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Two and Three Dimensional Network Polymers for Electrocatalysis

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th March 2014,
Accepted 00th March 2014

DOI: 10.1039/x0xx00000x

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Recently, two and three dimensional network polymers have started to gain traction in the research sphere as scientists look for ways to create materials with more tailored properties. These network polymers show high surface area and specific, sometimes periodic, functionality, providing perfect templates both to host electrocatalytic materials as well as function as electrocatalysts themselves. While doped carbon based materials such as graphene and carbon nanotubes, as well as diamond, have demonstrated their electrocatalytic potential, other network polymers have yet to be synthesized in a manner to optimize their potential. As these polymers are built of a periodic arrangement of appropriately functionalized monomers, an exact arrangement of functional sites should be possible, which combined with potentially high surface areas should lead to very high catalytic activity. This perspective will cover the synthesis and achievements of the mentioned doped carbon materials before taking a look at the strengths, shortcomings, and future goals in electrocatalysis as related to more novel network polymers.

1 Introduction

In recent times, global interest with “clean energy” has only accelerated as concerns about both the environmental impact and long-term viability of fossil fuels continue to grow. One particular technology that is often overlooked is that of fuel cells. Fuel cells have been around for a long time, and it was around the early 2000's that various car manufacturers trumpeted hydrogen fuel cells as the future of automobiles. That future mysteriously disappeared as the research challenges proved much greater and the cost much higher than originally anticipated. In fact, it is only recently that fuel cells have been brought back on the table as a potential candidate for powering the vehicles of the future. In addition, as the role of renewable energy has expanded, fuel cells are also potential candidates for power generation in remote areas, or as part of a system to store and convert the energy from intermittent renewable sources like solar or wind. However, no matter the application, there are a few limiting factors that are affecting the wide-spread implementation of fuel cells, according to the U.S. Department of Energy: cost, durability and reliability, system size, air thermal and water management, as well as improved heat recovery systems.¹ Of these limiting factors the cost and the durability are heavily influenced by a single component: the electrocatalyst.²

In the most highly researched type of fuel cell for transportation, the hydrogen fuel cell, the current catalyst is platinum nanoparticles suspended on glassy carbon. Platinum is obviously a poor choice from a cost perspective, being as it is a rare noble metal. In addition, platinum suffers from stability/durability issues; it is prone to be easily dissolved in electrolyte and agglomerates into larger particles, decreasing the active surface area, as well as suffers from poisoning issues from CO and methanol.^{3–5} Research efforts toward the improvement of catalytic properties have focused on the oxygen reduction reaction (ORR), as that is the rate-limiting step.^{6,7} There are generally three different research approaches taken to try and improve the electrocatalyst: (1) reduction of the Pt-loading,⁸ (2) development of non-precious metal catalysts,^{9–11} and (3) development of metal-free catalysts.^{6,12,13} While the properties of a typical Pt/C electrode are well known and fairly optimized, simply reducing the Pt loading will only lower the cost; poisoning will still remain as a major issue. Therefore, focusing on (2) and/or (3) will have the most long-term benefit. Network polymers can take advantage of both avenues of research, depending on the type of network. Overall, these networks generally include ordered carbon structures as well as the class of materials known as covalent organic frameworks (COFs). While the, generally metal-free, catalytic potential of the carbon structures has been demonstrated and continues to improve, research on COFs has

thus far focused on hydrogen storage applications,^{14–16} likely due to their large surface area and low electrical conductivity. However, these materials make prime candidates for highly tailored catalysts due to their periodic and specific functionality, as well as their high surface area. Here, recent advances in carbon-based structures will be reviewed first, followed by a review and perspective on the use of COFs in electrocatalysis.

2 Carbon-based Networks

In order for carbon structures to be useful for electrocatalytic purposes, they must be doped with other elements, which generally include nitrogen, boron, phosphorus, and sulphur.^{6,7,17} In particular, nitrogen is a favourite due to its larger electronegativity and extra electron pair, as well as the ease with which it can be doped into the carbon framework, due to its similar atomic size to carbon. There are many different methods that have been developed to introduce nitrogen into various carbon compounds and all are based on one of two different overall approaches: (1) direct incorporation in the carbon framework by displacing a carbon atom with a nitrogen atom, or (2) functionalization of the carbon framework with an additional nitrogen containing group. Both methods have produced compounds that have high electrochemical performance, though in most cases any sort of surface functionalization with a nitrogen-containing group, where the group is attached to the framework, is accompanied by direct (substitutionary) nitrogen doping into the carbon framework itself due to the harsh attachment methods used. The different carbon frameworks used for electrocatalytic purposes generally include graphite/graphene, carbon nanotubes (CNTs), and 3D carbon structures (ordered or otherwise). Graphene and CNTs share many of the same synthesis methods, while all of these materials share a few methods of doping. For the purposes of this review, graphene will be used as an illustrative example of the various synthetic and doping methods available, while a key aspect of 3D carbon networks will be mentioned as it pertains to COF use in electrocatalysis.

2.1 Graphene and CNTs

Graphene and carbon nanotubes (CNTs) are two highly ordered carbon network structures that are the focus of many research efforts in various fields including electrocatalysis due to their outstanding properties, which are high electrical conductivity, modestly high surface area (depending on treatment), high mechanical strength, high thermal conductivity, and high stability.^{18,19} While CNTs have their own challenges, the two materials share similar synthesis and doping methods; therefore, further discussion will be limited to examples from a graphene perspective. Only a modest overview will be given here, as a recent review covered the topic in an in-depth manner.²⁰

Graphene can be synthesized in a number of different ways including chemical vapour deposition (CVD),²¹ arc discharge,²² oxidation/reduction,²³ solvothermal reaction,²⁴ and by ball-milling.²⁵ All of these methods are capable of in-situ doping as well. As for post synthesis methods there are four different treatments for doping graphene: (1) a thermal treatment, (2) a plasma treatment, (3) an N_2H_4 treatment and (4) an NH_4OH treatment.

2.1.1 CHEMICAL VAPOR DEPOSITION

CVD is by far and away the most popular method of creating high quality graphene. In CVD, a carbon source, along with other elements if desired, is vaporized and deposited on a supporting substrate. Generally a metal support (Ni, Cu, or Pt) is used as a substrate to help catalyze the reaction.^{26–29} In order to create a nitrogen doped graphene, a gaseous mixture containing both a carbon source (e.g., methane or ethylene) and a nitrogen source (e.g., ammonia),^{27–29} or a liquid single source containing both carbon and nitrogen (e.g. pyridine or acrylonitrile),^{30,31} must be used. Following formation of the graphene layer(s), the metal is etched away using acid.^{26–30} Phosphorus and boron doped materials can also be obtained by using the appropriate precursors.^{32,33} Of interest is also the possibility of co-doping *via* CVD, in particular, boron-nitrogen co-doped graphenes.³⁴ Advantages of CVD are that it is straightforward, has a broad range of N sources available, and is generally scalable; disadvantages include corrosion of equipment due to precursors, very precise control needed over the gas flow rates, very harsh synthesis conditions, and most important from a commercialization perspective, high cost.

2.1.2 ARC DISCHARGE

In this method graphite electrodes are vaporized in the presence of a nitrogen precursor resulting in N-doped graphene.²⁰ Hydrogen gas should be present in the reaction environment in order to prevent the graphene sheets from rolling up into carbon nanotubes.^{35,36} B-doped graphene can be obtained by this method when B_2H_6 is added to the reaction mixture.^{35,36} Advantages include clean synthesis (no impurities to worry about) and potential large scale synthesis; the major disadvantage is the harsh reaction conditions.

2.1.3 SOLVOTHERMAL REACTION

A typical solvothermal synthesis involves mixing precursors and solvent in a sealable autoclave and then heating the mixture to a set temperature for a set time. One solvothermal approach in the literature to produce N-doped graphene is through the direct reaction of tetrachloromethane with lithium nitride.³⁷ A solvothermal synthesis of undoped graphene has also been reported using sodium and ethanol;³⁸ this method may be able to be modified to allow for the addition of a nitrogen precursor to facilitate nitrogen doping. The

Table 1. Overview of N-doped carbon synthesis methods with an eye toward commercialization

Synthesis Method	Well-studied	Control over Doping Position	Reaction Conditions	Quality of Product	Steps	Time	Quantity of Material Obtained	Scale up	Cost	Ref.
CVD	Yes	Yes	Harsh; corrosive reactants; precise control necessary	Best	2-3	~3 hr	Depends on substrate size	Easy; very straightforward	High	26-34
Arc Discharge	Yes	No	Harsh; plasma formation; large current	High	1-2	~1 hr	High	Easy; large area sheets possible	Moderate-high	35,36
Solvothermal	No	No	Mild; low temp	High	5	24 hr+	Depends on size of autoclave	Possible; large quantities possible but many washing steps	Moderate-high	37,38
Ball Milling	No	Yes	Mild; room temp	High	2	48 hr+	Depends on size of ball mill	Easy	Low	17,25,39
Thermal Treatment	Yes	No	High Temp	Medium-Poor	2-3	~4 hr	Limited by starting amount of graphene	Possible; creation of GO requires strong acids	N/A	40-46
Plasma Treatment	Yes	No	Harsh; plasma formation	Medium-Poor	1-2	<40 min	“	Possible; requires large plasma reactor	N/A	20,42,47,48
N ₂ H ₄ Treatment	Yes	Yes; low doping	Mild; low temp; possible ultrasonication	Poor	7	~17 hr+	“	Possible; lots of steps	N/A	47
NH ₄ OH Treatment	No	No	Mild; low temp; sonication	Medium	6+	~36 hr+	“	Possible; lots of steps	N/A	49,50

advantages of the solvothermal approach include easy scale-up, simplicity of method, and a low reaction temperature, with the disadvantages being that little research has been done into the method and graphene is of relatively poor quality compared with CVD.

2.1.4 BALL-MILLING

A very new technique involving ball milling of graphite in the presence of various gaseous elements to yield edge selectively functionalized graphene has recently been created by Jeon *et al.*^{17,25,39} In this method, graphite is loaded into a planetary ball-mill along with stainless steel balls and a choice of functionalizing compound, which can range from dry ice to various substances such as halogens, nitrogen and sulphur.

After ball-milling the final compound is washed with acid to remove any potential metallic impurities. Many different edge groups have been added to the graphene nanoplatelets (GNPs) using this method, including hydrogen, carboxylic acid, sulfonic acid, chlorine, bromine, iodine, and nitrogen. This method has a number of advantages among which are ease of synthesis, direct functionalization, diversity of functionalization, lack of damage to the basal plane of the graphene, mild reaction conditions, easy suspension in polar solvents (including water) for solution processing, and high scalability. The disadvantage of this method is that while the quality is quite high, it is still poorer than CVD grown graphene.

2.1.5 THERMAL TREATMENT

In a typical thermal treatment, nitrogen is introduced by subjecting carbon materials (typically oxidized) to a nitrogen rich atmosphere (NH_3 or melamine) at high temperature.^{40–43} This thermal annealing technique can also be used to synthesize B, S, or I-doped graphene, using boron oxide, benzyldisulfide, or iodine, respectively.^{44–46}

2.1.6 PLASMA TREATMENT

In this method graphene or graphene oxide (Fig. 1, synthesized from graphite by a modified Hummers method^{42,47}) is subjected to a N_2 or NH_3 plasma. The plasma treatment creates defect sites that can readily react with nitrogen, while the final N-content depends on the exposure time and plasma strength.^{20,48} A potential problem with this method is excess damage to the graphitic structure, which would decrease the electrocatalytic performance.

2.1.7 REDUCTION OF GRAPHENE OXIDE (GO)

A $\text{N}_2\text{H}_4/\text{NH}_3$ mixture may be used to simultaneously reduce and nitrogen dope GO at a temperature lower than 160 °C.⁴⁷ However this method has potential problems with agglomeration of the graphene sheets into a graphite-like structure.

Additionally NH_4OH can be used to reduce the graphene oxide instead of a $\text{N}_2\text{H}_4/\text{NH}_3$ mixture in order to produce what the authors term amine functionalized graphene (AFG).⁴⁹ This last approach has since been modified by Jiang *et al.* to include an additional “hole-creating” step in the graphene basal plane after successful doping to form amine functionalized holey graphene AFHG.⁵⁰ The advantages of this holey graphene are a highly increased surface area and the introduction of large pore channels. It appears that based on the results from this material, as well as the following ones, that creating a porous structure is the next step in increasing the utility of metal-free catalysts.

2.2 Three Dimensional Carbon Frameworks

The methods of synthesizing graphene discussed thus far usually lead to single or few layer sheets of graphene; while such sheets may agglomerate into a 3D structure such an action generally leads to a reduction in surface area and a reduction in electrocatalytic activity. Therefore it is highly desirable to disperse the graphene sheets. This can either be done chemically by functionalization or sonication or by using either spacers or a template to create a 3D structure with a high surface area.

2.2.1 CARBON AEROGELS

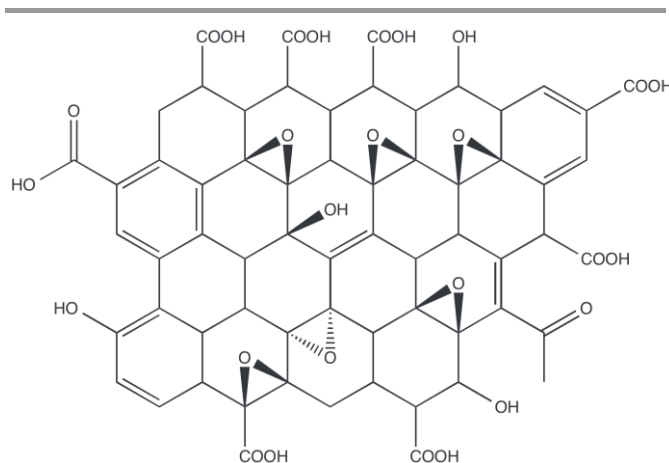


Fig. 1 Graphene oxide is used as the starting material for almost all post-synthesis doping. Due to the large amount of oxygen species the basal plane of the graphene is highly damaged, and successful reduction does not completely repair it, especially without an additional carbon source, leading to poor quality material.

A hydrothermal method for creating a nitrogen and sulphur dual-doped carbon aerogel has been reported by Wohlgemuth *et al* using glucose as the carbon source, ovalbumin as the nitrogen source, and either S-(2-Thienyl)-L-cysteine (TC) or 2-thienyl-carboxaldehyde (TCA) as a sulphur source.⁵¹ A typical synthesis involves mixing all of the precursors together with water in an autoclave and heating to a moderate temperature, followed by drying with supercritical CO_2 . The dried product is then pyrolyzed at high temperature. This method has the advantage of dual-doping elements, cheap precursors, and easy synthesis, with the disadvantage being lack of order.

2.2.2 CARBON HYDROGELS

Jiang *et al.* have recently reported the formation of a PN-doped carbon hydrogel.⁵² In order to form this hydrogel, gelation between precursors occurs at low temperature, followed by thawing and chemical crosslinking. Doping is accomplished by immersing the material in an appropriate solution, in this case cyanamide and phosphoric acid. The resulting product is then heat treated at high temperature. The material showed high surface area and electrocatalytic activity. This method has the advantage of high surface area, dual doping, and reasonably controllable doping levels.

2.2.3 GRAPHENE/CNT COMPOSITES

Using spacers to separate the graphene sheets and thus increase surface area has been investigated by a number of researchers, with schemes of varying levels of complexity. A favourite spacer for graphene is CNTs, due to the similar properties between the two materials, such as high conductivity, carbon based structure, and demonstrated electrocatalytic potential. CNTs have the benefit of being

rigid, which means they can be used to separate the graphene layers.

In a simple scheme Wang *et al.* mixed GO and partially opened multi-wall CNTs in water to form a layered structure with the CNTs spacing the graphene layers.⁵³ While this simple method resulted in a 3x increase of the surface area the CNTs were not arranged vertically but horizontally, limiting their spacing power and surface area.

Two more sophisticated methods for generating graphene/CNT composites have been reported. Although one of the reports is focused on capacitors, the method is illustrative of the synthesis route that may be used. The method reported by Du *et al.* begins by acid treating a piece of highly ordered pyrolytic graphite (HOPG), which is then heated to high temperature under argon. This expanded graphite is then treated using CVD, first to grow a layer of SiO₂, then to growth the CNTs.⁵⁴ It may be noted that there is no doping reported in this method, but that could potentially be easily overcome by changing the CNT precursor. Using a similar procedure Ma *et al.* starts with GO, reduces and loads the graphene with Ni in a sonication step, and then uses CVD, with pyridine as the precursor, to grow N-doped CNTs on the graphene surfaces, demonstrating a doped graphene-CNT composite.⁵⁵ This composite showed increase surface area and activity, but still left much room for improvement in terms of structural ordering and amount of doping.

2.2.4 ORDERED MESOPOROUS CARBONS

A potential way to overcome the ordering problem is to use a template. As such a class of materials that will be illustrative for later discussion are ordered mesoporous carbons (OMCs). OMCs are carbon materials characterized by regular arrays of uniform mesopores. The distinct advantage of the OMCs as compared to the carbon materials discussed in the previous section is that they can be more active because an ordered interconnected porous structure enhances the surface area (500–1900 m²/g) and the pore volume of the material.^{56–58} 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. While OMCs share in the advantages of the carbon materials discussed thus far, namely high electrical and thermal conductivity as well as high stability,⁵⁹ as well as dual doping,⁶⁰ these materials often require difficult synthesis methods, thus hindering their scale-up, though a recent report from Cheon *et al.* used a rather simple method (Fig. 2).^{56,59,61–63} Regardless of the difficulty of the synthesis, a weakness of OMCs is that they do not allow for tailored functionality. This is one of the main strengths of covalent organic frameworks, along with others that include numerous synthesis routes (many very amenable to scale-up), high surface areas, and tuneable pore size.

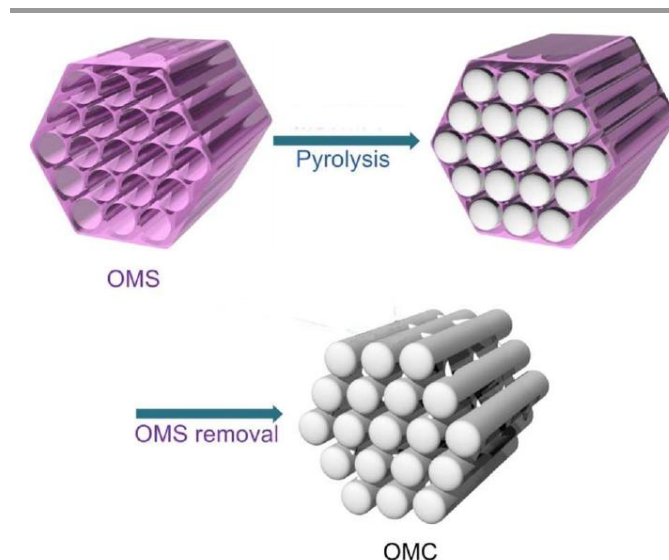


Fig. 2 Recent synthesis procedure for OMCs. Beginning with a template, in this case ordered mesoporous silica (OMS), a carbon and nitrogen source is mixed with the template and then pyrolyzed to cement the structure. The OMS is then removed by washing with HF. Adapted with permission from ref. ⁶³ © Nature Publishing Group.

3 Covalent Organic Frameworks

Covalent organic frameworks (COFs) are covalently linked networks of monomers that are ideally crystalline due to their periodic arrangements. Generally, COFs are also porous, but the definition is not incredibly well defined; graphene, though a single non-porous sheet, could be considered as one of two dimensional COFs. COFs are a more recent development that grew out of the metal organic framework (MOF) movement in order to address the shortcomings of that class of materials, namely, their issues with stability in harsh conditions, especially high temperatures and moisture.⁶⁴ The all-covalent bonding within the COF structure is much more stable than the metal coordination bonding in a MOF; nevertheless this very stability presents the greatest challenge to COF synthesis. Unlike in MOFs, where the weak metal-ligand coordination bond can be broken and restored many times during synthesis in order to create a highly crystalline framework (a so-called reversible reaction), many covalent bonding reactions are thermodynamically highly favourable, leading to strong, but ultimately irreversible bonds. This creates a lack of an error correcting mechanism during the formation of the COF, which makes synthesis of a highly crystalline framework extraordinarily difficult. Therefore, although the number and range of organic reactions, monomers, and functionalities is incredibly large, only a few distinct chemistries have emerged, based on the reversibility of the covalent bonding (Fig. 3B).^{65–67} The original COFs made use of boronic acid based linkers to form a boronate ester-linked network;⁶⁸ while providing proof of concept, these materials have a fatal weakness in their sensitivity to moisture and oxidation. For this reason nitrogen based linkers, due to their more stable bond formation, have started to gain

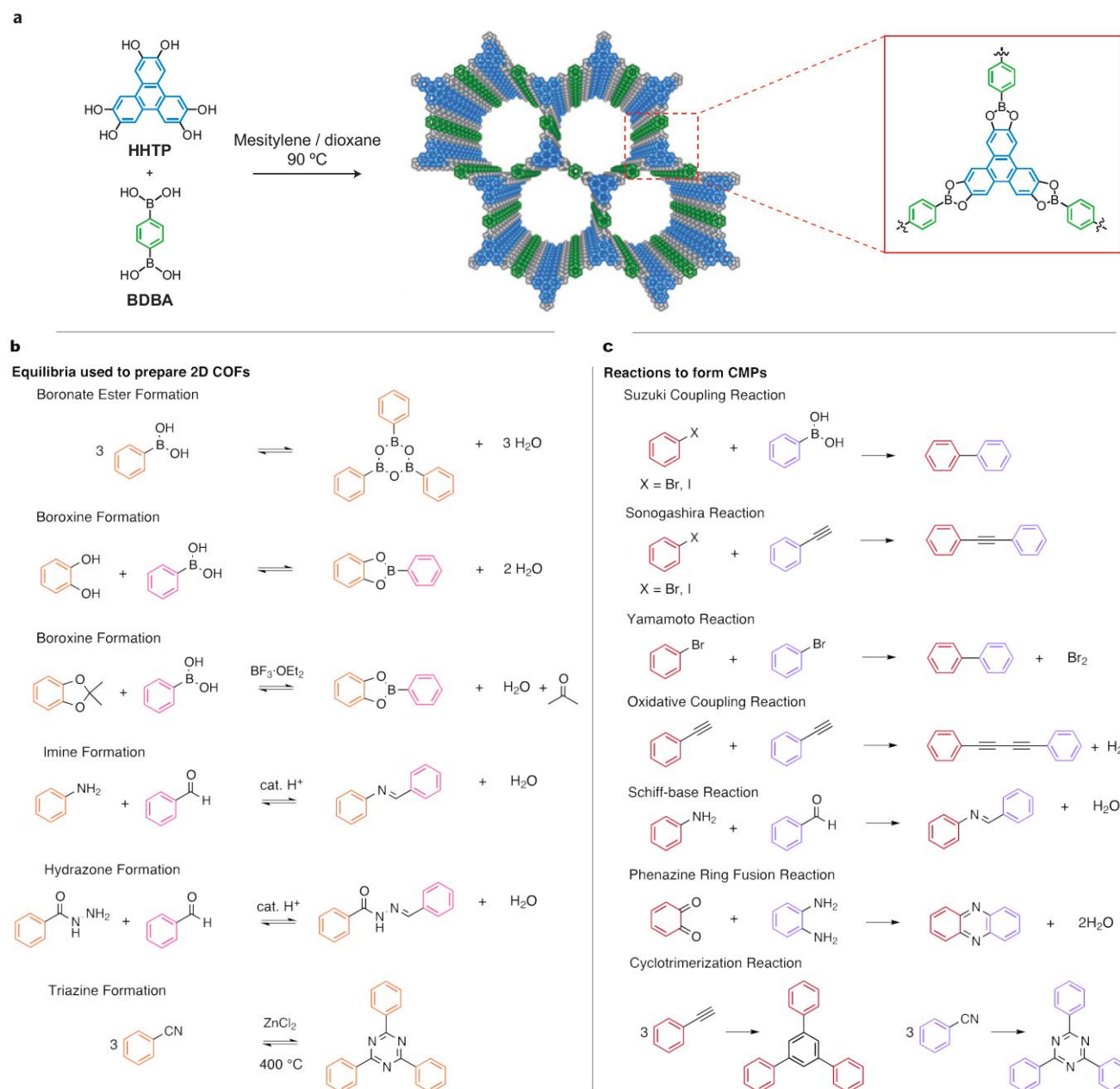


Fig. 3 (a) Condensation of HHTP and BDPA provides a prototypical 2D COF (COF-5). Unless one of the linkers has 3D functionality, most crystalline COFs will exhibit a stacked 2D layered structure. Various chemistries used for both (b) COF and (c) CMP formation. The COF reactions are generally reversible, while the CMP reactions are not. (a) and (b) Reproduced from ref. ⁶⁶ © Nature Publishing Group. (c) Modified from ref. ⁷².

traction in the research field. However, it is for this exact reason, increased bond stability and by extension decreased reversibility, that creating a crystalline version of many nitrogen linked compounds is such a challenge.^{69–71} In addition to the materials created by these reversible reactions, there is a specially related class of materials, termed conjugated microporous polymers (CMPs), made from largely irreversible reactions (Fig. 3C).⁷² The major differences between COFs and CMPs are the crystallinity (COF-crystalline and CMP-amorphous) and the conjugated structure.

However, although COFs and CMPs go under different names the terms are still by and large ill-defined; therefore, for the purposes of this review CMPs will be considered to be a special subset of COFs due to their properties, as the synthetic procedures are largely the same.

Here, the general synthetic procedures will be discussed followed by the electrocatalytic applications and challenges of the compounds discussed in this review as a whole thus far.

3.1 Synthetic Methods

3.1.1 SOLVOTHERMAL REACTION

The main method of creating COFs is a solvothermal reaction. A typical solvothermal method for preparing COFs involves the following monomers and mixed solvents are placed in a reactor under an inert atmosphere. Afterward the vessel is sealed and brought to temperature. After the reaction, the precipitate is then collected, washed with suitable solvents, and dried under vacuum to yield the COF as a solid powder. Issues such as the solubility, reaction rate, crystal nucleation, crystal growth rate, and 'self-healing' structure are important points to consider when selecting the reaction media and conditions.⁶⁵ Solvent combinations and ratios are important factors in balancing between framework formation and crystallization when synthesizing highly crystalline COFs. For boronate ester and boroxine linked COFs, solvent combinations such as dioxane/mesitylene,^{68,73} DMAc/*o*-dichlorobenzene,⁷⁴ and THF/methanol⁷⁵ have been employed. In contrast, dioxane/aqueous acetic acid has been used as the solvent for imine-linked COFs,⁷⁶ while mesitylene/dioxane/aqueous acetic acid was effective for hydrazone linked COFs.⁷⁰ In all cases, a suitable concentration of the building blocks in the solvent system is necessary for the reaction to proceed under thermodynamic control. At the same time, a suitable temperature is important to ensure the reversibility of the reaction. Generally, COFs have been prepared at temperatures ranging between 85–120 °C depending on the chemical reactivity of the building blocks. A closed reaction environment is required to allow the presence of water molecules that could trigger the reverse reaction in the system.

CMP formation follows the same basic solvothermal methods as mentioned above, but it does not generally use a sealed vessel; instead the reactants are simply allowed to stir at temperature, generally under reflux. There are many different chemical reactions for the formation of CMPs, including the Suzuki cross-coupling reaction, the Yamamoto reaction, the Sonogashira–Hagihara reaction, the oxidative coupling reaction, the Schiff-base reaction, the Friedel–Crafts reaction, the phenazine ring fusion reaction, and cyclotrimerization. For an in-depth look at the monomers and reactions available, please see the recent review by Xu et al.⁷²

3.1.2 MICROWAVE ASSISTED SYNTHESIS

An alternative method for the rapid synthesis of certain COFs is microwave-assisted synthesis. Microwave synthesis provides several advantages over solvothermal methods: microwave synthesis produces COFs rapidly, a sealed vessel is not required for the microwave synthesis, and the microwave solvent extraction process removes residues and impurities trapped in the frameworks more efficiently, which promotes better porosity.^{77,78} Of these advantages, the rapid synthesis makes a large difference from a scale up and application perspective. With further research the microwave protocol

could provide a powerful replacement for the solvothermal method.

3.1.3 IONOTHERMAL SYNTHESIS

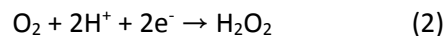
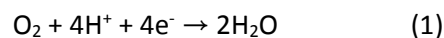
A third method for COF creation, ionothermal synthesis, has only been used to synthesize a small subset of COFs, namely covalent triazine frameworks (CTFs).^{69,79,80} The cyclotrimerization of aromatic nitrile building units in molten ZnCl₂ at 400 °C affords crystalline conjugated CTFs with robust chemical and thermal stabilities. ZnCl₂ acts as both the solvent and the catalyst for the trimerization reaction, which appears to be partially reversible. However, the harsh reaction conditions limit the useable monomers. Most of the synthesized CTFs are amorphous materials that lack long range order.

3.1.4 SURFACE ASSISTED SYNTHESIS

Because covalent linkers that are inherently three dimensional (as opposed to 2D planar) are a rarity, most COFs ideally exist as stacked 2D layers. In order for in-depth study, imaging, and application various methods have been employed to obtain a single layer (or few layers) of material. A general approach to do this is the use of a solid substrate/template during synthesis to direct the formation of a COF in the planar direction without allowing for many-layer formation (Fig.4). Two different deposition techniques, evaporation and solvothermal reaction, have been used with different substrate materials including the (111) face of Ag,⁸¹ highly ordered pyrolytic graphite (HOPG),^{82–84} as well as graphene.^{85–87} Only reversible COF reactions have been used with templates thus far; finding a method to be able to template generally irreversible reactions may lead to crystalline versions of many CMPs, which may show desirable electronic properties due to their fully conjugated nature. Choosing monomers that sublime easily could be one potential route for the formation of these highly ordered CMPs. These highly ordered COFs would be most useful for mechanistic studies, both in electrocatalysis and other fields.

4 Electrocatalysis

As was explained in the introduction to this review, electrocatalysis, especially the oxygen reduction reaction (ORR), is an active and important area of research. In a typical fuel cell, the ORR takes place at the cathode and can follow two pathways; the first is a four-electron reduction of oxygen directly to water (1) and the second is a two-step two-electron process with hydrogen peroxide as an intermediate (2 and 3).



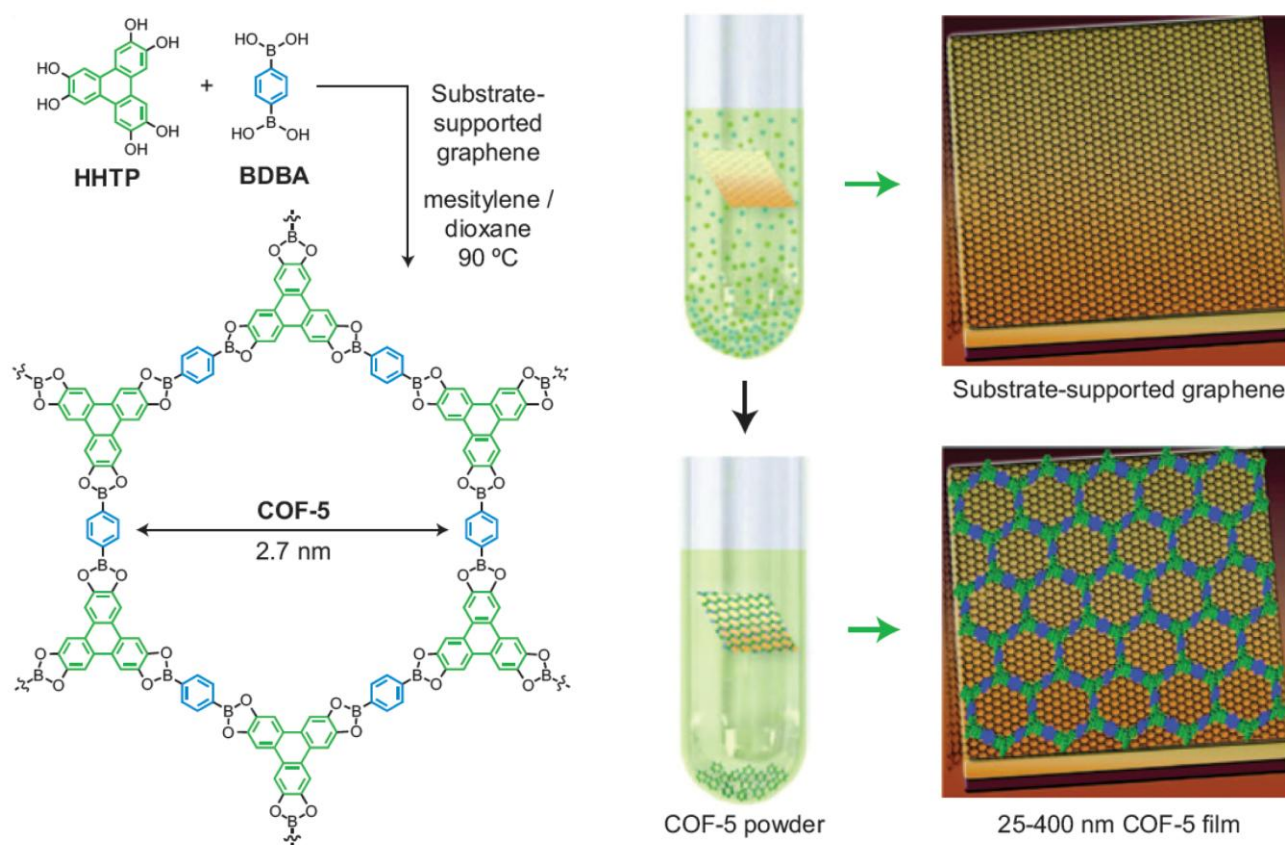
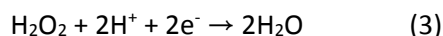


Fig. 4 Surface assisted synthesis of COF-5. The substrate directs the formation of single or few layer material (which helps with increased crystallinity); in addition, bulk powder COF will form in the solvothermal reaction conditions. This technique can be used with many different monomer systems using either solvothermal synthesis or sublimation. Reproduced with permission from ref. ⁶⁷ © Nature Publishing group.



efficient single step conversion to water is preferred. While the exact mechanics that determine whether a catalyst favors a two or four electron pathway is not known, the number of exchanged electrons, n , is still a useful measure for comparison of electrocatalytic activity. Other parameters used for comparison include the onset potential, kinetic current density (J_K), and diffusion-limited current density (J_D). Generally speaking, heteroatom-doped carbon materials show higher current densities, both kinetic and diffusion-limited, than commercially available platinum catalysts, while showing lower onset potentials (in an alkaline medium).¹² The number of electrons transferred is highly variable and only recent structures have an n value near 4.^{88–90} While the exact mechanics behind the electrocatalytic activity in doped carbon structures is still unknown, there are a few parameters that are known to have an effect on the activity level. In doped carbon structures these include the type of dopant site, the amount of carbon edge sites, the total dopant content, the surface area, and the degree of graphitization.

The presence of hydrogen peroxide is problematic as it can lead to corrosion of the fuel cell components; therefore, the more

As an example nitrogen can be found in four bonding configurations: pyridinic N (N1), pyrrolic N (N2), graphitic N (N3A&B) and oxidized pyridinic N (N4) (Fig. 5). Pyridinic N and pyrrolic N atoms are located at edge or defect sites; they do not increase the number of electrons in the delocalized π -system. Graphitic N atoms substitute carbon atoms within the basal plane (*i.e.* not at the edges). They have the same configuration as graphitic carbon atoms, but they introduce extra electrons in the delocalized π -system, due to the extra electron pair of nitrogen. Pyridinic N can also be present in its oxidized form.^{26,91} It has been observed that incorporation of nitrogen enhances the electron-donor or basic capacities of the carbon material, thereby enhancing its ORR activity. The enhanced basicity can be related to the lone-pair electron of pyridinic N and to the presence of more electrons in the delocalized π -orbitals of the carbon framework from the graphitic N. π -Electrons can perform a nucleophilic attack on oxygen and the more π -electrons the system contains, the higher the oxygen reduction activity. However, the exact nature of the active sites in N-doped carbons is still a matter

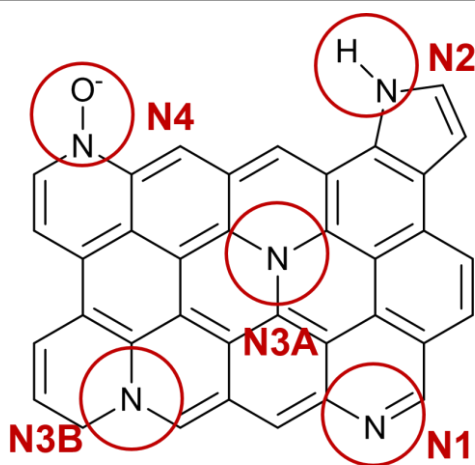


Fig. 5 Different nitrogen doping positions in the graphitic structure. The exact role of each position on the ORR is still highly debated.

of debate. Some researchers assume that pyridinic N is involved in the ORR activity,⁹² while others propose graphitic N.^{27,93} A recent study suggests that both sites might be equally important for the ORR, since it was proposed that graphitic and pyridinic N sites interconvert during the ORR.⁹⁴ Other reports mention that the type of dopant atom does not really matter, but the more important factor is that dopant atoms disrupt the electronic neutrality of the carbon framework, leading to charged locations for the oxygen to absorb onto the framework.⁹⁵ If that is true, multiple element doping should then lead to higher electrocatalytic activity, which it has been shown to do.^{34,39} While other dopant elements such as B, P, and S have been shown to increase the electrocatalytic activity of the material, they are almost always co-doped with nitrogen; therefore, studies on their solitary effect on the activity of the network are limited. However they are thought to follow the same mechanism of charge disruption of the framework due to the differing electronegativities and valence electron counts between the dopant atoms and the carbon framework. However in the case of sulphur a different mechanism of spin neutrality disruption has been proposed to try and account for the increased electrocatalytic activity despite the relative similarity in electronegativity between sulphur and carbon. This spin neutrality disruption could also potentially apply to the other elements.

Edge sites play a major role because they are the preferred spot for catalytic activity in a material.^{96–99} Dopant atoms are generally related to an increased formation of edge sites, because the lattice mismatches between the dopant and host atoms causes defects. Therefore, an increasing amount of dopant also increases the edge sites, which should lead to an increase in electrocatalytic activity. Nevertheless, if the edge sites cannot be reached by the reactant molecules (or any of the reactant sites), the sites do not contribute to increased catalytic activity. Therefore, a high accessible surface area is of paramount importance; creating a material with porosity can help increase the surface area, but the pores must be large

enough to accommodate the influx and outflow of reactant and reacted molecules. It must be noted that steric effects have not been a major issue with any of the compounds used for electrocatalysis. The oxygen molecule can absorb onto the framework either at the dopant atom or at the carbon atom next to the dopant since both will carry a slight charge. This vastly increases the available absorption sites, making the limiting factor the pore size. Most pores are large enough to accommodate the oxygen molecule, so the limiting factor is further reduced to if a reactant site is next to a pore. This is why increasing the surface area vastly increases the electrocatalytic activity.

Lastly, the degree of graphitization is related to the electrical conductivity of the material; the higher the conductivity, the higher the electrochemical activity. However, there is a trade-off between surface area and degree of graphitization, as increasing temperature decreases the surface area by sintering and increases the graphitization by rearrangement.

4.1 Carbon-Based Networks

Doped carbon structures already have high electrical conductivity, so a combination of increased dopant and accessible surface area seems like the most likely path forward in order to increase the catalytic activity in these materials. A recent example by Dai *et al.* describes the synthesis of a boron/nitrogen co-doped graphene foam.³⁴ Compared to pristine graphene foam, the individual B and N doped foams showed an increase in catalytic activity, but the BN doped foams were by far the most active. The authors speculate that not only both the isolated B and N atoms can act as active sites for the ORR through charge transfer with neighbouring C atoms, but also the interaction between adjacent B and N atoms could reduce the band-gap energy to further facilitate the ORR performance. In addition, B- and N-co-doping could also enhance the electroactive surface area, fulfilling all of the enhancement criteria of increased dopant amount and increased accessible surface area. Another example of the benefit of increased surface area is the amine functionalized holey graphene (AFHG, Fig. 6) by Jiang *et al.*⁵⁰

Compared to the regular amine functionalized graphene (AFG), the synthesized AFHG showed increased catalytic activity. This particular material provides even stronger evidence that increasing the accessible surface area increases the activity, as the amount of nitrogen doped into the structure remained approximately constant. It might also prove fruitful to try and increase the doping content, perhaps by creating a holey version of the graphene before doping or running a second doping step after the AFHG formation. Both materials have taken advantage of what is known thus far about increasing the catalytic activity; they have large accessible surface areas, high doping content, multi-element doping, and high electrical conductivity. Nevertheless, without a way to more precisely control the structure of the material, study of the mechanisms behind the ORR will prove difficult.

4.2 Perspective on COF use in Electrocatalysis

In light of this fact, COFs provide a large opportunity, as their main strength is their highly tailorable and potentially periodic functionality. A recent study by Xu *et al.* demonstrates the formation of a COF for organocatalysis.¹⁰⁰ In the study, the benefits of using a COF are readily apparent; the functional sites can be highly tailored, the sites are highly regular, and the surface area is large.¹⁰⁰ However, few have yet to take advantage of this opportunity in electrocatalysis. This is most likely due to a few reasons. COFs can have extremely high surface areas and the correct monomer combination can result in extraordinarily high levels of “dopant” atoms, but the conductivity of many COFs is extremely poor. This has led to a focus on storage applications, as the weakness of poor electrical conductivity is not an issue. Also the hydrolytic and oxidative stability of many COFs is not very good, due to the reversible reactions that are used in order to create highly crystalline and ordered frameworks. This is a problem as many fuel cells use an aqueous electrolyte, not to mention the large concentration of oxygen from the ORR itself. Use of a solid state electrolyte would help mitigate the corrosive effects of water on many COFs, but as the electrocatalytic reaction creates water as a by-product COFs that show low hydrolytic stability should not be considered. Overall these requirements mean that reactions that are more irreversible, and therefore create more stable COFs, should be the focus of research on COFs for electrocatalysis. This includes many of the nitrogen-linked compounds, but due to the requirement for electrical conductivity CMPs are probably the best option for a way forward. CMPs overcome the two major shortcomings just discussed as CMPs generally form aromatic systems, which are highly stable, as well as are fully conjugated, which may lead to higher electrical conductivity. However, CMPs are generally amorphous; if the framework still shows electrical conductivity then this is actually beneficial, as amorphous materials generally have a higher surface area. Nevertheless, for mechanistic studies, the challenge with CMPs is creating a non-amorphous framework, as a crystalline framework would allow for precise knowledge of the functional sites. This knowledge would allow for tailoring of the material in order to study the role of each type of functional site. A potential way past this barrier is using surface directed synthesis. Choosing appropriate monomers and conditions would be the most challenging aspect of the research required; monomers that can be sublimated may prove beneficial, or a particular solvent system may help increase the yield of a highly crystalline framework. Dogru *et al.* recently used a high throughput screening approach using a robotic dosing system to optimize the synthesis parameters of their COF.⁷⁷ This type of approach, combined with surface assisted synthesis would help to rapidly develop solvent systems that are capable of forming crystalline CMPs. In addition to the organic “doped” COFs thus far discussed, it is also possible to functionalize based COF loaded with either iron, cobalt, or manganese. COFs with metallic elements, as Xiang *et al.* have recently

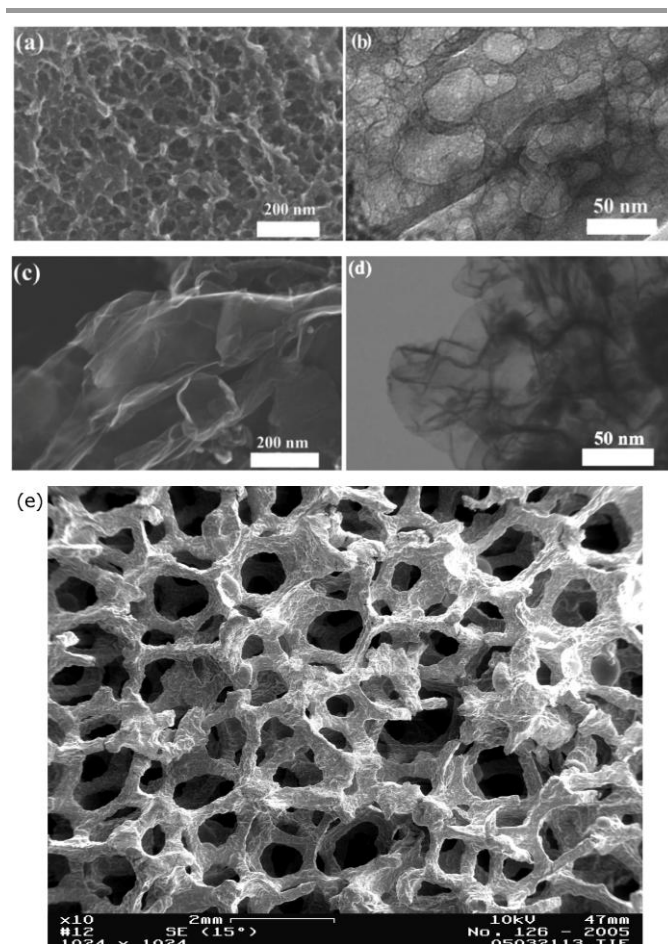


Fig. 6 (a, b) Amine functionalized holey graphene (AFHG) and (c, d) amine functionalized graphene (AFG). The porous nature of the AFHG increased its surface area and catalytic activity compared to AFG. (e) Metal foam that forms the framework for graphene foams. The metal is dissolved away using acid after CVD synthesis of graphene on the foam. Both the AFHG and graphene foams are porous but not ordered. (a-d) Reproduced from ref. 50.

demonstrated (Fig. 7).^{71,101} They demonstrate a porphyrin based COF loaded with either iron, cobalt, or manganese. These COFs should not be confused with MOFs, as the backbone structure is entirely organic, with transition metals simply loaded onto the structure. These transition metals provide active catalytic sites in the structure, although the structure must generally undergo carbonization in order to increase the electrical conductivity to an acceptable level. Nevertheless, the results show the power of metallic organic hybrid structures, with cobalt providing a large increase in both kinetic and diffusion-limited current density, and with iron increasing n to 3.93 as well as lowering the onset below that of platinum, which is remarkable. Perhaps a structure with both cobalt and iron could be synthesized to try and take advantage of all of these strengths. Another possibility is following a similar procedure to Jahan *et al.*, who recently created a graphene porphyrin-MOF hybrid structure.¹⁰² This structure used graphene to boost the electrical conductivity of the material, while using the porphyrin-MOF as both an active catalytic site and a spacer between graphene sheets in order to

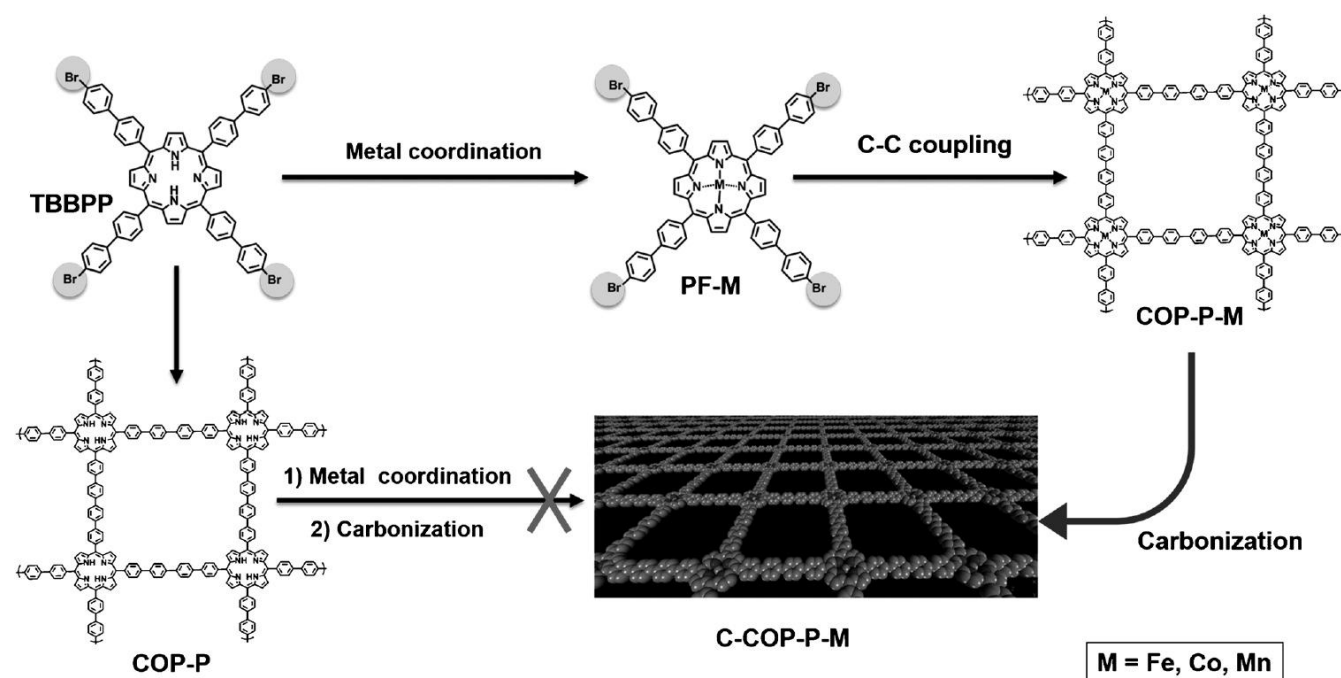


Fig. 7 Recent scheme for synthesizing a metal-doped COF for electrocatalysis. This framework is technically a CMP and demonstrates the utility of porphyrins in coordinating metals. A carbonization/graphitization step was required in order to increase the electrical conductivity to an acceptable level. Reproduced with permission from ref. ¹⁰¹ © John Wiley and Sons.

increase the surface area. This should be possible with purely organic linkers as well, given the right functionalities in the right places. The surface of graphene can be modified to have many different types of functional groups attached, which can be utilized to connect the different sheets. Given the right functionality, the linkers can provide catalytically active sites. This approach may prove to be very useful as the graphene porphyrin-MOF hybrid had high electrocatalytic activity with the largest benefit being a voltage independent 4-electron pathway.

5 Summary and Conclusions

Two and three dimensional polymeric networks have garnered lots of attention in the past decade due to their unique and manifold properties, and thus potential applications. Both carbon-based networks and COFs have been the subject of intensive study, but in very different arenas. Carbon based-networks due to their high stability and high conductivity have been extremely focused on electronic applications of all kinds, electrocatalysis included. They are fairly easily doped, but control of the final doping structure is difficult. On the other hand COFs have traditionally been researched in the gas storage and separation fields due to their large surface area and tuneable pore size and functionality. Nevertheless, COFs can be adapted for use in electrocatalysis. The COFs known as CMPs seem to provide the best chance for this transition due to their fully conjugated structure; in addition, COFs seem more likely to make better electrocatalysts from “doping” with metallic elements rather than intrinsic catalytic centers (like

N-doped graphene). The challenge going forward is finding how to create crystalline COFs, or how to take advantage of their ordered structure to lay out the catalytic centers in a precisely defined manner. Two and three dimensional network polymers are a recent hot area in scientific research due to their potential in many applications; COFs are just waiting for their chance to shine in electrocatalysis.

Acknowledgements

The authors acknowledge the support of Basic Research, BK21 Plus, Converging Research Center (CRC), Mid-Career Researcher, and Basic Research Laboratory (BRL) programs through the National Research Foundation (NRF), VPP supported by KSU and US Air Force Office of Scientific Research through Asian Office of Aerospace R&D (AFOSR-AOARD),

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Note: In regards to testing of the electrochemical properties of new materials, while the use of alkaline and acidic electrolytes is much easier than the use of a solid state proton exchange membrane (PEM), PEMs are the future of portable fuel cells (automotive and otherwise). A solid-state electrolyte provides a large number of benefits, least of which is the lack of flammability, corrosion, and a high power to weight ratio. PEM cells suffer from issues of catalyst poisoning and durability, which

is a large part of the research into non-platinum catalysts. Therefore testing of new materials with this future in mind should be encouraged.

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