Int. J. Electrochem. Sci., 11 **(2016)** 1821 - 1830

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Behaviors of Myoglobin on Graphene and Bi Film Modified Electrode and Electrocatalysis to Trichloroacetic Acid

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Received: 24 November 2015 / *Accepted:* 11 January 2016 / *Published:* 1 February 2016

Graphene (GR) and bismuth (Bi) film was directly electrodeposited on carbon ionic liquid electrode (CILE) surface, which was applied as the substrate electrode. Myoglobin (Mb) was fixed on the Bi/GR/CILE surface with a thin Nafion membrane to get a new electrochemical biosensor (Nafion/Mb/Bi/GR/CILE). Cyclic voltammetric results showed that a couple of well-defined redox peaks present on the voltammograms, exhibiting the achievement of direct electron transfer of Mb on the electrode. This result can be attributed to the existence of GR and Bi film with high electronic conductivity and big surface area. Electrochemical parameters were got with electron transfer coefficient (α) as 0.34 and heterogeneous electron transfer kinetic constant (k_s) as 1.15 s^{-1}. This Mb modified electrode reveals fine electrocatalytic activity to the reduction and detection of trichloroacetic acid (TCA) in the linear range from 0.5 to 46.0 mmol L^{-1} with the detection limit of 0.167 mmol L^{-1} (3σ). Therefore a promising electrochemical biosensor was constructed successfully.

Keywords: Graphene; Bismuth; Myoglobin; Carbon ionic liquid electrode; Direct electrochemistry

1. INTRODUCTION

Direct electron transfer of redox enzymes and proteins can be used to investigate on the redox process of the biological system and to establish the foundation for the fabrication of biosensors, bioreactors and biomedical apparatus [1]. Nevertheless, the electron transfer of redox proteins is hard to be realized because of its deep hidden of electroactive centers in the protective matrix and the negative orientation on the bare solid electrode with the loss of bioactivity [2]. Therefore various biocompatible and conductive films had been designed to realize the electron transfer from redox enzymes to basic electrode [3].

Graphene (GR) nanosheets are carbon nanomaterials with huge surface area and fine electronic conductivity, which has been applied to electrochemistry and electrochemical sensors [4,5]. Various methods including micromechanical cleavage, chemical vapor deposition, solvothermal and chemical method have been devised to synthesis of GR [6,7]. As a convenient method electrochemical reduction has the advantages of green, cheap and easily to be controlled [8,9]. By using electrochemical technique the oxygenal groups on the graphene oxide surface can be straightly eliminated with the recovery of structures and properties of GR. Chen et al. prepared the GR-based composite by electrochemical methods and applied to the fabrication of electrochemical devices [10]. Our groups also investigated the electrochemical reduced GR modified electrodes for the electrochemical sensing [11,12].

Bismuth (Bi) film modified electrode has been applied in electroanalysis, which exhibits high metal conductivity and excellent adsorption activity. Owing to the specific physicochemical characters like less toxicity, wide potential window and partial insensitive to dissolve oxygen, bismuth film electrode can be used to replace the mercury electrode [13]. Various carbon based electrode including carbon paste electrode (CPE) can be used as the electrode supports for Bi stripping voltammetry [14,15], which offers a readily renewable surface with low cost.

Carbon ionic liquid electrode (CILE) is manufactured by incorporating ionic liquid (IL) into CPE, which can be used as the working electrode with many merits such as simple procedure, fine reversibility, wide electrochemical windows, high conductivity, good antifouling capability and inherent electrocatalytic ability [16,17]. CILE can also be modified with nanomaterials and applied as the working electrode for the construction of electrochemical biosensors [18-20].

In this paper GR and Bi film were deposited on the surface of CILE by electroreduction to gain a decorated electrode (Bi/GR/CILE). Then myoglobin (Mb) was further immobilized on its surface to get an electrochemical sensor. Direct electrochemistry of Mb on Bi/GR/CILE was realized with a couple of redox peaks presented. Then electrochemical parameters of Mb were calculated and electrocatalysis to trichloroacetic acid (TCA) was further investigated.

2. EXPERIMENTAL

2.1 Apparatus

CHI 1210A and CHI 660D electrochemical workstation (Shanghai CH Instrument, China) were used for voltammetry and electrochemical impedance spectroscopy (EIS). The three-electrode was composed of a Nafion/Mb/Bi/GR/CILE (the working electrode), a platinum wire electrode (the auxiliary electrode) and a saturated calomel electrode (SCE, the reference electrode). Scanning electron microscopy (SEM) was recorded on a JSM-7100F scanning electron microscope (Japan Electron Company, Japan).

2.2 Reagents

Mb (MW 17800, Sigma), Nafion (5% ethanol solution, Sigma), 1-hexylpyridinium hexafluorophosphate ($HPPF_6$, Lanzhou Greenchem ILS. LICP. CAS., China), graphene oxide (GO, Taiyuan Tanmei Ltd. Co., China), lithium perchlorate ($LiClO_4$, Chengdu Kelong Chemical Reagent Co., China), graphite powder (average particle size 30 μm, Shanghai Colloid Chemical Co., China), bismuth nitrate pentahydrate (Tianjin Chemical Reagent) and TCA (Tianjin Kemiou Chemical Co., China) were used. 0.1 mol L^{-1} phosphate buffer solutions were used as electrolyte, which were maintained in the nitrogen atmosphere during the electrochemical measurements.

2.3 Construction of Nafion/Mb/Bi/GR/CILE

$HPPF_6$ based CILE was manufactured on the basis of the previous procedure [21]. In short, $HPPF_6$ (0.8 g) and graphite powder (1.6 g) were mingled in a mortar homogeneously and the resulted paste was crammed into a glass tube ($\Phi=4\times10^{-3}$ m). Finally a copper wire were inserted to the bottom of the paste as conductor.

GR modified CILE was got by electrodeposition with a potentiostatic method [22]. CILE was placed in the mixture of 3.0 mg mL^{-1} GO and 0.1 mol L^{-1} $LiClO_4$ solution with a magnetic stirring. Then electroreduction was performed at the potential of -1.30 V for 300 s, which resulted in a steady GR film on surface of CILE. After washing with ultrapure water and drying in the nitrogen gas environment, GR/CILE was put in a 2.0 μmol L^{-1} Bi(III) solution and electrodeposition was carried out at the potential of -1.10 V for 120 s to get Bi/GR/CILE. Electrochemical biosensor was prepared by dropping 8.0 μL of 15.0 mg mL^{-1} Mb solution directly onto Bi/GR/CILE and the electrode was dried at room temperature. Finally 5.0 μL of 0.5% Nafion solution was casted on Mb/Bi/GR/CILE and dried to obtain Nafion/Mb/Bi/GR/CILE, which was preserved at 4 °C before use. Other electrodes such as Nafion/CILE, Nafion/Mb/CILE, Nafion/Mb/Bi/CILE and Nafion/Mb/GR/CILE were prepared by the similar procedure.

3. RESULTS AND DISCUSSION

3.1 Characterizations of Nafion/Mb/Bi/GR/CILE

SEM image of the electroreduced GR modified electrode was shown in Figure 1A, which exhibited a well-defined and interconnected porous network with the typical characteristic of GR nanosheet appeared. After the electrodeposition of Bi(III), a continues Bi film could be found on the surface of GR (Figure 1B). The existence of Bi film on the GR can further enhance the roughness of modified electrode.

EIS is usually used to provide impedance information of the interface after the modification. The semicircle diameter of Nyquist plots reflected the electron transfer resistance (Ret) on the electrode surface and the linear part at lower frequencies conforms to the diffusion process. EIS experiments were performed in a 10.0 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ and 0.1 mol L^{-1} KCl mixture solution with the frequency swept from 10^4 to 10^{-1} Hz, and the results were exhibited in Figure 1C. On Nafion/CILE the Ret value was 107.3 Ω (curve b) and that of Nafion/Mb/CILE increased to 195.1 Ω (curve a), showing the existence of Mb on the electrode surface hampered the electron transfer of $[Fe(CN)_6]^{3-/4-}$ and increased the interfacial resistance. On Nafion/Mb/Bi/CILE (curve c) and Nafion/Mb/GR/CILE (curve d) the Ret values were got as 73.7 Ω and 65.6 Ω, which was ascribed to the existence of high conductive Bi membrane or GR nanosheet that decreased the resistance. On Nafion/Mb/Bi/GR/CILE (curve e) a straight line was present with the Ret value decreased to zero, which was ascribed to the highest conductivity of Bi/GR nanocomposite on the electrode surface.

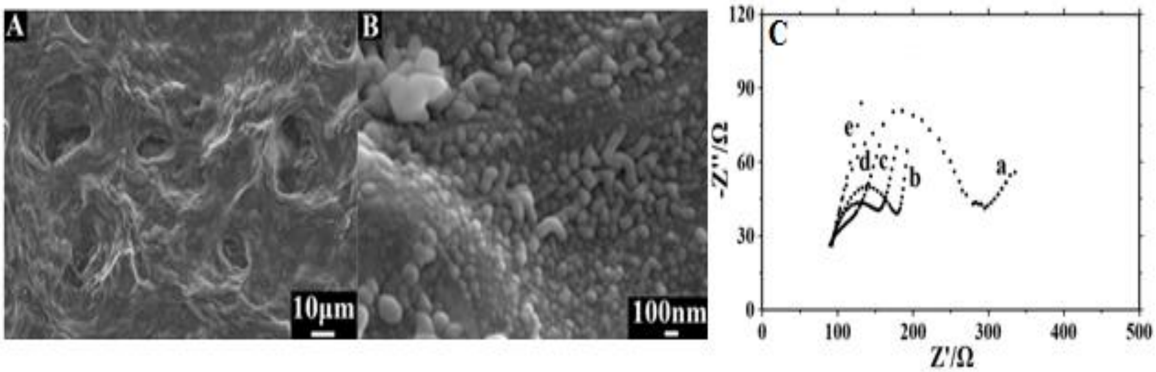

Figure 1. SEM images of GR/CILE (A) and Bi/GR/CILE (B); (C) EIS of (a) Nafion/Mb/CILE, (b) Nafion/CILE, (c) Nafion/Mb/Bi/CILE, (d) Nafion/Mb/GR/CILE and (e) Nafion/Mb/Bi/GR/CILE in a 10.0 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ and 0.1 mol L^{-1} KCl solution with the frequencies from 10^4 to 10^{-1} Hz.

3.2 Electrochemical response of Mb

Electrochemical behaviors of Mb on the electrode were investigated by cyclic voltammetry with the results displayed in Figure 2. No peaks could be observed on Nafion/CILE (curve a), revealing no electrochemical reaction in the potential range investigated. Meanwhile the presence of Mb on different electrodes resulted in a couple of redox peaks, indicating the electron transfer of Mb with CILE was realized. All data of the four Mb modified electrodes were summarized in table 1 for comparison and it could be observed that the redox peak currents improved slowly with the addition of GR and Bi film on the electrode surface. On Nafion/Mb/Bi/CILE (curve c) the redox peak currents was a little bigger than that of Nafion/Mb/CILE (curve b). On Nafion/Mb/GR/CILE (curve d) the redox peak of Mb was also realized with the background current increased, which was ascribed to the existence of GR nanosheet on CILE surface. On Nafion/Mb/Bi/GR/CILE (curve e) the biggest redox peak currents appeared. The presence of GR and Bi nanocomposite on the surface of CILE can offer a conductive interface with huge surface area, which is desirable for Mb loading with more contacting chance for electron transfer.

Table 1 Electrochemical data of four Mb modified electrodes in pH 3.0 PBS, scan rate: 0.1 V s^{-1}.

Electrode	*I*pc/μA	*I*pa/μA	*E*pc/V	*E*pa/V	*I*pa/*I*pc	Δ*E*p/V
Nafion/Mb/CILE	12.86	11.68	-0.205	-0.151	0.91	0.054
Nafion/Mb/Bi/CILE	15.81	14.95	-0.210	-0.151	0.95	0.059
Nafion/Mb/GR/CILE	22.22	22.78	-0.227	-0.150	1.03	0.077
Nafion/Mb/Bi/GR/CILE	27.30	26.50	-0.231	-0.150	0.97	0.081

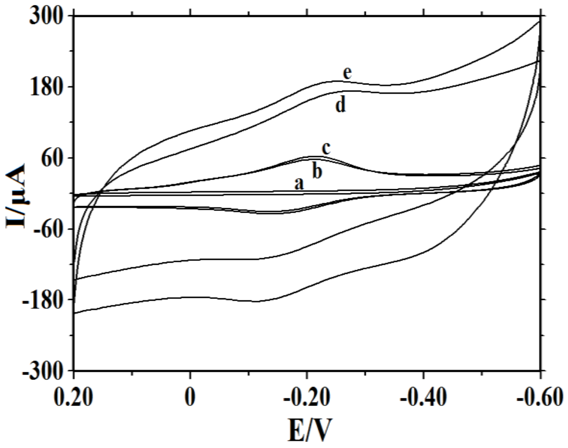

Figure 2. CV of (a) Nafion/CILE, (b) Nafion/Mb/CILE, (c) Nafion/Mb/Bi/CILE, (d) Nafion/Mb/GR/CILE and (e) Nafion/Mb/Bi/GR/CILE in pH 3.0 PBS, scan rate: 0.1 V s^{-1}.

3.3 Electrochemical investigation

The influence of scan rate on electrochemical responses of Nafion/Mb/Bi/GR/CILE was surveyed by cyclic voltammetry with the data revealed in Figure 3. In the scan rate scope from 100 to 900 mV s^{-1} a couple of quasi-symmetric redox peaks was present and the currents enhanced slowly with the increase of scan rate (Figure 3A). As shown in Figure 3B two linear relationships were established with linear regression equations as $I\text{pc}(\mu\text{A})=197.13\upsilon\ (\text{V s}^{-1})+13.40\ (\gamma=0.991)$ and $I\text{pa}(\mu\text{A})=-185.62\upsilon\ (\text{V s}^{-1})-13.71\ (\gamma=0.991)$, indicating a surface-controlled thin-layer electrode behavior. With the increase of scan rate Δ*E*p also enhanced slowly, which manifested a quasi-reversible electrochemical process. Therefore the electrochemical data could be gained according to the Laviron’s method [23], the kinetic of the redox reaction could be calculated with the electron transfer coefficient (α) and electron transfer rate constant (k_s) as 0.34 and 1.15 s^{-1}. This k_s value is greater than some reported values [24,25], suggesting a relatively fast rate of electron transfer. By integration of the reduction peaks, the surface concentration (Γ^*) of electroactive Mb can be got by the formula ($\Gamma^*=Q/nAF$) [26] and the value was calculated as 1.89×10^{-9} mol cm^{-2}, which was bigger than the monolayer coverage of 1.89×10^{-11} mol cm^{-2} [27].

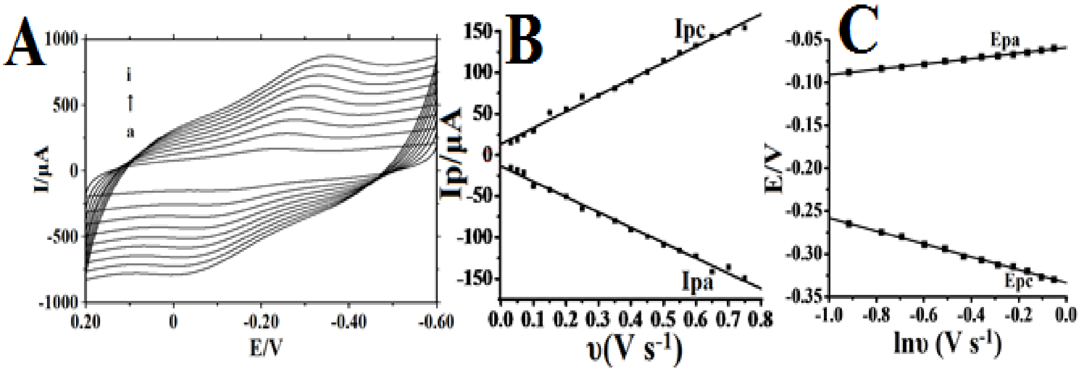

Figure 3. (A) Effect of scan rates (υ) (from a → i as 100, 200, 300, 400, 500, 600, 700, 800, 900 mV s^{-1}) on electrochemical responses of Nafion/Mb/Bi/GR/CILE in pH 3.0 PBS; (B) Plot of the redox peak currents against υ; (C) Plot of the redox peak potentials against lnυ.

The influence of buffer pH on electrochemical behaviors of Nafion/Mb/Bi/GR/CILE was studied in different PBS. Almost quasi-reversible voltammograms with steady and well-defined redox peaks appeared and the biggest redox peak currents was got at pH 3.0, which was chosen for the electrochemical experiments. Furthermore, the change of pH value from 2.0 to 6.0 resulted in negative shifts of the redox peaks, revealing that protons were involved in the electrode reaction. The linear equation between $E^{0'}$ and pH was got as $E^{0'}$(mV)=-43.9 pH- 21.2 (γ=0.990). The slope value (-43.9 mV pH^{-1}) was smaller as compared with the theoretical value (-59.0 mV pH^{-1}) for one-proton and one-electron transfer process.

3.4 Electrocatalysis

TCA is often used for the precipitation of macromolecules and in the cosmetic treatments, so it is necessary to establish sensitive method for TCA detection. Bioelectrocatalysis of Nafion/Mb/Bi/GR/CILE to the electroreduction of TCA was explored with cyclic voltammogram illustrated in Figure 4. Upon the addition of different concentrations of TCA in pH 3.0 PBS, the reduction peak appeared at -0.214 V with the disappearance of the oxidation peak. Also the reduction peak currents increased with the increase of TCA concentration gradually, which was a typical electrocatalytic behavior. The further increase of the TCA concentration led to appearance of the second reduction peak at -0.546 V. According to Fan's working [28], the reaction of electrocatalysis could be inferred from the following equations:

$$\text{Mb Fe(III)} + e \rightleftharpoons \text{Mb Fe(II)} \quad (1)$$

$$2\ \text{Mb Fe(II)} + Cl_3CCOOH + H^+ \rightarrow 2\ \text{Mb Fe(III)} + Cl_2CHCOOH + Cl^- \quad (2)$$

$$\text{Mb Fe(II)} + e \rightarrow \text{Mb Fe(I)} \quad (3)$$

$$2\ \text{Mb Fe(I)} + Cl_2CHCOOH + H^+ \rightarrow 2\ \text{Mb Fe(II)} + ClCH_2COOH + Cl^- \quad (4)$$

$$2\ \text{Mb Fe(I)} + ClCH_2COOH + H^+ \rightarrow 2\ \text{Mb Fe(II)} + CH_3COOH + Cl^- \quad (5)$$

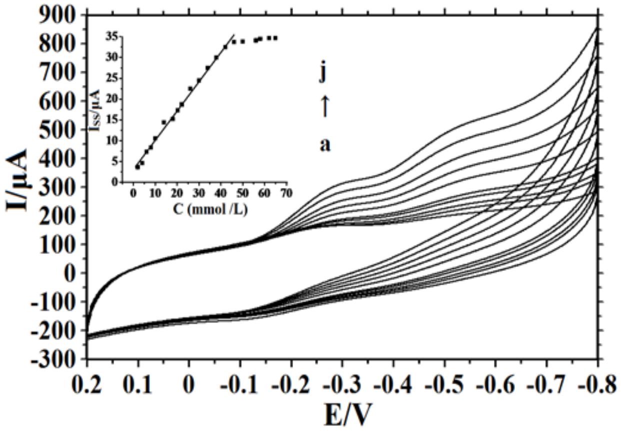

Figure 4. CV of Nafion/Mb/Bi/GR/CILE with 2, 4, 8, 18, 26, 30, 38, 46, 59, 65 mmol L^{-1} TCA (curves a → j), scan rate: 0.1 V s^{-1} (Inset was the linearity of catalytic reduction currents and TCA concentration).

A linear relationship between the catalytic cathodic peak current and the TCA concentration were obtained in the range of 0.5 ~ 46.0 mmol L^{-1} with the equation as Iss (μA) = 0.703C(mmol L^{-1}) +3.06 (γ=0.993) and the detection limit as 0.167 mmol L^{-1} (3σ). A comparison of the electrochemical data of the Mb modified electrode and the TCA detection was summarized in table 2, which indicated that this Mb modified electrode has a relative high k_s value, wide linear range and low detection limit. When the TCA concentration was bigger than 46.0 mmol L^{-1}, the reduction peak current was flatten, showing a representative Michaelis-Menten kinetic process. Then the apparent Michaelis-Menten constant (K_M^{app}) was got as 0.036 mmol L^{-1} according to the Lineweaver–Burk equation [29]. This K_M^{app} value is lower than that of some reported values such as Mb immobilized in agarose hydrogel films with 1-butyl-3-methylimidazolium hexafluorophosphate as electrolyte (177.0 mmol L^{-1}) [30] or Nafion/Mb/NiO/GR/CILE (10.67 mmol L^{-1}) [31], so the Mb molecules in Nafion/Mb/Bi/GR/CILE remained excellent bioactivity with high biological affinity to TCA.

Table 2 Electrochemical data of different Mb modified electrodes towards the detection of TCA

Modified electrodes	k_s	Linear range (mmol L^{-1})	Detection limit (mmol L^{-1})	K_M^{app} (mmol L^{-1})	Refs.
Mb-HSG-SN-CNTs/GCE	0.41	2.0×10^{-3}–1.2	3.6×10^{-4}	1.62	[24]
Nafion/Mb/MWCNTs/CILE	0.332	1.57-12.0	0.1	3.396	[25]
Nafion/Mb/Co/CILE	0.588	0.4-12.0	0.2	4.11	[29]
Nafion/Mb-Co_3O_4-Au/IL-CILE	0.799	2.0-20.0	0.5	4.70	[30]
Nafion-$BMIMPF_6$/Mb/CILE	0.532	1.6-19.6	0.2	90.8	[31]
Nafion/Mb/NiO/GR/CILE	1.27	0.69-30.0	0.23	10.67	[34]
Nafion/Mb/Bi/GR/CILE	1.15	0.5-46.0	0.167	0.036	This Work

3.5 Stability, reproducibility and repeatability of the modified electrode

The stability of Nafion/Mb/Bi/GR/CILE was surveyed by putting it into 4°C refrigerator for a certain period. The redox peak currents of the modified electrode reserved 95.8% of its original value after 10 days and the current reduced approximately 7.5% after 30 days. The reproducibility of the modified electrode was tested with a 6.0 mmol L^{-1} TCA solution and the relative standard deviation (RSD) could be calculated as 2.6% (n=10). Therefore the modified electrode indicated excellent stability and reproducibility. Seven Mb modified electrodes were manufactured by the same step and the RSD value for the 6.0 mmol L^{-1} TCA could be got as 3.55%, indicating the excellent repeatability for the preparation of Nafion/Mb/Bi/GR/CILE.

3.6 Analytical application

The application of this Mb modified electrode to TCA detection was investigated in lab water with the standard addition method to calculate the recovery. As shown in table 3, the recovery was in the range of 98.33 % -101.25%. Thus, the modified electrode can be used for the quantitative determination TCA in water samples with satisfactory results.

Table 3 Detection results of TCA in lab water sample (n=3).

Water Sample	Found (mmol L^{-1})	Added (mmol L^{-1})	Found (mmol L^{-1})	Recovery (%)	RSD (%)
1	0	4.0	3.99	99.75	1.09
2	0	6.0	5.90	98.33	2.16
3	0	8.0	8.10	101.25	2.37

4. CONCLUSIONS

In this work, a Bi film and GR modified CILE was designed by electrodeposition and applied to the fixation of Mb. Owing to the high conductivity of GR and Bi film, the immobilized Mb molecules exhibited an enhanced electron transfer rate with a couple of well-defined redox peaks presented, indicating that direct electrochemistry of Mb was accomplished on Bi/GR/CILE. The designed biosensor displayed good electrocatalytic response to the TCA reduction without the additional electron mediators. Hence Bi/GR/CILE worked as an excellent electrochemical sensing platform for the third-generation biosensor designs.

ACKNOWLEDGMENTS
The work was supported from the National Natural Science Foundation of China (No. 21365010), the Natural Science Foundation of Shandong Province (ZR2013BM014), the Natural Science Foundation of Hainan Province (20152016), and the International S&T Cooperation Project of Hainan Province (KJHZ2015-13).

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