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Application of Poly (3-methylthiophene) Modified Glassy Carbon Electrode as Riboflavin Sensor

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The electrochemical behavior of riboflavin (VB_2) at a glassy carbon electrode modified with poly (3-methylthiophene) (P3MT) was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The poly (3-methylthiophene) modified glassy carbon electrode (P3MT/GCE) can greatly enhance the peak currents and the detection sensitivity of VB_2 under optimal conditions. Cyclic measurements showed that the electron transfer number, n, was calculated to be 2 and the diffusivity (D_0) was 2.6×10^{-5} cm^2 s^{-1}. The quantitative analysis of VB_2 was made by the DPV method, the relative deviation was 1.5% for 7 successive determinations at 0.1 μmol L^{-1} VB_2 in 0.1 mol L^{-1} pH 4.0 phosphate buffer solution (PBS), and the peak current on the modified electrode was linear over a range from 1.0×10^{-7} to 2.0×10^{-4} mol L^{-1} riboflavin, with the detection limit of 5.0×10^{-8} mol L^{-1}(S/N=3).

Keywords: riboflavin, poly (3-methylthiophene) modified glassy carbon electrode (P3MT/GCE), cyclic voltammetry (CV), differential pulse voltammetry (DPV).

1. INTRODUCTION

Riboflavin (Vitamin B_2, VB_2) is a water-soluble biochemical molecule widely existing in food and pharmaceutical products. Riboflavin is the composition of coenzyme and involved in sugar, protein, fat metabolism, promoting growth and cell regeneration. It can promotion of skin, nails, hair's normal growth, and eliminate the mouth, lips, tongue inflammation, also can promotion of vision, reduce eye fatigue. At the same time, riboflavin is a kind of phototropism, phototaxis, and photodynamic therapy photosensitive agent [1-3]. Many methods for the determination of VB_2 have been reported, including HPLC [4], fluorescence [5], spectro-photometric [6], chemiluminescence methods [7] and cyclodextrin based optosensor [8]. However, these techniques are usually expensive, laborious and time-consuming with low sensitivity. Thus, the design and development of quick, simple, inexpensive and effective methods are of great importance in practice.

Electrochemical methods have been of great interest due to several advantages, including high sensitivity, comparative simplicity, rapid response and low cost. However, the direct electrochemical detection of VB_2 at common electrode materials showed important practical drawbacks, such as high over-potential, poor selectivity, high irreversibility and electrode fouling. In fact, most of the above-mentioned problems can be minimized or avoided by pretreatment of the electrodes with proper method. Up to now, only few methods, such as activation of glass carbon electrode at certain electric potentials have been purposed to improve the sensitivity of the electrical method, and none of the methods can meet the practical needs [9-12].

Poly (3-methylthiophene) (P3MT) is a widely used conducting polymer for sensor purpose, which can be easily electrodeposited onto electrode surface by electro-oxidation of its monomer [13-15]. P3MT modified electrodes have been extensively reported and have shown excellent electro-catalytic effect on some compounds which have conjugated double bond in molecular structure, such as phenolic compounds [16,17], dopamine [18], 8-Hydroxy-2'-deoxyguanosine (8-OH-dG) [19]. However, to the best of our knowledge, there have been no reports on the electrochemical behaviors of VB_2 at the P3MT-modified electrodes.

In this paper, a poly (3-methylthiophene) film modified electrode has been fabricated by the electrochemical polymerization. The electrochemical behavior of riboflavin at the modified electrode was investigated by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods. The sensor exhibited a high sensitivity and fast response.

2. EXPERIMENTAL PART

2.1. Apparatus

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using a CHI760C electrochemical workstation (CH Instruments, Shanghai, Chenhua Equipments, China). The conventional three-electrode system was employed with a bare GCE or a P3MT-modified GCE as working electrode, a platinum wire as auxiliary electrode, and the reference electrode was a saturated Ag/AgCl (3M KCl).

2.2. Chemicals and reagents

3-methythiohene (3MT) was obtained from Acros and was used without further purification. Acetonitrile (LC grade), $NaClO_4$, riboflavin were all obtained from Aldrich. All other reagents were analytical reagent grade, and all solutions were prepared using twice distilled water.

2.3. Fabrication of modified glassy carbon electrode

The preparation of P3MT modified glassy carbon electrode (P3MT/GCE) has been described in previous works [16, 18, 19, 20]. Briefly, prior to the polymer electro-synthesis, the surface of the GCE (diameter 3.0 mm) was polished with 0.05 μ m alumina slurry and cleaned by ultra-sonication in twice

distilled water. P3MT was electrode-posited on a GCE surface from a solution containing 0.1M 3MT and 0.1M $NaClO_4$ dissolved in acetonitrile. Both cyclic voltammetry and the potentiostatic mode were adapted for P3MT film preparation. Cyclic voltammetry was carried out between 0.0 and 1.7 V *vs.* Ag/AgCl at a scan rate of 20 mV s^{-1} for three cycles, and then the film was grown in potentiostatic mode at a potential of 0.7 V *vs.* Ag/AgCl for 10 s. After the polymerization, the electrode was treated in pH 7.0 phosphate buffer solution (PBS) by repetitive scanning in the potential range of 0.0 and 1.7 V *vs.* Ag/AgCl for 10 cycles and then between -0.2 and 0.5 V *vs.* Ag/AgCl at a scan rate of 100 mV s^{-1} until a stable background was obtained. Thus, the P3MT-modified GCE was achieved. The modified electrodes were stored in a dry chamber before use to keep their surface dried.

2.4. Electrochemical experiments

The DPV and CV experiments were performed in 0.1 mol L^{-1} PBS (pH 4.0) containing certain concentrations of VB_2. Under the various conditions, the differential pulse voltammetry (DPV) and cyclic voltammetry (CV) were recorded in a suitable potential range. All experiments were carried out at ambient temperature (about 25 °C) under a nitrogen atmosphere.

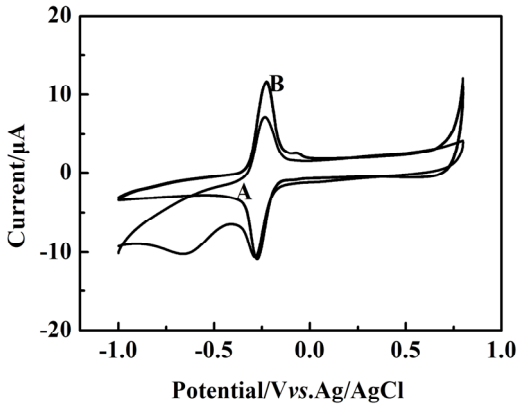


Figure 1. Cyclic voltammetric of 2×10^{-4} mol L^{-1} VB_2 at the bare GCE (A) and P3MT/ GCE (B) in 0.1 mol L^{-1} pH 4.0 PBS. Scan rate of 100 mV s^{-1}.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behaviors of VB_2 at the P3MT/GCE by cyclic voltammetric (CV)

Figure 1. showed cyclic voltammetric of 2×10^{-4} mol L^{-1} VB_2 at the bare GCE (A) and P3MT - modified GCE (B) in 0.1 mol L^{-1} pH 4.0 PBS with a scan rate of 100 mV s^{-1}.The potential range was controlled between -1.0 and +1.0 V *vs.* Ag/AgCl. At the bare GCE (A), a pair of redox peaks were

observed (Figure1, curve A).The oxidation and reduction peak potentials occurred at -0.23V *vs.* Ag/AgCl and -0.28 V *vs.* Ag/AgCl, respectively, the separation between peak potentials (ΔE_P) was 0.05 V *vs.* Ag/AgCl. Under the same measurement conditions, the ΔE_P was 0.04 V *vs.* Ag/AgCl at the P3MT/ GCE electrode (Figure1, curve B), which indicates that the reversibility of VB_2 on P3MT/GCE had been improved. As Figure1 (B) shown, the oxidative peak current on the P3MT/GCE was significantly higher than that on the bare electrode, which showed that P3MT had a better electro-catalysis effect on VB_2 than that of bare GCE. From the cyclic voltammetric measurement, it can be seen that P3MT/GCE was more sensitive than the bare electrode for Vitamin B assay.

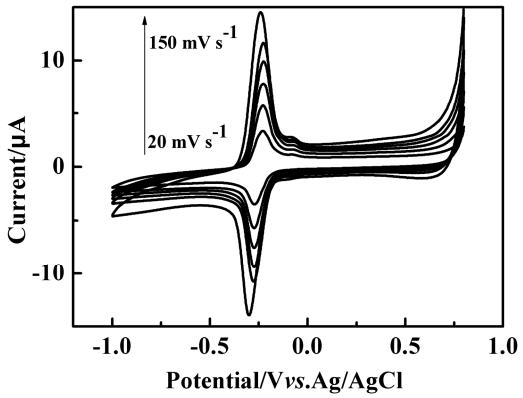


Figure 2. Cyclic voltammetric of 2×10^{-4} mol L^{-1} VB_2 at the P3MT/GCE in 0.1 mol L^{-1} pH 4.0 PBS. Scan rate: 150, 100, 80, 60, 40, 20 mV s^{-1}.

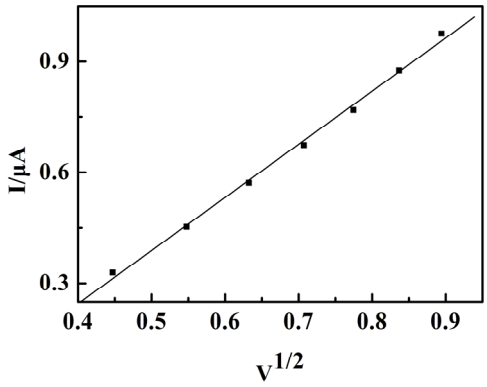


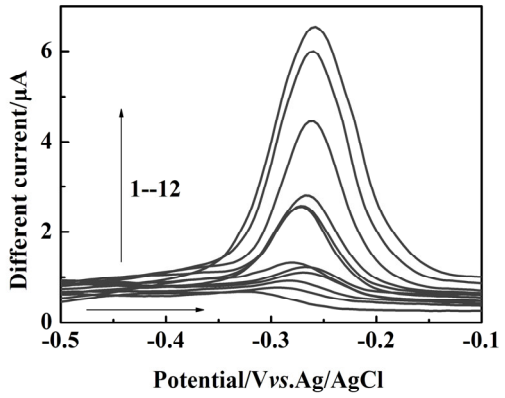
Figure 3. Relationship between peak current and $V^{1/2}$ of 2×10^{-4} mol L^{-1} VB_2 at the P3MT/GCE in 0.1 mol L^{-1} pH 4.0 PBS. Scan rate: 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 V s^{-1}

The effect of the scan rates on the electrochemical response of 2×10^{-4} mol L^{-1} VB_2 at the P3MT/GCE in 0.1 mol L^{-1} pH 4.0 PBS was investigated by CV and the results were shown in Figure 2. It can be seen that the peak current increased with the increase of scan rate. The plot of peak current against $V^{1/2}$ was linear over the range of 0.2-0.8 V s^{-1} and the linear regression equations: I_{Pa} = -3.304 + 1.437 $V^{1/2}$/V s^{-1} (I_{Pa} in μA, V in V s^{-1}) with a correlation coefficient of 0.9982 was obtained (Figure3). According to the formula of Randles [21], $i_p= 2.69\times10^5 n^{3/2} D_0^{1/2} C_0 V^{1/2}$, $i_p= i_{pa}/ i_{pc}$= 1.098, n=2, so the

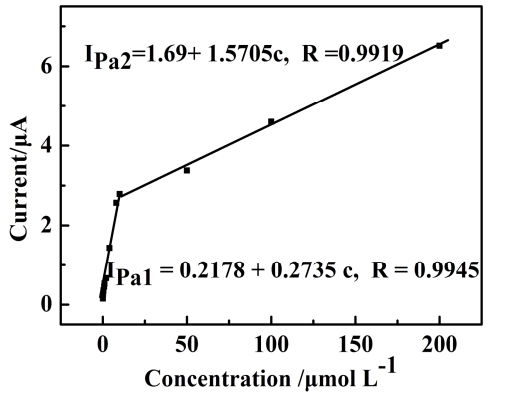
value of diffusivity (D_0) was $2.6\times10^{-5}cm^2.s^{-1}$. Thus, VB_2 had a diffusion-controlled process at the P3MT/GCE. In the light of the present results, it can be inferred that the two one-electron reactions would be involved in the electro-catalysis reduction of VB_2 at the P3MT/GCE, and can be shown as follows (RF referred to riboflavin):

$$RF+H^+ \rightleftharpoons RFH^+$$

$$RFH^+ + H^+ \rightleftharpoons RFH_2^{2+}$$



(A)



(B)

Figure 4. (A) Differential pulse voltammetry (background correction) for different concentrations VB_2 at the P3MT /GCE. Concentrations: 0.1, 0.2, 0.4, 0.8, 1, 2, 4, 8,10, 50, 100, 200 μmol L^{-1}. Potential range: -0.2-0.4 V (*vs*. Ag/AgCl); Incr E (V): 0.004; Amplitude (V):0.05; Pulse Width (sec): 0.2; Sample Width (sec):0.02; Pulse Period (sec): 0.5; Quiet Time (sec):2. Figure 4(B) the linear relationships in different concentrations VB_2 at the P3MT/GCE.

3.2 Determination VB_2 at the P3MT/GCE by differential pulse voltammetry (DPV)

Differential pulse voltammetry (DPV) was used for the determination of VB_2, because of its much higher current sensitivity and better resolution than cyclic voltammetry. Figure 4(A) showed the differential pulse voltammetry behavior of different concentrations VB_2 in 0.1 mol L^{-1} pH 4.0 PBS. The relative deviation was 1.5% for 7 successive determinations at 0.1 μmol L^{-1} VB_2. After each of determination the electrode was treated in pH 4.0 PBS by repetitive scanning until a stable background was obtained. As shown in Figure 4 (A), it was evident that electron transfer reaction was enhanced, and the modified electrode showed positive and effective electrochemical for the VB_2. It can be found that the differential pulse peak heights of VB_2 was linearly related to the VB_2 concentration over two concentration intervals, viz. 0.1-10 μmol L^{-1} and 50-200 μmol L^{-1}as shown in Figure 4(B), the linear regression equations, respectively:

$$I_{Pa1}/\mu A = 0.2178 + 0.2735\ c/(\mu mol\ L^{-1}),\ (r = 0.9945)\ (\ 0.1\text{-}10\ \mu mol\ L^{-1})$$

$$I_{Pa2}/\mu A = 1.690 + 1.5705\ c/(\mu mol\ L^{-1}),\ (\ r = 0.9919)\ (50\text{-}200\ \mu mol\ L^{-1})$$

The corresponding slopes (sensitivity) of the above equations were 0.2735, 1.5705 μA/(μmol L^{-1}), respectively. The detection limit of VB_2 can be estimated to be 5×10^{-8} mol L^{-1} (S/N=3). Thus, the proposed modified electrode may provide a potential application for the estimate of VB_2 level in human body and so on.

4. CONCLUSIONS

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) showed that the P3MT modified electrode had better sensitivity and detection limit towards VB_2 under certain conditions. The method was simple and rapid with high accuracy, and the determination results with great satisfaction. Thus, the poly (3-methylthiophene) modified glassy carbon electrode as riboflavin sensor had a better application prospect.

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References

1. A. Chatterjee, J.S. Foord, *Diamond & Related Materials* 18 (2009) 899.
2. R.M. Kotkar, P.B. Desai, A. K, *Sensors and Actuators B*.124 (2007) 90.
3. A.C. Pereira, A.S. Santos, L.T. Kubota, *Journal of Colloid and Interface Science* 265 (2003) 351.
4. G.M. Greenway, N. Kometa, *Analyst* 119 (5) (1994) 929.

5. E. Sikorska, A. Gliszczyńska-Świgło, M. Insińska-Rak, I. Khmelinskii, D.D. Keukeleire, M. Sikorski, *Anal Chim. Acta*. 613(2), 207 (2008).
6. T. Perez-Ruiz, C. Martinez-Lazazo.V. Tomas, O. Val, *Analyst* 119 (6) (1994) 1825.
7. T. Perez-Ruiz, C. Martinez-Lazazo. V. Tomas, O. Val, *Analyst* 119 (6) (1994) 1199.
8. Z.H. Gong, Z.J. Zhang, *Analyst* 121 (8) (1996) 1119.
9. A.L. Beilby, T.A. Sasaki, H.M. Stern, *Anal. Chem*. 67 (5) (1995) 976.
10. T. Nagaoka, T. Fukunage,T. Yoshino, I. Watanabe, T. Nakayama, S.Okazaki, *Anal. Chem*. 60 (24) (1988) 2766.
11. K.K. Shiu, K. Shi, *Electroanalysis* 12(2) (2000) 134.
12. R.F. Carvalhal, R.K. Mendes, L.T. Kubota, *Int. J. Electrochem. Sci.* 2 (2007) 973.
13. M. Ates, *Int. J. Electrochem. Sci.* 4 (2009) 1004.
14. A.S. Widge, M. Jeffries-El, X.Y. Cui, C.F. Lagenaur, *Yoky Matsuoka, Biosensors and Bioelectronics* 22 (2007) 1723.
15. Y. S. Kim, J. H. Park, S. Lee, Y. Lee, *Solar Energy Materials & Solar Cells* 93 (2009) 1398.
16. J. Wang, R.L.Li, *Anal. Chem.* 61 (1989) 2809.
17. L. Agüí, B. Serra, P. Yáñez-Sedeño, A. J. Reviejo, J. M. Pingarrón, *Electroanalysis* 13 (2001) 1231.
18. H.S. Wang, T. H. Li, W.L. Jia, H.Y. Xu, *Biosensors and Bioelectronics* 22(5) (2006) 664.
19. T.H. Li, W.L. Jia, H.S. Wang, R.M. Liu, *Biosensors and Bioelectronics* 22 (2007) 1245.
20. H.S. Wang, D.Q. Huang, R.M. Liu, *Electroanal. Chem*. 570 (2004) 83.
21. C.Y. Lu, Z.H. Han, *Scichina*.30 (5) (2000) 428.