

The Host – Guest Interaction Between Cucurbit[7]uril and Ferrocenemonocarboxylic Acid for Electrochemically Catalytic Determination of Glucose

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Abstract: A simple and sensitive method for glucose determination was described based on the host-guest inclusive complex of cucurbit[7]uril and ferrocenemonocarboxylic acid. In this work, the mixture of cucurbit[7]uril and graphene oxide, ferrocenemonocarboxylic acid as electron transfer mediator and glucose oxidase as catalytic material were modified successively on the electrode.

Under the optimized conditions, a linear response between current intensity and glucose concentrations over a range of 0.1–10 mM was obtained with a relatively low detection limit (27 μM , $S/N=3$). Meanwhile, this method exhibited high selectivity in the interference investigation, and the reliability and applicability in human serum samples analysis.

Keywords: Cucurbit[7]uril • Ferrocenemonocarboxylic acid • Host-guest interaction • Glucose determination • Human serum sample

1 Introduction

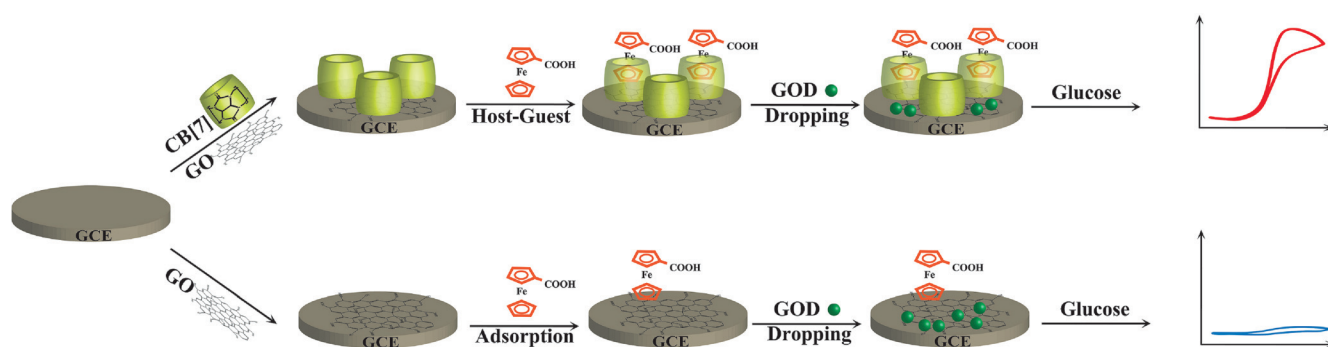
In recent years, the host – guest interactions exhibited by different macrocyclic receptors, such as cyclodextrins, crown ethers, calixarenes, have been extensively explored for bioanalysis [1–3]. Cucurbit[*n*]urils, which are found to be used very popular in electrochemical biosensing recently [4–6], are a group of macrocyclic compounds with polar carbonyl groups surrounding the portals and pumpkin-shaped molecules [7–9]. Compared to the other homologues, cucurbit[7]uril (CB[7]) has a relatively moderate solubility in water and appropriate cavity size to form very stable complexes with ferrocene (Fc) and its derivatives, such as 1,1'-bis(trimethylammoniomethyl)ferrocene (BAFc) ion, which has the binding constant as high as 10^{15} M^{-1} [10–13].

In the electrochemically catalytic determination of glucose, Fc and its derivatives, as the mediators [14], have been proved to be more efficient in the process of shuttling electrons between glucose oxidase (GOD) and the electrode owing to their good electrochemical reversibility and stability at low potential [15–17]. In the present literatures, Fc and its derivatives were entrapped on the electrode in different ways, such as direct adsorption [18], conjugation with active and inert proteins [19], cross-linking with polymer [20], synthesis of Fc derivatives with specific functional groups [21]. All these ways would result in some problems, including the leakage of the mediator, catalytic activity losing of active biomolecules, harsh conditions of the cross-linking experiments and complicated preparation [22–25]. However, these problems can be effectively resolved by the host-guest inclusion. Currently, it has been demonstrated that except the function of mediator, Fc and its derivatives also can be employed as a guest simultaneously [26–28]. In most researches, β -cyclodextrin (β -CD) was used as the host to

envelop Fc and its derivatives [29,30]. CB[7] with the comparable cavity size to β -CD can form the more stable inclusion complexes with them [31,32], because the host-guest recognition of β -CD primarily relies on hydrophobic interactions [33,34], while CB[7] not only relies on this kind of interaction but also depends on ion-dipole interactions owing to its carbonyl oxygen [10,31]. Therefore, the inclusive complex formed by CB[7] and Fc and its derivatives can be excellent candidates in application for glucose biosensing.

In our work, based on the host-guest interaction between CB[7] and ferrocenemonocarboxylic acid (Fc-COOH), a sensitive method for glucose biosensing has been proposed for the first time. In order to enhance the stability of CB[7] on the electrode and increase the electron transfer efficiency, graphene oxide (GO) is involved in this method, due to its unique advantages [35–37], such as large specific surface area, high electrical mobility, and low production cost. As illustrated in Scheme 1, the mixture of CB[7] and GO in a certain proportion was firstly immobilized on glassy carbon electrode (GCE), and Fc-COOH as the electron transfer mediator was captured on the electrode by host-guest recognition. Then, the catalytic agent – GOD was modified on Fc-COOH/CB[7]-GO/GCE for the further glucose biosensing. This developed glucose biosensing method shows the excellent performance in sensitivity and selectivity.

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Scheme 1. Schematic illustration of GOD/Fc-COOH/CB[7]-GO/GCE and GOD/Fc-COOH/GO/GCE for glucose detection.

2 Experimental

2.1 Instrumentation

Electrochemical experiments were all performed on a CHI 660C electrochemical workstation (Chenhua, Shanghai) at room temperature. A three-electrode system was utilized in a 10 mL electrochemical cell for electrochemical determination: GOD/Fc-COOH/CB[7]-GO/GCE as the working electrode, Ag/AgCl (saturated KCl solution) as reference electrode and platinum wire as counter electrode. The pH values of a series of 0.1 M PBS (containing Na_2HPO_4 - NaH_2PO_4 and KCl) were measured by a PHS-3C pH meter (Leici Instrumental Factory, Shanghai). The glucose in human serum sample was determined by a Yuezhun III glucose meter (Jiangsu Yuyue Medical Equipment & Supply Co., Ltd.). The ultrapure water was from a Millipore Milli-Q system.

2.2 Reagents

$\text{K}_3\text{Fe}(\text{CN})_6$, KCl, Na_2HPO_4 , NaH_2PO_4 , ascorbic acid (AA), uric acid (UA) and L-cysteine (Cys) were purchased from Sinopharm Chemical Reagent Co., Ltd. Cucurbit[7]uril (CB[7]) was obtained from Taiyuan Aisiweida Chemical Technology Co., Ltd. 3-Hydroxytyramine hydrochloride (DA-HCl) and glucose oxidase (GOD) were purchased from Sigma-Aldrich Chemical Company. All reagents were of analytical reagent grade and all the solutions were prepared with ultrapure water.

2.3 Preparation of GOD/Fc-COOH/CB[7]-GO/GCE and Electrochemical Detection

The bare GCE was firstly cleaned by ultrasonication in ethanol and ultrapure water for 5 min respectively, and then the electrode was carefully polished on the chamois leather with Al_2O_3 slurry (0.05 μm and 0.3 μm) to obtain a smooth surface and rinsed with ultrapure water. Subsequently, 5 μL of homogeneous CB[7]-GO suspension after ultrasonical mixing was dropped on the pretreated GCE and dried at 30 °C to form a uniform film. After that, the CB[7]-GO/GCE was immersed in the 1 mM Fc-COOH solution for host-guest recognition process. 3 h

later, Fc-COOH/CB[7]-GO/GCE was washed with ultrapure water, and 5 μL of GOD was dropped on it and dried at room temperature.

Electrochemical responses were recorded by cyclic voltammetry (CV) in 0.1 M PBS solution at room temperature in a range of 0–0.6 V with a scan rate of 10 mV/s.

2.4 Pretreatment of Serum Sample

Human serum samples were obtained from the local hospital and centrifuged before stored in the refrigerator at –20 °C. The supernatant was diluted with 0.1 M PBS: Sample 1, 2 and 3 was diluted 5 folds, 3 folds and 1 fold, respectively. Then each sample was divided into two portions for further analysis. The first portion was used for glucose determination in the real pretreated serum sample, while the second one was mixed with 4 mM glucose to determine the recovery with the standard addition method.

3 Results and Discussion

3.1 Recognition Ability of Different Modified Electrodes for Fc-COOH

The ability of different modified electrodes to envelop Fc-COOH was investigated by recording the CV responses of Fc-COOH (Figure 1). Compared to bare GCE (curve a) and GO/GCE (curve c), CB[7]/GCE (curve b) and CB[7]-GO/GCE (curve d) exhibited increased peak current after interacting with Fc-COOH for 3 h respectively, showing that CB[7] could effectively form inclusion complex with Fc-COOH. On the other hand, with the addition of GO, GO/GCE and CB[7]-GO/GCE presented better performance on current intensity than GCE and CB[7]/GCE. Moreover, a pair of nearly reversible redox peaks was obtained on CB[7]-GO/GCE. As we know that GO has large specific surface area and abundant functional groups, thus it can increase the immobilized amount of CB[7] on the electrode and the electron transfer efficiency in the electrocatalytic determination, leading to the improved stability, sensitivity and reversibility of CB[7]-GO/GCE.

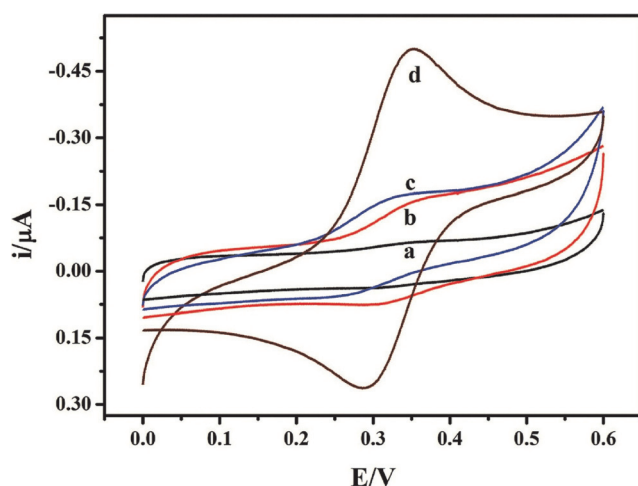


Fig. 1. CVs of Fc-COOH on different modified electrodes in 0.1 M PBS (pH 7.0) at a scan rate of 10 mV/s: (a) GCE; (b) CB[7]/GCE; (c) GO/GCE; (d) CB[7]-GO/GCE.

3.2 Electrocatalytic Oxidation of Glucose at Different Modified Electrodes

Figure 2 displays the electrocatalytic performance on glucose oxidation of different modified electrodes. Clearly, there was no electrochemical response without modifying Fc-COOH on the electrode (curve a). Even, when Fc-COOH was modified through the adsorption with GO rather than the host-guest interactions, no obvious current growth was observed (curve b). The reason maybe was that the adsorption amount of Fc-COOH was too small to cause the obvious electro-catalytic effect. Nevertheless, when the abundant Fc-COOH and GOD coexist on the modified electrode, the enhancement of oxidation current (curve c) can be presented clearly, indicating that CB[7] could effectively envelop Fc-COOH to produce distinct

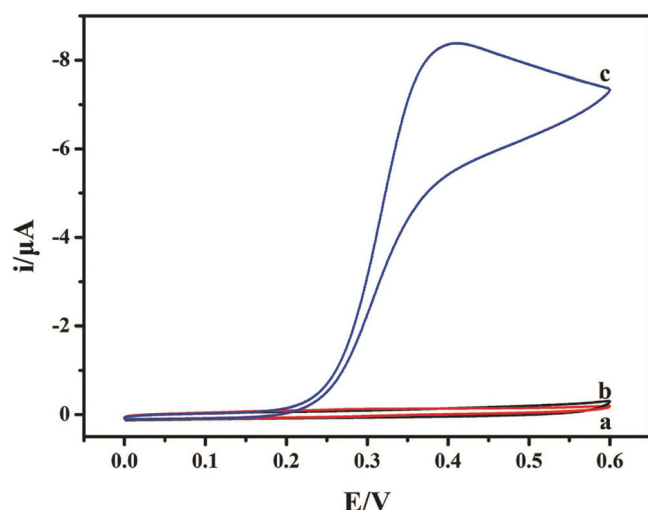


Fig. 2. CVs of 10 mM glucose (0.1 M PBS, pH 7.0) on different modified electrodes at a scan rate of 10 mV/s: (a) GOD/CB[7]-GO/GCE; (b) GOD/Fc-COOH/GO/GCE; (c) GOD/Fc-COOH/CB[7]-GO/GCE.

electrocatalytic oxidation of glucose due to their strong host-guest interaction. The inclusive complexes of Fc-COOH and CB[7] can be regarded as the electron mediator between the electrode and the enzyme. Thus, the GOD/Fc-COOH/CB[7]-GO/GCE can be used for further glucose biosensing.

3.3 Optimization of Experimental Variables

As known to all, various experimental variables would affect the determination of glucose. To further improve the detection sensitivity, the experimental conditions for glucose detection have been optimized, including the mixing ratio between GO and CB[7] along with their concentrations, pH value and ionic strength of PBS, and GOD concentration.

3.3.1 Optimization of the Mixing Ratio Between GO and CB[7] along with Their Concentrations

GO could immobilize CB[7] effectively, but too large proportion of the GO would affect the electron transfer rate, so it is important to seek out the optimal ratio between GO and CB[7]. The mixture of GO and CB[7] was prepared with constant concentration of CB[7] (0.6 mg/mL) and the variable concentrations of GO in the range of 0.15–2.4 mg/mL. Figure 3A shows that the peak current raised as the proportion of GO increased. When the mixing ratio reached 2 : 1, the catalytic effect was optimal. However, the peak current began to decrease as the ratios were higher than 2 : 1, perhaps because GO in too large proportion impeded the envelope process between Fc-COOH and CB[7], resulting in a little Fc-COOH captured on the electrode. Therefore, the ratio of 2 : 1 was selected as the optimum mixing condition.

The thickness of the modified film would also influence the current response of the electrode, therefore the effect of CB[7] concentration was investigated with the optimized ratio 2 : 1 between GO and CB[7]. In Figure 3B, it could be observed that the peak current enhanced with the increase of CB[7] concentration until 0.9 mg/mL, probably due to the unsaturated amount of CB[7] immobilized on electrode under this concentration. When it was above 0.9 mg/mL, the current declined, since the relatively thick modified film would generate the low electron transfer rate. Therefore, 0.9 mg/mL was selected as the optimum concentration.

3.3.2 Optimization of pH Value and Ionic Strength of PBS

The pH value of PBS has a huge impact on the catalytic rate and catalytic activity of GOD. Many studies [38,39] have been reported that neutral pH was more appropriate for glucose sensing application and the catalytic activity of GOD would be damaged while the pH was too low or too high. Herein, the effect of pH values was researched in the range of 5.0–9.0 and the results in Figure 3C demonstrated that the strongest current signal

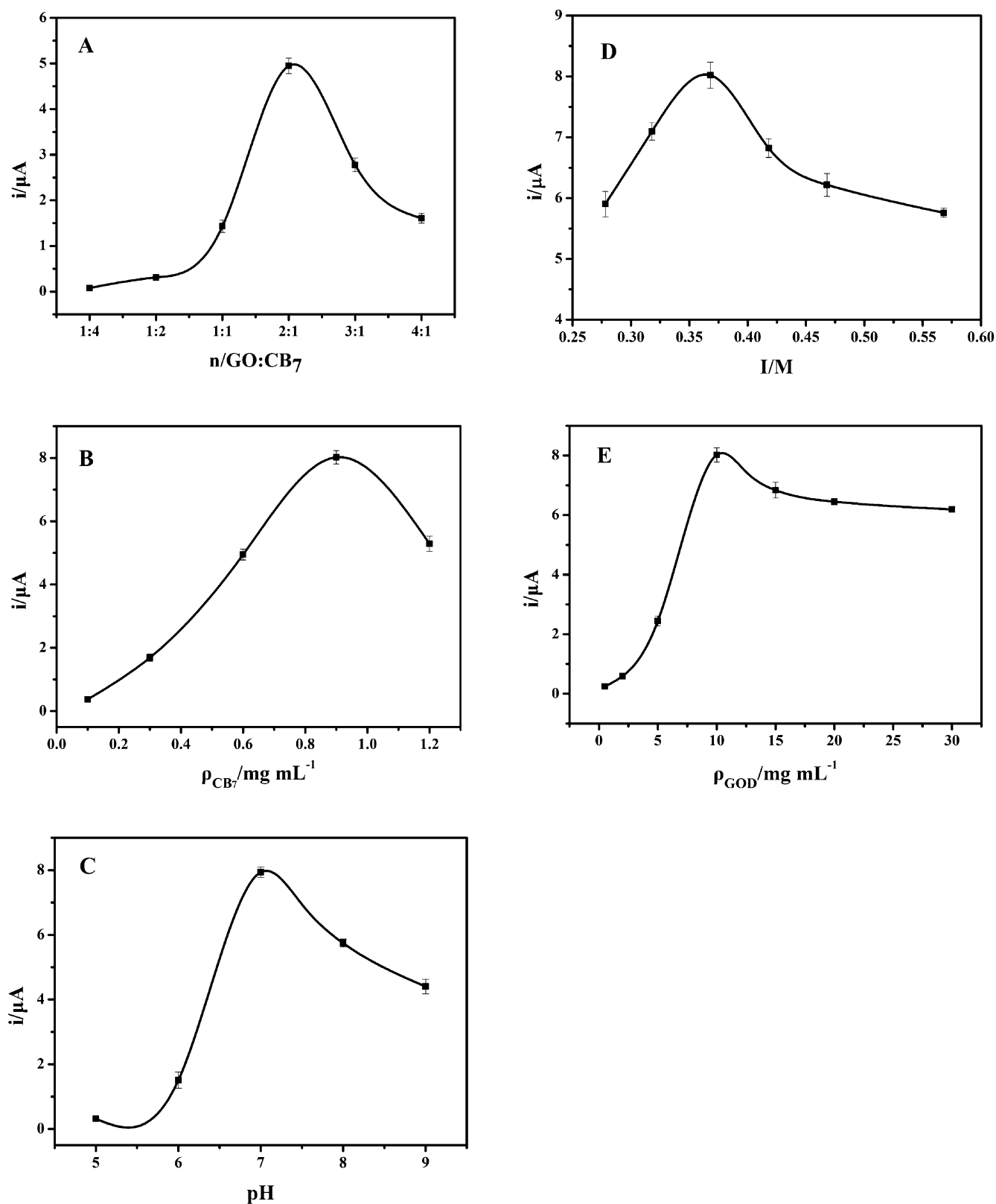


Fig. 3. (A) The effect of $n(\text{GO}:\text{CB}_7)$ on the peak current from 1:4 to 4:1 in 10 mM glucose (0.1 M PBS, pH 7.0) at room temperature. (B) The effect of ρ_{CB_7} on the peak current from 0.1 mg/mL to 1.2 mg/mL in 10 mM glucose (0.1 M PBS, pH 7.0) at room temperature. (C) The effect of pH on the peak current from 5.0 to 9.0 in 10 mM glucose (0.1 M PBS) at room temperature. (D) The effect of the ionic strength on the peak current from 0.278 M to 0.568 M in 10 mM glucose (0.1 M PBS, pH 7.0) at room temperature. (E) The effect of ρ_{GOD} on the peak current from 0.5 mg/mL to 30 mg/mL in 10 mM glucose (0.1 M PBS, pH 7.0) at room temperature.

could be obtained near pH 7.0. When it was below or above 7.0, the signal decreased. Besides, the normal value pH of human blood is known to be around 7.0. Thus, pH 7.0 was selected in the experiment as the optimum condition.

The effect of ionic strength was examined as well through changing the concentration of KCl in PBS, as it may influence the stability of the inclusion complex [40]. As shown in Figure 3D, the peak current increased when the ionic strength of PBS raised. As it reached 0.368 M, the peak current was the maximum. However, with the continuous increasing of ionic strength, the peak current decreased instead, probably because too high ionic strength would decrease the interaction between GOD and the modified electrode.

3.3.3 Optimization of GOD Concentration

The concentration of GOD was another important factor for its catalytic activity, because the high concentration would produce the thick film, and then bring about the decreased catalytic activity. As shown in Figure 3E, when the concentration of GOD increased from 0.5 mg/mL to 10 mg/mL, the response current enhanced rapidly. However, when the concentration continuously increased to 30 mg/mL, the response current gradually decreased on the contrary, which probably was caused by the resistance of the thick film. Consequently, 10 mg/mL was selected in the experiment as the optimum concentration of GOD.

3.4 Quantitative Determination of Glucose

The determination of glucose was performed at GOD/Fc-COOH/CB[7]-GO/GCE by cyclic voltammetry under the optimal conditions. As indicated in Figure 4, the catalytic peak current enhanced with glucose concentration increasing and the corresponding linear range of glucose is from 0.1 to 10 mM with a detection limit of 27 μM ($S/N = 3$). Compared with other methods to entrap the mediator (Table 1), the proposed glucose biosensing method using the host-guest interaction to capture Fc-COOH has a wider linear range and a higher sensitivity.

Table 1. Comparison of GOD/Fc-COOH/CB[7]-GO/GCE electrode with other reported glucose sensing method based on Fc and its derivatives as the mediator. GOx/paper disk: glucose oxidase/paper disk; Fc/Nafion/GOx: ferrocene/Nafion/glucose oxidase; PPy/Fc/GOx: polymer polypyrrole/ferrocene/glucose oxidase; Th/ThCO₂H/ThFc: poly(thiophene)/poly(3-thiophene acetic acid)/dicyclopentadienyl iron-1,4-dien; FC-20/Chi/GOx: ferrocene modified polysiloxane/chitosan/glucose oxidase; GOD/Fc-COOH/CB[7]-GO: glucose oxidase/ferrocenemonocarboxylic acid/cucurbit[7]uril-graphene oxide.

| Matrix | Immobilization method | Linear range | Detection limit | Sensitivity | References |
|-----------------------------|--------------------------|--------------|-------------------|--|------------|
| GOx/paper disk | In solution | 1.0–5.0 mM | 180 μM | 0.25 $\mu\text{A mM}^{-1}$ | [41] |
| Fc/Nafion/GOx | Incorporation | Up to 2.7 mM | 44 μM | 6.92 nA mM^{-1} | [42] |
| PPy/Fc/GOx | Electrochemical process | 0–25 mM | – | 20 nA mM^{-1} | [43] |
| Th/ThCO ₂ H/ThFc | Synthesis of derivatives | 0.5–3.0 mM | 2.5 μM | 40 $\text{nA mM}^{-1}\text{cm}^{-2}$ | [44] |
| FC-20/Chi/GOx | Cross-linking | Up to 6 mM | – | 0.86 $\mu\text{A mM}^{-1}\text{cm}^{-2}$ | [45] |
| GOD/Fc-COOH/CB[7]-GO | Host-guest | 0.1–10 mM | 27 μM | 0.80 $\mu\text{A mM}^{-1}$ | This work |

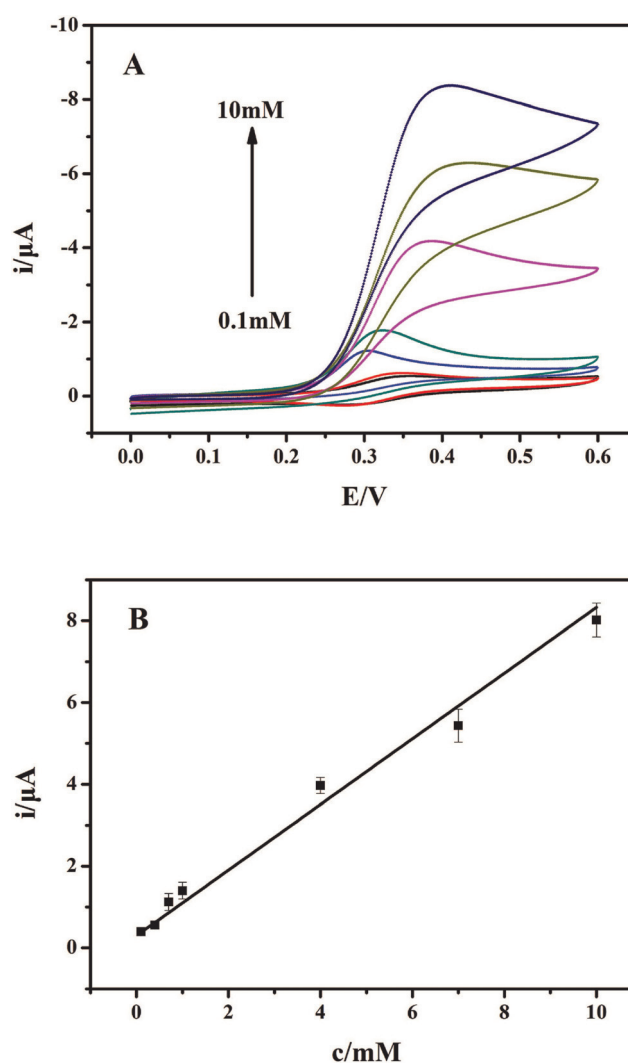


Fig. 4. (A) CV responses of glucose at different concentrations in 0.1 M PBS (pH 7.0) at a scan rate of 10 mV/s. (B) Calibration curve of response current towards different concentrations of glucose.

3.5 Interference Investigation

Cyclic voltammetric experiments proceed to study the interference effect of other oxidizable compounds co-existing with glucose in natural samples, such as ascorbic acid (AA), uric acid (UA), 3-hydroxytyramine hydrochloride

(DA-HCl), l-cysteine (Cys). It has been reported that the normal physiological levels of glucose is at least 30 times higher than that of AA, dopamine (DA) and UA [46]. In our work, there were essentially negligible current responses after additions of 0.4 mM AA, 0.4 mM UA, 0.4 mM DA-HCl and 4 mM Cys to 4 mM glucose solution, respectively (Table 2). Usually, AA and UA would

Table 2. Influence of interfering compounds on the response of glucose sensing. i_G : Current response to 4 mM glucose; i_{G+I} : current response to 4 mM glucose in presence of interfering compounds.

| Interfering compound | Concentration (mM) | $(i_{G+I}-i_G)/i_G$ (%) |
|----------------------|--------------------|-------------------------|
| AA | 0.4 | 6.71 |
| UA | 0.4 | 1.04 |
| DA-HCl | 0.4 | 4.19 |
| Cys | 4 | 1.76 |

affect the determination of glucose because of their overlapping oxidation peaks [27,47], but in this assay, they had hardly any interference to glucose. The reason maybe that the complex film Fc-COOH/CB[7]-GO could hinder the access of these interfering materials to the electrode surface, thereby almost avoiding the interference. Consequently, this sensing method is highly selective for the determination of glucose under physiological conditions.

3.6 Human Serum Sample Measurement

In order to study the practical application of the developed glucose sensing method in clinical analysis, it was applied to determine the real human serum samples with cyclic voltammetry technique under the optimized conditions. Obviously, the obtained results were very close to those determined by the glucose meter (Table 3). Moreover, with the standard addition method, the recovery of glucose in the real samples ranged from 92.60% to 98.99% ($n=3$), which indicated that the glucose sensing method was reliable and applicable in real human serum sample analysis.

4 Conclusions

In conclusion, this work described a novel and efficient detection protocol for glucose based on inclusive complex of cucurbit[7]uril and ferrocenemonocarboxylic acid and the involvement of graphene oxide with simplicity, high sensitivity and selectivity. GOD/Fc-COOH/CB[7]-GO/GCE was exploited to detect glucose with the electrochemical catalysis of GOD, in which, Fc-COOH captured

by CB[7] through host-guest interaction was utilized as electron mediator between GOD and the electrode. The biosensing method shows a broad linear range from 0.1–10 mM with low detection limit of 27 μ M ($S/N=3$) for glucose determination under the optimized conditions. It also exhibits that the coexisting interfering analytes under physiological conditions do not interfere with the glucose biosensing. Furthermore, our method was successfully applied to the detection of glucose in real human blood serum samples, which provides a facile and rapid detection approach in interrelated diseases diagnostic assays.

Acknowledgements

This work was financially supported by the *National Nature Science Foundation of China* (Grant No. 21275054).

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Table 3. Glucose determination in serum sample (G: glucose).

| Serum samples | Electrochemical result (mM) | Glucose meter (mM) | G added (mM) | G found (mM) | Recovery (%) |
|---------------|-----------------------------|--------------------|--------------|--------------|--------------|
| Sample 1 | 1.042 | 1.030 | 4 | 4.669 | 92.60 |
| Sample 2 | 1.819 | 1.724 | 4 | 5.482 | 94.21 |
| Sample 3 | 2.527 | 2.582 | 4 | 6.461 | 98.99 |

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Received: October 23, 2014
Accepted: December 7, 2014
Published online: April 24, 2015