Graphical Abstract

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

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Nitrogen and phosphorus co-doped graphene nanoribbons/CNTs composite with 3-D stereo structure obtained by oxidation and exfoliation of multi-walled carbon nanotubes and following high temperature heat-treatment work as efficient electro-catalyst for the oxygen reduction reaction.

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

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ARTICLE INFO

Article history:

Received 14 December 2015

Received in revised form 30 December 2015

Accepted 7 January 2016

Available online

Keywords:

Graphene nanoribbons

Carbon nanotube

Doping

Electrocatalyst

Oxygen reduction reaction

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.

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 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

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The graphene nanoribbons/CNTs composite was prepared via a Hummers method [18]. Firstly, 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 $^\circ\text{C}$ 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 ($\text{NH}_4\text{H}_2\text{PO}_4$) was first grounded into fine powder in a mortar, and then annealed in a tube furnace at a heating rate of 10 $^\circ\text{C}/\text{min}$ 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, $E^0 = -0.768 \text{ V vs. SHE}$) 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 $\mu\text{g cm}^{-2}$ 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:

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_D} \quad (1)$$

$$j_D = 0.62nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C_{\text{O}_2} \quad (2)$$

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 ($A = 0.196 \text{ cm}^2$), D is the O_2 diffusion coefficient ($D = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinematic viscosity of the electrolyte ($\nu = 1.13 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$), ω is the rotating speed of RDE, C_{O_2} is the concentration of O_2 ($C_{\text{O}_2} = 1.2 \times 10^{-3} \text{ mol L}^{-1}$).

3. Results and discussion

Graphene nanoribbons/CNTs composite derived from the oxidization and exfoliation of MWCNTs are usually employed as precursor for heteroatom doping. Figure 1(a-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. 1(c-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 (Figure 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 energy dispersive spectrometer (EDS) elemental distribution analysis in Fig. 2(a-d) show homogenous distribution of C,

N and P element. Due to the high annealing temperature of 900 °C, $\text{NH}_4\text{H}_2\text{PO}_4$ would experience a complete decomposition at the extreme temperature condition. Therefore, N and P elements were successfully doped into the carbon structure.

The surface elemental composition of NPCNT-2 was determined by XPS analysis. Fig. 3 (a-c) shows the high-resolution XPS spectrum of C 1s, N 1s and P 2p, respectively. The C 1s spectrum was deconvoluted into four single peaks which present C-C bond (284.6 eV), C-P bond (285.5 eV), C-N bond (287.2 eV) and COOH (289.0 eV) bond, further confirming that N and P atoms have been successfully doped into the stereo framework [19, 20]. The high-resolution N1s spectrum revealed three single N species peaks at 398.7 eV, 399.8 eV and 401.0 eV which correspond to pyridinic N, pyrrolic N and graphitic N, respectively [21]. Recent researches have been recognized that graphitic N and pyridinic N play critical roles in determining the ORR performance of the carbon based materials [5]. Graphitic N mainly accounts for the conductivity and determines the limiting current density, while pyridinic N leads to the interaction of oxygen and controls the onset potential. Moreover, NPCNT-2 containing P atoms deconvoluted into two characteristic peaks shown at 132.8 eV and 134.1 eV, attributing to the C-P bond and P-O bond, respectively [22, 23]. Raman spectra of all three samples in Figure 3d show the characteristic D band, G band and 2D band located at $1350 \pm 20 \text{ cm}^{-1}$, $1575 \pm 20 \text{ cm}^{-1}$ and $2750 \pm 20 \text{ cm}^{-1}$, respectively, which have been reported to be signatures of graphitic carbon materials [24]. The G band and 2D band are attributed to the first order scattering of the E_{2g} mode of sp² carbon atoms while the D band is induced by defects or disorder [25]. The intensity ratio (I_D/I_G) of NSCNT-0, NSCNT-2 and NSCNT-4 are calculated to be 0.90, 0.97 and 1.11, respectively. The increase of I_D/I_G is due to the partial exfoliation of MWCNT which produces lots of defects. Moreover, the G band of NSCNT-2 and NSCNT-4 slightly shift toward higher frequency with respect to that of NSCNT-0, indicating the successfully doping of heteroatoms in the composite [26, 27].

The electrocatalytic performance of the NPCNT samples towards ORR was first studied via cyclic voltammetry (CV) in N_2 - and O_2 -saturated 0.1 M KOH solution. Oxygen reduction peaks can be obviously seen in O_2 -saturated solution when compared with the CV curves in N_2 -saturated solution (Fig. 4a). Moreover, NPCNT-2 showed more positive oxygen reduction peak potential (0.76 V) than NPCNT-0 and NPCNT-4 samples (0.65 V and 0.74 V, respectively), indicating excellent electrocatalytic activity of the NPCNT-2 towards ORR. To better understand the ORR catalytic activity of the samples, linear sweep voltammetry (LSV) measurement was conducted and compared with Pt/C catalyst. Among the investigated samples, the NPCNT-2 displayed the best ORR activity in terms of onset and half wave potentials (0.90 V and 0.77 V vs. RHE) which was slightly lower than commercial Pt/C (0.99 V and 0.78 V, Fig. 4b), while the NPCNT-0 and NPCNT-4 showed poor onset and half wave potential and limiting diffusion current density. Therefore, we can conclude that a moderate exfoliation of MWCNT resulting in the remaining carbon nanotube skeleton supported the exfoliated graphene ribbons, forming a three dimensional structure, which promoted the limiting diffusion current density of NPCNT-2 (equal to Pt/C). However, fully or inadequate exfoliation would result in poor catalytic activity. The poor performance of NPCNT-4 was probably caused by the agglomeration of graphene ribbons after high temperature calcination procedure. The Tafel plots for ORR on the three samples and Pt/C were calculated by plotting the logarithm of the kinetic current density derived from the LSV curves of Figure 4b to further investigate the electrode kinetics. As shown in Figure 4c, the Tafel slope on NPCNT-2 is $\sim 46.7 \text{ mV dec}^{-1}$, which is much lower than that of NPCNT-0 ($\sim 57.8 \text{ mV dec}^{-1}$), NPCNT-4 ($\sim 50.0 \text{ mV dec}^{-1}$) and Pt/C ($\sim 92.3 \text{ mV dec}^{-1}$), indicating a more favorable ORR kinetic on NPCNT-2. The Tafel slope in low overpotential indicated the first electron transfer step by breaking the O-O bond is probably the rate determining step in a direct 4-electron O_2 reduction [28-30]. Therefore, the lower Tafel slope of NPCNT-2 undergoes a faster ORR rate.

The polarization curves for ORR with different rotation speeds are shown in Fig. 4d. The ORR polarization curves show a diffusion-controlled region at voltages lower than 0.6 V, a diffusion-kinetic combined region (0.6 – 0.8 V), and a kinetic-controlled region at voltages higher than 0.8 V (vs. RHE). The corresponding Koutecky-Levich plots (j vs. $\omega^{-1/2}$) in Fig. 4e constructed from equation (1) and (2) show that diffusion current linearly scale with $\omega^{-1/2}$ and demonstrate a first-order ORR kinetics at potentials of 0.65 V, 0.70 V and 0.75 V [6]. The electron transfer number (n) of NPCNT-2 was quantitatively calculated to be 3.82, 3.97 and 3.94 (at the above three potentials, respectively) by using the slopes of these plots, indicating a 4-electron pathway dominated ORR process.

Fuel crossover effect is an important issue challenging the cathode catalysts in current fuel cell techniques [31, 32]. The methanol tolerance of NPCNT-2 and Pt/C catalysts towards ORR were evaluated through chronoamperometric measurements at constant potential of 0.7 V and rotation speed of 1600 rpm. When injected 1 M methanol into the solution at 400 s (Fig. 4f), NPCNT-2 showed slight fluctuation and remains stable current response while Pt/C suffered a sharp loss of 23.5% activity. These results indicate the better methanol tolerance of NPCNT-2 than Pt/C catalyst which is suitable as cathode catalyst for alkaline fuel cells.

4. Conclusion

In summary, N and P co-doped 3-D structured graphene nanoribbons/CNTs composite was successfully prepared by unzipping of MWCNTs and following the heat-treatment with ammonium dihydrogen phosphate. The unique structure reserved both the properties of carbon nanotube and graphene, exhibited excellent catalytic performance for the ORR with excellent onset and half-wave potential when compared with NPCNT-0, NPCNT-4 and Pt/C. Moreover, NPCNT-2 catalyst showed much better methanol tolerance in comparison to Pt/C.

Acknowledgment (This section is optional)

This work was supported by the National Natural Science Foundation (Nos. 21306060, 21573083), the Program for New Century Excellent Talents in Universities of China (No. NCET-13-0237), the Doctoral Fund of Ministry of Education of China (No. 20130142120039), the Fundamental Research Funds for the Central University (Nos. 2013TS136, 2014YQ009). We thank Analytical and Testing Center of Huazhong University of Science and Technology for allowing us to use its facilities. S/TEM work was carried out at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences (No. DE-SC0012704).

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Figure 1. (a) TEM image of NPCNT-0; (b) DF-STEM image of NPCNT-4; (c-e) The enlarged DF-STEM images of NPCNT-2.

Figure 2. (a) DF-TEM image of NSCNT-2 with the corresponding carbon (b), nitrogen (c) and phosphorus (d) of elemental mapping images, respectively.

Figure 3. High-resolution XPS spectrum of C 1s (a), N 1s (b) and P 2p (c) for NPCNT-2; (d) Raman spectra of NPCNT-0, NPCNT-2 and NPCNT-4.

Figure 4. (a) CV curves of NPCNT samples at a scan rate of 50 mV s⁻¹ in N₂- and O₂- saturated 0.1 mol L⁻¹ KOH solution; (b) ORR polarization curves of NPCNT samples and Pt/C at a rotating speed of 1600 rpm in O₂-saturated 0.1 M KOH solution; (c) Tafel plots of ORR polarization curves of (b); (d) ORR polarization curves of NPCNT-2 in O₂-saturated 0.1 mol L⁻¹ KOH solution at different rotating speed; (e) Koutecky-Levich plots under potentials at 0.65 V, 0.70

V and 0.75 V; (f) i-t chronoamperometric methanol tolerance measurement of NPCNT-2 and Pt/C at potential of 0.7 V by injecting 1 mol L⁻¹ methanol at 400 s in 0.1 mol L⁻¹ KOH solution.