

Short Communication

Size-controlled Electrocatalysis of Glucose Oxidation in an Alkaline Solution at AuNPS Electrodeposited onto Glassy Carbon Electrodes

Sami BEN AOUN*

Department of Chemistry, Faculty of Science, Taibah University, PO. Box 30002 Al-Madinah Al-Munawarah, KSA

*E-mail: sbenaoun@taibahu.edu.sa; Tel. +966-590-900-727 ; Fax. +966-4847-0235

Received: 20 May 2013 / *Accepted:* 7 June 2013 / *Published:* 1 August 2013

The cyclic voltammetric investigation of the electrocatalytic oxidation of glucose in a (5 mM glucose + 0.1 M NaOH) solution has been conducted at Au nanoparticle-modified glassy carbon electrodes. In contrast to the absence of any oxidative current at bare unmodified electrodes, the effective electrocatalytic oxidation of glucose was observed upon the electrodeposition of gold nanoparticles onto the glassy carbon electrode surface. Two distinct oxidation peaks were observed that were attributed to the oxidation of glucose to gluconolactone which in turn was further oxidized at more positive potentials. An interesting size-dependence of the obtained catalytic activities was observed, affecting both the oxidation peak potential and current densities and the best catalyst was shown to be 18 nm Au-GCE with an oxidation peak potential of ca. -0.3 V vs. Ag|AgCl (Sat. KCl).

Keywords: Gold nanoparticles, Glucose Oxidation, Glassy Carbon Electrode, Electrocatalysis.

1. INTRODUCTION

A great deal of interest has been paid to the electrocatalytic oxidation of glucose at various substrates, including gold [1-12] and carbon [12-19]. Its importance lies on the various applications of such studies including, but not limited to, waste water treatment, blood sugar sensing and fuel cells. It has been shown that the under-potential deposition of metal ad-atoms onto gold electrodes had a positive impact on the observed catalytic activities [1, 2, 10, 11] where effective oxidation of glucose at relatively negative potentials was observed at Ag-UPD Au single crystal electrodes. Similar behavior was shown at nanoparticle-modified electrodes [13, 14, 20].

Gold nanoparticles (AuNPS) were mainly reported to be either chemically prepared via the reduction of aqueous solution of the chloro-metallate anion [20-23] or electrochemically deposited onto the substrate material [24-29].

In a recent work, we reported a very interesting electrocatalysis of glucose in an alkaline solution at chemically synthesized gold nanoparticles via a two-phase (water-toluene) reduction of AuCl_4^- by (NaBH_4) in the presence of decanethiol (DT)[20]. In the present work, we will report the study of gold nanoparticles (AuNPS) electrochemically deposited onto glassy carbon electrode (GCE) towards the electrocatalytic oxidation of glucose in a 0.1 M NaOH solution. We will show the AuNPS size-controlled catalytic activities investigated by cyclic voltammetry.

2. EXPERIMENTAL

2.1. Chemicals and Electrodes:

All solutions in the present study were prepared using ultra pure water (Milli-Q 18.2 M Ω .cm, Millipore System Inc.). D-glucose obtained from Wako Pure Chemical Industries, Ltd. NaOH and H_2SO_4 (ultra pure grade, Kanto Chemical Co., Inc.) were used as received.

Glassy Carbon Electrodes (GCE) having a diameter ($\phi = 6$ mm) were purchased from Nikko Keisoku, Japan and served as working electrodes. An Ag|AgCl|KCl(sat) electrode and a Pt-plate were used as reference and counter electrodes, respectively.

All electrochemical measurements were conducted using a CV-50 W voltammetric analyzer (Bioanalytical Systems, Inc.) in a conventional three-electrode electrochemical cell having a fritted glass-separated reference electrode's compartment. The prepared solutions were first purged with high-purity nitrogen for at least 20 minutes before the experiments, and during measurements the nitrogen flow was uninterrupted.

All glassware used in the present work were duly cleansed then further decontaminated in boiling nitric acid (30% v/v) and rinsed thoroughly with Milli-Q water.

2.2. Electrochemical deposition of gold nanoparticles

Au nanoparticles were electrodeposited onto GC electrodes from a (0.5 M H_2SO_4 + 0.2 mM HAuCl_4) solution by applying a 5 s potential step (unless specified otherwise) from 1.1 V to (0.4 V, 0.2 V and 0 V) leading, respectively, to the deposition of nanoparticles of (34 nm, 24 nm and 18 nm) diameter [24, 25].

Prior to each experiment, the GC electrode was polished with a 0.1 μm alumina polishing suspension (Baikalox®) on a polishing cloth (Bioanalytical Systems, Inc.) to a mirror-like finish and then cleaned by sonication for 20 minutes in Milli-Q water.

Upon deposition of Au nanoparticles, the electrode was immediately taken out of the solution, rinsed thoroughly with Milli-Q water then transferred to another electrochemical cell filled with a

(5mM glucose + 0.1 M NaOH) solution for voltammetric measurements. The potential was then scanned between -0.8 V to 0.8 V vs. Ag|AgCl (Sat. KCl) at a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$.

All current densities were calculated with respect to the apparent geometric surface area of the working electrode and all potentials were reported with reference to Ag|AgCl (Sat. KCl) electrode. The Pt-plate counter electrode was cleaned and freshly annealed in a hydrogen flame prior to each measurement. And all experiments were conducted at room temperature.

3. RESULTS AND DISCUSSION

The cyclic voltammetric results of a bare GC electrode in a (5 mM glucose + 0.1 M NaOH) solution didn't show, as expected, any oxidation peak for glucose in the potential of interest, in the present work conditions.

Results are displayed in figure 1, showing the absence of any significant current flow except for the potential range of the oxidation of the electrode surface itself confirming that carbon substrate is totally catalytically inactive towards glucose oxidation.

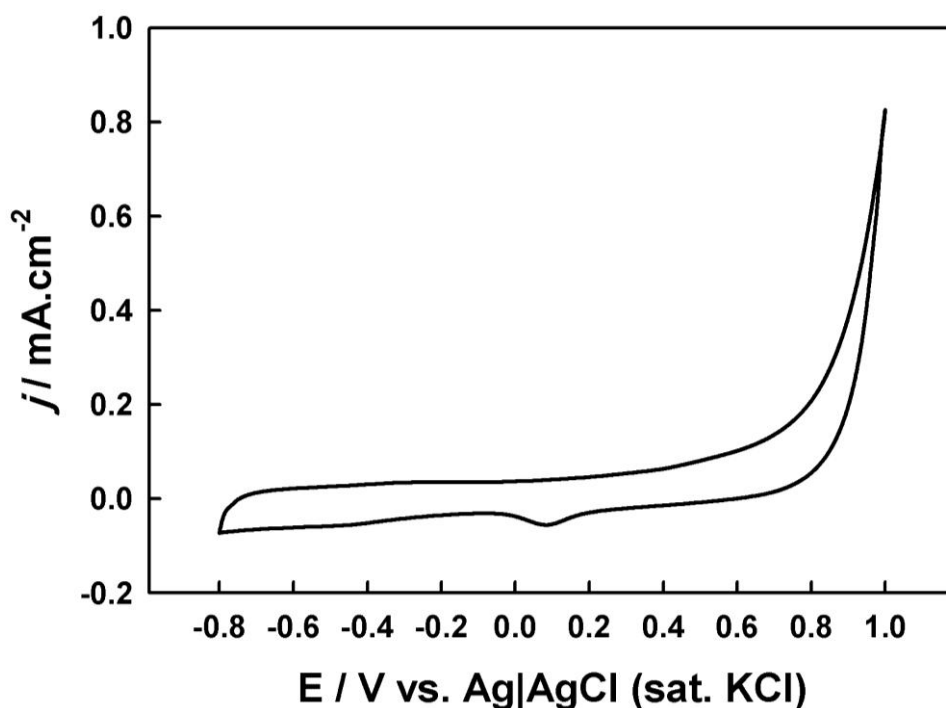


Figure 1. Cyclic voltammogram of GC electrode in a (5 mM glucose + 0.1 M NaOH) solution at a $50 \text{ mV}\cdot\text{s}^{-1}$ scan rate.

Interestingly, a minute amount of gold nanoparticles, prepared via a 5 s potential step as described in the experimental section, showed an extraordinary catalytic effect for glucose oxidation as displayed in figure 2.

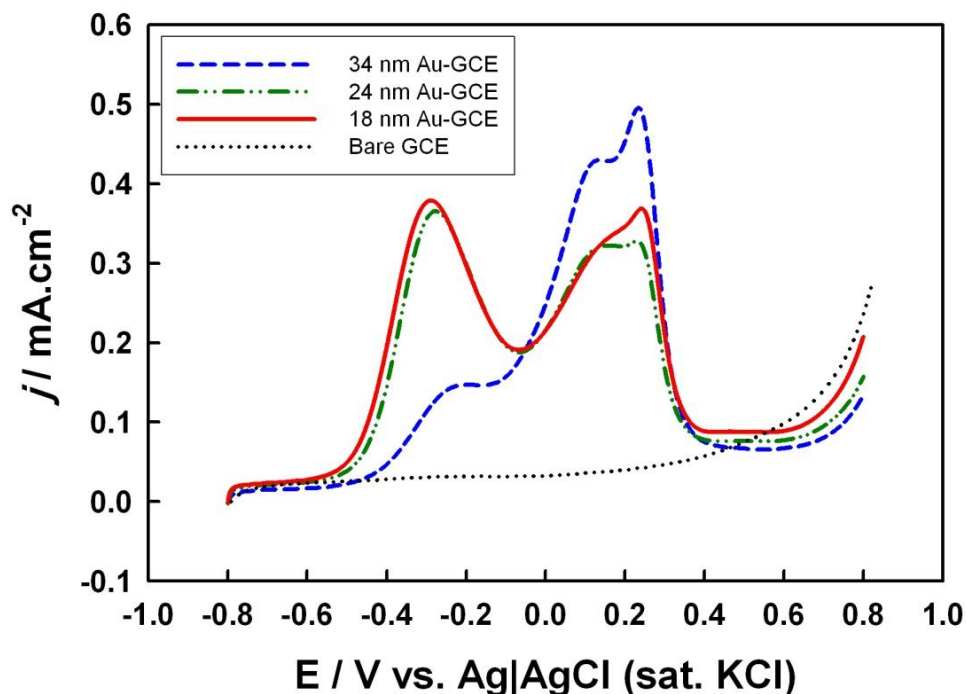
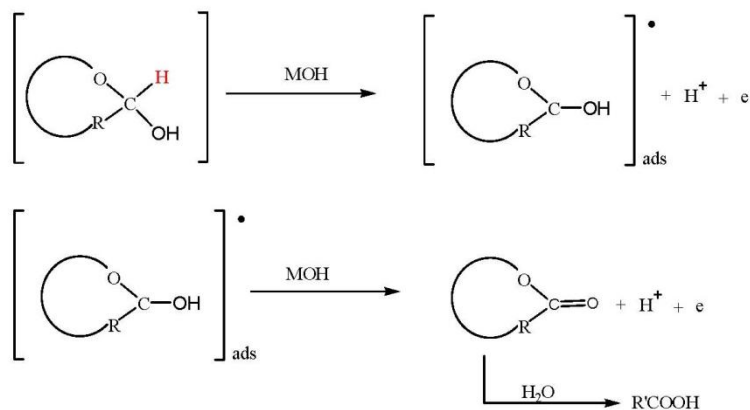


Figure 2. Voltammetric curves of glucose oxidation in a (5 mM glucose + 0.1 M NaOH) solution at bare and Au_{nano}-GC electrodes. Scan rate: 50 mV s⁻¹.

As shown, the smaller is the particle size, the better is the catalytic effect expressed as a steady increase in the oxidation peak current densities and a negative shift of the peak potential values in the order 34 nm Au-GCE < 24 nm Au-GCE < 18 nm Au-GCE. The most probable explanation would be the better dispersion of smaller nanoparticles onto the GC electrodes surface as reported by Mc.Dermott et. al. [24] where nanoparticles of 34, 24 and 18 nm in diameter have a particle density of 28, 54 and 89 particles/μm⁻², respectively. Several reports of size-controlled electrocatalysis are also found in literature [26, 30-32].

As displayed in figure2, at 18nm Au-GCE electrode, the oxidation peak of glucose occurred at ca. -0.3 V vs. Ag|AgCl (Sat. KCl) followed by the further oxidation of gluconolactone at more positive potentials around ca. 0.2 V vs. Ag|AgCl (Sat. KCl) according to the following scheme [1]:



Scheme 1. Oxidation mechanism of glucose at gold electrodes (M = Au) at potentials more negative than 0 V vs. Ag|AgCl. MOH denotes the active site on the electrode surface.

In order to possibly improve the catalytic activity of the prepared electrodes, we tried to change the conditions of the potential step electrodeposition by varying the time between 25 and 200 seconds while keeping the same potential range (i.e. stepping the potential from 1.1 V to 0 V).

Results for glucose oxidation at the as-prepared Au_{nano}-GCE electrodes are displayed in figure 3 showing that with increasing deposition time, a slight increase in the oxidation peak current is observed accompanied with a slight negative shift of the oxidation peak potential.

Interestingly, a 200 seconds deposition was enough to prepare a sufficiently highly active electrode surface for glucose oxidation compared with our previously reported Au_{2nm}-PFC electrodes [20] with an oxidation peak potential at ca. -0.37 V, without the need to fully cover the electrode surface with Au nanoparticles (i.e. as in the case of modified PFC electrodes) which means, in other words, that far less gold material is utilized.

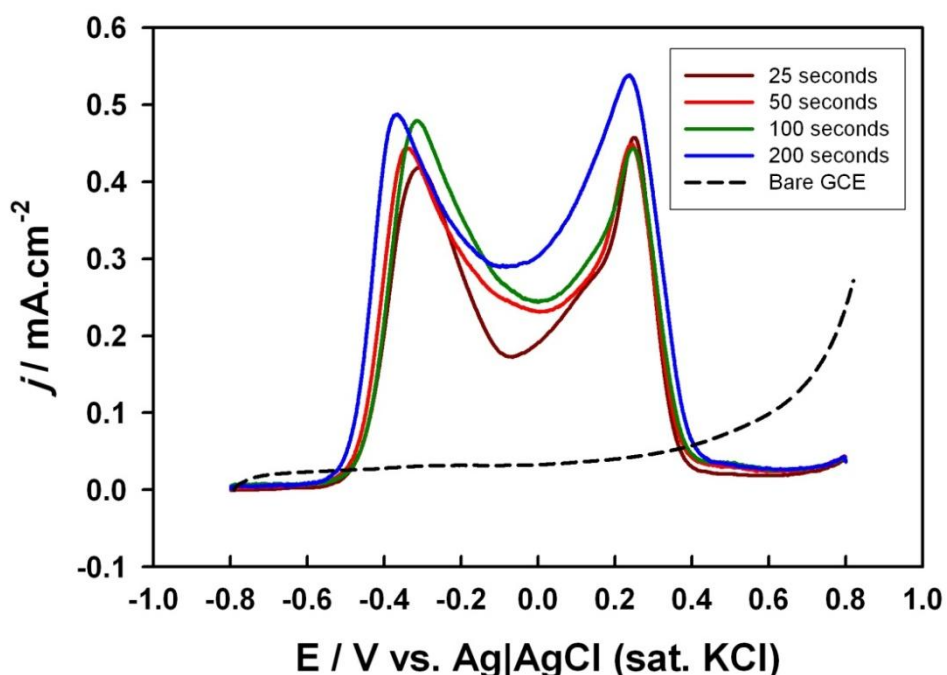


Figure 3. Voltammetric curves of glucose oxidation in a (5 mM glucose + 0.1 M NaOH) solution at bare and Au_{nano}-GC electrodes. Scan rate: 50 mV s⁻¹.

4. CONCLUSION

AuNPS electrodeposited onto glassy carbon electrodes showed a very interesting catalytic activity for glucose oxidation in alkaline media.

The obtained results in the present study can be summarized as follows:

- A tunable, size-controlled catalytic activity for the oxidation of glucose in alkaline media was successfully achieved.
- The highest catalytic activity, in the present work conditions, was observed at the as-prepared 18 nm Au-GCE electrodes.

- A further improvement was observed as a result of deposition time-dependence investigation.
- A nicely comparable catalytic activity to a previously reported AuNPS-PFC catalyst was obtained upon a brief electrodeposition of as short as 200 seconds.
- The prepared catalyst showed a higher cost-effectiveness compared with a similar catalyst reported earlier.

ACKNOWLEDGMENT

S. Ben Aoun acknowledges the partial financial support to this work from the Deanship of Scientific Research, Taibah Univeristy (Project No. 658/432).

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