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A facile one-step electrochemical synthesis of graphene/NiO nanocomposites as efficient electrocatalyst for glucose and methanol

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ABSTRACT

In the present paper, we demonstrated a facile one-step and effective electrochemical strategy to synthesize graphene/NiO nanocomposites, which represents a new type of graphene/transition metal complex heterostructure. For the electrochemical deposition at the potential range of −1.2 to 0 V, graphite oxide (GO) was electrochemically reduced to graphene, accompanied by the simultaneous formation of NiO with a nanoparticle morphology. The obtained nanocomposites were characterized by scanning electron microscopy and electrochemical techniques. It was found that a large amount of NiO nanoparticles with diameter of 100–200 nm were uniformly grown on both sides of graphene nanosheets. Electrochemical experiments indicated that the composite film had a large surface area and enhanced electron-transfer rate compared with only NiO nanoparticles, due to an efficient electrical network through NiO nanoparticles direct anchoring on the surface of graphene. Moreover, as a model, glucose and methanol were selected as small molecules to investigate the electrocatalytic properties of the nanocomposites. The results showed that an enhanced electrocatalytic performance of the nanocomposites was obtained. The nanocomposites based sensor exhibited a rapid and highly sensitive response to glucose and methanol, which might find promising applications in medical applications, biological fuel cells and food industries.

1. Introduction

The development of materials science has brought significant progress to applied electrochemical fields. A pressing example to demonstrate this is graphene-based nanomaterial, which has gained even more interest due to its fascinating properties, including huge specific surface area, superior mechanical properties, large thermal conductivity, remarkable electronic conductivity, etc. One exciting research field is that where graphene is been used as a promising two-dimensional (2D) support to load polymers or nanoparticles for applications in electrochemical devices, such as supercapacitors [1,2], rechargeable lithium-ion batteries [3], catalyst [4,5] and electrochemical sensors [6–8]. The resultant nanocomposites made from graphene (or its derivatives) and functional nanomaterials are expected to present the beneficial properties of each component, producing a material with improved performance via possible synergistic interaction. Driven by these reported attractive properties, increasing numbers of researches in this field have been committed to the incorporation of graphene into composite material, including metal nanoparticles [4,9,10], metal oxides [11–13], prussian blue nanoparticles [14,15], quantum dots [16,17], carbon nanotubes [18], and conducting polymers [19,20]. Among those materials, nickel oxides (NiO) have received a great deal of attention because of its good electrochemical stability and electrocatalytic activity as well as low cost for extensive applications. The combination of graphene with Ni-based nanomaterials have been developed by various strategies for highly sensitive electrochemical sensors. Lv et al. [21] prepared graphene nanosheet–NiO–DNA nanohybrids through a first self-assembly and subsequent thermal treatment process, and followed with DNA dispersing. The nanohybrids were utilized as the active material for high-performance non-enzymatic glucose sensors. Zhang et al. [22] proposed a simple one-pot method to in situ assemble $Ni(OH)_2$ nanoplates on reduced graphene oxide nanosheets and investigated the application of the prepared 2D nanocomposite for enzyme-free glucose sensing. Yuan et al. [23] prepared graphene oxide/nickel oxide modified electrode by multi-step electrochemical methods and employed it for supercapacitor and biosensing application. Jia and Wang [24] developed a nonenzymatic ethanol sensor by directly electrodepositing nickel nanoparticles on the electrode with a nafion/graphene modifier using electrochemical method. However, in these nanocomposites preparation process, both the introduction of insulated GO

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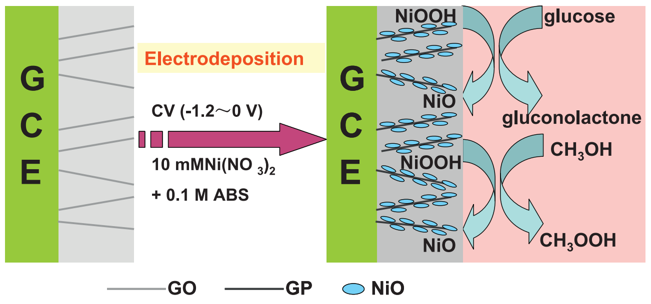

Scheme 1. Strategy for the electrochemical synthesis of GP/NiO/GCE and the electrocatalytic process of the resultant modified electrode for oxidation of glucose and methanol.

and the complicated multiple-step procedures will definitely limit their practical applications. Therefore, the development of facile and effective approaches for synthesis of graphene–NiO nanocomposites is highly desirable and remains a great challenge.

It is well-known that electrochemical method is an effective tool to modify electronic states by adjusting the external power source to change the Fermi energy level of the surfaces of conducting materials. Electrochemical synthesis of graphene at cathodic potentials from graphite oxide (GO) precursor has been reported by several research groups [25–27]. Thereafter, a possible one-step electrochemical route to prepare a wide range of graphene-based nanocomposite films has been opened up. For example, Pt nanoparticles@graphene nanocomposite [28], graphene/polyaniline composite [29], and graphene/MnO_2 nanowall hybrids [30] have been successfully synthesized through a one-step electrochemical method. The present one-step electrochemical method shows some clear advantages. First, it is very simple, green and fast; without any toxic reductive agents being used, therefore, it will not result in contamination of the resultant products. Second, the method is controllable by adjusting the exterior electrochemical parameters and the required reaction conditions are mild. Third, the resultant nanocomposites are especially for electrochemical applications due to their direct deposition onto conducting substrate.

In this work, we proposed a one-step electrochemical method for preparation of graphene/NiO nanocomposites by scanning the potential of the GO modified electrode in $Ni(NO_3)_2$ solution at cathodic potentials. During the scanning process, nickel ions were first reduced to metallic nickel and then nickel(s) could be oxidized, forming nickel oxides along the surface of GO. At the same time, GO was reduced to graphene, forming the graphene/NiO nanoparticles composites modified electrode. Chemically modified electrodes have been employed for the detection and determination of various organic molecules [31–34]. Due to the large specific area, high conductivity and good electrocatalytic properties, the graphene/NiO nanocomposite modified electrode was investigated as electrocatalyst for oxidation of glucose and methanol (as model analyte) and shows potentials for application in sensors to detect small organic molecules. The whole preparation and electrocatalytic oxidation process is displayed in Scheme 1. The method developed in this work provides a simple approach for large-scale production of graphene/NiO nanocomposite for practical applications in medical applications, biological fuel cells and food industries.

2. Experimental

2.1. Reagents and apparatus

Graphite powder (spectral requirement, Shanghai Chemicals) was used for synthesizing graphite oxide (GO) and graphene. Glucose, ascorbic acid, dopamine, uric acid and nickel(II) nitrate hexahydrate were purchased from Sigma Aldrich. Hydrogen peroxide and methanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of these reagents were of analytical grade and used as received. Unless otherwise stated, ultrapure water (18.2 MΩ cm) produced by a Milli-Q system was used as the solvent throughout this work.

Scanning electron microscopy (SEM) was conducted by JSM-6701F (Japan) for surface morphology observations. Electrochemical experiments were performed on a CHI 660D electrochemical station (Shanghai, China) with a conventional three-electrode system. The graphene/NiO nanocomposites modified glassy carbon electrode (GCE) was used as the working electrode. A Pt wire and a saturated calomel electrode (SCE) acted as the counter and reference electrodes, respectively.

2.2. Synthesis of graphene/NiO nanocomposites

The GO was synthesized from natural graphite powder based on a modified Hummers method as presented by Kovtyukhova and colleagues [35,36]. As-synthesized GO was dispersed in water, giving a yellow–brown dispersion with a concentration of 1 mg mL^{-1} by an ultrasonic technique. A 10 μL portion of the resulting GO dispersion was dropped onto a pretreated bare GCE (diameter of 3 mm) and dried at room temperature to obtain the GO-modified GCE (GO/GCE). Here, prior to the surface modification, GCE was polished with 0.3 and 0.05 μm alumina slurries, respectively, and then ultrasonically cleaned in water. The one-step electrochemical synthesis of graphene/NiO nanocomposites was conducted by scanning the potential of the GO/GCE between −1.2 and 0 V versus SCE at a scan rate of 50 mV s^{-1} for 20 cycles in 0.1 M acetate buffer solution (ABS, pH 4.0) containing 10 mM $Ni(NO_3)_2$. After deposition, the electrode was rinsed with distilled water. For comparison, a bare GCE was employed under the same conditions to obtain NiO nanoparticles modified GCE (NiO/GCE). The graphene modified GCE (GP/GCE) was prepared using the GO/GCE under the same conditions except that $Ni(NO_3)_2$ was not involved.

2.3. Electrochemistry measurements

Cyclic voltammetry (CV) and amperometric experiments were carried out at room temperature. A certain volume of stock solution of glucose or methanol and 10 mL 0.1 M NaOH were added into an electrochemical cell, and then the three-electrode system was inserted into the cell. The CV was carried out to investigate the electrochemical response of graphene/NiO/GCE toward glucose or methanol. The amperometric experiment was performed to achieve the quantitative analysis.

3. Results and discussion

3.1. Formation mechanism and characterization of graphene/NiO nanocomposites

It is well known that exfoliated GO precursor can be electrochemically reduced to graphene at cathodic potentials. Meanwhile, the cation of Ni^{2+} can also electrochemically converted to nickel oxides [37,38]. Based on these results, a one-step electrochemical method was utilized to prepare GP/NiO nanocomposites on the electrode using the resulting GO precursor. Typically, a GO/GCE was employed in pH 4.0 ABS containing $Ni(NO_3)_2$ using CV technique. The effect of the applied cathodic potential on the electrochemical reduction of GO was first investigated. Fig. 1a displays the cyclic voltammograms (CVs) of GO/GCE scanning in pH 4.0 ABS at a potential range from −1.2 to 0 V for 20 cycles. It is clear that a large cathodic current starting at potential of −0.8 V in the first

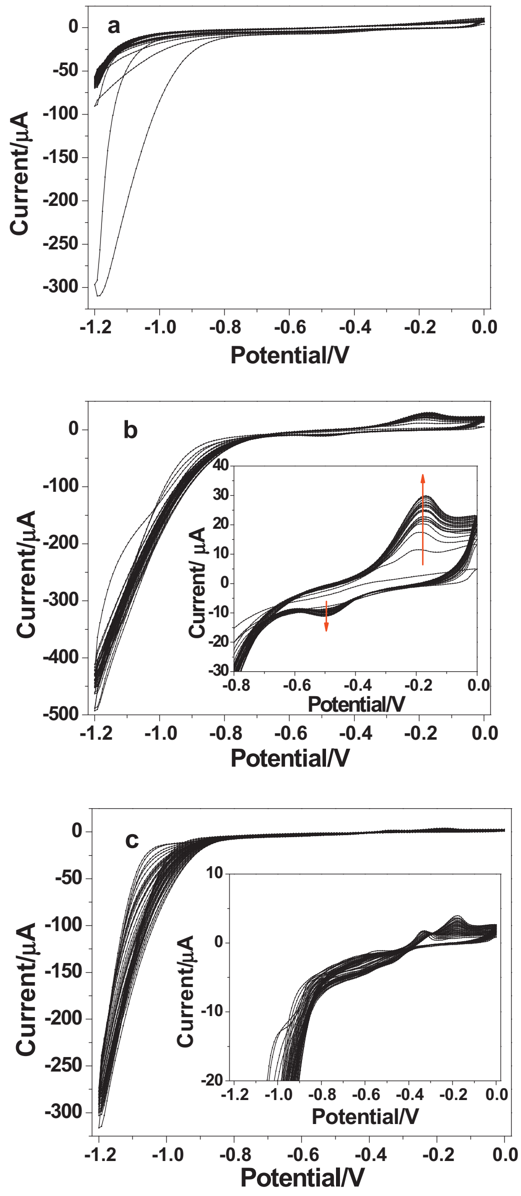

Fig. 1. (a) CVs of GO/GCE in 0.1 M pH 4.0 ABS; CVs of GO/GCE (b) and the bare GCE (c) in 0.1 M ABS (pH 4.0) containing 10 mM $Ni(NO_3)_2$. The inset of b and c is the corresponding magnified CVs.

cycle was found due to reduction of the high number of oxygen-containing functional groups in GO. With further increasing the scanning cycles, the cathodic current decreased considerably and disappeared after several potential cycles, indicating that the electrochemical reduction of GO was fast. There is no corresponding anodic wave in the CV curve, revealing that the electrochemical reduction of GO is irreversible. The control experiment was performed by conducting CV of GCE in ABS to confirm the significant contribution of GO reduction instead of oxygen at cathodic potentials. The result is shown in Fig. S1. As can be observed, the reduction current starting at a potential of −0.5 V is corresponding to reduction of oxygen. Compared with the reduction current of GO (Fig. 1a), the reduction current of oxygen is negligible. The resultant graphene modified electrode presents a typical wrinkled and flake-like shape with plenty of corrugations and scrollings (as shown in Fig. S2). By comparison, the same potential range and potential cycles were utilized for electrochemical synthesis of GP/NiO nanocomposites modified electrode. As shown in Fig. 1b, during the cathodic scan, the increment in current at −0.48 V (versus SCE) is due to reduction of Ni^{2+} ions ($Ni^{2+} + 2e \rightarrow Ni$). Besides, a large cathodic current with onset potential of −0.7 V was observed. The larger cathodic current, compared with those of GO/GCE, indicates that there are some other species simultaneously reduced. According to the previous reports [39], the reduction $Ni(OH)_2$ occurred when the potential was negative than −0.7 V. Meanwhile, the onset reduction potential (−0.7 V) is obviously more positive than those for individual GO (−0.8 V) and only $Ni(NO_3)_2$ solution (−0.85 V, as shown in Fig. 1c). Therefore, it can be concluded that the presence of GO or graphene catalyzed the reduction of $Ni(OH)_2$ to Ni(s). NiO growth takes place via intermediate steps of hydroxide formation given in the following equations:

$$Ni(NO_3)_2 + 2H_2O \rightarrow Ni(OH)_2 + 2HNO_3$$

$$Ni(OH)_2 \rightarrow NiO + H_2O$$

While during the anodic scan, the anodic peak at −0.18 V, corresponding to the dissolution of the formed nickel films ($Ni(s) - 2e \rightarrow Ni^{2+}$), increased with the increasing cycle number because more and more nickel films have been deposited onto the electrode surface.

The morphology of the synthesized GP/NiO nanocomposites modified electrode was characterized by SEM. As can be seen from Fig. 2a, NiO nanoparticles with an average diameter of 100–200 nm were largely homogeneously distributed on electrode surface. In the one-step electrochemical synthesis process, it can be seen from Fig. 2b that both sides of graphene have been decorated with NiO nanoparticles, which leads to an enhanced loading amount of electrocatalyst. Besides, it should be noted that there were some aggregation of nanoparticles especially on the wrinkled graphene layer. While for only NiO nanoparticles modified electrode prepared under the same conditions, heavily aggregated and compact nanoparticles were obtained (as shown in Fig. S3).

The electrochemical behavior of GP/NiO nanocomposites modified electrode was investigated using CV. Fig. 3a represents the CV responses on the GP/GCE, NiO/GCE, and GP/NiO/GCE in 0.1 M NaOH at a scan rate of 50 mV s^{-1}. It was found that no reaction peak current is observed at GP/GCE, indicating that graphene was electrochemically silent in the potential range of interest. However, in both NiO/GCE and GP/NiO/GCE, a pair of well-defined redox peaks corresponding to Ni^{2+}/Ni^{3+} redox couple was observed. The redox peak currents of GP/NiO/GCE are obviously stronger than those for the NiO/GCE, which is attributed to an enhanced loading amount of NiO electrocatalyst on support of graphene and the large surface area of composites. The redox peak currents of GP/NiO/GCE obtained at different scan rates in 0.1 mol L^{-1} NaOH are given in Fig. 3b. It can be seen that the peak-to-peak separation became widened with increase of scan rates. In the range of 5–300 mV s^{-1}, both the anodic and cathodic peak current grew linearly with the scan rates (correlation coefficients of 0.9959 and 0.9923 for anodic and cathodic peaks, respectively), suggesting a surface-controlled electrochemical process.

3.2. Electrochemical impedance spectroscopy studies of GP/NiO nanocomposites modified electrode

Electrochemical impedance spectroscopy (EIS) can reveal the impedance changes of the electrode surface during the modification process. Fig. 4 shows the EIS of different modified electrodes in 10 mM $Fe(CN)_6{}^{3-/4-}$ containing 0.1 M KCl as supporting electrolyte in the frequency range swept 10^5–0.1 Hz. The AC voltage amplitude was 5 mV and the applied potential was 180 mV. The interface can be modeled by an equivalent circuit (shown in the inset of Fig. 3). This equivalent circuit includes the ohmic resistance of the

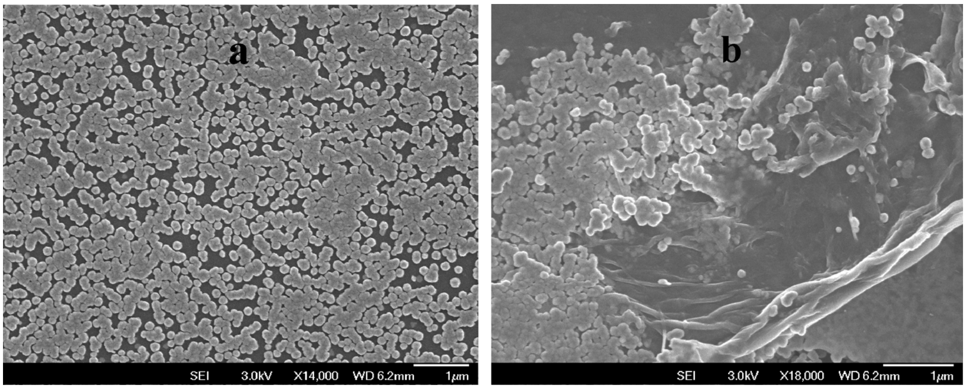

Fig. 2. The SEM images of GP/NiO nanocomposites modified electrode.

electrolyte (R_s), the electron-transfer resistance (R_{et}), the double layer capacitance (C_{dl}) and Warburg impedance (Z_W). The EIS includes a semicircular part and a linear part. The semicircular part at higher frequency corresponds to the electron-transfer limited process, and the diameter is equivalent to the R_{et}. The linear part at lower frequency corresponds to the diffusion process. Here, the R_{et} was concerned because the electron transfer properties of the modified materials is the most wanted to be known. On the bare GCE, the R_{et} value was got as 139.9 Ω. While on the GP/GCE, the R_{et} value was decreased to 124.7 Ω, which was due to the presence of highly conductive graphene nanosheets that could accelerate the electron transfer rate of $\mathrm{Fe(CN)_6}^{3-/4-}$. After NiO nanoparticles were deposited on the GCE surface, the low conductivity of NiO resulted in a high R_{et} value of 983.7 Ω. However, compared with NiO/GCE, GP/NiO composites modified electrode showed a lower R_{et} of 310.4 Ω, indicating that an efficient electrical network through NiO nanoparticles direct anchoring on the surface of graphene facilitates the electron-transfer.

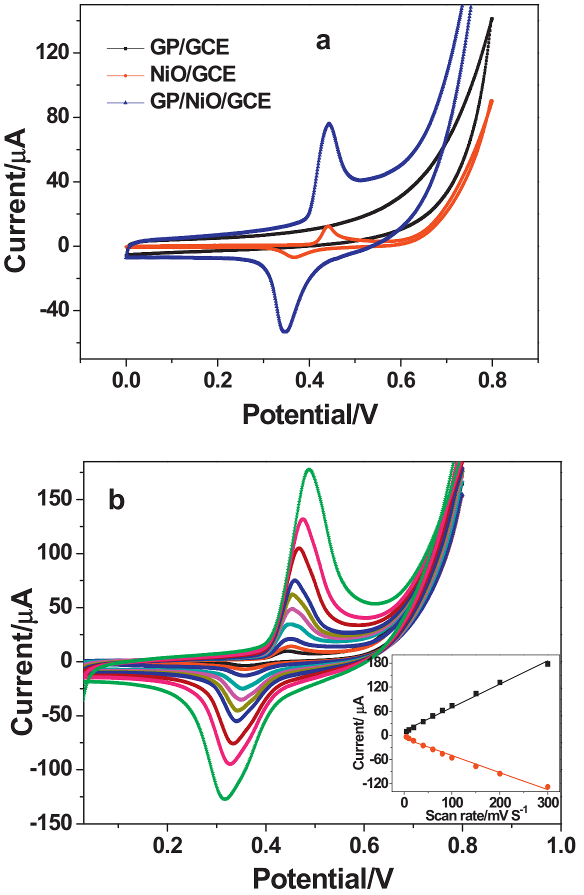

Fig. 3. (a) CVs obtained in 0.1 M NaOH solution at GP/GCE, NiO/GCE, and GP/NiO/GCE with a scan rate of 50 mV s^{-1}; (b) CVs of the GP/NiO/GCE in 0.1 M NaOH solution at scan rates (from inner to outer) of 5, 10, 20, 40, 60, 80, 100, 150, 200, 300 mV s^{-1}, the inset shows the plots of peak current versus scan rate.

3.3. Electrocatalytic oxidation of glucose at the GP/NiO nanocomposites modified electrode

Ni-based nanomaterials have been widely used to construct nonenzymatic glucose sensors owing to their electrocatalytic properties originating from the redox couple of NiO/NiOOH on the electrode surface in alkaline medium [40–43]. A comparative study on the electrocatalytic performance toward glucose oxidation at different electrodes was first carried out by CV. Fig. 5 presents the CV responses on different modified electrodes in 0.1 M NaOH with and without 2 mM glucose. As shown in Fig. 5a, the bare GCE shows no response to addition of glucose. In the case of GP/GCE (Fig. 5b), the response to glucose is very limited and the oxidation of glucose requires a very high positive potential, which will lead to a very slow electrode kinetic. In contrast, a pair of well-defined redox peaks obtained at NiO/GCE can be assigned to the $\mathrm{NiO + OH^- - e \rightarrow NiOOH}$ reaction and the added glucose was oxidized by NiOOH to gluconolactone (NiOOH + glucose → NiO + gluconolactone). As a result, obvious anodic peak current increase at starting potential of 0.32 V and completely disappearance of cathodic peak current can be observed at

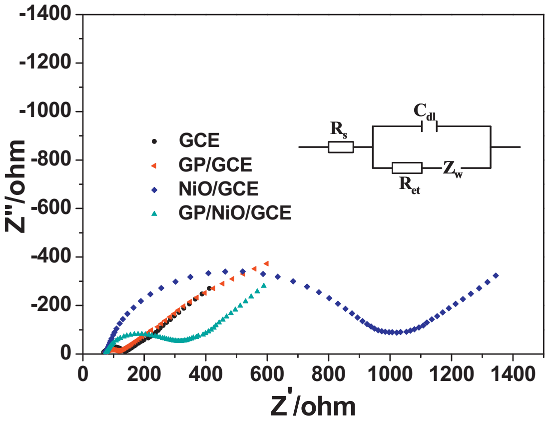

Fig. 4. Nyquist plots of EIS in the solution containing 10 mM $[\mathrm{Fe(CN)_6}]^{3-/4-}$ solution as probe and 0.1 M KCl as supporting electrolyte.

NiO/GCE due to direct electrooxidation of glucose catalyzed by NiO nanoparticles (Fig. 5c). While for GP/NiO nanocomposites modified electrode (Fig. 5d), upon the addition of glucose, much higher anodic current increase and lower starting potential of 0.25 V for glucose oxidation can be obtained. Such enhanced electrocatalytic performance of the nanocomposites may be ascribed to a synergistic effect between graphene and the loaded NiO nanoparticles, which includes high catalytic active sites for the glucose oxidation provided by the well-distributed and high loading amount of NiO nanoparticles and fast electron transfer channel offered by an efficient electrical network through one-step electrochemical method.

The influence of applied potentials was systemically investigated on the amperometric response of the GP/NiO nanocomposites modified electrode to glucose. Fig. 6a exhibits amperometric response of GP/NiO/GCE to successive additions of 50 μM glucose at different applied potentials. Obviously, the steady-state current response of 50 μM glucose increased rapidly from +0.3 to +0.4 V, and then gradually increased from +0.4 to +0.5 V. When the applied potential was +0.6 V, the current increase of glucose was lowered and the blank current was significantly enhanced. The detection sensitivity of glucose at +0.3, +0.4, +0.5, and +0.6 V, was calculated to be 3.52, 94.18, 126.8 and 51.42 μA mM^{-1}. Considering that the high detection sensitivity as well as the fact that serious interference at high applied potentials, +0.4 V was chosen as the optimum applied potential for glucose detection.

Fig. 6b presents the amperometric response at the GP/NiO nanocomposites modified electrode for successive additions of different concentrations of glucose in 0.1 M NaOH solution at an applied potential of +0.4 V, from which rapid response to the addition of glucose (within 3 s) can be obtained. The response to glucose shows a good linear range from 5 μM to 2.8 mM with a correlation coefficient of 0.9977 and a slope of 111 μA mM^{-1} (as shown in Fig. 6c). Based on the previous work described by Shi et al. [44,45], the electrode surface area of the NiO/GP nanocomposite modified electrode can be calculated to be about 0.07 cm^2. The sensitivity of the sensor is calculated to be 1571 μA mM^{-1} cm^{-2}, which is higher than the reported values at RGO-Ni(OH)$_2$ modified electrode (11.43 μA mM^{-1} cm^{-2}) [22], NiO nanoparticles/GO modified electrode (1087 μA mM^{-1} cm^{-2}) [37], Ni nanoparticlss/SWNT modified electrode (1438 μA mM^{-1} cm^{-2}) [40], CuO/TiO$_2$ modified electrode (1321 μA mM^{-1} cm^{-2}) [46] and CoOOH nanosheets modified electrode (341 μA mM^{-1} cm^{-2}) [47], but lowers that the Cu$_2$O/SMWNTs modified electrode with a sensitivity of 2143 μA mM^{-1} cm^{-2} [48]. The detection limit at a signal to noise ratio of 3 is estimated to be 1 μM. The performance of the as-prepared GP/NiO catalyst is compared with some of existing nonenzymatic glucose sensor. As shown in Table 1, it can be concluded that the as-prepared GP/NiO catalyst is among the top list of sensors with a faster response speed, a higher sensitivity, and a lower detection limit.

Some interference often co-existing with glucose in a biological sample, such as dopamine (DA), ascorbic acid (AA), uric acid (UA) and H$_2$O$_2$, could be easily oxidized and interfere with glucose detection. In the physiological sample, glucose concentration (4–7 mM) is generally much higher than those of interfering species. Therefore, the influence of 0.1 mM interference species on the current response of 1 mM glucose was evaluated. From the current response in Fig. 6d, a remarkable glucose signal was obtained comparing to the other four interfering species. Compared to glucose, all the interfering species yielded current response less than 6%. These results indicated that the present GP/NiO nanocomposite based sensor could be used for the sensitive and selective detection of glucose.

The GP/NiO nanocomposites modified electrode was applied for the analysis of glucose spiked in the urine sample. The urine samples spiked with 10 and 20 mM standard solution of glucose were

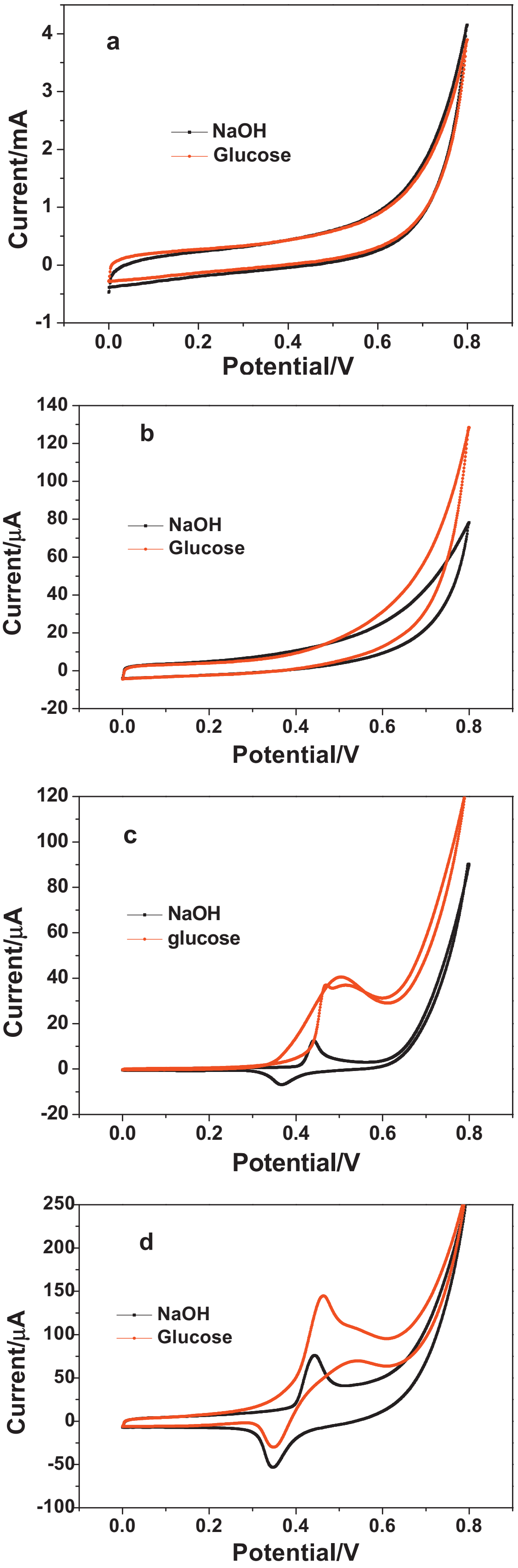

Fig. 5. CVs of (a) GCE, (b) GP/GCE, (c) NiO/GCE, and (d) GP/NiO/GCE in 0.1 mol L^{-1} NaOH in the absence (black curve) and the presence (red curve) of 2 mM glucose at a scan rate of 50 mV s^{-1}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

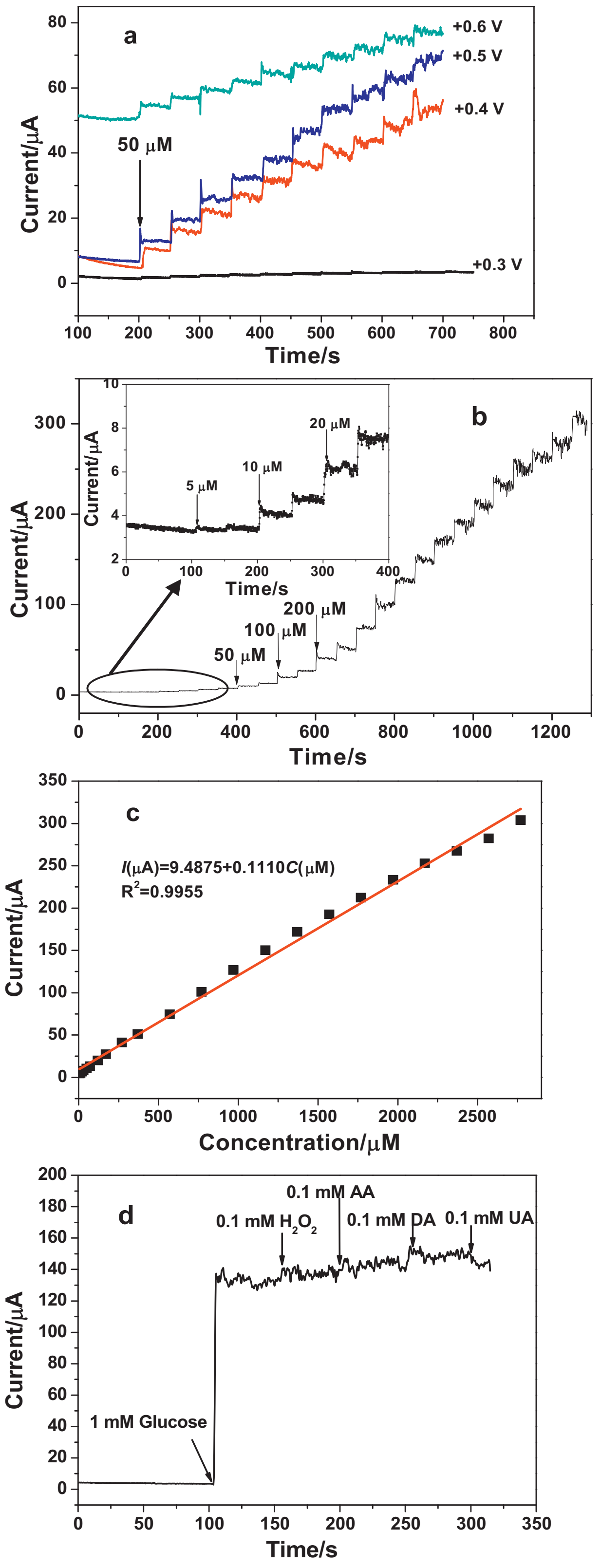

Fig. 6. Detection of glucose in 0.1 M NaOH solution using the GP/NiO/GCE: (a) Amperometric responses of GP/NiO/GCE to successive additions of 50 μM glucose at the applied potentials of +0.3, +0.4, +0.5 and +0.6 V, respectively; (b) Amperometric responses of the GP/NiO/GCE (holding at +0.40 V) upon addition of glucose to increasing concentrations; (c) the corresponding calibration curves; (d) Amperometric responses of the GP/NiO/GCE to successive additions of 1 mM glucose, 0.1 mM H_2O_2, 0.1 mM AA, 0.1 mM DA, and 0.1 mM UA in 0.1 M NaOH at +0.4 V.

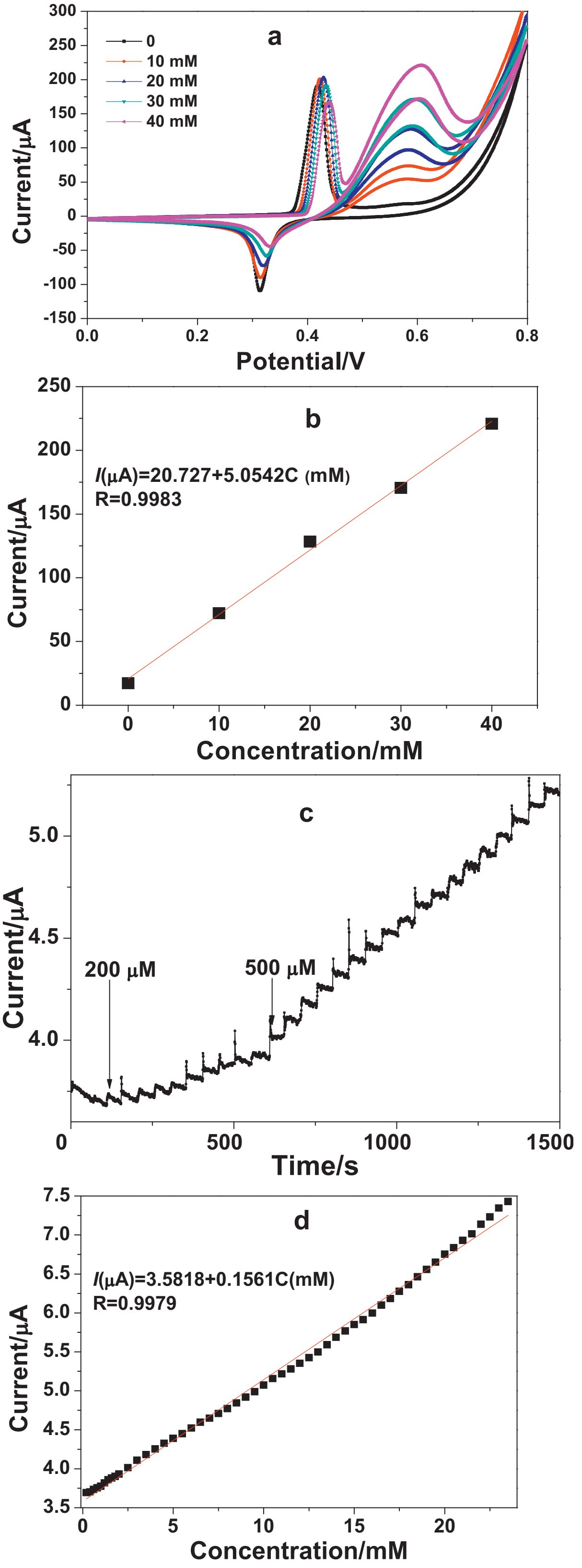

Fig. 7. (a) CVs of the GP/NiO/GCE with different methanol concentrations (0, 10, 20, 30, 40 mM) in 0.1 M NaOH at a scan rate of 100 mV s^{-1}; (b) relationship between the methanol oxidation peak current values of CVs and methanol concentration; (c) current–time responses of the GP/NiO/GCE upon addition of methanol to increasing concentrations; and (d) the plots of amperometric current versus methanol concentrations.

Table 1
Comparison of the present GP/NiO nanocomposites modified electrode with other nonenzymatic glucose sensors.

Electrode materials	Response time (s)	Potential (V)	Sensitivity (μA mM^{-1} cm^{-2})	Linear range	LOD (μM)	Reference
RGO-Ni(OH)$_2$	7	+0.54	11.43	2 μM–3.1 mM	0.6	[22]
NiONPs/GO	–	+0.6	1087	3.13 μM–3.05 mM	1	[37]
NiNP/SWNT	3	+0.4	1438	1 μM–1 mM	0.5	[40]
CuO/TiO$_2$	5	+0.7	1321	10 μM–2 mM	0.39	[46]
CoOOH nanosheets	4	+0.4	341	30 μM–0.7 mM	30.9	[47]
Cu$_2$O/SMWNTs	3	+0.4	2143	0.5 μM–2.5 mM	0.2	[48]
Ni–Cu/TiO$_2$NTs	5	+0.6	1590.9	10 μM–3.2 mM	5	[49]
NiO–graphene	<3	+0.35	–	20 μM–4.5 mM	5	[50]
CS-RGO-NiNPs	–	+0.6	318.4	0.2 mM–9 mM	4.4	[51]
GP/NiO	3	+0.4	1571	5 μM–2.8 mM	1	This work

Table 2
Amperometric determination of glucose spiked in urine samples ($n = 4$).

Urine samples	Spiked (μM)	Found (μM)	RSD (%)	Recovery (%)
Sample 1	10.0	10.3	2.64	103
Sample 2	20.0	19.5	2.08	97.5

signed as sample 1 and 2, respectively. The amperometric detection was carried out at the applied potential of 0.4 V in 10 mL 0.1 mol L^{-1} NaOH solution under stirring condition with the injection of 10 μL urine samples. The quantitative determination of urine samples was performed using the standard addition method and the results are shown in Table 2. The analytical recoveries indicate that the developed sensor could be used for the determination of glucose in urine samples.

3.4. *Electrocatalytic oxidation of methanol at the GP/NiO nanocomposites modified electrode*

A large number of transition metal and transition metal oxide electrodes have shown a good degree of electroactivity toward carbohydrates. Thus, the as-prepared GP/NiO nanocomposites modified electrode constructed by one-step electrochemical method is expected to be a promising catalyst material for methanol oxidation. Compared with the single component of GP/GCE and NiO/GCE, the GP/NiO/GCE exhibited the most significant methanol oxidation responses (as shown in Fig. S4). Fig. 7a presents the CVs recorded at 50 mV s^{-1} in the absence and presence of different concentrations of methanol (0.1–0.4 mM) in 0.1 M NaOH. Upon addition of methanol, a new anodic peak corresponding to oxidation of methanol emerged at 0.58 V. This anodic peak current was found to increase linearly with the methanol concentration (Fig. 7b). For the application of amperometric determination at applied potentials of +0.6 V, a stable and rapid change in current can be observed (Fig. 7c) with the successive additions of 200 and 500 μM methanol. The GP/NiO nanocomposites modified electrode exhibits sensitive and rapid current response to methanol addition, achieving steady-state current in <5 s. The amperometric currents versus total methanol concentrations and the corresponding calibration curve of current versus concentration are presented in Fig. 7d. The regression equation is $I\ (\mu A) = 3.5818 + 0.1561C$ (mM), with correlation coefficient of 0.9979. The present methanol sensor displays a linear range from 0.2 to 24 mM, with a sensitivity of 2.21 μA mM^{-1} cm^{-2} and a detection limit of 50 μM (signal/noise = 3). The facile analysis procedures based on GP/NiO nanocomposites electrochemical methanol sensor overcomes the limitations of the inevitable drawbacks for enzyme-based sensor, such as the chemical and thermal instabilities originated from the intrinsic nature of enzymes as well as the tedious fabrication procedures [52]. Therefore, it is potential for monitoring methanol levels in the environment, in alcoholic beverages and for clinical diagnostic measurements.

3.5. *Reproducibility and stability*

The inter-electrode reproducibility investigation was conducted by comparing the response currents of six GP/NiO composites modified electrodes prepared under the same conditions. The relative standard deviation (RSD) of response for amperometric determination of 50 μM glucose at 0.4 V and 200 μM methanol at 0.6 V was 4.6% and 5.8%, respectively. In addition, eight measurements of 50 μM glucose using the same electrode yielded a RSD of 3.5%, while for 200 μM methanol, the RSD was 3.9%. These results indicated excellent intra-electrode and inter-electrode reproducibility. Furthermore, the long-term stability of developed electrode was studied by analyzing its amperometric response after one-month storage. The results showed only 1.8% and 2.3% decrease in the current response to 50 μM glucose and 200 μM methanol, respectively.

4. Conclusions

We have demonstrated a facile and effective method to synthesize GP/NiO nanocomposites via a one-step electrochemical approach. Electrochemical reduction of GO and deposition of NiO nanoparticles were realized simultaneously at potential range of −1.2 to 0 V. Based on the high loading amount of NiO nanoparticles on both sides of graphene and its resulting efficient electrical network, the as-prepared GP/NiO nanocomposites modified electrode exhibited a high electrocatalytic activity toward oxidation of glucose and methanol in alkaline conditions. The GP/NiO nanocomposites based sensor showed potentials for detecting glucose and methanol, exhibited quick response in the wide linear range with a high detection sensitivity. The present developed method opens up a general route to prepare a wide range of graphene-based nanocomposite materials with extensive application prospects.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2013.09.047.

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