

Electrocatalytic Oxidation of D-Glucose Using a Cd ad-atom-Modified Au(111) Electrode in Alkaline Solution

Zekerya DURSUN^{1,*}, Sami BEN AOUN², Isao TANIGUCHI²

¹*Department of Chemistry Faculty of Science, Ege University, 35100 Bornova, İzmir-TURKEY
e-mail: zekerya.dursun@ege.edu.tr*

²*Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University,
2-39-1, Kurokami, Kumamoto 860-8555, JAPAN
e-mail: zekerya.dursun@ege.edu.tr*

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Au(111) single crystal electrodes were modified by underpotential deposition (UPD) of Cd ad-atoms with different coverages, which were used for the electrocatalytic oxidation of glucose in alkaline media. The catalytic activity of the electrodes was dependent on how the Cd ad-atoms covered the surface. Under the presented experimental conditions the monolayer (ML) Cd ad-atom-covered Au(111) electrode had the best catalytic activity on D-glucose oxidation, in terms of both potential shifts and peak current increases, as compared to the 0.11, 0.5, and 2 ML covered and bare Au(111) electrodes. Double layer capacity measurements revealed that the shifts of the potential of zero charge (pzc) were dependent on the different surface coverages of the Cd ad-atom-modified Au(111) electrodes, which is in good agreement with cyclic voltammetric results, as the current flow was initiated for glucose oxidation after a slightly more positive potential of pzc in all Cd ad-atom-modified Au(111) and bare Au(111) electrodes.

Key Words: Cadmium, UPD, D-glucose fuel cells, double layer capacity, single crystal gold electrode.

Introduction

The underpotential deposition (UPD) of ad-atoms (M) on a foreign metal substrate (S) as the sub-monolayer/monolayer (ML) at more positive potential than the reversible Nernst potential has received considerable attention.^{1–3} UPD occurs when the M-S interaction is stronger than the M-M interaction. The deposition potential of the metal on the electrode surface depends on the nature of the substrate and on the adsorption of the metal ions.⁴ Such phenomena allow for the precise and reproducible control of the surface coverage-dependent properties of the metal ad-atom structure and its electronic properties. The

*Corresponding author

study of UPD processes offers additional information about the mechanism of a number of electrochemical phenomena, such as adsorption, charge transfer, surface diffusion, crystal nucleation, growth, and double layer changes.⁵ The deposition of ad-atoms as a monolayer onto the surface of electrodes can improve electrocatalytic activity, selectivity, and corrosion stability. Since UPD can change the surface properties of a metal substrate, compared to both the metal substrate and isolated bulk deposited metal, surfaces prepared by UPD have been used for the electrocatalytic reaction of many compounds, such as glucose,^{6–10} methanol,^{11,13} carbon monoxide,^{15–17} formic acid,¹⁸ formaldehyde,¹⁹ nitrate,²⁰ and oxygen.^{21,22} Among these compounds, the electrochemical oxidation of glucose in aqueous solution plays an important role in many areas, such as blood sugar measurement in medical applications, and in cardiac pacemakers and glucose-oxygen fuel cells. A gold electrode is not a good catalyst in acidic solution, but the opposite behavior is observed in alkaline solution, especially when single crystal gold electrodes are used.²³ We are interested in fuel cell applications of the electrocatalytic oxidation of sugars in alkaline media on different ad-atom-modified single crystal gold surfaces. In our previous study the effect of UPD on glucose oxidation was studied using silver ad-atoms on Au(111) and it was observed that a 1/3 ML Ag ad-atom-modified Au(111) electrode demonstrated better electrocatalytic activity towards glucose oxidation in alkaline solution. As a result, the activity of the electrode was found to be strongly dependent on the coverage of the silver adlayer on the Au(111) surface.¹⁰ In the present study the effect of Cd ad-atom-modified Au(111) electrodes on the electrocatalytic oxidation of glucose was studied by cyclic voltammetry in alkaline solution. Double layer capacity measurements were carried out to clarify the ad-atom-modified Au(111) electrode surface conditions and to make a comparison to the bare Au(111) electrode. Details for each Cd ad-layer prepared in this study are presented and the electrocatalytic activity of each towards the oxidation of sugars was compared.

Experimental

Reagents and solutions

The solutions employed throughout the study were prepared using H₂SO₄ and NaOH (ultra-pure grade, Kanto Chemical Co., Inc.), D-glucose (Wako Pure Chemical Industries, Ltd), and ultra-pure water (Milli-Q 18.2 MΩg cm, Millipore system). CdSO₄(cadmium sulfate/water (3/8), 99.9%) was used for UPD onto Au(111) single crystal electrodes.

Gold single crystals were prepared by the so-called flame-annealing quenching method developed by Clavilier et al.²⁴ The crystallographic axes of the crystal were determined by the laser beam reflection from Au(111) surfaces and then the crystals were embedded in resin for cutting. The surfaces were exposed to mechanical polishing with finer grades of alumina paste. In order to remove mechanical damage from the polished surfaces, the single crystals were annealed at 950 °C for at least 12 h in an electric furnace. Finally, the electrode was annealed in a hydrogen flame; after cooling in a hydrogen gas stream, it was quickly dipped into ultra-pure water saturated with hydrogen. Contact of the working electrode with solution was carried out by the meniscus method in order to contact only the cut plane during the measurement of cyclic voltammograms. The single crystal Au(111) electrode surfaces were controlled by measuring the cyclic voltammograms in a 0.1 M H₂SO₄ solution. A 3-electrode-containing cell was utilized for preparation of Cd ad-atoms, the cyclic voltammetric measurements of D-glucose, and the blank 0.1 M NaOH solutions. Either a platinum or Ag/AgCl electrode was used as a reference electrode, and a platinum wire or Pt-Plate was used as a counter electrode. Cyclic voltammetry measurements were carried out using either a PS-06

manual polarization unit (Toho Giken, Japan) or a CV-50 W voltammetric analyzer (Bioanalytical Systems, Inc.). The cadmium UPD gold electrodes were prepared from

1 mM CdSO₄ in 0.1 M H₂SO₄ solution, and the UPD process was conducted by starting the scan immediately after immersion of the gold electrode at ca. 0.0 V (vs. Pt-plate) with a scan rate of 5 mV s⁻¹. Scanning was stopped with the deposition of 0.11 ML, 0.5 ML, 1.0 ML, and 2 ML of Cd ad-atoms forming at ca. -0.69 V, -1.02 V, -1.38, and -1.47 V vs. Pt-plate, respectively. All of the ad-atom-modified electrodes prepared were rinsed thoroughly with ultra-pure water (Milli-Q 18.2 MΩ cm, Millipore System Inc.) prior to transfer into another electrochemical cell that contained either glucose solution or 0.1 M NaOH blank solution. Cyclic voltammograms were measured at a scan rate of 50 mV s⁻¹ with Ag|AgCl (sat. KCl) and Pt-plate used as reference and counter electrodes, respectively. An Echochemie AUTOLAB PGSTAT 30 frequency response analyzer system was employed for double layer capacity measurements.

Results and Discussion

Preparation of Cd ad-atom-modified Au(111) and Application to D-glucose Oxidation

The cyclic voltammogram of the Au(111) single crystal electrode in 1 mM CdSO₄ + 0.1 M H₂SO₄ solution is shown in Figure 1. Cyclic voltammograms in the potential range of 0.0 V to -1.4 V were in good agreement with voltammograms reported by other groups^{3,25,26}. Peaks were observed at -0.69 V, -1.02 V, and 1.38 V vs. Pt-plate, with surface coverages of 0.11, 0.5, and 1 ML, respectively. Nonetheless, we observed another deposition peak at -1.47 V, which was less than 2 ML [24] for the UPD of Cd ad-atoms. The effect of the Cd ad-atom-modified Au(111) electrode on D-glucose oxidation was studied with different Cd ad-atom coverages. Figure 2 shows the electrochemical oxidation of D-glucose at the bare and Cd ad-atom-modified Au(111) electrodes. The current flow for glucose oxidation started at ca. -0.55 V (vs. Ag|AgCl) for both the bare and the Cd ad-atom-modified Au(111) electrodes. A small negative peak potential shift was observed in the 0.11 and 0.5 ML Cd ad-atom-modified Au(111) electrodes, as compared to the bare Au(111) electrode. The double layer capacity of both the bare and Cd-deposited Au(111) electrodes revealed that the potential of zero charge (pzc) shifted to slightly more negative potentials, from -0.60 to -0.63 and from -0.66 V (vs. Ag|AgCl) for 0.11 and 0.5 ML Cd coverages, respectively (Figure 3). The results indicated that the adsorption of OH⁻ ions on the bare Au(111) and Cd ad-atom-modified Au(111) electrodes to form AuOH species started at almost the same potentials.

In terms of the glucose oxidation potential, 1 ML and 2 ML Cd ad-atoms caused more positive effects. On the other hand, the oxidation peak current notably increased with both 1 and 2 ML Cd ad-atoms. However, the oxidation peak current of glucose at 2 ML Cd ad-atoms was still slightly higher than that of the bare Au(111) electrode, but was slightly less than in the case of the 1 ML Cd ad-layer. The current flow started at ca. -0.55 V for the bare electrode and this potential shifted to around -0.70 V (vs. Ag|AgCl) at the Cd-deposited Au(111) electrode, with 1ML and 2 ML coverages for D-glucose oxidation. The oxidation peak potential also shifted from ca. -0.26 V to ca. -0.40 V, vs. Ag|AgCl for both 1ML and 2 ML Cd coverages, respectively. A bulk deposition of Cd multi-layers was prepared to check the electrocatalytic activity of the Cd electrode. In this case, total inhibition of the catalytic activity of the Au(111) single crystal electrode surface for glucose oxidation was observed.

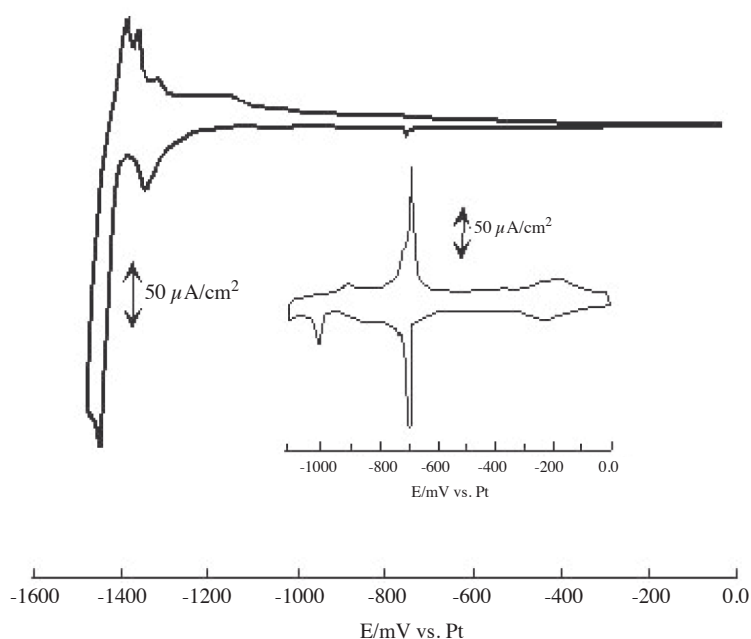


Figure 1. Cyclic voltammogram of an Au(111) electrode in 0.1 M H_2SO_4 + 1 mM CdSO_4 . Scan rate: 5 mV s^{-1} .

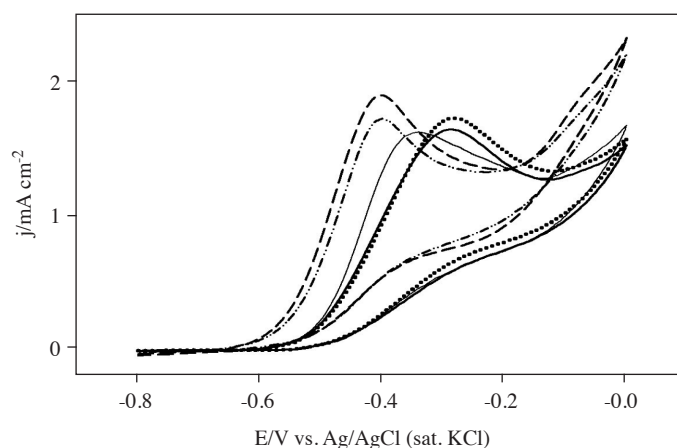


Figure 2. Cyclic voltammograms for glucose oxidation in a 10 mM glucose + 0.1 M NaOH solution at the Au(111) electrode (dotted line) and Au(111) electrodes deposited with Cd ad-atoms at -0.69 V (bold solid line), -1.02 V (solid line), -1.38 V (long dash line), and -1.47 V (dash dot-dot line), vs. Pt-plate. Scan rate: 50 mV s^{-1} .

In a previous study²⁷ in which the effect of UPD on glucose oxidation was studied using silver ad-atoms on Au(111), the 1/3 ML Ag ad-atom-modified Au(111) electrode, in which the metal surface coverage occurred via a layer-by-layer formation,²⁷ demonstrated better electrocatalytic activity towards glucose oxidation in alkaline solution.²⁷ In other words, after 1/3 ML layer deposition Au(111) catalytic activity increased. Normally, it is expected that 1 and 2 ML Cd ad-atom coverage on an Au(111) electrode would show either poor or no catalytic activity towards glucose oxidation. Because the Cd ad-atoms growing on the Au(111) surface were constructed as 2-dimensional islands instead of a layer-by-layer formation, this was not observed, leading to the higher catalytic activity towards glucose oxidation due to the existence of an uncovered Au surface among those islands. One other possibility is that Cd alloy formation may create

some defects on the Au(111) surface, based on experimental observation of a closed layer of Cd deposition in a UPD region where interfacial alloying was expected to appear.²⁶ The electrocatalytic activity of the Cd ad-atom-modified Au(111) electrode could also be explained by a change in the electrode surface charge after Cd deposition, allowing the formation of AuOH at more negative potentials on account of the Cd atoms being slightly more electropositively charged relative to Au on the surface. The best catalytic activity for glucose oxidation, therefore, was demonstrated by 1 and 2 ML Cd ad-atom coverages. To clarify the explanation, the double layer capacity measurements of 1 and 2 ML Cd-modified electrodes presented in Figure 3 show that the pzc shifted from ca. -0.60 V vs. Ag|AgCl in the case of the bare gold electrode to ca. -0.75 V vs. Ag|AgCl. As discussed above, a similar explanation can be given for 1 and 2 ML Cd ad-atom modified Au(111) surfaces. They enhanced the adsorption of OH^- on the electrode surface and this formation catalyzed D-glucose oxidation around -0.70 V. The slight increase in the peak current can be attributed to the increased AuOH population on the electrode surface.²⁸ A multilayer coverage Cd deposited on the Au(111) electrode did not show any catalytic activity of D-glucose at the studied potential range.

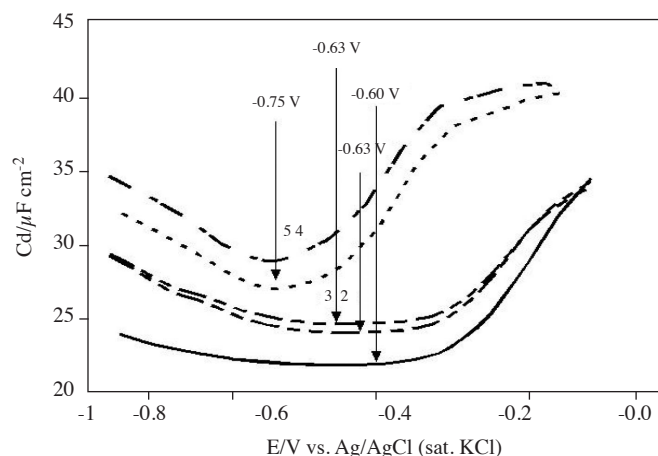


Figure 3. Double layer capacitance for 1) the Au(111) electrode, 2) 0.11 ML Cd-, 3) 0.5 ML Cd-, 4) 1 ML Cd-, and 5) 2 ML Cd-modified Au(111) electrodes in a 0.1 M NaOH solution.

Figure 4 shows a second current flow starting at ca. -50 and -170 mV vs. Ag|AgCl at both the bare and 1 ML Cd-deposited Au(111) electrodes, respectively, due to the oxidation of gluconolactone generated in the first oxidation peak. The oxidation peak potential shifted from 260 to 200 mV with the 1 ML Cd-deposited Au(111) electrode and a slight peak current decrease was observed. The oxidation reaction was suppressed on gold oxide and no poisoning of the Au(111) surface took place in the electrocatalytic oxidation of glucose, as observed with a Pt electrode.²⁸ Gluconolactone was also studied with the bare and Cd ad-atom modified Au(111) electrodes (Figure 5). The 1 ML Cd-deposited Au(111) electrode demonstrated better catalytic activity on the oxidation peak potential than the bare electrode. The peak potential was slightly shifted to a negative direction for the second oxidation peak of glucose because the pzc shifted to more negative potentials; at those potentials 1 ML deposition induced more AuOH formation on the Au surface. After the second oxidation peak, the current was suddenly decreased, as the higher Au-oxides (Au_2O_3) caused surface passivation in the bare and Cd-deposited Au(111) electrodes, which was also observed with the Ag-deposited Au(111) electrode.²⁷

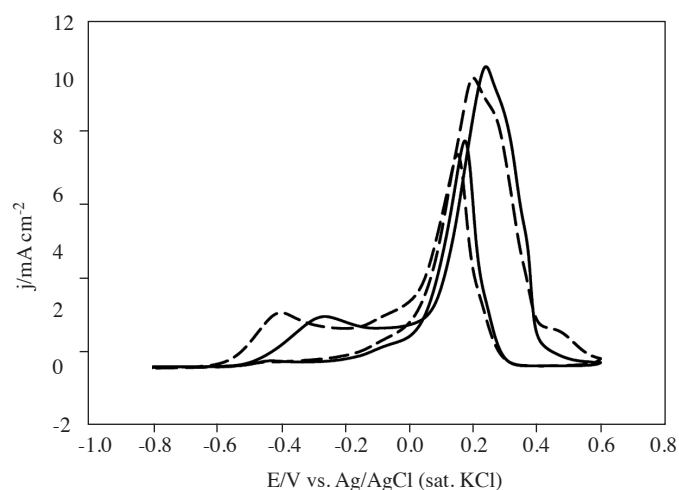


Figure 4. Voltammetric curves for oxidation of (a) 10 mM glucose in a 0.1 M NaOH solution at the Au(111) (solid lines) and the 1 ML Cd-modified Au(111) (dashed lines) electrodes. Scan rate: 50 mV s^{-1} .

A similar catalytic effect was observed on glucose oxidation with the Cd-deposited Au(100) electrode (Figure 6), and glucose oxidation was observed at ca. -370 mV (vs. Ag|AgCl), which was more positive than in the case of the Cd-deposited Au(111) electrode. From the above results, the 1 ML Cd ad-atom-modified Au(111) electrode had the best catalytic activity, as compared to the bare Au(111), bare Au(100), and other Cd ad-atom-modified Au(100) electrodes.

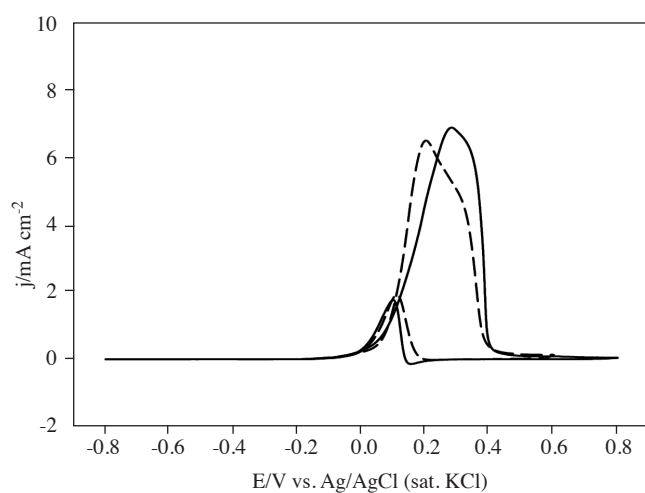


Figure 5. Voltammetric curves for oxidation of 10 mM gluconolactone in a 0.1 M NaOH solution at the Au(111) (solid lines) and the 1 ML Cd-modified Au(111) (dashed lines) electrodes. Scan rate: 50 mV s^{-1} .

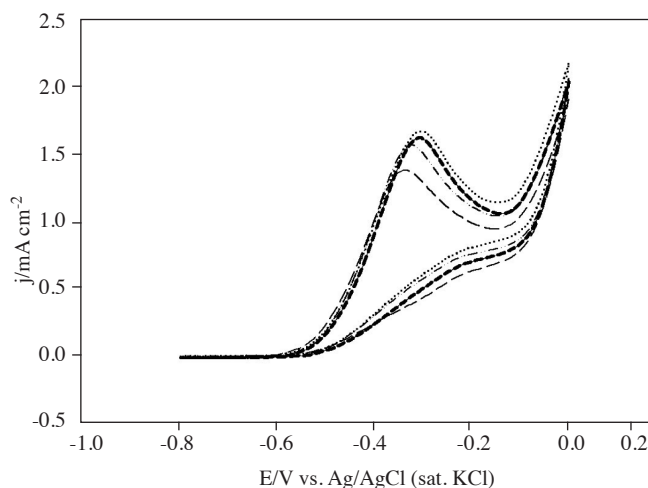


Figure 6. Cyclic voltammograms for glucose oxidation in a 10 mM glucose + 0.1 M NaOH solution at the Au(100) electrode (dotted line) and the Au(100) electrodes deposited with Cd ad-atoms at 0.2 ML (bold dash line), 0.5 ML (dash dot dot line), and 1 ML (long dash line), vs. Pt-plate. Scan rate: 50 mV s⁻¹.

Conclusion

A single crystal Au(111) electrode had activity towards D-glucose oxidation to gluconolactone in 0.1 M NaOH solution, and the activity increased after the Au surface was modified with Cd ad-atoms. The catalytic effect on the oxidation peak potential and peak current were dependent upon the surface coverage. The Cd ad-atom-modified Au(111) electrodes showed a positive catalytic effect on D-glucose oxidation, particularly with 1 and 2 ML coverage. The electrocatalytic oxidation of glucose was also studied with Cd ad-atom-modified Au(100) electrodes, and these electrodes also showed catalytic activity towards the oxidation of glucose. Nonetheless, the catalytic activity of Cd ad-atom-modified Au(100) electrodes was less than that of Cd ad-atom-modified Au(111) electrodes, in terms of oxidation potentials.

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