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Layer-by-layer assembly of 1,4-diaminoanthraquinone and glucose oxidase

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Abstract

Electrochemical sensing of glucose on a gold electrode modified by the sequential incorporation of the mediator, 1,4-diaminoanthraquinone (DAAQ) and the enzyme, glucose oxidase (GOD), through covalent linkage onto a self-assembled monolayer configuration is described in this paper. It has been shown that two alternate layers of enzyme and mediator could be formed on the surface. The modified electrode is catalytic towards glucose oxidation. The catalytic response becomes more well behaved with the two-layer configuration and it is demonstrated by the amperometric experiments. The results also indicated that the mediator catalyzes the oxidation of H_2O_2, and also it establishes a weak electrical communication between the enzyme and the electrode surface. The results present the scope for the fabrication of membrane-free biosensors of ultra-thin dimensions.

Keywords: Electrochemical sensing; 1,4-Diaminoanthraquinone; Glucose oxidase

1. Introduction

Development of amperometric biosensors using redox enzymes as biocatalysts has been an active field of research for the past two or three decades [1,2]. Glucose oxidase (GOD), a very common enzyme of oxidoreductase category, catalyzes the oxidation of glucose highly selective among the aldoses and produces H_2O_2 by a subsequent reaction with the dissolved oxygen according to the following reactions:

$$\text{GOD-FAD} + \text{glucose} \rightarrow \text{GOD-FADH}_2 + \text{gluconolactone} \quad (1)$$

$$\text{GOD-FADH}_2 + \text{O}_2 \rightarrow \text{GOD-FAD} + \text{H}_2\text{O}_2 \quad (2)$$

The H_2O_2 produced is detected amperometrically and the resulting current is then related to the concentration of glucose [3]. However, the electrochemical oxidation of H_2O_2 requires an electrode potential that is highly anodic to the reversible potential of the GOD-FAD/$FADH_2$ couple. Further, the oxidation of H_2O_2 takes place more readily on Pt than on gold surface [4]. To overcome this poor sensitivity of gold electrode for H_2O_2 measurement, mediators are usually employed [5].

Alternatively, small diffusing redox mediators, which enable facile electrical communication between the gold electrode and the enzyme [6–9] were employed. In such electrodes, reaction (1) is followed by (3) as below.

$$\text{GOD-FADH}_2 + 2\text{MED}_{ox} \rightarrow \text{GOD-FAD} + 2\text{MED}_{red} + 2\text{H}^+ \quad (3)$$

The reduced form of the mediator produced by the reaction (3) is immediately converted back to the oxidized form by electrooxidation on the electrode surface at potentials slightly positive of the formal potential of the mediator. However, in an oxygen-containing medium, the dissolved oxygen and the oxidized form of the mediator will compete with each other in regenerating the enzyme back to its oxidized form.

To fabricate an enzyme biosensor, it would be preferable to immobilize the electron transfer mediator and the enzyme onto the electrode surface. Mediators like quinones [10,11], ferrocenes [12–14], viologens [15] and Ru complexes [16] are commonly used. So far, enzyme biosensors have been developed with enzymes which have been either chemically modified with electron relays [17,18] or immobilized in the mediating polymers such as polypyrrole [19–22], polysilox-

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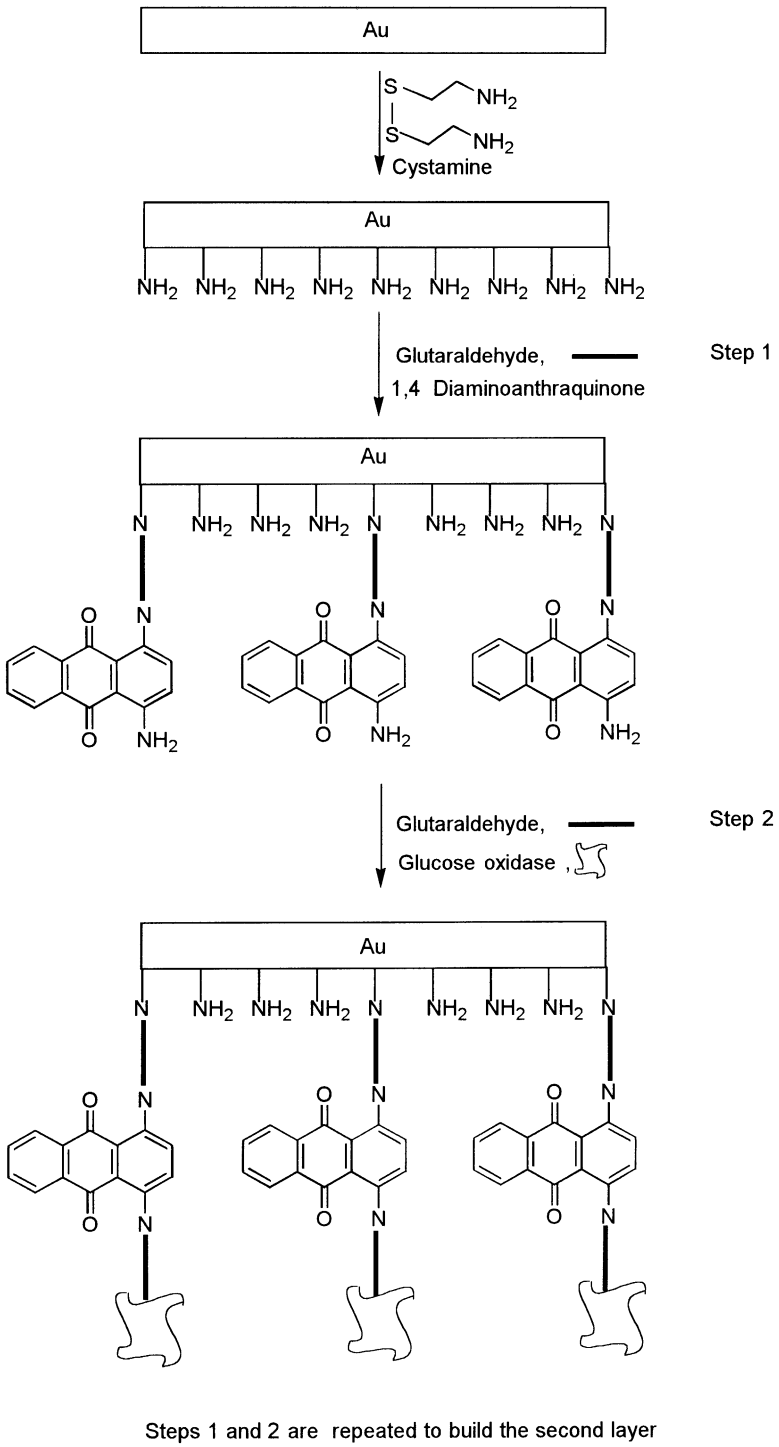
ane [23–25], polyethylene oxide and polyvinylpyridine [26,27].

Recently, self-assembly approach [28–31] is being employed for the immobilization of molecules to obtain chemically modified electrodes. This approach, which enables the formation of a monolayer of the chosen molecules on the electrode surface is very simple and is driven by the chemical affinity between the electrode material and the molecules to be immobilized. Based on this self-assembled monolayer (SAM) formation, electrodes have been chemically modified for functional applications such as molecular recognition [32,33], ion gating [34,35], molecular electronics [36], sensors [37], catalysis [38–40], understanding electron transfer characteristics [30,41–44], etc.



Scheme 1. Schematic description of the sequential modification of the gold electrode surface with a self-assembled monolayer of cystamine; cross-linking of 1,4-diaminoanthraquinone and then immobilization of GOD enzyme.

Very recently, the self-assembly technique is being exploited for the construction of amperometric enzyme biosensors [45–49]. The analytical advantages associated with SAM-based configurations are as follows.

1. The SAM approach is simple and elegant. It enables easy covalent binding of the enzyme and mediators onto the electrode surface.
2. Since the mediators are linked to the surface through covalent linkage, the problems of mediators diffusing away from the surface or mediator dissolution in the background electrolyte are not faced.
3. Nonfaradaic background currents are reduced to a great extent as the monolayer prevents close approach of the solvent molecules and ions to the electrode surface, thereby decreasing the double layer capacitance.
4. It is possible to covalently bind enzymes onto the electrode surfaces through SAMs and therefore membrane-free biosensors can be developed. The elimination of membrane in the configuration leads to rapid response time, free from diffusion problem of substrates or products through the enzyme membrane.

There are only few reports, which describe a combination of enzyme and mediator in the same SAM configuration [50–53]. In this work, attempt has been made to covalently link the mediator, 1,4-diaminoanthraquinone (DAAQ), and the enzyme GOD onto a SAM of cystamine through covalent linkage using glutaraldehyde (Scheme 1). It has been shown that two (mediator–enzyme) layers could be formed on the gold surface by this method. The results indicate that the mediator catalyzes the oxidation of H_2O_2, and also it establishes electrical communication between the enzyme and electrode surface. The investigations further present the scope for fabrication of membrane-free biosensors of ultra-thin dimensions with the molecules of the mediator and enzyme on the electrode surface linked alternately in a layer-by-layer configuration.

2. Experimental

2.1. Reagents and equipments

GOD (EC 1.1.3.4, Sigma, type VII), β-glucose (No. G-5250, Sigma), cystamine (Aldrich), glutaraldehyde (50% BDH) and 1,4-diaminoanthraquinone (Aldrich) were used. The electrolytic medium employed throughout the investigations was 0.1 M phosphate buffer at pH 7.0. The buffer solution was prepared from AR grade KH_2PO_4 and the pH was adjusted with NaOH solution, also made from the AR grade reagent.

A conventional three-electrode glass cell was used in the present studies. The working electrode was a polycrystalline gold disc electrode of 1.9 mm diameter, supplied by M/s BAS, USA. A platinum foil and a $Hg/Hg_2SO_4/H_2SO_4$ (MSE) served as the counter and the reference electrodes, respectively. All potential values in this study are referred to MSE. The cyclic voltammetric and the amperometric measurements were carried out using the Potentioscan (Wenking, Model POS 88) coupled to an *X-Y/t* Recorder (Rikadenki, Model RW 201-T).

2.2. Preparation of DAAQ modified electrode

Gold electrode was polished with alumina using different grades of emery paper, sonicated in distilled water and cleaned with *piranha* solution before modification. The cleaned electrode was dipped overnight in an ethanol solution of cystamine. Afterwards, the electrode was washed with ethanol and treated with an aqueous glutaraldehyde (5% (v/v)) solution for 1 h and then rinsed with water. Then the electrode is immersed in DAAQ solution in ethanol for 3 h. The electrode is washed with ethanol and then treated with GOD solution (1 mg ml^{-1} in buffer solution) for half-an-hour. The electrode is then washed with water, dried and tested for the response of glucose. The above procedure is repeated to yield another layer of DAAQ and GOD for obtaining layer-by-layer configuration.

The surface modification of the gold electrode based on SAM configuration is shown in the Scheme 1. The treatment of the gold electrode with cystamine results in the formation of a cystamine SAM through strong bonding of its sulfur center with the Au surface and leaving the terminal amino groups free for further functionalization. Accordingly, the amino tails of the cystamine SAM are linked to DAAQ through coupling reactions involving glutaraldehyde. The DAAQ-immobilized electrode surface was then treated again in the glutaraldehyde solution and then in the enzyme solution. A layer of GOD was incorporated onto Au/DAAQ electrode through covalent linkage using glutaraldehyde. The above procedure was repeated again to yield a second layer of the mediator and the enzyme. The modified electrodes were referred to as Au/DAAQ, Au/DAAQ/GOD(1) and Au/DAAQ/GOD(2) to denote the Au surfaces covered with a layer of mediator, one layer each of mediator and enzyme and two layers each of mediator and enzyme, respectively.

3. Results and discussions

Fig. 1 presents the cyclic voltammograms (CVs) of Au/DAAQ electrode in 0.1 M phosphate buffer (pH 7.0) at different scan rates. The surface-linked DAAQ exhibits a characteristic redox behavior. At a scan rate of 50 mV s^{-1}, the anodic peak potential (E_{pa}) and the cathodic peak potential (E_{pc}) occur at −220 and −280 mV, respectively, yielding a value of −250 mV for the formal potential of the DAAQ layer. The ΔE_p value was 60 mV. Observation of such ΔE_p values as against a theoretical value of 0 mV for surface-immobilized reversible redox species is not uncommon [53]. The surface coverage of DAAQ was

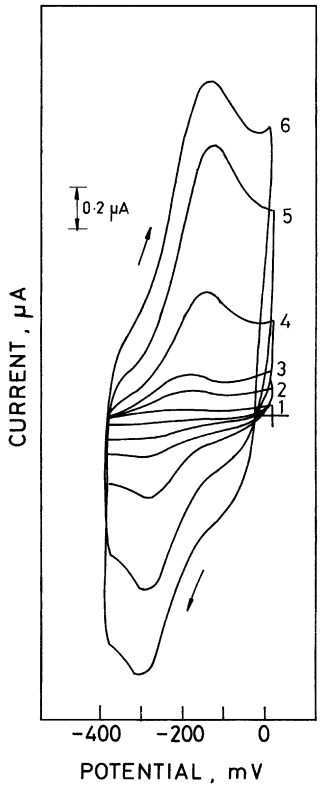


Fig. 1. Cyclic voltammograms showing the redox behavior of Au/DAAQ electrode in phosphate buffer (pH = 7.0; 0.1 M) at different scan rates: (1) $10\,mV\,s^{-1}$, (2) $50\,mV\,s^{-1}$, (3) $100\,mV\,s^{-1}$, (4) $250\,mV\,s^{-1}$, (5) $500\,mV\,s^{-1}$ and (6) $1000\,mV\,s^{-1}$.

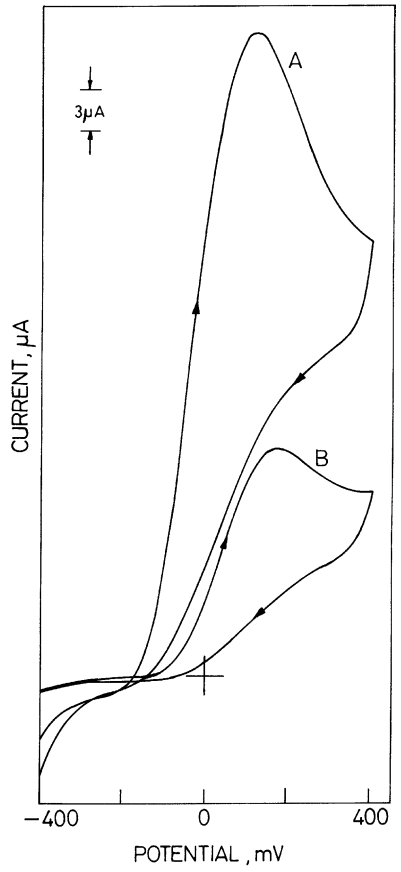


Fig. 2. Cyclic voltammetric response for 1.5 mM H_2O_2 in phosphate buffer (pH = 7.0; 0.1 M) at $5\,mV\,s^{-1}$ on Au/DAAQ (curve A) and bare Au electrodes (curve B).

estimated by the integration of charge under the anodic peaks at low scan rates. The charge was estimated to be $2.043\,\mu C\,cm^{-2}$ and this corresponds to a surface coverage of $1.056 \times 10^{-11}\,mol\,cm^{-2}$. This value of surface coverage approximates to a monolayer of redox species when compared with the data reported earlier [46,54].

It is known [3] that the glucose sensing on metal electrodes like Pt at bias potentials of 0.25 V (i.e., 0.6 V vs NCE) proceeds through anodic decomposition of H_2O_2. However, this reaction is found to be sluggish on a gold surface [55]. On the other hand, the CV and the amperometric investigations described here show that the modified-Au surface enables facile kinetics for the H_2O_2 decomposition reaction. In other words, the surface-immobilized DAAQ molecules are able to mediate and thereby catalyze the reaction. The observation receives a confirmatory support from the following experiments involving direct electrooxidation of H_2O_2. Fig. 2 (curve A) describes the CV recorded on Au/DAAQ electrode in phosphate buffer (pH 7.0) containing 1.5 mM H_2O_2 at $5\,mV\,s^{-1}$. The CV behavior under identical experimental conditions on bare Au is also presented (Fig. 2, curve B) for comparison. It is seen that DAAQ modification on Au could catalyze H_2O_2 decomposition by about three-fold increase which explains the observed ability of the Au/DAAQ/GOD electrodes for rapid sensing of glucose. Moreover, the potential at which the H_2O_2 decomposition reaction is catalyzed (Fig. 2, curve A) is identical with the potential value noticed for glucose sensing on the modified electrode (Fig. 5).

Generally, the presence of a mediator—be it immobilized on the surface or present in the solution—facilitates the electron transfer between the electrode and the FAD center of the enzyme. The foregoing results have shown the ability of the surface-immobilized DAAQ molecules to catalyze the H_2O_2 decomposition reaction. It will be interesting to see if the DAAQ molecules could also mediate electron transfer between the Au electrode and GOD. In other words, will there be glucose sensing in the absence of H_2O_2 decomposition reaction? To verify this, the buffer solution containing GOD and DAAQ was deoxygenated for about 2 h by purging the solution with pure nitrogen gas and then the voltammetric response was recorded in the presence of added glucose. The CV (Fig. 3) obtained for a 30 mM glucose concentration in 0.1 M phosphate buffer (pH 7.0) at $5\,mV\,s^{-1}$, shows the catalytic response involving glucose oxidation. Since the buffer solution has been deoxygenated, it is obvious that the glucose sensing at the electrode surface proceeds through direct mediation between the electrode

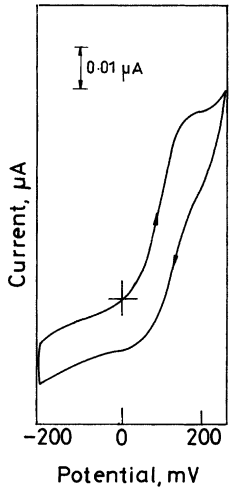


Fig. 3. Cyclic voltammogram depicting the catalytic oxidation of glucose (30 mM) in deoxygenated phosphate buffer (pH = 7.0; 0.1 M) containing GOD and DAAQ. Scan rate: 5 mV s^{-1}.

and the enzyme, according to reaction (3) described earlier. However, the potential (i.e., ∼100 mV) at which mediation occurs is considerably anodic to the formal potential of DAAQ molecules (−250 mV; cf. Fig. 1). It is likely that the relatively high orientation of the mediator molecules in the modified layers may offer steric hindrance in its communication with the enzyme moieties and thereby causes the observed anodic potential shift. Hence, only a weak link could be established by DAAQ with enzyme.

Since the mediator molecule DAAQ employed in the present study is found to catalyze the oxidation of H_2O_2 to a greater extent compared to currents produced in the deaerated conditions (due to weak electrical communication), we have employed the detection of H_2O_2 as the detection method for the estimation of glucose in nondeaerated solutions with the help of amperometry using the layer-by-layer configuration as described in Section 2.

Fig. 4 depicts the CV for the Au/DAAQ/GOD(1) electrode in 0.1 M phosphate (pH 7.0) buffer containing 30 mM of β-glucose at a scan rate of 5 mV s^{-1}. The glucose in solution is catalytically oxidized by GOD, which is sensed by the electrode with the help of the mediator layer.

Fig. 5 describes the CV response for the Au/DAAQ/GOD(2) in 0.1 M phosphate buffer containing 30 mM of β-glucose at a scan rate of 5 mV s^{-1}. From this, it can be seen that the catalytic current increases when compared to that obtained on Au/DAAQ/GOD(1) and the CV becomes well defined possibly due to the enhanced-catalytic activity resulting from the incorporation of more GOD. The mediator concentration also increases, with the increase in the number of layers. However, the rate determining step is the formation of H_2O_2 from the enzymatic reaction. Hence, the increase in the catalytic current is more likely to be due to increased concentration of GOD.

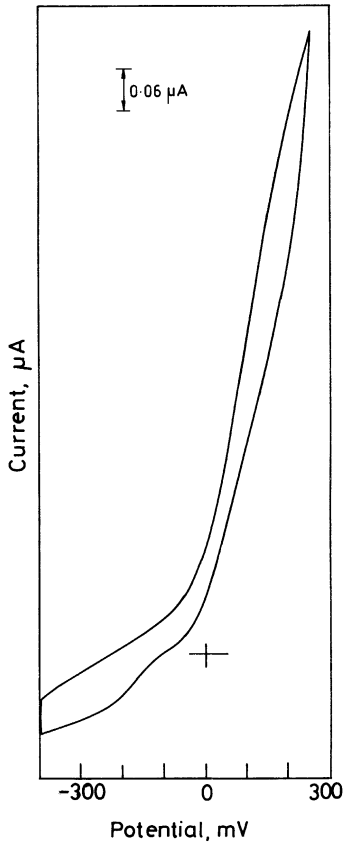


Fig. 4. Cyclic voltammogram for the Au/DAAQ/GOD(1) electrode in phosphate buffer (pH = 7.0; 0.1 M) containing 30 mM glucose at 5 mV s^{-1}.

The Au/DAAQ/GOD(1) and Au/DAAQ/GOD(2) electrodes were tested for their amperometric response to glucose in 0.1 M phosphate buffer medium at a bias potential of 0.25 V. The current observed on the Au/DAAQ/GOD(1)

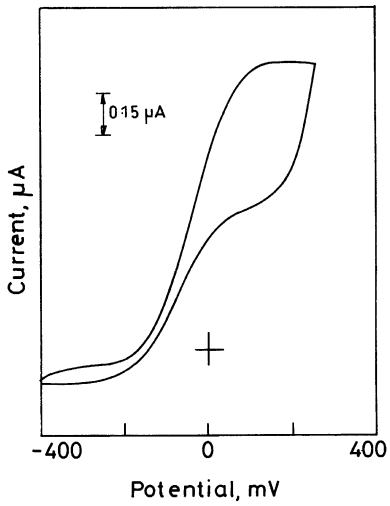


Fig. 5. Cyclic voltammogram for the Au/DAAQ/GOD(2) electrode in phosphate buffer (pH = 7.0; 0.1 M) containing 30 mM glucose at 5 mV s^{-1}.

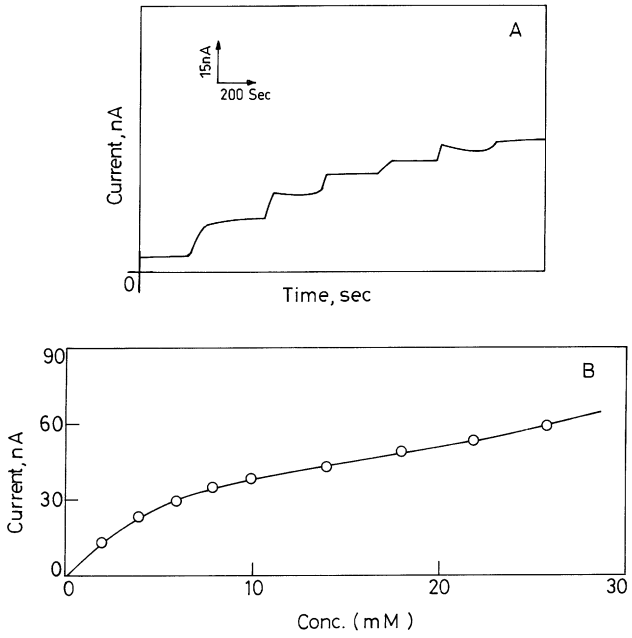


Fig. 6. (A) Amperometric response on Au/DAAQ/GOD(1) electrode for successive additions (2 mM each) of glucose bias potential: 250 mV. (B) Calibration plot based on the amperometric response in (A) above.

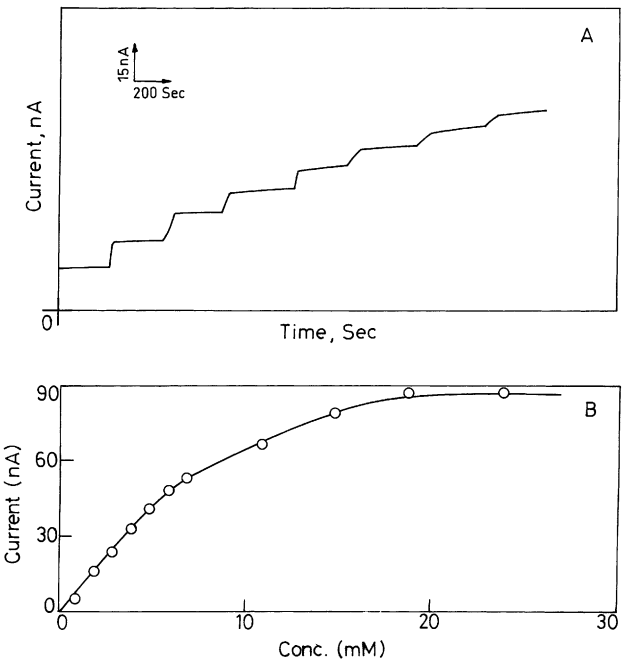


Fig. 7. (A) Amperometric response on Au/DAAQ/GOD(2) electrode for successive additions (2 mM each) of glucose bias potential: 250 mV. (B) Calibration plot based on the amperometric response in (A) above.

electrode increased after the addition of glucose and the steady state was achieved within 100 s (Fig. 6A). The amperometric currents were measured at different concentrations of glucose and the resulting calibration curve is presented in Fig. 6B. The calibration graph shows that the response varies linearly up to 4 mM and reaches saturation at high concentrations which is typical of an enzyme-catalyzed reaction. The amperometric response of the Au/DAAQ/GOD(2) electrode to different concentrations of glucose is depicted in Fig. 7A. The calibration curve obtained by plotting 'amperometric current vs glucose concentration' is presented in Fig. 7B. It could be observed that the amperometric currents obtained on Au/DAAQ/GOD(2) electrode are higher than those resulting from Au/DAAQ/GOD(1) electrode. The linear response range on the former electrode is 0–7 mM, while it is only up to 4 mM on the latter electrode. Moreover, the sensitivity is also higher on Au/DAAQ/GOD(2) than on the other as revealed by the higher slope values of 10.25 nA mM^{-1} on Au/DAAQ/GOD(2) as against 7.75 nA mM^{-1} on the other. This shows that the incorporation of a second layer of enzyme and the redox mediator does not detrimentally increase the resistivity of the film. On the other hand, the enhanced loading leads to improvement in catalytic activity, thereby yielding increased amperometric currents and enhanced slopes.

3.1. Calculation of Michaelis–Menten constants

Michaelis–Menten analysis of the biocatalyzed oxidation of glucose is carried out using Lineweaver Burk plots. Lineweaver Burk equation, a modified version of the Michaelis–Menten equation states that

$$\frac{1}{I_S} = \frac{K_m}{I_{max}} \times \frac{1}{[S]} + \frac{1}{I_{max}} \quad (4)$$

where I_S is the steady state current observed during the amperometric experiment, K_m the Michaelis–Menten constant, S the concentration in mM analyte of substrate (glucose), I_{max} the maximum steady state current that can be achieved from the system.

From the double reciprocal plot of $1/I_S$ vs $1/[S]$, the kinetic parameter K_m and I_{max} have been calculated.

Electrode	K_m (mM)	I_{max} (nA)
Au/DAAQ/GOD(1)	14	55
Au/DAAQ/GOD(2)	28	180

The values of K_m obtained are comparable to that of literature value [56]. The investigations show that increased loading of enzyme results in enhanced-catalytic activity and higher amperometric currents. This shows that the rate of the reaction at the enzyme electrode is not controlled by the diffusion of substrate (viz. glucose) within the SAM-modified film. However, substrate diffusion within the film controlling the reaction rate has been reported with relatively thicker films incorporated on the electrode surface [57].

4. Conclusion

The investigations have shown that DAAQ and GOD can be alternately linked to the gold electrode through a

self-assembled monolayer configuration through cystamine. It was possible to incorporate two alternate layers of enzyme and mediator onto the surface. The catalytic response becomes well behaved with two layer of configuration, and it is effectively shown in the amperometric experiments. We can further build up layers to enhance the performance. However, the possibility of good multilayer configuration depends on the ability to form covalent linkages with well-separated layers of mediators and enzymes. However, if we resort to linkage through electrostatic interactions, we can relatively build up the number of layers in an easy manner. The glucose sensing proceeds through the catalytic oxidation of H_2O_2 produced in the enzymatic reaction. Though gold is a poor catalyst for H_2O_2 electrooxidation, the presence of DAAQ on the electrode surface could make it electrocatalytic for the oxidation of H_2O_2. The scope for the preparation of membrane-free biosensors of ultra-thin dimensions is demonstrated in this work.

References

[1] G.S. Wilson, in: A.P.F. Turner, I. Karube, G.S. Wilson (Eds.), Biosensors: Fundamental and Applications, Oxford University Press, New York, 1987.
[2] A.E.G. Cass (Ed.), Biosensors: A Practical Approach, IRL press, Oxford, UK, 1990.
[3] G.G. Guilbault, G.J. Lubrano, J. Anal. Chim. Acta 64 (1973) 439.
[4] Y. Zhang, G.S. Wilson, J. Electroanal. Chem. 345 (1993) 253.
[5] I. Willner, A. Riklin, B. Shoham, D. Rivenzon, E. Katz, Adv. Mater. 5 (1993) 912.
[6] P. Yeh, T. Kuwana, J. Electrochem. Soc. 123 (1976) 1334.
[7] A.E.G. Cass, G. Davis, M.J. Green, H.A.O. Hill, J. Electroanal. Chem. 190 (1985) 117.
[8] A.L. Crumbliss, H.A.O. Hill, D.J. Page, J. Electroanal. Chem. 206 (1986) 327.
[9] I. Taniguchi, S. Miyamoto, S. Tomimura, F.M. Hawkridge, J. Electroanal. Chem. 240 (1988) 333.
[10] T. Kaku, H.I. Karan, Y. Okamoto, Anal. Chem. 66 (1994) 123.
[11] T. Keda, T. Shibatta, M. Senda, J. Electroanal. Chem. 261 (1989) 351.
[12] A.E.G. Cass, G. Davis, G.D. Francis, H.A.O. Hill, W.J. Aston, I.J. Higgins, E.V. Plotkin, L.D.L. Scott, A.P.F. Turner, Anal. Chem. 56 (1984) 667.
[13] C. Iwakura, Y. Kagiya, H. Yoneyama, J. Chem. Soc., Chem. Commun. (1988) 1019.
[14] G. Joensson, L. Gorton, L. Peterson, Electroanalysis 1 (1989) 49.
[15] E. Katz, N. Itzhak, I. Wilner, J. Electroanal. Chem. 332 (1992) 357.
[16] H.O. Finklea, D.D. Hanshew, J. Am. Chem. Soc. 114 (1992) 3173.
[17] Y. Degani, A. Heller, J. Phys. Chem. 91 (1987) 1285.
[18] Y. Degani, A. Heller, J. Am. Chem. Soc. 110 (1988) 2615.
[19] D. Belanger, D. Nadream, J. Fortier, J. Electroanal. Chem. 274 (1989) 143.
[20] S. Yabuki, H. Shinohara, M. Aizawa, J. Chem. Soc., Chem. Commun. (1989) 945.
[21] M. Trojanavicz, W. Matuszewski, M. Podsiadla, Biosens. Bioelectron. 5 (1990) 149.
[22] N.C. Foulds, C.R. Lowe, Anal. Chem. 60 (1988) 2473.
[23] P.D. Hale, T. Inagaki, H.I. Karan, Y. Okamoto, T.A. Skotheim, J. Am. Chem. Soc. 111 (1989) 3482.
[24] T. Inagaki, H.S. Lee, T.A. Skotheim, Y. Okamoto, J. Chem. Soc., Chem. Commun. (1989) 1181.
[25] P.D. Hale, L.I. Boguslavsky, T. Inagaki, H.I. Karan, H.S. Lee, T.A. Skotheim, Y. Okamoto, Anal. Chem. 63 (1991) 677.
[26] Y. Degani, A. Heller, J. Am. Chem. Soc. 111 (1989) 2357.
[27] B.A. Gregg, A. Heller, Anal. Chem. 62 (1990) 258.
[28] A. Ulman, An Introduction to Ultrathin Organic Films: From Langmuir–Blodgett to Self Assembly, Academic Press, New York, 1991.
[29] H.O. Finklea, in: A.J. Bard, I. Rubinstein (Eds.), Electroanalytical Chemistry, Vol. 19, Marcel Dekker, New York, 1996.
[30] M.D. Porter, T.B. Bright, D.L. Allara, C.E.D. Chidsey, J. Am. Chem. Soc. 109 (1987) 3559.
[31] C.D. Bain, E.B. Troughton, Y.T. Tao, J. Evall, G.M. Whitesides, R.G. Nuzzo, J. Am. Chem. Soc. 111 (1989) 321.
[32] S. Bharathi, V. Yegnaraman, G. Prabhakara Rao, Langmuir 11 (1995) 666.
[33] Q. Cheng, A.B. Toth, Anal. Chem. 64 (1992) 1998.
[34] S. Bharathi, V. Yegnaraman, G. Prabhakara Rao, Langmuir 9 (1993) 1614.
[35] S. Steinberg, Y. Tor, E. Sabatani, I. Rubinstein, J. Am. Chem. Soc. 113 (1991) 5176.
[36] F.L. Center (Ed.), Molecular Electronic Devices, Vol. I, Marcel Dekker, New York, 1982.;
F.L. Center (Ed.), Molecular Electronic Devices, Vol. II, Marcel Dekker, New York, 1987.
[37] I. Turyan, D. Mandler, Electroanalysis 8 (1996) 207.
[38] S. Berchmans, V. Yegnaraman, N. Sandhyarani, K.V.G.K. Murty, T. Pradeep, J. Electroanal. Chem. 468 (1999) 170–179.
[39] D.N. Upadhyay, V. Yegnaraman, G. Prabhakara Rao, Langmuir 12 (1996) 4249.
[40] E. Sabatani, I. Rubinstein, J. Phys. Chem. 91 (1987) 6663.
[41] S. Berchmans, V. Yegnaraman, G. Prabhakara Rao, Proc. Indian Acad. Sci. (Chem. Sci.) 109 (1997) 277–287.
[42] S. Berchmans, V. Yegnaraman, G. Prabhakara Rao, J. Solid State Electrochem. 3 (1998) 52–54.
[43] E. Sabatani, I. Rubinstein, R. Maoz, J. Sagiv, J. Electroanal. Chem. 219 (1987) 365.
[44] C. Miller, P. Cuendet, M. Gratzel, J. Phys. Chem. 95 (1991) 877.
[45] E. Katz, D.D. Schlereth, H.L. Schmidt, A.J.J. Olsthoorn, J. Electroanal. Chem. 368 (1994) 165.
[46] I. Willner, N. Lapidot, A. Riklin, R. Kasher, E. Zahavy, E. Katz, J. Am. Chem. Soc. 116 (1994) 1428.
[47] E. Katz, M. Lion-Dagon, I. Willner, J. Electroanal. Chem. 382 (1995) 25.
[48] T. Lotzbeyer, W. Schuhmann, E. Katz, J. Falter, H.L. Schmidt, J. Electroanal. Chem. 377 (1994) 291.
[49] I. Willner, E. Katz, A. Riklin, R. Kasher, J. Am. Chem. Soc. 114 (1992) 10965.
[50] I. Willner, V. Helg-Shabtai, R. Blonder, E. Katz, G. Tao, J. Am. Chem. Soc. 118 (1996) 10321.
[51] I. Willner, A. Riklin, Anal. Chem. 66 (1994) 1535.
[52] C. Ruan, F. Yang, C. Lei, J. Deng, Anal. Chem. 70 (1998) 1721.
[53] C. Ruan, R. Yang, X. Chen, J. Deng, J. Electroanal. Chem. 455 (1998) 121.
[54] E. Laviron, J. Electroanal. Chem. 101 (1979) 19.
[55] K.J. Sung, G.S. Wilson, Anal. Chem. 68 (1996) 591.
[56] R. Wilson, A.P.F. Turner, Biosens. Bioelectron. 7 (1992) 165.
[57] D.L. Mell, J.T. Maloy, Anal. Chem. 47 (1976) 299.