Porous Carbon Networks Derived From Graphitic Carbon Nitride for Efficient Oxygen Reduction Reaction

Chenxia Li¹, Xuesong Li¹*, Xiajuan Sun², Xueyu Zhang¹, Lianfeng Duan¹, Xijia Yang¹, Liying Wang¹ and Wei Lü¹*

Abstract

Great efforts have been dedicated to finding economic and efficient oxygen reduction reaction (ORR) for fuel cell technology. Among various catalysts, N-doped carbon-based nanomaterials have attracted much attention due to low-cost, noble metal free, and good durability. Herein, we developed a facile and economic strategy to prepare nitrogen-doped carbon networks for efficient ORR application. The g-C₃N₄ is used as the template and N source, and dopamine is used as the carbon source. By simple hydrothermal treatment and sintering, N-doped carbon network structures with high specific surface area, effective ORR activity, and superior durability could be acquired. The present strategy is free of involving generally multistep, poisonous reagents, and complication of removing template for fabrication of 3D carbon structures.

Keywords: Mesoporous carbon, Carbon-based materials, Metal free, Oxygen reduction reaction

Background

The oxygen reduction reaction (ORR) is a crucial step for further development of clean energy conversion strategies such as fuel cells and metal-air batteries [1–3]. The traditional Pt-based cathode materials for ORR are generally suffered from high cost, limited stability, and poor tolerance to methanol [1, 4–8]. Therefore, to develop a low cost, highly active, durable material towards ORR has received great attention [9, 10]. Numerous efforts have been dedicated to searching replacement for Pt-based electrocatalysts, such as transition-metal catalysts [5, 11–13], and carbon-based nanomaterials [4, 8, 13–16].

Notably, as metal-free electrocatalysts, carbon-based nanomaterials are promising materials for ORR due to good durability, noble metal free, and low-cost [17]. By elegant design of material system, 3D porous carbon structures could be achieved and provided high specific area and pore volume, which is extremely important for efficient ORR [7, 18]. Desirable three-dimensional carbon structures generally derived from various templates including ice, silica, and polystyrene [19]. The fabrication of 3D carbon structure generally involved multistep, poisonous reagents, and complication of removing template [6, 20, 21]. Thus, facile preparation strategy is still a main obstacle. In addition, the introduction of N atoms in carbon materials significantly enhances electrocatalytic activity thus inducing efficient ORR [22, 23]. Great efforts have reported N-doped carbon materials by introducing nitrogen-rich source such as melamine [24, 25], urea [26], dopamine [27], and pyrrole followed by sintering. For ORR applications, a facile way to realize porous structure and efficient N doping is still highly desired.

Herein, we developed a strategy to prepare nitrogen-doped carbon networks for efficient ORR application using metal-free graphitic carbon nitride (g-C₃N₄) and dopamine (DA) as N source and C source, respectively. Metal-free g-C₃N₄ has been intensively investigated due to its potential application for photocatalysis [9, 28–30] and ORR [30–33] etc. The N-doped materials could be achieved using g-C₃N₄ as the N source due to its high N content [20, 23, 34, 35]. The g-C₃N₄ is a typical two-dimensional conjugated polymer material [36, 37]. It has received extensive attention as an inexpensive, metal-free, visible light-responsive photocatalyst [38, 39]. The g-C₃N₄ has excellent electronic band structure, surface...
functionalization modification, and high physical and chemical stability and is non-toxic and rich in raw materials [40–42]. In addition, the nitrogen content is high, making it one of the known N-rich compounds [43]. The most important thing is that it has a variety of 2D or 3D structures that can be obtained by controlling the synthesis conditions [44–46]. Nitrogen-doped carbon materials generally have a synthesis temperature above 800 °C, which satisfies the requirements for removing the template [47]. Therefore, it is possible to utilize g-C₃N₄ that only contains carbon and nitrogen elements to synthesize N-doped carbon materials [48]. In the present work, g-C₃N₄ is used as a template and N source simultaneously to prepare porous carbon structures with high specific surface area (954 m² g⁻¹) and 5.71% N content is achieved, which exhibits comparable ORR activity, superior durability, and methanol tolerance to Pt/C reference electrocatalyst.

**Methods**

**Materials**

Potassium hydroxide (KOH) and potassium chloride (KCl) were obtained from Sinopharm Chemical Reagent Co., Ltd. Potassium hexacyanoferrate (K₃[Fe(CN)]₆) were obtained from Tianjin Yongsheng Fine Chemical Co., Ltd. Urea were obtained from Beijing Chemical Corp. All of the above drugs are analytically pure. Naifon® perfluorinated solution (5 wt. % in mixture of lower aliphatic alcohols and water, contains 45% water) was purchased from Sigma-Aldrich.

**Synthesis of g-C₃N₄ Template**

Typically, 15 g of urea in 100 mL crucible was kept at 550 °C for 4 h. The g-C₃N₄ was acquired and grounded to light yellow powder for later use after cooling to room temperature.

**Synthesis of g-C₃N₄@dopamine Precursors**

0.5 g g-C₃N₄ was dispersed in 20 mL DA solution. The concentration of DA was 0.3 M. The mixture was ultrasonicated for 2 h and transferred into an autoclave followed by heating at 120 °C for 10 h. The resulted sample was centrifuged and washed followed by drying at 80 °C overnight. Three heating temperatures of 120 °C, 140 °C, and 160 °C were used for preparing g-C₃N₄/PDA precursors, and the corresponding samples were named g-C₃N₄/PDA-120, g-C₃N₄/PDA-140, and g-C₃N₄/PDA-160, respectively.

**Preparation of Nitrogen-Doped 2D Carbon Materials**

The precursors of g-C₃N₄/PDA-120, g-C₃N₄/PDA-140, and g-C₃N₄/PDA-160 were heated to 900 °C for 2 h in nitrogen atmosphere. After cooling to room temperature, nitrogen-doped porous carbon samples named NC-120, NC-140, and NC-160 (NC-T) were synthesized. However, the attempt for further decreasing heating temperature to 100 °C induced very poor coating of DA on g-C₃N₄, which resulted in low yield after sintering at 900 °C. Therefore, three temperatures of 120 °C, 140 °C, and 160 °C were chosen for further investigation. The synthesis process of nitrogen-doped porous carbon samples is shown in Scheme 1.

**Electrochemical Measurement**

Electrochemical analysis was fulfilled by the DynecChem electrochemical workstation, and Ag/AgCl and platinum are used as reference electrode and counter electrode, respectively. The cyclic voltampis was tested in 0.1 M potassium hydroxide solution. The glass carbon electrode (GCE) was polished and washed before using. To prepare the working electrodes, aliquots of 5 μL and 2.5 mg/mL NC-120, NC-140, NC-160, Pt/C solutions were dipped on to GCE for further test.

**Characterization**

The structure and chemical composition of the NC-T was analyzed by X-ray diffraction (XRD) (D-MAX II A X-ray diffractometer), transmission electron microscopy (TEM) (Tecnai F20), scanning electron microscope (SEM) (JEOL7610), fourier transform infrared (FT-IR) (Nicolet iS50) spectra, X-ray photoelectron spectroscopy (XPS) (Kratos Axis UltraDLD), and Raman (Horiba, Japan); N₂ adsorption-desorption (77 K) isotherms were carried out on a Micromeritics ASAP 2020 instrument (MICROSENSOR, USA).

**Results and Discussion**

**SEM and TEM Characterization**

In order to determine the morphology of the synthesized samples, SEM and TEM are used for structure observation as shown in Fig. 1. Figure 1a represents the sheet structure of as-synthesized g-C₃N₄. The 2D structure of g-C₃N₄ is further confirmed from Fig. 1b, which is similar with the previous report [48]. For g-C₃N₄/PDA-120 as shown in Fig. 1c, d, the SEM image is similar with that of g-C₃N₄. However, the TEM image of g-C₃N₄/PDA-120 shows well-dispersed sheet like morphology, compared with as-synthesized g-C₃N₄. With the increasing heating temperature from 120 to 160 °C, the thin lamellar structure of carbonized layer could be observed (Additional file 1: Figure S1). After sintering at 900 °C, the SEM images appear honeycomb-like structures as shown in Fig. 1e due to the pyrolysis of g-C₃N₄ template, inducing porous carbon structures as shown in Fig. 1f and Additional file 1: Figure S2. The thermo-gravity test of g-C₃N₄ was carried out to determine the residue of g-C₃N₄, and g-C₃N₄ begins to decompose at 520 °C. Under nitrogen protection, fully decomposition is confirmed at 760 °C.
Scheme 1 The synthetic process of NC-T electrocatalysts

Fig. 1 Structural characterizations of samples like carbon nanosheets. a SEM and b TEM images of g-C$_3$N$_4$. c SEM and d TEM images of g-C$_3$N$_4$/PDA-120, e SEM and f TEM images of NC-120
as shown in Additional file 1: Figure S3. Between 80 and 100 °C, g-C₃N₄ will slightly lose its quality due to the evaporation of moisture, and the research result is consistent with previous reports [47]. This indicates that g-C₃N₄ could be used as an efficient template for preparing porous carbon structures.

**XRD, FT-IR, and Raman Characterization**

Hydrothermal temperature not only affects the structure of samples but also changes the peak of XRD. The three DA-coated g-C₃N₄ samples all exhibit two diffraction peaks at 13.0° and 27.4° attributing to (100) and (002) crystal planes of g-C₃N₄ template as shown in Fig. 2a. After calcination at 900 °C, the obvious variation for all three samples could be found. The peak at 13.0° vanished, and two new peaks occur around 26.3° and 44.1° relevant to the (002) and (100) planes of graphene, indicating the formation of a new graphitic carbon structure as shown in Additional file 1: Figure S4 [4]. With the increasing hydrothermal temperature, the degree of graphitization and crystalline increases gradually. This is further confirmed by Raman and FT-IR test.

FT-IR spectrometry was performed to analyze the functional groups present on the surfaces of NC-T hybrids. FT-IR spectra of g-C₃N₄, g-C₃N₄/PDA-120, g-C₃N₄/PDA-140, and g-C₃N₄/PDA-160 indicate that these samples include similar carbon and oxygen containing functional groups as shown in Fig. 2b. The peaks between 1200 and 1650 cm⁻¹ belong to stretching methods of CN heterocycles, and the broad peaks located in the range of 3000–3500 cm⁻¹ are ascribed to the N-H group stretching vibration [49]. With the increasing hydrothermal temperature, the two peaks at 1650 cm⁻¹ (C=C) and 3350 cm⁻¹ (O-H) are more evident due to DA wrapped on g-C₃N₄. After high-temperature carbonization, only three weak peaks remain for NC-120 at 1600 cm⁻¹, 1260 cm⁻¹, and 3450 cm⁻¹ (Fig. 2c), which are ascribed to the C-C and C-N vibration. This indicates that high-temperature carbonization destroys O-H, N-H, and other chemical bonds, while C-N bonds are stable, thus ensuring the effective doping of nitrogen elements.

Raman spectroscopy is employed to evaluate the structural evolution of NC-T. Figure 2d is the Raman spectra of NC-120, NC-140, and NC-160, and the peaks at 1350 and 1580 cm⁻¹ correspond to the D and G band, respectively [50, 51]. With the increasing hydrothermal temperature, the intensity ratio of I_D/I_G decreases from 2.34 to 2.08, indicating the enhanced graphitization degree with the increasing temperature.

**XPS Characterization**

XPS is used to explore the elemental composition of the samples as shown in Fig. 3. Compared with g-C₃N₄, three g-C₃N₄/PDA-T samples exhibit increased oxygen...
content due to the carbonized DA coating on g-C₃N₄ (Additional file 1: Table S1). With the increasing hydrothermal temperature from 120 to 160 °C, the N content decreases (Fig. 3a). For C-related peaks, the intensities of C-C/C=C and C-O peaks enhance, while the peak of N-C=C gradually decreases with the increasing hydrothermal temperature as shown in Fig. 3b. According to previous report [24], desirable electrochemical performance could be achieved by samples with high effective N-doping content. Based on XPS spectra of NC-T, C content increases after 900 °C heat treatment with the increase of hydrothermal temperature (Additional file 1: Figure S6). Table 1 gives effective N content of the three samples. The NC-T displays the presence of pyridinic N (398.5 eV) and graphitic N (401.1 eV) [25]. When the hydrothermal temperature is raised to 160 °C, the N content decreased significantly. Figure 4 shows high-resolution N 1 s XPS spectra of NC-T samples. The percentage of pyridinic N and graphitic N as a function of hydrothermal temperature is shown in Fig. 4d. The N content decreases gradually with the increasing hydrothermal temperature.

Brunauer–Emmett–Teller (BET) Characterization

The catalytic activity is related to the specific surface area and the pore structure. The BET specific surface areas of samples are decided by N₂ adsorption isotherms test at 77 K, and all samples show type IV curves [19]. This implies that the samples have micropores and mesoporous structures as shown in Additional file 1: Figure S5. The specific surface areas of NC-120, NC-140, and NC-160 are 954, 824, and 517 m² g⁻¹, respectively, which are significantly higher than those of original g-C₃N₄ (85 m² g⁻¹). The results show that lower temperature contributes to the formation of large specific surface area and pore size. For the ORR catalyst, the benefit of the layered structure, high specific surface areas, and high nitrogen contents are very significant. The SEM and TEM images of g-C₃N₄/PDA-T showed the three samples have a similar-layered structure with pristine g-C₃N₄ (Additional file 1: Figure S1). NC-120 exhibits the largest large specific surface area (954 m² g⁻¹), and it has a suitable mesoporous structure (= 5 nm). The large specific surface area helps to increase the contact area with the reactants and accelerate the reaction [52].

Electrocatalytic Performance and Discussion

It could be concluded from the above results that NC-120 has the largest specific surface area and the highest nitrogen content, which is very beneficial for ORR [46]. The electrochemical properties of the samples are investigated by cyclic voltammetry (CV) and compared with commercial Pt/C catalysts. The results are shown in Fig. 5 and Table 2. There is no oxygen reduction peak observed for all samples under nitrogen saturated condition (Fig. 5a and Additional file 1: Figure S8). For oxygen saturated condition, there is an obvious oxygen reduction peak, and it becomes more obvious with the decreasing hydrothermal temperature. The results suggest that CV behaviors are associated with the structure of catalysts. In O₂-saturated 0.1 M KOH solutions, the NC-120 sample expresses the best performance, which is close to Pt-based catalyst and its half-peak potential is 0.224 V, and its ultimate current density is 5.04 mA cm⁻² (Additional file 1: Figure S7). Figure 5b is the linear scan voltammogram (LSV) curve, showing the limiting current density and onset potentials of the NC-T samples. With the decreasing hydrothermal temperature, the voltage and current density is enhanced, and the performance of catalyst is improved gradually. It can be seen from Fig. 5c that a
small movement of that curve is found after the addition of methanol, suggesting that NC-120 has excellent tolerance to methanol. In the Fig. 5(e), the NC-120 exhibited good oxygen reduction properties, which could be due to the large specific surface area and nitrogen content (Additional file 1: Figure S7). For NC-120 (Fig. 5d, f), the number of electron transfer in the process of oxygen reduction is calculated to be 3.9–4.1, indicating that the oxygen reduction reaction of NC-120 catalytic is four electronic processes. NC-120 has the best electrochemical performance, which is attributed to the effective N doping by present strategy.

As shown in Scheme 1, DA is used as carbon source and g-C$_3$N$_4$ nanosheet is used as template and nitrogen source. There are three reasons for choosing this strategy: Firstly, g-C$_3$N$_4$ can provide multi-layer structure and it could fully disappear at 900 °C. Secondly, DA can provide carbon atom and carbonized DA could cover on both sides of g-C$_3$N$_4$. PDA was formed on the template of g-C$_3$N$_4$ in a hydrothermal process using DA as a carbon source. In hydrothermal processes, PDA can strongly adhere to substrate surface of organic or inorganic materials by forming strong covalent and non-covalent bonds on the surface of the substrate. After the coating material is formed, pyrolysis under nitrogen conditions results in the formation of porous carbon materials with large specific surface area. Finally, the decomposed g-C$_3$N$_4$ would provide N atoms for doping carbon structure, thus effectively increasing active sites for ORR. In previous reports, Liu et al. prepared g-C$_3$N$_4$@PDA composites by dropping DA solution directly into g-C$_3$N$_4$ solution under stirring for enhancing visible light photocatalytic H$_2$ production activity, which exhibits promising results [37]. In present work, as discussed above, we developed a new strategy to prepare N-doped porous carbon structures with high specific surface area (954 m$^2$ g$^{-1}$) and high N content (5.71%) using g-C$_3$N$_4$ as template and N source simultaneously. The acquired composites exhibit comparable ORR activity, superior durability, and methanol tolerance to Pt/C reference electrocatalyst.

**Conclusion**

In summary, we developed a strategy to synthesize N-doped carbon structures. The first step is mainly the
hydrothermal process, and the second step is the heat treatment process. With g-C$_3$N$_4$ as the template and DA as the carbon source, porous carbon networks with high N doping content could be achieved. The resulted network structures can increase the specific surface area of the catalyst and thus provide excellent electrochemical properties including good methanol tolerance effect and stability compared with Pt/C catalyst. The performance of these excellent electrocatalysis may be attributed to the following reasons: (1) N-doped C-layered structure with high content of graphite-N and pyridine-N species provides a highly active site for oxygen reduction.

Table 2 Elemental composition, surface area, and electroactivity of samples

| Samples | N content at % (pyridinic N+ graphitic N) | $S_{BET}$ (m$^2$ g$^{-1}$) | $E_{\text{half-peak voltage}}$ (V) | $n$ | $J_1$ (mA cm$^{-2}$) |
|---------|----------------------------------------|-----------------------------|---------------------------------|-----|---------------------|
| NC-120  | 5.71 at % (2.04 at % + 3.67 at %)       | 954                         | $-0.224$                       | 3.9–4.1 | 5.040               |
| NC-140  | 5.43 at % (2.68 at % + 2.65 at %)       | 833                         | $-0.257$                       | 3.5–3.7 | 4.072               |
| NC-160  | 3.45 at % (1.21 at % + 2.24 at %)       | 517                         | $-0.327$                       | 3.0–3.2 | 3.165               |
| Pt/C    | –                                      | –                           | $-0.175$                       | –    | –                   |

Fig. 5 a CV curves of NC-120 in N$_2$ and O$_2$ saturated 0.1 M KOH aqueous solution with a scan rate of 100 mV s$^{-1}$. b LSV curves of NC-T at 1600 rpm rotating speeds. c Linear polarization curves of NC-120 with different rotation rates at a sweep rate of 5 mV s$^{-1}$ in O$_2$-saturated 0.1 M KOH. d K-L plots at different potentials based on the results of c. e CVs of NC-120 in O$_2$-saturated 0.1 M KOH solution with 3 M CH$_3$OH. f CV curves of NC-T in O$_2$ saturated 0.1 M KOH aqueous solution with a scan rate of 100 mV s$^{-1}$.
reaction. (2) The high specific surface area (954 m² g⁻¹) coexists with high graphitic carbon and amorphous carbon, contributing to the electron conduction of the ORR. (3) The porous structures accelerate the transfer of electrons and promote the full utilization of active sites. These advantages all determine the good catalytic effect of this material. In addition, the present method to prepare N-doped carbon-based nanomaterials is economic, eco-friendly, and efficient, making them widely available in fuel cells in future.

Additional file

Additional file 1: Figure S1. (A) SEM and (B) TEM images of g-C₃N₄@PDA-120. (C) TEM and (D) TEM images of g-C₃N₄@PDA-140. (E) SEM and (F) TEM images of g-C₃N₄@PDA-160. Figure S2. (A) SEM and (B) TEM images of NC-120. (C) SEM and (D) TEM images of NC-140. (E) SEM and (F) TEM images of NC-160. Figure S3. TG of g-C₃N₄ in N₂ with a temperature rise rate of 5 °C min⁻¹. Figure S4. XRD patterns of NC-120, NC-140, and NC-160. Figure S5. N₂ adsorption/desorption isotherms (inset, pore size distribution of g-C₃N₄ and all NC-T). Figure S6. CVs of PtC and NC-T in N₂ and O₂ saturated 0.1 M KOH aqueous solution with a scan rate of 100 mV s⁻¹. (a) CV curves of NC-T (T = 120°C 140°C 160°C) with different rotation rates at a sweep rate of 5 mV s⁻¹. (b) c and (d) Linear polarization curves of NC-T (T = 120°C 140°C 160°C) saturated with O₂. (e) CV curves of CN-T in N₂ and O₂ saturated 0.1 M KOH aqueous solution with a scan rate of 100 mV s⁻¹ (t = 120°C, 140°C, 160°C). Supplementary data related to this article can be found at journal website. (DOC 17806 kb)

Abbreviations

BET: Brunauer–Emmett–Teller; CV: Cyclic voltammetry; DA: Dopamine; g-C₃N₄: Graphitic carbon nitride; GCE: Glass carbon electrode; LSV: Linear scan voltammetry; ORR: Oxygen reduction reaction; SEM: Scanning electron microscope; TEM: Transmission electron microscope; XPS: X-ray photoelectron spectroscopy

Authors’ Contributions

WL and XL conceived the idea. CL carried out the experiments. XS, XZ, LD, and CL drafted the manuscript. All authors read and approved the final manuscript.

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Availability of Data and Materials

The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Competing Interests

The authors declare that they have no competing interests.

Author details

1 Key Laboratory of Advanced Structural Materials, Ministry of Education & Advanced Institute of Materials Science, Changchun University of Technology, Changchun, Changchun 130012, China. 2 State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130012, China.

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