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Covalent Organic Frameworks: Emerging Organic Solid Materials for Energy and Electrochemical Applications

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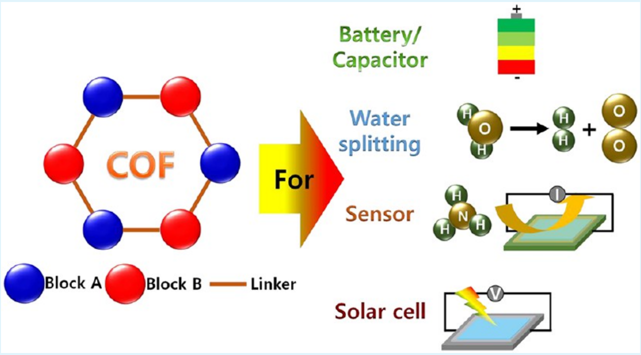
ABSTRACT: Covalent organic frameworks (COFs), materials constructed from organic building blocks joined by robust covalent bonds, have emerged as attractive materials in the context of electrochemical applications because of their high, intrinsic porosities and crystalline frameworks, as well as their ability to be tuned across two- and three-dimensions by the judicious selection of building blocks. Because of the recent and rapid development of this field, we have summarized COFs employed for electrochemical applications, such as batteries and capacitors, water splitting, solar cells, and sensors, with an emphasis on the structural design and resulting performance of the targeted electrochemical system. Overall, we anticipate this review will stimulate the design and synthesis of the next generation of COFs for use in electrochemical applications and beyond.



KEYWORDS: *covalent organic frameworks, structural design and synthesis, electrochemical applications, energy conversion and storage, porous crystalline materials*

1. INTRODUCTION

As the world population diverts away from conventional energy sources derived from fossil fuels, focus has shifted toward the utilization of green and sustainable energy resources, such as wind and solar energy, which can potentially address the shortcomings of conventional energy resources.[1−5] However, despite significant advances in the integration of these natural energy resources, their intermittent nature has limited the implementation of this technology on a large scale. For example, the dependence of renewable energy sources on natural phenomena (e.g., wind and sunlight) influences when that energy can be drawn, which has significant consequences in the context of grid balancing, or ensuring the correct amount of electricity is supplied to the grid. Batteries and capacitors have emerged as devices that can potentially solve this problem because of their ability to store and carry electrochemical energy in applications ranging from the large scale, such as electric grids, to small-scale portable electronics, such as cell phones.[6−9] Currently, several electrochemical systems, including metal-ion batteries, metal−air batteries, metal−sulfur batteries, and hybrid capacitors, are all studied for a diverse range of potential applications,[10−12] and the continued advancement of devices incorporating the electrochemical systems relies on the development of advanced materials with superior physical and chemical properties. As the development of novel materials plays a pivotal role in the progression in this field, more advanced materials must be developed for continued progress. In this context, we aim to provide an overview of an emerging class of materials for use in high-performance electrochemical devices, which we hope will facilitate innovative design and the synthesis of advanced energy materials for the next generation of electrochemical systems.

Specifically, we have focused our discussion on covalent organic frameworks (COFs) and their unique advantages in the context of electrochemical applications, which cannot be obtained using other materials. COFs are named after the covalent bonds that form between the organic building blocks, leading to robust frameworks that extend in two and three dimensions. Although structurally reminiscent of metal−organic frameworks, one crucial difference between the two frameworks is the absence of metal cations or connecting nodes in COFs, which leads to porous and crystalline materials that generally have relatively lower densities. As a result of their tunable nature, permanent porosities, and extremely high surface areas, COFs have found use in various fields ranging from gas and ion filtrations, batteries and capacitors, solar cells, and electrochemical catalysis.[13−17] As the synthesis and

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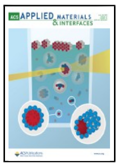

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understanding of COF-based materials become more sophisticated, these purely organic materials have emerged in areas that have been typically dominated by metal-containing composites or materials. For example, organic materials have often been overlooked for use in electrode materials in metal-ion batteries because of their poor electronic conductivity, and as a result, the exploration of electrode materials for this application has mainly been limited to composites bearing metal species or other inorganic materials, which typically exhibit much higher conductivites.[18−21] Based on the recently reported use of COFs as electrode materials, COF-based electrode materials could potentially solve the current challenges related to the storage of electric energy.[21−23] To improve the electronic conductivity, we discussed several potential solutions in the subsequent sections, namely, the introduction of conductive agents and functionalization with specific groups.

On the basis of the previous reviews on these materials, it can be seen that multiple structural, morphological, synthetic, and design concepts have been reported.[24−26] Just as with small organic molecules, the reactivity of COF precursors can be tuned by varying the functional groups on the organic building blocks; a variety of well-defined organic reactions have proven useful for the synthesis of COFs, ranging from the boronic ether,[27] aldehyde/amine,[28] and Schiff base reactions,[29] among others. As a result, both two- and three-dimensional spatially expended layered or framework-structuring materials with tunable pore sizes can be precisely formed. The inherent porosity of COFs renders electrolyte permeability in these materials, presenting an innate advantage in comparison with conventional bulk composites.[30,31] Furthermore, access to straightforward methods to modify pore sizes enables the precise tunability of COFs for desired battery applications (i.e., tailor the pore size to a specific cation or anion present in an electrolyte for improved electrochemical performance). Finally, functionalization of COFs via chemical reactivity offers the potential straightforward transformation of an electrochemically inactive, as-prepared COF material into an attractive material with the desired charge-storage properties.

As a result of these key features, COFs are purely organic materials that are attractive and multifunctional candidates for electric energy storage. To further stimulate the research efforts in this area and open up new potential avenues for research, we reviewed the recent reports on COFs in the context of electric energy storage, including electrochemical batteries and capacitors, as well as in other electrochemistry-related applications, such as solar cells, water splitting, and sensors. Specifically, we discuss the structure and design of COFs and the established synthetic protocols used to access these materials. Finally, we highlight the remaining challenges related to COF-based materials employed in electrochemical applications and offer potential opportunities toward future developments for materials in this regard. Overall, researchers around the world may benefit from this review as increasing efforts are being put into obtaining insights into the design of functional COF materials.

2. CONSIDERATION OF DESIGN

2.1. COF Structure. Generally, COFs can be classified into two- and three-dimensional porous and crystalline structures, which can be tuned by modifying the organic building blocks. Two-dimensional, or layered, COFs feature strong covalent bonds between atoms throughout the layer and relatively weaker hydrogen bonding or van der Waals interactions between the layers. The large variety in structural features enables COFs to be used for diverse applications; for example, highly porous, crystalline structures can serve as both robust hosts and self-active materials, with accessible active sites on the COF tunnel walls. Thus far, the use of two-dimensional COFs has been documented in many applications, such as water splitting, solar cells, metal-ion batteries, and sensors.[32,33] However, one potential issue for the two-dimensional COFs arises from the weak van der Waals forces at the interlaminations in the reported layered-COFs with staggered arrangements, which can lead to loss of performance, if the layers shift.[34,35] In comparison, three-dimensional COFs provide inherent robust backbones solely comprised of covalent bonds, which can more readily maintain the structure of the material during extensive use in a variety of applications,[36,37] suggesting high-performance materials may potentially be more readily derived from three-dimensional COFs. High structural fidelity of both two- and three-dimensional COFs is essential to achieve desired performances for applications in which these materials are employed. Despite improved chemical stability relative to their two-dimensional counterparts, three-dimensional COFs still face challenges from their formation to utilization; for example, spontaneous hydrolytic decomposition occurs after the short-term use of three-dimensional COFs in aqueous media, resulting in a significant decrease in application efficiency due to the degradation of the COF material—structural performance of COF materials has been extensively reviewed by Kandambeth and co-workers,[38] so we refer the reader there for more information on this topic. To mitigate structural decomposition, Liu et al.[39] explored the concept of a self-healing COF comprising boronate ether bonds that form via the reaction between diboronic acid and azobenzene precursors. Following deconstruction by UV light, this two-dimensional, single-layered COF can be healed by annealing treatment, and the recovery of performance can be achieved even after long-term use. This self-healing material has enormous potential in applications, such as gas absorption and electrochemical batteries, in which the improved lifespan of this material may potentially lead to a more-cost-efficient system.

As an alternative strategy to structural self-healing, the design of COFs that exhibit high chemical and thermal stability can also be employed for a range of applications. For example, Wei et al.[40] demonstrated that a dual bonding approach, reminiscent of a mortise and tenon joint, is one effective approach toward constructing COFs with superior stability (Figure 1a). In this work, the authors prepared a series of benzoxazole-based COFs via continuous imine formation, cyclization, and oxidation/dehydrogenation reactions to reinforce the material structure. The structure can be manipulated at the molecular level to achieve desired performances. Yang et al. have proved this concept by altering the linker in naphthalimide-based COFs.[41] Excellent electrochemical performances were obtained by using these COFs as cathode materials in lithium-ion batteries (Figure 1b, c).

2.2. Constitution. Thus far in this review, the reported COFs have been formed through covalent bonds between the building blocks in which the presence of specific functional groups is determined by the target application for the COF material. In these materials, the resulting pore sizes are mainly determined by the length of the linkers; however, the final crystalline structures are limited by steric features of the building blocks. These inherently porous organic frameworks are attractive because of the variety of both structures and constitutions. Pore sizes, together with intrinsic and postsynthetically implanted functional groups at the matrices, determine their performance when employed in an electrochemical application.

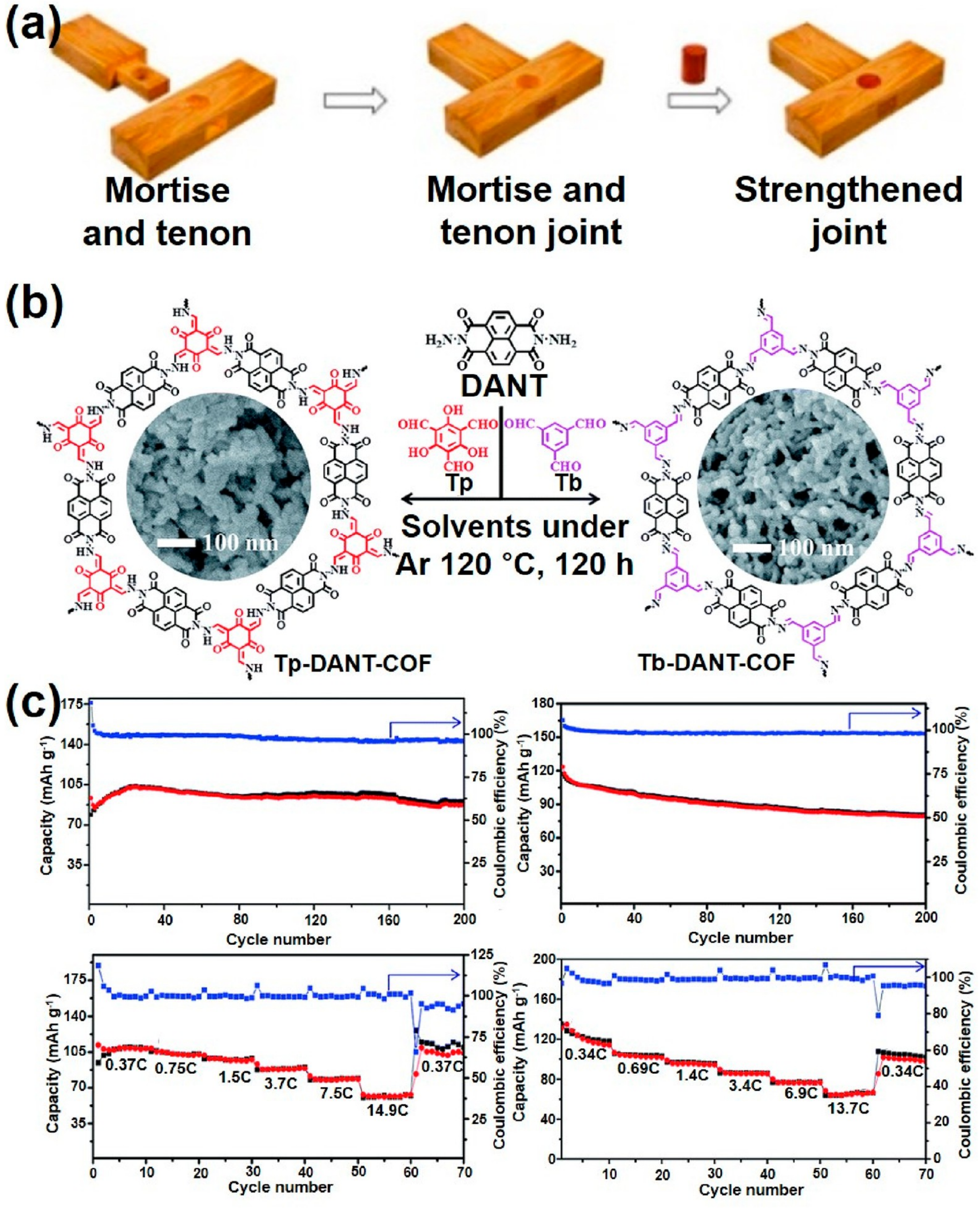

Figure 1. (a) Schematic illustration of the mortise and tenon concept. Reprinted with permission from ref 40. Copyright 2018 American Chemical Society. (b) Schematic illustration of two different types of COFs. (c) Cycling and rate performance tests of COF electrodes. Reprinted with permission from ref 41. Copyright 2016 Royal Society of Chemistry.

COFs mainly comprise carbon and hydrogen species, which makes them favorable porous carbon precursors. Furthermore, metal-embedded or doped composites can serve as platforms for functionalized materials.[42]

As a result of the extended conjugated framework inherent to COFs, charged cations or anions can be introduced into the COF walls or interfaces, making charged COFs attractive candidates for certain applications in which electrostatic attraction is required, such as cation filtration or polysulfide absorption. For example, depending on the voltage applied to a COF film (e.g., positive or negative), cations and anions can potentially be separated in a variety of solvents. Indeed, Huang et al. have demonstrated this concept by forming COFs using 4,4′,4′′,4′′′-(pyrene-1,3,6,8-tetrayl)tetra-aniline and 5,6-bis(4-formylbenzyl)-1,3-dimethyl-benzimidazolium

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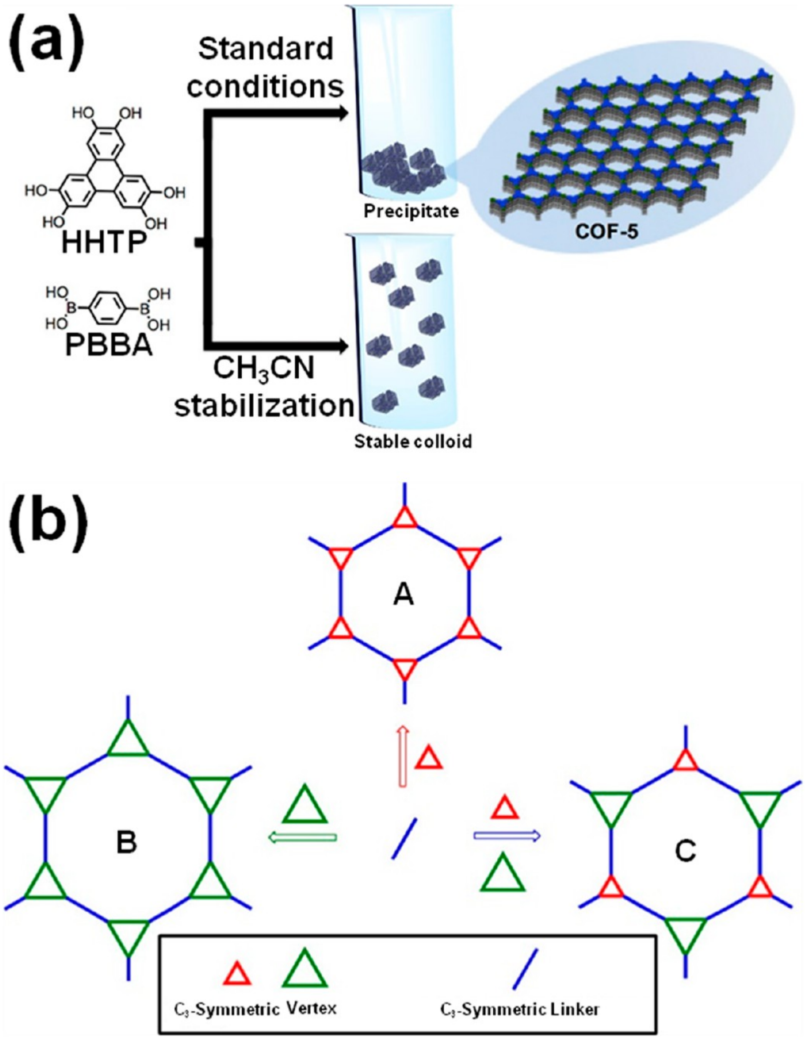

Figure 2. (a) Schematic illustration of the synthesis process of boronate ester-linked two-dimensional COFs. Reprinted with permission from ref 49. Copyright 2017 American Chemical Society. (b) Illustration of the mechanism of dehydrobenzoannulene-COFs. Reprinted with permission from ref 50. Copyright 2016 American Chemical Society.

bromide, with cation centers alternatively decorated on both sides of the walls to have a unique ionic interface construction.[43] This report may stimulate more relevant research on charged COFs.

Simulation is an efficient tool used to estimate and calculate the performances of the designed COF materials. For example, Guo et al. studied Li-doped phthalocyanine using simulations and found that one Li$^+$ cation insertion corresponds to the adsorption of three H$_2$ molecules with an energy barrier of 0.11 eV, suggesting the potential use of this material in gas absorption applications.[44] Lin et al. employed first-principle calculations to demonstrate the correlation between the bonding structure and orbital energy of porphyrin-based COF materials.[45] A series of porphyrin-containing COFs decorated with 3d transition metals in the center of porphyrin have been synthesized to demonstrate the catalytic activities of the COFs. Electron transfer in these systems is dependent on the identity of the transition metal, which can be ascertained through analysis of the energy band gap diagram; different energy barriers during the reactions with 3d metals are depicted in this study. These results can be employed to predict the limitation of overpotential of transition-metal-based COFs, which is a key parameter for the understanding of energy barriers in both the oxygen evolution and the oxygen reduction reactions.

2.3. Synthesis Strategies of COFs. Many factors related to the synthetic strategy of a COF, such as cost-efficiency, time, and environmental influence, need to be considered in order to determine the commercialization potential for COF-based materials.[46] So far, the documented synthetic methods for COFs mainly rely on two strategies involving either liquid- or solid-state fabrications, and factors ranging from the reversibility of covalent bonding to the isolation of products must be considered in both systems.[47] Most current synthetic protocols suffer from poor control over the final morphologies, forming insoluble and unprocessable aggregations.[48] A novel solvent-controlled synthesis method has been reported by Smith et al. in which CH$_3$CN was employed to stabilize the COF during construction, and it was found that different ratios of precursors can also result in the formation of various crystalline COFs (Figure 2a).[49] The introduction of CH$_3$CN can effectively inhibit the crystallite precipitation during the synthesis process, which is an important discovery for the future preparation of well-dispersed COFs. Crowe et al. demonstrated a facile method for the preparation of heterogeneous COFs by tuning the reactant ratios, leading to the formation of three different types of COF products.[50]

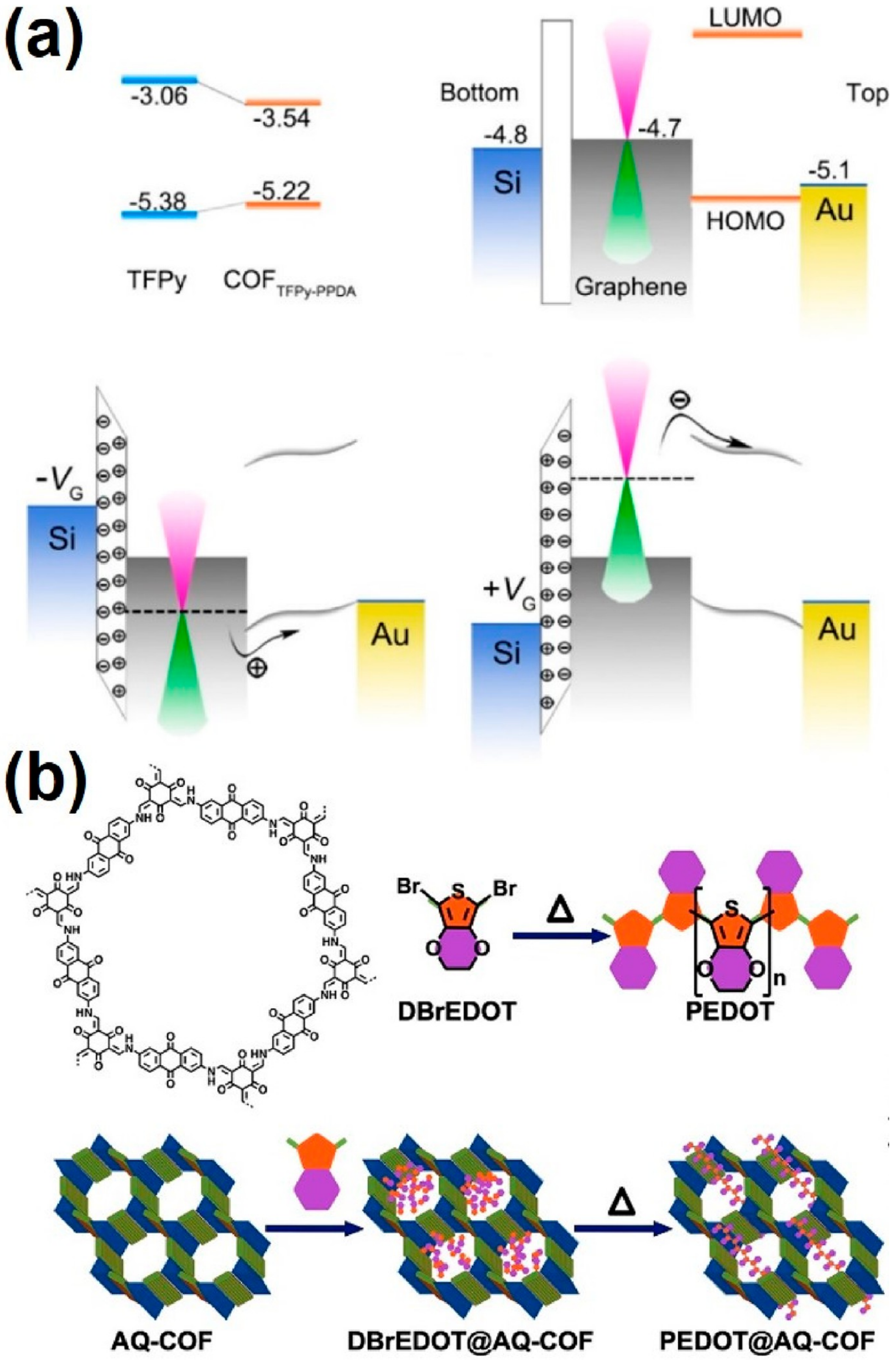

Figure 3. (a) Band diagrams of the COF. Reprinted with permission from ref 60. Copyright 2017 American Chemical Society. (b) Chemical structure of the poly(3,4-ethylenedioxythiophene)/COF. Reprinted with permission from ref 62. Copyright 2019 American Chemical Society.

The COFs were prepared by reacting different ratios of C3-symmetric dehydrobenzoannulene monomers with C2-symmetric linkers to yield three types of COFs (Figure 2b). Additionally, manipulating the crystallizing process of COFs is a potentially effective method to functionalize the final products. This concept has been demonstrated in a recent study by Tan et al., where an amorphous polyimine product formed through a Schiff-base reaction was transformed into crystalline polyimine following the heat treatment.[51] Typically, a Fe_3O_4 template-mediated method was employed to prepare the crystalline COFs, in which

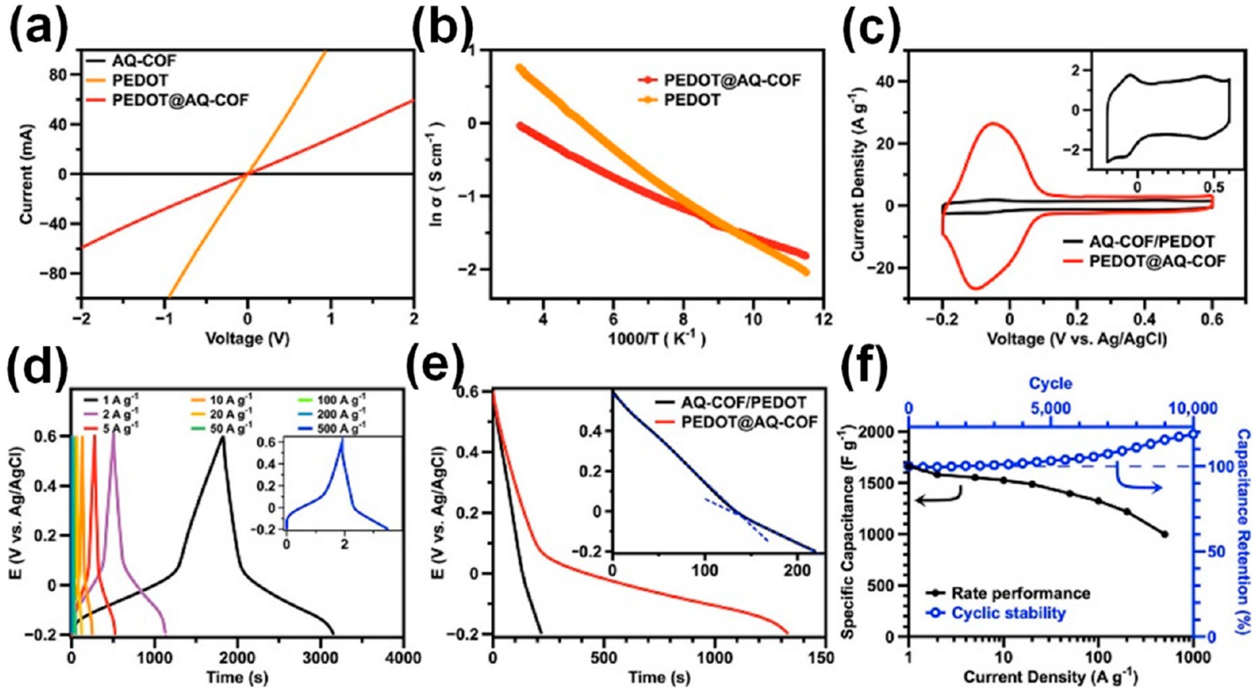

Figure 4. (a) Current–voltage plots. (b) Conductivity profiles with temperature dependent. (c) Cyclic voltammetry curves. (d) Voltage profiles of galvanastatic charge/discharge process. (e) Voltage profiles of discharge profiles. (f) Rate performance and lifetime results. Reprinted with permission from ref 62. Copyright 2019 American Chemical Society.

an amorphous polyimine network intermediate was formed, followed by a solvothermal-assisted disorder-to-order transformation to the desired crystalline product.

As demonstrated above, researchers should pay special attention to the stability and the composition of the COF when designing new synthetic methods. Water sensitivity remains a challenge that currently profits the widespread application of COFs as it limits the synthesis process, as well as the realistic use of these materials outside of a laboratory setting. As for the composition, researchers should consider synthesitic routes that avoid the use of metal species in COFs, and particularly noble metal speices, in order to reduce the manufacturing costs associated with these materials. Finally, researchers should continue to leverage organic chemical methods to tune the properties of COFs through the introduction of various functional groups.

3. METAL-ION BATTERIES

3.1. COFs Working as Host Materials.

Since their introduction several decades ago, metal-ion batteries have received great attention and are considered to be a promising solution to address both the ever-decreasing fossil energy resources and ever-increasing demand for electric vehicles, in addition to powering various electronic devices and storing energy generated from natural energy resources. Although metal-ion batteries have seen great advances in recent years, the avenues for further development seem to be limited to new composite materials that incorporate metal salts, such as metal oxides, selenides, and sulfides, which typically have high densities due to the metallic components.[52,53] In contrast, COFs built with nonmetal species are relatively less dense and lighter weight——a significant advantage for improving the energy densities of batteries. However, poor electronic conductivity, limited tolerance toward acidic and basic solutions, and sensitivity toward water molecules are considered potential roadblocks for the implementation of COFs in battery materials.[54]

Battery systems are mainly constructed with anode, cathode, and electrolyte components, among which the capacity values are determined by the electrode materials. Generally, electrode materials are comprised of either single phase components, which are used as the electrochemically active species, or composites, which serve as either the support materials or as the electrochemically active materials. Because of their versatility, COFs incorporated in electrode materials can act as efficient support matrices for functional group loading, as well as the independent electrochemically active species in metal-ion batteries. In brief, incorporating redox-active functional groups within COF matrices is an efficient approach for creating multiple redox couples. Furthermore, COFs represent a class of promising precursors for the preparation of microporous and mesoporous carbon materials,[55] which play a key role in electrochemical systems as their large surface areas can result in higher capacities and fast dynamic exchange. Although COFs provide a new methodology for fabricating highly porous carbon materials, the poor conductivity of COFs limits their implementation as electrode materials. The ionic conductivity of COFs can be manipulated by modulating the pore size through the appropriate selection of linkers, which results in an appropriate aperture that facilitates ion diffusion. Though some COFs exhibit inherent conductivity, most of them show unsatisfactory electronic conductivity for use as electrode materials in batteries. One potential strategy to circumvent this issue involves the introduction of conductive skeletons, such as carbon nanotubes, metal foams, and conductive powders, which enable the construction of electronically conductive channels inside the COF matrices.[56] In this regard, Zha et al. employed graphene for improving the electronic conductivity of anthraquinone electrodes, in which anthraquinone-based COFs were introduced on a graphene through a Schiff-base reaction.[57] However, one of the disadvantages with this system is that the electrostatic repulsion between graphene and the formed COF results in poor conductivity, thereby rapidly reducing the capacitance values.

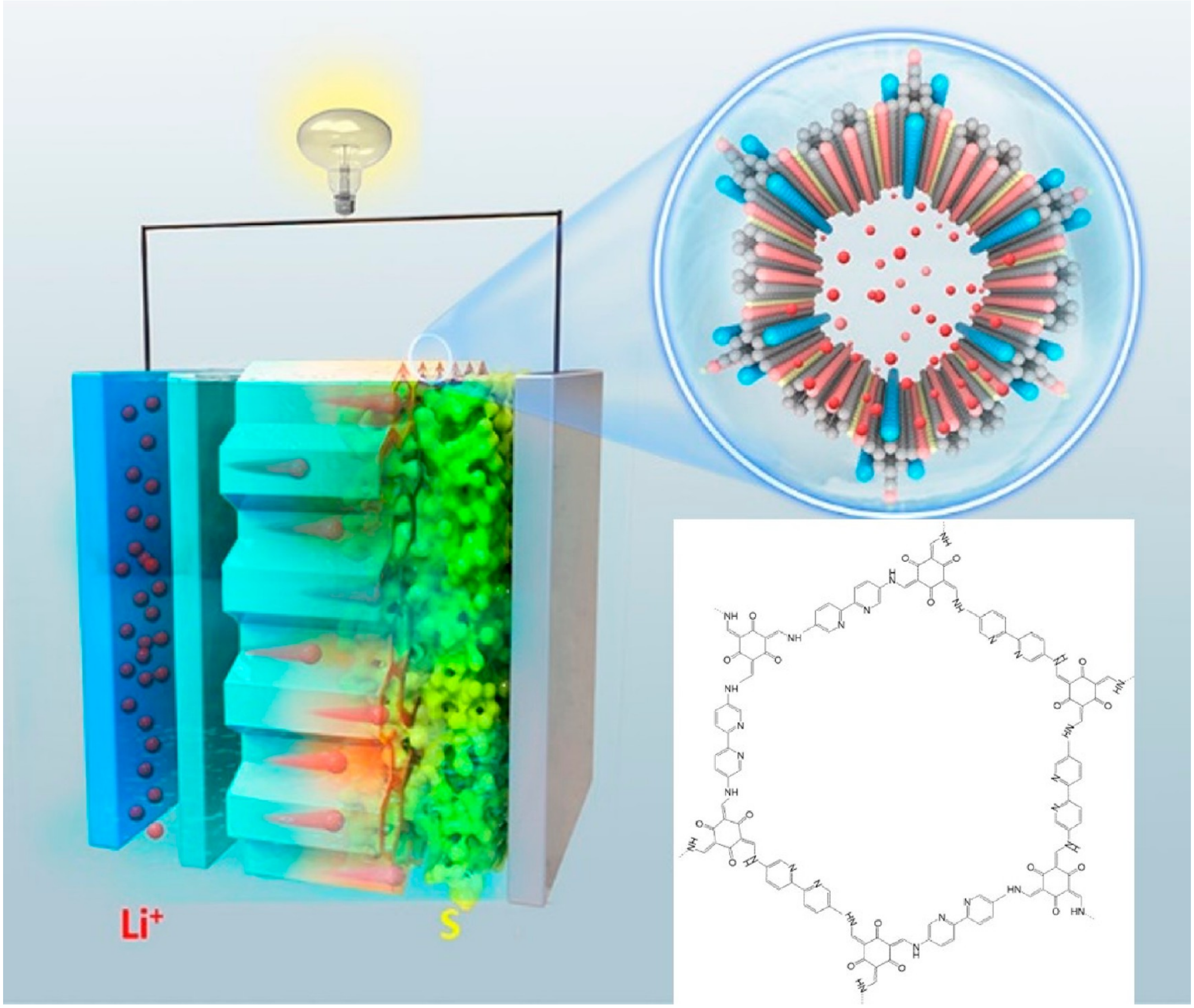

Figure 5. Schematic illustration of the Li−S battery. Reprinted with permission from ref 64. Copyright 2019 American Chemical Society.

Alternatively, implanting conductive functional groups or conductive polymers on the COFs can potentially introduce electrical conductivity to the ensuing material. Xu et al. have also reported the use of electronic conductive supports for improving the electrochemical reaction dynamics and structural stability of COFs.[58,59] The highly improved ionic conductivity is evaluated using electrochemical impedance spectroscopy, in which the charge-transfer resistance was reduced from 129 to 8.5 Ohm following the introduction of carbon nanotubes into the structure. Overall, this improved ionic conductivity may potentially facilitate the utilization of COF-based active materials. Sun et al. demonstrated an organic electronic device constructed from single-layer graphene and an oriented COF that was prepared through a solvothermal method using 1,3,6,8-tetrakis(*p*-formylphenyl)-pyrene and *p*-phenylenediamine as the building blocks.[60] High on-current densities, current densities, and on/off ratios were obtained because of the tunability of the work function between single-layer graphene and the two-dimensional COF (Figure 3a). The band gap was reduced by 0.64 eV, resulting in a lower energy barrier for the injection of electrons and holes. In this study, the introduced COF layers in between graphene layer and gold serves as a charge flow channel. When positive voltage was loaded, an electron could inject in the COF layer (n-type channel); in contrast, the p-type channel was constructed when negative voltage was loaded enhancing the work function of the graphene. The reasonable band gap of COF effectively allows the flow of charge carriers under certain confinement conditions.

Typically, the attachment between graphene and the COF was mainly nonselective, resulting in small enhancements in conductivity. However, Colson et al. reported a well-defined COF on single-layered graphene that was synthesized through a graphene-template method to control the COF growth on the photolithography-derived graphene layers;[61] overall, this breakthrough processing technique facilitates the integration of graphene into diverse devices. Alternatively, electronic conductivity can also be enhanced by building an electron transfer pathway inside the pores of COFs. As demonstrated by Wu and co-workers,[62] electronically conductive chains comprising poly(3,4-ethylenedioxythiophene) are formed inside COFs (Figure 3b), resulting in an all-organic electrode with capacitance values up to 1663 F g^{-1} at a current density of 1 A g^{-1}. Furthermore, ultrafast charge/discharge capabilities and excellent device lifespans have

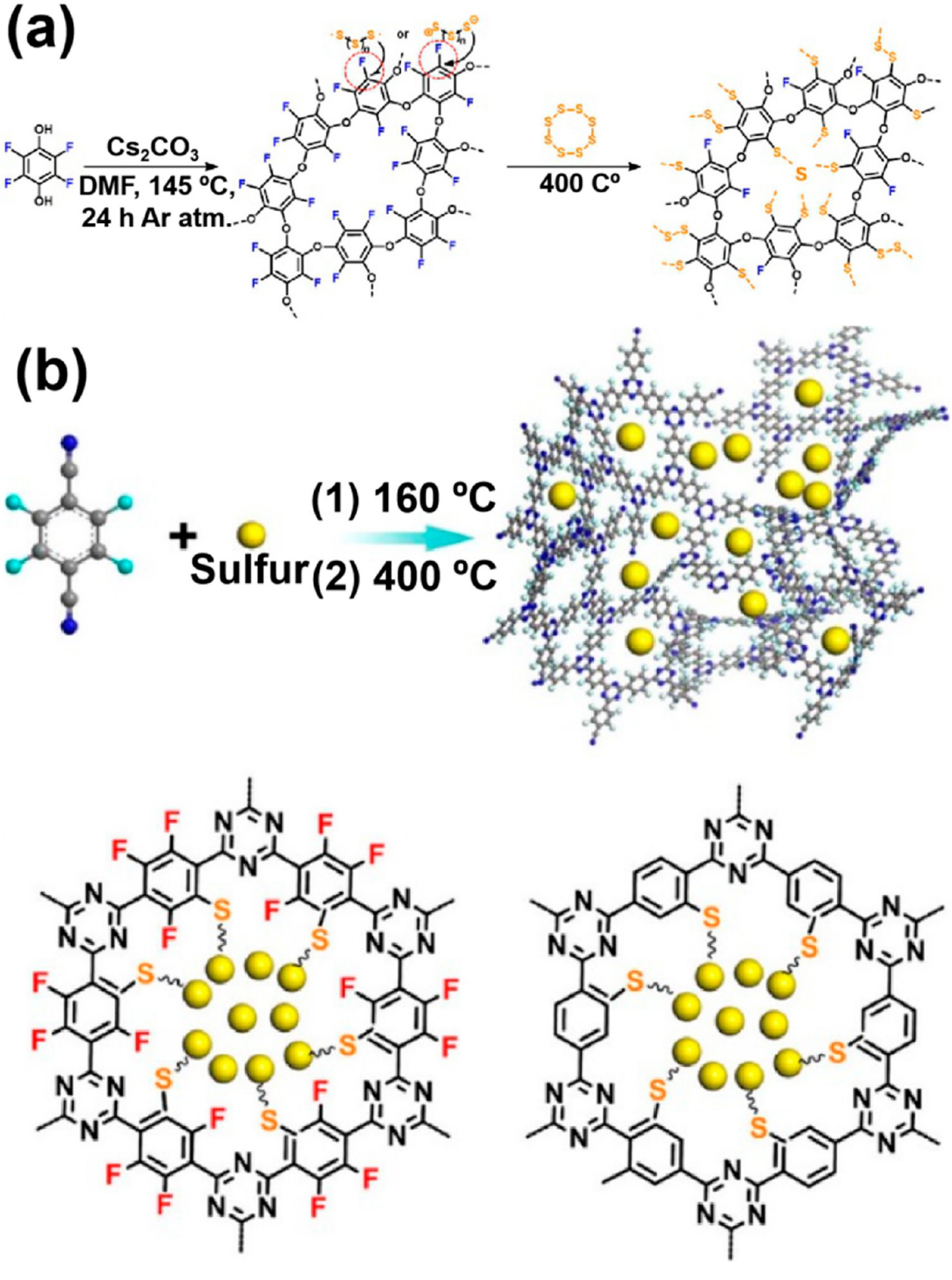

Figure 6. (a) Schematic illustration of the S absorption process. Reprinted with permission from ref 69. Copyright 2019 American Chemical Society. (b) Schematic illustration of S fixing process. Reprinted with permission from ref 70. Copyright 2017 American Chemical Society.

been reported with a capacitance of 998 F g^{-1} at a high current density of 500 A g^{-1} (Figure 4). This innovative design unprecedentedly combines the favorable structural features of the inner channels in the COFs with nanolevel control in postprocessing techniques. Importantly, this method successfully avoids alterations of the as-prepared COFs, a common problem with many postprocessing techniques that are currently utilized.

3.2. Elimination of Polysulfide Shuttling. Li−S batteries represent a class of promising candidates for effective energy storage in the future. The construction of Li−S batteries is similar to the Li-ion batteries, in which the active species in cathode materials are mainly elemental sulfur for storing the lithium ions. The lithium polysulfide is formed upon discharge, some of which is soluble in the organic electrolyte. Lithium ions migrate

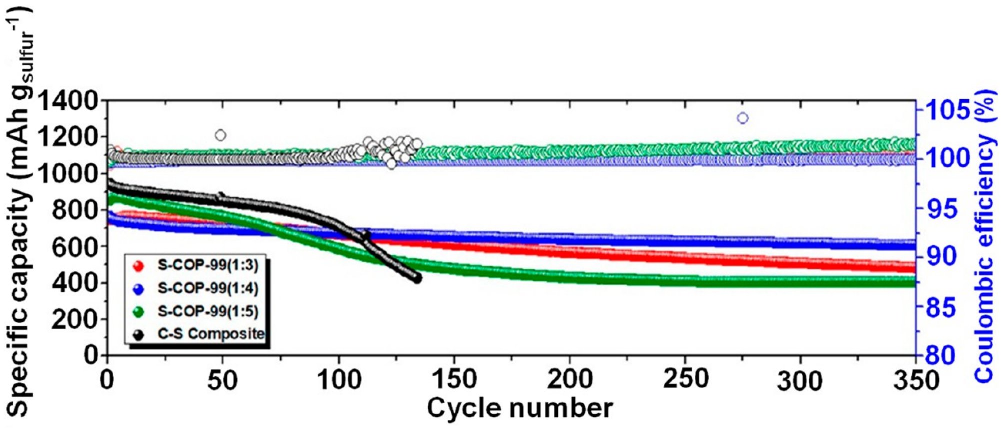

Figure 7. Cycling performance of the products with different ratios. Reprinted with permission from ref 69. Copyright 2019 American Chemical Society.

back to the anode upon charge process. However, the dissolution of polysulfide, or the polysulfide shuttling effect, is a crucial disadvantage that has been hampering the use of Li−S batteries in practical applications.[63] Some two-dimensional COFs have been found to absorb polysulfides, presenting a potential strategy to inhibit the dissolution of polysulfide in Li−S batteries. In this regard, Liao et al. prepared porphyrin-based COFs to be used as sulfur hosts in the rechargeable Li−S batteries. In repeated charge/discharge processes at a current density of 840 mA g^{-1}, a capacity of 633 mA h g^{-1} was obtained with a sulfur loading amount of 55%,[58] demonstrating the feasibility of storing sulfur in nanopore environments. Xu et al. prepared 2,4,6-triformylphloroglucinol and 5,5′-diamino-2,2′-bipyridine-based COFs through the Schiff base reaction,[64] resulting in a material that combines the benefits of the fast lithium-ion transfer pathway, which is provided by the one-dimensional pathway in the as-prepared COF, as well as the polysulfide adsorption properties that are enabled by the pyridine units (Figure 5). Furthermore, Ghazi et al. demonstrated chemisorption of polysulfides by COFs:[65] Both the COF-1 and *N*-doped covalent organic framework can effectively trap polysulfides, with binding energies of 34 and 24 kcal mol^{-1}, respectively, with a decrease in bonding energies as the lengths of polysulfide chains are shortened. The good integrity is widely demonstrated.[66,67] Talapaneni et al. provided a new approach for the synthesis of covalent triazine-based frameworks.[68] Following preparation of this material from elemental sulfur, a high sulfur loading of up to 62% was observed with spatially refined micropores effectively leading to a homogeneous distribution of polysulfide throughout the COF.

Another innovative method to avoid the detrimental polysulfide shuttling behavior is to limit diffusion of the polysulfide through the use of nucleophilic aromatic substitution reaction (S$_N$Ar). Shin et al. demonstrated this concept through the use of fluorinated COFs as a sulfur host (Figure 6a).[69] During the electrochemical reaction, the fluorinated compound can trap the polysulfide by both steric (pore size of around 1 nm) and electrostatic confinements. Following this reaction, a high sulfur loading amount of 70% is achieved, in addition to 79.9% capacity retention of the initial 762 mAh g^{-1} capacity (Figure 7); this work represents a breakthrough in the study of the S$_N$Ar-based inhibition of polysulfide dissolution. Similarly, Xu et al. demonstrated this concept by using fluorinated porous triazine-based frameworks (Figure 6b), which exhibits enhanced capacity relative to that of either N-doped covalent organic framework-S or porous carbon (Figure 8).[70]

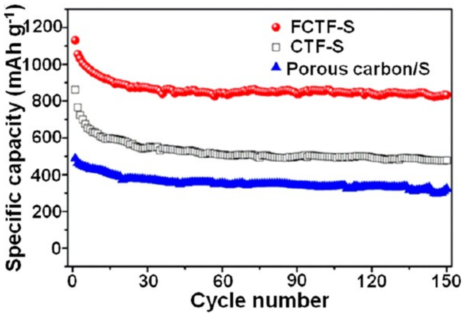

Figure 8. Cycling performance of the prepared COFs. Reprinted with permission from ref 70. Copyright 2017 American Chemical Society.

Furthermore, the observed enhancement in capacities (Figure 9) may also ensue from high crystallinity of the sulfide-based COFs prepared using the S$_N$Ar reaction.[71] The well-refined crystalline structures form smooth charge transfer tunnels inside the active materials while ensuring sufficient exposure of redox active sites (Figure 10). Recently, a simultaneously lithiophilic and sulfiphilic COF-based material was prepared through the use of a single building block, 4-cyanophenylboronic acid, that contains both N (lithiophilic) and B (sulfiphilic) species (Figure 11).[72] In the electrochemical study, the feasibility of combining the oppositely charged features by the single COF material is demonstrated, which provides a new concept of dual-affinity. To synthesize frameworks in a controlled fashion, Li et al. fabricated hollow COFs using porphyrin blocks via a template-based method in which both the shell thickness and the pore size could be tuned from 40 to 500 nm. The resulting COF exhibits good electrochemical stability with high retained capacity values of 773 mAh g^{-1} after 200 cycles, whereas the capacity of the carbon black-based one quickly decayed to 477 mAh g^{-1} under analogous conditions.[73] This strategy combines the advantages of both physical confinement and chemical adsorption for mitigating the undesired polysulfide shuttling.

3.3. COFs as Cathode Materials.

In order for electrodes to achieve high specific capacities, high electrochemical activity and lower density (lightweight) are the two most vital design parameters for electrode materials. In this regard, COFs are great potential electrode material candidates due to their high redox activity and absence of metal species. The performance of most previously reported metal-based electrode materials was dependent on the change in the valence of metal ions, despite the presence of several nonmetals, such as S, Si, and Se. In contrast,

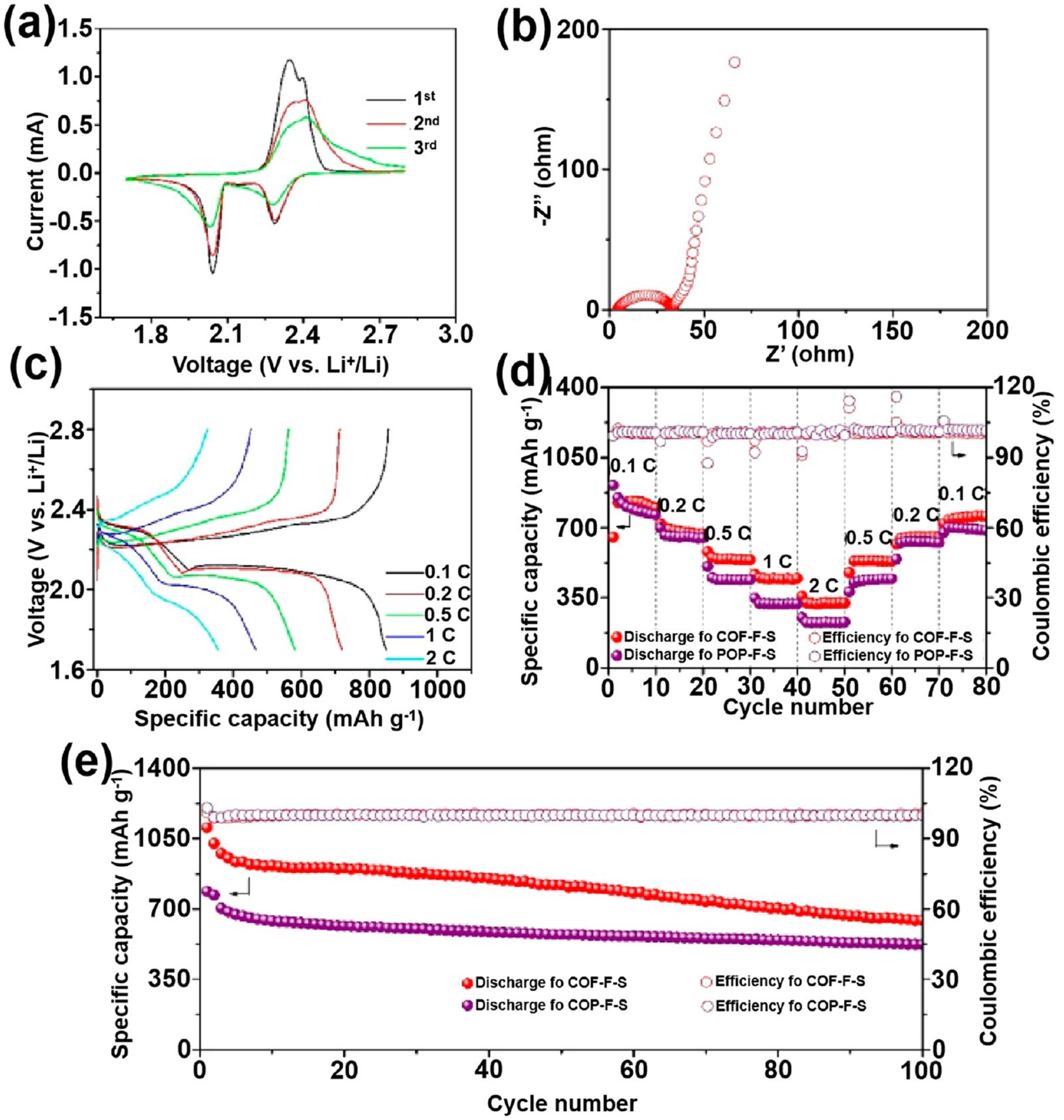

Figure 9. Electrochemical performance of the cells: (a) cyclic voltametry curves; (b) electrochemical impedance spectrum; (c) voltage profiles; (d) rate performances; (e) repeated charge/discharge cycling measurements. Reprinted with permission from ref 71. Copyright 2018 American Chemical Society.

the direct use of COFs as electrode materials is an innovative method whereby redox active functional groups in the matrices govern the performance of these materials. Ding et al. prepared tetrathiafulvalene-based COFs and examined their redox activity using a cyclic voltammetry study,[74] indicating that the introduction of tetrathiafulvalene endows the matrix COF with surface-controlled processes, with two pairs of redox peaks at 0.69 and 1.07 V vs Ag/AgCl, respectively. Luo et al. demonstrated the electrochemical activity of the carbonyl functional groups in poly(imide-benzoquinone) with a 10 Li^+ redox capability.[75] Furthermore, a 14-electron redox reaction was reported by Lei et al.[76] in which Li^+ ions can be electrochemically absorbed by both the C═N group (1 Li^+) and benzene rings (6 Li^+). Combined, these works strongly suggest the feasibility of incorporating multiple redox-active groups within the COF matrix, which can be potentially beneficial for improving the energy density, in terms of specific capacity, for metal-free COF-based electrode materials.

The active sites at the COFs play a crucial role during electrochemical reactions and exposing redox active sites can potentially further improve the electrochemical performance of COF materials. Wang et al.[77] exfoliated stacked, layered COFs and carried out lithium-ion storage capability measurements, finding that the redox reactions are dominated by a charge-transfer process rather than a diffusion-controlled process as in pristine COFs (Figure 12a). Typically, delaminating anthraquinone-based COFs results in materials with excellent electrochemical properties, such as long lifetimes (up to 1800 cycles) and good rate capability (74% capacity retention at a current density of 500 mA g^{-1}, in comparison with that at 20 mA g^{-1} for the control material). Finally, the capacity can potentially

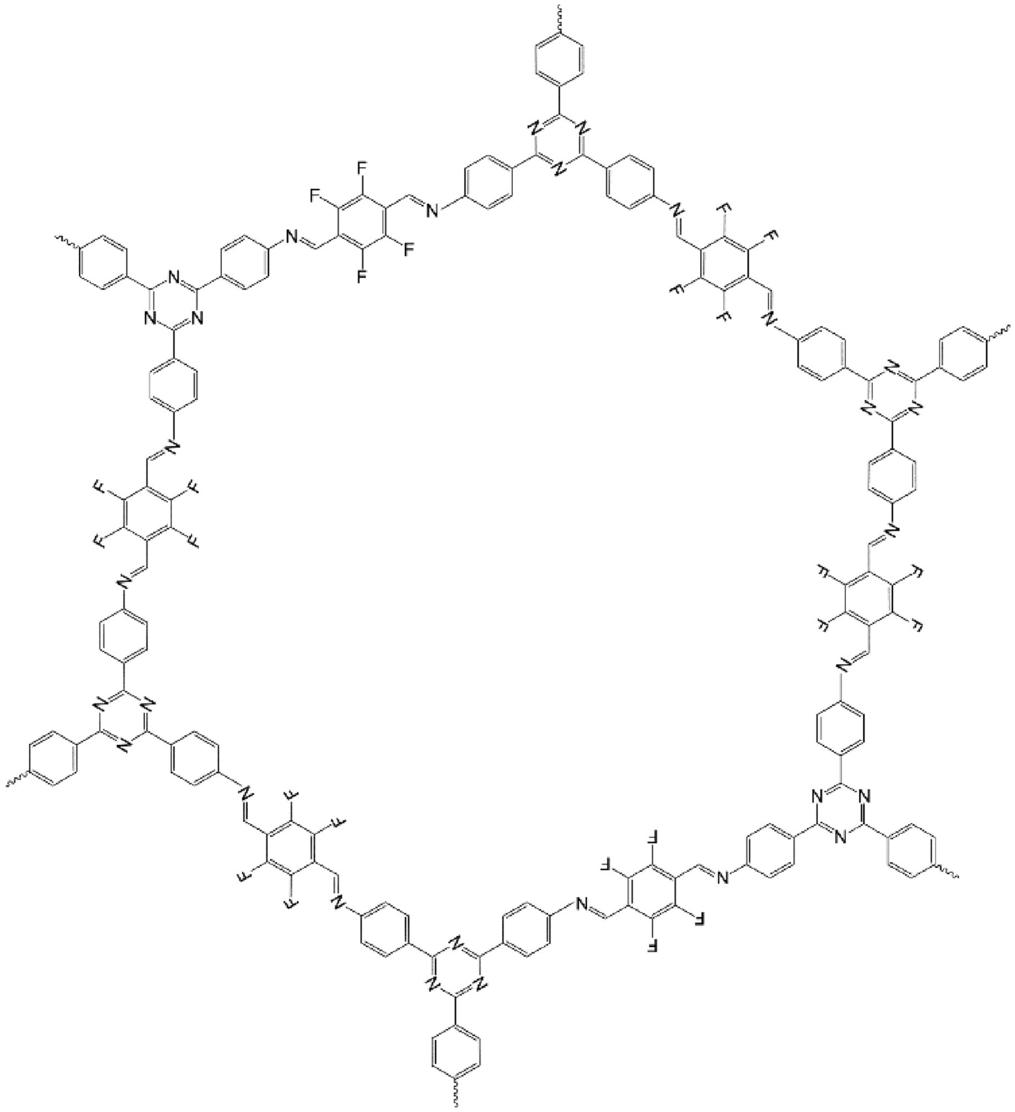

Figure 10. Material structure of the synthesized COF through S_NAr reaction.

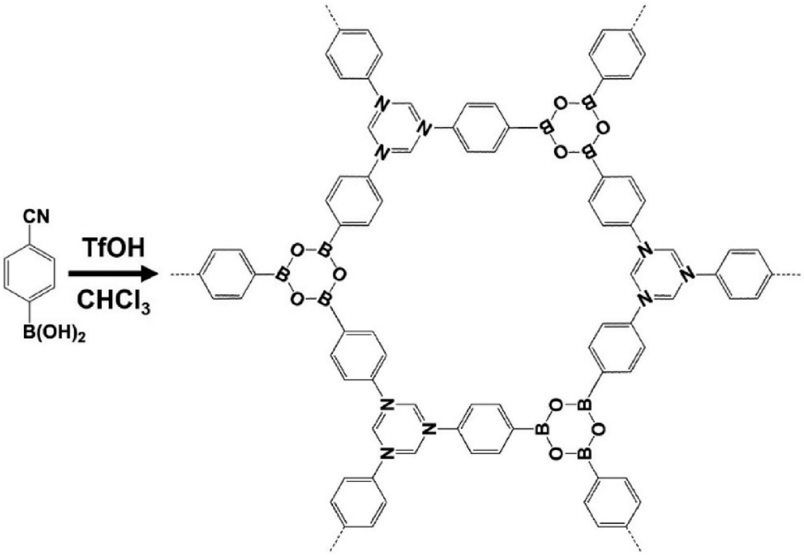

Figure 11. Schematic illustration of the COF synthesis mechanism.

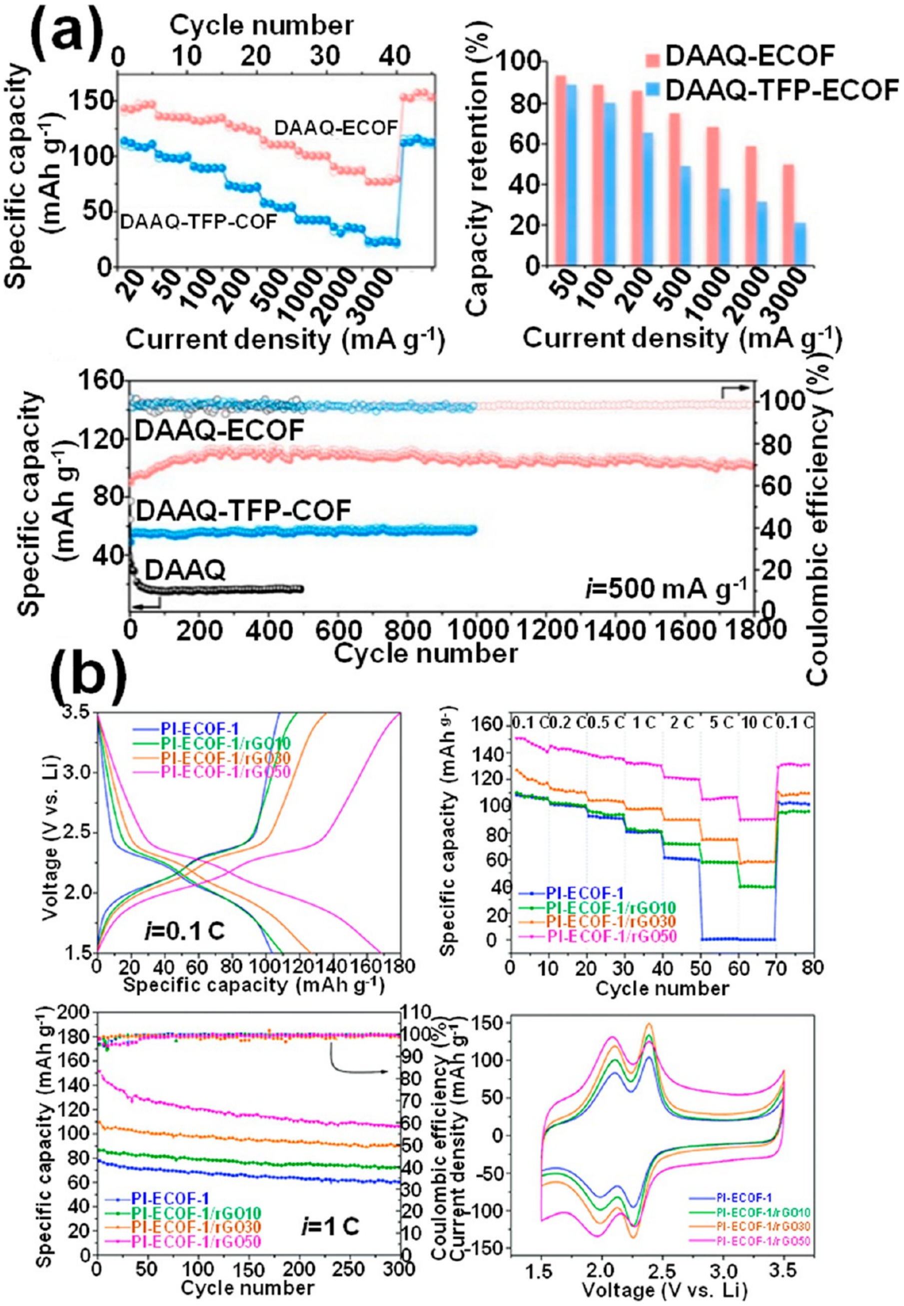

Figure 12. (a) Rate performance, capacity retention, and long-term cyclability and Coulombic efficiencies. Reprinted with permission from ref 77. Copyright 2017 American Chemical Society. (b) Charge/discharge profiles, rate performance, repeated charge/discharge cycling performance and Coulombic efficiency, and cyclic voltammetry curves. Reprinted with permission from ref 80. Copyright 2019 Royal Society of Chemistry.

be further modified through the use of a reticular design strategy.

Alternatively, enhanced conductivity can also be obtained through the enforcement of backbone planarity, or by increasing the surface areas of the COF material.[78] Indeed, these two methods result in the construction of wide, robust charge-transfer tunnels during electrochemical reactions. In one example, improved conductivity in COFs has been achieved through the use of oriented benzodithiophene COF thin films that exhibit improved electron and hole conductivities.[79] The electrochemical dynamics and capacities can be simultaneously modified by integrating conductive supports and thinner active materials. Wang et al. reported composite electrode materials using pyromellitic dianhydride and tris(4-aminophenyl)amine or 1,3,5-tris(4-aminophenyl)benzene (Figure 13).[80] The products have increased graphene oxide content relative to the control materials and display significant enhancements in their electrochemical capacities, increasing from 103 to 167 mAh g^{-1} at 14.2 mA g^{-1} (Figure 12b). Additionally, poly(1,4-anthraquinone) and poly(1,5-anthraquinone) were found to be suitable cathode materials for lithium-ion batteries as the systems that incorporate these materials exhibit an electrochemical capacity of 257 mAh g^{-1}, which approaches the theoretical capacity value of 260 mAh g^{-1}, while also displaying a small charge/discharge voltage gap of 0.04 V that is attributed to lower hysteresis.[81] The orientation of the COF matrix can effectively expose the redox-active functional groups and facilitate the electrochemical reactions, which was demonstrated by DeBlase et al. in which well-oriented anthraquinone groups were synthesized

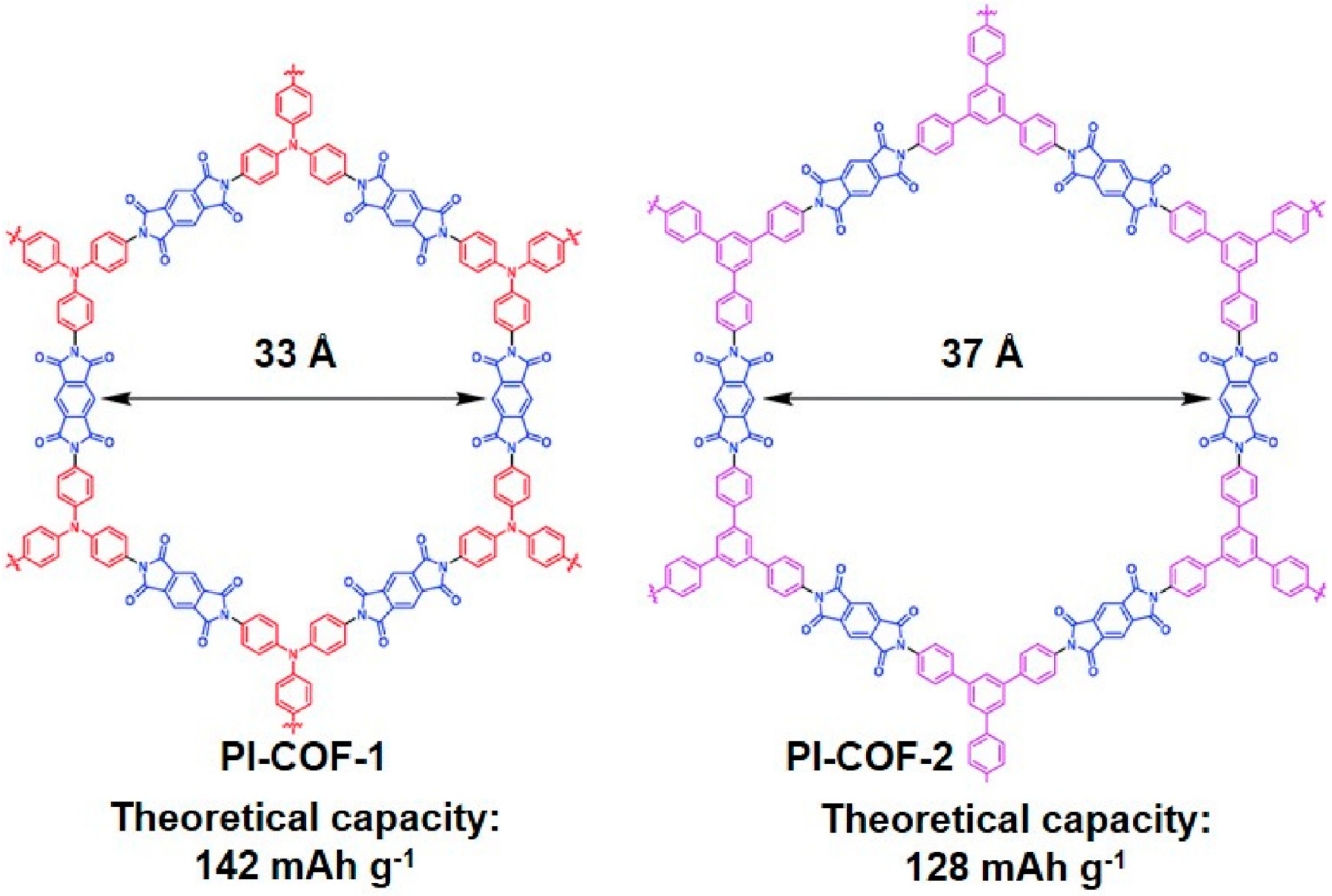

Figure 13. Material structures of two different types of COFs. Reprinted with permission from ref 80. Copyright 2019 Royal Society of Chemistry.

on a COF with a thickness of less than 200 nm (Figure 14).[82] Although the accessibility of redox-active functional groups presents a current roadblock that limits the potential for these materials in energy-storage application, postsynthetic engineering is an efficient strategy to immobilize the active radicals on the framework, resulting in materials that exhibit highly reversible electrochemical reactions.[83]

3.4. COFs as Anode Materials. Because of safety issues resulting from the uncontrolled growth of lithium dendrites in Li-ion batteries, the search for new anode materials that can mitigate this undesired process represents a significant focus in this field. Similar to the desired features for cathodes, alternative anode materials also need high specific capacities and good reaction dynamics; as such, COFs with high transport dynamics are appropriate for use as anode materials. Zhang et al. demonstrated the feasibility of using COF-derived porous carbon materials with N dopants as anode materials for Li- and Na-ion batteries.[84] Similarly, a novel two-dimensional COF prepared from polyporphyrin and 4-thiophenephenyl precursors was used as an anode material in Li-ion batteries in a study by Yang et al. (Figure 15a), resulting in a battery with a high lithium-ion storage capacity of up to 666 mAh g^{-1} (Figure 15b).[85] Liu et al. demonstrated that exfoliated trizaine-based COFs with AB-type stacking act as excellent anode materials for Na-ion storage due to the robust and conjugated porous structure, resulting in a battery with a capacity of 262 mAh g^{-1} at a current density of 0.1 A g^{-1}.[86] In this study, both micromechanical and liquid methods were employed for the exfoliation of bulk COFs.

3.5. COFs as Electrode Materials for Electrochemical Capacitors. Capacitors are devices that can be used to achieve momentary high-power densities, which is a shortcoming of battery systems as they only exhibit high energy densities. Generally, the difference between charge/discharge mechanisms (physically for capacitors, electrochemically for batteries) determines the final energy-storage feature of devices. Because of the increasing demand for electric vehicles, studies on electrochemical batteries with satisfactory power densities are being pursued. Additionally, a hybrid type of electric energy-storage system prepared from a battery-type anode and capacitor-type cathode is being studied as a potential route to achieve both high energy and power densities.[87] This methodology has shown some promise relative to systems incorporating conventional designs;[88] despite these advances, however, the preparation of promising electrode materials remains a challenge because of difficulties related to unbalanced reaction kinetics and specific capacity amounts. The straightforward methods for the tunability of pore sizes in COFs, in addition to the large number of organic groups available for functionalization, enable effective electrode material engineering to match with the charge carriers in electrolytes.

Recently, researchers have designed and synthesized innovative COFs that exhibit improved efficiencies, and their highly porous crystalline structures and a tunable pore size suggest the feasibility of their use as electrode materials for high-performance capacitors. Patra et al. prepared a benzimidazole-based covalent-organic polymer via the Schiff base condensation reaction that exhibited

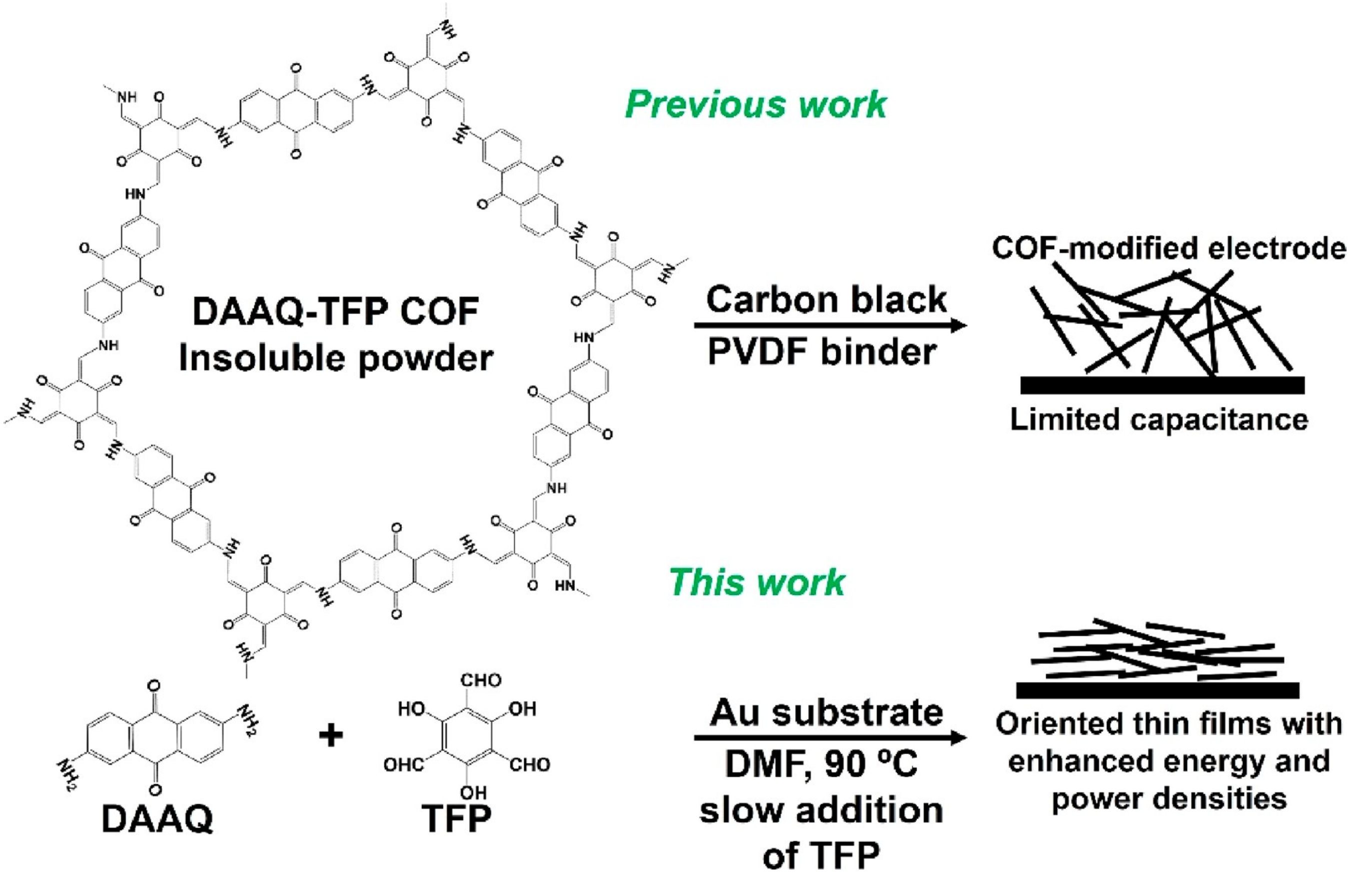

Figure 14. Structure of the hexagonal subunit of the 2,6-diaminoanthraquinone-1,3,5-triformylphluroglucinol COF.

a high capacitance of 335 F g^{-1} and good cyclic stability of up to 1000 cycles (Figures 16a, b and 17).[89]

Khattak et al. synthesized a series of pyridine-based COFs and demonstrated the redox activity of the pyridyl functional group in H_2SO_4 solution through a controlled method (Figures 16c, d and 18).[90] A long-term lifetime of up to 6000 charge/discharge cycles has been demonstrated for the pyridine-containing COF, and a 2D−2D electrode material with an edge-ion (vertical) orientation has also been developed.[91] This innovative structure was achieved by vertically coordinating the diboronic acid molecules onto graphene sheets before the growth process takes place. After carbonization treatment, the electrochemical performance of this material was evaluated in a supercapacitor to provide insights into the structural design of the electrode materials, where it was found that electrochemical activity can also be improved by enriching the π-electron communication throughout the framework. The structural engineering plays a significant role for the high-performance capacitors.[92−95] Graphene is an important component,[96−100] together with others, such as MXene and organics,[101,102] for capacitor construction. In the report by Xu et al., Knoevenagel condensation reaction was employed for integrating the 3,5-dicyano-2,4,6-trimethylpyridine and 1,3,5-triazine units into a COF material.[103] Bhanja et al. synthesized TDFP-1 through a Schiff base condensation reaction of two monomers, 1,3,5-tris(4-aminophenyl)triazine and 2,6-diformyl-4-methylphenol.[104] A diffusion-controlled charge storage process was determined, with a pair of redox peaks resulting from the COF, and a superior capacitance of 354 F g^{-1} at 2 mV s^{-1} was obtained together with a good capacitance retention. In addition, doped and highly porous carbon materials can also be prepared by carbonization operations at various temperatures. An N-doped amorphous carbon material formed by the carbonization of a COF precursor at 800 °C exhibited a capacitance of 230 F g^{-1} at a current density of 0.5 A g^{-1} (Figure 19a).[105] The COFs used in capacitors allow molecular-level control to manipulate the capacitance. For example, TpPa-$(OH)_2$ was found to have excellent capacitances of 416 F g^{-1} at 0.5 A g^{-1} in a three-electrode system.[106] This superior result was attained because of the reversible proton-coupled electron transfer (Figure 19b).

3.6. Solid-State Electrolyte.

Electrolytes in battery systems serve both as electronic insulators and as ion conductive components, and the excellent ionic conductivity of liquid electrolytes has made them attractive for use in batteries despite several potential disadvantages, such as leakage and flammability. Recently, solid-state electrolytes have received growing attention because of improvements in ionic conductivity, as well as the safer operation relative to their liquid counterparts, following the discovery of perovskite-type solid electrolytes in all solid-state Li-ion batteries. Importantly, the absence of flammable components and the lack of susceptibility to leakage of solid electrolytes make them potential candidates for incorporation into the next generation of battery and capacitor systems. Pioneering reports have demonstrated the feasibility of using metal−organic framework materials as solid electrolytes,[107−114] and the inherent porosity of these structures allows for the introduction of other species inside metal−organic frameworks, such as metal ions and functional groups, that can further improve performace.[115] Thus, researchers envisioned extending the concept of building solid-state electrolytes materials from using porous frameworks to include COFs, which are

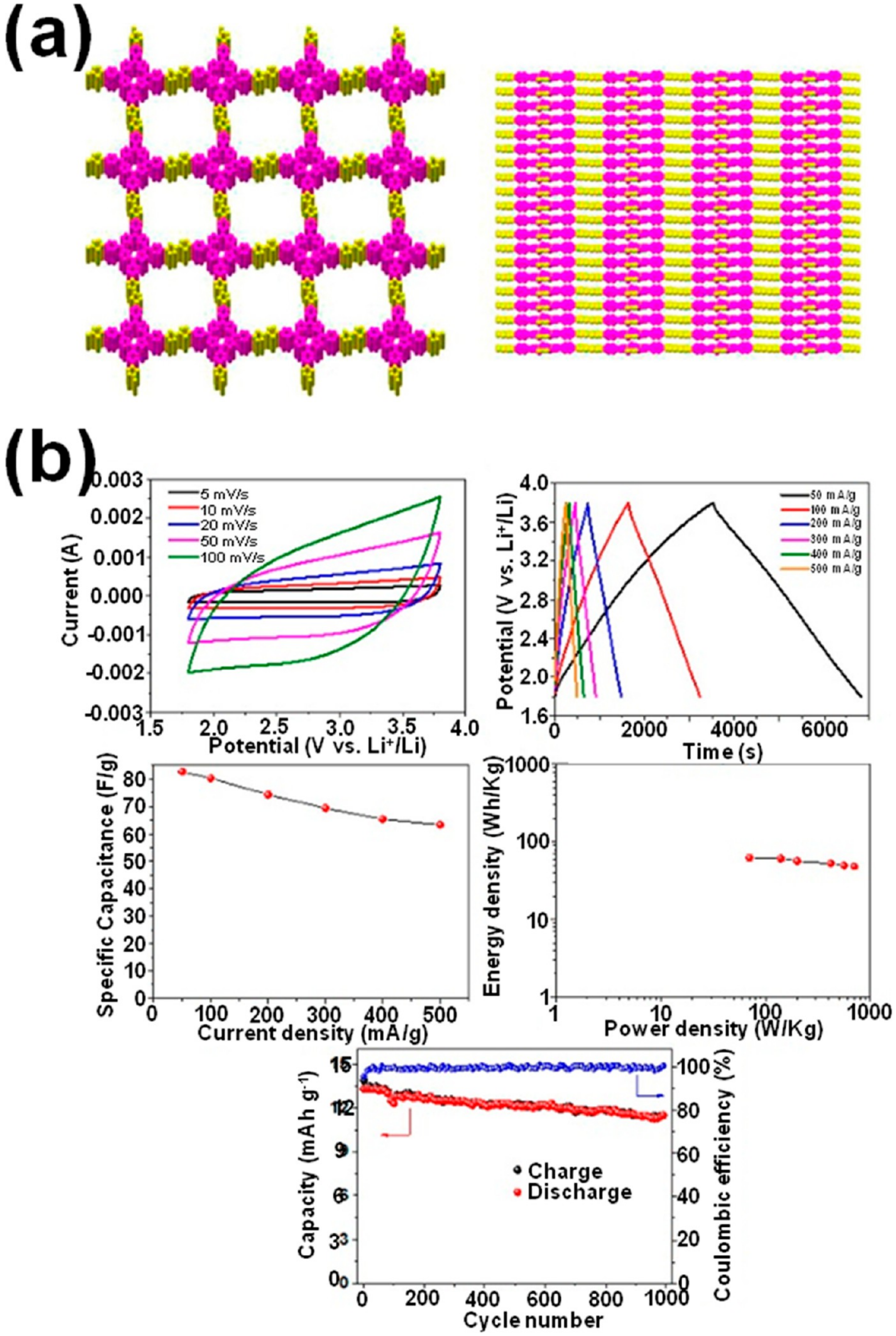

Figure 15. (a) Pursued material morphologies of the simulated COF. (b) Cyclic voltammetry curves, voltage profiles, rate performances, Ragone plot, and repeated charge/discharge capacities and Coulombic efficiencies. Reprinted with permission from ref 85. Copyright 2016 American Chemical Society.

potentially advantageous because of the lower densities of these materials as the absence of heavy metal species, which may ultimately result in batteries with lower cell weights. Shinde et al. reported the first mechanochemically fabricated bipyridine-based solid electrolyte for use as a solid electrolyte in fuel cells, achieving an open circuit voltage of 0.93 V and proton conductivity of 1.4×10^{-2} S cm^{-1}.[116] Notably, these values are better than those obtained from the solid electrolyte comprising the solvothermal-synthesized COF, thus highlighting the importance of this preparation method for COFs, which is more eco-friendly.

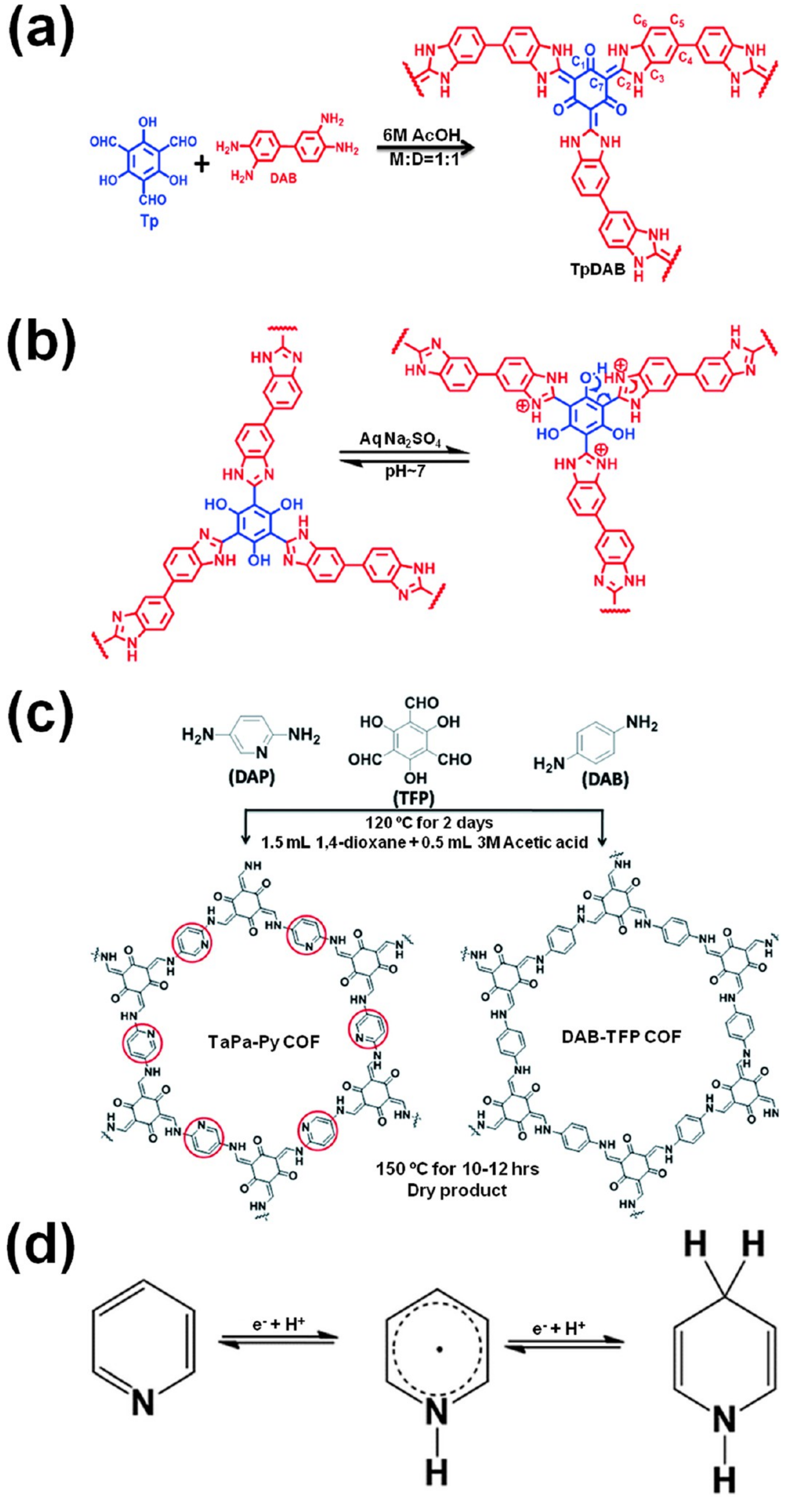

Figure 16. (a) Schematic illustration of the COF synthesis process, (b) oxidation/reduction mechanism of 1,3,5-triformylphloroglucinol 3,3-diaminobenzidine. Reprinted with permission from ref 89. Copyright 2016 Royal Society of Chemistry. (c) Synthetic procedure of the COFs, (d) proposed mechanism for the redox reaction. Reprinted with permission from ref 90. Copyright 2016 Royal Society of Chemistry.

An innovative strategy to improve the Li-ion conductivity inside the COFs was demonstrated by Chen et al. in which Li-associating ion pairs are screened by the incorporation of a cationic skeleton (Figure 20a, b), leading to a facile method to enhance Li-ion concentrations in the material that results in highly improved Li-ion conductivity (up to 2.09×10^{-4} S cm^{-1} at 70 °C).[117] Chandra et al. demonstrated that sulfonic acid-containing COFs built from 1,3,5-triformylphloroglucinol and

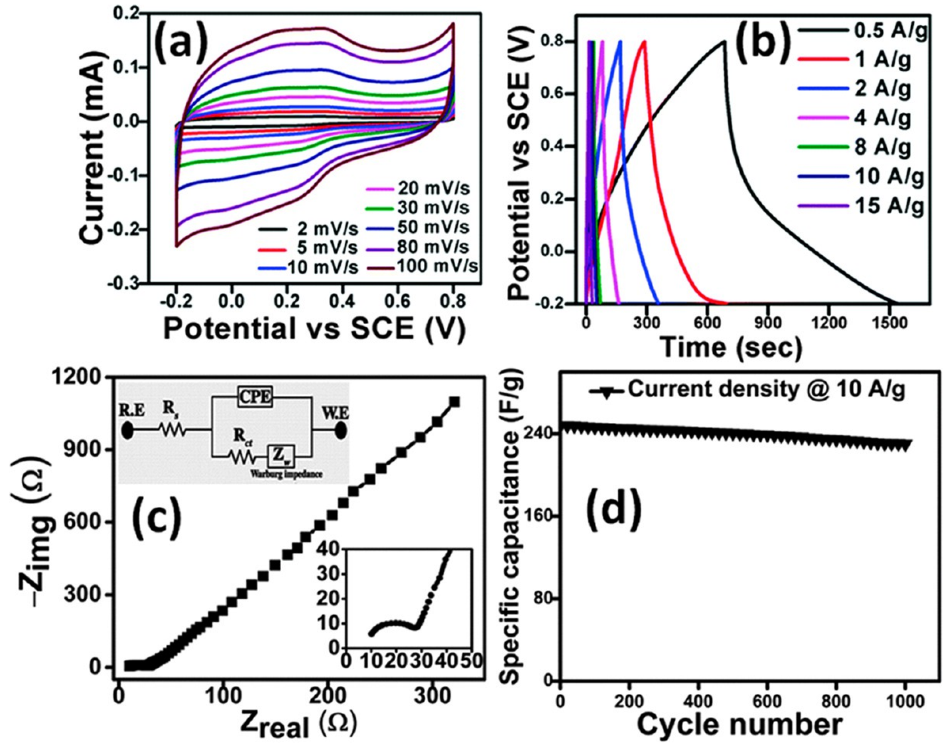

Figure 17. (a) Cyclic voltammetry curves, (b) voltage profiles at different current densities, (c) electrochemical impedance curves, and (d) repeated charge/discharge measurements. Reprinted with permission from ref 89. Copyright 2016 Royal Society of Chemistry.

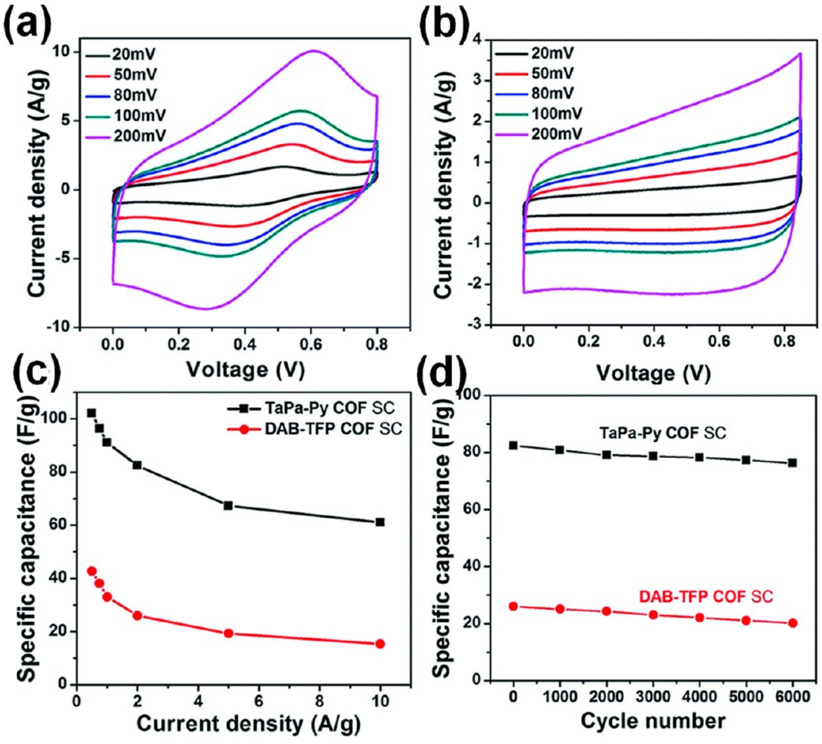

Figure 18. (a, b) Cyclic voltammetry curves, (c) rate performances, and (d) repeated charge/discharge performance. Reprinted with permission from ref 90. Copyright 2016 Royal Society of Chemistry.

2,5-diaminobenzenesulfonic acid exhibit an intrinsic proton conductivity of 1.7×10^{-5} S cm^{-1}.[118] In addition, a COF comprising alkaline pyridine and acidic sulfonic groups was also prepared in order to immobilize the proton carriers. Ultimately, this work provides greater insights into the engineering of COFs for improving the ionic conductivity in the context of electrolytes in electrochemical systems (Figure 21). In a related study, a quasi-transparent and flexible solid-state electrolyte with high proton conductivity of 6.45×10^{-3} S cm^{-1} at 313 K and 100% relative humidity was reported for use in fuel cells (Figure 22a),[119] in which an animine-based COF was formed by a direct Schiff base reaction using 1,3,5-tris(4-aminophenyl)benzene and

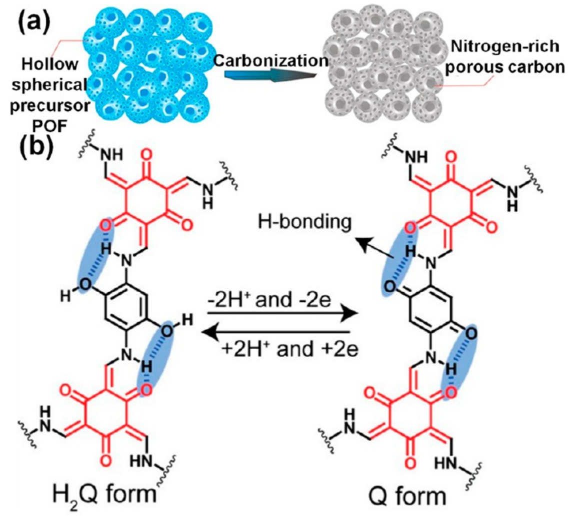

Figure 19. (a) Schematic illustration of the synthesis of nitrogen-rich porous carbon. Reprinted with permission from ref 105. Copyright 2013 American Chemical Society. (b) Proposed H-bonding that stabilizes the formed COFs. Reprinted with permission from ref 106. Copyright 2017 American Chemical Society.

1,3,5-benzenetricarbaldehyde. The fabricated fuel cell has a power density of 12.95 mW cm^{-2} at a specific current of 53.1 mA cm^{-2} at 323 K. Alternatively, mechanical processing offers another effective approach toward the fabrication of crystalline and functionalized COFs.

Vazquez-Molina et al. demonstrated the feasibility of mechanically pressing COFs into different shapes (Figure 22b),[120] and as a result, the products exhibit similar crystallographic properties. Furthermore, the pressed COF pellets impregnated with Li-cation sources reveal good Li^+-ion conductivities; overall, this work provides a facile strategy for fabricating battery cells with desired shapes. In a related mechanochemical synthetic example provided by Peng et al.,[121] diaminobenzene precursors with pendent intrinsic sulfonic acid groups are subjected to a mechanoassisted synthesis (Figures 22c and 23a, b). The resulting products exhibit good proton conductivities (3.96×10^{-2} S cm^{-1} for bare product and 1.58×10^{-2} S cm^{-1} for the COF mixed with polyvinylidene fluoride) in combination with a low activation energy of 0.21 eV.

3.7. COFs in Flexible Electrochemical Energy-Storage Devices.

With an increasing demand for foldable and flexible electronics, internal power sources with structural flexibility are required more than ever before. One of the unique structural merits of highly porous and crystalline COFs is their ability to be fabricated into flexible electrochemical devices, which may potentially lead to suitable flexible battery systems for use in foldable electronics. In conventional battery systems, both the anode and cathode comprising solid, bulk materials, despite the use of liquid electrolytes, and these solid-state electrodes are difficult to manipulate structurally. One innovative approach involves the loading of nanosized active materials onto some flexible supports; however, these materials do not meet the requirements for implementation in electronics applications. Alternatively, the use of inherently flexible, COF-based electrode materials can potentially meet the stringent structural requirements required for these applications. To probe this concept, Li et al. prepared porphyrin-based COFs for flexible and wearable Zn−air batteries and found that the nonmetal cathode exhibited outstanding stability and high energy efficiency.[122] Although the reported device can successfully light a 2.0 V LED lamp under various bending degrees, many potential hurdles remain, such as how to synthesize large-sized COFs with only a few layers, in order for flexible COF-based batteries to be implemented in commercial applications.

Overall, the use of COFs in metal-ion batteries may provide two main insights for future progress. First, elemental sulfur is a competitive material for use as a cathode material of metal-ion batteries because of its low costs and high capacities, as demonstrated in the large number of previous studies, and studies on the interactions between COFs and sulfur represent the main

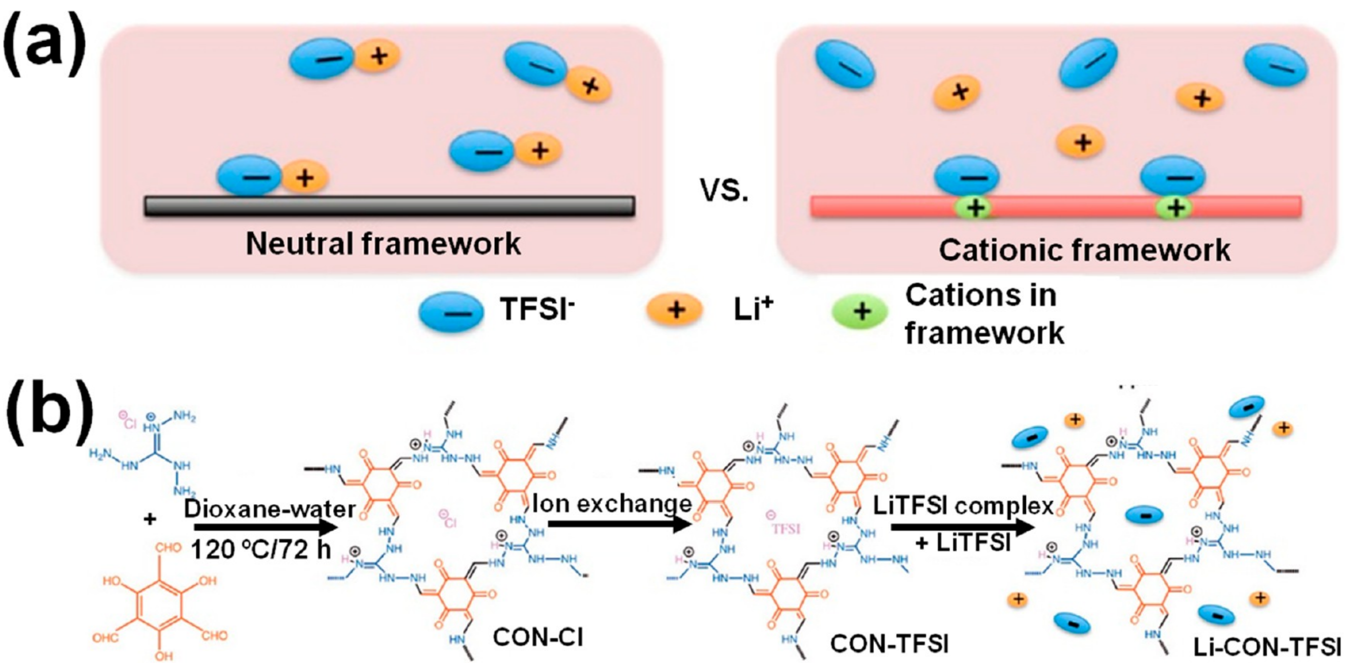

Figure 20. (a) Schematic illustrations of types of COFs, (b) schematical illustration of the synthesis procedure. Reprinted with permission from ref 117. Copyright 2018 ACS Publishing Group.

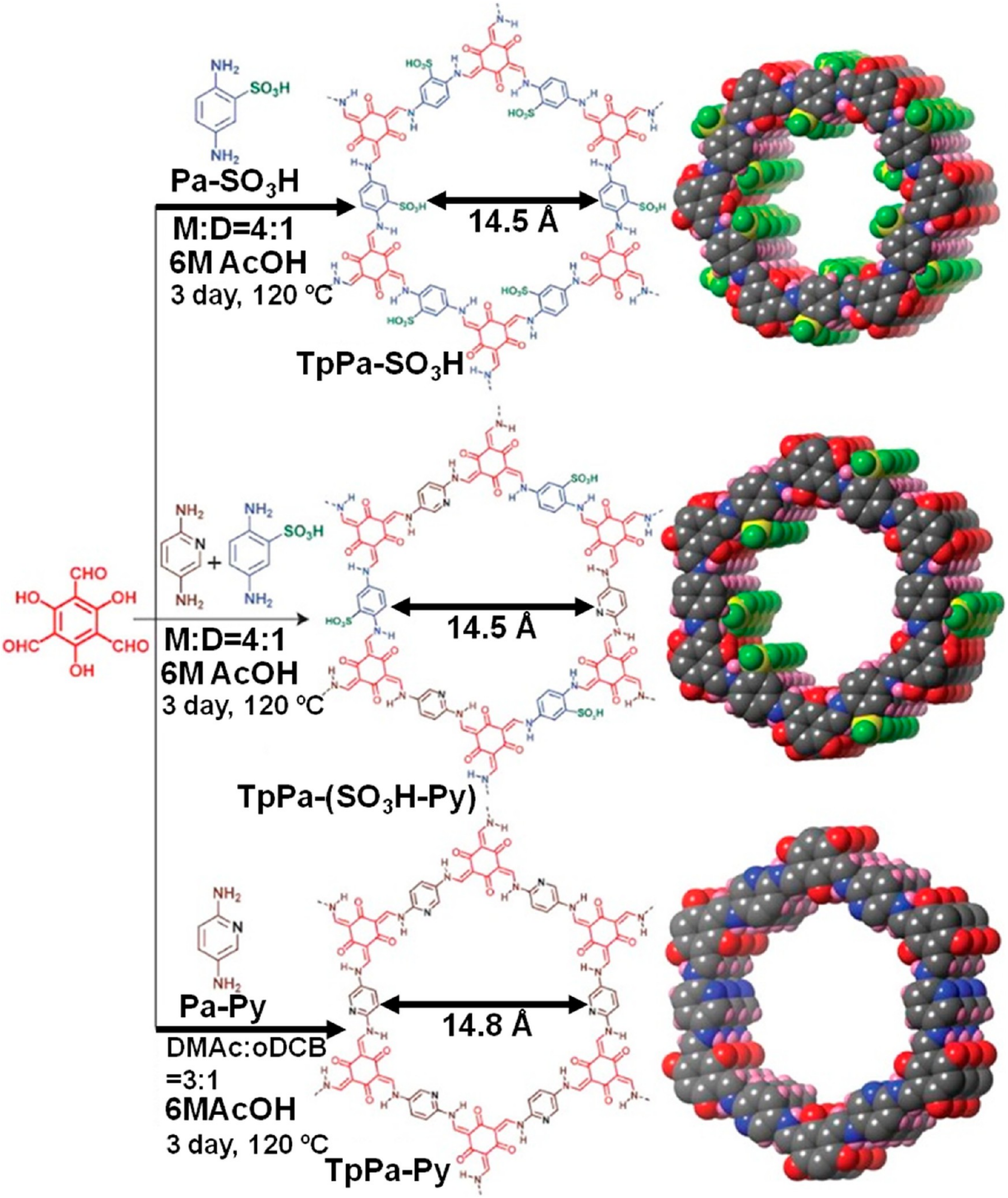

Figure 21. Schematic illustration of the sulfonic COFs. Reprinted with permission from ref 118. Copyright 2016 American Chemical Society.

focus for this research in the future. Second, almost all COFs are solid-state materials with a certain mechanical strength, which may provide inspiration for using COFs as protective layers against the issues regarding the formation of metal dendrites and potentially result in a possible solution regarding the safety issues associated with metal-ion batteries.

4. COFS AS PHOTOELECTROCHEMICAL CATYALYSTS FOR WATER SPLITTING

Nanocatalysts, which play a crucial role in water splitting applications, are generally comprised of metals, metal oxides, and metal sulfide nanoparticles, resulting in increased materials

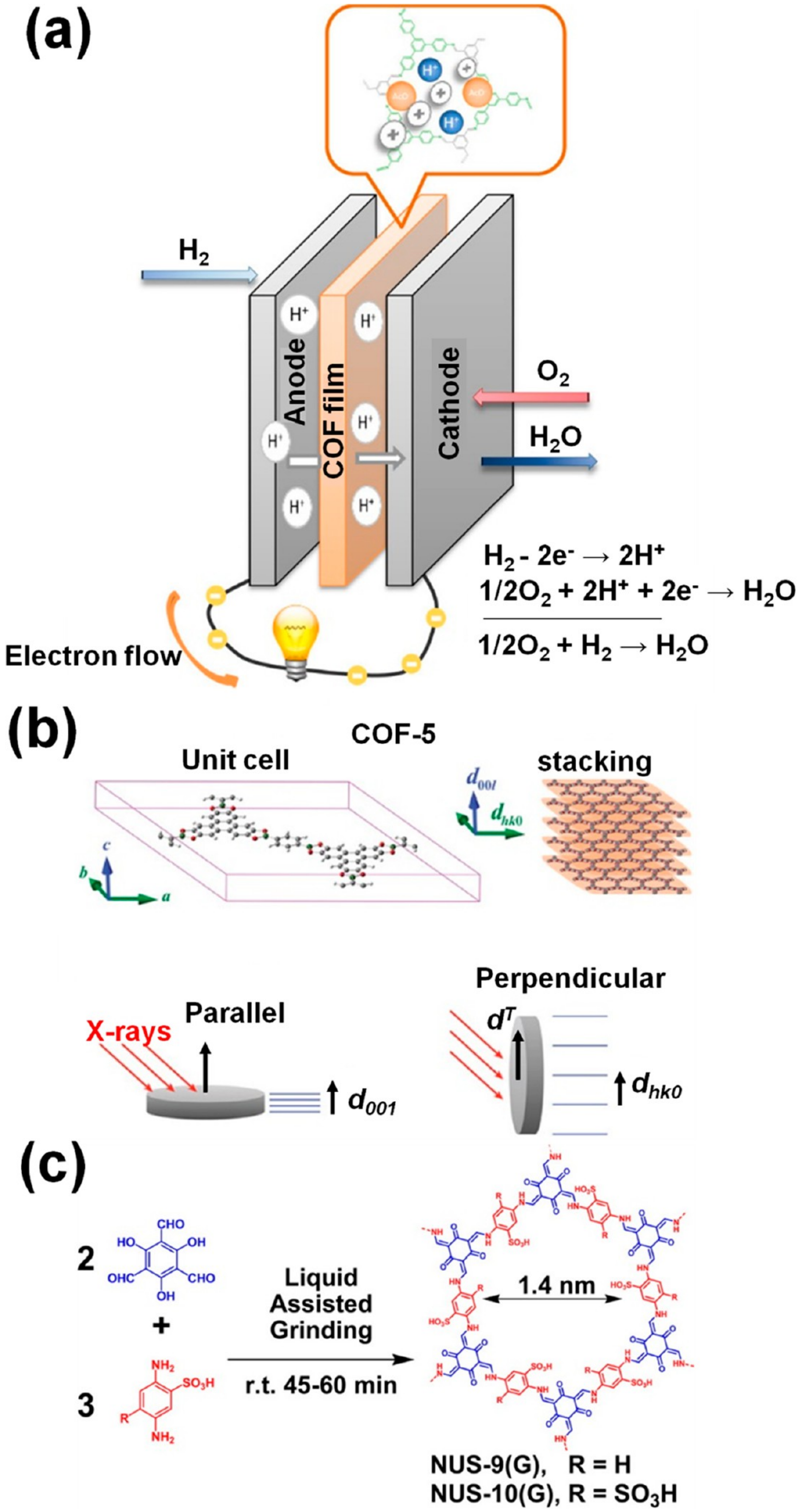

Figure 22. (a) Schematic illustration of the proton exchange membrane made by the COF material. Reprinted with permission from ref 119. Copyright 2017 American Chemical Society. (b) Schematic illustration of the two-dimensional COF stacking methods. Reprinted with permission from ref 120. Copyright 2016 American Chemical Society. (c) Schematic illustration of the COF synthesis process. Reprinted with permission from ref 121. Copyright 2016 American Chemical Society.

cost and a greater consumption of resources. Although the development of metal-free nanocatalysts would potentially address these drawbacks, many metal-free nanomaterials exhibit poor conductivity, limiting their implementation as effective catalysts, although some reports suggest the activity of metal-free nanocatalysts can be improved upon photoirradiation

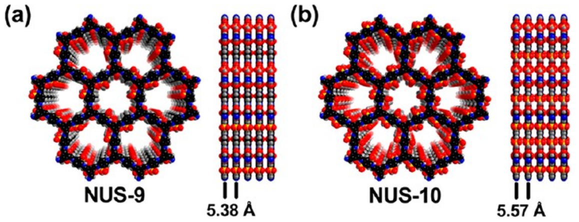

Figure 23. Schematic illustration of the AA-type stacking method for (a) NUS-9 and (b) NUS-10 COFs. Reprinted with permission from ref 121. Copyright 2016 American Chemical Society.

(i.e., photocatalytic conditions). As such, the intrinsic crystallinity, porosity, and tunability of COFs make them a promising class of potential photoelectrocatalysts for water splitting reactions. Jiménez-Almarza et al. documented a metal-free catalyst composed of bare phenyl rings and imines, which works as a photoelectrocatalyst in oxidative transformations.[123]

Another photosensitive COF was prepared by Huang et al. using $[4\pi+4\pi]$ cycloaddition of anthracene,[124] which results in a switchable COF that can be resettled and regenerated thermally. The performance of this COF-based photoelectrocatalyst is influenced by external-stimuli-induced structural evolution, making it a potentially useful material in smart materials applications.

Acetylene-based COFs are also favorable for use as heterogeneous photoelectroncatalysts for hydrogenation reactions because of their oxidative stability. COFs have shown promise as host materials for photoelectrocatalysts. Aiyappa et al. demonstrated that the inherent porosity can be used to trap Co species in the bipyridine-containing COFs deployed in oxygen evolution reactions,[125] and as a result, an overpotential of 400 mV at a current density of 1 mA cm^{-1} was attained together with an excellent stability of 1000 cycles and 24 h of oxygen evolution reaction activity (Figure 24).

Sick and co-workers studied aromatic amine-functionalized polyimine sheets formed via thiophene dialdehyde and tetraphenylethylene building blocks (Figure 25).[126] The sheets formed three-dimensional, porous, and photoelectroactive frameworks via π-stacking interactions that absorb visible light to generate photoexcited electrons, which then diffuse to the COF surface to reduce protons for subsequent hydrogen evolution. Importantly, this work provides a methodology to tune currently available photoabsorbers by incorporating different building blocks and facilitating their three-dimensional stacking. In an alternative approach, Bi et al. examined triazine-based COFs with a two-dimensional structure that were decorated with Pd nanoparticles, finding that this system exhibits excellent photoelectrocatalytic activity and sustainability in water splitting by taking advantage of the synergetic effect between the nanoscale size and triazine moieties.[127] Jin and co-workers constructed Pt-doped COFs for use in water splitting, taking advantage of three unique properties of π-conjugated COFs: (i) harvesting a wide range of energy (from visible light to infrared light); (ii) ordered pathways for exciton and charge transport; (iii) multiple reaction centers for promoting the reaction efficiency (Figure 26).[128]

In a theoretical study, Jiang and co-workers demonstrated that the interlayer coupling of multilayer triazine-based COFs contributes to enhanced visible-light absorption relative to that of the monolayer COFs.[129] Mullangi and co-workers developed a novel metal-free catalyst for water splitting, which was formed from building blocks functionalized with sp^3 nitrogen.[130] Notably, when this catalyst was used for oxygen evolution in an alkaline solution, it exhibited the best overpotential among the noble metal-free catalyst systems with outstanding kinetics. Furthermore, the sp^3 nitrogen in the backbone facilitated bonding with other small-sized nanoparticles in a sandwiched structure without the need for a capping agent.

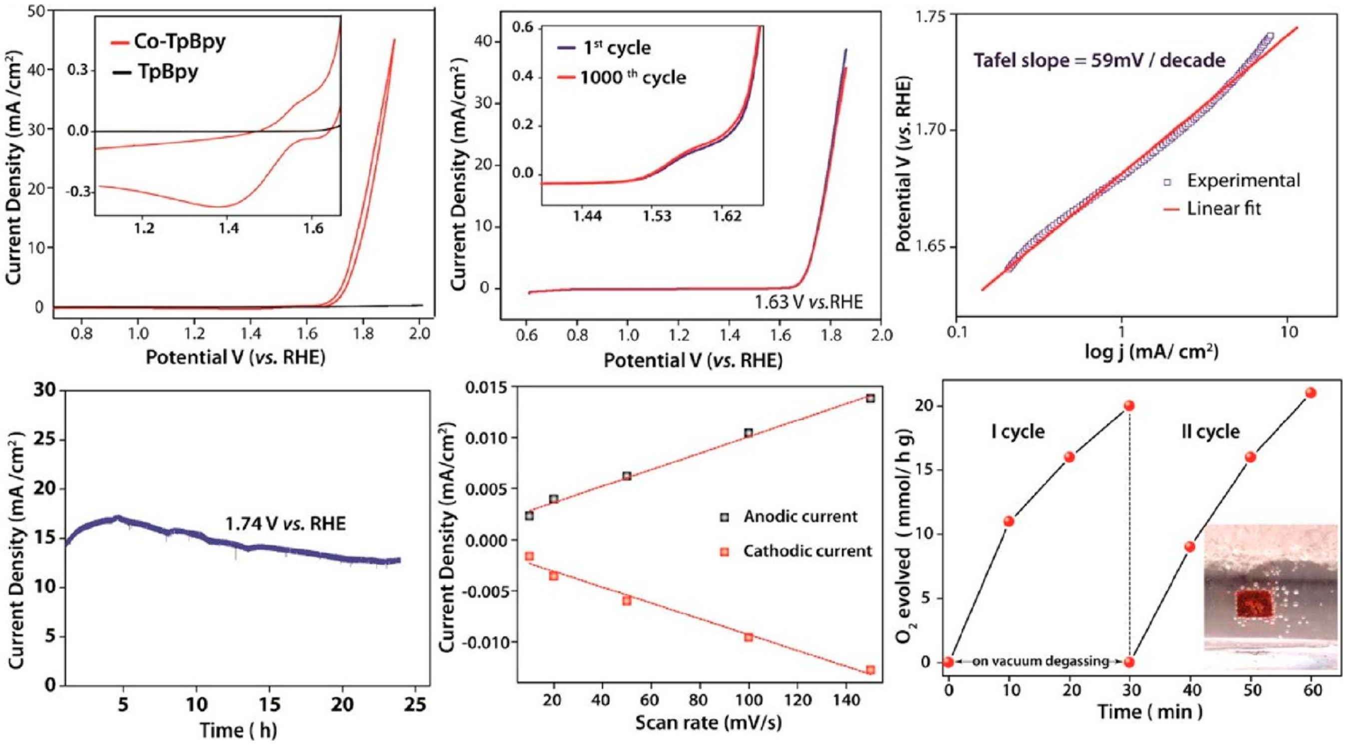

Figure 24. Cyclic voltammetry profiles of different COF-based catalysts; Tafel plot; current density of the electrode; response current evolution at different scan rates; oxygen evolution and demonstration. Reprinted with permission from ref 125. Copyright 2016 American Chemical Society.

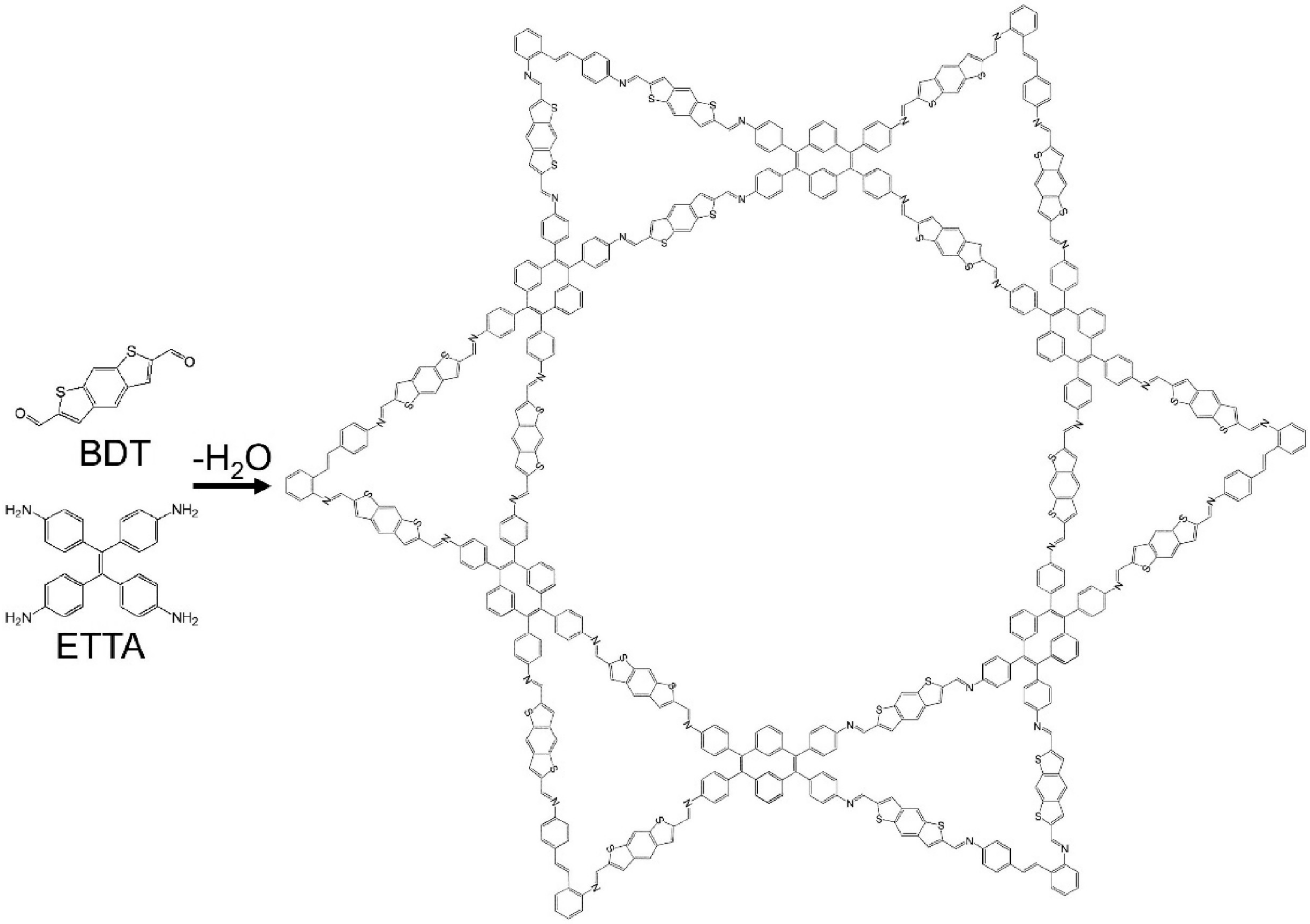

Figure 25. Schematic illustration of the COF formation.

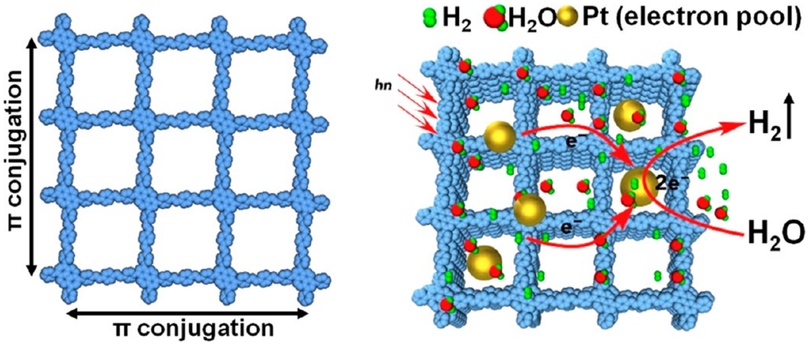

Figure 26. Two-dimensional COF (left) and the catalyzed water splitting process (right). Reprinted with permission from ref 128. Copyright 2019 Elsevier.

The effect of spacer length in COFs on the water splitting efficiency has been studied by Meier and co-workersin which seven types of materials with different spacer units were prepared via either Suzuki–Miyaura polycondensation reactions or trifluoromethanesulfonic acid catalysis from nitrile-functionalized precursors (Figure 27).[131] These materials exhibited similar hydrogen evolution efficiencies, yet different optical absorption properties were observed depending on the functional groups present. Through density functional theory calculations, a trade-off between increased light absorption and decreased thermodynamic driving force was found, corroborating the experimental data. Kuecken and co-workers demonstrated a facile synthetic strategy to optimizing the catalytic activity of a COF-based material employed for hydrogen evolution.[132] The product formed under the optimized conditions (the COF precursor in the presence of $ZnCl_2$ at 400 °C for 10 min) exhibits an average hydrogen evolution rate as high as 1072 μmol h^{-1} g^{-1} when irradiated with visible light.

Furthermore, Patra et al. synthesized a porphyrin-based COF through a condensation reaction between triformyl phloroglucinol and 5,10,15,20-tetra(4-aminophenyl)-21H,23H-porphyrin. This COF demonstrated systematically improved performance such as low overpotential and a small Tafel slope, surpassing the performance of metal-free photoelectrochemical catalysts.[133]

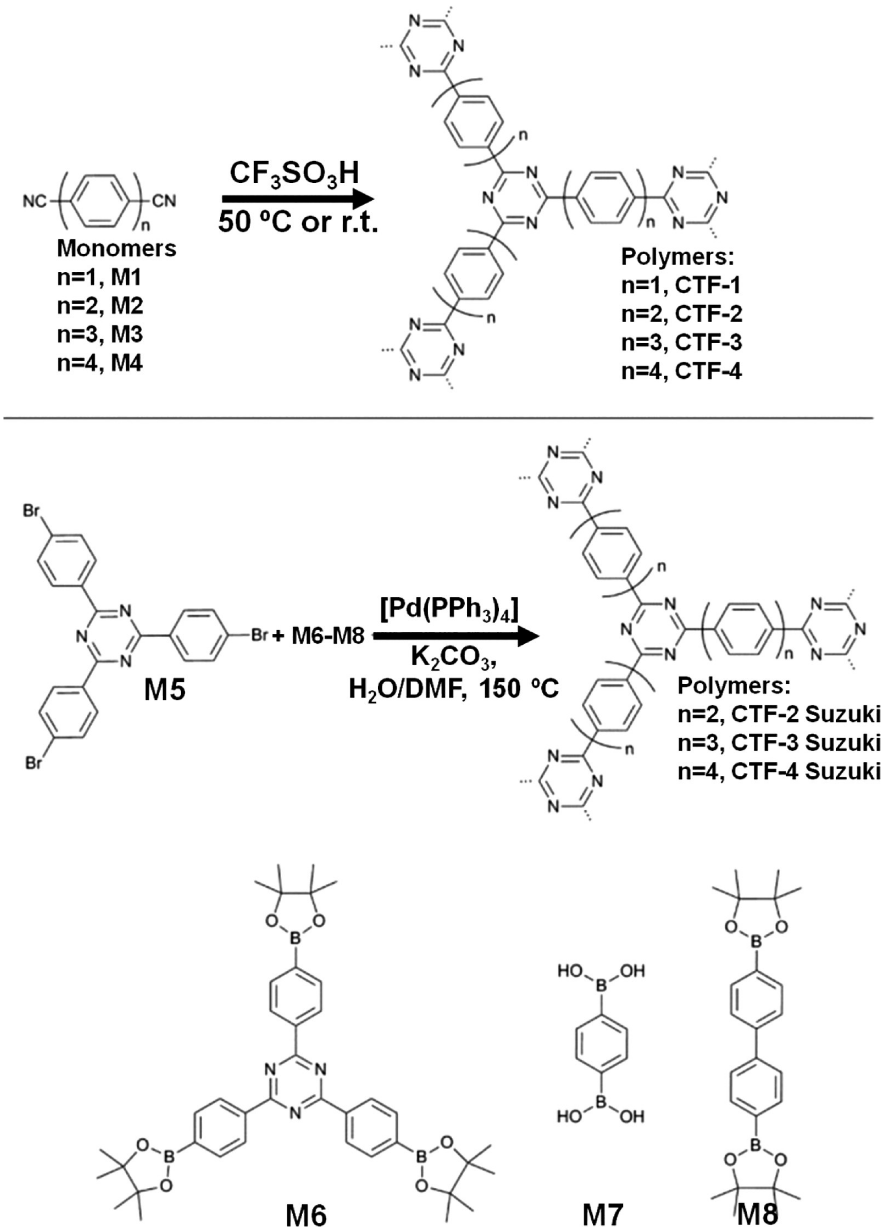

Figure 27. Schematic illustration for the triazine-based COFs. Reprinted with permission from ref 131. Copyright 2017 Elsevier.

Importantly, Wan et al. demonstrated that the 2,4,6-tris(4-methylphenyl)-1,3,5-triazine-based two-dimensional COFs can achieve water splitting under the irradiation of visible light,[134] and tuning the adjustable band gap also provides one reference.[135]

The combinatory concept has also been studied by Wang et al. in which MXene and other photoelectrochemical active species-containing functional groups were introduced into COFs.[136,137] Liu et al. demonstrated the supporting effect of COFs for water splitting applications by forming an organic hybridized photoelectrocatalyst in which carbon-encapsulated nickel phosphide particle is loaded on a fully conjugated organic polymer.[138] Similarly, Aiyappa et al. further demonstrated the benefits of the supporting effect with a Co-containing COF based on bipyridine, reflecting exceptional stability and an overpotential of 400 mV at a sepcific current of 1 mA cm^{-2}.[139]

Transition metals like Co, together with other noble metal species such as Au, have been demonstrated to be efficient catalysts.[140] On the basis of this technique, Jia et al. demonstated a further modification strategy in which the authors introduced

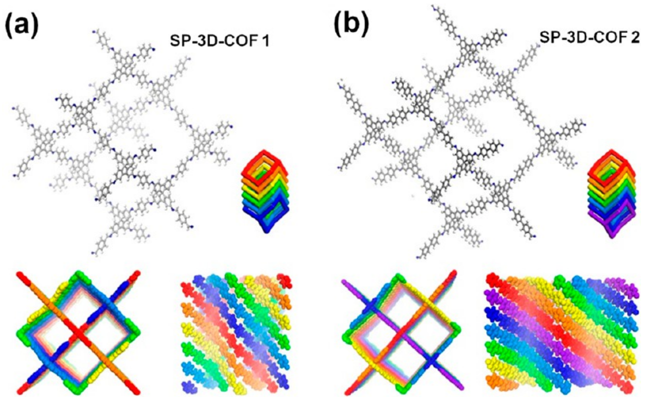

Figure 28. Structural illustration of conjugated COFs. Reprinted with permission from ref 144. Copyright 2018 American Chemical Society.

multiwall carbon nanotubes in the composite of porphyrin-based COFs and cobalt, resulting in an improvement in performance

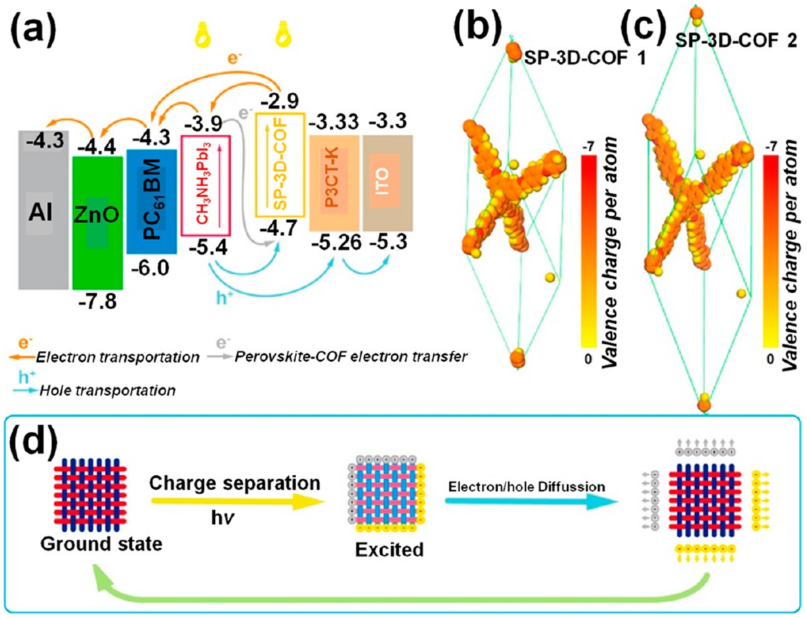

Figure 29. (a) Band diagram, (b,c) optimized COFs based on the DFT calculations, and (d) proposed mechanism for the light motivation reaction. Reprinted with permission from ref 144. Copyright 2018 American Chemical Society.

when employed for water splitting. Importantly, this work highlights the synergetic effect of a COF-based composite catalyst for water splitting application, as it relies on the combination of a conductive agent, COFs, and catalytically active elements.[141]

Semiconductors comprise an alternative class of catalytically active species, and in particular, some of these catalysts can be excited upon the irradiance of UV or visible light. This concept has been demonstrated by Pan et al. as they reported that triazine-based COFs can further manipulate the energy band of $BiVO_4$ to improve the photoelectrochemical performance.[142]

COFs that serve as photoelectrochemical catalysts are crucial for the reformation of conventional noble metal-based catalysts. Currently, research in this area may need to focus on the development of organic catalysts to reduce material costs. Pioneering work has demonstrated the feasibility of this concept, which will potentially pave the way toward continued development in the future.

5. COFS FOR SOLAR CELL APPLICATIONS

Solar cells have received tremendous attention as promising devices for the continued development of sustainable and green energy sources.[143] Several generations of solar cells, including Si-based solar cells, dye-sensitized solar cells, and perovskite-type solar cells, have been successfully designed and fabricated. Thus, far, the conversion efficiency of solar energy has been limited to less than 30%. Because of their reversible redox activity and excellent tunability, COFs are a class of materials that exhibit great potential for use in the next generation of solar cell devices, with some COFs having already exhibited promising performances in this setting. For example, Wu and co-workers synthesized highly conjugated, three-dimensional COFs through the use of imine-linked spirobifluorene cores (Figure 28a, b) that exhibit desirable permanent porosity and thermal stability.[144] Interestingly, a 6- or 7-fold interpenetration can be obtained depending on the structure of linking units employed. Under controlled conditions, solar cell devices containing the synthesized products display an increase in power conversion efficiency by 15.9 to 18.0% relative to the control devices, while also exhibiting excellent leakage prevention (Figure 29a−d).

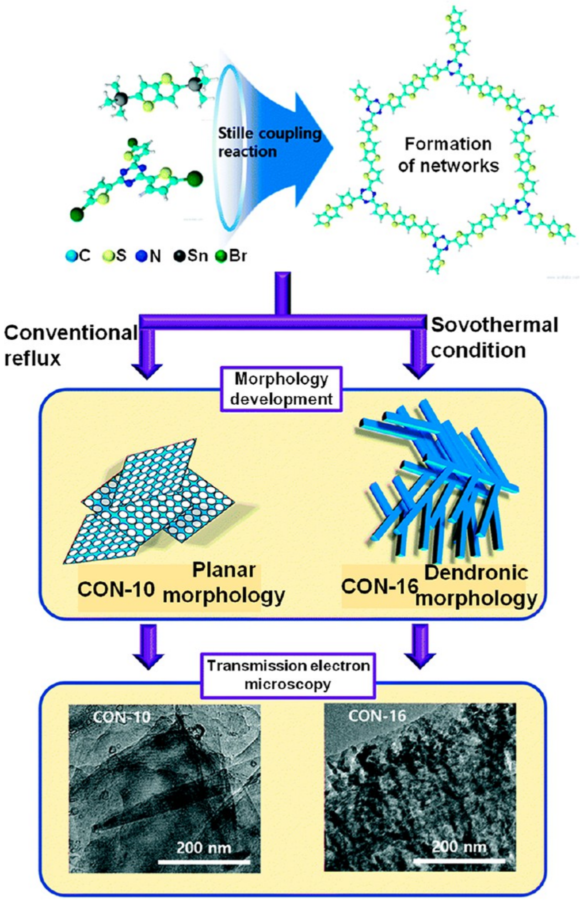

Figure 30. Schematic illustration of the COF synthesis process; transmission electron microscopy images of the as-synthesized COF nanosheets. Reprinted with permission from ref 145. Copyright 2020 Royal Society of Chemistry.

Park and co-workers synthesized an efficient hole-transport layer using boronate-ether-based COF nanosheets, which were

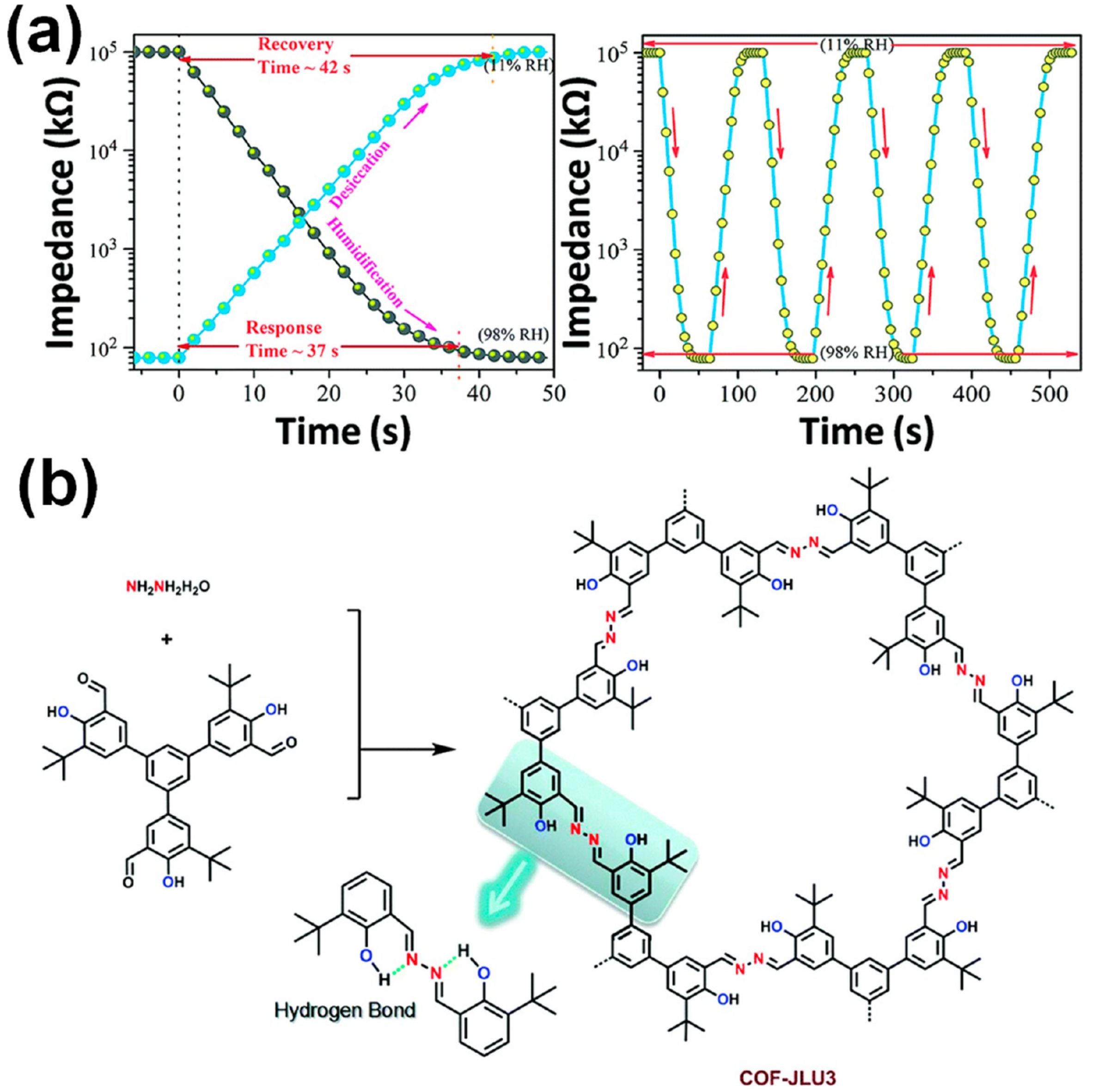

Figure 31. (a) Impedance variation curves. Reprinted with permission from ref 148. Copyright 2017 Royal Society of Chemistry. (b) Mechanism illustration of the COF synthesis process. Reprinted with permission from ref 149. Copyright 2016 Royal Society of Chemistry.

synthesized through the Stille cross-coupling reaction (Figure 30).[145] The device incorporating COF-10 as the hole-transport layer displays a conversion efficiency of 10.2%, which is a significant increase of 1% over that of the reference devices. Lv and co-workers synthesized two-dimensional COF nanosheets from naphthalenediimide and triphenylamine building blocks that demonstrated higher charge transfer efficiency, high specific areas (up to 1276 m^2 g^{-1}), and ultrahigh intramolecular charge transfer efficiency that enables a synergetic effect with respect to electrochemical reactions.[147]

6. SENSORS

Improvements in sensing technology can be realized through the development of upgraded materials that exhibit selective reactivity. In this regard, COFs can potentially be employed in multiple types of sensing applications depending on the interactions between functional groups on the COF and extrinsic molecules or ions present in the analyte.[146] For example, COFs that exhibit sensitivity toward water suggests their potential use as humidity sensors, as reported by Singh and co-workers.[147,148] In this report, interactions between COF-based boron ester linkages and water molecules were exploited to develop a highly sensitive COF-based humidity sensor that exhibits excellent stability and reversibility (Figure 31a).

Li et al. demonstrated that a COF-based luminescent sensor can be used to detect toxic metal ions with high sensitivity and selectivity toward Cu^{2+} ions.[149] In this system, the strong luminescence originates from salicylaldehyde and bulky groups as building blocks for the vertices (Figure 31b). Similarly, a ratiometric sensor for detecting water has been developed by Qian et al. through the use of a dual-fluorescence emission mechanism[150] in which an imine-based two-dimensional COF was fabricated. When used for detecting water in organic solvents, this COF exhibits fluorescent emissions with peaks at about 500 and 590 nm that result from excited-state intramolecular proton transfer and intramolecular charge transfer effects (Figure 32a). A new imide-based COF sensor used for the detection of the nitroaromatic molecules, namely 2,4,6-trinitrophenol, has been fabricated by Das et al. through Schiff-base reactions using a

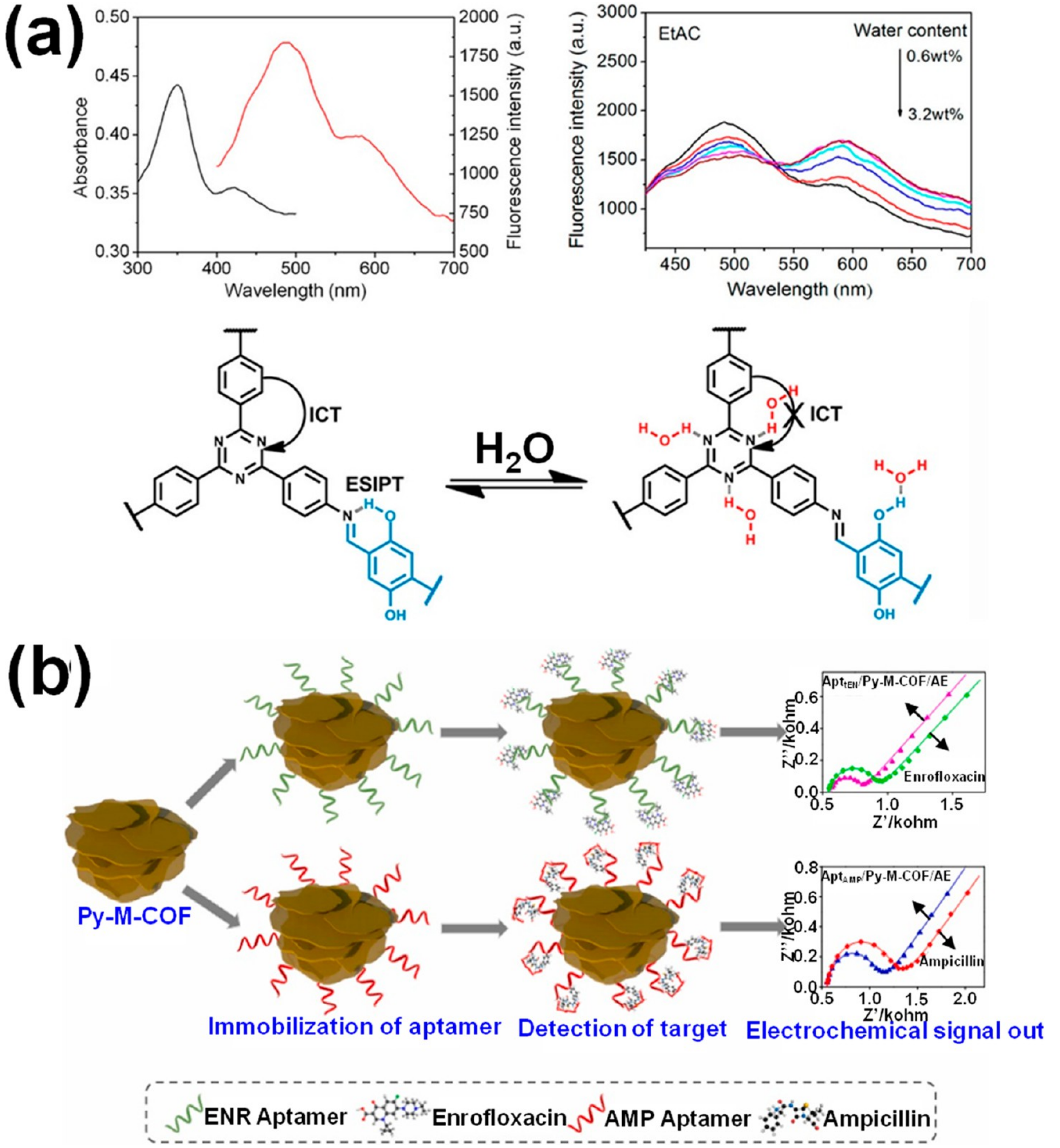

Figure 32. (a) UV−vis absorption and fluorescence spectra, and schematic illustration of the water sensing mechanism. Reprinted with permission from ref 150. Copyright 2017 American Chemical Society. (b) Schematic illustration of the detection process and the impedance variation. Reprinted with permission from ref 152. Copyright 2019 Elsevier.

solvothermal strategy, followed by liquid phase exfoliation which resulted in the preparation of two-dimensional COFs.[151] Notably, this work provides the first report of two-dimensional COFs employed to detect nitroaromatic analytes via turn-on/off luminescence mechanisms. A similar COF system developed using imine-based 1,3,6,8-tetrakis(4-formylphenyl)pyrene and melamine was used as a sensor for antibiotics as shown in Figure 32b. In this system, the COFs serve as scaffolds of aptamer strands via $\pi-\pi$ stacking and electrostatic interactions, which enable the sensing interactions to occur.[152]

7. SUMMARY AND PERSPECTIVES ON REMAINING CHALLENGES AND POTENTIAL OPPORTUNITIES

COFs represent an exciting class of materials that exhibit unique properties relative to those of other composites. In particular, COFs are constructed with tunable building blocks that are connected through robust covalent bonds and exhibit permanent porosities, as well as favorable chemical and thermal stabilities. Additionally, the large number of potential building blocks and unique bonding interactions available to COFs enables numerous opportunities for optimizing this platform. Importantly, COFs can be tailored to exhibit desired functions through the judicious selection linkers and functional groups. Furthermore, the additive processing can potentially be used to further functionalize the final products. Herein, we reviewed the documented COF-based materials in the context of energy-related and electrochemical applications. Specifically, these reports have been summarized in terms of materials design and synthesis, as well as their use in diverse electrochemical-related applications, including batteries and capacitors, solar cells, water splitting, and sensors. Together, these COF matrix design and postfunctionalization methods play a crucial role in the performance improvements of these materials in electrochemical applications, which greatly influences the efficiencies of the final devices, such as batteries and solar cells. Thus, COFs provide an emerging platform for researchers to design favorable materials.

Despite many of these unique advantages, several challenges regarding this class of materials persist. For example, although these structures exhibit superiority to other types of materials in some aspects, issues regarding the synthesis of high-quality, crystalline materials in large quantities limit their potential use in many applications. Furthermore, the sensitivity of many covalent bonds in COFs toward water molecules presents a great challenge in the fabrication and postprocessing of COF materials. Currently, the electronic conductivities of many COFs are much lower relative to those of metal-based materials, and although significant progress has been made in this regard, many COFs are still not suitable for use in electrochemical applications. Combined, these properties make optimization difficult, even in laboratory-scale studies. In addition, the delamination of the two-dimensional COFs can be an issue. Thus, the two-dimensional and wire-type materials can be suggested as a confinement media to improve the structural integrity of the host materials. Considering both the current advantages and disadvantages of COFs, the future development of COFs for use in different energy-related applications should mainly target organic materials that are low cost, eco-friendly, easy to fabricate, and high performance. Moving forward, we encourage researchers take advantages of the vast array of functionalization strategies available in order to engineer solid-stage COFs that meet these design critera for use in broad applications. Thus, many potential opportunities exist in this emerging field for researchers to develop advanced materials that can potentially make a significant impact in many different energy-related applications.

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Notes

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