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Highly Exposed Active Sites of defects enriched Derived MOFs for enhanced Oxygen Reduction Reaction

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ABSTRACT:

The low utilization of active sites of metal-organic frameworks (MOFs)-derived nanostructured carbon materials are considerable challenges in practical applications. Here, we develop a MOFs (ZIF-8)-derived N-doped porous carbon (NPC) nanomaterials as high active oxygen reduction reaction (ORR) catalysts with enhancing both the exposed active sites and surface defects of NPC resulting from the enlarged pore of NPC by KOH activation strategy. The experiments show that the KOH activation not only enlarged the pore size of ZIF-8-derived NPC nanomaterials creating numerous mesopores but also generated abundant defects in NPC nanomaterilas. The 4h KOH activated MOFs-derived NPC (NPC-4) nanomaterials show an activity of 0.257 mA cm$^{-2}$ at 0.9V (vs. RHE), which was almost 10 times greater than that of NPC nanomaterials (0.0265 mA cm$^{-2}$). The NPC-4 exhibits comparable ORR activity, higher stability, and better tolerance to methanol compared with the commercial Pt/C. The density functional theory (DFT) results show that N-doped carbon along with the defects are more favorable for ORR compared with N-doped carbon because the present of defect lead to enhanced O adsorption ability and promote the ORR process.
INTRODUCTION

Metal-organic frameworks (MOFs)-derived carbon nanomaterials have attracted considerable attention in catalysis owing to their superior properties, such as high surface area, large pore volumes, excellent chemical stabilities and an excellent electrical conductivity.\textsuperscript{1-6} Especially, MOFs-derived N-doped porous carbon (NPC) nanomaterials have been widely investigated as oxygen reduction reaction (ORR) electrocatalysts to avoid or minimize the use of precious metals such as Pt in fuel cells.\textsuperscript{7-11} N-doped carbon (N-C) or N-coordinated metals on NPC nanomaterials can be achieved as a highly ORR active sites by pyrolysis of various MOFs precursors.\textsuperscript{12-15} The surface area and porosity of MOFs-derived NPC nanomaterials plays an important role in determining their ORR catalytic properties. The best ORR performance of catalysts derived from MOFs precursors were usually obtained through optimizing the porosity and surface area of those derived catalysts.\textsuperscript{16-18}

Although MOFs-derived NPC nanomaterials possess high porosity and large surface area with numerous active sites, how to create highly exposed active sites and thus improve the utilization of active sites of MOFs-derived NPCs still remains a big challenge. Generally, a high surface area with the maximum exposed active sites to the electrolyte is crucial for the performance of nanoporous electrode materials.\textsuperscript{19} Numerous N-containing active sites can be easily obtained by the direct pyrolysis/carbonization of MOFs with N-containing ligands at high temperatures. N-containing active sites are uniformly distributed throughout of MOFs-derived NPC nanomaterials with a significant thickness and most of those N-containing active sites mainly locate at the micropore surface inside MOFs-derived NPC nanomaterials.\textsuperscript{20-21} The utilization of active sites inside MOFs-derived NPC catalysts are hindered by the limited mass transfer because of small pore size, disorder and their lengthy diffusion path.\textsuperscript{18, 22} There are large transfer resistance for
reactants (such as oxygen) to reach the active sites inside MOFs-derived NPC nanomaterials through micropores which decrease the utilization of active sites of MOFs-derived nanomaterials.\textsuperscript{23-24} The optimizing porosity of MOFs-derived NPC nanomaterials creating mesopores by NH\textsubscript{3} activation showed higher ORR performance compared with nanomaterials derived from their pure MOFs due to a faster mass transfer,\textsuperscript{25-26} Xie et al. reported a biomass-derived hierarchical porous carbon material by KOH activation with unique porous structural properties as electrode materials.\textsuperscript{27} Recently, experiments and theoretical calculations demonstrated that adjusting surface defects in the carbon nanomaterials is one of most effective strategies to enhance the ORR activity.\textsuperscript{28-31} Therefore, it is desirable to explore an effective way to enlarge the pore size of MOFs-derived NPC nanomaterials generating mesopores and defects and thus providing more exposed active sites and facilitating the mass transfer to enhance the ORR activity.

Here, we demonstrate a novel strategy to enhance the ORR activity of MOFs-derived nanomaterials through enlarging the pore size and adjusting surface defects of the MOFs-derived NPC nanomaterials by the KOH activation. In this work, the Zn-based zeolitic imidazolate framework (ZIF-8) is used as a mode MOFs to produce NPC nanomaterials. The experiments show that the KOH activation not only enlarged the pore size of ZIF-8-derived NPC nanomaterials but also generated defects in NPC nanomaterials, which expose more active sites and facilitate the mass transfer of ORR reactants. The pore-enlarged ZIF-8-derived NPC nanomaterials have higher ORR activity than the pure ZIF-8-derived NPC.

EXPERIMENTAL SECTION

Synthesis of pore size enlarged NPC derived from ZIF-8 precursor
The ZIF-8 was synthesized according to a reported procedure. The as-prepared ZIF-8 was
grounded into a powder and transferred into a quartz tube, followed by the heat treatment
temperature 900°C for 2h under N₂ atmosphere, the obtained black powder is washed with 1 M
HCl and then washed with deionized water three times (labeled as NPC). For the KOH activation
process, a mass ratio of 1:1 of NPC and KOH was added in 15 ml deionized water and
ultrasonicated for 1h. Then the suspension was evaporated to form a smooth and thick slurry by
heating under magnetic stirring at 80°C, followed drying at 60 °C in a vacuum oven. After being
ground in an agate mortar, samples was heated in a tube furnace at 750 °C for 1h, 2h, 4h, 5h
(labeled as NPC-1, NPC-2, NPC-4, NPC-5, respectively) at N₂ atmosphere. The resulting products
were firstly washed with 1M HCl and then washed with deionized water three times, followed
drying 70°C in a vacuum oven.

Materials Characterization

The morphology and structure of the samples were characterized by scanning electron
microscopy (SEM, SUPRA 55), transmission electron microscopy (TEM, TECNAL G2F2O) and
X-ray powder diffraction (XRD, ULTIMA III). X-ray photoelectron spectroscopy (XPS)
characterization was performed by a K-Alpha. Nitrogen adsorption-desorption isotherms were
determined by the Brunauer-Emmett-Teller (BET) equation using the equipment of
MICROMERITICES 3Flex. Material surface analysis were determined by Raman.

Electrochemical Testing

All electrochemical measurements were carried out at room temperature using an Autolab
electrochemistry station in a standard three-electrode cell. A catalyst modified glassy carbon
electrode was used as the working electrode. Ag/AgCl (sat. KCl) and platinum wire were used as
reference and counter electrodes, respectively. The working electrodes were prepared as follows. The catalyst slurry was prepared by mixing 5.0 mg of catalyst in 350µL ethanol and 150µL water and 50µL Nafion (5 wt. %) and then ultrasonicated for 15 minutes to form a uniform black ink. Subsequently, 5.6 µL of prepared catalyst ink was pipetted onto rotating disk electrode (RDE, 3.00 mm diameter). For the commercial Pt/C (20 wt. %), 3.0 mg sample was added in 3ml deionized water contained 10µL Nafion (5 wt. %), followed by ultrasonicated for 15min, and then 3.6µL ink was pipetted onto RDE. The potentials presented in this study are referred with respect to reversible hydrogen electrode (RHE). Cyclic voltammetry (CV) measurements were performed at a scan rate of 10 mV·s⁻¹ within a potential range from 0.05 V to 1.2 V (vs. RHE) in 0.1 M KOH. ORR linear sweep voltammetry (LSV) measurements were conducted on a RDE in O₂-satureted 0.1 M KOH solution at a scan rate of 10 mV·s⁻¹ and at rotating speed of 1600 rpm. The electrochemical impedance spectroscopy (EIS) are recorded in O₂-saturated 0.1 M KOH at 0.82 V (vs. RHE) with 5 mV ac potential from 10 kHz to 0.01 Hz (rotation speed:1600 rpm). Methanol tolerability tests were performed in 0.1 M KOH contained 1 M methanol. Accelerated durability tests (ADT) were performed by sweeping electrode between 0.6 V-1.0 V (vs. RHE) at 50 mV/s for 10000 cycles in oxygen saturated 0.1 M KOH.

**Density Functional Theory Calculation**

Geometric optimization and total energy calculations were performed within DFT framework as implemented with Vienna ab initio simulation package (VASP) in which spin-polarization was all considered. We used the Projector-augmented wave (PAW) potentials’ database to simulate the interaction between valence electrons and cores. In addition, the Perdew-Burke-Ernzerh (PBE) of exchange correlational function and the Generalized-Gradient Approximation (GGA) was adopted to investigate the transfer and correlation of electrons. It is reasonable to choose the
kinetic energy cutoff for plane wave expansion at 450 eV and a 2×2×1 Monkhorst-Pack k-point grid sampling of the first Brillouin zone.\textsuperscript{40} In order to determine the occupancy, we set the Gaussian smearing width to 0.1 eV. The adsorption surface, of which the unit lattice constant is set to 12.792Å×14.772Å and the vacuum layer is set to 15Å, was calculated the structural relaxation by using a conjugate gradient algorithm, limiting the maximum force and energy of unconstrained atoms to less than 0.01 eV/Å and 1×10\textsuperscript{-5} eV, respectively. The electronic iteration convergence value for self-consistent field (SCF) calculation was set to 1×10\textsuperscript{-4} eV.

RESULTS AND DISCUSSION

The fabrication strategy of the pore size enlarged NPC nanomaterials derived from ZIF-8 precursors is schematically illustrated in Scheme 1. First, the average particle size of prepared ZIF-8 is 40-50 nm (Figure S1). The ZIF-8 crystals are converted into N-doped graphitic porous carbon nanomaterials retaining its original morphology after carbonization at 900°C under N\textsubscript{2} atmosphere (Figure S2). After KOH activation, it is obvious that a much rougher surface formed on the KOH activated NPC nanoparticles in comparison with parent ZIF-8 derived NPC. The surface roughness of NPC nanoparticles increase with the time of KOH activation (Figure 1 and Figure S3-S5), mainly originating from the generation of numerous surface defects on the NPC.\textsuperscript{41}

Scheme 1. Schematic diagram of the synthesis of the pore size enlarged N-doped porous carbon (NPC) nanomaterials derived from ZIF-8 precursors.
More importantly, we found that the pore size of ZIF-8 derived NPC nanoparticles enlarged after KOH activation and the pore size increase with prolonged time of KOH activation. As shown in Figure S3, it is observed that most pores formed on the surface of ZIF-8 derived NPC nanoparticles are micropores (in red cycle). Some larger pores (>1nm) were found on the surface for 1h and 2h KOH activated ZIF-8 derived NPC nanoparticles (Figure S3 and Figure S4). When activation time is prolonged to 4h, micropores decrease and most of pore size is more than 1nm on the surface of NPC-4 nanoparticles (Figure 1c and Figure 1d). Furthermore, mesopores formed

![Fig. 1](image)

Fig. 1. (a) SEM image of NPC-4 sample, (b) Low-resolution and (c and d) high-resolution TEM images of NPC-4 sample.
in NPC-4 nanoparticle. It is worth mentioned that larger pore in KOH activated ZIF-8 derived NPC formed through coalescing of unconnected micropores of NPC. These findings suggest that KOH activation is a good strategy to enlarge the pore size of MOFs derived NPC nanomaterials. However, it is very important to control the KOH activation time and the framework of ZIF-8 derived NPC nanoparticles collapsed during the KOH activation process when KOH activation time increases to 5h (Figure S5). The framework collapse of NPC-5 will lower mass transfer and thus decrease the ORR activity.

The pore structure of nanoporous electrode materials plays an important role in determining the ORR activity because the pore size will affect diffusion of reactants and mass transport. The nitrogen absorption/desorption isotherms were used to further investigate the details of pore size change of KOH activated ZIF-8 derived NPC nanoparticles. The isotherms as shown in Figure 2a indicate that the 4h KOH activation can obviously increase the BET surface area of ZIF-8 derived NPC nanoparticles. More important, compared with NPC sample, the distinct hysteresis loop in the range of $P/P_0$ 0.4-0.8 for NPC-4 sample suggests that 4h KOH activation significantly increase the mesopore (pore size of 2-50 nm) of NPC sample, which is beneficial for mass transfer through the entire NPC and promotes the interfacial catalytic reaction. The pore size distribution (PSD) while the ZIF-8 derived NPC nanomaterials mainly have micropore structure with pore size between 0.5 and 1 nm (Figure 2b). It is well known that MOF derived nanomaterials with abundant mesopores can provide a favorable mass transport platform and expose more active sites. To understand how the mesopore formed in NPC-4 nanomaterials, we carefully check the pore size of different KOH time activated NPC. After 1h KOH activation, the micropore centred at 1.2 nm increased and mesopore centred at 2.3 nm formed on the NPC-1 samples (Figure S6).
Fig. 2. (a) N\textsubscript{2} adsorption-desorption isotherms of ZIF-8 derived NPC nanomaterial and KOH activated ZIF-8 derived NPC nanomaterials. (b) Pore size distribution data obtained by the density functional theory (DFT) method of NPC and NPC-4 samples. (c) High-resolution N 1s spectra and (d) the contents of four kinds of nitrogen species of ZIF-8 derived NPC nanomaterial and KOH activated ZIF-8 derived NPC nanomaterials.

In addition, some pore size (< 0.5 nm) appeared. When KOH activation time increase to 2h, the pore size ranging from 1nm to 4 nm increased compared with the NPC-1 samples (Figure S6). It is obvious that the pore size (< 1nm) decreased when KOH activation time increase to 5h (Figure S6). The surface area and pore area characteristics of NPC and KOH activated NPC samples were summarized in Table 1. The KOH activation can firstly create micropores on the surface of NPC through the etching reaction between KOH and carbon, confirmed by the analysis of BET results. The size of newly generated micropores increase with etching reaction and then enlarge or coalesce
the unconnected micropores of NPC to new mesopores with the increase in the activation time (Scheme 1). The mechanism of KOH activation for the enlarged pore structure of NPC materials may considered as the etching reaction of carbon in ZIF-8-derived NPC according to the following equation (1):  

$$6\text{KOH} + 2\text{C} \rightarrow 2\text{K} + 2\text{K}_2\text{CO}_3 + 3\text{H}_2$$  

(1)

### Table 1. Surface area and pore area characteristics of NPC, NPC-1, NPC-2, NPC-4 and NPC-5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m$^2$ g$^{-1}$)</th>
<th>Micropore area (m$^2$ g$^{-1}$)</th>
<th>Mesopore area (m$^2$ g$^{-1}$)</th>
<th>$S_{\text{Meso}}/S_{\text{BET}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPC</td>
<td>1003</td>
<td>936</td>
<td>67</td>
<td>6.7</td>
</tr>
<tr>
<td>NPC-1</td>
<td>3077</td>
<td>2461</td>
<td>616</td>
<td>20</td>
</tr>
<tr>
<td>NPC-2</td>
<td>3074</td>
<td>2360</td>
<td>714</td>
<td>23.2</td>
</tr>
<tr>
<td>NPC-4</td>
<td>2928</td>
<td>2047</td>
<td>881</td>
<td>30</td>
</tr>
<tr>
<td>NPC-5</td>
<td>2818</td>
<td>1862</td>
<td>956</td>
<td>33.9</td>
</tr>
</tbody>
</table>

The nanoporous electrode materials containing both micropores and mesopores will increase the utilization of active sites because mesopores facilitate the mass transfer, while micropores provide numerous accessible active sites. BET results further confirm that the KOH activation is an effective way to enlarge the pore size of MOFs derived NPC nanomaterials to create numerous mesopores and expose more active sites, thus increasing the utilization of active sites within whole nonporous catalysts.

XPS measurements were used to analyze the surface chemical states of KOH activated ZIF-8 derived NPC nanomaterials. Figure S7 show the XPS survey spectra of KOH activated ZIF-8
derived NPC nanomaterials. The high resolution N1s spectra of NPC nanomaterials as shown in Figure 2c display the existence of four nitrogen species: pyridinic-N (~398.6 eV), pyrrolic-N (~400.1 eV), graphitic-N (~401.2 eV) and oxidized-N (~404.1 eV). It is believed that pyridinic-N or graphitic-N species are the dominant active sites for ORR.\textsuperscript{51-56} We found that the content of different N type of as-prepared samples change with the KOH activation (Figure 2d). After 1h KOH activation, the content of pyridinic-N and pyrrolic-N decrease while the content of graphitic-N and oxidized-N slight increase, which may be attributed to the different KOH etching speed for various N-C configuration. With prolonged time KOH activation, the NPC-2 samples have 25% pyridinic-N and 26% graphitic-N while the NPC-4 samples possess 26% pyridinic-N and 31% graphitic-N. Therefore, the NPC-4 nanomaterials contain more pyridinic-N and graphitic-N atoms than other KOH-activated NPC samples, which considered to be highly active sites for the ORR.\textsuperscript{12} Figure 3a displays the raman spectra of KOH activated ZIF-8 derived NPC nanomaterials with a typical D-band ($\sim$1350 cm\textsuperscript{-1}) and G-band ($\sim$1580 cm\textsuperscript{-1}) corresponding to the disorder carbon and the highly order graphitic carbon, respectively.\textsuperscript{57-58} The intensity ratio ($I_D/I_G$) of NPC is 0.95 and

![Fig. 3. (a) Raman spectra and (b) XRD of the ZIF-8 derived NPC nanomaterial and KOH activated ZIF-8 derived NPC nanomaterials.](image-url)
the ratio of $I_D/I_G$ gradually increases to 1.08 with KOH etching time, indicating the KOH activation generates the defects in NPC. The more defects in KOH activated NPC are further confirmed by the X-ray diffraction (XRD) patterns (Figure 3b). NPC displayed two broad peaks at 25° and 43°, corresponding to the (002) and (101) planes of graphitic carbon while KOH activated NPC show very weak peaks at 25° and 43°, suggesting that the KOH activation can generate defects on the surface of NPC. Our finding is also in consistent with the previous studies which shows the KOH activation can effective generate the defects on carbon materials.\textsuperscript{41} It is observed that abundant defects on carbon material can serve as efficient active sites for ORR.\textsuperscript{53, 59-60}

The electrochemical performance of the as-prepared samples was carried out to investigate the effects of the KOH activation on NPC nanomaterials as electrochemical catalysts towards ORR. The NPC nanomaterials without KOH activation show poor ORR activity with a large overpotential (Figure 4a). The KOH activation can gradually enhance the ORR activity with an increased activation time ranging from 1h to 4h (Figure 4a). The ORR activity of NPC-4 nanomaterials at 0.9V is 0.257 mA cm\textsuperscript{-2}, which was almost 10 times greater than that of NPC nanomaterials (0.0265 mA cm\textsuperscript{-2}). The NPC-4 nanomaterials exhibited highest catalytic activities towards ORR, which is comparable to that of Pt/C catalysts. In addition, the Tafel slopes for NPC-4 and Pt/C were observed to be very similar (Figure S8). However, it was observed that the ORR catalytic activity of the NPC-5 nanomaterials decreased (Figure 4a). This is likely ascribed to the collapse of ZIF-8 derived NPC framework in consistent with the analysis of TEM images, which will decrease the ORR activity due to the increase in the mass transport resistance. So, it is very important to control KOH activation time to keep NPC morphology and optimize porosity. The enhanced ORR activity of NPC-4 nanomaterials should be attributed the more active sites resulting from optimization of N species and enlarged pore of NPC, which create numerous mesopores
facilitating the mass transfer of ORR reactants and increasing the utilization of active sites. The electrochemical impedance spectroscopy measurements (Figure 4b) also reveal that the NPC-4 has much lower the charge-transfer resistance and the intrinsic resistance compared with the other as-prepared samples. To further investigate the ORR kinetics of the NPC-4 samples, LSV polarization curves at various rotating rates are performed using a rotating disc electrode (RDE).
The n value for NPC-4 sample is calculated to be 3.94 according to the slope of K-L plots in the potential range of 0.3 V to 0.6 V (Figure 4c), which is close to the four-electron ORR process. Comparison of ORR activities NPC-4 catalyst and latest N-doped carbon catalysts reported previously further verifies that our synthesis strategy is very effective in improving ORR performance (Table S1).

The evaluation of stability is crucial for development of new electrocatalyst for practical application. The accelerated durability tests (ADT) were conducted using a thin-film catalyst coated on a RDE. The electrode potential was cycled between 0.6 V-1.0 V (vs. RHE) at 50 mV/s for 10000 cycles in oxygen saturated 0.1 M KOH. It is observed that the NPC-4 catalyst is more stable than the commercial Pt/C catalyst. After 10000 cycles, the $E_{1/2}$ value of NPC-4 catalyst exhibits a small negative shift of 10 mV (Figure 4d), while the commercial Pt/C catalyst shows larger negative shift of 41 mV during potential cycling (Figure S9). Furthermore, compared with Pt/C catalyst, the NPC-4 catalyst shows better tolerance to the methanol poison (Figure S10), suggesting an excellent ORR selectivity.

To further explore the intrinsic ORR catalytic mechanism of the N-doped carbon, density functional theory (DFT) calculations are carried out to determine the dominant catalytic sites of different doping configurations. We first used principles DFT calculations to evaluate graphitic-N and pyridinic-N species toward ORR activity in alkaline solution. The calculated free energy profiles on these two N doping configurations are shown in Figure S11. Our DFT study predicted that the ORR catalytic activity of the graphitic-N species is similar to the pyridinic-N species in alkaline media. To study the influence of N-doped carbon nanomaterials along with the defects, we calculated the ORR processes on pyridinic-N and defect- pyridinc-N models (Figure 5a and...
Figure 5b). In alkaline media, after O$_2$ molecule firstly adsorbed on the top of the active sites on NPC-4 sample, O$_2$ will be protonated to form OOH*, the OOH* will then dissociate into O* and OH*, and finally both O* and OH* form product OH$^-$. The oxygen molecules adsorbed the surface of catalysts as the initial step play an important role in the ORR activity. Figure 5c revealed that the defect- pyridinic-N has lower energy barrier for O$_2$ chemisorption in first step of ORR process (O$_2$ +* $\rightarrow$ O$_2$*), which will benefit for the high ORR activity. Moreover, the rate determining step for the ORR process (OH*+e$^-$$\rightarrow$OH$^-$) has a lower overpotential in defect-pyridinic-N. Those data suggested that the defects on KOH activated NPC will facilitate the ORR process. As shown in Figure 5d, the increased electronic states around the Fermi level in defect-
pyridinic-N may be ascribed to the formation of defects around pyridinic-N, leading to the enhanced O adsorption ability and thereby the ORR activity. In summary, the presence of defects structure helps to improve ORR activity in alkaline electrolytes.

CONCLUSION

In conclusion, we successfully synthesized a highly active ORR metal-free N-doped carbon catalyst through both enlarging the pore size and generating surface defects of the ZIF-8-derived NPC nanomaterials by KOH activation. The 4h KOH activated MOF derived NPC (NPC-4) nanomaterials show almost 10 times higher than that of NPC nanomaterials. It is found that the optimized NPC-4 exhibits comparable ORR catalytic activity, higher stability, and better tolerance to methanol compared with the commercial Pt/C. The enhanced ORR activity of NPC-4 nanomaterials is attributed to the abundant surface defects and the highly exposed active sites enabled by KOH activation creating numerous mesopores, which facilitate the mass transfer of ORR reactants. The density functional theory (DFT) results show that N-doped carbon along with the defects are more favorable for ORR compared with N-doped carbon because the present of defect lead to enhanced O adsorption ability and promote the ORR process. We believe that the general synthetic strategy presented here can be extended to other catalytic systems increasing the exposed of active sites.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:
SEM images, XRD patterns, TEM images, nitrogen adsorption/desorption isotherms, XPS spectra, Tafel plots, Durability tests, Methanol poison tests, Free energy profiles, Comparison of ORR activities

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The authors declare no competing financial interest.

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SYNOPSIS

A highly active ORR catalyst is achieved through enhancing the exposed active sites and surface defects of the ZIF-8-derived carbon by KOH activation.