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Original Paper

A novel carbon nanotube-modified biosensor containing a dsDNA-Ni(II) complex membrane, and its use for electro-catalytic oxidation of methanol in alkaline medium

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Abstract. A novel biosensor was fabricated by using a DNA-Ni(II)/MWNTs/Chitosan complex membrane, and the synergistic electrocatalytic effect of the complex membrane for the electro-oxidation of methanol was observed. The membrane composed of DNA, MWNTs and chitosan functioned as a support matrix for the immobilization of the electrocatalytic nickel cation. The good electrocatalytic activity of the resulting DNA-Ni(II)/MWNTs/chitosan/GC electrode was demonstrated by electro-oxidation of methanol in alkaline medium. A linear range from 0.2 to 5.0 mM for the detection of methanol in alkaline medium was observed with a rapid response (within 3 s) and a detection limit of 10 μM based on a signal-to-noise ratio of 3. In addition, the sensor exhibited good stability.

Keywords: DNA, synergistic electrocatalytic, complex membrane, carbon nanotubes, biosensor.

DNA is an important and promising molecule with all the basic properties necessary for the assembly of nano-scale electronic devices. The DNA film may provide unique electron transfer properties improving electron transfer characteristics between redox active species and the electrode surface [1, 2]. On the other hand, it is known that some transition metal ions (Cu^{2+}, Ni^{2+}, and Zn^{2+}, etc.) coordinate between the DNA-base pairs [3, 4]. Gu et al. reported in detail about the electrochemical behavior of copper ions in the DNA/PAA membrane and the responsive characteristics of the DNA-Cu(II)/PAA/GC electrode for the determination of H_2O_2 [5]. Gao et al. reported that the copper ions could strongly bind to DNA, primarily through the N7 of guanine [6]. So we supposed that the linkage between DNA molecules and Ni(II) was similar to the DNA and copper ions', although there are no reports stating exactly through what linkage the Ni(II) could bind to DNA.

Many studies on carbon nanotubes modified with metal nanoparticle or ion coating using different methods were reported. Guillermina et al. made a new glucose biosensor by dispersing the metal particles, enzyme and multi-wall carbon nanotubes within a mineral oil binder, and strong electrocatalytic activity to the reduction of hydrogen peroxide was observed [7]. George et al. made up the CNT/Al composites [8]. However, direct electrostatic interaction between the metal nanoparticles or ions and the CNTs was weak. Many materials and methods were used to make the metal immobilized on the CNTs firm. The combination of CNTs with DNA has recently attracted the attention of several research groups.

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The DNA-based biomolecular recognition principle has been applied to CNTs to construct nanotube electronic devices as well as CNT–DNA electrochemical sensors [9]. Guo et al. described the electrochemical characteristics of the immobilization of both double-stranded and single-stranded calf thymus DNA molecules on the surface of MWNTs [10]. Nepal et al. made out DNA-wrapped nanotubes of both multi-walled and single-walled carbon nanotubes by a solid-state mechanochemical reaction, and nonspecific interactions occurring between the CNTs and the amphiphilic DNA were observed by SEM photography. The high binding affinity of DNA to the nanotube backbones due to π-stacking led to the wrapping with DNA [11].

In our study, the cation Ni^{2+} was immobilized on the dsDNA molecules to form a DNA-Ni^{2+} compound, and then the DNA-Ni^{2+} compound was immobilized on the CNTs directly. The chitosan was covered onto the modified electrode to form a membrane and prevent the DNA-Ni(II)/MWNTs compound from falling off the electrode surface in the electrochemical determination process. Then a DNA-Ni(II)/MWNTs/chitosan/GC electrode was fabricated. The synergistic effect of the metal ion Ni(II) and MWNTs to the electrocatalytic oxidation of methanol was shown by cyclic voltammetry and typical current-time analysis. MWNTs were first treated with nitric acid prior to the immobilization of DNA in order to introduce carboxylic acid groups into the surfaces of the carbon nanotubes.

Experimental

Reagents and chemicals

Double-stranded DNA was purchased from Sigma (USA, www.sigma-aldrich.com). Multi-wall carbon nanotubes were purchased from Shenzhen Nanotech Port Co. Ltd. (ShenZhen, China, www.seasunnano.com). Chitosan was purchased from Sigma (USA www.sigma-aldrich.com). All other chemicals were of analytical grade and used without further purification. Doubly distilled water was used for the preparation of buffer and standard solutions.

Electrochemical measurements

All electrochemical measurements were carried out with a three-electrode system comprising a DNA-Ni(II)/MWNTs/Chitosan/GC electrode as a working electrode, an Ag/AgCl (sat. KCl) reference electrode and a platinum wire auxiliary electrode (1 mm diameter). An 0.1 M NaOH solution was used as an electrolyte solution. Cyclic voltammetry (CV) was performed with an electrochemical analyzer (CHI 660a, CH Instrument Inc.). The air-saturated electrolyte solution was gently stirred during the amperometric measurements. All measurements were carried out at room temperature (25 °C).

Preparation of DNA-Ni(II)/MWNTs/Chitosan/GCE

A glassy carbon (GC) electrode (3 mm diameter, Bioanalytical Systems (BAS), West Lafayette, IN) was carefully polished with emery paper and aqueous slurries of fine alumina powders (0.3 and 0.05 μm) on a polishing cloth until a mirror finish was obtained. After sonicating in water for 2 min, the electrodes were immersed in phosphate buffer (pH = 7.0) and first oxidized at 2.0 V for 100 s followed by reduction to −1.1 V for 50 s. Then the electrodes were cleaned by cyclic voltammetry between −1.1 V and +0.9 V at $50\,mV \cdot s^{-1}$ until a stable profile was obtained. The prepared electrodes were dried under a nitrogen stream and used for modification immediately. The MWNTs layer modified electrode was prepared by casting 10 μL of the dispersion on the surface of a GC electrode, which had been air-dried at room temperature. The DNA-Ni(II)/Chitosan complex-immobilized electrode was prepared as follows: aqueous solutions of dsDNA (0.5 mL, $2.4\,mg \cdot mL^{-1}$) and $NiCl_2$ (0.5 mL, 0.1 M) were mixed for at least 2 h to form the DNA-Ni(II) complex. Then 40 μL of the mixture of DNA and Ni(II) and 5 μL of chitosan (1%) aqueous solution were successively placed on the MWNTs/GC electrode surface to form a complex layer. The electrode was allowed to dry for 1 day under a 500 mL beaker at room temperature. After rinsing it with distilled water, the resulting DNA-Ni(II)/MWNTs/Chitosan membrane-modified GC electrode was stored in the refrigerator at 4 °C. A DNA-Ni(II)/Chitosan membrane without MWNTs was also prepared in a similar manner.

Results and discussion

Electrochemical properties of the DNA-Ni(II)/MWNTs/Chitosan/GC electrode

The DNA-Ni(II)/MWNTs/Chitosan/GC electrode was studied in 0.1 M NaOH solution in the potential range of 0.2–0.7 V, scan rate = $50\,mV \cdot s^{-1}$. A pair of well-defined redox peaks could be obtained at 0.426 and 0.518 V. These redox waves were obviously attributed to the electrochemical reaction of $NiCl_2$, since no apparent voltammetric response was observed at a Nickel ion free DNA/Chitosan membrane in the same experimental conditions. The redox system corresponding to these peaks was assigned to the redox process Ni(II)/Ni(III) and could be written as [12]:

$$Ni(OH)_2 + HO^- \rightarrow NiO(OH) + H_2O + e^-$$

or as represented elsewhere [13, 14]:

$$Ni(OH)_2 \rightarrow NiO(OH) + H^+ + e^-$$

The cyclic voltammograms of the DNA-Ni(II)/MWNTs/Chitosan/GC electrode were stable during the repeated potential sweeps, so the sweep rate behavior could be assessed. Figure 1A shows the CV of the DNA-Ni(II)/MWNTs/Chitosan/GC electrode

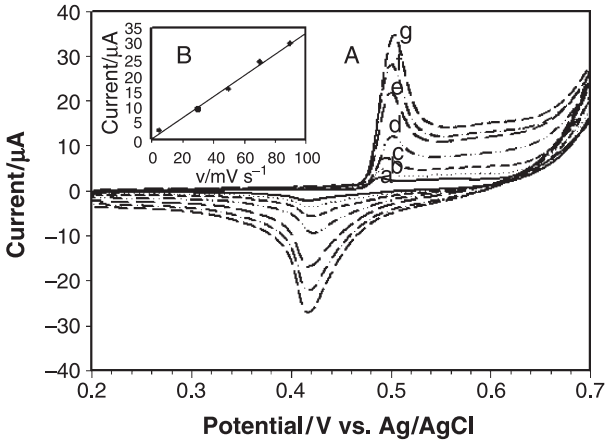

Fig. 1. (A) Cyclic voltammograms of the DNA-Ni(II)/MWNTs/Chitosan/GC electrode in 0.1 M NaOH solution at different scan rates: (*a*) $5\,mV \cdot s^{-1}$, (*b*) $10\,mV \cdot s^{-1}$, (*c*) $20\,mV \cdot s^{-1}$, (*d*) $40\,mV \cdot s^{-1}$, (*e*) $60\,mV \cdot s^{-1}$, (*f*) $80\,mV \cdot s^{-1}$, (*g*) $100\,mV \cdot s^{-1}$. (B) The plots of current vs. scan rate

obtained at different potential scan rates. The cathodic and anodic peak currents linearly increased with increasing scan rates from 0.005 to $0.1\,V \cdot s^{-1}$ (shown in Fig. 1B), and none of the peak potentials changed. This result indicates that the electrode reaction of nickel ion within the DNA/MWNTs/Chitosan layer on the GC electrode is mainly controlled by a surface-confined redox process.

SEM of the DNA/MWNTs membrane

Figure 2 shows the SEM photograph of pristine MWNTs membrane (Fig. 2a) and MWNTs/DNA membrane (Fig. 2b). As shown in Fig. 2a, the small bundles of MWNTs are distributed very homogeneously on the surface of the GC electrode. After addition of dsDNA to the pristine MWNTs, it could be observed from the SEM photograph that the small bundles of MWNTs became illegible and the diameters of MWNTs/DNA were slightly thicker than those of pristine MWNTs. Singh et al. obtained the SEM photograph of MWNT-NH_3^+:DNA complexes, where DNA condensates to form a concrete-like planar structure with nanotubes buried within [15]. In the study of Nepal et al., the SEM photograph showed that DNA was wrapped onto the CNTs [11]. In their study, the nanotubes were cut into shorter lengths and were fully covered with DNA. However, the MWNTs in our study were obviously longer, and it could be concluded that the MWNTs were not entirely covered by DNA. The contrast of Fig. 2a and b showed that the DNA molecules were wrapped closely but not fully onto the carbon nanotubes. The interaction of the DNA molecules with the carbon nanotubes produced a particularly large surface area structure. The large-surface area membrane was expected to be an attractive platform for the adsorption of metal ions or other molecules and could be constructed as highly catalyzed electrochemical sensors.

Response of the DNA-Ni(II)/MWNTs/Chitosan/GC electrode to methanol in alkaline medium

It is found that the addition of 0.2 M methanol to the electrolyte changes the voltammetric response of the modified electrode (DNA-Ni(II)/MWNTs/Chitosan/

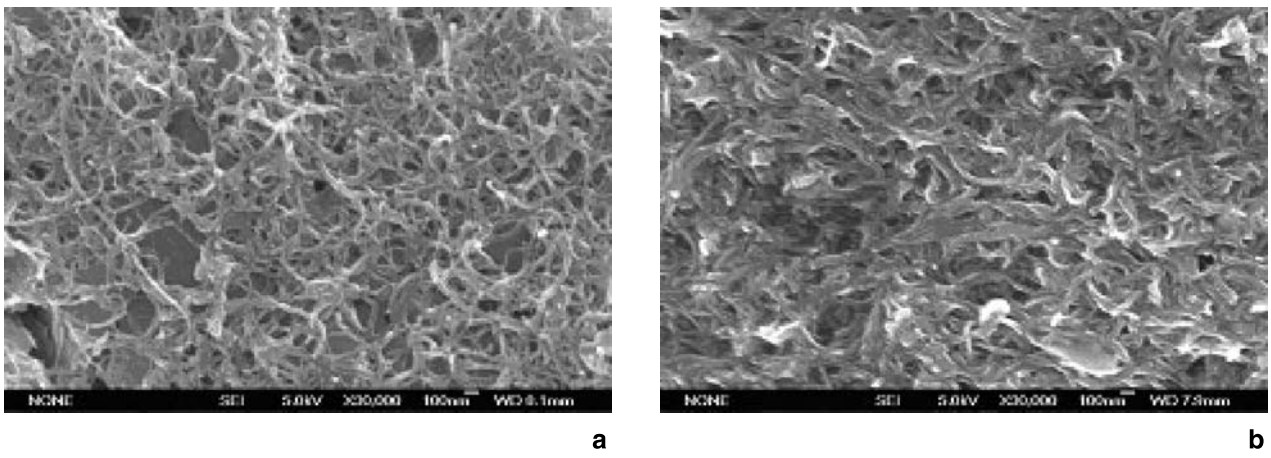

Fig. 2. SEM photograph of the pristine MWNTs (a) membrane and MWNTs/DNA (b) membrane on the GC electrode

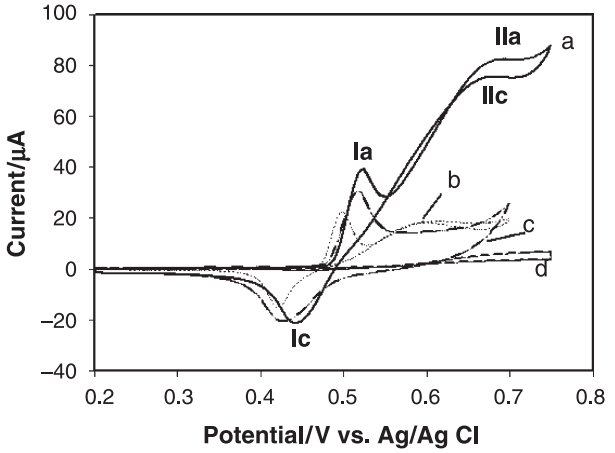

Fig. 3. Cyclic voltammograms of the DNA-Ni(II)/MWNTs/Chitosan/GC electrode with (*a*) and without (*c*) the addition of 0.2 M methanol, DNA-Ni(II)/Chitosan/GC electrode (*b*) and MWNTs/GC electrode (*d*) with the addition of 0.2 M methanol in 0.1 M NaOH solution (scan rate = 50 mV · s^{-1})

GC electrode). Figure 3a shows the cyclic voltammograms of the DNA-Ni(II)/MWNTs/Chitosan/GC electrode in 0.1 M NaOH solution in the presence of 0.2 M methanol, in the potential range of 0.20–0.75 V (Ag/AgCl). The electro-oxidation of methanol on the DNA-Ni(II)/MWNTs/Chitosan/GC electrode is represented in Fig. 3 by two oxidation peaks, which are related to the oxidation of methanol and the corresponding intermediates produced during the methanol oxidation at 0.67 and 0.65 V (peak IIa, IIc, Fig. 3), respectively [16]. A similar shape of a cyclic voltammogram was observed recently by Taraszewska and Roslonek [17, 18] for methanol oxidation in NaOH solution on a GC electrode modified by nickel hydroxide formed from ex situ chemical precipitation or tetraazamacrocyclic complexes of nickel.

Methanol oxidation is a very complex process since up to six electrons can be transferred when CO_2 is the final product. In this transformation, formaldehyde, formic acid and CO appear as stable reaction intermediates [19]. Despite many attempts to determine the mechanism of methanol electro-oxidation, surprisingly little is known with certainty. According to the data in the literature, it is evident that the oxidation of methanol depends on the concentration of OH^-, the morphology of the modifying film, its thickness and permeability, the surface concentration of active sites, and the charge transport through the film. The results presented here are not sufficient to discuss the mechanism of methanol oxidation in detail; however, summarizing the main results obtained in this study, it must be possible to explain the following facts based on the reaction mechanism.

(1) The methanol electro-oxidation was observed only using the DNA-Ni(II)/MWNTs/Chitosan films. Cyclic voltammograms recorded for modified electrodes after the demetalation processes were almost flat.
(2) The electro-oxidation process of methanol was always observed at potentials more positive than the potential of the Ni(II)/Ni(III) redox couple (peak Ia, Fig. 3).
(3) The reaction mechanism must involve adsorbed hydroxyl because the oxidation of the methanol adsorption intermediate occurs only at potentials positive enough for the electrode surface to be partially covered by OH_{ads}. Moreover, the complete oxidation process to formate or carbonate ions needs oxygen atoms, which implies the participation of water or hydroxyl ions.

On the basis of the above facts, and in the light of the literature data relating to the oxidation of alcohols in basic media on electrodes modified by an Ni(II)/Ni(III) redox couple [17–21], a plausible mechanism of methanol oxidation on our modified electrode may be written as follows:

$$\text{Methanol} + \text{NiO(OH)} \rightarrow \text{Ni(OH)}_2 + \text{intermediate(s)} + \text{H}_2\text{O} + \text{e}^-$$

$$\text{intermediate(s)} + 2\text{n(OH)}^- \rightarrow \text{product} + \text{nH}_2\text{O} + 2\text{ne}^-$$

where $n = 1$ (oxidation of primary alcohols except methanol), or $n = 2$ (oxidation of methanol). This plausible reaction mechanism may qualitatively explain all the experimental facts observed.

As shown in Fig. 3a, the current peak of methanol oxidation on the DNA-Ni(II)/MWNTs/Chitosan/GC electrode in the 0.1 M NaOH solution is observed to be almost 80 μA. Without the MWNTs, the current peak of methanol oxidation of the DNA-Ni(II)/Chitosan/GC electrode is no more than 20 μA (Fig. 3b). The MWNTs/GC electrode shows little current response to the oxidation of methanol (Fig. 3d). The DNA-Ni(II)/MWNTs modified GC electrode has a higher electrocatalytic activity towards the oxidation of methanol than both the DNA-Ni(II) modified and the MWNTs modified GC electrode. It was concluded that the carbon nanotubes and Ni(II) in the complex

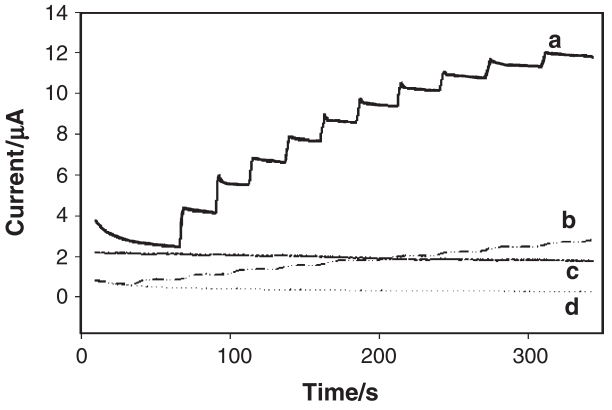

Fig. 4. Typical current-time curve of the DNA-Ni(II)/MWNTs/Chitosan/GC electrode (*a*), DNA-Ni(II)/Chitosan/GC electrode (*b*), MWNTs/Chitosan/GC electrode (*c*) and bare GC electrode (*d*) in 0.1 M NaOH solution upon successive addition of 0.8 mM methanol. The applied potential was 0.6 V (vs. Ag/AgCl)

membrane had a synergistic electrocatalytic effect on the oxidation of the methanol.

In order to further investigate the synergistic effect of the MWNTs and Ni ions on the oxidation of methanol, typical current-time curves of different electrodes were calculated. The electrocatalytic activity of the DNA-Ni(II)/MWNTs/Chitosan/GC, DNA-Ni(II)/Chitosan/GC, MWNTs/Chitosan/GC and bare GC electrodes was investigated by observing the current response curves upon successive addition of 0.8 mM methanol in 0.1 M NaOH solution. The oxidation potential of the methanol (0.6 V) was chosen as the potential to be applied. The results are displayed in Fig. 4. Without adding Ni ions to the membrane, the response of oxidation to methanol on the MWNTs/Chitosan/GC electrode (Fig. 4c) is about 0.1 μA. The DNA-Ni(II)/Chitosan/GC electrode (Fig. 4b) (not loaded with MWNTs) has a current response of 0.5 μA. However, the response current on MWNTs/Chitosan/GC (Fig. 4a) is about 1.6 μA. This implies that the DNA-Ni(II)/MWNTs/Chitosan/GC electrode has a much higher sensitivity than the other two modified electrodes. Furthermore, the response time of the DNA-Ni(II)/MWNTs/Chitosan/GC electrode is much faster (within 3 s) than in the absence of MWNTs (about 20 s).

According to the above facts it could be concluded that the Ni(II) ions are the major catalysts for the oxidation of methanol and that the MWNTs could also catalyze the oxidation of methanol due to their electrical conductivity. However, when the Ni(II) ions bind to MWNTs via dsDNA molecules, the electrochemical property of the DNA-Ni(II)/MWNTs/Chitosan membrane is exhibited. Moreover, the improvement of the electrochemical properties of the complex membrane is not only the additive effect of the catalytic ability of the Ni(II) ions and the MWNTs. In fact, the response current of oxidation to methanol on the DNA-Ni(II)/MWNTs/Chitosan/GC electrode is almost three times larger than the sum of the response current on the MWNTs/Chitosan/GC and DNA-Ni(II)/Chitosan/GC electrode. This could be explained by the synergistic electrocatalytic effect of the MWNTs and Ni(II) ions in the DNA-Ni(II)/MWNTs/Chitosan membrane. The detailed mechanism of this synergistic electrocatalytic effect between the MWNTs and Ni(II) ions is currently uncertain and might be considered in future work of ours.

Figure 5A shows the typical current-time curve of the DNA-Ni(II)/MWNTs/Chitosan/GC electrode in the 0.1 M NaOH solution upon successive addition of 0.2, 0.4, 0.8, 3.2, 5.0, 6.0, 7.0, 8.0, and 10.0 mM methanol at the applied potential of 0.6 V versus Ag/AgCl. After the addition of methanol, the steady-state currents reached another steady-state value (95% of the maximum) in less than 5 s. Such a fast response may be attributed to fast diffusion of methanol within the complex membrane. The corresponding calibration curves are shown in Fig. 5B and C. A linear range of 0.2–5.0 mM with a detection limit of 10 μM was observed.

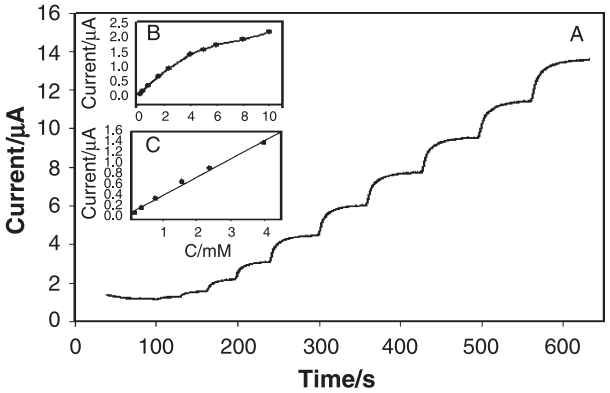

Fig. 5. (A) Typical current-time curve of the DNA-Ni(II)/MWNTs/Chitosan/GC electrode in 0.1 M NaOH solution upon successive addition of 0.2, 0.4, 0.8, 3.2, 5.0, 6.0, 7.0, 8.0 and 10.0 mM methanol. (B) Dependence of the methanol oxidation current on the methanol concentration. (C) Linear part of the (B) curve

Optimization of analytical conditions

Effect of amounts of MWNTs, concentration of $NiCl_2$, concentration of DNA

The synergistic effect of the MWNTs and the Ni ions was expected to be affected by the amounts of MWNTs and Ni ions in the complex membrane on the electrode surface, which can be controlled by changing the amounts of MWNTs and Ni ions with other conditions unchanged. The relationship between the response current and the amounts of MWNTs, the response current and Ni ions was studied. With increasing MWNTs and Ni ions, the response current increased correspondingly, which might imply that more MWNTs and Ni ions result in higher sensitivity. However, it was observed that the background current and noise level also increased with additional amounts of MWNTs. Hence, a moderate MWNTs concentration of 20 μL (1 mg · mL^{-1}) and a $NiCl_2$ concentration of 3 mM was selected for the fabrication of the DNA-Ni(II)/MWNTs/Chitosan/GC electrode.

In our study, it was also found that the higher the concentration of DNA, the higher the current response of the modified electrode to the electrocatalytic oxidation of methanol. This is because the Ni^{2+} ions were modified on the MWNTs via dsDNA, so more Ni^{2+} could be immobilized on the electrode if more DNA molecules were added. Thus, the modified electrode could obtain a much higher current response to the oxidation of methanol. However, too large amounts of DNA molecules may also increase the background current and noise level correspondingly. The concentration of 2.4 mg · mL^{-1} of dsDNA was selected for the fabrication of the DNA-Ni(II)/MWNTs/Chitosan/GC electrode in our study.

Stability of the modified electrode

The long-term cycle stabilities of the DNA-Ni(II)/MWNTs/Chitosan/GC electrode for methanol oxidation were also studied. i^0 and i are the oxidation peak current densities of the forward CV scan at the first cycle after the complete activation of catalysts and the corresponding cycles, respectively. It is observed that the ratio of i to i^0 decreases gradually with an increasing number of cycles. When the cycle number reaches 500, almost 30% of the electrocatalytic activity of the modified electrode is observed to be lost, implying that the DNA-Ni(II)/MWNTs/Chitosan/GC electrode has good stability for the oxidation of methanol.

Conclusions

In this paper, a novel DNA-Ni(II)/MWNTs/Chitosan/GC electrode was fabricated using a membrane composed of MWNTs and Ni(II) and dsDNA molecules to immobilize the Ni(II) ions on the MWNTs. The electrochemical behavior of the modified GC electrode was studied by cyclic voltammetry and typical current-time analysis. The synergistic electrocatalytic effect of the MWNTs and Ni(II) ions on the oxidation of methanol in alkaline medium was observed. The response current of the DNA-Ni(II)/MWNTs/Chitosan/GC is much larger than that of the MWNTs/ Chitosan/GC and DNA-Ni(II)/Chitosan/GC electrode, and its response time is less than 3 s. It also showed good stability in the experiment. We observed a linear range for the determination of methanol on our modified electrode of 0.2–5.0 mM and a detection limit of 10 μM.

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