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A novel platform based on defect-rich knotted graphene nanotubes for detection of small biomolecules

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ABSTRACT

Detection of disease-related small biomolecules was of great significance for clinical diagnostics and treatment. In this work, we synthesized defect-rich knotted graphene nanotubes (k-GNTs) via chemical oxidative etching of stacked-up carbon nanotubes (SC-CNTs) followed by chemical reduction, to detect disease-related small biomolecules. We further studied the electrochemical properties using three representative redox probes and analyzed their biosensitivity using five biomolecules. The k-GNT-modified electrodes exhibited excellent electrochemical response, with the lowest ΔE_p and the highest k^0. Besides, the modified electrodes could simultaneously detect and discriminate between dopamine (DA), ascorbic acid and uric acid (UA), as well as differentiate phenethylamine (PEA) and epinephrine (EP) existed in newborn rat serum, providing the wide linear detection ranges with high sensitivities for DA, UA, PEA, and EP. These excellent electrocatalytic properties could be ascribe to the unique knotted graphene nanotube structure with high proportion of defect/edge sites, large, accessible, three-dimensional, accessible surface area, fewer oxygen-containing groups and doped N atoms. Our work reveals defect-rich k-GNTs as a promising platform for further applications in electrochemical biosensing and electrocatalysis.

1. Introduction

The detection of disease-related small biomolecules, such as dopamine (DA), uric acid (UA), ascorbic acid (AA), epinephrine (EP) and phenethylamine (PEA), is important in the field of clinical diagnostics and treatment [1–5]. Therefore, it is of great significance to understand the electrochemical reactions and quantify the contents of these molecules in human body fluids [6]. However, coexisting compounds, such as DA, UA and AA or EP and PEA, in the extracellular fluid of the central nervous system and serum cause great interference due to the overlapping oxidation potentials of commercial conventional electrodes [7,8]. To resolve this problem, various materials or substrates have been extensively studied to modify the surfaces of working electrodes or use carbon based materials such as carbon nanotubes, carbon dots, and graphene as electrode materials [1,9–13].

To date, the structural defects of a wide variety of carbon based materials have drawn widespread attention to various research fields with respect to their influence on the chemical and structural properties of the carbon nanostructures [14–16]. Structural defects are generated during the production process or are intentionally induced in materials by post-treatment, including the plasma treatment, amorphization, doping and so on [17–19]. Moreover, defect modification of nano-carbon materials is a powerful means to improve the electrical conductivity, which was proved by studying heterogeneous electrochemical reactions at the surface of nano-carbon based electrodes [20].

Among the various nano-carbon materials based options, graphene holds great promise as a next-generation material due to its better wettability, high surface area and excellent mechanical strength [21–24]. Ideal-structured graphene materials' side wall is inert and hydrophobic, which points to a limited surface area and few available active sites. This limits its applications in electrochemistry [25,26]. Accordingly, chemically modified graphene is necessary [27,28]. Graphene oxide (GO), a specific modified graphene, derived its name from the oxidation process of graphite, is known to be extensively researched materials [29]. Compared with other carbon materials, GO has many edge-plan sites. However, its defects are exposed to the mismatch between theory and reality. Besides, GO tends to aggregate due to the π–π interaction between individual sheets [30,31]. Moreover, the oxygen-containing groups in GO actually impeded the rate of heterogeneous electron transfer [32–34].

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To solve this problem, we prepared a novel modified graphene, knotted graphene nanotubes (k-GNTs), which are relatively straight nanotubes that are divided into sections by "knots". In k-GNTs, there existed abundant edge-plane like-sites/defects located along the nanotubes, which are responsible for the fast electron transfer rate [35–37]. Moreover, k-GNTs intertwine to form a three-dimensional spatial configuration on the electrode surface, which could greatly increase the electrode surface area. Besides, k-GNTs have fewer oxygen-containing groups, which is good for the electrochemical conductivity. Additionally, N atoms can be introduced to produce more defect sites on the graphene sheets, endowing the k-GNTs with higher electrical conductivity [38,39].

In this work, we synthesized k-GNTs via chemical oxidative etching of carbon nanotubes [40], followed by chemical reduction [41]. We used three representative redox probes to study the electrochemical properties of k-GNTs using stacked-up carbon nanotubes (SC-CNTs), oxidative graphene nanotubes (ox-GNTs) and glassy carbon electrodes (GCEs) as referring materials. Our work provides further insight into the electrochemistry of k-GNT-modified glassy carbon electrodes using five biomolecules, DA, UA, AA, EP and PEA. In addition, the modified electrodes were applied to detect EP and PEA in newborn rat serum.

2. Experimental method

2.1. Reagents

Stacked-up carbon nanotubes (SC-CNTs, impurities (iron −free, < 100 ppm Iron content), ca. 100 nm in diameter and 20–200 μm in length) and $Ru(NH_3)_6Cl_3$ (stored at 2–8 °C) were purchased from Sigma-Aldrich Co., Llc., USA. HCl, HNO_3, H_2SO_4, $KMnO_4$, NH_2-NH_2 (85 wt% in H_2O), H_2O_2 (30 wt% in H_2O), $K_3Fe(CN)_6$, $NaNO_3$, KCl, $K_2HPO_4{\cdot}3H_2O$ and KH_2PO_4 were obtained from Sinopharm Chemical Reagent Co., Ltd., China, and were of analytical grade. K_2IrCl_6, dopamine (DA), ascorbic acid (AA), and uric acid (UA) were purchased from Alfa Aesar. Phenethylamine (PEA) was purchased from Sigma-Aldrich. Epinephrine (EP) was purchased from Aladdin. All solutions were prepared with ultrapure water (resistivity of 18.25 MΩ cm^{-1}). K_2IrCl_6, $K_3Fe(CN)_6$, and $Ru(NH_3)_6Cl_3$ were utilized at a concentration of 5 mM in 0.1 M KCl supporting electrolyte. PBS (phosphate buffer saline) solution (0.1 M, pH = 7.0) were prepared with $K_2HPO_4{\cdot}3H_2O$ and KH_2PO_4. Different concentrations of AA, DA, UA, PEA, and EP solutions were prepared with PBS depending on the needs of the measurement. The newborn rat serum (NRS) was diluted 10 times with 0.1 M PBS before electrochemical measurements.

2.2. Apparatus

The microstructure characteristics of the SC-CNFs, ox-GNTs and k-GNTs were investigated using a FEI Tecnai G2 F20 S-TWIN transmission electron microscope (TEM). Raman spectroscopy (Renishaw, UK) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific, USA) were also carried out. Powder X-ray diffraction (XRD) patterns were obtained using an X'Pert-PMD system, with Cu Ka radiation (λ = 0.15405 nm, 40 kV, 100 mA). UV–vis absorption spectra were obtained using a Cary 50 spectrophotometer (UV-2450). Electrochemical experiments were carried out using a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument, China). All the experiments were performed using a three-electrode system consisting of platinum wire as the auxiliary electrode, a glassy carbon electrode (GCE, Φ = 3 mm) as the working electrode, and a saturated calomel electrode (SCE) as the reference electrode.

2.3. Material synthesis

The ox-GNTs were prepared using a method adapted from Liu' method [40]. Briefly, SC-CNTs (0.2 g) and $NaNO_3$ (1.0 g) were mixed in concentrated H_2SO_4 at 0°§≥. $KMnO_4$ was added (6 g) slowly. The mixture was stirred for 90 min at 0°C and then heated at 35°C for an additional 60 min. The mixture was then poured slowly into 250 mL of water with 10 mL of 30% H_2O_2. After stirring, the products were washed with deionized-ultrafiltered water until the pH was neutral (pH = 7).

The k-GNTs were prepared using a typical procedure [41]. The ox-GNTs (100 mg) were loaded in a 250 mL roundbottom flask and water (100 mL) was then added, yielding a dispersion. This dispersion was sonicated until it became clear with no visible particulate matter. Hydrazine hydrate (1.00 mL, 32.1 mmol) was then added and the solution heated in an oil bath at 100 °C under a water-cooled condenser for 24 h over which the reduced GO gradually precipitated out as a black solid. This product was isolated by filtration over a medium fritted glass funnel, washed copiously with water and dried on the funnel under a continuous air flow through the solid product cake.

2.4. Electrode preparation

The GCE was polished using 1.0 μm, 0.5 μm and 0.05 μm alumina powder and was then sonicated with ethanol and deionized-ultrafiltered water for 5 min, respectively. The GCE was then dried. Next, the surface of GCE was then coated with 8 μL aqueous dispersion of 1 mg/mL k-GNTs, ox-GNTs and SC-CNTs to fabricate k-GNTs/GCE, ox-GNTs/GCE and SC-CNTs/GCE electrodes. All the electrodes were dried in air.

3. Results and discussion

3.1. Structural characterizations

Fig. 1 and Fig. S1 showed the typical low and high magnification TEM images of the SC-CNTs, ox-GNTs and k-GNTs. It was obvious from the TEM images (Fig. 1A and Fig. S1A) that SC-CNTs had a diameter of approximately 150 nm. Unlike the common CNTs with an integrated hollow cylindrical structure, the inner region of the SC-CNTs was a stacked-cup-like structure, with bending graphite-like sheets as the outer shell that form multiple separated cavities. After chemical oxidative treatment, based on Fig. 1B and Fig. S1B, we determined that ox-GNTs had a larger diameter than SC-CNTs. Moreover, the inner walls of the ox-GNTs retained hollow tubular-like structures, whereas the outer walls had unfolded GO-like structure strongly connected to the inner walls. The k-GNTs were shown in Fig. 1C and Fig. S1C. Increased thickness of the nanotube-wall was observed, indicating the outer wall of the k-GNTs was successfully reduced and re-stacked. Moreover, k-GNTs are divided into sections by knots and the outside GO-like structure reunited and became crumpled sheets on the surface, which seamlessly associated with the inner wall to form a disordered surface.

The schematic representation of the production of ox-GNTs and k-GNTs was illustrated in Scheme 1. The stacked cup-like structure of SC-CNTs might play an important role in preparing k-GNTs. On the one hand, the outer wall of the SC-CNTs was easily attacked by oxidants, forming an unfolded GO-like structure seamlessly connected with the inner walls. On the other hand, the curvature of the tubes cavities, particularly close to the dome part, had more local pressure than the open channel tubes, indicating that the oxidative reaction will be significantly increased with curvature of the carbon nanotubes during the chemical oxidative etching [42,43]. After chemical reduction, the outer wall GO-like structure re-stacked disorderly and the knots of ox-GNTs enlarged, forming a