Ferric Citrate-derived N-doped Hierarchical Porous Carbons for Oxygen Reduction Reaction and Electrochemical Supercapacitors

Jingyue Zhu, Dan Xu, Cancan Wang, Wenjing Qian, Jun Guo, and Feng Yan*

Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, China.

Abstract: This work reports a facile strategy for the preparation of Nitrogen-doped porous carbons via carbonization of a mixture containing ferric citrate (FC) and ammonium chloride (NH_4Cl). FC provides carbon and iron element sources, while ammonium chloride acts as both the porogen and nitrogen dopant during the carbonization process. The formed hierarchical porous structures facilitate the ion diffusion/transport, and nitrogen-doping provides more active sites, which contribute to both oxygen reduction reaction (ORR) and supercapacitor applications. Compared with KOH and NaCl, the utilization of NH_4Cl as porogen shows the best ORR performance in this work might due to the dual functions of NH_4Cl . Ferric citrate- NH_4Cl carbonized at 700°C exhibits good capacity of 242 F g^{-1} and stability in 6 M KOH at a current density of 1 A g^{-1} . Since both FC and NH_4Cl are cheap and easily available, this work provides a facile and effective method to obtain carbons with superb electrochemical performances.

* Corresponding author. Tel: +86-512-65880973. E-mail: fyan@suda.edu.cn (Feng Yan)

1. Introduction

With the increasing demand for energy and the consumption of fossil fuels, it is imperative to develop alternative electrochemical devices, such as fuel cells, lithium ion batteries and supercapacitors with low cost, high efficiency and renewability [1-4]. Oxygen reduction reaction (ORR) is a key issue for electrochemical devices, such as metal-air batteries and low temperature fuel cells. The power densities of devices are highly dependent on the cathode catalysts. Although Pt-based catalysts show high ORR activity, the limited resources and high cost hinder their practical applications. Therefore, development of Pt-free catalysts using transition metal oxides [5-8], transition metal macrocyclic compounds [9, 10], chalcogenide [11, 12], or carbon materials (CMs) [13, 14] is highly required.

Recently, porous CMs with controlled architectures have been widely applied in energy conversion and storage devices, as an electrocatalyst for ORR on cathode [15-17], and as electrode materials for supercapacitors [18, 19]. Among the CMs studied, the heteroatom-doped CMs have shown great potential in ORR, because the electrocatalysis performance can be greatly enhanced by modulating the catalytic sites, and chemisorption energy of O_2 [20]. In addition, doping of transition metals (such as Fe or Co) into CM frameworks usually leads to high performance due to the synergistic effect of metal, nitrogen and carbon elementals [21]. For example, the N-doped carbons with encapsulated nanoparticles (i.e. Fe_3C) could provide more active sites for ORR to superior catalytic activity [22-24]. In addition, the porosity of CMs is another critical factor to influence the ORR electrocatalytic activity [25]. The high surface area and hierarchical porous structure can promote the mass transport of ions and improve the electrochemical activity per active area [26]. On the other hand, nitrogen doping can improve the surface wettability to electrolyte and conductivity of carbons, followed with the Faradaic reactions to make a contribution to supercapacitors[27]. Meanwhile, the micropores/mesopores

structure can provide large surface area and fast ions delivering [28]. Therefore, the rational design of carbons with large specific surface area, hierarchical pore-size distribution and high content of heteroatoms is of great interest to obtain the superior performance for both ORR and electrochemical supercapacitors [29-31].

With the urgent desire for environmental protection and resource conservation, the low-cost precursor and simplified synthesis process play critical role for the immediate practical utilizations. Recently, CMs derived from organic salts (such as potassium citrate and sodium glutamate) have drawn considerable attention because they are easily available and relatively cheap [32, 33]. In this study, we report a facile and efficient procedure for the preparation of Nitrogen-doped porous carbons via carbonization of a mixture containing ferric citrate (FC) and ammonium chloride (NH_4Cl). Here, FC, which consists of organic moiety and iron atoms, provides carbon and iron element sources. Ammonium chloride, which completely decompose into NH_3 and HCl during the carbonization acts as both the porogen and N dopant for the preparation of N-doped CMs with hierarchical porous structures [34]. The chemical composition and porous structures can be easily tuned by the amount of ammonium chloride and (or) carbonization temperature. Among all the FC-derived CMs investigated, FC- NH_4Cl carbonized at 800 °C exhibited the optimal activities when applied for oxygen reduction reaction, while FC- NH_4Cl carbonized at 700 °C exhibited a capacitance of 242 F g⁻¹ at a current density of 1 A g⁻¹ in 6 M KOH and good stability for supercapacitors.

2. Experimental Section

2.1 Materials

Ferric citrate ($\text{FeC}_6\text{H}_5\text{O}_7$) was obtained from Shanghai Qiangshun Chemical Reagents Co., Ltd. Ammonium chloride, potassium hydroxide, sodium chloride, hydrochloric acid were bought from

Sinopharm Chemical Reagents Co., Ltd. Nafion perfluorinated resin solution (5 wt %) was purchased from Sigma–Aldrich Co. Polytetrafluoroethylene (PTFE) solution (60 wt %) was ordered from Aladdin chemistry Co., Ltd. JM Pt/C (20 wt %), acetylene black, and nickel foam were used as received. Distilled deionized water was used throughout the experiments.

2.2 Preparation of ferric citrate-derived hierarchical porous N-doped carbons (FC-NH₄Cl-T-n)

In a typical synthesis, a mixture containing NH₄Cl and FC (NH₄Cl: FC= 0.5, 1, 2, mass ratio) was grinded homogeneously. The mixture was carbonized in a ceramic crucible to high temperatures (700 °C, 800 °C, or 900 °C) under a nitrogen atmosphere, at a heating rate of 5 °C min⁻¹. Each sample was held at the setting temperature for 1 h. The resulting black solid was washed with 1 M HCl solution and distilled water, and then dried at 80 °C overnight under vacuum. The FC-derived N-doped hierarchical porous carbons are denoted as FC-NH₄Cl-T-n, where T represents the pyrolysis temperature and n indicates the mass ratio of NH₄Cl to FC.

For comparison, the carbon synthesized via solely pyrolysis (at 800 °C) of ferric citrate was denoted as FC-800. Potassium hydroxide and sodium chloride were used as the porogen to replace NH₄Cl for the preparation of CMs (carbonized at 800 °C). The corresponding carbon samples were denoted as FC-KOH-800-1.0 and FC-NaCl-800-1.0, respectively.

2.3 Material characterization

The thermogravimetric analysis (TGA) was tested by TGA 4000 (Perkin Elmer Co., Ltd). The TGA curves were collected with the program temperature set from room temperature to 900 °C under N₂. The measurements were performed at a heating rate of 20 °C min⁻¹. X-ray diffraction (XRD) recorded in 2θ range from 5° to 85° was conducted by a Philips X'Pert Pro diffractometer. Raman spectra were measured using a LabRAM HR800 with the range from 500 to 2500 cm⁻¹. Iron content was measured by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) with

a ICP Varian 710es. X-ray photoelectron spectroscopy (XPS) experiments were carried out from an XPS-7000 spectrometer. The transmission electron microscopy (TEM) were examined by a Tecnai G220. High resolution (HR)-TEM images and scanning transmission electron microscopy (STEM) were examined by a Tecnai F20. The scanning electron microscopy (SEM) images were collected using Hitachi Model S-4700 field emission. The energy-dispersive X-ray spectroscopy (EDX) data were measured with a spectrometer attached to the SEM. ASAP 2020 accelerated surface area and porosimetry instrument (Micromeritics) was used to obtain nitrogen sorption isotherms. The special surface area was calculated by Brunauer–Emmett–Teller (BET) method and the pore-size distribution (PSD) plots were acquired by density function theory (DFT) calculations.

2.4 *Electrochemical measurement*

All the electrochemical experiments were measured via a CHI660C electrochemical workstation (Shanghai Chenhua Instruments Co.) with a three-electrode system. Hg/HgO electrode and Pt foil were used as the reference and counter electrodes, respectively.

2.4.1 *Oxygen reduction reaction (ORR) measurements*

For rotating disk electrode (RDE) measurements, the working electrode was prepared as the following: FC-derived carbon materials (1 mg), deionized water (0.10 mL), ethanol (0.15 mL), and Nafion (8 μ L) were mixed and ultrasonicated to form a well-dispersed catalyst ink. Then 20 μ L of prepared ink was cast onto a glassy carbon electrode (5 mm in diameter). The catalyst loading of the samples is controlled to be 0.4 mg cm⁻². For comparison, the commercially available Pt/C catalyst solution (20 wt%) was also prepared with catalyst loading of 0.2 mg cm⁻².

Cyclic voltammogram (CV) curves were carried out in N₂ or O₂-saturated 0.1 M KOH solution from -0.8 to 0.2 V (vs. Hg/HgO) at 100 mV s⁻¹. The ORR polarization curves were obtained at a scanning rate of 10 mV s⁻¹ range from 400 to 1600 rpm. The ORR kinetics can be analysed through the

Koutecky-Levich equations:

$$\frac{1}{J} = \frac{1}{J_0} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (1)$$

$$B = 0.62nFC_0(D_0)^{2/3}(v)^{-1/6} \quad (2)$$

$$J_K = nFkC_0 \quad (3)$$

For rotating ring disk electrode (RRDE) measurements, the catalysts were prepared follow the method described above. The catalyst loading was about 0.4 mg cm⁻². The ring potential was set at 1.2 V (vs. RHE) in O₂-saturated 0.1 M KOH solution. The H₂O₂ yield and electron transfer number (n) were calculated by the following equations:

$$\%(H_2O_2) = 200 \times \frac{I_r / N}{I_d + I_r / N} \quad (4)$$

$$n = 4 \times \frac{I_d}{I_d + I_r / N} \quad (5)$$

All the potentials were conducted using Hg/HgO as the reference electrode and converted to the RHE ($E_{RHE} = E_{Hg/HgO} + 0.059pH + E_{Hg/HgO}^0$, where $E_{Hg/HgO}$ is the measured potential, and $E_{Hg/HgO}^0 = 0.098$ V).

2.4.2 Supercapacitor measurements

The working electrode was prepared as the following: FC-NH₄Cl-T-1.0 (80 wt %), carbon black (10 wt %), and PTFE (10 wt %) were well-mixed to obtain a viscous slurry. Then the electrode material was pressed onto a nickel foam (1.0 cm²), which was conducted as the current collector. A 6 M KOH was employed as the electrolyte. Electrochemical impedance spectroscopy (EIS) curves were acquired within a frequency range of 10 kHz-0.01 Hz. CV curves were conducted at the scanning rate of 5-100 mV s⁻¹ from -1.0 to 0 V (vs Hg/HgO). Galvanostatic charge-discharge (GCD) measurements were carried out at 0.5 to 30 A g⁻¹. In a three-electrode system, the specific capacitance was calculated from

GCD curves by equation (6):

$$C = \frac{I\Delta t}{m\Delta V} \quad (6)$$

3. Results and Discussion

Figure 1 shows the synthetic route for the preparation of N-doped hierarchical porous carbons with encapsulated Fe_3C . The resulting carbons were synthesized by the pyrolysis of a mixture containing ferric citrate and ammonium chloride, followed by acid-leaching. For simplicity, the prepared CMs are denoted as FC- NH_4Cl -T-n (T indicates the pyrolysis temperature, and n represents the mass ratio of NH_4Cl to FC).

Figure 1. Schematic procedure for the synthesis of N-doped hierarchical porous CMs with encapsulated Fe_3C and their electrochemical applications in ORR and supercapacitor. The structure and composition of carbons were controlled by the carbonization temperature and (or) NH_4Cl content. FC- NH_4Cl pyrolyzed at 800 °C exhibited the optimal activities for ORR, while pyrolyzed at 700 °C showed high capacitance and stability for supercapacitor.

Figure 2 shows the thermogravimetric analysis (TGA) curves of FC, NH_4Cl , and a FC- NH_4Cl

mixture under a nitrogen atmosphere. The pyrolysis of FC alone shows the mass loss in the temperature range of 180-480 °C and 660-720 °C, which can be mostly attributed to the transformation from citrate ion to citraconic and itaconic anhydrides, and the continue elimination the functional groups of amorphous carbons, respectively [22]. At high temperatures (660-720 °C), the iron species can be reduced by carbon which also contributes to the weight loss due to the yielded CO/CO₂ gas [35]. The residue of FC under N₂ is determined to be about 24.5%. It is not surprising that the NH₄Cl may be completely decomposed below 400 °C (NH₄Cl→NH₃+HCl). However, it should be noted that the yield of FC-NH₄Cl (1:1, mass ratio) is about 18.35 %, which is higher than that of the calculated stoichiometric value (12.3%). A possible reason of the increased yield is that the ammonia gas derived from NH₄Cl may form free radicals (such as NH₂ and NH) to react with carbon, which can incorporate the nitrogen atoms into CMs to improve the overall yield [36].

Figure 2. Thermogravimetric analysis (TGA) curves of ferric citrate, ammonium chloride and FC-NH₄Cl-1.0 under N₂ atmosphere.

The crystalline structure of carbons was further characterized by X-ray diffraction (XRD). **Figures 3a, b** shows all of the FC-derived N-doped carbons have similar XRD patterns of Fe₃C and graphite

phase. The detailed diffraction peaks of FC-NH₄Cl-700-1.0 and FC-NH₄Cl-800-1.0 were demonstrated in **Figure S1**, demonstrating the formation of Fe₃C (JCPDS No. 35-0772) [37]. After the acid-leaching, only Fe₃C nanoparticles encapsulated in carbon layers were retained, leading to the weak diffraction peaks. The peaks at 26.1° and 43° are indexed to (002) and (100) planes of the graphitic carbons, respectively [22]. The intralayer condensation behaved at 43° can improve the conductivity of carbons [38]. It can be seen that the higher pyrolysis temperature resulted in a sharper and stronger (002) peak, suggesting a higher graphitization degree. In addition, a higher NH₄Cl amount may result in a weaker peak of (002). The formation of CMs was further characterized by Raman spectra (**Figures 3c, d, and S2**). Two peaks centered at 1340 and 1580 cm⁻¹ reflect the characteristic D (defects and disorder) and G (graphitic) peaks of CMs, respectively [28, 39]. The order degree of graphitic structure could be determined by the D/G ratio of band intensities. Here, the D/G intensity ratios of FC-NH₄Cl-700-1.0, FC-NH₄Cl-800-1.0 and FC-NH₄Cl-900-1.0 were calculated to be 1.37, 1.28, and 0.82, respectively, indicating that higher pyrolysis temperature benefited the formation of high degree graphitic carbons. In addition, the high amount of NH₄Cl may lead to higher I_D/I_G value (from 1.22 to 1.49, for FC-NH₄Cl-800-0.5 and FC-NH₄Cl-800-2.0, respectively), because the decomposition of the NH₄Cl released the gas, which may act as a pore-forming agent to obtain disordered and defective carbons. The results of Raman spectra agree well with those of XRD.

Figure 3. X-ray diffraction (XRD) patterns of FC-derived N-doped carbons (a) at various pyrolysis temperatures, (b) and with different amount of NH_4Cl . (c), (d) Raman spectra of $\text{FC-NH}_4\text{Cl-T-n}$. The peaks at about 1340 and 1580 cm^{-1} are ascribed to D (disordered carbon) and G (graphitic carbon) bands of the CMs.

Table 1 lists the chemical compositions of FC-derived CMs tested by energy-dispersive X-ray spectroscopy (EDX). All the CMs derived from the mixture of FC and NH_4Cl consist of C, N, Fe, and O atoms. Moreover, the higher content of NH_4Cl and lower carbonization temperature lead to the higher amount of N-doping degree. Therefore, it can be confirmed that the ammonia gas generated by pyrolysis process of NH_4Cl may be subsequently doped into FC-derived product to bring nitrogen into carbon matrix, which made it possible to prepare N-doped CMs. However, no nitrogen atoms were

observed for FC-KOH-800-1.0 and FC-NaCl-800-1.0 derived carbons, further confirmed that NH_4Cl could acts as the N dopant for the preparation of N-doped CMs. To analyze more precise elemental composition, X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma optical emission spectrometry (ICP-OES) were employed to analyze the composition of FC- NH_4Cl -T-n more precisely (see **Table S1**).

Table 1. Chemical composition of FC-derived CMs tested by energy-dispersive X-ray spectroscopy measurements.

Sample	EDX (wt %)			
	C	N	Fe	O
FC- NH_4Cl -700-1.0	78.93	10.12	1.54	9.41
FC- NH_4Cl -800-1.0	87.57	4.43	1.02	6.98
FC- NH_4Cl -900-1.0	94.48	1.81	0.63	3.08
FC- NH_4Cl -800-0.5	86.38	3.35	1.58	8.69
FC- NH_4Cl -800-2.0	84.64	7.16	0.67	7.53
FC-800	85.72	—	2.51	11.77
FC-KOH-800-1.0	88.79	—	1.19	10.02
FC-NaCl-800-1.0	91.57	—	0.34	8.09

X-ray photoelectron spectroscopy was performed to probe the binding environment of elements doped in CMs. **Figures 4, S3** show the high-resolution N1s, C1s, and O1s XPS spectra of FC- NH_4Cl -T-n. The XPS spectra of C1s (see **Figure S3**) show three peaks at around 284.6 eV (C-C), 285.6 eV (C-N), and 288.7 eV (O-C=O), respectively[33]. The deconvoluted peak of C-N indicating that the nitrogen has been successfully incorporated into carbon frameworks. The surface nitrogen functional groups could be revealed by N1s spectra. **Figure 4** shows the N1s XPS spectra of FC- NH_4Cl -700-1.0

and FC-NH₄Cl-800-1.0. The binding energies were divided into three peaks: 398.0, 400.1, and 400.8 eV, corresponding to pyridinic N (N-6), pyrrolic N (N-5) and quaternary N (N-Q), respectively [40, 41]. Meanwhile, the quaternary nitrogen can bring higher electrical conductivity to carbons [42]. Three types of O-containing groups, including quinone-type groups (C=O at 531.5 eV), phenol or ether-type groups (C-OH or C-O-C at 533.5), and carboxylic groups (COOH at 535 eV) were detected by O1s XPS spectra (see **Figure S3**) [43]. Note that no obvious iron signal was observed by XPS spectra, indicating that the formed Fe₃C was covered by graphitic carbon layer which may block the detection [44]. The encapsulated Fe₃C will be further proved by TEM images (**Figure 5**).

Figure 4. High-resolution N1s X-ray photoelectron spectroscopy of (a) FC-NH₄Cl-700-1.0 and (b) FC-NH₄Cl-800-1.0 derived carbons.

Figures 5a, b show SEM images of the prepared FC-NH₄Cl-700-1.0 and FC-NH₄Cl-800-1.0. The interconnected porous carbon nanosheets were observed to form three-dimensional (3D) nanostructure, which was quite different from the sponge-like CMs derived from pure FC (see **Figure S4a**). Such a difference may be due to the addition of NH₄Cl as the porogen. The presented 3D interpenetrating structure may effectively offer continuous pathways for electron and ion transfer, which can enhance the electrochemical property for both ORR and supercapacitor [45]. **Figure S4** also shows the

topography of FC-NH₄Cl-800-0.5, NH₄Cl-800-2.0, FC-NH₄Cl-900-1.0 and the carbons derived from FC-KOH and FC-NaCl. The TEM images of FC-NH₄Cl-700-1.0 and FC-NH₄Cl-800-1.0 show that the Fe₃C nanoparticles of 50-100 nm in diameter were well encapsulated in the carbon matrix, which may provide the protection from the acid-leaching (**Figure 5c,d**). In addition, the micro/mesopores architectures were developed whether the pyrolysis temperature was 700 °C or 800 °C (**Figures 5g, h**). **Figure 5d** shows onion-like carbon structures of FC-NH₄Cl-800-1.0, which are different from the nanosheet carbons shown in **Figure 5c**, probably due to the higher graphitization structure. **Figures 5e, f** show that the spacing of lattice fringe is about 0.200 nm, implying the formation of iron-rich nanoparticles during the heat-treatment [22]. Based on the XRD results, it can be concluded that the iron-rich nanoparticles were mainly Fe₃C. **Figure S5** showed the scanning transmission electron microscopy (STEM) and elemental mapping analysis of FC-NH₄Cl-700-1.0 and FC-NH₄Cl-800-1.0. Distributions of heteroatoms (O, N, and Fe) could be observed, suggesting that the iron nanoparticles, doped O and N atoms are homogeneously dispersed in carbon skeletons.

By means of the carbonization of FC-NH₄Cl, followed by acid treatment, a series of hierarchical porous CMs were produced. **Figure 6a** shows nitrogen adsorption/desorption isotherms of FC-NH₄Cl-T-1.0. According to the IUPAC classification, the FC-NH₄Cl-700-1.0 exhibits a type-I sorption isotherm, which mainly consisted of microporous structure. FC-NH₄Cl-800-1.0 and FC-NH₄Cl-900-1.0 show hysteresis loop representing the type-IV curves, which indicated the existent of both micropores and mesopores. The pore-size distribution (PSD) curves of the three carbons are further proved in **Figure 6b**. From the pore characteristics listed in **Table 2**, the specific surface areas of the resulting samples were 1181, 1103, and 153 m² g⁻¹, and the pore volumes were 0.50, 0.54, and 0.38 cm³ g⁻¹, respectively. It can be seen that the S_{BET} values of FC-NH₄Cl-700-1.0 and FC-NH₄Cl-800-1.0 are much higher than that of FC-NH₄Cl-900-1.0. The lower S_{BET} value of FC-NH₄Cl-900-1.0 may be due to the pore collapse and enhanced crystallization at higher carbonization temperature [46, 47]. The

S_{BET} value of FC-800 (without NH_4Cl) was determined to be $513 \text{ m}^2 \text{ g}^{-1}$ (see **Table S2**), which was ascribable to the removal of nanoparticles and effect of CO/CO_2 , produced by the reaction between iron compounds and carbon [35]. Meanwhile, FC- NH_4Cl -800-0.5 and FC- NH_4Cl -800-2.0 also show a higher S_{BET} value than that of pure FC (**Figure S6** and **Table S2**). The high S_{BET} value was due to the addition of NH_4Cl , which acts as self-porogen with the elimination of generated gas. Therefore, it can be concluded that the formed porous network originated from the coefficient between NH_4Cl as pore former and the activation of iron compounds, which made it possible to prepare the hierarchical porous carbons by modulating the temperature and (or) mass ratio of NH_4Cl to FC.

Figure 5. Scanning electron microscopy (SEM) images of (a) FC- NH_4Cl -700-1.0 and (b) FC- NH_4Cl -800-1.0; and TEM images of (c, g) FC- NH_4Cl -700-1.0 and (d, h) FC- NH_4Cl -800-1.0. High resolution transmission electron microscopy (HR-TEM) images of (e) FC- NH_4Cl -700-1.0 and (f) FC- NH_4Cl -800-1.0. The spacing of lattice fringe of iron-rich nanoparticles was signed in the pictures. Fe_3C nanoparticles of 50-100 nm in diameter were well encapsulated in the carbon matrix, which may provide the protection from acid-leaching.

Figure 6. (a) Nitrogen adsorption/desorption isotherms of FC-NH₄Cl-700-1.0, FC-NH₄Cl-800-1.0, and FC-NH₄Cl-900-1.0. The sample of FC-NH₄Cl-700-1.0 exhibits a type-I sorption isotherm. The FC-NH₄Cl-800-1.0 and FC-NH₄Cl-900-1.0 exhibit type-IV shaped curves. The corresponding specific surface areas are 1181, 1103, and 153 m² g⁻¹, respectively. (b) Pore-size distribution curves of FC-NH₄Cl-T-1.0.

Table 2. Pore characteristics of FC-NH₄Cl-T-1.0.

Sample	S _{BET} [m ² g ⁻¹]	S _{langmuir} [m ² g ⁻¹]	V _{pore} [cm ³ g ⁻¹]	D _{aver} [nm]
FC-NH ₄ Cl-700-1.0	1180.92	1350.46	0.50	1.70
FC-NH ₄ Cl-800-1.0	1102.74	1306.10	0.54	1.96
FC-NH ₄ Cl-900-1.0	152.96	233.38	0.38	9.86

The FC-derived carbon materials were further applied for ORR, as shown in **Figure 7**. The ORR catalytic performance of the carbons was investigated by rotating disk electrode (RDE) in 0.1 M KOH solution. **Figure 7a** shows that the FC-NH₄Cl-800-1.0 exhibits superior ORR activity than those carbonized at 700 or 900 °C according to the more positive onset potential (E_{onset}), half-wave potential ($E_{1/2}$), and larger limiting current density in linear-sweep voltammograms (LSV) [48]. From the result, we can see that FC-NH₄Cl-800-1.0 and FC-NH₄Cl-700-1.0 have similar specific surface area, while

some mesopores existed in FC-NH₄Cl-800-1.0 may provide better mass diffusion to boost the ORR [49]. In addition, the higher carbonization temperature may cause the higher degree of graphitization. Although FC-NH₄Cl-900-1.0 has high graphitic degree, the relatively lower specific surface area, N and Fe content may limit its activity. Nitrogen atom can provide the active sites to a positive correlation [21, 50], and the encapsulated Fe₃C can activate the surrounding carbon layer which was beneficial for ORR [24]. Moreover, the nitrogen groups coordinated with Fe may form the Fe-N_x sites to provide active centers for ORR [51-55]. Therefore, the best catalytic performance of FC-NH₄Cl-800-1.0 should account the synergistic effect of the multi-factor among specific surface area, hierarchically porous structures, graphitic degree, and the content of N and Fe. Hence, the carbonization temperature of 800 °C was chosen for pyrolysis of FC, FC-KOH, and FC-NaCl for further research. **Figure 7b** demonstrates that among the three small-molecular porogen (NH₄Cl, KOH, and NaCl), only NH₄Cl exhibits high electrochemical performance in this work, because it acts as not only porogen but also N-dopant. More important, FC-NH₄Cl-800-1.0 with E_{onset} of 0.94 V and E_{1/2} of 0.85 V (vs. RHE) was close to the commercial Pt/C (0.93 V for E_{onset} and 0.83 V for E_{1/2}). FC-800 with low surface area and no N atoms doping shows the weaker catalytic activity (0.83 V for E_{onset} and 0.72 V for E_{1/2}). Compared with N-doped porous carbons reported, the FC-NH₄Cl-800-1.0 material presents one of the highest catalytic activities for ORR (see **Table 3**). The cyclic voltammogram (CV) curves of FC-NH₄Cl-800-1.0 were recorded in N₂ and O₂-saturated 0.1 M KOH solutions, respectively (see **Figure S7**). When the electrolyte was saturated with N₂, no redox peaks appeared for FC-NH₄Cl-800-1.0. By contrast, the peak at 0.68 V can be detected in O₂-saturated environment, indicating the electrocatalytic activity of FC-NH₄Cl-800-1.0 [56]. **Figure 7c** and **Figure S8** show the RDE voltammograms of FC-NH₄Cl-T-1.0 and Pt/C at rotating speeds from 400 to 1600 rpm. It can be seen that the limiting current density increases with the higher rotation rate, because the higher rotation rates may shorten the diffusion distance. The corresponding Koutecky-Levich (K-L) plots of FC-

NH₄Cl-800-1.0 were shown in **Figure 7d** to study the ORR kinetics. The electron transfer number (n) was calculated from the slopes of lines, which is about 3.7 to 3.9 for FC-NH₄Cl-800-1.0 at the potential from 0.55 to 0.25 V. Therefore, the ORR of FC-NH₄Cl-800-1.0 occurs a 4e reaction to reduce oxygen molecule to hydroxyl ion in alkaline electrolyte ($\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$) [57]. The rotation ring disk electrode (RRDE) technique was employed to show the four-electron selectivity of FC-NH₄Cl-800-1.0 (see **Figure S9**). The low amount of peroxide yield (lower than 4.5%) and nearly four electron transfer (see **Figure S9b-c**), suggest the direct four-electron process for ORR.

Table 3. ORR performance of N-doped porous carbons reported in the representative literature. The values of potential provided are versus reversible hydrogen electrode (RHE).*

Sample	Electrolyte	E _{onset} (V)	E _{1/2} (V)	Reference
FC-NH ₄ Cl-800-1.0	0.1 M KOH	0.94	0.85	This work
FC-800	0.1 M KOH	0.83	0.72	This work
CCa	0.1 M KOH	0.90	0.75	[58]
PDI-900	0.1 M KOH	0.87	0.76	[59]
NPC-F	0.1 M KOH	~0.90	0.84	[60]
N-doped Fe-Fe ₃ C @graphitic layer	0.1 M KOH	0.92	~0.77	[61]
Fe-N/C-800	0.1 M KOH	0.92	0.81	[62]

The tolerance performance to fuel molecule was evaluated in O₂-saturated 0.1 M KOH solution with or without 0.5 M methanol (see **Figure 7e** and **S10**). As can be seen from **Figure 7e**, FC-NH₄Cl-800-1.0 shows negligible change with the addition of 0.5 M methanol, indicating the excellent tolerance to methanol. **Figure 7f** shows the durability for ORR conducted by current–time (i–t)

chronoamperometric response. It should be noted that FC-NH₄Cl-800-1.0 retains 81.8 % of initial current in alkaline medium after 5000 seconds, suggesting better catalytic stability than that of Pt/C (retains 76.6 %).

Figure 7. Rotating disk electrode (RDE) polarization curves of (a) FC-NH₄Cl-T-1.0 and (b) FC-derived carbons pyrolyzed at 800 °C and Pt/C, in O₂-saturated 0.1 M KOH solution at 1600 rpm; (c) Linear-sweep voltammograms (LSV) curves of FC-NH₄Cl-800-1.0 at different rotation speeds; (d) The Koutecky-Levich (K-L) plots of FC-NH₄Cl-800-1.0. (e) LSV curves of FC-NH₄Cl-800-1.0 in O₂-saturated 0.1 M KOH solution with or without 0.5 M methanol; (f) current–time (i–t) chronoamperometric response of FC-NH₄Cl-800-1.0 and Pt/C in O₂-saturated 0.1 M KOH solution at 1600 rpm. The loading of all the FC-derived carbons was 0.4 mg cm⁻² and was 0.2 mg cm⁻² for commercial Pt/C.

To extend the application of obtained porous CMs, FC-NH₄Cl-T-1.0 materials were also applied as electrodes in 6 M KOH solution for supercapacitive behaviour. **Figure 8a** shows the electrochemical impedance spectroscopy (EIS) curves of FC-NH₄Cl-T-1.0 from 10 kHz to 0.01 Hz (inset shows the

equivalent circuit). The magnified region of FC-NH₄Cl-700-1.0 was demonstrated in **Figure S11**. For circuit, R_s represents the solution resistance. R_{ct} is the charge transfer resistance, while W is the Warburg impedance. Two capacitors C stand for double-layer capacitance (C_1) and Faradic capacitance (C_2), respectively [63]. At high frequencies, R_s and R_{ct} for FC-NH₄Cl-700-1.0 electrode were 1.16 and 0.15 Ω , respectively, which were higher than those of FC-NH₄Cl-800-1.0 ($R_s=0.91$ Ω , $R_{ct}=0.04$ Ω) and FC-NH₄Cl-900-1.0 ($R_s=0.84$ Ω , $R_{ct}=0.03$ Ω). The lower carbonization temperature for FC-NH₄Cl-700-1.0 resulted in a relative lower conductivity, due to the lower graphitic degree. In addition, three samples show almost 90° to X-axis, indicating the effect of standard double layer capacitors [64]. FC-NH₄Cl-700-1.0 exhibits a slight deviation to the ideal vertical line, suggesting pseudofaradaic reactions to supplement the supercapacitive behaviour [65]. The middle frequencies at a phase shift of 45° was accounted as the Warburg impedance, suggesting the ion diffusion/transport [28]. The microporous structure and abundance of functional groups hinder the ion diffusion/transport to electrode surface, leading to the high impedance of FC-NH₄Cl-700-1.0 [66]. **Figure 8b** exhibits CV curves of FC-NH₄Cl-T-1.0 at a scan rate of 5 mV s⁻¹. FC-NH₄Cl-700-1.0 displays the largest loop area among the three samples, and well-developed CV curves at various scan rates (see **Figure 8c**), implying the most appealing supercapacitor electrode in this work. Hence, the good performance of supercapacitor was not only due to the high graphitic degree and porous structure, but also affected by other factors, including the heteroatomic impact and high specific surface area. In addition, we can see a redox peak at about -0.4 V for FC-NH₄Cl-700-1.0, probably due to the high content of nitrogen (10.12 %) [40]. The absence of apparent Faradaic hump of iron was probably due to the low content of Fe (1.54 %).

Figure 8. (a) Electrochemical impedance spectroscopy (EIS) curves of FC-NH₄Cl-T-1.0 (inset: equivalent circuit). (b) CV curves of FC-NH₄Cl-T-1.0 at a scan rate of 5 mV s⁻¹ in 6 M KOH solution. (c) Cyclic voltammogram (CV) curves of FC-NH₄Cl-700-1.0 at different scan rates. (d) Galvanostatic charge-discharge (GCD) curves of FC-NH₄Cl-700-1.0 at various current densities from 1 to 10 A g⁻¹. (e) Specific capacitances of FC-NH₄Cl-T-1.0 in various current densities. (f) Cyclic stability of FC-NH₄Cl-700-1.0 at a current density of 1 A g⁻¹ in 6 M KOH after 5000 cycles. The capacitance retained about 92 % of the initial specific capacitance.

The galvanostatic charge–discharge (GCD) curves were also used (**Figures 8d** and **S13a, b**). At a current density of 1 A g⁻¹, the specific capacitances of FC-NH₄Cl-700-1.0, FC-NH₄Cl-800-1.0, and FC-NH₄Cl-900-1.0 were calculated to be 242, 163, and 13 F g⁻¹ by **equation 6**. FC-NH₄Cl-700-1.0 owns the best specific capacitance greatly depends on the highest specific surface area (1181 m² g⁻¹) and heteroatom doping content. A high surface area with 3D pore structure can block the dense agglomeration, which is in favour of the full utilization to electrochemical interface for electrolyte and electrochemical reactions [67]. While doping heteroatom into the carbon can gain additional

pseudocapacitance to supercapacitance. The doped heteroatom of N and O may bring the electrochemical active sites to contribute the Faradaic reaction and improve hydrophilicity of electrode to enhance the contact area with aqueous electrolyte [68]. It could be seen that the iron content of FC-NH₄Cl-700-1.0 was higher than that of FC-NH₄Cl-800-1.0 and FC-NH₄Cl-900-1.0. The encapsulated Fe₃C nanoparticles, obtained by the interaction of metallic iron and carbon during the heat-treatment, can form Fe (III) and Fe (II) species on the process of charge/discharge redox reactions, playing a partial role to contribute the pseudocapacitance [69, 70]. Therefore, it is supposed that the high specific surface area, doped heteroatoms (N and O), and encapsulated Fe₃C nanoparticles highly improved the supercapacitor performance. Besides, the electrochemical tests of the undoped FC carbons (derived from direct carbonization of FC) were shown in **Figure S13c**. It can be seen that the specific capacitance of FC-800 was calculated to be 100 F g⁻¹ at a current density of 1 A g⁻¹, which was about twice lower than that of FC-NH₄Cl-700-1.0. **Table 4** exhibits the capacitances of N-doped porous carbons reported in the representative literature. The FC-NH₄Cl-700-1.0 showed relatively high supercapacitor performance among the CMs reported.

Table 4. Capacitances of N-doped porous carbons reported in the representative literature.

Sample	Electrolyte	Capacitance (F g ⁻¹)	Current density (A g ⁻¹)	Reference
FC-NH ₄ Cl-700-1.0	6 M KOH	242	1	This work
FC-800	6 M KOH	100	1	This work
3D graphene layers	1 M H ₂ SO ₄	231.2	1	[71]
CCa-800-N	1 M H ₂ SO ₄	208	0.1	[72]
C-900	6 M KOH	210	1	[73]
CNCs-800	6 M KOH	248	1	[74]
CA-GA-2	6 M KOH	220	0.1	[75]

Figure 8e shows the specific capacitances of FC-NH₄Cl-T-1.0 in various current densities. As we can see that the calculated specific capacitance of FC-NH₄Cl-700-1.0 was higher than other two samples in a current density from 0.5 to 30 A g⁻¹. Moreover, FC-NH₄Cl-700-1.0 maintained specific capacitances of 155 F g⁻¹ at 30 A g⁻¹, suggesting a good stability at high current density. The cycling capability is another important factor for the application of supercapacitor (see **Figure 8f**). The measurement for FC-NH₄Cl-700-1.0 was conducted by galvanostatic charge/discharge method in 1 A g⁻¹. After 5000 cycles, about 92 % of the initial specific capacitance was retained, suggesting the promising supercapacitor electrode material of FC-NH₄Cl-700-1.0 for practical application.

4. Conclusions

In conclusion, a series of N-doped hierarchical porous carbons were prepared via carbonizing the ferric citrate-ammonium chloride. Ferric citrate provides both carbon and iron sources, while ammonium chloride acts as both the porogen and nitrogen dopant. The textural structure and chemical composition can be regulated by pyrolysis temperature and mass ration of NH₄Cl to FC. Compared with KOH and NaCl, NH₄Cl exhibits the best ORR activity, probably due to the role for both dopant and porogen. In addition, Fe₃C nanoparticles were formed during the carbonization process and be well-encapsulated in carbon layer, which can be protected from the acid etching. FC-NH₄Cl-800-1.0 showed the best ORR activity and FC-NH₄Cl-700-1.0 exhibit high specific capacitance and good stability. Since ferric citrate and ammonium chloride are low-cost and easily available, this work provided a facile and effective method to obtain carbons with superb electrochemical performance.

Acknowledgements

This work was supported by the National Science Foundation for Distinguished Young Scholars (No.

21425417), the Natural Science Foundation of China (No. 21274101), and the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

References

- [1] A.S. Arico, P. Bruce, B. Scrosati, J.-M. Tarascon, W. Van Schalkwijk, Nanostructured materials for advanced energy conversion and storage devices, *Nat. Mater.* 4(5) (2005) 366-377.
- [2] M.K. Debe, Electrocatalyst approaches and challenges for automotive fuel cells, *Nature* 486(7401) (2012) 43-51.
- [3] G. Wang, L. Zhang, J. Zhang, A review of electrode materials for electrochemical supercapacitors, *Chem. Soc. Rev.* 41(2) (2012) 797-828.
- [4] Y. Peng, X. Wu, L. Qiu, C. Liu, S. Wang, F. Yan, Synthesis of carbon-PtAu nanoparticle hybrids originating from triethoxysilane-derivatized ionic liquids for methanol electrooxidation and the catalytic reduction of 4-nitrophenol, *J. Mater. Chem. A* 1(32) (2013) 9257-9263.
- [5] X. Liu, W. Liu, M. Ko, M. Park, M.G. Kim, P. Oh, et al, Metal (Ni, Co)-Metal Oxides/Graphene Nanocomposites as Multifunctional Electrocatalysts, *Adv. Funct. Mater.* 25(36) (2015) 5799-5808.
- [6] G. Li, X. Wang, J. Fu, J. Li, M.G. Park, Y. Zhang, et al, Pomegranate-Inspired Design of Highly Active and Durable Bifunctional Electrocatalysts for Rechargeable Meta-Air Batteries, *Angew. Chem. Int. Ed.* 55(16) (2016) 4977-4982.
- [7] D. Xu, Y. Xie, Y.-J. Song, W.-Q. Deng, A green and facile method toward synthesis of waste paper-derived 3D functional porous graphene via in situ activation of cobalt(ii), *J. Mater. Chem. A* 3(31) (2015) 16072-16078.
- [8] Y. Liang, H. Wang, P. Diao, W. Chang, G. Hong, Y. Li, et al, Oxygen reduction electrocatalyst based on strongly coupled cobalt oxide nanocrystals and carbon nanotubes, *J. Am. Chem. Soc.* 134(38) (2012) 15849-15857.
- [9] I. Hijazi, T. Bourgeteau, R. Cornut, A. Morozan, A. Filoramo, J. Leroy, et al, Carbon nanotube-templated synthesis of covalent porphyrin network for oxygen reduction reaction, *J. Am. Chem. Soc.* 136(17) (2014) 6348-6354.

- [10] Y. Liu, X. Yue, K. Li, J. Qiao, D.P. Wilkinson, J. Zhang, PEM fuel cell electrocatalysts based on transition metal macrocyclic compounds, *Coordin. Chem. Rev.* 315 (2016) 153-177.
- [11] J. Masud, A.T. Swesi, W.P. Liyanage, M. Nath, Cobalt Selenide Nanostructures: An Efficient Bifunctional Catalyst with High Current Density at Low Coverage, *ACS Appl. Mater. Interfaces* 8(27) (2016) 17292-17302.
- [12] S. Dou, L. Tao, J. Huo, S. Wang, L. Dai, Etched and doped Co₉S₈/graphene hybrid for oxygen electrocatalysis, *Energy Environ. Sci.* 9(4) (2016) 1320-1326.
- [13] S. Zhang, M.S. Miran, A. Ikoma, K. Dokko, M. Watanabe, Protic ionic liquids and salts as versatile carbon precursors, *J. Am. Chem. Soc.* 136(5) (2014) 1690-1693.
- [14] H. Yu, L. Shang, T. Bian, R. Shi, G.I. Waterhouse, Y. Zhao, et al, Nitrogen-Doped Porous Carbon Nanosheets Templated from g-C₃N₄ as Metal-Free Electrocatalysts for Efficient Oxygen Reduction Reaction, *Adv. Mater.* 28 (2016) 5080-5086.
- [15] V. Perazzolo, C. Durante, R. Pilot, A. Paduano, J. Zheng, G.A. Rizzi, et al, Nitrogen and sulfur doped mesoporous carbon as metal-free electrocatalysts for the in situ production of hydrogen peroxide, *Carbon* 95 (2015) 949-963.
- [16] G. Tao, L. Zhang, L. Chen, X. Cui, Z. Hua, M. Wang, et al, N-doped hierarchically macro/mesoporous carbon with excellent electrocatalytic activity and durability for oxygen reduction reaction, *Carbon* 86 (2015) 108-117.
- [17] F.P. Pan, Z.Y. Cao, Q.P. Zhao, H.Y. Liang, J.Y. Zhang, Nitrogen-doped porous carbon nanosheets made from biomass as highly active electrocatalyst for oxygen reduction reaction, *J. Power Sources* 272 (2014) 8-15.
- [18] L. Li, Q. Zhong, N.D. Kim, G. Ruan, Y. Yang, C. Gao, et al, Nitrogen-doped carbonized cotton for highly flexible supercapacitors, *Carbon* 105 (2016) 260-267.
- [19] G.-X. Li, P.-X. Hou, S.-Y. Zhao, C. Liu, H.-M. Cheng, A flexible cotton-derived carbon sponge for high-performance capacitive deionization, *Carbon* 101 (2016) 1-8.
- [20] W. He, Y. Wang, C. Jiang, L. Lu, Structural effects of a carbon matrix in non-precious metal O₂-reduction electrocatalysts, *Chem. Soc. Rev.* 45(9) (2016) 2396-2409.
- [21] W. Xia, A. Mahmood, Z. Liang, R. Zou, S. Guo, Earth-Abundant Nanomaterials for Oxygen Reduction, *Angew. Chem. Int. Ed.* 55(8) (2016) 2650-2676.
- [22] J. Wang, G. Wang, S. Miao, X. Jiang, J. Li, X. Bao, Synthesis of Fe/Fe₃C nanoparticles encapsulated in nitrogen-doped carbon with single-source molecular precursor for the oxygen reduction reaction, *Carbon* 75 (2014) 381-389.

- [23] Y. Hu, J.O. Jensen, W. Zhang, L.N. Cleemann, W. Xing, N.J. Bjerrum, et al, Hollow spheres of iron carbide nanoparticles encased in graphitic layers as oxygen reduction catalysts, *Angew. Chem. Int. Ed.* 53(14) (2014) 3675-3679.
- [24] M. Xiao, J. Zhu, L. Feng, C. Liu, W. Xing, Meso/Macroporous Nitrogen-Doped Carbon Architectures with Iron Carbide Encapsulated in Graphitic Layers as an Efficient and Robust Catalyst for the Oxygen Reduction Reaction in Both Acidic and Alkaline Solutions, *Adv. Mater.* 27(15) (2015) 2521-2527.
- [25] K.P. Qiu, Z.X. Guo, Hierarchically porous graphene sheets and graphitic carbon nitride intercalated composites for enhanced oxygen reduction reaction, *J. Mater. Chem. A* 2(9) (2014) 3209-3215.
- [26] P. Chen, L.-K. Wang, G. Wang, M.-R. Gao, J. Ge, W.-J. Yuan, et al, Nitrogen-doped nanoporous carbon nanosheets derived from plant biomass: an efficient catalyst for oxygen reduction reaction, *Energy Environ. Sci.* 7(12) (2014) 4095-4103.
- [27] J. Zhang, D. Xu, W. Qian, J. Zhu, F. Yan, Host-guest inclusion complexes derived heteroatom-doped porous carbon materials, *Carbon* 105 (2016) 183-190.
- [28] J. Zhu, D. Xu, W. Qian, J. Zhang, F. Yan, Heteroatom-Containing Porous Carbons Derived from Ionic Liquid - Doped Alkali Organic Salts for Supercapacitors, *Small* 12(14) (2016) 1935-1944.
- [29] Y. He, X. Han, Y. Du, B. Song, P. Xu, B. Zhang, Bifunctional Nitrogen-Doped Microporous Carbon Microspheres Derived from Poly (o-methylaniline) for Oxygen Reduction and Supercapacitors, *ACS Appl. Mater. Interfaces* 8(6) (2015) 3601-3608.
- [30] D.Y. Chung, K.J. Lee, S.H. Yu, M. Kim, S.Y. Lee, O.H. Kim, et al, Alveoli-Inspired Facile Transport Structure of N-Doped Porous Carbon for Electrochemical Energy Applications, *Adv. Energy Mater.* 5(3) (2015) 1401309.
- [31] M. Vujković, N. Gavrilov, I. Pašti, J. Krstić, J. Trivas-Sejdic, G. Ćirić-Marjanović, et al, Superior capacitive and electrocatalytic properties of carbonized nanostructured polyaniline upon a low-temperature hydrothermal treatment, *Carbon* 64 (2013) 472-486.
- [32] M. Sevilla, A.B. Fuertes, Direct synthesis of highly porous interconnected carbon nanosheets and their application as high-performance supercapacitors, *ACS Nano* 8(5) (2014) 5069-5078.
- [33] W. Qian, J. Zhu, Y. Zhang, X. Wu, F. Yan, Condiment-Derived 3D Architecture Porous Carbon for Electrochemical Supercapacitors, *Small* 11(37) (2015) 4959-4969.

- [34] X. Wang, Y. Zhang, C. Zhi, X. Wang, D. Tang, Y. Xu, et al, Three-dimensional strutted graphene grown by substrate-free sugar blowing for high-power-density supercapacitors, *Nat. Commun.* 4 (2013) 2905.
- [35] X. Zhu, F. Qian, Y. Liu, D. Matera, G. Wu, S. Zhang, et al, Controllable synthesis of magnetic carbon composites with high porosity and strong acid resistance from hydrochar for efficient removal of organic pollutants: An overlooked influence, *Carbon* 99 (2016) 338-347.
- [36] W. Shen, W. Fan, Nitrogen-containing porous carbons: synthesis and application, *J. Mater. Chem. A* 1(4) (2013) 999-1013.
- [37] W.-J. Jiang, L. Gu, L. Li, Y. Zhang, X. Zhang, L.-J. Zhang, et al, Understanding the High Activity of Fe-N-C Electrocatalysts in Oxygen Reduction: Fe/Fe₃C Nanoparticles Boost the Activity of Fe-Nx, *J. Am. Chem. Soc.* 138(10) (2016) 3570-3578.
- [38] J.P. Paraknowitsch, J. Zhang, D. Su, A. Thomas, M. Antonietti, Ionic Liquids as Precursors for Nitrogen-Doped Graphitic Carbon, *Adv. Mater.* 22(1) (2010) 87-92.
- [39] H. Wang, Z. Xu, A. Kohandehghan, Z. Li, K. Cui, X. Tan, et al, Interconnected carbon nanosheets derived from hemp for ultrafast supercapacitors with high energy, *ACS Nano* 7(6) (2013) 5131-5141.
- [40] W. Qian, F. Sun, Y. Xu, L. Qiu, C. Liu, S. Wang, et al, Human hair-derived carbon flakes for electrochemical supercapacitors, *Energy Environ. Sci.* 7(1) (2014) 379-386.
- [41] C. Pan, L. Qiu, Y. Peng, F. Yan, Facile synthesis of nitrogen-doped carbon-Pt nanoparticle hybrids via carbonization of poly ([Bvim][Br]-co-acrylonitrile) for electrocatalytic oxidation of methanol, *J. Mater. Chem.* 22(27) (2012) 13578-13584.
- [42] L. Hao, X. Li, L. Zhi, Carbonaceous electrode materials for supercapacitors, *Adv. Mater.* 25(28) (2013) 3899-3904.
- [43] B. Xu, D. Zheng, M. Jia, G. Cao, Y. Yang, Nitrogen-doped porous carbon simply prepared by pyrolyzing a nitrogen-containing organic salt for supercapacitors, *Electrochim. Acta* 98 (2013) 176-182.
- [44] J. Wei, Y. Liang, Y. Hu, B. Kong, G.P. Simon, J. Zhang, et al, A Versatile Iron-Tannin-Framework Ink Coating Strategy to Fabricate Biomass-Derived Iron Carbide/Fe-N-Carbon Catalysts for Efficient Oxygen Reduction, *Angew. Chem.* 128(4) (2016) 1377-1381.
- [45] X. Yang, A. Liu, Y. Zhao, H. Lu, Y. Zhang, W. Wei, et al, Three-dimensional macroporous polypyrrole-derived graphene electrode prepared by the hydrogen bubble dynamic template for supercapacitors and metal-free catalysts, *ACS Appl. Mater. Interfaces* 7(42) (2015) 23731-23740.

- [46] H. Zhu, X. Wang, X. Liu, X. Yang, Integrated Synthesis of Poly (o-phenylenediamine)-Derived Carbon Materials for High Performance Supercapacitors, *Adv. Mater.* 24(48) (2012) 6524-6529.
- [47] C. Wang, Y. Wang, J. Graser, R. Zhao, F. Gao, M.J. O'Connell, Solution-Based Carbohydrate Synthesis of Individual Solid, Hollow, and Porous Carbon Nanospheres Using Spray Pyrolysis, *ACS Nano* 7(12) (2013) 11156-11165.
- [48] S. Gao, K. Geng, H. Liu, X. Wei, M. Zhang, P. Wang, et al, Transforming organic-rich amaranthus waste into nitrogen-doped carbon with superior performance of the oxygen reduction reaction, *Energy Environ. Sci.* 8(1) (2015) 221-229.
- [49] J.Y. Cheon, T. Kim, Y. Choi, H.Y. Jeong, M.G. Kim, Y.J. Sa, et al, Ordered mesoporous porphyrinic carbons with very high electrocatalytic activity for the oxygen reduction reaction, *Sci. Rep.* 3 (2013) 2715.
- [50] D. Eisenberg, W. Stroek, N.J. Geels, S. Tanase, M. Ferbinteanu, S.J. Teat, et al, A rational synthesis of hierarchically porous, N-doped carbon from Mg-based MOFs: understanding the link between nitrogen content and oxygen reduction electrocatalysis, *Phys. Chem. Chem. Phys.* 18(30) (2016) 20778-20783.
- [51] G. Wu, P. Zelenay, Nanostructured nonprecious metal catalysts for oxygen reduction reaction, *Acc. Chem. Res.* 46(8) (2013) 1878-1889.
- [52] A. Serov, M.H. Robson, B. Halevi, K. Artyushkova, P. Atanasov, Highly active and durable templated non-PGM cathode catalysts derived from iron and aminoantipyrine, *Electrochem. Commun.* 22 (2012) 53-56.
- [53] M. Ferrandon, A.J. Kropf, D.J. Myers, K. Artyushkova, U. Kramm, P. Bogdanoff, et al, Multitechnique characterization of a polyaniline-iron-carbon oxygen reduction catalyst, *J. Phys. Chem. C* 116(30) (2012) 16001-16013.
- [54] K. Artyushkova, A. Serov, S. Rojas-Carbonell, P. Atanasov, Chemistry of multitudinous active sites for oxygen reduction reaction in transition metal-nitrogen-carbon electrocatalysts, *J. Phys. Chem. C* 119(46) (2015) 25917-25928.
- [55] G. Wu, K.L. More, C.M. Johnston, P. Zelenay, High-performance electrocatalysts for oxygen reduction derived from polyaniline, iron, and cobalt, *Science* 332(6028) (2011) 443-447.
- [56] Z.Y. Wu, X.X. Xu, B.C. Hu, H.W. Liang, Y. Lin, L.F. Chen, et al, Iron Carbide Nanoparticles Encapsulated in Mesoporous Fe-N-Doped Carbon Nanofibers for Efficient Electrocatalysis, *Angew. Chem.* 127(28) (2015) 8297-8301.

- [57] L. Liu, X. Yang, N. Ma, H. Liu, Y. Xia, C. Chen, et al, Scalable and Cost-Effective Synthesis of Highly Efficient Fe₂N-Based Oxygen Reduction Catalyst Derived from Seaweed Biomass, *Small* 12(10) (2016) 1295-1301.
- [58] G.A. Ferrero, A.B. Fuertes, M. Sevilla, M.-M. Titirici, Efficient metal-free N-doped mesoporous carbon catalysts for ORR by a template-free approach, *Carbon* 106 (2016) 179-187.
- [59] R. Liu, D. Wu, X. Feng, K. Müllen, Nitrogen-doped ordered mesoporous graphitic arrays with high electrocatalytic activity for oxygen reduction, *Angew. Chem.* 122(14) (2010) 2619-2623.
- [60] Z. Xu, X. Zhuang, C. Yang, J. Cao, Z. Yao, Y. Tang, et al, Nitrogen-Doped Porous Carbon Superstructures Derived from Hierarchical Assembly of Polyimide Nanosheets, *Adv. Mater.* 28(10) (2016) 1981-1987.
- [61] B.K. Barman, K.K. Nanda, Prussian blue as a single precursor for synthesis of Fe/Fe₃C encapsulated N-doped graphitic nanostructures as bi-functional catalysts, *Green Chem.* 18(2) (2016) 427-432.
- [62] L. Lin, Q. Zhu, A.-W. Xu, Noble-metal-free Fe-N/C catalyst for highly efficient oxygen reduction reaction under both alkaline and acidic conditions, *J. Am. Chem. Soc.* 136(31) (2014) 11027-11033.
- [63] X.-L. Wu, T. Wen, H.-L. Guo, S. Yang, X. Wang, A.-W. Xu, Biomass-derived sponge-like carbonaceous hydrogels and aerogels for supercapacitors, *ACS Nano* 7(4) (2013) 3589-3597.
- [64] M. Biswal, A. Banerjee, M. Deo, S. Ogale, From dead leaves to high energy density supercapacitors, *Energy Environ. Sci.* 6(4) (2013) 1249-1259.
- [65] L.-F. Chen, X.-D. Zhang, H.-W. Liang, M. Kong, Q.-F. Guan, P. Chen, et al, Synthesis of nitrogen-doped porous carbon nanofibers as an efficient electrode material for supercapacitors, *ACS Nano* 6(8) (2012) 7092-7102.
- [66] L. Lai, H. Yang, L. Wang, B.K. Teh, J. Zhong, H. Chou, et al, Preparation of supercapacitor electrodes through selection of graphene surface functionalities, *ACS Nano* 6(7) (2012) 5941-5951.
- [67] Y.S. Yun, S.Y. Cho, J. Shim, B.H. Kim, S.J. Chang, S.J. Baek, et al, Microporous carbon nanoplates from regenerated silk proteins for supercapacitors, *Adv. Mater.* 25(14) (2013) 1993-1998.
- [68] Q. Wang, J. Yan, Z. Fan, Carbon materials for high volumetric performance supercapacitors: design, progress, challenges and opportunities, *Energy Environ. Sci.* 9(3) (2016) 729-762.
- [69] Y. Xie, Y. Chen, Y. Zhou, K.M. Unruh, J.Q. Xiao, A negative working potential supercapacitor electrode consisting of a continuous nanoporous Fe-Ni network, *Nanoscale* 8(23) (2016) 11875-11881.

- [70] E. Fedorovskaya, L. Bulusheva, A. Kurennya, I. Asanov, N. Rudina, K. Funtov, et al, Supercapacitor performance of vertically aligned multiwall carbon nanotubes produced by aerosol-assisted CCVD method, *Electrochim. Acta* 139 (2014) 165-172.
- [71] J. Hao, Y. Liao, Y. Zhong, D. Shu, C. He, S. Guo, et al, Three-dimensional graphene layers prepared by a gas-foaming method for supercapacitor applications, *Carbon* 94 (2015) 879-887.
- [72] G. Ferrero, M. Sevilla, A. Fuertes, Mesoporous carbons synthesized by direct carbonization of citrate salts for use as high-performance capacitors, *Carbon* 88 (2015) 239-251.
- [73] B. Qiu, C. Pan, W. Qian, Y. Peng, L. Qiu, F. Yan, Nitrogen-doped mesoporous carbons originated from ionic liquids as electrode materials for supercapacitors, *J. Mater. Chem. A* 1(21) (2013) 6373-6378.
- [74] Y. Tan, C. Xu, G. Chen, Z. Liu, M. Ma, Q. Xie, et al, Synthesis of ultrathin nitrogen-doped graphitic carbon nanocages as advanced electrode materials for supercapacitor, *ACS Appl. Mater. Interfaces* 5(6) (2013) 2241-2248.
- [75] L. Zhao, L.Z. Fan, M.Q. Zhou, H. Guan, S. Qiao, M. Antonietti, et al, Nitrogen-Containing Hydrothermal Carbons with Superior Performance in Supercapacitors, *Adv. Mater.* 22(45) (2010) 5202-5206.

Graphical abstract