

D-4-1

Self Assembled Viologen Modified Electrode as Mediator of Glucose Sensor

Dong-Yun Lee, A.K.M. Kafi, Sang-Hyun Park, Dong-Jin Qian¹ and Young-Soo Kwon*

Department of Electrical Engineering & CIIPMS, Dong-A University,

840, Hadan-2dong, Saha-gu, Busan 604-714, Korea

Phone: +82-51-200-7738, Fax: +82-51-200-6552, E-mail: yskwon@dau.ac.kr

¹Institute of Advanced Materials, Fudan University,

220, Handan Road, Shanghai 200433, China

1. Introduction

Viologen derivatives have been widely investigated their redox activity and electrochromic properties [1,2]. They are attractive materials because of their chemical stability, their relatively simple behavior of redox reaction and their possible practical applications due to their electrochemical properties.

Since Clark and Lyons first proposed the initial idea of glucose enzyme electrodes in 1962, an increasing interest has been paid toward development of the biosensor for glucose measurement [3]. Most of the known glucose sensors are based on the electrochemical oxidation of hydrogen peroxide which is produced from immobilized enzyme with the help of dissolved oxygen [4]. However, the amperometric measurement of hydrogen peroxide oxidation requires a relatively high working potential (over 0.6 V), at which other species such as uric acid and ascorbic acid are also electro-active. Therefore, researchers attempted to minimize errors by interfering electro-active species in glucose sensors. In the case of this the consumption of oxygen by mediator can be used to design more sophisticated glucose sensor.

In this work, thiol modified viologen has been used to design glucose biosensor as redox mediator. Viologen ($VC_{10}SH$) play an important role as electron relays in systems in which electron transfer is initiated by electrochemical process [5]. It exhibits fast reversible electrochemical characteristics at negative potentials that can make it useful as redox mediators for enzymatic reaction [6]. In this present work, glucose oxidase (GOD) was immobilized onto the thiol-functionalized self assembled viologen modified gold (Au) electrode. It is expected to increase the efficiency of electron transport and the sensitivity of the GOD modified electrode by viologen as electron mediator. The sensor based on this, exhibits excellent performance, a fast response, nice sensitivity, and low detection limit.

2. Experimental

2.1 Reagents

Viologen derivative ($VC_{10}SH$) was synthesized by Dr. Qian (Fudan University, China). Fig. 1 shows the chemical structure of the viologen bonded with a thiol group. The rest of the reagents used in this experiments were of analytical grade and used without any purification. All solutions were prepared using Milli-Q water. Glucose oxidase and glucose were purchased from Sigma. Their stock solutions were stored at a temperature of 4°C. All other reagents were of analytical grade. The experimental solutions were prepared everyday by appropriate dilution of the stock solution. All the stock solutions were prepared fresh with distilled water. Water was purified with a Milli-Q purification system.

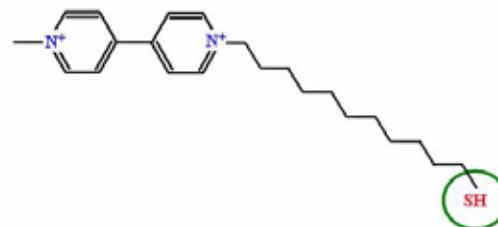


Fig. 1 The Chemical Structure of viologen

2.2 Electrode modification

At First, the gold electrode was cleaned by piranha solution ($H_2SO_4:H_2O_2=3:1$) solution subsequently cleaned by cycling between potential windows of 0 to + 1.5 V versus Ag/AgCl in 0.05 M H_2SO_4 solution at a scan rate of 100 mV/s for nearly 25 minutes until stable scans were recorded. Then the electrode was thoroughly rinsed with the water. After pretreatment, the electrode was immersed in an ethanol-acetonitrile (1:1) solution containing 2 mM thiol-functionalized viologen for 24 hours. After self-assembled, the electrode was removed from the deposition solution and rinsed with ethanol and water to remove weakly adsorbed viologen. After then, the viologen-modified electrode was immersed into phosphate buffer solution containing 5 mg/ml Glucose oxidase for 5 hours.

2.3 Apparatus and electrochemical measurement

Cyclic voltammetry (CV) and chronoamperometry (CA) were carried out with the CHI (630B) workstation. A three electrode configuration was employed for these experiments. The self-assembled viologen monolayer onto gold electrode was used as the working electrode. The Pt wire and KCl saturated Ag/AgCl electrodes were used as counter and reference electrodes, respectively

3. Results and Discussion

The modified electrodes were characterized by cyclic voltammetry to confirm the electron flow from the gold electrode. Fig. 2 shows the voltammogram of the GOD/Viologen/ Au electrode in phosphate buffer solution at pH 7.0. The oxygen reduction peak can be observed at about -0.5 V together with typical redox peak of viologen. Fig. 3 shows the voltammogram of the GOD/Viologen/Au electrode in the phosphate buffer solution containing 5 mM glucose. Interestingly, in the presence of glucose the reduction peak of oxygen completely disappears. It is assumed that the catalytic effect of the oxygen reduction was occurred by the viologen derivative. The mechanism of the reduction of oxygen by viologen can be described as similar as follows [7,8].

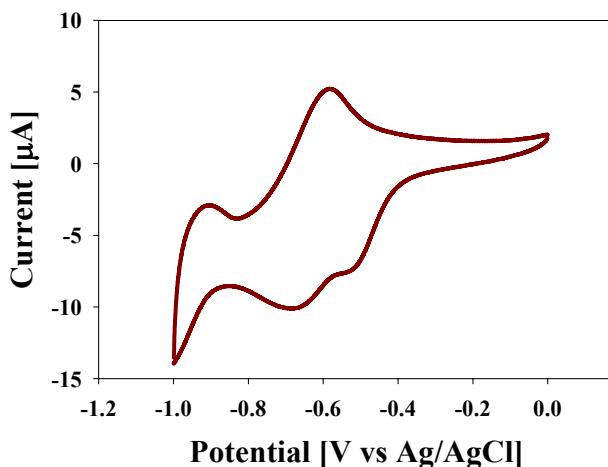
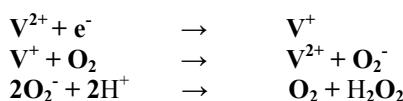


Fig. 2 GOD/Viologen/Au electrode in the absence of glucose.

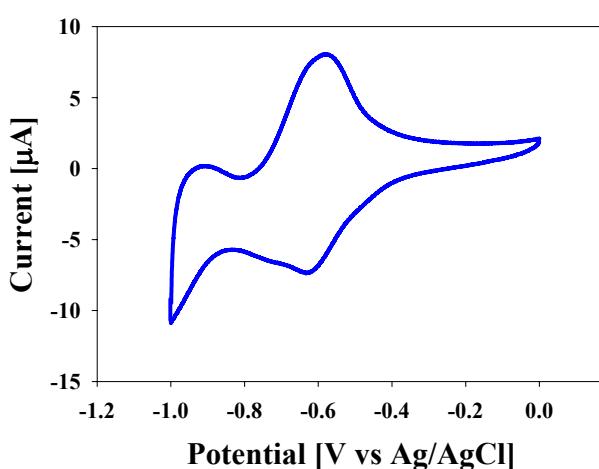


Fig. 3 GOD/Viologen/Au electrode in the presence of 5 mM glucose.

In the presence of glucose, there is also the reaction:



Through the optimal conditions, the plot of current as a function of glucose concentration shows a linear line in glucose concentration between 3×10^{-5} and 4.5×10^{-4} M with a detection limit of 3×10^{-6} M.

4. Conclusion

We designed novel amperometric biosensor for glucose determination using viologen derivatives as an electron mediator. The proposed biosensor showed nice sensitivity and stability, and low detection limit. Low cost, ease of fabrication, fast response time, nice sensitivity, and stability are obvious advantages for this newly proposed modified electrode.

Acknowledgement

This work was supported by grant No. R01-2006-000-11120-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

References

- [1] D. I. Gittins, D. Bethell, R. J. Nichols, and D. J. Schiffrin, *Adv. Mater.*, **11** (9) (1999) 737.
- [2] J.-Y. Ock, H.-K. Shin, D.-J. Qian, J. Miyake, and Y.-S. Kwon, *Jpn. J. Appl. Phys.*, **43** (4B) (2004) 2376.
- [3] L. Clark and C. Lyons, *Ann. NY Acad. Sci.*, **102** (1962) 29.
- [4] S. J. Updike and J. P. Hicks, *Nature*, **214** (1967) 986.
- [5] N. Nakamura, H.-X. Huang, D.-J. Qian and J. Miyake, *Langmuir*, **18** (2002) 5804.
- [6] D.-Y. Lee, A.K.M. Kafi, S.-H. Park, D.-J. Qian and Y.-S. Kwon, *Jpn. J. Appl. Phys.*, **45** (4B) (2006) 3772.
- [7] S. Hu, C. C. Liu, *Electroanalysis*, **9** (1997) 372.
- [8] M. E. Ghica, Christopher M.A. Brett, *Analytica Chimica Acta* **532** (2005) 145.