Highly Catalytic Electrode for Glucose Electro-oxidation Based on Au Nanoparticles Electrodeposited onto HOPG Substrate

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The electrocatalytic oxidation of glucose at Au nanoparticles-modified highly oriented pyrolytic graphite (HOPG) electrode has been investigated, for the first time. Catalytic oxidation of glucose to gluconolactone was observed and an electro-oxidative pretreatment of the HOPG electrode showed a significant enhancement of the catalytic activity as a consequence of the significant change in the crystallographic orientations through enrichment in the Au(100) facets of the electrodeposited Au nanoparticles.

The electrocatalytic oxidation of glucose has been examined extensively especially on gold substrates,[1–9] that has been paid much attention so far due to an increasing interest in its fuel cells applications. In this respect, underpotential-deposited metal ad-atoms modified gold electrodes exhibited interesting catalytic activities,[1–3] where effective oxidation of glucose at relatively negative potentials was observed at Ag-UPD Au single crystal electrodes. On the other hand, Au nanoparticles showed interesting electrocatalytic activity towards many reactions like CO oxidation,[10] O_2 reduction,[11] and glucose oxidation.[12] The preparation of Au nanoparticles by electrochemical deposition on an inert substrate is well documented in the literature,[11,13–16] and followed by in the present work. The HOPG substrate has been selected in the current study as it encounters two significant properties; Firstly, it has good crystalline nature, and secondly, it can be easily pretreated oxidatively, which in turn affects the catalytic activity of the electrodeposited Au nanoparticles,[15] while maintaining the same degree of crystallinity.[17] Such properties are of prime importance in view of previously reported studies showing a clear dependence of the catalytic activity on the crystallographic orientations of Au single crystals.[1–3]

Freshly cleaved HOPG plates (Veeco Metrology Group Co., Ltd., Japan) were used either untreated or after electro-oxidizing in a 0.5 M H_2SO_4 solution.[15] Au nanoparticles were then electrodeposited on the thus-prepared HOPG electrodes from a (0.5 M H_2SO_4 + 1 mM $HAuCl_4$) solution by applying a 300 s potential step from 1.1 to 0 V vs Ag|AgCl|KCl(sat). The morphology of the prepared Au nanoparticles was investigated using scanning electron microscopy (SEM) analysis, conducted with a (JSM-6060LV, JEOL Ltd., Japan) scanning electron microscope.

Figure 1 (left) shows the characteristic cyclic voltammograms of the prepared Au nanoparticles-deposited HOPG electrodes (Au_{nano}–HOPG) in an N_2-saturated 0.5 M H_2SO_4 solution at a potential scan rate of 100 mV s^{-1}. The extracted data show a significant increase of nearly 2.5 folds when comparing the real surface area of the electrodeposited Au nanoparticles onto electro-oxidized HOPG and untreated HOPG electrodes, respectively (cf. Table 1). The significant difference in the behavior of (Au_{nano}–HOPG) in the case of untreated and electro-oxidized HOPG electrodes shown in Figure 1 (left) is related to the difference in the amount and the average particle size of the electrodeposited Au nanoparticles in the two cases as depicted in the SEM images as well as the ratios of the different crystallographic orientations of the deposited Au nanoparticles as will be discussed below. In this respect, we monitored the oxygen reduction reaction (ORR) by measuring the cyclic voltammograms in an O_2-saturated 0.5 M KOH solution at both electrodes (Figure 1, right). While ORR proceeds via two two-electron reduction processes at untreated electrodes (Peaks I and II), significant tendency towards the direct four-electron reduction process, shown as an increase in the current density of Peak I at the expense of Peak II, is obtained at electro-oxidized (Au_{nano}–HOPG) electrode. This can be safely attributed to an increase in the relative ratio of Au(100) single crystal facets of the deposited Au nanoparticles which is in agreement with the reported XRD analysis.[17]

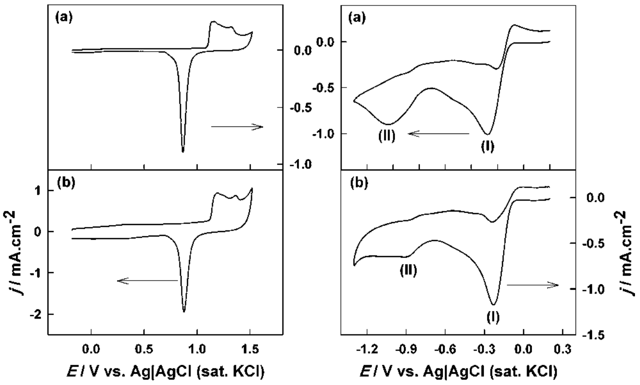

Figure 1. Left: Cyclic voltammograms of Au_{nano}–HOPG electrodes in the case of (a) untreated and (b) electro-oxidized HOPG electrodes in an N_2-saturated 0.5 M H_2SO_4 solution; Right: Cyclic voltammograms in an O_2-saturated 0.5 M KOH solution at Au_{nano}–HOPG electrodes in the case of (a) untreated and (b) electro-oxidized HOPG electrodes. Potential scan rate: 100 mV s^{-1} in all cases.

On the other hand, the obtained SEM micrographs of the prepared electrodes, that are in good agreement with those in the literature,[15,18] reveal that the electro-oxidation of HOPG electrode results in the deposition of well-dispersed, smaller-sized gold nanoparticles (cf. Table 1).

Figure 2A displays the cyclic voltammogram of untreated bare (Au_{nano}–HOPG) electrode in an N_2-saturated (10 mM glucose + 0.1 M NaOH) solution, showing an extraordinary high electrocatalytic activity towards glucose oxidation with two distinct oxidation peaks at ca. −0.26 V and ca. 0.25 V vs Ag|AgCl|KCl(sat) related to the two-electron oxidation of glucose into gluconolactone and further oxidation of the latter

Table 1. Characterization of the electrodeposited Au nanoparticles at different Au_{nano}–HOPG electrodes

Substrate[a]	Amount of deposited Au nanoparticles[b] / $\mu g\,cm^{-2}$	Real surface area[c] / $10^{-1}\,cm^2$	Specific surface area / $10^4\,cm^2\,g^{-1}$	Particle size distribution / nm	Average particle density[d] / particle μm^{-2}
1	24.8	3.3	7.2	150–600	4
2	88.8	8.7	4.9	70–150	45

[a] Untreated (1) and electro-oxidized (2) HOPG electrodes. [b] As calculated from the *i–t* curves measured during the potential-step electrodeposition. [c] As estimated from the charge consumed during the reduction of the surface oxide monolayer of Au (peak at ca. −0.87 V vs Ag|AgCl|KCl(sat) in Figure (1, left) using a reported value of ($400\,\mu C\,cm^{-2}$).[18] [d] The number of particles per $1\,\mu m^2$, as estimated from an area of ca. $30\,\mu m^2$.

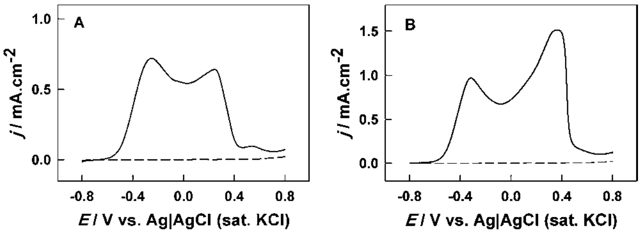

Figure 2. Voltammetric curves of glucose oxidation in an N_2-saturated (10 mM glucose + 0.1 M NaOH) solution at **(A)** untreated and **(B)** pretreated bare HOPG (dashed line) and Au_{nano}–HOPG (solid line) electrodes. Potential scan rate: $50\,mV\,s^{-1}$.

at more positive potentials, respectively.[1–3] Further interesting catalytic activity was obtained when the HOPG electrodes were subjected to an electrochemical oxidative pretreatment prior to the electrodeposition of Au nanoparticles, and results are displayed in Figure 2B.

By comparing this behavior to that observed at an untreated modified HOPG electrode, one can depict the following main features: (a) An interesting peak current increase of around ca. 50% for glucose oxidation and it nearly tripled for the further gluconolactone oxidation and (b) an interesting negative shift of the oxidation potential of glucose: the starting of current flow shifted from ca. −0.60 to −0.67 V and, accordingly, the oxidation peak potential shifted from ca. −0.26 to −0.32 V at (Au_{nano}–HOPG) in the case of untreated and electro-oxidized HOPG electrodes, respectively. A most probable explanation of this interesting catalytic activity would be: (a) The significant increase both in the real surface area and in the average density of the electrodeposited Au nanoparticles in the case of electro-oxidized HOPG electrodes (cf. Table 1) enabling the formation of more active sites for glucose oxidation (i.e. Au–OH),[1–3] and (b) the significant change in the degree of crystallinity of the Au nanoparticles as a consequence of the electro-oxidative pretreatment of the HOPG electrode. In fact, a relative enrichment in the Au(200) facet at the expense of Au(111) was reported for similar electrodes as clearly evidenced with the XRD data,[17] and the prepared Au_{nano}–HOPG electrode in the case of electro-oxidized HOPG showed an Au(100)-like electrocatalytic activity as concluded from ORR investigation (i.e. Figure 1, left) in good agreement with that in the literature.[15] This explanation is further strengthened with the previously reported study at single crystal electrodes,[1–3] where the peak potential for glucose oxidation shifted from ca. −0.26 to −0.3 V at Au(111) and Au(100) single crystal electrodes, respectively, as a consequence of a negative shift in the point of zero charge (pzc).

To the best of our knowledge, (Au_{nano}–HOPG) electrodes were used for the first time for the electrocatalytic oxidation of glucose and it was found that an electro-oxidative pretreatment of HOPG electrode caused the enrichment in Au(100) facets of the electrodeposited Au nanoparticles, which resulted in clear catalytic effect on the oxidation of glucose to gluconolactone in an alkaline solution. It is noteworthy that this behavior is typical of HOPG substrate as concluded from similar work, currently under way, for other carbon-based electrodes.

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