

Electrodeposition of Nickel Nanoparticles Modified Glassy Carbon Electrode for Nonenzymatic Glucose Biosensing

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We report the electrocatalytic activity of nickel nanoparticles (NPs) modified glassy carbon electrode (GCE), prepared by potentiostatic electrodeposition, toward glucose electro-oxidation in alkaline medium. The morphology image of nickel on the GCE surface was characterized by scanning electron microscope (SEM). Electrochemical oxidation of glucose with this sensor was examined by cyclic voltammetry (CV) and chronoamperometry in alkaline aqueous solutions. Amperometric response of the electrocatalytic oxidation to glucose at the potential of 500 mV presents a linear dependence ($R=0.9941$) in the glucose concentration range of 5 μM -1.155 mM, with a 1 μM detection limit ($S/N = 3$). The biologic compounds probably existed in human serum sample, such as ascorbic acid, uric acid, and dopamine, do not disturb the determination of glucose. The relative standard deviation (RSD) of the determination of practical serum samples is less than 7% compared with the results obtained from clinical examination. The proposed sensor exhibits excellent electrocatalytic activity toward the oxidation of glucose, which is a good candidate for glucose quantification.

Keywords: Nickel nanoparticles, Electrodeposition, Glassy carbon electrode, Nonenzymatic glucose biosensing

1. INTRODUCTION

Recently, diabetes mellitus has become a major public health problem worldwide drawing extensive attention[1]. People with diabetes are more prone to suffer renal, retinal and neural complications. They need to constantly monitor their blood glucose level so as to control disease[2].

Therefore, the accurate, rapid and automatic determination of glucose concentration in blood is very important in biological and clinical analysis [3]. Numerous methods by using enzymes such as glucose oxidase have been reported for the determination of glucose, the signal transduction is based on the oxidation of the hydrogen peroxide which is produced by the enzymatic reaction [4]. Although there have been already tremendous benefits from the use of those enzymatic sensors, inevitable drawbacks such as high cost of enzymes, chemical and thermal instability as well as the severe interferences from other oxidable species in blood samples may limit their applications [1,5].

To solve these problems, nonenzymatic glucose sensor is of great demand, and it is becoming an intense research subject. Nowadays, various metal electrodes, alloy electrodes or metal oxide materials have been explored for enzyme-free electrochemical glucose sensors[6], such as Ni [7,8], Co [9], Au [10], Cu[11], Pt [12], Pt-Pd [13], NiO [14], CuO [15-17], Co₃O₄[18] *etc.*. However, considering the major market requirement, the reported sensor based on noble metals may limit their commercial applications due to the high cost. Among these low-cost metal materials, nickel is an attractive electrocatalyst for glucose oxidation. It is well-known that nickel exhibits excellent electrocatalytic performance in alkaline medium [19,20]. In previous reports, Zhao *et al.* [2] used a metallic nickel electrode directly for the nonenzymatic glucose sensor. The amperometric signal at the potential of 550 mV shows a linear correlation to glucose concentration in the range of 0.10-2.50 mmol l⁻¹, with a detection limit of 0.04 mmol l⁻¹ [2]. Wang *et al.* prepared nickel-cobalt nanostructures electrodeposited on reduced graphene oxide-modified glassy carbon electrode (GCE) for highly sensitive glucose detection [8]. Linear calibration range for determining glucose is from 10 μM to 2.65 mM and the detection limit was 3.79 μM. Recent reported performances of determining glucose based on nonenzymatic sensors are still somewhat poor, and need improve. In additional, the fabrication process and cost of the existing nonenzymatic sensors based on metal or metal oxide are not an ideal routine. It is highly demand to develop a facile prepared process of nonenzymatic glucose sensor with excellent performance and cheapness.

In this work, nickel nanoparticles (Ni NPs) modified GCE (Ni NPs/GCE) as the detector for convenient and low-cost blood glucose biosensing was facile fabricated with electrodeposition. The morphology and composition of the modified electrode were characterized with scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The electrochemical and electrocatalytic behaviors of the Ni NPs/GCE toward the oxidation of glucose were discussed detailed. In additional, the detecting performance of Ni NPs/GCE towards glucose was evaluated. Inspiringly, significant performance in catalytic activity, sensitivity, and real applications to glucose have been achieved based on the prepared Ni NPs/GCE with acceptable stability in this work.

2. EXPERIMENTAL

2.1. Chemicals and reagents

Glucose, glycine, tyrosine and NiSO₄ were purchased from Sinopharm Group Chemical Reagent Co., Ltd(Shanghai, China). Ascorbic acid(AA), Uric acid(UA) and dopamine(DA) were

obtained from Sigma-Aldrich. Human serum samples were provided from the local Hospital. All reagents were of analytical grade and used without further purification. All solutions were prepared with ultrapure water.

2.2. Instrumentation

The morphology and composition were studied by Hitachi S-4800 scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS). All electrochemical measurements were performed on a CHI660C electrochemical workstation (CH instruments, China) at the room temperature. A conventional three-electrode system was adopted including a bare or modified GCE (3 mm diameter) as working electrode, a Ag/AgCl electrode as reference electrode and a platinum wire as counter electrode. The electrodeposition of Ni NPs/GCE was performed in a quiescent solution. The amperometric experiments were carried out in 0.1 M NaOH with continuous stirring.

2.3. Preparation of Ni NPs/GCE

GCE modification with Ni nanoparticles was achieved by electrodeposition. Firstly, the GCE was polished carefully with alumina powder. Then, the polished GCE was cleaned with ultrapure water, and dried at room temperature. The potentiostatic deposition of metallic nickel on the GCE electrode from an aqueous solution of 1 M H₂SO₄ solution containing 0.2 M NiSO₄ by applying a constant potential electrolysis at -1.25 V for 40 s. After electrodeposition, the Ni NPs/GCE was washed with ultrapure water and purged with high purity nitrogen for use.

3. RESULTS AND DISCUSSION

3.1. Electrodeposition and morphology of Ni NPs/GCE electrode

Potentiostatic deposition was utilized to prepare metallic Ni modified GCE. Figure 1 shows the electric current as a function of time for potentiostatic deposition of Ni at -1.25 V on the GCE. The chronoamperometry result indicates that the current increases rapidly at the onset of the applied cathodic potential and Ni²⁺ has been reduced and deposited on the surface of GCE electrode for the first 15 s. Then, the electrodeposition rate slows down and the current fluctuates between 0.25 and 0.35 A, accompanied with bubbles growing on the electrode surface, which may be the simultaneous H₂ reduction. In this electrodeposited process, Ni²⁺ ions are quickly exhausted with the applied potential of -1.25 V. In the meantime, numerous bubbles originated from hydrogen evolution happened to effect the diffusion and reaction of Ni²⁺ ions on the electrode surface. As hydrogen bubbles formed and moved off the electrode surface, the formation of H₂ may help to impact the morphology of the deposited Ni. Compared to other methods, including hydrothermal, template-directed for materials prepared, the proposed electrodeposition strategy is facile and cheap without any complex

requirements [21,22].

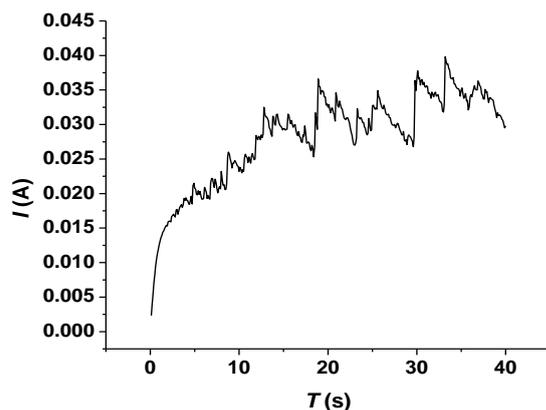


Figure 1. Amperometric *i-t* curve of the preparation of Ni nanoparticles modified GCE electrode

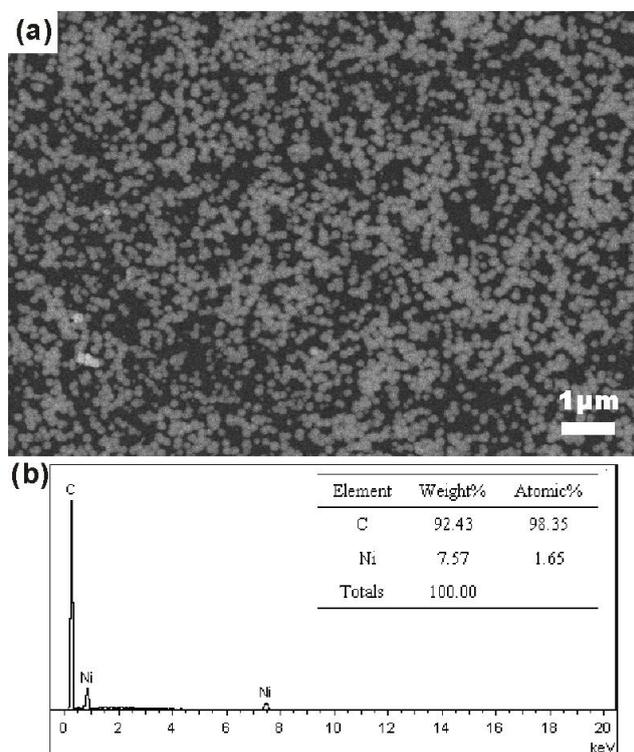


Figure 2. SEM image(a) and EDS pattern(b) of the Ni nanoparticles modified GCE electrode

Figure 2 shows the SEM image and EDS pattern of Ni NPs modified GCE obtained at the constant potential of -0.25 V for 40 s, which clearly illustrates that the metallic Ni has been successfully electrodeposited on the GCE substrate. The Ni nanoparticles closely packed on GCE have a spherical shape and a uniform size distribution, with a diameter of about 100 nm. Some Ni particles aggregate together to form quasi-3-dimensional structure. The uniform structure may facilitate electron transfer and promote electrocatalytic reaction. The peaks of C and Ni elements appear in the EDS pattern illustrate the fact that a thin layer of Ni nanoparticles is deposited on GCE electrode.

3.2. Electrocatalytic oxidation of glucose on Ni NPs/GCE

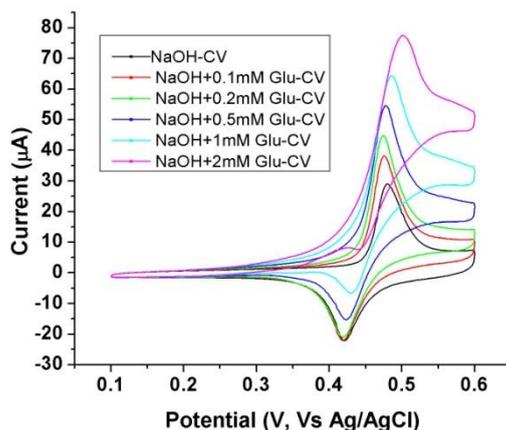
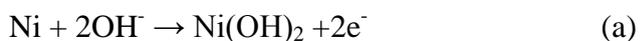
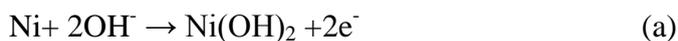


Figure 3. Cyclic voltammograms of Ni NPs/GCE in the absence and presence of different concentrations of glucose in 0.1 M NaOH solution

In alkaline solution, the cyclic voltammograms on the Ni NPs/GCE in the absence and presence of glucose with different concentrations are shown in Figure 3. A pair of well-defined redox peaks is obtained in the cyclic voltammogram of the nickel nanoparticles modified GCE in 0.1 M NaOH without glucose. The anodic peak potential observed at about 480 mV, and the cathodic peak potential at about 420 mV are ascribed to the Ni(III)/(II) redox couple in strong basic condition. Compared with reported metallic nickel electrode[2], Ni NPs/GCE exhibited a more remarkable current response, indicating an excellent electrocatalytic property of glucose oxidation. The electrochemical reactions of the Ni(III)/(II) couple in alkaline solution may be as follows [2,22]:



In the presence of glucose in alkaline solution, the effect of different glucose concentrations on Ni NPs/GCE was investigated. The results (Figure3) showed that the peak currents with the potential at around 0.5 V were gradually increased by increasing glucose concentrations. As can be seen clearly, glucose can be oxidized at alkaline pH and the Ni(III)/(II) species on the electrode surface acts as a catalyst for the oxidation of glucose. When glucose is added into NaOH solution, the Ni(III) species on the electrode can rapidly oxidize glucose to glucolactone, which lead to a significant increase in the anodic peak current. The electrocatalytic oxidation mechanism of glucose at the Ni NPs/GCE may be simply described by the following reactions in alkaline solution [5,22]: The Ni(III)/(II) redox couple serve double function of the electronical medium and enzyme.



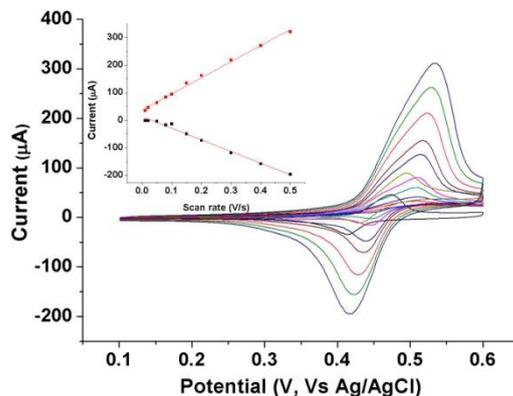
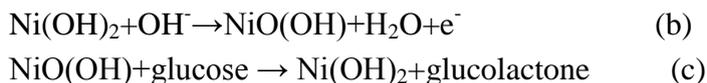


Figure 4. Cyclic voltammograms of Ni nanoparticles modified electrode at scan rates of 10, 20, 50, 80, 100, 150, 200, 300, 400, 500 mV/s. The inset shows plots of peak current versus scan rate

In order to better understand the electrocatalytic properties of the Ni NPs/GCE for glucose oxidation, cyclic voltammetric measurements at different scan rates were carried out. Figure 4 depicts the CV curves of Ni NPs/GCE in 0.1 M NaOH containing 1 mM glucose at various scan rates. As the scan rate increases, the anodic peak potentials shift to more positive and the cathodic peak potentials convert to negative direction. And the peak currents are enhanced with the increasing of the scan rate. According to the plot of the anodic and the cathodic peak currents against the scan rate shown in insert of Figure 4, it is found that the anodic and the cathodic peak currents are linearly proportional to potential sweep rate, indicating that oxidation of glucose is surface-controlled in this range of potential scan rate [1,9].

3.3. Performance of glucose sensing

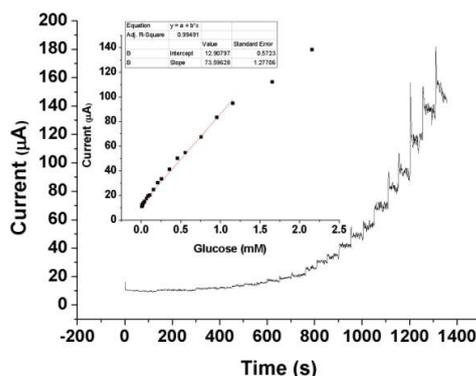


Figure 5. Chronoamperometric responses of glucose sensor upon successive addition of glucose. The inset shows the correlation between the amperometric responses and the glucose concentrations

Figure 5 shows the typical current-time dynamic response of the Ni NPs/GCE upon the successive addition of a certain concentration of glucose into 0.1 M NaOH at the optimal potential of 0.5 V under constantly stirring. Well-defined amperometric currents are increasing quickly and gaining steadily with some level of glucose added, with a response time of about 4 s, illustrating efficient catalytic ability of Ni NPs/GCE for glucose oxidation. The catalytic current is linear with the concentration of glucose in the range from 5 μM to 1.155 mM, as shown in the inset of Figure 5. The calibration curve of $i(\mu\text{A})=12.91+73.60 c$ (mM) (i and c express the height of peak current and concentration of glucose, respectively) was obtained with correlation coefficient of $R=0.9941$. When the concentration of glucose is higher than 1.2 mM, the amperometric responses are gradually saturated due to the lack of sufficient sites on the covered electrode surface to accommodate the added glucose [22]. The sensitivity was $1041.2 \mu\text{A mM}^{-1}\text{cm}^{-2}$ and the detection limit was estimated to be 1 μM based on $S/N=3$, being low enough for the requirement of the accurate detection of human serum sample.

A comparison of the performance of Ni NPs/GCE with other nickel-based glucose sensors is shown in Table 1. All of them have some advantages and limitations. As-prepared Ni NPs/GCE offered a lower detection limit than nickel electrode, Ni-Co nanostructures/GCE and Pt/Ni nanowires/GCE. Pt/Ni nanowires/GCE and Ni nanowire arrays/GCE exhibited wide linear ranges. However, their methods were somewhat complicated, and the materials used in the fabrication step were more expensive, because a precious metal, platinum, had been used. The low cost of electrode material and the simple preparation approach make Ni NPs/GCE prominent. In comparison with Ni/ITO and Ni-nanospheres/reduced grapheme oxide, Ni NPs/GCE in this work offered a more reasonable linear range. By comparing, it can be seen that Ni NPs/GCE is a promising candidate for application of real glucose detection.

Table 1. Performance of Ni NPs/GCE compared with other reported nickel-based glucose sensors via amperometry technique

Modified electrode	Sensitivity ($\mu\text{A cm}^{-2} \text{mM}^{-1}$)	Linear range (μM)	Detection limit (μM)	Ref.
Nickel electrode	-	100-2500	40	2
Ni-Co nanostructures/GCE	878.05	10-2650	6.83	8
Pt/Ni nanowires/GCE	920	2-2000	1.5	23
Ni/ITO	189.5	1-350	0.5	1
Ni nanowire arrays/GCE	1043	0.5-7000	0.1	24
Ni-nanospheres/reduced grapheme oxide	813	1-110	-	25
Ni NPs /GCE	1041.2	5-1155	1	This work

In practical applications, the interfering species such as uric acid (UA), ascorbic acid (AA) and dopamine (DA) normally co-existed with glucose in human blood may be oxidized simultaneously with glucose because of their similar electroactivities [3,5]. Although the normal physiological level of glucose (3–8 mM) in human blood is much higher than the concentrations of interfering species like DA (less than 5 μM), UA (0.02 mM), and AA (0.1 mM), they still may interfere with the determination of glucose. In the present work, the interference experiments were carried out by successive addition of 1 mM glucose, 0.01 mM DA, 0.02 mM UA, 0.1 mM AA, 0.01 mM ethanol, 0.1 mM glycine, and 0.1 mM tyrosine into 0.1 M NaOH. The anti-interference effect of Ni NPs/GCE to interfering reagents toward the determination of glucose at +0.5 V was investigated (Figure 6). It can be seen that these species produce negligible current responses in comparison with that of glucose. This may be related to the rough surface of Ni NPs/GCE, because a rough-surface electrode favors kinetically controlled reaction (the electro-oxidation for glucose), while the electro-oxidation of the interfering species being diffusion-controlled does not depend significantly on the electrode roughness[26]. The specificity results agree well with the other Ni-based electrodes [24,27]. The results imply that Ni NPs/GCE presents high selectivity for the glucose oxidation and can be used for the specific detection of glucose in real samples. Furthermore, the stability of Ni NPs/GCE was evaluated by amperometric measurement under a constant potential of +0.5 V for 2000 s. The result (data not shown) indicates that the current response of Ni NPs/GCE towards glucose detection remains stable due to the favorable electrocatalytic stability. In additional, the response of Ni NPs/GCE for glucose detection can remain more than 85% of the initial response when the prepared Ni NPs/GCE stored at ambient environment for half a month.

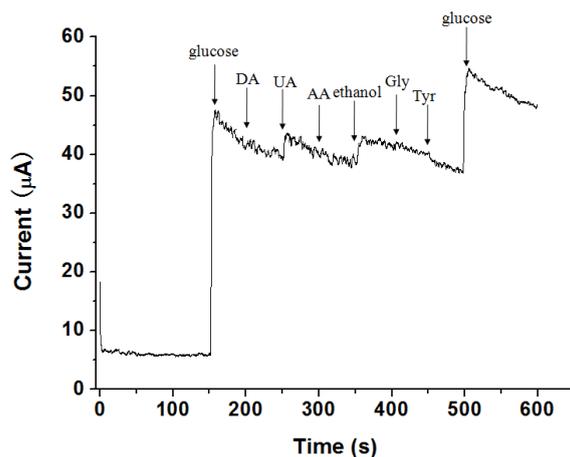


Figure 6. The amperometric *i-t* curve of Ni nanoparticles modified GCE with additions of glucose and different substances

3.4. Application for real samples

The practical application of proposed Ni NPs/GCE was evaluated by testing the glucose concentration in human serum samples. Glucose quantities for four different serum samples were determined and summarized in Table 2. The relative standard deviation was less than 7% to three parallel measurements of same sample. Furthermore, the low absolute values of the relative errors

indicates that the experimental results are comparable with those measured by a hospital-used method, which was Enzymatic (GOD/POD) colorimetric method on automatic biochemical analyzer. The results suggests the fact that the Ni NPs/GCE can be utilized for real human serum samples with favorable accuracy and precision, illustrating the effective performance for further potential applications .

Table 2. Determination of glucose in human blood serum

Serum sample	Measured by this method (mmol/L)	Compared (mmol/L)	RSD%(n=3)	Relative error(%)
1	8.97	9.11	2.2	-1.4
2	8.16	8.15	1.1	0.1
3	7.60	7.25	1.6	4.8
4	12.72	12.50	6.5	1.8

4. CONCLUSION

Nickel nanoparticles adhered tightly to the GCE surface through facile potentiostatic deposition showed good electrocatalytic activity toward oxidation of glucose in 0.1 M NaOH. Such established Ni NPs/GCE was convenient, inexpensive and efficient. Linear range for monitoring glucose is 5 μM to 1.155 mM, with a 1 μM detection limit and a sensitivity of 1041.2 $\mu\text{A mM}^{-1}\text{cm}^{-2}$. The relative standard deviation (R.S.D.) is less than 7% for the determination of practical serum samples. Although other biological compound such as UA, AA in human blood may interfere with determination of glucose, the Ni NPs/GCE shows high selectivity for the glucose oxidation. The proposed Ni NPs/GCE holds the great potential for glucose oxidation and detection, which indeed demonstrates it could be used as a nonenzymatic glucose sensor.

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