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Two-Dimensional Carbon-Rich Conjugated Frameworks for Electrochemical Energy Applications

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Abstract

Following the 15-year-long investigation on graphene, two-dimensional (2D) carbon-rich conjugated frameworks (CCFs) have drawn growing research interests as a new generation of multifunctional materials. Typical 2D CCFs include 2D π -conjugated polymers (also classified as 2D π -conjugated covalent organic frameworks) and 2D π -conjugated metal-organic frameworks. They are characterized by the layer-stacked periodic frameworks with high in-plane π -conjugation. The unique structures endow 2D CCFs with regular porosities, large specific surface areas, and superior chemical stability. Besides, 2D CCFs depict notable properties in common (*e.g.*, excellent electronic conductivity, designable topologies, defined catalytic/redox-active sites), which have motivated increasing efforts devoted to exploring 2D CCFs for electrochemical energy applications. In this Perspective, the structural features and synthetic principles of 2D CCFs are briefly introduced. Subsequently, we discuss the recent achievements in 2D CCFs designed for diverse electrochemical energy conversion (electrocatalysis) and storage (supercapacitors and batteries) applications. Particular emphasis is put on analyzing the precise structural regulation of 2D CCFs. Finally, we provide an outlook about the future development of synthetic 2D CCFs for electrochemical applications, which concerns with the novel monomer design, the chemical methodology/strategy establishment, [as well as the roadmap towards practical applications](#).

1. Introduction

Exploiting clean and sustainable energy resources represents one of the most feasible approaches to mitigate the current heavy energy dependence on fossil fuels.¹ In this regard, the latest decades have witnessed significant advances in a variety of electrochemical energy applications (EEAs), such as fuel cells, metal-air batteries, water-splitting/CO₂-reduction electrolyzers, supercapacitors, and rechargeable batteries.^{2, 3} These electrochemical devices can either convert chemical energy into electrical energy through efficient and green manners,³ or store the intermittent electrical energy harvested from renewable energy sources (*e.g.*, wind, tide, and solar).⁴ The operation simplicity, configuration flexibility, and eco-friendly features empower these energy conversion/storage devices to embrace broad market prospects in many areas. As the core part of EEAs, active electrode materials for different electrochemical devices share specific criteria in common, such as excellent chemical stability, continuous conductive pathways, efficient mass transport channels, and rich catalytic/redox-active centers. Currently, the main bottleneck of these EEAs that restricts their rapid penetration into the market lies in the unsatisfactory electrochemical performance. To this end, the exploration of high-performance active materials is highly demanded.

Due to the abundant resources and non-toxic properties, carbon materials have been extensively utilized as active materials for EEAs. In particular, graphene and its derivatives, single-/few-layer hexagonal sp²-hybridized carbon nanosheets, are of great interest. The two-dimensional (2D) fully π -conjugated aromatic structure renders graphene with large surface-to-volume ratio, high mechanical strength, outstanding electronic conductivity, and excellent chemical/electrochemical stability.⁵ These superior properties ensure graphene to be a robust active material applicable to most EEAs. The encouraging success of graphene has further stimulated the exploration of other synthetic 2D carbon-rich materials with similar structural features, which has brought 2D carbon-rich conjugated frameworks (CCFs) into the spotlight. Similar to graphene, 2D CCFs are built up with atomically ordered planar networks with high in-plane π -conjugation and weak out-of-plane π - π stacking. Especially, sub-nanosized/nanosized in-plane pores are periodically distributed on 2D CCF planes, allowing layer-stacked 2D CCFs with deep electrolyte infiltration and efficient mass transport through the pore channels. More importantly, 2D CCFs are prepared via bottom-up synthetic strategies, which makes it convenient to precisely tailor their geometries, catalytic/redox sites, and chemical/physical properties at the molecular level by adapting modern organic and polymer chemistries. All these features enable 2D CCFs with great promise as the superior active materials for EEAs, as well as the ideal model systems to derive insights into the molecular design principles towards varying EEAs.

Figure 1. Basic structures of (a) 2D CPF and (b) 2D *c*-MOF.

The research on 2D CCFs is a complex integration involving the exploration of theoretical molecular design, synthetic organic/polymer chemistry, and functional applications. To date, intensive synthetic efforts have been dedicated to the preparation of new 2D CCFs,^{6, 7} and 2D CCF structures will continue to evolve in aspects of their complexity and diversity. However, the exploration of 2D CCFs for EEAs has only attained scientific attention in the last few years. As an emerging research field, there remain critical challenges, particularly in establishing an unambiguous correlation between 2D CCF structures and their electrochemical performances in different EEAs. Herein, we first briefly introduce the structural features and the synthetic principles of 2D CCFs (including 2D conjugated polymer frameworks (CPFs, Figure 1a) and 2D conjugated metal-organic frameworks (*c*-MOFs, Figure 1b)). Next, we present the representative 2D CCFs in various electrochemical energy conversion (electrocatalysis) and energy storage (supercapacitors and batteries) applications by emphasizing on our recent studies. By doing so, we hope to offer a clear view of this emerging field to accelerate the future explorations of 2D CCFs for electrochemical applications.

2. Structural Features and Chemical Synthesis

2D CPFs. Linear conjugated polymers with continuous π -electron delocalization along the chain direction have been intensively explored as the active materials for EEAs (*e.g.*, polythiophene, polypyrrole, and polyaniline).⁸⁻¹⁰ Extending the conjugation systems into the second dimension is essential to address the short conjugation length and rich point defects associated with the linear conjugated polymers,¹¹ which however requires critical breakthroughs in the synthetic chemistry for 2D conjugated polymers. Dynamic covalent chemistry, which has been widely explored for the synthesis of 2D covalent organic frameworks (COFs) in the last decade, may provide possible synthetic pathways.^{12, 13} However, the long-range π -conjugation of most reported 2D COFs is interrupted by the non-conjugated (*e.g.*, boroxine and boronate ester) or low-efficient conjugated (*e.g.*, Schiff-base) linkages. Therefore, searching for new synthetic strategies and methodologies is imperative to bridge the two fields (conjugated polymers and 2D COFs) by developing 2D CPFs (also classified as 2D π -conjugated COFs).

Currently reported conjugated linkages of 2D CPFs are dominated by imine bond (C=N) formed via the Schiff-base reaction (Figure 2a).⁶ Unfortunately, the polarized C=N bond restricts the efficient charge carrier delocalization over the whole 2D polymer backbones. In 2016, we reported a crystalline sp²-carbon (C=C) linked 2D conjugated framework of poly(phenylenevinylene), which was synthesized through the Knoevenagel condensation of 1,4-phenylenediacetonitrile and three armed aromatic aldehyde.¹² Sp²-carbon linkages with efficient π -electron delocalization endow 2D CPFs with uninterrupted in-plane π -conjugation. Moreover, 2D CPFs show exceptional chemical stability, which contrasts significantly with other reported COFs. For example, Jin *et al.*¹⁴ synthesized three kinds of sp²-carbon linked 2D CPFs by coupling 1,3,6,8-tetrakis(4-formylphenyl)pyrene with 2,2'-(1,4-phenylene)diacetonitrile, 2,2'-(biphenyl-4,4'-diyl)diacetonitrile, and 2,2'-([1,1':4',1''-terphenyl]-4,4''-diyl)diacetonitrile, respectively. These 2D CPFs retained unchanged structures under various conditions, such as immersion in aggressive aqueous solutions (12 M HCl and 14 M NaOH) for one week and exposure to air for one year. Remarkable electronic and magnetic properties were uncovered for the sp²-carbon-linked 2D CPFs after iodine doping by Jiang *et al.*¹³ These exciting results have stimulated the growing interest in developing sp²-carbon-linked 2D CPFs employing diverse conjugated monomers or building blocks.

Figure 2. (a) Schiff-base reaction. (b) Knoevenagel condensation reaction. Representative (c) benzyl cyanide monomers and (d) aldehyde monomers. (e) Aldol condensation reaction. (f) Representative electron-deficient arylmethyl monomers.

The employed Knoevenagel condensation reaction (Figure 2b) using a base catalyst can convert benzyl cyanides (Figure 2c) and aldehydes (Figure 2d) into cyano-substituted olefin linkage.^{12, 14-17} Besides, non-substituted olefin-linked 2D CPFs can be prepared through the Aldol condensation reaction (Figure 2e) of aldehydes (Figure 2d) with electron-deficient arylmethyl monomers (Figure

2f), as recently reported by Yaghi, Zhang and others.¹⁸⁻²¹ The synthesis of highly crystalline 2D CPFs relies on readily regulating the thermodynamic equilibrium of covalent reactions through adjusting reaction media and conditions. Recently, we unveiled the essential role of the employed inorganic bases in catalyzing the formation of C=C double bonds via Knoevenagel condensation.¹¹ Cs₂CO₃ mediated reaction pathway was revealed to facilitate the reversible C-C single bond formation of the first-step intermediate, which was beneficial for achieving the final crystalline polymers after the elimination reaction in the second step. 2D CPFs are generally synthesized through solvothermal synthesis approaches, and they are obtained in the form of powder samples.⁶

2D *c*-MOFs. 2D *c*-MOFs represent the new-generation MOFs with strong in-plane conjugation and weak out-of-plane π - π stacking.²² Thus far, they have been synthesized by building monomers based on benzene (Figure 3a),^{23, 24} benzoquinone/benzene (Figure 3b),^{25, 26} triphenylene (Figure 3c),²⁷⁻²⁹ coronene (Figure 3d),³⁰ phthalocyanine (Figure 3e),³¹⁻³³ dibenzo[g,p]chrysene (Figure 3f),³⁴ and some others^{35, 36}. These monomers are equipped with ortho-substituted groups (*e.g.*, -OH, -SH, -NH₂), which are capable of forming square-planar coordination complexes with transition metals (*e.g.*, Zn, Cu, Ni, Co, Fe, Pd). In this context, the topological structures of the constructed 2D *c*-MOFs can be feasibly tailored by the ligand design, showing different pore geometries (*e.g.*, triangle, square, and hexagonal) and pore size (from non-porous to 2 nm in diameter). A variety of methods have been utilized to synthesize 2D *c*-MOFs, such as solvothermal synthesis,^{37, 31} interface-assisted synthesis,^{27, 38} on-surface synthesis,³⁹ and surfactant-assisted synthesis,⁴⁰ which render 2D *c*-MOFs with various morphologies such as bulk crystals, ultra-thin nanosheets (<5 nm), and single-/few-layer films.

Figure 3. Typical organic ligands and the relevant 2D *c*-MOFs. (a) Benzene based, (b) benzoquinone/benzene based, (c) triphenylene based, (d) coronene based, (e) phthalocyanine based, and (f) dibenzo[g,p]chrysene based ligand monomers.

Properties associated with EEAs. Porosity, conductivity, and active sites (catalytic/redox) are three basic parameters required for active materials towards electrochemical applications. For instance, 2D CPFs generally exhibit semi-conductive properties with tunable bandgaps (~ 1.0 eV to ~ 2.5 eV) and low intrinsic electronic conductivity (up to $\sim 10^{-4}$ S cm $^{-1}$)¹³. As similar to linear conjugated polymers, doping can be an effective strategy to boost up the electronic conductivity of 2D CPFs. The relatively low conductivity limits the application scope of 2D CPF for electrocatalysis and supercapacitors. However, the semi-conductive feature and abundant redox sites could render them to be excellent candidates for photo/(electro)-catalysis⁴¹ and batteries⁴². Benefiting from the favorable π -d conjugation and the planar structures, 2D *c*-MOFs generally display narrow bandgaps (< 1.0 eV) and metallic conductivities. The conductivity of 2D *c*-MOFs outclasses that of non-conjugated MOFs. For instance, Ni₃(HITP)₂ (HITP = 2,3,6,7,10,11-hexaiminotriphenylene) 2D *c*-MOF exhibits the bulk electronic conductivity of 2 S cm $^{-1}$ and the surface conductivity of 40 S cm $^{-1}$.²⁹ The record-high conductivity for 2D *c*-MOFs was reported for non-porous Cu₃BHT (BHT = benzenehexathiolate), reaching 2500 S cm $^{-1}$.²³ Therefore, 2D *c*-MOFs have demonstrated versatile applications in electrocatalysis,³² supercapacitors,⁴³ and batteries⁴⁰.

The stacking modes of layered 2D CCFs can influence the porosity and conductivity of 2D CCFs.⁷ For instance, the slipped parallel and eclipsed stacking modes in an AA pattern induce extended 1D pore channels of multi-layer 2D CCFs, while the staggered mode leads to a relatively narrowed 1D channels. Moreover, the theoretical simulation indicates that the AA-inclined stacking mode of 2D MOF Fe₃(THT)₂ (THT = 2,3,6,7,10,11-triphenylenehexathiol) exhibits a bandgap of ~ 0.35 eV, while the AA-eclipsed stacking mode provides a wider gap of ~ 0.65 eV.⁴⁴ In this regard, strategies to control the topological stacking mode of 2D CCFs are highly attractive.

Besides, 2D CCFs with thin-layer morphologies are highly desired for energy applications, as they can expose most build-in active centers on the surfaces. Thin-layer 2D CCFs can be fabricated by two strategies, namely bottom-up synthesis and top-down exfoliation. The challenge of bottom-up synthesis lies in restricting the growth of 2D CCFs in the vertical direction. Interfacial synthesis is an effective approach to achieve 2D CCF thin films by controlling the growth of 2D CCFs along the interfaces. So far, various interfacial synthetic strategies have been developed, including liquid-liquid,^{24, 26, 38, 44} liquid-air,²⁷ and solid-air⁴⁵ methods. The lateral size can be controlled by tuning the interface shapes, while the thickness of the thin films (from single layer to several μ m) can be adjusted by changing the synthesis time. In the category of top-down exfoliation, layer-stacked 2D CCFs are delaminated into single-/few-layer nanosheets by overcoming the weak interlayer interaction. Sonication is the most common approach to breakdown layer-stacked structures into thin nanosheets.¹⁹ The employed solvent, the concentration of 2D CCFs, as well as the sonication power and time, play significant roles in determining the exfoliation efficiency. Moreover, we recently found that ball milling was an efficient way to exfoliate phthalocyanine-based 2D *c*-MOFs.⁴³ Although top-down exfoliation approaches are straightforward and promising to obtain 2D CCF nanosheets, it remains challenging to achieve homogeneous lateral size and thickness, as well as high exfoliation yield.

3. Electrochemical Energy Conversion

Gas-involved reactions such as hydrogen evolution reaction (HER), oxygen evolution reaction

(OER), oxygen reduction reaction (ORR), and carbon dioxide reduction reaction (CO₂RR), are the heart of electrochemical energy conversion technologies.^{3, 46} However, the sluggish kinetics and the large overpotential of these electrochemical reactions have restricted the energy conversion efficiency. Thereby, developing electrocatalysts to promote the reactivity of these gas-involved reactions has been considered as the main task in the development of electrochemical energy conversion devices. The significance of 2D CCFs as electrocatalysts lies in their capability to offer a large density of atomic-level dispersed catalytic sites. To this end, catalytic center engineering plays a critical role in determining the electrocatalytic activity of 2D CCF-based catalysts.

Owing to the outstanding chemical stability, carbon materials (*e.g.*, carbon nanotubes, graphene, porous carbon) can serve as superior skeletons to arrange electrocatalytic sites (*e.g.*, heteroatoms, atomically dispersed metal species).⁴⁷ The key limitation of carbon catalysts is the lack of defined and dense active sites, which makes it challenging to fully understand the fundamental mechanism. By contrast, 2D *c*-MOFs are superb platforms to periodically immobilize defined single-metal species into carbon-rich frameworks, allowing dense catalytic sites and adjustable catalytic selectivity. In particular, triphenylene- and phthalocyanine-based 2D *c*-MOFs with large in-plane pores have attracted great interests for electrocatalysis. Diverse square-planar linkages were selected as the active sites towards catalyzing distinct electrochemical reactions, *e.g.*, metal-S₄ complex for HER,^{27, 38, 48} metal-N₄ complex for OER,⁴⁹ metal-N₄/metal-O₄ complexes for ORR,^{31, 49} and metal-O₄ complex for CO₂RR.³²

Figure 4. (a) Synthesis of Ni₃(THT)₂ film by using the LB method. (b) HER polarization plots and Tafel curve of Ni₃(THT)₂ film. Adapted with permission from ref. ²⁷. Copyright 2015 Wiley-VCH.

(c) Chemical structure of THTA-Co. (d) HER polarization plots of THTA-Co/G in comparison with those of graphene-based hybrids with $\text{Co}_3(\text{THA})_2$, $\text{Co}_3(\text{THT})_2$, and their mixture. Adapted with permission from ref. ⁴⁸. Copyright 2017 Wiley-VCH.

In 2015, our group used the Langmuir-Blodgett (LB) method to prepare an ultrathin $\text{Ni}_3(\text{THT})_2$ 2D *c*-MOF film with a lateral size of several square millimeters (Figure 4a).²⁷ The atomic force microscopy image revealed a single-layer $\text{Ni}_3(\text{THT})_2$ film with a thickness of 0.7 nm. The high exposure of Ni bis(dithiolene) moieties enabled the obtained $\text{Ni}_3(\text{THT})_2$ film with good electrocatalytic performance towards HER, showing an overpotential of 333 mV at 10 mA cm^{-2} and a Tafel slope of 80.5 mV decade^{-1} in 0.5 M H_2SO_4 (Figure 4b). Furthermore, we extended the LB method to synthesize 2D *c*-MOFs with CoS_2N_2 complexes (denoted as THTA-Co) by simultaneously coupling THT and THA (THA = 1,2,5,6,9,10-triphenylenehexamine) with Co centers (Figure 4c).⁴⁸ Moreover, the hybrid of THTA-Co and graphene (denoted as THTA-Co/G) delivered an overpotential of 230 mV at 10 mA cm^{-2} , substantially outclassing graphene-based hybrids with $\text{Co}_3(\text{THA})_2$, $\text{Co}_3(\text{THT})_2$, and their mixture (Figure 4d). These findings manifested that CoS_2N_2 complexes in triphenylene based 2D *c*-MOFs were superior catalytic centers over CoS_4 and CoN_4 complexes. Theoretical calculation suggested that the Co-N units in CoS_2N_2 complexes severed as the most active sites with the lowest H^* adsorption Gibbs free energy. Most recently, Huang *et al.*³⁵ reported a *c*-MOF by linking hexaiminohexaazatrinaphthalene (HAHATN) ligands with Ni nodes. The *c*-MOF (denoted as $\text{Ni}_3(\text{Ni}_3\text{HAHATN})_2$) has extra bidentate NiN_2 sites, which showed stronger electron-donating ability and thus higher catalytic activity towards HER than NiN_4 linkages. In an alkaline electrolyte (0.1 M KOH), $\text{Ni}_3(\text{Ni}_3\text{HAHATN})_2$ nanosheets depicted a small overpotential (115 mV) at 10 mA cm^{-2} and a low Tafel slope (45.6 mV dec^{-1}) for HER.

Figure 5. (a) Structure of PcCu-O₈-Co. (b) ORR polarization curves of PcCu-O₈-Co/CNTs at different rotating speeds. (c) ORR polarization curves of PcCu-O₈-Co/CNTs before and after the life test. Adapted with permission from ref. ³¹. Copyright 2019 Wiley-VCH. (d) Free energy profiles for HER and CO₂RR, and (e) Faradic efficiency of CO and H₂ of PcCu-O₈-Cu, PcZn-O₈-Cu, PcCu-O₈-Zn, and PcZn-O₈-Zn. (f) Schematic HER and CO₂RR processes of PcCu-O₈-Zn. Adapted with

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Towards ORR, CoO₄ complexes are efficient electrocatalytic centers in a copper phthalocyanine (PcCu) based 2D c-MOF (denoted as PcCu-O₈-Co, Figure 5a).³¹ The Co atoms in PcCu-O₈-Co were revealed to possess single electron occupied e_g orbitals, which explains the record ORR electrocatalytic performance of PcCu-O₈-Co among intrinsic MOF catalysts. PcCu-O₈-Co synthesized on carbon nanotubes (CNTs) showed a halfwave overpotential of 400 mV and a limited current density of 5.3 mA cm⁻² at 1600 rpm (Figure 5b). Importantly, the excellent long-term catalytic stability of PcCu-O₈-Co/CNTs was indicated by the almost identical polarization curves of PcCu-O₈-Co/CNTs before and after 5000 electrochemical cycles (Figure 5c). Besides, Peng with his colleagues⁴⁹ studied the role of metal centers in determining the ORR activity of HITP ligand-based c-MOFs. The unpaired 3d electrons of Co centers induced the less coplanarity of CoN₄ linkages compared with NiN₄ linkages, which further led to the lower crystallinity and less conductivity of Co₃(HITP)₂ than those of Ni₃(HITP)₂. Nevertheless, among HITP-based c-MOFs with different Co/Ni ratio, Co₃(HITP)₂ exhibited the highest catalytic activity towards ORR (halfwave overpotential: 430 mV), revealing Co centers to be superior active sites to Ni centers.

The electrocatalytic activity and selectivity of 2D c-MOFs towards catalyzing CO₂RR can be precisely manipulated at the molecular level, which was exemplified by our recent study on phthalocyanine-based 2D c-MOFs.³² Four 2D c-MOFs were constructed by linking PcCu or zinc phthalocyanine (PcZn) ligands via CuO₄ or ZnO₄ complexes (defined as PcCu-O₈-Cu, PcZn-O₈-Cu, PcCu-O₈-Zn, and PcZn-O₈-Zn). These 2D c-MOFs presented distinct selectivity for the CO₂-to-CO conversion and the competing HER (Figure 5d), which generated syngas with molar H₂/CO ratios ranging from 1:7 to 4:1 (Figure 5e). Amongst, PcCu-O₈-Zn displayed the optimal CO₂RR catalytic performance with a large CO₂-to-CO conversion efficiency of 88% and a turnover frequency of 0.39 s⁻¹ at -0.7 V vs. RHE. This excellent performance was co-contributed by the CO₂RR-active ZnO₄ sites and the facilitated CO₂ protonation enabled by the CuN₄ sites (Figure 5f).

Besides, metal porphyrin structures equipped with metal-N₄ species provide favorable catalytic sites (e.g., CoN₄ towards CO₂RR), which can be easily incorporated into 2D CPFs. It is also feasible to manipulate the catalytic activity of 2D CPFs through the choice of building blocks. For instance, Diercks *et al.*⁵⁰ reported an imine-linked 2D CPF synthesized by the condensation of 5,10,15,20-tetrakis(4-aminophenyl)porphyrinato cobalt and 2,5-dimethoxyterephthalaldehyde. The 2D CPF exhibited electrocatalytic activity for CO₂RR with a CO₂-to-CO conversion efficiency of 87% and a current density of 65 mA per mg of cobalt at -0.67 V vs. RHE. On the other hand, benefiting from the semiconducting characteristics, 2D CPFs have been investigated as photocatalysts⁵¹ and photoelectrocatalysts⁴¹ for water splitting. For instance, Jiang *et al.*⁵¹ fabricated an sp²-carbon linked 2D CPF formed by tetrakis(4-formylphenyl)pyrene and 1,4-phenylenediacetonitrile. It exhibited a photocatalytic activity with a high H₂ production rate of 2120 μmol h⁻¹ g⁻¹ under irradiation at wavelengths > 420 nm.

4. Electrochemical Energy Storage

The ideal electrochemical energy storage devices should have the ability to store massive energy and output energy in a fast and reversible way.⁵²⁻⁵⁵ Supercapacitors and alkali metal-ion batteries,

as the two electrochemical energy storage technologies on the market today, possess striking differences in charge-storage behavior.⁵⁶⁻⁵⁸ Supercapacitors based on surface-controlled charge storage deliver high power density and ultralong cycle life, but relatively low energy density. Conductivity is a crucial requirement for supercapacitor electrodes, which thus motivates the recent exploration of highly conductive 2D *c*-MOFs for supercapacitors. By contrast, alkali metal-ion batteries rely on diffusion-controlled bulk Faradic redox reactions to store charges, generally presenting large energy density, but low power and decent cycling stability. Compared with supercapacitor electrodes, battery electrodes depict less dependency on electronic conductivity. Therefore, both 2D CPFs and 2D *c*-MOFs have attracted increasing research interests as the active materials for batteries.

4.1 Supercapacitors

Figure 6. (a) Chemical structure and (b) CV curves of $\text{Ni}_3(\text{HITP})_2$. (c) Relative size of $\text{Ni}_3(\text{HITP})_2$ pores, ions, and solvent molecules in $\text{TEABF}_4/\text{acetonitrile}$ electrolyte. Adapted with permission from ref. ³⁷. Copyright Springer Nature. (d) Ligands, (e) differential capacitance per unit pore surface area, and (f) gravimetric Ragone plots of $\text{Ni}_3(\text{HHB})_2$, $\text{Ni}_3(\text{HITP})_2$, and $\text{Ni}_3(\text{HITN})_2$. Adapted with permission from ref. ⁵⁹. Copyright Springer Nature.

Depending on the charge-storage mechanism, active materials for supercapacitors are divided into electrical double layer capacitor (EDLC)-type materials and pseudocapacitive materials. EDLCs store charges by physical ion adsorption, whilst pseudocapacitors involve surface Faradic redox reactions. Since supercapacitors are large-power featured devices, the primary considerations for supercapacitor electrode materials are large specific surface area, high electronic conductivity, and efficient ion diffusion channels.^{4, 60} 2D *c*-MOFs stand out as potential electrodes for supercapacitors because of their high intrinsic conductivity and well-organized porous structures. In 2017, Dincă *et al.*³⁷ explored neat $\text{Ni}_3(\text{HITP})_2$ (Figure 6a) as an supercapacitor electrode in 1 M

tetraethylammonium tetrafluoroborate dissolved in acetonitrile. $\text{Ni}_3(\text{HITP})_2$ presented typical EDLC behavior with an areal capacitance of $18 \mu\text{F cm}^{-2}$ normalized to its specific surface area (Figure 6b). The important role of 1D cylindrical channels was highlighted, as they can well accommodate electrolyte ions (Figure 6c). To provide insights into the relationship between the 1D channel diameters of 2D *c*-MOFs and EDLC models, Bi *et al.*⁵⁹ utilized constant-potential molecular dynamic simulation to assess the EDLC behavior of $\text{Ni}_3(\text{HHB})_2$ (HHB = hexahydroxybenzene), $\text{Ni}_3(\text{HITP})_2$, and $\text{Ni}_3(\text{HITN})_2$ (HITN = 2,3,8,9,14,15-hexamino-trinaphthalene) in room-temperature ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate (Ligands are shown in Figure 6d). As revealed by the simulation results, $\text{Ni}_3(\text{HHB})_2$ with the smallest pore channels showed a double-hump capacitance-potential curve, which contrasted with the bell-shaped curves presented by $\text{Ni}_3(\text{HITP})_2$ and $\text{Ni}_3(\text{HITN})_2$ (Figure 6e). Among these three types of 2D *c*-MOFs, the larger 1D pore channel was disclosed to induce the higher gravimetric energy and power densities (Figure 6f). These findings offer essential guidance for the structural design of EDLC-type 2D *c*-MOFs.

Figure 7. (a) Chemical structure of $\text{Cu}_3(\text{HAB})_2$ and $\text{Ni}_3(\text{HAB})_2$. CV profiles of (b) $\text{Cu}_3(\text{HAB})_2$ and (c) $\text{Ni}_3(\text{HAB})_2$. Adapted with permission from ref.⁶¹. Copyright Springer Nature. (d) Chemical structure of $\text{PcCu}-(\text{NH})_8-\text{Ni}$. (e) Charge-discharge profiles of the MSC device fabricated with the $\text{PcCu}-(\text{NH})_8-\text{Ni}$ /graphene hybrid film. (f) Capacitance retention in the alternative flat and bent configurations after 3000 cycles at 20 mV s^{-1} . Adapted with permission from ref.⁴³. Copyright 2020 Wiley-VCH.

2D *c*-MOFs can show pseudocapacitive charge storage in alkaline aqueous electrolytes. Feng *et al.*⁶¹ synthesized $\text{Cu}_3(\text{HAB})_2$ and $\text{Ni}_3(\text{HAB})_2$ (HAB = hexaaminobenzene) powder by reactions of HAB linkers and Cu (II) or Ni(II) salts in water (Figure 7a). Cyclic voltammetry (CV) profiles of both $\text{Cu}_3(\text{HAB})_2$ (Figure 7b) and $\text{Ni}_3(\text{HAB})_2$ (Figure 7c) presented pseudocapacitance-indicative redox peaks. The redox behavior of $\text{Ni}_3(\text{HAB})_2$ was speculated to originate from the ligands, as Ni valence

change was excluded by ex-situ X-ray photoelectron spectroscopy (XPS) analysis. The pseudocapacitive behavior enabled $\text{Ni}_3(\text{HAB})_2$ (a 50 μm thick pellet) to present a high volumetric capacitance of 760 F cm^{-3} (427 F g^{-1}) at 0.2 mV s^{-1} . Pseudocapacitive behavior was also observed for a *c*-MOF synthesized by dibenzo[*g,p*]chrysene-2,3,6,7,10,11,14,15-octaol and Cu centers (the *c*-MOF is denoted as Cu-DBC).³⁴ In a neutral aqueous electrolyte (1M NaCl), Cu-DBC achieved a high specific capacitance of 479 F g^{-1} at 0.2 A g^{-1} with a potential window of 0.7 V.

Apart from conventional supercapacitor devices, in-plane micro-supercapacitors (MSCs) were also built based on 2D *c*-MOFs,^{43, 62} which could function as promising power sources for next-generation miniaturized electronics. Our group employed a layer-by-layer fabrication method to construct MSCs based on azulene-bridged 2D coordination polymer films.⁶² The device exhibited a remarkable EDLC performance with a volumetric capacitance of 34.1 F cm^{-3} . It also depicted potential capability as high-performance AC line filters with a small resistance-capacitance constant of 0.83 ms. Very recently, we reported the synthesis of phthalocyanine-based 2D *c*-MOF nanosheets linked by NiN_4 complexes (denoted as $\text{PcCu}(\text{NH})_8\text{-Ni}$, Figure 7d).⁴³ The achieved 2D *c*-MOF nanosheets with an average lateral size of $\sim 160 \text{ nm}$ and thickness of $\sim 7 \text{ nm}$ could be homogeneously dispersed in dimethylformamide. MSCs were fabricated based on $\text{PcCu}(\text{NH})_8\text{-Ni}$ /graphene hybrid film electrodes and polyvinyl alcohol (PVA)/LiCl gel electrolyte, which exhibited typical EDLC behaviors and a high areal capacitance of 18.9 mF cm^{-2} (Figure 7e). The device also displayed excellent mechanical flexibility. Even at an alternative flat and bent state, the device still maintained 86.2% of its initial performance after 3000 cycles (Figure 7f).

The relatively low conductivity certainly limits the research interests of 2D CPFs for supercapacitors. So far, only a few studies reported the direct use of 2D CPFs as supercapacitor electrodes. For instance, Jiang *et al.*⁶³ reported a kind of aza-fused 2D CPF, which was ionothermally synthesized by the condensation reaction of 1,2,4,5-benzenetetramine and triquinoyl hydrate. The high specific surface area ($> 1000 \text{ m}^2 \text{ g}^{-1}$), rich micropores (0.9 nm), and the favorable ion-adsorption aza units endowed the achieved aza-fused 2D CPF to be an excellent EDLC-type electrode material.

4.2 Alkali metal-ion batteries.

2D CPFs hold the capability to periodically integrate different ion-storage groups (*e.g.*, benzene ring,⁶⁴ TEMPO,⁶⁵ hexaazatrinaphthalene (HATN)⁴², pyrazine^{45, 66}) with varying redox potentials, and thus can be engineered as either anode or cathode materials for lithium-ion batteries (LIBs) and sodium-ion batteries (NIBs). To shorten the ion/charge transport distance and promote the utilization efficiency of active sites, constructing hybrids with conductive carbon materials⁶⁴ and exfoliating 2D CPFs into a few layers⁶⁵ are two feasible strategies. Most recently, our group⁴² developed an sp^2 -carbon linked 2D CPF (defined as 2D CCP-HATN) cathode for LIBs, which precisely integrated 6-electron redox-active hexaazatrinaphthalene units (Figure 8a) into the long-range conjugation system. Knoevenagel condensation reaction of 2,3,8,9,14,15-hexa(4-formyl-phenyl)diquinoxalino[2,3-*a*:2',3'-*c*]phenazine (HATN-6CHO, Figure 8b) and 1,4-phenylenediacetonitrile (PDAN, Figure 8c) was utilized to generate the dual-pore 2D CCP-HATN (Figure 8d). As a control experiment, an imine-linked 2D CPF (defined as 2D C=N HATN) with the same topology was also synthesized by substituting PDAN with 1,4-phenylenediamine. CV curves (Figure 8e) identified that 2D CCP-HATN presented higher redox activities than 2D C=N HATN,

which verified the important role of sp^2 -conjugated carbon linkage. Moreover, the Li-ion storage performance of 2D CCP-HATN was further enhanced by in-situ growth on CNTs (50 wt.%), delivering a high specific capacity of 117 mAh g^{-1} and 94 mAh g^{-1} at 100 mA g^{-1} and 1 A g^{-1} , respectively (Figure 8f).

Figure 8. (a) Li-ion storage mechanism of hexaazatrinaphthalene unites. Chemical structures of (b) HATN-6CHO, (c) PDAN, and (d) 2D CCP-HATN. (e) CV curves of 2D C=N HATN, 2D CCP-HATN, and 2D CCP-HATN@CNT at 1 mV s^{-1} . (f) Charge-discharge profiles of 2D CCP-HATN@CNT. Adapted with permission from ref. ⁴². Copyright 2019 Wiley-VCH.

2D *c*-MOFs are potential cathode materials for LIBs^{25, 40, 67} and NIBs⁶⁸, because their square-planar metal coordination linkages exhibit multi-electron redox capability. Importantly, the narrow bandgap and high conductivity of 2D *c*-MOFs make it possible to use 2D *c*-MOFs as battery electrodes without using much conductive additive. As a typical example, we recently reported the use of $Cu_3(HHB)_2$ (Figure 9a, HHB = hexahydroxybenzene) for Li^+ storage.⁴⁰ The employed surfactant-assisted solution synthesis approach enabled the fabrication of single-crystalline $Cu_3(HHB)_2$ nanosheets (4-7 nm in thickness). Compared with the bulk powders, the ultrathin *c*-MOFs nanosheets as battery electrodes showed the advantages of fast ion diffusion and high active-site utilization (Figure 9b). $Cu_3(HHB)_2$ nanosheets delivered a high specific capacity of 153 mAh

g^{-1} and stable cycle life of 1000 cycles. CuO_4 units were recognized as the Li^+ -storage sites, which involves ligand redox (from $\text{C}=\text{O}$ to $\text{C}-\text{O}-\text{Li}$) and $\text{Cu}^{2+}/\text{Cu}^+$ redox reactions. This mechanism was also verified by a recent study that involves a series of *ex-situ* characterizations.²⁵ Besides, $\text{Co}_3(\text{HAB})_2$ for Na^+ storage delivered a reversible specific capacity of 291 mAh g^{-1} in the potential range of $0.5\sim 3 \text{ V vs. Na}^+/\text{Na}$.⁶⁸ In this case, the redox activity of $\text{Co}_3(\text{HAB})_2$ originated from the conversion of benzoid imine/quinoid amine, rather than the Co valence change.

Figure 9. (a) Chemical structure of $\text{Cu}_3(\text{HHB})_2$. (b) Schematic illustration of the advantage of $\text{Cu}_3(\text{HHB})_2$ nanosheets as cathodes for Li -ion storage. Adapted with permission from ref. ⁴⁰. Copyright The Royal Society of Chemistry 2020. (c) Schematic illustration of the rechargeable $\text{Zn}-\text{Cu}_3(\text{HHTP})_2$ cell. Adapted with permission from ref. ⁶⁹. Copyright Springer Nature.

In addition, recent efforts have also been devoted to investigating 2D *c*-MOFs as electrode materials for emerging battery technologies. For example, Stoddart's group recently reported the use of $\text{Cu}_3(\text{HHTP})_2$ ($\text{HHTP} = 2,3,6,7,10,11$ -hexahydroxytriphenylene) as cathodes of aqueous zinc-ion batteries to couple with Zn metal anodes (Figure 9c).⁶⁹ The fabricated electrodes achieved a Zn^{2+} -storage capacity of 228 mAh g^{-1} , indicating an average 2.3-electron redox reaction per Cu atom.

Due to the excellent conductive and porous characteristics, 2D *c*-MOFs are also excellent supports to load other non-conductive active materials. Most recently, we demonstrated that PcCu based 2D *c*-MOFs linked by metal- O_4 complexes (*i.e.*, FeO_4 , NiO_4 , and ZnO_4 , corresponding 2D *c*-MOFs are denoted as $\text{Fe}_2\text{-O}_8\text{-PcCu}$, $\text{Ni}_2\text{-O}_8\text{-PcCu}$, and $\text{Zn}_2\text{-O}_8\text{-PcCu}$) were superior hosts for I_2 cathode in $\text{Na}-\text{I}_2$ batteries, which could resolve the poor cycle stability faced by I_2 cathode.⁷⁰ Metal- O_4 sites functioned as I_3^- adsorption sites, effectively restraining the I_3^- dissolution. Moreover, the I_3^- adsorption ability of 2D *c*-MOFs could be well tailored by selecting different metal elements (*i.e.*, Fe, Ni, Zn). Amongst, FeO_4 sites of $\text{Fe}_2\text{-O}_8\text{-PcCu}$ allowed the best I_3^- binding capability (Figure 10a). The constructed $\text{Fe}_2\text{-O}_8\text{-PcCu}/\text{I}_2$ electrode exhibited a high discharge capacity of 208 mAh g^{-1} at 0.3 A g^{-1} and capacity retention of 57% at 1.5 A g^{-1} (Figure 10b). Moreover, an ultralong cycle life was demonstrated for $\text{Fe}_2\text{-O}_8\text{-PcCu}/\text{I}_2$ electrode with almost no capacity decay over 3200 cycles (Figure 10 c).

Figure 10. (a) The comparison of different sites for polyiodide adsorption energy in Fe₂-O₈-PcCu, Ni₂-O₈-PcCu, and Zn₂-O₈-PcCu. (b) The galvanostatic discharge profiles of Fe₂-O₈-PcCu/I₂ electrode at various current densities. (c) The long-time cycle of Fe₂-O₈-PcCu/I₂ electrode at 1.5 A g⁻¹. Adapted with permission from ref. ⁷⁰. Copyright 2020 Wiley-VCH.

5. Conclusions and outlook

Overall, featured by the typical layered conjugated structures, synthetic 2D CCFs have emerged as a group of intelligent multifunctional materials. Our Perspective has examined the recent exploration of 2D CCFs for diverse EEAs. Precise control over the structures and functionalities of 2D CCFs has been illustrated through the multivariate bottom-up synthesis, offering opportunities for 2D CCFs as the robust electrode materials in various electrochemical reactions. The building monomers, linkages, and topologies of 2D CCFs can be tailored at the molecular level, which further determines their porosity, electrical properties, as well as catalytic/redox activities. Given that the understanding in the synthetic chemistry of 2D CCFs will continue to be deepened, the explosive development of 2D CCFs towards EEAs is expected. On the other hand, the research on 2D CCFs for EEAs remains at the primary stage. Thereby, some of the most intriguing questions about the future development are highlighted below.

Improving the crystallinity of 2D CCFs (crystalline degree and crystalline domain size) is a major challenge to be solved. The large ratio of disordered structure in 2D CCFs can block the long-range charge and mass transport pathways, which causes considerable inconsistency between theoretical

expectation and experimentally determined electrochemical properties. Concerning this, particular emphasis should be put on expanding the toolbox of synthetic protocols, while also considering means to control the crystal growth.

Another main challenge is the synthesis of 2D CCFs with high electronic conductivity (or even metallic conductivity). The electronic conductivity of 2D CCFs mainly relies on the through-space and the in-plane extended conjugation pathways, which are dependent on the selected conjugated building blocks and linkage chemistries. Strategic design of π -electron delocalized monomers will be crucial for the construction of 2D CCFs with high conductivity and good structural stability. In this regard, plenty of electroactive molecular units (e.g., thiophene-rich monomers) remain to be explored for 2D CCFs.

Apart from high conductivity, large porosity and dense catalytic-/redox-active sites are two factors that affect the performance of 2D CCFs towards EEAs. To pursue high electrochemical performance, 2D CCFs should be designed with specific regular pores to allow barrier-low mass transport. Meanwhile, 2D CCFs should contain non-active components as few as possible. The layer stacking mode of 2D CCFs (e.g., slipped parallel, eclipsed, and staggers) can significantly influence the porosity and charge transfer efficiency. In this regard, exploiting synthetic routes for 2D CCFs that can control the stacking arrangement is demanded. Additionally, depending on the application scopes, suitable bottom-up synthetic methods for 2D CCFs with controlled morphologies (e.g., powders, ultrathin nanosheets, thin films) are highly pursued. Top-down strategies that enable controlled exfoliation are also desired to expose build-in active sites of 2D CCFs on the surface and thus boost the performance of 2D CCFs towards EEAs.

Given that the electronic conductivity of the reported 2D CCFs are still not comparable with many carbon materials and inorganic metallic materials, one future direction is to incorporate the guest dopants into 2D CCFs or to construct 2D CCFs-based hybrids with other metallic materials. In this respect, strategies for constructing pore-confined nanoclusters and 2D-2D van der Waals heterostructures require to be explored, which will bring plenty of opportunities for advanced electrode materials toward EEAs. Moreover, the development of multi-component 2D CCFs containing multi-metal centers will open new avenues for electrocatalysts with superb activity/selectivity, as well as multifunctional supercapacitors and batteries.

The unique structures of 2D CCFs can offer potential opportunities in some emerging EEAs, which deserve future exploration efforts. For instance, multivalent metal-ion (Zn-ion, Ca-ion, Mg-ion, and Al-ion) batteries are promising next-generation energy storage technologies due to the direct use of low-cost multivalent metal anodes.⁷¹ However, the large-size charge-carrier cations and the strong cation-host repulsive interaction cause the sluggish ion-diffusion kinetics and the large volume change of conventional inorganic cathodes. The well-defined 1D pore channels and highly accessible redox-sites of suitable building monomers may enable 2D CCFs to address the kinetics and volume change issues, and thus to be alternative cathode materials for multivalent metal-ion batteries.⁷² On the other hand, 2D CCFs with defined growth orientation hold the possibility to realize the selective and orientated ion transport. In this regard, 2D CCFs can be used for applications such as solid-state electrolytes, hosting materials, and protective coating layers for

other active materials.

The ultimate application of 2D CCFs in EEAs requires also competitive cost-efficiency and industrial scalability. Therefore, developing the low-cost, scalable, and industrial technique for producing 2D CCFs will be needed. [Advanced processing and manufacturing techniques, such as different printing, spray/spin coating, and roll-to-roll assembly methods, should be also taken into consideration in the future.](#)

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