Recent progress in two-dimensional polymers for energy storage and conversion: design, synthesis, and applications

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The increasing concerns about environmental issues caused by fossil fuels, and the demand for renewable energy have triggered extensive research into efficient energy storage and conversion systems. Owing to their unique properties of a high specific area, well-defined pore size, and tunable molecular structure, 2D metal–organic frameworks (MOFs) and covalent–organic frameworks (COFs), as two typical classes of 2D porous polymers, have been considered as intriguing materials for energy storage and conversion. This review provides a comprehensive overview of the up-to-date synthesis strategies of 2D MOFs and COFs, and their further applications. We mainly focus on the top-down and bottom-up synthesis methods, and applications in supercapacitors, lithium-ion batteries, batteries beyond lithium-ion batteries (lithium–sulfur batteries, and sodium-ion batteries), and electrocatalysts for CO2 reduction, oxygen evolution, oxygen reduction, and hydrogen evolution.

1. Introduction

The rapid development of electrical vehicles, portable electronics, and the grid has trigged increasing demand for efficient and economical electrical energy storage and conversion systems. Although tremendous studies have been conducted to explore novel electrode materials or develop new energy storage and conversion techniques, such as sodium-ion batteries,1−3 lithium–sulfur batteries,4−7 lithium–oxygen batteries,8 and fuel cells, since the commercialization of lithium-ion batteries (LIBs) in 1990s,9,10 there have been few breakthroughs in practical energy storage applications. Because of the low capacities of commercial anodes (372 mAh g−1 for graphite) and cathodes (LiCoO2, LiFePO4), the design and synthesis of novel electrode materials is urgently desired.

Since the successful exfoliation of monolayer graphene from graphite by a micromechanical cleavage technique in 2004,11 two-dimensional (2D) materials, such as transition metal dichalcogenides (TMDs), layered metal oxides, layered double hydroxides, hexagonal boron nitride, MXenes, silicene, and black phosphorus,12 have drawn unprecedented attention because of their unique physical, electronic, and chemical properties induced by electron confinement in two dimensions. Due to their unique properties, 2D materials have been widely investigated in various fields, such as optoelectronics,13,14 sensors,15 catalysis,16−18 biomedicine,19−21 and especially in...
energy storage and conversion,18,22,23 because of the ultrahigh specific area of 2D materials, disclosing much more surface active sites and ion-transport pathways, and enhanced ion transport between layers.

In 1995, Yaghi and co-workers first synthesized MOFs with metal ions and organic building blocks using reticular chemistry.24 Later in 2005, they successfully prepared several novel porous organic frameworks connected by covalent bonds, which were the first examples of COFs.25 Because of their high surface area, well-defined pore structure, and abundant building blocks, and especially the specific functionality by tailoring structures with different building blocks, MOFs and COFs have drawn tremendous attention in various applications. More importantly, 2D porous polymers (2D MOFs and COFs) also possess abundant accessible active sites for improved electrochemical performance, just like other 2D materials.

However, for most 2D porous polymers, their relatively low electrical conductivity severely restricts their application in energy storage and conversion. Although the pyrolysis of 2D polymers into carbon-based composite materials has been adopted as an alternative way to improve the conductivity,26–28 it could change the physicochemical properties of 2D polymers, thus restricting their further applications.

Due to the synergistic merits discussed above, increasing efforts have been conducted to design and synthesize novel functional 2D porous polymers. Although there are a few reviews about synthesis strategies for 2D COFs, 2D MOFs, and/or their applications, a relatively comprehensive review about the synthesis methods and energy storage applications of 2D porous polymers has not been provided so far. Consequently, herein, we present a special summary of the rational design and synthesis of 2D COFs and MOFs, and their energy storage and conversion applications (supercapacitors, LIBs, batteries beyond LIBs, and electrocatalysts), providing a relatively comprehensive basis for future research. Because of their similarity of the structures and properties, we review the synthesis strategy and applications of 2D COFs and 2D MOFs as a whole.

2. Synthesis of 2D porous polymers

Because of the unique properties of 2D porous polymers and their high potential in various applications, many strategies have been explored to synthesize novel and high quality 2D COFs and 2D MOFs. In general, there are two strategies to fabricate 2D porous polymers: the top-down and bottom-up methods.

2.1. Top-down methods

Like graphite, layered bulk porous polymers are composed of stacked monolayers by weak interactions, such as hydrogen bonding or van der Waals forces. A straightforward way to obtain monolayer or few-layer 2D porous polymers is to break the interactions between the layers of bulk porous polymers, for which sonication, electrochemical, and/or mechanical delamination are used.29–35 The first successful exfoliation of 2D porous polymers (MOFs) was conducted by Zamora and co-workers in 2010.36 They first synthesized black lustrous crystals of [Cu2Br(IN)2]n (IN = isonicotinato) by hydrothermal reactions using KBr, KOH, isonicotinic acid, and CuBr2. The structure of single-layer [Cu2Br(IN)2]n is shown in Fig. 1a. After sonication of the bulk layered MOFs, a single atomic layer with a height of ~0.5 nm was obtained, as shown in Fig. 1b. Then, they applied a sonication technique to exfoliate the 2D COFs.37 The bulk COF-8 (Fig. 1c) was synthesized by the condensation of 1,3,5-tris[4-phenylboronic acid] benzene (BTPB) and 2,3,6,7,20,11-hexa-hydroxytriphenylene (HHTP), followed by the sonication of COF-8 in dry CH3Cl for 15 min. The AFM results showed that the exfoliated 2D COFs consisted of only 10–25 layers of COF-8 (with a thickness of 4–10 nm) with lateral dimensions of several micrometers, as shown in Fig. 1d. Later, using similar sonication methods, other 2D porous polymers, including MOF-2 (ZnBDC, BDC = 1,4-bezenedicarboxylate),29 [Fe(Py2th)2]n (iron(ii)-pyrimidine-2-thiolate),39 and COF-43,40 were also successfully exfoliated.

Inspired by the phenomenon of the delamination of bulk COFs during the mechanochemical synthesis process, Banerjee and co-workers used mechanical grinding to exfoliate a series of synthesized functionalized COFs.41 Interestingly, the exfoliated few-layer 2D COFs retained their structural integrity during the exfoliation process, and remained stable even in basic and acidic conditions. In addition, they also synthesized self-exfoliated guanidinium-halide-based ionic COFs.42 Recently, Yang et al. applied a new method combining wet ball-milling and sonication for the delamination of layered Zn2(bim)4 (bim = benzimidazole) using a mixture of methanol and n-propanol as the solvent, since wet ball-milling prompted the diffusion of
small methanol molecules into the interlayer spaces, while n-propanol stabilized the exfoliated few-layer 2D MOFs.\textsuperscript{42}

Although top-down methods are facile and efficient to exfoliate 2D porous polymers, the disadvantages, such as low yield, slow production rate, mechanical damage, and the restacking of obtained mono- or few-layer nanosheets, seriously hinder their application in the large-scale fabrication of high-quality mono- or few-layer 2D polymers. Therefore, it is necessary to develop other alternative methods.

2.2. Bottom-up methods

Different from top-down methods, in bottom-up methods, various building blocks are used directly to synthesize 2D porous polymers. The key principle in bottom-up methods is to prevent polymerization along the vertical direction, while retaining the in-plane growth at the same time, or avoid the restacking of 2D nanosheets during the synthesis process. In this section, we discuss briefly the methods for the direct synthesis of 2D porous polymers.

2.2.1. Interfacial synthesis. A precisely designed surface can provide an ideal template to control the growth of porous polymers in 2D. Therefore, interfacial synthesis methods, including liquid–liquid,\textsuperscript{43–46} liquid–air,\textsuperscript{47–50} solid–liquid,\textsuperscript{51} and solid–vapor\textsuperscript{52–54} interface reactions, have been widely used in the fabrication of 2D porous polymers.

The most widely used interfacial technique to synthesize 2D MOFs is the liquid–liquid or liquid–air interfacial reaction. For instance, Kitagawa and co-workers successfully fabricated NASF-1 and NASF-2 by a liquid–liquid interfacial method.\textsuperscript{55,56} Recently, Nishihara and co-workers used a liquid–air interfacial reaction to prepare single-layer nanosheets of nickel bis(di-thiolene) using benzenhexahthiol (BHT) and nickel acetate [Ni(OAc)\textsubscript{2}] as building blocks.\textsuperscript{47} As shown in Fig. 2a, using a micro-syringe, they gently sparged an ethyl acetate solution of BHT on the surface of an aqueous solution of NaBr and Ni(OAc)\textsubscript{2}. The ethyl acetate evaporated during the reaction process, leaving the obtained monolayer nano-1 nanosheet at the liquid–air interface. The AFM results showed a smooth surface with a thickness of 0.6 nm (Fig. 2b and c), in accordance with STM analysis (Fig. 2c and d). The same group also used a liquid–air interfacial reaction to prepare monolayer or few-layer nanosheets of bis(dipyrrinato)zinc(II) MOFs.\textsuperscript{48} Liquid–liquid and liquid–air interfacial reactions are also widely used in preparation of 2D COFs.\textsuperscript{45,46,50,57} For instance, our group reported the first preparation of monolayer or few-layer triazine-based 2D COFs (2DP) by the liquid–liquid interfacial synthesis of 1,4-dicyanobenzene (DCB) (Fig. 2e). In this process, dichloromethane was employed as the good solvent for DCB, and trifluoromethanesulfonic acid served as a catalyst for nitrile cyclotrimerization. The TEM results (Fig. 2f) clearly showed the hexagonal patterns of the triazine-based 2D COFs of few-layer, in accordance with the AFM results in Fig. 2g.\textsuperscript{45}

Another widely used interfacial method is the solid–liquid interfacial reaction. Using this method, Lei and co-workers conducted a Schiff-base condensation between aromatic diamine and aromatic aldehyde monomers on a highly oriented pyrolytic graphite (HOPG) surface, as shown in Fig. 3a and b.\textsuperscript{58} The resulting surface-confined 2D COFs, with almost an entire

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**Fig. 2** (a) Illustration of the synthesis of nano-1. (b) AFM topological image of single-layer nano-1 and (inset) its cross-sectional analysis. (c) STM topological image of single-layer nano-1 on HOPG. The inset shows a cross-sectional analysis. (d) Close-up of the hexagonal pattern shown in the white square in (c). The upper-right and lower-left insets are the fast Fourier transform (FFT) of the STM image and the FFT-filtered image, respectively. Reproduced with permission from ref. 47. Copyright\textsuperscript{©} 2013 American Chemical Society. (e) HR-TEM image of 2DP showing few-layer (three-layer) thickness. (f) Higher-magnification HR-TEM image a of the 2DP. (g) AFM images of few-layer 2DP. Reproduced with permission from ref. 45, copyright\textsuperscript{©} 2017, American Chemical Society.

**Fig. 3** (a) Schematic illustration of the synthesis of COFs. (b) Molecular structure of the monomers: 1, benzene-1,3,5-tricarbaldehyde; 2, p-phenylenediamine; 3, benzidine; 4, o-tolidine; 5, 4400-diamino-p-terphenyl. (c) Large-scale STM image of the bilayer surface of COF\textsubscript{1,5}. (d) Digital magnification of the area marked by the blue rectangle. (e) Height AFM image of the surface COF\textsubscript{1,5} showing excellent full surface coverage. Reproduced with permission from ref. 58, copyright\textsuperscript{©} 2013, American Chemical Society.
surface coverage and few defects, had tunable pore sizes from 1.7 to 3.5 nm. More importantly, a bilayer nanosheet of 2D COFs was successfully fabricated, which was confirmed by the high-resolution STM and AFM images in Fig. 3c–e. In addition to HOPG, Dichtel and co-workers prepared a series of 2D COFs on single-layer graphene using a solid–liquid interfacial reaction.\textsuperscript{59-62} Meanwhile, some other materials, such as Au,\textsuperscript{63} three-dimensional (3D) graphene,\textsuperscript{64} and silicon,\textsuperscript{65} have also been used as substrates in the liquid–solid interfacial method. Although substrate patterning is usually necessary to obtain long-range order and orientation during the synthesis of 2D polymers, different thicknesses and surface roughness of 2D polymers could be obtained with different substrates, and specific substrate can be used for different devices and applications.\textsuperscript{59}

A self-limiting solid–vapor interfacial strategy was reported to fabricate highly ordered monolayer 2D COFs.\textsuperscript{66} As shown in Fig. 4a, first, one precursor (A) was preloaded onto the surface of the substrate by drop-casting, then precursor (B) was introduced. The whole system was sealed in a closed reactor with a thermodynamic regulation agent. Precursor B first vaporizes and reacts with precursor A on the surface by heating the reactor to a designated temperature. Highly ordered 2D COFs, i.e., SCOF-IC1 (obtained by 1,3,5-tris(4-aminophenyl)benzene and terephthaldicarbox-aldehyde), and SCOF-LZU1 (obtained by the condensation of 1,3,5-triformyl-benzene and p-phenylenediamine) were fabricated by this method, which was confirmed by the STM results in Fig. 4b–e. The author also thoroughly investigated the effect of precursor coverage, temperature, and...
the thermodynamic regulation agent on the quality of the resulting 2D COFs.

In the interfacial methods discussed above, the yield of the resulting 2D porous polymers is highly dependent on the area of the interface, which heavily restricts their application in large-scale fabrication. Recently, Gascon and co-workers developed a three liquid layers strategy based on diffusion-mediated modulation to synthesize copper 1,4-benzenedicarboxylate (CuBDC) 2D MOFs. As shown in Fig. 5a, the three liquid layers, as a synthesis medium, comprised mixtures of N,N-dimethyl formamide (DMF) and a suitable miscible acetonitrile with different ratios (the volume ratios of DMF to acetonitrile are, from top to bottom, 1 : 2, 1 : 1, and 2 : 1, respectively). Under static conditions, Cu$^{2+}$ cations in the top layer and 1,4-benzenedicarboxylic acid (BDCA) in the bottom layer diffuse slowly into the middle layer, leading to the growth of 2D MOFs nanosheets. The overgrowth of nascent nanosheets can be avoided because of the sediment of MOFs from the middle layer. The results of different characterizations showed that the resulting 2D MOFs possessed a lamellae structure with a thickness of 5–25 nm, as shown in Fig. 5b–d. Meanwhile, this facile method can be successfully applied to other 2D MOFs, such as...
copper 1,4-naphthalenedicarboxylate, copper 2,6-naphthalenedicarboxylate, and cobalt 1,4-benzenedicarboxylate.

2.2.2. Other methods. Recently, our group synthesized, for the first time, 2D aromatic polyamides (2DAPA-1, 2DAPA-2) with high crystallinity, excellent thermal stability, and solvent dispersibility by mechanochemical ball-milling. As shown in Fig. 6a–d, these 2D aromatic polyamides have a lateral size of micrometers, and an ultrathin thickness of a few nanometers. It was also found that solvent-free conditions were indispensable for the successful preparation of the 2DAPAs.

A surfactant-assisted synthetic method, proposed by Zhang and co-workers, recently was used to produce ultrathin 2D MOF nanosheets, since the surfactant can not only restrict the growth of nanosheets along the vertical direction, but also stabilize the few-layer 2D MOFs, as shown in Fig. 6e. In the 2D Zn-TCPP (TCPP = tetakis(4-carboxyphenyl)porphyrin) MOFs, a 2D layered sheet was formed by the linkage of one TCPP ligand with four Zn paddle-wheel metal nodes. In the presence of polyvinylpyrrolidone (PVP) as a surfactant, the obtained Zn-TCPP nanosheets possessed a lateral size of micrometers and a thickness of sub-10 nm, as shown in Fig. 6f and g.

3. Application of 2D porous polymers in energy storage and conversion

As highly potential useful materials for energy storage and conversion applications, 2D porous polymers have the following...
merits: (a) high specific area for more accessible active sites; (b) various building blocks for the judicious synthesis of 2D porous polymers with much more redox-active groups; (c) easily tunable pore sizes for ion transport, and a nanometer thickness to allow rapid mass and electron transport. Therefore, many studies have been performed to investigate the application of 2D porous polymers in energy storage and conversion. In this section, we mainly focus on the application of 2D COFs and MOFs in supercapacitors (SCs), LIBs, batteries beyond LIBs, and electrochemical catalysis.

3.1. Supercapacitors (SCs)

SCs have drawn extensive attention due to their ultralong cycle life, pulse power supply, high power density, and high dynamic of charge propagation. Generally, on the basis of their energy storage mechanism, there are two classes of SCs: the electrical double-layer capacitor and pseudocapacitor, the performance of which is highly dependent on the specific area and redox-active sites, respectively. Owe to their advantages, such as high specific areas and tunable structure and functional groups, 2D porous polymers have drawn increasing interest in SCs applications. However, in order to obtain high crystallinity, the majority of COFs are prepared via reversible organic reactions. However, reversibility during the synthesis of COFs makes these crystalline COFs unstable at acidic, basic, or even under ambient conditions. Meanwhile, most MOFs are also unstable in the acidic or basic conditions under which supercapacitors are usually performed. Because of the chemical instability and relatively low capacitance, it is still a great challenge to prepare novel 2D porous polymers with redox-active moieties.

Using 2,6-diaminoanthraquinone (DAAQ) and 1,3,5-triformylphloroglucinol (TFP), Dichtel and co-workers successfully synthesized β-ketoenamine-linked 2D COFs (DAAQ-TFP COF) with double-layer capacitor and pseudocapacitor, the performance of which is highly dependent on the specific area and redox-active sites, respectively. Owe to their advantages, such as high specific areas and tunable structure and functional groups, 2D porous polymers have drawn increasing interest in SCs applications. However, in order to obtain high crystallinity, the majority of COFs are prepared via reversible organic reactions. However, reversibility during the synthesis of COFs makes these crystalline COFs unstable at acidic, basic, or even under ambient conditions. Meanwhile, most MOFs are also unstable in the acidic or basic conditions under which supercapacitors are usually performed. Because of the chemical instability and relatively low capacitance, it is still a great challenge to prepare novel 2D porous polymers with redox-active moieties.

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excellent chemical stability. With the incorporation of anthraquinones, these 2D COFs with the highest surface area (435 m² g⁻¹) in the COFs linked by imines or enamines possessed a rapid reversible redox process. As shown in Fig. 7a, in the galvanostatic charge–discharge (GCDC) curves, DAAQ-TFP COF and DAAQ monomer showed voltage plateaus at −0.05 V (Ag/T-Ag), induced by the redox process of anthraquinones. In contrast, the GCDC result of DAB-TFP COF displayed a “shark-fin” curve, indicating a double-layer capacitance mechanism. The capacitance of DAAQ-TFP COF had an initial value of 48 ± 10 F g⁻¹, which was stabilized at 40 ± 9 F g⁻¹ after 10 cycles, and showed no further decrease even after 5000 cycles, while the DAB-TFP COF only provided an initial capacitance of 15 ± 6 F g⁻¹, as shown in Fig. 7b and c. Later, they further developed a method for synthesizing 2D DAB-TFP COFs films with a thickness less than 200 nm on Au working electrodes. Compared with their random powder, the oriented COFs film electrodes exhibited a 400% increase in capacitance.⁴³

Recently, Jiang and co-workers incorporated a redox-active group into conventional COFs for energy storage by post-synthetic channel-wall functionalization with organic radicals.⁷³ They first synthesized [HC≡C]₃₀%NiP-COF and [HC≡C]₁₀₀%NiP-COF by a solvothermal reaction of nickel 5,10,15,20-tetrakis(4-tert-butylpyridine) porphyrin (NiP) with different ratios of 2,5-bis(2-propynoxy) terephthalaldehyde (BPTA) and 2,5-dimethoxyterephthalaldehyde (DMTA), followed by a click reaction with 4-azido-2,2,6,6-tetramethyl-1-piperidinyloxy to prepare [TEMPO]₅₀%-NiP-COF and [TEMPO]₁₀₀%NiP-COF. [TEMPO]₅₀%-NiP-COF delivered capacitance of 167 and 113 F g⁻¹ at current densities of 100 and 2000 mA g⁻¹, respectively, while those of [TEMPO]₁₀₀%NiP-COF were 124 and 101 F g⁻¹, which were low but much more stable, as shown in Fig. 8a and b. Meanwhile, at 500 mA g⁻¹, the charge and discharge curves of [TEMPO]₅₀%-NiP-COF retained their shape and the capacitance was constant after 100 cycles, due to the covalently immobilized TEMPO radicals, as shown in Fig. 8c. In addition, Tang and co-workers first prepared 2D COFs with redox-active pyridine moieties using diamino pyridine (DAP) with triformylphloroglucinol (TFP) under solvothermal conditions. This novel 2D COF exhibited faradaic behavior with a high capacitance (209 F g⁻¹ at 0.5 A g⁻¹), excellent rate performance (164 F g⁻¹ at 5 A g⁻¹), and superior long-term stability (capacitance retention of 92% after 6000 cycles at 2 A g⁻¹). Lei and co-workers synthesized 2D COFs on graphene by a Schiff-base reaction using 2,6-diamino-anthraquinone and benzene-1,3,5-tricarbonyl. This composite showed a high specific capacitance of 31.7 mF cm⁻², but poor cycling stability.⁴⁴

![Fig. 12](image-url) (a) Schematic of the AA-stacking of DTP-ANDi-COF with redox-active naphthalene diimide walls (red) and one-dimensional mesoscale channels. (b) Chemical structure of one pore in DTP-ANDi-COF. (c) (top) Electrochemical redox reaction of a naphthalene diimide unit, (bottom) photographs of a coin-type battery. (d) Capacities of DTP-ANDi-COF@CNTs (red line) and CNT (dotted black line) batteries and coulombic efficiency of DTP-ANDi-COF@CNTs for 100 cycles (black line). (e) Capacity (red line) of DTP-ANDi-COF@CNTs batteries upon continuous cycling at a high current density and coulombic efficiency (black line). (f) Capacity (red line) and coulombic efficiency (black line) of DTP-ANDi-COF@CNTs for 700 cycles at 2.4 C. Reproduced with permission from ref. 89, copyright© 2015, Springer Nature.

![Fig. 13](image-url) (a) TEM photo, (b) AFM topographical image and (c) height profile of DAAQ-ECOF. (d) Rate performance of DAAQ-ECOF. (e) Capacity retention of DAAQ-ECOF and DAAQ-TFP-COF compared with their capacities measured at 20 mA g⁻¹. (f) Long-term cycling and coulombic efficiencies measured at a current density of 500 mA g⁻¹. Reproduced with permission from ref. 34. copyright© 2017, American Chemical Society.
As for MOFs, the relatively low electrical conductivity, which hinders the effective utilization of active materials, and poor chemical stability, which leads to inferior long-term cycling performance, significantly restrict their application in SCs. Recently, a class of highly conductive 2D π-conjugated MOFs, made from triphenylene- or benzene-derived ligands with ortho-disubstituted S, N, or O donor atoms that define planar coordination environment with various transition metal nodes,\textsuperscript{47,75–80} have attracted tremendous attention for SCs. For instance, Sheberla and co-workers prepared Ni\(_3\)(2,3,6,7,10,11-hexaiminotriphenylene)\(_2\) (Ni\(_3\)(HITP)\(_2\)), as shown in Fig. 9a, with a bulk conductivity greater than 5000 S m\(^{-1}\), under relatively mild conditions.\textsuperscript{81} Directly used as a binder-free electrode for SCs, these MOFs exhibited a volumetric capacitance of 118 F cm\(^{-3}\) at 50 mA g\(^{-1}\), and a capacity retention greater than 90% at 2 A g\(^{-1}\) over 10 000 cycles, as shown in Fig. 9b. Later, Bao and co-workers reported an electrode with high performance based on hexaaminobenzene (HAB)-derived 2D MOFs (Ni-HAB, Fig. 9c). Because of the high conductivity and excellent chemical stability, the electrode of Ni-HAB, with a pseudocapacitive mechanism, exhibited high areal capacitances over 20 F cm\(^{-2}\), volumetric capacitance up to 760 F cm\(^{-3}\), and superior cycling stability with a capacitance retention of 90% after 12 000 cycles, as shown in Fig. 9d–f. \textsuperscript{82} Meanwhile, there are also some reports of using 2D MOFs composites or derivatives as electrodes for SCs.\textsuperscript{28,83}

3.2. Lithium-ion batteries

Over the past two decades, though LIBs have become prominent in electrical vehicles, portable electronics, and other applications, little breakthrough has been made, given the relatively low capacity of commercial anodes (372 mA h g\(^{-1}\) for graphite) and cathodes (a limited capacity of about 250 mA h g\(^{-1}\) for insertion-oxide cathodes).\textsuperscript{84} On the other hand, because of the abundant building blocks, various redox-active groups can be incorporated into the 2D COFs and MOFs. Combined with a high specific area and tuneable pore sizes, 2D porous polymers possess huge potential in applications in LIBs. However, the low electrical conductivity of many 2D porous polymers highly hinders their practical applications. Therefore, the exploration of novel 2D materials for high-performance electrodes for LIBs is of great importance to meet the increasing energy consumption demands.\textsuperscript{85}

Li and co-workers first reported highly conductive 2D poly-porphyrin (TThPP) COFs used as an anode for LIBs with a reversible capacity of 666 mA h g\(^{-1}\), much higher than that of graphite.\textsuperscript{86} Zhao and co-workers synthesis two 2D COFs (N2-COF and N3-COF) by a condensation reaction of 1,3,5-triformylbenzene and two amino derivatives under solvothermal condition, as shown in Fig. 10a and b. Because of their uniform porosity for the enhanced transport of electrolyte and highly conjugated layered stacking for excellent conductivity, these two

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**Fig. 14**  (a) Schematic diagram of the composite synthesis from CTF-1 by the impregnation of molten sulfur. The carbon is shown in gray, the nitrogen in blue, the hydrogen in red, and the sulfur in yellow. Reproduced with permission from ref. 93, copyright © 2014, The Royal Society of Chemistry  (b) cycling performance of Por-COF/S composite at 0.5C rate.  (c) Discharge–capacity for the Por-COF/S composite at different rates. Reproduced with permission from ref. 94, copyright © 2016, The Royal Society of Chemistry.

**Fig. 15**  (a) Synthesis of S-CTF-1 from elemental sulfur and an optical image of S-CTF-1.  (b) First discharge and charge curves of S-CTF-1 measured at 0.05C.  (c) Cycling performance and CEs of S-CTF-1 in comparison with a control sample, KB-S. The tests were performed at 0.2C.  (d) Rate performance of S-CTF-1 measured at various current densities.  (e) Cycling performance of S-CTF-1 measured at 1C and 2C. Reproduced with permission from ref. 95, copyright © 2016, Wiley-VCH Verlag GmbH &Co. KGaA, Weinheim.
fully conjugated COFs exhibit excellent rate performance and cycling stability with high specific capacities, as shown in Fig. 10c–f. Recently, in order to overcome their intrinsic disadvantages, such as low theoretic capacity, sluggish electron/ion diffusion kinetics, and poor structural stability, Wang and co-workers prepared few-layered 2D COFs, trapped by carbon nanotubes (CNTs), with 14-electron redox sites per monomer by the reaction of 1,3,5-Benzene-tricarboxaldehyde and 1,4-diaminobenzene, as shown in Fig. 11a. From the transmission electron microscopy (TEM) results in Fig. 11b and c, it can be clearly seen that a thin COF layer with a thickness of ~5 nm was coated on the surface of CNTs. Because of this unique structure, electrodes of COF@CNTs for LIBs have delivered an ultrahigh reversible capacity of 1536 mA h g\(^{-1}\) at 0.1 A g\(^{-1}\), and remained stable after 500 cycles, as shown in Fig. 11d. More importantly, the structure of COF@CNTs remained stable even after 500 discharge–charge cycles. According to the results of theoretical calculations and different measurements, the storage mechanism involving 14-electron redox chemistry for a COF monomer has been proposed, and the increase of capacity during the activation process has been ascribed to the expansion of the interlamellar spacing induced by the lithiation/delithiation process.

Besides anodes, 2D porous polymers also possess huge potential as cathodes for LIBs. Jiang and co-workers reported redox-active 2D materials as cathodes for LIBs. They employed a new class of redox-active materials, carbon-based organic frameworks (COFs), which exhibit excellent electrochemical properties. COFs are obtained from the condensation of aromatic amines and aldehydes and exhibit excellent rate capability and cycling stability. The excellent electrochemical performance is attributed to the unique framework structure and the presence of redox-active sites.

**Fig. 16** Chemical structures of (a) COF-1 and (b) COF-5. (c) Cycling performance (at a charge/discharge current density of 2.0C/2.0C). (d) Discharge C-rate capability (discharge current densities varied from 0.2 to 10.0C under a fixed charge current density of 0.2C). (e) AC impedance spectra after 300 cycles. Reproduced with permission from ref. 96, copyright © 2016, American Chemical Society.
COFs (DTP-ANDI-COF@CNTs) by the reaction of 2,3,6,7,10,11-hexahydroxytriphenylene and N,N-di-(4-boronophenyl)-naphthalene-1,4,5,8-tetracarboxylic acid diimide on the surface of CNTs, as shown in Fig. 12a–c. Because of the improved structural stability boosted by the covalent network, enhanced electron conductivity of CNTs, and excellent ion transport benefiting from the open meso-channels, DTP-ANDI-COF@CNTs, as a cathode for LIBs, have exhibited superior rate capability and robust cycling stability with nearly 100% coulombic efficiency, as shown in Fig. 12d–f.90 Recently, Wang and co-workers presented exfoliated 2D COFs (DAAQ-ECOFs) by the ball-milling of layered DAAQ-TFP-COF, which was synthesized by the reaction of 2,6-diaminoanthraquinone (DAAQ) and 1,3,5-tris(4-formylphenyl)benzene (TFP). The TEM and AFM results in
Fig. 13a–c show that the DAAQ-ECOFs possessed an ultrathin, slightly wrinkled, and transparent layer structure with a thickness of 3 to 5 nm. Due to the ultrathin structure, an improved utilization of redox sites and enhanced electrochemical kinetics are anticipated. As cathodes for LSBs, DAAQ-ECOFs have shown a superior rate performance and long-term cycling stability (a capacity retention of 98% over 1800 cycles) with high specific capacities, as shown in Fig. 13d–f. In addition, 2D MOFs have also been used as a cathode for LSBs. For instance, Kimizuka and et al. reported the first 2D phthalocyanine-based MOF (Cu–CuPc) by the complexation of copper(n) ions with copper(n) 2,3,9,10,16,17,23,24-octahydroxy-29H,31H-phthalocyanine (CuPcOH). A cathode of Cu–CuPc 2D MOFs exhibited large capacities of 128 mA h g⁻¹, and good stability during 200 electrochemical cycles.

3.3. Batteries beyond LIBs

The rapid development of portable electronics, transportation, and grid applications has trigged the exploration of novel rechargeable energy storage systems with high power density and low cost. However, the relatively low power density and limited lithium resource seriously restrict the further application of LIBs in modern society. Thus, batteries beyond LIBs, such as lithium–sulfur batteries (LSBs) and sodium-ion batteries (SIBs), have attracted increasing attention.

Recently, LSBs have drawn increasing attention because of their high theoretical energy density (2600 Wh kg⁻¹ or 2800 Wh L⁻¹), low cost, and abundant resource of the element sulfur. However, some issues, such as the low conductivity of discharging (Li₂S or Li[S]) and charging products (S), dissolubility and shuttle effect of intermediate polysulfide, and large volume change heavily restrict the commercial applications of LSBs. 2D COFs or MOFs not only provide high specific area for a high loading of S, but also effectively suppress the shuttle effect of polysulfide because of both physical and chemical confinements, resulting in an excellent electrochemical performance of LSBs with high S loading. Since Nazar et al. reported CMK-3 as a host material for LSBs, many other nanostructure materials have been used for sulfur impregnation in LSBs. Wang and co-workers synthesized 2D COFs (CTF-1) by the cyclotrimerization of 1,4-dicyanobenzene, which was mixed with sulfur by a melt diffusion strategy at 155 °C, as shown in Fig. 14a. The cathode of CTF-1/S@155 °C delivered 1197 mA h g⁻¹ at the second cycle and 762 mA h g⁻¹ at the 50th cycle with a coulombic efficiency of about 97%, indicating the efficiency in depressing the shuttling effect of polysulfide. Later, the same group synthesized porphyrin-based 2D COFs (Por-COF) with a large pore volume and narrow pore size. After combination with sulfur by melt diffusion, the cathodes of Por-COF/S exhibited better long-term cycling stability (capacity of 633 mA h g⁻¹ after 200 cycles at 0.5C with a capacity decay rate of 0.16% per cycle) and rate performance (670 mA h g⁻¹ at 1C), as shown in Fig. 14b and c.

Further, Coskun and co-workers reported a 2D covalent triazine framework (CTF) with embedded polymeric sulfur by the reaction of 1,4-dicyanobenzene and elemental sulfur under a solvent- and catalyst-free condition. As shown in Fig. 15a, the obtained S-CTF-1 had strong sulfur binding and an ordered pore structure for sulfur distribution. The cathode of S-CTF-1 showed typical discharge–charge curves of S₈ (Fig. 15b). After 50 cycles at 0.2C, he capacity retention remained at 84.3% with a coulombic efficiency of 99.7% (Fig. 15c). When tested at 1 and 2C after 300 cycles, capacity retentions of 85.8% and 81%, respectively, were obtained (Fig. 15e). Meanwhile, S-CTF-1 also showed excellent rate performance (Fig. 15d).

Because of the low conductivity, the low sulfur loading (usually lower than 50% based on the whole electrode) has severely restricted the application of 2D porous polymers as hosts for sulfur impregnation. However, as an interlayer, 2D porous polymers can efficiently suppress the shuttling effect because of physical entrapment (tunable pore size) and chemical interaction (polar–polar interaction between lithium polysulfide and hetero-atoms of N, O, S, and etc., and/or metal–sulfur bonding). Lee and co-workers synthesized two CNT-templated 2D COFs (COF-1 and COF-5) with pore sizes of 0.7 and 2.7 nm, respectively, as shown in Fig. 16a and b. The cathodes of LSBs with the COF-1 (COF-1 NN) interlayer exhibited improved capacity retention of 84% after 300 cycles at 2C, which was much better than that with other interlayers, as shown in Fig. 16c. Meanwhile, the rate performance of LSBs with the COF-1 NN interlayer was also significantly enhanced in...
the wide range of current densities (0.2–10 C, Fig. 16d), which was induced by the lowest charge transfer resistance, as shown in Fig. 16e. The excellent electrochemical performance was in accordance with density functional theory (DFT) calculations, which demonstrated that COF-1 had the strongest adsorption of lithium polysulfide (Li$_2$S$_n$).

Recently, Li and co-workers reported a facile and scalable method for preparing a free-standing 2D MOF, Zn$_2$[benzimidazolate]$_2$(OH)$_2$ (ZBCP), at the air–water interface as a charge barrier in LSBs, as shown in Fig. 17a. The SEM result (Fig. 17b) showed that the ZBCP layer was a continuous and large-scale film with a thickness of ~3 nm (Fig. 17c–e). Because

![Diagram](image_url)

**Fig. 19** (a) Design and synthesis of metalloporphyrin-derived 2D covalent–organic frameworks. (b) Cyclic voltammograms of COF-366-Co and COF-367-Co in a carbon dioxide-saturated medium (blue and red solid lines, respectively) or nitrogen-saturated medium (blue and red dotted lines, respectively). The black solid line shows the background (bare carbon electrode) CV responses in the carbon dioxide-saturated medium. (c) Long-term bulk electrolyses at −0.67 V (versus RHE). Reproduced with permission from ref. 101, copyright © 2015, American Association for the Advancement of Science. (d) Illustration of the electrolysis cell and the two respective half reactions. (e) Cyclic voltammograms of COF-366-Co, COF-366-(OMe)$_2$-Co, COF-366-F-Co, and COF-366-(F)$_4$-Co in N$_2$N-dimethylformamide with tetrabutylammonium hexafluorophosphate as the electrolyte. (f) Current densities per milligram of cobalt in the different COF catalysts under an applied potential of −0.67 V vs. RHE in 0.5 M aqueous potassium bicarbonate buffer. Reproduced with permission from ref. 102, copyright © 2017, American Chemical Society.
the hydroxyl groups in ZBCP could implement electrostatic charges in this ultrathin 2D MOF, which could efficiently mitigate the shuttling effect of Li2S as a charge barrier, the electrochemical performance of LSBs could be highly enhanced. As shown in Fig. 17f and g, LSBs with the ZBCP exhibited a better rate performance and cycling stability, compared with those without ZBCP.

Besides LSBs, SIBs have also drawn tremendous attention owing to the similar electrochemical property of sodium with lithium and the earth-abundant resource of sodium. Our group reported the synthesis of millimeter-sized crystalline covalent triazine frameworks (CTFs) by a one-pot trimerization reaction of 1,4-dicyanobenzene in a solvent system, followed by further exfoliation of this CTFs into few-layer 2D polymers (2DPs) by both sonication and micromechanical cleavage. The 2DPs had a lateral size of micrometers with a thickness of about 2–3 nm, as shown in Fig. 18a and b. When used as anodes for SIBs, due to their robust porous structure, both electrodes of CTFs and 2DPs exhibited good rate performance and cycling stability with high specific capacities (Fig. 18 c–e).

3.4. Electrocatalysis

With the overexploitation of fossil fuels, the exploration of renewable energy, such as wind, solar, and tide energy, has raised overwhelming interest. However, the intermittence of such renewable energy can result in a mismatch of energy supply and demand, which severely impedes its exploitation. Therefore, converting the intermittent energy into chemical

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**Fig. 20**  (a) Polarization curves of NiCo-UMOFNs, Ni-UMOFNs, Co-UMOFNs, RuO2, and bulk NiCo-MOFs in O2-saturated 1 M KOH solution at a scan rate of 5 mV s\(^{-1}\). The dotted horizontal line is a guide to the eye showing a current density of 10 mA cm\(^{-2}\). (b) Tafel plots of NiCo-UMOFNs, Ni-UMOFNs, Co-UMOFNs, and bulk NiCo-MOFs derived from Koutecky–Levich plots in O2-saturated 1 M KOH solution. (c) RRDE measurement of NiCo-UMOFNs in O2-saturated 1 M KOH solution at a rotation speed of 1500 rpm (ring potential: 1.50 V versus RHE). (d) Faraday efficiency testing of NiCo-UMOFNs using the RRDE technique in N2-saturated 1 M KOH solution. The inset presents the Faraday efficiency testing mechanism of the RRDE, the black columns on the sides are Pt ring electrodes. The Pt ring electrode and glassy carbon electrode are separated by a non-conductive PTFE barrier (white columns). When a constant current (300 μA) is applied to the disk electrode for O2 generation at 20 s, a ring current of ~59.6 μA, caused by O2 reduction, is detected immediately. Reproduced with permission from ref. 104, copyright© 2016, Springer Nature.
energy by the oxygen reduction reaction (OER), oxygen evolution reaction (ORR), hydrogen evolution reaction (HER), or carbon dioxide (CO₂) reduction reaction (CRR), has drawn increasing attention. Because of their large specific area, 2D porous polymers can provide more active sites. Meanwhile, specific atoms with high catalytic efficiency can be incorporated into different 2D porous polymers for specific electrocatalysis reactions. Therefore, 2D porous polymers are attracting increasing attention in electrocatalysis.

### 3.4.1. CO₂ reduction reaction (CRR)

The reduction of CO₂ into other carbon products (carbon monoxide, methanol, methane, ethylene) is a sustainable challenge, but necessary strategy to meet the increasing global energy demand and to mitigate climate change. However, the usually used molecular catalysts for CRR typically require an organic reaction medium because of the competitive HER in aqueous media. Meanwhile, heterogeneous catalysts suffer from optimization of their activity by structural changes at a molecular level.

Chang and co-workers reported two COFs (COF-366-Co and COF-367-Co) as tunable materials for electrocatalysis, which were synthesized by the imine condensation of 5,10,15,20-tetrakis(4-aminophenyl)porphinato)cobalt [Co(TAP)] with 1,4-benzenedicarboxaldehyde (BDA) and biphenyl-4,4’-dicarboxaldehyde (BPDA), respectively, as shown in Fig. 19a. Because of the ability to achieve a precise control of the spatial arrangement of their catalytic centers, the facile expansion and function of their frameworks, and ability to tune their pore environment electronically and sterically, both COFs showed a high faradaic efficiency (90%) and improved turnover numbers at pH 7 with an overpotential of ~0.55 V, which represented, compared with the molecular cobalt complex, a 26-fold improvement in activity. Meanwhile, because of its larger pore size for a higher capacity of CO₂ adsorption and more electrochemical and chemical accessible active sites, COF-367-Co exhibited a greater enhanced electrocatalytic activity than COF-366-Co, as shown in Fig. 19b and c. In addition, they also investigated the effect of the remote functionalization of linker units on the reactivity of the molecular active sites in the reticular frameworks by preparation of a series of COFs, termed as COF-366-Co, COF-366-(OMe)₂-Co, COF-366-F-Co, and COF-366-(F)₄-Co, with different electron-withdrawing groups on the organic linkers. Since the impact of electron withdrawing on the cobalt center is proportional to the electronegativity and the amount of functional groups, remote functional groups have a significant effect on the electronic character of the porphyrin active sites for CRR. As a result, COF-366-F-Co, with the largest electron-withdrawing impact, had, compared with COF-366-Co, higher cathode peaks (Fig. 19d-f). This work illustrated the direct electronic structure–function relationship of COFs as electrocatalysts, which should enlighten future research into COFs as highly efficient catalysts.

### 3.4.2. Oxygen evolution reaction (OER)

OER, which is of great importance in water splitting and metal–air batteries, usually demands the use of costly noble metal oxides (RuO₂ and IrO₂) to mitigate the sluggish kinetics. Meanwhile, the energy conversion efficiency of OER is severely jeopardized by the high overpotentials to drive this reaction. Thus, huge efforts have been devoted to design and fabricate alternative catalysts. Because of their ultrathin layer that can aid rapid mass and electron transport, high surface area for accessible catalytic active sites, and easily tunable atomic structures and bonding arrangements, 2D MOFs have huge potential as a substitute for noble metal oxide catalysts.

Ultrathin NiCo bimetal–organic frameworks (NiCo-UMOFNs) with a thickness of ~3 nm were synthesized by Tang and co-workers from a mixed solution of BDC, Ni²⁺, and Co²⁺ under ultrasonic conditions. When used as electrocatalysts for OER in alkaline conditions, the NiCo-UMOFNs showed an overpotential of ~189 mV at 10 mA cm⁻² with a low onset potential of 1.39 V, and an excellent stable current density for more than 200 h at an overpotential of 0.25 V with a faradaic efficiency of 99.3% (Fig. 20a–d). In addition, they also demonstrated that the coordinatively unsaturated metal atoms and the coupling effect of different metals were crucial for this excellent electrocatalytic performance by X-ray spectroscopy (XPS) and density functional theory (DFT). In addition, a novel nickel phthalocyanine-based 2D MOF (NiPc-MOF) was first
synthesized by Du and co-workers, and then used as electrocatalysts for OER, showing excellent performance.\textsuperscript{105}

Recently, Zhang and co-workers reported a novel way to prepare 2D pillar-layered MOFs by electrochemical exfoliation. 2D-Co-NS MOFs with a thickness of about 2 nm were obtained by the direct electrochemical exfoliation of 3D-Co, which was synthesized by solvothermal reactions of Co(CH$_3$-hydroxy-1,4-benzenedicarboxylic acid (H$_4$dhbdc), as shown in Fig. 21a. Fe-doped 2D-Co-NS (Fe: 2D-Co-NS@Ni) was further prepared and used as an electrocatalyst for OER. The Fe: 2D-Co-NS@Ni exhibited an ultralow overpotential of 211 mV at 10 mA cm$^{-2}$ with a Tafel slope of 46 mV dec$^{-1}$, and a high turnover frequency of 30 s$^{-1}$ at an overpotential of 0.3 V (Fig. 21b–e).\textsuperscript{35}

In order to further improve the electrocatalytic performance, conductive nanostructures are usually used to enhance the electrical conductivity of 2D porous polymers. For instance, Huang and co-workers reported the synthesis of a 2D MOFs/MXene hybrid (Ti$_3$C$_2$T$_x$–CoBDC) using exfoliated MXene nanosheets, 1,4-benzenedicarboxylic acid (1,4-BDC), and cobalt(II) acetate tetrahydrate (Co(CH$_3$COO)$_2$·4H$_2$O) by a diffusion-mediated method, and used this as an electrocatalyst for OER, as schematically shown in Fig. 22. Owning to the synergistic effect of the porous structure and high surface area of 2D MOFs, as well as the conductivity of MXene, the Ti$_3$C$_2$T$_x$–CoBDC hybrid showed a current density of 10 mA cm$^{-2}$ at a potential of 1.64 V vs. a reversible hydrogen electrode (RHE) in 0.1 M KOH, and a Tafel slope of 48.2 mV dec$^{-1}$, which surpassed the performance of the standard IrO$_2$-based catalyst.\textsuperscript{106}

### 3.4.3. Oxygen reduction reaction (ORR).

The exploration of novel electrocatalysts for ORR with high active site density and catalytic activity, long-term stability, and low overpotential, is

**Fig. 22** Schematic illustration of the fabrication process of Ti$_3$C$_2$T$_x$–CoBDC hybrid for oxygen evolution reaction. Reproduced with permission from ref. 106, copyright© 2017, American Chemical Society.

**Fig. 23** (a) Polarization curves of Ni$_3$(HITP)$_2$ under N$_2$ (green) versus O$_2$ atmosphere (red) as well as of a blank glassy carbon electrode under N$_2$ versus O$_2$ atmosphere (blue and purple, respectively). (b) Activation-controlled Tafel plot for Ni$_3$(HITP)$_2$-electrocatalyzed ORR. Reproduced with permission from ref. 108, copyright© 2016, Springer Nature. (c) Proposed mechanism for 2e$^-$ O$_2$ electroreduction with Ni$_3$(HITP)$_2$. Reproduced with permission from ref. 109, copyright© 2017, American Chemical Society.
crucial to the large-scale application of fuel cells. Although Pt-based catalysts have achieved superior electrocatalytic performance for ORR, their large-scale applications are seriously hindered by their high cost and restricted stability. 2D porous polymers with a high surface area, stable chemical structure, and tunable moieties and porous sizes have raised increasing interest in electrocatalysis for ORR. However, post-synthetic treatment or modification are usually needed to further tailor traditional neat 2D MOFs or COFs because of their limited electronic conductivity and catalytic activity.197

Recently, Marinescu and co-workers reported highly conductive 2D MOFs [Ni3(HITP)2] with a surface conductivity value of 40 S cm−1, which is the best among coordination polymers. Because of the intrinsic merits of MOFs and their high conductivity, when used as electrocatalysts for ORR, [Ni3(HITP)2] exhibited an onset potential of 0.82 V (−50 μA cm−2) in a solution of KOH, and a Tafel slope of −128 mV dec−1 (Fig. 23a and b), which were comparable with the performances of other state-of-the-art catalysts for ORR.188 They further conducted experimental and computational research to elucidate the catalytic mechanism of [Ni3(HITP)2] for ORR. From the results of their experiments and computations, they found that it was the ligand, rather than the metal atom in MOFs, that played a key role in ORR, and so they proposed a reasonable mechanism for the oxygen reduction reaction, as shown in Fig. 23c.189 This work provided details of the precise structure–function relationships in non-platinum metal electrocatalysts for ORR, paving the way to design novel catalysts with excellent catalytic activity, stability, and selectivity.

3.4.4. Hydrogen evolution reaction (HER). Highly conductive 2D MOFs have also been used as electrocatalysts for HER. Marinescu and co-workers synthesized MOS-1 and MOS-2 through a liquid–liquid interfacial method using [Co(MeCN)6] [BF4]2 with BHT and THT, respectively. With the decrease of pH of the aqueous medium, MOS-1 exhibited a catalytic peak in the polarization curves, as shown in Fig. 24a. Meanwhile, low overpotentials of 0.34 and 0.53 V were needed to obtain a current density of 10 mA cm−2 for MOS-1 and MOS-2, respectively (Fig. 24b).44 Lately, Pradhan and co-workers reported 2D COFs (SB-PORPy-COF) as metal-free catalysts for HER by a Schiff condensation using 5,10,15,20-tetrakis(4-aminophenyl) porphyrin (TAP) and 1,3,6,8-tetakis (4-formylphenyl) pyrene (TFFPy). Because of the high surface area and promising chemical stability, SB-PORPy-COF showed an onset potential of 50 mV and a Tafel slope of 116 mV dec−1 (Fig. 24c and d).190

4. Summary and outlook

The review presents the recent progress in strategies (top-down and bottom-up methods) to design and fabricate 2D MOFs and COFs, and their applications in energy storage and conversion, including supercapacitors, lithium-ion batteries, batteries beyond LIBs, and electrolyzers for various electrocatalytic reactions, such as CRR, OER, ORR, and HER. Because of the highly structural similarity of 2D MOFs and COFs, similar synthesis strategies and applications are also anticipated. Therefore, we discussed the synthesis strategies and applications of 2D MOFs and COFs as a whole, not only providing a comprehensive understanding for their design principles and possible applications, but also to enlighten the further research to prepare novel 2D MOFs or COFs for suitable applications by comparison of the differences in synthesis methods and applications of the reported 2D porous polymers. For instance, though some top-down (sonication, ball-milling) and bottom-up (solid–liquid, liquid–liquid, and liquid–air) methods are adopted for the fabrication of both 2D MOFs and COFs, electrochemical exfoliation and three-layer diffusion-mediated synthesis of 2D MOFs have not yet been applied in the design of 2D COFs.

Indeed, using the reported strategies, a myriad of 2D porous polymers with different building blocks has been successfully fabricated, and remarkable progress has been made in energy storage and conversion applications, such as the conductive 2D MOFs in SCs and ORR, and 2D porous polymers in high-performance LSBs. Meanwhile, the unique 2D structure can serve as an ideal platform to study the structure–property relationship during the electrochemical process, which is of great importance for the further design of novel electrodes and for understanding other complex systems. Generally, the precise design of 2D MOFs or COFs with specific active materials for high-performance electrochemical processes is still in its infancy. More strategies or building blocks are necessary to explore novel 2D porous polymers. If the intrinsic merits (high surface area, porosity, tunable structures) can be fully exploited, we believe that 2D porous polymers possess huge potential in energy storage and conversion applications.
Conflicts of interest

There are no conflicts to declare.

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References