Fabrication of Myoglobin-Sodium Alginate-Graphene Composite Modified Carbon ionic liquid electrode via the Electrodeposition Method and Its Electrocatalysis toward Trichloroacetic Acid

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To achieve the accurate determination of trichloroacetic acid (TCA) in water chlorination, the sensitive electrochemical biosensor, Nafion/myoglobin-sodium alginate-graphene composite modified carbon ionic liquid electrode (Nafion/Mb-SA-GR/CILE), was fabricated by the electrodeposition method. Spectroscopic results implied that Mb could keep its biological activity in the SA-GR composite film. Direct electrochemistry of Nafion/Mb-SA-GR/CILE indicated that direct electron transfer of Mb was realized on the modified electrode, which was attributed to the synergistic effects of SA-GR composite film with excellent electrocatalytic capability and good biocompatibility. Furthermore, the modified electrode displayed good electrocatalytic ability towards TCA with the linear range from 7.5 to 69.0 mmol/L and a low detection limit of 0.163 mmol/L (3σ). Meanwhile, the modified electrode possessed good stability, reproducibility and excellent accuracy for the detection of tap-water, exhibiting great potentials for electroanalysis and electrocatalysis applications.

Keywords: electrodeposition, trichloroacetic acid, direct electrochemistry, sodium alginate, graphene

1. INTRODUCTION

Chlorination is the most commonly used disinfection method for the production of drinking water in the water plant, which is used to inhibit the spread of waterborne diseases such as cholera, dysentery, typhoid etc [1]. Trichloroacetic acid (TCA) is a non-volatile chlorinated organic matter
produced by water chlorination. As a major disinfection by-product, it poses a significant threat to human health due to its carcinogenicity, teratogenicity and mutagenicity [2]. Therefore, accurate determination and regular monitoring of TCA concentration is very important to environmental protection and human health [3].

Among the various methods for the determination of TCA, redox proteins based electrochemical biosensors have exhibited great merits in terms of the simplicity of operation, high sensitivity and substrate selectivity of the enzymes [4]. As a common and important redox protein, myoglobin (Mb) could be employed to construct electrochemical biosensors for the presence of the bioactive heme Fe (III)/Fe (II) redox couple in its molecular structure. But the possible application of electrochemical biosensors is usually limited by their poor stability and short shelf life. For this reason, various methods such as cross-linking [5], sol-gel [6], self-assembly [7], covalent binding [8], surfactant-enzyme complex [9] and electrodeposition [10] have been explored. Among these methods, electrodeposition technology, as a simple and convenient technique, is considered to be an effective way for the construction of protein electrodes with the aid of biocompatible material. Firstly, this method could efficiently immobilize proteins with minimum denaturation, which could also closely adhere to the surface of the substrate electrode. Secondly, it achieves the uniform dispersion of the electroactive materials in the resulting biocomposite film, making the fabrication of biosensor reproducible [11]. Alginate is one of the main biocompatible materials, belonging to the anionic natural polymer. It has been used for the immobilization of proteins by electrodeposition method in previous reports [12]. Because of the presence of abundant carboxyl groups on alginate molecular chains, it could form alginate acid film due to the pH decrease at the anode during the electrodeposition process. Eventually, the formed film was uniformly coated on the substrate electrode, which could provide proteins microenvironments to keep their native structure and improve the stability of biosensor [13].

However, due to the deep burying of redox active center in the structure of redox protein, the direct electron transfer between the redox protein and the electrode is hard to be realized [14, 15]. Hence the substrate electrode is required to be further modified by the use of different materials, including organic materials [16, 17], inorganic materials [18, 19] and metal materials [10, 20], to keep the redox protein’s bio-structure and enhance the electron transfer rate between the redox protein’s active centers and the electrode. In particular, graphene (GR), possesses a lot of unique advantages, such as high thermal conductivity, excellent mechanical stiffness, fast electron transportation and good biocompatibility, which displays great potentials for sensor application [21, 22]. Gan and Hu had reviewed potential applications for electrochemistry and electroanalysis of GR [23]. Chen et al. [24] electrodeposited Fe$_3$O$_4$-graphene, sodium alginate and Mb on the carbon ionic liquid electrode to achieve direct electrochemistry and electrocatalysis of myoglobin. Sun et al. [25] applied GR and multi-walled carbon nanotubes on carbon ionic liquid electrode surface for the immobilization of Hb, revealing good electrocatalytic ability toward the reduction of different substrates such as TCA.

In this work, we prepared carbon ionic liquid electrode (CILE) by simply incorporating the binder and the ionic liquid into the carbon past electrode. The as-prepared CILE possess excellent conductivity, wide electrochemical windows, high sensitivity and good anti-fouling ability, which has been proved to be an effective working electrode for electrochemical sensor [26, 27]. From previous
work, the fabrications of electrochemical sensor via the electrodeposition method are performed on the metal electrode, such as the bulk gold electrode [11], while the use of CILE as the substrate electrode for electrodeposition has been rarely reported so far. This study attempted to achieve electrodeposition of Mb, sodium alginate (SA) and GR on CILE to fabricate myoglobin-sodium alginate-graphene composite modified CILE, using Nafion as the film forming material, which was labeled as Nafion/Mb-SA-GR/CILE. During the electrodeposition process, the formed Mb-SA-GR composite film could efficiently immobilize Mb and keep its native structure. The direct electrochemistry of the resultant Nafion/Mb-SA-GR/CILE was studied. Meanwhile, the electrocatalytic ability of the modified electrode to the reduction of TCA and the determination of TCA in real samples were also investigated.

2. EXPERIMENTAL

2.1. Materials

The standard trichloroacetic acid (TCA) was bought from Tianjin Kemiou Chemical Ltd. Co., China. Polymers such as sodium alginate (SA), myoglobin (Mb) and Nafion (5% ethanol solution) were purchased from Sigma. Superior graphene (GR) was purchased from Sinocarbon Technology Co. Ltd., China. In addition, the materials such as Graphite powder (particle size R= 30 mm), Ionic liquid N-hexylpyridinium hexafluorophosphate (HPPF₆) and liquid paraffin were respectively purchased from Shanghai Colloid Chem. Co., China, Lanzhou Greenchem, ILS, LICP, CAS., China and Aladdin Chemical Reagent Co., Ltd., Shanghai, China. USA. 0.1 mol/L pH 7.0 phosphate buffer solutions (PBS) were used as the supporting electrolyte. The chemicals were of analytical grade and the deionized water was used throughout.

2.2. Apparatus

A CHI 750B electrochemical workstation was used to conduct cyclic voltammetry at an ambient temperature, which involves a common three-electrode system that includes a modified electrode as working electrode, a platinum wire electrode as auxiliary electrode and a saturated calomel electrode as reference electrode. The morphology of the electrode was recorded with a JSM-7100F scanning electron microscope (Electron, Japan). FT-IR spectra of sample were recorded on a Nicolet 6700 Fourier transform infrared spectrometer (Thermo Fisher Scientific Inc., US). UV-vis spectra were recorded on a UV-2700 spectrophotometer (Shimadzu, Japan).

2.3. Fabrication of Nafion/Mb-SA-GR/CILE

Firstly, CILE was prepared according to previous method [28]. Then, a blend solution containing 10.0 mg/mL Mb, 1.67 mg/mL SA and 1.25 mg/mL GR were mixed homogeneously. Before the electrodeposition process, the highly purified nitrogen was used to purge the blend solution for 30
min. Subsequently, Electrodeposition of Mb, SA and GR on CILE was performed on the continuous cyclic voltammetric sweep for 15 cycles between $-1.1$ and $+1.1$ V (vs. SCE) at a scan rate of 100 mV/s under a nitrogen atmosphere. Finally, to avoid the leakage of protein that immobilized on the electrode surface, thus improving its stability, the modified electrode surface was covered evenly with 5.0 μL of 0.5% Nafion solution to obtained Nafion/Mb-SA-GR/CILE. For comparison, other modified electrodes such as Nafion/SA/CILE, Nafion/Mb-SA/CILE and Nafion/GR-SA/CILE were also prepared by the same method.

2.4. Electrochemical measurement of Nafion/Mb-SA-GR/CILE

Cyclic voltammetry was performed in a 10 mL electrochemical cell containing 0.1 mol/L pH 7.0 PBS to measure the electrochemical properties of the modified electrode. To note, the electrocatalysis of Nafion/Mb-SA-GR/CILE to the reduction of TCA was conducted in 0.1 mol/L PBS containing different concentrations of TCA. The PBS was deoxygenated thoroughly with highly purified nitrogen for at least 30 min before the further experiments. Meanwhile, the nitrogen atmosphere was maintained in the electrochemical cell during the experiments.

Scheme 1. Schematic diagram for the fabrication of Nafion/Mb-SA-GR/CILE

3. RESULTS AND DISCUSSION

3.1. Electrodeposition of Mb-SA-GR composite on CILE

As shown in Scheme 1, the fabrication of Nafion/Mb-SA-GR/CILE was achieved via the electro-co-deposition of Mb, GR, and SA on CILE, followed by the coating of Nafion film to improve the stability of the modified electrode. Since there are large amounts of carboxyl groups along the backbone, alginate is considered to be pH dependent, which makes it become suitable material for the immobilization of proteins on the electrode by local formation of alginate acid during the electrodeposition process [11]. The cyclic voltammograms of the electrodeposition of the mixture solution of 10.0 mg/mL Mb, 1.67 mg/mL SA and 1.25 mg/mL GR on CILE was shown in Fig. 1. Along with the cycle increase, a relatively strong peak at about $-0.387$ V (vs. SCE) gradually appeared which was assigned to the oxidation peak current that was ascribed to the electrochemical decomposition of water [12]. During the electrodeposition process, the water at the anode was electrochemically decomposed, which resulted in the production of $H^+$, making the pH decrease around the anode. Furthermore, the low pH made the alginate anionic species form alginate acid gel on
the surface of the electrode. Based on this reason, the Mb, GR and SA composite could uniformly electro-co-deposite on the anode surface (CILE) to achieve the immobilization of proteins and provide them microenvironments to keep their native structure [24, 28]. At last, Nafion film was coated on the electrode to further prevent the leakage of Mb out of Mb-SA-GR composite.

Figure 1. Cyclic voltammograms of electrodeposition of Mb-SA-GR composite on CILE for 15 cycles’ continuous sweep between −1.1 and +1.1 V (vs. SCE) at a scan rate of 100 mV/s

3.2. Characterization of the modified electrode

Figure 2. SEM images of (a) Mb, (b) SA, (c) GR and (d) Mb-SA-GR composite

The surface morphologies of Mb, SA, GR and Mb-SA-GR composite film that prepared by electrodeposition method were examined by SEM. As shown in Fig. 2a, single Mb exhibited the
cluster shape, resulting from the small deformation of the molecular structure during the process of drying. The results implied that without the protection of the biocompatible materials, the active Mb may easily suffer from denaturation. Thank to the good film-forming property of SA, it generated a uniform alginate acid film on the CILE (Fig. 2b), which were attributed to the decrease of pH around the electrode. The large sheet-like shape with slightly scrolled edges of GR can be clearly seen from Fig. 4c, but it is a hydrophobic material that is loose and easy to disengage from the electrode surface. After co-deposition by SA, Mb-SA-GR composite film mainly exhibited the morphology of SA with the increase of surface roughness, implying that Mb and GR had been successfully immobilized on the CILE during the electrodeposition process.

FT-IR and UV-vis absorption spectra were used to confirm the conformational integrity of Mb in Mb-SA-GR composite film. As shown in Fig. 3, Mb revealed characteristic amide I and II infrared absorbance peaks at respectively 1654.74 and 1542.03 cm\(^{-1}\). It is reported that the shape and position of the amide I and II infrared absorbance peaks of Mb can provide detailed information on the secondary structure of the polypeptide chain [27]. As Mb-SA-GR composite film displayed similar amide I and II infrared absorbance peaks at 1647.51 and 1547.81 cm\(^{-1}\) (Fig. 3b), the results implied that Mb could remain its native structure in SA-GR composite film.

![FT-IR spectra of (a) Mb and (b) Mb-SA-GR composite film](image)

**Figure 3.** FT-IR spectra of (a) Mb and (b) Mb-SA-GR composite film

UV-Vis adsorption spectrum could be also test the structure change of Mb. As can be seen from Fig. 4, Mb displayed a strong peak at 409 nm in pH 7.0 PBS, which was assigned to the characteristic Soret absorption [28]. And the Soret peaks of Mb-SA (Fig. 4b) and Mb-SA-GR (Fig. 4c) mixture solutions appeared at the same position (409 nm). The results implied that Mb molecules could keep its biological activity in the mixture, and SA could provide a good microenvironment to the redox proteins.
3.3. Direct electrochemistry of Nafion/Mb-SA-GR/CILE

Cyclic voltammetry of different modified electrodes in deaerated pH 7.0 PBS were performed at the scan rate of 100 mV s\(^{-1}\) with the result shown in Fig. 5. From the cyclic voltammograms, Nafion/SA/CILE (curve a) and Nafion/GR-SA/CILE (curve b) exhibited no obvious voltammetric response, demonstrating no electroactive substances existed on the electrode. Due to the redox of immobilized Mb, Nafion/Mb-SA/CILE and Nafion/Mb-SA-GR/CILE revealed a pair of symmetric redox peaks. Since the good biocompatibility of SA could provide redox proteins suitable microenvironment to keep their biological activity, thus facilitating the electron transfer between redox proteins and the electrode [28-29], Nafion/Mb-SA/CILE exhibited high reduction peak current (curve c). It is reported that GR possesses high conductivity with big porous structure, which is benefit to improve the electron transfer rate of redox proteins with underlying electrode [25]. Therefore, the synergistic effects of SA and GR composite film accelerated the electron transfer rate, making Nafion/Mb-SA-GR/CILE present bigger redox peak current in comparison with Nafion/Mb-SA/CILE. From cyclic voltammetry curve of Nafion/Mb-SA-GR/CILE, the cathodic peak potential (\(E_{pc}\)) and the anodic peak potential (\(E_{pa}\)) were respectively -0.308 V and -0.212 V, while the peak-to-peak separation (\(\Delta E_p\)) was 96 mV. Based on these data, the formal peak potential (\(E^0\)) could be calculated as -0.260 V (vs. SCE) and the ratio of redox peak currents was nearly a unity, which was the typical value of the active center of Mb Fe (III)/Fe (II) redox couple [27]. So the direct electron transfer of Mb could be achieved on Nafion/Mb-SA-GR/CILE with fast electron transfer rate.

The effect of scan rate on the electrochemical responses of Nafion/Mb-SA-GR/CILE was further investigated by cyclic voltammetry, and the result was presented in Fig. 6. During the cyclic scanning, a pair of symmetric redox peaks appeared in the cyclic voltammograms, which was assigned to the reduction and reoxidation of electroactive Mb Fe (III)/Fe (II) redox couple in the Mb-SA-GR composite.
Figure 5. Cyclic voltammograms of different electrodes at the scan rate of 100 mV/s in pH 7.0 PBS: (a) Nafion/SA/CILE, (b) Nafion/GR-SA/CILE, (c) Nafion/Mb-SA/CILE and (d) Nafion/Mb-SA-GR/CILE.

Figure 6. (a) Cyclic voltammograms of Nafion/Mb-SA-GR/CILE in pH 7.0 PBS at different scan rates (from a to t are 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950, 1000 mV/s, respectively); (b) Linear relationship of the cathodic and anodic peak current (Ip) versus scan rate (v); (c) Linear relationship of the anodic and cathodic peak potential versus ln(v).
With the increase of scan rate from 50 to 1000 mV/s, the redox peak currents and scan rate showed good linear relationship which were respectively calculated as 
\[ I_{pc} (\mu A) = 175.326v (V/s) + 18.447 \] 
\( (n=22, \gamma=0.998) \) and 
\[ I_{pa} (\mu A) = -103.564v (V/s) - 4.265 \] 
\( (n=22, \gamma=0.997) \), indicating a surface controlled thin-layer electrochemical reaction. The surface concentration \( (\Gamma^*) \) of electroactive Mb on the electrode surface could be calculated with the Faraday’s law \( (\Gamma^* = Q/nAF) \), where \( Q \) is the integration charge of the reduction peak, \( n \) is the number of electron transferred, \( A \) is the surface area of the electrode, \( F \) is the Faraday constant \([15]\). The charge value \( (Q) \) was nearly constant at different scan rates and the average value of \( \Gamma^* \) was got as \( 3.415 \times 10^{-9} \text{mol/cm}^2 \), which was much larger than that of monolayer coverage \( (2.0 \times 10^{-11} \text{mol/cm}^2) \) \([30]\). The results indicated that SA-GR composite film contained multilayers of Mb, which may be attributed to the three dimensional structure of GR with the increased surface area. In addition, the redox peak potentials and natural logarithm of scan rate \( (\ln v) \) also exhibited good linear relationship with the linear regression equations as 
\[ E_{pc} (V) = -0.086lnv (V/s) - 0.454 \] 
\( (n=13, \gamma=0.989) \) and 
\[ E_{pa} (V) = 0.061lnv (V/s) - 0.295 \] 
\( (n=13, \gamma=0.986) \), respectively. Based on the Laviron’s equation \([31-32]\), the electrochemical parameters of the electrode reaction, such as the electron transfer coefficient \( (\alpha) \) and the apparent heterogeneous electron transfer rate constant \( (k_s) \) could be calculated as 0.384 and 0.207 s\(^{-1}\), respectively.

### 3.4. Electrocatalytic ability towards TCA

The electrocatalytic ability of Nafion/Mb-SA-GR/CILE towards TCA was investigated by cyclic voltammetry with the results shown in Fig. 7. Since the redox proteins usually have good electrocatalytic activity to TCA \([15]\), Nafion/Mb-SA-GR/CILE could reveal reduction peak in PBS with the presence of TCA. With the increase of TCA concentration, the reduction peak currents appeared at -0.288 V (vs. SCE) and -0.513 V (vs. SCE) gradually improved, while the oxidation peak current disappeared. This phenomenon was considered to be the typical characteristic of the electrocatalytic reaction \([28]\). The two reduction peaks corresponded to the electrocatalytic reduction of Mb in the modified electrode for TCA and the formation of a highly reduced form of Mb, which may be dechlorinate di- and mono-chloroacetic acid after the dechlorination of TCA with Mb Fe(II) \([15]\).

The statistical data for TCA determination was shown in Table 1. The reduction peak current increased linearly with TCA concentration in the range from 7.5 to 69.0 mmol/L with the linear regression equation as 
\[ \text{Iss}(\mu A) = 4.856C(\text{mmol/L}) + 26.160 \] 
\( (n=24, \gamma=0.996) \) and the detection limit as 0.163 mmol/L\((3\sigma)\). When the TCA concentration was more than 69.0 mmol/L, the catalytic reduction peak currents began to level off, exhibiting a Michaelis-Menten kinetic process. As the enzyme-substrate kinetics, the apparent Michaelis-Menten constant \( (K_{M^{app}}) \), could be obtained with the Lineweaver–Burk equation \( (1/\text{Iss}=1/\text{I}_{\text{max}}+K_{M^{app}}/\text{I}_{\text{max}}C) \), where \( \text{Iss} \) is the steady-state current, \( \text{I}_{\text{max}} \) is the maximum current under saturated substrate condition, and \( C \) is the bulk concentration of the substrate \([33]\). According to Lineweaver–Burk equation, the \( K_{M^{app}} \) value was calculated as 8.71 mmol/L. The comparisons of the electrochemical parameters of Nafion/Mb-SA-GR/CILE with other similar TCA sensors or modified electrodes were displayed in Table 2 \([10, 24, 27-28, 30, 34]\). It was observed that
this electrochemical sensor exhibited a comparable linear range and smaller detection limit for TCA detection, revealing that the immobilized Mb in SA-GR composite film by electrodeposition method exhibited high affinity to TCA with good enzymatic activity.

![Figure 7](image.png)

**Figure 7.** Cyclic voltammograms of Nafion/Mb-SA-GR/CILE in pH 7.0 PBS containing 7.5, 9.0, 11.0, 13.0, 15.0, 19.0, 22.0, 25.0, 28.0, 34.0, 37.0, 40.0, 46.0, 49.0, 57.0, 69.0 mmol/L TCA (curves a-p), respectively, with the scan rate as 100 mV/s (Inset was the linear relationship of catalytic reduction peak currents and the TCA concentration).

**Table 1.** Statistical Parameters of the regression equation for the determination of TCA

<table>
<thead>
<tr>
<th>Modified electrode</th>
<th>Linear Range (mmol/L)</th>
<th>γ</th>
<th>Detection limit (mmol/L)</th>
<th>Linear regression equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion/Mb-SA-GR/CILE</td>
<td>7.5~69.0</td>
<td>0.996</td>
<td>0.163</td>
<td>Iss(μA)= 26.160 + 4.856C(mmol/L)</td>
</tr>
</tbody>
</table>

**Table 2.** Electrochemical parameters of different modified electrodes for the detection of TCA

<table>
<thead>
<tr>
<th>Modified electrode formulation</th>
<th>Linear range (mmol/L)</th>
<th>Detection limit (mmol/L)</th>
<th>$K_{M^{app}}$ (mmol/L)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion/Mb-SA-GR/CILE</td>
<td>7.5~69</td>
<td>0.163</td>
<td>8.71</td>
<td>Presented method</td>
</tr>
<tr>
<td>Nafion/Mb/Co/CILE</td>
<td>0.4~12.0</td>
<td>0.2</td>
<td>4.11</td>
<td>[10]</td>
</tr>
<tr>
<td>Nafion/Mb-SA-Fe$_3$O$_4$-GR/CILE</td>
<td>1.4~119.4</td>
<td>0.174</td>
<td>29.1</td>
<td>[24]</td>
</tr>
<tr>
<td>Nafion/Mb-Co$_3$O$_4$-Au/IL-CPE</td>
<td>2.0~20.0</td>
<td>0.5</td>
<td>4.7</td>
<td>[27]</td>
</tr>
<tr>
<td>Nafion/Mb-SA-TiO$_2$/CILE</td>
<td>5.3~114.2</td>
<td>0.152</td>
<td>32.3</td>
<td>[28]</td>
</tr>
<tr>
<td>agarose-[bmim][PF$_6$]/Mb/GCE</td>
<td>-</td>
<td>-</td>
<td>47.0</td>
<td>[30]</td>
</tr>
<tr>
<td>Nafion-BMIMPF$_6$/Mb/CILE</td>
<td>1.6~19.6</td>
<td>0.2</td>
<td>90.8</td>
<td>[34]</td>
</tr>
</tbody>
</table>
3.5. Stability and reproducibility

The stability and reproducibility of Nafion/Mb-SA-GR/CILE was further investigated by cyclic voltammetry. Firstly, Nafion/Mb-SA-GR/CILE could keep constant peak currents during continuous scanning for 130 cycles. After storing at 4 °C for more than 4 weeks, the Nafion/Mb-SA-GR/CILE retained 93.5 % of the initial current response. The good long-term stability can be owing to the good biocompatibility of SA and film-forming property of Nafion that retained proteins’ native structure and prevented their leakage. In addition, the cyclic voltammetry was also used to investigate the reproducibility of Nafion/Mb-SA-GR/CILE. The relative standard deviation (RSD) of 8 successive measurements for the current determinations of 10.0 mmol/L TCA was 3.45%, which indicated acceptable reproducibility. Therefore, the modified electrode displayed good stability and reproducibility, according to the above results.

3.6. Determination of TCA in real samples

The modified electrode’s capability of determining TCA in real samples was evaluated via a recovery study [35]. The recovery performance of the modified electrode was investigated by spiking TCA at different concentrations (10, 20 and 30 mmol/L) in tap-water. Meanwhile, a standard method of GC-MS was used for comparison. As shown in Table 3, the recovery of electrochemical biosensor was in the range from 97.0% to 102.5% with small RSD value in the range from 1.5% to 2.7%, which was desirably consistent with the results of GC-MS. The results indicated that the fabricated electrochemical biosensor had excellent accuracy for the detection of tap-water.

Table 3. Determination of TCA in tap-water samples using the modified electrode and the standard GC-MS method

<table>
<thead>
<tr>
<th>Samples</th>
<th>Added (mmol/L)</th>
<th>Electrochemical biosensor</th>
<th>GC-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Found (mmol/L)</td>
<td>Recovery (%)</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>9.7</td>
<td>97.0</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>20.5</td>
<td>102.5</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>30.4</td>
<td>101.3</td>
</tr>
</tbody>
</table>

4. CONCLUSION

In summarize, the Mb-SA-GR composite was successfully deposited on the surface of CILE to construct Nafion/Mb-SA-GR/CILE by cyclic voltammetric electrodeposition. The electrochemical performance of the modified electrode at pH = 7.0 PBS buffer and its electrocatalytic activity to TCA
were investigated. The obtained SA-GR composite film has good biocompatibility and electrical conductivity, which can provide a good microenvironment for Mb, improve its stability and biological activity, and accelerate the direct electron transfer rate between Mb and underlying CILE. The fabricated Nafion/Mb-SA-GR/CILE revealed good electrocatalytic activity to TCA with the linear range from 7.5 to 69.0 mmol/L and a low detection limit of 0.163 mmol/L (3σ). And it also possessed good stability, reproducibility and excellent accuracy for the detection of tap-water, which made it a promising biosensor for electroanalysis and electrocatalysis in the environmental protection field.

References


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