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Non-enzymatic electrochemical glucose sensor based on platinum nanoflowers supported on graphene oxide

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ABSTRACT

A non-enzymatic electrochemical method was developed for glucose detection using a glassy carbon electrode modified with platinum nanoflowers supported on graphene oxide (PtNFs-GO). PtNFs-GO was synthesized using a nontoxic, rapid, one-pot and template-free method. Low-cost, green solvent ethanol acted as the reductant, and the advanced and effective 2D carbon material-GO nanosheet acted as the stabilizing material. Their morphologies were characterized using transmission electron microscopy. Cyclic voltammetry and amperometric methods were used to evaluate the electrocatalytic activity towards glucose in neutral media. The modified electrode exhibited strong and sensitive amperometric responses to glucose even in the presence of a high concentration of chloride ions. The response time was within 5 s. The interference effects from ascorbic acid and uric acid were comparatively small when operated at suitable potential. Under optimal detection potential (0.47 V with a saturated calomel reference electrode) the PtNFs-GO modified electrode performed a current response towards glucose at a broad concentration range from 2 μM to 20.3 mM. Two linear regions could be observed at 2 μM to 10.3 mM with a sensitivity of 1.26 μA mM^{-1} cm^{-2} (correlation coefficient 0.9968), and at 10.3 mM to 20.3 mM with a sensitivity of 0.64 μA mM^{-1} cm^{-2}(correlation coefficient 0.9969). The LOD of 2 μM was lower than many non-enzymatic electrochemical glucose sensors. The modified electrode was also applied to the determination of glucose in glucose injection solutions, and the satisfactory results obtained indicated that it was promising for the development of a novel non-enzymatic electrochemical glucose sensor.

1. Introduction

Diabetes mellitus is a chronic but treatable disease affecting about 200 million people around the world [1]. The diagnosis and control of diabetes mellitus requires a tight monitoring of blood glucose levels. As a result, the rising demand for glucose sensors with high sensitivity and selectivity, good stability, fast response, and low cost has driven tremendous research efforts for decades. Electrochemical biosensors for glucose play a leading role in this direction [2]. Most studies on this subject are based on glucose oxidase bound to electrode transducers, in which hydrogen peroxide is catalytically produced from the oxidation of glucose in the presence of oxygen, and which can be amperometrically detected. Although enzymatic detection usually shows good selectivity and high sensitivity [3–5], the most serious problem of the enzymatic sensors is lack of stability due to the intrinsic nature of the enzyme. Their activity is easily affected by temperature, pH, toxic chemicals and even humidity [6], and this is difficult to overcome. To address this problem, many studies have attempted to detect glucose based on enzyme-free electrochemical oxidation, especially using non-enzymatic amperometric glucose sensors.

Recently, metal nanoparticles (MNPs) have attracted much attention for the development of catalytic systems. The direct electro-catalytic oxidation of glucose on metal and alloy nanomaterials such as Ag [7], Au [8], Ni [9], Pd [10], Pt [11–13], Pt-Pd [14], Pt_2Pd [15] and metal oxides such as CuO_x [16] and MnO_2 [17] have been studied. Among the non-enzymatic glucose sensors, Pt has been the most popular material due to its high catalytic activity toward glucose oxidation [18]. Compared with smooth Pt, nanostructured Pt offers three advantages. First, the electro-oxidation of glucose is a kinetic-controlled electrochemical event and sensitive to the nanoscopic surface area of the electrode, rather than to its geometric area [11–14]. Nanostructured Pt with its large specific surface area favors kinetic control and a higher sensitivity can be obtained in the sensing of glucose. Second, electroactive species such as ascorbic acid (AA) and uric acid (UA) are oxidized in the potential range of glucose oxidation, resulting in a poor selectivity. Because the electro-oxidation of AA and UA is diffusion-controlled and does not significantly depend on the electrode specific surface [12], this means that nanostructured Pt with a higher sensitivity for

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glucose can also obtain a better selectivity. Third, Pt based electrodes are easily poisoned by adsorbed intermediates and chloride ions, resulting in a low sensitivity. Fortunately, nanostructured Pt such as mesoporous Pt [11], Pt nanotube arrays [12], Pt based nanocomposites such as PtNPs supported on a carbon nanotube [19], Pt nanoflowers (PtNFs) supported on a carbon nanotube [20] are able to retain sufficient sensitivity even in the presence of chloride ions. Therefore, much effort has been put into the design of novel Pt and Pt based nanomaterials to acquire higher electrocatalytic activity and stability.

Graphene, consisting of a single atomic layer of conjugated sp^2 carbon atoms, has attracted considerable attention from both experimental and theoretical scientific communities in recent years [21,22]. Graphene oxide (GO), one of the most important derivatives of graphene, has also received a great deal of attention because of its importance in nanoscience [23] and it is conveniently prepared on a large-scale [24]. GO is a pseudo-two-dimensional carbon material with several oxygen functional groups such as hydroxyl, carboxyl and epoxy groups on its basal planes and edges, which makes possible the sorption and intercalation of ions and molecules. This feature, together with high specific surface area and easy dispersion, makes GO a promising material for the immobilization of a large amount of substances including a wide range of metals, NPs, bimolecular and further fabricated novel electrochemical sensors [25,26].

The hybridization of graphene (or its derivatives) with functional nanomaterials can result in physical properties being derived synergistically from both components, such as enhancement in electrical conductivity and mechanical strength, provide a new way to develop catalytic, magnetic, and optoelectronic materials [27]. Many efforts have been made to develop MNPs/GO nanocomposites [28–30]. Recently, we have found that PtNFs supported on GO could be synthesized using an in situ reduction process and revealed an unusually high activity for the methanol oxidation reaction [31]. In this process, low-cost, green solvent ethanol acts as the reductant and GO nanosheet act as the stabilizing material. In order to take advantage of the structural properties of GO as well as the excellent electro-catalytic activity of nanoplatinum, in this study, we proposed a novel non-enzymatic electrochemical glucose sensor based on PtNFs supported on GO (PtNFs-GO). PtNFs-GO modified glassy carbon electrodes (GCEs) were applied in the non-enzymatic detection of glucose. As proposed, cyclic voltammetric results showed that the PtNFs-GO exhibited excellent electrocatalytic activity towards glucose and retained sufficient sensitivity even in the presence of 0.1 M chloride ions. Amperometric curves indicated that the modified electrode was highly sensitive with stable sensing characteristics for glucose and a response time within 5 s. The PtNFs-GO modified electrode performed a current response towards glucose at a broad concentration range from 2 μM to 20.3 mM. The LOD of 2 μM was lower than many non-enzymatic electrochemical glucose sensors. In addition, interference from the oxidation of common interfering species, such as AA and UA was investigated and satisfactory selectivity was obtained.

2. Experimental section

2.1. Materials

Graphite powders were purchased from Lvyin Co. (Xiamen, China); potassium permanganate, concentrated sulfuric acid and sodium nitrate were obtained from the Chemical Reagent Company of Shanghai (China); K_2PtCl_4 was purchased from Wake Pure Chemicals, Co. Ltd. (Osaka, Japan); 5% Nafion ethanol solution and UA were from the Aldrich Chem. Co. (USA); and glucose and AA were from the Chemical Reagent Company of Guangzhou (China). The 0.05 M phosphate buffer saline (PBS, pH 7.4) was employed as a supporting electrolyte. Rod GCEs were from BAS Co. Ltd. (Tokyo, Japan). All other reagents were of analytical grade and used without further purification. The pure water for solution preparation was from a Millipore Autopure WR600A system (Millipore, Ltd., USA).

2.2. Instruments

The morphology of the PtNFs-GO was examined using a high resolution transmission electron microscope (HRTEM, FEI Tecnai-F30 FEG). Electrochemical measurements were performed using a CHI 660B Electrochemical Analyzer (CHI Co. Shanghai, China) equipped with a conventional three-electrode system, a GCE coated with PtNFs-GO-Nafion film, a Pt auxiliary electrode and a saturated calomel reference electrode, was used.

2.3. Preparation of GO and PtNFs-GO

GO was prepared from natural graphite using the modified Hummers' method [32,33]. 50 mg as-synthesized GO was dispersed in 100 mL water to obtain a yellow–brown aqueous solution with the aid of ultrasonication. The resulting GO solution was heated in an oil bath at 100 °C for 24 h to obtain thermal reduction [34].

Synthesis of PtNFs modified GO was achieved using an in situ reduction based on our previous studies [31]. In a typical experiment, homogeneous GO suspension (0.5 mL 0.5 mg mL^{-1}) and K_2PtCl_4 (0.65 mL to 10 mM) aqueous solution were first mixed in a vial and then 1.15 mL ethanol was added under vigorous stirring. The mixture was stirred for 60 min at 30 °C, and then the reaction mixture was washed with pure water and centrifuged to remove the remaining reagents.

2.4. Preparation of the PtNFs and the PtNFs-GO/Nafion-modified GCE

Before modification, a GCE was polished with 1, 0.3, and 0.05 μm α-Al_2O_3, sequentially. After ultrasonic concussion, the polished GCE was dried at room temperature and then 2 μL PtNFs-GO suspensions were dropped onto the GCE surface. For stable coating by the catalysts, 2 μL 0.5% Nafion ethanol solution was placed on the GC electrode surface and it was subsequently dried for 4 h in the air at room temperature.

3. Results and discussion

3.1. Characterization of PtNFs-GO

The TEM and HRTEM images depicted in Fig. 1 are direct morphological observations of the as-prepared PtNFs-GO. Fig. 1a shows that PtNFs uniformly distributed on the GO surface with a flower-like shape and a high density. The average overall dimension of these PtNFs was found to be about 30 nm. Furthermore, the GO sheets have a large surface area, and PtNFs can be deposited on both sides of the sheets which are both accessible during their application. Fig. 1b shows that each of the as-synthesized PtNFs was composed of many small spherical PtNPs which were around 4 nm. The high-resolution TEM (HRTEM) image (Fig. 1c) indicates that each PtNP in the PtNFs presented a crystalline structure. The interplanar spacing was 0.224 nm, which agreed well with the (1 1 1) lattice spacing of face-centered-cubic Pt (0.225 nm). For comparison, PtNFs were also synthesized in the absence of GO and only severely aggregated PtNFs could be seen (see Supplementary material Fig. S1).

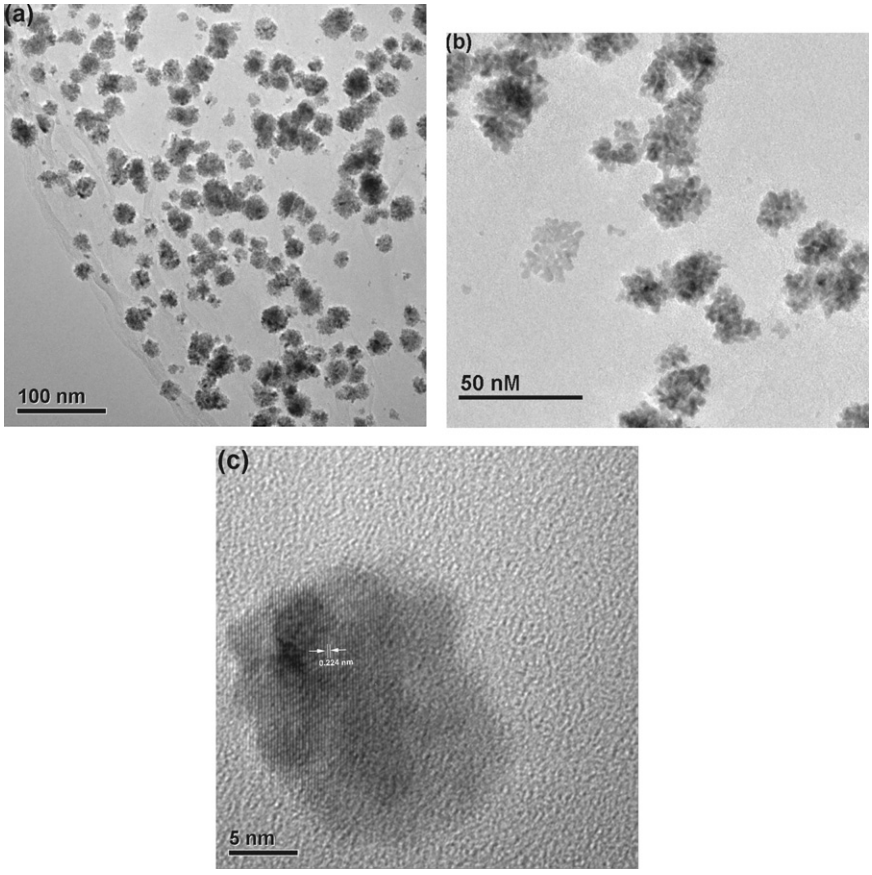

Fig. 1. (a) and (b) TEM and (c) HRTEM images of the synthesized PtNFs-GO.

In an acidic medium, hydrogen adsorption and desorption on a Pt surface is an effective technique for determining the active surface area of a Pt-based electrode [35]. Thus, cyclic voltammetry (CV) was used to characterize the PtNFs-GO modified GCE in a solution of 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1} (see supplementary material Fig. S2). It is clear that three pairs of reversible peaks could be observed at −0.15 V, −0.08 V and 0 V, corresponding to hydrogen adsorption/desorption on the electrode surfaces. The peaks at −0.15 V and −0.08 V could attributed to the (1 1 0) and (1 0 0) Pt facets [36]. The anodic oxidation of the PtNFs-GO modified GCE starting at 0.727 V was a result of the formation of platinum oxide that was subsequently stripped at 0.590 V in the reverse scan. All the peaks exhibited the characteristic features expected for polycrystalline Pt [37] and agreed with the results of TEM observation. By integrating the charge associated with hydrogen adsorption and when an integrated charge of 0.21 mC cm^{-2} was introduced, the real surface of the modified electrode was calculated to be 0.699 cm^2.

3.2. Electrocatalytic oxidation of glucose in neutral media

In order to investigate the electrocatalytic oxidation activity of the PtNFs-GO modified GCE in neutral media, CV results were recorded in 0.05 M PBS (pH 7.4). For comparison, an aggregated PtNFs (with ECSA of 0.368 cm^2) modified GCE was also tested. Fig. 2 presents the CV results of the PtNFs-GO and PtNFs modified GCE in the PBS in the presence and absence of 20 mM glucose at a potential scan rate of 20 mV s^{-1}. As shown in Fig. 2a, in the blank PBS, both electrodes were characterized by hydrogen adsorption/desorption peaks in the hydrogen region (−0.6 to −0.3 V), a flat double layer region (−0.3–0.2 V), a platinum oxide formation region (0.2–0.8 V) and corresponding reduction peaks at 0.03 V in the reverse scan. These results were in good agreement with those investigated in acid media in Fig. S2. The CV results recorded in the PBS with 20 mM glucose are presented in Fig. 2b. The characteristics changed significantly and showed a very complicated electrochemical behavior. During the positive scan, three peaks appeared using the PtNFs-GO modified GCE. The first peak at −0.40 V was due to the electrochemical adsorption of glucose and the dehydrogenation of the anomeric carbon [38]. The second peak appearing at 0.09 V could have resulted from the electrosorption glucose to form gluconic acid by releasing one proton [35]. At potentials move positive, an accumulation of intermediates on the electrode surface inhibited further electrosorption of glucose, resulting in a current decrease [12,39]. Then, at a potential of 0.28 V, Pt-OH surface species appeared which could catalyze the oxidation of the poisoning intermediates. Thus, further oxidation of glucose and its intermediates might have occurred forming products such as glucono lactone or gluconic acid and resulting in the third peak appearance at 0.60 V. The decrease in current at more positive potential was caused by the formation of thick Pt oxide, which competed for the surface adsorption sites with glucose, and inhibited the direct electrocatalytic oxidation of glucose. During the negative toward scan, with the reduction of platinum oxide at a potential around 0.05 V, more and more surface sites would be re-activated and available for the direct oxidation of glucose, resulting in a sharp increase in anodic current with the peak at −0.11 V. With the applied potential moving to more negative values, the electrosorption of glucose at the PtNFs appeared again, resulting in an accumulation of intermediates on the electrode surface. This effect led to the decrease in the anodic current. As for PtNFs modified GCE, the electrochemical characteristics of the oxidation of glucose were similar to those for PtNFs-GO. However, both the anodic peak and

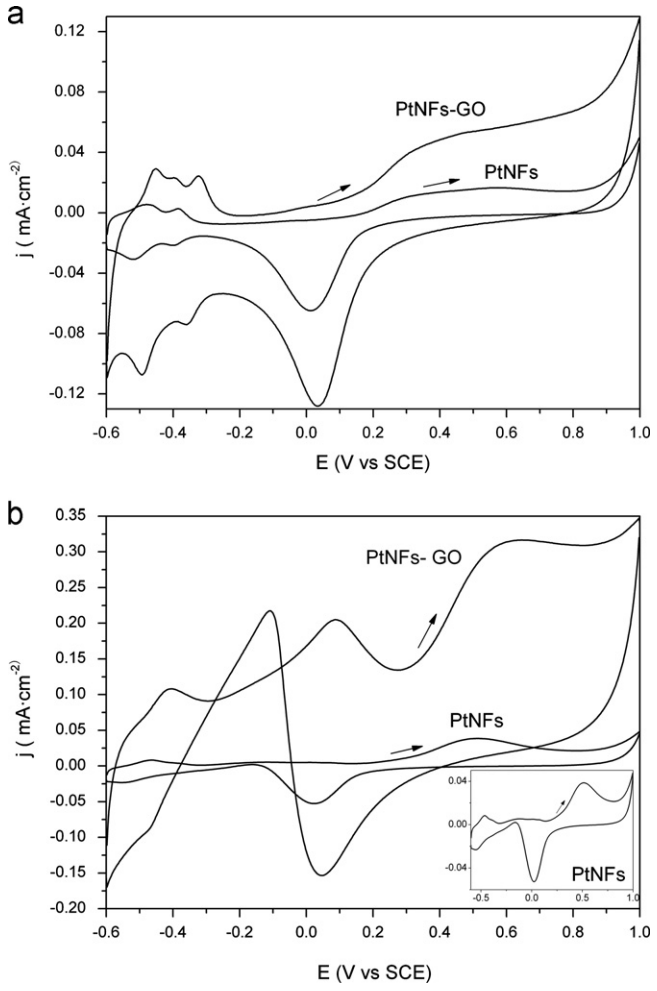

Fig. 2. CV curves of PtNFs and PtNFs-GO modified GCE in 0.05 M PBS (pH 7.4) with (b) and without (a) 20 mM glucose at a scan rate of 20 mV s^{-1}. Insets are the magnified CVs of the corresponding PtNFs/Nafion modified GCE.

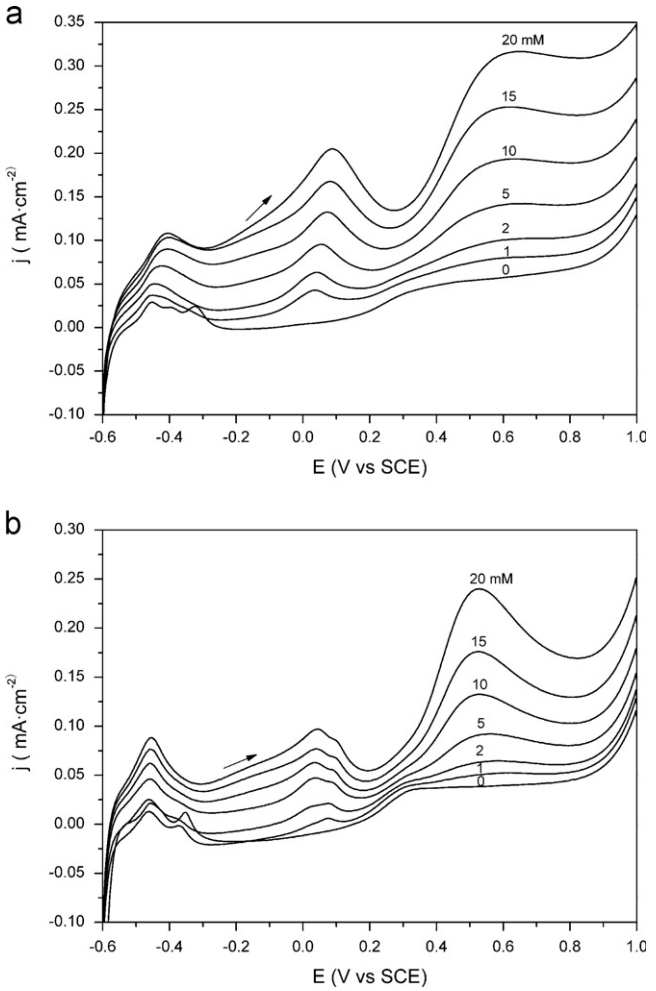

Fig. 3. Positive-going portions of CV curves of PtNFs-GO modified GCE in 0.05 M PBS (pH 7.4)+x mM glucose (where x was 0, 1, 2, 5, 10, 15, 20) with (b) and without (a) 0.1 M NaCl.

the catholic peak current density were much lower than those obtained using the PtNFs-GO modified GCE (ca. 1/8). The present results clearly showed that the electrocatalytic oxidation of glucose at the surface of the PtNFs-GO catalyst was effective and that the electrocatalytic activity of PtNFs-GO was much higher than that of aggregated PtNFs. Two factors could be ascribed to the discrepancy in electrocatalytic activity: on the one hand, the high density, well-distributed and porous PtNFs on the surface of the GO would induce more active sites for the catalytic redox reaction; while on the other hand, the presence of the oxygen-containing groups such as hydroxyl and carboxyl etc. on the surface of SWNTs can improve the electrocatalytic activity of the Pt-SWNT catalyst [40,41]. Thus, it was believed that the large surface area and edge-plane like defective sites on GO could also enhance the catalytic activity due to the synergistic effect of the GO and PtNFs [42,43].

It was obvious that the PtNFs-GO modified GCE showed excellent electrocatalytic activity toward glucose oxidation in a neutral PBS. Therefore, assessment of its performance towards the tolerance of chloride ions was necessary to ensure possible applications in physiological environments. Fig. 3 presents the CV results of the PtNFs-GO modified GCE in 0.05 M PBS (pH 7.4) and various concentrations of glucose (from 0 mM to 20 mM) with (b) and without (a) 0.1 M NaCl. For convenience, only the positive-going portions are presented. The position of the redox peaks for the oxidation of glucose remained unchanged under the presence of chloride ions. However, two obvious differences could be distinguished. First, the anodic current peaks at the potential around 0 V were significantly decreased. Chloride ions preferentially block active sites on the electrode surface, which means less chance of reactive species approaching the surface, and results in the suppression of glucose adsorption and decreasing the oxidation rate; second, the height of the anodic current at a potential around 0.60 V was decreased slightly and the curve shape looked more symmetrical in the presence of chloride ions, indicating that chloride ions had little effect in the direct electrocatalytic oxidation of glucose. These results demonstrated that the PtNFs-GO catalyst can be used for glucose sensing even in the presence of a high concentration of chloride ions.

3.3. Amperometric responses to glucose and interfering electroactive species

It is clear from Fig. 3, that two current peaks are apparently associated with the glucose concentration in the presence of 0.1 M chloride ion. Thus, the detection potential which affected the amperometric detection of glucose needed to be investigated. Fig. 4a shows a comparison of the amperometric responses of the PtNFs-GO modified GCE at the potentials around 0.60 V with successive 1 mM additions of glucose to the stirred solution. When 1 mM glucose was successively added into the stirred test solution, the current varied steeply to reach a stable value.

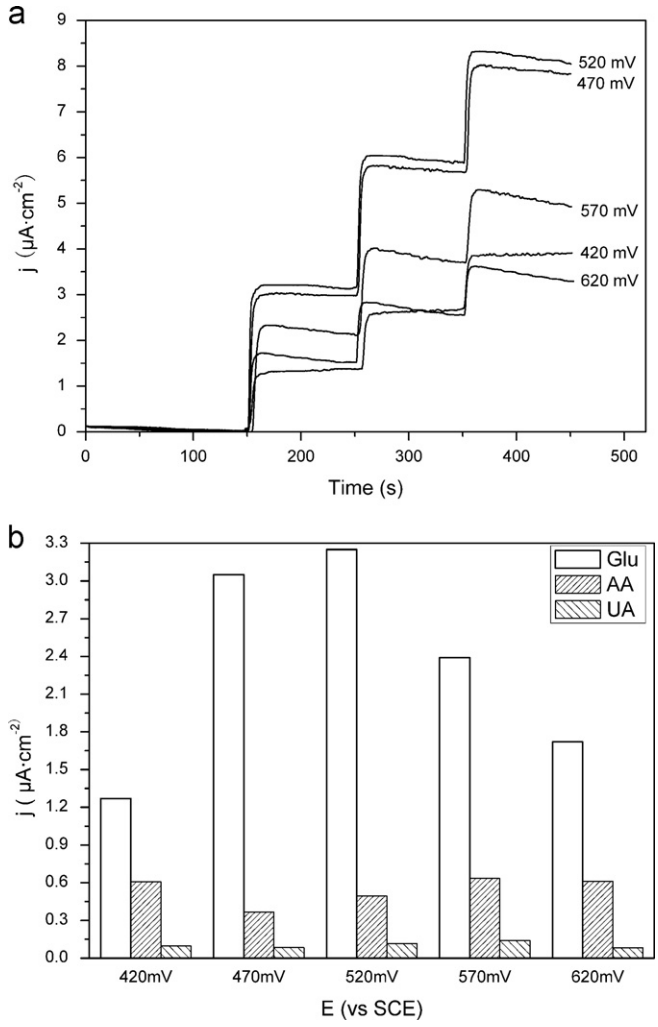

Fig. 4. (a) Amperometric responses of PtNFs-GO modified GCE in 0.05 M PBS (pH 7.4) containing 0.1 M NaCl with the successive addition of 1 mM glucose at different potentials. (b) Selectivity of the modified electrode at different potentials in 0.05 M PBS (pH 7.4) containing 0.1 M NaCl upon addition of 1 mM glucose, 0.02 mM UA or 0.10 mM AA, respectively.

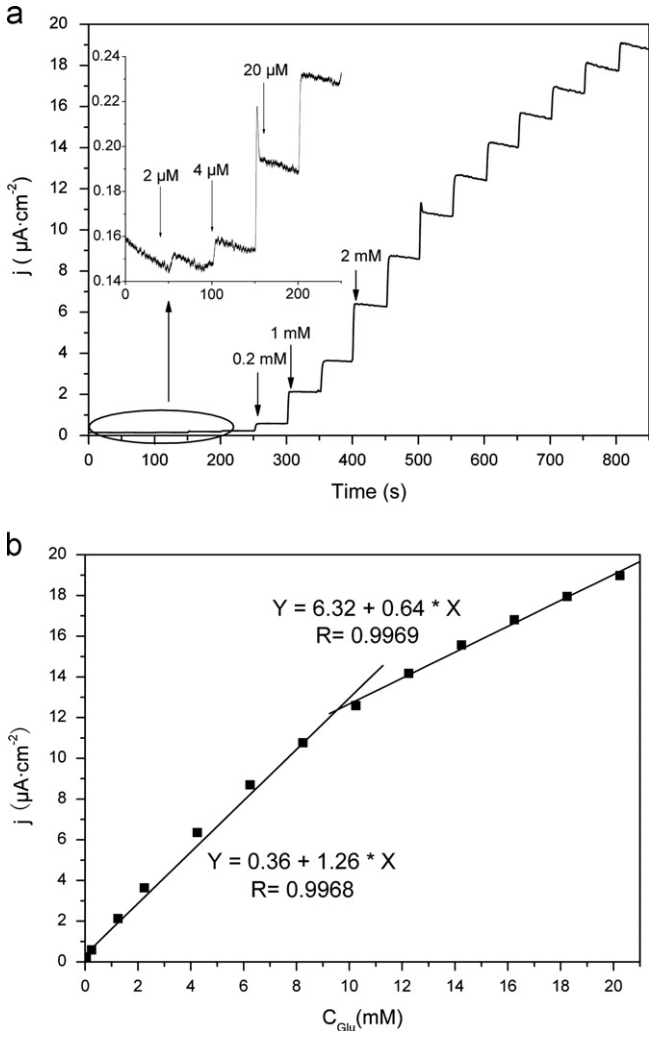

Fig. 5. (a) Typical amperometric responses of PtNFs-GO modified GCE in 0.05 M PBS (pH 7.4) containing 0.1 M NaCl with successive addition an aliquot of glucose at 50 s intervals and a potential of 0.47 V. Inset shows the amperometric responses of four sensors to glucose in 200 s. (b) Calibration curve between the current and the concentration of glucose.

The response time was within 5 s. At a potential of 0.42 V, the amperometric response was quite stable, but the sensitivity was not so satisfactory because of the insufficient potential. As for the results from the potentials of 0.57 V and 0.62 V, the signal decreased rapidly due to the formation of thick Pt oxide. However, at the potentials of 0.47 V and 0.52 V, the signals were quite sensitive and stable. Amperometric responses were also tested at low potentials around 0 V, however, no steady signals could be found because glucose could not be completely oxidized at such a low potential and intermediates were generated on the electrode surface, which blocked some of the active catalytic sites (see Supplementary material Fig. S3).

As mentioned previously, one of the major challenges in non-enzymatic glucose detection is the interfering electrochemical signals caused by some coexisting organic substances, such as UA and AA. The normal physiological level of glucose is 3–8 mM, which is much higher than those of interfering species of AA (~0.1 mM) and UA (~0.02 mM) [19,44]. Therefore, the amperometric responses of the modified electrode in solutions of 0.05 M PBS containing 0.1 M NaCl with the addition of 1 mM glucose, 0.1 mM AA and 0.02 mM UA at different potentials were evaluated. As shown in Fig. 4b, at the potentials of 0.47 V and 0.52 V, the highest selectivity was acquired. At 0.47 V, the current responses for AA and UA were 12.0% and 3.9% compared to that of glucose; while at 0.52 V, they were 15.2% and 4.7%. The results indicated that the PtNFs-GO modified GCE had good anti-interference ability towards the interferents and the selective and sensitive detection of glucose on the modified electrode could be achieved by applying a suitable detection potential.

Based on the above experiments, a potential of 0.47 V was chosen for the amperometric sensing of glucose. Fig. 4a illustrates the current variation with successive changes of glucose concentration under the optimized experimental conditions. Upon addition of an aliquot of glucose to the stirred PBS, the oxidation current increased steeply and reached a steady-state current within 5 s. Fig. 5b shows the calibration curve for the amperometric responses of the PtNFs-GO modified GCE towards glucose in the concentration range from 2 μM to 20.3 mM. There are two linear regions, respectively, in 2 μM to 10.3 mM with a sensitivity of 1.26 $\mu A\,mM^{-1}\,cm^{-2}$ (correlation coefficient 0.9968) and in 10.3 mM–20.3 mM with a lower sensitivity of 0.64 $\mu A\,mM^{-1}\,cm^{-2}$(correlation coefficient 0.9969) due to the adsorption of intermediates derived from the electrocatalytic oxidation of glucose at high concentration of glucose. Comparisons with some previously reported non-enzymatic glucose sensing methods and materials were made and the results are given in Table 1. The advantage of the proposed glucose sensor was obvious and it

Table 1
Comparison of some Pt based non-enzymatic glucose sensors in terms of LOD, linear range, and sensitivity.

Electrode materials	LOD (μM)	Linear range (mM)	Sensitivity ($\mu M\ mM^{-1}\ cm^{-2}$)	References
Pt NTAEs	1.0	2–14	0.1	[12]
PtNFs-MWCNT	2.0	0.002–10.0	7.266	[13]
Pt-Pd NWAs	8.0	1–11	11.25	[45]
PtM (M=Ru, Pd and Au)	50	up to 15	10.6	[46]
Pt/MWCNT	Not given	2–20	1.10	[47]
Pt-Au/MWCNT	10	0.04–24.4	10.71	[18]
Macroporous Au-Pt	25	1–20	39.53	[48]
Ni/POAP modified CPE	90	0.1–2.7	–	[49]
MnO_2/MWNTs	10	0.010–28	–	[50]
PtNFs/GO	2.0	0.002–10.3	1.26	
		10.3–20.3	0.64	This work

showed good sensing performance in terms of LOD and linear range, which meant that the PtNFs-GO was promising for analytical applications.

3.4. Stability and reproducibility

The storage stability of the modified GCEs was investigated by comparing the changes of current response of the electrode, stored in a dry state at room temperature, before and after two weeks storage with additions of 1 mM of glucose in PBS (pH 7.4) containing 0.1 M NaCl. It retained 73.4% of its initial response current after the two weeks of storage. Concerning the reproducibility, PtNFs-GO modified GCEs were evaluated by comparing their current responses in different batches. The amperometric responses of six different batches of electrodes to 1 mM glucose solution were independently tested. The result was satisfactory for the electrode-to-electrode reproducibility with a relative standard deviation (RSD) value of 7.6%. Additionally, the RSD (6.3%, $n=5$) for 1 mM glucose determination demonstrated good intra-electrode reproducibility (The tested electrode was cleaned and refreshed by cyclic scanning in a solution of 0.5 M H_2SO_4 before each measurement). These results indicated that the PtNFs-GO was suitable for the preparation of sensitive, stable and reproducible amperometric sensors in glucose determination.

3.5. Sample analysis

In order to study the applicability of the PtNFs-GO modified electrode, it was applied to the determination of glucose in glucose injection samples. Glucose injection samples were obtained from a local hospital and diluted with PBS (pH 7.4) containing 0.1 M NaCl. The standard addition method was applied in the determination. The recovery for the determination of glucose was in the range of 111.6–118.2% for three samples (see Supplementary material Table S1), indicating the potential usefulness of the PtNFs-GO modified GCE for the practical determination of glucose in real samples.

4. Conclusion

In summary, we successfully constructed a non-enzymatic glucose sensor based on PtNFs-GO modified GC electrodes. The PtNFs-GO was synthesized using a nontoxic, rapid, one-pot and template-free method. Low-cost, green solvent ethanol acted as the reductant and advanced, powerful 2D carbon material-GO nanosheet acted as the stabilizing material. Direct glucose oxidation on the modified electrode was investigated both using voltammetric and amperometric methods. The modified electrode gave strong and sensitive current responses to glucose owing to its highly active surface area and the synergistic effect of the GO and PtNFs. The modified electrode retained sufficient sensitivity in the presence of high concentrations of chloride ions. In addition, the interference effects of AA and UA were comparatively small using a suitable applied potential. The proposed sensor provided good reproducibility for glucose determination in real samples such as glucose injection solution.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.10.066.

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