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A novel N-doped carbon nanotube fiber for selective and reliable electrochemical determination of ascorbic acid in rat brain microdialysates

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ABSTRACT

Selective and reliable method is of great importance for in vivo analysis in the complicated brain. In this work, we developed a new approach for detection of ascorbic acid (AA) based on a new nitrogen-doped nanotube fiber (NCNF) microelectrode. After electrochemical pre-treatment, the NCNF microelectrode (e-NCNF) demonstrated high electrocatalytic capability for AA oxidation with a low working potential, 0 V, resulting in high selectivity for detection of AA level against other biological species in brain, as well as producing high sensitivity. Moreover, the e-NCNF was directly assembled by carbon nanotube bundles, free from the post-modification, thus showing high reproducibility, in which the deviation of anodic current intensity of six electrodes prepared with same method did not exceed 4% (RSD, $n = 6$). Based on the remarkable analytical performance, the e-NCNF with good biocompatibility was successfully applied to determine the AA level as 134 ± 7 mM, in rat brain microdialysates.
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1. Introduction

Development of microelectrode with remarkable analytical performance such as high selectivity and good reproducibility, is of great importance for in vivo analysis in the complicated rat brain [1–5]. On the one hand, there are an amount of interferences coexisting in cerebral systems. Several electroactive species, for example, metal ions like copper ion, and neurotransmitters, can generate interference responses over that of target molecules, leading to the difficulty for selective detection in rat brain [3–7]. On the other hand, reproducible electrode performance is essentially important to provide reliable information, avoiding the determination error of person-to-person and electrode-to-electrode [6–10]. As one of the most popular microelectrodes, carbon fiber (CF) microelectrode has been widely employed for in vivo determination because of its high conductivity, excellent biocompatibility, and easy to be miniaturized [11–14]. Such CF microelectrode generally is subjected to surface modification by nanomaterials or organic molecules, in order to improve the selectivity and sensitivity. However, the manual modification for microelectrode surface usually makes the electrode performance inevitably influenced by the amount of nanomaterials or organic molecules, modification time, temperature, and so on [15–16], resulting in the difficulty for obtaining good reproducibility [17–19]. Therefore, development of novel microelectrode with engineered surface without post-modification is an urgent demand for in vivo analysis with high selectivity and good reproducibility.

Herein, we developed a new electrochemical approach for detection of cerebral ascorbic acid (AA) in rat brain microdialysates based on a novel nitrogen-doped carbon nanotube fiber (NCNF) microelectrode. As one of important antioxidants in brain science, alteration of AA level in the brain was considered as one of the biomarkers for brain diseases, such as ischemia, Alzheimer's disease, and Parkinson's disease, and so on [20–25]. AA is a typical inner-sphere reaction species, consequently, its electron-transfer kinetics highly sensitive to the electrode surface [26]. AA can be oxidized into dehydroascorbic acid through a two-electron and one-proton process followed by an irreversible hydrolysis to finally produce and electroinactive product of 2, 3-diketongulanic acid [27]. However, such irreversible electrochemical redox process of the ascorbate oxidation generally need a high overpotential at most types of electrodes, essentially making it difficult to selective detection of AA in practical sample because the coexisting electroactive species will produce great interferences on measurement signal. In view of distinct electronic and structural properties from other kinds of carbon nanomaterials, carbon nanotubes have become the star nanomaterials for AA determination [28–31]. The previous investigation has demonstrated that the carbon nanotubes could greatly facilitate the oxidation of AA at low potential [32–33]. Different from previous carbon fiber microelectrode modified by carbon nanotubes, the present NCNF was directly assembled by carbon nanotube bundles with uniform diameter. Thus, the NCNF electrode remained the excellent electrochemical catalytic properties for AA oxidation with a low working potential, 0.0 V vs. Ag/AgCl, as well as high sensitivity. More

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importantly, such NCNF essentially provided a facile way for microelectrode fabrication, and greatly improved the reproducibility of electrode due to avoiding the manual modification procedures. Finally, the NCNF microelectrode was successfully applied to determine the concentration of AA in rat brain microdialysates.

2. Experimental

2.1. Reagents and chemicals

Dopamine (DA), AA, iron(II) phthalocyanine (FePc), γ-aminobutyric acid (GABA), uric acid (UA), 3,4-dihydroxyphenylacetic acid (DOPAC), L-tyrosine (Tyr), D-tryptophan (Trp), homovanillic acid (HVA), D (+)-glucose, 5-hydroxyindole-3-acetic acid (5-HIAA), adenosine Association Tennis Professional (ATP), lactate (Lac), 5-hydroxytryptamine (5-HT), ascorbate oxidase (AAox) (Cucurbita species, EC 1.10.3.3), ammonium persulfate (APS), and *N*, *N*-methylene bisacrylamide (BIS) were all purchased from Sigma and used as supplied. Sodium chloride (NaCl), potassium chloride (KCl), monopotassium phosphate (KH_2PO4), magnesium chloride ($MgCl_2$), sodium bicarbonate ($NaHCO_3$), sodium sulfate (Na_2SO_4), and calcium chloride ($CaCl_2$) were purchased from Aladdin. Acrylic acid was obtained from Shanghai Dahe Chemical (Shanghai, China). Chemicals were at least analytical reagent grade and were used without further purification. Artificial cerebrospinal fluid (aCSF) was prepared by mixing NaCl (126 mM), KCl (2.4 mM), KH_2PO_4 (0.5 mM), $MgCl_2$ (0.85 mM), $NaHCO_3$ (27.5 mM), Na_2SO_4 (0.5 mM), and $CaCl_2$ (1.1 mM) into Milli-Q water, and the solution pH was adjusted to pH 7.4.

2.2. Synthesis of NCNF

The N-doped carbon nanotube film was synthesized from a template of aligned carbon nanotube sheet by chemical vapor deposition as previously reported [34]. The carbon nanotube fiber was dry-spun from N-doped carbon nanotube array at a rotating rate of 2000 rpm. The multiwalled carbon nanotube arrays were synthesized by chemical vapor deposition in a quartz tube furnace with a diameter of 2 in. In a typical synthesis, Fe (1 nm) and Al_2O_3 (10 nm) were sequentially deposited on a silicon substrate by electron beam evaporation and used as the catalyst. Ethylene with a flowing rate of 90 sccm was used as carbon source, and a mixture of Ar (400 sccm) and H_2 (30 sccm) was used as carrying gas. The synthetic reaction was performed at 740 °C for 15 min.

2.3. Preparation of CNTF microelectrodes

A NCNF was attached to a copper wire with silver conducting paste. Next, the NCNF together with the attached copper wire was carefully inserted into the capillary, in which the NCNF was exposed to one open tip of the capillary and Cu wire was extended to the other end of the capillary. Epoxy resin was injected drop-by-drop into the capillary for fixation. Excess epoxy on the NCNF was carefully removed with acetone to form microelectrodes. The microelectrode was thus dried at room temperature for one day and the exposed NCNF was carefully cut down to 4 mm length under microscopy. The as-prepared NCNF microelectrode was then sequentially sonicated in acetone, 3 M HNO_3, 1.0 M NaOH and water, each for 3 min, and finally subjected to electrochemical activation. The NCNF microelectrode was electrochemically pretreated in 0.1 M NaOH with +1.5 V for 100 s. The NCNF microelectrode was further electrochemically treated in 0.5 M H_2SO_4 with cyclic voltammetry within a potential range from −1.0 V to +1.0 V at a scan rate of 0.1 V s^{-1} until a stable cyclic voltammogram was obtained. The fabricated microelectrode was denoted as e-NCNF microelectrode hereafter. All potentials in the electrochemical measurement mentioned in this article were obtained using Ag/AgCl (saturated KCl) as reference electrode.

2.4. Apparatus and measurements

Electrochemical measurement was performed on a computer-controlled electrochemical analyzer (CHI 832, CHI instrument). The CF or NCNF microelectrode was used as working electrode and a platinum wire served as counter electrode. Scanning electron microscopy (SEM, Hitachi S4300-F microscope, Japan) and transmission electron microscopy (TEM JEOL JEM-2100F operated at 200 kV) were employed for characterization of NCNF. The morphology of the CNFs was observed by field emission scanning electron microscopy (FE-SEM) on a Hitachi S-4800 SEM. HRTEM observation was performed using a field emission transmission electron microscopy (FE-TEM) on a JEM-2100F operated at 200 kV. In order to avoid the beam damage on the MWCNTs, a very low electron dose was used during the observation. X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Japan) equipped with an Al Kα (1486.6 eV photons) was used to characterize the carbon nanotube fiber.

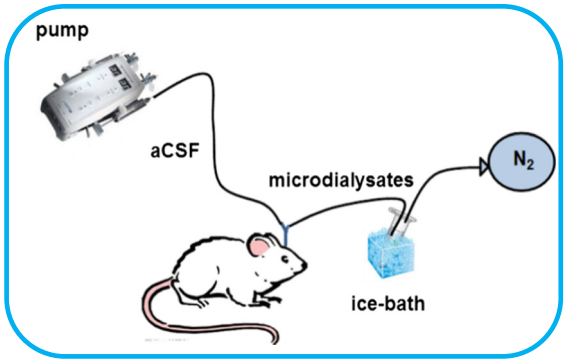
2.5. In vivo experiments

All procedures involving animals were conducted with approval of the Animal Ethics Committee in East China Normal University, China. Male Wistar normal rats (100–120 g) were purchased from Shanghai Yisen Biotechnology Co., Ltd., China. Then, the rat (200–250 g) was used for in vivo experiments and anesthetized with chloral hydrate (initial dose of 300 mg kg^{-1} (i. p.) with additional doses of 50 mg kg^{-1} (i. p.) as needed to maintain anesthesia and wrapped in a homeothermic blanket (Beijing Tide-Gene Biotechnology Development Center). The rat was placed in a stereotaxic frame with the incisor bar set at 5 mm above the interaural line and appropriately placed holes were drilled through the skull. The microdialysis probe (CMA/110/111 Tub) was implanted in the striatum at the site of 2.5 mm anterior to bregma, 2.5 mm lateral from midline, and 7.0 mm below dura. In order to reduce injury to the rat, the microdialysis probe should be implanted into the striatum of rats slowly within 30 min with special care. The experimental setup of microdialysis is shown in Scheme 1. Throughout the surgery, the body temperature of the animals was maintained at 37 °C with a homeothermic blanket. The microdialysis probe (CMA/110/111 Tub) was implanted into the striatum of rats and was perfused with aCSF solution at 2 μL min^{-1} for at least 90 min for equilibration. Cyclic voltammetry (CV) was employed to study electrochemical behavior of AA oxidation.

3. Results and discussion

3.1. Characterization of NCNF

Pure nanotube fiber was spun from nanotube arrays synthesized by a chemical vapor deposition process. A typical SEM image of NCNF was shown in Fig. 1A. In contrast to conventional CF, The NCNF was assembled by carbon nanotube bundles, exhibiting an array structure with a



Scheme 1. The schematic illustration about the experimental setup of microdialysis.

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