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Study of the nonenzymatic glucose sensor based on highly dispersed Pt nanoparticles supported on carbon nanotubes

Lian-Qing Rong [a,b], Chen Yang [a], Qing-Yun Qian [a], Xing-Hua Xia [a,*]

[a] *Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China*

[b] *Department of Chemical Engineering, Pingxiang College, Pingxiang 337055, China*

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Abstract

An amperometric biosensor for sensitive and selective detection of glucose has been constructed by using highly dispersed Pt nanoparticles supported on carbon nanotubes (Pt-MWCNTs) as sensing interface. The Pt-MWCNTs were synthesized by using the two-step pyrolysis method. This composite shows good electrocatalytic activity towards the oxidation of glucose in alkaline and thus can be used to selectively detect glucose. We found that detection potential and Nafion amount covered on the Pt-MWCNTs modified glassy carbon electrode had considerable influence on the selectivity for amperometric detection of glucose. Under optimal detection conditions (detection potential of 0.0 V versus SCE and 10 μL 1.5% Nafion), selective detection of glucose in the glucose concentration range of 1.0–26.5 mM (correlation coefficient, >0.999) can be performed. The results demonstrate that the Pt-MWCNTs composite is promising for the fabrication of nonenzymatic glucose sensors.

Keywords: Carbon nanotubes; Platinum; Nonenzymatic biosensor; Glucose; Electroanalysis

1. Introduction

Determination of dissolved glucose is of great importance in various areas [1–4]. Many previous studies on glucose detection included the use of enzyme glucose oxidase [2,5], which catalyzes the oxidation of glucose in the presence of oxygen to hydrogen peroxide that can be amperometric detected. However, due to the intrinsic nature of enzymes, such enzyme-based sensors suffer from the instability problem [6–8]. Studies have been attempted to detect glucose based on its direct electrochemical oxidation. However, conventional platinum or gold electrodes have the shortcoming of low electrocatalytic activity towards the oxidation of glucose due to the poisoning effect of reaction intermediates (e.g., adsorbed CO) [6,9], resulting in low sensibility, poor selectivity. On the other hand, the electrochemical detection of glucose with conventional electrodes was influenced heavily by the interfering electroactive species such as ascorbic acid (AA), uric acid (UA), and *p*-acetamidophenol (PP) under physiological conditions [10,11]. Since the electrocatalytic oxidation of glucose on platinum electrodes is a kinetic controlled reaction, its oxidation rate can be enhanced by increasing the real surface area. While the electrochemical responses of the common interfering species of ascorbic acid, uric acid and *p*-acetamedophenol will not be changed significantly since their electrochemical oxidation are diffusion controlled. Therefore, porous platinum electrodes with high roughness factors can be used to sensitively and selectively detect glucose without interference from the common interfering electroactive species. We and others reported that mesoporous platinum [12], three-dimensionally ordered macroporous platinum [9], and highly ordered platinum-nanotubes arrays [11,13,14] could be the potential catalytic interfaces for construction of nonenzymatic glucose sensors with high selectivity and sensitivity.

Carbon nanotube (CNT) has been proven to be one of the most functional nanomaterials because of its remarkable electronic and mechanical properties [15]. Explorations of the CNTs in biological and medical applications have become a rapidly expanding research field [16,17], especially in electrochemistry.

* Corresponding author. Tel.: +86 25 83597436; fax: +86 25 83597436.
E-mail address: xhxia@nju.edu.cn (X.-H. Xia).

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Ye et al. [2] for the first time reported the nonenzymatic detection of glucose using a CNTs modified Glass Carbon (GC) electrode. Electrochemical detection of carbohydrates at carbon nanotube modified glassy carbon electrodes was also reported [3]. However, Compton and his coworkers recently reported that the previously reported electrocatalytic activity of carbon nanotubes came from the metal impurities [18]. They also demonstrated that the electrocatalytic reduction of hydrogen peroxide at a multi-walled carbon nanotube modified electrode is due to the iron oxide particles arising from the chemical vapor deposition process rather than due to the intrinsic catalytic activity of the carbon nanotubes [19].

We recently reported a method for the fabrication of noble metallic nanoparticles supported on carbon nanotubes by using a two-step approach including adsorption and pyrolysis [20,21]. In this method, the functional groups of the carbon nanotubes act as nucleation sites for the growth of platinum particles, thus, the platinum nanoparticles are highly dispersed on the side wall of the carbon nanotubes (Pt-MWCNTs) and have good stability. As mentioned above, glucose can be electrochemically oxidized to gluconic acid at a platinum electrode. Parallel to this reaction, poisoning intermediate (adsorbed CO) is formed, which poisons the electrode surface. The total oxidation mechanism of glucose at platinum electrode is similar to that of ethanol. The generally accepted dual-pathway mechanism of the electrooxidation of ethanol has been demonstrated [22–25]. The ethanol molecules adsorb on a site which is initially covered by a water molecule. Adsorbed ethanol can dissociate to produce adsorbed CO and some other H-containing adsorbed residues. Platinum electrode surface will be rapidly poisoned by the strongly adsorbed CO and ethanol electrooxidation is thus prevented before CO being oxidized at much higher overpotentials. In another oxidation way, ethanol is directly oxidized to form solvable intermediates of acetaldehyde or acetic acid. We believe that the Pt-MWCNTs composite could be an active electrocatalyst towards the oxidation of glucose and is promising for the fabrication of a nonenzymatic glucose sensor.

In this communication, we report the fabrication of a nonenzymatic biosensor for selective detection of glucose by using platinum nanoparticles supported on multi-walled carbon nanotubes as the catalyst. The Pt-MWCNTs composite was prepared as we reported previously [20,26] and characterized by Transmission Electron Microscope (TEM). Electrochemical methods were used to characterize the electrocatalytic activity of the Pt-MWCNTs towards the oxidation of glucose. Selective detection of glucose using the present catalyst was optimized by choosing proper experimental conditions.

2. Materials and methods

2.1. Functionalization of multi-walled carbon nanotubes

Carbon nanotube is very hydrophobic and cannot be wetted by aqueous solution for its high surface tension [27]. Surface modification is of importance to improve metal ions adhesion to the carbon nanotube. According to our previous report [20,21], the multi-walled carbon nanotube (Shenzhen Nanotech Co. Ltd.) was purified by refluxing in a 5 M HNO_3 aqueous solution for 5 h to remove the metallic nickel particles that served as a catalyst for the growth of MWCNTs, and then washed with deionized water for several times. The purified MWCNTs were refluxed in a mixture of HNO_3 and H_2SO_4 (1:1) for 2 h and then filtrated and washed with deionized water until the solution pH approached 7.0. FTIR analysis of the resulting MWCNTs shows that the MWCNTs surface has functional groups such as phenol, carbonyl and carboxyl groups located at ca. 1720 and 3440 cm^{-1}, respectively [20].

2.2. Deposition of Pt nanoparticles on the multi-walled carbon nanotubes

The functional MWCNTs were stirred in 0.04 M $PtCl_4$–C_2H_5OH solution for ca. 2 h. Then, they were filtrated and dried at room temperature. Pyrolysis of the pretreated MWCNTs adsorbed with platinum salts was carried out in a self-made furnace at 500 °C for 1 h to form black powder of Pt-MWCNTs composite. The whole process was carried out under N_2 atmosphere for avoiding the incursion of oxygen and at the meantime removing the gaseous byproducts formed during the pyrolysis process.

Infrared spectroscopic analysis of the functional carbon nanotube was carried out on a Tensor-27 Fourier IR spectrometer (Bruker, USA) equipped with a MCT detector. Transmission electron microscopic (TEM) images and X-ray diffraction patterns were measured on JEM 200CX (JEOL, Japan), ESCALAB MKII (VG company, United Kingdom) using an Mg Kα X-ray source, X'Pert X-ray diffraction spectrometer (Philips, USA), respectively.

2.3. Preparation of Pt-MWCNTs electrode

1.2 mg Pt-MWCNTs powder was dispersed in 300 μL dimethylformamide (DMF). Nafion solution (1.5%) was prepared by diluting 5% Nafion solution (Aldrich) with ethanol. 2.5 μL Pt-MWCNTs composite in DMF was cast on a well-polished glassy carbon electrode ($\phi = 3$ mm) twice under atmosphere. After the film was dried, Nafion solution (1.5% in ethanol) was pipetted on the catalyst surface for protection.

Electrochemical characterization of the Pt-MWCNTs-Nafion modified GC electrode was performed on a CHI 800 Electrochemical Station (CH Instrument, USA) with a modified electrode as the working electrode, a platinum sheet as the counter electrode and a Saturated Calomel Electrode (SCE) as the reference, respectively. All potentials in this work refer to the SCE. Amperometric measurements were carried out under stirred condition, and the response currents were marked with the change value between the steady-state current and background current.

All chemicals were of analytical grade and solutions were prepared with deionized water from a pure system (>18 MΩ, Purelab Classic Corp., USA). All the electrochemical experiments were carried out in nitrogen saturated solutions and at room temperature.

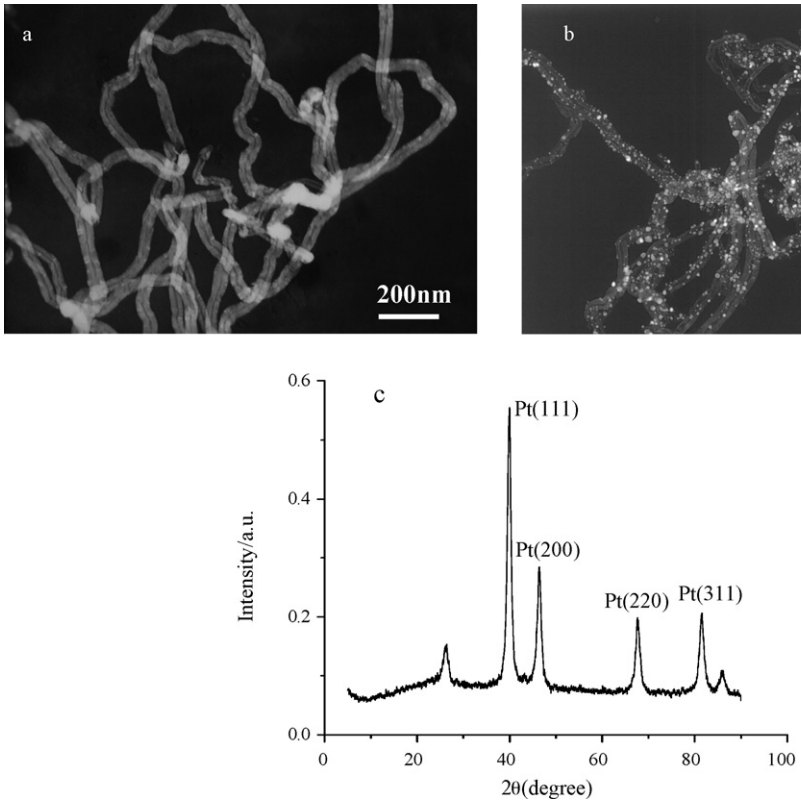

Fig. 1. (a) TEM image of the functional MWCNTs; (b) TEM image of the Pt-MWCNTs; (c) XRD pattern of the Pt-MWCNTs.

3. Results and discussion

3.1. Characterization of the Pt-MWCNTs composite

Fig. 1 shows the TEM images of the functional multi-walled carbon nanotube (a) and the Pt nanoparticles supported on the MWCNTs (b), respectively. As shown in Fig. 1a, the functional MWCNTs has an outer diameter of ca. 40 nm and inner diameter of ca. 5 nm. After deposition of Pt, the TEM image shows that highly dispersed Pt nanoparticles evenly distributed on the sidewall of the MWCNTs. The highly dispersed Pt nanoparticles on the sidewall of the MWCNTs may provide large available surface and enhance the electrocatalytic activity towards the oxidation of glucose.

Fig. 1c shows the X-ray diffraction pattern of the Pt nanoparticles supported on carbon nanotubes. The diffraction peaks at around 2θ of 39.7° (1 1 1), 46.2° (2 0 0), 67.4° (2 2 0), and 81.2° (3 1 1) can be assigned to the Pt face-centered cubic (fcc) structure. The diffraction peak at 26.5° can be attributed to the hexagonal graphite structures (0 0 2). The average particle size of the deposited Pt-catalysts was calculated to be ca. 9 nm from the (1 1 1), (2 0 0) and (2 2 0) X-ray diffraction peaks of the Pt cubic (fcc) lattice in terms of the Scherrer's equation [28].

3.2. Electrocatalysis of glucose at a Pt-MWCNTs composite modified electrode

The electrocatalytic activity of the Pt-MWCNTs composite towards the oxidation of glucose in an alkaline solution was first demonstrated. Fig. 2 shows the cyclic voltammograms of the Pt-MWCNTs-Nafion modified GC electrode in a 0.1 M NaOH solution with (solid curve) and without (dashed curve) 5 mM glucose at a scan rate of 100 mV s^{-1}. In the alkaline solution, the CV shows the characteristics of a platinum electrode including the hydrogen region (−1.0 to −0.6 V), double layer region (−0.6 to −0.3 V) and the oxide formation region (−0.4 to +0.6 V). With glucose in solution, the CV shows a very complicated electrochemical behavior. In the positive potential scan, three anodic current peaks appear at −0.73, −0.25 and +0.11 V, respectively.

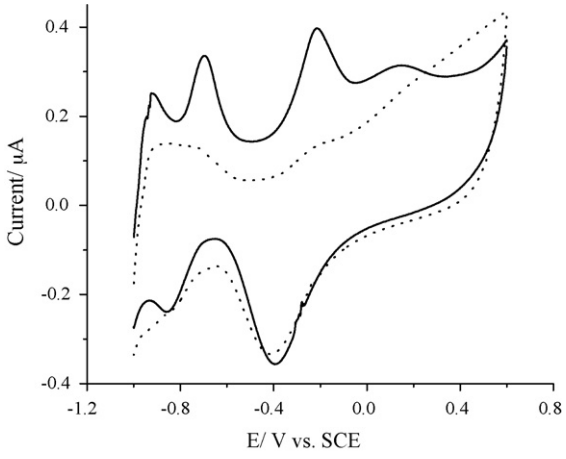

Fig. 2. Cyclic voltammograms (CVs) of a Pt-MWCNTs-Nafion modified GC electrode in a 0.1 M NaOH solution in the presence (solid curve) and absence (dotted curve) of 5 mM glucose at a scan rate of 100 mV s^{-1}.

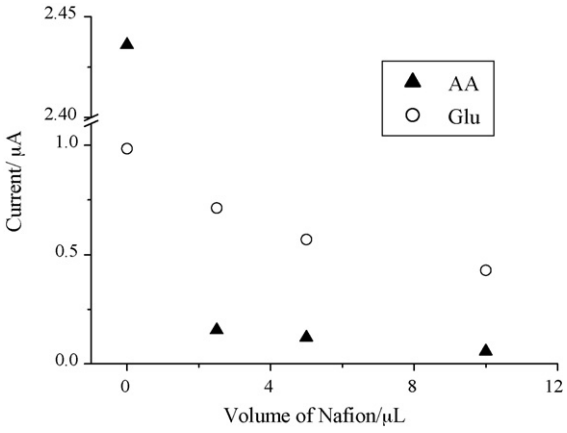

Fig. 3. Effect of the volume of 1.5 wt% Nafion solution on the amperometric response of the Pt-MWCNTs modified GC electrode at 0.0 V in a solution of 0.1 M NaOH containing 0.1 mM ascorbic acid (solid triangles) or 1 mM glucose (empty circle).

The first current peak should be due to the electrochemical adsorption of glucose to form an adsorbed intermediate. At potentials positive with respect to this peak, accumulation of the intermediates (e.g., adsorbed CO) on the electrode surface inhibits the further adsorption of glucose, resulting in a decrease in current. At a potential of about −0.53 V, Pt–OH surface species start to form in the NaOH solution (compare with the CV in alkaline solution without glucose). The Pt–OH species can then oxidize the poisoning intermediates derived from the electrochemical adsorption of glucose to form the anodic current peak at −0.25 V. This process releases free platinum active sites for the direct oxidation of glucose, resulting in the third anodic current peak at +0.11 V. The decrease in current after the third current peak could be due to the formation of thick platinum oxide which in turn inhibits the oxidation of glucose as well. In the negative potential scan, two cathodic current peaks appear. The cathodic current peak at −0.40 V should be due to the reduction of platinum oxide that is formed in the positive potential scan. The peak at −0.82 V could be due to the reduction of the oxidized products of glucose or desorption of the oxidation products (gluconic acid and any derivatives), since this peak is only apparent in the presence of glucose.

In order to understand the observed electrochemical behavior of the Pt-MWCNTs-Nafion modified GC electrode for glucose oxidation, CVs of glucose on MWCNTs that experienced the same pyrolysis conditions as the Pt-MWCNTs was also carried out. In this experiment, cyclic voltammograms (CVs) of

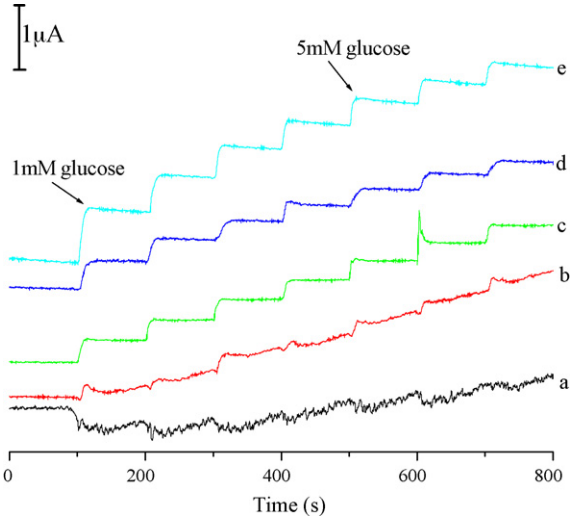

Fig. 4. Amperometric responses of the Pt-MWCNTs-Nafion modified GC electrode at different detection potential upon successive additions of 80 μL solution containing 0.5 M glucose into 40 mL 0.1 M NaOH. The detection solution was continuously stirred. Detection potential: −0.2 V (a), −0.1 V (b), 0.0 V (c), +0.1 V (d) and +0.2 V (e).

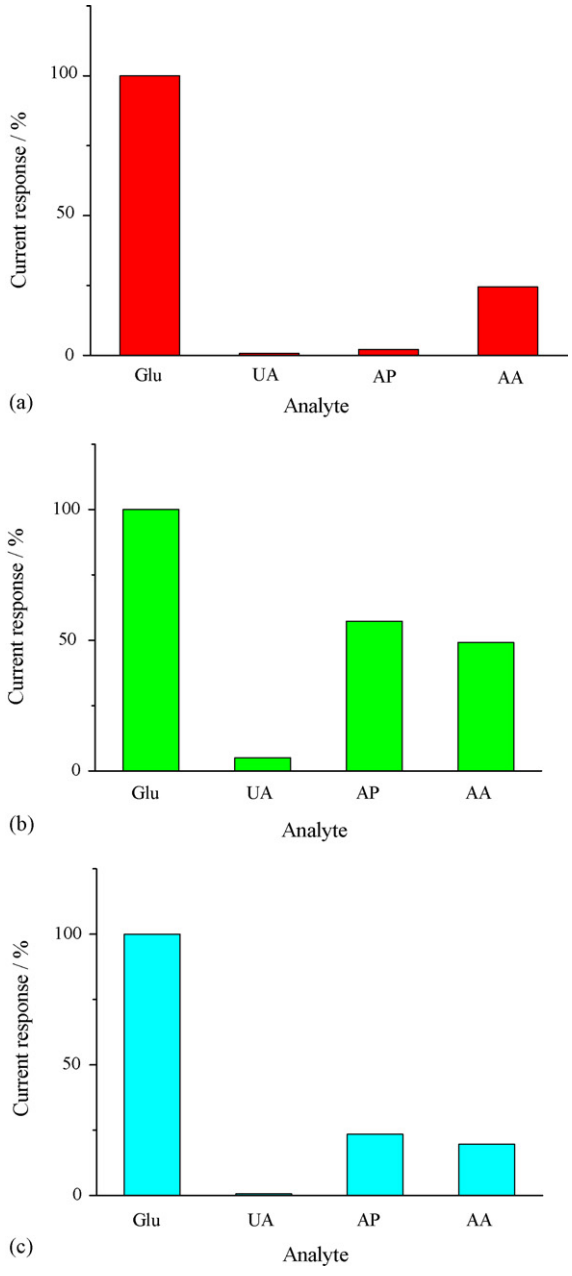

Fig. 5. Selectivity of the modified electrode at 0.0 V (a), 0.1 V (b) and 0.2 V (c) in a solution of 0.1 M NaOH + 1.0 mM glucose upon continuous addition of 0.02 mM UA, 0.10 mM AP, and 0.10 mM AA in 0.1 M NaOH. The current for glucose on the modified electrode was taken as 100%, and the currents for the interfering electroactive species were normalized to the current for glucose.

the MWCNTs-Nafion modified GC electrode in a 0.1 M NaOH solution with and without glucose are almost the same, only showing a peak pair located at around −0.4 V which is due to the redox behavior of the carboxylic acid groups on the functional MWCNTs surface [29]. Obviously, the functional MWCNTs do not show obvious electrocatalytic activity towards the oxidation of glucose in alkaline solution. Therefore, the observed electrocatalytic oxidation of glucose on the Pt-MWCNTs composite modified electrode is due to the presence of platinum nanoparticles, but not the MWCNTs itself or impurities such as iron oxide, which is in good agreement with that reported recently [18,19].

3.3. Effect of Nafion on the electrochemical response of the modified electrode

Curulli et al. [30] reported a glucose biosensor based on PB supported on non-conventional conducting polymer nanotubes. It had high selectivity for H_2O_2 and high rejection towards the common interferences. Alternatively, we used Prussian blue as electrocatalyst for the reduction of hydrogen peroxide generated from an enzymatic reaction [31]. In addition, we suggested a dual-electrode pair system with diffusion layer distance gap to completely deplete interfering species, thus, selective and sensitive detection of glucose can be realized [32,33]. In addition, Tang et al. [14] reported that Nafion film has good anti-interferent ability to ascorbic acid during glucose detection.

Fig. 3 indicates that the anodic response of the Pt-MWCNTs modified GC electrode at 0.0 V in a solution of 0.1 M NaOH containing 0.1 mM ascorbic acid or 1 mM glucose decreases with the increase of Nafion amount covered on the electrode surface. As the Nafion volume increased from 0 to 10 μL, the amperometric response of AA significantly decreased from 2.44 to 0.06 μA; while for glucose, it decreases slightly from 0.99 to 0.43 μA. It is clear that the decrease in amperometric response for ascorbic acid upon increase of Nafion is much faster than for glucose. Therefore, we can selectively detect glucose simply by increasing the Nafion amount. In the following experiments, 10 μL 1.5% Nafion solution was cast on the modified electrodes.

3.4. Amperometric response to glucose and interfering electroactive species

In this section, the effect of detection potential on the amperometric detection of glucose was investigated. In the measurements, the amperometric responses of the Pt-MWCNTs-Nafion modified GC electrode at different detection potential in a solution of 0.1 M NaOH upon addition of glucose were recorded. The results are shown in Fig. 4. Addition of glucose was marked with arrows to the concentrations mentioned. It is clear that the response current of the modified electrode abruptly increases to steady-state values upon addition of glucose. The response time is only about 10 s. In addition, the response sensitivity of glucose increases significantly with the potential increasing from −0.1 to 0.0 V. At more positive detection potentials (0.0 to +0.2 V), it changes slightly.

The normal physiological level of glucose is 3–8 mM, which is much higher than that of the interfering species, AA, UA and PP, ∼0.1 mM. Since the interfering species have higher electron transfer rates than glucose, their oxidation currents are comparable to that from highly concentrated glucose. Therefore, the amperometric responses of the modified electrode at 0.0, 0.1 and 0.2 V in solutions of 0.1 M NaOH + 1 mM glucose and 0.1 M NaOH with continuous addition of 0.02 mM UA, 0.10 mM AP, and 0.10 mM AA were evaluated, respectively. For a better comparison, the response current of 1 mM glucose is set as 100%, and the responses of the interfering species are normalized by this value. The results are shown in Fig. 5. For all these three detection potentials, the interference from UA is neglectable; while interferences from the AP and AA are significant and they increase with the increase of the detection potential. At the detection potential of 0.0 V (Fig. 5a), the interferences from UA, AP and AA are only 0.72%, and 2.14% and 24.5%, respectively. This indicates that at the detection potential of 0.0 V, the present sensor has good anti-interfere ability towards the three interferents and the selective and sensitive detection of glucose on the modified electrode can be achieved.

Based on the above measurements, the optimal detection conditions of the modified electrode towards glucose can be summarized as: the volume of 1.5% Nafion is 10 μL and the

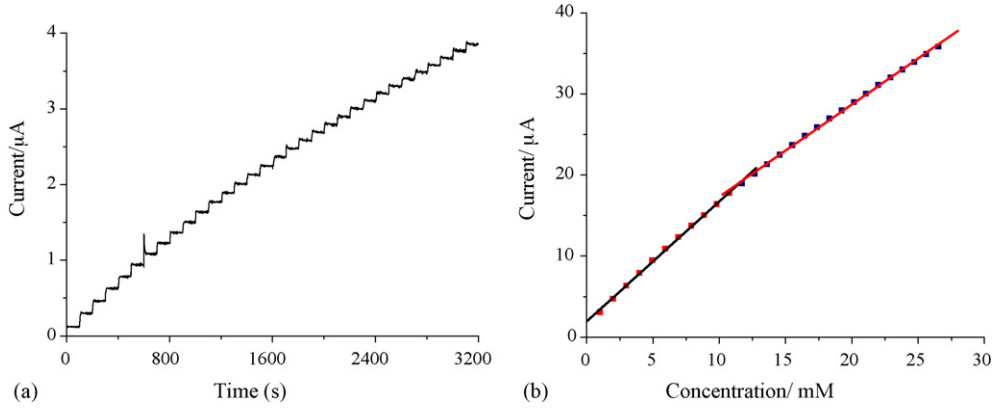

Fig. 6. Hydrodynamic response (a) of the Pt-MWCNTs-Nafion modified gold electrode at 0.0 V upon addition of 80 μL solution containing 0.5 M glucose into 40 mL 0.1 M NaOH (volume correction considered) for each current step and the corresponding calibration curve (b).

detection potential is 0.0 V. Under these optimal conditions, amperometric determination of glucose was carried out. As shown in Fig. 6a, the amperometric response of glucose on this modified electrode shows good stability over long term performance. The corresponding calibration curve (Fig. 6b) shows two linear regions of glucose concentration, respectively, in 1.0–11.7 mM (correlation coefficient, 0.9993) and 11.7–26.5 mM (correlation coefficient, 0.9995).

4. Conclusions

We have synthesized Pt-catalysts supported on carbon nanotubes by using the two-step process including adsorption and pyrolysis. The Pt nanoparticles disperse uniformly on the sidewalls of the carbon nanotubes. The resulting Pt-MWCNTs catalyst shows high electrocatalytic activity towards the oxidation of glucose in alkaline solution, and thus can be successfully used to selectively detect glucose. Results showed that the Pt-MWCNTs catalyst modified electrode covered with 10 μL 1.5% Nafion at a detection potential of 0.0 V versus SCE had good anti-interfere ability towards UA, AP and AA. Good linear dependence of the amperometric response of the modified electrode on the glucose concentration range from 1 to 26.5 mM was achieved. The present communication shows that the Pt-MWCNTs composite is promising for the fabrication of nonenzymatic glucose sensors.

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