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Short communication

Electrochemical biosensing platforms using poly-cyclodextrin and carbon nanotube composite

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ABSTRACT

Carbon nanotubes (CNTs) were "dissolved" in mixed solution of cyclodextrin (CD) and cyclodextrin pre-polymer (pre-CDP) and were used as modifier to fabricate chemical modified electrode. The dispersions of CNTs in different solutions were characterized using UV–vis spectrophotometer. The insoluble conducting composite film of poly-cyclodextrin (CDP) and carbon nanotube was synthesized, and glucose oxidase (GOx) was immobilized on the film to fabricate amperometric biosensor. The CNT–CDP electrode was stable. It can keep the exceptional chemical and physical properties of CNTs and the host–guest chemical reaction ability of cyclodextrins. Cyclic voltammetry measurements of potassium ferricyanide solution (50 mM, and scan rate 100 mV s^{-1}) shows that the CDP film was compact and the CNT–CDP film maintains the electrocatalytic activity of CNT. Glucose oxidase was used as a model enzyme to prepare a glucose biosensor. The bioactivity of immobilized glucose oxidase was maintained due to the biocompatibility of cyclodextrin. Amperometric measurements were done with different concentrations of glucose. The CNT–CDP/GCE–GOx biosensor has wide concentration ranges and good sensitivity to glucose. It showed a detection limit of 3.5 μM with a linear range from 0.004 to 3.23 mM and from 4.26 to 10.00 mM. In addition, the biosensor can be operated under wide pH range (pH 5.6–7.8) without great changes in its sensitivity.

1. Introduction

Biosensors utilizing immobilized oxidase for the conversion of the target analyte into electrochemically detectable products are sensitive, selective, and efficient analytical devices and can be used for determining specific substances in biological, clinical, environmental, or other samples (Kros et al., 2001; Bakker, 2004; Yang and Zhu, 2006; Fotouhi et al., 2010). Many studies have been carried out to improve the performances of biosensors (Tu and Chen, 2001; Zhang et al., 2007; Ramanavicius et al., 2008; Zhao et al., 2010; Manesh et al., 2010). The methods of enzyme immobilization on electrodes include immobilization of enzyme in gels, cross-linked polymers, or mixing into nanomaterials/polymer composite, etc. (Yang and Zhu, 2007; German et al., 2010). Recently, the application of CNTs provides new way to design novel electrochemical biosensors since it has the ability to promote electron-transfer reactions of enzymes and other biomolecules (Jacobs et al., 2010). CNTs have been intensively studied due to their distinct physical properties such as high electrical conductivity, chemical stability and high mechanical strength and modulus (Tagmatarchis et al., 2002; Lin et al., 2004; Lozano et al., 2010). But one major barrier for developing CNT-based biosensors is the insolubility of CNTs in all solvents (Wang et al., 2003a). In order to incorporate CNTs into the biological system, the task of solubilizing CNTs has been studied extensively through covalent modification or noncovalent functionalization. In particular, "wrapping" CNTs into polymeric materials is useful to facilitate the solubilization of CNTs in aqueous solutions without impairing their physical properties (Wang et al., 2003a; Hrapovic et al., 2004). Based on this method, CNTs had been dispersed into polymers (such as nafion and chitosan) to form CNT/polymer composite films and the composite films can be used as versatile biosensors when enzymes were attached on it (Hrapovic et al., 2004; Zhang et al., 2004, 2006; Liu et al., 2005; Zeng et al., 2007; Manesh et al., 2008). However, polymers that render CNT soluble in aqueous solutions are still desired (Zhao and Stoddart, 2009).

Cyclodextrins (CDs) are a group of naturally occurring cyclic oligosaccharides, often with six, seven or eight D-glucopyranose units. β-Cyclodextrin (β-CD) is a cyclic oligosaccharide that consists of seven glucopyranose units. It possesses an electronic and hydrophobic interior microenvironment in its cavity structure, which allows hydrophobic molecules to be easily incorporated into its cavity by displacing the water (Breslow and Dong, 1998; Szejtli, 1998). β-CD cross-linked polymer (β-CDP) displays excellent film-forming ability. It provides not only a large surface for enzyme

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and mediator loading, but also a desirable microenvironment to enzyme (Liu et al., 1998; Zhu et al., 2000). It was for these reasons that we decided to explore the possibility of using the CNT–CDP system as a platform for the development of electrochemical sensors and biosensors.

Wang et al. (2003b) and He et al. (2006) have reported electrocatalytic response behavior of CD/CNTs modified electrodes. In their papers, CNTs and CD were adsorbed on the base electrodes physically. Together with the water-soluble characteristics of CD, the long time stability of this kind of electrodes is not satisfied. Thus the reported CD/CNTs modified electrodes are not suitable for the immobilization of enzyme to construct biosensors. In order to construct a biosensing platform, water-insoluble poly-cyclodextrin and CNT composite is needed.

In this paper, CNTs were "dissolved" in mixed solution of CD and pre-CDP and were used as modifier to fabricate chemical modified electrode. The CNT–CDP electrode was stable and can keep the exceptional chemical and physical properties of CNTs and the host–guest chemical reaction ability of cyclodextrins. The CNT–CDP composite has the potential to provide operational access to a large group of enzymes and electron-transfer mediators.

2. Experimental

2.1. Chemicals and reagents

Multi-walled CNTs which have 95% purity or more were obtained from the Department of Physics, Tsinghua University and were purified by heating under reflux conditions in 6 mol L^{-1} HNO_3 for 2 h. The diameter of the CNTs was in the range of 10–20 nm. Glucose oxidase (GOx) was purchased from Sigma Company, the activity was about 178 U mg^{-1}. β-D-Glucose, β-cyclodextrin (CD), 3-chloro-1,2-epoxypropane, glutaraldehyde (GD) and other chemicals used in this work were available with analytical reagent grade. Dialysis tube with molecular weight cut-off, 3500 (#MD34-3.5) was purchased from Jingke Hongda Biotechnology Co., Ltd. Electrochemistry measurements were carried out in 0.1 M phosphate buffer solution (PBS) (pH = 7.2), which was prepared by dissolving 0.061 mol di-sodium hydrogen phosphate and 0.039 mol sodium di-hydrogen phosphate in 1 L of double distilled water. Also 0.1 mol potassium chloride was added to the solution to increase conductivity of the solution. 100 mM of glucose solution was prepared by dissolving anhydrous β-D-glucose in the phosphate buffer solution and was stored at 4 °C when not in use (mutarotation was allowed for at least 12 h before use). GOx was dissolved in the phosphate buffer solution with a concentration of 4.5 mg mL^{-1} and stored at 4 °C.

2.2. Instrumentation

Absorbance measurement is using Hitachi U-3010 UV–visible spectrophotometer. Cyclic voltammetry (CV) and amperometric measurements were performed using a CHI 660C electrochemical workstation. A three electrode cell with a platinum foil (10 mm × 5 mm × 0.1 mm) as counter electrode and a saturated calomel electrode (SCE) as reference electrode were used for electrochemical measurements. All experiments were conducted at 25 ± 0.5 °C if no special announcement.

2.3. Preparation of β-cyclodextrin prepolymer (pre-CDP)

The polycondensation of CD with GD often achieves water-soluble poly-cyclodextrin. In order to get insoluble poly-cyclodextrin, the β-cyclodextrin prepolymer (pre-CDP) is needed (Kutner et al., 1992; Wu and Wu, 1998). The pre-CDP was prepared by cross-linking β-cyclodextrin under strongly alkaline conditions with epichlorhydrin (Ekberg et al., 1989). In detail, 10.5 g of β-cyclodextrin was dissolved in 25 mL of 35% NaOH, 8.5 mL of epichlorhydrin was added into the CD solution drop by drop with stirring, and the reaction solution was heated to 90 °C for 5 min with stirring. After cooling to room temperature, the solution was neutralized with 6 mol L^{-1} HCl. The final volume of the solution was about 50 mL. The solution was subjected to dialysis (molecular weight cut-off, 3500). The dialysate was dried by the low-temperature vacuum drying process. Thus water-soluble pre-CDP was obtained.

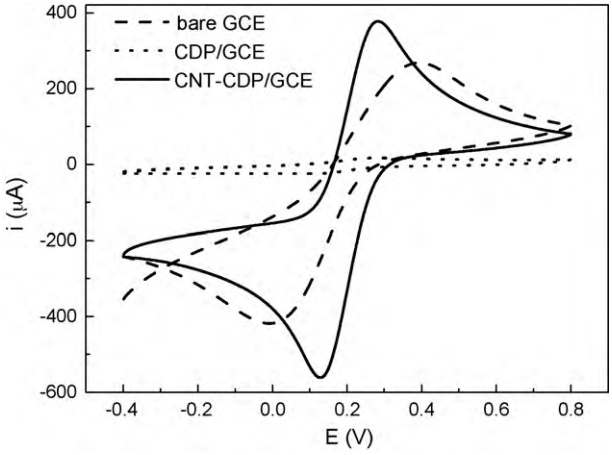

Fig. 1. The cyclic voltammetry curves of three different types of electrodes: bare glass carbon electrode (GCE), CDP modified GCE (CDP/GCE), CDP and CNT modified GCE (CNT–CDP/GCE) (50 mM $Fe(CN)_6^{3-}$ and 0.2 M KCl at 100 mV s^{-1}).

2.4. Sensor fabrication

The purified CNTs could disperse in the solution of CD (Wang et al., 2003b; He et al., 2006), but could not disperse in the solution of pre-CDP (see Fig. 1). Here 5 mg of the purified CNTs were dispersed in 10 mL of mixed solution of CD (2 wt.%) and pre-CDP (2 wt.%.) by ultrasonication for 5 min to get black suspension. The suspension was used as modifier to fabricate chemical modified electrode.

The basal glass carbon electrode (GCE) was washed sequentially with 0.1 M HNO_3, ethanol, and distilled water. 30 μL black suspension (mixed solution of CD (2 wt.%), pre-CDP (2 wt.%) and CNTs), 20 μL GD (0.25 M) and 20 μL HCl (0.2 M) solutions were mixed completely. 5 μL of the mixed solution was dropped on the surface of the GCE, and was kept at room temperature for about 2 h to get the modified electrode, CNT–CDP/GCE. Also a CDP/GCE was prepared according to above sequence but without CNTs in the mixed solutions. A 3 μL drop of glucose oxidase solution (4.5 mg mL^{-1}) was dried on the CNT–CDP/GCE. Then 3.5 μL of glutaraldehyde (0.25 M) was applied on the resulting electrode to cross-link the enzyme in 1–2 h. The resulted biosensor (CNT–CDP/GCE–GOx) was washed thoroughly with phosphate buffer solution and stored at 4 °C when not in use.

3. Results and discussion

3.1. The dispersion of CNTs in cyclodextrin solution

The dispersions of CNTs in different solutions were characterized using UV–vis spectrophotometer (Hitachi U-3010) operating between the ranges of 400 and 800 nm. Bundled carbon nanotubes are not active in the UV–vis region (Rastogi et al., 2008; Yu et al., 2007). Only individual carbon nanotubes absorb in this region. Therefore, dispersion of carbon nanotubes can be characterized

using UV–vis absorption spectroscopy. The absorbance values at 500 nm are the measure of dispersion of carbon nanotubes in solution (all the solutions remained static for at least 30 min after ultrasonication) (Rastogi et al., 2008; Yu et al., 2007). Absorbance value is the logarithm of the ratio of the intensities of the incident light (I_o) and the transmitted light (I): $A = \log(I_o/I)$. The absorbance values of CD and pre-CDP are very low in the ranges of 400–800 nm. The absorbance values at 500 nm for CD and pre-CDP solutions both are lower than 0.002. The absorbance values at 500 nm for 4% CDP–CNT (CNTs in solution of 4 wt.% pre-CDP) is only 0.06, and the aggradation of the CNTs is visible. For the solution of 2% CD–CNT (CD (2 wt.%)), 2% CD–CDP–CNT (CD (2 wt.%) and pre-CDP (2 wt.%)), 4% CD–CDP–CNT (CD (2 wt.%) and pre-CDP (4 wt.%)), the absorbance values are all beyond the range of the instrument, so the absorption spectra are the diluted solutions (15 times). The absorbance values at 500 nm for the diluted solutions of 2% CD–CNT, 2% CD–CDP–CNT and 4% CD–CDP–CNT are 3.07, 2.89 and 1.47, respectively. With the increase in concentration of the pre-CDP, the CNTs tend to aggregate, but without pre-CDP, the prepared film of CDP/CNT is soluble and is not suitable for biosensing purpose. Here the solution of 2% CD–CDP–CNT was chosen, that is, 0.5 mg of CNTs dispersed in 1 mL of solutions of CD (2 wt.%) and pre-CDP (2 wt.%).

3.2. Electrochemical characterization of the modified electrode

Cyclic voltammetry of ferricyanide system is a valuable and convenient tool to monitor the characteristic of the surface of modified electrode. Cyclic voltammetry was conducted in 50 mM $Fe(CN)_6^{3-}$ and 0.2 M KCl at 100 mV s^{-1} for three different types of electrodes: bare glass carbon electrode (GCE), CDP modified GCE (CDP/GCE), CDP and CNT modified GCE (CNT–CDP/GCE). Fig. 1 shows the steady-state CVs for the bare and the two modified GCE. For the bare GCE, the oxidation and reduction peaks caused by the $[Fe(CN)_6]^{3-/4-}$ redox couples were noticeable at +0.40 and +0.02 V vs. SCE in forward and reverse scans, respectively. For the CDP/GCE, the oxidation and reduction peaks disappeared. This means that the CDP film which coating the bare GCE is dense and can prevent the penetration of electroactive substance. While for the CNT–CDP/GCE, the oxidation peak potential of the $[Fe(CN)_6]^{3-/4-}$ redox couples shifted more negatively and the reduction peak potential shifted more positively than that at bare GCE, which suggested that the CNT–CDP film promoted the electrochemical reaction of $[Fe(CN)_6]^{3-/4-}$ more efficiently. Furthermore, the oxidation peak current of $[Fe(CN)_6]^{3-/4-}$ at CNT–CDP/GCE was stronger than those at bare GCE. The peak current of CNT–CDP/GCE was increased because of the large surface area of CNTs dispersed in the modifying layer. According to Randles–Sevcik equation (Hrapovic et al., 2004): $I_p = 2.69 \times 10^5 AD^{1/2}n^{3/2}\gamma^{1/2}C$, where A represents the area of the electrode (cm^2); n, the number of electrons participating in the reaction, is equal to 1; D, the diffusion coefficient of the molecule in solution, is $(6.70 \pm 0.02) \times 10^{-6}$ cm^2 s^{-1}; C, the concentration of the probe molecule in the solution, is 50 mM, and γ, the scan rate (V s^{-1}). The calculated electroactive surface area of the CNT–CDP/GCE was 3.42 mm^2, compared to 2.43 mm^2 for the bare GCE and 0.15 mm^2 for the CDP/GCE.

3.3. Amperometric response to hydrogen peroxide

The amperometric responses of the electrodes to successive additions of 0.5 mM hydrogen peroxide were tested using a CHI660C electrochemical workstation. During chronoamperometric measurements, the working electrode was poised at +0.60 V vs. SCE. The i–t curves of GCE, CDP/GCE, and CNT–CDP/GCE were shown in Fig. 2, respectively. The amperometric response to hydrogen peroxide of the bare GCE has a rate of 0.073 μA mM^{-1}. When the CDP/GCE was tested, the response current was too small to be noticed (about 0.1 nA mM^{-1}), which confirmed that the CDP film can prevent the penetration of hydrogen peroxide. When the bare electrode was modified with CDP–CNT film (CNT–CDP/GCE), the response current increased markedly, the sensitivity (current vs. concentration of hydrogen peroxide) was 1.90 μA mM^{-1}, that is about 25 times higher than bare GCE. This suggests that the CDP–CNT film modified on the bare GCE promoted the electrochemical reaction of hydrogen peroxide more efficiently. The detection limit (S/N = 3) were 340 (M (CDP/GCE), 62 (M (GCE), and 7.3 (M (CNT–CDP/GCE). There is a disadvantage that the noise level of the CNT–CDP/GCE electrode is larger than CDP/GCE electrode.

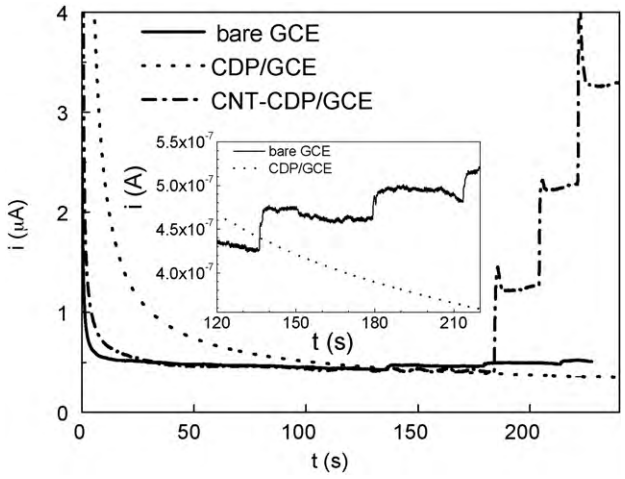

Fig. 2. Amperometric responses to hydrogen peroxide in 0.1 M phosphate buffer (pH 7.2) at 0.6 V vs. SCE of the three electrodes: GCE, CDP/GCE, and CNT–CDP/GCE. The concentration of hydrogen peroxide changes with 0.5 mM each time. The inset shows the enlarged response curves of the bare GCE and CDP/GCE.

3.4. The performance of glucose biosensor

Glucose oxidase was used as a model enzyme to construct CNT–CDP/GCE–GOx sensors by immobilizing GOx on the CNT–CDP/GCE. The CNT–CDP/GCE–GOx sensor was tested using a CHI660C electrochemical workstation. During chronoamperometric measurements, the working electrode was poised at +0.60 V vs. SCE. At each amperometric measurement, 100 μL of glucose solution (100 mM) was added into 9.0 mL of PBS with stir when the background current was stable (stirring rate: ~1000 rpm).

The i–t curves of CNT–CDP/GCE–GOx sensor were shown in Fig. 3. The volume of enzyme on the biosensor was 3 μL (about 2.4 U). The sensor could work linearly in glucose solution. When the glucose concentration is lower than 3.23 mM, the corresponding regression equation of the linear plot was: $I/\mu A = 0.015 + 0.74c$, $N = 4$, $SD = 9.3 \times 10^{-8}$, $R = 0.997$, where c is the glucose concentration in mM (the upper inset in Fig. 3). The sensitivity was thus estimated as 21.6 μA mM^{-1} cm^{-2} (0.74 μA mM^{-1}). The detection limit (S/N = 3) were determined to be 3.5 μM. Additionally, the biosensor is stable. It could keep about 85% of its response activity compared with its first measurement in 5.0 mM glucose solution after 2 weeks.

The i–c curve of the sensor deviates from linearity at higher concentration representing a typical characteristic of Michaelis–Menten kinetics. The Lineweaver–Burk equation could be expressed as follows: $1/i = (K_m/i_{max})1/c + 1/i_{max}$, where i represents the initial velocity of reaction, i_{max} represents the saturated initial velocity, K_m is the Michaelis–Menten constant, and c is the concentration of substrate (glucose). Thus K_m is evaluated to be 9.5 mM and i_{max} is evaluated to be 9.88 μA derived from Lineweaver–Burk equation (lower inset in Fig. 3). The value of K_m

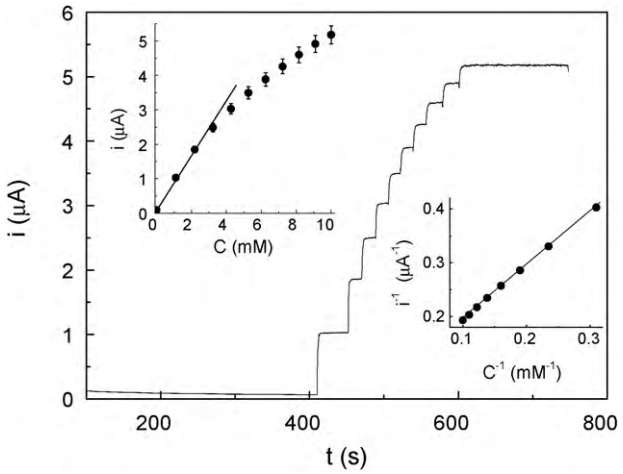

Fig. 3. Amperometric responses of CNT–CDP/GCE–GOx electrodes with successive glucose injection (stirring rate: ~1000 rpm). The applied potential was 0.6 V vs. SCE. The upper inset shows the corrected *i–c* curve of the sensor. The relative standard deviation (RSD) is 5%. The lower inset is the "double reciprocal" curve corresponds to the Lineweaver–Burk equation.

is comparable to the reported 8.2 mM and is much lower than the mentioned data in the same article (Liu et al., 2005). These results show that the biosensor possesses higher biological affinity to glucose.

The investigation of the effect of pH value toward the biosensor was carried out. The pH dependence of the sensor was evaluated at 5.0 mM glucose solution over the pH range from 4.7 to 8.2 (response currents at different pH value were 2.12 μA with pH 4.7, 2.33 μA with pH 5.2, 3.42 μA with pH 5.6, 3.23 μA with pH 6.4, 3.29 μA with pH 6.8, 3.36 μA with pH 7.0, 3.26 μA with pH 7.2, 3.30 μA with pH 7.4, 3.28 μA with pH 7.8, 3.02 μA with pH 8.0 and 2.75 μA with pH 8.2). The isoelectric point of GOx is about 4.2. For soluble native GOx, its pH optimum often showed at about 5.5. However, the CNT–CDP/GCE–GOx biosensor displayed pH independent in the pH range 5.6–7.8. This behavior is consistent with the previous results about the conducting composite of nano-Pt and nano-SiO_2 (Yang and Zhu, 2007).

4. Conclusions

In brief, this present work demonstrates that it is possible to construct insoluble CNT–CDP film for biosensing purpose by dissolving multi-walled CNTs in a mixed aqueous solution of β-cyclodextrin and β-cyclodextrin prepolymer. The CNT–CDP system represents a new biocomposite platform for the development of oxidase-based electrochemical biosensors. In such a system, cyclodextrin provides not only a large surface for enzyme and mediator loading, but also a desirable microenvironment to enzyme, while the CNTs could promote the electro-redox reaction of the active center of the oxidase. The CNT–CDP biocomposites provides promising electrode materials for the development of biosensors and other bioelectrochemical devices.

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