Contents lists available at ScienceDirect

Chinese Chemical Letters

Original article

Rational design of three-dimensional nitrogen and phosphorus co-doped graphene nanoribbons/CNTs composite for the oxygen reduction

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ARTICLE INFO

ABSTRACT

In the present work, we report nitrogen and phosphorus co-doped 3-D structured carbon nanotube intercalated graphene nanoribbon composite. The graphene nanoribbons are prepared via partial exfoliation of multi-walled carbon nanotubes. In the graphene nanoribbons/CNTs composite, carbon nanotubes play a role of skeleton and support the exfoliated graphene nanoribbons to form the stereo structure. After high temperature heat-treatment with ammonium dihydrogen phosphate, the unique structure reserves both the properties of carbon nanotube and graphene, exhibiting excellent catalytic performance for the ORR with excellent onset and half-wave potential, which is similar to commercial Pt/C electrocatalysts.

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1. Introduction

The massive consumption of global energy resources resulted in the shortage of fossil fuels and severe environmental problems. Proton exchange membrane fuel cells (PEMFCs) have attracted widespread interests due to their high energy density and negligible emission of harmful byproducts. Oxygen reduction reaction, the reaction rate control step in PEMFCs, has been extensively studied due to the urgent requirement of efficient electrocatalysts to accelerate its reaction rate. Platinum-based catalysts are well-known as the most active catalysts for the ORR. However, the scarcity resource, high cost and poor durability hinder its further commercialization. Therefore, it is of vital importance to explore platinum-free catalyst to improve the sluggish kinetics of the ORR [1].

In recent years, graphene-based nanomaterials have shown excellent electrocatalytic performance for ORR [2,3]. However, the two-dimensional graphene sheets incline to agglomerate during thermal annealing and electrochemical measurements due to the strong π–π interaction. The agglomeration of graphene layers would significantly reduce the specific surface area and even lower the electrocatalytic performance. Therefore, it is of vital importance to explore proper methods to avoid the re-stacking of graphene layers. Yu et al. incorporated multi-walled carbon nanotubes (MWCNTs) with graphene layers to form a three dimensional N doped aerogel structure [4]. Qiao et al. grew graphene layers on hierarchical ordered porous carbon materials which combined the advantages of both hierarchical porous carbon and graphene [5]. Moreover, the kinetics of the ORR would be significantly enhanced via heteroatom (e.g. B [6,7], N [8–11], P [12,13], S [14,15] and I [16]) doping. Recent studies have also revealed the existence of a synergistic coupling effect, predicting that co-doping would offer much more active sites than single atomic doping [17].

In this paper, graphene nanoribbons/CNTs composite was successfully obtained by unzipping MWCNTs with different exfoliation degree. The CNT with partially unzipped outer-wall formed a remained inner CNT skeleton supported graphene nanoribbons, with a three dimensional structure, inhibiting the restacking of graphene layers. After heat-treatment with

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ammonium dihydrogen phosphate at high temperature, N and P atoms were successfully co-doped in the nanocomposite. The unique 3-D structure reserves both the properties of CNT and graphene, exhibiting excellent catalytic performance for the ORR with excellent onset and half-wave potential.

2. Experimental

2.1. Preparation of graphene/nanotubes composite

The graphene nanoribbons/CNTs composite was prepared via a Hummers method [18]. First, 2.0 g of MWCNT (20–30 nm in diameter and 10–20 μm in length) was added into a 500 mL three-necked round-bottomed flask filled with 300 mL concentrated H_2SO_4. The mixture was continuously mechanical stirred for 12 h at room temperature. 4.0 g of $KMnO_4$ was then slowly added into the flask and mechanical stirred for 1 h, and then heated to 70 °C for 1 h. After cooled down to room temperature, the mixture was poured into a 3000 mL baker filled with 25 mL of H_2O_2 and 500 mL of ice. Resulting precipitate was obtained by suction-filtered in air and washed with copious amounts of distilled water until the pH was 7 and then underwent a freeze-drying process. The obtained material was denoted as CNT-2 (the mass ratio of MWCNT to $KMnO_4$ was 1:2). Similarly, by changing the ratio of MWCNT to $KMnO_4$ to 1:0 and 1:4, the materials were denoted as CNT-0 and CNT-4, respectively.

2.2. Preparation of N/P co-doped exfoliation MWCNT

The mixture of 0.1 mg of partially unzipped CNTs and 1.0 g of ammonium dihydrogen phosphate ($NH_4H_2PO_4$) was first grounded into fine powder in a mortar, and then annealed in a tube furnace at a heating rate of 10 °C min^{-1} for 2 h under the protection of N_2 to obtain nitrogen and phosphorus co-doped graphene nanoribbons/CNTs composite (NPCNT-2). For comparison, NSCNT-0 and NSCNT-4 were also prepared accordingly.

2.3. Physical characterization

X-ray photoelectron spectroscopy (XPS) data were obtained by using an AXIS-ULTRA DLD-600W Instrument. Fourier transform infrared (FT-IR) spectra of the samples were collected on VERTEX 70, BRUKER Inc. S/TEM images were obtained using an 300 keV field-emission scanning transmission electron microscopy. Raman spectra were taken by a LabRam HR800 spectrometer with a 532 nm laser excitation.

2.4. Electrochemical measurements

The electrochemical measurements were performed on a CHI 760e electrochemical workstation equipped with a high speed rotator from Pine Instruments in which a three-electrode system consisting of a glassy carbon working electrode (5 mm in diameter), a piece of carbon paper as counter electrode to

eliminate the contamination from Pt, and reverse hydrogen electrode (RHE, $E^\theta = -0.768$ V vs. SHE) as reference electrode at room temperature (298 K) in 0.1 mol L^{-1} KOH solution. 5 mg of samples was dispersed in 1 mL of isopropanol/Nafion hybrid solutions and ultrasonic dispersed to form homogeneous ink. 16 μL of ink was drop onto the glassy carbon substrate, and dried naturally. The mass loading of commercial Pt/C is about 15 μg cm^{-2} which worked as a benchmark for the comparison of the as synthesized samples. The cyclic voltammetry and linear sweep voltammetry of the samples were operated in N_2- or O_2-saturated 0.1 mol L^{-1} KOH solution at a scanning rate of 50 mV s^{-1} or sweep rate of 5 mV s^{-1}. Electrons transfer number (n) was calculated from the following Koutecky–Levich (K–L) equation:

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_D} \tag{1}$$

$$j_D = 0.62nFAD^{2/3}v^{-1/6}w^{1/2}C_{O_2} \tag{2}$$

In the two equations, j, j_K, j_D represent the measured current, kinetic current and limiting diffusion current, respectively, n is the overall electrons transfer number, F is the Faraday constant (96,485 C mol^{-1}), A is the electrode area ($A = 0.196$ cm^2), D is the O_2 diffusion coefficient ($D = 1.9 \times 10^{-5}$ cm^2 s^{-1}), v is the kinematic viscosity of the electrolyte ($v = 1.13 \times 10^{-2}$ cm^2 s^{-1}), ω is the rotating speed of RDE, C_{O_2} is the concentration of O_2 $\left(C_{O_2} = 1.2 \times 10^{-3} \text{ mol L}^{-1} \right)$.

3. Results and discussion

Graphene nanoribbons/CNTs composite derived from the oxidization and exfoliation of MWCNTs are usually employed as precursor for heteroatom doping. Fig. 1a and b shows the transmission electron microscopy (TEM) image of NPCNT-0 and dark-field scanning transmission electron microscopy (DF-STEM) image of NPCNT-4, respectively. NPCNT-0 remains integrated one-dimensional tubular structure while NPCNT-4 was almost completely exfoliated and increased the layer thickness due to the strong π–π interaction during thermal annealing process. Enlarged magnification DF-STEM images of NPCNT-2 can be seen from Fig. 1c–e. A network structure with CNTs supported exfoliated graphene nano-ribbons can be seen from the overview DF-STEM image (Fig. 1c). Moreover, longitude opening "mouth" like structure (Fig. 1d–e) on CNTs indicated the longitude unzipping of MWCNTs. The unique opening structure enables the electrolyte easily entering the CNTs and facilitated the contact between oxygen and electrolyte. However, the mechanical incorporating of MWCNTs with graphene layers is difficult to form a uniform graphene layer-MWCNTs-graphene layer structure via a mechanical incorporating method. Therefore, this unique stereo structure obtained by partial exfoliation of MWCNTs would combine the high electro-conductivity of CNTs and ultra-high specific surface area of graphene nanoribbons together which is better than the simple mechanical incorporating MWCNTs with graphene layers. The DF-STEM image and the corresponding
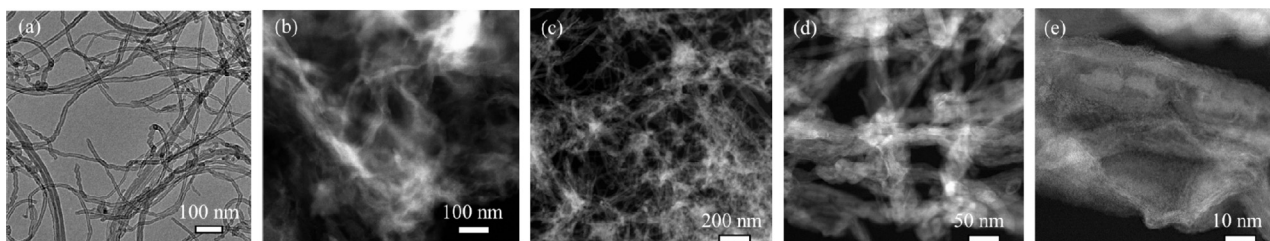

Fig. 1. (a) TEM image of NPCNT-0, (b) DF-STEM image of NPCNT-4 and (c–e) the enlarged DF-STEM images of NPCNT-2.