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Surface nitrogen-enriched carbon nanotubes for uniform dispersion of platinum nanoparticles and their electrochemical biosensing property

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ABSTRACT

Nitrogen containing carbon layer-coated carbon nanotubes (CNx-CNTs) was prepared as the support for platinum nanoparticles (Pt NPs) and their enhanced properties for electrochemical biosensor has been demonstrated in this paper. The CNx-CNTs were obtained from pyrolysis of polydopamine-wrapped CNTs, which were synthesized by a single deposition process based on the oxidative self-polymerization of dopamine on CNTs. It is found that Pt NPs are deposited on the surface of the CNx-CNTs (Pt/CNx-CNTs) with highly dispersion and small particle size (with an average diameter of 1.7 ± 0.3 nm). Compared to the nitrogen-free CNTs supported Pt NP composite (Pt/CNTs), the Pt/CNx-CNTs modified glassy carbon (GC) electrode exhibits superior electrocatalytic performance towards the oxidation of hydrogen peroxide (increase by about 55% of response current). Taking glucose oxidase (GOD) as the model, the proposed amperometric enzyme biosensor based on the Pt/CNx-CNTs shows excellent analytical characteristics to glucose detection, such as excellent sustainability in large range of pH values, high sensitivity (66.51 μA (mmol dm^{-3})$^{-1}$ cm^{-2}), wide linear range (0.01-6.1 mmol dm^{-3}) and low detection limit (0.4 μmol dm^{-3}).

1. Introduction

Carbon nanotubes (CNTs) have been employed as support for transition metal nanoparticles (NPs) in a broad range of applications (eg. biosensor, fuel cell and heterogeneous catalysis) [1–9], owing to their fascinating properties like large accessible surface areas, low electric resistance, and high chemical and electrochemical stability. The performance of CNTs/NPs is strongly affected by many factors, such as the sizes, amount and uniformity of the metal NPs and the total surface area of carbon supports. In order to establish a uniform coverage of metal particles on the surface of CNTs, it is necessary to activate the graphitic surface of the tubes, which is extremely inert, to introduce more reactive sites [10]. Several methods have been applied and typically involve harsh chemical or electrochemical oxidation at defect sites of CNTs [11,12], grafting of polymer [4,13,14], etc. Unfortunately, these treatments considerably harm the mechanical and/or electronic properties of the tubes due to the introduction of either large numbers of oxidative damage on graphite structures or non-conductive functional groups. In addition, the weak bonding interaction between metal and support could potentially lead to detachment of NPs from the CNTs surface, and thereby affect the durability and utilization of composite material [15–17].

Alternatively, doping carbon materials with heteroatoms (e.g., nitrogen) represents a feasible pathway to provide chemically active sites on carbon surface whereas without significant degradation of their electrical properties, hence improving the dispersion of metal NPs on carbon materials and retarding the degradation of metal nanoparticles [17–24]. Nitrogen-doped CNTs (NCNTs) have been reported as excellent support materials for uniform Pt NPs dispersion with significantly better electro-catalytic performance and durability than that of nitrogen-free Pt/CNT in the application of fuel cell and sensing [10,23–26]. Furthermore, nitrogen-doped carbon itself is also already known to act as metal-free catalyst for oxygen reduction [27–32]. Currently, one of the most common methods to synthesis NCNTs is direct CVD deposition by using nitrogen-containing carbon precursor. However, the NCNTs prepared by CVD usually have low nitrogen content, resulting in a dispersion and particle size of noble metal NPs on CNTs which are still unsatisfactory. If the nitrogen content of NCNTs is extensively increased by a direct nitrogen-doping strategy, the nature of the CNTs may change due to the introduction of lots of disordered sites

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into the CNT lattice during the nitrogen-doping process, leading to the formation of a less stable structure of NCNTs. To minimize the above disadvantages, it is highly desirable to develop an effective surface-nitrogen-enrichment method in order to increase the surface nitrogen content of CNTs but cause limited structural damage to CNTs.

A promising method to form nitrogen containing CNTs is based on the pyrolysis of nitrogen-containing polymer functionalized CNTs to obtain a nitrogen-containing carbon layer (CNx) covered on the surface of CNTs [10]. Polydopamine has great adhesive properties on a range of substrates (CNTs [33–35] and SiO_2 [36] etc), which can be easily obtained via exposing a solution of dopamine to air at room temperature. Pyrolyzing dopamine and its polymer to synthesize nitrogen-containing carbon materials has advantages of generalized and robust synthesis, film thickness control, without heating and avoiding metal and organic catalysts. Recently we have employed this approach to generate hollow nitrogen-doped carbon spheres (HNCS) for applications of electrochemical sensors and fuel cells [32,37,38]. Due to the presence of nitrogen species, the HNCS has shown admirable properties towards electrocatalytic oxidation of small molecular compounds (DA, UA, AA and oxygen) as well as Au NPs uniformly loading. Herein, we successfully synthesized nitrogen-doped carbon layer-coated CNTs (CNx-CNTs) composite by heating PDA wrapped CNTs to temperature of 1000 °C, which were fabricated by the spontaneous self-polymerization of dopamine onto CNTs surface. The surface-nitrogen-enriched CNTs not only introduce a uniform distribution of nitrogen atoms on the CNT surface to anchor and grow platinum NPs with ultra-uniform dispersion and narrow size distribution, but also maintain the intrinsic nature of CNTs (as shown in Scheme 1). Furthermore, taking glucose oxidase (GOD) as a model, this Pt/CNx-CNTs was utilized as an enzyme-immobilization electrode material in an amperometric biosensor with significant superior characteristics than nitrogen free CNTs supported Pt NPs (Pt/CNTs).

2. Experimental

2.1. Reagents and Apparatus

Multi-walled carbon nanotubes (CNTs, >95%, diameter 20-60 nm, length 5-15 μm) prepared by CVD were purchased from Shenzhen Nanotech Port Ltd. Glucose oxidase (E.C. 1.1.3.4, Type X-S, 136100 U/G from Aspergillus niger), Dopamine hydrochloride was purchased from Alfa Aesar (USA) and used as received. 5 wt% Nafion 117 solution was purchased from Sigma-Aldrich (USA). Glucose stock solution was stored overnight at room temperature before use. All other chemicals were of analytical grade. Aqueous solutions used throughout were prepared with ultra-pure water obtained from a Millipore system (>18 MΩ cm). All of the electrochemical measurements were carried out at room temperature (25 ± 2 °C).

Micrographs of transmission electron microscopy (TEM) were obtained on a JEOL 3010 transmission electron microscope operating at 200 kV. Nitrogen sorption isotherms and Brunauer–Emmett–Teller (BET) surface areas of the materials were determined by an ASAP 2010 Micrometrics sorptometer (America). Nitrogen content in CNx-CNTs was determined by elemental analyzer (TCH-600, America). Thermogravimetric analysis (TGA) of CNx-CNTs was carried out on Luxx STA 409 PC with 5 K min^{-1} heating rate with oxygen flow. All of the electrochemical measurements were performed on a CHI 660D electrochemical workstation (Chenhua Instrument Company of Shanghai, China) with a conventional three-electrode system. Platinum wire was used as counter electrode, Ag/AgCl electrode as reference electrode, and modified GC electrode as working electrode.

2.2. Preparation of CNx-CNTs

The preparation of CNx-CNTs consists of two steps. Firstly, PDA/CNTs composite was synthesized according to the literature [33,36]. In brief, 100 mg CNTs was washed thoroughly with 50 mM tris(hydroxymethyl)aminomethane-chloride acid (Tris-HCl) buffer (pH = 8.5) and centrifuged three times alternatively. The deposit was re-suspended in 100 ml 50 mM Tris buffer (pH = 8.5) containing 2 mg mL^{-1} DA, followed by vigorous stirring for 24 h to form PDA/CNTs composite. Then the dark-coloured precipitate was centrifuged (5000 rpm, 2 min) and washed with fresh Tris buffer (three times) to remove the tan solution, followed by drying in vacuum at 60 °C overnight. Finally, CNx-CNTs were synthesized by the pyrolysis of the prepared PDA/CNTs in a nitrogen atmosphere at 1000 °C for 2 h.

2.3. Preparation of Pt/CNx-CNTs

Deposition of the Pt NPs on the CNx-CNTs was carried out via a microwave-assisted reduction process in ethylene glycol solution. The details were as follows: 20 mg of CNx-CNTs was mixed with 665 μL H_2PtCl_6 (38.6 mmol dm^{-3}) in 25 mL ethylene glycol solution under ultra-sonication for 30 min. The pH value of the solution was adjusted to 10 with 1.0 M KOH aqueous solution. Then, the mixture was placed in a microwave oven and heated by microwave irradiation (800 W) for 10 min at 120 °C. The products were centrifuged and washed three times with distilled water. The CNx-CNTs-supported Pt NPs, denoted as Pt/CNx-CNTs, was dried in a vacuum oven at 60 °C overnight. For comparison, Pt NPs supported on the acid-treated CNTs, labeled as Pt/CNTs, was prepared under the same procedure as described above.

2.4. Preparation of GOD/Pt/CNx-CNTs/GC electrode

Prior to use, GC electrodes (diameter = 3 mm) were carefully polished to a mirror-like plane with 0.5 and 0.05 μm alumina slurries, successively. Afterward, the electrodes were washed thoroughly with excess amount of water and dried under nitrogen gas.

The CNx-CNTs modified GC (CNx-CNTs/GC) electrode was prepared by casting 5 μL CNx-CNTs suspension (2 mg mL^{-1} CNx-CNTs in mixture of water and ethanol (v:v = 1:1)) on GC surface and dried at room temperature for 24 hours. For comparison, the CNTs/GC electrode was also prepared by the same procedure.

For fabricating GOD biosensor, a 5 μL of GOD solution (10 mg mL^{-1} GOD in PBS, pH 7.0) was dropped on the CNx-CNTs/GC electrode and dried at less than 4 °C overnight, the obtained GOD/CNx-CNTs modified electrode was then rinsed carefully with double-distilled water and dried, followed by coating 4 μL of Nafion ethanol solution (1 wt%) onto the electrode surface to avoid the leak of the GOD. The Nafion/GOD/CNx-CNTs electrode was washed thoroughly with water. For comparison, the CNTs modified electrode was also prepared to immobilize GOD via the same procedure.

3. Results and discussion

3.1. Characterization of CNx-CNTs and Pt/CNx-CNTs

Fig. 1A and B shows the TEM images of obtained CNx-CNTs composite. It displays clearly the tubular morphology and typical graphite layered structure in the inner wall of the tubes, indicating that the framework of CNTs is well-preserved after the pyrolysis in nitrogen atmosphere. Furthermore, it can be observed that the outside surface of CNTs is covered by an amorphous structured shell (CNx) with thickness of ~12 nm, which should be the carbonization product of PDA on the surface of CNTs.