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No cytotoxic nitrogen-doped carbon nanotubes as efficient metal-free electrocatalyst for oxygen reduction in fuel cells

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ABSTRACT

Bamboo-like nitrogen-doped carbon nanotubes (NCNTs) with different nitrogen content have been synthesized by chemical vapor deposition (CVD) under different reaction temperature of 600–900 °C. The butylamine and FeY have been used as precursor and catalyst, respectively. The electrocatalytic property of the NCNTs catalyst in oxygen reduction was examined by cyclic voltammetry. The results revealed that the NCNTs catalyst has higher catalytic activity than the commonly used Pt/C catalyst (Pt-CNTs, 20% of Pt/C, BASF), suggesting potential applications in fuel cells. On the other hand, the cytotoxic effects of NCNTs materials showed no cytotoxic to SPCA-1 cells, of which Pt-CNTs and CNTs particles indicated notably high cytotoxic. From these results, more application fields might be found for NCNTs except for as cathodic catalyst in fuel cells (FCs).

1. Introduction

Alkaline fuel cells with platinum-loaded carbon as an electrocatalyst for the four-electron the oxygen reduction reaction (ORR) were developed for the Apollo lunar mission in the 1960s [1], and platinum (Pt) nanoparticles have long been regarded as the best catalyst for ORR in fuel cells [2]. But the large-scale practical application of fuel cells has not been realized. That is because that the high cost of the Pt catalysts, together with the limited reserves of Pt in nature, has been shown to be the major “showstopper” to mass market fuel cells for commercial applications.

Recently, intensive research efforts in reducing or replacing Pt-based electrode in fuel cells have led to the development of new ORR electrocatalysts, including Pt-based alloys [3], transition metal chalcogenides [4], enzymatic electrocatalytic systems [5], conducting poly (3,4-ethylenedioxythiophene) (PEDOT)-coated membranes [6], and carbon nanotube-supported metal particles [5–7]. Apart from their use as the noble metal-catalyst supports, nanotubes have shown outstanding electrocatalytic activities due to their unique electrical and chemical properties [8]. Doping with different elements could make carbon-based nanomaterials even better electrocatalytic activities and could provide a promising method to tailor specific properties of carbon nanomaterials [9]. Such as, nitrogen-in-corporation could efficiently introduce chemically active sites into carbon nanomaterials because conjugation between the nitrogen lone-pair electrons and the graphene π-system [3,4,7] may create nanomaterials with regulated electronic properties. Dai et al. reported that the vertically aligned nitrogen-doped carbon nanotube arrays demonstrated high electrocatalytic activities for ORR [10], which possessed a great potential for low-cost nonplatinum catalysts for fuel cell cathodes. Bamboo-like nitrogen-doped carbon nanotubes have been used as hemoglobin immobilization [11] and metal-free cathodic catalysts for oxygen reduction in microbial fuel cells under neutral conditions [12]. However, as far as we are aware, there are a few studies which are aimed at the applications of bamboo-like nitrogen-doped carbon nanotubes synthesized by simple CVD method at FCs cathode [1,2]. The cytotoxic effects of NCNTs against cells have never been reported.

Thus, the main purpose of this study is to examine the feasibility of bamboo-like NCNTs synthesized by simple CVD method as metal-free cathodic catalysts for oxygen reduction, and compare electrocatalytic activities of NCNTs with that of commercial Pt-carbon and CNTs as the cathodic catalyst in FCs. To achieve these aims, the performance of NCNTs as catalyst on cathodic oxygen reduction is elucidated by electrochemical measurements. The electrocatalytic activities of NCNTs as catalyst were evaluated by comparison with the commercially available Pt-CNTs catalyst and CNTs particles, demonstrating obviously high catalytic activity. In addition, the cytotoxic effect of NCNTs have been studied by cell

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assay and showed the higher safeness than commercial Pt-CNTs and CNTs. These results indicated that NCNTs materials have better practical application than Pt-CNTs and CNTs as cathodic catalyst in FCs and might be used in more other fields.

2. Experimental

2.1. NCNTs preparation

Bamboo-like NCNTs with nitrogen content of 2.7–7.8% were synthesized at different reaction temperature by CVD as described previously [13], about 0.5 g FeY catalyst powder was placed in the central part of a horizontal quartz tube in the furnace. After the reaction chamber was evacuated and flushed with N_2 for several times to remove oxygen and moisture, the reactor was heated to reaction temperature at a rate of 20 °C/min in N_2. Butylamine was then switched into the system for about 120 min, by the carrying gas of N_2 at a flow rate of 20 mL/min passing through a butylamine saturator at room temperature. The feed rate of butylamine was estimated to be about 10 mg/min. After that, the reactor was cooled to room temperature in N_2 and dark product was obtained. Commonly, the purification process for NCNTs was as follows: NCNTs were firstly washed three times by 20% HF solution, then soaked in 20% HF solution overnight and finally heat-dried at 105 °C for 2 h. Unless otherwise stated, all chemicals were purchased from Sigma–Aldrich and used without any further purification. All the solutions were prepared with doubly distilled water.

2.2. Material and electrochemical analyses

The NCNTs were characterized by transmission electron microscopy (TEM, JEOL-JEM-1005) and high-resolution TEM HRTEM, JEM2010. Characterization: Powder XRD patterns were recorded on a (D8-Advance, Germany) equipped with CuKa radiation (40 kV, 20 mA) at a rate of 0.1°/min over the range of 10–70° (2θ). The N/C atomic ratio was analyzed by X-ray photoelectron spectroscopy (XPS, VG ESCALAB MK- II) excited by an X-ray source of Mg $K\alpha$ ($h\nu$ = 1253.6 eV) in an ultrahigh vacuum chamber with a base pressure of $<2 \times 10^{-8}$ Torr.

Electrochemical measurements were conducted on a computer-controlled electrochemical workstation (CHI 760C, CH Instrument, USA) with a typical three-electrode cell equipped with gas flow systems. A glassy carbon (GC) electrode coated with NCNTs (NCNTs/GC), Pt/C (Pt/C/GC) or CNTs was used as the working electrode, an Ag/AgCl electrode (3 M KCl-filled) as the reference electrode, and a platinum wire as the counter electrode. All of the potentials in this study were with respect to the Ag/AgCl reference electrode. 0.1 M KOH solution saturated with oxygen was applied as the electrolyte for both cyclic voltammogram (CV). CV was used to characterize electrochemical activities on the electrode surface by measuring the current response at an electrode surface to a specific range of potentials with a scan rate of 0.1 V s^{-1}. The potential was varied from 1.0 to −1.0 V vs. Before the CV experiments, catalyst ink was coated onto the glassy carbon electrode and oxygen gas was saturated in the electrolyte by bubbling the gas for 20 min. All electrochemical experiments (except as noted) were carried out at room temperature (25 ± 1 °C).

2.3. Cell assay

Briefly, SPCA-1 cancer cells were seeded into 35 mm × 10 mm petri dish (corning) at the concentration of 1×10^5 cells/ml in RPMI-1640 plus 10% FBS culture medium in 2 mL. Cells were allowed to adhere to the petri dish for 24 h. Before adding particles, the culture media were replaced with pH 7.4 RPMI-1640 plus 10% FBS with 1% penicillin and streptomycin. To each petri dish, 100 μL of the BLM

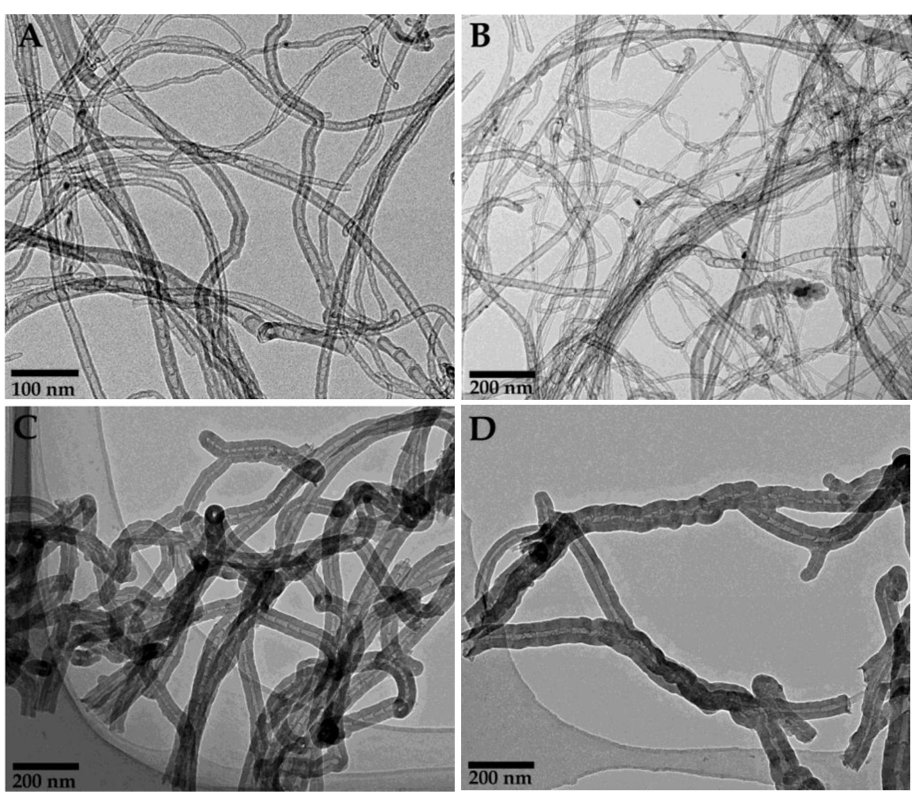

Fig. 1. TEM images of NCNTs synthesized at different reaction temperature. A: 600 °C; B: 700 °C; C: 800 °C; D: 900 °C.