



Nitrogen-doped ultrathin carbon nanofibers derived from electrospinning: Large-scale production, unique structure, and application as electrocatalysts for oxygen reduction

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ABSTRACT

Ultrathin nitrogen-doped carbon nanofibers (NCNFs) with unique structure are prepared by electrospinning. The ultrathin NCNFs are produced in the form of large-area membranes by carbonizing electrospun polyacrylonitrile (PAN) nanofibers in NH₃. The diameter of the NCNFs can be effectively reduced due to the etching reactivity of NH₃ with carbon and the average diameter down to 20 nm is obtained. The NCNFs carbonized in NH₃ possess unique structure that many graphitic layers protrude from the fiber surface with their edges exposed. The nitrogen doped in the NCNFs is mainly from that contained in the PAN molecules and partially from ambient NH₃. The membranes of the ultrathin NCNFs exhibit high electrocatalytic activity, long-term operation stability, and excellent tolerance to crossover effect during oxygen reduction reaction in fuel cells. The high electrocatalytic activity of the ultrathin NCNFs may be mainly ascribed to their small diameter and exposed graphitic layer edges apart from N doping. Due to the simplicity in production, low cost, absence of metal residue, and the material form of freestanding membrane with large area the ultrathin NCNFs derived from electrospinning hold high promise for the practical application of fuel cells.

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1. Introduction

Fuel cells are attracting increasing interest as clean and efficient power sources [1,2]. The oxygen reduction reaction (ORR) at the cathode is one of the most important factors influencing the performance of a fuel cell and efficient electrocatalysts are crucial for the occurrence of the ORR with desired current density, overpotential, and stability [1,3,4]. Conventionally, platinum (Pt)-based materials are widely used as the electrocatalysts for ORR [4–6]. However, the Pt catalysts suffer from the disadvantages of high cost, limited supply, activity deterioration with time, and CO poisoning [5,7], which hinders the commercialization of fuel cells. Much effort has been devoted to the search for alternative catalysts to Pt and some Pt-free catalysts such as transition metal chalcogenides [8,9], Pd-based alloys [10], gold nanoclusters [11], and cobalt–polypyrrole–carbon composites [6] have been found to have electrocatalytic activity on ORR. Particularly, nitrogen (N)-doped carbon materials such as nonotubes [12–14], nanotube cups [15], graphene [16], and mesoporous carbon [17] exhibit excellent

electrocatalytic activity, long-term operation stability, and tolerance to crossover effect for ORR, indicating a tremendous potential for applications as low cost cathodic catalysts for fuel cells. Currently, the research on the N-doped carbon catalysts is still at its beginning stage and further work is urgently needed to understand the electrocatalytic mechanism and develop new N-doped carbon catalysts with high purity, easiness in large-scale production, and convenience in practical application.

Electrospinning is a simple and versatile method capable of producing continuous polymer nanofibers with diameters down to a few nanometers [18,19]. The electrospun nanofibers are generally prepared in the form of membranes with large area. Many polymers and polymer-based composites have been made into nanofibers by electrospinning. Inorganic nanofibers such as carbon [20–22], boron nitride [23], and oxides [24] can be obtained by calcining the electrospun precursor fibers. The carbon nanofibers are generally made by using electrospun polyacrylonitrile (PAN) nanofibers as the precursors. Some promising applications such as supercapacitors [20], electrodes for Li-ion batteries [21], and catalyst supports [22] have been demonstrated for the electrospun carbon nanofibers. However, the investigation of N-doped carbon nanofibers (NCNFs) derived from electrospinning and their applications as electrocatalysts for ORR have not been reported so far.

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Herein we report the large-scale production of ultrathin NCNFs and their electrocatalytic performance for ORR in fuel cells. The NCNFs were prepared in the form of free standing membrane with large area by carbonizing the electrospun PAN nanofibers at high temperature in N_2 or NH_3 atmosphere. The ultrathin NCNFs with average diameters as small as 20 nm were obtained when carbonizing the PAN nanofibers in NH_3 due to the etching reactivity of NH_3 with carbon. The electrocatalytic activity of the NCNFs is strongly dependant on the carbonizing atmosphere, temperature, and their diameter. The NCNFs carbonized in NH_3 show excellent electrocatalytic performance for ORR, which is much better than that of the NCNFs carbonized in N_2 and increases with increasing the carbonizing temperature. The experimental results suggest that the doping state of pyrrolic-N may contribute greatly to the excellent electrocatalytic activity of the NCNFs prepared in NH_3 .

2. Experimental

The electrospinning solutions with concentrations (wt./v, %) of 5.3%, 7%, 8%, and 9% were prepared by dissolving PAN (Aldrich, $M_w = 150,000$) in dimethylformamide (DMF). The PAN nanofibers were prepared by a conventional electrospinning setup [19], which mainly consists of a high voltage power supply (0–50 kV) (DW-P503-2ACCD, Dongwen High Voltage Power Supply Company, China) and an ordinary hypodermic syringe with a stainless steel needle. Graphitic papers were used as substrates to collect the electrospun nanofibers. During electrospinning the positive terminal (copper wire) of the power supply is connected with the syringe needle and the ground electrode is connected with the graphitic papers. The distance between the needle nozzle and collecting substrates was set at about 15 cm and the electrospinning voltage is 25 kV. No syringe pump was used during electrospinning.

The preparation of the NCNFs includes two steps, namely, stabilization and carbonization of the electrospun PAN nanofibers. The stabilization was carried out in air at 250 °C for 2 h with a heating rate of 3 °C min^{-1} . The carbonization was carried out in NH_3 or N_2 atmosphere with a flow rate of 100 mL min^{-1} for 3 h at given temperatures and a heating rate of 7 °C min^{-1} .

Scanning electron microscopy (SEM, HITACHI S-4700), transmission electron microscopy (TEM, JEM-2010), Raman spectroscopy (Renishaw RM-1000), and X-ray diffraction (XRD, Rigaku D/Max 2500/PC) were used to characterize the structure of the NCNFs. X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was used to determine the composition and bonding states of the NCNFs and the binding energy (B.E.) of the C 1s (284.6 eV) peak was taken as an internal standard.

The electrochemical characterization were performed on an electrochemical workstation (CHI760C, Shanghai Chenhua Instrument Co., Ltd., China). Cyclic voltammogram (CV) and rotating-disk electrode (RDE) polarization curves were carried out at room temperature (~ 25 °C) in a conventional three-electrode electrochemical cell. A platinum wire (CHI115) and an Ag/AgCl (sat.) (CHI111) electrode were used as the counter and reference electrode, respectively. A glassy carbon (GC) electrode (3 mm in diameter, 0.0707 cm^2 , CHI104) and GC disk (3.5 mm in diameter, 0.0962 cm^2 , Jiangsu Jiangfen Electroanalytical Instrument Co., Ltd.) were employed as the working electrodes for CV and RDE tests, respectively. Before use, the GC electrodes were carefully polished with gamma alumina powders (0.05 μm) until a mirror-like surface was obtained, followed by washing with double distilled water and drying in vacuum. During CV and RDE tests, a certain amount of electrocatalyst samples (250 $\mu g cm^{-2}$) were adhered onto the GC electrode with a drop of water. After drying, a drop of Nafion solution (5 wt.%, Alfa Aesar) was dripped onto the catalyst layer to improve the adhesion of the catalysts on the GC surface. The

RDE polarization curves were recorded by scanning the disk potential from -1.2 to 0.2 V vs. Ag/AgCl at a fixed scan rate of 10 $mV s^{-1}$ and different rotation rates from 400 to 3600 rpm in O_2 -saturated 0.1 M KOH solution. The CV curves were recorded from -1.2 to 0.2 V vs. Ag/AgCl at a scan rate of 100 $mV s^{-1}$ in O_2 -saturated 0.1 M KOH solution. Before each RDE and CV measurements O_2 gas was bubbled directly into the cell for 15 min to obtain O_2 -saturated solutions. The current–time ($i-t$) curves were tested at a constant voltage of -0.40 V for more than 20,000 s in 0.1 M KOH solution under continuous O_2 bubbling with a flow rate of 40 mL min^{-1} at a fixed rotation rate of 1600 rpm.

3. Results and discussion

The PAN nanofibers were electrospun from the PAN/DMF solutions. The diameter of the PAN nanofibers can be controlled by changing the solution concentration. In this paper the applied PAN nanofibers were electrospun at the solution concentration of 5.3% unless otherwise stated. Fig. 1a–c shows the SEM images of the NCNFs carbonized at 1000 °C in N_2 and NH_3 , the diameters of which were measured to be about 130 and 20 nm, respectively. It is clearly indicated that much thinner NCNFs were obtained when carbonizing in NH_3 than in N_2 although the used PAN nanofibers are similar in diameter. We consider that the diameter reduction of the NCNFs carbonized in NH_3 is due to the etching reactivity of NH_3 with carbon. At high temperature NH_3 can decompose to generate H atoms or H containing active species, which are capable of reacting with carbon to form carbon containing active species or molecules, resulting in the decrease of the fiber diameter. To the best of our knowledge, this is the thinnest carbon nanofibers derived from electrospinning so far reported. The diameter of the NCNFs increases with decreasing the carbonizing temperature due to the decreased etching reactivity of NH_3 and the diameters of 20, 40, and 90 nm were obtained at 1000, 900, and 800 °C, respectively. The present work established an effective method to fabricate ultrathin NCNFs. Fig. 1d is an optical photo of a NCNF membrane with a size of 5.5×14.5 cm^2 , indicating that the NCNFs can be easily produced with large area by the electrospinning technique. Comparing with the powder form for carbon nanotubes and graphene the present NCNF membranes may be more convenient in practical application as catalysts for fuel cells.

Fig. 2 shows the TEM images of the obtained NCNFs. The diameters of the NCNFs measured from the TEM images (Fig. 2 and Supplementary data, Figs. S1) are about similar to that measured from the SEM images. We noticed that the NCNFs obtained in NH_3 are rougher than that obtained in N_2 . In the high resolution TEM images the lattice fringes corresponding to (002) planes can be clearly seen. For the NCNFs carbonized in N_2 the graphitic layers are generally aligned along the fiber axis to form smooth surface (Fig. 2b). However, the NCNFs prepared in NH_3 possess a unique structure composed of two different parts, i.e., in the outer part of the nanofibers many graphitic layers radially protrude from the fiber surface with their edges exposed but in the inner part the lattice fringes are in parallel to the fiber axis (Fig. 2d and Supplementary data, Figs. S1 and S2). These protruding graphitic layers exhibit single or few fringe lines at the layer edges, suggesting that they are likely mono- or few-atomic-layered according to the study on graphene [25]. This unique structure has not been reported previously for carbon nanofibers and may be highly advantageous for applications such as electrocatalysts and supercapacitor electrodes due to the exposed edges of the graphitic layers. We consider that the inner part of the NCNFs forms due to the carbonization of PAN while the outer part forms through a growth process occurring in the carbonizing process. As stated above, NH_3 will react with the carbon elements in the fibers to gen-

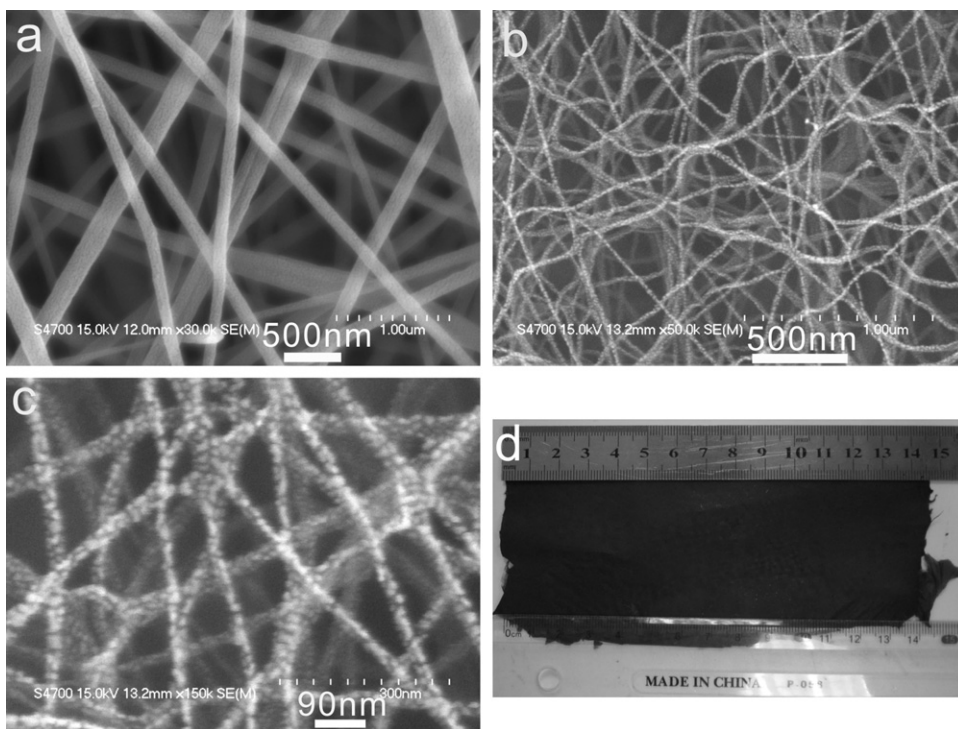


Fig. 1. (a–c) SEM images of the NCNFs carbonized at 1000 °C in N₂ (a) and NH₃ (b and c). (d) An optical photo showing the size of a NCNF membrane.

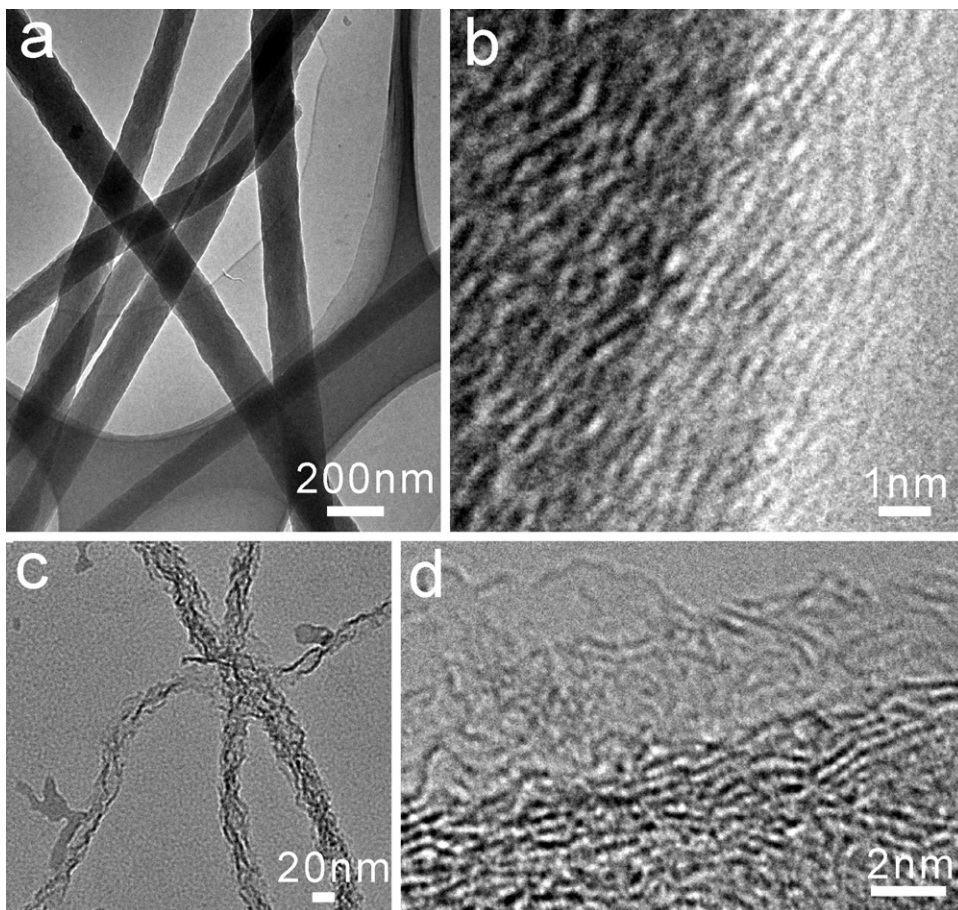


Fig. 2. TEM images of the NCNFs obtained at 1000 °C in N₂ (a and b) and NH₃ (c and d).

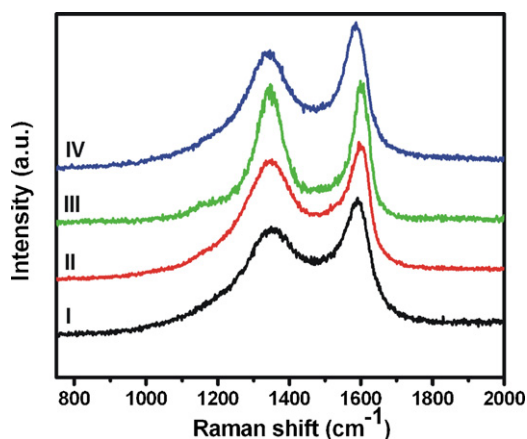


Fig. 3. Raman spectra of the NCNFs carbonized under different atmosphere and temperature: I – NH₃, 800 °C; II – NH₃, 900 °C; III – NH₃, 1000 °C; IV – N₂, 1000 °C.

erate carbon containing active species in vapor phase and reduce the fiber diameter. Simultaneously, the carbon containing active species can also be adsorbed on the surface of the carbon nanofibers and incorporate into the graphitic lattice, resulting in a growth process resembling chemical vapor deposition and forming the radially protruding graphitic layers. The TEM images were also taken for the NCNFs carbonized in NH₃ at 900 and 800 °C (not shown). We found that the protruding layers tend to form at higher temperature and almost no protruding layers were observed for the NCNFs carbonized at 800 °C. This is mainly because the carbon containing active species for the growth of the protruding layers decrease due to the decreased reactivity of NH₃ at lower temperature.

Fig. 3 shows the first-order Raman spectra of the NCNFs carbonized under different conditions. All samples exhibit the well-known D and G peaks associated with the disordered and graphitized structures, respectively, showing the characteristics of microcrystalline graphitic materials [26,27]. The peak parameters including position, full width at half maximum (FWHM), and integrated intensity ratio I_D/I_G were determined by Gaussian fitting on the D and G peaks (Supplementary data, Table S1). Obvious decrease of the FWHM and the I_D/I_G ratio with increasing carbonizing temperature is observed, indicating a corresponding increase of the graphitization degree. The dependence of graphitization degree on the heat treatment temperature has been observed frequently and can be easily understood [28,29]. It is also found that the FWHM and I_D/I_G ratio are smaller for the NCNFs prepared in NH₃ than prepared in N₂, indicating a higher graphitization degree for the former than the latter. The higher graphitization degree obtained in NH₃ should be caused by the presence of H elements in the gas mixtures, which promotes the crystallizing process by bonding with the surface atoms on the carbon nanofibers to increase the mobility of the carbon atoms and inducing a growth process.

The electrocatalytic activity of the NCNFs was investigated as a function of carbonizing temperature and atmosphere. For the NCNFs obtained in NH₃ at 800, 900, and 1000 °C obvious ORR peaks in the CV curves are observed at –0.43, –0.36, and –0.25 V with the corresponding peak current densities to be 1.05, 1.96, and 3.73 mA cm⁻², respectively, and their onset potentials are –0.23, –0.14, and –0.09 V, respectively (Fig. 4a). As for the NCNFs carbonized in N₂ at 1000 °C, the onset potential, peak position, and peak current density are –0.13 V, –0.46 V, and 1.07 mA cm⁻², respectively (Fig. 4a). This indicates that all the NCNFs obtained under the applied conditions have obvious electrocatalytic activity for ORR. Clearly, the electrocatalytic activity of the NCNFs is strongly dependent on the carbonizing atmosphere and temperature. Much better electrocatalytic activity was obtained for the

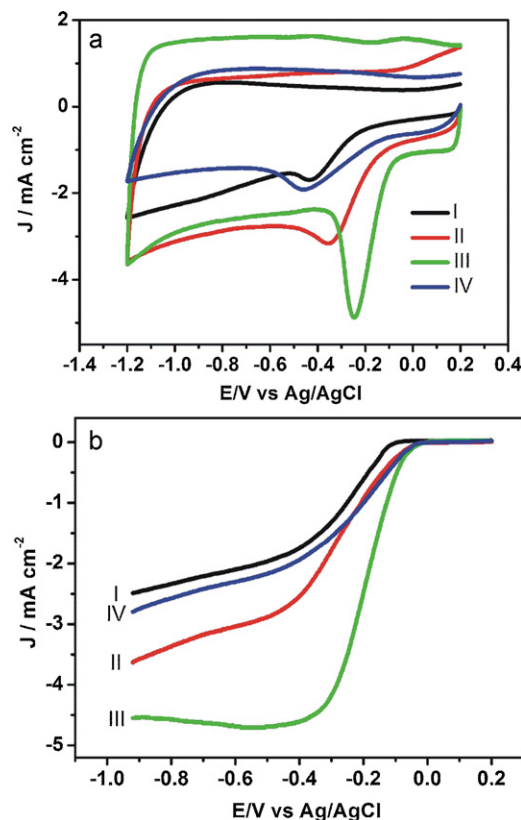


Fig. 4. CV curves (a) and RDE voltammograms (b) of the NCNFs carbonized under different atmosphere and temperature in O₂-saturated 0.1 M KOH solution: I – NH₃, 800 °C; II – NH₃, 900 °C; III – NH₃, 1000 °C; IV – N₂, 1000 °C. The applied scan rates for CV and RDE measurements are 100 mV s⁻¹ and 10 mV s⁻¹, respectively, and the rotating rate is 1600 rpm during RDE measurements.

NCNFs carbonized in NH₃ than that in N₂ and at higher temperature. RDE voltammetry measurements were carried out to further investigate the electrocatalytic process of the NCNFs. Fig. 4b compares the RDE voltammograms of the different NCNFs. Similar changing trend to the CV measurements was observed in the RDE voltammograms, i.e., much better electrocatalytic activity appears for the NCNFs carbonized in NH₃ and at higher temperature. The onset potentials are –0.1, –0.04, –0.02, and –0.03 V for the NCNFs carbonized in NH₃ at 800, 900, and 1000 °C and in N₂ at 1000 °C, respectively. A high steady-state diffusion current density over 4.5 mA cm⁻² was observed in a large potential range for the NCNFs carbonized in NH₃ at 1000 °C, which is about twice as high as that obtained for the NCNFs carbonized in NH₃ at 800 °C and in N₂ at 1000 °C. The electron numbers transferred (n) per oxygen molecule during ORR and the kinetic-limiting current density (J_K) can be obtained from the slope and intercept of the Koutecky–Levich plots (Supplementary data, Fig. S3) [11]. For the NCNFs carbonized in NH₃ at 800, 900, and 1000 °C and that in N₂ at 1000 °C, the overall electron numbers transferred during ORR at –0.40 V are 2.48, 3.40, 3.96 and 3.51 and the J_K are 3.46, 5.26, 21.50, and 3.10 mA cm⁻², respectively. It can be seen that the increase of the carbonizing temperature and the application of NH₃ as the carbonizing atmosphere substantially facilitate electron-transfer kinetics of oxygen reduction. These results indicate that the NCNFs especially carbonized at 1000 °C in NH₃ possess high electrocatalytic activity rarely seen so far for the N-doped carbon materials [14–17] and hold high promise for application as cheap and efficient metal-free electrocatalysts for ORR.

Tolerance to crossover effect and stability are very important criteria to evaluate the quality of an electrocatalyst for ORR. We

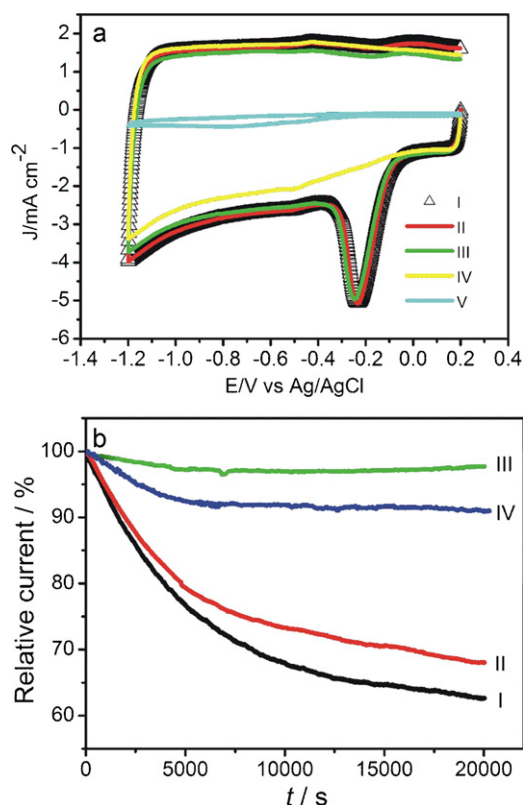


Fig. 5. (a) CV curves for the NCNFs (I–IV) carbonized in NH_3 at 1000°C and the bare GC electrode (V) in 0.1 M KOH solution under different conditions: I – saturated with O_2 , II – saturated with O_2 in the presence of 3.0 M methanol, III – saturated with O_2 in the presence of 3.0 M methanol and after a continuous potential cycling of about 1000 cycles, IV – saturated with N_2 , V – saturated with O_2 , bare GC electrode. Scan rate 100 mV s^{-1} . (b) Current–time (i – t) chronoamperometric response obtained for the NCNFs carbonized in NH_3 at 800°C (I), 900°C (II), 1000°C (III), and in N_2 at 1000°C (IV) in O_2 -saturated 0.1 M KOH at -0.4 V and a rotation rate of 1600 rpm .

investigated the crossover effect of the NCNFs by measuring the CV curves in 0.1 M KOH solution in the presence of methanol. In Fig. 5a the CV curves in O_2 -saturated 0.1 M KOH solutions without and with addition of 3 M methanol are compared for the NCNFs carbonized in NH_3 at 1000°C (curves I and II). It is clearly indicated that the two CV curves almost overlap each other, demonstrating a good tolerance to the crossover effect. Furthermore, no notable changes were observed for the CV curves in the presence of 3 M methanol even after 1000 cycles, further confirming the good tolerance to crossover effect and high stability of the NCNF catalysts (Fig. 5a-III). The electrocatalytic stability of the NCNFs was further measured at -0.40 V for 20,000 s in O_2 saturated 0.1 M KOH solution at a rotating rate of 1600 rpm (Fig. 5b). It is observed that the NCNFs carbonized in NH_3 at 1000°C exhibits a very slow attenuation after a decrease of about 2% within the first 3000 s, and a rather high relative current of 97.7% still persists after 20,000 s. In our experiments, the NCNFs obtained in N_2 show similar stability to that obtained in NH_3 . We noticed that the electrocatalytic stability of the NCNFs is more sensitive to the carbonizing temperature but less sensitive to the carbonizing atmosphere, as indicated by the great decrease in the relative current density with prolonging the duration for the NCNFs obtained at 800 and 900°C (Fig. 5b). This may be because the structure of the NCNFs obtained at higher temperature is more stable than that obtained at lower temperature. To confirm the origin of the electrocatalytic activity of the NCNFs the CV curves were measured for the NCNFs in N_2 -saturated 0.1 M KOH solution and the bare GC electrode in O_2 -saturated 0.1 M KOH solution (Fig. 5a-IV and V). It is clearly seen that no obvious peaks

were observed on the CVs obtained in the above two cases, indicating that the obtained high electrocatalytic activity are exclusively from the ORR catalyzed by the NCNFs.

Up to now, the reported electrocatalytic activities of N-doped carbon materials were mainly obtained for those with nanoscale features such as carbon nanotubes, mesoporous graphitic arrays, and graphene [12–17]. It was also reported that the electrocatalytic activity of the carbon nanotubes for ORR can be substantially enhanced by the alignment structure [14]. In the present work, we found that the electrocatalytic activity of the NCNFs can be greatly enhanced by the reduction of their diameters. We prepared the NCNFs with average diameters of about 180, 120, 70, and 20 nm by carbonization in NH_3 at 1000°C from the PAN nanofibers electrospun at the concentrations of 9%, 8%, 7%, and 5.3%, respectively. The CV measurements show that with decreasing the diameter from 180 to 20 nm the peak current density increases from 2.26 to 3.73 mA cm^{-2} with the onset potential shifting from -0.15 to -0.09 V (Supplementary data, Fig. S4). Size dependence of electrocatalytic activity was frequently observed for nanoscale catalysts. For example, significant enhancement of electrocatalytic activity can be obtained for gold nanoparticles by decreasing particle size [11], which was ascribed to the corresponding changes in chemical states of the surface atoms. In the present work, the enhancement of the electrocatalytic activity with decreasing fiber diameter may be mainly ascribed to the corresponding increase of the active surface area. However, further work is needed to understand the precise mechanism.

As stated above, application of NH_3 and higher temperature during carbonization and reduction of the diameter highly favor the electrocatalytic activity of the NCNFs. To understand the influencing mechanism of the above factors XPS was used to identify the concentration and doping states of N in graphitic network. The C1s peaks for all the NCNFs are centered at about 284.7 eV with slight asymmetry, showing the characteristics of N doped graphitic carbon structure (Supplementary data, Fig. S5) [17]. Fig. 6 shows the XPS N1s spectra of the NCNFs carbonized at different temperatures and atmospheres, where fitting lines indicating the bonding states of the doped N are also shown. The total N concentrations (at.%) calculated from the XPS spectra for the NCNFs carbonized in NH_3 at 800 , 900 , and 1000°C and in N_2 at 1000°C are 3.3%, 2.0%, 0.75%, and 0.47%, respectively. This indicates that the electrocatalytic activity is not directly related to the N concentration, in agreement with the previous report [17]. Due to the fully metal-free fabrication process the electrocatalytic activity of the NCNFs can be exclusively attributed to NCNFs. The nitrogen content in the NCNFs is mainly from the nitrogen contained in the PAN precursor (molecular formula $(\text{C}_3\text{H}_3\text{N})_n$) and may be partially from the ambient atmosphere (N_2 or NH_3). The higher N concentration for the NCNFs carbonized in NH_3 than that in N_2 should be caused by the higher reactivity of NH_3 than N_2 . Generally, N can be doped into the graphitic structure in the form of pyridinic-N, pyrrolic-N, graphitic-N, and pyridine-N-oxide N with the XPS peaks at $398.7 \pm 0.3\text{ eV}$, $400.4 \pm 0.3\text{ eV}$, $401.4 \pm 0.3\text{ eV}$, and $402\text{--}404\text{ eV}$ [12,30], respectively. In the present work all the four N doping forms are present in the NCNFs carbonized in NH_3 and only pyridinic-N and graphitic-N are present in the NCNFs carbonized in N_2 (Fig. 6 and Supplementary data, Table S2). Formation of the pyrrolic-N in NH_3 atmosphere should be because H atoms or H containing active species produced due to NH_3 decomposition participate in the carbonization reaction. It is found that only the pyrrolic-N monotonically increases with increasing the carbonizing temperature for the NCNFs obtained in NH_3 (Supplementary data, Table S2), revealing a possible correlation between the pyrrolic-N and the ORR electrocatalytic activity. The XPS results suggest that the pyrrolic-N may play important roles in the electrocatalytic activity of the NCNFs although pyridinic-N and graphitic-N may all

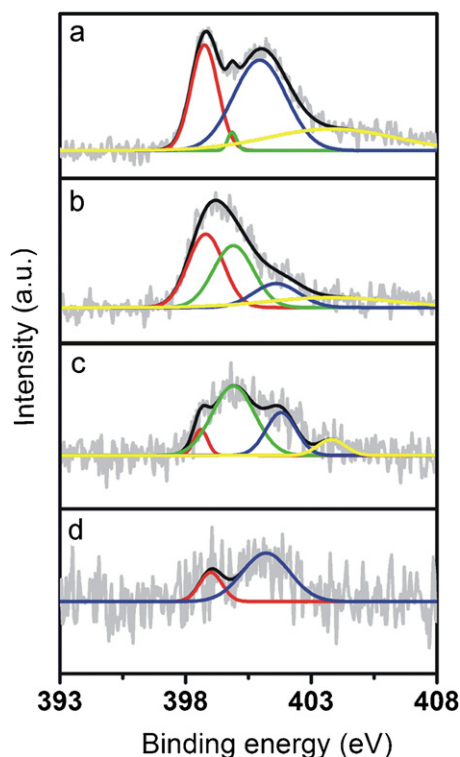


Fig. 6. XPS N1s spectra of the NCNFs carbonized under different atmosphere and temperature: (a) NH_3 , 800 °C; (b) NH_3 , 900 °C; (c) NH_3 , 1000 °C; (d) N_2 , 1000 °C. (fitting lines are also shown. Red: pyridinic-N, green: pyrrolic-N, blue: graphitic-N, yellow: pyridine-N-oxide N). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

contribute to it. Based on the above characterizing results it can be tentatively understood that the much higher electrocatalytic activity of the NCNFs obtained in NH_3 than that in N_2 is mainly caused by the presence of the pyrrolic-N, smaller diameter, and exposed layer edges for the former. The increase of the pyrrolic-N, reduction in diameter, and the increase of the exposed layer edges account for the increase of the electrocatalytic activity with increasing the carbonizing temperature for the NCNFs carbonized in NH_3 .

4. Conclusions

In conclusion, a simple and cheap technique producing ultrathin NCNFs on a large scale has been established based on electrospinning. The ultrathin NCNFs with average diameter down to 20 nm were prepared by heating the electrospun PAN nanofibers in NH_3 atmosphere. The diameter reduction of the NCNFs is caused by the etching reactivity of NH_3 with carbon at high temperature during carbonization. Unique structure was obtained for the NCNFs carbonized in NH_3 , where many graphitic layers protrude from the fiber surface with their edges exposed. The obtained ultrathin NCNFs possess high electrocatalytic activity, long-term stability, and excellent tolerance to crossover effects for ORR. The presence

of the pyrrolic-N and exposed layer edges and small diameter may be the cause of the high electrocatalytic activity of the ultrathin NCNFs. Considering the simplicity in production, low cost, absence of metal catalysts, and the material form of freestanding membrane with large area the electrospun NCNFs hold high promise for the practical application of fuel cells.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2011.08.013.

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