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# Recent development of efficient electrocatalysts derived from porous organic polymers for oxygen reduction reaction

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Porous organic polymers (POPs) have recently emerged as promising candidates for catalyzing oxygen reduction reaction (ORR). Compared to conventional Pt-based ORR catalysts, these newly developed porous materials, including both non-precious metal based catalysts and metal-free catalysts, are more sustainable and cost-effective. Their porous structures and large surface areas facilitate mass and electron transport and boost the ORR kinetics. This mini-review will give a brief summary of recent development of POPs as electrocatalysts for the ORR. Some design principles, different POP structures, key factors for their ORR catalytic performance, and outlook of POP materials will be discussed.

**porous organic polymers, oxygen reduction reaction, electrocatalysis, metalloporphyrin**

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## 1 Introduction

With the rising concerns about environmental problems and energy crisis, developing environment-friendly and renewable energy resources is highly demanded. Among the new generation of energy devices, fuel cells [1–3], microbial fuel cells [4,5] and metal-air batteries [6,7] have attracted broad interest from researchers all around the world. One of the standing problems involved in these three emerging technologies is the sluggish reaction kinetics of the oxygen reduction reaction (ORR) [8,9]. The ORR is the critical process in these energy converting systems that normally occurs at the cathode. Two main mechanisms are usually involved in either acidic or basic aqueous solutions: the direct 4-electron reduction pathway from O<sub>2</sub> to H<sub>2</sub>O and the 2-electron reduction pathway from O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. To facilitate the reaction to go

through the direct 4-electron mechanism and speed up the low kinetics of ORR, various cathode ORR catalysts have been developed over the past few decades. At the current stage, platinum (Pt)-based materials are still the most widely studied and traditionally regarded as the best group of ORR catalysts due to their excellent catalytic activities [10–13]. Unfortunately, Pt is a noble metal and Pt-based catalysts are usually not cost-effective due to the limited sources. Moreover, they tend to suffer other problems such as susceptibility to intermediate (i.e. H<sub>2</sub>O<sub>2</sub>) poisoning and aggregation of active species.

To address these problems, tremendous efforts have been made within the past few years, including alloying Pt with non-noble metals, metal oxides, non-noble metal complexes and metal-free heteroatom-doped carbons [14–17]. Notably, porous organic polymers (POPs) have recently emerged as a highly promising class of catalysts alternative to conventional Pt-based ORR catalysts [8,14,18]. POPs, including

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conjugated microporous polymers (CMPs), covalent organic frameworks (COFs), etc. usually have large specific surface area and customizable pore size distribution. It has been proved these features can enhance the mass transport and thus increase the efficiency of catalytic activity [19–22]. Their chemical compositions are usually well-defined and inter-monomer connectivity (covalent bonding) is much more stable than similar and widely studied metal-organic frameworks (MOFs). Moreover, heteroatoms, such as N, S, B and F can be introduced into the catalyst in a controlled fashion through rational design of the precursors [23–25]. Compared with MOFs, POPs possess higher chemical and thermal stabilities, which are highly desired for the energy-related applications. Most importantly, POPs are usually free of noble metals, thus having much more abundant sources compared to conventional Pt-based ORR catalysts. This feature is critical for the development of cost-effective and sustainable ORR catalysts for practical applications. In this minireview, we will give a brief introduction on some basic design principles for POPs used in ORR. Then, recent progress in this area will be briefly reviewed, including several different types of POPs. We will also discuss several main factors that determine the ORR performance.

## 2 Porous organic polymers used in ORR

### 2.1 Design principles

To make POPs applicable in ORR, the most important design criterion is the introduction of catalytically active sites. Unlike size and shape effect observed in Pt-based ORR catalysts, POPs are much more sensitive to the electronic effect on the active sites. For non-precious metal catalysts, they usually need to create ORR active M–N sites (M=Fe, Co, etc.; N=nitrogen containing ligand), while for metal-free catalysts, doped heteroatoms are required to modulate the charge redistribution. Many non-precious metal catalysts for ORR have been obtained from POPs containing metal complexes (M–N<sub>4</sub>) with N<sub>4</sub>-chelating ligands (e.g. porphyrins, phthalocyanines), either as such or upon pyrolysis. It has been reported that nitrogen-enriched porous carbon networks containing metal-nanoparticles, metal-bonded N, and pyrrolic N atoms are formed upon pyrolysis [26–28]. Metal-free catalysts have been derived from POPs with high nitrogen content, which form N-doped graphitic carbon materials upon pyrolysis. However, the exact catalytic centers have not been fully identified in all these catalysts.

A large accessible surface area and abundant pore distributions are also of paramount importance, since they can increase the exposure of active sites and facilitate the mass transport. Usually, mesopores are particularly advantageous, since the pore size can be sufficiently large (2 to 50 nm) to

allow the reactants to reach the active sites without diffusion limitations [18].

Besides, catalysts which can catalyze direct conversion of O<sub>2</sub> to H<sub>2</sub>O through 4-electron mechanism are preferred since the possible intermediate, hydrogen peroxide, produced in 2-electron reduction process can cause corrosion damage to the instruments. The detailed 4-electron pathway mechanism of the O<sub>2</sub> reduction catalyzed by electrocatalysts derived from POPs is not well understood due to ill-defined catalyst structures after carbonization [29,9]. However, thorough mechanistic investigations have been conducted using small molecular co-facial bimetallic porphyrins as the ORR catalysts [30–36]. The study revealed that rapid electron and proton transfer is critical to suppress side reactions such as hydrolysis or premature dissociation of reactants as well as intermediates. In that context, POPs, featuring high surface area with well-defined porous structures, uniformly distributed active sites, and carbon-rich conjugated skeleton, which facilitate mass transport and electron transfer, would be favorable substrates for ORR catalyst development.

The ideal ORR catalysts should be inert to the methanol oxidation and tolerant to the presence of methanol which is crossed-over from the anode to the cathode through the proton exchange membrane. The isolation of the active centers from methanol and design of active centers inert toward methanol oxidation are highly important to obtain a methanol-tolerant electrocatalyst. Many electrocatalysts derived from POPs are reported to have excellent methanol tolerance [26,28,37].

Finally, better conductivity can enhance the electron transfer, thus improving the oxygen reduction activity. Commonly used methods include thermal pyrolysis treatment to form graphitic carbons, template directed synthesis, or mixing with conductive species, such as the conductivity booster carbon black or easily polymerizable carbon precursors, e.g. furfuryl alcohol.

### 2.2 Different types of porous organic polymers

During the past few years, a few POPs have been developed for ORR applications. Herein, we classified them into mainly three groups based on their components, namely, non-precious metal-containing POPs, metal-free POPs and template-directed POPs. The properties and catalytic activities of different types of those ORR catalysts derived from POPs are summarized in Table 1.

Porphyrin- or phthalocyanine-based porous polymers contain a high density of macrocyclic nitrogen-coordinated metal centers, which account for their enhanced ORR catalytic activity. It has attracted increasing attention since the first demonstration of cobalt phthalocyanine as ORR electrocatalyst in alkaline electrolytes in 1964 [38–40]. Recently, Liu and coworkers [24] reported a new non-precious-metal catalyst based on a porous organic polymer (PFeTTPP),

**Table 1** A summary of POPs derived ORR catalyst

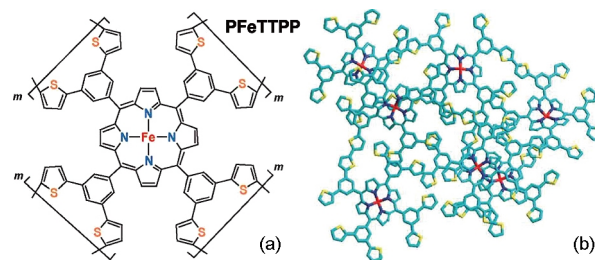
Types	POPs	Pyrolysis temperature (°C)	BET surface area (m <sup>2</sup> g <sup>-1</sup> )		Electrolyte	ORR performance			Ref.
			Before pyrolysis	After pyrolysis		$E_o^a)$ (V)	$I_d^b)$ (mA cm <sup>-2</sup> )	$N_e^c)$	
Nonprecious metal-containing porphyrin-based POPs	PFeTTPP	700	2303	903	0.1 M HClO <sub>4</sub>	0.93	~5.0	3.96	[24]
	CoP-CMP	800	1158	480	0.1 M KOH	0.84	4.6	~3.85	[27]
					0.5 M H <sub>2</sub> SO <sub>4</sub>	0.74	4.8	~3.93	
	COP-P-Fe	950	/	/	0.1 M KOH	0.98	/	3.81	[28]
					0.1 M HClO <sub>4</sub>	0.89	/	3.82	
	COP-P-Co	950	/	/	0.1 M KOH	~0.90	~5.0	3.56	[41]
					0.1 M HClO <sub>4</sub>	/	~5.7	3.61	
	PCN-FeCo	800	1260	930	0.1 M KOH	0.88	~5.2	~4.20	[41]
					0.1 M HClO <sub>4</sub>	0.90	~5.4	~4.20	
	CoPEF	/	/	/	0.1 M KOH	0.83	4.5	3.78	[37]
0.5 M H <sub>2</sub> SO <sub>4</sub>					0.62	4.5	3.83		
CoPOP	800	1069	764	0.1 M KOH	~0.90	5.4	3.92	[26]	
				0.5 M H <sub>2</sub> SO <sub>4</sub>	~0.80	5.3	3.93		
FePOP	800	854	608	0.1 M PBS	0.80	/	~3.77	[46]	
Metal-free triazine-based POPs	COP-4	950	2015	569	0.1 M KOH	~0.90	/	3.90	[47]
	CTF, B doping	700	/	1694		~0.82	~4.6	~3.84	[25]
	CTF, F doping	700	/	2570		~0.90	6.2	3.70	
POF (PAF-6)	1000	/	785		/	5.2	3.75	[48]	
Template-directed POPs	CMPs-2D	800	593	573	0.1 M KOH	/	~6.0	3.85	[51]
	M-CMP	800	1625	850		0.92	5.4	~4.00	[52]

a)  $E_o$ : onset potential; b)  $I_d$ : diffusion-limiting current density; c)  $N_e$ : electron transfer number.

which has an ultrahigh surface area (BET surface area of 2303 m<sup>2</sup>g<sup>-1</sup>) and a high density of iron-porphyrin groups (Figure 1). After thermolysis of the porous precursors, the as-prepared catalysts show excellent ORR catalytic activity in acidic electrolyte (see Table 1).

Similar catalysts were reported by Müllen *et al.* [27] using cobalt porphyrin-based conjugated mesoporous polymer CoP-CMP (Figure 2). The precursor was synthesized via Yamamoto poly-condensation of Co-porphyrin. Subsequent thermal treatment of the CoP-CMP yielded nitrogen-enriched porous carbons with cobalt nanoparticles incorporated. For comparison, they also obtained the metal-free analog under the same reaction conditions. After evaluating parameters, e.g. half-wave potential and limiting current, they found the Co-containing catalyst was superior to metal-free catalysts and even commercial 20 wt% Pt/C catalysts in both alkaline and acidic media, showing excellent stability and electron transfer number comparable to Pt/C.

Dai group [28] later also explored similar porphyrin containing POPs (two more benzene rings between two porphyrins compared to CoP-CMP) with other metals such as Fe and Mn. They found that due to the poor solubility of POPs in most common solvents, it is hard to introduce metals through post-synthetic method into the as-formed polymers,



**Figure 1** (a) Molecular structure of PFeTTPP; (b) simulated 3D stacking of iron-metallated species. Fe: red, N: blue, C: light blue, S: yellow; H not shown for clarity (color online).

which indicates that it is very important to rationally design the initial metal-containing precursor through bottom-up strategy. Regarding ORR performance, Dai demonstrated that the Fe-incorporated POPs exhibited a similar onset potential as that of the bench-mark Pt/C in both alkaline and acid media, while for the Co-containing polymer, the material displayed an even higher kinetic current and diffusion-limiting current in alkaline solution compared to Pt/C.

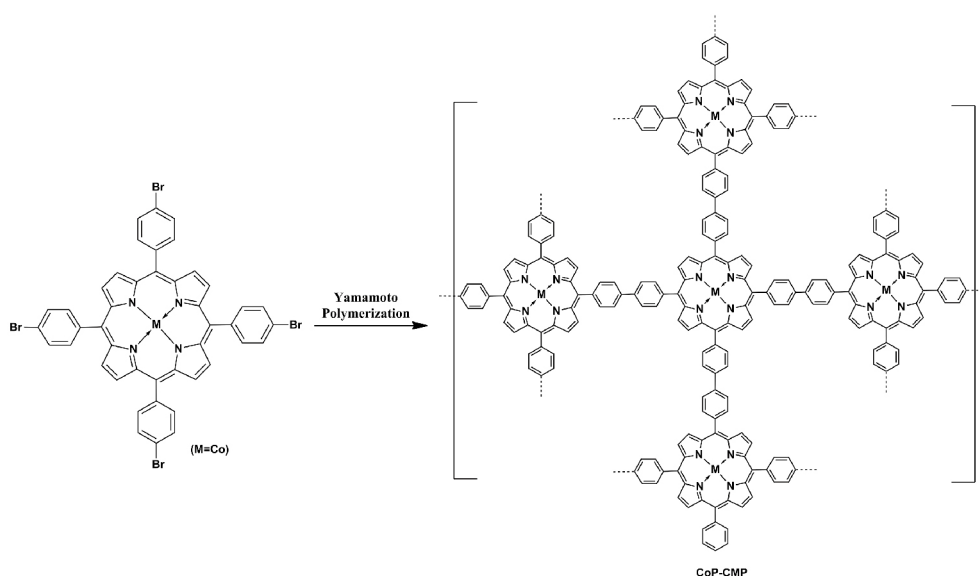
The examples that have been discussed above are generally homometallic POPs, which may limit their applications. To overcome such a problem, Feng *et al.* [41] reported a hetero-metal-embedded porous catalyst (PCN-Fe/Co/C)

derived from well-designed organic conjugated framework PCN-Fe/Co (Figure 3). The synthesis started from two different types of porphyrinic monomers with different metals (Fe and Co) and peripheral functionalities. The two monomers were co-polymerized through Sonogashira-Hagihara coupling reaction to get the Fe and Co heterometalporphyrinic porous conjugated polymers. This is the first example of heterometallic POPs used as electrode catalysts in ORR. The derived heterometallic porous catalysts exhibit high ORR activity and remarkable electrochemical stability in both alkaline and acidic electrolyte, which are superior to their monometallic counterparts and commercial Pt/C.

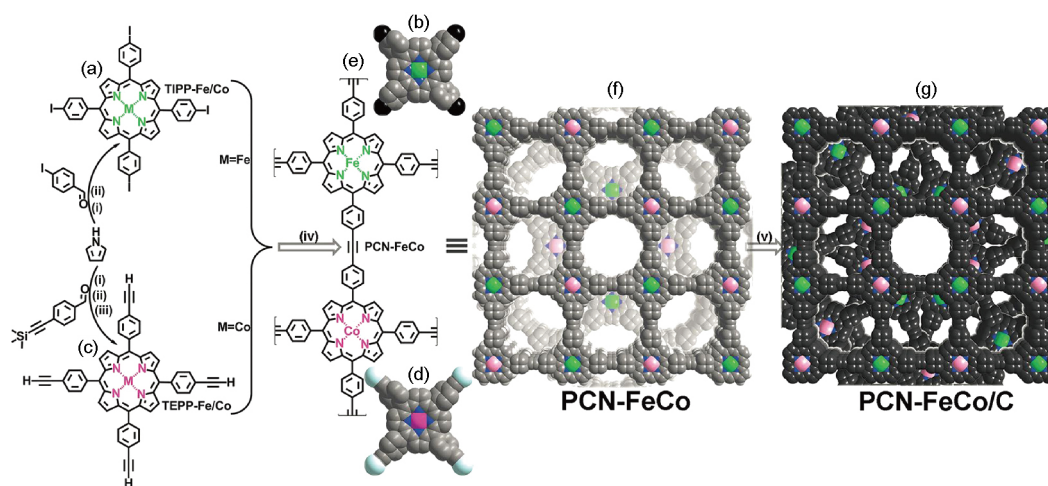
Recently, Zhang and coworkers [37,42–45] reported more porous and thermally stable poly(aryleneethynylene) networks that were synthesized through dynamic alkyne

metathesis. Compared with commonly-practiced irreversible cross-coupling reactions, porous organic polymer CoPEF obtained through this strategy shows some structural order, which might provide better conjunction. They used a highly active multidentate molybdenum carbyne catalyst to perform the alkyne metathesis polymerization of Co-porphyrin-based monomers (Figure 4). The obtained polymer framework CoPEF was mixed with conductive carbon black to make the electrode catalyst instead of thermal treatment of the porous polymer (no pyrolysis). The resulting materials show excellent ORR catalytic activity in both acidic and alkaline media. Moreover, the catalyst was resistant to methanol-poisoning, thus demonstrating excellent durability.

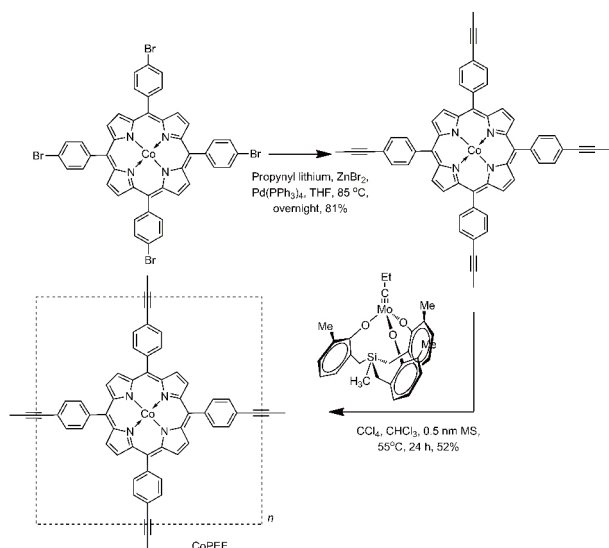
In addition to conventional two dimensional POPs used in ORR, Zhang [26] also developed three-dimensional electrode



**Figure 2** Schematic representation of the chemical synthesis of metalloporphyrin-based conjugated mesoporous polymer frameworks (CoP-CMP).



**Figure 3** Schematic diagram of the synthesis of (a, b) 5,10,15,20-tetrakis-(4-iodophenyl)porphyrin coordinated metals and (c, d) 5,10,15,20-tetrakis-(4-ethynylphenyl)porphyrin coordinated metals (metal=Fe, Co) monomers, (e, f) porphyrinic conjugated network, PCN-FeCo, and (g) carbonization product PCN-FeCo/C (FeFe/C and CoCo/C are prepared by the same synthetic route). Reprinted from Ref. [32] with permission. Copyright 2015 Wiley (color online).



**Figure 4** Schematic diagram of the synthesis of Co(II) porphyrinylene-ethynylene framework (CoPEF) using multidentate molybdenum caybyne as catalysts.

catalysts through coupling of tetratopic connectors and Co-porphyrins. The three dimensional network provided higher porosity and showed enhanced catalytic activity. When the coordinated metal was changed to iron, pyrolyzed material displayed excellent ORR activity even in pH-neutral medium, which makes it a promising cathode candidate to replace Pt in microbial fuel cells [46].

Very recently, triazine-based POPs with high density of N atoms have been developed as promising metal-free electrocatalysts for ORR. Dai group [47] reported four POPs with varied N doping levels and porous structures (Figure 5). The resulting N-rich POPs were subjected to carbonization in an inert atmosphere to produce the N-doped graphitic carbon materials. Among them, COP-4 with triazine-based building blocks show the best ORR activity with the most positive potential (0.79 vs. RHE) and higher diffusion current density. In addition, the onset potential was similar to that of commercial 20 wt% Pt/C and the transferred electron number is 3.90, indicating close to the full reduction of oxygen to water.

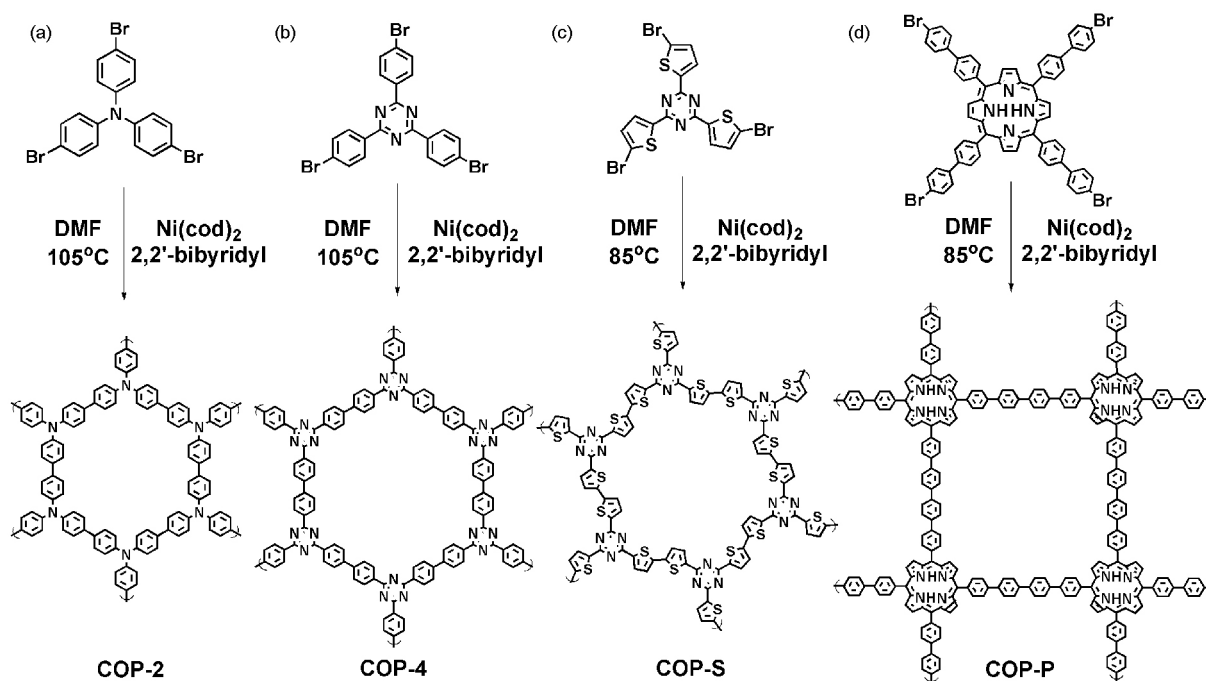
A triazine-based framework similar to COP-4, where two triazine rings are connected by one benzene ring instead of two benzene rings, was also prepared by Zhi and coworkers [25] through trimerization of terephthalo-nitrile. In their research, they found the conductivity of the as-prepared porous materials can be significantly improved by elevating their thermal treatment temperature. The conductivity significantly contributes to the enhancement of catalytic activities. Interestingly, their bottom-up strategy can afford other atom dopant, such as boron and fluorine (CTF, B-doping and CTF, F-doping, Table 1), which will bring great opportunity for gaining deeper understanding of the structure-property relationship of metal-free electrocatalysts for ORR.

Another way to enhance the conductivity in the metal-free catalyst is introducing some carbon precursors before the carbonization, as reported by the Banerjee group [48]. They used piperazine and cyanuric chloride to construct the triazine-based POPs. The POPs were then mixed with furfuryl alcohol, which can be easily polymerized to form polyfurfuryl alcohol inside the organic framework at 150 °C. After pyrolyzed at 1000 °C, the obtained porous materials displayed better activity than commercially available Pt/C catalyst in alkaline conditions. Polymerized furfuryl alcohol acts as the carbon precursors, which was proposed to improve the yield as well as the porosity of the resulting carbon.

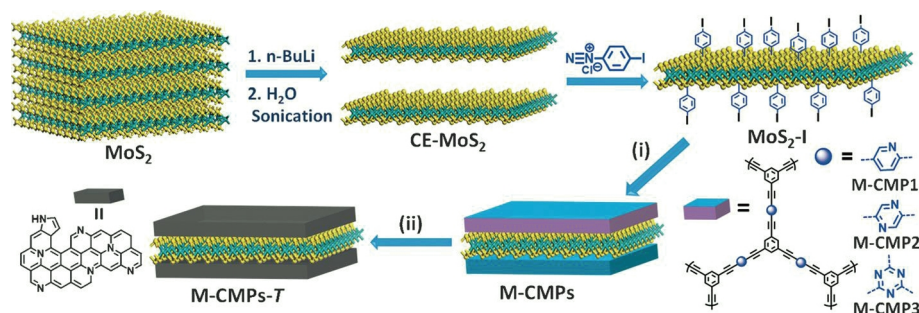
Triazine-based POPs can also be combined with non-precious metals through controllable pyrolysis of triazine-based frameworks with iron chloride hexahydrate. Very similar to the porphyrin-based nitrogen-coordinated metal macrocyclic centers, Fe–N functions as active sites. Impressively, after acid leaching, both mesopores and macropores were created in the porous structure, which is desired for electron and mass transportation [49].

The two types of ORR catalysts discussed above are both based on template-free synthesis. Due to the limitation of the synthetic protocols, most of these reported POPs do not have uniform morphologies. It has been shown that the morphologies and microstructures of porous polymers may affect the performance of these derived catalysts in ORR [50]. Therefore, template-directed synthesis is attractive in the view of shape control of the final POPs. Feng group [51] reported shape controlled conjugated porous polymers with different dimensions. Bromo-functionalized carbon nanospheres (zero dimension), single-walled carbon nanotubes (one dimension) and reduced graphene oxide (two dimensions) served as structurally directing templates. Sonogashira-Hagihara reaction was used to couple the templates with conjugated porous polymers. After pyrolysis, all three types of morphologies were preserved with boron and nitrogen co-doped. These POPs show clear morphology-performance relationship in both ORR and air cathode in Zn-air batteries (activity: 2D>1D>0D).

Recently, Feng group [52], collaborating with Scherf group, published another work using MoS<sub>2</sub>, which has unique electronic properties, as a novel template. The bulk MoS<sub>2</sub> was first treated with *n*-butyllithium to obtain chemically exfoliated MoS<sub>2</sub> (Figure 6). Then, the surface of the MoS<sub>2</sub> was functionalized with 4-iodophenyl diazonium (MoS<sub>2</sub>-I). This Sonogashira-Hagihara reaction was applied using 1,3,5-triethynylbenzene and aryl di- or tri-halides as building blocks to form the pyridine-, pyrazine- and triazine-containing polymers. After pyrolysis, core-shelled sandwich-like porous hybrids (M-CMPs-T) were obtained with large specific surface areas and hierarchical porous structure, which worked as efficient catalysts in 0.1M KOH solutions for ORR.



**Figure 5** Schematic diagrams of the synthesis of different types of covalent organic polymers derived from different N-rich precursors using nickel catalyzed Yamamoto-type Ullmann cross-coupling reaction. (a–d) Monomers tris(4-bromophenyl)amine, 2,4,6-tris-(4-bromo-phenyl)-[1,3,5] triazine, (4'-bromobiphenyl-4-yl)-porphyrin and 2,4,6-tris (5-bromothiophen-2-yl)-1,3,5-triazine, respectively.



**Figure 6** Schematic diagrams of the chemical exfoliation of bulk MoS<sub>2</sub> and subsequent functionalization with 4-iodophenyl substituents under formation of MoS<sub>2</sub>-I as well as the preparation of MoS<sub>2</sub>-templated conjugated microporous polymers and the corresponding MoS<sub>2</sub>/nitrogen-doped porous carbon hybrids. Reprinted from Ref. [44] with permission. Copyright 2016 Wiley (color online).

Impressively, lower energy consumption and operation voltage were observed for the hybrid material in comparison to corresponding MoS<sub>2</sub>-free counterparts.

### 2.3 What determines the ORR performance

In addition to gaining a deeper insight into the relationship between the structure and the ORR performance, to guide the rational design of porous organic polymers that can be used as ORR catalysts, it is highly important to figure out what exactly determines the ORR performance in terms of both activity and stability. Based on the literature reports, the following two factors are important: (1) the creation and exposure of active sites; (2) efficient mass and electron transfer. Incorporation of interconnected catalytic centers into conjugated porous networks with high porosity is believed to be

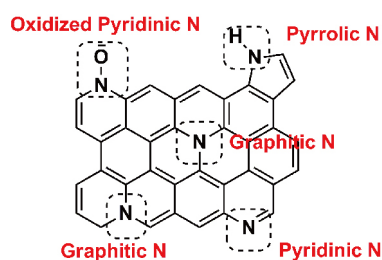
beneficial for sufficient exposure of active centers and efficient electron and mass transfer.

The density of catalytically active sites and the rate of catalysis per active site directly affect the electrocatalytic current achievable at electrode. The rate of catalysis per active site is determined by the average turnover frequency of the catalytic center, which largely depends on the design of catalytic centers (e.g. choice of transition metals). Transition metal nitrogen coordination M–N (M=Co, Fe and Mn) is commonly regarded as the real active site for non-noble metal catalysts. Even though the exact mechanism is still unclear, high content of coordinated M–N species are proved to be favorable for the enhancement of the catalytic activities [27]. Without the metal coordinated species, the electrocatalytic performance was poor [24,47]. Co, Fe and Mn are commonly used metal centers which exhibit reasonable binding affinity to

wards molecular oxygen and the most positive  $M^{2+}/M^{3+}$  redox potentials [53]. There is no concrete relationship observed between the N-content and the ORR performance [27].

For the metal-free ORR catalysts, N-doping, especially nitrogen with certain configurations is related to the creation of active sites for ORR. Figure 7 shows different N configurations that can be found in metal-free catalysts. Usually, pyridinic N with lone-pair and graphitic N with delocalized  $\pi$ -orbitals are assumed to be responsible for the catalytic activity. It is reasonable that  $\pi$ -electrons can perform a nucleophilic attack on oxygen and the more  $\pi$ -electrons the system contains, the higher the oxygen reduction activity. In order to achieve high efficiency of these active sites, it is important to maximize their exposure to the external substances, which calls for high surface area and abundant porosity.

Efficient mass and electron transfer is another crucial factor for enhancing the ORR performance. That is, reactant oxygen molecules and electron from the electrode should be efficiently transferred to the active sites, and products should be removed away from the active sites. Porous structure again should be highlighted here for the efficient mass transfer. Most POPs reported thus far were pyrolyzed before their electrocatalysis applications. Heat-treatment of POPs at a temperature above 600°C significantly improves the catalytic activities of the materials. It has been proposed that the decomposition of these carbon-rich materials occurs during heat-treatment, forming conductive graphitic structure, therefore facilitating electron transfer [54]. The pyrolysis temperature is reported to be critical for the catalytic activity of POPs [27]. A low pyrolysis temperature cannot lead to a high graphitization degree to ensure a good conductivity for the porous carbon materials, while a too high pyrolysis temperature could destroy their porous structure and thus dramatically decrease the surface area. However, the detailed chemistry behind the catalysis by these pyrolyzed polymer frameworks is still poorly understood, largely due to the ill-defined structure of the pyrolyzed materials and complicate structural variations under high temperature treatment. When unpyrolyzed POPs (e.g. CoPEF) are used as ORR electrocatalysts, carbon black is generally used as a conductivity booster to achieve high catalytic activity.



**Figure 7** Schematic diagrams of different nitrogen doping positions in the graphitic structure (color online).

### 3 Summary and outlook

In this minireview, we give a brief introduction on the recent progress made in the ORR catalysts derived from porous organic polymers and discuss the relationship between the structures and properties. Although significant progress has been made to develop various POPs as ORR catalysts, there are still various limitations needed to be addressed to make them practically applicable in electrocatalysis. First of all, even though N-doping is demonstrated to be one of the key factors for the improvement of catalytic activity of electrocatalysts, controlling the final doping, including the amount and configuration, is difficult. It not only requires more accurate design of the porous polymer precursors, but also the well-optimized pyrolysis conditions. Secondly, a better understanding of catalysis mechanism is needed to explain the detailed structure-property relationships. Till now, theories like charge disruption or spin neutrality are proposed to explain the ORR catalytic activity of POPs. However, the exact mechanism is still a matter of debate. The exploration of structure-property relationships depends on systematic study of the differences resulting from variation in chemical structures of the catalysts. In this view, the bottom-up synthesis shows its advantages. Also, theoretical calculations of some already reported experimental results and predictions on potential compositions are highly desired. Thirdly, compared with Pt-based ORR catalysts, the low conductivity of POPs represents a big challenge. Higher conductivity can enable fast electron transport through the catalyst during the ORR process. Even though methods like adding additional conductive substrates or applying conductive templates have been taken to solve the problem, more research work is still needed to increase the intrinsic conductivity of the porous materials. Developing more conjugated microporous polymers may be a useful route to enhance the conductivity from the sources. Last but not least, the stability and poison tolerance of POPs in all kinds of ORR environments need to be improved for practical applications. That means more stable skeleton and active sites should be introduced into the materials. All basic and acidic sensitive groups should be avoided to give robust catalysts for practical applications. Overall, POPs represent promising candidates for ORR catalysis in many energy devices. We believe that in the near future, the research in this area will lead to the development of cost-effective alternative of Pt-based materials with comparable or even better stability and activity.

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**Conflict of interest** The authors declare that they have no conflict of interest.



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