Biosensors and Bioelectronics 25 (2009) 218–223

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

A nano-Ni based ultrasensitive nonenzymatic electrochemical sensor for glucose: Enhancing sensitivity through a nanowire array strategy

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ARTICLE INFO

Article history:
Received 29 April 2009
Received in revised form 12 June 2009
Accepted 26 June 2009
Available online 7 July 2009

Keywords:
Ni nanowire arrays
Glucose
Amperometry
Nonenzymatic sensor
Electropolymerization

ABSTRACT

Highly ordered Ni nanowire arrays (NiNWAs) were synthesized for the first time using a template-directed electropolymerization strategy with a nanopore polycarbonate (PC) membrane template, and their morphological characterization were examined by scanning electron microscopy (SEM) and transmission electron microscope (TEM). A NiNWAs based electrode shows very high electrochemical activity for electrocatalytic oxidation of glucose in alkaline medium, which has been utilized as the basis of the fabrication of a nonenzymatic biosensor for electrochemical detection of glucose. The biosensor can be applied to the quantification of glucose with a linear range covering from 5.0×10^{-7} to 7.0×10^{-3} M, a high sensitivity of 1043 $\mu A\,mM^{-1}\,cm^{-2}$, and a low detection limit of 1×10^{-7} M. The experiment results also showed that the sensor exhibits good reproducibility and long-term stability, as well as high selectivity with no interference from other oxidable species.

1. Introduction

It was demonstrated by modern pathology and medicine investigation that, in diabetes patients, the risk for renal, retinal and neural complications is directly related to the magnitude of chronic elevations of blood glucose (Turner et al., 1999). Therefore, the development of fast and reliable methods for glucose determination is of considerable importance. Conventional spectrophotometric methods are limited in detection of glucose due to the lack of chromophoric or fluorophoric ligands for glucose. Electrochemical biosensors have received increasing attention due to their remarkable features such as high sensitivity, simple instrumentation, low production cost and promising response speed. Glucose oxidase (GOx) (Liu et al., 2007; Salimi et al., 2007; Kaushik et al., 2008; Liu et al., 2008) as enzymatic catalyst has been widely used for such kind of biosensor fabrication. However, the activity of GOx can be easily affected by temperature, pH, humidity, and toxic chemicals (Wilson and Turner, 1992). Another limitation is the severe interferences from other oxidable species in blood samples such as ascorbic and uric acids, since the electrode must be poised at +0.7 V (versus Ag/AgCl) or higher for the electrochemical detection of hydrogen peroxide generated as a co-product by enzyme-catalyzed oxidation of glucose (Hrapovic and Luong, 2003). Nonenzymatic glucose sensor seems to be an attractively alternative technique free from above-mentioned drawbacks.

The majority of reported nonenzymatic electrochemical glucose sensors are direct amperometric ones, which rely on the current response of glucose oxidation directly at the electrode surface. The electrocatalytic activity of the electrode material is, therefore, the key factor that affects both the sensitivity and selectivity of glucose detection for nonenzymatic glucose sensors (Safavi et al., 2009). Different metals such as platinum (Beden et al., 1996; Bae et al., 1991), gold (Hsiao et al., 1996), alloys (containing Pt, Pb, Au, Pd and Rh) (Sun et al., 2001) have been explored as electrode materials to develop enzyme-free sensors for glucose. However, these electrodes suffer from slow kinetics and surface fouling due to the absorption of intermediates and chloride ion (Ye et al., 2004). Recent years have seen a growing interest in development of nonenzymatic glucose sensors based on metallic nanoparticles, as such materials showed some unique features such as high surface area-to-volume ratios, rapid mass transport, improved electrocatalytic activity as well as biocompatibility with comparison to bulk electrode metallic materials (Lin et al., 2005; Mena et al., 2005; Welch and Compton, 2006). Several metallic nanoparticles such as Au (Tominaga et al., 2005, 2006), Cu (Casella et al., 1997; Xu et al., 2006), Pt (Rong et al., 2007), Pt/Pb (Cui et al., 2007) and Pt/Ir nanoparticles (Holt-Hindle et al., 2008) have been used to prepare nonenzymatic glucose sensors and exhibited good analytical performance for glucose detection.

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doi:10.1016/j.bios.2009.06.041

The nickel electrode (Luo et al., 1991; Casella et al., 1991; Fermier and Colon, 1996) has been the most widely utilized electrode for determining glucose in alkaline media and the electrochemical property of metallic nickel electrode has been well investigated. It was suggested that the mechanism for its response involves $Ni^{2+/3+}$ couple on the oxidized Ni surface. Several Ni nanoparticles based enzyme-free biosensors for glucose have also been reported which showed great enhancement in the electro-oxidation of glucose compared to other metallic nanoparticles based electrodes. You et al. (2003) reported a nonenzymatic glucose electrode based on Ni nanoparticles dispersed in disordered graphite-like carbon (Ni–NDC), which showed at least 1 order of magnitude enhancement of the sensitivity to glucose compared to the bulk-Ni electrode. Cheng et al. (2008) reported the application of a nano-NiO modified carbon paste electrode to detect carbohydrates with high sensitivity and stability. Safavi et al. (2009) reported the fabrication of a novel nonenzymatic composite electrode based on the mixing powdered nanoscale nickel hydroxide with graphite powder and ionic liquid, which shows a highly sensitive, selective and extraordinary stable response towards glucose. Nanowires have attracted an increasing interest in the past five years, due to their promising applications in sensor development, nanoscale electronic and photonic devices fabrication. Compared to spherical nanoparticles, nanowires possess a number of unique optical, electrical and catalytic properties that endue them with new and important activities (Salem et al., 2004; Granot et al., 2005). And the high surface area-to-volume ratios of nanowires could increase the voltammetric signals for electroactive species that diffused from the bulk solution. Combining the advantageous features of the metallic Ni (You et al., 2005; Salimi and Roushani, 2005; Liu et al., 2009) and the three-dimensional nanostructured arrays (Bai et al., 2008) in electrocatalytic oxidation of glucose, we developed an enzyme-free glucose sensor based on the Ni nanowire arrays (NiNWAs), which was synthesized using a template-directed electropolymerization strategy with a nanopore polycarbonate (PC) membrane template. The proposed NiNWAs electrode allows highly sensitive, stable, and fast amperometric sensing of glucose. In addition, interference from the oxidation of common interfering species, such as ascorbic acid and uric acid, is effectively avoided.

2. Experimental

2.1. Apparatus and reagents

Scanning electron microscopy (SEM) analysis was performed using a JSM-5600LV microscope (JEOL Ltd., Japan). Transmission electron microscope (TEM) image was taken with a JEM-3010 transmission electron microscope (JEOL Co. Ltd., Japan). The Cyclic voltammetric and amperometric measurements were carried out on a CHI 760B electrochemical workstation (Shanghai, China). A three-electrode cell (10 mL) was used with the modified glassy carbon (GC) electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum foil electrode as the counter electrode.

All potentials were measured versus the SCE, and all experiments were carried out at room temperature. Track-etched porous PC (0.2 μm) membrane was provided by Whatman (Anodisc 47, 0.2 μm). D-(+)-Glucose was obtained from Merck. Nickel sulfate hexahydrate ($NiSO_4{\cdot}6H_2O$) was purchased from Sigma, and nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), hydroxide (NaOH), boric acid (H_3BO_3) from Kermel Chemical Reagent Company (Tianjin, China). A 0.1 M NaOH solution was used as supporting electrolyte. All other reagents were of analytical grade, and doubly distilled water was used throughout the experiments.

2.2. Fabrication of Ni nanowire array electrode

For the electrodeposition of NiNWAs, a thin film of platinum (~30 nm) was first sputtered onto one face of the PC template to make the template conductive. In a typical experiment, the membrane was attached platinum-side down on the GC (4 mm diameter) electrode surface and covered by a rubber O-ring. The NiNWAs were deposited using chronoamperometry under the potential of +1.35 V for 30 min by immersing the GC electrode in a mixture of 100 g/L $NiSO_4{\cdot}6H_2O$, 30 g/L $NiCl_2{\cdot}6H_2O$ and 40 g/L H_3BO_3, the pH value of which was adjusted to 2.5 with 1 M H_2SO_4 (Wang et al., 2005). After deposition, the PC template was dissolved by immersing the electrode in chloroform. The resulting GC electrode modified by NiNWAs was washed repeatedly with ethanol and deionized water.

3. Results and discussion

3.1. Characterization of the prepared NiNWAs

A NiNWAs platform for glucose detection was generated by electrodeposition of Ni into the pores of a polycarbonate membrane and subsequent chemical etching of the template. The nanowires are highly regular and uniform, and vertically oriented with an average diameter of about 250 nm, which corresponds to the size of the nanopore in the template (Fig. 1A). Fig. 1B shows SEM images of the Ni nanowire arrays, which confirmed the formation of nanowires. It can also be seen from the image that for most of the nanowires the spacing between two nanowires is larger than the diameter of the nanowire, making each nanowire work as an individual nanoelectrode (Lin et al., 2004). Counting the number of the fibers observed in such images allows for an experimental evaluation of the nanowire density. The nanowire density is about 5×10^8 cm^{-2}. TEM image of the Ni nanowires is shown in Fig. 1C. A straight nanowire can be seen with a diameter of about 250 nm, which is in accordance with the SEM image.

3.2. Electrochemical property of the NiNWAs electrode

To investigate the electrochemical performance of the NiNWAs electrode, cyclic voltammetry was employed over a potential range from +0.1 to +0.7 V. Fig. 2 shows the cyclic voltammogram of the bare (a) and the NiNWAs electrode (b) in 0.1 M NaOH solution. There is no reaction peak current observed for the bare electrode at the electrochemical window. However, a pair of well-defined redox peaks with cathodic peak at 338 mV and the corresponding anodic peak at 477 mV are observed at the NiNWAs electrode, corresponding to the Ni(III)/(II) redox couple. The experimental results are consistent with the literature observation that the cyclic voltammogram of the nickel substrate in 0.1 mol L^{-1} NaOH shows a nonsymmetrical face wave associated with an irreversible process of oxidation-reduction (Zhao et al., 2007). The electrochemical reactions of the Ni(III)/(II) peaks may be as follows (Zhao et al., 2007; Luo et al., 1996):

$$NiO + OH^- - e^- \rightarrow NiO(OH) \quad (1)$$

or

$$Ni(OH)_2 + OH^- - e^- \rightarrow NiO(OH) + H_2O \quad (2)$$

where NiO and $Ni(OH)_2$ are due to the oxidation of Ni(0) to Ni(II) at potential of less than −600 mV.

$$Ni + 2OH^- - 2e^- \rightarrow NiO + H_2O \quad (3)$$

or

$$Ni + 2OH^- - 2e^- \rightarrow Ni(OH)_2 \quad (4)$$

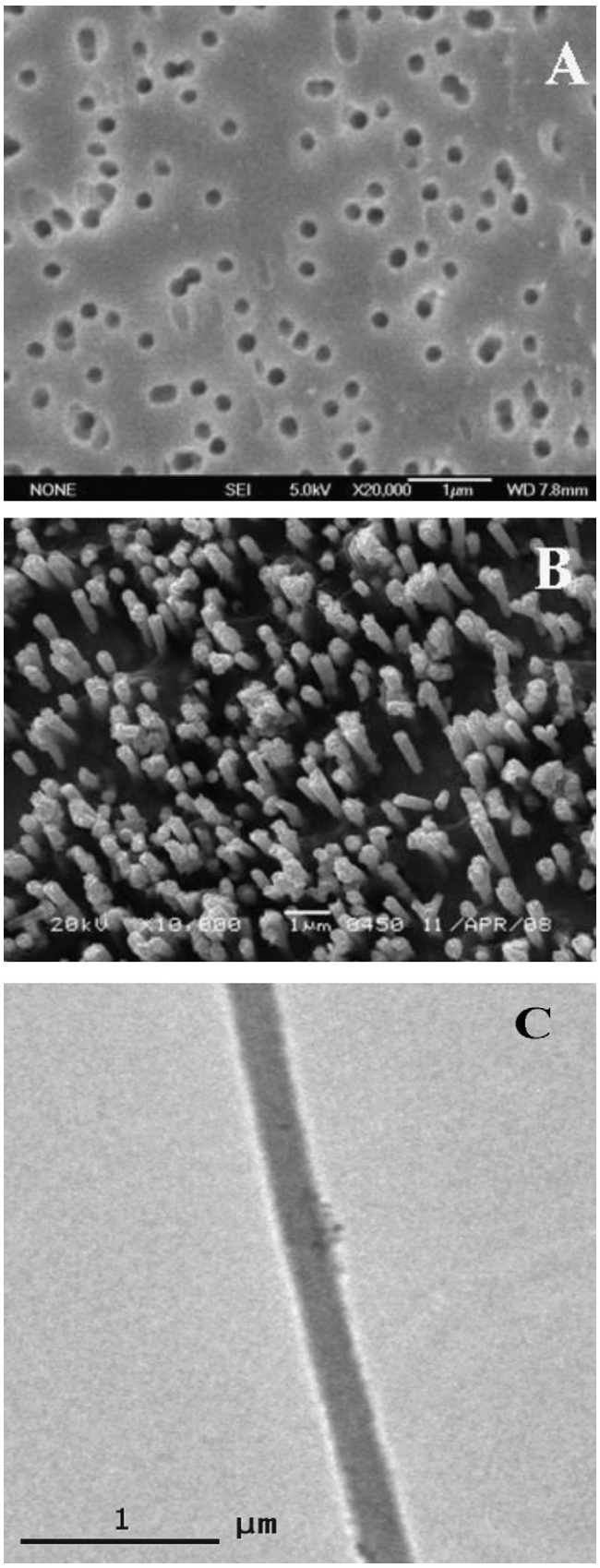

Fig. 1. SEM image of the nanopore polycarbonate membrane template (A), the Ni nanowire array (B); and TEM image of a single Ni nanowire (C).

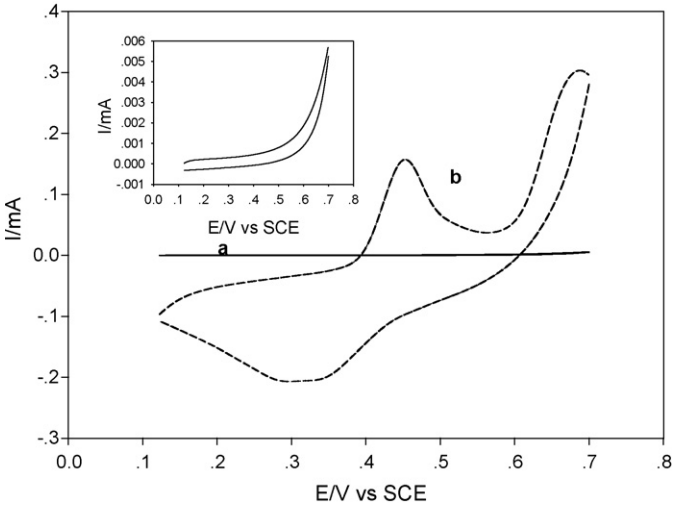

Fig. 2. Cyclic voltammograms obtained in 0.1 M NaOH solution at bare and the NiNWAs modified GC electrode. (Inset) Bare electrode in 0.1 M NaOH.

Eqs. (1) and (2) may be simply described by

$$\mathrm{Ni(II)} - \mathrm{e^-} \rightarrow \mathrm{Ni(III)} \quad (5)$$

Fig. 3A shows the cyclic voltammograms of the NiNWAs electrode recorded in 0.1 M NaOH solution at different scan rates. It is found that both anodic and cathodic peak currents increase clearly with increasing potential scan rate. In the range of 0.02–0.5 V s^{-1}, both the anodic and cathodic peak current were linearly correlated to the scan rates (inset plot in Fig. 3A), implying that the electrochemical kinetics is a typical surface-controlled electrochemical process. Stability for the NiNWAs modified electrode was also examined by recording its 20 consecutive CV curves in NaOH at a scan rate of 50 mV s^{-1}, and results are given in Fig. 3B. No obvious peak current change is found during 20 consecutive CV curves, implying that the NiNWAs are very stably electrochemical modified onto the surface of GC electrode.

3.3. Electrocatalytic oxidation of glucose at the NiNWAs electrode

In order to test the electrocatalytic activity of the NiNWAs electrode, the cyclic voltammograms were obtained in the absence and presence of glucose, and the curves are presented in Fig. 4A. In the absence of glucose (curve a), one couple of well-behaved redox peaks for the NiNWAs on the electrode can be observed. Upon the addition of 50 μL of 1.0 M glucose in 10 mL NaOH (the concentration of glucose being 5 mM), there is a great enhancement of the anodic peak current (curve b). At the same time, the cathodic peak current decreases. This indicates that the NiNWAs can catalyze the oxidation of glucose. As indicated in literatures (Zhao et al., 2007; Safavi et al., 2009), the oxidation of glucose to glucolactone (two hydrogen are liberated in this process) was catalyzed by the Ni(III)/(II) redox couple according to the following reactions:

$$\mathrm{Ni(OH)_2} + \mathrm{OH^-} \rightarrow \mathrm{NiO(OH)} + \mathrm{H_2O} + \mathrm{e^-}$$

$$\mathrm{NiO(OH)} + \mathrm{glucose} \rightarrow \mathrm{Ni(OH)_2} + \mathrm{glucolactone}$$

The Ni(III) species on the electrode surface rapidly oxidizes glucose at the anodic, producing Ni(II) species and sacrificing Ni(III) ones. As a result, the change in concentrations of Ni(II) and Ni(III) species causes the increase of the anodic peak current and the decrease of the cathodic peak current.

It is well known that the applied potential strongly affects the amperometric response of a biosensor. We have systemically

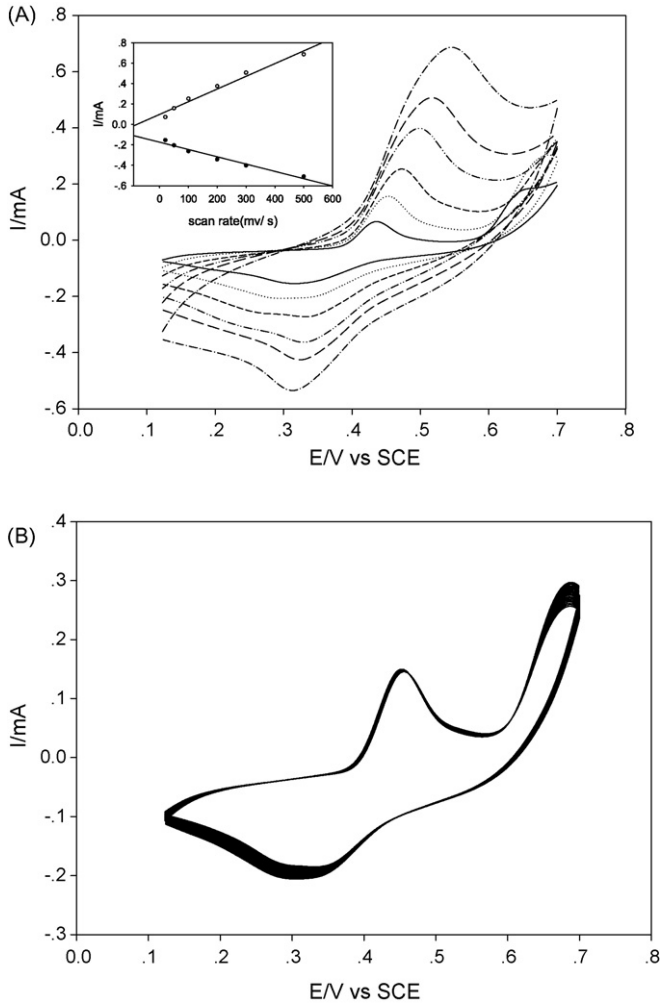

Fig. 3. Cyclic voltammograms curves of the NiNWAs electrode recorded in 0.1 M NaOH solution at different scan rates (inner to outer): 0.02, 0.05, 0.1, 0.2, 0.3, and 0.5 V s^{-1}; and peak current as a function of different scan rate (left inset) (A), and 20 consecutive CV curves of the NiNWAs electrode in 0.1 M NaOH solution at 50 mV s^{-1} (B).

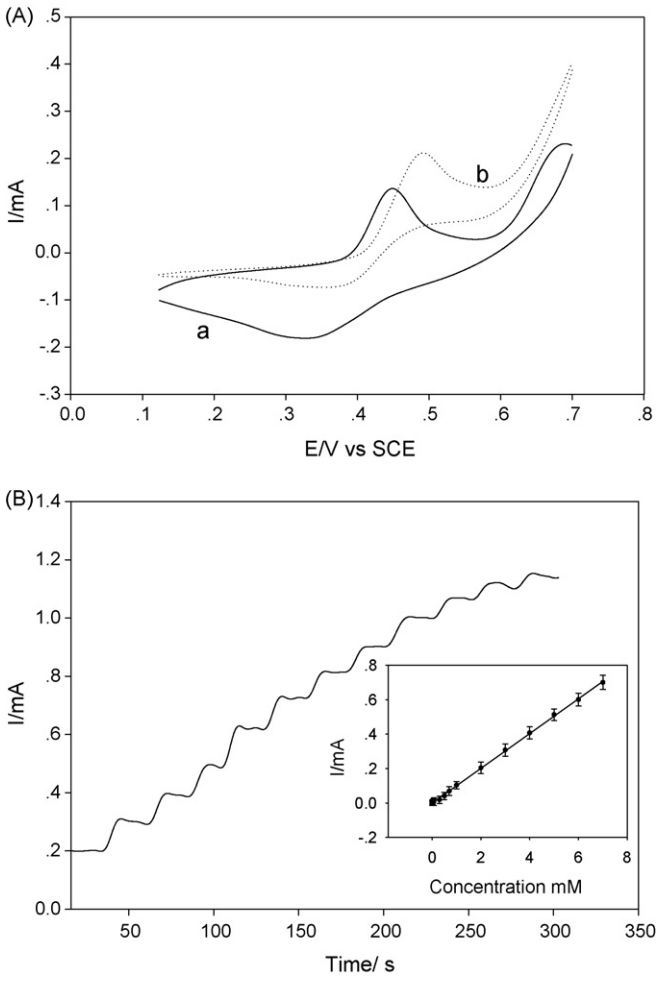

Fig. 4. Cyclic voltammograms of the NiNWAs modified GC electrode recorded in 0.1 M NaOH solution (a) and in NaOH solution with 5 mM glucose (b) between +0.1 and +0.7 V at the scan rate of 50 mV s^{-1} (A), and Amperometric responses for the NiNWAs modified GC electrode to subsequent additions of 10 μL of 1.0 M glucose in 10 mL 0.1 M NaOH solution (the change of concentration for glucose being 1.0 mM) at +0.55 V (B). The error bars indicated the standard deviation of triplicate determinations for each concentration of analyte.

investigated the impact of applied potentials on the amperometric response of the NiNWAs electrode to glucose. Constant potential chronoamperometry was performed by varying the potential (in 0.05 V steps) of the NiNWAs electrode between +0.2 and +0.7 V in the presence of 0.2 mM glucose. The steady-state reduction current increases gradually from +0.2 to +0.55 V, and reach the maximum at +0.55 V, then decreases at more negative potentials than +0.55 V. Taking the sensitivity and the signal/noise ratio into consideration, +0.55 V was chosen as the optimum applied potential.

An alkaline medium is required for enhancing the electrocatalytic activity of several transition metals for oxidation of carbohydrate compounds. Therefore, we investigated the influence of hydroxide concentration on the performance of the sensor over the hydroxide concentration range of 0–0.5 M. No response current of the oxidation of glucose was acquired in the absence of NaOH. With the concentration of NaOH increasing from 0 to 0.1 M, the currents increased, because glucose is easily oxidized at high pH. However, when the concentration of NaOH increased above 0.1 M, a high background noise was seen. The results obtained are consistent with the experimental phenomena that an increased background current was observed at a high NaOH concentration (Wang, 2001). In our experiment, a 0.1 M NaOH solution was chosen as the medium. The optimal applied potential was obtained at +0.55 V in 0.1 M NaOH solution. Therefore, these conditions were used for subsequent experiments.

Fig. 4B shows amperometric responses for the NiNWAs electrode to subsequent additions of 10 μL of 1.0 M glucose in 10 mL 0.1 M NaOH solution (the change of concentration for glucose being 1.0 mM) at +0.55 V. It is observed that the NiNWAs electrode responds quickly to the change of glucose concentration and reaches a steady-state signal within 10 s, and the amperometric signal shows linear correlation to glucose concentration in the range from 5×10^{-7} to 7×10^{-3} M with a correlation coefficient of 0.998, which covers five orders of magnitude of glucose concentrations. The sensitivity was 1043 μA mM^{-1} cm^{-2}, and the detection limit was obtained as 1×10^{-7} M (based on S/N = 3), demonstrating that NiNWAs electrode yielded the most advantageous analytical performance in glucose detection, as compared with the existing glucose sensors. The average relative standard deviation (RSD) is not more than 5.6%. The comparison of NiNWAs electrode with different nonenzymatic glucose sensors are shown in Table 1. The overall performance reveals that this sensor displays a good superiority in terms of sensitivity, selectivity and linear calibration.

Table 1
Comparison of the present NiNWAs electrode with different nonenzymatic glucose sensors.

Type of electrode	Detection potential (V)	Sensitivity ($\mu A\,mM^{-1}\,cm^{-2}$)	Linear range	Detection limit (μM)	Stability	Ref.
Ni powder modified electrode	0.4	40	0.5 μM–5mM	2 μM	–	You et al. (2003)
Ni nanoparticle modified carbon paste electrode	0.55	–	1.0 μM–1.0mM	0.3 μM	One week	Cheng et al. (2008)
Pt–Pb nanowire array electrode	−0.2	11.25	−11 mM	8 μM	30 days	Bai et al. (2008)
Nanoscale nickel hydroxide modified carbon ionic liquide electrode	0.55	202	50 μM–23 mM	6 μM	100 days	Safavi et al. (2009)
Copper nanocluster/MWCNT	0.65	251.38	0.7–3.5 mM	0.21 μM	35 days	Kang et al. (2007)
Copper nanoparticles	0.65	–	1 μM–5 mM	0.5 μM	60 days	Xu et al. (2006)
Cu/SAMs	0.6	–	3.0 μM–10 mM	0.7 μM	–	Zhao et al. (2006)
Nickel electrode	0.55	–	0.1–2.5 mM	0.04mM	–	Zhao et al. (2007)
Ni nanoparticle loaded carbon nanofiber paste electrode	0.6	420.4	2.0 μM–2.5 mM	1 μM	–	Liu et al. (2009)
NiNWAs	0.55	1043	0.5 μM–7 mM	0.1 μM	65 days	This paper

3.4. Interference study

One of the most important analytical factors for an amperometric biosensor is the ability of the sensor to discriminate the interfering species having electroactivities similar to the target analyte. The oxidizable compounds such as ascorbic acid (AA) and uric acid (UA) are normally co-existed with glucose in real samples. The normal physiological level of glucose is about 3–8 mM, which is much higher than the concentrations of interfering species like UA (0.1 mM) and AA (0.1 mM) (Kang et al., 2007; Safavi et al., 2009). In the present work, we studied the interference effect of 0.1 mM UA and 0.1 mM AA on the amperometric response of 1 mM glucose. At this level, almost no current response for such electroactive interfering species was detected in comparison to that of glucose by the sensor at an applied potential of +0.55 V in 0.1 M NaOH solution (Fig. 5).

3.5. Reproducibility and stability

The reproducibility and repeatability of the developed biosensor were determined. In a series of 10 sensors prepared in the same way, a relative standard deviation of 3.5% was obtained toward 2 mM glucose, indicating the reliability of the method. A set of 10 different amperometric measurements for 2 mM glucose with a single biosensor yield a R.S.D. of 3.4%.

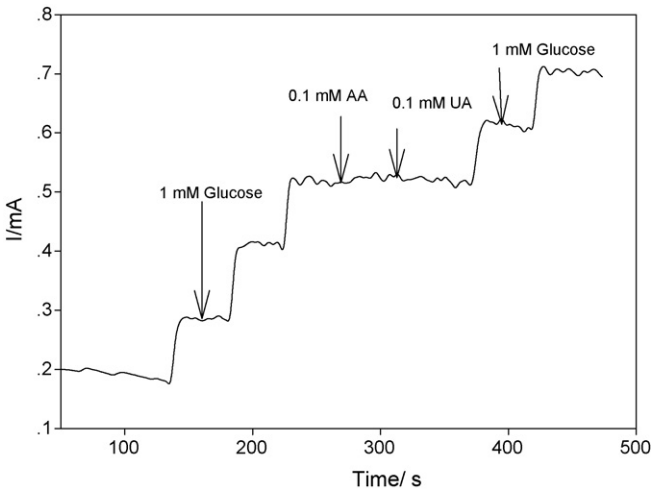

Fig. 5. Amperometric response of glucose (1 mM) in the absence and presence of 0.1 mM AA and UA, at the NiNWAs modified GC electrode in 0.1 M NaOH at an applied potential of +0.55 V.

The stability of the glucose biosensor was explored. The proposed sensor was stored in air at ambient conditions. The response to 2 mM glucose was tested each week, after 65 days of storage, the response of the biosensor only decreased 7% compared to the initial response, which shows long-term stability.

4. Conclusions

In this work, an enzyme-free glucose sensor based on the NiNWAs was fabricated by electrochemical template deposition of Ni into the pores of track-etched polycarbonate host membrane and the following chemical remove of the template. NiNWAs electrode shows a very high electrochemical active surface area and high electrocatalytic activity for the glucose electrooxidation. A lower detection limit of 1×10^{-7} M, a high sensitivity of $1043\,\mu A\,mM^{-1}\,cm^{-2}$ and a wider linear range of 5×10^{-7} to 7×10^{-3} M were obtained compared with those previously reported. More importantly, the interference from the oxidation of common interfering species such as ascorbic acid and uric acid is effectively avoided. Thus, the NiNWAs holds the promise for the development of nonenzymatic glucose sensor.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant 20505008, 20675028), "973" National Key Basic Research Program of China (2007CB310500), Ministry of Education of China (NCET-07-0272), and Hunan Natural Science Foundation (06JJ4010, 07JJ3025).

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