Structural Characteristics and Environmental Applications of Covalent Organic Frameworks

Niaz Ali Khan [1], Muhammad Humayun [2], Muhammad Usman [3], Zahid Ali Ghazi [4], Abdul Naeem [4], Abbas Khan [5,*], Asim Laeeq Khan [6], Asif Ali Tahir [7,*] and Habib Ullah [7,*]

1   Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China; niaz@tju.edu.cn
2   Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, China; 2017511018@hust.edu.cn
3   Center of Research Excellence in Nanotechnology, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran 31261, Saudi Arabia; muhammadu@kfupm.edu.sa
4   National Centre of Excellence in Physical Chemistry (NCEPC), University of Peshawar, Peshawar 25120, Pakistan; zghazi@uop.edu.pk (Z.A.G.); naeem@uop.edu.pk (A.N.)
5   Department of Chemistry, Abdul Wali Khan University, Mardan 23200, Pakistan
6   Membrane Systems Research Group, Department of Chemical Engineering, Lahore Campus, COMSATS University Islamabad, Lahore 54000, Pakistan; alaeeqkhan@cuilahore.edu.pk
7   Environment and Sustainability Institute, University of Exeter, Penryn, Cornwall TR10 9FE, UK
*   Correspondence: abbas053@gmail.com (A.K.); A.Tahir@exeter.ac.uk (A.A.T.); hu203@exeter.ac.uk (H.U.)

Abstract: Covalent organic frameworks (COFs) are emerging crystalline polymeric materials with highly ordered intrinsic and uniform pores. Their synthesis involves reticular chemistry, which offers the freedom of choosing building precursors from a large bank with distinct geometries and functionalities. The pore sizes of COFs, as well as their geometry and functionalities, can be pre-designed, giving them an immense opportunity in various fields. In this mini-review, we will focus on the use of COFs in the removal of environmentally hazardous metal ions and chemicals through adsorption and separation. The review will introduce basic aspects of COFs and their advantages over other purification materials. Various fabrication strategies of COFs will be introduced in relation to the separation field. Finally, the challenges of COFs and their future perspectives in this field will be briefly outlined.

Keywords: covalent organic frameworks; synthesis; functionalities; adsorption; separation

1. Introduction

Purification processes such as distillation, evaporation, concentration, and crystallization are important in basic research as well as playing an important role in industries. These processes, however, operate at the expense of environmental deterioration by consuming an enormous amount of energy, further promoting global warming. Industrial effluents also contain a large amount of chemical and bio-chemical hazardous ingredients polluting the already scarce freshwater resources. Moreover, many industries waste a large amount of precious chemical compounds and organic solvents due to the lack of economical separation/purification materials. Therefore, purification processes with low energy requirements may benefit the environment by saving energy on one hand and saving important capital costs on the other. In recent years, adsorption- (entrapment) and membrane (size exclusion)-based purification have attracted immense research and industrial interest due to their low energy consumption as well as simple and environmentally friendly operation. Various amorphous materials such as hyper-cross-linked polymers (HCPs) [1,2], porous organic polymers (POPs) [3,4], conjugated microporous polymers (CMPs) [5–7], and activated carbon [8–10]; and crystalline materials such as metal-organic frameworks (MOFs) [11–14] and zeolites [15–19], have shown excellent preliminary separation performance. Covalent

organic frameworks (COFs) are a class of crystalline framework material synthesized from purely organic building blocks. Their synthesis involves reticular chemistry, which gives immense freedom of pre-design. Their pore geometry, size, and functionalities can be pre-determined by choosing building units from a large bank. Yaghi and co-workers first reported COFs based on boroxine and boronate ester rings [20]. These COFs, however, are prone to deformation in the presence of even trace amounts of humidity rendering them unsuitable in aqueous conditions. Later, imine-based COFs were reported to have superior chemical and solvent stability. Banerjee and co-workers prepared β-ketoenamine COFs with exceptional stability at high temperatures and in extreme acidic and basic conditions [21]. Similarly, Thomas and co-workers reported triazine-based COFs prepared at 400 °C, exhibiting excellent thermo-chemical stabilities [22]. Some of the important applications and various types of COFs are shown in Scheme 1 and Figure 1, respectively. Among many important aspects, COFs offer pore post-functionalization due to their organic nature, for specific desirable applications such as gas storage [23–25], catalysis [26,27], electronic devices [11,28], electrode material for batteries [29–32], etc.

Scheme 1. The applications of COFs in various technologies.

The most attractive feature of COFs is their framework structure with uniform and extended porous channels, attracting the interest of scientists in the purification/separation field. Earth's environment is under threat from the increasing disposal of hazardous ingredients such as heavy metals and poisonous organic and bio-organic chemicals [33–39]. Due to their distinct features, COFs represent themselves as viable alternative materials to address these issues [40,41]. Suitable pore designs and functionalities can render COFs as adsorbents for trapping hazardous metals, organic and bio-pollutants, and greenhouse gases [39,42–47]. As adsorbents, COF pores attract and trap pollutants based on their affinity towards functional COFs. COFs are also touted as excellent robust materials to fabricate separation membranes [48,49]. In the membrane form, pollutants are separated based on diffusion rates relying on the size, geometry, or charge of permeate and retentate. COFs have been reported to remove toxic components from both gases and liquids. Moreover, functionally decorated COFs can facilitate catalytic degradation of pollutants and convert them to clean energy. Our group has extensively worked on metal oxides and their composites for the application of photo- and electro-catalytic process [50–67], but recently

we have shifted our focus towards COFs due to their excellent characteristic properties. Although COFs were first reported in 2005, their environmental applications have only attracted interest very recently [68]. Since then, COFs have been extensively explored for various environmentally related applications. We believe that an up-to-date account is urgently required for scientists in this field. A review on a similar topic was published elsewhere in 2019 [69]. However, great progress has been made since then in this field and a review covering the new methods and strategies for the synthesis of COF materials towards environmental application is urgently needed to guide emerging scientists in this field.
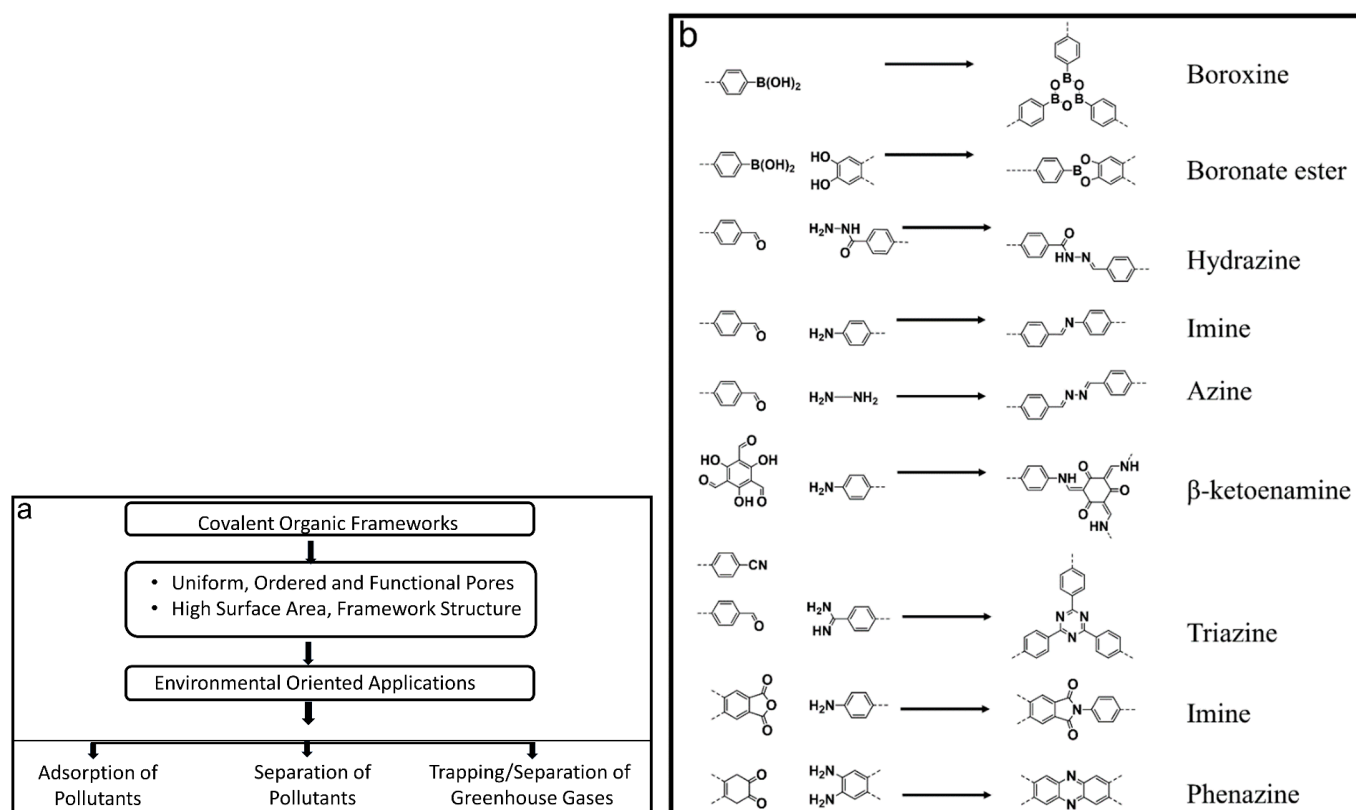

Figure 1. (**a**) Illustration of COFs towards environmental applications and (**b**) important classes of COFs and their pore geometry by binding different linkers.

2. Evolution of COF Synthesis through Time

A brief evolution overview of various COF synthetic methods since their first report will be discussed here. The first COF was based on boroxine and boronate-ester linkages [20]. Although highly crystalline, these COFs are not suitable for an aqueous environment as the crystallinity and framework nature is destroyed even in the presence of a trace amount of water due to the electron-deficient boron. Later on, various other COFs based on imine [27,70], triazine [71], hydrazine [72], and keto-enol [29,73] linkages were reported, exhibiting excellent stability in organic, aqueous environments as well as harsh acidic and basic conditions. The synthesis of COFs intended for environmental applications generally follows bottom-up and top-down approaches. The former involves solvothermal [20], interfacial polymerization [74,75], in-situ growth [76], micro-wave assisted [77], and on-surface crystallization [78,79] methods, and the latter involves delamination of COF powders into mono/few-layer sheets for further applications [80]. COF pore geometry can be pre-determined by choosing suitable linker symmetry (Figure 1) or modified through post-functionalization. Further elaboration of these synthetic and post-functionalization methods is beyond the scope of this review. Many other reviews have covered various aspects of COF reticular synthesis and properties in detail [81–90].

3. Important Aspects of COF Materials towards Cleaner Environment

Industries are polluting our environment in two ways: (i) disposal of hazardous chemicals in water reservoirs; (ii) and greenhouse gases into the air. Materials with advanced functionalities to trap these hazardous chemicals and gases are urgently required to address these issues [91]. COFs are materials that have intrinsic, uniform, ordered and tailorable pores along with high surface area, making them very attractive for trapping and separating these hazardous molecules. COFs with multi-functional pores have extended their applicability in environmental cleansing. Due to their high surface area and ordered porous channels, they can not only be used to trap/store gas molecules but can also function as separating media to remove unwanted chemicals from the waste solution. This application can reduce environmental pollution as well as help in the recovery of precious solvents to be re-used in industries, rendering the whole operation environmentally and economically friendly. Recent development has yielded COFs with extraordinary stability in harsh acidic and basic conditions, rendering them highly desirable in industrial purification and trapping applications [21,92]. The rational design of COFs needs careful consideration of many aspects for intended purification applications. In this section, we will discuss some important aspects of COFs such as structure, morphology, and charge of their pores, as well as their stability, which makes them ideal alternative materials for environmental applications.

3.1. Pore Structure

Trapping or separation processes involve distinct characters of pores, the most important being their size. The pore geometry and structure can be pre-designed by choosing monomers with appropriate symmetry, as shown in Figure 1. The size of environmental pollutants ranges from sub-nanometer (metals) to several nanometers (dyes) and even up to micrometer (bio-pollutants such as bacteria, etc.) [93,94]. Therefore, careful consideration should be given to designing COFs for specific purification applications. COFs with pore sizes ranging from 0.5–5 nm have been reported so far, making them highly desirable in size-dependent separation processes. Banerjee et al. exhibited control over pore size by cross-linking precursors of different lengths and obtained COFs with pores in the range of 1.4–2.6 nm. 1,3,5-trifromylphloroglucinol (TFP) was chosen as the aldehyde-bearing monomer, whereas four amine-bearing monomers with different lengths were chosen as linkers (Figure 2) [74].

Similarly, Ditchel et al. efficiently reduced the pore size of COFs by choosing linkers with six methyl or ethyl groups directing into the pores of the framework [95]. Pore surface engineering or pore post-functionalization is another strategy to tune the pore structure of COFs. Jiang et al., for the first time, reported an interesting strategy to first synthesize COFs with azide functionalities [96]. The COFs were synthesized through the condensation reaction between azide-appended benzene diboronic acid (N3-BDBA) and benzene diboronic acid (BDBA) with hexahydroxytriphenylene (HHTP). The azide could be easily cross-linked with many moieties such as propyl acetate, –COOH, –NH$_2$, –COOMe, –OH, and –C≡C through click chemistry. The pore size was controlled between 1.2 and 3 nm by employing this strategy. Moreover, introducing these functional groups through post-functionalization also rendered COFs with desirable wettability and charge surfaces.

3.2. Hydrophobicity/Hydrophilicity of COFs

The morphology of COFs, such as their surface area and hydrophilic/hydrophobic nature, is very important for purification processes. COFs with a surface area of >2000 m$^2 \cdot$g^{-1} have already been reported [73,97]. Ordered porous channels along with such high surface area are highly desired for purification/trapping applications. Hydrophilic/hydrophobic properties of COFs are another important controllable aspect, which are exploited by merely choosing desired linkers or through post-functionalization. COFs with hydrophobic nature [98] will enhance their applications in organic media, whereas hydrophilic COFs [99] will work better in aqueous media. Zhang et al. prepared a superhydrophobic COF through

pore surface functionalization and evaluated their application in harsh conditions [100]. They first synthesized the COF and the pores were grafted with fluoride. The contact angle was increased from 0° to 150° by varying fluoride grafting. The modified COF retained its crystallinity and hydrophobicity under extremely harsh conditions such as in boiling water and in solutions with pH ranging from 1 to 14. Similarly, Hu et al. synthesized a hydrophilic triazine-based COF (Figure 3) and used it as a sensor for the detection of gallic acid (GA) and uric acid (UA) [101].

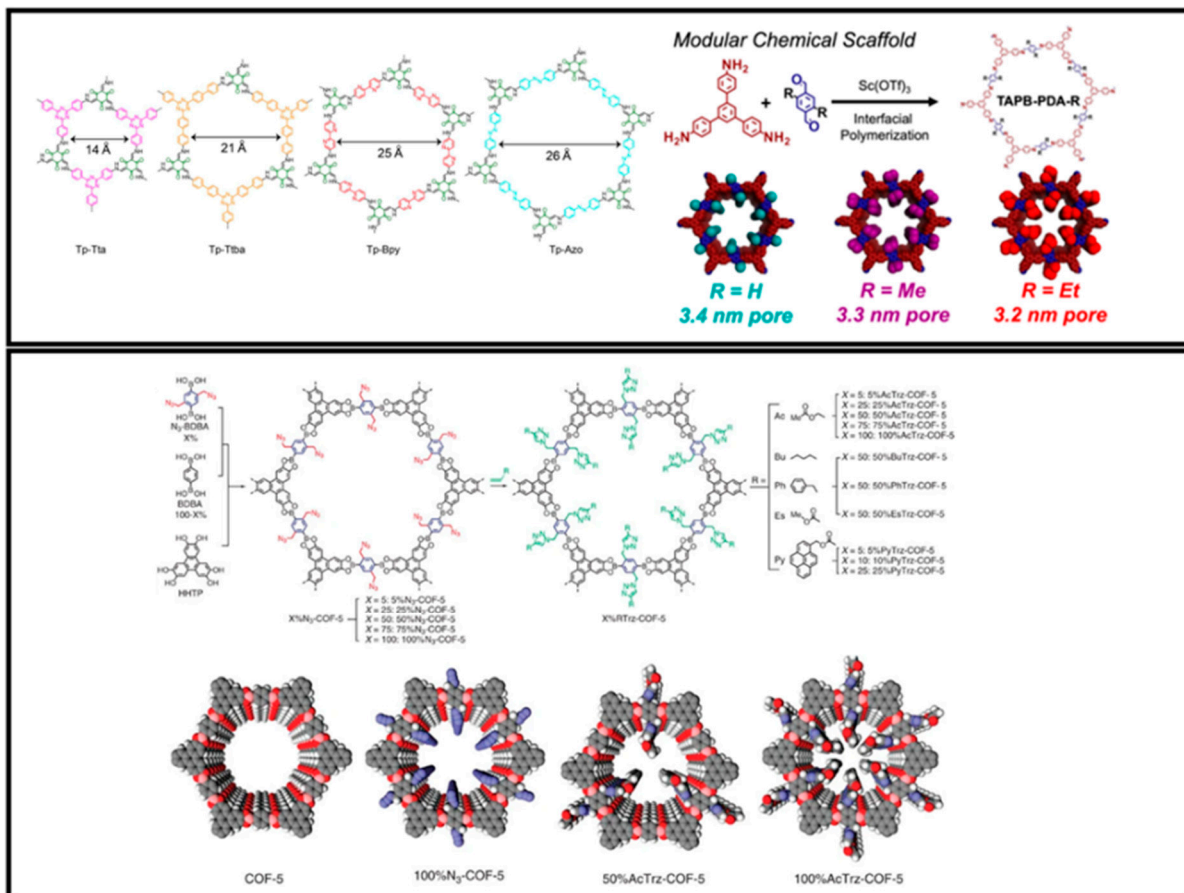**Figure 2.** Control of pore size through linker selection (**top**) and post-functionalization (**bottom**). Adapted with permission from references [74,95], copyright 2017 and 2019 American Chemical Society.
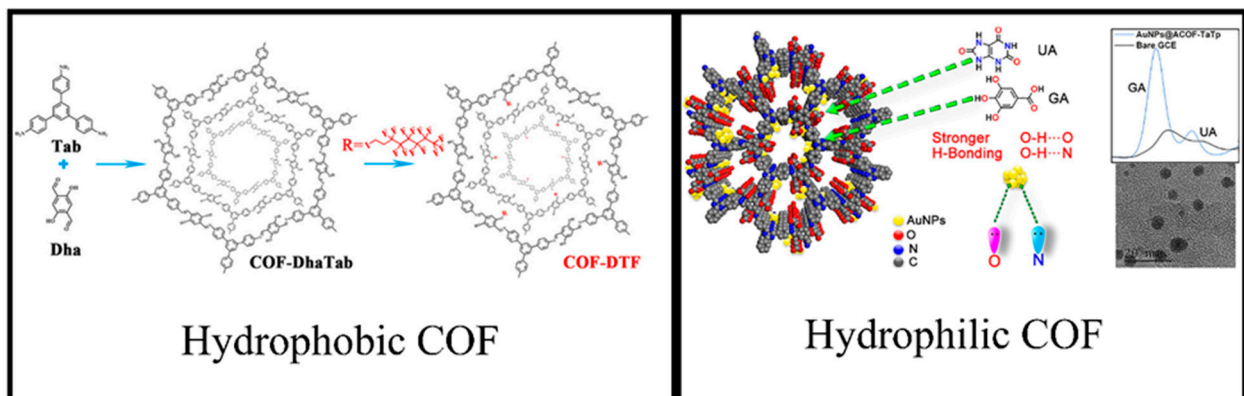

Figure 3. Examples of hydrophobic and hydrophilic COFs. Adapted with permission from references [100], copyright 2020 American Chemical Society and [101], copyright 2021 Elsevier.

3.3. Structural Stability

The first reported COFs based on boroxine and boronate ester linkages had poor stability in even a small amount of water. This phenomenon arises from the fact that the boron sites are electron deficient and can undergo nucleophilic reaction, resulting in structural degradation through hydrolysis. The effect is more severe as water is produced as a by-product during COF synthesis, which can facilitate the backward reaction and therefore severely affect their industrial applications. For environmental applications, COFs need to retain their ordered structure in practically harsh conditions. Linkers with strong covalent bonding to extend the framework, along with hydrogen bonding between interlayers, can overcome this shortcoming to some extent. Imine, azines, hydrazine, imides, and triazine-based COFs exhibit exceptional stability in harsh conditions because they are synthesized through acidic catalyst-based reversible reactions. Therefore, the backward reaction will be facilitated in an acidic environment but the COF should be stable in water as well as organic solvents [102]. Banerjee et al. explored a reversible/irreversible approach to improve COF stability one step further in solvents with pH ranging from 1 to 14 [21]. The same group also exhibited that increasing hydrogen bonding in the framework can also improve the stability of COFs [103]. They incorporated –OH functionalities adjacent to the –C=N bonds to introduce –OH–N=C hydrogen bonds, which ultimately safeguarded the imine nitrogen from hydrolysis in the presence of both acids and water. Similarly, other groups have improved COF stability through increasing intra-molecular hydrogen bonding to improve the COFs overall thermo-chemical stability [104,105].

3.4. Pore Charge

Pore charge is a crucial factor in the separation or trapping of hazardous chemicals through electrostatic interactions. According to Donnan's theory, a negative charge-separating barrier will repulse divalent anions whereas divalent cations will be attracted. Therefore, if the negatively charged separating barrier is an adsorption agent then the cations will be trapped inside the matrix, but if the barrier is a membrane then the positively charged ions will transport more efficiently leaving anions in the feed. The same phenomenon is applied to the oppositely charged separating barrier. So far, very little attention has been given to design-charged COFs. Ma and co-workers introduced cationic sites in the COF (EB-COF:Br) by reacting 1,3,5-triformylphloroglucnol and ethidium bromide (EB) (3,8-diamino-5-ethyl-6-phenylphenanthridinium bromide) [106]. Similarly, Oakey et al. prepared a negatively charged COF by introducing carboxyl functional groups in the COF's backbone and introduced them as fillers in the preparation of mixed matrix membranes [107]. In addition to the narrow size distribution of COF pores, the deprotonated -COOH$^-$ enhanced the rejection of bovine serum albumin (negatively charged protein) to as high as 81% at a COF loading of 0.8%. A similar approach was adopted to prepare a COF with modifiable carboxyl functional groups to prepare 12 COFs with variable aperture size and was self-assembled as continuous membranes [108]. It is expected that the synthesis of COFs based on charged pores for environmental application will attract more attention in coming years by incorporating functional groups such as hydroxyl, sulfonic acid, amine, etc.

4. Applications of COFs towards Environment

COFs are touted as ideal candidates for applications towards a clean environment. COFs can function as adsorbent/trapping materials for hazardous moieties. In addition, COFs can be used as a catalyst for green energy production, catalytic degradation of pollutants, as a sensor for gas detection, and as membrane-forming materials to separate solid as well as gaseous pollutants. The applications of COFs have been summarized in Table 1.

4.1. Adsorption

Thanks to their ordered porous framework structure and ease of functionalization, COFs can be used to adsorb many hazardous pollutants and toxic metals as well as adsorb hazardous gases. Several aspects of COFs such as their tunable architecture, uniform and tailorable pores, ease of incorporation of functional sites, low density, and large surface area make them appealing for adsorption applications.

4.1.1. Adsorption of Heavy Metals

The presence of heavy metals in water even in trace amounts poses a great threat to human health. The capture of these heavy metals is of crucial importance for a healthy environment. Hu et al. employed an interesting strategy to coat COFs with polydopamine (PDA) [109]. The COF@PDA showed an excellent adsorption affinity towards Cu(II) and the adsorption equilibrium was achieved within ten minutes with an adsorption capacity of 109.2 mg/g. Furthermore, the adsorbed Cu(II) was heated to obtain (COF@PDA@CuO) and used as a fire-retardant of epoxy resins. Tong et al. incorporated a thiol (-SH) group in the COF framework to adsorb Hg(II) from contaminated water [110]. In another work, three different covalent triazine framework-based COFs decorated with S ((MSCTF-1, MSCTF-2, and xSCTF-2) were synthesized and evaluated for Hg^{2+} adsorption [111]. These COFs exhibited high adoption efficiency towards Hg^{2+} (840.5 mg/g) thanks to the S in the backbone of COFs. Ma et al. employed a post-functionalization strategy to prepare a COF for mercury removal through adsorption [112]. They first synthesized the COF with vinyl functionalities that could be easily modified with S functionalities through a thiol-ene click reaction to obtain modified COF (COF-S-SH). The resulting COF exhibited unprecedented adsorption capacity for mercury. More importantly, COF-S-SH mercury concentration could be reduced from 5 ppm to 0.1 ppb, which is below the consumable limit of 2 ppb. They attributed such high adsorption to factors such as ordered porous structure and the existence of abundant chelating groups. Another serious threat to the environment is caused by radioactive metals such as effluents containing UO_2^{2+}/Eu^{3+}. Removal of these metals from the effluents needs urgent attention. Hu et al. proposed a composite material containing an MOF and a COF decorated with -NH_2 functionalities ((NH$_2$-MIL-125(Ti)@TpPa-1) [113–115]. The composite material was able to remove both UO_2^{2+} and Eu^{3+} at fast rates of 536.73 mg/g and 593.97 mg/g respectively (Figure 4).

4.1.2. Adsorption of Hazardous Chemicals and Gases

Zhao et al. synthesized a composite containing metal oxide, an MOF, and a COF (Fe_3O_4@TAPB-COF@ZIF-8) and applied it for the adsorption of bisphenol, an endocrine-disrupting chemical interfering with the human hormonal system [116]. The composite materials achieved detection of concentrations as low as 0.04 ng/mL in a wider range of 0.25–1000 ng/mL. Due to its stable organic framework structure, the composite material exhibited excellent repeatability and reproducibility. The same group also reported a type of COF (TAPT-DHTA) and employed it for the adsorption of phenoxy carboxylic acid (PCA) pesticides in plant food derivatives [117]. Effluents from textile industries containing organic dyes are posing one of the biggest challenges to our environment. Removal of these dyes also needs attention to safeguard the environment. Jamshidian et al. reported a composite material of MOF–COF (MIL-101-NH$_2$@COF) to remove acid blue 9 dye, a type of carcinogenic organic chemical [114]. They obtained an adsorption capacity of 256 mg/g thanks to the enhanced affinity between the dye and the functionalities of composite materials. Greenhouse gases such as CO, CO_2, and CH_4 pose yet another threat to the ozone layer and subsequently to the life on Earth. Porphyrin-based COFs were synthesized and evaluated as adsorbents for these greenhouse gases [115]. Due to the high surface area, sheet-like structure, and uniform pores, the metal-free porphyrin sheets exhibited excellent affinity towards these gases. In another report, triazine-based COFs were synthesized by trimerization reaction of 1,3-bis-, 1,3,5-tris- and 1,3,5,7-tetrakis(4-cyanophenyl)adamantane and employed for the adsorption of CO_2 [118]. Due to the stable structure and high

BET surface area (1180 m^2/g) with ideal pore size distribution (0.4–1 nm), an excellent CO$_2$ uptake of 58.1 cm^3 g^{-1} at 273 K was achieved. Similarly, a triazine-based COF was synthesized with a pore size in the range 0.52–0.54 nm [119]. The resulting COF (CTF-FUM-350) exhibited excellent adsorption for CO$_2$ while N$_2$, a valuable gas, could be easily collected in the permeate.
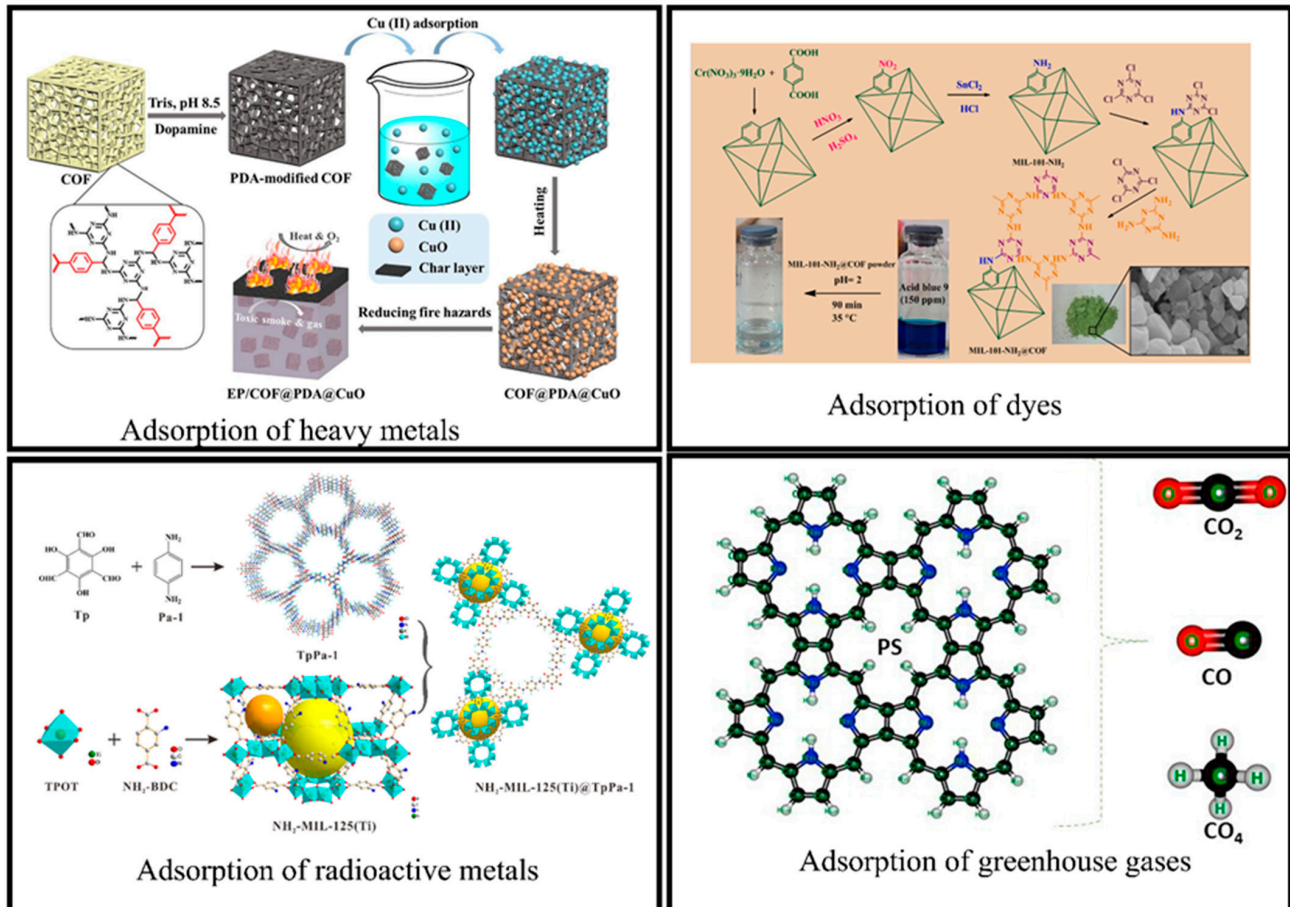

Figure 4. Adsorption of metals, toxic chemicals, and greenhouse gases. Adapted with permission from references [109], copyright 2021 Elsevier, [113] copyright 2021 American Chemical Society, [116] copyright 2021 Elsevier, and [117] copyright 2021 Elsevier.

4.2. COFs as Sensors for Chemicals

Alongside adsorption, detection and sensing of heavy metals is also an important area of research focus. Timely detection of these hazardous elements can prevent the pollution of the environment. Wang et al. prepared a thioether-functionalized COF for the detection of Hg^{2+}. The π-conjugated framework functioned as a signal transducer, the densely packed and evenly distributed thioether as a receptor, and the uniform pores as mass transfer enhancers [68]. The resulting COF exhibited high sensitivity, selectivity, and visibility thanks to these combined factors. Recently, N, S-rich COF$_{BTT-TZT}$ was synthesized by Song et al. [120]. The COF showed excellent sensing of Hg^{2+} in the range 0.54 nM–5.0 μM at a sensing limit of 0.18 nM. In the same report, they converted COF$_{BTT-TZT}$ (functioning as precursor and template) to hollow N, S-doped C@Pd nanorods to design electrochemical sensors for paracetamol. Similarly, Banerjee et al. synthesized imide-based COFs for the detection of hazardous nitrophenols [121]. The exfoliated COF nanosheets of TpBDH and TfpBDH showed excellent "turn-on" and "turn-off" effects in solid and dispersed states, respectively. Similarly, COFs have been reported for the detection of ammonia [122], nitroaromatic explosives [123–125], Cu^{2+} [126], picric acid [127], gallic acid (GA) and uric acid (UA) [128], levodopa content in human urine and blood serum samples [129], etc.

4.3. COF as Pollutant Degradation Agent for Clean Environment

Catalytic degradation of pollutants is an attractive alternative to a clean environment. However, traditional catalysts face the challenges of low surface area, stability, and recyclability. Materials to address these issues are highly desired [130,131]. COFs are ideal candidates for the above-mentioned applications due to their ordered structure with high surface area and excellent thermo-chemical stability. Cai et al. reported a triazine functionalized COF (TTO-COF) based on olefin linkages, which exhibited excellent chemical stability under severe conditions (see Figure 5) [132]. 4-formyl phenyl) triazine and 2,4,6-trimethyl-1,3,5-triazine were used as precursors to synthesize the COF, which was stable at temperatures as high as 400 °C. More importantly, TTO-COF exhibited excellent photocatalytic degradation of organic dyes and organic pollutants. In another report, a series of COFs denoted as CuPor-Ph-COF were grown in situ on a g-C_3N_4 support (CuPor-Ph-COF/g-C_3N_4) (see Figure 5) [133]. Rhodamine B was chosen as a model pollutant for degradation. Due to the faster separation of photogenerated charges in COF pores, the composite CuPor-Ph-COF/g-C_3N_4 exhibited higher photocatalytic activity compared to pure COF and g-C_3N_4. The Fenton reaction is an advanced oxidation process (AOP) for organic pollutant degradation that involves the generation of hydroxyl or peroxyl radicals from ferrous ion-activated hydrogen peroxide. Traditionally, the Fenton reaction is carried out through a homogenous catalyst that is not recyclable and makes the process expensive. Fang et al. synthesized a functionalized COF (JUC-521-Fe) and employed it as a heterogeneous catalyst to carry the Fenton reaction [134]. Rhodamine 6G, a highly toxic dye, was used as a model pollutant. JUC-521-Fe achieved a very high catalytic activity with a reaction rate constant of 2.8×10^{-2}/min and more than 95% degradation efficiency in just 90 min. Similar approaches have been employed by other groups to degrade pollutants such as phenol [135], BPA [136], and organic dyes [137–141].
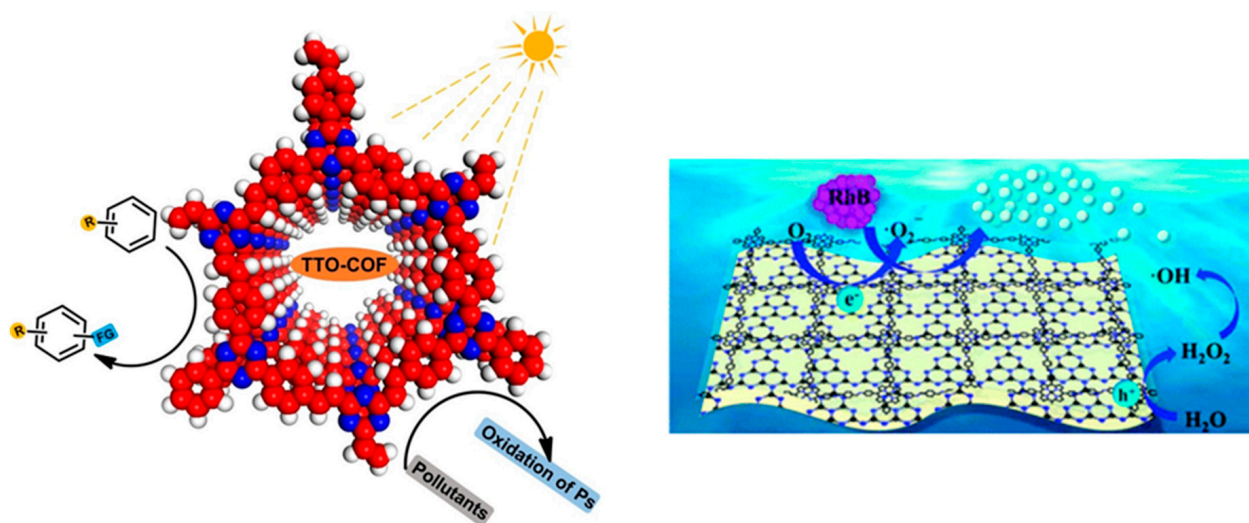

Figure 5. Illustration of photodegradation applications of COFs. Adapted with permission from references [132] copyright 2020 Elsevier and [133] copyright 2019 The Royal Chemical Society.

4.4. COFs as Membrane-Forming Materials

Due to their tunable pore aperture and pore environment, COFs are touted as ideal candidates to be employed in separation membranes. The traditional separation membranes to separate pollutants either in the gaseous form or in the solid form from the aqueous or organic solvents usually lack regular porous channels, rendering them with low permeance performance. In this section, we will discuss different strategies to use COFs in the separation field towards environmental protection.

4.4.1. Mixed Matrix Membranes (MMMs)

Incorporation of COFs in the traditional polymeric materials to enhance their flux/permeance is perhaps the most explored approach. Polymeric membranes exhibit low flux due to their dense and irregularly porous structure. MMMs are prepared by adding a filler material to make their structure loose and enhance the porosity. However, MMMs face the challenge of a trade-off between permeance and selectivity. Materials with regular porous structures and functionalities are highly desired to function as fillers [13]. COFs provide such opportunities. Dan et al. exfoliated COF (NUS-2 and NUS-3) into mono/few-layer nanosheets and embedded them in a poly(ether imide) (Ultem) or polybenzimidazole (PBI) matrix to fabricate mixed matrix membranes [142]. The resulting MMMs exhibited excellent trapping performance for CO_2, an extremely alarming greenhouse gas. Using a similar approach, another highly selective MMM was fabricated by employing COF nanosheets as filler materials [143]. Due to the adsorption of gases in pores of COFs, a mixture of gases such as CO_2/N_2 and CO_2/CH_4 could be separated with a high degree of accuracy. Recently, Jiang et al. designed an innovative strategy of using COF hollow microspheres and incorporated them as fillers into Pebaxmatrix [144]. The COF microsphere surfaces were decorated with polyethylene glycol monomethyl ether (PEG) before their embedment in MMMs. COFs played a dual role in flux enhancement; the transport resistance was reduced due to the COFs' regular pores while the ethylene oxide groups on PEG reduced the pore size of COFs as well as enhancing their compatibility with the polymer matrix. As a result, an excellent CO_2/CH_4 separation performance was achieved even surpassing the 2008 Robenson's upper bound. A more detailed review specifically on the CO_2 separation via COF is available elsewhere [145].

Besides hazardous gas separation, removal of pollutants from water as well as the transformation of unhealthy water into drinkable water (desalination) is another pressing issue that needs urgent attention. A cationic COF (TpEB) was employed as a filler during the fabrication of polyacrylonitrile (PAN) membranes. The charge on the COF enhanced the compatibility of the COF with the polymer matrix. As a result, a high rejection rate for BSA (an organic pollutant and fouling material) along with an excellent water permeance performance of 380 L/m^2.h.bar [146] were obtained. Our group employed an interesting strategy to exploit the low-density nature of COFs [147]. A COF (COF TpHZ) was mixed as a filler in the polymeric matrix of poly(ether sulfone). Due to the low density of the COF compared to the polymer, they migrated to the upper surface during membrane formation to form a density-based gradient distribution. COFs endowed the membrane with enhanced hydrophilicity with a permeance of 2.48 kg/m^2 and a separation factor of 1430 for a water/ethanol mixture. The morphology of the filler material also has a distinct impact on the resulting MMMs. Gao et al. synthesized COF (TpPa-2) through microwave (MW) and mechanochemical (MC) methods [148]. They observed that compared to the MC method, the COF synthesized via the MW method exhibited a much higher surface area, good stability, small particle size, and lower agglomeration tendency. As a result, even a small amount of 0.2% COF as a filler improved the permeance manifolds while still keeping excellent selectivity, addressing the trade-off challenge. As mentioned earlier, the compatibility of filler material plays an important role in the resulting MMMs. Polymers that are organic in nature are more compatible with organic fillers compared to their inorganic counterparts. Xu et al. incorporated carboxylated COF (COF-COOH) as a filler in the preparation of MMMs [149]. The resulting MMMs showed enhanced hydrophilicity and negative charge rendering the MMMs a 4-fold higher permeance and excellent rejection rate for NaCl. Slowing the reaction rate of polyamide (PA) membrane synthesis can also enhance the denseness of the PA layer, thus enhancing the permeance. Gao et al. proposed that reducing the diffusion rate of an amine-bearing monomer from the aqueous to the organic phase can yield microdefects in the PA layer, which was proposed by Alan Turing many years ago (See Figure 6) [150]. They achieved this degree of slow diffusion by using polyvinyl alcohol as the filler material, which could slow down the diffusion of piperazine through hydrogen bonding interactions. Our group recently employed reactive

COF nanosheets as fillers in the fabrication of MMMs [80]. The COF nanosheets played a dual role. In the aqueous phase, they interacted with piperazine through hydrogen bonding, therefore reducing its diffusion rate into an organic phase. During the interfacial polymerization stage, the COF nanosheets reacted with trimesoyl chloride (TMC) through their peripheral –NH$_2$ groups. Due to the synergistic effect, the resulting MMMs obtained an extraordinary 6.8-fold flux enhancement while keeping a steady salt rejection rate. Similarly, we reacted COF nanosheets with graphene oxide (GO) nanosheets for the first time to prepare a mixed nanosheet membrane assembled from the reacted two kinds of nanosheets [151]. GO nanosheets have mechanical stability but are non-porous, whereas COF nanosheets are porous. By reacting these two kinds of nanosheets and self-assembling them in membrane form, the water pathway was shortened by manifolds. Compared to a flux of ≈16 L/m^2.h.bar for a pristine GO membrane, the GO-COF membranes exhibited 226 L/m^2.h.bar permeance with similar dye rejection rates.
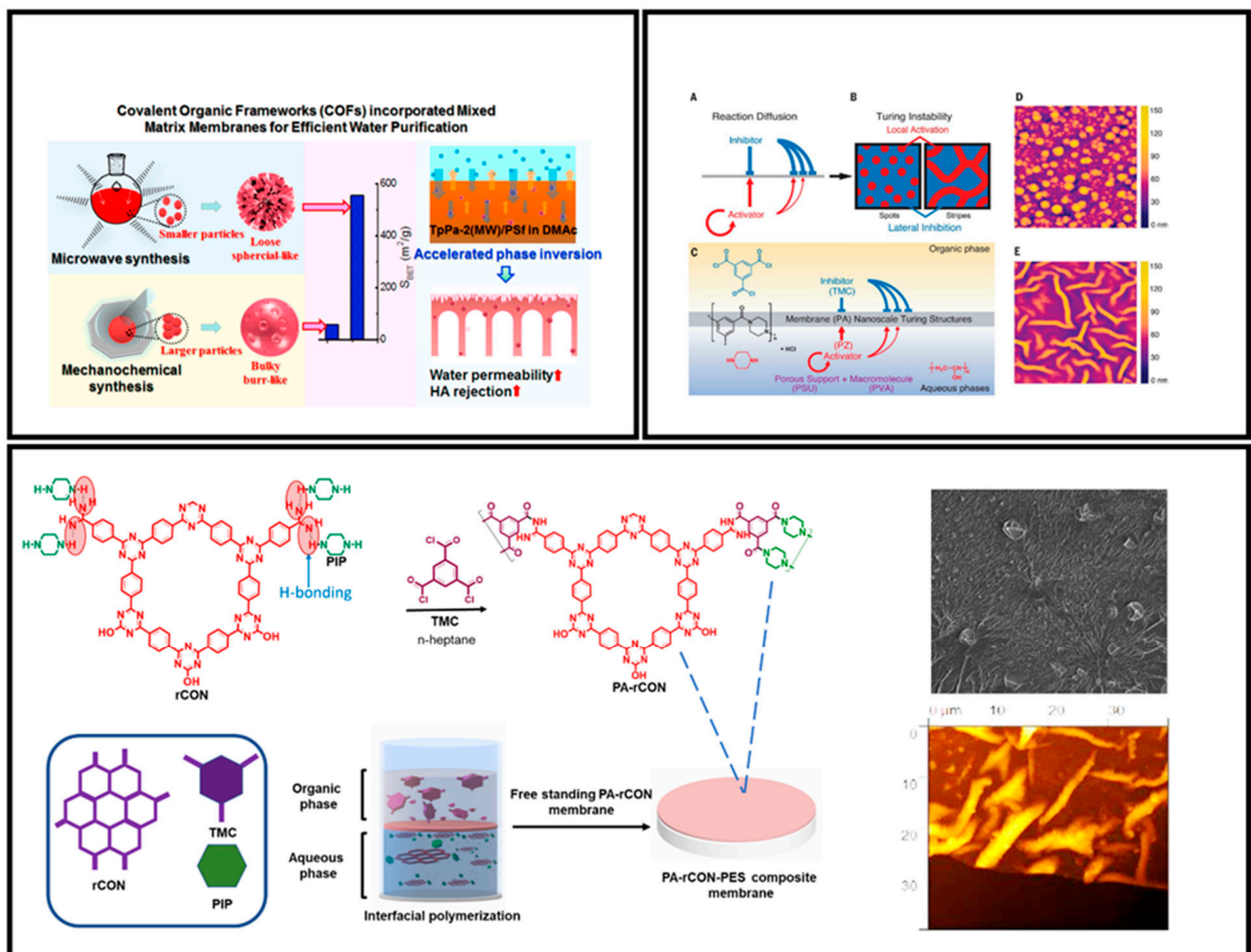

Figure 6. Different strategies to fabricate MMMs. Adapted with permission from reference [80] copyright 2020 American Chemical Society and [150] copyright 2018 Science.

Table 1. Summary of various applications of COFs.

COFs as Adsorbent Materials			
Abbreviation	**Adsorbed Material**	**Capacity**	**Reference**
COF@PDA	Cu(II)	109.2 mg/g	[109]
COF-SH	Hg(II)	1283 mg/g	[110]
MSCTF-1, MSCTF-2, xSCTF-2	Hg^{+2}	840.5 mg/g	[111]
COF-S-SH	Hg^{+2} and Hg^0	1350 and 863 mg/g	[112]
NH_2-MIL-125(Ti)@TpPa-1	UO_2^{2+} and Eu^{3+}	536.73 and 593.97 mg/g	[113]
Fe_3O_4@TAPB-COF@ZIF-8	Bisphenol	Detection limit (0.04 ng/mL)	[114]
TAPT-DHTA	Phenoxy carboxylic acids (PCAs) pesticides	Detection limit (0.007 ng/g)	[115]
MIL-101-NH_2@COF	Blue 9 dye	256 mg/g	[116]
Porphyrin sheets	Greenhouse gases	NA	[117]
PCTF5	CO_2	CO_2 uptake of 58.1 cm^3/g at 273 K	[118]
CTF-FUM-350	CO_2	57.2 cm^3/g at 298 K	[119]
COFs as Sensor Materials			
Abbreviation	**Sensing Materials**	**Reference**	
COF-LZU8	Hg^{+2}	[68]	
$COF_{BTT-TZT}$	Paracetamol	[120]	
TpBDH and TfpBDH	Nitrophenols	[121]	
TPE-Ph COF	Ammonia	[122]	
COP-3 and COP-4	Nitroaromatic explosives	[123]	
COF-Cage 4	Picric acid	[127]	
ACOF-TaTp	Gallic acid and uric acid	[128]	
AgCo/TAPB-DMTP-COF	Levodopa	[129]	
COFs as Fillers in Mixed Matrix Membranes			
Abbreviation	**Application**	**Reference**	
COF-Ultem and COF-PBI	CO_2 separation	[142]	
TpPa-1@PBI-BuI and TpBD@PBI-BuI	Greenhouse gases separation	[143]	
COF-MMM	CO_2/CH_4 separation	[144]	
TpEB	BSA removal	[146]	
COF TpHZ	Water/ethanol separation	[147]	
COF (TpPa-2)	Organic foulant removal	[148]	
COF (COF-COOH)	Desalination	[149]	
PA-rCON	Desalination	[80]	
GO-CTN	Dye removal	[151]	
COFs as Active Layers in Separation Membranes			
Abbreviation	**Method of Preparation**	**Application**	**Reference**
Tp-PA1, TpPA-2 etc	Liquid-liquid interfacial polymerization	Dye separation	[74]
TFP-PDA	Solid-vapor interfacial polymerization	Dye separation	[75]
COF-LZU1	In-situ polymerization	Dye separation	[76]

4.4.2. Stacking of COF Nanosheets in the Membrane Form

COFs are crystalline materials with layered structures assembled through pi-*pi* stacking. Several reports have highlighted the exfoliation or delamination of COFs into single or few layers [152,153]. Self-assembling these COF nanosheets (CONs) is yet another attractive approach towards fabricating COF membranes for environmental applications; yet very few reports exist on this topic. Jiang et al. reported an interesting strategy to exfoliate COFs into CONs and self-assemble them with cellulose nanofibers through a mixed dimensional assembly [154]. Due to the shielding effect, membranes with precise pore sizes in the range 0.45–1.0 nm were obtained. The resulting membrane exhibited a very high flux of 8.53 kg/m^2.h.bar. The membranes could be used both for dehydration

of n-butanol (separation factor of 3876) and desalination with 96.8% Na_2SO_4 rejection. Li et al. explored the use of photo-isomerizable azobenzene as a driving agent for the exfoliation of a variety of COFs into CONs [155]. They obtained CONs with a larger lateral area compared to traditional exfoliated CONs due to the high compatibility between COF structure and azobenzene molecules. The membranes obtained from the resulting CONs exhibited very high permeance of 596 L/m^2.h.bar with excellent retention of hazardous dye molecules. Similarly, Liu et al. exfoliated COF into CONs and self-assembled them into membrane [156]. Due to the ultralow solvent-interface interaction and plethora of porous channels, the membranes exhibited water permeance of 141.5 L/m^2.h.bar and excellent molecular and ion separation. In another report, a cationic COF (EB-COF:Br) was synthesized through a bottom-up approach and then exfoliated into CONs [106]. These CONs were self-assembled with vacuum assistance into stacked COF membranes. Due to the high positive charge density on the membrane, they exhibited selective separation of hazardous dyes with different charges. These membranes obtained 98% rejection of anionic dyes.

4.4.3. Pure COF as Active Separation Layer in Membranes

Membranes with a purely COF selective layer are an attractive goal, yet are very challenging to achieve. In fact, very few reports have so far exhibited successful membrane fabrication with COF as an active layer. The biggest challenge is the processability of COFs as the traditional COFs are synthesized as insoluble and unprocessable powders. Translating the porous structure of these powders into membrane form is a daunting challenge. Banerjee et al. reported an interfacial crystallization method to obtain various defect-free COF membranes [74]. To slow down the initial polymerization, they employed an interlayer containing water. The aldehyde monomer was dissolved in an organic solvent followed by the interlayer of water and then an aqueous solution containing a catalyst and an amine-bearing monomer. The reaction was kept in static conditions for 3–5 days to obtain highly crystalline COF membranes that exhibited an unprecedented high permeance both towards the water and organic solvents along with good dye rejection rates. This work still faced some challenges, such as the amine-bearing monomer also being soluble in the organic solvent. It led to a thicker membrane because the polymerization could not be limited to the interface. Besides, the liquid–liquid interface is very fragile and could be disrupted with even a gentle shaking. The membrane formation also took longer due to room temperature. Our group addressed those challenges by employing a solid-vapor interface to crystallize COF membranes as described in Figure 7 [75]. One monomer was grown on solid support. The second monomer was vaporized to react with the first monomer. Due to the static and stable solid-vapor interface, the reaction temperature could be increased up to 150 °C. Secondly, the reaction was confined at the interface. Therefore, highly crystalline and ultra-thin (120 nm) membranes were fabricated in just 9 h. Due to high crystallinity and low thickness; these membranes outperformed all other reported COF membranes by manifolds. Caro et al. employed an in-situ polymerization method to fabricate COF membranes directly on the alumina support [76]. The alumina support was first functionalized with APTES and a thin layer of aldehyde monomer was grown on it through in-situ polymerization. Later, the alumina support with aldehyde monomer was immersed in a mixed monomer solution to grow a thin layer of COF on top of the support. The composite membranes were used as such for nanofiltration purposes. They exhibited good permeance as well as dye rejection performance.
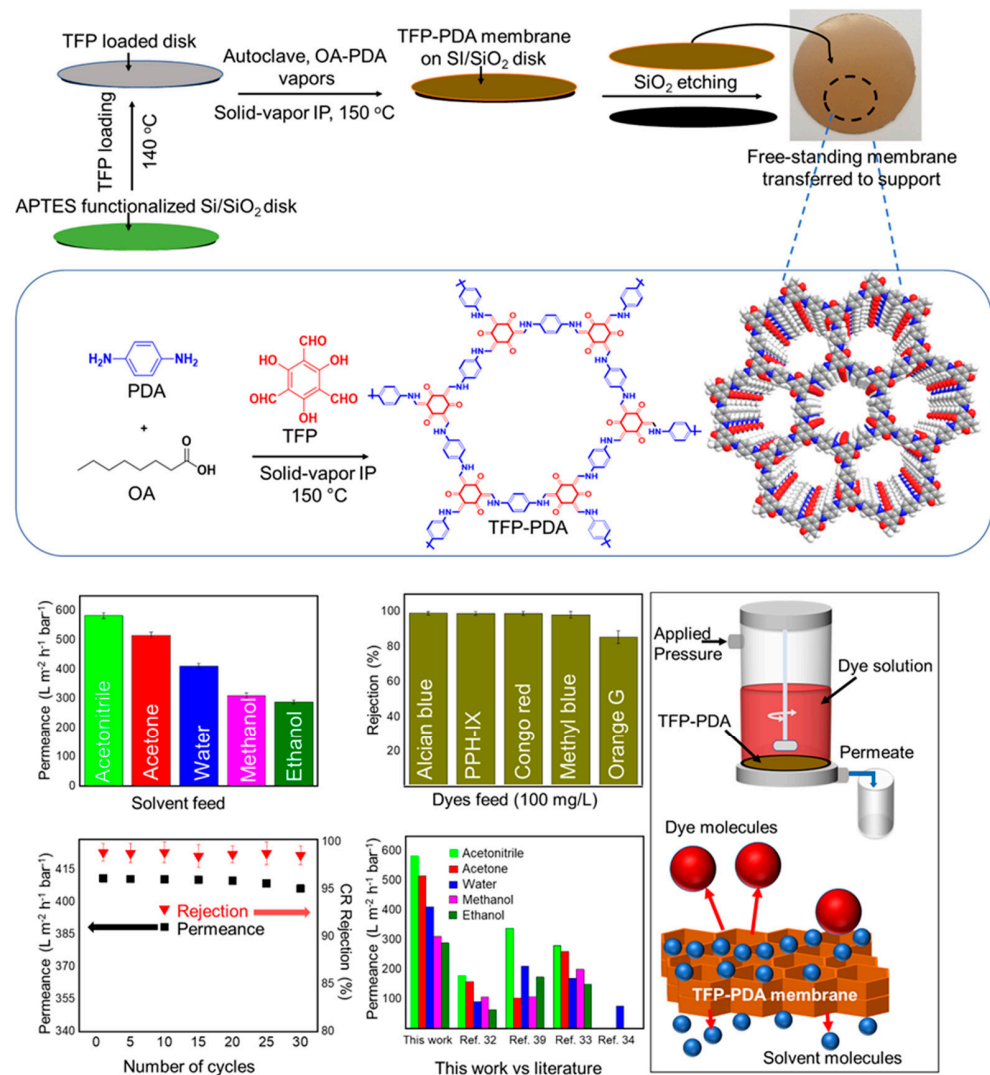
Figure 7. Employment of solid-vapor interface for the fabrication of COF membranes. Adapted with permission from reference [75] copyright 2020 American Chemical Society.

5. Conclusions and Perspectives

Reticular chemistry composed of COFs is the most advanced emerging materials science. Although the developments in COFs are still in the early stage, the salient feature of these materials, like the ease of functionalization with tailored pore windows and sizes, reflect their potential for certain applications. These characteristics suggest that these are an emerging class of material in a wide range of applications including photocatalysts, adsorbents for heavy metals and dyes, membranes for gas, and metal separation. A vast amount of the literature has been reviewed in this article. Emphasis has been given to highlighting the main characteristic features of COFs and their role in environmental remediation.

The structure, morphology, pores, and charge on COF pores were elaborated on for their role in environmental applications. Several COFs have been synthesized using various synthetic approaches comprising solvothermal methods. Although initially reported COFs were not stable, however, introducing hydrogen bonding and other functional groups has increased the stability of current COFs. The pore size of COFs can be pre-designed by choosing specific sizes of monomers for particular applications. The pore size ranging from 0.5–5 nm has been reported so far making them highly desirable in size-dependent separation processes. The pore charge is crucial when COFs are used as adsorbents

or membranes for separation. The negatively charged pore separates the cations and vice versa.

Due to their pore and structural tunability, COFs have been extensively used as good adsorbents for hazardous materials. Heavy metals in water like Cu, Hg, Eu, organic dyes, and greenhouse gases have been removed effectively through COF chemistry. COFs have also shown excellent sensing for heavy metals with low detection limits in water and human urine and blood samples. COFs are ideal candidates for the photocatalytic degradation of organic dyes and pollutants with high stability and recyclability. Due to functionality and pore window size, COFs have been used in the preparation of defect-free membranes. MMMs have excellent separation performance for CO_2 separation from the air and natural gas, surpassing the upper bound curve. Besides, nanosheets of COFs have been fabricated on porous supports, which exhibited high selectivity. In the future, intense research is required for the application-oriented synthesis of COFs, such as COFs with large porosity for adsorption, active sites for photodegradation, and the ability of linkers to form defect-free films for separation membranes.

Despite such huge advancements in COF chemistry for environmental applications, several challenges can still be addressed.

1. COFs with certain functionalities are still needed.
2. Economically viable preparation methods are needed for commercialization.
3. The crystallinity of the COF materials is still an issue that needs further incitement.
4. Many COFs are not stable in humid conditions and this is a serious issue.
5. CO_2 separation in the presence of water and other acidic gases is not well explored.
6. More structural performance of COFs need to be designed for environmental applications.
7. The fragile nature of a pure nanosheet of COFs is challenging for industrial applications. Thus, flexible COF membranes would be an attractive approach.
8. The environmental risk management data for COFs is still lacking, which needs to be addressed.

Author Contributions: Conceptualization, N.A.K., M.H., M.U., Z.A.G., A.N., A.K., A.L.K., A.A.T. and H.U.; validation, M.H., M.U., A.K., A.A.T. and H.U.; writing—original draft preparation, N.A.K.; writing—review and editing, N.A.K., M.H., M.U.; visualization, M.H., A.K., A.A.T., M.U. and H.U.; supervision, M.H., M.U., A.K., A.A.T. and H.U. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Sheng, Y.; Chen, Q.; Mahurin, S.M.; Mayes, R.T.; Zhan, W.; Zhang, J.; Liu, H.; Dai, S. Fibers with Hyper-Crosslinked Functional Porous Frameworks. *Macromol. Rapid Commun.* **2018**, *39*, 1700767. [CrossRef] [PubMed]
2. Li, H.; Meng, B.; Mahurin, S.M.; Chai, S.-H.; Nelson, K.M.; Baker, D.C.; Liu, H.; Dai, S. Carbohydrate based hyper-crosslinked organic polymers with -OH functional groups for CO_2 separation. *J. Mater. Chem. A* **2015**, *3*, 20913–20918. [CrossRef]
3. Dawson, R.; Cooper, A.I.; Adams, D.J. Nanoporous organic polymer networks. *Prog. Polym. Sci.* **2012**, *37*, 530–563. [CrossRef]
4. Kitagawa, S.; Kitaura, R.; Noro, S. Functional porous coordination polymers. *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375. [CrossRef]
5. Li, A.; Sun, H.-X.; Tan, D.-Z.; Fan, W.-J.; Wen, S.-H.; Qing, X.-J.; Li, G.-X.; Li, S.-Y.; Deng, W.-Q. Superhydrophobic conjugated microporous polymers for separation and adsorption. *Energy Environ. Sci.* **2011**, *4*, 2062–2065. [CrossRef]
6. Liang, B.; Wang, H.; Shi, X.; Shen, B.; He, X.; Ghazi, Z.A.; Khan, N.A.; Sin, H.; Khattak, A.M.; Li, L.; et al. Microporous membranes comprising conjugated polymers with rigid backbones enable ultrafast organic-solvent nanofiltration. *Nat. Chem.* **2018**, *10*, 961–967. [CrossRef] [PubMed]
7. He, X.; Sin, H.; Liang, B.; Ghazi, Z.A.; Khattak, A.M.; Khan, N.A.; Alanagh, H.R.; Li, L.; Lu, X.; Tang, Z. Controlling the Selectivity of Conjugated Microporous Polymer Membrane for Efficient Organic Solvent Nanofiltration. *Adv. Funct. Mater.* **2019**, *29*, 1900134. [CrossRef]

8. Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361–1403. [CrossRef]

9. Dillon, A.C.; Jones, K.M.; Bekkedahl, T.A.; Kiang, C.H.; Bethune, D.S.; Heben, M.J. Storage of hydrogen in single-walled carbon nanotubes. *Nature* **1997**, *386*, 377–379. [CrossRef]

10. Adio, S.O.; Ganiyu, S.A.; Usman, M.; Abdulazeez, I.; Alhooshani, K. Facile and efficient nitrogen modified porous carbon derived from sugarcane bagasse for CO_2 capture: Experimental and DFT investigation of nitrogen atoms on carbon frameworks. *Chem. Eng. J.* **2020**, *382*, 122964. [CrossRef]

11. Yildirim, O.; Bonomo, M.; Barbero, N.; Atzori, C.; Civalleri, B.; Bonino, F.; Viscardi, G.; Barolo, C. Application of Metal-Organic Frameworks and Covalent Organic Frameworks as (Photo)Active Material in Hybrid Photovoltaic Technologies. *Energies* **2020**, *13*, 5602. [CrossRef]

12. Li, J.-R.; Kuppler, R.J.; Zhou, H.-C. Selective gas adsorption and separation in metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1477–1504. [CrossRef]

13. Usman, M.; Ali, M.; Al-Maythalony, B.A.; Ghanem, A.S.; Saadi, O.W.; Ali, M.; Jafar Mazumder, M.A.; Abdel-Azeim, S.; Habib, M.A.; Yamani, Z.H.; et al. Highly Efficient Permeation and Separation of Gases with Metal–Organic Frameworks Confined in Polymeric Nanochannels. *ACS Appl. Mater. Interfaces* **2020**, *12*, 49992–50001. [CrossRef]

14. Ghanem, A.S.; Ba-Shammakh, M.; Usman, M.; Khan, M.F.; Dafallah, H.; Habib, M.A.; Al-Maythalony, B.A. High gas permselectivity in ZIF-302/polyimide self-consistent mixed-matrix membrane. *J. Appl. Polym. Sci.* **2020**, *137*, 48513. [CrossRef]

15. Boyd, G.E.; Adamson, A.W.; Myers, L.S. The exchange adsorption of ions from aqueous solutions by organic zeolites 2. *J. Am. Chem. Soc.* **1947**, *69*, 2836–2848. [CrossRef] [PubMed]

16. Wang, S.; Peng, Y. Natural zeolites as effective adsorbents in water and wastewater treatment. *Chem. Eng. J.* **2010**, *156*, 11–24. [CrossRef]

17. Imran, A.; Bramer, E.A.; Seshan, K.; Brem, G. Catalytic Flash Pyrolysis of Biomass Using Different Types of Zeolite and Online Vapor Fractionation. *Energies* **2016**, *9*, 187. [CrossRef]

18. Luis Miguez, J.; Porteiro, J.; Perez-Orozco, R.; Angel Gomez, M. Technology Evolution in Membrane-Based CCS. *Energies* **2018**, *11*, 3153. [CrossRef]

19. Usman, M.; Zhu, J.; Chuiyang, K.; Arslan, M.T.; Khan, A.; Galadima, A.; Muraza, O.; Khan, I.; Helal, A.; Al-Maythalony, B.A.; et al. Propene Adsorption-Chemisorption Behaviors on H-SAPO-34 Zeolite Catalysts at Different Temperatures. *Catalysts* **2019**, *9*, 919. [CrossRef]

20. Côté, A.P.; Benin, A.I.; Ockwig, N.W.; O'Keeffe, M.; Matzger, A.J.; Yaghi, O.M. Porous, Crystalline, Covalent Organic Frameworks. *Science* **2005**, *310*, 1166–1170. [CrossRef]

21. Kandambeth, S.; Mallick, A.; Lukose, B.; Mane, M.V.; Heine, T.; Banerjee, R. Construction of Crystalline 2D Covalent Organic Frameworks with Remarkable Chemical (Acid/Base) Stability via a Combined Reversible and Irreversible Route. *J. Am. Chem. Soc.* **2012**, *134*, 19524–19527. [CrossRef] [PubMed]

22. Katekomol, P.; Roeser, J.; Bojdys, M.; Weber, J.; Thomas, A. Covalent Triazine Frameworks Prepared from 1,3,5-Tricyanobenzene. *Chem. Mater.* **2013**, *25*, 1542–1548. [CrossRef]

23. Furukawa, H.; Yaghi, O.M. Storage of Hydrogen, Methane, and Carbon Dioxide in Highly Porous Covalent Organic Frameworks for Clean Energy Applications. *J. Am. Chem. Soc.* **2009**, *131*, 8875–8883. [CrossRef]

24. Alahakoon, S.B.; Thompson, C.M.; Occhialini, G.; Smaldone, R.A. Design Principles for Covalent Organic Frameworks in Energy Storage Applications. *Chemsuschem* **2017**, *10*, 2116–2129. [CrossRef]

25. Khattak, A.M.; Ghazi, Z.A.; Liang, B.; Khan, N.A.; Iqbal, A.; Li, L.; Tang, Z. A redox-active 2D covalent organic framework with pyridine moieties capable of faradaic energy storage. *J. Mater. Chem. A* **2016**, *4*, 16312–16317. [CrossRef]

26. Royuela, S.; Gil-San Millan, R.; Mancheno, M.J.; Mar Ramos, M.; Segura, J.L.; Navarro, J.A.R.; Zamora, F. Catalytically Active Imine-based Covalent Organic Frameworks for Detoxification of Nerve Agent Simulants in Aqueous Media. *Materials* **2019**, *12*, 1974. [CrossRef]

27. Ding, S.-Y.; Gao, J.; Wang, Q.; Zhang, Y.; Song, W.-G.; Su, C.-Y.; Wang, W. Construction of Covalent Organic Framework for Catalysis: Pd/COF-LZU1 in Suzuki-Miyaura Coupling Reaction. *J. Am. Chem. Soc.* **2011**, *133*, 19816–19822. [CrossRef] [PubMed]

28. Calik, M.; Auras, F.; Salonen, L.M.; Bader, K.; Grill, I.; Handloser, M.; Medina, D.D.; Dogru, M.; Loebermann, F.; Trauner, D.; et al. Extraction of Photogenerated Electrons and Holes from a Covalent Organic Framework Integrated Heterojunction. *J. Am. Chem. Soc.* **2014**, *136*, 17802–17807. [CrossRef] [PubMed]

29. DeBlase, C.R.; Silberstein, K.E.; Thanh-Tam, T.; Abruna, H.D.; Dichtel, W.R. beta-Ketoenamine-Linked Covalent Organic Frameworks Capable of Pseudocapacitive Energy Storage. *J. Am. Chem. Soc.* **2013**, *135*, 16821–16824. [CrossRef] [PubMed]

30. Wang, S.; Wang, Q.; Shao, P.; Han, Y.; Gao, X.; Ma, L.; Yuan, S.; Ma, X.; Zhou, J.; Feng, X.; et al. Exfoliation of Covalent Organic Frameworks into Few-Layer Redox-Active Nanosheets as Cathode Materials for Lithium-Ion Batteries. *J. Am. Chem. Soc.* **2017**, *139*, 4258–4261. [CrossRef] [PubMed]

31. Sun, T.; Xie, J.; Guo, W.; Li, D.-S.; Zhang, Q. Covalent-Organic Frameworks: Advanced Organic Electrode Materials for Rechargeable Batteries. *Adv. Energy Mater.* **2020**, *10*, 1904199. [CrossRef]

32. Ghazi, Z.A.; Zhu, L.; Wang, H.; Naeem, A.; Khattak, A.M.; Liang, B.; Khan, N.A.; Wei, Z.; Li, L.; Tang, Z. Efficient Polysulfide Chemisorption in Covalent Organic Frameworks for High-Performance Lithium-Sulfur Batteries. *Adv. Energy Mater.* **2016**, *6*, 1601250. [CrossRef]

33. Delrue, F.; Alvarez-Diaz, P.D.; Fon-Sing, S.; Fleury, G.; Sassi, J.-F. The Environmental Biorefinery: Using Microalgae to Remediate Wastewater, a Win-Win Paradigm. *Energies* **2016**, *9*, 132. [CrossRef]

34. Song, W.; Deng, X. Effects of Urbanization-Induced Cultivated Land Loss on Ecosystem Services in the North China Plain. *Energies* **2015**, *8*, 5678–5693. [CrossRef]

35. Fu, F.; Wang, Q. Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manag.* **2011**, *92*, 407–418. [CrossRef]

36. Jarup, L. Hazards of heavy metal contamination. *Br. Med. Bull.* **2003**, *68*, 167–182. [CrossRef]

37. Raju, K.A.; Ramakrishna, C. The effects of heavy metals on the anatomical structures of *Avicennia marina* (Forssk.) Vierh. *Braz. J. Bot.* **2021**, *54*, 1–9.

38. Abrham, F.; Gholap, A.V. Analysis of heavy metal concentration in some vegetables using atomic absorption spectroscopy. *Pollution* **2021**, *7*, 205–216.

39. Ghazi, Z.A.; Khattak, A.M.; Iqbal, R.; Ahmad, R.; Khan, A.A.; Usman, M.; Nawaz, F.; Ali, W.; Felegari, Z.; Jan, S.U.; et al. Adsorptive removal of Cd2+ from aqueous solutions by a highly stable covalent triazine-based framework. *New J. Chem.* **2018**, *42*, 10234–10242. [CrossRef]

40. Liu, L.; Wang, X.-X.; Wang, X.; Xu, G.-J.; Zhao, Y.-F.; Wang, M.-L.; Lin, J.-M.; Zhao, R.-S.; Wu, Y. Triazine-cored covalent organic framework for ultrasensitive detection of polybrominated diphenyl ethers from real samples: Experimental and DFT study. *J. Hazard. Mater.* **2021**, *403*, 123917. [CrossRef]

41. Zhang, Y.; Li, H.; Chang, J.; Guan, X.; Tang, L.; Fang, Q.; Valtchev, V.; Yan, Y.; Qiu, S. 3D Thioether-Based Covalent Organic Frameworks for Selective and Efficient Mercury Removal. *Small* **2021**, e2006112. [CrossRef] [PubMed]

42. Huang, L.; Shen, R.; Liu, R.; Xu, S.; Shuai, Q. Facile fabrication of magnetic covalent organic frameworks for magnetic solid-phase extraction of diclofenac sodium in milk. *Food Chem.* **2021**, *347*, 129002. [CrossRef] [PubMed]

43. Jiang, H.-L.; Lin, Y.-L.; Li, N.; Wang, Z.-W.; Liu, M.; Zhao, R.-S.; Lin, J.-M. Application of magnetic N-doped carbon nanotubes in solid-phase extraction of trace bisphenols from fruit juices. *Food Chem.* **2018**, *269*, 413–418. [CrossRef]

44. Li, X.; Cui, Y.-Y.; Yang, C.-X. Covalent coupling fabrication of microporous organic network bonded capillary columns for gas chromatographic separation. *Talanta* **2021**, *224*, 121914. [CrossRef]

45. Xiao, Y.; Ma, C.; Jin, Z.; Wang, J.; He, L.; Mu, X.; Song, L.; Hu, Y. Functional covalent organic framework for exceptional Fe2+, Co2+ and Ni2+ removal: An upcycling strategy to achieve water decontamination and reutilization as smoke suppressant and flame retardant simultaneously. *Chem. Eng. J.* **2020**, 127837. [CrossRef]

46. Xin, J.; Zhou, Y.; Wang, X.; Xu, G.; Xie, M.; Liu, L.; Zhao, R.; Wu, Y.; Wang, M. Room-temperature synthesis of magnetic covalent organic frameworks for analyzing trace benzoylurea insecticide residue in tea beverages. *Food Chem.* **2021**, *347*, 129075. [CrossRef] [PubMed]

47. Garba, M.D.; Usman, M.; Mazumder, M.A.J.; Al-Ahmed, A. Inamuddin, Complexing agents for metal removal using ultrafiltration membranes: A review. *Environ. Chem. Lett.* **2019**, *17*, 1195–1208. [CrossRef]

48. Turangan, N.; Xu, Y.; Spratt, H.; Rintoul, L.; Bottle, S.; MacLeod, J. Self-supporting covalent organic framework membranes synthesized through two different processes: Solvothermal annealing and solvent vapor annealing. *Nanotechnology* **2021**, *32*, 075604. [CrossRef] [PubMed]

49. Zhang, L.; Li, Y.; Wang, Y.; Ma, S.; Ou, J.; Shen, Y.; Ye, M.; Uyama, H. Integration of covalent organic frameworks into hydrophilic membrane with hierarchical porous structure for fast adsorption of metal ions. *J. Hazard. Mater.* **2021**, *407*, 124390. [CrossRef]

50. Ullah, H.; Tahir, A.A.; Mallick, T.K. Structural and electronic properties of oxygen defective and Se-doped p-type BiVO4 (001) thin film for the applications of photocatalysis. *Appl. Catal. B* **2018**, *224*, 895–903. [CrossRef]

51. Ullah, H.; Tahir, A.A.; Mallick, T.K. Polypyrrole/TiO2 composites for the application of photocatalysis. *Sens. Actuators B* **2017**, *241*, 1161–1169. [CrossRef]

52. Ullah, H.; Tahir, A.A.; Bibi, S.; Mallick, T.K.; Karazhanov, S.Z. Electronic properties of β-TaON and its surfaces for solar water splitting. *Appl. Catal. B* **2018**, *229*, 24–31. [CrossRef]

53. Ullah, H.; Loh, A.; Trudgeon, D.P.; Li, X. Density Functional Theory Study of NiFeCo Trinary Oxy-Hydroxides for an Efficient and Stable Oxygen Evolution Reaction Catalyst. *ACS Omega* **2020**, *5*, 20517–20524. [CrossRef]

54. Ullah, H.; Bibi, S.; Tahir, A.A.; Mallick, T.K. Donor-acceptor polymer for the design of all-solid-state dye-sensitized solar cells. *J. Alloy. Compd.* **2017**, *696*, 914–922. [CrossRef]

55. Ullah, H.; Bibi, S.; Tahir, A.A.; Mallick, T.K. Density functional theory study of selenium-substituted low-bandgap donor–acceptor–donor polymer. *J. Phys. Chem. C* **2016**, *120*, 27200–27211. [CrossRef]

56. Nasir, S.N.F.M.; Ullah, H.; Ebadi, M.; Tahir, A.A.; Sagu, J.S.; Mat Teridi, M.A. New insights into Se/BiVO4 heterostructure for photoelectrochemical water splitting: A combined experimental and DFT study. *J. Phys. Chem. C* **2017**, *121*, 6218–6228. [CrossRef]

57. Humayun, M.; Ullah, H.; Cao, J.; Pi, W.; Yuan, Y.; Ali, S.; Tahir, A.A.; Yue, P.; Khan, A.; Zheng, Z. Experimental and DFT Studies of Au Deposition Over WO 3/gC 3 N 4 Z-Scheme Heterojunction. *Nano-Micro Lett.* **2020**, *12*, 1–18. [CrossRef]

58. Samsudin, M.F.R.; Ullah, H.; Tahir, A.A.; Li, X.; Ng, Y.H.; Sufian, S. Superior photoelectrocatalytic performance of ternary structural BiVO4/GQD/g-C3N4 heterojunction. *J. Colloid Interface Sci.* **2021**, *586*, 785–796. [CrossRef]

59. Samsudin, M.F.R.; Ullah, H.; Bashiri, R.; Mohamed, N.M.; Sufian, S.; Ng, Y.H. Experimental and DFT insights on microflower g-C3N4/BiVO4 photocatalyst for enhanced photoelectrochemical hydrogen generation from lake water. *ACS Sustain. Chem. Eng.* **2020**, *8*, 9393–9403. [CrossRef]

60. Noh, M.F.M.; Ullah, H.; Arzaee, N.A.; Ab Halim, A.; Rahim, M.A.F.A.; Mohamed, N.A.; Safaei, J.; Nasir, S.N.F.M.; Wang, G.; Teridi, M.A.M. Rapid fabrication of oxygen defective α-Fe₂O₃ (110) for enhanced photoelectrochemical activities. *Dalton Trans.* **2020**, *49*, 12037–12048.

61. Mohamed, N.A.; Ullah, H.; Safaei, J.; Ismail, A.F.; Mohamad Noh, M.F.; Soh, M.F.; Ibrahim, M.A.; Ludin, N.A.; Mat Teridi, M.A. Efficient Photoelectrochemical Performance of γ Irradiated g-C3N4 and Its g-C3N4@BiVO4 Heterojunction for Solar Water Splitting. *J. Phys. Chem. C* **2019**, *123*, 9013–9026. [CrossRef]

62. Safaei, J.; Ullah, H.; Mohamed, N.A.; Mohamad Noh, M.F.; Soh, M.F.; Tahir, A.A.; Ahmad Ludin, N.; Ibrahim, M.A.; Wan Isahak, W.N.R.; Mat Teridi, M.A. Enhanced photoelectrochemical performance of Z-scheme g-C3N4/BiVO4 photocatalyst. *Appl. Catal. B* **2018**, *234*, 296–310. [CrossRef]

63. Ola, O.; Ullah, H.; Chen, Y.; Thummavichai, K.; Wang, N.; Zhu, Y. DFT and Experimental Studies of Iron Oxide-based Nanocomposites for Efficient Electrocatalysis. *J. Mater. Chem. C* **2021**. [CrossRef]

64. Lin, Y.; Wang, P.; Loh, A.; Wan, L.; Habib, U.; Xu, Z.; Li, X.; Wang, B. Assembling flower-on-sheet CoP–NiCoP nanohybrids as efficient self-supported electrocatalysts for hydrogen evolution reaction in both acidic and alkaline media. *J. Mater. Sci.* **2021**, *56*, 3375–3386. [CrossRef]

65. Sookhakian, M.; Ullah, H.; Teridi, M.A.M.; Tong, G.B.; Basirun, W.J.; Alias, Y. Boron-doped graphene-supported manganese oxide nanotubes as an efficient non-metal catalyst for the oxygen reduction reaction. *Sustain. Energy Fuels* **2020**, *4*, 737–749. [CrossRef]

66. Kim, H.P.; Vasilopoulou, M.; Ullah, H.; Bibi, S.; Gavim, A.E.X.; Macedo, A.G.; da Silva, W.J.; Schneider, F.K.; Tahir, A.A.; Teridi, M.A.M. A hysteresis-free perovskite transistor with exceptional stability through molecular cross-linking and amine-based surface passivation. *Nanoscale* **2020**, *12*, 7641–7650. [CrossRef]

67. Bin Mohd Yusoff, A.R.; Mahata, A.; Vasilopoulou, M.; Ullah, H.; Hu, B.; da Silva, W.J.; Schneider, F.K.; Gao, P.; Ievlev, A.V.; Liu, Y. Observation of large Rashba spin–orbit coupling at room temperature in compositionally engineered perovskite single crystals and application in high performance photodetectors. *Mater. Today* **2021**, in press.

68. Ding, S.-Y.; Dong, M.; Wang, Y.-W.; Chen, Y.-T.; Wang, H.-Z.; Su, C.-Y.; Wang, W. Thioether-Based Fluorescent Covalent Organic Framework for Selective Detection and Facile Removal of Mercury(II). *J. Am. Chem. Soc.* **2016**, *138*, 3031–3037. [CrossRef]

69. Wang, J.; Zhuang, S. Covalent organic frameworks (COFs) for environmental applications. *Coord. Chem. Rev.* **2019**, *400*, 213046. [CrossRef]

70. Uribe-Romo, F.J.; Hunt, J.R.; Furukawa, H.; Klock, C.; O'Keeffe, M.; Yaghi, O.M. A Crystalline Imine-Linked 3-D Porous Covalent Organic Framework. *J. Am. Chem. Soc.* **2009**, *131*, 4570–4571. [CrossRef]

71. Kuhn, P.; Antonietti, M.; Thomas, A. Porous, covalent triazine-based frameworks prepared by ionothermal synthesis. *Angew. Chem. Int. Ed.* **2008**, *47*, 3450–3453. [CrossRef]

72. Uribe-Romo, F.J.; Doonan, C.J.; Furukawa, H.; Oisaki, K.; Yaghi, O.M. Crystalline Covalent Organic Frameworks with Hydrazone Linkages. *J. Am. Chem. Soc.* **2011**, *133*, 11478–11481. [CrossRef]

73. Karak, S.; Kandambeth, S.; Biswal, B.P.; Sasmal, H.S.; Kumar, S.; Pachfule, P.; Banerjee, R. Constructing Ultraporous Covalent Organic Frameworks in Seconds via an Organic Terracotta Process. *J. Am. Chem. Soc.* **2017**, *139*, 1856–1862. [CrossRef] [PubMed]

74. Dey, K.; Pal, M.; Rout, K.C.; Kunjattu, H.S.; Das, A.; Mukherjee, R.; Kharul, U.K.; Banerjee, R. Selective Molecular Separation by Interfacially Crystallized Covalent Organic Framework Thin Films. *J. Am. Chem. Soc.* **2017**, *139*, 13083–13091. [CrossRef]

75. Khan, N.A.; Zhang, R.; Wu, H.; Shen, J.; Yuan, J.; Fan, C.; Cao, L.; Olson, M.A.; Jiang, Z. Solid–Vapor Interface Engineered Covalent Organic Framework Membranes for Molecular Separation. *J. Am. Chem. Soc.* **2020**, *142*, 13450–13458. [CrossRef]

76. Fan, H.; Gu, J.; Meng, H.; Knebel, A.; Caro, J. High-Flux Membranes Based on the Covalent Organic Framework COF-LZU1 for Selective Dye Separation by Nanofiltration. *Angew. Chem. Int. Ed.* **2018**, *57*, 4083–4087. [CrossRef] [PubMed]

77. Diaz de Grenu, B.; Torres, J.; Garcia-Gonzalez, J.; Munoz-Pina, S.; de los Reyes, R.; Costero, A.M.; Amoros, P.; Ros-Lis, J.V. Microwave-Assisted Synthesis of Covalent Organic Frameworks: A Review. *ChemSusChem* **2021**, *14*, 208–233. [CrossRef]

78. Liu, X.-H.; Guan, C.-Z.; Ding, S.-Y.; Wang, W.; Yan, H.-J.; Wang, D.; Wan, L.-J. On-Surface Synthesis of Single-Layered Two-Dimensional Covalent Organic Frameworks via Solid–Vapor Interface Reactions. *J. Am. Chem. Soc.* **2013**, *135*, 10470–10474. [CrossRef] [PubMed]

79. Xu, L.; Zhou, X.; Tian, W.Q.; Gao, T.; Zhang, Y.F.; Lei, S.; Liu, Z.F. Surface-Confined Single-Layer Covalent Organic Framework on Single-Layer Graphene Grown on Copper Foil. *Angew. Chem. Int. Ed.* **2014**, *53*, 9564–9568. [CrossRef]

80. Khan, N.A.; Yuan, J.; Wu, H.; Huang, T.; You, X.; Olson, M.A.; Azad, C.S.; Rahman, A.U.; Jiang, Z. Covalent Organic Framework Nanosheets as Reactive Fillers to Fabricate Free-Standing Polyamide Membranes for Efficient Desalination. *ACS Appl. Mater. Interfaces* **2020**, *12*, 27777–27785. [CrossRef]

81. Bian, G.; Yin, J.; Zhu, J. Recent Advances on Conductive 2D Covalent Organic Frameworks. *Small* **2021**, e2006043. [CrossRef]

82. Liu, Y.; Zhou, W.; Teo, W.L.; Wang, K.; Zhang, L.; Zeng, Y.; Zhao, Y. Covalent-Organic-Framework-Based Composite Materials. *Chem* **2020**, *6*, 3172–3202. [CrossRef]

83. Ren, D.; Ren, S.; Lin, Y.; Xu, J.; Wang, X. Recent developments of organic solvent resistant materials for membrane separations. *Chemosphere* **2020**, *271*, 129425. [CrossRef]

84. Zhang, Y.; Jin, X.; Ma, X.; Wang, Y. Chiral porous organic frameworks and their application in enantioseparation. *Anal. Methods* **2021**, *13*, 8–33. [CrossRef] [PubMed]

85. Diercks, C.S.; Yaghi, O.M. The atom, the molecule, and the covalent organic framework. *Science* **2017**, *355*, eaal1585. [CrossRef]

86. Ding, S.-Y.; Wang, W. Covalent organic frameworks (COFs): From design to applications. *Chem. Soc. Rev.* **2013**, *42*, 548–568. [CrossRef]
87. Feng, X.; Ding, X.; Jiang, D. Covalent organic frameworks. *Chem. Soc. Rev.* **2012**, *41*, 6010–6022. [CrossRef]
88. Huang, N.; Wang, P.; Jiang, D. Covalent organic frameworks: A materials platform for structural and functional designs. *Nat. Rev. Mater.* **2016**, *1*, 1–19. [CrossRef]
89. Segura, J.L.; Mancheno, M.J.; Zamora, F. Covalent organic frameworks based on Schiff-base chemistry: Synthesis, properties and potential applications. *Chem. Soc. Rev.* **2016**, *45*, 5635–5671. [CrossRef] [PubMed]
90. Waller, P.J.; Gandara, F.; Yaghi, O.M. Chemistry of Covalent Organic Frameworks. *Acc. Chem. Res.* **2015**, *48*, 3053–3063. [CrossRef]
91. Ashraf, M.; Khan, I.; Usman, M.; Khan, A.; Shah, S.S.; Khan, A.Z.; Saeed, K.; Yaseen, M.; Ehsan, M.F.; Tahir, M.N.; et al. Hematite and Magnetite Nanostructures for Green and Sustainable Energy Harnessing and Environmental Pollution Control: A Review. *Chem. Res. Toxicol.* **2020**, *33*, 1292–1311. [CrossRef] [PubMed]
92. Halder, A.; Karak, S.; Addicoat, M.; Bera, S.; Chakraborty, A.; Kunjattu, S.H.; Pachfule, P.; Heine, T.; Banerjee, R. Ultrastable Imine-Based Covalent Organic Frameworks for Sulfuric Acid Recovery: An Effect of Interlayer Hydrogen Bonding. *Angew. Chem. Int. Ed.* **2018**, *57*, 5797–5802. [CrossRef]
93. Ehsan, M.F.; Fazal, A.; Hamid, S.; Arfan, M.; Khan, I.; Usman, M.; Shafiee, A.; Ashiq, M.N. $CoFe_2O_4$ decorated g-C3N4 nanosheets: New insights into superoxide anion mediated photomineralization of methylene blue. *J. Environ. Chem. Eng.* **2020**, *8*, 104556. [CrossRef]
94. Ehsan, M.F.; Shafiq, M.; Hamid, S.; Shafiee, A.; Usman, M.; Khan, I.; Ashiq, M.N.; Arfan, M. Reactive oxygen species: New insights into photocatalytic pollutant degradation over g-C3N4/ZnSe nanocomposite. *Appl. Surf. Sci.* **2020**, *532*, 147418. [CrossRef]
95. Corcos, A.R.; Levato, G.A.; Jiang, Z.; Evans, A.M.; Livingston, A.G.; Mariñas, B.J.; Dichtel, W.R. Reducing the Pore Size of Covalent Organic Frameworks in Thin-Film Composite Membranes Enhances Solute Rejection. *ACS Mater. Lett.* **2019**, *1*, 440–446. [CrossRef]
96. Nagai, A.; Guo, Z.; Feng, X.; Jin, S.; Chen, X.; Ding, X.; Jiang, D. Pore surface engineering in covalent organic frameworks. *Nat. Commun.* **2011**, *2*, 536. [CrossRef]
97. Zhuang, S.; Liu, Y.; Wang, J. Covalent organic frameworks as efficient adsorbent for sulfamerazine removal from aqueous solution. *J. Hazard. Mater.* **2020**, *383*, 121126. [CrossRef]
98. Mullangi, D.; Shalini, S.; Nandi, S.; Choksi, B.; Vaidhyanathan, R. Super-hydrophobic covalent organic frameworks for chemical resistant coatings and hydrophobic paper and textile composites. *J. Mater. Chem. A* **2017**, *5*, 8376–8384. [CrossRef]
99. Liu, Z.; Su, Q.; Ju, P.; Li, X.; Li, G.; Wu, Q.; Yang, B. A hydrophilic covalent organic framework for photocatalytic oxidation of benzylamine in water. *Chem. Commun.* **2020**, *56*, 766–769. [CrossRef]
100. Han, N.; Zhang, Z.; Gao, H.; Qian, Y.; Tan, L.; Yang, C.; Zhang, H.; Cui, Z.; Li, W.; Zhang, X. Superhydrophobic Covalent Organic Frameworks Prepared via Pore Surface Modifications for Functional Coatings under Harsh Conditions. *ACS Appl. Mater. Interfaces* **2020**, *12*, 2926–2934. [CrossRef] [PubMed]
101. Lin, X.; Deng, Y.; He, Y.; Chen, J.; Hu, S. Construction of hydrophilic N, O-rich carboxylated triazine-covalent organic frameworks for the application in selective simultaneous electrochemical detection. *Appl. Surf. Sci.* **2021**, *545*, 149047. [CrossRef]
102. Yuan, S.; Li, X.; Zhu, J.; Zhang, G.; Van Puyvelde, P.; Van der Bruggen, B. Covalent organic frameworks for membrane separation. *Chem. Soc. Rev.* **2019**, *48*, 2665–2681. [CrossRef]
103. Kandambeth, S.; Shinde, D.B.; Panda, M.K.; Lukose, B.; Heine, T.; Banerjee, R. Enhancement of Chemical Stability and Crystallinity in Porphyrin-Containing Covalent Organic Frameworks by Intramolecular Hydrogen Bonds. *Angew. Chem. Int. Ed.* **2013**, *52*, 13052–13056. [CrossRef] [PubMed]
104. Xu, H.; Gao, J.; Jiang, D. Stable, crystalline, porous, covalent organic frameworks as a platform for chiral organocatalysts. *Nat. Chem.* **2015**, *7*, 905–912. [CrossRef] [PubMed]
105. Li, Z.; Zhang, Y.; Xia, H.; Mu, Y.; Liu, X. A robust and luminescent covalent organic framework as a highly sensitive and selective sensor for the detection of Cu2+ ions. *Chem. Commun.* **2016**, *52*, 6613–6616. [CrossRef]
106. Zhang, W.; Zhang, L.; Zhao, H.; Li, B.; Ma, H. A two-dimensional cationic covalent organic framework membrane for selective molecular sieving. *J. Mater. Chem. A* **2018**, *6*, 13331–13339. [CrossRef]
107. Duong, P.H.H.; Kuehl, V.A.; Mastorovich, B.; Hoberg, J.O.; Parkinson, B.A.; Li-Oakey, K.D. Carboxyl-functionalized covalent organic framework as a two-dimensional nanofiller for mixed-matrix ultrafiltration membranes. *J. Membr. Sci.* **2019**, *574*, 338–348. [CrossRef]
108. Kuehl, V.A.; Yin, J.; Duong, P.H.H.; Mastorovich, B.; Newell, B.; Li-Oakey, K.D.; Parkinson, B.A.; Hoberg, J.O. A Highly Ordered Nanoporous, Two-Dimensional Covalent Organic Framework with Modifiable Pores, and Its Application in Water Purification and Ion Sieving. *J. Am. Chem. Soc.* **2018**, *140*, 18200–18207. [CrossRef]
109. Xiao, Y.; Ma, C.; Jin, Z.; Wang, C.; Wang, J.; Wang, H.; Mu, X.; Song, L.; Hu, Y. Functional covalent organic framework illuminate rapid and efficient capture of Cu (II) and reutilization to reduce fire hazards of epoxy resin. *Sep. Purif. Technol.* **2021**, *259*, 118119. [CrossRef]
110. Ma, Z.; Liu, F.; Liu, N.; Liu, W.; Tong, M. Facile synthesis of sulfhydryl modified covalent organic frameworks for high efficient Hg(II) removal from water. *J. Hazard. Mater.* **2021**, *405*, 124190. [CrossRef]
111. Yang, Z.; Gu, Y.; Yuan, B.; Tian, Y.; Shang, J.; Tsang, D.C.W.; Liu, M.; Gan, L.; Mao, S.; Li, L. Thio-groups decorated covalent triazine frameworks for selective mercury removal. *J. Hazard. Mater.* **2021**, *403*, 123702. [CrossRef] [PubMed]

112. Sun, Q.; Aguila, B.; Perman, J.; Earl, L.D.; Abney, C.W.; Cheng, Y.; Wei, H.; Nguyen, N.; Wojtas, L.; Ma, S. Postsynthetically Modified Covalent Organic Frameworks for Efficient and Effective Mercury Removal. *J. Am. Chem. Soc.* **2017**, *139*, 2786–2793. [CrossRef]

113. Zhong, X.; Liu, Y.; Liang, W.; Zhu, Y.; Hu, B. Construction of Core-Shell MOFs@COF Hybrids as a Platform for the Removal of UO_2^{2+} and Eu^{3+} Ions from Solution. *ACS Appl. Mater. Interfaces* **2021**, *13*, 13883–13985. [CrossRef]

114. Jiang, H.-L.; Fu, Q.-B.; Wang, M.-L.; Lin, J.-M.; Zhao, R.-S. Determination of trace bisphenols in functional beverages through the magnetic solid-phase extraction with MOF-COF composite. *Food Chem.* **2021**, *345*, 128841. [CrossRef]

115. Xu, G.; Hou, L.; Li, B.; Wang, X.; Liu, L.; Li, N.; Wang, M.-L.; Zhao, R.-S. Facile preparation of hydroxyl bearing covalent organic frameworks for analysis of phenoxy carboxylic acid pesticide residue in plant-derived food. *Food Chem.* **2021**, *345*, 128749. [CrossRef] [PubMed]

116. Dinari, M.; Jamshidian, F. Preparation of MIL-101-NH2 MOF/triazine based covalent organic framework hybrid and its application in acid blue 9 removals. *Polymer* **2021**, *215*, 123383. [CrossRef]

117. Suresh, R.; Vijayakumar, S. Adsorption of greenhouse gases on the surface of covalent organic framework of porphyrin—An ab initio study. *Phys. E Low-Dimens. Syst. Nanostruct.* **2021**, *126*, 114448. [CrossRef]

118. Bhunia, A.; Boldog, I.; Moeller, A.; Janiak, C. Highly stable nanoporous covalent triazine-based frameworks with an adamantane core for carbon dioxide sorption and separation. *J. Mater. Chem. A* **2013**, *1*, 14990–14999. [CrossRef]

119. Wang, K.; Huang, H.; Liu, D.; Wang, C.; Li, J.; Zhong, C. Covalent Triazine-Based Frameworks with Ultramicropores and High Nitrogen Contents for Highly Selective CO_2 Capture. *Environ. Sci. Technol.* **2016**, *50*, 4869–4876. [CrossRef]

120. Wang, L.; Yang, Y.; Liang, H.; Wu, N.; Peng, X.; Wang, L.; Song, Y. A novel N,S-rich COF and its derived hollow N,S-doped carbon@Pd nanorods for electrochemical detection of Hg2+ and paracetamol. *J. Hazard. Mater.* **2021**, *409*, 124528. [CrossRef] [PubMed]

121. Das, G.; Biswal, B.P.; Kandambeth, S.; Venkatesh, V.; Kaur, G.; Addicoat, M.; Heine, T.; Verma, S.; Banerjee, R. Chemical sensing in two dimensional porous covalent organic nanosheets. *Chem. Sci.* **2015**, *6*, 3931–3939. [CrossRef]

122. Dalapati, S.; Jin, E.Q.; Addicoat, M.; Heine, T.; Jiang, D.L. Highly Emissive Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2016**, *138*, 5797–5800. [CrossRef]

123. Xiang, Z.H.; Cao, D.P. Synthesis of Luminescent Covalent-Organic Polymers for Detecting Nitroaromatic Explosives and Small Organic Molecules. *Macromol. Rapid Commun.* **2012**, *33*, 1184–1190. [CrossRef] [PubMed]

124. Sang, N.N.; Zhan, C.X.; Cao, D.P. Highly sensitive and selective detection of 2,4,6-trinitrophenol using covalent-organic polymer luminescent probes. *J. Mater. Chem. A* **2015**, *3*, 92–96. [CrossRef]

125. Zhang, W.; Qiu, L.G.; Yuan, Y.P.; Xie, A.J.; Shen, Y.H.; Zhu, J.F. Microwave-assisted synthesis of highly fluorescent nanoparticles of a melamine-based porous covalent organic framework for trace-level detection of nitroaromatic explosives. *J. Hazard. Mater.* **2012**, *221*, 147–154. [CrossRef]

126. Cui, C.; Wang, Q.; Xin, C.; Liu, Q.; Deng, X.; Liu, T.; Xu, X.; Zhang, X. Covalent organic framework with bidentate ligand sites as reliable fluorescent sensor for Cu2+. *Microporous Mesoporous Mater.* **2020**, *299*, 110122. [CrossRef]

127. Acharyya, K.; Mukherjee, P.S. A fluorescent organic cage for picric acid detection. *Chem. Commun.* **2014**, *50*, 15788–15791. [CrossRef] [PubMed]

128. Guan, Q.L.; Sun, Y.; Huo, R.; Xin, Y.; Bai, F.Y.; Xing, Y.H.; Sun, L.X. Cu-MOF Material Constructed with a Triazine Polycarboxylate Skeleton: Multifunctional Identify and Microdetecting of the Aromatic Diamine Family (o, m, p-Phenylenediamine) Based on the Luminescent Response. *Inorg. Chem.* **2021**, *60*, 2829–2838. [CrossRef]

129. Sun, X.; Wang, N.; Xie, Y.; Chu, H.; Wang, Y.; Wang, Y. In-situ anchoring bimetallic nanoparticles on covalent organic framework as an ultrasensitive electrochemical sensor for levodopa detection. *Talanta* **2021**, *225*, 122072. [CrossRef] [PubMed]

130. Garba, M.D.; Usman, M.; Khan, S.; Shehzad, F.; Galadima, A.; Ehsan, M.F.; Ghanem, A.S.; Humayun, M. CO_2 towards fuels: A review of catalytic conversion of carbon dioxide to hydrocarbons. *J. Environ. Chem. Eng.* **2020**, *9*, 104756. [CrossRef]

131. Yaseen, M.; Humayun, M.; Khan, A.; Usman, M.; Ullah, H.; Tahir, A.A. Preparation, Functionalization, Modification, and Applications of Nanostructured Gold: A Critical Review. *Energies* **2021**, *14*, 1278. [CrossRef]

132. Yang, Y.; Niu, H.; Xu, L.; Zhang, H.; Cai, Y. Triazine functionalized fully conjugated covalent organic framework for efficient photocatalysis. *Appl. Catal. B Environ.* **2020**, *269*, 118799. [CrossRef]

133. Hou, Y.; Cui, C.-X.; Zhang, E.; Wang, J.-C.; Li, Y.; Zhang, Y.; Zhang, Y.; Wang, Q.; Jiang, J. A hybrid of g-C3N4 and porphyrin-based covalent organic frameworks via liquid-assisted grinding for enhanced visible-light-driven photoactivity. *Dalton Trans.* **2019**, *48*, 14989–14995. [CrossRef] [PubMed]

134. Liu, Y.; Wang, Y.; Li, H.; Guan, X.; Zhu, L.; Xue, M.; Yan, Y.; Valtchev, V.; Qiu, S.; Fang, Q. Ambient aqueous-phase synthesis of covalent organic frameworks for degradation of organic pollutants. *Chem. Sci.* **2019**, *10*, 10815–10820. [CrossRef]

135. Lv, H.; Zhao, X.; Niu, H.; He, S.; Tang, Z.; Wu, F.; Giesy, J.P. Ball milling synthesis of covalent organic framework as a highly active photocatalyst for degradation of organic contaminants. *J. Hazard. Mater.* **2019**, *369*, 494–502. [CrossRef] [PubMed]

136. Lv, S.W.; Liu, J.M.; Li, C.Y.; Zhao, N.; Wang, Z.H.; Wang, S. Two novel MOFs@COFs hybrid-based photocatalytic platforms coupling with sulfate radical-involved advanced oxidation processes for enhanced degradation of bisphenol A. *Chemosphere* **2020**, *243*, 125378. [CrossRef]

137. Preet, K.; Gupta, G.; Kotal, M.; Kansal, S.K.; Salunke, D.B.; Sharma, H.K.; Chandra Sahoo, S.; Van Der Voort, P.; Roy, S. Mechanochemical Synthesis of a New Triptycene-Based Imine-Linked Covalent Organic Polymer for Degradation of Organic Dye. *Cryst. Growth Des.* **2019**, *19*, 2525–2530. [CrossRef]

138. Wang, R.-L.; Li, D.-P.; Wang, L.-J.; Zhang, X.; Zhou, Z.-Y.; Mu, J.-L.; Su, Z.-M. The preparation of new covalent organic framework embedded with silver nanoparticles and its applications in degradation of organic pollutants from waste water. *Dalton Trans.* **2019**, *48*, 1051–1059. [CrossRef] [PubMed]

139. Yao, Y.; Hu, Y.; Hu, H.; Chen, L.; Yu, M.; Gao, M.; Wang, S. Metal-free catalysts of graphitic carbon nitride–covalent organic frameworks for efficient pollutant destruction in water. *J. Colloid Interface Sci.* **2019**, *554*, 376–387. [CrossRef]

140. Ma, R.; Liu, N.; Lin, T.-T.; Zhao, T.; Huang, S.-L.; Yang, G.-Y. Anderson polyoxometalate built-in covalent organic frameworks for enhancing catalytic performances. *J. Mater. Chem. A* **2020**, *8*, 8548–8553. [CrossRef]

141. Wei, Y.; Zhang, F.; Hao, J.; Ling, Y.; Gong, Y.; Wang, S.; Wei, J.; Yang, Z. Boosting the photocatalytic performances of covalent organic frameworks enabled by spatial modulation of plasmonic nanocrystals. *Appl. Catal. B Environ.* **2020**, *272*, 119035. [CrossRef]

142. Kang, Z.X.; Peng, Y.W.; Qian, Y.H.; Yuan, D.Q.; Addicoat, M.A.; Heine, T.; Hu, Z.G.; Tee, L.; Guo, Z.G.; Zhao, D. Mixed Matrix Membranes (MMMs) Comprising Exfoliated 2D Covalent Organic Frameworks (COFs) for Efficient CO_2 Separation. *Chem. Mater.* **2016**, *28*, 1277–1285. [CrossRef]

143. Biswal, B.P.; Chaudhari, H.D.; Banerjee, R.; Kharul, U.K. Chemically Stable Covalent Organic Framework (COF)-Polybenzimidazole Hybrid Membranes: Enhanced Gas Separation through Pore Modulation. *Chem. Eur. J.* **2016**, *22*, 4695–4699. [CrossRef]

144. Liu, Y.T.; Wu, H.; Wu, S.Q.; Song, S.Q.; Guo, Z.Y.; Ren, Y.X.; Zhao, R.; Yang, L.X.; Wu, Y.Z.; Jiang, Z.Y. Multifunctional covalent organic framework (COF)-Based mixed matrix membranes for enhanced CO_2 separation. *J. Membr. Sci.* **2021**, *618*, 9. [CrossRef]

145. Xiong, S.H.; Li, L.; Dong, L.; Tang, J.T.; Yu, G.P.; Pan, C.Y. Covalent-organic frameworks (COFs)-based membranes for CO_2 separation. *J. CO2 Util.* **2020**, *41*, 12. [CrossRef]

146. Wang, X.; Shi, X.; Wang, Y. In Situ Growth of Cationic Covalent Organic Frameworks (COFs) for Mixed Matrix Membranes with Enhanced Performances. *Langmuir* **2020**, *36*, 10970–10978. [CrossRef] [PubMed]

147. Yang, H.; Wu, H.; Yao, Z.Q.; Shi, B.B.; Xu, Z.; Cheng, X.X.; Pan, F.S.; Liu, G.H.; Jiang, Z.Y.; Cao, X.Z. Functionally graded membranes from nanoporous covalent organic frameworks for highly selective water permeation. *J. Mater. Chem. A* **2018**, *6*, 583–591. [CrossRef]

148. Xu, L.; Xu, J.; Shan, B.T.; Wang, X.L.; Gao, C.J. TpPa-2-incorporated mixed matrix membranes for efficient water purification. *J. Membr. Sci.* **2017**, *526*, 355–366. [CrossRef]

149. Xu, L.; Yang, T.; Li, M.; Chang, J.; Xu, J. Thin-film nanocomposite membrane doped with carboxylated covalent organic frameworks for efficient forward osmosis desalination. *J. Membr. Sci.* **2020**, *610*, 118111. [CrossRef]

150. Tan, Z.; Chen, S.; Peng, X.; Zhang, L.; Gao, C. Polyamide membranes with nanoscale Turing structures for water purification. *Science* **2018**, *360*, 518–521. [CrossRef] [PubMed]

151. Khan, N.A.; Yuan, J.; Wu, H.; Cao, L.; Zhang, R.; Liu, Y.; Li, L.; Rahman, A.U.; Kasher, R.; Jiang, Z. Mixed Nanosheet Membranes Assembled from Chemically Grafted Graphene Oxide and Covalent Organic Frameworks for Ultra-high Water Flux. *ACS Appl. Mater. Interfaces* **2019**, *11*, 28978–28986. [CrossRef] [PubMed]

152. Berlanga, I.; Ruiz-González, M.L.; González-Calbet, J.M.; Fierro, J.L.G.; Mas-Ballesté, R.; Zamora, F. Delamination of Layered Covalent Organic Frameworks. *Small* **2011**, *7*, 1207–1211. [CrossRef] [PubMed]

153. Chandra, S.; Kandambeth, S.; Biswal, B.P.; Lukose, B.; Kunjir, S.M.; Chaudhary, M.; Babarao, R.; Heine, T.; Banerjee, R. Chemically Stable Multilayered Covalent Organic Nanosheets from Covalent Organic Frameworks via Mechanical Delamination. *J. Am. Chem. Soc.* **2013**, *135*, 17853–17861. [CrossRef]

154. Yang, H.; Yang, L.; Wang, H.; Xu, Z.; Zhao, Y.; Luo, Y.; Nasir, N.; Song, Y.; Wu, H.; Pan, F.; et al. Covalent organic framework membranes through a mixed-dimensional assembly for molecular separations. *Nat. Commun.* **2019**, *10*, 1–10. [CrossRef]

155. Yao, J.; Liu, C.; Liu, X.; Guo, J.; Zhang, S.; Zheng, J.; Li, S. Azobenzene-assisted exfoliation of 2D covalent organic frameworks into large-area, few-layer nanosheets for high flux and selective molecular separation membrane. *J. Membr. Sci.* **2020**, *601*, 117864. [CrossRef]

156. Li, G.L.; Wang, W.; Fang, Q.L.; Liu, F. Covalent triazine frameworks membrane with highly ordered skeleton nanopores for robust and precise molecule/ion separation. *J. Membr. Sci.* **2020**, *595*, 9. [CrossRef]