



Perspective

On-Surface Synthesis and Applications of 2D Covalent Organic Framework Nanosheets

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Abstract: Covalent organic framework nanosheets (COF nanosheets) are two-dimensional crystalline porous polymers with in-plane covalent bonds and out-of-plane Van der Waals forces. Owing to the customizable structure, chemical modification, and ultra-high porosity, COF nanosheets show many fascinating properties unique to traditional two-dimensional materials, and have shown potential applications in gas separation, sensors, electronic, and optoelectronic devices. This minireview aims to illustrate recent progress on two-dimensional covalent organic framework nanosheets, from two aspects of on-surface synthesis and potential applications. We first review the synthesis of COF nanosheets at the gas–solid interface. On-surface synthesis under ultrahigh vacuum and on-surface synthesis under vapor are highlighted. In addition, we also review the liquid–solid interface synthesis of COF nanosheets at various substrates, i.e., both crystalline and amorphous substrates. Beyond the synthesis, we highlight state-of-the-art applications of the COF nanosheets, particularly in charge transport, chemical sensors, and gas separation.

Keywords: on-surface synthesis; covalent organic framework; thin film; device application; scanning tunneling microscopy



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1. Introduction

Covalent organic frameworks (COFs) are long-range, ordered, covalently bonded polymers, showing crystallinity and porosity [1–3]. COFs form via covalently bonding molecular building blocks [4]. Due to their fascinating properties, including thermal stability and rich chemical/physical properties, COFs have shown potential applications in many emerging fields, such as catalysts [5], sensors [6,7], gas separation [8,9], and energy storage [10,11]. Furthermore, the pore size of COFs can also be artificially regulated to achieve the specific properties, which can broaden the scope of their application [12–14].

Covalent organic framework nanosheets (COF nanosheets), derived from COFs, are two-dimensional materials with in-plane covalent bonds and out-of-plane weak Van der Waals forces. Due to the rich architecture and ultra-high porosity, COF nanosheets show many fascinating properties unique to other 2D materials and have been applied in gas separation [15], sensors [7], and optoelectronic devices [16–18]. COF nanosheets have attracted extensive research interest, and currently COF reviews mainly focus on the solution-based synthesis of COF powder and nanosheets [19–21]. Reviews on the substrate-supported synthesis of COF nanosheets are still rare.

In this minireview, we will summarize recent progress on the on-surface synthesis and state-of-the-art applications of COF nanosheets. We first review the history of COF nanosheets in Section 2. In Section 3, we summarize the COF nanosheet synthesis at the gas–solid interface, including on-surface synthesis under ultrahigh vacuum and on-surface synthesis under vapor. In Section 4, we illustrate the COF nanosheet synthesis at the

liquid–solid interface. Lastly, in Section 5, we highlight the applications of COF nanosheets in charge transport, chemical sensors, and gas separation.

2. The History of COF Nanosheets

The first COF was reported by Yaghi and Adrien P. Côté et al. in 2005 via solution-based wet chemistry [22]. A condensation reaction of 1,4-benzenediboronic acid (BDDBA) precursors was employed to synthesize COF-1 (Figure 1a) under 120 °C by heating for 72 h in the mesitylene-dioxane solution. These circumstances made it possible for the BDDBA dehydration to gradually carry on, which benefits the crystallite growth. The COF-5 was also synthesized via a dehydration reaction between BDDBA and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP), as shown in Figure 1a. Powder X-ray diffraction (PXRD) was carried out to characterize the as-synthesized COFs shown in Figure 1b, which verified that the crystalline COF-1 and COF-5 were indeed obtained. Based on the powder XRD, structural models of COF-1 and COF-5 are proposed in Figure 1c by exchanging the place of certain atoms in graphite. After that, various kinds of COFs have been synthesized by using various molecular units or different types of chemical reactions [23–28].

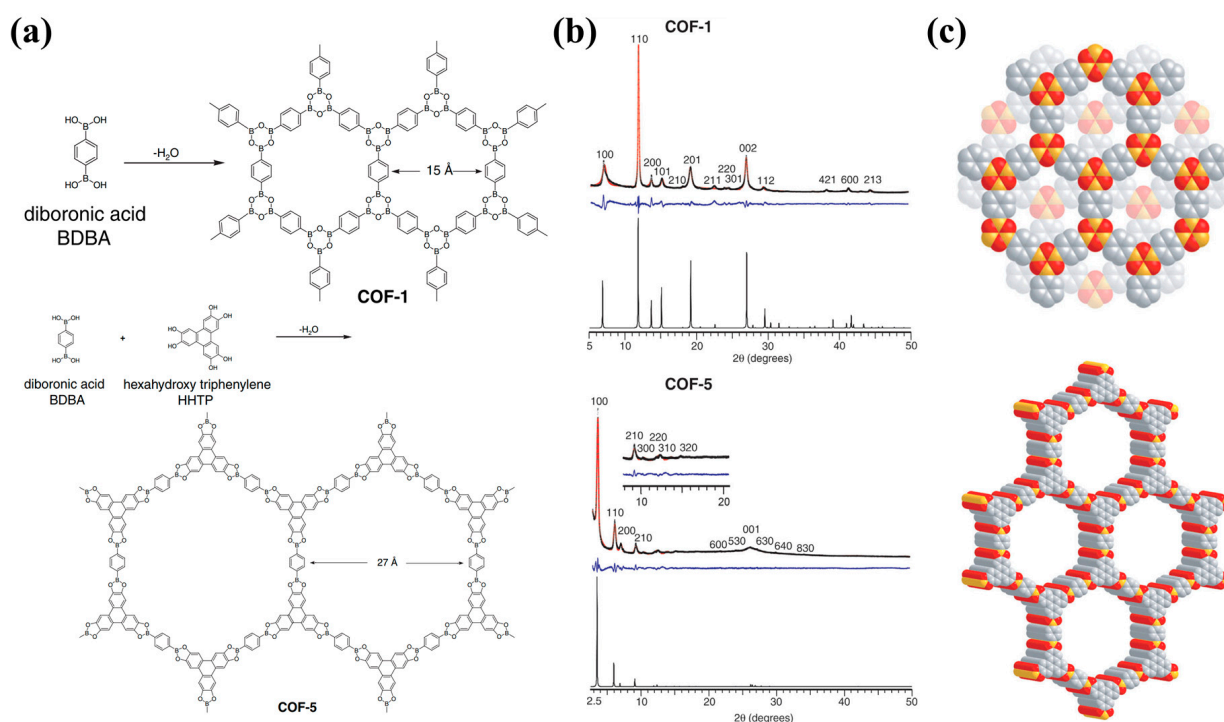


Figure 1. Two kinds of COFs obtained via traditional solution-based wet chemistry. (a) Condensation reactions of boronic acids used to synthesize COF-1 and COF-5, respectively. (b) X-ray analysis of COF-1 and COF-5 structures, and the corresponding calculated powder XRD. (c) Structural models of COF-1 and COF-5, where carbon, boron, and oxygen are represented as gray, orange, and red spheres, respectively. Figures are reproduced with permission from Ref. [15], Copyright © 2005, AAAS.

In 2007, Grill and Hecht et al. came up with a method of on-surface synthesis to construct organic networks via covalently bonding molecular units on an Au (111) surface under ultrahigh-vacuum [29]. The basic principle is that, via exciting molecular units with functional substituent groups on the metal crystal by heating, the substituent groups dissociate from molecules, and then cross-linkages form between activated molecular units. Figure 2a shows STM images of three kinds of covalent organic nanostructures formed on the Au (111) surface. By changing molecular units with different substituent groups at different sites using Br-TPP (5-(4-Bromophenyl)-10,15,20-tri(phenyl)porphyrin), Br₂-TPP (5,15-Bis(4-bromophenyl)-10,20-bisphenylporphyrin), and Br₄-TPP (tetra (4-bromophenyl)

porphyrin) as precursors, respectively, the final organic nanostructures of dimers, one-dimensional chains, and two-dimensional networks were obtained on the Au (111) substrate. Corresponding chemical structures of the organic nanostructures are presented in Figure 2b. On-surface synthesis has emerged as a powerful method to obtain 2D COF monolayers on the surface under high vacuum [30–36]. Since the COF sheets show good charge transport, these research works help us to design the functionalized nanostructures, integrating the electronics, optics, and magnetism [37,38]. This will definitely benefit the application of COFs in molecular electronic devices.

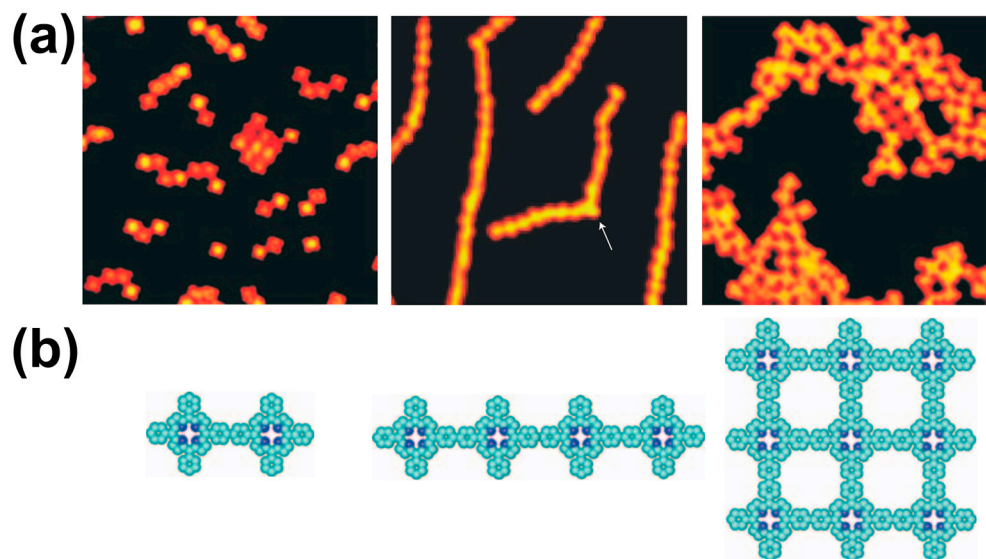


Figure 2. On-surface synthesis of COF monolayer under high vacuum. (a) STM images of three kinds of organic nanostructures formed on the Au (111) surface using precursors of Br-TPP, Br₂-TPP, and Br₄-TPP, respectively. (b) Corresponding chemical structures of the organic nanostructures. Figures are reproduced with permission from Ref. [21], Copyright © 2007, Springer Nature.

3. Methods to Prepare COF Nanosheets

The methods to synthesize COF nanosheets can be categorized as the top-down approach or the bottom-up approach [2,39]. Although bottom-up approaches make it easier to control the sample thickness and orientation of COF nanosheets, the top-down approach is chosen more often for practical applications due to its simplicity and scalability.

The basic principle of the top-down strategy is to exfoliate the as-synthesized layered COF bulk into COF nanosheets [2]. This strategy mainly consists of mechanical exfoliation (ME) and liquid phase exfoliation (LPE) [40,41]. ME refers to a method of repeatedly sticking and peeling bulk COFs by transparent tape to obtain 2D thin films. The advantages of the ME method are low cost, easy operation, and the high quality of materials obtained, while the drawbacks are low yield and the difficulty to obtain large-scale thin films. By providing external energy, the LPE method can destroy the Van der Waals force between layers, so that the layered bulk COFs disintegrate into 2D few-layer nanosheets. The LPE method shows advantages in simple operation, such as easy expansion and high yield, while the final products may have a small domain size and structural defects.

On the other hand, the bottom-up strategy is applied on the surface and/or at various interfaces to synthesize porous nanosheets through various coupling reactions, such as Ullman coupling, imine coupling, the boronic dehydration reaction, and so on. Several bottom-up methods, including on-surface synthesis under high vacuum, vapor-assisted synthesis, and solid–liquid interface synthesis, are illustrated below.

3.1. On-Surface Synthesis

Zwaneveld et al. reported surface covalent organic frameworks (SCOFs, a kind of COF nanosheet) in 2008 [35]. The SCOF-1 was synthesized by the dehydration reaction of BDBA precursors, and another type of COF (SCOF-2) was synthesized by the condensation reaction between BDBA and HHTP precursors. The precursors were sublimated by heating under ultra-high vacuum (UHV), and then deposited on an Ag (111) substrate. The side products, such as H₂O, formed on the surface, were finally removed by sample annealing. The network structures remained intact after annealing, suggesting thermal stability and structural permanence. The STM technique was employed to in situ-probe the morphology of the samples. The pore sizes can be directly measured by high-resolution STM images, which shows that the pore size can be regulated from 15.3 Å to 29.8 Å, as in Figure 3a,b, respectively. Their work was the early attempt to synthesize a large, stable, and size-controllable COFs.

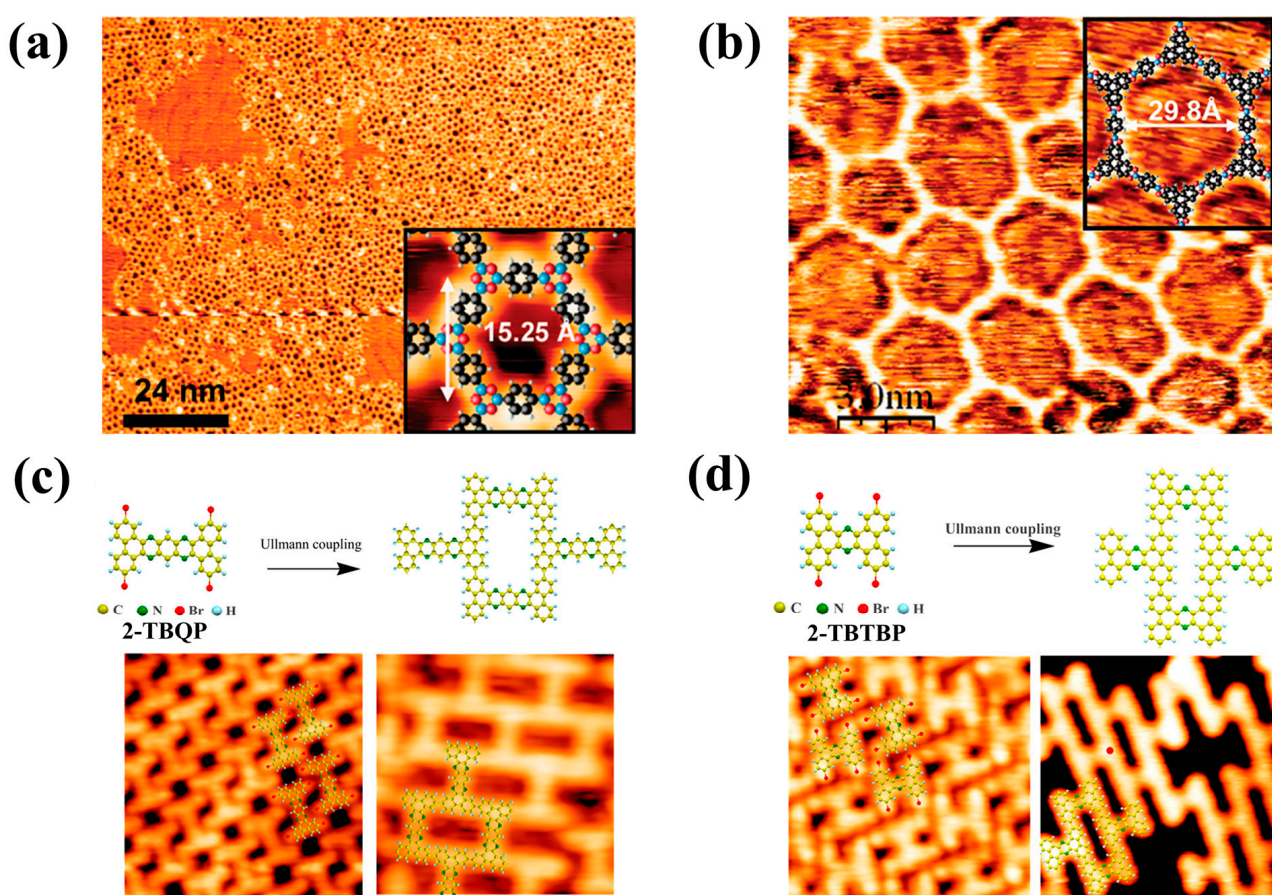


Figure 3. Custom-designed COF monolayers via on-surface synthesis. (a,b) STM images of SCOF-1 and SCOF-2 networks. The apertures of SCOF-1 and SCOF-2 are 15.25 Å and 29.8 Å, respectively. The insets show the overlaid chemical structures obtained by DFT calculations. Pentagonal and heptagonal structures, resulting from defects in covalent bond formation, can be observed in (b). (c) Chemical structure, corresponding STM images of self-assembly, and monolayer carbon nitride (4N-doping carbon nitride) after annealing, image size: 6 nm × 6 nm. (d) Chemical structure, corresponding STM images of self-assembly, and monolayer carbon nitride (2N-doping carbon nitride) after annealing, image size: 6 nm × 6 nm. (a,b) Figures are reproduced with permission from Ref. [35], Copyright © 2008, American Chemical Society. (c,d) Figures are reproduced with permission from Ref. [42], Copyright © 2020, American Chemical Society.

In 2020, a single-layer carbon nitride 2D network with control over the pore sizes and nitrogen-doping was synthesized by Wang et al. [42,43]. After being sublimated from a Knudsen effusion cell under UHV conditions, 2-TBQP precursors were deposited onto an Au (111) substrate at room temperature to obtain a self-assembly structure, as shown in Figure 3c. After annealing the sample, a 2D carbon nitride monolayer with adjusted nanopores and expected nitrogen doping was obtained via Ullman cross-coupling of the precursors. Using a different precursor of 2-TBTBP, another carbon nitride monolayer was also obtained in Figure 3d. The high-resolution STM images indicate that the carbon nitride monolayer can be tailored in N-doping level, pore sizes, and dimensions (1D or 2D). An atomic-scale investigation of the heteroatom-doped carbon was achieved.

3.2. Vapor-Assisted Synthesis

SCOFs obtained via on-surface synthesis are polycrystalline with defects and are always small in size. To promote the large-area synthesis of COF thin films, reversible reactions with self-repair ability were employed by Wan et al. [44,45]. The schematic diagram is shown in Figure 4a,b. Precursor A was drop-casted onto the substrate surface. Precursor B, with a low vaporization point, and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were also introduced into a closed reactor. After heating the reactor, precursor B will vaporize and react with precursor A on the surface. The introduced $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ can maintain a water vapor environment to regulate the reversible dehydration reaction. As a result, highly ordered SCOF-1 forms on the highly oriented pyrolytic graphite (HOPG) substrate. Using a similar vapor-assisted strategy, other large-area SCOFs were also obtained using various precursors.

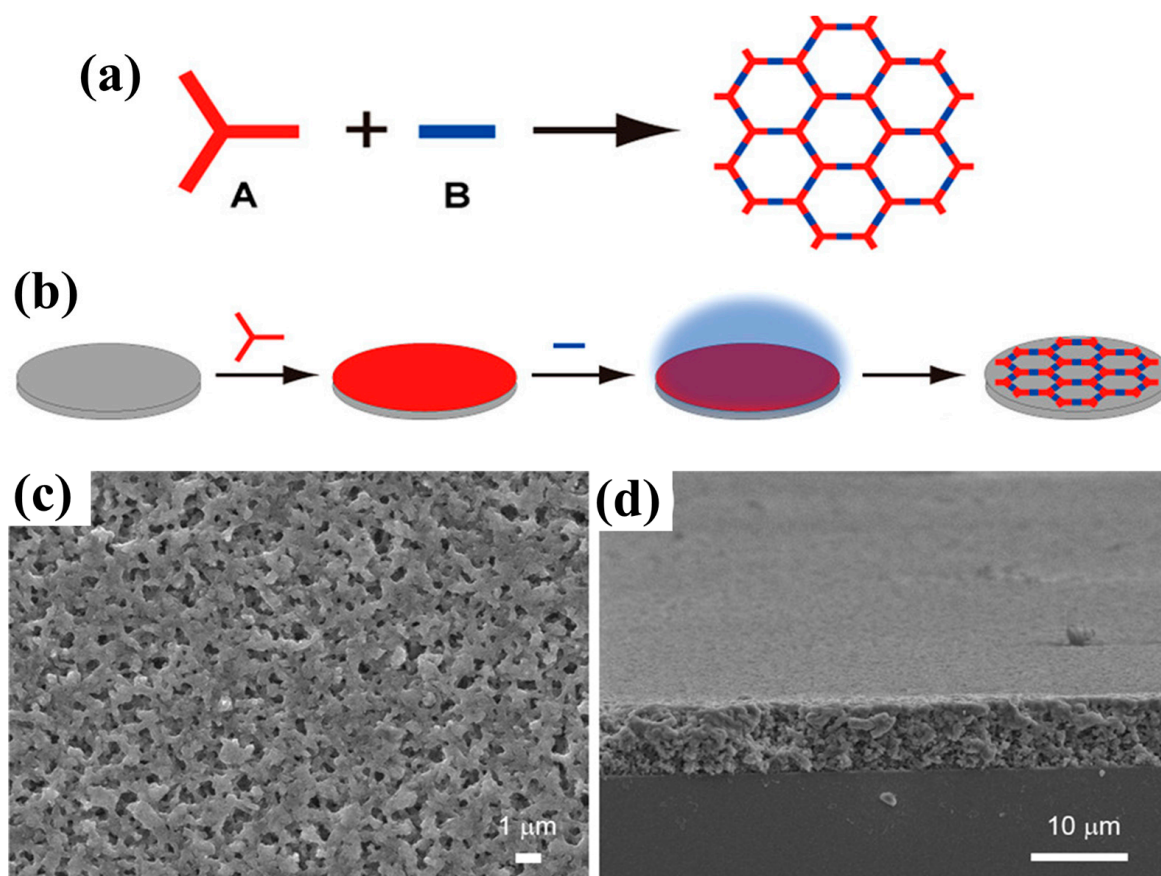


Figure 4. Cont.

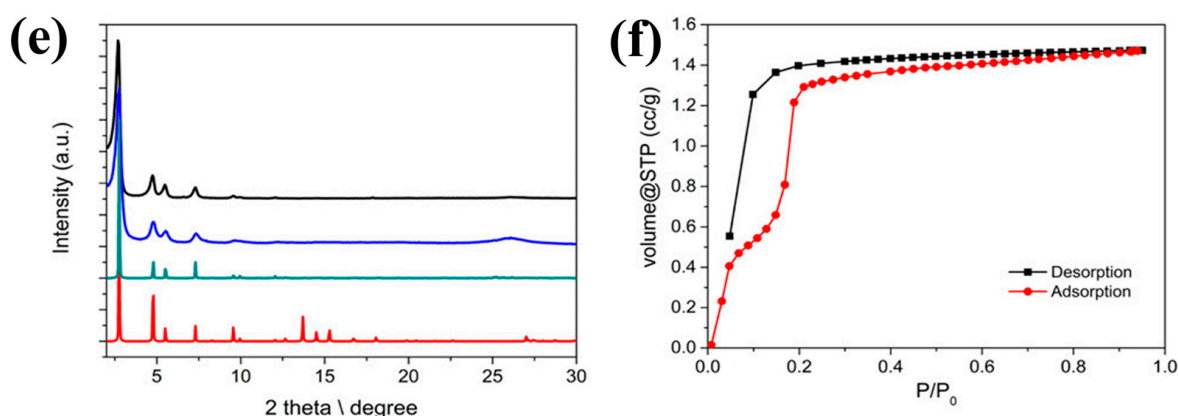


Figure 4. Vapor-assisted synthesis of large-area SCOFs. (a,b) Schematic diagrams of SCOFs' formation. (c,d) Top view and cross-section SEM images of BDT-COF thin film. (e) Experimental powder X-ray diffraction (PXRD) pattern of a BDT-COF film synthesized on an amorphous glass substrate by vapor-assisted reaction (black), solvothermal synthesis (blue), simulated PXRD patterns based on an eclipsed AA stacking (green), and a staggered AB stacking (red). (f) Krypton sorption isotherm of degassed BDT-COF thin film on an amorphous glass substrate. (a,b) Figures are reproduced with permission from Ref. [45], Copyright © 2013, American Chemical Society. (c–f) Figures are reproduced with permission from Ref. [46], Copyright © 2015, American Chemical Society.

Vapor-assisted on-surface synthesis is also feasible for forming COFs on amorphous substrates. Dana et al. reported in 2015 that the BDT-COF, COF-5, and pyrene-COF films were obtained on an amorphous glass substrate [46]. Precursor 1 was dissolved in organic solvent, and the solution was drop-casted onto the amorphous glass substrate. The glass substrate was put into a closed reactor containing precursor 2 vapor and reacted for 72 h at room temperature. The as-synthesized COFs have been characterized by SEM, PXRD, and sorption isotherm, as shown in Figure 4c–f, suggesting that a crystalline COF film can be grown on an amorphous substrate. Their work shows that the vapor-assisted synthesis was an effective way to prepare the COF thin films.

3.3. Solid–Liquid Interface Synthesis

The COF nanosheets can also be synthesized on a solid surface by using a solid–liquid interface. Zhan et al. recently reported the polymerization and crystallization process of a 2D boroxine covalent polymer at a solid–liquid interface [47]. Figure 5a shows the reaction pathway of the 2D boroxine covalent polymer, and Figure 5b shows a liquid STM image of the 2D porous polymer that was synthesized by dropping 5 μ L of a 1-octanoic acid solution of pyrene-2,7-diboronic acid (PDBA) onto a clean HOPG surface. Figure 5c presents the nucleation and growth process of the 2D boroxine covalent polymer over time, suggesting that a single domain evolved from the oligomeric nuclei to a larger 2D polymer domain. A statistical investigation was carried out based on the STM observations, revealing the key parameters for COF crystallization at the solid–liquid interface, such as the growth rate, critical nucleation size, and nucleation rate. Furthermore, Zhan et al. studied the domain coalescence process from a kinetic point of view at the single-molecule level. Figure 5d shows the crystallographic orientations, grain boundary (GB) migration rate, and grain misorientation of each GB. These investigations help us understand the polymerization and crystallization parameters for 2D COF nanosheet growth.

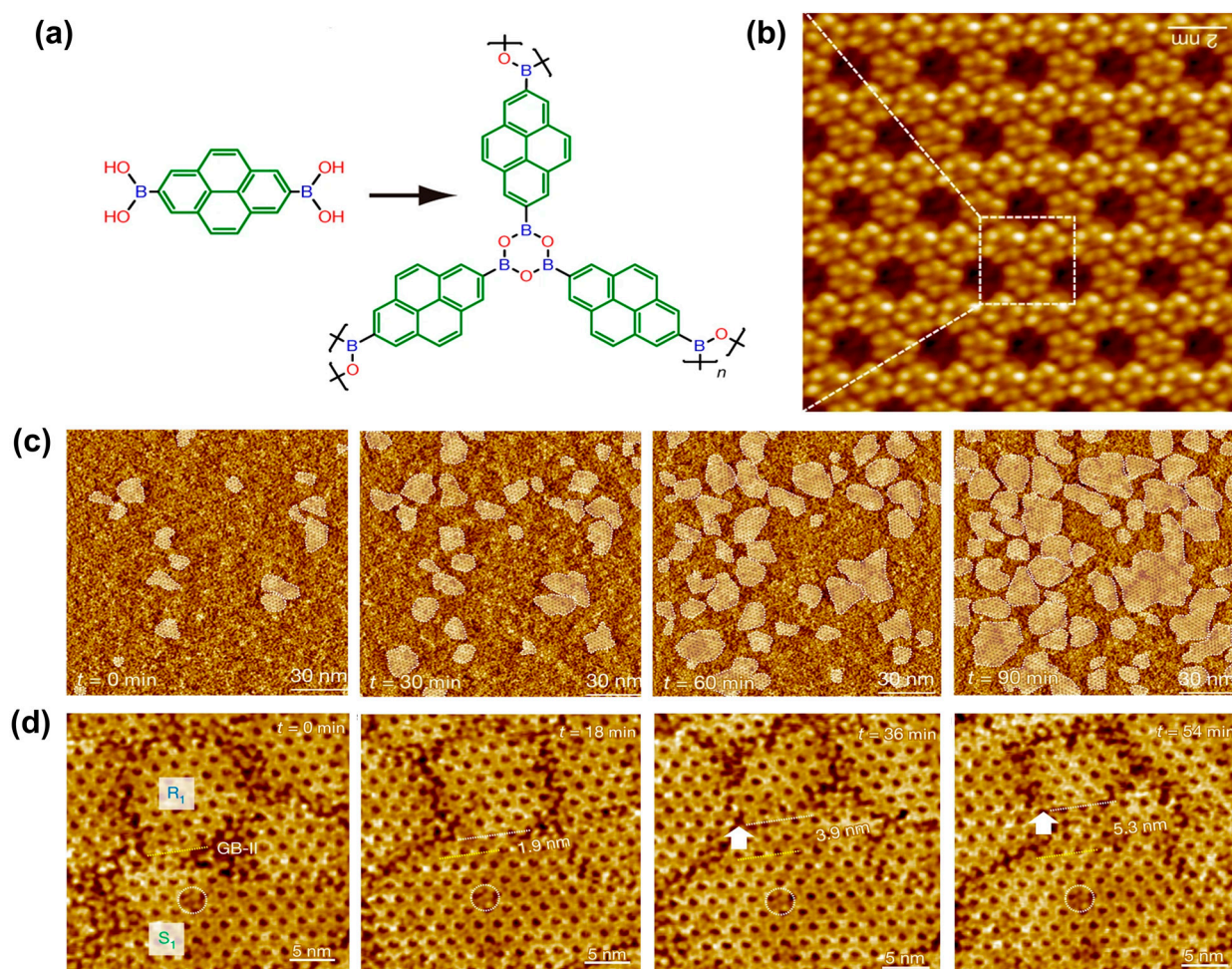


Figure 5. The polymerization process of COF nanosheet at a solid–liquid interface. (a) Reaction pathway of the 2D boroxine covalent polymer. (b) Liquid STM images of the 2D covalent polymer. The corresponding chemical structure marked by the white dashed line is shown in (a). (c) Nucleation and growth process recorded by STM, image size: 12 nm × 12 nm. (d) Liquid STM images of grain boundaries and their movement. Figures are reproduced with permission from Ref. [47], Copyright © 2022, Springer Nature.

Using a similar solid–liquid interface, Colson et al. reported the growth of COF films on a single-layer graphene (SLG) substrate [48]. Firstly, a well-known COF-5 film was synthesized on a SLG/Cu substrate, as shown in Figure 6a. The SLG/Cu substrate was prepared by growing SLG on Cu through the chemical vapor deposition method. The SLG/Cu substrate was inserted into the solution for COF film growth. Grazing incidence diffraction (GID) shows that the as-synthesized COF film on the SLG/Cu substrate has a better crystallinity compared with the COF powder (Figure 6b). To prove the universality of the synthetic method, the COF-5 films were also grown on the SLG/SiO₂ and SLG/SiC substrates, respectively. The diffraction patterns in Figure 6c,d suggest the long-range order structures, the same as that on the SLG/Cu substrate. The COF films on the SLG/Cu substrate were thicker than those on SLG/SiO₂ and SLG/SiC substrates under the same reaction time, indicating that the underlying substrate played a key role in controlling the thickness of the films. As discussed in Figure 4, COF thin films can also be grown on the amorphous glass substrates.

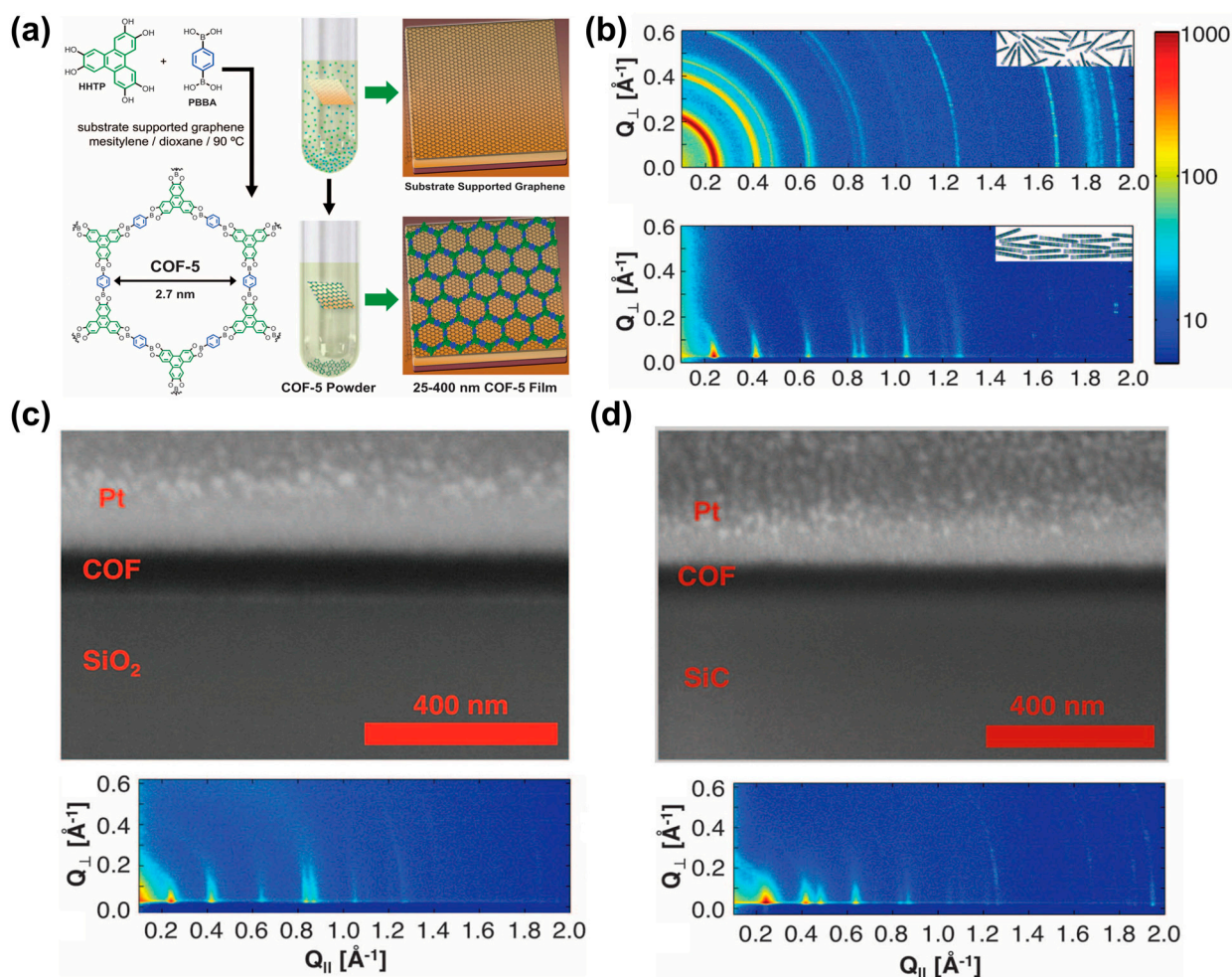


Figure 6. The solid–liquid interface growth of COF nanosheets on a single-layer graphene (SLG) substrate. (a) Chemical structure and solid–liquid interface preparation of COF-5 on the SLG/Cu substrate. (b) GID patterns of COF-5 powder (up) and COF-5 films on SLG/Cu (down). (c) SEM image of COF-5 film on SLG/SiO₂ and its GID pattern. (d) SEM image of COF-5 film on SLG/SiC and its GID pattern. Figures are reproduced with permission from Ref. [48], Copyright © 2011, AAAS.

4. Applications of COF Nanosheets

Due to their ultra-high porosity, low mass density, rich chemical/physical properties, and high structure tunability at the atomic level, 2D COF films have shown potential applications in various emerging fields [49,50], such as field effect transistors (FETs) [51,52], light-emitting diodes (LEDs) [53,54], gas separation [14,15,55], energy storage [56], and sensors [57]. A few cutting-edge applications of 2D COFs are illustrated in Figure 7. These applications of COF nanosheets are in charge transport (a–c), chemical sensors (d–f), and gas separation (g–i).

4.1. Charge Transport

Due to the high-order molecular array and structural tunability, 2D COF nanosheets can provide large amounts of channels for charge and exciton transfer, which is essential in the field of electronic devices. Frey et al. investigated the charge transportation in COFs by detecting the electrical conductivity in different directions [58]. As shown in Figure 7a, the in-plane electrical conductivity of the BTT COFs was investigated by analyzing the relationship between temperature and conductivity, showing a defect-dominated hopping type of charge transport in the COF film. The out-of-plane charge transport was obtained by conductive atomic force microscopy measurement, which was smaller than the in-plane

direction since the conjugated structure is only in-plane (Figure 7b). The pathways of charge transfer in the COF films were also stimulated in Figure 7c, which suggested that the type of charge transport in the 2D plane was hopping, and that the grain boundary formation due to the rotated COF layers reduced charge transport in the out-of-plane direction.

4.2. Chemical Sensor

Owing to their high thermal stabilities, porousness, and structural designability, COF nanosheets have also shown applications in the field of chemical sensors and biosensors [59,60]. Yuan et al. reported a chemical capacitive sensor that was made of COFs with interdigitated electrodes (IDEs) [61]. The strategy was to directly grow BTA-TAPT COF films onto IDEs to detect the benzene since the benzene molecule interacts with the triazine moieties of the COFs. Figure 7d shows the schematic representation of this chemical sensor. By monitoring the capacitance of the sensor under benzene, CO₂, CH₄, and C₃H₈, respectively, Figure 7e shows that the chemical sensor exhibited a high selectivity towards benzene, indicating a strong interaction between benzene and the COF nanosheet. The COF-based sensor was compared with other detectors or sensors, as shown in Figure 7f. The COF-based sensor shows a relatively higher level of selectivity and a lower operating temperature.

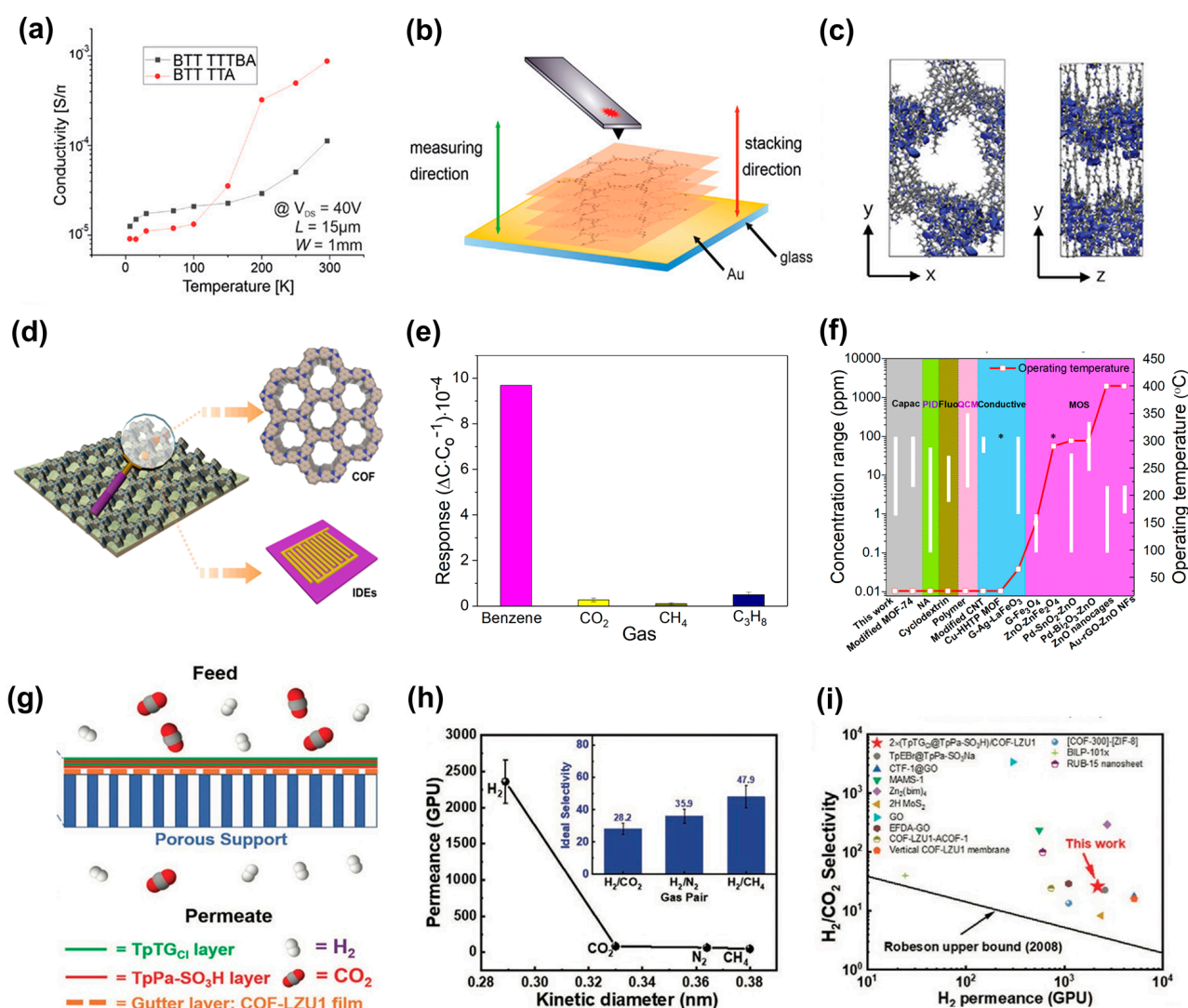


Figure 7. Applications of COF nanosheets in charge transport (a–c), chemical sensors (d–f), and gas separation (g–i). (a) In-plane conductivity performance at different temperatures. (b) Schematic

representation of conductive AFM measurements of the charge transport in the out-of-plane direction. (c) Simulations of the charge transport in the COF film based on electron affinity. (d) Schematic representation of the COF-based chemical sensor. (e) Selectivity of the sensor towards benzene, CO₂, CH₄, and C₃H₈. (f) The performance comparison with the latest types of chemical sensors. (g) Schematic representation of multilayer COF-based membranes. (h) Permeance performance for different individual-component gases. The insert illustrates the ideal selectivity for different gas mixtures. (i) The comparison of H₂/CO₂ separation performance among the state-of-the-art membranes. (a–c) Figures are reproduced with permission from Ref. [58], Copyright © 2022, Wiley-VCH GmbH. (d–f) Figures are reproduced with permission from Ref. [61], Copyright © 2022, American Chemical Society. (g–i) Figures are reproduced with permission from Ref. [62], Copyright © 2022, American Chemical Society.

4.3. Gas Separation

In addition, because of the ordered, regular, and adjustable pore structure in the framework, COF nanosheets are ideal functional films for separating gases or liquids [9,55,63–66]. Ying et al. proposed a multi-interfacial strategy to prepare COF heterojunction membranes for gas separation [62]. As shown in Figure 7g, based on the interfacial reaction between TpPa-SO₃H and Tptg_{cl}, a COF nanosheet was grown on the other kind of COF nanosheet to form a COF heterostructure with nanopores. The COF heterostructure was interfaced with a buffer layer of COF-LZU1 film to fight against resistance during gas transport. The COF bilayer number was optimal to enhance H₂ and CO₂ separation permeance and H₂/CO₂ selectivity. The permeance dramatically decreased when the kinetic diameter increased, suggesting the effective sieving ability of this membrane (Figure 7h). Compared with other membranes in Figure 7i, the COF membranes exhibited excellent performance on H₂/CO₂ separation.

5. Conclusions

COF nanosheets have emerged as a promising porous material for next-generation functional applications since the first COF-1 was synthesized in 2005. The bottom-up synthesis discussed in this minireview possesses the advantages of adjusting the film thickness, heteroatom doping, and pore sizes, which are crucial in practical applications. Two strategies of the bottom-up method were included, namely solid–gas interface synthesis and solid–liquid interface synthesis. For on-surface synthesis, the COF nanosheets are mainly synthesized under UHV conditions by evaporating the reactants on metal crystals. On-surface synthesis has been a powerful strategy for the synthesis of novel low-dimensional COF nanosheets. Combined with STM, the as-synthesized COF nanosheets can be in situ imaged at a single-molecule level. However, the order domain size of COF nanosheets obtained via on-surface synthesis is still very small, and structural defects always exist. To fix these problems, reversible chemistry was developed in the field of on-surface synthesis. For the solid–liquid interface, an in situ liquid STM study of the formation mechanism of 2D COFs growth has been reported. In addition, COF thin-film growth on both the crystalline substrate and the amorphous substrate was also discussed, suggesting the feasibility of applying the solid–liquid interface strategy to synthesize COF nanosheets on various other kinds of 2D materials or substrates for functional devices.

Finally, several examples were highlighted to illustrate the state-of-the-art applications of COF nanosheets. COF nanosheet-based devices have shown applications in charge transport, chemical sensing, gas separation membranes, and so on. These works suggest COF nanosheets as a promising 2D material for next-generation functional devices. Further research is needed to realize the large-scale preparation of highly ordered COF nanosheets.

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