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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 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ (correlation coefficient 0.9968), and at 10.3 mM to 20.3 mM with a sensitivity of 0.64 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ (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.

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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], Pt₂Pd [15] and metal oxides such as CuO_x [16] and MnO₂ [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 μ M to 20.3 mM. The LOD of 2 μ M 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 $0.05 \mu\text{m } \alpha\text{-Al}_2\text{O}_3$, sequentially. After ultrasonic concussion, the polished GCE was dried at room temperature and then 2 μ L PtNFs-GO suspensions were dropped onto the GCE surface. For stable coating by the catalysts, 2 μ L 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 (111) 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).

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