Covalent Organic Framework/Graphene Hybrids: Synthesis, Properties, and Applications

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To address current energy crises and environmental concerns, it is imperative to develop and design versatile porous materials ideal for water purification and energy storage. The advent of covalent organic frameworks (COFs), a revolutionary terrain of porous materials, is underscored by their superlative features such as divinable structure, adjustable aperture, and high specific surface area. However, issues like inferior electric conductivity, inaccessible active sites impede mass transfer and poor processability of bulky COFs restrict their wider application. As a herculean stride forward, COF/graphene hybrids amalgamate the strengths of their constituent components and have in consequence, enticed significant scientific intrigue. Herein, the current progress on the structure and properties of graphene-based materials and COFs are systematically outlined. Then, synthetic strategies for preparing COF/graphene hybrids, including one-pot synthesis, ex situ synthesis, and in situ growth, are comprehensively reviewed. Afterward, the pivotal attributes of COF/graphene hybrids are dissected in conjunction with their multifaceted applications spanning adsorption, separation, catalysis, sensing, and energy storage. Finally, this review is concluded by elucidating prevailing challenges and gesturing toward prospective strides within the realm of COF/graphene hybrids research.

1. Introduction

Covalent organic frameworks (COFs) have garnered considerable interest as a novel type of porous organic material,

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following the pioneering research conducted by Yaghi et al. in 2005.^[1–3] COFs are a class of highly porous crystalline polymeric materials composed of lightweight elements such as C, N, O, B, Si, and H, which are held together by strong covalent bonds among the organic linkers. COFs distinguish themselves from their macromolecular counterparts through an array of unparalleled attributes, including their structural diversity, large surface area, permanent porosity, long-range order, and versatile functionalities.[4,5] Effortlessly straddling multiple applications,^[6] COFs have unfurled their enormous potential in realms such as water purification,^[7] photocatalysis,^[8–10] environmental sensing,^[11] energy storage,^[12-14] and gas storage/separation.[15-18] Nevertheless, an objective appraisal reveals that certain inadequacies persist within solid-state COFs, which include inferior conductivity,^[19,20] electric inaccessible active sites,^[21] impeded mass transfer, and

poor processability. These shortcomings have curtailed their application across novel sectors such as electrochemistry,^[22] catalysis,^[23] and membrane separation.^[24] In response, contemporary research indicates an augmenting interest in constructing COF-anchored composites that amalgamate the strengths of their foundational materials to circumvent persisting flaws. The reinstated COFs thus produced, represent a radical advancement over conventionally synthesized counterparts, proposing a promising avenue for overcoming challenges that previously remained unaddressed by mono-constituent COFs.

In recent years, graphene-based materials have emerged as a promising additive to address the challenges faced by COFs due to their unique structures and exceptional electronic, thermal, electrochemical, and mechanical properties. Several empirical validations have elucidated that the infusion of graphenecentric constituents into COFs can instigate substantial augmentation in sought-after attributes and performance indices.^[25–28] COF/graphene-based hybrids were first reported by Colson and co-workers in 2011,^[29] and have attracted significant academic interest, resulting in the publication of a growing number of research articles on the topic (**Figures 1** and 2). Recent research indicates that COF/graphene-based hybrids are adept at merging the distinct advantages of each of the individual components while simultaneously resolving their limitations. This



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Figure 1. Number of published articles on graphene and COF in the past decade. (Search engine: Web of Science).

integration has resulted in significant improvements in stability, electrical conductivity, and accessibility to desirable active sites of the composites.^[26,30,31] The presence of ionic groups and aromatic sp² domains in graphene-based materials enables them to serve not only as structural nodes but also actively participate in bonding formation.^[32] Furthermore, the carboxylate and pyridine groups on graphene-based materials have been found to play a vital role in the assembly process,^[33] effectively promoting covalent bonding and directing the growth of COFs,^[34] and providing a more beneficial structure and bringing unique performance across diverse applications. The integration of graphene-centric constituents has been shown to substantially amplify the properties of composite materials, hence emphasizing the necessity for heightened scrutiny of such hybrid configurations. This stratagem not only proliferates potential applications far exceeding those of traditional materials, but also warrants enhanced efficacy and results. Thus, the commitment of further research toward the proliferation and application of such hybrid constructs represents an endeavor of supreme significance.

Despite the extensive coverage found in prior literature regarding COFs, placing focus primarily on their architectural features, synthetic methods, and highlighted properties, along with their potential implementation in the realms of sensing, membrane separation, and photocatalysis, it is notable that certain aspects of this field still call for heightened scrutiny.^[1,35,36] It is also noteworthy to mention the distinct absence of a comprehensive review encapsulating the array of synthetical approaches and wideranging applications of COF/graphene hybrids, underscoring the necessity to shed light on these innovative materials. In the quest to fill this apparent scholarly void, first, a critical examination of the contemporary advancements in the growth, structuring, and attributes of graphene, its derivatives, and COFs is depicted (Section 2). Following this, the existing synthetical methods aimed at crafting COF/graphene hybrids are meticulously condensed (Section 3). Subsequent to this, a robust discussion ensues on the fundamental attributes of COF/graphene hybrids, which range from their specific surface area and pore size to their inherent stability, conductivity, and wettability. These properties are comparatively analyzed with those of their root materials to craft a theoretical structure for the development of hybrids fit for niche applications (Section 4). As a natural sequel, potential deployment scenarios for COF/graphene hybrids in contexts like adsorption, separation, catalysis, sensing, and energy storage are strictly considered (Section 5). Concluding the review, emerging trajectories and formidable challenges associated with COF/graphene hybrids are contemplated meticulously (Section 6).

2. Structure and Properties of Pristine Materials

COF/graphene hybrids consist of a single primitive material with inherent advantages, yet these materials face limitations that hinder their use. This section provides an overview of the fundamental properties and challenges associated with graphene, graphene derivatives, and COF materials.

2.1. Graphene

Graphene is a 2D monolayer honeycomb crystal that is structured by sp² hybridization of carbon atoms,^[49] which is considered the fundamental building block of several carbon materials (like carbon nanotube and fullerene) (Figure 3a-c).^[50] Monolayer graphene has only one carbon atomic layer thickness (0.35 nm), and three electrons in the outer layer of carbon atom form σ bonds through sp² hybridization.^[51] Each lattice contains three σ bonds, forming a stable hexagon with a bond angle of 120° and a C-C bond length of ≈ 0.142 nm. The p orbitals perpendicular to the sp² hybrid plane in each carbon atom form delocalized large π bonds side-by-side throughout the graphene plane.^[52] Due to the lack of thermodynamic stability in 2D graphene crystals, monodisperse graphene sheets loaded onto a substrate exhibit non-planar surface features with micro-scale fold structures.^[53] For a prolonged period, graphene remained a theoretical structure, deemed incapable of survival in isolation. It wasn't until 2004 that high-quality graphene was successfully extracted from graphite via micromechanical exfoliation using adhesive tape.^[54] The realization of such high-quality graphene crystals allowed for the exploration of their astounding electronic properties. Geim and Novoselov were jointly awarded the 2010 Nobel Prize in Physics for their pioneering work on 2D graphene materials. Since then, research on graphene, including its controlled synthesis, functional modification, and emerging applications, has burgeoned exponentially. Although the micromechanical exfoliation method produces superior graphene constructs, it is challenged by scalability and practicability constraints for mass production. Instead of this, synthesis methods such as chemical vapor deposition (CVD),^[55–59] epitaxial growth,^[60–63] and chemical exfoliation^[64-66] have emerged as viable alternatives for graphene manufacturing.

The exceptional chemical structure of graphene gives rise to its remarkable properties. Graphene possesses a theoretical specific surface area of 2630 m² g,^[67] along with high mechanical strength (rupture strength of 42 N/m and Young's modulus of \approx 1 TPa),^[68–72] superfast electron mobility at low temperature

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Figure 2. Development of COF/graphene hybrids and their first application in various fields. Reproduced with permission.^[28,29,33,37–48] Copyright 2005, 2011, Science. Copyright 2015, 2016, 2017, 2019, 2020, 2023, The Royal Society of Chemistry. Copyright 2018, 2022, Wiley-VCH. Copyright 2018, 2019, Elsevier B.V. Copyright 2019, 2022, American Chemical Society. Copyright 2020, Nature.

(over 200 000 cm² V⁻¹ s⁻¹),^[73] and outstanding thermal conductivity at room temperature (\approx 5000 W mK⁻¹).^[74] Owing to these unique physical and chemical properties, graphene exhibits vast potential for applications in electronic devices,^[75] energy conversion, storage,^[76–78] sensors, biotechnology,^[79] environmental management,^[42] and other fields.

2.2. Graphene Derivatives

Although pristine graphene nanosheets have excellent physicochemical properties, the insolubility of graphene itself and the presence of van der Waals forces and π – π stacking between the nanosheets often result in irreversible aggregation and precipitation of graphene in water and organic solvents, which is not favorable for the preparation of graphene composites. Graphene derivatives with some oxygen-containing functional groups can overcome these shortcomings. Graphene oxide (GO) is the primary oxygen-containing derivative of graphene, which shares a similar planar structure to graphene and has excellent water solubility (Figure 3d,e).^[50] GO is usually composed of graphene-like aromatic structures and polar oxygen-containing groups. These aromatic areas are randomly sized and separated by sp³ hybrid carbon atoms. The surface of GO features an abundance of epoxy and hydroxyl groups, while hydrophilic carboxyl (-COOH) and aldehyde (-CHO) groups are predominantly situated near the edges.^[80] The reduction of GO can facilitate the partial restoration of the sp² carbon network (Figure 3f), making it an effective method for producing reduced GO (rGO).^[50] GO possesses several distinctive structural features that give rise to intriguing surface chemical properties, such as amphiphilicity, electronegativity, and dispersity.^[81] Despite some of its physical properties being lower than graphene, the presence of oxygencontaining functional groups in GO provides it with good dispersity and reactivity.^[82] Moreover, these functional groups can easily react with compounds containing amino, carboxyl, and isocyanate groups to achieve covalent modification of GO, facilitating the hybridization with other materials.^[83,84] Additionally, GO can also realize non-covalent bonding with other compounds through hydrogen bonding, $\pi - \pi$ bonding, etc. The assembly of GO nanosheets can easily produce graphene macroscopic materials such as graphene fibers, graphene membranes, and graphene



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Figure 3. Structures of a) graphene, b) carbon nanotube and c) fullerene (C₆₀). The chemical structures of pristine graphene d), GO e), and rGO f). Reproduced with permission.^[50] Copyright 2020, Wiley-VCH.

aerogels (GAs). Thus, compared with graphene, GO is a preferred choice for preparing COF/graphene hybrids due to its tunable chemical structure.

In addition to GO, other graphene derivatives, such as graphene acid and amine-modified reduced GO (NH₂-rGO), are also ideal graphene-based materials for COFs due to their single active functional group.^[46] These graphene derivatives can be obtained by pre-modification of GO, facilitating the further growth of COF nanosheets on these graphene derivatives.^[85] Doped graphene has also been used for compounding with COF.^[86] Doped graphene can be made by in-plane modification, where carbon atoms in graphene are replaced by other elements, such as B and N. The characteristics of doped graphene are dependent on the type and concentration of the doping element. Doping elements can regulate the bandgap of graphene and act as the reaction center in the catalytic reaction, giving graphene more excellent properties.^[87]

2.3. COFs

COFs are a subclass of porous polymers that are composed of small organic monomers which are joined together by strong covalent bonds.^[1–3] Unlike conventional linear polymers, the structure of COFs can be precisely manipulated across both two- and three-dimensional space. Such unique capability allows for the creation of highly-ordered, crystalline porous materials with rigid skeletons. As a result, the chemical and physical properties of COFs can be regulated with high accuracy. The nanostructures and voids that are created in COFs provide an optimal environment for molecular storage, release, and separation. This makes them highly appropriate for a diverse array of applications, such as energy storage,^[88–90] catalysis,^[91–93] and separation.^[8,94]

The synthesis of COFs relies on the reversible covalent bonding between organic building blocks. The typical building blocks utilized for this process are aromatic di- or triamines, aldehydes, or carboxylic acids, which can undergo condensation reactions to form imine or amide bonds. In addition to these, other functional groups such as boronic acids, thiol groups, and azides have also been employed to synthesize COFs with unique structures and properties. According to the linkage type between monomers, COFs can be divided into imine COFs,^[25] boron-containing COFs,^[95] triazine COFs,^[96] azine hydrazone COFs,^[97] anhydride type COFs,^[98,99] phenazine linkage COFs,^[100] benzimidazole linkage COFs,^[101] benzobisoxazole linkage COFs,^[102] borazine linkage COFs,^[103] squaraine type COFs^[104] and olefin linkage COFs (**Figure 4**).^[105,106] Among them, boron-containing COFs,^[95] imine COFs,^[107] and triazine COFs^[96] are the three widely investigated COFs. Boron-containing COFs are composed of boric acid or its derivatives as nodes and organic molecules as connected units. They usually have high thermal (450–600 °C)^[106] and chemical stability, which can be used as catalysts, drug delivery bodies, and pollutant sensors.^[108] However, a prominent drawback of the majority of the boron-containing COFs is their susceptibility to moisture, causing framework degradation when exposed to high humidity or aqueous environments. In contrast,

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Figure 4. Chemical formulae for the reactions of different types of COFs, which include imine COFs, boron-containing COFs, triazine COFs, anhydride type COFs, phenazine lineage COFs, benzimidazole linkage COFs, benzobisoxazole linkage COFs, borazine linkage COFs, squaraine type COFs, olefin linkage COFs, and azine hydrazine COFs.

imine COFs can be synthesized under milder conditions, thereby reducing the defect formation arising from extreme synthesis conditions. This offers a novel approach to the production of COF materials. Imine-bonded COFs are COFs with high crystallinity and stability, which are also the most adjustable kind of COFs.^[109] Triazine-based COFs^[96] are photocatalytic COFs materials formed directly from triazine rings, which can broaden their visible light absorption range to improve light utilization. Furthermore, similar to (polymeric carbon nitrides) PCN polymers, the triazine-based COFs feature a nitrogen-rich structure that confers a pronounced heteroatomic effect and a highly porous and reactive active site. Such merits indicate the great photocatalytic potential of covalent triazine frameworks (CTFs). Additionally, COFs derived from benzobisoxazole show promising catalytic properties, and the incorporation of a benzoxazole ring creates a heterojunction with eosin Y catalyst, thereby enabling effective catalytic degradation of pollutants under visible light irradiation.^[110]

The selection of building blocks, reaction parameters, and post-synthetic modifications are all significant in adjusting the properties of COFs. One of the main challenges in COF synthesis is the control of their crystallinity and porosity.^[112] Reaction conditions, such as solvent selection, temperature, and reaction duration, can impact the degree of COF crystallinity and porosity.^[113] Generally, a slower reaction rate and a higher degree of supersaturation can generate more crystalline and porous COFs.^[114] Template-assisted synthesis, such as the use of surfactants or micelles as templates, can also regulate COF porosity.^[115] This technique has been shown to promote the formation of COFs with orderly mesopores or micropores. In addition, we can use topological technology to synthesize the desired COFs,^[111] design the framework structure of the function that we need in advance, and then find the appropriate monomer to synthesize it.^[116] At the same time, the monomers can be selected for COF synthesis according to the specific applications which is another major advantage of this material (Figure 5a–e).^[117]

As we have discussed above, COFs have been found to possess high surface areas, ranging from a few hundred to a few thousand square meters per gram, rendering them attractive for a variety of applications including gas storage,^[108,118] catalysis,^[97,119,120] and energy conversion^[121] and storage.^[118,122] However, the insolubility and poor processability of bulk COF materials limit their practical applications. Additionally, the weak conductivity of bulk COFs is a major obstacle to their use in energy storage applications, which reduces the advantage of their large specific surface area and stability. This limitation is particularly evident in the context of energy batteries, where COFs are sometimes employed as electrodes and suffer from poor electron transfer rates and limited availability of active sites.^[38,123] To address this problem, it is necessary to combine it with some conductive materials. Therefore, more and more recent research focused on the development of composite materials of COFs, which could potentially overcome these limitations.

3. Synthetic Strategies for COF/Graphene Hybrids

3.1. One-Pot Synthesis

The preparation of COF/graphene hybrids involves numerous methods, but the most significant one is the one-pot synthesis





Figure 5. Schematic of 2D COFs with a) hexagonal, b) tetragonal, c) trigonal, d) herringbone, and e) brick-wall topologies based on different multitopic organic building blocks (BBs). Reproduced with permission.^[111] Copyright 2016, American Chemical Society.

method due to its convenience and time efficiency. This method enables the precise control of reaction conditions such as temperature, pressure, and reaction time, leading to the formation of homogeneous and high-quality materials.^[124] The one-pot approach is also highly efficient because it reduces material loss during transfer, resulting in higher yields.^[125] Furthermore, it is a cost-effective approach that eliminates the need for additional equipment and processing steps.

The pioneering one-pot synthesis of COF/graphene hybrids was developed by Wen et al.^[33] in 2018. Briefly, the first step involved adding 1,3,5-triformylphloroglucinol (TFP) and 2,6diaminoanthraquinone (DAAQ) into a glass tube. Following this, the dispersant mesitylene/dioxane and acetic acid were added and the mixture was ultrasonically dispersed evenly. The GO dispersion was then added before sealing the glass tube reaction and incubating it at 120°C for three days. Finally, the solid hybrid material was cleaned and dried (Figure 6a). Later in 2020, Abdellah et al.^[126] reported a GO@COF-1 composite material using a similar one-pot method. They utilized a dimethyl sulfoxide (DMSO) solution to disperse GO through ultrasonic treatment. Afterward, they added COF monomers, including melamine and terephthaldehyde, to the dispersion. The reaction was then conducted at 180°C for 3 days under vigorous stirring. Subsequently, the precipitate underwent filtration and washing with tetrahydrofuran (THF), acetone, and N, N-dimethylformamide (DMF). Finally, the GO@COF-1 composites were obtained by vacuum drying at 120°C. In 2022, Liang et al.^[31] also reported the eco-friendly preparation of GO/COF composites at ambient temperature using this method, with a composite yield exceeding 90%. Initially, the authors dissolved 1,3,5-tris(4-aminophenyl)benzene (TPB)

and HAc in acetonitrile (ACN). Then, GO was introduced into the ACN dispersion and thoroughly mixed for 30 min. Another monomer, 2,5-divinylterephthalaldehyde (DVA), was solubilized in ACN and blended with the preconfigured GO/TPB dispersion after vigorous stirring, and then allowed to react fully at ambient temperature for 72 h. After thrice washing with THF and ethanol, and subsequently drying, the GO/COFs hybrid material was obtained (Figure 6b). In another work, Shen and coworkers developed a simplified solvent-free method to synthesize COF/GO composite materials using magnetic COF (MCOF) and GO.^[124] To impart the composite with magnetic property, the authors first modified the COF monomer 1, 4-diaminoanthraquinone (Dq). Superficially, Dq, along with p-toluene sulfonic acid (PTSA), Fe₃O₄@SiO₂-NH₂, and GO was added to a mortar. Another COF monomer, triformylphloroglucinol (Tp), was added after grinding for 5 min. After grinding for an additional 10 min, the paste substance was mixed with the right amount of ultra-pure water and then transferred to an environment of 170°C for 5 min. Finally, the paste was cleaned with water, dimethylacetamide (DMAc), and acetone to remove the unreacted monomers. MCOF/GO hybrid materials were obtained after vacuum drying at 60°C. Zhang and coworkers also reported a TpPa@rGO composite by adopting a typical one-pot method.[32] To synthesize TpPa@rGO powder, initially, Tp was mixed with p-phenylenediamine (Pa) and thoroughly polished to yield yellow powder. Next, DMF was used to dissolve the yellow powder with the addition of GO. Following this, acetic acid was added to accelerate the reaction process. The resulting dispersion was then placed in an autoclave and allowed to react under N₂ at 120 °C for 72 h. Finally, the TpPa@rGO powder was procured after the process of centrifugation, cleansing with DMF and anhydrous ethanol to remove excess impurities,





Figure 6. a) One-pot synthesis of o-TDCOF and o-GS-COF. Reproduced with permission.^[33] Copyright 2018, Elsevier B.V. b) Preparation process of COF/graphene hybrids materials. Reproduced with permission.^[31] Copyright 2022, The Royal Society of Chemistry. c) Synthesis process of TpPa@rGO. Reproduced with permission.^[32] Copyright 2022, Elsevier B.V.

and drying, resulting in a dark red powder (Figure 6c). Similarly, Mervat et al.^[86] reported a composite made from graphene and a COF using the one-pot method to prepare N-doped C/rGO composites. Initially, they added melamine and p-phenylaldehyde into a GO/DMSO solution. The mixture was then heated and stirred at 180 °C for 72 h until the condensation reaction was completed. After cleaning the precipitate with THF and acetone, the N-doped COF/rGO composite was obtained through vacuum drying at 120 °C.

The main advantage of the one-pot synthesis method lies in its ability to reduce the loss of synthesis monomers due to transfer processes, thereby improving the utilization of synthetic materials. Compared to multi-step synthesis, the one-pot method offers the advantages of time and labor savings by eliminating the need for intermediate purification. However, one-pot synthesis often comes with the occurrence of some side reactions during the reaction process, as well as the risk of contamination of intermediate products by chemical reagents. Therefore, researchers need to assess whether the entire reaction process meets the standards for one-pot synthesis before proceeding.

3.2. Ex Situ Synthesis

Ex situ synthesis stands in contrast to the in situ synthesis technique, by providing a more expansive range of materials that can be synthesized, as it is not constricted by the particular reaction conditions required by in-situ synthesis. Moreover, ex situ synthesis is often more conducive to scaling up for large-scale production, as it can be conveniently executed with standard equipment and processes, and can be employed to yield materials with tailored characteristics and properties by modifying the synthesis conditions.

The first study on the ex situ synthesis of COF/graphene hybrids was conducted by Guo et al.^[127] in 2018. They prepared a covalent organic polymer/rGO (COP/rGO) hybrid catalyst using this method. The authors initially synthesized a COP that

had been modified with metal ions and functional groups. Subsequently, they combined this COP with rGO, resulting in the formation of a COP@rGO composite material due to the electrostatic interaction between the positively charged metal ions on the COP and the negatively charged rGO surface (Figure 7a). In 2021, Zhao et al. also applied the ex-situ method to synthesize a COF/rGO hybrid material.^[128] Initially, piperazine, melamine, and KCO3 were dissolved in 1,4-dioxane and stirred magnetically for 1 h. Subsequently, the resulting mixture was refluxed at 110 °C for 48 h to obtain COF. The pre-prepared COF and GO were individually dissolved in 50 mL of deionized water, followed by 3 h of ultrasonic treatment to facilitate complete dissolution. Subsequently, ascorbic acid was introduced into the mixture of COF and GO solution, and the resulting mixture was refluxed at 80 °C for 3 h. The resultants were then collected through centrifugation and subsequently washed with deionized water to ultimately obtain the COF/rGO hybrids (Figure 7b). Similarly, Wang et al.^[30] also reported a COF/rGO-x composite material using this method. In this work, TFP and 1,4-diaminobenzene (DAPy) were dissolved in a blend of trimethylbenzene and 1,4-dioxane (4:1, v/v). The reaction underwent condensation with Schiff base at a temperature of 120 °C for 72 h. Upon completion of the reaction, the resulting mixture was subjected to washing and subsequent drying, resulting in the formation of deep red TaPa-Py COF crystals with a yield of 72%. To achieve the exfoliation of these COF crystals into 2D nanosheets, ultrasound was employed, followed by dispersing the 2D-COF nanosheets in n-methyl-2-pyrrolidone (NMP) upon successful exfoliation. The suspension of 2D-COF nanosheets was then combined with different amounts of GO suspension and reacted at 180 °C for 6 h, leading to the formation of COF/rGO hybrids (Figure 7c).

Ex situ synthesis is also a commonly utilized method for preparing COF/graphene hybrid membranes. GO is highly dispersible, making it ideal for aiding the dispersion of COF. When the mixture of GO and COFs is filtered under vacuum, an ultra-thin composite membrane can be formed. For instance, Kong and colleagues reported the fabrication of a COF-TpPa/GO

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Figure 7. a) The preparation process of COP/rGO. Reproduced with permission.^[127] Copyright 2018, Wiley-VCH. b) Illustration of the synthesis of COF/rGO composites. Reproduced with permission.^[128] Copyright 2021, American Chemical Society. c) Preparation process of COF/rGO-x composite materials. Reproduced with permission.^[30] Copyright 2022, Elsevier B.V. d) Preparation process of TpPa-1/GO composite membrane for gas separation. Reproduced with permission.^[130] Copyright 2019, Elsevier B.V. d) Preparation process of TpPa-1/GO composite membrane for gas separation.

membrane using this method. The COF-TpPa/GO suspension was uniformly mixed and filtered under a vacuum. The resulting membrane was then subjected to hot pressing to enhance the stability of the COF-TpPa/GO membrane.^[129] In another work, Tang et al.^[130] also developed a composite membrane through the ex-situ approach. Initially, they synthesized two-dimensional COFs, TpPa-1, TpPa-2, and TpPa-NO₂, which possessed a uniform pore size. Subsequently, these COFs were mixed with a GO solution, filtered, and then a composite separation membrane was obtained. The notable merit of this approach is that it does not alter the structure of the two-dimensional COFs, thereby enabling the complete expression of their unique properties (Figure 7d).

Ex-situ synthesis can be utilized to synthesize the desired hybrid materials using different processes, often resulting in higher purity of the target product. For COFs/graphene-based hybrid materials, one can first synthesize high-quality COF materials and then combine them with graphene-based materials. This significantly reduces the impact of graphene-based materials on COF synthesis during the hybridization process. Additionally, it's worth mentioning that the synthesis conditions of COFs do not limit the extent of their hybridization with graphene-based materials. This allows COF/graphene hybrid materials to have even greater advantages.

3.3. In Situ Growth

To optimize the synthesis of composite materials for specific applications, it is crucial to improve the synthesis approach. In situ growth method refers to first modifying GO with the organic unit of COF, and then guiding the subsequent growth of COF. In contrast to the aforementioned methods, the in-situ growth method offers certain advantages that can contribute to the experimental outcomes.

The first reported in-situ growth of COF on graphene was conducted by Sun and colleagues in 2017.^[34] They initially dissolved GO and 1,4-benzenediboronic acid (DBA) in a methanol solution for a solvothermal reaction, enabling DBA to anchor onto the GO surface via functional groups without any condensation occurring between the DBA molecules. The remaining two unreacted hydroxyl groups on the DBA molecule served as nucleation sites for the condensation reaction with the DBA molecule, leading to the vertical growth of COF-1 on the GO surface (Figure 8a). In 2019, Zhang and colleagues reported a study in which COF-1 was loaded onto a GO layer using an in-situ growth technique. The resulting GO nanosheet loaded with COF-1 was then processed using an extraction and filtration method to create a film, which was used for separating dyes and salts (Figure 8b).^[131] The researchers first prepared a GO/methanol dispersion and subsequently added DBA to the GO dispersion. After thoroughly mixing, the solution was transferred to a stainless vessel and allowed to react for 12 h at 90 °C. Following the reaction, the excess DBA was removed through multiple washes with methanol. The resulting GO/DBA was then dispersed in a mesitylene/dioxane solution. The reaction continued for 72 h at 120 °C after introducing additional DBA to the GO/DBA dispersion, facilitating the condensation of DBA with the DBA on the GO sheet layer. Finally, the reaction was washed with acetone and dried at 50 °C. Later, Li et al.^[43] also utilized the in-situ growth method to create a COF/rGO aerogel. Initially, they combined GO with a COF monomer, Dq, and loaded it onto the GO nanosheet layer. Subsequently, they introduced another COF monomer, Tp, to





Figure 8. a) Diagram of COF growing vertically on GO nanosheets. Reproduced with permission.^[34] Copyright 2017, Wiley-VCH. b) Synthesis of COF-1/GO with in situ growth. Reproduced with permission.^[131] Copyright 2019, Elsevier B.V. c) In situ synthesis of COF/rGO aerogel. Reproduced with permission.^[43] Copyright 2020, Nature. d) COF nanosheets grown vertically on graphene aerosol. Reproduced with permission.^[132] Copyright 2022, Wiley-VCH.

initiate polycondensation with Dq. TpDq grew in situ on the lamellar structure, following which the composites underwent freeze-drying to obtain COF-TpDq/rGO aerogel (Figure 8c).

COF nanosheets can also be grown directly on the surface of the GA, thereby allowing for the regulation of the original pore structure of GA. Recently, Jiang et al. presented the modification of GAs with vertically grown COF nanosheets using the in-situ growth method.^[132] First, freeze-dried GA possessed high porosity, and macropores of roughly 5 μ m were synthesized. Then, the GA was submerged in a dispersion containing TPB and 1,3,5benzenetricarbaldehyde (BTCA), together with monofunctional competitors' benzaldehyde and aniline, as well as scandium (III) trifluoromethanesulfonate. The two monomers could produce highly crystalline COFs on GA scaffolds in the presence of monofunctional competitors. Following a reaction period of 48 h, the products were washed and annealed for 2 h under argon protection to obtain highly conductive v-COF-GAs (Figure 8d).

This approach can minimize impurities and byproducts in the synthesis process, leading to improved purity of the composite materials. Moreover, the morphology and size of the material can be regulated by manipulating the growth conditions such as temperature and reactant concentration. From an economic perspective, the in-situ growth method avoids the need for excessive solvents and reagents, resulting in significant cost savings during synthesis.

4. Enhanced Properties of COF/graphene Hybrids

To address the shortcomings of individual materials, one approach is to create hybrids by combining them with other materials. The preceding discussion provided a brief overview of

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Figure 9. a) N₂ adsorption–desorption curves of COF/rGO. b) Pore size distribution of materials calculated by NLDFT method. Reproduced with permission.^[43] Copyright 2020, Nature. c) Water transport channels of GO–CTF membrane. Reproduced with permission.^[40] Copyright 2019, American Chemical Society.

the preparation of COF/graphene hybrids. The subsequent sections will delve into the effects of hybridization on the properties of COF/graphene hybrids, especially the synergistic effects between COFs and graphene. Several examples will be presented in this part to showcase the remarkable performance of the enhanced properties, including specific surface area, pore size, stability, conductivity, and wettability.

4.1. Surface Area and Pore Structure

The surface area and pore structure are crucial structural features of COF/graphene hybrids, significantly impacting their performance in diverse applications. Specifically, a larger surface area facilitates applications like absorption by increasing the contact possibility between the targeted pollutant and the adsorption material, thereby enhancing both the capacity and rate of pollutant adsorption. Because COF/graphene hybrids are composed of COF and graphene, their surface area and pore structure can be adjusted by manipulating these components.

Earlier studies have indicated the clear synergistic effect between COF and graphene. COF/graphene hybrids have a higher surface area than pure COF and graphene. In 2018, Wen et al.^[33] reported the utilization of a graphene-synergized 2D COF (GS-COF) to concentrate uranium, a radioactive element, in aqueous solutions. The study observed synergistic effects between COF and graphene, demonstrating improved efficiency of the uranium adsorption process through the combination of the two materials. The N_2 adsorption experiments conducted on GS-COF demonstrated that the specific surface area of the composite material is 313.2 $m^2~g^{-1}$. Importantly, this specific surface area was larger than that of the pristine GO (74.8 $m^2~g^{-1}$) and TDCOF (210.3 $m^2~g^{-1}$), respectively. This result was attributed to the interlayering of the two nanomaterials, which minimized the polymer-polymer interaction and enhanced the dispersion, thereby increasing the specific surface area.

It is worth noting that some studies have also indicated that the combination with graphene will reduce the specific surface area. In 2020, Li et al. also reported a COF/rGO composite aerogel, but what's different is that they found the specific surface area of hybrid materials is between TPDq-COF and rGO. The obtained TPDq-COF had a specific surface area of 498 m² g⁻¹. When this COF is combined with reduced GO, the specific surface area is reduced to 246 m² g⁻¹, but this value is still larger than that of the pure rGO (37 m² g⁻¹) (Figure 9a).^[43] The lower specific surface area of the pure rGO is ascribed to the π - π interaction between the rGO nanosheets. After compounding TPDq-COF with rGO, the presence of COF can increase the layer spacing of rGO to improve the specific surface area. Conversely, the specific surface area of TPDq-COF is partially masked by rGO, Conversely, the specific surface area of TPDq-COF is partially masked by rGO, leading to the specific surface area of hybrids materials being between TPDq-COF and rGO. Nevertheless, the deficiency of the specific surface area can be compensated by the creation of an extra porosity (Figure 9b), facilitating the adsorption process. The combination with COF can effectively solve the

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problem that graphene sheets are easy to stack. For this purpose, Zhong et al.^[25] coupled GO nanosheets and TpPa-1 framework for the adsorption of U(VI) and Eu(III) in water. The BET-specific surface area of GO@TpPa-1 was determined to be 500.8 m² g⁻¹, while those of TpPa-1 and GO were 688.8 and 373.5 m² g⁻¹, respectively. Compared with pure GO, the specific surface area of GO@TpPa-1 increased by 127.3 m² g⁻¹. Yao and coworkers also fabricated hybrid materials composed of rGO and TpPa-1-COF.^[47] The surface areas of TpPa-1-COF and rGO (5%)-TpPa-1-COF were determined to be 569.06 and 520.23 m² g⁻¹, respectively. The incorporation of rGO caused a reduction in the exposed area of TpPa-1-COF, ultimately resulting in a reduction of the surface area of the composite material.

Expanding pore size is an important aspect of regulating hybrid performance, as pore sizes determine the transport of substances within the composite. For instance, to enlarge the pore size for oil droplets to pass through, Wang et al. reported the growth of COFs on GO lamella.^[123] They found that the composite coating showed extremely high oil permeability. This was mainly due to the growth of COFs leading to a large increase in the ratio of pore size and macropore volume of the hybrid material, so the channel for oil to pass through the coating expanded. COFs with an ordered pore structure can not only increase the pore size of the membrane, but also adjust the interlayer channel of the GO by combining with the GO sheet to provide a vertical channel for the composite membrane and accelerate the membrane penetration. As a typical example, Khan et al. utilized CTF to integrate with GO by incorporating some vertical channels without altering the layer spacing of GO (Figure 9c).^[40] Upon the combination of GO and COF, a significant cooperative effect was observed, where COF intercalation led to an improvement in the specific surface area of the composite. Furthermore, the composite's overall flux was enhanced due to the presence of a vertical channel in COF.

The control of the surface area and pore structure of COF/graphene hybrid materials is aimed at improving their potential in various applications, especially in adsorption processes. Future research could focus on fine-tuning synthesis methods to obtain the optimal surface area and pore structure for specific applications. In addition, the interaction between COFs and graphene remains an interesting area of exploration. When these materials are combined, understanding the factors that control synergies and specific surface area changes could pave the way for designing more efficient and versatile COF/graphene hybrids. Moreover, expanding pore size as a means of improving transport performance opens up opportunities for the application of filtration, separation, and membrane technologies. Overall, the interplay between specific surface areas, pore structures, and composites provides a rich area of research with the potential to address environmental and energy challenges in innovative ways.

4.2. Stability

The stability of COF/graphene hybrids is of paramount importance for their practical application under industry-related conditions. They must exhibit a high degree of stability to withstand harsh chemical and thermal conditions without compromising their structural integrity, even when exposed to extreme environmental conditions. While the original COF may be unstable under such conditions, prior research has shown that COF/graphene hybrids possess superior chemical and thermal stability in comparison.

Imine COFs, a significant subclass of COFs, possess a reversible imine bond that is susceptible to hydrolysis in acidic environments, which hinders their widespread use. Zhong and colleagues suggested that incorporating acid and base-resistant GO could enhance the stability of imine COFs. In their work, TpPa-1 anchored on GO nanosheets achieved improved stability, while also facilitating the heavy metal ion adsorption.^[25] The thermogravimetric analyses (TGA) of GO and GO@TpPa-1 were performed to compare their thermal stability. GO exhibited a weight loss of \approx 6.6% below 100 °C due to the evaporation of adsorbed water molecules. Further heating to 100-200 °C resulted in a weight loss of 24% as the oxygen-containing groups on GO undergo decomposition. As the temperature continued to rise, the carbon skeleton of GO began to pyrolyze at \approx 503 °C, leading to a weight loss of up to 72.5%. In contrast, the weight loss of GO@TpPa-1 started at a higher temperature of 403 °C and continued until 617 °C, suggesting its structural stability (Figure 10a,b). Hence, GO@TpPa-1 exhibited superior thermal stability in comparison to GO. In another work, Liu and coworkers conducted TGA to investigate the thermal stability of CTF-1 and CTF-1/GO-3.0 under N2 conditions.^[133] TGA results showed that CTF-1/GO-3.0 remained stable at 220 °C, while CTF-1 began to lose weight at 220 °C. The initial pyrolysis temperature of CTF-1/GO-3.0 is higher (276 °C), indicative of enhanced thermal stability of CTF-1/GO-3.0 in comparison to that of CTF-1 (Figure 10c). However, a recent work conducted by Roys et al.^[135] indicated that the thermal stability of ternary WO3@TpPa-1-COF/rGO composite slightly decreased compared to that of single COF and binary WO₃@TpPa-1-COF. The ternary composite WO₃@TpPa-1-COF/rGO (30%) exhibited a slow weight loss below 300 °C, attributed to the pyrolysis of oxygen-containing groups in rGO structure. However, at 300 °C, the ternary component structure collapsed and the reduction in thermal stability was ascribed to the weak π - π interaction between TpPa-1-COF and rGO.

Pure GO membranes are prone to structural collapse due to repulsive forces between GO nanosheets, which poses a major challenge for their practical application. Introducing COF as a cross-linking agent between GO nanosheets can significantly reduce the electrostatic repulsion effect and form a more stable membrane structure.^[123] Based on this, Khan et al.^[40] presented the fabrication of GO-CTF₅ membranes with improved pure water flux and stability in aqueous media. The stability of pure GO membranes and $\text{GO-CTF}_{\scriptscriptstyle{\mathsf{S}}}$ membranes was evaluated under various pH conditions accompanied by ultrasound, as depicted in Figure 10d. The results demonstrated that both pure GO membrane and GO-CTF₅ membranes were stable without peeling off from the basement membrane under acidic conditions. While under neutral and alkaline conditions, significant shedding occurred in the pure GO membrane, whereas the GO-CTF₅ membrane remained intact. These findings indicated that the GO-CTF₅ composite membrane possessed superior chemical stability in comparison to the pure GO membrane. In 2020, Sui et al. reported the use of a two-dimensional COF nanosheet as a crosslinking agent to enhance the stability of the rGO membrane.

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Figure 10. a) TGA of GO; b) TGA of GO@TpPa-1. Reproduced with permission.^[25] Copyright 2021, Elsevier B.V. c) TGA of CTF-1 and CTF-1/GO-3.0 under N₂ condition. Reproduced with permission.^[133] Copyright 2021, Wiley-VCH. d) Digital photos of GO film and GO-CTF₅ film under different extreme conditions. Reproduced with permission.^[40] Copyright 2019, American Chemical Society. e) The flux of the composite membrane prGO/COF and the retention rate for MB at different pressures. Reproduced with permission.^[134] Copyright 2020, The Royal Society of Chemistry.

The intercalation of COF not only improved the structural stability of the hybrid membrane but also increased the transport channels of water molecules by utilizing the vertical channels of COF.^[134] Figure 10e illustrated that the flux and rejection rate of the rGO/COF nanolaminate membrane remained stable under different pressures, indicating its improved structural stability.

The interaction between COFs and graphene in enhancing stability remains an area of interest and should be investigated further. Understanding the mechanisms behind stability improvements and identifying the conditions under which stability may be compromised will guide the development of more resilient hybrid materials. Additionally, the use of COF as a cross-linker in graphene-based membranes offers exciting opportunities to improve structural stability and performance. This method can be applied to a variety of applications, such as water purification, seawater desalination, and energy conversion.

4.3. Conductivity

Typically, COFs demonstrate low electrical conductivity, whereas graphene and its derivatives exhibit high conductivity. Hence, COF/graphene hybrids commonly demonstrate superior electrical conductivity as compared to pure COFs.

To fully harness the enormous potential of COF's large specific surface area, uniform pores, and compact active sites in the energy sector. In 2018, Luo and colleagues reported the in-situ polymerization of tetramino-benzoquinone (TABQ) and pyromellitic dianhydride (PMDA) on graphene to produce poly(imide-benzoquinone)-graphene (PIBN-G) heterogeneous materials with exceptional electrical conductivity, which served as an anode for lithium-ion batteries.^[45] The electrochemical impedance spectrum (EIS) revealed that the charge transfer resistance (R_{et}) of PIBN-G is considerably smaller than that of PIBN (PIBN-G: 169.4 Ω , PIBN: 280.2 Ω), indicating a significant increase in conductivity. Sun and colleagues prepared porous carbon material by surface modification of reduced graphene oxide (rGO) with 2D COF nanosheets, resulting in vertically aligned CNS-rGO (v-CNS-rGO) hybrids. This modification significantly improved the energy storage efficiency of the resulting material.^[85] Utilizing vertical nanosheets in the hybrid material resulted in a shortened path for electron transfer, hence enhancing its conductivity. The Nyquist plots of various proportions of v-CNS-rGO revealed that the semicircle located in the high-frequency region has a small radius, indicating low electron transfer resistance for the v-CNS-rGO composite material (Figure 11a). Additionally, the authors created a composite by directly blending COF powder (CNP) with rGO, which they named CNP/rGO. However, EIS testing results of v-CNSrGO-3 and CNP/rGO-3 showed that v-CNS-rGO-3 still possessed a lower electron transfer resistance compared to CNP/rGO-3 (Figure 11b). Later in 2019, Huang and colleagues also found that the graphene@COF composite could limit the formation of large Li₂CO₃ particles and facilitate the decomposition of small Li₂CO₃ particles, leading to an increase in electron transfer rate and a reduction in charging voltage. The resistances of graphene and

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Figure 11. a) Nyquist plots of different ratios of v-CNS-rGO. b) Nyquist plots of v-CNS-rGO-3 and CNP/rGO-3. Reproduced with permission.^[85] Copyright 2018, Wiley-VCH. c) EIS of graphene and graphene@COF after 30 cycles. Reproduced with permission.^[136] Copyright 2019, Wiley-VCH. d) EIS of USTB-6, USTB-6/G, and USTB-6@G. Reproduced with permission.^[132] Copyright 2022, Wiley-VCH.

graphene@COF were found to be 8.0 and 9.1 Ω , respectively.^[136] Although the introduction of COF somewhat decreased the electron transfer rate of the composite material, its conductivity remained higher than that of pure COF. After 30 cycles, the performance of both graphene and graphene@COF was tested again, revealing that the resistance of graphene increased significantly, whereas graphene@COF maintained a high level of electrical conductivity (Figure 11c).

Recently, An and his colleagues demonstrated the fabrication of a DAAQ-COF/GA 3D composite aerogel electrode to overcome the issues of low electron transfer rate and ineffective use of active sites associated with DAAQ-COFs.^[137] The Nyquist plot of DAAQ-COF/GA indicated that various COF/GO ratios had relatively low electron transfer resistance and ion diffusion resistance. By merging COFs with 2D graphene-based materials, the poor electrical conductivity and low active site utilization of single COFs could be improved, resulting in improved electrical conductivity and remarkable energy storage performance. Liu et al. also utilized a solvothermal method to create a COF/graphene hybrid material named USTB-6@G (USTB representing the University of Science and Technology Beijing) and utilized it as a cathode substance in lithium-ion batteries to maximize the active sites of porous COF.^[138] The radius of the Nyquist curve in the high-frequency region of USTB-6@G was smaller than that of USTB-6/G (USTB-6 mixed with graphene directly) and USTB-6, implying a higher electron transfer rate and enhanced conductivity of USTB-6@G (Figure 11d).

Adding graphene to COFs materials is expected to improve electrical conductivity, making it more suitable for energy-related applications, including batteries and supercapacitors. Future research could delve deeper into the mechanisms that control the enhanced conductivity of COF/graphene hybrid materials, allowing for more precise control and optimization of these properties. Overall, the synergies of COFs and graphene in improving electrical conductivity open the door to innovative solutions in the energy sector to solve the challenges associated with energy storage and conversion sustainably and efficiently.

4.4. Wettability

The wettability of a material is determined by its surface chemical composition and roughness. The surface properties and wettability of COFs can be modulated by hybridizing them with graphene derivatives. The COFs reported in previous studies are highly sensitive to water due to the abundant polar functional groups on their surface, which gives them hydrophilicity. In the presence of water, the reverse reaction is promoted, leading to the degradation of COFs. The hydrophilicity of graphene and its derivatives is also related to the polar groups on their surface, which can be easily regulated to control the surface properties and water sensitivity of COFs.

For example, in 2019, Kong and co-workers embed hydrophobic COF-TpPa into the GO sheet.^[129] They discovered that the initial COF-TpPa had a contact angle of 125.78°, whereas the hybrid membrane displayed a water contact angle of 60.92°. The incorporation of COFs not only alleviated the energy barrier for





Figure 12. a) Dynamic water contact angle of GO, COF, and GO/COF. Reproduced with permission.^[139] Copyright 2020, Elsevier B.V. b) Water contact angle of GO, TTF-BN-AO, and rGO-TTF-BN-AO. Reproduced with permission.^[140] Copyright 2022, Elsevier B.V.

water permeation through the GO membrane, thus benefiting the transmembrane transport of water molecules, but also facilitated the dispersion of COFs in an aqueous solution, which overcame the insolubility issue. A recent study in 2020 reported a fascinating superhydrophilic GO/COF composite membrane.^[139] Superhydrophilic COF nanomaterials were synthesized in advance by using TFB and PDA monomers. The hydrophilicity of these COFs is mainly attributed to their hydrophilic functional groups, like carboxylic, hydroxyl, and sulfonic groups. As can be seen from Figure 12a, the water contact angle of GO/COF rapidly decreased from 33° to 0° within just 2 s, while the water contact angle of GO only decreased from 41.4° to 28.6° within 5 s, indicating that the hydrophilicity of the composite was significantly enhanced. Zhang et al.^[140] also used hydrophilic COF to enhance the overall hydrophilicity of composites in 2022. The researchers developed an rGO-TTF-BN-AO hydrogel. As evidenced by Figure 12b, the water contact angle of the original rGO was 83.6°, and after the addition of TTF-BN, the water contact angle was significantly reduced to 44.1°, indicating the enhanced hydrophilicity of the hydrogel. Wang et al.^[123] synthesized a series of superhydrophobic COF/GO membranes. The roughness of COF particles and the hydrophobicity of COFs contributed to the superhydrophobicity of the composite. They also found that increasing the GO amount would reduce the surface roughness and water contact angle of the membranes. As a result, the contact angle of GO, COF/GO₂₅, and COF/GO₅₀ were found to be 160°, whereas the contact angle of COF/GO₇₅ and COF/GO₁₀₀ decreased to 150°. In addition, the authors also investigated the water contact angle of COF/GO₅₀ at different pH values and found that it stabilized at 160°, indicating that the composite membrane has a stable superhydrophobicity.

Moreover, the stability of wettability, as demonstrated by stable superhydrophobicity, is essential for long-term applications. Investigating the durability and robustness of wettability modifications under various conditions can provide insights into the practical utility of COF/graphene hybrids in real-world scenarios.

5. Applications of COF/Graphene Hybrids

In the following section, the environmental and energy applications of COF/graphene hybrids are discussed in detail.

5.1. Adsorption

The adsorption process relies heavily on the physicochemical properties of porous nanomaterials. Developing materials with high adsorption capacity is critical. However, using these materials alone may not produce satisfactory results, so combining them for the adsorption of organic pollutants is a favorable strategy. The adsorption efficiency of COF/graphene hybrids for organic pollutants is found to be better than that of single GO or COF. These COF/graphene hybrids show significant effectiveness in heavy metal ion adsorption, organic pollutant adsorption, and carbon dioxide adsorption (shown in **Table 1**).

5.1.1. Heavy Metal Ions Adsorption

Heavy metals are metallic elements with high density and atomic weight that tend to accumulate in the environment and cause

Table	1.	The	adsor	ption	performance	e of variou	s COF	/grap	nene h	vbrids.
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Materials	COF	Graphene	Preparation methods	Pollutants	Performance [mg g ⁻¹]	References
COF/graphene aerogel	COF-SO ₃ Na	GO	One-pot synthesis	MB, RhB, CV	34.0, 368.0, 328.0	[42]
COF/rGO	TpDq-COF	rGO	In situ Growth	Organic solvents/oil	98.0-240.0	[43]
COF@PGO	COF _{TFA}	PGO	Ex situ synthesis	Chlorogenic acid, caffeic acid	17.0, 17.2	[141]
o-GS-COF	TDCOF	GO	One-pot synthesis	U (VI)	220.1	[33]
rGO-TTF-BN-AO	TTF-BN	GO	One-pot synthesis	U (VI)	521.6	[140]
GO@TpPa-1	TpPa-1	GO	Ex situ synthesis	U(VI), Eu(III)	1532.4, 886.4	[25]
TpPa@rGO	ТрРа	rGO	One-pot synthesis	Pb ²⁺	137.8	[32]
a-GO@COF-F	COF-F	a-GO	One-pot synthesis	CO ₂	67.9	[78]

irreversible damage to the nervous system, liver, and kidneys of humans.^[142] COF/graphene hybrids, owing to their high specific surface area and abundant surface functional groups, have been extensively utilized for adsorbing heavy metal ions in a variety of applications.

While some porous polymeric and metal-organic framework materials with numerous active functional groups of donor heteroatoms may exhibit better adsorption capacity, the requirement for extracting and recovering radioactive metal uranium from nuclear wastewater is an adsorbent material that possesses superior acid-base stability and radioactivity resistance. In 2018, Wen et al.^[33] reported the preparation of o-GS-COF complexes by a one-pot method for the adsorption of radioactive material uranium. The composite material exhibited significantly enhanced uranium adsorption capabilities in comparison to the original GO and o-TDCOF (COF synthesized by TFP and DAAQ). The adsorption capacity of the o-GS-COF composite was measured to be 144.2 mg g^{-1} , which surpassed that of GO (92.5 mg g^{-1}), TDCOF (98.8 mg g^{-1}), o-TDCOF (105.0 mg g^{-1}), and GS-COF (115.4 mg g⁻¹). The increase in adsorption capacity was ascribed to two factors. First, the combination of GO and COF significantly increased the specific surface area of the hybrid material. Second, the oxidation of the composite material produced more oxygen-containing groups, which was conducive to the adsorption of uranium (Figure 13a). In addition, the composite could stably adsorb radioactive ions even under strongly acidic conditions. Later, a study on the adsorption of heavy metal ions using GO@TPPA-1 hybrids was also presented by Zhong et al.^[25] in 2021. The researchers utilized an ex-situ synthesis method to increase the trapping of radionuclide ions by reducing the selfstacking of COF using GO nanosheets. The key structure involved was the -C=N···H···O=on the skeleton structure, forming a hexagonal potential well for efficient trapping of uranium U(VI)/europium Eu(III) ions (Figure 13b). The adsorption capacity of GO@TPPA-1 for U(VI) and Eu(III) was determined to be 1532.35 and 886.44 mg g^{-1} , respectively, which was much higher than the adsorption capacity of U(VI) by the hybrid material reported by Wen et al. (144.2 mg g⁻¹) in 2018.^[33]

In 2022, Zhang et al. developed hydrogels consisting of rGO and COF to facilitate U(VI) enrichment in seawater using photothermal conversion desalination. The hydrogel relied on light irradiation to generate a substantial amount of heat on the surface of the hydrogel, which caused water vapor release and promoted U(VI) diffusion in the three-dimensional hydrogel network, thus enhancing the enrichment of U(VI). There were two major factors governing the adsorption of hydrogels throughout the adsorption process. The first factor was pH, due to H⁺ competing with U(VI) for the adsorption site. The temperature was another crucial driving force that played a dominant role in the adsorption process, and the adsorption amount under optimal conditions was 521.6 mg g^{-1} . In addition, light was also an important factor in achieving the desired adsorption capacity, which also proved the synergistic effect of photothermal. At pH = 8, the adsorption capacity of hydrogel reached 352.6 mg g⁻¹ under light conditions, which was 33.9% higher than that under dark conditions (263.2 mg g⁻¹).^[140] Different from previously reported physical adsorption techniques, Zhang et al. recently proposed a groundbreaking technique for electroadsorbing Pb2+ present in water by employing TPPA@rGO as an electrode. Here, rGO served as a substrate to furnish the necessary conductivity and expedite the transfer of electrons, while COF-TPPA selectively captured Pb²⁺ via its inherent redox-active site.^[32]

5.1.2. Organic Pollutants Adsorption

Organic pollutants are the most serious form in wastewater, especially the wastewater generated from the pharmaceutical, printing, and dyeing industries. The persistence of these pollutants has caused serious environmental problems, so there is an urgent need to treat the pollutants. Among them, the use of adsorbent adsorption has become a convenient method to remove organic pollutants.

The highly porous structure of COF/graphene hybrids is conducive to their absorption of organic solvents or oil pollutants. In 2020, Li et al.^[43] reported the synthesis of COF/rGO aerogels to achieve efficient adsorption of organic solvents. They utilized an in-situ growth method to uniformly load TPDQ-COF on the surface of rGO. 16 types of organic solvents were selected as target pollutants, and the results showed that the absorption amount for almost all 16 types of organic solvents was higher than 10 000 wt.% (Figure 13c,d).^[43] This high adsorption amount was ascribed to the large specific surface area and superhydrophobic properties of TPDQ-COF.

Although COF alone is an efficient adsorbent, it is susceptible to pore blockage which can cause a reduction in its adsorption capacity. To overcome this, Li et al.^[42] recently combined ultra-thin COF containing sulfonic acid ions and graphene by a one-pot hydrothermal method to prepare a COF/graphene aerogel (CGA) for dye adsorption. They found that the COF powder alone took SCIENCE NEWS _____

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Figure 13. a) The possible adsorption mechanism of o-GS-COF. Reproduced with permission.^[33] Copyright 2018, Elsevier B.V. b) Schematic diagram showing the adsorption of U(VI) and Eu(III) on GO@TpPa-1. Reproduced with permission.^[25] Copyright 2021, Elsevier B.V. c) Pictures showing the absorption of dyed silicone oil (up)and chloroform (down) by COF/rGO aerogels. d) Absorption capacity of COF/rGO for various organic solvents. Reproduced with permission.^[43] Copyright 2020, Springer Nature. Comparison of equilibrium times e) and maximum adsorption capacities f) of bulk COF powder and CGA for RhB. g) Schematic illustration of the adsorption mechanism of bulk COF and ultrathin COF. Reproduced with permission.^[42] Copyright 2022, Wiley-VCH.

3 h to adsorb these dyes, while the hybrid aerogel took only 3 min. The density of the aerogel was only 7.1 mg cm⁻³, and the removal rate of Rhodamine B (RhB) reached more than 99% within 3 min (Figure 13e,f). The significant enhancement in the absorption capability can be traced back to the three-dimensional interconnected macroporous framework and prominently-exposed adsorption sites. This advancement overcomes the limitations of conventional bulk COFs, which are inherently comprised of a stacked 2D structure and devoid of macropores (Figure 13g). In another work, Liang et al.^[31] prepared GO/COFs composites by Schiff base coupling reaction for the adsorption removal of three different organic pollutants (naphthalene, 1-naphthalamine, and 1-naphthol). The results indicated that the adsorption capacities of GO for three organic pollutants were 112, 96.6, and

87.5 mg g⁻¹, respectively, while the adsorption capacities of COFs were 182, 63.1, and 71.9 mg g⁻¹, respectively. It is noteworthy that the adsorption capacity of GO/COFs for naphthalene (211 mg g⁻¹), 1-naphthalamine (110 mg g⁻¹), and 1-naphthol (98.2 mg g⁻¹) was significantly improved compared with a single component. The whole adsorption process mainly depended on π - π interaction, hydrophobic interaction, and pore size effect. Wang et al.^[141] also synthesized a hybrid material called COF_{TFA}@PGO to selectively adsorb organic pollutants. This adsorbent predominantly utilized cation- π interaction forces to capture pollutants, which in turn enhanced the stability of the hybrid material. The adsorption capacity of the COF_{TFA}@PGO composite for chlorogenic acid and caffeic acid was \approx 20 mg g⁻¹, significantly exceeding that of the other two reference substrates. These

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Table 2.	Liquid	Separation	performance	of different	COF/graphene	hybrid membranes.
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Materials	COF	Graphene	Preparation methods	Pollutants	Flux [L m ⁻² h ⁻¹ bar ⁻¹]	Rejection [%]	References
GO/COF	TFB+PDA	GO	Vacuum filtration	MB, CR	59.0	99.0, 99.8	[139]
GO–CTF	CTFn	GO	Vacuum filtration	EBT, CR, MB, AB	226.3	98.1, 97.5, 97.5, 96.7	[40]
HP-COF-TpPa/GO	COF-TpPa	GO	Vacuum filtration	MB	166.8	97.1	[129]
GO/v-COF@GO	v-COF	GO	In Situ Growth	Oil	10 000.0	99.9	[44]
30-COF@rGO	COF-LZU1	rGO	Vacuum filtration	BB, RB, MB, AO7, RhB	135.0	96.0, 90.0, 85.0, 81.0, 77.0	[144]
prGO/COF	COF-4	prGO	Vacuum filtration	RhB, MB, AO7	194.0	98.0	[134]
COF/GO _x	COF	GOx	One-pot synthesis	Oil	26 000.0	98.3	[123]
AGO	ACOF-1	GO	One-pot synthesis	Methyl blue, MB, MO, CBT, AC, CR, RB, vitamin B12	47.0	95.0–99.2	[145]
GO/COF-1	COF-1	GO	In Situ Growth	CR, DR, MB, RB5, RhB	31.0	99.0	[131]

CR, Congo red. EBT, Erichrome black T. AB, Alcian blue. RB, Rose bengal. BB, Brilliant blue G. AO7, Acid orange 7. MO, Methyl orange. CBT, chrome black T. AC, Acid fuchsin. RB, Reactive black. DR, Direct red. RB5, Reactive black 5.

results indicated that COF_{TFA} @PGO possesses favorable selectivity for organic acids (chlorogenic acid and caffeic acid).

COF/graphene hybrids are anticipated to be the forthcoming generation of exceptional adsorbent materials in facilitating the elimination of organic pollutants. However, further research is required to explore the adsorption abilities of diverse emerging organic pollutants, as well as to develop advanced COF/graphene hybrids that offer better performance.

5.1.3. CO₂ Adsorption

Global warming represents a paramount climate challenge that we must address. Carbon dioxide (CO₂), a significant constituent of greenhouse gases, has emerged as a key target for mitigation efforts.^[143] COF/graphene hybrids are also efficient for CO₂ adsorption. For example, an a-GO@COF-F hybrid material consisting of two-dimensional mesoporous COF-F and anilinefunctionalized GO (a-GO) was proposed for CO2 adsorption recently.^[38] The results showed that the optimal CO₂ adsorption capacity of a-GO@COF-F-2 at 273 and 298 K are 67.8 and 52.8 mg g^{-1} , respectively, which exceeded the adsorption capacity of pure a-GO (47.1 and 34.9 mg g^{-1}). The superior adsorption performance was primarily attributed to the adjustment of pore size and functional surface in the composite material. Given the lack of research on gas adsorption by COF/graphene hybrids, there is still considerable room for the development of high-performance COF/graphene hybrids with ideal pore sizes, strong π - π interactions, and multiple active sites for gas adsorption.

5.2. Separation

Membrane separation technology is a common method for wastewater treatment, and there is a considerable demand for membranes with high throughput and high retention rates. The properties of GO, including its ease of modification, dispersion, and exceptional solution processing abilities, make it a highly sought-after membrane material that has garnered significant attention in current research. Despite its many advantages, the low permeability of GO membranes, attributed to their narrow layer spacing and intricate water transport path, still requires further improvement. Modification of GO membranes is crucial in this regard. The addition of COF nanomaterials to GO membranes can expand the layer spacing of GO membranes and increase the water flux, but it does not significantly affect the retention performance. Consequently, COF/graphene hybrid membranes have been increasingly favored in diverse membrane separation systems (Table 2).

5.2.1. Liquid Separation

The hybrid membrane can enhance the stability of pure GO membrane by mitigating the impact of electrostatic repulsion between GO nanosheets, thus prolonging the longevity in water.^[139] Besides, the two-dimensional COF nano-sheet can fill in the gaps between some adjacent GO sheets, regulating the distance between adjacent GO sheets to enhance the rejection rate or improve solvent selectivity. As a typical example, In 2019, Kong et al.^[129] presented a GO@COF-TpPa membrane prepared by hot pressing and used for dye separation. They investigated the removal of three typical dyes, crystal violet (CV), methylene blue (MB), and acid chromium Blue K. The molecular size of CV and MB is smaller than the pore size of COF, while the size of acid chromium blue K is larger than the pore size of COF. However, the results showed that the retention effect of dye molecules does not depend on the molecular pore size. Conversely, smaller CV and MB exhibited higher rejection rates than acidic chromium blue K due to the attraction between negatively charged acidic chromium Blue K and positively charged membrane pores. Khan and coworkers designed a hybrid membrane with vertical pores composed of GO and CTF nanosheets. By introducing CTF nanosheets, they obtained a GO-CTF membrane with a thickness of \approx 32 nm. Compared with the stacking of pure GO nanosheets, the introduction of CTF could shorten the path of water molecules and increase the pure water flux of the membrane. The organic dye removal rate of GO-CTF membrane was more than 90%, and the water flux reached 226.3 L m⁻² h⁻¹ bar⁻¹, which was more than 12 times that of the original membrane.^[40]





Figure 14. a) The rejection of MB, RhB, AO7. Reproduced with permission.^[134] Copyright 2020, The Royal Society of Chemistry. b) Culture of E. coli a,b) and S. aureus c,d) in pre-filter and post-filter solutions. Reproduced with permission.^[145] Copyright 2022, Elsevier B.V. c) Three key roles of 2D-COFs. Reproduced with permission.^[144] Copyright 2021, Elsevier B.V. c)

Moreover, some other work also indicated that the intercalation of GO membranes with COF materials could increase the interlayer spacing of the GO membranes, thereby enhancing their permeability. For instance, a porous rGO membrane (prGO) with COF intercalation was prepared by Sui et al.in 2020.^[134] The composite membrane not only had improved pure water flux due to increased interlayer spacing, but also could retain the initial high retention rate. In addition, the embedding of COF improved the mechanical strength of the composite membrane and increased the self-supporting ability of prGO in the macroporous matrix. With the increase in the amount of COF, the maximum water flux of the membrane could reach 194.0 L m⁻² h⁻¹ bar⁻¹, which was more than 10 times that of the original membrane. The removal rates of MB, lime 7 (AO7), and RhB were over 98% (Figure 14a). Recently, Ye and coworkers modified GO membranes with nitrogen-containing COF for the separation of dyes and salts in wastewater. The results showed that over 90% of the dyes with a molecular weight of 319.85-1355.37 Da were retained by the composite membrane. The retention rate of the membrane for small inorganic salt was also up to 80%. It is worth noting that the microorganisms could also be completely removed with no bacteria in the filtered solution, as shown in Figure 14b.^[145]

COF/graphene composite membranes have also been used for organic solvent nanofiltration. Compared to pure GO membrane and COF membrane, the GO@COF hybrid membrane has shown significant improvement in organic solvent nanofiltration performance. For example, Sui et al.^[144] prepared COF/graphene composites and used them for organic solvent nanofiltration in 2021. The hybrid membrane with intercalated COF LZU1 showed that the methanol permeability of the mixed membrane loaded with 30% COF LZU1 was 162% higher than that of the pure rGO membrane, with a permeability of 76 m⁻² h⁻¹ bar⁻¹, compared with 28 m⁻² h⁻¹ bar⁻¹ in the pure rGO membrane, without sacrificing selectivity. COF LZU1 has a triple function (Figure 14c), the first of which is to increase the water flux by increasing the nanosheet layer spacing. The second function is to improve the stability of the base film by acting as a stabilizing cross-linking agent. A third effect is due to the porous nature of

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Figure 15. a) Tunable separation performance with different thicknesses of the ultrathin CTF-1 membranes. Reproduced with permission.^[48] Copyright 2016, The Royal Society of Chemistry. b) H_2/CO_2 separation diagram; c) H_2 and CO_2 separation performance at TpPa-1 (30 mL) with different volumes of GO. Reproduced with permission.^[130] Copyright 2019, Elsevier B.V. d) Mechanism of borate promoting CO_2 transfer. Reproduced with permission.^[146] Copyright 2021, The Royal Society of Chemistry.

COF LZU1, which, when added between graphene sheets, forms a vertical channel through which the solvent passes, thereby increasing the flux.

COF/graphene hybrid membranes have demonstrated the potential to achieve selective nanofiltration. Researchers can investigate the development of membranes with tailored selectivity for specific molecules or ions, enabling targeted separation in various industries.

5.2.2. Gas Separation

In the current industrial development environment, the pursuit of green energy is increasingly important, and the recycling of energy gas is particularly important. Therefore, the separation of energy gases, especially the separation of hydrogen and methane from mixed gases, has become a hot issue in the field of separation in recent years.

In 2016, Ying et al.^[48] first applied COF/graphene hybrid membrane to gas separation. They prepared GO/twodimensional CTF-1 composite films and applied them to the selective separation of H_2/CO_2 . The results showed that the composite membrane could stably separate CO₂ and H₂. The H₂ permeability of the 100 nm composite film reached 1.7×10^{-6} mol m⁻² s⁻¹ Pa⁻¹. In addition, the separation selectivity also increased with the increase of membrane thickness, and the H_2/CO_2 separation coefficient was as high as 22 (Figure 15a). Tang et al. then constructed a composite membrane using GO and three COF materials, TPA-1, TPA-2, and TPA-NO₂, and used it for H_2/CO_2 separation (Figure 15b). The obtained TPA-1-30/GO-10 membrane exhibited exceptional gas separation capabilities, as indicated by an H₂ permeability of 1.067×10^{-6} mol m⁻² s⁻¹ Pa⁻¹ and an H₂/CO₂ separation coefficient of 25.57 (Figure 15c).^[130] Yang et al.^[146] prepared borate-containing COF (TpTGB) in 2021, and then used vacuum filtration-assisted self-assembly to form GO-TPTGB membrane containing a small amount of GO for the separation of CO₂ and CH_4 . With the help of borates (Figure 15d), CO_2 could be transported to the other side of the membrane easily, resulting in a high separation constant of 27. It is pertinent to note that the use of COF/graphene hybrid membranes in gas separation is still a nascent field, and requires further investigation into COFs with





Figure 16. a) Mechanism schematic of the photocatalytic H2 evolution of rGO(5%)-TpPa-1-COF. Reproduced with permission.^[47] Copyright 2020, The Royal Society of Chemistry. b) Mechanism schematic of the photocatalytic H2 evolution of WO3@TpPa-1-COF/rGO(30%) composite materials. Reproduced with permission.^[147] Copyright 2022, Elsevier B.V.

appropriate pore sizes, as well as effective strategies for compounding with graphene, in order to achieve highly efficient separation of gas mixtures.

5.3. Catalysis

The utilization of visible light in catalytic processes represents an eco-friendly and sustainable approach to generating hydrogen and oxygen.

5.3.1. Catalytic Hydrogen Evolution

Currently, excessive energy demand calls for the extraction of energy fuels which is a challenging area that researchers must prioritize. Among these, H_2 , as a pollution-free source of energy, has gained wide acceptance, making the development of hydrogen evolution technology a critical focus. The utilization of visible light for catalyzing hydrogen production is undoubtedly an eco-friendly approach.

Porous COFs with multi-active sites are commonly used in catalysis, but they still suffer from slow electron transfer rates, which restrict their practical application. However, this issue can be resolved through the combination of graphene-based materials with high electrical conductivity. The earliest application of this hybrid material for hydrogen evolution was presented by Yao et al in 2020. They prepared a series of rGO-TpPa-1-COFs using a one-pot method, in which GO was reduced, functionalized, and covalently connected with COF. Covalent bonding imparted greater stability to the hybrid material, while rGO promoted photogenerated electron migration to enhance H₂ evolution activity. The observed H₂ production rate was 11.98 mmol g⁻¹ h⁻¹ under visible light irradiation, showcasing a remarkable increase of 4.85 times and 2.50 times when compared to pure TpPa-1-COF and 5% rGO/TpPa-1-COF without covalent bonding, respectively.^[47] The TpPa-1-COF located on the surface of rGO during the catalytic process had a certain absorption effect on light, and the rGO layer played a carrier transport role for photoelectrons, and greatly shortened the electron migration path. Thus, it enabled the rapid separation of photo-generated electrons and holes to occur and improved the catalytic hydrogen production capacity (Figure 16a).

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In the subsequent year, Liu and coworkers synthesized hydrogen-evolving materials consisting of GO and CTF-1 through π -conjugate linkage via an in-situ reaction. The introduction of GO facilitated the transport of electrons, enabling photogenerated electrons to move through CTF-1 more efficiently after being excited by visible light. This resulted in the separation of photogenerated charges from holes, while shortening the electron migration path. The most optimal hybrid ratio of CTF-1/GO-3.0 exhibited a hydrogen evolution rate of 2262.4 μ mol g⁻¹ h⁻¹, which was 8.9 times higher than pure CTF-1 (256 μ mol g⁻¹ h⁻¹).^[133] To further enhance the hydrogen evolution rate, Yan and his colleagues^[147] synthesized a ternary hybrid hydrogen-evolving material. Initially, a Z-type heterojunction, specifically WO₃@TpPa-1-COF, was synthesized to facilitate the separation of photogenerated electrons and holes. It was then compounded with rGO. The observed hydrogen evolution rate of the WO3@TpPa-1-COF/rGO (30%) composite was noted to be 26.73 mmol g⁻¹ h⁻¹ under visible light irradiation. This value was 11.73 times that of TpPa-1-COF (2.28 mmol $g^{-1} h^{-1}$) and 1.6 times that of WO₃@TpPa-1-COF (16.65 mmol g⁻¹ h⁻¹). The integrated rGO in the composite acted as an electron acceptor during the photocatalytic process, thereby augmenting the transfer of photogenerated electrons to the active center. As a result, the photocatalytic activity was promoted, and the efficiency of electron-hole separation was improved, leading to a higher hydrogen evolution rate (Figure 16b).

A deeper understanding of the underlying photocatalysis mechanisms in COF-graphene hybrids can guide the design of more efficient materials. Researchers should delve into the electron transfer processes and explore ways to optimize charge separation and migration.

5.3.2. Catalytic Oxygen Reduction

Oxygen reduction reaction (ORR) is a key reaction in energy conversion technologies involving fuel cells and metal-air



batteries. To achieve efficient ORR performance, COF/graphene hybrids have also been extensively explored. For example, Guo et al.^[127] employed self-assembled COP and rGO to form a hybrid electrocatalyst for catalyzing ORR. Their study revealed that the electrical conductivity of the hybrid COP/rGO substantially increased by over seven orders of magnitude (from 3.06×10^{-9} to 0.256 S m⁻¹) compared to pure COP. The resultant COP/rGO hybrid catalyst displayed a noteworthy positive half-wave potential (150 mV). The potential of COF/GO hybrid materials for electrocatalytic oxygen reduction applications is greatly increased by improving the electrical conductivity of the copolymer without changing the COF structure. Pyrolysis is expected to further improve the properties of the materials. To this end, Jiao and coworkers modified CTF with rGO to create a composite with high electrical conductivity and subsequently pyrolyzed the hybrid material to form an N-doped and hierarchically porous carbons/rGO (NHC/rGO) composite with a sandwich morphology. The findings revealed that in an alkaline solution, NHC/rGO-950 exhibited greater onset and half-wave potentials, higher diffusion-limited current density, and superior long-term stability when compared to the existing Pt/C.^[39] The use of pyrolysis to enhance the properties of COF/graphene hybrids shows promise. Future studies should delve deeper into optimizing pyrolysis conditions, such as temperature and duration, to fine-tune the electrocatalytic performance of these materials.

5.4. Sensing

As crucial as advancing environmental protection measures, quantitative and qualitative identification of polluting agents in the environment is equally paramount. Due to their low cost and short analysis time, electrochemical techniques offer several advantages over traditional analytical methods for trace-level analyte detection. Glass carbon electrodes (GCE) serve as the primary substrate for the development of electrochemical sensors, where the electrode surface is modified using conductive nanomaterials that improve target analyte sensitivity. The highly conductive hybrids of COF and graphene typically demonstrate excellent electrochemical properties, making them an ideal choice for developing electrochemical sensors with widespread applications.

A highly sensitive electrochemical sensor capable of simultaneously detecting sulfadiazine (SDZ) and acetaminophen (AP) was first reported by Sun et al. in 2019.^[28] The sensor was constructed using GO and COF (Figure 17a). They used molecularly imprinted polymers deposited on GO/COF sheets to identify SDZ and AP, using the conductivity of GO/COF to transmit altered electrical signals. Linear correction curves were obtained for SDZ and AP at concentration ranges of 0.5–200 and 0.05–20 $\mu \textsc{m},$ respectively. Under optimal test conditions, detection limits were determined to be 0.16 and 0.032 µM, respectively. Different pollutants can be detected by utilizing different aptamers. In 2021, Han et al. developed an electrochemical sensor that can detect chloramphenicol (CAP) by combining gold nanoparticles with COF and aminated GO to form a detection platform. The developed electrochemical sensor demonstrated exceptional sensitivity, with the ability to quantitatively detect ultra-trace amounts of AP at concentrations as low as 0.0001-1 ng mL⁻¹. In addition to the high selectivity of the sensor, they observed good reproducibility and long-term stability, making it a reliable analytical tool for the detection of AP in complex real-world samples.^[149] The use of graphene-based and COF materials for electrical signal transmission showed great promise in the field of electrochemical sensing and broadened the application field of these materials. Recently, Wang et al. also synthesized a CTF with abundant active sites. They grew Au nanoparticles on the surface of triazine covalent organic skeleton (TS-COF) to improve detection sensitivity, thus preparing AuNPs@TS-COF hybrid materials with enhanced electrical activity. To speed up the electron transfer rate, the authors introduced rGO with high conductivity to accelerate the transmission of electrical signals. The CV curves of the AuNPS@TS-COF/rGO nanocomposite modified electrode and the variation of oxidation peak currents at different pH are shown in Figure 17b,c. The results indicated that the composite electrode exhibited both high sensitivity and selectivity for target analytes. Moreover, the sensitivity of the sensor increased with an increase in pH. The optimum pH for the electrochemical sensor was determined to be 6.5.^[148] The composite electrode demonstrated exceptional analytical performance, with detection limits of 0.07, 0.03, and 4.30 μ M (S/N = 3) for uric acid (UA), dopamine (DA), and ascorbic acid (AA), respectively. The combination of graphene-based and COF materials in electrochemical sensing has ushered in a new era of highly sensitive and selective detection capabilities.

5.5. Energy Storage

The development of the world has always relied on the availability of energy, and researchers have always been focused on exploring materials for energy storage. The potential of COF/graphene as an inorganic carbon material for energy storage has garnered significant attention. **Table 3**t briefly lists the performance of various COF/graphene hybrid materials as energy materials.

5.5.1. Supercapacitor

Graphene is a highly robust conductor that has traditionally been limited to the field of supercapacitors due to the selfagglomerating tendency caused by van der Waals forces. However, if this problem is corrected, graphene will be an outstanding candidate in the field of supercapacitors. To solve this problem, some researchers have proposed cross-linking graphene with COFs to create hybrid materials that perform well in the field of supercapacitors.

The performance of supercapacitors depends on electron transfer rate, interlayer spacing between graphene, and other factors, which can be addressed by using specific COFs. For example, in 2020, Wang et al. reported the application of combined rGO and COF in supercapacitors. The optimal gravimetric specific capacitance and volumetric specific capacitance in aqueous electrolytes were 321 F g⁻¹ and 237 F cm⁻³, respectively (**Figure 18**a,b).^[26] A comparison between the developed composite materials and those reported in the literature highlights a significant breakthrough in the field of capacitive graphene electrodes. In another study by Wang et al.,^[30] they synthesized a two-dimensional COF/graphene composite by hydrothermal method



Figure 17. a) Schematic illustration of MIP/GO@COF/GCE sensor fabrication. Reproduced with permission.^[28] Copyright 2019, Elsevier B.V. b) Current change curve of the modified electrode at different pH. c) The steady photocurrent produced by a light switch. Reproduced with permission.^[148] Copyright 2022, Elsevier B.V.

to solve the laminate tilt problem in electron transfer. The hybrid material exhibited a weight capacitance of 599 F g⁻¹, significantly higher than the original GO (203 F g⁻¹) and COFs (110 F g⁻¹). The impedance spectra of COF/graphene hybrid materials were analyzed and proved their excellent electronic conductivity. COFs could also make the capacity retention rate of supercapacitors reach more than 80%, while the charge and discharge current density increased by 40 times. The conductivity of rGO can alleviate the problem of insufficient conductivity of bulk COFs. While the presence of COFs is conducive to better transport of electrolyte ions. In 2022, Yao et al.^[154] discovered the complementary effect of rGO/COF composites (Figure 18c). The test results

showed that the conductivity and current response of graphene and COF hybrid materials were superior to those of individual materials. In addition, the structural stability of the device was commendable, with a capacitance retention rate of 94.02% even after 10000 cycles, indicating that the COF provided reliable support.

Due to its excellent electrical conductivity and unique mechanical properties, three-dimensional GA has received great attention in the field of energy storage. It is also feasible to combine COF materials with GAs to significantly improve the overall conductivity by constructing a three-dimensional conductive network.^[150] The use of three-dimensional graphene aerogels
 Table 3. Energy storage performance of different COF/graphene hybrids.

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Materials	COF	Graphene	Preparation methods	Application field	Condition	Capacitance	References
DAAQ-COF/GA	DAAQ-COFs	GO	Self-assembly	supercapacitor	1.0 A g ⁻¹	378.0 F g ⁻¹	[79]
a-GO@COF-F	COF-F	a-GO	One-pot synthesis	supercapacitor	1.0 A g ⁻¹	295.0 F g ⁻¹	[78]
S/P-CTF@rGO	S/P-CTF	rGO	In situ growth	Li–S batteries	0.5 C	1130.0 mAh g ⁻¹	[150]
COF@GO/S	COF	GO	Ex situ synthesis	Li–S batteries	1.0 C	848.4 mAh g ⁻¹	[9]
graphene@COF	imine COF	Graphene	In situ growth	Li–CO ₂ batteries	75.0 mA g ⁻¹	27 833.0 mAh g ⁻¹	[136]
COF/GO	COF	N-doped C/rGO	In situ growth	supercapacitor	0.8 A g ⁻¹	234.0 F g ⁻¹	[86]
v-COF-GA	COF NPs	GA	In situ growth	supercapacitor	0.5 A g ⁻¹	289.0 F g ⁻¹	[132]
USTB-6@G	USTB-6	Graphene	In situ growth	Li-ion batteries	0.2 C	285.0 mAh g ⁻¹	[132]
PIBN-G	COF	Graphene	In situ growth	Li-ion batteries	0.1 C	271.0 mAh g ⁻¹	[45]
COF–SO₃H@rGO	COF-TpPa	rGO	One-pot synthesis	Li–S batteries	0.2 C	1163.4 mAh g ⁻¹	[151]
v-CNS-RGO	COF-1	GO	In situ growth	supercapacitor	1.0 A g ⁻¹	160.0–170.0 F g ⁻¹	[34]
NCM	COF	Graphene	In situ growth	supercapacitor	0.1 A g ⁻¹	1162.0 mAh g ⁻¹	[152]
rGO/COF	COF-1	GO	Ex situ synthesis	supercapacitor	1.0 A g ⁻¹	321.0 F g ⁻¹	[26]
COF/rGO-30	TaPa-Py COF	rGO	Ex situ synthesis	supercapacitor	0.5 A g ⁻¹	599.0 F g ⁻¹	[30]
COF/NH ₂ -rGO	COF	NH ₂ -rGO	One-pot synthesis	supercapacitor	0.2 A g ⁻¹	533.0 F g ⁻¹	[46]
PI-ECOF/rGO	PI-COFs	rGO	Ex situ synthesis	Li-ion batteries	0.1 C	167.0 mAh g ⁻¹	[153]
COF@rGO	COF	rGO	Ex situ synthesis	supercapacitor	0.2 A g ⁻¹	451.9 F g ⁻¹	[154]
CTF-rGO	CTFs	rGO	Ex situ synthesis	supercapacitor	0.1 A g ⁻¹	235.0 mAh g ⁻¹	[155]
COF _{DAAQ-BTA} -3DG	COF _{DAAQ-BTA}	Graphene	In situ growth	supercapacitor	0.5 mA cm^{-2}	7.6 mF cm ⁻²	[156]

(GAs) combined with COFs presents an exciting avenue for improving conductivity and energy storage capacity. Future studies should delve deeper into the design and fabrication of 3D conductive networks to unlock the full potential of these materials. To this end, An et al. employed an anthraquinone-type COF featuring highly reactive positively charged sites to facilitate electrostatic self-assembly with negatively charged GO, generating a hybrid aerogel for supercapacitor applications.^[137] Performance tests showed that the hybrid aerogel has enhanced specific capacitance since anthraquinone-based COF overcame the shortcomings of early supercapacitor materials in active site utilization and electron transfer. Notably, the heterogeneous aerogel electrode exhibited an ultra-high specific capacitance of 378 F g⁻¹ at 1 A g⁻¹, maintaining 88.9% capacity retention even after 2000 cycles (Figure 18d). In a recent study, Jiang and his colleagues also reported the fabrication of a COF/graphene mixed aerogel. They grew COF vertically on the surface of a macroporous GA and layered it as an electron transport highway.^[132] These hybrid aerogels demonstrated impressive weight capacitance of 289 F g⁻¹ and excellent capacitance retention, achieving 77% from 0.5 to 50 A g^{-1} at large charge/discharge rates and 74% from 1.2 to 10.4 mg cm⁻². The outstanding conductivity of graphene and the tunable properties of COFs offer a synergistic platform for supercapacitor enhancement. Future research should aim to unravel the precise mechanisms behind this synergy and further optimize the combination for improved performance.

5.5.2. Battery

The growing demand for sustainable and clean energy has stimulated the development of the energy storage industry, with a focus on researching high-capacity batteries. Among battery technologies, lithium-sulfur batteries are an important type. However, their drawbacks are quite apparent. The "shuttle effect" of lithium polysulfides (LiPSs) results in active material loss and cycle instability, greatly hindering the practical application of these batteries. To address this issue, Hu et al.^[9] put forward a report in 2022 that GO was coated on the COFs as the main material of lithium-sulfur batteries, and GO was used to wrap the discrete sulfur (Figure 19a). To mitigate the undesired depletion of active components and improve the cycle stability of the electrode, a novel cathode material comprising COF@GO/S was utilized in lithium-sulfur batteries. They found that the initial specific capacity could be elevated to 848.4 mAh g⁻¹, and it could be maintained at over 600 mAh g⁻¹ even after 500 cycles, emphasizing the high stability and excellent electrochemical performance of the COF@GO/S cathode material. The results of DFT calculation showed that COF had good adsorption properties and could carry out ion transport well. The use of nanoporous structures to capture free sulfur, or strong covalent bonding for sulfur chemical attachment and adsorption was the approach to solve the shuttle effect of lithium-sulfur batteries. Based on this, S/P-CTF@rGO hybrids were constructed by Guan and coworkers.^[150] The covalent binding of diazinone and triazinone polar groups on P-CTFs chains to sulfur in heterogeneous materials further limited the diffusion of polysulfides and significantly extended the service life of lithium-sulfur batteries.

Rechargeable lithium-ion (Li-ion) batteries have become ubiquitous in daily life and are increasingly relied upon to power portable electronic devices. Organic electrode materials, characterized by simple, reversible redox reactions, have demonstrated higher rate performance compared to inorganic electrode materials based on traditional intercalation reactions. As such, organic electrode materials represent an auspicious avenue toward the development of next-generation, high-performance, sustainable

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Figure 18. a) The gravimetric specific capacitance (C_m) and b) volumetric capacitance (C_ν) under different current densities based on the mass and volume of electrode materials, respectively. Reproduced with permission.^[26] Copyright 2020, Elsevier B.V. c) Internal structures of rGO/COF@rGO. Reproduced with permission.^[154] Copyright 2022, American Chemical Society. d) Cycling stability test at 5 A g⁻¹ for 20 000 cycles. Reproduced with permission.^[137] Copyright 2021, The Royal Society of Chemistry.

lithium-ion batteries with fast charging capabilities. Nonetheless, electrodes based on small organic molecules are prone to dissolution in organic electrolytes, leading to poor cycling stability. To address this issue, Liu et al.^[138] prepared dual-porous COF USTB-6 with exceptional crystallinity and abundant redox active sites. They incorporated graphene into the composite material, which played a non-uniform nucleation role, guiding the uniform growth of thin COF nanosheets on the carbon layer. As a result, the electronic conductivity of the COF-based electrode was greatly enhanced, allowing for improved battery performance. The specific capacity of graphene-supported USTB-6 nanosheet cathode is 285 mAh g⁻¹ at 0.2 C current density, and 188 mAh g⁻¹ at 10 C, which has excellent magnification

performance. In addition, after 6000 charge–discharge tests at 5 C, the USTB-6 nanosheet cathode still maintained a capacity of 170 mAh g^{-1} .

In summary, the development of high-capacity batteries, such as lithium-sulfur and lithium-ion batteries, holds great promise for meeting the growing demand for sustainable and clean energy storage solutions. Innovative approaches based on COF/graphene hybrids have shown significant improvements in the stability, electrochemical performance, and cycling capabilities of these batteries. Looking ahead, further research should focus on optimizing the performance and stability of these battery technologies to enable their practical application in sustainable energy systems. ADVANCED SCIENCE NEWS ______



Figure 19. a) Role of GO and COF in lithium-sulfur batteries. Reproduced with permission.^[9] Copyright 2022, Institute of Physics. b) Schematic diagram of $COF_{ETBC-TAPT}$ -graphene film location in sensing fibers and gas absorption and charge transfer. c) The steady photocurrent under a light switch. Reproduced with permission.^[157] Copyright 2020, Wiley-VCH. d) Variation of water contact angle of COF/graphene composite hydrogel with different hydrophilic COF loadings. Reproduced with permission.^[41] Copyright 2022, American Chemical Society.

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5.6. Other Application

2D materials have garnered significant interest in the fields of electronics and optoelectronics due to their exceptional properties. The wide demand for high-performance optoelectronic devices has driven the exploration of diverse 2D composites. These materials can exhibit even more exceptional properties than standalone 2D materials, providing promising avenues for the development of advanced electronic and optoelectronic applications. For instance, Xiong et al.^[157] overcame the unmachinable nature of COF powder and directly grow a photosensitive COF_{ETBC-TAPT} (COF synthesized by 4',4'",4""',4""''-(1,2-ethenediylidene)tetrakis[1,1'-biphenyl]-4-carboxaldehyde (ETBC) and 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPT)) in situ on the strongly conducting graphene. The heterostructure formed by graphene and ${\rm COF}_{\rm ETBC-TAPT}$ accelerated the transfer of photogenerated electrons and produced a relatively obvious photocurrent (Figure 19b). COF_{ETBC-TAPT}-graphene photodetectors had an optical response rate of 3.2×107 A W⁻¹ and a time response of 1.14 ms at 473 nm, demonstrating excellent overall performance. The authors performed periodic illumination within 2 h to study the stability of COF_{ETBC-TAPT}-graphene composite as a photosensitive detector. The results showed that the photocurrent was switched synchronously with illumination, and the photocurrent was stable (Figure 19c). Additionally, the high surface area of COF_{ETBC-TAPT} could be reversibly regulated by specific molecules, showcasing its potential for the application of COF/graphene hybrids in the realm of photodetection.

The integration of solar power and water treatment technology offers a promising and sustainable approach to producing clean drinking water. Photothermal conversion, which is the conversion of light energy into heat energy, functions as a vital link between these two technologies. The utilization of photothermal conversion materials enables the production of water vapor, which can be collected and purified to produce potable water. Recently, a COF/graphene composite hydrogel with hydrophilic and hydrophobic regions was presented by Li et al. The wettability of the hydrogel could be regulated by using hydrophilic COF. As the loading of COF-SO₃H increased, the overall hydrophilicity of the hydrogel also increased (Figure 19d).^[41] Under one solar irradiation, the water evaporation rate of the dual-zone regulated hybrid hydrogel was 3.69 kg⁻¹ m⁻² h⁻¹ with an energy efficiency of 92%. Remarkably, the hydrogel could also maintain a high evaporation rate under weak sunlight, which greatly increased the possibility of practical application of this hydrogel. The ability of COF/graphene composite hydrogels for seawater desalination and wastewater treatment further demonstrated the potential promise of this material for environmental applications.

6. Conclusion and Perspectives

The hybridization of graphene and COFs has given rise to a novel category of composite materials featuring enriched attributes and manifold applications in the fields of energy and environment. The distinctive properties of graphene, notably its elevated electrical conductivity and large surface area, in conjunction with the adjustable chemical configuration and porousness of COFs, have offered opportunities for the creation of composites having fascinating features such as remarkable adsorption capacity, selectiv-

ity, sensitivity, and photocatalytic activity. Therefore, we reviewed in detail the changes in the properties of COF/graphene hybrids before and after forming composite, as well as the applications of graphene-based/COF hybrid materials in adsorption, membrane separation, catalysis, sensing, and energy storage. The combination of covalent organic framework (COF) and graphene offers several advantages. First, the high surface area of both COF and graphene is further augmented, providing more active sites for interactions with molecules, which is beneficial for applications such as gas storage, catalysis, and sensing. Additionally, the combination improves the conductivity of the material, making it suitable for energy storage and electronic devices. Moreover, the tunable properties of COF and graphene can be tailored to specific applications, allowing for a wide range of potential uses. Overall, the versatility of this combination makes it highly attractive for various industrial and technological applications. Nevertheless, several hindrances still need to be overcome to unlock the complete potential of graphene-based COF hybrids.

First, one of the challenges is the preparation of composites with uniform dispersion and strong interaction between the graphene and COF components. The force between hybrid materials is an important factor to evaluate whether they can maintain stability in the process of application, especially the graphenebased/COF hybrid materials in reaction systems where electron transfer occurs. Hybrid materials connected between graphenebased materials and COF using covalent bonding have a strong facilitation effect on electron transfer compared to those combined through noncovalent bonds. Therefore, the development of graphene and COF components connected by strong interaction forces is important to maintain the stability of the reaction system.

Second, another challenge is the scalability of the synthesis methods, as most of the reported methods are limited to smallscale synthesis. The more common one-pot method can be used to produce hybrid materials on a large scale, but this method is time-consuming and the purity of the hybrid materials is not high. The one-pot method cannot be utilized for applications that require higher-purity hybrid materials to complete. In-situ growth is a preparation method to improve the purity of hybrid materials, but it is limited to small-scale synthesis. Therefore, the development of a suitable preparation approach is also a future investigation direction.

For future research, two points need to be noted, in addition to the above-mentioned preparation methods. First, research should focus on addressing these challenges and exploring new graphene-based COF hybrids for application in environmental remediation. One promising direction is the development of multifunctional composites that can simultaneously perform multiple tasks, such as adsorption and photocatalysis. The integration of multiple functions into a single material can reduce the complexity and cost of the remediation process and provide a more efficient and sustainable solution.

Second, another direction for future research is the exploration of new graphene-based COF hybrid materials with structural and compositional variations. The development of new COFs with different pore sizes, shapes, and surface functionalities can expand the scope of applications and provide new opportunities for adsorption, separation, catalysis, sensing, and energy storage. Apart from material innovation, forthcoming analyses ought to prioritize examining the ecological implications and safety considerations associated with graphene-based COF hybrid materials. The potential release of graphene and COF components into the environment and their long-term effects on ecosystems and human health should be carefully studied to ensure the safe use and disposal of these materials.

In conclusion, the development of graphene-based COF hybrid materials has opened new opportunities for environmental remediation and energy application. These materials exhibit enhanced properties such as high adsorption capacity, selectivity, sensitivity, and photocatalytic activity, and can provide a more efficient and sustainable solution for environmental challenges. However, further research is needed to address the challenges and explore the full potential of these materials in environmental applications.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

covalent organic frameworks, energy storage, graphene, hybrids, water purification

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