

# Application of Ionic Liquid-Graphene-NiO Hollowsphere Composite Modified Electrode for Electrochemical Investigation on Hemoglobin and Electrocatalysis to Trichloroacetic Acid

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Received: 2 January 2017 / Accepted: 8 March 2017 / Published: 12 April 2017

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In this present paper NiO hollowsphere was synthesized by a solvothermal method. Then it characterized by different methods including powder X-ray diffraction and scanning electron microscopy. NiO hollowsphere was further mixed with hemoglobin (Hb), ionic liquid and graphene (GR) to get a biocomposite, which was casted on carbon ionic liquid electrode. Spectroscopic data showed that Hb kept its native structure in the mixture. Direct electron transfer of Hb were investigated with a pair of well-defined quasi-reversible redox peaks appeared and the formal peak potential ( $E^0$ ) was got at -0.341 V (vs. SCE). The Hb modified electrode showed excellent electrocatalysis to trichloroacetic acid (TCA) reduction. Under the selected conditions the currents had a good linear relationship with TCA concentration from 1.5 to 10.0 mmol L<sup>-1</sup> and the detection limit was 0.5 mmol L<sup>-1</sup> ( $3\sigma$ ). This Hb based electrode exhibited good stability and reproducibility, which could be used for third-generation electrochemical biosensor.

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**Keywords:** NiO hollowsphere, Direct electrochemistry, Hemoglobin, Carbon ionic liquid electrode, Trichloroacetic acid.

## 1. INTRODUCTION

In recent years great efforts are put on electrochemical investigation on redox proteins/enzymes due to their usages in biological analysis and electrocatalytic biosensor [1]. However, electron transfer of proteins on the commonly used working electrode is hard due to the deeply burying of electroactive center [2]. To offer a specific interface for keeping the nature conformation of protein and improving

direct electron transfer rate from proteins to electrode, various materials are proposed for protein modified electrodes [3-6]. Ionic liquids (IL) are organic compounds that composed of organic cations with different anions, which are often present as liquid at room temperature. In the area of electrochemistry, ILs have been widely used due to their unique physicochemical characteristics, including relatively high ionic conductivity, good chemical stability, less vapor pressure, stable electrochemical windows and good biocompatibility [7, 8]. ILs can also be modified on the working electrodes [9]. Zhao et al. [10] applied ILs/carbon composite for the direct electrochemical behaviors of microperoxidase. Maleki et al. [11] mixed N-octylpyridinium hexafluorophosphate with carbon paste for the preparation of a high-performance carbon paste electrode. Sun et al. applied ILs based carbon paste electrodes for protein electrochemistry [12, 13] or drug analysis [14, 15].

As a metal oxide nanosized NiO nanoparticles have been widely used for the electrode modification due to large surface area, good chemical stability, excellent electrocatalysis and fast electron transfer capability [16]. Various NiO morphologies have been synthesized via different methods [17, 18], which can be used as the immobilization matrix for redox protein with direct electron transfer realized. Li et al. applied NiO hollow nanospheres for amperometric glucose sensor [19]. Zong et al. immobilized myoglobin to NiO nanoparticles modified graphite electrode [20].

As a thin-layer carbon nanosheet, graphene (GR) has attracted tremendous attentions due to its unique electronic, optical and chemical characteristics [21]. Because of the fast electron transport rate and large specific surface area, functionalized GR can accelerate the electron transfer from redox enzymes to electrodes [22]. Therefore GR has been widely applied to the preparation of electrochemical based sensors with improved performances [23]. GR has large surface area and can be used for loading of other nanomaterials. The composites exhibit the synergistic effects, which are promising in the electrode modification for sensing. GR based composites are used for electrode modifications and electrochemical sensors [24, 25].

In this paper NiO hollowsphere was synthesized and mixed with IL ([EMIM]EtOSO<sub>3</sub>), GR and hemoglobin (Hb) get a biocomposite, which was further applied to prepare an electrochemical sensing platform with carbon ionic liquid electrode (CILE). Nafion is a perfluorosulfonate linear ion-exchange polymer that has good proton conductivity and film forming ability, which is selected as an immobilization matrix for fixation [26]. Direct electrochemical investigation on Hb was realized and this Hb based sensor exhibited better electrocatalysis to trichloroacetic acid (TCA) reduction.

## 2. EXPERIMENTAL

### 2.1. Apparatus and reagents

A CHI 440A electrochemical analyzer (Shanghai Chenhua Instrument, China) was applied to the electrochemical measurements with a three-electrode model. The composite modified electrode was working electrode with a platinum wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. Scanning electron microscopy (SEM) was on a JSM-6700F scanning electron microscope (Japan Electron Company, Japan). X-ray powder diffraction (XRD) was operated

on a Japan RigakuD/Maxr-A X-ray diffractometer with graphite monochromatized high-intensity Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). UV-Vis and FT-IR spectra were on Cary 50 probe spectrophotometer (Varian Co., Australia) and Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific Inc., USA).

1-Ethyl-3-methyl-imidazolium tetrafluoroborate ([EMIM]BF<sub>4</sub>) and 1-ethyl-3-methyl-imidazolium ethylsulphate ([EMIM]EtOSO<sub>3</sub>) were got from Lanzhou Yulu Fine Chemical Co. Ltd. GR (Taiyuan Tanmei Co., China), Hb (Sigma-Aldrich Co., USA), Nafion (5% ethanol solution, Sigma-Aldrich Co., USA), carbon powder (particle size 30  $\mu\text{m}$ , Shanghai Colloid Chem. Co., China) and TCA (Tianjin Kemiou Chem. Ltd. Co., China) were used as received. 0.1 mol L<sup>-1</sup> phosphate buffer solutions (PBS) were prepared as the supporting electrolyte. The reagents were of analytical grade with doubly distilled water used throughout.

## 2.2. Preparation of NiO hollowsphere

NiO hollowsphere was synthesized with following procedure. 1.0696 g NiCl<sub>2</sub>·6H<sub>2</sub>O and 0.4 mL ammonia were dissolved homogeneously in 39.6 mL water. Then 4.0000 g glucose and 0.8225 g cetyltrimethyl ammoniumbromide was added with the mixture stirred for 60 min. The resulted solution was put into a 100 mL Teflon-lined stainless-steel autoclave with heating at 140 °C for 12 h. After cooled naturally to room temperature, the resulted material was collected by filtration, washed with water and absolute ethyl alcohol. Then it was heated at 60 °C for 6 h to obtain the black powder precursor. Finally NiO hollowspheres were got by calcining the obtained precursor at 600 °C for 5 h.

## 2.3. Preparation of modified electrode

According to the reference [27] CILE was home-made with [EMIM]BF<sub>4</sub> as the modifier, which was polished on a weighing paper before use. The composite was prepared by mixing 78  $\mu\text{L}$  31.0 mg mL<sup>-1</sup> Hb, 12  $\mu\text{L}$  [EMIM]EtOSO<sub>3</sub>, 13  $\mu\text{L}$  3.0 mg mL<sup>-1</sup> GR and 50  $\mu\text{L}$  0.8 mg mL<sup>-1</sup> NiO hollowsphere together, which was diluted to 200  $\mu\text{L}$  with 0.1 mol L<sup>-1</sup> PBS (pH 7.7). After sonicated homogeneously, 6.0  $\mu\text{L}$  Hb-IL-GR-NiO mixture was modified on CILE and dry at room temperature. Finally 7.0  $\mu\text{L}$  0.5 % Nafion solution was casted on the electrode and dried to get the resulted electrode (Nafion/Hb-IL-GR-NiO/CILE), which was stored at 4 °C refrigerator when not used. Other electrodes were fabricated with the similar methods for comparison.

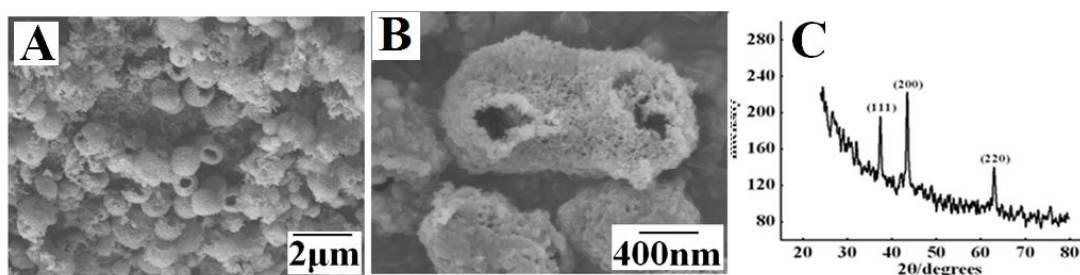
## 2.4. Procedure

Electrochemical experiments were performed in a 10 mL voltammetric cell with 0.1 mol L<sup>-1</sup> PBS that deoxygenated with highly purified nitrogen thoroughly for 30 min prior to experiments, which was kept in a nitrogen atmosphere during the measurements. UV-Vis spectroscopy were done with a mixture solution of Hb, [EMIM]EtOSO<sub>3</sub>, GR and NiO hollowsphere. Hb-IL-GR-NiO and Hb on a glass slide were prepared for FT-IR experiments.

### 3. RESULTS AND DISCUSSION

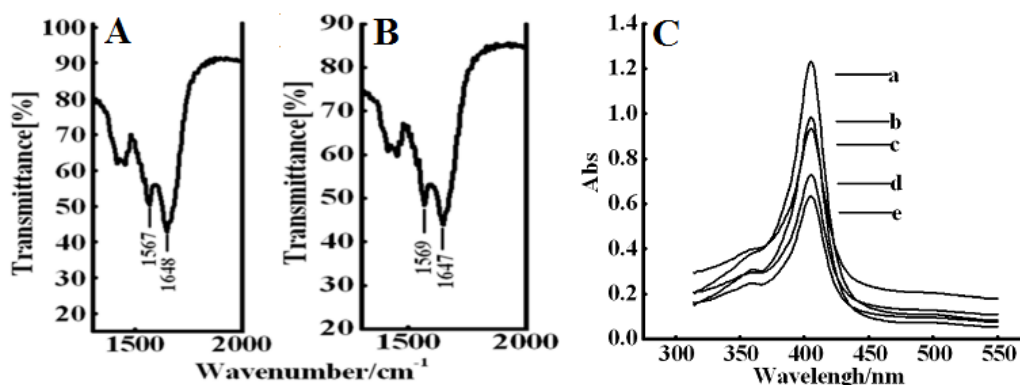
#### 3.1. Characteristics of NiO hollowsphere

As shown in Fig. 1 A and B, the panoramic morphology of NiO hollowsphere was present. All samples appeared as hollow sphere structure and the diameter was 1  $\mu\text{m}$  (Fig. 1A). The proportion of hollowsphere in the whole sample was more than 95 %. Enlarged observation indicated that on the surface of hollowsphere many holes appeared (Fig. 1B), which increased the surface area and enhanced the adsorption capacity on its surface. Fig. 1C showed a typical XRD data of NiO hollowsphere. The diffraction peaks at  $2\theta$  values of  $37.32^\circ$ ,  $43.47^\circ$ ,  $63.04^\circ$  were due to the reflection of (111), (200), (220) planes of NiO, which could be readily indexed to cubic crystalline phase NiO (JCPDS card 73-1591,  $a = 4.1684 \text{ \AA}$ ).



**Figure 1.** SEM images of NiO hollowsphere with different amplification multiples (A, B) and (C) XRD of the sample.

#### 3.2. Spectroscopic results



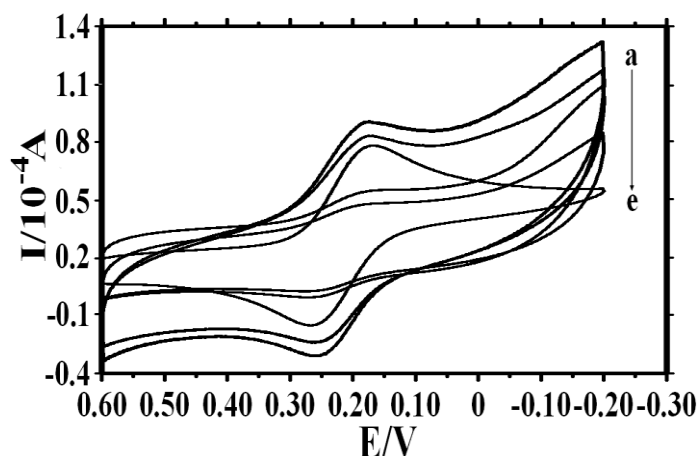
**Figure 2.** FT-IR spectra of (A) Hb and (B) Hb-IL-GR-NiO mixture, (C) UV-Vis absorption spectra of Hb-NiO (a), Hb (b), Hb-IL-NiO (c), Hb-GR-NiO (d) and Hb-IL-GR-NiO (e).

FT-IR spectroscopy is often used to check protein structure. The amide I ( $1700\text{--}1600 \text{ cm}^{-1}$ ) and amide II ( $1600\text{--}1500 \text{ cm}^{-1}$ ) infrared absorbance give detailed data about the secondary structure of the polypeptide chain [28]. The denatured Hb molecule will result in the diminish or even disappear of these bands. As shown in Fig. 2, FT-IR results of Hb amide bands appeared at  $1648$  and  $1567 \text{ cm}^{-1}$  (Fig. 2A), which was almost the same as that of Hb mixed with IL, GR and NiO together ( $1647$  and

1569  $\text{cm}^{-1}$ , Fig. 2B). In UV-Vis absorption spectrum the Soret absorption band of redox proteins also provide the information about the conformational integrity [29]. As shown in Fig. 2C, the Soret band of Hb could be observed at 405.0 nm in 0.1 mol  $\text{L}^{-1}$  PBS before or after mixed with other materials. The data indicated that Hb had its native structure remained due to the biocompatibility of IL, GR and NiO hollowsphere.

### 3.3 Electrochemical characteristics of the modified electrodes

Cyclic voltammograms of different modified electrodes in a ferricyanide solution were recorded to evaluate the modification effects. As shown in Fig. 3, a pair of well-defined redox peaks could be observed on the different modified electrodes. On CILE (curve c) the peak-to-peak separation was 0.093 V (vs. SCE), indicating a relative good reversibility on CILE. On Nafion/Hb/CILE (curve e) the redox peak currents decreased to the smallest value, which was due to the presence of Hb on the electrode hindered the electron transfer rate. The redox peak currents increased step-by-step on Nafion/Hb-NiO/CILE (curve d), Nafion/Hb-IL-NiO/CILE (curve b) and Nafion/Hb-IL-GR-NiO/CILE (curve a) with the incorporation of NiO, IL and GR on the electrode gradually. Therefore the interfacial conductivity was increased with the addition of high conductive IL and GR, or the incorporation of semiconductive NiO hollowsphere, which exhibited the synergistic effects and enhanced the electron transfer rate of ferricyanide.

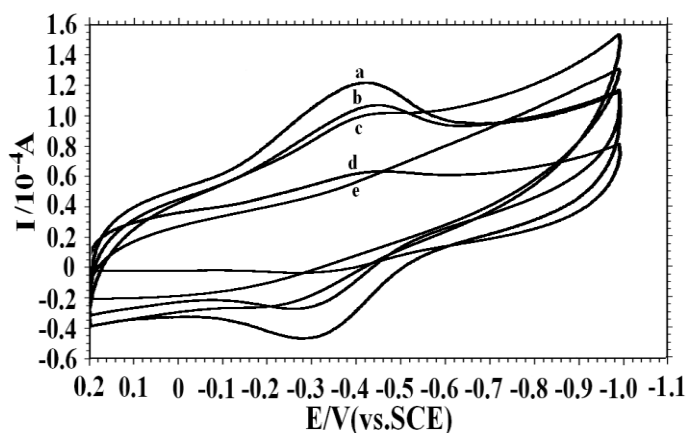


**Figure 3.** Cyclic voltammograms of (a) Nafion/Hb-IL-GR-NiO/CILE, (b) Nafion/Hb-IL-NiO/CILE, (c) CILE, (d) Nafion/Hb-NiO/CILE and (e) Nafion/Hb/CILE in a mixture solution of 1.0 mmol  $\text{L}^{-1}$   $[\text{Fe}(\text{CN})_6]^{3-}$  and 0.1 mol  $\text{L}^{-1}$  KCl with the scan rate as 100  $\text{mV s}^{-1}$ .

### 3.4 Direct electrochemistry of Hb modified electrode

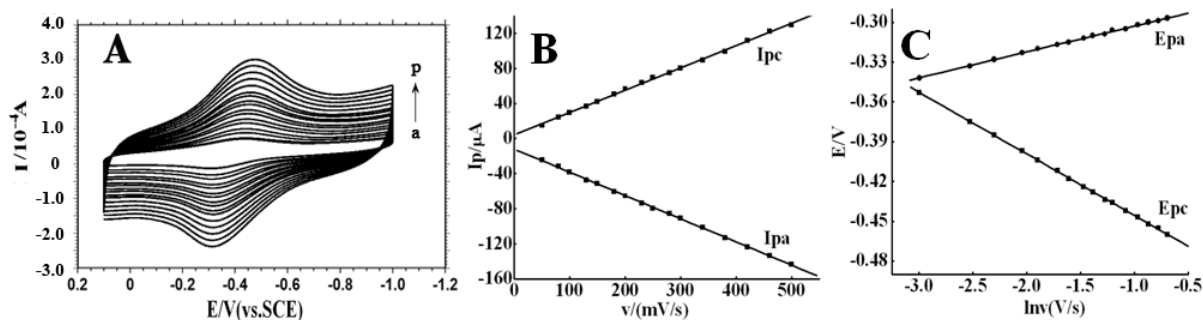
Direct electrochemical investigations were performed by cyclic voltammetry and the curves were listed in Fig. 4. On Nafion/IL-GR-NiO/CILE (curve e) no redox peaks appeared in the selected potential range. On Nafion/Hb/CILE (curve d) a pair of unsymmetric redox peaks with low redox peak currents was observed, indicating a slow direct electron transfer from Hb to CILE. On Nafion/Hb-

NiO/CILE (curve c) the redox peak current enhanced due to the presence of NiO hollowsphere that could facilitate the electron transfer. NiO hollowsphere with many mesoporous on its surface could form a three-dimensional structure for the loading of protein. On Nafion/Hb-IL-NiO/CILE (curve b) a couple of stable and well-defined redox peaks appeared due to the high conductivity of IL. While on Nafion/Hb-IL-GR-NiO/CILE (curve a) the biggest peak currents appeared with symmetric curves, showing a fast electron transfer rate. The cathodic ( $E_{pc}$ ) and anodic ( $E_{pa}$ ) peak potential were located at -0.382 V and -0.300 V, and the formal peak potential ( $E^{0'}$ ) was got as -0.341 V (vs. SCE). The high of redox peak currents was almost the same, indicating a quasi-reversible electrochemical reaction.



**Figure 4.** Cyclic voltammograms of (a) Nafion/Hb-IL-GR-NiO/CILE, (b) Nafion/Hb-IL-NiO/CILE, (c) Nafion/Hb-NiO/CILE, (d) Nafion/Hb/CILE and (e) Nafion/IL-GR-NiO/CILE at the scan rate of  $100 \text{ mV s}^{-1}$  in pH 7.7 PBS.

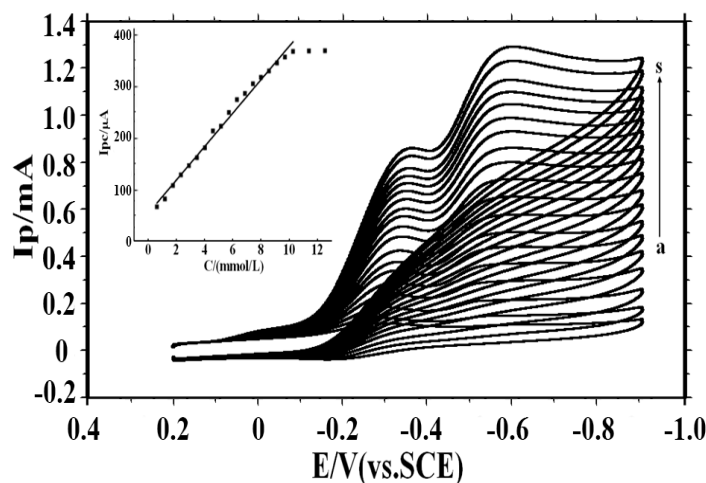
Fig. 5A showed the influence of scan rate on cyclic voltammograms of Nafion/Hb-IL-GR-NiO/CILE in pH 7.7 PBS. The peak currents increased with scan rate from  $50$  to  $500 \text{ mV s}^{-1}$  with the data shown in Fig. 5B. Two linear regression equations between the peak currents and scan rate were got as  $I_{pc} (\mu\text{A}) = 0.25v (\text{mV s}^{-1}) + 4.07$  ( $\gamma = 0.999$ ) and  $I_{pa} (\mu\text{A}) = -0.260 v (\text{mV s}^{-1}) - 11.92$  ( $\gamma = 0.999$ ), showing a surface-controlled thin-layer process. From the equation  $Q = nAF\Gamma^*$  [30], the surface concentration of electroactive Hb ( $\Gamma^*$ ) was  $2.16 \times 10^{-9} \text{ mol cm}^{-2}$ , which counted for 24.11% of the total Hb present on the electrode. The result was ascribed to the large and specific sphere surface for Hb to exchange the electron at higher efficiency. The increase of scan rate also led to the increase of the peak-to-peak separation without the change of the formal peak potential. Based on Laviron's equations [31], the electrochemical parameters of the Hb electrode reaction could be calculated. As shown in Fig. 5C, two linear regression equations of  $E_p$  and  $\ln v$  were constructed and the results were  $E_{pa} (\text{V}) = 0.019 \ln v - 0.283$  ( $\gamma = 0.999$ ) and  $E_{pc} (\text{V}) = -0.046 \ln v - 0.492$  ( $\gamma = 0.999$ ). Then the electron transfer coefficient ( $\alpha$ ) and the apparent heterogeneous electron transfer rate constant ( $k_s$ ) were 0.55 and  $0.703 \text{ s}^{-1}$ . This  $k_s$  value was larger than some former references [32-34], proving a fast electron transfer rate of Hb in IL-GR-NiO composite.



**Figure 5.** (A) Influence of scan rate on cyclic voltammograms of Nafion/Hb-IL-GR-NiO/CILE in pH 7.7 PBS, the scan rates from a to p were 50, 80, 100, 130, 150, 180, 200, 230, 250, 280, 300, 340, 380, 420, 460, 500  $\text{mV s}^{-1}$ . (B) Linear relationship of  $I_{pc}$  and  $I_{pa}$  versus scan rate ( $v$ ). (C) Linear relationship of  $E_{pa}$  and  $E_{pc}$  versus  $\ln v$ .

### 3.5. Electrocatalysis

Electrocatalysis of this Hb based electrode to the TCA reduction was checked by cyclic voltammetry with the curves shown in Fig. 6. Different concentrations of TCA added in PBS resulted in significant increase of the reduction peak current at  $-0.29$  V and the oxidation peak disappeared, which was ascribed to the presence of Hb molecules on the electrode that exhibited good catalytic ability to TCA. The catalytic reduction currents increased with the TCA concentration from  $1.5$  to  $10.0$   $\text{mmol L}^{-1}$  and the linear regression equation was  $I_{ss} (\mu\text{A}) = 38.10 \pm 1.52 C (\text{mmol L}^{-1}) + 18.78 \pm 0.76$  ( $n = 26$ ,  $\gamma = 0.998$ ) with the detection limit as  $0.5$   $\text{mmol L}^{-1}$  ( $3\sigma$ ).



**Figure 6.** Cyclic voltammograms of Nafion/Hb-IL-GR-NiO/CILE in  $0.1$   $\text{mol L}^{-1}$  pH 7.7 PBS with different concentrations of TCA at the scan rate of  $100$   $\text{mV s}^{-1}$ . (curve a to s was  $1.5$ ,  $1.8$ ,  $2.0$ ,  $2.5$ ,  $3.0$ ,  $3.5$ ,  $4.0$ ,  $4.5$ ,  $5.0$ ,  $5.5$ ,  $6.0$ ,  $6.5$ ,  $7.0$ ,  $7.5$ ,  $8.0$ ,  $8.5$ ,  $9.0$ ,  $9.5$ ,  $10.0$   $\text{mmol L}^{-1}$ ). Inset is linear relationship of catalytic reduction peak currents and the TCA concentration.

### 3.6. Stability of the electrodes

The stability of Nafion/Hb-IL-GR-NiO/CILE was investigated by cyclic voltammetric scan for 100 cycles, which had no obvious decrease of the response. When the electrode was stored at  $4$   $^{\circ}\text{C}$ ,

96% of its initial response current remained after 2 weeks storage and 94.3% remained after 1 month, demonstrating a good long-term stability. Eight Hb modified electrodes were fabricated by the same procedure for the determination of 5.0 mmol L<sup>-1</sup> TCA, which had the relative standard deviation (RSD) value of 2.1%, indicating a good repeatability.

#### 4. CONCLUSION

In this paper Hb, IL, GR and NiO hollowsphere were mixed to form a biocomposite, which was casted on the electrode surface to obtain an electrochemical sensor. Electrochemistry of this Hb modified electrode was carefully investigated with direct electrochemical responses of Hb greatly enhanced, which was attributed to the synergistic effects. A systematic comparison of different electrochemical TCA sensors were summarized in table 1, which indicated that this modified electrode was able to detect TCA with lower detection limit due to the specific composition of the modifier used. Therefore this electrochemical sensor exhibited excellent electrocatalytic activity to the TCA reduction with well-defined analytical results.

**Table 1.** Comparison of electrocatalytic TCA analysis with various protein modified electrodes.

Modified electrodes	Linear range (mmol·L <sup>-1</sup> )	Detection limit (mmol·L <sup>-1</sup> )	Refs.
CTS/CMS-Hb/CILE	2.0 - 70.0	0.30	5
CTS/Mb/ZrO <sub>2</sub> /GR/CILE	0.4 - 29.0	0.13	13
CTS-Hb-CNT-IL/CILE	1.6 - 12.0	0.40	35
Nafion/Mb-SA-TiO <sub>2</sub> /CILE	5.3 - 114.2	0.152	36
Nafion/Mb-SA-Fe <sub>3</sub> O <sub>4</sub> -GR/CILE	1.4 - 119.4	0.174	37
Nafion/HRP/MoS <sub>2</sub> /CILE	10.0 - 63.0	0.67	38
CS/Mb/3DrGO-Au/CILE	0.2 - 36.0	0.06	39
CTS/NiO-HRP/CILE	0.8 - 38.0	0.26	40
CTS/GR-CuS/CILE	1.0 - 64.0	0.20	41
AFIL-LDH-Hbcop/GCE	0.8 - 430	0.194	42
Nafion/Hb-IL-GR-NiO/CILE	1.5 - 10.0	0.5	This work

#### ACKNOWLEDGEMENTS

We acknowledge the financial support of the Program for Innovative Research Team in University (IRT-16R19), and the Science and Research Key Project of Universities of Hainan Province (Hnky2016ZD-10).

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