PAF-derived nitrogen-doped 3D Carbon Materials for Efficient Energy Conversion and Storage

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Owing to the shortage of the traditional fossil fuels caused by fast consumption, it is an urgent task to develop the renewable and clean energy sources. Thus, advanced technologies for both energy conversion (e.g., solar cells and fuel cells) and storage (e.g., supercapacitors and batteries) are being studied extensively. In this work, we use porous aromatic framework (PAF) as precursor to produce nitrogen-doped 3D carbon materials, i.e., N-PAF-Carbon, by exposing NH3 media. The “graphitic” and “pyridinic” N species, large surface area, and similar pore size as electrolyte ions endow the nitrogen-doped PAF-Carbon with outstanding electronic performance. Our results suggest the N-doping enhance not only the ORR electronic catalysis but also the supercapacitive performance. Actually, the N-PAF-Carbon obtains ~70 mV half-wave potential enhancement and 80% increase as to the limiting current after N doping. Moreover, the N-PAF-Carbon displays free from the CO and methanol crossover effect and better long-term durability compared with the commercial Pt/C benchmark. Moreover, N-PAF-Carbon also possesses large capacitance (385 F g⁻¹) and excellent performance stability without any loss in capacitance after 9000 charge–discharge cycles. These results clearly suggest that PAF-derived N-doped carbon material is promising metal-free ORR catalyst for fuel cells and capacitor electrode materials.

Since the shortage of the traditional fossil fuels and CO2 emission issues1-2, it become an urgent task to develop the renewable and clean energy sources. Toward this end, advanced technologies for both energy conversion (e.g., solar cells3-4 and fuel cells5) and storage (e.g., supercapacitors6 and batteries7-9) are being studied extensively. Actually, the catalysts for oxygen reduction play a key role in regulating the performance of fuel cells. However, it is still a great challenge to develop highly efficient and stable oxygen reduction reaction (ORR) electrocatalysts at a low cost since the scarcity, high cost and poor long-term stability of the Pt-based ORR catalysts are main obstacles for commercialization of the fuel cell technology.

The porous carbon family has been demonstrated to be promising candidates for high-performance energy-conversion and storage devices. Recently, N-doping has been widely considered as one of the most feasible approaches to modulate the electronic and catalytic properties of graphene and its derivatives9-16. A large variety of heteroatom-doped carbon materials, including vertically-aligned nitrogen-containing carbon nanotubes (VANCNTs)12, N-doped graphene17, nitrogen carbide, and N-doped ordered mesoporous graphitic arrays18, have been demonstrated to be efficient metal-free ORR electrocatalysts free from CO “poisoning” with a comparable even higher electrocatalytic activity and better long-term operation stability than the commercially available Pt-based electrodes (e.g., C2-20, 20% platinum on Vulcan XC-72R; E-TEK) in alkaline electrolytes. Moreover, N-doping technology has also been extensively used in highly efficient supercapacitors9,10,19,20.

Recently, porous covalent organic materials (COMs)21-28 with high porosity and controllable structural characteristics as well as multi-chemical functionality have been considered as self-sacrificed precursor to fabricate novel nanoporous carbons including graphene analogues. The COM-derived porous carbons show a lot of advantages. For example, their inherent optimized pore size allows ion migration, and high surface area provides the possibility of formation of an electrostatic charge-separation layer, and a highly ordered structure enables the formation of conductive paths. All these characteristics suggest that COM-derived porous carbon is a class of promising electrocatalyst materials. Pachfule et al. employed N-rich porous-organic-frameworks as template to prepare porous nitrogen-rich carbon under 1000°C and obtained ~40 mV enhancement in the onset potential compared to that of a commercial Pt/C catalyst29. Zhuang et al. prepared the S-/N-doped 2D porous carbons by...
the combination of graphene with 2D conjugated microporous polymers as metal-free catalysts for ORR and as supercapacitors. Kou et al. synthesized a Aza-fused p-conjugated microporous framework (Aza-CMP) via phenazing ring fusion reaction and Aza-CMP@450 shows large capacitance of ∼530 F g⁻¹ at 0.2 A g⁻¹.

3D structures provide an ideal platform towards the maximization of high specific surface areas, strong mechanical strengths and fast mass and electron transport kinetics for the development of high-performance catalysts, electromechanical and electrochemical devices. Actually, the composition and structure of COM materials would determine the electrochemical properties of the resulting porous carbons. Here, to synthesize 3D carbon and reduce the effects of other elements in COM materials, we select porous aromatic porous carbons. N-PAF-Carbon.

Results

Material characterizations. The FT-IR (Figure S1) and solid-state ¹³C/MAS NMR (Figure S2) measurements reveal the success of C-C coupling in synthesis processes, which is consistent with the previous report. The pore size distribution derived from the N₂ adsorption at 77 K shows that the pore size of as-synthesized PAF-1 is ∼1.27 nm (Figure 1b), which also consists with the reported one. Our thermo gravimetric (TG) results suggest the carbonization should be carried out with two steps, i.e., first preheated at 350 °C for a period of time and subsequently carbonized at a given high temperature. As shown in Figure 1c, the sample heated directly under N₂ atmosphere without preheating at 350 °C almost loss all the weight before 900 °C, while the sample with preheating at 350 °C for 2 hours can reserve up 70% weight even under 900 °C. The 1.54 wt% weight (the inset in Figure 1c) during this process can be ascribed to the adsorbed guests (e.g. O₂, CO₂) in the air due to ultrahigh surface area and the as-synthesized PAF-1 sample can be almost burned with the only adsorbed O₂ molecules in the air.

For comparison, we also prepared undoped 3D PAF derived carbon material. For simplicity, we marked the carbonized PAF carbon materials as PAF-Carbon-T (T= 600, 800 and 1000 °C and T is omitted when T = 800 °C). As shown in Figure 2a, the sample PAF-Carbon-800 show the best graphitization degree (I_G/I_D=1.07, Figure 2a) among the three PAF-derived carbon samples. The intensity of D band becomes higher than that of G band when the temperature is increased to 1000 °C, suggesting the structure of PAF-1 may be completely destroyed and the disordered carbons dominate under 1000 °C. The powder X-ray diffraction (XRD) spectra with two pronounced (0 0 2) graphitic peaks at 26° and (1 0 0) at 43° (Figure S3), indicate the formation of graphitic structures during carbonization. Combining the above results with the following ORR activities (vide infra), we employed 800 °C as the optimal carbonization temperature for preparing N-PAF-Carbon. The Raman results of N-PAF-Carbon show a high ratio of I_G/I_D (1.23, Figure 2a), suggesting good graphitization degree. The X-ray photoelectron spectroscopic (XPS) measurements show that the atomic percentage of N in N-PAF-Carbon reaches 4.1% (Figure 2b). The XPS N 1s spectra of N-PAF-Carbon (Figure 2c) could be deconvoluted into three sub-peaks: “graphitic” N at 401.1 eV, “pyrrolic” N at 400.1 eV and “pyridinic” N at 398.6 eV, in which the “graphitic” and “pyridinic” N dominate (Figure 2d). Transmission electron microscopic (TEM) images show porous texture in N-PAF-Carbon (Figure 2e). The XRD spectra of N-PAF-Carbon also shows two pronounced (0 0 2) graphitic peaks at 26° and (1 0 0) at 43° (Figure S3), suggesting that the N-PAF-Carbon has good crystalline quality.

Oxygen reduction reaction (ORR) evaluation. The electrocatalytic activities of the non- and N-doped PAF derived carbon materials were explored through cyclic voltammetry (CV), rotating disk

Figure 1 | (a) The scheme for synthesis of PAF-1 materials. The cyan sphere in the right structure refers to the pore in PAF-1 and the purple lines refer to the framework of diamond structure. The actual structures of the statistical PAF-1 materials will be more complex than the one represented. (b) Pore size distribution and cumulative pore volume of PAF-1 obtained by non-local density functional theory modelling on the N₂ adsorption curve. (b) TG analysis of as synthesized PAF-1. The inset refers to the enlargement of the TG analysis in blue circle region.
electrode (RDE), rotating ring disk electrode (RRDE), and chronoamperometric measurements in 0.1 M KOH aqueous solution. Pt/C was also measured for comparison. The RDE measurements show the optimized annealing temperature is to be 800 °C since the sample PAF-Carbon-800 possess the highest positive onset and half-wave potential (Figure 3b). Therefore, combining with the above characterization (vide supra), we employ 800 °C as the carbonization temperature to obtain N-PAF-Carbon. As shown as in Figure 3a, both PAF-Carbon and N-PAF-Carbon show a well-defined cathodic peak centered in the CV curve when the electrolyte was saturated with O₂-saturated 0.1 M KOH, and present a featureless slope for the cathodic current with N₂-saturated 0.1 M KOH within the entire potential range (Figure S4a and S5a). N-PAF-Carbon possesses about 20 mV positive cathodic peak than that of PAF-Carbon, suggesting a more pronounced catalytic activity of N-PAF-Carbon compared with non-doped PAF carbon.

To gain further insight into the ORR process of PAF-Carbon and N-PAF-Carbon, RDE measurements were performed in O₂-saturated 0.1 M KOH electrolyte at a scan rate of 5 mV s⁻¹. As can be seen in Figure 3b, the N-doped sample exhibits much better catalytic activity compared with the non-doped PAF-Carbon. N-PAF-Carbon obtains about 70 mV enhancement for the half-wave potential compared with PAF-Carbon (0.75 vs. 0.68 V) and the limiting current is also improved as much as 80% (from 2.39 mA cm⁻² to 4.30 mA cm⁻²) after nitrogen doping. In particular, the N-doped PAF sample shows only about 44 mV less for the half-wave potential than the commercial Pt/C. Subsequently, RRDE measurements were carried out to determine their catalytic reaction pathway (Figure 4c). On the basis of the ring and disk currents, the electron transfer number (n) of N-PAF-Carbon was calculated to be 3.50–3.55 at 0 to 0.8 V (vs. reversible hydrogen electrode: RHE), suggesting a mainly four-electron oxygen reduction process. These results consist with those derived from RDE with K-L equation (Figures S5 and S6). In contrast, the electron transfer number for PAF-Carbon was less than 3 under similar condition. Particularly, the peroxide percentage for N-PAF-Carbon was remarkably reduced to <30% from 80% of non-doped PAF-Carbon sample. Basing on the above result, we can infer that the N-doping remarkably enhances the electrocatalytic activity of the PAF-Carbon for ORR. Furthermore, the chronoamperometric measurements show the N-PAF-Carbon is almost free from the CO and methanol crossover effects and holds better long-term durability compared with the commercial Pt/C. These results indicate that N-PAF-Carbon material is promising metal-free ORR electrocatalyst for fuel cells.

Supercapacitance performance. Apart from enhancement for ORR activity of the N-doped technique, we also investigated the effect of N-doping on the supercapacitive behavior. As shown in Figure 4a and 4c, one significant feature in the I–V profiles is that no redox peaks are observable, which indicates that PAF derived carbon do not involve redox-related faradic processes during the charge-discharge processes. The I–V curves of both PAF-Carbon and N-PAF-Carbon at the different scan rates retain good symmetry, which confirms good electrochemical stability and capacitance. The current of the N-PAF-Carbon is more than 40% larger than those of non-doped PAF-Carbon. The specific capacitance was evaluated from the discharge curves (Figure. 4b and 4d). Under higher current densities than 0.5 A g⁻¹, the capacitances of PAF-Carbon were largely enhanced after N-doping. In particular, the capacitance of PAF-Carbon is increased from 75 to 135 F g⁻¹ (with 80% increment) after N-doping at 10 A g⁻¹. When the current density was reduced to 0.2 A g⁻¹, the charge-discharge profiles of PAF-Carbon show remarkable asymmetry character and the hysteresis appears in the discharge process, which may arise from the relatively poor electronic conductivity of PAF-Carbon. In a sharp contrast, the charge-discharge curves of N-PAF-Carbon sample exhibits good symmetry under low current density, even at 0.2 A g⁻¹, which confirms the electronic conductivity of N-PAF-Carbon is largely enhanced after N-doping. The hysteresis results in the ‘inflated’ supercapacitance of PAF-Carbon (Figure 4c) compared with that...
of N-PAF-Carbon. Particularly, the supercapacitance of N-PAF-Carbon at 0.1 A g⁻¹ reaches 385 F g⁻¹, which is close to the previously reported ‘ultrahigh’ supercapacitance of Aza-CMPs (93–549 F g⁻¹),¹³ N-doped graphene foam (484 F g⁻¹)¹⁹ but superior to the state-of-the-art nanostructured carbon, e.g., activated carbon materials (<270 F g⁻¹),²⁷–²⁹ N-rich porous carbon materials (50–330 F g⁻¹), carbon nanotubes (50–120 F g⁻¹),⁴⁰ graphene (135 F g⁻¹), N-doped graphene film (280 F g⁻¹)¹⁹, and carbon fibers (120–370 F g⁻¹)³⁵ and remarkably outperform those carbons derived from metal organic frameworks (MOFs).²⁴–²⁶ (See more results in Table S1 in the Supporting Information).

Discussion

To gain insight into the kinetic behavior of N-doping enhancement for supercapacitance, we further carried out electrochemical impedance spectroscopic (EIS) measurements. In Figure 5a, N-PAF-Carbon exhibits an approximately vertical line, which suggests that N-PAF-Carbon possesses lower diffusive resistivity for the electrolyte ions within the pores. N-PAF-Carbon show a near vertical line, which suggests that N-PAF-Carbon possesses lower diffusive resistivity for the electrolyte ions within the pores. N-PAF-Carbon possesses a larger specific surface area (SSA) (764 vs. 600, PAF-Carbon-800, PAF-Carbon-1000, N-PAF-Carbon and Pt/C in O₂-saturated 0.1 M KOH at 1600 rpm at a sweep rate of 5 mV s⁻¹). (c) RRDE curves for PAF-Carbon and N-PAF-Carbon at 1600 rpm. The calculated H₂O₂ yield derived from RRDE is also inserted. (d)–(f), Methanol and CO-poison effects and durability evaluation on i-t chronoamperometric responses for ORR at Pt/C (red) and N-PAF-Carbon (black) electrodes. In figure d, the arrow indicates the addition of 3 mL methanol into the O₂-saturated electrochemical cell after about 400 s. In figure e, the addition of 55 mL min⁻¹ CO gas into the 550 mL min⁻¹ O₂ flow saturated electrochemical cell after about 250 s.

Figure 3 | (a) CV curves of PAF-Carbon and N-PAF-Carbon in O₂-saturated 0.1 M KOH at a sweep rate of 50 mV s⁻¹. (b) LSV curves for PAF-Carbon-600, PAF-Carbon-800, PAF-Carbon-1000, PAF-Carbon and Pt/C in O₂-saturated 0.1 M KOH at 1600 rpm at a sweep rate of 5 mV s⁻¹. (c) RRDE curves for PAF-Carbon and N-PAF-Carbon at 1600 rpm. The calculated H₂O₂ yield derived from RRDE is also inserted. (d)–(f), Methanol and CO-poison effects and durability evaluation on i-t chronoamperometric responses for ORR at Pt/C (red) and N-PAF-Carbon (black) electrodes. In figure d, the arrow indicates the addition of 3 mL methanol into the O₂-saturated electrochemical cell after about 400 s. In figure e, the addition of 55 mL min⁻¹ CO gas into the 550 mL min⁻¹ O₂ flow saturated electrochemical cell after about 250 s.
Furthermore, N-PAF-Carbon also exhibits excellent stability without any loss in capacitance after 9000 charge–discharge cycles at a current density of 5 A g$^{-1}$ and the charge–discharge profiles retain the linearity and symmetry well (Figures 5e and 5f). In short, N-PAF-Carbon possesses not only large capacitance but also an excellent cycle life, and is very promising capacitor electrode materials.

In summary, we firstly developed the physical exposure to nitrogen-containing moieties doping approach to introduce N heteroatom into covalent organic materials. Our results suggest the N-doping technique enhance not only the ORR electronic catalysis but also supercapacitive behavior. The N-doped PAF derived carbon obtains ~70 mV enhancement as to half-wave potential and 80% increase as to the limiting current for ORR catalysis. Moreover, the N-doped PAF derived carbon displays free from the CO and methanol crossover effect and better long-term durability compared with the commercial Pt/C benchmark. Furthermore, N-PAF-Carbon based capacitor device is only 0.96 Ω equivalent series resistance.
Figure 5 | (a) Nyquist plots of PAF-Carbon and N-PAF-Carbon. Inset shows the impedance in the high and medium-frequency regions and an equivalent circuit as electrode materials is also inserted. (b) Plot of imaginary capacitance versus frequency. The inset shows a plot of the time constant $\tau_0$ of PAF-Carbon and N-PAF-Carbon. (c) $N_2$ adsorption isotherms of PAF-Carbon and N-PAF-Carbon at 77K. Solid and open symbols represent adsorption and desorption, respectively. (d) NLDFT pore size distributions of PAF-Carbon and N-PAF-Carbon by incremental pore volume. (e) Charge–discharge curves of N-PAF-Carbon during a test of 9000 cycles. The profiles of three time zones of the initial, middle, and last 700 seconds are selected to confirm that they are identical to each other in shape and symmetry. (f) Capacitance percentage of N-PAF-Carbon for a 9000-cycle charge–discharge test at a current density of 5 A g$^{-1}$.

Table 1 | Summary of porosities, and supercapacitive behaviour of PAF-Carbon and N-PAF-Carbon

| Materials          | BET SSA$^a$ [m$^2$ g$^{-1}$] | Langmuir SSA [m$^2$ g$^{-1}$] | Pore volume$^b$ [cm$^3$ g$^{-1}$] | Pore size distribution [nm] | Capacitance [F g$^{-1}$] | $R_s$ [Ω] | $R_{ct}$ [Ω] | $R_s + R_{ct}$ [Ω] |
|--------------------|-------------------------------|-------------------------------|-----------------------------------|-------------------------------|--------------------------|-----------|-------------|------------------|
| PAF-Carbon         | 418                           | 665                           | 0.24                              | 1.29                          | 336$^c$                  | 0.98      | 1.02        | 2.00             |
| N-PAF-Carbon       | 764                           | 1246                          | 0.45                              | 1.37; 1.09                    | 385$^d$                  | 0.76      | 0.20        | 0.96             |

$^a$BET specific surface area (SSA) calculated in the region of $P/P_0 = 0.05$ to 0.3.
$^b$Determined at $P/P_0 = 0.9997$. The pore volume in this work refers to the total pore volume including the surface condensation.
$^c$The capacitance at 0.2 A g$^{-1}$.
$^d$The capacitance at 0.1 A g$^{-1}$.
low diffusive resistivity of the electrolyte ions within the pores and N-PAF-Carbon possesses not only large capacitance (385 F g⁻¹) but also an excellent performance stability without any loss in capacitance after 9000 charge–discharge cycles. These results clearly indicate that N-PAF-Carbon material is promising metal-free ORR catalyst for fuel cells and promising capacitor electrode materials.

**Methods**

PAF-1 was prepared according with the previous reported method. By heating the bis(1,5-cyclooctadiene)nickel(0) ([Ni(cod)]₂) and 2,2’-bipyridyl in dehydrated DMF with Tetrakis(4-bromophenyl)methane at 85 °C for overnight, we obtained the PAF-1 powder after drying in vacuum. The scheme for synthesis of PAF was shown in Figure 1a. The activated PAF-1 sample was put into the temperature programming–furnace for degassing at 350 °C for 3 hours and then carbonized at a given temperature. The resulting sample was marked as PAF-Carbon. To prepare nitrogen doped 3D carbons (marked as N-PAF-Carbon), we employ the above similar carbonization method, i.e., the activated PAF-1 was put into the temperature programming–furnace for degassing at 350 °C for 3 hours and then further carbonized under N₂ media at a given temperature to produce the final products. The detailed synthetic methods can be found in the supporting information.

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