A novel amperometric glucose sensor based on PtIr nanoparticles uniformly dispersed on carbon nanotubes

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A novel amperometric nonenzymatic glucose sensor based on PtIr nanoparticles deposited on carbon nanotubes (PtIr/CNT hybrids) has been successfully fabricated and applied to the nonenzymatic glucose detection. Their electrochemical behavior toward the oxidation of glucose was compared with Pt/CNT nanoparticles deposited on carbon nanotubes (Pt/CNT hybrids) prepared with a similar procedure. In PtIr/CNT hybrids, PtIr nanoparticles were homogeneously dispersed on carbon nanotubes with an average diameter of 2.0 nm. Their size can be controlled by tuning the Pt/Ir ratio. In contrast, Pt nanoparticles are unevenly distributed on carbon nanotubes with an average diameter of 5.0 nm. The PtIr/CNT hybrids modified electrode shows a highly electroactive surface area, and displays a greatly enhanced electrocatalytic activity toward glucose oxidation. Chronoamperometry was applied to glucose detection in 0.2 M phosphate buffer solution (pH 7.4). The effect of the size of PtIr nanoparticles and the applied potential was investigated. The as-prepared PtIr/CNT hybrid based glucose sensor significantly shows a higher sensitivity, a lower detection limit and a wider linear range than those of Pt/CNT modified electrode. Moreover, Ir addition in Pt catalysts can enable the amperometric glucose detection with longer stability even in the presence of the interference such as ascorbic acid, uric acid, 4-acetamidophenol, creatinine and cholesterol. These results indicate that the PtIr/CNT hybrids are a promising candidate for a highly sensitive and selective nonenzymatic glucose sensor.

1. Introduction

Glucose level control in blood is a key clinical parameter due to the worldwide increasing incidence of diabetes [1]. Electrochemical determination of glucose has gained considerable attention because of its practicality, simplicity, and low-cost [2]. Generally, this method will do with glucose oxidase in virtue of its high selectivity and sensitivity [3]. However, as to these biosensors, the enzymes are instable and their responses will be dependent on environment parameters, such as temperature, pH value, humidity and toxic chemicals on account of the nature of enzymes [4]. These drawbacks will hinder the commercialization of the glucose biosensors.

Nonenzymatic glucose detection has been put forward as a promising alternative to cope with these difficulties. In this strategy, Glucose can be determined in the absence of enzymes by using nano-structured materials as the electrocatalysts including metal alloy [5,6] and metal oxide [7,8]. Among these electro-catalysts, Pt is a popular candidate used in nonenzymatic glucose detection. But Pt based electrode is susceptible to poisoning by adsorbed intermediates [6,9]. In addition, its wide application is constrained for its low sensitivity and poor selectivity toward glucose oxidation [10,11].

Many efforts have been devoted to improve the analytic performance of Pt sensors for glucose detection. The facile access is to fabricate novel Pt nanomaterials with high surface area. Park et al. use mesoporous Pt to detect glucose without enzyme, the current response of glucose increase significantly for high roughness of mesoporous structure on the Pt electrode surface [12]. Besides, Modification of Pt with another metal or metal oxide has been proved to be effective in terms of glucose detection, Pb [9], Pd [2] and Ru [5] has been applied to nonenzymatic glucose detection, but the dissolution of these metal ions and the toxicities of these metal elements involved prevent these methods from being put into practical use. Ir is unique, it has a relative high oxidation potential of 1.26 V (Ir4+/Ir vs. SCE). Therefore, the addition of Ir into Pt electrocatalysts can make them robust enough to provide reproducible current responses of glucose. Moreover, PtIr electrocatalysts...
exhibit a good stability and increased sensitivity toward glucose in the absence of enzyme when compared with Pt electrocatalysts. Peter et al. has reported nanoporous PtIr catalysts is promising for nonenzymatic glucose even in the presence of a high concentration of Cl\(^-\) and other common interfering species such as ascorbic acid, acetamidophenol and uric acid [6].

On the other hand, the economical and efficient use of Pt catalysts should be taken into consideration during the construction of nonenzyme glucose sensors. Herein, we demonstrated an efficient strategy to prepare PtIr catalyst deposited on the surface of carbon nanotubes (CNTs) for nonenzymatic glucose detection. The introduction of CNTs can reduce the amount that use of for the synthesis of PtIr catalysts. Moreover, the presence of CNTs can favor the electron transfer on the electrode interface, which will upgrade the electrochemical activity of PtIr catalysts toward glucose oxidation.

2. Experimental

2.1. Chemicals and materials

H\(_2\)PtCl\(_6\) and IrCl\(_3\), \(\delta\)-glucose, l-ascorbic acid (AA), uric acid (UA), 4-acetamidophenol (AP), creatinine, cholesterol, potassium
phosphate dibasic, potassium phosphate monobasic and sodium chloride are analytic pure, which were purchased from ACROS. Milli-Q system (18.2 MΩ cm) was used for the preparation of all solution.

Multiwalled carbon nanotubes (MWCNTs) were obtained from Chengdu organic Chemistry Co., Ltd (purity >95%, out diameter 10~20 nm, length ~30 μm) and purified as follows [1]: the raw MWCNTs were dispersed by ultrasonication in water for several minutes. A concentrated HNO₃ (65%) solution was added into this solution to decompose amorphous carbon by boiling for several hours. Then, a concentrated HCl (63%) solution was introduced to dissolve the metal particles inside the raw MWCNTs by refluxing for 8 h. After the solution was filtered through a 0.45 μm PTFE filter membrane, the filtered mass was collected and dried at 100 °C in vacuum.

2.2. Preparation of PtIr/MWCNT hybrids

PtIr/MWCNT hybrids were synthesized by thermo-reduction in the mixture solution of water and ethanol with a volume ratio of 1:1. In brief, 10 mg carbon nanotube was dispersed into the solution of 20 mL ethylene glycol and 20 mL deionized water. Then the pH was adjusted to 10 with 0.05 M KOH solution. Then, a fixed total amount (100 μmol) of H₂PtCl₆ and IrCl₃ with a different molecular ratio of Pt/Ir was added in batches. The mixture solution was transferred into a 100 mL flask charged with a magnetic bar after 2 h ultrasonication. Then, this flask was placed in a thermostated oil bath. The reaction solution was deoxygenated by nitrogen for 15 min and heated under reflux at 140 °C for 12 h. Finally, these products were centrifuged, washed with deionized water and ethanol for 3 times and dried in vacuum at 80 °C.

For comparison, Pt/MWCNT and Ir/MWCNT hybrids were prepared in accordance with the preparation of PtIr/MWCNT hybrids with 100 μmol H₂PtCl₆ (for Pt/MWCNT hybrids) or 100 μmol IrCl₃ (for Ir/MWCNT hybrids).

2.3. Characterization

Inductively coupled plasma-atom emission spectroscopy (ICP-AES) was performed on Agilent 7500ce quadrupole ICP-AES. Different catalysts, PtₓIr₁/MWCNT (x = 1, 2, 4) and Pt/MWCNT were sampled by treatment with aqua regia. MWCNTs cannot be dissolved, and can be discarded by centrifugation. The elements, Pt and Ir were dissolved and left in solution for ICP-AES analysis.

Transmission electron microscopy (TEM) observation was performed on a JEOL 2010 microscope equipped with an electron energy dispersive X-ray spectroscopy (EDS), operating at 200 kV using a high-brightness LaB₆ electron gun. The composition of different catalysts was determined by their energy dispersive spectroscopy (EDS) at 150 kV. A drop of 8 μL as-prepared suspensions containing PtIr/MWCNT, Pt/MWCNT or Ir/MWCNT hybrids was gently deposited onto a carbon-coated copper grid and dried in air prior to TEM observation.

2.4. Electrochemical investigation

We used a 15 mL glass electrochemical cell containing three electrodes: a glassy carbon disk working electrode (3 mm or 6 mm in diameter) embedded in Teflon, a platinum wire counter electrode (1 mm in diameter, 5 cm in length), and a saturated KCl Ag/AgCl electrode as the reference electrode. Before use, the glassy carbon or bare Pt disc electrodes were polished with 0.5 μm alumina slurry, washed with the deionized water, then immersed for 20 min in a sonicator bath, and finally washed with the deionized water.

To modify the glassy carbon electrode with MWCNT, Ir/MWCNT or different Pt catalysts, 4.0 mg of these materials (MWCNT, PtIr/MWCNT, Pt/MWCNT or Ir/MWCNT hybrids) were dispersed in 400 μL deionized water to form a homogenous catalyst ink by sonication, and then a 5 μL of these catalysts ink was mixed with a 2.5 μL of 0.5% Nafion®117 ethanol solution. The mixture was spread and air-dried on a glassy carbon electrode at room temperature.
A three-electrode setup was configured with CHI 660C interfaced to a personal computer at room temperature for the electrochemical characterization. The electrolytic solution was bubbled with nitrogen for 15 min before the electrochemical experiment.

Glucose oxidation was investigated by cyclic voltammetry in 0.2 M phosphate buffer solution (PBS, pH 7.4) containing 1 mM glucose. The working electrode was a glassy carbon disk working electrode (3 mm in diameter), and scanned from −0.8 V to +0.8 V at the scan rate of 50 mV/s. Glucose detection was performed under the potentiostatic mode at the operating potential of 0.10 V in 0.2 M PBS (pH 7.4). The amperometric measurement was carried out by using a rotating disk electrode system (RDE) with a glassy carbon disk (6 mm in diameter) controlled by a Pine analytical rotor (Model AFMSRX) under a rotate rate of 500 rpm.

The electrolytic solution was bubbled with nitrogen for 15 min before the electrochemical experiment and the electrochemical experiments were conducted at the room temperature in ambient condition.

3. Result and discussion

3.1. Characterization of PtIr/MWCNT, Pt/MWCNT and Ir/MWCNT hybrids

The morphology of Pt$_x$Ir$_1$/MWCNT hybrids with different Pt/Ir ratio = $x$ ($x = 1, 2, 4$) was imaged by TEM. As shown in Fig. 1, the PtIr nanoparticles in Pt$_x$Ir$_1$/MWCNT hybrids were uniformly deposited in high density on the surface of MWCNTs without aggregation. On the contrary, the dispersion of Pt nanoparticles is uneven. It is obvious that some small Pt nanoparticles are aggregated and
overgrew into a big one on the surface of MWCNTs. On the other hand, Ir nanoparticles are homogeneously dispersed on the surface of MWCNTs in high density, suggesting that the addition of Ir element will be in favor of the deposition of Pt nanoparticles (Fig. S1).

Their size distributions (Fig. 2) were evaluated statistically by measuring the diameter of PtIr or Pt nanoparticles on the surface of MWCNTs in the selected area. The average diameter of PtIr nanoparticles in PtIr/MWCNT hybrids ranged from 2.0 nm to 3.0 nm with different Pt/Ir ratio. Among these PtIr nanoparticles, the PtIr nanoparticles prepared at Pt/Ir ratio of 4:1 have a smallest average diameter, which is 2.0 nm. In contrast, the sizes of Pt nanoparticles distributes from 2.0 to 8.0 nm with an average diameter of 5.2 nm, much bigger than those of PtIr and Ir nanoparticles. For latter, as shown in Fig. S2, the average diameter of Ir nanoparticles is estimated to be 1.82 nm.

The composition of PtIr/MWCNT hybrids is measured by EDS attached to TEM (Fig. 3). Cu Ka peak is presented at 8.0 KeV (its relative peak La 1.2 KeV, and Kb 8.8 KeV), which comes from the copper grids used as a support in TEM observation [13]. As to PtIr/MWCNT hybrids, both Pt and Ir Ma peaks take place at 2.1 KeV. Pt La peak exists at 9.5 KeV and Lb peak at 11.1 KeV, while Ir La peak occurs at 9.2 KeV and Lb peak at 10.8 KeV [6]. The molar ratio of Pt/Ir for PtIr/MWCNT hybrids can be estimated by normalizing the intensity of Pt L and Ir L signal on the EDS curves. The results were listed in Table S1, which was consistent with the data of ICP-AES.

3.2. Electrochemical investigation of PtIr/MWCNT hybrids

The electrochemical behavior of PtIr/MWCNT and Pt/MWCNT hybrids (x = 1, 2, 4) was conducted by cyclic voltammetry. Fig. 4 shows the CVs of PtIr/MWCNT/GC in N2-saturated 0.5 M H2SO4 solution. The PtIr nanoparticles show the signatures of polycrystalline Pt in the potential interval between −0.2 and 0.1 V, which can be divided into the reductive adsorption region of protons in the reverse cathodic scan and the oxidative desorption region of hydrogen atom in the forward anodic scan [14]. This potential region is defined as the hydrogen area, which can be used to calculate the electroactive surface area (ESA) of Pt based hybrids [15]. The ESAs of PtIr/MWCNT hybrids are estimated by integrating the hydrogen region, which were listed in Table S2. It is clear from Table S2 that the ESAs of PtIr/MWCNT hybrids are mostly dependent on the size of PtIr nanoparticles supported on MWCNTs. Given the mass of PtIr nanoparticles, as discussed above, a decrease of their average diameter will give rise to an increase of their specific surface areas. Therefore, the ESA sequence of PtIr nanoparticles among PtIr/MWCNT and Pt/MWCNT hybrids follows this order of decrease: PtIr/MWCNT (116.7 m2 g−1 Pt), PtIr/MWCNT (95.3 m2 g−1 Pt), PtIr/MWCNT (78.2 m2 g−1 Pt) and Pt/MWCNT hybrids (58.3 m2 g−1 Pt).

3.3. Electro-catalytic oxidation of glucose

The catalytic properties of hybrids were also investigated using cyclic voltammetry. In the interest of developing novel electrode catalysts suitable for application in glucose biosensors, a PBS (pH 7.4) was chosen as the electrolyte as it is comparable to physiological conditions. Fig. 5 shows the CVs of the electrode modified with PtIr/MWCNT hybrids (abbreviated as PtIr/MWCNT/GC) in 0.2 M PBS (pH 7.4) in the presence (Fig. 5a) and absence (Fig. 5b) of 1 mM glucose. For comparison, the CVs of the electrode modified with MWCNTs, Pt/MWCNT, Ir/MWCNT hybrids are also presented and denoted as MWCNT/GC (Fig. 5c and d), Pt/MWCNT/GC (Fig. 5e and f) and Ir/MWCNT/GC (Fig. S2a and b), respectively. The oxidation current of glucose is neither observed at MWCNT/GC nor at Ir/MWCNT/GC in the applied potential range from −0.6 to 0.8 V (Fig. 5e). However, both Pt/MWCNT/GC and PtIr/MWCNT/GC exhibit a good catalytic activity as evident by the multiple peaks attributed to the adsorption and redox of glucose and its intermediates [16]. These peaks can be explained by the well-established mechanism of direct electro-oxidation of glucose on Pt electrodes in neutral media [17]. For convenience, only the anodic oxidation peaks were discussed below. Peak I is ascribed to the chemisorption and dehydrogenation of glucose, and takes place at the hydrogen region (below −0.3 V). Peak II is associated with the electrooxidation of glucose, and occurs at the double layer region (spanning −0.2 to 0.2 V). In this region, the abundance of adsorbed OH species increases at the increasingly anodic potentials, as the fast dissociation of water reaction. This incipient hydroxide is catalytic to the oxidation of glucose. Peaks III is related to oxygen evolution in the oxygen region from ca. 0.4 V. Herein the platinum surface is covered by a monolayer of adsorbed oxygen, which will inhibit glucose oxidation as OH ads is desorbed and replaced by less catalytically active Oads. For Pt/MWCNT/GC, Peaks II and III are unsharped, and overlapped with each other (Fig. 5c). In contrast, for PtIr/MWCNT/GC, Peaks II and III are well-defined, and the current of Peak II at 0.1 V is about 1.7 times higher than that of Pt/MWCNT/GC after normalizing the current of these Pt catalysts in the potential of ca. 0.1 V in the absence of glucose (Fig. 5a). It is clear that the current of Peak II responding to glucose oxidation enhanced significantly after Ir content was introduced into Pt catalysts. The unique structure of PtIr/MWCNT hybrids may be contributed to their higher catalytic activity on glucose oxidation. As discussed above, the PtIr nanoparticles are smaller, and their dispersion on MWCNTs is more uniform, which will enable PtIr/MWCNT hybrids to supply more active Pt site for glucose oxidation. Therefore, PtIr/MWCNT/GC shows a higher current response to glucose than Pt/MWCNT/GC in the applied potential. In addition, the bare Pt disc electrode (diameter 3 mm) also shows a current response to glucose oxidation, which amounts to 5–6% of the oxidative current of glucose obtained at PtIr/MWCNT/GC in the applied potential range from −0.6 to 0.8 V (Fig. S2).

3.4. Amperometric determination of glucose

The glucose concentration in solution was determined by chronoamperometry. Fig. 6A shows typical amperometric response
of the RDE modified with Pt2Ir1/MWCNT and Pt/MWCNT hybrids to subsequent addition of glucose in 0.2 M PBS (pH 7.4) at 0.1 V. For convenience, the working electrode is denoted as Pt2Ir1/MWCNT/RDE-GC and Pt/MWCNT/RDE-GC, respectively. It is observed that both Pt2Ir1/MWCNT/RDE-GC and Pt/MWCNT/RDE-GC respond quickly to the change of glucose concentration and reach a steady-state signal within 5 s at higher concentration. When the concentration of glucose is below 3 μM, as shown in Fig. 6A inset, Pt/MWCNT/RDE-GC has no obvious current response, but Pt2Ir1/MWCNT/RDE-GC shows an obvious anodic current associated with glucose oxidation, which is estimated to be 0.235 μA cm⁻². Fig. 6B shows the corresponding calibration curve of Pt2Ir1/MWCNT/RDE-GC and Pt/MWCNT/RDE-GC. As to Pt2Ir1/MWCNT/RDE-GC, its calibration curve displays a linear range of 1.0–1000 μM with a sensitive of 206 μA mM⁻¹ cm⁻² (r = 0.9987), and a detection limit of 0.5 μM (signal/noise = 3). By contrast, the calibration curve of Pt/MWCNT/RDE-GC for glucose sensing shows a shorter linear range (60–800 μM), a less sensitive (48 μA mM⁻¹ cm⁻² (r = 0.9065)) and a lower detection limit (40 μM). The composition effect of PtIr nanoparticles was also investigated by chronoamperometry, as shown in Fig. 6C, all PtIr/MWCNT/RDE-GC electrodes show a linear current response to glucose concentrations (40 μM), the calibration plots presented in Fig. 6C inset indicated that amperometric sensitivities increase in the following order: Pt2Ir1/MWCNTs (206 μA mM⁻¹ cm⁻²) > PtIr1/MWCNTs (162 μA mM⁻¹ cm⁻²) > PtIr1/MWCNTs (114 μA mM⁻¹ cm⁻²). The sensitivity sequence of glucose detection is in good agreement with the ESAs of these Pt catalysts. Other detection parameters of glucose were listed in Table S3. Obviously, Pt2Ir1/MWCNT/RDE-GC is superior to Pt4Ir1/MWCNTs/RDE-GC and Pt1Ir1/MWCNT/RDE-GC in term of linear range and detection limit in glucose sensing apart from sensitivity. The impact of the electrode potential on Pt2Ir1/MWCNT/RDE-GC and Pt/MWCNT/RDE-GC was further investigated by the chronoamperometry at fixed concentration of glucose (40 μM) in 0.2 M PBS (pH 7.4). Fig. 6D shows their
dependence of amperometric response on the applied potentials ranged from −0.3 to 0.3 V. It is clear that PtIr/MWCNT/RDE-GC also exhibit a higher current response of glucose oxidation than Pt/MWCNT/RDE-GC at all the investigated potential. The optimum oxidation potential in glucose detection is 0.1 V, which fits well with the CV curves. For comparison, the detection parameters on glucose at several modified electrodes were listed in Table S4. The detection limit, linear calibration range and sensitivity for glucose determination at PtIr/MWCNT/RDE-GC are comparable and even better than those obtained at the electrodes reported recently.

3.5. Selectively and stability

In real samples, the easily oxidative species such as AA, UA, AP and creatinine, co-exist with glucose in human blood, which will affect the sensor response [18]. Considering the concentration of glucose is at least 30 times as much as the interfering species in human blood such as UA, AP, AA and creatinine [19], the selectivity of PtIr/MWCNT/RDE-GC was studied by comparing the amperometric responses of these electroactive species at 0.10 V in 0.2 M PBS (pH 7.4) upon subsequent additions of 25 μM UA, 25 μM AP, 25 μM AA, 25 μM creatinine, 180 μM cholesterol and 180 μM glucose. As shown in Fig. 7, the injection of glucose gives rise to a remarkable current response immediately, while the addition of UA, AP and cholesterol causes a negligible current response. Compared to glucose, AA and creatinine yield current response 5.6% and 4.1% of glucose oxidation current obtained at PtIr/MWCNT/RDE-GC, respectively. Therefore, the interference of AA and creatinine can be neglected during glucose detection in human blood when used PtIr/MWCNT/RDE-GC as biosensor.

Another attractive feature of PtIr/MWCNT/RDE-GC was its highly operational stability for amperometric determination of glucose. Control experiments were performed on Pt/MWCNT/RDE-GC due to the similar principle of electrocatalysis. Fig. 8 compares the current responses of PtIr/MWCNT/RDE-GC with that of Pt/MWCNT/RDE-GC to 300 μM glucose in 0.2 M PBS recorded over about 12 min. Pt/MWCNT/GC showed a rapid decay of the current with 45% signal depressions after 12 min. In contrast, the response of PtIr/MWCNT/RDE-GC remained constant throughout the entire experiment, suggesting that there was no inhibition effect of glucose and its oxidation products on the surface of the electrode [20].

4. Conclusion

In summary, we have demonstrated a novel nonenzymatic electrochemical glucose sensor based on PtIr/MWCNT electrocatalysts. PtIr nanoparticles with different Pt/Ir ratio were homogenously deposited on the surface of multi-walled carbon nanotubes using a one-step facile hydrothermal method. The as-prepared PtIr/MWCNT modified electrode exhibits very strong and sensitive amperometric responses to glucose even in the presence of the common interfering species, such as ascorbic acid, uric acid, 4-acetamidophenol, creatinine and cholesterol. Ease of fabrication, fast response and high sensitivity and long stability make the nonenzymatic glucose sensor proposed in this study very promising in the pharmaceutical and clinical detection of glucose.

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Appendix A. Supplementary data


References


