Crucial role for oxygen functional groups in the oxygen reduction reaction electrocatalytic activity of nitrogen-doped carbons

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Abstract

Generally, a significant amount of oxygen functional groups (OFGs) usually exist on the surface of nitrogen-doped carbons. Unfortunately, the role of OFGs on the oxygen reduction reaction (ORR) electrocatalytic activity of nitrogen-doped carbons is rarely discussed. Herein, we report that the OFGs play a crucial role on the ORR electrocatalytic activity of nitrogen-doped carbons. A nitrogen doped carbon foam (NCF) containing OFGs was prepared by pyrolysis of melamine foam. The species of the OFGs were then tuned by chemical reduction, and their effects on the ORR electrocatalytic activity of the NCF were investigated by electrochemical measurements, X-ray photoelectron spectroscopy and solid-state NMR spectroscopy. Results showed that the ORR electrocatalytic activity of the NCF greatly decreased after chemical reduction. The OFGs in the form of quinone were found to be crucial for the ORR electrocatalytic activity of the NCF. This study not only provided a new and effective strategy for investigating the effect of OFGs on the ORR electrocatalytic activity of nitrogen-doped carbons, but also presented a new insight into understanding their electrocatalytic mechanism.

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1. Introduction

As an indispensable oxygen electrode reaction, oxygen reduction reaction (ORR) is of great importance for electrochemical energy devices, such as fuel cells [1–5], metal-air batteries [6,7], electrocatalytic and photocatalytic water splitting [8]. Generally, efficient electrocatalysts are required for the ORR due to its low kinetics. Until now, platinum/carbon (Pt/C)-based catalysts have been believed to be the best electrocatalysts for ORR. However, they suffer from several drawbacks, including the limited resources, high cost and CO deactivation [1]. Recently, a number of non-precious materials had been developed to replace the Pt/C catalyst for the ORR. Among these materials, the metal-free heteroatom-doped carbons had attracted special attentions [9–16], e.g. nitrogen-doped carbons (NCs) [10,14,17–21] due to their low-cost, high-efficient ORR catalytic activities and excellent durability and selectivity. It had reported that the introduction of electron-rich N atoms can activate surrounding carbon atoms and create a net positive charge, thus facilitates ORR electrocatalytic activities of the NCs [4,17]. There is a matter of fact that should not be ignored: a significant amount of oxygen functional groups (OFGs) usually exist in NCs, even more than 10 at.% [22,23], which could be derived from nitrogen-containing precursors or introduced during preparation process [24,25]. Moreover, the content of O atoms is much higher than that of N atoms [22,26].

In recent years, numerous studies had reported that the existence of OFGs endowed carbon nanomaterials with ORR electrocatalytic activity [27–35]. Waki et al. reported that the OFGs on the edge site and hole defect site on MWCNTs led to a significant improvement on the ORR electrocatalytic activity [31]. The electrocatalytic effect of the OFGs was also confirmed in oxygen-functionalized graphene from carbon fibers [35]. Calculation results showed that the enhancement of electrocatalytic activities could be attributed to the high electronegativity of oxygen atoms. The OFGs connected with the carbon framework would induce the
charge delocalization of their adjacent C atoms, leading to charge redistribution among those carbon atoms. These positively charged carbon atoms demonstrated as active sites for enhancing the adsorption of intermediate species in ORR, and thus enhanced the ORR electrocatalytic activity. In addition to the improvement in the ORR electrocatalytic activity, the advantages of oxygen species on the surface of NCs were also widely recognized for the applications of energy conversion, such as lithium-ion batteries [36], Li-S batteries [37,38], Li-Se batteries [39], supercapacitors [22,40], hydrogen evolution reaction [41] and oxygen evolution reaction [42,43]. The primarily reason was the incorporation of oxygen atoms in carbon network that changes the electronic and geometric properties of their peripheral carbon atoms. This, in turn affected their electrocatalytic performance or introduced additional capacitance, i.e. pseudocapacitance through redox reaction [22,43]. However, the role of OFGs on the ORR activity of the NCs was rarely discussed. For instance, Liu et al. reported a novel high-efficient ORR catalyst, nitrogen-doped ordered mesoporous graphic arrays (NOMGAs). The outstanding ORR activity the NOMGAs was attributed to the graphite-like N atoms [21]. Nevertheless, the O content (6.1%) was even higher than the N content (2.7%) in NOMGAs, but the effect of OFGs on the ORR electrocatalytic activity of the NOMGAs was unfortunately not discussed. Silva et al. firstly reported that the OFGs had positive effect on the ORR catalytic activity of the NCs. The N and O co-doped mesoporous carbons prepared by pyrolysis of polyaniline exhibited outstanding electrocatalytic activity toward ORR. Their outstanding ORR performance was primarily proposed to be ascribed to the synergetic effect of N and O doping in pyridone group formed during the pyrolysis process [18]. However, the contribution of the OFGs on the ORR electrocatalytic activity of the NCs was not distinguished.

Herein, we reported the crucial role of OFGs on the ORR electrocatalytic activity of the NCs. A nitrogen doped carbon foam (NCF) containing OFGs prepared by pyrolysis of melamine foam was used as an example of NCs. A strategy of chemical reduction treatment was employed to tune the OFGs of the NCF. The changes of ORR electrocatalytic activity and OFGs of the NCF during the chemical reduction treatment were detected by using electrochemical measurements, X-ray photoelectron spectroscopy and solid-state NMR spectroscopy. The OFGs in quinone species were found to be crucial for the ORR electrocatalytic activity of the NCF.

2. Experimental

2.1. Preparation of NCFs

The NCFs were prepared by pyrolyzing a nitrogen containing precursor, melamine foam (MF), as reported in our previous works [44,45]. Typically, MFs were cut into pieces of cubic shape. They were firstly washed with acetone and deionized water for several times to remove the impurities, then dried overnight at 80 °C under vacuum. Thereafter, the samples were placed on a porcelain boat and put into a high-temperature tube furnace. The samples firstly suffered from an oxidation process at 300 °C for 30 min in air; subsequently, further heated to 1000 °C with a heating rate of 10 °C per min 1 and annealed for 60 min under the protection of N2 gas. After naturally cooling down to room temperature, the NCFs were obtained.

2.2. Chemical reduction of NCFs

The chemical reduction of the NCFs was performed in hydrazine hydrate solutions at 100 °C for overnight. After that, the NCF samples were taken out, washed with ethanol and deionized water for several times, and finally dried at 60 °C overnight to obtain the reduced nitrogen doped carbon foams (rNCFs). The rNCFs reduced with hydrazine hydrate mass fraction of 9%, 10% and 12% were denoted as rNCF-9%, rNCF-10% and rNCF-12%, respectively.

2.3. Electrochemical measurements

In this study, cyclic voltammetry (CV) measurements were conducted with a bi-potentiostat (Biologic, VMP3) by using a typical three-electrode electrochemical system. The system was equipped with a Pt wire as the counter electrode, an Ag/AgCl (saturated KCl internal solution) as the reference electrode, and glass carbon (GC) loaded with ORR catalysts as the working electrode, respectively. The electrocatalyst was loaded onto the GC according to the following steps. Typically, 1 mg of the as-prepared catalyst was dispersed in 250 μL deionized water and 25 μL 5wt.% Nafion solution under sonication to form a homogeneous dispersion. Subsequently, 5 μL catalyst dispersion was drop-casted onto the GC and then dried naturally at room temperature. To further verify electrocatalytic behavior of the ORR catalysts, linear sweep voltammetry (LSV) tests was performed by using a rotating ring-disk electrode (RRDE). The catalyst loading process onto the RRDE was similar to that onto the GC, but 15 μL catalyst dispersion was used instead of 5 μL. The scanning rates of the CV and LSV tests were 100 and 10 mV/s-1, respectively. The electrolyte in all the electrochemical measurements was 0.1 M KOH solution. The peroxide yield (H2O2%) and the electron transfer numbers (n) were calculated according to the following equations [3,46]:

\[
H_2O_2(\%) = 200 \times \frac{I_R/N}{I_D + I_R/N} 
\]

\[
n = 4 \times \frac{I_D}{I_D + I_R/N} 
\]

where, \(I_D\) and \(I_R\) are the disk and ring currents, respectively. All measurements were conducted at 25 °C, and the collection efficiency (N) of Pt ring was taken as 40% determined from the redox reaction of K3[Fe(CN)6].

2.4. Characterization

The microstructures of the NCFs and the rNCFs were characterized by transmission electron microscopy (TEM, JEM-2100, JEOL) at an accelerating voltage of 200 kV. The crystalline structure was characterized using Raman spectroscopy (LABRAM HR-800, Horiba) with Al Kα source. Raman spectra were recorded with a laser at an excitation wavelength of 532 nm. The elemental composition and chemical state of the NCFs were characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Scientific). The XPS analysis were conducted by using a monochromatic Al Kα X-ray source with an energy of 1253.6 eV. The pore features of the NCFs were measured by nitrogen adsorption–desorption isotherms at 77 K with a Micromeritics apparatus (ASAP 2020). The specific surface area was determined according to the Brunauer-Emmett-Teller (BET) equations, and the pore size distribution (PSD) was obtained by the Barrett-Joyner-Halenda [BJH] method.

Solid-state magic-angle spinning (MAS) NMR spectra were recorded on a Bruker AVIIIHD 400WB spectrometer with a field strength of 9.4T, equipped with a MASDVT400WB BL2.5 HXY probe. Samples were packed in 2.5 mm rotors and spun at the magic angle with 25 kHz. Temperature for data collection was 20 °C. 13C direct excitation spectra were acquired by employing a Hahn Echo pulse sequence to remove background signal [47].
total number of scans was 49,152, amounting to six days of measurement time. Applied carbon power was 50 kHz, the recycle delay was 10 s, and acquisition time was 9.94 ms. 

$^{13}$C detected $^1$H–$^{13}$C cross polarization (CP) spectra were acquired with 286,720 scans [48,49], amounting to seven days of measurement time. Proton excitation power was 66.7 kHz. CP contact power was 59.3 kHz for proton and 36.5 kHz for carbon, applied for a contact time of 600 ms on the proton channel with a decreasing power ramp from 100 to 80%. Recycle delay was 2 s, and acquisition time was 10.24 ms. Carrier frequencies were 4 ppm for proton and 100 ppm for carbon. SPINAL64 was used in all recordings for proton decoupling [50]. Spectra were processed with Bruker TopSpin 3.5 and externally referenced to adamantane [51]. A line broadening of 200 Hz was applied to all spectra.

3. Results and discussion

3.1. Electrocatalytic performance of the NCF and the rNCFs

In order to study the effect of oxygen species on the ORR activity, CV measurements of the NCF and the rNCFs were first performed in oxygen or nitrogen-saturated 0.1 M KOH solution using a typical three-electrode electrochemical system. As shown in Fig. 1, the initial NCF exhibits an excellent electrocatalytic activity towards ORR with a peak potential ($E_{\text{peak}}$) of about $-0.19$ V (Fig. 1A), which is very close to commercial 20 wt% Pt/C with peak potential of about $-0.16$ V in alkaline media. After chemical reduction by hydrazine hydrate, the ORR peak potential of the rNCF catalysts strongly decreased, implying a great decrease of ORR electrocatalytic activity. For instance, the ORR peak potential of rNCFs negatively shifted to around $-0.22$ V for rNCF-9%, $-0.35$ V for rNCF-10% and $-0.38$ V for rNCF-12%, respectively. In addition, the ORR current density of the rNCFs also significantly decreased compared to the initial NCF at a given applied potential of $-0.5$ V (Fig. 1). The negative shift of the peak potential and the decrease of ORR current density obviously indicated that the rNCFs exhibited a much lower catalytic activity for ORR as comparison to the initial NCF.

To further quantitatively evaluate the ORR performance of the NCF and rNCFs, RDE measurements were conducted and the corresponding results were presented in Fig. 2 and Fig. S1. Generally, the ORR process in alkaline solution involves in two pathways, a four-electron pathway to directly convert oxygen to water and a two-electron pathway with the generation of hydrogen peroxide [46]. The former pathway is preferred for efficient ORR electrocatalytic activity. It can be observed that the RDE LSV curves of the NCF (Fig. 2A) at different rotating speeds exhibited a predominantly one-step process, indicating a desired four-electron ORR pathway of the NCF. In contrast, the resulted RDE LSVs of the rNCFs (Fig. 2B and Fig. S1) displayed a possibly hybrid four-electron and two-electron pathway. Furthermore, in comparison with the ORR onset potential ($E_{\text{onset}}$) of the NCF ($E_{\text{onset}} = -0.05$ V, Fig. 2C), the rNCFs exhibited more negative onset potentials along with the increasing concentration of hydrazine hydrate solution. As shown in Table 1, the $E_{\text{onset}}$ of rNCFs negatively shifted from $-0.05$ V to $-0.10$, $-0.14$ and $-0.16$ V for the rNCF-9%, rNCF-10% and rNCF-12%, respectively. Similarly, the ORR current densities of rNCFs were also significantly lower than the initial NCF. To shed insight on the transfer kinetics and catalytic activity of ORR, we also carried out the RRDE measurements and the ring current was monitored accurately to measure the yield of peroxide species (H$_2$O$_2$). As indicated in Fig. 2D and E, the initial NCF showed the lowest H$_2$O$_2$ yield ($2.43 \pm 2.56\%$) in the potential ranging from $-0.25$ to $-0.50$ V (vs Ag/AgCl), whereas the rNCFs exhibited higher H$_2$O$_2$ yields. The average electron transfer number ($n$) of the NCF (Fig. 2F) is about 3.8, suggesting approximately a four-electron reaction, which is much higher than that of rNCFs. As discussed in the preceding paragraph, all the electrochemical results indicate a significant decrease of ORR electrocatalytic activity after chemical reduction of the NCF.

![Fig. 1. CV curves of the initial NCF and the rNCFs in nitrogen (red) and oxygen-saturated (black) 0.1 M KOH solutions at a scan rate of 100 mV s$^{-1}$: (A) NCF, (B) rNCF-9%, (C) rNCF-10% and (D) rNCF-12%. The blue arrows refer to the ORR current densities at a given applied potential of $-0.5$ V. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)](image-url)
3.2. Pore structure characterization of the NCF and rNCFs

To explore the reasons of ORR performance reduction of the rNCFs, further physical and chemical characterization of the NCF and rNCF catalysts were performed. High-resolution TEM (HR-TEM) images (Fig. 3 and Fig. S3) demonstrate that both NCF and rNCFs contain typically amorphous carbon structure. Compared with the initial NCF, no defects were observed in the rNCFs, indicating that the chemical reduction process exerts little influence on the crystalline structure. This result was also confirmed by Raman spectroscopy. Raman spectra in Fig. S2 showed two characteristic D and G bands at ~1328 and 1585 cm$^{-1}$ for all samples. The intensity ratios of D-band to G-band ($I_D/I_G$) for NCF, rNCF-9%, rNCF-10% and rNCF-12% were calculated to be 1.18, 1.19, 1.22 and 1.21, respectively, indicating a similar graphitization degree after the chemical reduction treatment.

To get insight into the effect of chemical reduction on the porous structures of the NCF catalysts, the nitrogen adsorption/desorption analyses were conducted. As shown in Fig. 4 and Fig. S4, the isotherms of the NCF and rNCFs exhibit an IV-type curve, indicating the presence of micro- and mesopores in all products. Table 2 shows detail parameters of pore structure calculated from nitrogen adsorption/desorption. The specific surface area ($S_{BET}$) and total pore volume ($V_t$) of rNCFs are between 787.6–737.9 m$^2$ g$^{-1}$ and 0.413–0.401 cm$^3$ g$^{-1}$, respectively. These are comparable to $S_{BET}$ (809.3 m$^2$ g$^{-1}$) and $V_t$ (0.427 cm$^3$ g$^{-1}$) of the pristine NCF. Moreover, the NCF and rNCFs show a narrow pore width distribution in the range of 2.153–2.175 nm, as displayed in the PSD curves. These

![Fig. 2. RDE voltammograms of (A) NCF and (B) rNCF-10% measured at different rotating rates ranging from 2500 to 400 rpm with a scanning rate of 10 mV s$^{-1}$. (C) Disc and (D) ring current response of the NCF and rNCFs at a rotating rate of 1600 rpm in O$_2$-saturated 0.1 M KOH solution. (E) Percentage of peroxide and (F) electron transfer number ($n$) for NCF and rNCFs catalysts at various potentials.](image)

### Table 1
Summary of electrochemical performance of NCFs in alkaline solution.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_{peak}$ (V)</th>
<th>$E_{onset}$ (V)</th>
<th>H$_2$O$_2$ yield (%)</th>
<th>Average electron transfer number ($n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCF</td>
<td>-0.19</td>
<td>-0.05</td>
<td>2.43–12.56</td>
<td>3.8</td>
</tr>
<tr>
<td>rNCF-9%</td>
<td>-0.22</td>
<td>-0.10</td>
<td>4.38–20.62</td>
<td>3.4</td>
</tr>
<tr>
<td>rNCF-10%</td>
<td>-0.35</td>
<td>-0.14</td>
<td>6.40–34.24</td>
<td>3.2</td>
</tr>
<tr>
<td>rNCF-12%</td>
<td>-0.38</td>
<td>-0.16</td>
<td>8.26–38.10</td>
<td>2.8</td>
</tr>
</tbody>
</table>

![image](image)

![image](image)
results reveal that the pore structures of the rNCFs showed no markedly difference in comparison with that of the initial NCF. It also indicates that the reason for the great decrease of the ORR electrocatalytic activity of the rNCFs after chemical reduction is not the change of crystalline and pore structures.

3.3. Surface chemistry characterization of the NCF and rNCFs

The surface chemistry of catalysts is of significant importance for the ORR activity, since the ORR reaction is a surface process. Therefore, the NCF samples were investigated before and after chemical reduction using XPS spectroscopy and elemental analysis. The atomic contents of elements on the surface were presented in Table S1. Within the XPS survey spectra of the NCF and rNCFs (Fig. S5), all products contain three peaks, associated with C1s, N1s and O1s peaks. The initial NCF contains 72.1 at% C, 4.8 at% N and 20.1 at% O element (Table S1). In comparison, a great decrease of O content is observed for the rNCFs with the oxygen content of 17.3, 7.5 and 7.2 for rNCF-9%, rNCF-10% and rNCF-12%, respectively. This result is also confirmed by elemental analysis. The O/C atomic ratio of the NCF (20.5%) is much higher than that of the rNCFs in the range from 16.7 to 6.18% (Table S1). In comparison, the change in the N/C atomic ratio of the NCF (6.19%) and the rNCFs (5.30–5.51%) is relatively small.

To further understand the change of the surface properties, high resolution C1s, O1s and N1s XPS spectra of the NCF and rNCFs were collected (Fig. 5 and Fig. S5). The detailed contents of these species were calculated and listed in Table 3. As can be seen, the C1s XPS spectra could be split into three bands: sp²-carbon in graphite (C=C=C–C=C) at 284.6 ± 0.2 eV, carbon singly bound to oxygen in phenolic, alcoholic or etheric (C=O) at 286.1 ± 0.2 eV, carbon doubly bound to oxygen in carbonyl or quinone (C=O) at
It is noteworthy that the C=O groups of NCF in phenol or alcohol ether species greatly increase after suffering from the chemical reduction, while the content of the C=O group in carbonyl or quinone species decrease. Similarly, the high resolution O1s XPS spectra of the NCF and rNCFs display three peaks, which distinguished as oxygen doubly bound to carbon in quinone or carbonyl (O=C in quinone or carbonyl, 288.8 ± 0.2 eV), oxygen singly bound to carbon in epoxy (C=O in epoxy, 532.3 ± 0.2 eV), and oxygen doubly bound to carbon in phenolic or alcoholic moieties (C==O in phenolic or alcoholic, 533.1 ± 0.2 eV), respectively [34]. Further quantitative analysis exhibits a significant conversion of the oxygen functional groups from C==O to C—OH (Table 3) after the chemical reduction. In comparison to the initial NCF, the content of O==C in the rNCFs significantly decreases from 45.04% to 23.57%, while the fraction of C—OH increases from 21.29% to 36.6% after the chemical reduction treatment. These results demonstrate that the OFGs on NCF and rNCFs surfaces can be effectively tuned by chemical reduction.

Besides tuning of the OFGs, e.g. C=O and C==O functional groups, the chemical reduction also changes the doping state of N within the NCF. The high-resolution N1s XPS spectra of NCF and rNCFs

Table 2
Parameters of pore structure calculated from nitrogen adsorption measurements.

<table>
<thead>
<tr>
<th>Samples</th>
<th>(S_{\text{BET}}) (m(^2) g(^{-1}))</th>
<th>(V_{\text{t}}) (cm(^3) g(^{-1}))</th>
<th>(V_{\text{micro}}) (cm(^3) g(^{-1}))</th>
<th>(V_{\text{micro}}/V_{\text{t}}) (%)</th>
<th>(D_{\text{BJH}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCF</td>
<td>809.3</td>
<td>0.427</td>
<td>0.193</td>
<td>45.2</td>
<td>2.165</td>
</tr>
<tr>
<td>rNCF-9%</td>
<td>787.6</td>
<td>0.413</td>
<td>0.184</td>
<td>44.56</td>
<td>2.168</td>
</tr>
<tr>
<td>rNCF-10%</td>
<td>747.5</td>
<td>0.398</td>
<td>0.179</td>
<td>44.97</td>
<td>2.153</td>
</tr>
<tr>
<td>rNCF-12%</td>
<td>737.9</td>
<td>0.401</td>
<td>0.187</td>
<td>46.63</td>
<td>2.175</td>
</tr>
</tbody>
</table>

\(\text{a}\) \(S_{\text{BET}}\) refers to the specific surface area determined by BET method.

\(\text{b}\) \(V_{\text{t}}\) imply the total pore volume determined at \(P/P_0=0.9997\).

\(\text{c}\) \(V_{\text{micro}}\) indicates the micropore volume.

\(\text{d}\) \(D_{\text{BJH}}\) represents the average pore width calculated by BJH model.

Fig. 5. High resolution XPS survey spectra of (A, B) C1s, (C, D) O1s and (E, F) N1s peaks for NCF and rNCF-10% catalysts, respectively.
show that four peaks could be observed after deconvolution, which are assigned to pyridinic-N (398.2 ± 0.2 eV), pyrrolic-N/pyridone (400.3 ± 0.2 eV), graphitic-N (401.3 ± 0.2 eV) and pyridinic N=O (402.5 ± 0.2 eV) [18]. As seen in Table 3, compared to that in the initial NCF, the content of pyridinic-N in the rNCFs increases along with a decrease in pyrrolic-N/pyridone.

### 3.4. Key for the ORR activity of the NCF

According to the characterization and discussion in the preceding paragraph, the chemical reduction treatment did not change the pore structure and crystallinity, but decreased —C=—O moieties and increased pyridinic-N content in the NCF. As reported previously, pyridinic-N refers to as N bonded to two carbon atoms at the edges of graphene planes, which was definitely ascribed to create ORR active sites for NCs [53]. However, the rNCFs with higher content of pyridinic-N (Table 3) shows lower ORR performance than the initial NCF (Figs. 1 and 2). It is proposed that the decrease in pyrrolic-N/pyridone is crucial for the ORR catalytic activity of the NCF, while the quinone/C14-C. It was reported previously ascribed to amide in a pyridine configuration due to the absence of carboxyl derivatives in the NCF prepared at high temperature of 1000 °C. It was reported that pyridone species can undergo tautomeration with 2-hydroxypyridine, which was stable during the chemical reduction treatment [57]. Moreover, this species is proved to catalyze the ORR towards a two-electron pathway [58]. Therefore, it can be induced that the C=—O moieties mainly in quinone-type configuration were of great significant to enhance the ORR activity of NCF. The quinone-type species on the NCF surface enhance the interaction of edge active sites with molecular oxygen, thus facilitating the measured in N2-saturated acid electrolyte (0.5 M H2SO4 solutions). As shown in Fig. 6B, the initial NCF displays a pair of quasi-reversible redox peaks, which assigned to the redox pair of quinone and phenol groups [55]. In contrast, the rNCFs presents much weaker redox peaks, indicating a very low density of quinoid structures. Accordingly, the carbonyl groups are apparently converted to phenol or hydroxyl groups in the rNCF after the reduction with hydrazine hydrate solutions. This result confirms the existence of quinone-type groups in the NCF and is consistent with the XPS results.

To confirm the presence of pyridone-type species and highlight functional groups that introduce protons, we used cross polarization (CP) magic-angle-spinning (MAS) NMR. The signal for such a 13C spectrum originates from protons, and highlights regions within several angstroms from the source proton. Although not quantitative, we can therefore measure whether we can detect differences between the differentially treated samples. The 1H—13C cross polarization (CP) spectra in Fig. S6 reveal that NCF and rNCF-10% both contain aromatic carbon (125 ppm), aliphatic carbons (25, 10 ppm), alcohol (69 ppm), which is in consistent with the XPS results [56]. A shoulder at about 167 ppm appears in both NCF and rNCF-10%, which originated from amide or ester groups. In this study, this signal is believed to be solely corresponded to amide in a pyridone configuration due to the absence of carboxyl derivatives in the NCF prepared at high temperature of 1000 °C. It was reported that pyridone species can undergo tautomeration with 2-hydroxypyridine, which was stable during the chemical reduction treatment [57]. Moreover, this species is proved to catalyze the ORR towards a two-electron pathway [58]. Therefore, it can be induced that the C=—O moieties mainly in quinone-type configuration were of great significant to enhance the ORR activity of NCF. The quinone-type species on the NCF surface enhance the interaction of edge active sites with molecular oxygen, thus facilitating the

### Table 3

Summary of deconvoluted signals for C1s, O1s and N1s core energy levels.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Energy (eV)</th>
<th>Band assignment</th>
<th>NCF</th>
<th>rNCF-9%</th>
<th>rNCF-10%</th>
<th>rNCF-12%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>284.8 ± 0.2</td>
<td>C=C—C=C (sp² graphitic carbon)</td>
<td>62.57</td>
<td>63.42</td>
<td>61.32</td>
<td>62.72</td>
</tr>
<tr>
<td></td>
<td>286.1 ± 0.2</td>
<td>C=—O (phenolic or alcoholic or)</td>
<td>20.83</td>
<td>22.54</td>
<td>29.08</td>
<td>30.23</td>
</tr>
<tr>
<td></td>
<td>288.6 ± 0.2</td>
<td>C=—O (carbonyl or quinone)</td>
<td>16.60</td>
<td>14.04</td>
<td>9.60</td>
<td>7.05</td>
</tr>
<tr>
<td>O1s</td>
<td>531.5 ± 0.2</td>
<td>O=C (quinone or carbonyl)</td>
<td>45.04</td>
<td>38.56</td>
<td>25.78</td>
<td>23.54</td>
</tr>
<tr>
<td></td>
<td>532.3 ± 0.2</td>
<td>C—O=C (epoxy)</td>
<td>33.67</td>
<td>37.99</td>
<td>40.81</td>
<td>39.86</td>
</tr>
<tr>
<td></td>
<td>533.5 ± 0.2</td>
<td>C—OH (phenolic or alcoholic)</td>
<td>21.29</td>
<td>23.45</td>
<td>33.41</td>
<td>36.60</td>
</tr>
<tr>
<td>N1s</td>
<td>398.3 ± 0.2</td>
<td>Pyridinic-N</td>
<td>24.20</td>
<td>26.50</td>
<td>34.70</td>
<td>36.40</td>
</tr>
<tr>
<td></td>
<td>400.3 ± 0.2</td>
<td>Pyrrolic-N/Pyridone</td>
<td>41.60</td>
<td>39.20</td>
<td>28.00</td>
<td>25.30</td>
</tr>
<tr>
<td></td>
<td>401.3 ± 0.2</td>
<td>Graphitic-N</td>
<td>25.50</td>
<td>24.90</td>
<td>24.50</td>
<td>25.10</td>
</tr>
<tr>
<td></td>
<td>402.5 ± 0.2</td>
<td>Pyridinic N—O</td>
<td>8.70</td>
<td>9.40</td>
<td>10.80</td>
<td>13.20</td>
</tr>
</tbody>
</table>

**Fig. 6.** (A) Schematic illustration of nitrogen and oxygen species on the surface of the NCF and rNCFs. (B) CV curves of the NCF and rNCFs measured in N2-saturated 0.5 M H2SO4 solution with a scanning rate of 10 mV s⁻¹. The blue arrows pointed out the redox pair of quinone/phenol groups. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
reduction of O\textsubscript{2} towards a four-electron pathway.

4. Conclusions

In summary, the crucial role for the oxygen functional groups (OFGs) on oxygen reduction reaction (ORR) electrocatalytic activity of NCF was reported. A strategy of chemical reduction was employed to tune the species of the OFGs in the NCFs. After chemical reduction, the rNCFs showed a much lower ORR electrocatalytic activity than the initial NCF in terms of the more negative onset potential, low ORR current density and higher peroxide yield. The characterization tests results showed that the chemical reduction process did not change the physical structures of the NCF, like crystalline and pore structures, but the species of the OFGs. The \( C=\equiv O \) groups in the form of quinone were believed to play the crucial role on the ORR electrocatalytic activity of the NCF. Our findings provided a new insight into understanding of the catalyst mechanism on NCS, and would be beneficial for the design of high-efficient metal-free carbon-based catalysts.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.electacta.2018.09.175.

References


