microcloth. The bare GCEs were then sonicated for 10 min in Milli-Q water. Au nanoparticles were electrodeposited from acidic bath of 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing either 0.11 or 1.0 mM Na[AuCl<sub>4</sub>] by applying a potential step from 1.1 to 0.0 V vs. Ag/AgCl/KCl (sat).<sup>20</sup> The duration time of the potential step was varied from 5 to 600 s to obtain Au deposits with different characteristics (cf. Table I). The Au electrodes were first polished in a similar manner to the GCE and then electrochemically pretreated in N<sub>2</sub>-saturated 0.05 M H<sub>2</sub>SO<sub>4</sub> solution by repeating the potential scan in the range -0.2 to 1.5 V vs. Ag/AgCl/KCl (sat.) at 100 mV/s for 10 min or until the CV characteristic for a clean Au electrode was obtained. Scanning electron microscopy (SEM) analysis of the Au particles deposited on GCE was carried out using a JSM-T220 scanning electron microscope (JEOL Optical Laboratory, Japan) at an acceleration voltage of 15 kV and a working distance of 4-5 mm.

Oxygen reduction was studied in 0.1 M phosphate buffer solution (PBS) of pH 7.2 using a conventional two-compartment Pyrex glass container. Milli-Q water (Millipore, Japan) was used to prepare all solutions. Prior to each experiment,  $O_2$  gas was bubbled directly into the cell for 30 min to obtain an  $O_2$ -saturated solution, and during the measurements  $O_2$  gas was flushed over the cell solution. For the RDE experiments, the working electrode compartment was 200 cm<sup>3</sup> to eliminate possible change of the  $O_2$ concentration during the measurements. All the measurements were performed at room temperature ( $25 \pm 1$  °C). Electrochemical measurements were performed using a BAS 100 B/W electrochemical analyzer. Steady-state voltammograms were obtained at a bare GC and at a Au nanoparticle-electrodeposited GC disk

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Electrode no.	Deposition time (s)	Bath composition	Au loading <sup>a</sup> (g cm <sup>-2</sup> )	Average surface area of Au loading <sup>b</sup> (cm <sup>2</sup> )	Equivalent film thickness <sup>c</sup> (nm)
1	5	0.11 mM Na[AuCl <sub>4</sub> ] in 0.5 M H <sub>2</sub> SO <sub>4</sub>	$2.78 \times 10^{-7}$	$5.40 \times 10^{-3}$	0.14
2	5	1.0 mM Na[AuCl <sub>4</sub> ] in 0.5 M H <sub>2</sub> SO <sub>4</sub>	$1.50 \times 10^{-6}$	$1.68 \times 10^{-2}$	0.77
3	300	As above	$1.98 \times 10^{-5}$	$1.07 \times 10^{-1}$	10.3
4	600	As above	$4.16 \times 10^{-5}$	$1.46 \times 10^{-1}$	21.6

## Table I. Characterization of the Au loadings on GCE under different conditions of electrodeposition.

<sup>a</sup> As calculated from the i-t curve during the potential-step electrodeposition.

<sup>b</sup> As estimated from the charge consumed for the reduction peak of the surface oxide monolayer of Au (the peak at 900 mV in Fig. 2) using a reported value of 400  $\mu$ C cm<sup>-2.21-23</sup> <sup>c</sup> It is the thickness of a homogeneous Au film that covers the entire surface area of the GCE and has the same Au loading as that of nanoparticles.

 $(\phi = 3.0 \text{ mm})$ -Pt ring electrode (RRDE) using a rotary system from Nikko Keisoku, Japan. The Pt ring was potentiostated at 0.8 V vs. Ag/AgCl/KCl (sat), where oxidation of hydrogen peroxide arriving to the ring is under diffusion control. The current density was calculated on the basis of the geometric surface area of the GCEs. Electrolyte solutions were, if necessary, deaerated by bubbling N<sub>2</sub> gas for at least 30 min prior to electrochemical measurements.

#### **Results and Discussion**

Characterization of the Au deposits.—The typical SEM micrographs of the Au nanoparticles electrodeposited onto the GCEs under different operating conditions are shown in Fig. 1a-h. It is clear from these figures that the increase of either the time of deposition or the concentration of the  $AuCl_4^-$  resulted in an increase in the



Figure 1. SEM micrographs of (a) bare GCE and Au nanoparticle-electrodeposited GCEs prepared from 0.5 M  $H_2SO_4$  solution containing (b and c) 0.11 mM  $Na[AuCl_4]$  or (d-h) 1.0 mM  $Na[AuCl_4]$  via (b-d) 5, (e,g) 300, and (f,h) 600 s potential steps from 1.1 to 0.0 V vs. Ag/AgCl/KCl (sat).



Figure 2. CV response, in N<sub>2</sub>-saturated 0.05 M H<sub>2</sub>SO<sub>4</sub>, for Au nanoparticle-electrodeposited GCEs prepared from 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing (a) 0.11 mM Na[AuCl<sub>4</sub>] or (b-d) 1.0 mM Na[AuCl<sub>4</sub>] via (a and b) 5, (c) 300, and (d) 600 s potential steps from 1.1 to 0.0 V vs. Ag/AgCl/KCl (sat). Potential scan rate 100 mV s<sup>-1</sup>. Curve (e) represents the CV response of the bulk Au electrode.

average particle size of the Au nanoparticles. Furthermore, the Au particles deposited from the 0.11 mM Na[AuCl<sub>4</sub>] solution are in the nanoscale size (typically  $\sim$ 20 nm) and homogeneously distributed throughout the GC surface (Fig. 1b and c), while in the case of the electrodeposition from the 1.0 mM Na[AuCl<sub>4</sub>] solution, in addition to the 20 nm scale particles, bigger particles of about 80-100 nm (clusters) are formed (Fig. 1d).

In order to estimate the real surface area of the Au nanoparticles electrodeposited on the GCEs, the characteristic CV response of each electrode is measured in N<sub>2</sub>-saturated 0.05 M H<sub>2</sub>SO<sub>4</sub>. Figure 2 shows such CV response. The increase of the reduction peak current at *ca.* +900 mV reflects the increase of the Au loading on the GCE. The real surface area of the Au loading was estimated by calculating the amount of charge consumed during the reduction of the Au surface oxide monolayer using a reported value of 400  $\mu$ C cm<sup>-2</sup>.<sup>21-23</sup> Table I summarizes the loading characteristics of the Au nanoparticles electrodeposited on GCE under different conditions of electrodeposition.

Electrochemical reduction of O2 at Au nanoparticleelectrodeposited GCEs.—Figure 3 shows the CVs for the oxygen reduction at bare (curve a) and Au nanoparticle-electrodeposited (electrode no. 1, curve b) GCEs in O2-saturated 0.1 M phosphate buffer solution of pH 7.2 (0.1 M PBS pH 7.2). In curve a, the first reduction peak of  $O_2$  is observed at *ca.* -750 mV and the second one is obtained as a shoulder at around -2000 mV. The first peak is due to the two-electron reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>, while the second one is due to the further reduction of H<sub>2</sub>O<sub>2</sub> formed to H<sub>2</sub>O (cf. Fig. 4). Interestingly, a considerable positive shift of these two reduction peaks of  $O_2$  from *ca*. -750 and *ca*. -2000 mV (on the bare GCE) to -350 and -880 mV, respectively, was observed at the GCE loaded with a very minute amount of Au  $(2.78 \times 10^{-7} \text{ g cm}^{-1})$ curve b). The Au nanoparticle-electrodeposited GCE is considered a microdisk array-type electrode (see Fig. 1b and c) at which the diffusion layers at individual Au nanoparticles overlap each other to



Figure 3. CVs obtained for the  $O_2$  reduction at (a) bare GC and (b) Au nanoparticle-deposited GC (electrode no. 1) in  $O_2$ -saturated 0.1 M PBS (pH 7.2). Potential scan rate 100 mV s<sup>-1</sup>.

form a linearly expanding diffusion region, as can be expected by comparison of the average distance between the Au nanoparticles ( $\sim 0.02 \mu m$ , see Fig. 1b) and the diffusion layer thickness ( $\sim 2.1$  $\times$  10<sup>-2</sup> cm, under the experimental conditions of Fig. 3b). Consequently, the CV response (i.e., the voltammetric shape of the O<sub>2</sub> reduction wave) of this electrode is similar to that observed at the GCE with the same apparent geometric surface area. Figure 4 compares the CVs obtained with the bare and Au-deposited (electrode no. 1) GCEs in 0.1 M PBS saturated with  $N_2$  or  $O_2$  in the absence and presence of 1.8 mM H<sub>2</sub>O<sub>2</sub>. It is clear from this figure that the addition of H<sub>2</sub>O<sub>2</sub> to the O<sub>2</sub>-saturated 0.1 PBS resulted in an increase in the reduction peak current at -880 mV, while the peak current at -350 mV was not affected (compare curves d and e for electrode 1). The addition of H<sub>2</sub>O<sub>2</sub> to the N<sub>2</sub>-saturated solution caused the appearance of a reduction peak at -880 mV, and no peak was observed at -350 mV (compare curves a and f). As expected, the first reduction peak of O2 on GCE was not affected by the addition of  $H_2O_2$  (curves b and c).

Figure 5 shows the CV response obtained for the  $O_2$  reduction at the Au nanoparticle-electrodeposited GCEs in 0.1 M PBS (pH 7.2). This figure shows that the increase of the Au loading time (and in turn the average film thickness) leads to a more positive shift of the two reduction peaks (curves a-c). The first and second reduction peak potentials in curve c are almost the same as those obtained at the bulk Au electrode (curve d).

Consequently, from a practical point of view, the loading of a very minute amount of Au nanoparticles on the GCE (*e.g.*, curve b in Fig. 3 and curve a in Fig. 5) is most desirable for the following reasons: (*i*) it utilizes a small amount of a precise metal (*i.e.*, saving in the cost), and (*ii*) it can efficiently and selectively produce  $H_2O_2$  without interference from the second reduction peak, which becomes closer to the  $H_2O_2$  production peak upon increase of the Au loading (see Fig. 5).

Steady-state hydrodynamic voltammetric studies.—Figures 6-8 show the steady-state hydrodynamic voltammograms for the  $O_2$  reduction at a GCE, a Au nanoparticle-electrodeposited GCE





Figure 4. CV response obtained at the bare GC (a-c) and Au nanoparticle-deposited GC (electrode no. 1 curves d-f) in 0.1 M PBS pH 7.2 solution saturated with (a and f) N<sub>2</sub> or (b-e) O<sub>2</sub> in the absence (a, b, d) and the presence (c, e, f) of 1.8 mM H<sub>2</sub>O<sub>2</sub>. Potential scan rate 100 mV s<sup>-1</sup>.

**Figure 6.** Hydrodynamic voltammograms for the oxygen reduction at bare GC RDE ( $\phi = 3.0 \text{ mm}$ ) in O<sub>2</sub>-saturated 0.1 M PBS (pH 7.2) at different rotation rates of (a) 100, (b) 200, (c) 400, (d) 600, (e) 800, (f) 1000, (g) 1200, (h) 1600, (i) 2000, and (j) 2400 rpm. Potential scan rate 10 mV s<sup>-1</sup>.



(electrode no. 2), and a bulk Au electrode, respectively, in O<sub>2</sub>-saturated 0.1 M PBS (pH 7.2). The ill-defined two reduction waves were observed for the O<sub>2</sub> reduction on the Au-electrodeposited GCE and the bulk Au electrode in the potential range of +0.2 to -1.1 V (Fig. 7 and 8), while only one reduction



**Figure 5.** CVs obtained for the O<sub>2</sub> reduction at Au nanoparticle-deposited GC electrodes in O<sub>2</sub>-saturated 0.1 M PBS (pH 7.2). A potential step from 1.1 to 0.0 V was used for the electrodeposition of Au particles from 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 1.0 mM Na[AuCl<sub>4</sub>] with deposition time of (a) 5, (b) 300, and (c) 600 s. Curve d represents the CV response of the bulk Au electrode. Potential scan rate 100 mV s<sup>-1</sup>.

**Figure 7.** Hydrodynamic voltammograms for the oxygen reduction at a Au nanoparticle-electrodeposited GC RDE ( $\phi = 3.0 \text{ mm}$ ) (electrode 2) in O<sub>2</sub>-saturated 0.1 M PBS (pH 7.2) at different rotation rates of (a) 100, (b) 200, (c) 400, (d) 600, (e) 800, and (f) 1200 rpm. Potential scan rate 10 mV s<sup>-1</sup>.



**Figure 8.** Hydrodynamic voltammograms for the oxygen reduction at bare Au RDE ( $\phi = 2.0 \text{ mm}$ ) in O<sub>2</sub>-saturated 0.1 M PBS (pH 7.2) at different rotation rates of (a) 200, (b) 400, (c) 600, (d) 800, (e) 1000, (f) 1200, (g) 1600, (h) 2000, and (i) 2400 rpm. Potential scan rate 10 mV s<sup>-1</sup>.

wave could be obtained on GCE in the same potential domain (Fig. 6). The data are analyzed using the Koutecky-Levich equation given  $by^{24}$ 

$$1/i = 1/i_{\rm k} + 1/i_{\rm d} = -1/(nFAkC^{\rm o}) - 1/(0.62nFAD_{\rm O_2}^{2/3}\nu^{-1/6}C^{\rm 0}\omega^{1/2})$$
[1]

where *i* is the measured current at a given potential,  $i_k$  and  $i_d$  are the kinetic and diffusion-limited currents, respectively, *k* is the rate constant for O<sub>2</sub> reduction, *n* is the number of electrons involved in the oxygen reduction reaction, *F* is Faraday constant (96,484 C mol<sup>-1</sup>), *A* is the geometric electrode area (cm<sup>2</sup>),  $\omega$  is the rotation rate (rad s<sup>-1</sup>), *C*<sup>0</sup> is the saturated concentration of O<sub>2</sub> in 0.1 M PBS (pH 7.2, 8.8 × 10<sup>-7</sup> mol cm<sup>-3</sup>),  $D_{O_2}$  is the diffusion coefficient of O<sub>2</sub> (2.7 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>), and  $\nu$  is the kinematic viscosity of the solution (0.010 cm<sup>2</sup> s<sup>-1</sup>). The values of *C*<sup>o</sup> and  $D_{O_2}$  were determined by the hydrodynamic chronocoulometric technique<sup>25</sup> (the data are not shown here), while the value of  $\nu$  was measured using an Ubbelohde viscometer at 25°C.

Figures 9-11 show typical K-L plots for the data shown in Fig. 6-8, respectively. The dotted lines represent the theoretical predictions from Eq. 1 using an effective value of n = 2 (for Fig. 9) and n = 4 (for Fig. 10 and 11) and  $i_k \rightarrow \infty$ . Good agreement is found between the experimentally measured currents and those predicted using Eq. 1. These results confirm the conclusion of Fig. 4 (*i.e.*, the two-step four-electron reduction pathway for O<sub>2</sub> reduction). In other words, the values of *n*, for example, at -800 mV, are 2 at bare GCE and 4 at both Au nanoparticle-deposited GCE and Au bulk electrode. There is no intercept for the K-L plots (Fig. 10 and 11) at the potential at which the limiting current is reached, *i.e.*, the O<sub>2</sub> reduction is under diffusion control (as expected from the theory), but at other potentials we have intercept depending on the potential. The values of these intercepts refer to the kinetic current component of the total measured current (see Eq. 1).

Figure 12 compares the steady-state hydrodynamic voltammograms for the  $O_2$  reduction obtained at a bare GC disk ( $\phi = 3.0$  mm)-Pt ring (curves a and a') with those obtained at Au



Figure 9. K-L plots for the  $O_2$  reduction at the bulk GC RDE in  $O_2$ -saturated 0.1 M PBS (pH 7.2). The dotted line represents the theoretical K-L line calculated using n = 2. The electrode potential: (a) -600, (b) -700, (c) -800, and (d) -900 mV vs. Ag/AgCl/KCl (sat.). The data were taken from Fig. 6.

nanoparticle-electrodeposited GC disk (electrode no. 2)-Pt ring RRDE electrodes (curves b and b') in O<sub>2</sub>-saturated 0.1 M PBS pH 7.2. The measurements were performed at a scan rate of 20 mV s<sup>-1</sup> and a rotation speed of 400 rpm. The Au nanoparticles were electrodeposited onto the GC electrode from 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 1.0 mM Na[AuCl<sub>4</sub>] by applying a potential step from 1.1 to 0.0 V for 5 s. The top of this figure (*i.e.*, curves a' and b') shows the ring currents, which correspond to the oxidation of hydrogen



**Figure 10.** K-L plots for the O<sub>2</sub> reduction at the Au nanoparticleelectrodeposited GC RDE (electrode 2) in O<sub>2</sub>-saturated 0.1 M PBS (pH 7.2).  $(\cdot \cdot \cdot \cdot)$  The theoretical K-L line calculated using n = 2 and 4. The electrode potential: (a) -200, (b) -240, (c) -280, (d) -300, (e) -360, (f) -400, (g) -500, (h) -600, (i) -700, (j) -800, (k) -900, and (l) -1000 mV vs. Ag/AgCl/KCl (sat.). The data were taken from Fig. 7.



**Figure 11.** K-L plots for the O<sub>2</sub> reduction at the bulk Au RDE in O<sub>2</sub>-saturated 0.1 M PBS (pH 7.2).  $(\cdot \cdot \cdot \cdot)$  The theoretical K-L line calculated using n = 4. The electrode potential: (a) -200, (b) -300, (c) -400, (d) -500, (e) -600, (f) -700, and (g) -800 mV vs. Ag/AgCl/KCl (sat.). The data were taken from Fig. 8.

peroxide  $(H_2O_2)$  produced on the disk, while the bottom panel shows disk currents. A large positive shift in the first reduction peak of  $O_2$  is evident upon loading a minute amount of Au onto the GCE (compare curves a and b); at the same time the corresponding ring current starts to rise and reaches its maximum at a more positive



**Figure 12.** Steady-state voltammograms for O<sub>2</sub> reduction at (a) bare GC and (b) Au nanoparticle-electrodeposited GC disk electrodes and for H<sub>2</sub>O<sub>2</sub> oxidation at (a' and b') Pt ring electrode in O<sub>2</sub>-saturated 0.1 M PBS (pH 7.2). The Pt ring was potentiostated at 800 mV *vs.* Ag/AgCl/KCl (sat). Rotation rate 400 rpm, potential scan rate 20 mV s<sup>-1</sup>. A 5 s potential step from 1.1 to 0.0 V was used for the electrodeposition of Au nanoparticles from 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 1.0 mM Na[AuCl<sub>4</sub>].



Figure 13. Relation between the extent of the Au nanoparticle loading and the specific energy savings at the GC cathode during the reduction of  $O_2$  to  $H_2O_2$  in 0.1 M PBS (pH 7.2).

potential (compare curves a' and b'). This clearly indicates the electrocatalytic enhancement of the Au nanoparticles toward the  $O_2$  reduction compared to the bare GCE.

Energy savings during  $H_2O_2$  production.—The significant positive shift of the cathodic peak potential for the reduction of  $O_2$  to  $H_2O_2$  upon loading the Au nanoparticles on the GCEs corresponds to a remarkable reduction in the energy consumption at the cathode. At a particular current, *i*, the energy savings,  $\xi_s$ , in watt hours is given by<sup>26</sup>

$$\xi_{\rm s} = i\Delta E_{\rm (c)} t/3600 \qquad [2]$$

where *t* is the electrolysis time in seconds, and  $\Delta E_{(c)}$  is the shift in the peak potential at a certain rate of H<sub>2</sub>O<sub>2</sub> production (*i.e.*, at a constant current) brought about by the Au nanoparticles loading on the GCE. The amount of H<sub>2</sub>O<sub>2</sub> produced (in g mol) is given by the Faraday law as *it/nF*, where *n*(=2) is the number of electrons consumed per H<sub>2</sub>O<sub>2</sub> molecule produced. Thus, the energy savings at the cathode per g mol of H<sub>2</sub>O<sub>2</sub>,  $\xi'_{s}$ , is given by

$$\xi'_{s} = \xi_{s}/(it/nF) = (i\Delta E_{(c)}t/3600)/(it/nF) = \Delta E_{(c)}nF/3600$$
[3]

The values of  $\Delta E_{(c)}$  were obtained from Fig. 3 and 5. The energy savings at the cathode per gram of Au nanoparticle loading (*i.e.*, the specific energy savings) was calculated using Eq. 3 and is plotted in Fig. 13. As a conclusion of this figure, the most beneficial effect of the Au loading appears upon loading a minute amount of Au (*i.e.*, 5 s electrodeposition, in the nanoscale range, typically ~20 nm, with an equivalent film thickness of 0.14 nm) on the GCE, resulting in the highest specific energy savings of the electrode.

### Conclusion

The electrochemical reduction of  $O_2$  at Au nanoparticleelectrodeposited GCEs has been performed in 0.1 M PBS (pH 7.2). A regular positive shift of the cathodic peak potentials corresponding to the reduction of  $O_2$  to  $H_2O_2$  and  $H_2O_2$  to  $H_2O$  with a concurrent decrease in the peak separation is achieved upon the increase of the Au loading. The most beneficial effect of the Au nanoparticle electrodeposition for the selective reduction of  $O_2$  to  $H_2O_2$  is obtained upon loading a minute amount of Au on GCE (5 s electrodeposition; equivalent thickness 0.14 nm). Further increase in the Au loading (*e.g.*, 600 s electrodeposition) resulted in CV behavior similar to that at the bulk Au electrode, at which the selective electroreduction of  $O_2$  to  $H_2O_2$  is hindered by the interference of the second reduction peak of  $H_2O_2$  to  $H_2O$ .

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