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Recent Progress in Template-Assisted Synthesis of Nitrogen-Doped Porous Carbons for Oxygen Electoreduction

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Abstract: Nitrogen (N)-doped porous carbons are potential alternatives to precious metal catalysts for oxygen reduction reaction (ORR) at the cathodes of proton exchange membrane fuel cells and metal-air batteries. Template-assisted synthesis has been used extensively as a robust and versatile method in the preparation of such carbon catalysts, where the ORR activity has been found to be dependent on various structural parameters, such as the concentrations and molecular configurations of the dopants, and the porosity, surface accessibility and electrical conductivity of the carbon materials. In this review, we summarize recent progress in this area of research focusing on the design, preparation and engineering of N-doped porous carbons, as well as their ORR catalytic activity. Future trends in the development of N-doped porous carbons are also pointed out.

Key words: oxygen reduction reaction; N-doped porous carbon; template-assisted synthesis; thermally removable template

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Heteroatom-doped carbons have emerged as viable catalysts for oxygen reduction reaction (ORR), a critical process taking place at the cathodes of proton exchange membrane fuel cells and metal-air batteries that has been recognized as a major bottleneck limiting the device performance^[1-4]. Of these, N-doped carbons are of particular interest because of their remarkable ORR activity, as compared to other heteroatom-doped carbons, and hence, are deemed as a promising alternative to Pt for ORR^[5-8]. The ORR activity of N-doped carbons is mostly dictated by two factors: (a) the concentration and molecular configuration of the nitrogen dopants; and (b) the accessibility of ORR active sites that governs the transport of ORR relevant species such as H⁺, OH⁻, O₂, H₂O, etc., as manifested by the specific surface area and porosity of the carbon structures^[9-12]. Normally, a high content of homogeneously distributed active nitrogen dopants in the carbon catalysts is desired to ensure a

high ORR activity. However, to date it remains unclear which nitrogen dopant is responsible for the ORR activity because multiple nitrogen doping configurations are formed in the carbon molecular skeletons, e.g., pyrrolic N, pyridinic N and graphitic N. Wei et al.^[13] proposed that the active sites for ORR were carbon atoms adjacent to both pyridinic and pyrrolic N. Recently, Nakamura et al.^[14] suggested that the ORR active sites were the carbon atoms directly bonded to pyridinic N alone by examining the ORR activity of highly oriented pyrolytic graphite (HOPG) with controlled N-doping. More recently, Dai and co-workers^[15] claimed that graphitic N was responsible for the ORR activity of N-doped graphene nanoribbon networks.

In addition to the uncertainty about the identification of the ORR active sites of N-doped carbons, controllable synthesis of active nitrogen dopants via direct pyrolysis of N-containing carbonaceous precur-

sors is another challenge^[16]. For maximal surface accessibility, a high specific surface area of the carbon catalysts is generally desired and produced by implanting abundant hierarchical porous textures into the carbon matrix that serve as mass transport channels for ORR-relevant species^[10, 17]. In the large number of literature studies, N-doped porous carbons are typically synthesized by the following methods: (i) chemical activation, physical activation, or a combination of both; (ii) template-assisted synthesis; and (iii) direct carbonization of intrinsic porous precursors such as metal organic frameworks (MOFs) or covalent organic frameworks (COFs)^[10, 13, 18]. Among these, template-assisted synthesis is a robust and versatile method which has been extensively used in the preparation of porous carbon catalysts for ORR with controllable pore structures^[19-22].

Therefore, in the present review, we will summarize recent progress in the template-assisted preparation of N-doped porous carbons for ORR, with a focus on methods based on conventional rigid/soft templates and novel thermally removable templates. Comparisons among these template-assisted methods are also included.

1 Template-Assisted Synthesis of N-doped Porous Carbons

1.1 Conventional Rigid-Template Method

In a typical rigid-template method, carbonaceous precursors are injected into preformed nanostructured templates, and then subjected to high-temperature carbonization. The rigid templates prevent the collapse of the carbon matrix during pyrolysis. After pyrolysis, the rigid templates are removed by, for instance, chemical etching, leading to the formation of a porous structure^[23-27]. For example, Silva et al.^[23] utilized mesoporous silica SBA-15 as rigid templates to prepare N- and O-doped mesoporous carbons (Figure 1). The synthetic process is illustrated in Figure 1, where aniline was anchored and *in situ* polymerized within the channels of mesoporous silica that had been pre-functionalized with diaminosilane, the resulting polyaniline (PANI)/SBA-15 hybrids were then subjected to thermal

treatment under an inert atmosphere, and removal of the silica frameworks by chemical etching led to the formation of a porous carbon matrix.

In another study, Liu and co-workers^[5] used ordered mesoporous silica SBA-15 as rigid templates which were filled with a N-containing aromatic dyestuff, N,N'-bis(2,6-diisopropylphenyl)-3,4,9,10-perylenetetra-carboxylic diimide, and then underwent high-temperature pyrolysis. Subsequent removal of the SBA-15 templates by HF etching led to the production of N-doped ordered mesoporous graphitic arrays, which showed a high surface area of $510 \text{ m}^2 \cdot \text{g}^{-1}$ with a very narrow pore-size distribution centered at about 3.8 nm, a graphitized framework with a moderate nitrogen content, and a high ORR electrocatalytic activity in an alkaline electrolyte, along with an excellent long-term stability, and a strong resistance to fuel crossover.

More recently, Feng and coworkers^[28] also used the rigid-template method to synthesize metal-free, highly active N-doped, hierarchical porous carbon electrocatalysts for ORR. As depicted in Figure 2,

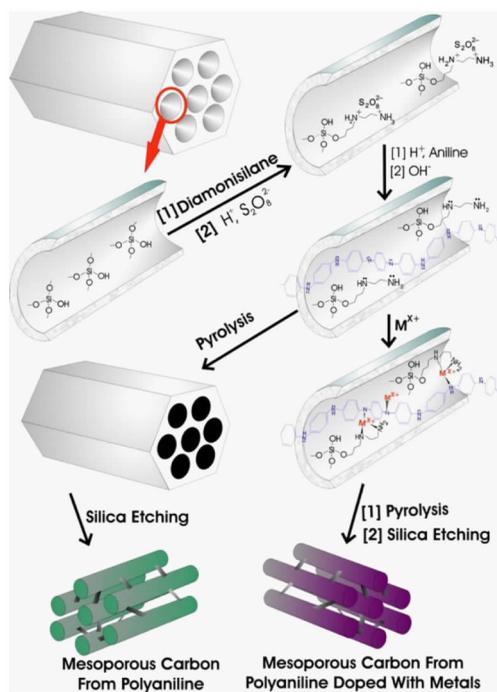


Fig. 1 Schematic illustration of the syntheses of N- and O-doped mesoporous carbons with or without metal dopants. Reprinted with permission from Ref.^[23].

they firstly polymerized *o*-phenylenediamine (oPD) on the surface of colloidal silica in the presence of ammonium peroxydisulphate (APS). The resultant PoPD/SiO₂ nanocomposite was then pyrolyzed in a nitrogen atmosphere, and the SiO₂ template was removed by NaOH etching to yield mesoporous N-doped carbons (meso-PoPD), which might be further activated by NH₃ treatment forming meso/micro-PoPD catalysts. This protocol allows for the simultaneous optimization of both porous textures and functionalization of the N-doped carbons.

Wei et al.^[20] synthesized N-doped carbon nanosheets by using a different rigid template, where colloidal silica nanoparticles were homogeneously grown on the surface of graphene oxide by hydrolysis of tetraethylorthosilicate, and then coated with polydopamine via *in situ* polymerization of dopamine and subsequently pyrolyzed at the controlled temperatures. Removal of the silica nanoparticles by HF etching yielded the mesoporous N-doped carbon nanosheets with abundant pores of 22 nm, which exhibited a more positive ORR half-wave potential than that of commercial Pt/C catalyst with a diffusion-limited current comparable to that of Pt/C in alkaline media.

In a separate study, Hu and co-workers^[29] prepared cubic-like N-doped carbon nanocages (NCNCs), where by N-containing carbonaceous precursors such as pyridine were directly polymerized and pyrolyzed on the surface of MgO nanocrystals derived *in situ* from basic magnesium carbonate (4MgCO₃·Mg(OH)₂·5H₂O) at high temperatures. The resulting NCNCs

showed a large specific surface area of *ca.* 900 m²·g⁻¹ and a high nitrogen content, leading to an excellent ORR catalytic activity in an alkaline solution that was comparable to that of commercial Pt/C catalyst. Interestingly, the thus-synthesized carbon nanocages could also be used as templates to prepare Fe- and N-codoped nanocages for further enhancement of the ORR activity^[30].

1.2 Conventional Soft-Template Method

Porous carbons may also be prepared by using soft templates based on organic polymers. For instance, Sun et al.^[31] reported a simple soft template method for the fabrication of graphene sheets sandwiched by nanoporous N-doped carbon layers. Experimentally, a triblock copolymer, Pluronic F127, was used as the template to guide the growth of a nanoporous phenol-melamine-formaldehyde (PMF) prepolymer on the graphene sheets. After carbonization at 700 °C, a sandwich structure (G-PMFs) was obtained (Figure 3), which exhibited a large specific surface area, an excellent electrocatalytic activity, a good electrochemical stability and a high selectivity for ORR in an alkaline electrolyte. In some other studies, mesoporous N-doped carbons with pore sizes larger than 10 nm were successfully prepared by using various high-molecular-weight block polymers as soft templates, such as polystyrene-block-poly(ethylene oxide) (PS-*b*-PEO), polyisobutylene-block-PEO (PIB-*b*-PEO), PS-block-poly(4-vinylpyridine) (PS-*b*-P4VP), and PEO-block-poly(methyl methacrylate) (PEO-*b*-PMMA)^[32-34]. In another study^[35], using the micelles of a high-molecular-weight block polymer PS-*b*-PEO as soft templates, Tang and co-workers developed a facile route to prepare the N-doped mesoporous carbon spheres with small particle size of *ca.* 200 nm and large pore size of *ca.* 16 nm. The resultant mesoporous N-doped carbon nanospheres showed an excellent electrocatalytic activity toward ORR in an alkaline electrolyte. It is worthy to note that in the preparation process, they used the PDA/PS-*b*-PEO composite spheres (where PDA denotes polymerized dopamine) as the precursor. The stable pre-formed PS-*b*-PEO micelles served as a sacrificial pore-form

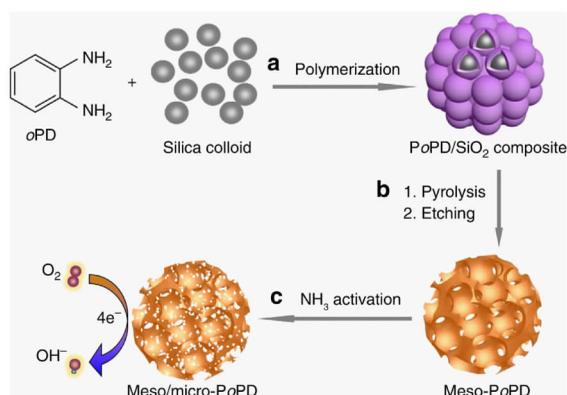


Fig. 2 Scheme for the preparation of meso/micro-PoPD electrocatalyst. Reprinted with permission from Ref.^[28].

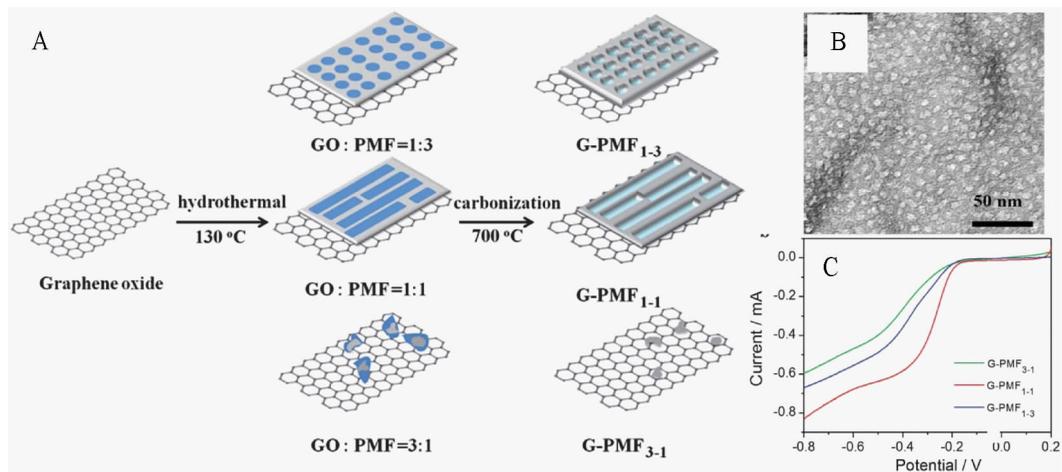


Fig. 3 A. Schematic illustration for the synthesis of nanoporous N-doped carbon modified graphene sheets (G-PMFs); B. A typical TEM image of G-PMFs; C. RDE voltammograms of G-PMF electrodes at a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$ and a rotation rate of $1600 \text{ r} \cdot \text{min}^{-1}$ in an O_2 -saturated $0.1 \text{ mol} \cdot \text{L}^{-1}$ KOH solution. Adapted with permission from Ref.^[31].

ing agent which were thermally removed during the carbonization process, leaving abundant mesopores in the final carbon nanospheres.

Separately, Wei et al.^[36] developed a simple organic-phase acid-assisted self-assembly route to synthesize nearly uniform mesoporous carbon nanospheres (MCNs) by direct hydrothermal treatment of triblock copolymers Pluronic F127 and phenol-formaldehyde-resol in a $2 \text{ mol} \cdot \text{L}^{-1}$ HCl aqueous solution, followed by high-temperature carbonization. Because both

F127 and resol were partly protonated in HCl, the hydrogen-bonding interaction between resol and F127 was enhanced by Coulombic interactions with Cl^- as a mediator, which impeded the crosslinking rate of resol molecules trapped in the triblock copolymer micelles, and thus, the macroscopic phase separation during the hydrothermal process (Figure 4). The resultant MCNs displayed a high surface area of $596 \text{ m}^2 \cdot \text{g}^{-1}$, a large pore volume of $0.77 \text{ cm}^3 \cdot \text{g}^{-1}$, along with a highly controllable diameter by changing the

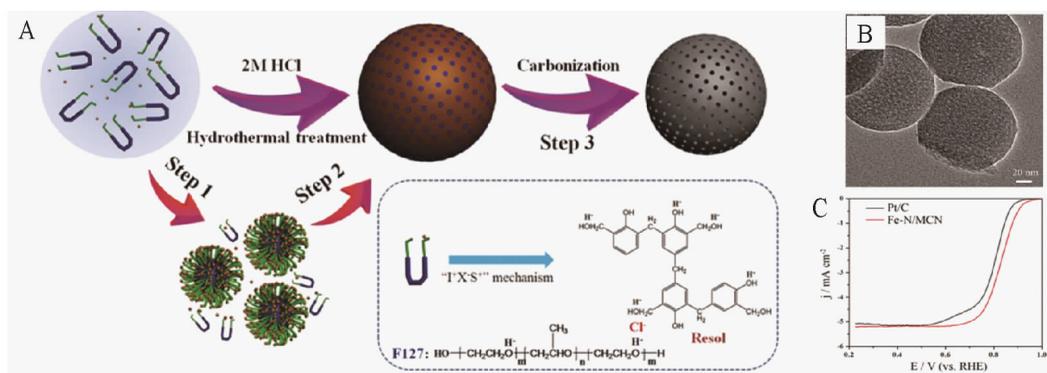


Fig. 4 A. Schematic illustration for the preparation of uniform mesoporous carbon nanospheres (MCNs): Step 1) the polymerization of resol induces the phase separation of F127 to form spherical micelles with a PPO core and PEO shell, where the resol is located in the PEO shell due to the strong Coulombic interactions between the protonated resol and PEO via the $\text{I}^+\text{X}^-\text{S}^+$ mechanism; Step 2) the further polymerization of resol induces the aggregation of composited spherical micelles to polymer nanospheres; and Step 3) carbonization under an inert atmosphere to selectively remove F127 and form a carbon framework; B. A typical TEM image of MCNs; C. The ORR activity of commercial Pt/C and Fe-N/MCNs at $1600 \text{ r} \cdot \text{min}^{-1}$ in O_2 -saturated $0.1 \text{ mol} \cdot \text{L}^{-1}$ KOH solution. Adapted with permission from Ref.^[36].

mass ratio of the template to resol. With their various unique structural characteristics, such as uniform spherical morphology, small diameter, high surface area and mesoporous structure, MCNs were further modified with Fe and N species to produce non-precious Fe-N/MCN catalysts, which exhibited a high catalytic activity, enhanced stability and excellent methanol tolerance, as compared to commercial Pt/C catalyst under alkaline conditions.

Alternatively, sheet-like polymers with aromatic backbones, such as polypyrrole and polyaniline, have also been used as structural templates for the preparation of carbon nanosheets^[17]. For instance, very recently, Xu et al. developed a novel approach to the fabrication of 3D carbon superstructures by thermal pyrolysis of flower-like microstructures derived from hierarchical assembly of fine-tunable polyimide nanosheets. These flower-like microstructures were employed as soft templates and their morphology was dependent on the concentration of the intermediate product of polyamic acid. Thanks to the high specific surface area as well as hierarchical porous structure, the thus-synthesized flower-like N-doped 3D carbon superstructures exhibited outstanding catalytic activity toward ORR in an alkaline electrolyte and an excellent capacitive and charge-discharge cycling performance as supercapacitor electrode materials^[37].

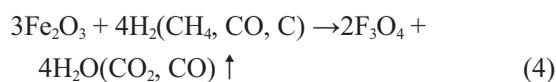
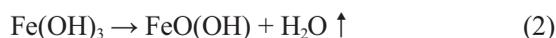
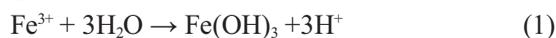
One may note that the aforementioned conventional template-assisted methods generally entail multiple time- and energy-consuming procedures, such as the preparation of nanostructured templates, homogeneous dispersion/impregnation of preformed templates, tedious wet-chemical etching, sample separation and purification, which complicate the synthesis process and make it difficult for efficient mass production^[38-40]. Furthermore, the post-synthesis removal of sacrificial templates by harsh acid/base etching may compromise ORR activity because part of the active components is inevitably removed.

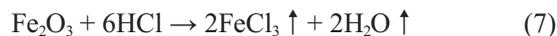
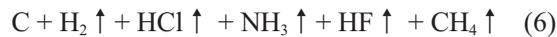
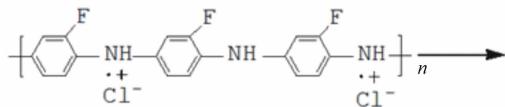
Furthermore, despite great effort in the development of N-doped porous carbon catalysts by using conventional template methods, most of these catalysts still exhibit ORR activity inferior to that of com-

mercial Pt/C catalysts in both alkaline and acidic electrolytes^[3]. This suggests that there is room for further improvement in the ORR activity of N-doped carbons. As mentioned above, it is of paramount significance to maximize the electrochemical surface area, especially the contribution from mesopores, so that the transport of ORR-relevant species may be facilitated and the ORR catalytic activity can be enhanced and even optimized^[10,41-42]. Considering the drawbacks of conventional “rigid template” and “soft template” methods, it is highly desired to develop novel template-assisted routes in the preparation of mesoporous N-doped carbons with a high surface area, where a large number of homogeneously distributed nanoscale templates can be formed *in situ* in the synthesis of carbonaceous precursors and subsequently removed during the thermal carbonization of precursors at high temperatures, as detailed below.

1.3 Thermally Removable Template Method

We have recently developed a novel template method for the preparation of N-doped porous carbons with thermally removable nanoparticles. As shown in Figure 5, 2-fluoroaniline was firstly polymerized in the presence of FeCl₃ by a hydrothermal method to form a poly(2-fluoroaniline) matrix embedded with a large number of homogeneously distributed FeO(OH) nanorods. Pyrolysis of the thus-prepared poly(2-fluoroaniline) yielded mesoporous N-doped carbon catalysts without post-synthesis removal of the templates. The FeO(OH) nanocrystals not only acted as rigid templates to prevent the collapse of poly(2-fluoroaniline) during carbonization, but also facilitated the formation of mesopores in the carbonized skeletons by thermal decomposition and evaporation at high temperatures. The reactions involved in the thermally removable template method were proposed as follows^[9,43],





In the aqueous solution of FeCl_3 and 2-fluoroaniline, FeCl_3 was hydrolyzed to form an amorphous $\text{Fe}(\text{OH})_3$ sol in the presence of alkaline 2-fluoroaniline (Eq. 1), and concurrently 2-fluoroaniline was protonated by hydrochloric acid that resulted from FeCl_3 hydrolysis. The protonated 2-fluoroaniline was hydrothermally polymerized into poly(2-fluoroaniline) sheets doped with HCl, where the amorphous $\text{Fe}(\text{OH})_3$ sol was also converted into homogeneously distributed $\text{FeO}(\text{OH})$ nanocrystals (Eq.2) in the polymer matrix. During the pyrolysis process, the $\text{FeO}(\text{OH})$ nanocrystals were converted to Fe_2O_3 (Eq. 3), and polymers of low molecular weights were partially degraded. At higher temperatures ($> 700\text{ }^\circ\text{C}$), most polymers were degraded to form graphitic carbons with the release of a series of volatile species, such as HCl, HF, NH_3 , H_2 , and CH_4 (Eqs. 4-6). HCl reacted with Fe_2O_3 to generate volatile FeCl_3 (Eq 7), hence, leading to the formation of abundant holes/cavities in the carbonized matrix.

The resulting mesoporous N-doped carbon catalysts with a trace amount of iron(Fe-N/C-800) exhib-

ited a specific surface area up to $934.8\text{ m}^2 \cdot \text{g}^{-1}$. In addition, electrochemical measurements showed a higher ORR activity and durability for the mesoporous Fe-N/C catalyst than that of commercial Pt/C catalyst in alkaline media (Figure 6). These results highlight the unique potential of using thermally sacrificial templates in the synthesis of highly porous carbons and their applications in ORR electrocatalysis.

In a later study, Wang and co-workers^[44] used ZnO nanocrystals as alternative thermally sacrificial templates, instead of $\text{FeO}(\text{OH})$ compounds used above, to prepare hierarchically porous N-doped carbon nanofibers (HP-NCNFs). The ZnO nano-templates were *in situ* generated and homogeneously embedded in the precursor fibers by electro-spinning. When the N-containing precursor with a number of ZnO nanocrystals was thermally treated at high temperatures, ZnO nano-templates acted as a thermally removable template because they were decomposed into ZnCl_2 and readily evaporated, hence, minimizing negative effects of residual metals on the active sites. The eventual HP-NCNFs showed a high specific surface area of $829.5\text{ m}^2 \cdot \text{g}^{-1}$ with a 3D hierarchically porous structure. Moreover, the HP-NCNFs showed better stability and stronger resistance against methanol crossover than commercial Pt/C catalyst in an alkaline electrolyte.

Whereas excellent ORR performance of N-doped

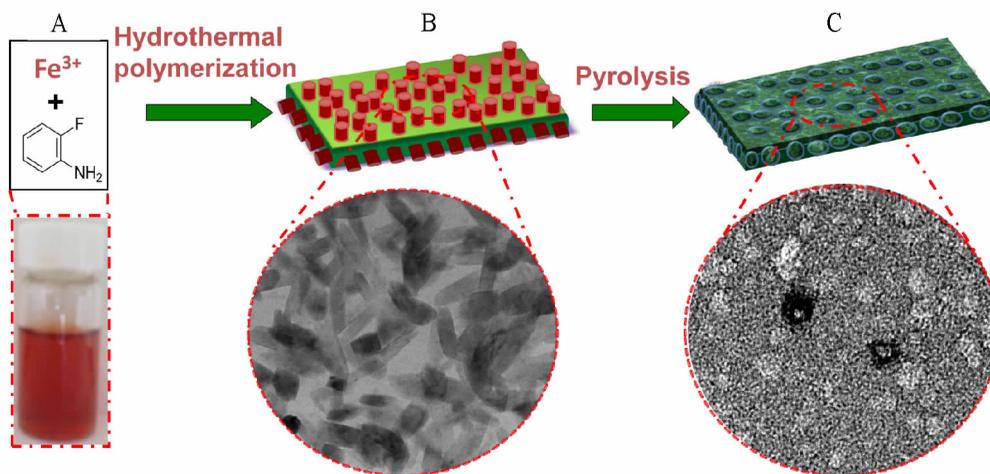


Fig. 5 Preparation of N-doped mesoporous carbon catalyst (Fe-N/C) with thermally removable nanoparticles. Reprinted with permission from Ref.^[9].

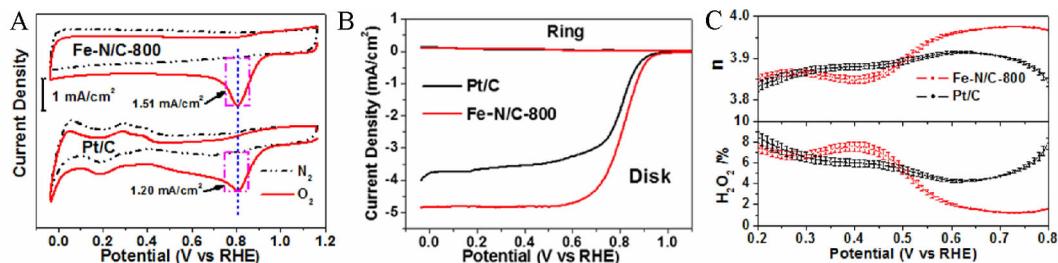


Fig. 6 A-B. Cyclic and RRDE voltammograms; C. Plots of H_2O_2 yield and number of electron transfer of a glassy carbon electrode modified with Fe-N/C-800 and Pt/C catalysts at the rotation speed of $1600\text{ r}\cdot\text{min}^{-1}$. Reprinted with permission from Ref.^[9].

porous carbon catalysts can be obtained through the thermally removable template method, the catalysts generally lack long-term durability under practical working conditions due to low graphitization of the carbon materials^[14,46-47]. Therefore, in the preparation of carbon-based ORR catalysts, maximizing the degree of graphitization is highly desired. This may be achieved by incorporating reduced graphene oxide as a conductive substrate to improve the electrocatalytic activity and durability of porous carbon catalysts^[8]. Note that reduced graphene oxides are easily restacked/aggregated after reduction by strong reducing agents such as hydrazine and $NaBH_4$, or high-temperature thermal treatment because of the strong π - π interactions between the graphene sheets. This may compromise the electrochemical surface area that is of importance in catalysis^[11,45,48-50]. To mitigate restacking of graphene sheets, several methods have been proposed in the literature. For example, deposition of porous carbon derived from polymers onto the surface of graphene represents an effective route. Unfortunately, this method usually involves multiple organic synthesis/polymerization processes. In addition, direct carbonization of the polymer/graphene precursors generally leads to severe diminishment of the

surface area due to collapse of pores at high temperatures.

Within this context, in a recent study we showed that a sandwich-like polymer/graphene oxide/polymer structure might be produced by hydrothermal polymerization of 2-fluoroaniline on the surface of graphene oxide sheets, with a large number of amorphous Fe-containing species embedded in the resulting poly(2-fluoroaniline), as depicted in Figure 7^[45]. These amorphous Fe-containing species were converted into nanoparticles during the pyrolysis process, and finally removed through the generation of volatile $FeCl_3$, $FeCl_2$ and other gaseous compounds, leading to the formation of a sandwich-like N-MC/rGO composite with rich nitrogen self-doped active sites and large specific surface areas. The preparation process is simple, based on direct carbonization of polymer/graphene oxide hybrid precursors without any additional foreign template and post-synthesis treatments. The resultant N-MC/rGO catalyst not only exhibited a high specific surface area, but also apparent ORR activity and substantially higher stability in alkaline electrolytes, as compared to that without the addition of reduced graphene oxides (Figure 8)^[45]. The excellent ORR performance of N-MC/rGO was

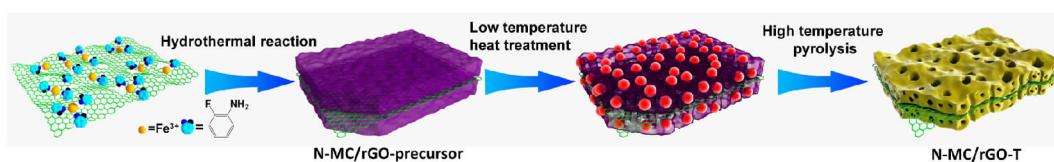


Fig. 7 Schematic illustration for the preparation process of N-MC/rGO-T catalysts by the thermally removable template method. Reprinted with permission from Ref.^[45].

attributed to the synergistic effect between the graphene and nitrogen doped porous carbon layer: the *in situ* formation of a sandwich-like structure effectively prevented the restacking of graphene sheets, and hence, exposed active sites to ORR relevant

species; in addition, the highly crystalline, conductive graphene sheets served as efficient 2D conductors for electrons, as well as an anti-corrosion coating layer for porous carbons.

The key point in the above thermally removable

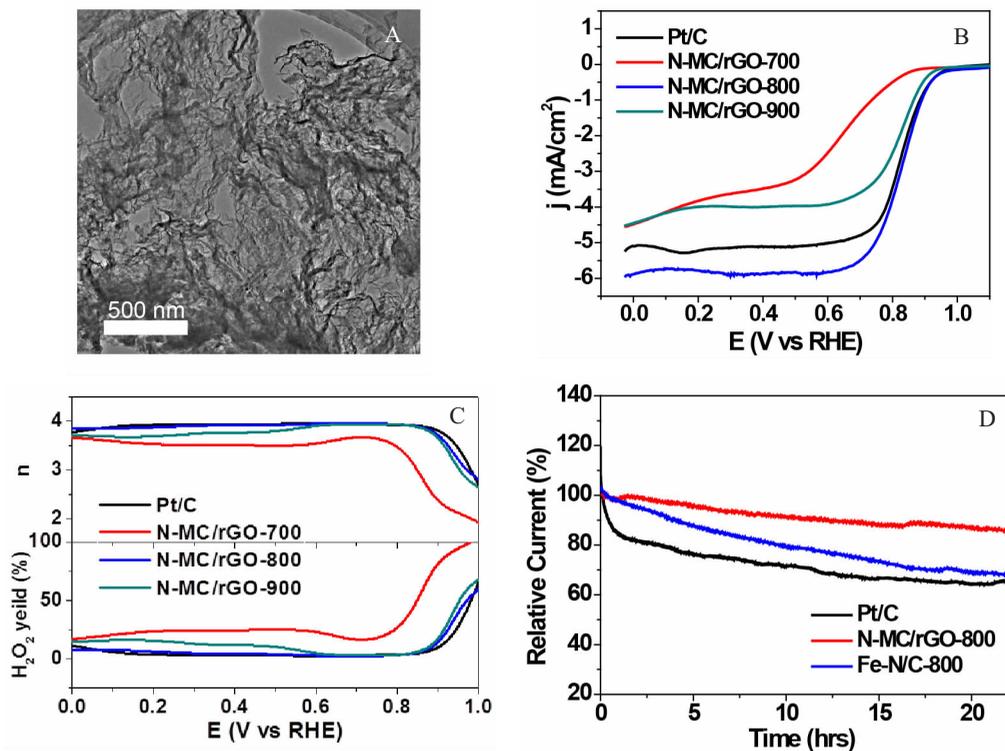


Fig. 8 A. TEM image of N-MC/rGO-800; B. Rotating disk electrode voltammograms; C. Plots of hydrogen peroxide yield and electron transfer number of Pt/C, N-MC/rGO-T (T=700, 800 and 900); D. Chronoamperometric curves of Pt/C, Fe-NC-800 and N-MC/rGO at 0.70 V versus RHE. Reprinted with permission from Ref.^[45].

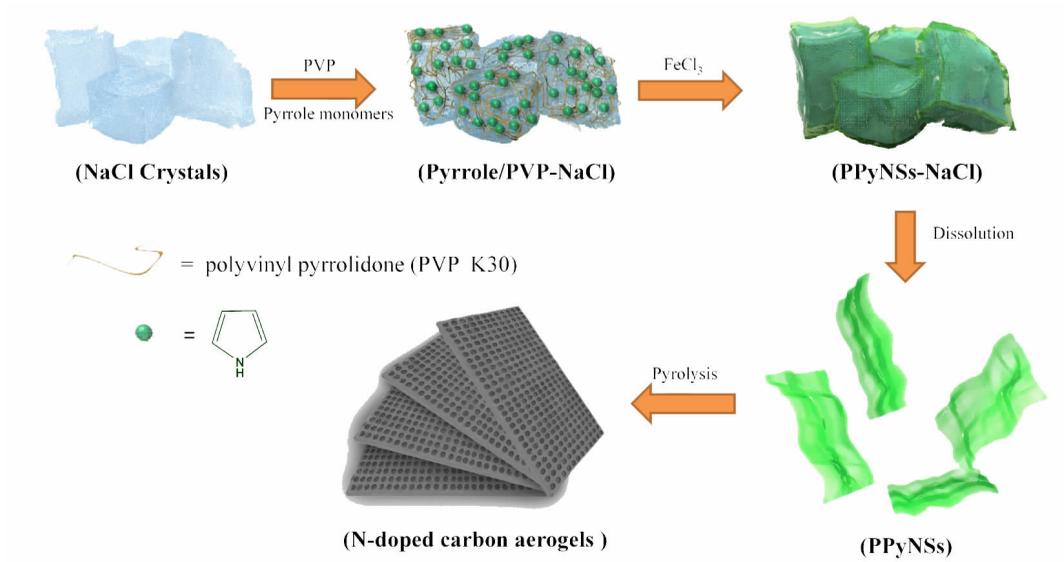


Fig. 9 Schematic illustration for the preparation of nitrogen-doped honeycomb-like porous carbons. Reproduced with permission from Ref.^[51].

template method is to form nanosheet precursors embedded with a high concentration of volatile nanotemplates. This is non-trivial, as typically the loading of nanoscale templates in polymer nanofibers and nanoparticles is rather limited. Furthermore, hydrothermal polymerization is generally needed to prepare N-containing polymer nanosheets, in which reaction vessels that can withstand high temperatures and high pressures are required, and hence, the process is difficult to be scaled up. Therefore, it remains desired to develop facile methods for the preparation of

high-performance porous carbon-based ORR catalysts that do not entail a solvo- or hydrothermal process and are viable for mass production^[51].

Very recently, we have developed a novel route for the rational design and readily scalable fabrication of N-doped honeycomb-like porous carbons (HPCs) with abundant hierarchical macro- and meso-pores by direct pyrolysis of polypyrrole nanosheets doped with FeCl₃ that were prepared by interfacially confined polymerization of pyrrole on the surface of NaCl crystals (Figure 9)^[51]. The homogeneously distributed

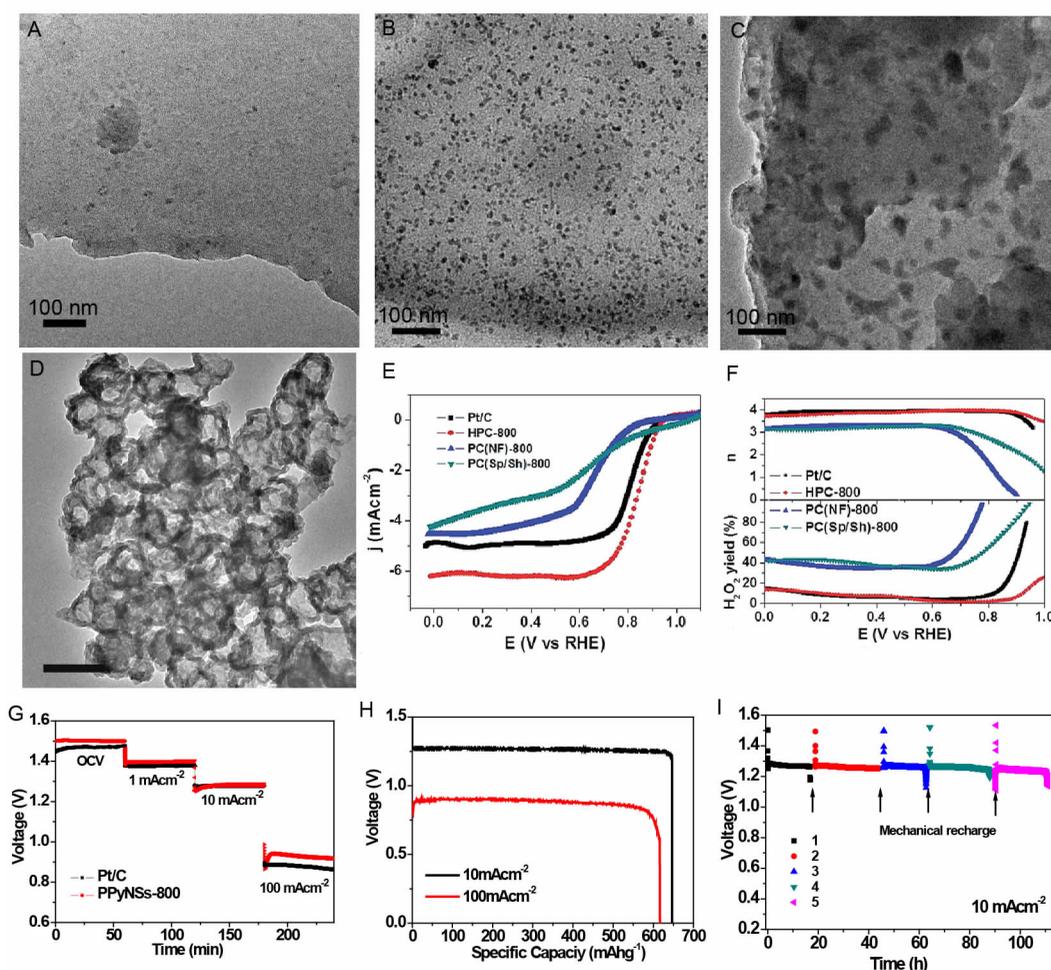


Fig. 10 TEM images showing the evolution of Fe-containing species in polypyrrole nanosheets prepared at room temperature (A), 300 °C(B), 500°C(C); TEM image of HPC-800 (D); RDE voltammograms (E) and plots of H₂O₂ yield (F) and number of electrons transferred (*n*) of HPC-800, PC(NF)-800, PC(Sp/Sh)-800 and 0.2 mg · cm⁻² of Pt/C in O₂-saturated 0.1 mol · L⁻¹ KOH solution at a rotation speed of 1600 r · min⁻¹. The potential sweep rate was 10 mV · s⁻¹; G. Typical galvanostatic discharge curves of a Zn-air battery with HPC-800 and Pt/C as air-diffusion cathode at various current densities (1, 10, and 100 mA · cm⁻²); H. Long-time galvanostatic discharge curves of a Zn-air battery using HPC-800 as the air-diffusion cathode; I. ‘Recharging’ the Zn-air battery using HPC-800 as the cathode catalyst by refilling the Zn anode and electrolyte. The catalyst loading in air cathode was 2.0 mg · cm⁻² for HPC-800 and 1.0 mg · cm⁻² for Pt/C, and the electrolyte for Zn-air cell measurements was 6.0 mol · L⁻¹ KOH. Reproduced with permission from Ref.^[51].

FeCl₃ and its derivatives were converted into thermally removable nanocrystals which not only helped to generate multi-hierarchical pores in the carbonized matrix during pyrolysis, but also promoted the formation of active sites such as pyridinic nitrogens and FeN_x/C moieties in the carbon skeletons. The resulting honeycomb-like porous carbons exhibited a high specific surface area of 796.8 m²·g⁻¹, along with a significant content of nitrogen dopants ranging from 7 to 18 at.%, leading to a remarkable ORR activity in alkaline electrolytes. Electrochemical measurements revealed that the honeycomb-like ORR carbon catalyst prepared at 800 °C stood out as the best one among the series, which featured a half-wave potential 40 mV more positive than that of commercial Pt/C catalysts, along with a higher diffusion-limited current, an electron-transfer number over 3.95 even at low overpotentials, much longer durability and stronger resistance against methanol crossover and CO poisoning. Moreover, by using thus-synthesized honeycomb-like porous carbons as the air-diffusion cathode, a Zn-air battery was assembled with a performance surpassing that based on Pt/C (Figure 10)^[51].

The results described above unambiguously highlight the significance of volatile templates in the preparation and engineering of N-doped porous carbons as a viable alternative to Pt-based noble metal nanocatalysts in important electrochemical devices, such as metal-air batteries, alkaline fuel cells and chlor-alkali electrolyzers.

2 Conclusions and Outlook

Remarkable progress has been made in the development of N-doped porous carbon catalysts for ORR based on rigid- and soft-template methods. The thermally removable template method represents a more facile and efficient route in the preparation of N-doped carbons with a large surface area and predominant mesopores for the enhanced ORR electrocatalysis. This method may be further extended to volatile organic materials, such as C₃N₄, and used as a general strategy in the preparation and engineering of highly porous carbons^[6, 12, 52]. Yet it remains challenging to prepare N-doped porous carbon catalysts with

controllable pores and preferred dopant configurations. Further research is desired towards this end. Meanwhile, multiple heteroatoms, including both metal and nonmetal elements (such as B, P, S, Fe, and Co), may be integrated into the carbon skeletons as codopants to further improve the ORR activity for practical applications.

Acknowledgments

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References:

- [1] Lin L, Zhu Q, Xu A W. Noble-metal-free Fe-N/C catalyst for highly efficient oxygen reduction reaction under both alkaline and acidic conditions[J]. *Journal of the American Chemical Society*, 2014, 136(31): 11027-11033.
- [2] Yin H, Zhang C Z, Liu F, et al. Hybrid of iron nitride and nitrogen-doped graphene aerogel as synergistic catalyst for oxygen reduction reaction[J]. *Advanced Functional Materials*, 2014, 24(20): 2930-2937.
- [3] Wang H B, Maiyalagan T, Wang X. Review on recent progress in nitrogen-doped graphene: Synthesis, characterization, and its potential applications[J]. *ACS Catalysis*, 2012, 2(5): 781-794.
- [4] Santoro C, Serov A, Villarrubia C W N, et al. Double-chamber microbial fuel cell with a non-platinum-group metal Fe-N-C cathode catalyst[J]. *ChemSusChem*, 2015, 8(5): 828-834.
- [5] Liu R, Wu D, Feng X L, et al. Nitrogen-doped ordered mesoporous graphitic arrays with high electrocatalytic activity for oxygen reduction[J]. *Angewandte Chemie-International Edition*, 2010, 49(14): 2565-2569.
- [6] Yu H, Shang L, Bian T, et al. Nitrogen-doped porous carbon nanosheets templated from g-C₃N₄ as metal-free electrocatalysts for efficient oxygen reduction reaction[J]. *Advanced Materials*, 2016, 28(25): 5080-5086.
- [7] Liu M, Zhang R, Chen W. Graphene-supported nanoelectrocatalysts for fuel cells: Synthesis, properties, and applications[J]. *Chemical Reviews*, 2014, 114(10): 5117-5160.
- [8] Higgins D, Zamani P, Yu A P, et al. The application of graphene and its composites in oxygen reduction electro-

- catalysis: A perspective and review of recent progress[J]. *Energy & Environmental Science*, 2016, 9(2): 357-390.
- [9] Niu W H, Li L G, Liu X J, et al. Mesoporous N-doped carbons prepared with thermally removable nanoparticle templates: An efficient electrocatalyst for oxygen reduction reaction[J]. *Journal of the American Chemical Society*, 2015, 137(16): 5555-5562.
- [10] Zhu Q L, Xia W, Akita T, et al. Metal-organic framework-derived honeycomb-like open porous nanostructures as precious-metal-free catalysts for highly efficient oxygen electroreduction[J]. *Advanced Materials*, 2016, 28(30): 6391-6398.
- [11] Zhong H X, Wang J, Zhang Y W, et al. ZIF-8 derived graphene-based nitrogen-doped porous carbon sheets as highly efficient and durable oxygen reduction electrocatalysts[J]. *Angewandte Chemie-International Edition*, 2014, 53(51): 14235-14239.
- [12] Zhang L J, Wang X Y, Wang R H, et al. Structural evolution from metal-organic framework to hybrids of nitrogen-doped porous carbon and carbon nanotubes for enhanced oxygen reduction activity[J]. *Chemistry of Materials*, 2015, 27(22): 7610-7618.
- [13] Ding S Y, Wang W. Covalent organic frameworks (COFs): From design to applications[J]. *Chemical Society Reviews*, 2013, 42(2): 548-568.
- [14] Zhou M, Wang H L, Guo S. Towards high-efficiency nanoelectrocatalysts for oxygen reduction through engineering advanced carbon nanomaterials[J]. *Chemical Society Reviews*, 2016, 45(5): 1273-1307.
- [15] Yang H B, Miao J W, Hung S F, et al. Identification of catalytic sites for oxygen reduction and oxygen evolution in N-doped graphene materials: Development of highly efficient metal-free bifunctional electrocatalyst[J]. *Science Advances*, 2016, 2: e1501122.
- [16] Wood K N, Ryan O H, Pylypenko S. Recent progress on nitrogen carbon structures designed for use in energy and sustainability applications[J]. *Energy & Environmental Science*, 2014, 7(4): 1212-1249.
- [17] Xu Z X, Zhuang X D, Yang C Q, et al. Nitrogen-doped porous carbon superstructures derived from hierarchical assembly of polyimide nanosheets[J]. *Advanced Materials*, 2016, 28(10): 1981-1987.
- [18] Li Z H, Shao M F, Zhou L, et al. Directed growth of metal-organic frameworks and their derived carbon-based network for efficient electrocatalytic oxygen reduction[J]. *Advanced Materials*, 2016, 28(12): 2337-2344.
- [19] Mane G P, Talapaneni S N, Anand C, et al. Preparation of highly ordered nitrogen-containing mesoporous carbon from a gelatin biomolecule and its excellent sensing of acetic acid[J]. *Advanced Functional Materials*, 2012, 22(17): 3596-3604.
- [20] Wei W, Liang H W, Parvez K, et al. Nitrogen-doped carbon nanosheets with size-defined mesopores as highly efficient metal-free catalyst for the oxygen reduction reaction[J]. *Angewandte Chemie-International Edition*, 2014, 53(6): 1570-1574.
- [21] Lee J, Kim J, Hyeon T. Recent progress in the synthesis of porous carbon materials[J]. *Advanced Materials*, 2006, 18(16): 2073-2094.
- [22] Liang H W, Wei W, Wu Z S, et al. Mesoporous metal-nitrogen-doped carbon electrocatalysts for highly efficient oxygen reduction reaction[J]. *Journal of the American Chemical Society*, 2013, 135(43): 16002-16005.
- [23] Silva R, Voiry D, Chhowalla M, et al. Efficient metal-free electrocatalysts for oxygen reduction: polyaniline-derived N- and O-doped mesoporous carbons[J]. *Journal of the American Chemical Society*, 2013, 135(21): 7823-7826.
- [24] Liang C, Li Z, Dai S. Mesoporous carbon materials: Synthesis and modification[J]. *Angewandte Chemie International Edition*, 2008, 47(20): 3696-3717.
- [25] Stein A, Wang Z Y, Fierke M A. Functionalization of porous carbon materials with designed pore architecture [J]. *Advanced Materials*, 2009, 21(3): 265-293.
- [26] Han J P, Xu G Y, Ding B, et al. Porous nitrogen-doped hollow carbon spheres derived from polyaniline for high performance supercapacitors[J]. *Journal of Materials Chemistry A*, 2014, 2(15): 5352-5357.
- [27] Liu X J, Zou S Z, Chen S W. Ordered mesoporous carbons codoped with nitrogen and iron as effective catalysts for oxygen reduction reaction[J]. *Nanoscale*, 2016, 8(46): 19249-19255.
- [28] Liang H W, X D Zhuang, Bruller S, et al. Hierarchically porous carbons with optimized nitrogen doping as highly active electrocatalysts for oxygen reduction[J]. *Nature Communications*, 2014, 5: 4973.
- [29] Chen S, Bi J, Zhao Y, et al. Nitrogen-doped carbon nanocages as efficient metal-free electrocatalysts for oxygen reduction reaction[J]. *Advanced Materials*, 2012, 24(41): 5593-5597.
- [30] Sun T, Wu Q, Zhuo O, et al. Manganese oxide-induced strategy to high-performance iron/nitrogen/carbon electrocatalysts with highly exposed active sites[J]. *Nanoscale*, 2016, 8(16): 8480-8485.
- [31] Sun Y Q, Sun C, Shi G Q. Nanoporous nitrogen doped carbon modified graphene as electrocatalyst for oxygen reduction reaction[J]. *Journal of Materials Chemistry*, 2012,

- 22(25): 12810-12816.
- [32] Deng Y H, Wei J, Sun Z K, et al. Large-pore ordered mesoporous materials templated from non-Pluronic amphiphilic block copolymers[J]. *Chemical Society Reviews*, 2013, 42(9): 4054-4070.
- [33] Liang C, Hong K, Guiochon G A, et al. Synthesis of a large-scale highly ordered porous carbon film by self-assembly of block copolymers[J]. *Angewandte Chemie-International Edition*, 2004, 43(43): 5785-5789.
- [34] Lee H I, Kim J H, You D J, et al. Rational synthesis pathway for ordered mesoporous carbon with controllable 30- to 100-angstrom pores[J]. *Advanced Materials*, 2008, 20(4): 757-762.
- [35] Tang J, Liu J, Li C, et al. Synthesis of nitrogen-doped mesoporous carbon spheres with extra-large pores through assembly of diblock copolymer micelles[J]. *Angewandte Chemie-International Edition*, 2015, 54(2): 588-593.
- [36] Wei J, Liang Y, Zhang X, et al. Controllable synthesis of mesoporous carbon nanospheres and Fe-N/carbon nanospheres as efficient oxygen reduction electrocatalysts[J]. *Nanoscale*, 2015, 7(14): 6247-6254.
- [37] Xu Z, Zhuang X, Yang C, et al. Nitrogen-doped porous carbon superstructures derived from hierarchical assembly of polyimide nanosheets[J]. *Advanced Materials*, 2016, 28(10): 1981-1987.
- [38] Liang J, Du X, Gibson C, et al. N-doped graphene natively grown on hierarchical ordered porous carbon for enhanced oxygen reduction[J]. *Advanced Materials*, 2013, 25(43): 6226-6231.
- [39] Dutta S, Bhaumik A, Wu K C W. Hierarchically porous carbon derived from polymers and biomass: effect of interconnected pores on energy applications[J]. *Energy & Environmental Science*, 2014, 7(11): 3574-3592.
- [40] Roberts A D, Li X, Zhang H. Porous carbon spheres and monoliths: Morphology control, pore size tuning and their applications as Li-ion battery anode materials [J]. *Chemical Society Reviews*, 2014, 43(13): 4341-4356.
- [41] Xiao M, Zhu J, Feng L, et al. 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[J]. *Advanced Materials*, 2015, 27(15): 2521-2527.
- [42] Liu Y L, Shi C X, Xu X Y, et al. Nitrogen-doped hierarchically porous carbon spheres as efficient metal-free electrocatalysts for an oxygen reduction reaction[J]. *Journal of Power Sources*, 2015, 283: 389-396.
- [43] Liu W J, Tian K, He Y R, et al. High-yield harvest of nanofibers/mesoporous carbon composite by pyrolysis of waste biomass and its application for high durability electrochemical energy storage[J]. *Environmental Science & Technology*, 2014, 48(23): 13951-13959.
- [44] Wang S G, Cui Z T, Qin J W, et al. Thermally removable *in-situ* formed ZnO template for synthesis of hierarchically porous N-doped carbon nanofibers for enhanced electrocatalysis[J]. *Nano Research*, 2016, 9(8): 2270-2283.
- [45] Niu W H, Li L G, Liu J, et al. Graphene-supported mesoporous carbons prepared with thermally removable templates as efficient catalysts for oxygen electroreduction [J]. *Small*, 2016, 12(14): 1900-1908.
- [46] Naveen M H, Shim K, Hossain M S A, et al. Template free preparation of heteroatoms doped carbon spheres with trace Fe for efficient oxygen reduction reaction and supercapacitor[J]. *Advanced Energy Materials*, DOI:10.1002/aenm.201602002.
- [47] Shi H, Shen Y F, He F, et al. Recent advances of doped carbon as non-precious catalysts for oxygen reduction reaction[J]. *Journal of Materials Chemistry A*, 2014, 2(38): 15704-15716.
- [48] Chabot V, Higgins D, Yu A, et al. A review of graphene and graphene oxide sponge: material synthesis and applications to energy and the environment[J]. *Energy & Environmental Science*, 2014, 7(5): 1564-1596.
- [49] Yang S, Feng X L, Wang X, et al. Graphene-based carbon nitride nanosheets as efficient metal-free electrocatalysts for oxygen reduction reactions[J]. *Angewandte Chemie-International Edition*, 2011, 50(23): 5339-5343.
- [50] Zhou X J, Qiao J L, Yang L, et al. A review of graphene-based nanostructural materials for both catalyst supports and metal-free catalysts in PEM fuel cell oxygen reduction reactions[J]. *Advanced Energy Materials*, 2014, 4(8): 1301523.
- [51] Niu W H, Li L G, Wang N, et al. Volatilizable template-assisted scalable preparation of honeycomb-like porous carbons for efficient oxygen electroreduction[J]. *Journal of Materials Chemistry A*, 2016, 4(28): 10820-10827.
- [52] Su Y Z, Yao Z Q, Zhang F, et al. Sulfur-enriched conjugated polymer nanosheet derived sulfur and nitrogen co-doped porous carbon nanosheets as electrocatalysts for oxygen reduction reaction and zinc-air battery[J]. *Advanced Functional Materials*, 2016, 26(32) : 5893-5902.

模板辅助合成氮掺杂的多孔碳基氧还原电催化剂的研究进展

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摘要: 氮掺杂的多孔碳材料有望能取代当前普遍应用于质子交换膜燃料电池和金属-空气电池阴极中的贵金属氧还原催化剂, 因而备受关注. 模板辅助合成技术作为一种可靠、通用的方法已经在多孔碳电催化剂的制备中得到了广泛的应用. 在碳基 ORR 电催化剂中, 其 ORR 活性受到诸多因素的影响, 如掺杂剂的浓度及其在碳上的分子掺杂态、孔洞结构、比表面积以及碳基材料的导电性等. 本文对近期氮掺杂多孔碳电催化剂的设计、制备、功能化及其在氧还原电催化中的应用研究进展进行了总结, 同时展望了模板辅助合成法的一些发展趋势.

关键词: 氧还原反应; 氮掺杂多孔碳; 模板辅助合成; 热可移模板