



Urea-treated carbon nanofibers as efficient catalytic materials for oxygen reduction reaction



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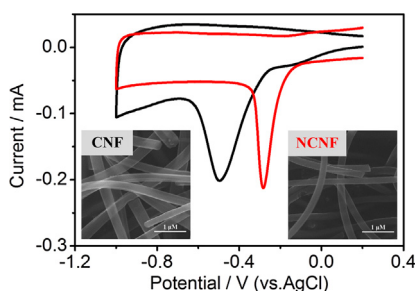
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HIGHLIGHTS

- Nitrogen-doped carbon nanofibers (NCNFs) were prepared by post-treatment method.
- Higher content of pyrrolic-N was observed in NCNFs than that of CNFs.
- NCNFs exhibited enhanced electrocatalytic performance for oxygen reduction reaction.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 10 August 2014

Received in revised form

10 September 2014

Accepted 16 September 2014

Available online 28 September 2014

Keywords:

Electrospinning

Nitrogen-doped carbon nanofibers

Oxygen reduction reaction

Electrocatalysis

ABSTRACT

Nitrogen-doped carbon nanofibers (NCNFs) are prepared by the thermal treatment of carbon nanofibers (CNFs) using urea as nitrogen source. Scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy have been employed to characterize the morphology and composition of CNFs and NCNFs. Compared with CNFs, NCNFs display thinner diameter, rougher surface and higher content of pyrrolic-N. As a metal-free catalyst for ORR, NCNFs exhibit comparable catalytic activity, significantly enhanced long-time stability and selectivity in comparison with commercial available Pt/C catalyst. Importantly, the self-supported NCNFs films could be conveniently utilized for electrode modification which is attractive in fuel cells. This work offers a promising metal-free catalyst as an alternative for Pt/C catalyst.

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1. Introduction

High-performance catalysts for the oxygen reduction reactions (ORR) have been considered as one of critical issues in the field of fuel cells. [1,2] Pt-based catalysts have been extensively explored for the excellent electrocatalytic activity. However, high cost, poor stability and low tolerance to the crossover effect significantly limit their large-scale applications in fuel cells [3].

Recently, state-of-the-art nitrogen-doped carbon nanomaterials have attracted enormous interest as promising substitutes for Pt-based catalysts [4–6]. According to previous reports, doping nitrogen into the carbon nanomaterials could improve the interaction between carbon atoms and guest molecules, leading to the enhancement of electrocatalytic performance [7]. Up to now, the incorporation of nitrogen into the carbon matrix could be achieved during the preparation procedure or through the post-treatment of carbon nanomaterials. To dope nitrogen into the carbon structure in situ, nitrogen-doped carbon nanomaterials are always directly synthesized using nitrogen-containing precursors such as melamine [8], urea [9], pyrrole [10] and acetonitrile [11]. As for the

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latter method, the carbons are usually treated in the ammonia (NH_3) containing atmosphere at elevated temperature. Most of these studies are focused on the nitrogen-doped carbon nanotubes and graphene; however, few investigations are aimed at the electrospun nitrogen-doped carbon nanofibers (NCNFs) [12,13]. Although carbon nanofibers (CNFs) with certain content of nitrogen could be obtained simply by the carbonization of electrospun polyacrylonitrile (PAN) nanofibers, the resulting CNFs show poor catalytic activity toward ORR. In fact, the nitrogen types in the carbons played an important role on the catalytic ability [14]. Qiu et al. carbonized the electrospun PAN nanofibers in NH_3 leading to the high content of pyrrolic-N and superior electrocatalytic activity toward ORR [15]. Our group has also synthesized electrospun NCNFs with high oxygen reduction activity by reutilizing the nitrogen-containing by-products as the nitrogen source [16]. Nevertheless, how to improve electrocatalytic activity of the electrospun CNFs for ORR is rarely studied.

Herein, we developed a simple method for the preparation of NCNFs by thermal post-treatment of electrospun carbon nanofibers using urea as nitrogen source. Compared with CNFs, the as-prepared NCNFs show smaller diameter, rougher surface and higher content of pyrrolic-N. When utilized as metal-free electrocatalyst for ORR, NCNFs exhibited comparable catalytic activity, enhanced long-time stability and better electrochemical selectivity in comparison with commercial Pt/C catalyst.

2. Experimental section

2.1. Materials

Polyacrylonitrile (PAN, $M_w = 150,000$) and nafion solution (5 wt.%) were purchased from Sigma–Aldrich. Potassium hydroxide (KOH), dimethylformamide (DMF, $\geq 99\%$) and methanol ($\geq 99\%$) were acquired from Beijing Chemical Co.; urea and platinum on carbon (20 wt. % Pt/C, Johnson Matthey) was obtained from Aladdin Industrial Inc. and Alfa Aesar, respectively. All other reagents were used as received. All the solutions were prepared by the double-distilled water.

2.2. Preparation of self-supported NCNFs films

The pristine CNFs were prepared by the carbonization of electrospun PAN nanofibers films. Typically, electrospun PAN nanofibers were prepared by 10 wt. % PAN electrospinning solution. Stabilization and carbonization was performed as follows: (1) stabilized at 250°C in air for 180 min, (2) heat up to 900°C for 60 min, (3) cooled down to room temperature in nitrogen.

For NCNFs, CNFs and urea were placed in a high-temperature furnace with the mass ratio of 1: 10 as shown in Scheme 1. Then, carbonization was performed by heating up to 900°C for 30 min with a heating-up rate of $10^\circ\text{C min}^{-1}$, then cooling down in nitrogen atmosphere.

2.3. Characterization

Scanning electron microscopy (SEM) experiments were performed on a PHILIPS XL-30 ESEM with an accelerating voltage of



Scheme 1. The preparation of NCNFs.

20 kV. Transmission electron microscopy (TEM) images were obtained on a TECNAI G2 with the accelerating voltage of 200 kV. X-Ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo ESCALAB 250 instrument equipped with Al $K\alpha$ radiation.

2.4. Electrochemical measurements

The NCNFs film was cut to the disk shape, and then adhered onto the glassy carbon electrode (GCE) using 0.5 wt. % nafion solution. For comparison, commercial Pt/C catalyst and pristine CNFs suspension was prepared in ethanol with the content of 4 mg mL^{-1} . The suspension was casted on the GCE, and nafion solution was also used. All the electrochemical measurements were performed on a CHI 832C electrochemical workstation, using a three-electrode system comprising by the modified GCE as the working electrode, a Pt plate as the counter electrode, and an Ag/AgCl (saturated KCl) electrode as reference electrode. The sample-modified working electrode was prepared by the same method as for CVs. The electrolyte saturated with O_2 or N_2 was bubbled for at least 30 min before experiments.

3. Results and discussion

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to characterize the structure and morphology of CNFs and NCNFs. The average diameter of NCNFs (ca. 232 nm) displays an obviously decrease in contrast to that of CNFs (ca. 303 nm) (Fig. 1). Additionally, a rougher surface for NCNFs could be observed in comparison with CNFs (Fig. 1C and D). These results may origin from the surface etching and nitrogen doping by nitrogen-containing gaseous compounds, particularly NH_3 , formed during the decomposition process of urea [17]. The radicals (such as NH and NH_2) generated by NH_3 at elevated temperature could replace the oxygen-containing groups by nitrogen-containing groups on the surface of carbons [18,19].

The XPS spectra for CNFs (Fig. 2A) and NCNFs (Fig. 2C) demonstrate the presence of C 1s (284 eV), O 1s (540 eV) and N 1s (400 eV). The nitrogen content of CNFs and NCNFs were estimated to be 5.5% and 2.1%, respectively. Moreover, it is reported that the forms of nitrogen in carbons play a more important role compared with the content of nitrogen for catalytic properties [15]. To exploit the forms of nitrogen in CNFs and NCNFs, high-resolution N 1s spectra measurements were carried out. Generally, the nitrogen doped into carbon nanomaterials could be in the forms of pyridinic-N ($398.7 \pm 0.3\text{ eV}$), pyrrolic-N ($400.4 \pm 0.3\text{ eV}$) and graphitic-N ($401.4 \pm 0.3\text{ eV}$) [20,21]. All these forms of nitrogen were found in CNFs and NCNFs (Fig. 2B and D). It is noteworthy that higher content of pyrrolic-N was observed in NCNFs (53%) than that in CNFs (26%) which is in good agreement with our previous work [16].

Benefiting from the unique self-supported structure, NCNFs films could be directly utilized as the electrode for electrochemical experiments. In this work, the electrocatalytic performance of NCNFs was evaluated by ORR using a NCNFs modified GCE as working electrode in the O_2 -saturated 0.1 M KOH solution (Fig. 3). The ORR peak potential at NCNFs is -0.27 V , significantly positive than that at CNFs (-0.50 V), suggesting a superior oxygen reduction ability. Moreover, rotating disk electrode (RDE) measurements were also performed to study the electrocatalytic activity at NCNFs, commercial Pt/C and CNFs toward ORR. As shown in Fig. 3B, the onset potential at CNFs, NCNFs and Pt/C is -0.17 V , -0.031 V and 0.048 V , respectively. Accordingly, the ORR onset potential at NCNFs is only ca. 79 mV negatively than that at Pt/C, indicating a comparable catalytic activity toward ORR.

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