



SPECIAL ISSUE: Energy Transitions towards Carbon Neutrality

Influence of the molecular structure of metal-phthalocyanine on electrocatalytic reactions

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ABSTRACT The demand for new catalysts for renewable energy production has become crucial. As an alternative to metal catalysts for electrocatalysis to produce energy sources, metal-phthalocyanine (MPc) electrocatalysts have shown potential. Their physicochemical and electrochemical properties depend on the chemical structure of the MPc and the central metal atom. Recent reviews of MPcs focused on their electrochemical performance in specific catalytic reactions, such as oxygen reduction reaction and CO₂ reduction reaction. However, understanding the structure of MPcs in depth is important, since their electrochemical catalytic activity is affected by structural modifications of MPcs. Therefore, this minireview focuses on how the molecular structure of MPcs affects electrochemical catalysis.

Keywords: metal-phthalocyanine, oxygen reduction reaction, carbon dioxide reduction reaction, hydrogen evolution reaction, oxygen evolution reaction, electrocatalytic activities

INTRODUCTION

The importance of producing renewable energy sources cannot be overstated. Hydrogen and oxygen, which can be used as energy sources, can be produced *via* electrochemical water splitting. Carbon dioxide can also be reduced to fuel sources through electrocatalytic reactions. The electrochemical reactions are carried out with catalysts: platinum as a noble metal for hydrogen production and oxygen reduction, IrO₂ or RuO₂ for oxygen generation, and gold or copper for carbon dioxide reduction [1–7]. The application of noble metal catalysts has always been limited for their high cost and low abundance. Therefore, synthesizing non-noble metal electrochemical catalysts with enhanced electrocatalytic activities is indispensable.

Metal-phthalocyanines (MPcs) have advantages as electrocatalysts over metals and metal oxides. The physicochemical properties of MPcs can vary depending on the structure and the central metal atom of the MPc, which makes it possible to extend the electrochemical properties of these materials. In 1960, the catalytic activity of cobalt-phthalocyanine (CoPc) for oxygen reduction reaction (ORR) was reported for the first time [8]. The redox reaction of the central cobalt atom from Co²⁺ to Co³⁺ has been considered as the mechanism behind the ORR. The metal

center (Co²⁺) induces an oxygen reduction process that simultaneously causes the oxidation of the metal (Co³⁺). Oxygen molecules are adsorbed onto the oxidized metal (Co³⁺), and the metal sites are reduced by the applied negative potential, which allows the electrochemical reaction. After a series of studies, the central transition metal in phthalocyanine is now considered to be the catalytically active site. Zagal *et al.* [9] found that the catalytic activity for ORR is influenced by the metal center, as the electron density of the central metal varies.

MPcs are versatile molecules capable of attaching functional groups and interacting with various materials. Recent studies also show that their electrochemical performance could be affected by the functional groups on the MPcs, the redox properties of the metal centers, and metal-ligand interactions. The electrochemical reactions on structurally modified MPcs have been broadly studied.

In this review, we contemplate the correlation between the electrocatalytic performance and the structure of MPcs, and present the pertinent factors of the structural configuration of MPcs that enhance the electrochemical activity.

STRUCTURE OF MPcs

Phthalocyanines consist of four isoindole units connected by a ring of nitrogen atoms and a cavity with hydrogen atoms, displaying a planar geometry with 18 π -electrons and this configuration allows delocalization leaving the molecules with interesting properties. Various 3d transition metals such as Fe, Ni, Cu, Co, and Zn, which have 2+ valance states, can replace the hydrogen atoms while retaining a planar structure [10–12]. The advantage of MPc is its single metal atom in the center. Single-metal sites are traditionally considered as catalytic active sites for electrocatalysts, and the single atoms show improved activities compared with corresponding nanoparticles and clusters. Therefore, the synthesis of single-atom catalysts has become necessary in the field of electrocatalysis. Taking this into account, MPcs have a significant advantage because the single metal atom in the centers of MPcs can be a catalytic active site. Various transition metals can replace these metal atoms in the center of MPcs and induce new and unexpected catalytic properties. For example, CoPc is favorable for the CO₂ reduction reaction (CO₂RR) owing to the reasonable binding energy between CO₂ molecules and the cobalt in CoPc, whereas iron-

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phtalocyanine (FePc) has strong binding energy with CO_2 . Hence, the CO_2RR on FePc is not preferred [13]. Most MPCs are insoluble in an aqueous solution, which hinders their applications in electrocatalysis. The terminal of isoindole in MPCs can be functionalized by functional groups such as sulfonates and, octa-alkoxy which are highly soluble in an aqueous solution and thus overcome the insolubility of MPCs [14,15]. Functionalized MPCs can also affect the electrocatalytic activities because the functional groups can change the electron density of the central metal atom in MPCs [16,17]. Another advantage of MPCs is the presence of aromatic rings with π electrons in the structure. MPCs are hybridized with molecules or substrate with aromatic rings, allowing intermolecular π - π interactions and vertically stacking of MPCs. In addition, the nature of abundant aromatic rings allows co-polymerization to construct a two-dimensional (2D) organic framework. The tunable structure of MPCs affects the electrocatalysis performance. Therefore, we classify the factors affecting the electrocatalytic reaction into four parts: the supporting materials, the functional groups on MPCs, changes of the axial coordination of metal center on MPCs, and polymerization of MPCs (Fig. 1).

Supporting materials

Most MPCs are deposited on a conducting substrate for electrocatalytic reactions to improve the electron transfer during the catalytic reactions. The assistance of the conducting substrates is necessary because of the semiconducting nature of MPCs. The planar structures, including the aromatic rings of MPCs, afford interactions with various carbon substrates such as carbon

nanotubes (CNTs) and graphene *via* π - π interactions. It causes the delocalization of π -electron density resulting in strong interactions between MPCs and carbon substrates [15,18–20]. Conducting substrates such as MXene or pure metal can also be used to support MPCs. FePc on the MXene shows increased ORR activity compared with the reactions on pure FePc. Hydroxyl or fluorine functional groups in the MXene can interact with Fe in FePc and stabilize the highest occupied molecular orbital (HOMO) of Fe by reducing the electron density of Fe [17]. Combination with pure metal substrates and MPCs also affects the ORR performance. CoPc was deposited on the Ag (111) by sublimation under ultrahigh vacuum condition. Co atoms in the monolayer of CoPc receive more charge from the Ag surface (0.98e of charge) compared with the pristine CoPc (0.77e of charge). This cobalt atom with a higher electron charge strengthens the Co–O interaction and weakens O–O stretching resulting in improved ORR activity on Co [21].

Functional groups attached to a terminal MPC

Effect of steric hindrance

The aromatic rings of MPCs trigger intermolecular π - π interaction, resulting in aggregation. This prohibits the charge transfer to active sites and reduces the electrocatalytic surface area. Well-dispersed MPCs without aggregation are crucial for rapid and continuous electron transfer to the active sites for the catalytic reaction. The aggregation can be avoided by adding functional groups capable of causing steric hindrance. The functional groups can be attached to the end of the aromatic ring of the

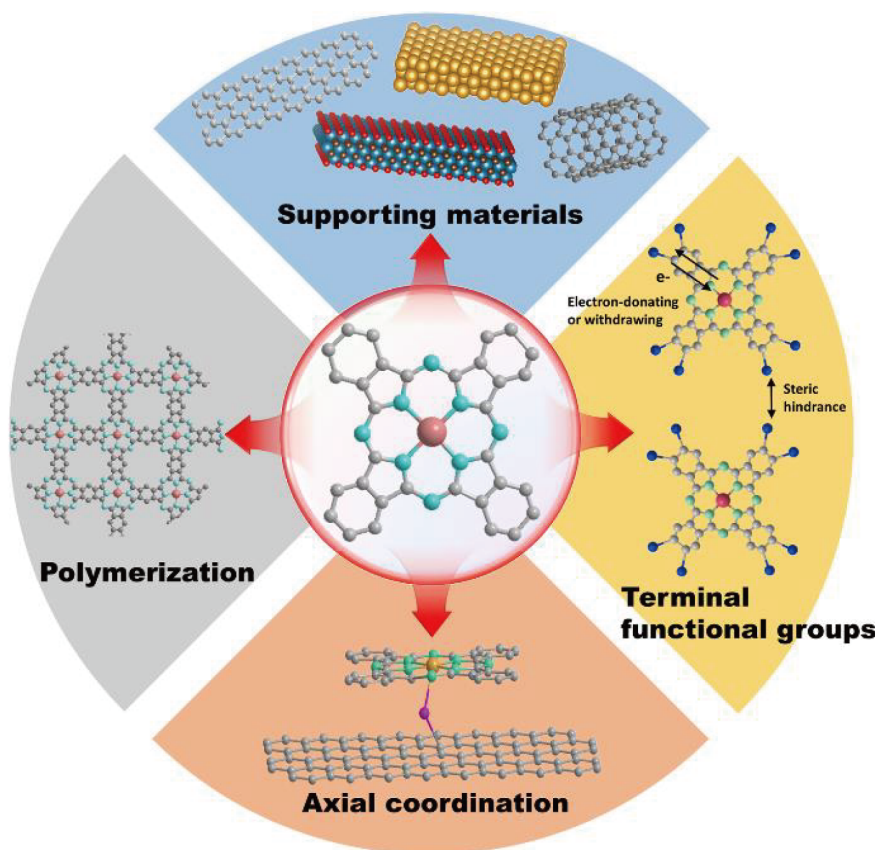


Figure 1 Molecular structures of MPCs with different supporting materials, terminal functionalization effect, axial coordination, and polymerization.

isoindole of MPc. Functionalized MPcs enhance the solubility and affect the homogeneous distribution of MPcs, in turn preventing the aggregation of MPcs [22,23]. Octa-alkoxy chain length is long enough to prevent the aggregation of molecules (Fig. 2a). The octa-alkoxy functional group makes the molecule highly soluble and sterically hindered. Due to this effect, octa-alkoxy-functionalized MPcs can be laterally constructed with homogeneously thin layers on graphene. From ultraviolet-visible (UV-Vis) spectra, the less red shift of Q-band appears in octa-alkoxy-functionalized CoPc (CoPc-A) on the chemically converted graphene (CCG), which shows the less aggregation of molecules. The Q-band indicates π - π interaction between molecules. Moreover, the intensity ratio of D and G bands (I_D/I_G) of the Raman spectrum has not changed after the adsorption of the molecules on the CCG, suggesting CoPc-A is deposited homogeneously on CCG. CoPc-A/CCG is favorable for transferring electrons along the z -axis direction from graphene to the central metal atoms, which are catalytic active sites [15]. Thus, CoPc-A on graphene improves the catalytic activity for reducing CO_2 to CO. Similarly, pyrrolidinonyl ligand-incorporated nickel-phthalocyanine (PyNiPc) lead to the efficient reduction of CO_2 to CO (Fig. 2b). The pyrrolidinonyl ligands in NiPc contribute to the single-molecular level distribution of PyNiPc on CNT, ultimately preventing the aggregation between NiPc molecules as shown by the main absorption band of UV-Vis of PyNiPc/CNT, rather than J-aggregation. The

Raman spectrum of PyNiPc molecules on CNT is not observed, which suggests that PyNiPc is dispersed homogeneously on CNTs and the strong PyNiPc-CNT electronic interactions. This highly distributed structure promotes the transfer of electrons. It also enhances the CO_2 to CO reduction reaction recording nearly 100% of faradaic efficiency and a superior CO/H_2 ratio of 640 at -0.88 V (vs. reversible hydrogen electrode (RHE)), suppressing the hydrogen evolution reaction (HER), which competes for the CO_2RR [24]. Diphenyl thiophenol functional groups can provide a high degree of steric hindrance owing to the enormous size of the molecules. FePc functionalized by diphenyl thiophenol groups can maintain the isolation of the single-metal active site. High-resolution electron spray ionization mass spectroscopy (ESI-MS) confirms that O_2 is easily trapped in between the diphenyl thiophenol-functionalized FePcs because the functional group induces the large gap between the molecules. Isolated Fe single-atom sites with large distance show a higher level of ORR activity with a higher current density by 7.4 times compared with the pristine FePc [25].

Effect of electron donors and acceptors

Functional groups that donate or accept electrons can tune the electron density of the metal center. Electron-donating functional groups can increase the electron density of the metal center by supplying more electrons to the π -conjugated system

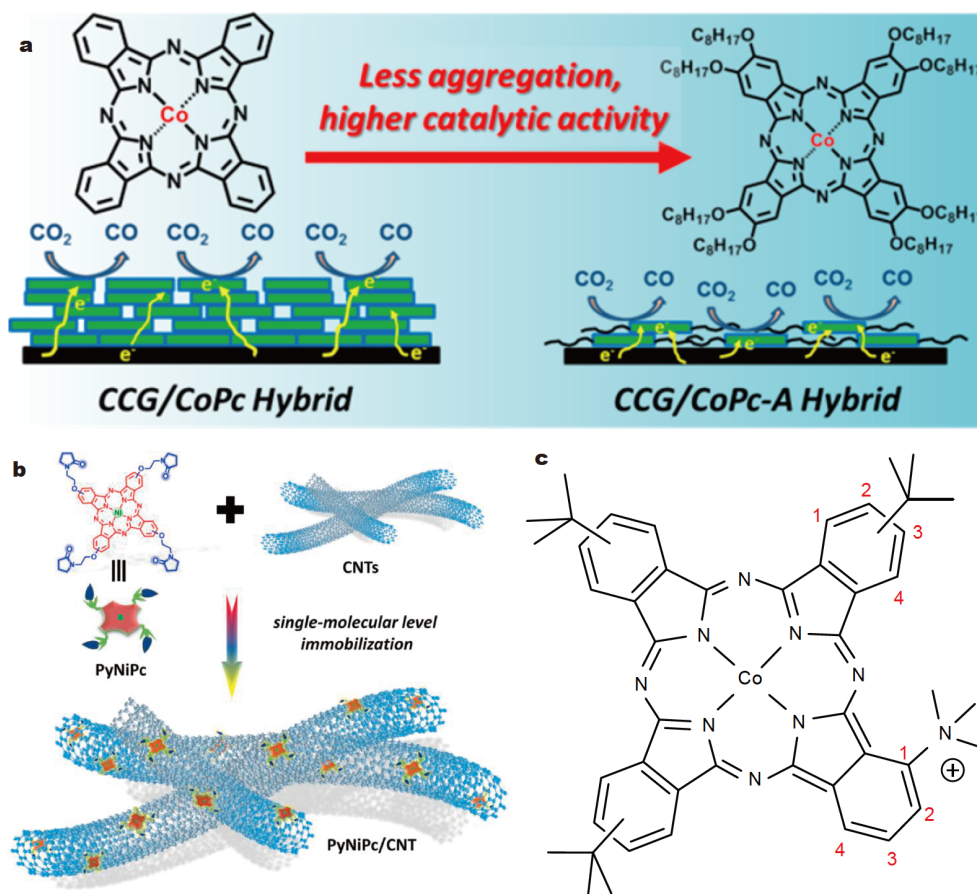


Figure 2 Terminal functionalized MPcs. (a) Schematic illustration of the octa-alkoxy-modified CoPc for CO_2RR . Reprinted with permission from Ref. [15]. Copyright 2019, American Chemical Society. (b) Illustration of single-molecule level immobilized PyNiPc on the CNT. Reprinted with permission from Ref. [24]. Copyright 2019, Elsevier. (c) Structure of trimethylammonium-functionalized CoPc. Reprinted with permission from Ref. [35]. Copyright 2019, Springer Nature.

of MPcs [26,27]. Electron-withdrawing groups give the metal center a favorable charge [28,29]. NiPc functionalized with NH_2 , a representative electron-donating group, shows improved adsorption of CO_2 at active sites and better CO_2 reduction efficiency of 99.8% compared with the pristine NiPc. The functional group donates electrons to the Ni center with an interior inductive effect, leading to a higher degree of electron localization [30,31]. The primary step for the CO_2 RR is the reduction from CO_2 to CO. However, most MPc electrocatalysts tend to degrade after the formation of CO gas, making it difficult to proceed to the next step. Therefore, the catalysts should be stable and moderate binding energy of CO at the active sites is required. Wu *et al.* [32] reported remarkable results showing that NH_2 -functionalized CoPc on CNT can reduce CO_2 to methanol, which can be used as an energy source. The Co atom in the pristine CoPc is oxidized to CoO_x , because the metal center is not stable under the reduction potential of CO_2 RR. In contrast, after CO_2 RR, CoPc- NH_2 molecules show the same UV-Vis absorption band as that of the prepared CoPc- NH_2 , suggesting that the CoPc- NH_2 structure is sustained under the reaction conditions. Perfluorinated CoPc (CoFPc) is well known as an efficient catalyst for water oxidation. Morlanés *et al.* [33] demonstrated that CoFPc immobilized on carbon cloth can reduce CO_2 selectively to CO in an aqueous solution. The immobilized CoFPc has no variation in the UV-Vis and Raman spectra after the electrocatalytic reaction, indicating that the immobilized structure remains chemically unchanged. Highly stable electrolysis of CO_2 to CO was achieved for 12 h because the fluorine groups on CoFPcs decrease the affinity of CoFPc toward CO, suppressing the poisoning from the reduced products, CO. Wang's group [34] found that the electron-withdrawing cyano groups can enhance the catalytic performance for the CO_2 RR on CoPcs. The CO_2 RR occurs during the reduction of Co^{2+} to Co^+ , because Co^+ is the active site for reducing CO_2 . The cyano functional groups on CoPcs promote the formation of Co^+ supported by the more dramatic Co(II)/Co(I) redox peak observed at more positive potential for CoPc-CN/CNT compared with CoPc/CNT. The Co^+ sites are less nucleophilic, and CO_2 is less strongly attached to the metal center, thus providing a higher fraction of Co^+ sites. This causes the efficient reduction of CO_2 on the Co center to CO, improving product removal and turnover. Large functional groups also enhance the activity of CO_2 RR. The positive charge of the trimethylammonium substituent in the CoPc structure shows three reversible faradaic waves that could be assigned to the Co(II)/Co(I) redox couple and ligand reduction peaks. This structure facilitates the C–O bond cleavage, leading to favorable CO reduction (Fig. 2c) [35].

Change of the axial coordination of the metal centers in MPcs

The planar structure of the M-N4 (a metal center coordinated with four nitrogen atoms) site usually shows unsatisfactory catalytic performance due to its inertness for activation. Therefore, attempts have been made to change the coordination around the metal center. The M-N4 center offers extra coordination sites in the axial direction by aligning functional groups or ligands vertically. Axial ligands are directly connected to the metal center, tuning the coordination from four to five to enhance the catalytic activity. Cho *et al.* [36] found the old ORR catalyst, cytochrome C oxidase, has five-coordinated Fe. Thus, they used pyridine-functionalized CNTs to change the coordination of FePc. The pyridine molecule, an axial ligand, is ver-

tically attached to the Fe center. As Fe ion is coordinated with the pyridine group at the axial direction in the FePc-pyridine system, the extra coordination leads to the change of electron density on Fe, resulting in higher binding energy of Fe 2p in X-ray photoelectron spectroscopy (XPS). In addition, the shoulder peak negatively shifts in FePc-pyridine-CNT, compared with FePc and FePc-CNT, suggesting an effective change of local symmetry from D_{4h} to five-coordination system by additional interaction with axial direction. They found that the five-coordinated Fe in FePc has a high charge density near the Fermi level, which makes the ORR process favorable. Moreover, the binding energy of O_2 and OOH on the pyridine-anchored FePc was found to be slightly higher than that on the pristine FePc, facilitating the adsorption of O_2 and OOH on the active sites. In addition, the HOO-FePc-pyridine system has a lower spin state than the HOO-FePc system. It is well known that the lower spin states in catalysts are responsible for the ORR activity [37]. Similarly, Chen *et al.* [38] synthesized an oxygen functional group with the axial direction anchored to Fe in FePc (O-FePc) (Fig. 3a). The oxygen functional group was introduced into acetylene black by O_2 plasma and the carbon supports were mixed with FePc. The positive shift of the X-ray absorption near-edge spectra (XANES) of Fe K-edge in O-FePc compared with FePc indicates the axial coordination of FePc on the oxygen. Moreover, the Mössbauer spectrum of O-FePc has D2 peaks corresponding the O-Fe-N4 coordination, while the FePc shows D1 peaks which are assigned to the square planar Fe-N4. The Fe sites with axially coordinated oxygen lead to electron localization which is beneficial for O_2 adsorption and activation for ORR. Thus, the O-FePc catalysts show fast kinetics for the ORR. The amine functional groups can also be used as an axial ligand. Zhang *et al.* [16] prepared FePc coated on NH_2 -functionalized CNTs. The shoulder shifts in XANES indicate a change in the local symmetry of Fe-N4 with the additional coordination of NH_2 in FePc. The NH_2 groups act as axial ligands that coordinate to Fe sites. The electron-donating NH_2 axial ligand leads to favorable O_2 adsorption on Fe sites for ORR. As mentioned previously, electron-withdrawing groups decrease the electron density from the metal center, resulting in a shift of the $M^{n+}/M^{(n-1)+}$ redox potential to more positive values, enhancing the electrocatalytic reaction. Pyridiniums are molecular entities that consist of 6-membered rings with a positively charged nitrogen atom, called core pyridium; they can also act as an electron-withdrawing group. Pizarro *et al.* [39] synthesized two structural pyridiniums isomers, where the only difference is the core positions (Up or Down, Fig. 3b) and attached the isomers to FePc vertically. The UV-Vis spectra of pyridiniums show very different intensities of absorbance regarding different core positions, which indicates that the changing core positions in the molecular backbone modify their electronic features. The influence of the core positions for the ORR was examined. Ultimately, the Up position of the pyridiniums changes the Fe- O_2 binding energy and leads to higher activity for the ORR than the pristine FePc. Coordination engineering affects the CO_2 RR as well as the ORR. Li *et al.* [40] prepared CNT functionalized by amino, hydroxyl, and carboxyl groups for anchoring onto the Co center of CoPc. In the XPS Co 2p spectrum of CoPc/CNT, the binding energy of CoPc/OH-CNT and CoPc/ NH_2 -CNT is slightly reduced due to the donation effect of $-\text{NH}_2$ and $-\text{OH}$, while the binding energy of CoPc/ COOH -CNT is slightly increased due to the electron-withdrawing effect of the $-\text{COOH}$

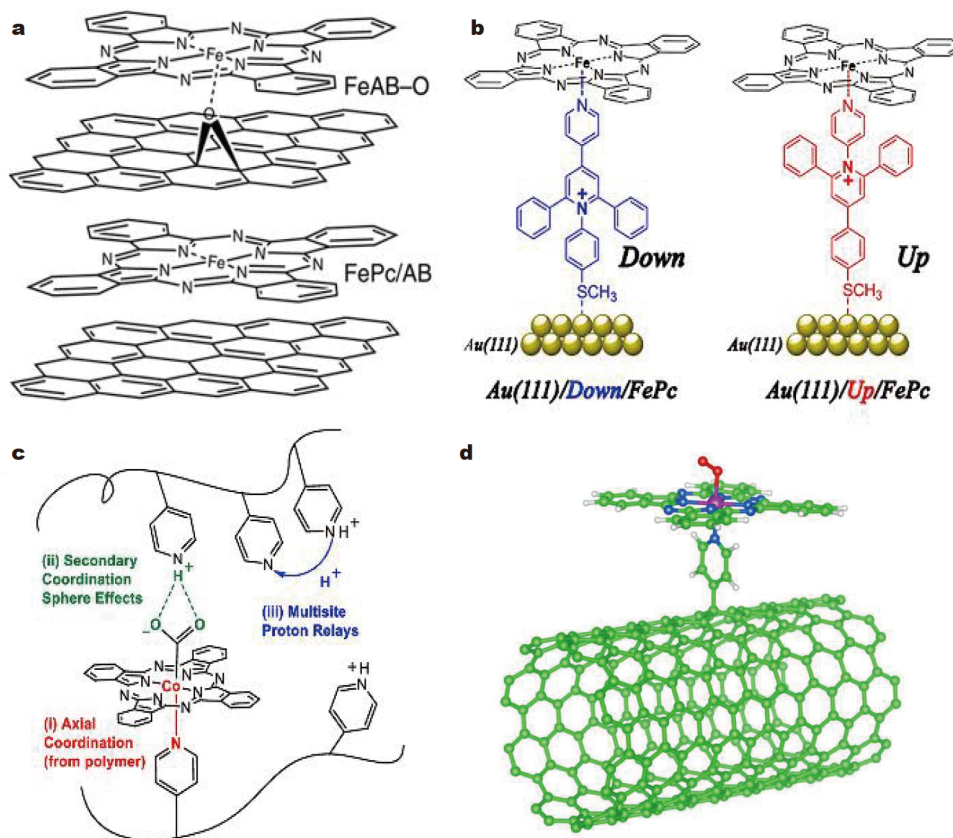


Figure 3 Axial ligand interactions of MPcs. (a) Molecular structure of FePc anchored onto oxygen-functionalized acetylene black. Reprinted with permission from Ref. [38]. Copyright 2020, Springer Nature. (b) Structure of self-assembled Au (111)/Down or Up/FePc. Reprinted with permission from Ref. [39]. Copyright 2018, American Chemical Society. (c) CoPc molecule surrounded by P4VP and its process for CO₂RR. Reprinted with permission from Ref. [43]. Copyright 2021, American Chemical Society. (d) Schematic illustration of the CoPc-py-CNT. Reprinted with permission from Ref. [50]. Copyright 2018, Elsevier.

group. Coordination engineered CoPcs are beneficial to the formation of *COOH and the desorption of *CO (intermediates for CO₂RR), thus increasing the activity for the CO₂RR. CoPcs coated with a poly-4-vinylpyridine (P4VP) film show higher activity and selectivity compared with the pristine CoPc. Pyridine-coordinated CoPc has a nucleophilic Co center, enhancing the binding with CO₂ (Fig. 3c). The axially coordinated ligand increases the electron density on Co as evidenced by the red shifts in the Q band absorption in UV-Vis spectrum. Surprisingly, the P4VP film can suppress the HER without hindering the CO₂RR, meaning that both factors contribute to the increase in the CO₂RR [41–43].

Polymerization of MPcs

The aggregation of MPcs inhibits catalytic reactions, because the active sites are blocked in MPcs. Polymerization of MPcs has been used to prevent such aggregation. The 2D structure of MPc allows polymerization between MPcs, leading to the formation of well-assembled thin layers on substrates. Han *et al.* [44] synthesized polymerized 1,2,4,5-tetracyanobenzene with CoPc on CNT (cobalt polyphthalocyanine on CNT, CoPPc/CNT). They observed *via* high-resolution transmission electron microscope (HRTEM) that the amorphous polymeric layer of CoPPc with a thickness of approximately 5 nm was coated onto CNT. The polymerized film is uniformly deposited on CNT *via* strong π - π interaction and active sites (Co²⁺) are exposed without blocking

(Fig. 4a). The structure could provide high conductivity and a high surface area, indicating that the CoPPc induces a very high turnover frequency (4900 h⁻¹ at 0.5 V) for the CO₂RR with long-term stability. Two-dimensionally polymerized MPcs construct metal-organic frameworks with mass structures with covalent bonds between the MPcs. Once the molecules are connected alongside each other with a covalent bond, they can form a well-aligned single-atom site without stacking, and the improved conjugation also enhances the charge transfer during high π -electron delocalization in the polymerized structure [45,46]. The 2D closely packed amide iron phthalocyanine polymer has good oxygen reduction activity due to the free electrons from highly delocalized π -bond. The flat-chained structure derived from the close-packed polymer of phthalocyanine forms the more delocalized and stronger π bond (Fig. 4b). This structure was confirmed by HRTEM with the interplanar spacing of the lattice fringes of 2.8 Å, indicating the existence of the regular planar phthalocyanine molecular structure [47]. Linker-free polymer structure of FePc was synthesized using a closing agent, resulting in a closed-edged structure without anhydride groups on FePc (Fig. 4c). The disappearance of X-ray diffraction (XRD) peak, which corresponds to FePc monomer aggregation, suggests the formation of the close-edged FePc polymer without aggregation. The close-edged FePc polymer increases the stability in electrolytes due to the absence of reactive groups such as O–H, N–H, C=O or C=N, which may

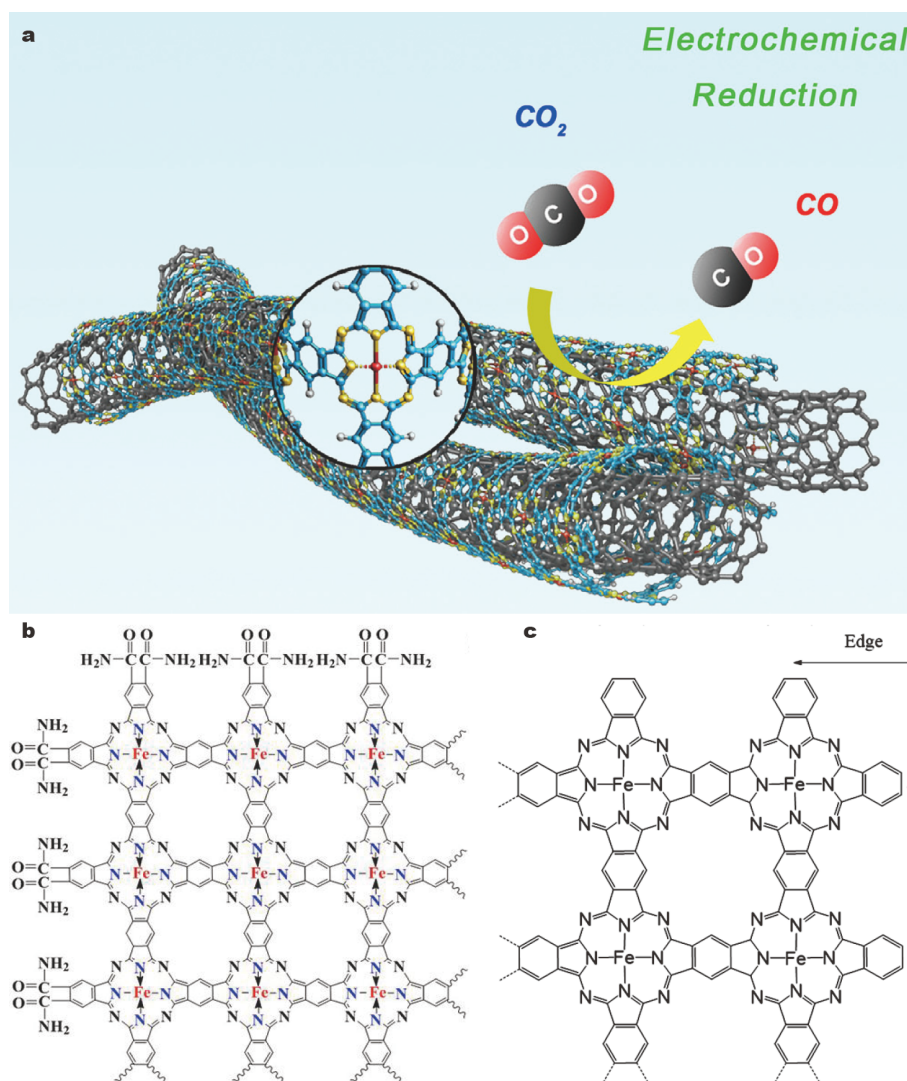


Figure 4 Polymerization of MPC. (a) Structure of polymerized CoPc surrounding CNT for CO₂RR. Reprinted with permission from Ref. [44]. Copyright 2017, Elsevier. (b) Closely packed amide FePc polymer. Reprinted with permission from Ref. [47]. Copyright 2020, Elsevier. (c) Linker-free polymer of FePc. Reprinted with permission from Ref. [20]. Copyright 2018, American Chemical Society.

cause the dissociation of FePc in an alkaline condition during ORR [20]. The well-distributed bimetallic Fe and Co phthalocyanines constructed by the Sonogashira-Hagihara coupling reaction form carbon-carbon bonds between the edge alkynes in each precursor molecule. Slightly red-shifted Q-band of UV-Vis absorbance compared with those of the corresponding phthalocyanine monomers, suggests the highly conjugated nature of the polymer [48]. The heterometallic 2D conjugated polymers (CPs) show synergetic catalytic ORRs.

Electrocatalytic reactions on MPCs

ORR

ORR is a cathode reaction in the fuel cell that converts the chemical energy of the fuel into electricity [49]. Oxygen (O₂) is reduced to water (H₂O) through a four-electron pathway, or hydrogen peroxide (H₂O₂) is produced *via* a two-electron pathway. The double bond of O₂ for an efficient ORR is completely broken by receiving four electrons producing H₂O, whereas the sluggish kinetics of ORR can lead to a two-electron

pathway, producing H₂O₂. FePc has been mainly studied for ORR because Fe is a well-known active site that can attract O₂. We discussed how the coordination of the center metal can affect the ORR performance earlier. FePc with pyridine ligand (penta-coordinated structure) shows a favorable adsorption process of O₂ and OOH on Fe sites and the spin state of OOH-FePc-pyridine is lower than that of OOH-FePc, improving the ORR activity. The higher binding energy of O₂ and OOH leads to a half-wave potential of 0.915 V (*vs.* RHE), a value of ~35 mV more positive than that of commercial Pt/C [36]. The O-functional group also contributes to O₂ adsorption and activation, while breaking the symmetrical electronic density and promoting the electronic localization of Fe sites. Fe-O coordination-induced electronic localization increases the adsorption energy of O₂ and the charge transfer from the Fe-O site to the adsorbed O₂, promoting the reduction of oxygen. As a result, Fe-O shows a superior half-wave potential of 0.9 V (*vs.* RHE), which is 30 and 50 mV more positive than the corresponding values of the pristine FePc without O-coordination and Pt/C (Fig. 5a) [38]. FePc with an NH₂ axial ligand also shows efficient ORR per-

formance. The high electron-donating property of NH_2 plays an essential role in the electron-deficient Fe active sites. As seen in Fig. 5b, the NH_2 axial ligand attached onto FePc shows the most positive half-wave potential (0.92 V vs. RHE), compared with other axial ligand catalysts of FePc/CNT-OH (0.89 V vs. RHE), FePc/CNT-COOH (0.87 V vs. RHE), and bare FePc/CNT (0.85 V vs. RHE) [16]. MXene also contributes to the ORR by reducing the electron density of Fe. The hydroxyl and fluorine terminations on MXene which have high electronegativity decrease the local electron density of Fe active sites. It causes electron delocalization around Fe. The strong delocalization of Fe induces the orbital overlap of Fe 3d with O 2p, and favors the Fe d_{z^2} electron transfer to O 2p orbitals. This facile electron transfer boosts the oxygen adsorption on Fe active sites and the reduction of O_2 , presenting a more positive half-wave potential of 0.9 V (vs. RHE) than pure FePc (0.85 V vs. RHE) and Pt/C (0.84 V vs. RHE) [17]. There are a few CoPc catalysts for the ORR. CoPc usually promotes the two-electron pathway in ORR due to its low adsorption energy for O_2 molecules. However, increasing the coordination number from Co-N4 to Co-N5 leads to the four-electron pathway. Pyridine-anchored CoPc which has a Co-N5 structure is shown in Fig. 3d [50]. Interaction between the metal substrates and metal center of MPCs can

also change the coordination of the metal center. The changed coordination of CoPc contributes to the breakage of the O-O bond for ORR. The Ag (111) surface can act as a fifth axial ligand for Co sites in CoPc. Thus, the electron transfer from Ag (111) to CoPc promotes the adsorption of O_2 . It has been verified from a charge analysis that the Co metal of bare CoPc receives a charge of 0.77e. However, the Co metal of the CoPc on the Ag (111) receives more charge (0.98e) [21].

The covalent bonds between MPCs induce free electrons in polymerized structures, which contributes to faster electron transfer and superior stability for ORR. The 2D closely packed amide polymer of FePc can hold a larger π -bond than a single FePc. The enlarged π -bond increases the delocalization energy, making the polymerized structure more facile to gain or lose electrons. Therefore, this structure shows a more positive half-wave potential (0.87 V vs. RHE), compared with that of FePc (0.71 V vs. RHE) and even better than commercial Pt/C (0.83 V vs. RHE) [47]. The linker-free 2D polymer of FePc has the closed edge structure that enhances the stability of the polymeric system in an alkaline electrolyte, and the absence of the anhydride groups at the edge may prevent the dissociation of the catalyst in the electrolyte during the ORR. The half-wave potential for the linker-free FePc polymer has been found to be 30 mV, more

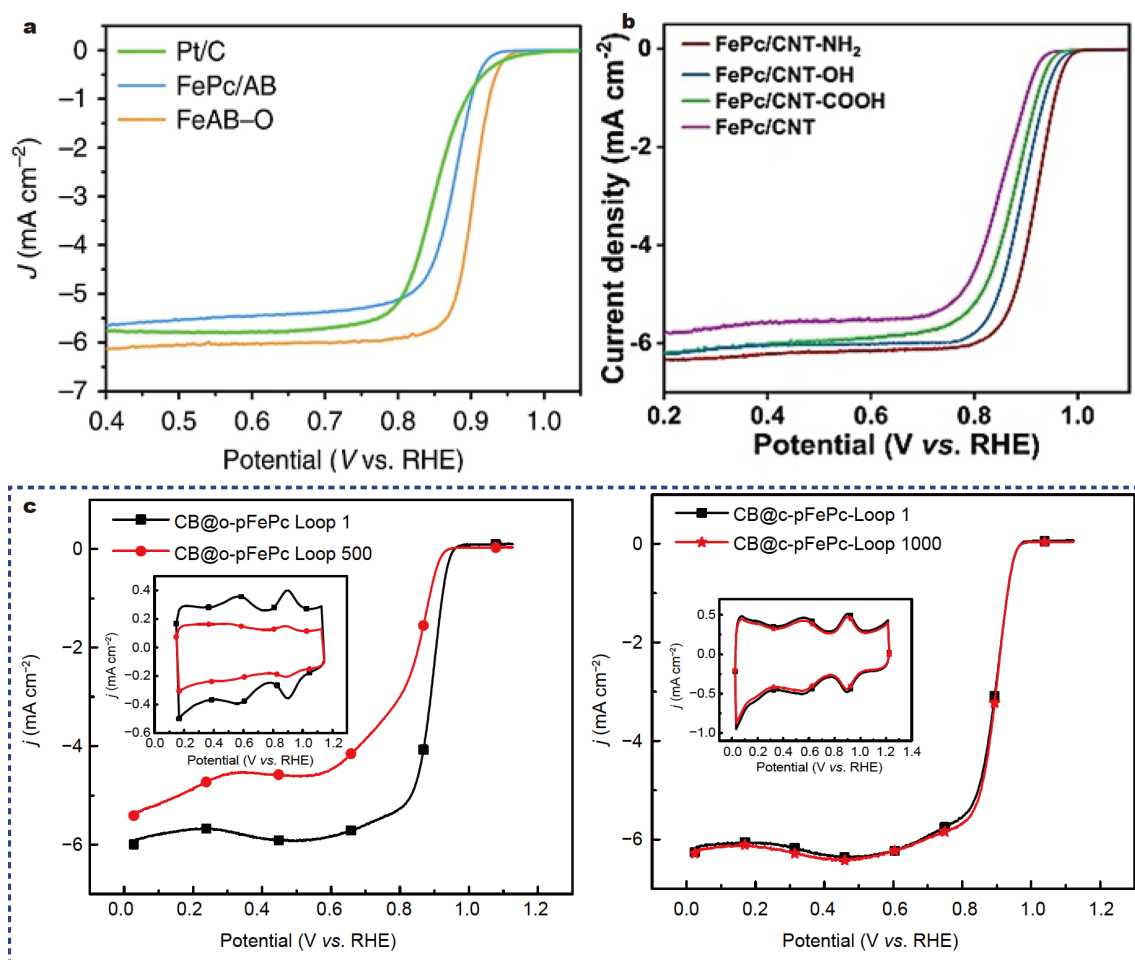


Figure 5 ORR performance of MPCs. (a) Linear sweep voltammetry (LSV) curves for FePc with O-coordination on the CNT. Reprinted with permission from Ref. [38]. Copyright 2020, Springer Nature. (b) LSV curves for FePc/CNT with different substituents. Reprinted with permission from Ref. [16]. Copyright 2021, Wiley. (c) LSV curves for the open-edged FePc polymer before and after 500 potential cycles (left) and LSV curves for the close-edged FePc polymer before and after 1000 potential cycles (right). Reprinted with permission from Ref. [20]. Copyright 2018, American Chemical Society.

positive than those of the FePc monomer or commercial Pt/C. Moreover, the closed-edge polymer shows no change of the catalytic activity even after 1000 cycles of potential cycling, whereas the open-edge polymer shows a dramatic loss of oxygen reduction performance after 500 potential cycles (Fig. 5c) [20]. Heterometallic 2D polymer promotes the $2e^- + 2e^-$ pathway for ORR by providing multi-metal active sites, Fe and Co. Oxygen reduction in the heterometallic FePc/CoPc firstly proceeds at the Co center by a $2e^-$ reduction pathway *via* peroxide generation. Then, the Fe center reduces the peroxide by another $2e^-$ reduction pathway to complete the whole oxygen reduction process, with a smaller activation barrier than those of both homometallic models. The well-arranged heterometallic structure stemming from the Sonogashira-Hagihara coupling reaction between the terminal groups from Co[Pc(ethynyl)₄] and the Fe[Pc(I)₄] can more capably utilize the multi-active sites to reduce oxygen. The synthesized catalyst reveals significantly enhanced ORR performance with a half-wave potential of 0.86 V *vs.* RHE, compared with the CoPc polymer (0.72 V *vs.* RHE) and the FePc polymer (0.80 V *vs.* RHE) [48].

CO₂RR

Electrocatalytic CO₂RR can facilitate the conversion from CO₂ to fuels or valuable carbon-based chemicals [51,52]. CO₂RR involves multi-proton coupled electron transfers, producing various C1 products with a relatively low potential range, which is overlapped with HER. The transition-metal center on MPCs has higher selectivity for CO₂RR than for HER, because its aromatic sites prevent short *H binding distances, reducing the potential for the Volmer-Heyrovsky pathway to appear [53]. CoPc and NiPc are well-known electrocatalysts for CO₂RR among transition metal phthalocyanines [54,55]. The conversion from CO₂ to CO on CoPc has been studied extensively. Density functional theory (DFT) simulations reveal that the Co metal in CoPc has profit binding energy of CO₂ reduction intermediates, *CO₂ and *CO, leading to the efficient production of CO on the active Co sites [56]. Similar to ORR catalysts, coordination-modified CoPc shows enhanced catalytic activity for CO₂RR. The NH₂ axial ligand on CoPcs makes the Co metal center nucleophilic, because it receives electrons from the electron-donating NH₂ group, affecting the binding energy of CO₂. NH₂-CoPcs shows high faradaic efficiency for CO production (~100% at -225 mA cm⁻²) at -0.6 V *vs.* RHE, maintaining their stability for 100 h of operation [40]. The coordination of CoPc can be also changed by the pyridine axial ligand. The axial ligand cre-

ates a gap in the faradaic efficiency between the pristine CoPc (60%) and pyridine coordinated CoPc (92%) at -1.25 V *vs.* RHE [42]. A functional group can prevent the aggregation of MPCs, contributing to efficient CO₂RR. CoPc-A on graphene forms a homogeneous thin layer on graphene instead of causing the aggregation of CoPc molecules. The thin layer leads to efficient electron transfer from graphene to CoPc. In Fig. 6a, the catalytic activity clearly shows enhanced faradaic efficiency from CO₂ to CO of 77% at -0.59 V *vs.* RHE, while the pristine CoPc has a faradaic efficiency of 63% [15]. NiPc functionalized with a pyrrolidone group constructs single-molecule level dispersion strongly immobilized on CNT. This highly dispersed structure shows nearly 100% CO faradaic efficiency at each potential range (-0.63 to -0.93 V *vs.* RHE) while also, providing a superior CO/H₂ ratio up to 640 at -0.88 V *vs.* RHE (Fig. 6b) [22].

NH₂-group substituted NiPc shows better faradaic efficiency of CO (almost 100% at -0.58, -0.62 V *vs.* RHE), compared with bare NiPc or hydroxyl-group-functionalized NiPc, due to the electron-donating NH₂ group that enhances the electron-donating reaction (Fig. 6c) [30]. NH₂-functionalized CoPc on CNT can prevent the harmful reduction of CoPc by lowering the reduction potential of CoPc. It shows an entirely stable current density under electrolysis at -1.0 V *vs.* RHE (between 30 and 33 mA cm⁻²), preserving the faradaic efficiency for MeOH from the pristine state (32%) for more than 12 h (28%) [32]. Perfluorinated CoPc was studied for its ability to increase the stability of the active sites for CO₂RR. Fluorine terminals decrease the affinity of the molecule toward CO, reducing the deterioration of active site with the faradaic efficiency of the reduction of CO₂ to CO up to 93% [33]. The polymerized CoPc suppresses the aggregation of CoPcs and maximizes their electrochemically active surface area, strengthening their physical and chemical properties. Template-directed polymerized CoPc on CNT presents a large faradaic efficiency of ~90% with remarkable stability for more than 24 h [44].

HER and oxygen evolution reaction (OER)

Although there are fewer electrocatalysts for HER and OER, compared with ORR and CO₂RR, the structural configuration of MPCs also affects the activities for HER and OER. *n*-Octylselanyl-functionalized copper phthalocyanine (CuPc) was prepared and characterized systematically. Interestingly, the Se-Se linkage was observed between CuPcs, and it formed a well-ordered hierarchical structure that influenced the charge transport and electronic structure, contributing to lower overpotential

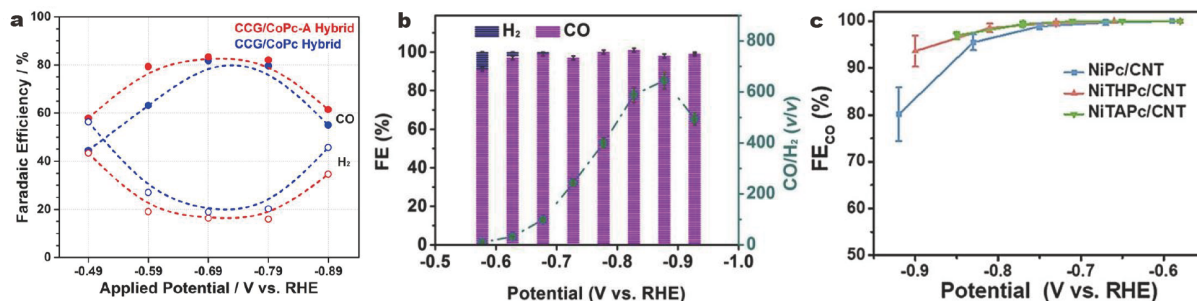


Figure 6 CO₂RR of MPCs. (a) Faradaic efficiency of CO and H₂ for CCG/CoPc-A and CCG/CoPc. Reprinted with permission from Ref. [15]. Copyright 2019, American Chemical Society. (b) Faradaic efficiency of CO and CO/H₂ ratio for pyrrolidone group-functionalized NiPc on CNT. Reprinted with permission from Ref. [24]. Copyright 2019, Elsevier. (c) Faradaic efficiency of CO for NiPc with terminal groups. Reprinted with permission from Ref. [30]. Copyright 2021, Wiley.

(-0.172 V vs. RHE at 10 mA cm $^{-2}$) and greater stability [57]. The electron-withdrawing SO $_3$ H functional group changes the electron density of CoPc and imparts enhanced activity for OER (the overpotential of 0.390 V vs. RHE at 10 mA cm $^{-2}$) [58]. Polymerized CoPc can also be used for OER with an overpotential value of 0.370 V vs. RHE, owing to its favorable adsorption property for intermediates of OER [59].

SUMMARY AND OUTLOOK

This review summarized the promising electrochemical performance of MPcs with structural modification for ORR, CO $_2$ RR, HER and OER. Nitrogen reduction reaction (NRR) using MPC has also been reported, but the number of reports is very small. Although the feasibility of NRR is controversial, the strategies used above can be used in NRR. We classified the four factors related to the structural configuration of MPcs: first, the supporting materials. It is necessary to deposit the MPcs on conducting substrates due to its semiconducting property. Second, terminal functionalized MPcs enhance the solubility and contribute to the homogeneous distribution of MPcs, preventing the aggregation of MPcs. The homogeneous thin layer of MPcs has the advantage to accept electrons, which makes a facile catalytic reaction. Additionally, terminal functional groups that donate or accept electrons can tune the electron density of the metal center. Third, the extra coordination of the M-N $_4$ center in the axial direction is built by vertically aligning functional groups or ligands. This interaction tunes the coordination of M-N $_4$ from four to five to enhance the catalytic activity. Last, polymerization of MPcs has been used to prevent molecular aggregation. The 2D structure of MPC constructs polymerization between MPcs, leading to the formation of finely assembled thin layers of MPcs.

Although previous studies make an effort to promote the electrocatalytic reaction of MPcs, which have modified geometric structures for enhancing catalytic performance, they still face challenges, such as the precise investigation of the configuration of MPcs. Most previous reports focus on tuning the molecular structure but not the bulk scale. It is necessary to observe the specific arrangement of the molecules on a few-layer scale. Therefore, the synthesis of well-aligned MPcs and the understanding of their structure are two emerging issues in the research of MPcs as electrocatalysts. Thus, researchers need to develop an in-depth study of the molecular orientation and its effect on the electrocatalytic mechanism.

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



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