Heterostructured hybrids of metal–organic frameworks (MOFs) and covalent–organic frameworks (COFs)

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Metal–organic frameworks (MOFs) and covalent–organic frameworks (COFs) with highly ordered crystalline structures show numerous advantages such as large surface areas, structural tunability, well-defined accessible pores, and thermo/chemical stability. Thus, combining different types of MOFs and COFs into one system can generate abundant MOF/COF-based hybrid nanomaterials with superior performances. In comparison to single MOFs or COFs, MOF/COF heterostructures show fantastic properties due to the synergistic effects of their different components. Accordingly, in recent years, MOF/COF-based heterostructures have received increasing attention and rapid advancements, exhibiting a broad range of potential applications in gas sorption and separation, catalysis, energy transfer, biomedicine, etc. Herein, the design principles, assembly mechanisms, synthetic approaches, and applications of different MOF/COF-based hybrids are summarized in detail. The current challenges and future perspectives for MOF/COF-based hybrids are also discussed. This review can provide deep insights into MOF/COF-based heterostructures, which will be helpful for the further development of these hybrid materials with advanced applications.

1. Introduction

Reticular chemistry focuses on the development of framework materials prepared by linking molecular building units via coordination or covalent bonding. Highly ordered crystalline metal–organic frameworks (MOFs) and covalent–organic frameworks (COFs) have attracted interest due to their structural features and advantageous properties, such as large specific surface area, programmable structures, tunable pore size, and readily available building blocks. Their applications have been explored in various fields, including gas adsorption or separation, electrocatalysis, photocatalysis, energy storage, ion batteries, biosensors, and controlled delivery. Further, MOFs/COFs have unique features of tunable pore size and periodic pores, which allow the incorporation of heteroatoms/metal coordinating moieties in a periodic way. However, some challenges still exist including their synthesis and functionalization, development of new nanostructures, and application in industry. For example, the instability of MOFs cannot meet the industry requirement of long lifetime of commercial products. Also, their commercialization requires their large-scale production with uniform properties, and the development of simple and green synthetic methods is a current challenge to achieve their mass production at a lower cost. Alternatively, COFs are rapidly expanding porous crystalline polymers that are constructed from organic building blocks via reversible covalent bonds and have gained increasing attention from scientists. Two-dimensional (2D) or 3D COFs consisting of accessible nanoscale channels or pores with uniform size and tunability have been widely prepared. Their channel structures and pore walls provide a well-defined nanospace as reaction centers, thus leading to vast applications, such as in photocatalysis, bioimaging and therapy, electrochemical energy storage and conversion, and electrocatalysis.

However, although great efforts have been focused on the preparation, nanostructure formation, and wide applications of MOFs and COFs, individually they cannot meet the specific demand in various fields due to their intrinsic features. For example, pristine MOFs show intrinsic deficiencies such as unsatisfactory stability and limited electrical conductivity and functionality. Moreover, although COFs show enhanced chemical stability, their specific surface areas and degree of crystallinity are poor. Therefore, the hybridization of MOFs and COFs has been intensively studied to obtain superior performances (Fig. 1). For instance, the good photoconductivity and/or fast charge transfer features of COFs can remedy poor conductivity of MOFs or can promote the separation ability of photogenerated electrons and holes in MOF/COF-based hybrids. Consequently, the photoelectrochemical and electrochemical properties are improved, and thus MOF@COF hybrids...
can be employed for the construction of sensors to detect various targets. Moreover, the photocatalytic efficiency of MOF/COF-based hybrids also can be greatly enhanced, broadening their applications in the field of photocatalysis. Besides, MOF/COF hybrids possess an enhanced surface area and large pore volume due to the formation of quasi-micro-scaled pores at the interface between MOFs and COFs, thus manifesting enhanced hydrogen uptake capacity in the field of energy storage. By integrating different functionalized MOF and COFs, various fantastic properties are generated due to the synergistic effects of each component for extensive applications in diverse fields. For instance, MOFs with large specific surface areas can serve as carriers for loading drugs, photosensitizers, and near infrared dyes, while some COFs with strong photothermal conversion or efficient reactive oxygen species can be explored as photothermal therapy (PTT) and photodynamic therapy (PDT) agents. These hybrids possess the merits of each component, showing synergistic effects such as chemotherapy, PTT, PDT, and imaging ability. Thereby, different types of MOF- and COF-hybrids have also been developed to further widen their potential applications in gas storage and separation, catalysis, batteries, and biomedicine and biosensing.

According to the nanostructures and components, diverse MOF/COF-based heterostructures have been manufactured, including MOF-on-MOF (core–shell or layered structure), MOF@COF, and COF-to-COF (or COF@COF). This review outlines the recent advances on MOF/COF-based hybrids, including the classification, design principles, synthetic approaches, and applications of different MOF/COF-based hybrids (Fig. 2). Although there are many reviews on the design principles and methods for the synthesis of MOFs and COFs, the heterostructures of MOFs/COFs have rarely been explored. Haldar et al. reviewed the hierarchical assemblies of MOF-on-MOF heterostructures, in which the layer-by-layer (LBL) and liquid-phase epitaxy (LPE) approaches for the preparation of surface-anchored MOF thin films and one-pot synthesis methods for these hierarchically designed structures, as well as their applications were discussed. In addition, Liu’s group discussed the current advancements on the combination of MOFs and COFs, in which only MOF@COF composites, ranging from their synthesis to enhanced applications, were provided. Zhang et al. also reviewed crystalline porous materials for electrochemical energy storage application, which summarized several hybridization techniques according to the dimensionality of hybridization. Recently, a similar review was reported by Chen et al., which focused on the synthetic approaches for MOF/COF hybrids and their applications. Herein, a comprehensive overview of the nanostructure formation, synthesis approaches, and diverse applications of these hybrids is provided with particular focus on the following aspects: (1) the classification of MOF- and COF-related hybrids with specific nanostructures (Section 2), (2) the design principles and approaches for the synthesis of MOF- and COF-related hybrids (Section 3), (3) the detailed applications and functions of MOF- and COF-based hybrids (Section 4), and (4) the present challenges and future prospects for these hybrids (Section 5). This work aims to review the development progress,
state-of-the-art designs of hybrid nanostructures, synthetic strategies, and different applications of MOF- and COF-related hybrids to provide insights into the construction of MOF/COF hybrids and deep understanding in this field.

2. Heterostructures and hybrid types of MOFs/COFs

Hybridizing diverse types of MOFs/COFs is a promising strategy to manipulate their compositions and structures and precisely tune their basic properties (such as structural flexibility, ordered pores, high surface area, and chemical functionality). MOF/COF-based heterostructures and hybrids with precise heterostructures tend to efficiently provide vast possibilities to extend their applicability. The following discussion focuses on the construction mechanism of different types of heterostructured MOF/COF-based hybrid materials.

2.1 MOF-on-MOF heterostructures

MOF-on-MOF hybrid materials are generated by introducing various organic ligands after crystal nucleation, which can conjugate two or more different types of MOFs into one whole MOF-on-MOF hybrid material. Generally, these hybrids include two categories of architectures, namely one MOF fully enclosed by another MOF (called core–shell MOF@MOF) and one MOF grown on another MOF surface in an isotropic/anisotropic manner (called layered MOF-on-MOF). Usually, in the notation for MOF@MOF heterostructures, that on the left is the core MOF and that on the right is the grown MOF. The introduction of different MOF crystals has been extensively applied to form different types of core–shell MOF@COF heteropitaxial crystals, while maintaining the intrinsic features of MOF crystals. As early as 2009, Sakata and Kitagawa’s group synthesized a core–shell MOF@MOF hybrid using the epitaxial growth approach. In 2015, Yamauchi’s group developed core–shell ZIF-8@ZIF-67 nanohybrids through a seed-mediated growth method. Subsequently, great efforts have been devoted to developing diverse ZIF@ZIF heterostructures. Coordinating the lattice of the second metal building unit with that of the first MOF core is essential in the construction of MOF@MOF hybrids. For example, MIL (Materials of Institute Lavoisier) MOFs, ZIF (Zeolitic Imidazolate Framework), PBAs (Prussian blue analogs), and other types of nanoMOF nanostructures are usually used as the core and embedded within a second MOF layer. Core–shell MOF-on-MOF heterostructures can combine the superior properties of their core and shell MOFs and substantially overcome the shortcomings of single MOFs. Their enhanced synergistic selective performance can be designed through the lattice choice and synthetic route for application in catalysis, sorption or separation, and molecular recognition. Therefore, these materials often exhibit specific features that differentiate them from individual MOFs.

Further, layered MOF-on-MOF structures are prepared using the initial MOF layer as a substrate, on which another MOF grows in situ. Heterostructured and layered MOF-on-MOF can be synthesized via the liquid phase epitaxial and vapor phase growth methods. In 2017, Eddaoudi’s group reported a synthetic strategy to precisely control the epitaxial growth of an MOF-on-MOF film, i.e., ordered hierarchical Cu-tho-MOF-5 on HKUST-1 structure. Takahashi’s group presented a strategy for the macroscopic length scale precise alignment of multiple layers of MOF-on-MOF films, which were fabricated by epitaxially matching the interface. An oriented Cu(OH)2 film acted as the substrate to form the first Cu(OH)(BPDC) (BPDC = bipyridine-5,5′-dicarboxylate) MOF layer via a “one-pot” approach. Then, the second Cu(BPDC)2 (BPDC = 2,2′- bipyridine-5,5′-dicarboxylate) MOF was deposited via liquid-phase epitaxy. Simultaneously, the layered MOF-on-MOF thin film was achieved via van der Waals interactions, favoring the formation of highly oriented MOF-on-MOF thin films. Hence, layered MOF-on-MOF heterostructures provide a good opportunity to construct MOF films with a controllable layer thickness, good orientation and crystallinity.

MOFs with similar lattices can easily form MOF@MOF hybrids. In 2012, Oh’s group developed a series of MOF@MOF heterostructures, including MIL-68@MIL-68–Br, MIL-88B@MIL-88A, MIL-68@MOF-NDC, MIL-68@MIL-68–Br, and MIL-68@MIL-68–X (X = NO2 or NH2). With the development of synthetic approaches for MOF@MOF heterostructures, MOFs with diverse lattice crystals also can be conjugated to form hybrids such as MIL-801@Ni-MOF-74, HKUST-1@MOF-5, UIO-67@HKUST-1, HKUST-1@IMOF-18, UIO-66@MIL-88B(Fe), UIO-67@MIL-88C(Fe), PCN-68@MOF-5, and UIO-66@ZIF-8. and other types of Zn-MOF-on-Zr-MOF and Fe-MOF-on-Tb-MOF through the MOF-on-MOF strategy.

2.1.1 MIL-based MOF-on-MOF. A series of MOF-on-MOF heterostructures, including Fe–MIL-88B@Ga–MIL-88, MIL-68@MIL-68–X, MIL-68@MIL-68–Br, MIL-88B@MIL-88A, In–MIL-68@MIL-68–X, has recently been designed and synthesized via the anisotropic growth method. In 2012, Oh’s group prepared MOF-MOF heterostructures using Fe–MIL-88B, In–MIL-88B and Ga–MIL-88B. The 3D hexagonal Fe–MIL-88B nanorods were comprised of FeO6 octahedral trimers, which were connected to the building block of BDC (BDC = 1,4-benzenedicarboxylate) (Fig. 3a). The resulting Fe–MIL-88B then served as a template for the preparation of the secondary MOF. Subsequently, the Fe–MIL-88B@m-MIL-88B heterostructure was prepared by consecutively growing secondary metal clusters (H2BDC and Mn(NO3)3, M = Ga3+ or In3+) using the solvothermal method, resulting in multiple functional and modulated properties. They also synthesized the core–shell MIL-68@MIL-68–Br, where the MIL-68 template was initially synthesized, followed by isotopically growing MIL-68–Br (Fig. 3b). Owing to the similar nanostructures of the first MIL-68 and the MIL-68–Br layer, the core–shell MIL-68@MIL-68–Br hybrid was obtained. The detailed characterizations revealed that using the crystalline MIL-68 resulted in the formation of an MIL-68–X shell on the MIL-68 surface. However, the MIL-68–X structures showed poor crystallinity when the template was not used. By contrast, the enhanced crystallinity of MIL-68–X remarkably improved their porosities and surface areas. Especially, MIL-68–NH2 with high crystallinity had a substantially larger surface...
area than that with low crystallinity. A similar result was obtained for MIL-68@MIL-68–X (X = NO₂ or NH₃), which was prepared (Fig. 3c) by reacting H₂BDC–NO₂ with In(NO₃)₃ with the help of the crystalline MIL-68, resulting in the oriented growth of MIL-68–NO₂ on the surface of MIL-68. ⁴⁰

Moreover, Oh’s group developed the MIL-88B@MIL-88A heterostructure through the unbalanced MOF-on-MOF growth method (Fig. 3d). Given their similar 3D hexagonal structural but mismatched cell parameters, the preparation of MIL-88A on MIL-88B gave rise to an atypical MIL-88B@MIL-88A with an off-centered core. Nano-sized hexagonal MIL-88B rods with a 3D hexagonal structure were synthesized, and then used as a template to grow MIL-88A and form the core–shell MIL-88B@MIL-88A hybrid. ⁴⁹

Based on previous work, Oh’s group constructed a core–shell MOF hybrid using the isotropic or anisotropic growth approach (Fig. 3e). The MIL-88B and MIL-88C nanostructures exhibited different chemical structures and/or cell lattices on the MIL-88B surface. Ga–MIL-88B was isotypically prepared on the Fe–MIL-88B template surface and also formed a core–shell MOF hybrid. Moreover, the core–shell hybrids of single-shelled Fe–MIL-88B@Fe–MIL-88C and double-shelled Fe–MIL-88B@Ga–MIL-88B@Fe–MIL-88C were prepared via the growth of Fe–MIL-88C on the MIL-88B core. The basic characterization revealed the change in the chemical structures and component during the growth of the MOF-on-MOF hybrids, thus showing the applicability of the unique tip-to-middle anisotropic growth approach and the unprecedented self-adjustment and self-reversion of the MOF cell lattices. All these effects finally led to the formation of the core–shell MOF@MOF hybrid via anisotropic growth. ⁵⁰ Besides these MOF-on-MOF heterostructures, Oh’s group developed novel ZIF-8@ZIF-67(Co, Zn) rings using the MOF-on-MOF method via three preparation steps, including the growth of 3D ZIF on a ZIF-L surface, partially etching the 2D ZIF-L template, and transforming the 2D ZIF-L into a 3D ZIF (Fig. 3f). The core–shell MOF@MOF rings and plates were modulated by changing the three steps. ⁵¹ In 2020, an MIL-88B-on-Uio-66 hybrid phase was prepared. ² The atypical-shaped NPs were composed of eight precisely aligned 3D hexagonal rods grown on the eight faces of one octahedron. Apparently, these core–shell MIL-MOF@MIL-MOF heterostructures were prepared using two MOFs with the same lattice crystals. Thus, the exploration of the potential applications of these well-designed MOF-on-MOF hybrid materials will be promising in the near future.

2.1.2 ZIF-based MOF-on-MOF. The isomorphism of some ZIFs can boost heterogeneous nucleation, whereas the fast addition of precursors is unfavorable for the heterogeneous nucleation induced by seeds. A series of ZIF@ZIF heterostructures have been prepared using the MOF-on-MOF strategy, showing great potential and wide applications in diverse fields. In 2015, Kang et al. provided an engineering strategy to obtain core–shell ZIF-L@ZIF-8 nanocomposites via the preparation of ZIF-8 crystals on ZIF-L nanosheets (Fig. 4a). The functionality of ZIF-8 was introduced into the ZIF-L@ZIF-8 hybrids. ²³ Zhang et al. developed uniform double-layered core–shell ZIF-67@ZIF-8 and ZIF-8@ZIF-67 crystals, as well as three-layered core–shell ZIF-67@ZIF-8@ZIF-67 and ZIF-8@ZIF-67@ZIF-8 crystals. In this case, the core diameter and shell thickness were strictly modulated using different seed sizes and molar feeding ratios of Zn²⁺/Co²⁺, respectively (Fig. 4b).²⁴ Guo et al. investigated different core–shell ZIF-67@ZIF-8@ZIF-67 nanocrystals, which were also obtained by modulating the core/shell thickness ratio, depending on the intervals after the initial addition of Co⁵⁺ (Fig. 4c). Only nanostructured hybrids of ZIF-67 and ZIF-8 were obtained, and it was found that agglomerates with an irregular shape were formed when Zn²⁺ ions were added first due to their inferior nucleation activity. When Co and Zn ions were introduced in the solution initially, a homogeneous distribution of these two metals was obtained at a high Co/Zn ratio, while a gradient from Co-rich cores to Zn-rich shells was formed at a low Co/Zn ratio. ²⁵ Ghalei’s group prepared nano-sized core–shell ZIF-67@ZIF-8 crystals using ZIF-67 as the core and ZIF-8 as

Fig. 3 Structure of MIL-MOF-based core–shell MOF-on-MOF or layered MOF-on-MOF heterostructure. (a) Heterometalation of Fe–MIL-88B@MIL-88B heterostructure (core–shell-type hybrid A@B and layer-type hybrid C/A/C) using Fe–MIL-88B nanorods as the seeds. Reproduced from ref. 47 with permission from the American Chemical Society. Copyright 2012. (b) MIL-68@MIL-68–Br and MIL-68@MIL-68–NDC obtained by isotropic and anisotropic growth with the 3D hexagonal-structured MIL-68 as the template. Reproduced from ref. 42, with permission from the American Chemical Society. Copyright 2016. (c) MIL-68@MIL-68–X (X = NO₂ or NH₃) hybrid-induced growth on 3D hexagonal-structured MIL-68. Reproduced from ref. 48 with permission from the American Chemical Society. Copyright 2018. (d) Mechanism for the unbalanced MOF-on-MOF growth of MIL-88A on the MIL-88B template for the production of the lopsided core–shell of MIL-88B@MIL-88A. Reproduced from ref. 49 with permission from The Royal Society of Chemistry. Copyright 2019. (e) Tip-to-middle MOF-on-MOF growth of the core–shell hybrids of single-shelled Fe–MIL-88B@Fe–MIL-88C and double-shelled Fe–MIL-88B@Ga–MIL-88B@Fe–MIL-88B. Reproduced from ref. 50 with permission from the American Chemical Society. Copyright 2020. (f) Formation of ZIF-8@ZIF-67(Co, Zn) rings using the MOF-on-MOF method via three preparation steps, including the growth of 3D ZIF on a ZIF-L surface, partially etching the 2D ZIF-L template, and transforming the 2D ZIF-L into a 3D ZIF. Reproduced from ref. 51 with permission from Wiley. Copyright 2020.
the shell (Fig. 4d), which were embedded in polyimide and Pebax 1657 substrates. Krishna et al. studied the differences in the structures and mechanisms for the synthesis of the mixed-linker ZIF by manufacturing a series of ZIF-8-90 hybrids (Fig. 4e). The results revealed the feasibility of integrating diverse ZIFs with a similar linker for the construction of MOF@MOF and MOF-on-MOF hybrids.

Fig. 4 Structure of ZIF-based core–shell MOF-on-MOF hybrid. (a) Illustration and SEM images of ZIF-L@ZIF-8 core–shell nanocomposite. Reproduced from ref. 53 with permission from the American Chemical Society, Copyright 2015. (b) Synthetic scheme for the preparation of core–shell ZIF-8@ZIF-67 core–shell ZIF-8@ZIF-67@ZIF-8 crystals, core–shell ZIF-67@ZIF-8 core–shell ZIF-67@ZIF-867@ZIF-8 crystals, and core–shell ZIF-8@ZIF-90@ZIF-8 crystals. Reproduced from ref. 54 with permission from the American Chemical Society, Copyright 2016. (c) Core–shell ZIF-67@ZIF-8@ZIF-67 with tunable core/shell thickness. Reproduced from ref. 55 with permission from Wiley, Copyright 2017. (d) Synthesis of nanosized core–shell ZIF-67@ZIF-8 crystals via seed-mediated growth and their loading in polyimide and Pebax 1657 for gas separation. Reproduced from ref. 56 with permission from Wiley. Copyright 2020. (e) Schematic mechanism for the synthesis of ZIF-8@ZIF-90 via solvent-assisted linker exchange. Reproduced from ref. 57 with permission from Elsevier, Copyright 2020.

It is difficult to precisely control the synthesis of MOFs with different ligands and morphological structures are owing to their high surface energy. These types of MOF@MOF heterostructures are usually synthesized via surfactant-mediated overgrowth to reduce their surface energy. Zhuang et al. synthesized uniform and solid UiO-66@ZIF-8 particles with diverse crystalline structures and chemical components with the aid of a surfactant called cetyltrimethylammonium bromide (CTAB). A similar Pd–UiO–NH2@ZIF-8 hybrid was also synthesized and used as a catalyst, where UiO-66–NH2 NPs were applied as the core MOF to load Pd NPs and ZIF-8. Consequently, the Pd–UiO–NH2@ZIF-8 hybrid demonstrated remarkable molecular sieving behaviour. Song et al. developed the ZIF-8@UiO-66–NH2 hybrid using UiO-66–NH2 and ZIF-8 as the core and shell, respectively, for boosting transport pathways and molecular sieving properties. The ZIF-8 layer was synthesized over the external UiO-66–NH2 surface via the LBL solution deposition method and the UiO-66–NH2 core was sequentially added to the preparation system of ZIF-8 via the internally extended growth method in the presence of polyvinyl pyrrolidone (PVP) (Fig. 5b). UiO–NH2–MIL-101(Al)@ZIF-8 nanoflower was used as the core, while ZIF-8 was utilized as the shell. According to the above-mentioned examples, PVP with a long-chain can endow different MOFs with the ability of uniform growth by reducing their surface energy. For instance, Xiong et al. prepared two types of UiO-66–NH2@ZIF-8-20 and ZIF-8/UiO-66–NH2 heterostructures by using PVP as a regulator, where ZIF-8 changed from a dodecahedron to a lamellar direction growth (Fig. 5c).

2.1.3 PBA-based MOF-on-MOF. Different types of Prussian blue (PB) and PBAs have been employed in different fields, such as clean energy, catalysis, biomedicine, and biosensing, owing to their nano-sized size, good compatibility with other layers, and multifarious functionality. PB or PBA NPs have been conjugated with diverse nanomaterials and MOFs. Wang et al. developed core–shell PB@ZIF-8 NPs as an excellent drug delivery system for loading doxorubicin (DOX) for cancer treatment. An electronegative surface was first formed by modifying PB with poly(sodium-4-styrenesulfonate), which was then attracted to the positively charged Zn2+ ions of ZIF-8, thus forming the ZIF-8 shell. The formation of isolated and coated ZIF-8 NPs was mainly due to homogeneous and heterogeneous nucleation, respectively. When the precursor concentration was low, NP-induced heterogeneous nucleation occurred easier than homogeneous nucleation because the synthetic system only
needed to overcome a low energy barrier. Hence, small ZIF-8 crystal nuclei were obtained on the PB nanocube surface, thereby forming uniform ZIF-8 shells. When the precursor concentration was high, homogeneous and heterogeneous nucleation simultaneously and competitively occurred, resulting in the coexistence of isolated and coated ZIF-8 NPs. Small ZIF-8 NPs with an irregular shape were prepared via homogeneous nucleation at a high precursor concentration (Fig. 6a). Yu et al. proposed a one-pot method for the synthesis of core–shell PBA@PBA nanostructures using an ion-modulation strategy (Fig. 6b), where Fe$^{3+}$ was used as the indicator. A certain amount of Fe$^{3+}$ ions underwent a partial phase transition to form new PBA NPs, which were epitaxially grown onto the original PBA core. The charge transfer band between ligand-to-metal was excited, resulting in charge transfer from CN$^-$/C0$^-$ to Fe$^{3+}$, thus causing a phase change occur. Subsequently, charges were provided from Mn$^{II}$ to CN$^-$/C0$^-$.

Moreover, a PB MOF and a porphyrin-doped UiO-66–TCPP MOF (TCPP = 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin) were used as the core and shell, respectively, to develop a novel core–shell MOF hybrid. Due to the defects present in the UiO-66 network, porphyrin ligands were introduced into the UiO-66 crystal. The outer surface of the PB MOF was modified with PVP, in which the oxygen in the carbonyl group of PVP bound with the Zr ions of UiO-66. The formed Zr–O bonds remarkably enhanced the further growth of the MOF over the PB surface. Consequently, the core–shell PB@MOF hybrid was prepared by using PB modified with PVP as a crystal nucleus (Fig. 6c). Also, using PVP as an activator, the ZIF-8/NH$_2$–MIL-53(Al) hybrid was

![Fig. 6 Structure of PBA-based MOF@MOF heterostructures. (a) Schematic illustration of procedure for the synthesis of PB@ZIF-8. Reproduced from ref. 62 with permission from Ivyspring International Publisher, Copyright 2017. (b) Fe$^{3+}$-modulated shape control of PBA@PBA. Reproduced from ref. 63 with permission from The Royal Society of Chemistry, Copyright 2018. (c) PB as the core for the growth of a porphyrin-doped UiO-66 MOF. Reproduced from ref. 64 with permission from The Royal Society of Chemistry, Copyright 2020. (d) ZIF-8/NH$_2$–MIL-53(Al) obtained by anchoring ZIF-8 on 2D NH$_2$–MIL-53(Al) nanoplates. Reproduced from ref. 65 with permission from Elsevier, Copyright 2019.](https://example.com/fig6.png)

Fig. 7 Structure of MOF-on-MOF heterostructures. (a) nHKUST-1⊂MOF-5 structure formed by embedding nanocrystalline HKUST-1 (nHKUST-1) in MOF-5 crystals. Reproduced from ref. 66 with permission from the American Chemical Society, Copyright 2015. (b) Core–shell UiO-67–BPY@UiO-66. Reproduced from ref. 67 with permission from Elsevier, Copyright 2019. (c) Core–shell MOFs (PCN-222@Zr-BPDC) with mismatching lattices by epitaxial growth. Reproduced from ref. 30 with permission from the American Chemical Society, Copyright 2018. (d) Selective epitaxial growth of PCN-222 nanorods on 0D PCN-608 nanoparticle, 1D UN-1000 nanorod, and 2D PCN-134 nanoplate. Reproduced from ref. 68 with permission from Elsevier, Copyright 2019. (e) Two MOF-on-MOF of Zn-MOF-on-Zr-MOF and Zr-MOF-on-Zn-MOF hybrids. Reproduced from ref. 45 with permission from Elsevier, Copyright 2018. (f) Bimetallic core–shell Tb-MOF-on-Fe-MOF and Fe-MOF-on-Tb-MOF nanostructures formed by Tb-MOF nanorod and hexagon-structured Fe-MOF. Reproduced from ref. 46 with permission from Elsevier, Copyright 2019. (g) Multiple layered MOF-on-MOF films using liquid-phase epitaxy. Reproduced from ref. 40 with permission from the American Chemical Society, Copyright 2020. (h) Selective growth of ZIF-8 on the side (110) facets of f$_4$MIL-125. Reproduced from ref. 69 with permission from The Royal Society of Chemistry, Copyright 2020. (i) NH$_2$–UiO-66(Zr)$@NH$_2$–MIL-125(Ti) nanohybrid. Reproduced from ref. 70 with permission from Wiley, Copyright 2017.)
obtained because of the pre-concentration effect of ZIF-8 adsorbing the 2D NH₂-MIL-53(Al) surface (Fig. 6d).  

2.1.4 Other types of MOF-on-MOF. Various core–shell MOF@MOF hybrids are often prepared through a stepwise approach, where the MOF core is firstly generated and further explored as a template for growing the shell.  

Aiming at the full combination of the shell and core components, lattice matching is necessary. However, this increases the difficulty in the development of synthetic methods to meet the requirement of lattice-matching for core–shell MOF@MOF nanohybrids. In addition to ZIFs and PBs, other types of MOFs have been utilized for the synthesis of MOF-on-MOF. Kang’s group synthesized a core–shell “nHKUST-1(nHKUST-1) ⊂ MOF-5” structure by introducing MOF-5 into HKUST-1 hybrids (Fig. 7a). This specific nanostructure resulted in new interfaces between the MOF core and MOF shell, producing different properties from their MOF parents. Specifically, MOF-5 [Zn₆O(BDC)₃] was embedded in the nanocrystalline HKUST-1 to construct the “nHKUST-1 ⊂ MOF-5” heterostructure, which encapsulated guest molecules.  

Similarly, Kwon et al. combined the metal clusters of one MOF with organic linkers of a second MOF to form a series of single crystalline MOF@MOF hybrids.  

Gong et al. presented a core–shell UiO-67–BPY@UiO-66 nanohybrid by combining UiO-66 and UiO-67–BPY (Fig. 7b). Moreover, Zhou’s group prepared a core–shell PCN-222@Zr–BPDC structure via a one-pot synthetic method (Fig. 7c). PCN-222 and Zr–BPDC both exhibited mismatched lattices. TCPP on PCN-222 bound strongly with Zr⁴⁺, thus affording fast and homogeneous crystal nucleation. However, a longer time was needed for crystal formation with BPDC (BPDC = biphenyl-4,4’-dicarboxylate) than TCPP under similar experimental conditions. When the seed crystal was used as the core for preparing the second MOF, heterogeneous nucleation occurred faster than its homogenous counterpart. Accordingly, the core–shell PCN-222@Zr–BPDC hybrid was synthesized by binding Zr⁴⁺ ions with H₂TCPP and H₂BPDC.  

Although many individual MOFs and COFs have been synthesized and applied in diverse fields, their exploration and applications are less than satisfactory due to the limited types and monotonous structures. The MOF/COF-based hybrids obtained by combining different types of MOFs and COFs can produce multifunctional porous MOF@COF heterostructures.  

To date, the growth of MOF@COF nanohybrids mainly depends on the formation of an imine bond (–C=N–) between the reserved –NH₂ groups of MOFs and aldehydes present on COFs via a condensation reaction. In particular, UiO-MOFs and MIL-MOFs are often employed for the fabrication of MOF@COF heterostructures because of their good chemical stability, flexible synthetic strategies, multifunctional properties, and good crystallization. Moreover, COF nanospheres can also serve as the core, and MOF layers synthesized around them via covalent bonds to obtain core–shell MOF@COF heterostructures. In this part, the current MOF@COF nanohybrids are summarized according to their MOF type.

2.2 MOF@COF heterostructures

Although various individual MOFs and COFs have been synthesized and applied in diverse fields, their exploration and applications are less than satisfactory due to the limited types and monotonous structures. The MOF/COF-based hybrids obtained by combining different types of MOFs and COFs can produce multifunctional porous MOF@COF heterostructures.  

To date, the growth of MOF@COF nanohybrids mainly depends on the formation of an imine bond (–C=N–) between the reserved –NH₂ groups of MOFs and aldehydes present on COFs via a condensation reaction. In particular, UiO-MOFs and MIL-MOFs are often employed for the fabrication of MOF@COF heterostructures because of their good chemical stability, flexible synthetic strategies, multifunctional properties, and good crystallization. Moreover, COF nanospheres can also serve as the core, and MOF layers synthesized around them via covalent bonds to obtain core–shell MOF@COF heterostructures. In this part, the current MOF@COF nanohybrids are summarized according to their MOF type.

2.2.1 UiO-based MOF@COF. Diverse UiO-66 and UiO-like MOFs can be combined with nanomaterials to enhance their potential applications in various fields. A series of UiO-66-based MOF@COF heterostructures was synthesized via the covalent binding of the functional groups on MOFs or COFs. Zheng et al. synthesized a nanoscale UiO-AM@COF composite using UiO-type NMOFs as self-templates (Fig. 8a). An amine-based porphyrin molecule, tetrakis(4-aminophenyl)porphine (H₄P), and various functional-substituted terephthalaldehydes have been employed as linking ligands to obtain diverse MOF/COF bearing imine groups and regular 2D networks. The size distribution and surface morphology of UiO-AM@COF were feasibly modulated by changing amine positions on the exterior of the UiO-AM seed and the used ratios of H₄P and terephthalaldehyde. Consequently, after chemical modification with MOF/COF, the obtained NPs exhibited high potential applications in various fields. A series of UiO-66-based MOF@COF heterostructures was synthesized via the covalent binding of the functional groups on MOFs or COFs. Zheng et al. synthesized a nanoscale UiO-AM@COF composite using UiO-type NMOFs as self-templates (Fig. 8a). An amine-based porphyrin molecule, tetrakis(4-aminophenyl)porphine (H₄P), and various functional-substituted terephthalaldehydes have been employed as linking ligands to obtain diverse MOF/COF bearing imine groups and regular 2D networks. The size distribution and surface morphology of UiO-AM@COF were feasibly modulated by changing amine positions on the exterior of the UiO-AM seed and the used ratios of H₄P and terephthalaldehyde. Consequently, after chemical modification with MOF/COF, the obtained NPs exhibited high
crystallization, well-dispersed size distribution, and integrated pore, similar to that of UiO-AM.77 In 2018, Zhan et al. and Cheng et al. prepared NH2–UiO-66/TpPa-1-COF composites by covalently linking NH2–UiO-66 on the surface of the TpPa-1 COF. TpPa-1-COF was synthesized by reacting p-phenylenediamine (PDA) and 1,3,5-triformylphloroglucinol (Tp) (Fig. 8b). The results revealed that NH2–UiO-66 particles were uniformly distributed on the surface of TpPa-1-1-COF.78 Qi et al. reported a new MOF@POP composite (UiO-66@SNW-1) comprised of Lewis acid sites (Zr clusters in UiO-66) and Brunsted base sites (amino groups in SNW-1) (Fig. 8c). Thereby, these functional groups served as a superior bifunctional catalyst. The results revealed that the UiO-66 crystals were embedded in the SNW-1 layer, leading to the formation of a rough UiO-66 surface.79 Yao and co-workers developed a UiO-66@COF-2 hybrid material for eliminating aggregation-caused quenching and enhancing the emission of COFs (Fig. 8d). UiO-66–NH2 crystals were selected as the MOF core, while the –NH2 group on UiO-66–NH2 could be tightly bonded for the synthesis of a COF-2 layer with 2,4,6-benzenetricarboxaldehyde and tetra-amino-tetraphenylethylene via a Schiff base reaction. Consequently, the UiO-66 core could improve the fluorescence of the bulky COFs, and also boost the sensing selectivity for adenosine triphosphate (ATP) owing to the high affinity of ZrIV toward the phosphate group.80 Chen et al. provided a novel core–shell NH2–UiO-66@TFPT–DETH heterostructure photocatalyst (DETH, hydrazine monomer and TFPT, aldehyde monomer). Herein, the TFPT–DETH COF was explored as the outer layer because of its good stability. For the preparation of the heterostructure, the TFPT monomer was anchored on the surface of NH2–UiO-66, thus forming NH2–UiO-66@TFPT via the Schiff-base reaction between the aldehyde group and amino group on NH2–UiO-66. After the pre-coated TFPT molecules were added, DETH and TFPT were exclusively in situ polymerized on the NH2–UiO-66 surface to form the core–shell NH2–UiO-66@TFPT–DETH heterostructure.81 Peng et al. prepared an aza-MOF@COF hybrid material, where the dispersion of the UiO-66–NH2 crystals was improved by adding PVP to easily coat the imine-linked COF. The porous aza-MOF@COF hybrid was synthesized using the following three steps: the surface modification of UiO-66–NH2 with 1,3,5-benzenetricarboxaldehyde (BTCA), producing UiO-66–CHO, the in situ growth of the COF layer on UiO-66 through condensation between the aldehydes on UiO-66–CHO and PDA, and the modification of MOF@COF-LZU1 via the aza-Diels–Alder reaction (Fig. 8e).82 Similar to UiO-66, HF-MOF can be prepared through the coordination of Hf6O4(OH)4 clusters with organic ligands. Zheng et al. synthesized an Hf–UiO-AM@POP-PEG nanocomposite (POP: porous-organic polymer) via the growth of tetrakis(4-aminophenyl)-21H,23H-chlorin (TAPC), terephthalaldehyde and PEG5k-NH2 on the outer surface of NH2–Hf–UiO-66 (Hf–UiO-AM).83

For MOF@COF hybrids, their MOF component can efficiently modulate their quality, surface morphology, optical performance, and catalytic properties. The N heteroatoms in COFs endow them high ability for binding Pd or Pt species.84 Zhu et al. provided a new UiO-66–NH2@COF@Pd hybrid using UiO-66–NH2 as the core and the covalently linked COF as the shell. Here, Pd nanoclusters (~0.8 nm) were successfully confined in UiO-66–NH2@COF. The obtained UiO-66–NH2@COF@Pd had high porosity, good stability and large specific surface area (Fig. 8f). The prepared UiO-66–NH2@COF@Pd hybrid had a hierarchical porous structure and was loaded with abundant Pd nanoclusters. The strong synergism of each component of the hybrid led to excellent catalytic performances.84

2.2.2 MIL-based MOF@COF. MOF crystals often bear a functional amino group (such as NH2–MIL-68, NH2–MIL-125(Ti) MOF, and NH2–MIL-101(Fe)), which can covalently link with the carboxyl or aldehyde groups in the building blocks of COFs, thus leading to the tight binding of MOFs and COFs (Fig. 9a).85 Hence, developing the series of NH2–MIL-MOF@COF hybrids can remarkably extend their potential applications. Zhang’s group prepared NH2–MIL-68@TPA-COF and explored it as an effective photodegradation catalyst (Fig. 9b). After NH2–MIL-68 was modified with tris[4-formylphenyl] amine (TPA), TPA-COF was synthesized around the NH2–MIL-68(CHO) surface by linking TPA and tris[4-aminophenyl]amine (TAPA) via a feasible condensation synthesis method to produce the NH2–MIL-68@TPA-COF hybrid material. Given the rod-like morphology of NH2–MIL-68, the obtained NH2–MIL-68(CHO) exhibited a similar surface morphology.79 In addition, Ti-based MOFs exhibit superior photocatalytic ability because of their high chemical stability, redox ability, and photocatalytic performances.86,87 In this regard, NH2–MIL-125(Ti)-based MOF@COF hybrids show promising applications. Sun et al. developed a Pd-doped core–shell MOF@COF hybrid using TiATA and the 2D imine-based COF-LZU1 as the core and shell, respectively, [Pd/TiATA@LZU1]. NH2–MIL-125(Ti) allowed the direct growth of the COF shell without a modification step, followed by the doping of Pd NPs. The MOF@COF hybrid had an octahedral shape similar to TiATA, where the TiATA surface in the MOF@COF hybrid was coated by COF nanosheets.88
et al. also prepared a variety of MOF/COF hybrids by separately integrating NH$_2$-MIL-53(Al), NH$_2$-UiO-66(Zr), and NH$_2$-MIL-125(Ti) with TTB-TTA (a COF synthesized from 4,4',4''-(1,3,5-triazine-2,4,6-triyl) trivalent trianiline (TTA)) layer. The obtained NH$_2$-MIL-125(Ti) with TTB-TTA composite with a double p-n heterojunction via a self-assembly strategy. The spherical COF-TPA/TPB was fabricated by compositing with SiO$_2$. Subsequently, it was added during the procedure for the synthesis of MIL-88B, thus gaining MIL-88B@COF hybrids. Furthermore, these hybrids were introduced into a certain amount of PANI solution, assembling MIL-88B@COF-PANI composites with significant photocatalytic activity.\textsuperscript{92}

2.2.3 Other types of MOF@COF. Besides covalent binding at the interface between amino-functionalized MOFs and COFs bearing aldehyde groups for the development of core–shell nanostructured MOF@COF hybrids, other types of MOF@COF composites have been prepared via hydrogen bonds and π–π stacking. Fu et al. developed a ZIF-8@COF-300 composite membrane, where COF-800 was synthesized using terephthalaldehyde and tetra-(4-anilyl)methane as monomers via a condensation reaction (Fig. 10a). The polyaniline layer was first coated on an SiO$_2$ disk, followed by the surface modification of polyaniline with terephthalaldehyde. Free C=O groups then reacted with tetra-(4-anilyl)-methane to produce a uniform COF-300 layer. Subsequently, hydrogen bonds were formed between terephthalic acid and the amine groups on COF-300, thus boosting the integration of the ZIF-8 top layer.\textsuperscript{93}

In addition to hydrogen bonds, the coordination binding between the zinc cation and amine group can enhance the binding of the COF and MOF components. In our previous work, a Co-MOF was synthesized over a terephthalonitrile-derived nitrogen-rich network surface, thus leading to the formation of the Co-MOF@TPN-COF hybrid. Co(NO$_3$)$_2$·6H$_2$O and 2-methylimidazole were used to prepare Co-MOF, and terephthalonitrile was polymerized over the Co-MOF surface (Fig. 10b). The proposed Co-MOF@TPN-COF displayed the advantages of MOFs and COFs, such as abundant nitrogen-related groups and excellent conductivity.\textsuperscript{94} Gao and co-workers constructed core–shell PCN-222-Co@TpPa-1 hybrid materials via strong π–π stacking to overcome their disadvantages and produce a synergistic effect, which afforded multifunctional properties (Fig. 10c). The obtained core–shell PCN-222-Co@TpPa-1 exhibited good stability and superior catalytic activity.\textsuperscript{71} Moreover, the Ce-MOF@MCA nanohybrid was
synthesized via the COF-on-MOF strategy, where MCA was prepared by reacting melamine and cyanuric acid [Fig. 10d].

2.3 COF-to-COF heterostructures

Imine-, azine-, hydrazone- and enamine-linked COF frameworks can be combined with other types of COFs and MOFs and serve as sieving membranes. Although COF membranes have been investigated, continuous progress on this area is highly restricted. In 2018, Fan et al. constructed a bilayer COF-to-COF membrane, which was prepared by synthesizing a 2D-COF layer over the another type of 2D-COF layer. The 2D-COFs of imine-linked COF-LZU1 and azine-linked ACOF-1 were used as building blocks due to their hexagonal pore structure. Ying et al. developed cationic TpEBr and anionic TpPa-SO\textsubscript{3}Na nanosheets, where the two building blocks with opposite charges were assembled to form an ultrathin membrane architecture. Consequently, different effects were integrated, forming ultrathin compact layers.

3. Design principles and synthetic approaches

High surface energy is often generated at the interfaces between different MOFs or COFs because of their various morphologies. Hence, suitable methods to prepare core–shell MOF-on-MOF and other types of MOFs- or COFs-based heterostructures must be explored (Fig. 11). Among the diverse preparation methods, seed-mediated growth, epitaxial and internally extended growth, and ligand exchange are usually used for the synthesis of core–shell MOF-on-MOF heterostructures. Anisotropic growth and induced growth, internal and epitaxial growth, and template methods are also applied for the development of other types of MOF-on-MOF heterostructures. The interfacial design strategy, one-step synthesis method, and \textit{in situ} polymerization approaches have been explored for MOF@COF hybrids. Temperature-swing solvothermal synthesis and LBL assembly methods are appropriate for the construction of COF-to-COF hybrids. This work provides the design principles and reviews the synthetic approaches that correspond to the classifications of MOF/COF-based hybrids with different nanostructures and morphologies.

3.1 MOF-on-MOF heterostructures

Owing to the well-defined and modulated heterocompositions and heterostructures of MOF-on-MOF nanohybrids, they have been explored as efficient platforms to overcome the inherent shortcomings in basic performances of their components (e.g., poor chemical stability, structural stability, and crystallinity) and realize desirable and applicable properties (e.g., reactivity, functionality, and thermodynamic stability). Growing a secondary MOF shell on an MOF core can efficiently form complex heterostructures that protect the inner MOF cores and afford functional domains of the MOF shell in MOF hybrid materials. Different strategies for the fabrication of core–shell MOF@MOF heterostructures have been developed, such as seed-mediated growth, one-pot synthesis, epitaxial and internally extended growth, ligand exchange, and surfactant-mediated overgrowth. As an alternative method, the synthesis method of MOF-on-MOF hybrids shows potential in constructing well-defined MOF hybrids with a heterogeneous interface between two different MOFs. Generally, two MOFs with lattice matching of their cell parameters are often used for the preparation of core–shell MOF-on-MOF hybrids by growing the second MOF using the isotropic growth method. Furthermore, MOF-on-MOF hybrid materials are obtained by anisotropically growing the second MOF on the template MOF with mismatched cell parameters. These methods for the synthesis of MOF-on-MOF hybrids will be discussed in the following sections.

3.1.1 Core–shell MOF@MOF

3.1.1.1 Seed-mediated growth methodology. During the seed-induced growth procedure, the introduction of seed crystals in the starting preparation system of MOFs can accelerate their crystallization rate significantly. However, the traditional seed-induced growth approach for the preparation of core–shell MOF@MOF hybrids often has shortcomings, such as the possible nucleation of the shell MOF in solution and seed aggregation, thus leading to structural incompleteness and reduction in the desired performances for the hybrids. In 2015, Yamauchi’s group prepared core–shell ZIF-8@ZIF-67 hybrids using the seed-mediated growth method, in which ZIF MOFs were synthesized \textit{via} the coordination reaction between diverse metal clusters and imidazole-related ligands. ZIF-8 crystals were explored as the core, while ZIF-67 was used as the shell. ZIF-8 seeds with a uniform size of approximately 50 nm were prepared \textit{via} the coordination of Zn\textsuperscript{2+} ions and 2-methyl-1H-imidazole (MeIm) using PVP as the capping agent. Co\textsuperscript{2+} ions
were firstly prepared as the core crystals, and then added to a fresh solution containing metal ions, linkers, and CTAB surfactant, resulting in heterogeneous nucleation on the ZIF core via vertically epitaxial growth owing to the matched lattice parameters.107

For the core–shell MOF@MOF hybrid materials prepared using two MOFs with different ligands and morphological structures, it is difficult to precisely control the regular epitaxial growth owing to their high surface energy. These types of MOF@MOF heterostructures are usually synthesized via surfactant-mediated overgrowth. Surfactants, such as CTAB and PVP, can efficiently modulate the formation of MOF@MOF heterostructures by lowering their surface energy.44 Therefore, the conformation and orientation of MOFs on solid surfaces can be sustained by using cationic surfactant capping agents despite their minimal structural similarity. Tsung’s group developed even UiO-66@ZIF-8 heterostructures. As is known, ZIF-8 and UiO-66 have distinct chemical structures and morphologies. Zn clusters and imidazolate were found in the ZIF-8 crystals and Zr6O4(OH)4 clusters and dicarboxylate linkers were present in UiO-66. With assistance from CTAB, homogeneous ZIF-8 outer layers were generated on homogeneously distributed UiO-66 crystals, thus forming the UiO-66@ZIF-8 hybrid.44 A core-shell NH2–MIL-101[Al]@ZIF-8 nanoflower was also prepared via an internal extended growth mode under PVP regulation. PVP molecules with long-chains were aligned along the [001] plane direction because of the high surface density of Cu(n). The efficient capping of PVP in the [001] plane greatly improved the formation of ZIF-8 from polyhedra to nanosheets by lowering its surface energy.59 Moreover, diverse core–shell or striped hetero Ln-MOF crystals have been synthesized via the anisotropic epitaxial growth method. Monometallic LIFM-18/19(Eu) crystals were prepared using TMPBPO and Eu nitrate through a simple diffusion method, followed by immersion in an acetone/water mixture solution (v/v = 3/1) containing saturated Tb(NO3)3·6H2O and TMPBPO. The second layer was propagated around the original core crystal due to the slow diffusion of acetone, thus forming a bimetallic hierarchical Eu@Tb-MOF hybrid.108

In addition to the use of surfactants, oriented hierarchical MOF heterostructures can also be constructed by dedicately choosing MOF seeds with similar ligands as the second MOF to match the crystal lattice. This leads to the epitaxial growth of the second MOF over the MOF seed with a small lattice mismatch. As shown in Fig. 13, three different 0D PCN-608 NPs and 1D NU-1000 nanorods, and 2D PCN-134 nanoplates were applied as templates for epitaxially growing PCN-222 nanorods. Depending on the size, shapes, and dimensionalities of these MOF cores, three different types of MOF heterostructures were achieved owing to the lattice mismatch between PCN-222 and the MOF seeds by selective epitaxial growth.68

3.1.1.3 One-pot synthesis. Among the different preparation approaches, one-pot synthesis is the most convenient to combine the multiple functionalities and performances of each component in a single platform, and thus is often applied to prepare MOF@MOF heterostructures.109 The core–shell MOF@MOF hybrids with structural integrity constructed via the one-pot synthesis method109 can remarkably avoid the possibility

Fig. 12 Schematic illustration of the synthesis of core–shell MOF@MOF nanohybrids. (a) Reproduced from ref. 104 with permission from The Royal Society of Chemistry, Copyright 2017. (b) Reproduced from ref. 107, with permission from Springer, copyright 2018. (c) Reproduced from ref. 55 with permission from Wiley, Copyright 2017. (d) Reproduced from ref. 111 with permission from the American Chemical Society, Copyright 2012. (f) Reproduced from ref. 43 with permission from the American Chemical Society, Copyright 2020.
of producing a new surface and reduce the requirements of incipient surface energy. As shown in Fig. 12c, Guo et al. proposed the prototypical bimetallic ZIF-8/ZIF-67 heterostructures within a single MOF crystal due to distinct reaction kinetics, leading to partial distribution of different metals during the formation of the MOF.29 Similar sizes of metal ions readily were adapted to blend in the same porous framework. Uniform distributions of the two metals in the ZIF-8/ZIF-67 heterostructures were obtained at a high Co/Zn ratio of Co2+ and Zn2+ ions in the initial solution. The ZIF-8/ZIF-67 heterostructures were observed at a low Co/Zn ratio concentration gradient from Co-rich cores to Zn-rich shells. When Co2+ was added initially, the core-shell ZIF-67@ZIF-8/67 hybrids were produced, and their core/shell thickness was modulated by the reaction time interval. In contrast, when Zn2+ was introduced initially, only irregular aggregates were produced because of the low nucleation capability of Zn2+.

In addition to the ZIF-8/ZIF-67 heterostructures obtained from MOFs with the same morphology and similar sizes, core-shell MOF@MOF nanostructures have also been obtained via the one-pot synthesis method using MOFs with diverse crystal lattices. Zhou’s group developed the PCN-222@Zr-BPDC hybrid via one-pot synthesis. The individual components of PCN-222@Zr-BPDC displayed mismatching lattices. The strong binding interaction between TCPB and metal cations resulted in fast homogeneous nucleation. By contrast, BPDC with low connectivity often took longer for the preparation of crystals than TCPB under similar conditions. However, heterogeneous nucleation occurred faster than its homogeneous counterpart because the seed crystal was used as a core for growing the second MOF.30 Besides the ZIF@ZIF and PCN@UiO core–shell structures, monodisperse MOF@MOF comprised of two PBAs was also prepared via the one-pot synthesis strategy.31

3.1.1.4 Ligand exchange. The post-synthesis ligand exchange method (PSE) exhibits some intrinsic advantages, such as operational simplicity, widespread generality, and thus extensive applications.199 PSE is typically performed by incubating MOF crystals in a solution containing another pure ligand in the presence of a suitable solvent (DMF or water). Two possible structures of the core–shell and uniformly distributed MOF@MOF heterostructures can be constructed using this technique. A homogeneous and mixed organic building blocks was achieved, in which ligand diffusion in the MOF was faster than its exchange. When the diffusion in the MOF was slow or if the exchange was faster at the edges of the crystal, the core–shell MOF@MOF nanohybrid was obtained (Fig. 12d).111 Moreover, the core–shell ZIF-67@Co-MOF-74 hybrid was constructed by exchanging the ligands on the ZIF-67 surface with 2,5-dihydroxyterephthalic acid (DHTP) molecules. During the preparation of this nanohybrid, DHTP molecules showed higher coordination ability than 2-MeIm. When adding ZIF-67, DHTP molecules competed with 2-MeIm on the surface of ZIF-67 to coordinate with cobalt, thus generating Co-MOF-74 on ZIF-67. Finally, a ZIF-67@Co-MOF-74 core–shell structure was achieved.112

3.1.1.5 Thermodynamically controlled complete replacement. Lah’s group reported a series of highly porous isostructural MOF heterostructures through the thermodynamically controlled complete replacement method, which was achieved by soaking the thermodynamically more stable MOF seeds as the core in a metal ion solution in the presence of ligands with a potentially less stable framework (Fig. 12e). This new type of MOF heterostructures demonstrated uniformly transmetalated framework structures, illustrating the boosted framework stabilities. The core–shell heterostructures were selectively transmetalated by kinetically controlling the replacement of the framework metal ions with the second MOF grown on the external MOF shell.113

3.1.1.6 Dual-interfacial engineering approach. Interfacial compatibility in mixed-matrix membranes can be realized via a dual-interfacial approach for the fabrication of MOF@MOF hybrids.114 Fig. 12f shows that the ultrathin MOF-74 layer was grown on the MOF core via the dual-interfacial engineering method. This layer was comprised two interfaces of MOF–MOF and MOF-polymer. Between them, the interface at the two MOFs, MOF–MOF, was formed due to the lattice matching between the two MOFs and was strongly integrated by the coordination bonds between the metal and ligand because of the chemical similarity of the two MOFs.43 Apparently, among the methods for constructing diverse MOF@MOF hybrids, the seed-mediated growth methodology is feasible for the preparation of MOF@MOF heterostructures with a matched lattice, such as ZIF-based hybrids. Meanwhile, the epitaxial and internally extended growth methods are helpful for the development of MOF@MOF hybrids using various MOFs. In addition, the presence of a surfactant can lower the surface energy at the interface between two MOFs, thereby facilitating the formation of MOF@MOF hybrids from diverse ligands.

3.1.2 Other types of MOF-on-MOF. Besides the core–shell MOF@MOF heterostructures, other categories of MOF-on-MOF hybrids have also been constructed through unique synthetic methods, which are apparently different from that of the MOF@MOF hybrids.

3.1.2.1 Isotropic and anisotropic growth. Presently, several types of MOF-on-MOF nanohybrids, including In–MIL-88B-on-Fe–MIL-88, MIL-68@MIL-68–Br, MIL-68@MIL-68–X (X = NO2 or NH2), MIL-88B@MIL-88A, Fe–MIL-88B@Fe–MIL-88C, and...
double-shelled Fe–MIL-88B@Ga–MIL-88B@Fe–MIL-88C, have been fabricated using isotropic or anisotropic growth and induced growth (Fig. 14a). Thus far, different MOF-on-MOF hybrid heteroparticles have been obtained by precisely modulating the isotropic and/or anisotropic nanoscale growth of various MOFs. Fe–MIL-88B, Ga–MIL-88B, and In–MIL-88B have been used for the heterometalation of MOF hybrids via the isotropic and anisotropic growth methods. Fe–MIL-88B nanorods with a hexagonal 3D structure were first prepared and explored as seeds for growing the secondary MOFs. The MOF-on-MOF heterostructure was obtained by hybridizing Fe–MIL-88B and M–MIL-88B (M = Ga or In).47 MIL-68–Br and MOF-NDC (NDC stands for naphthalene-1,4-dicarboxylic acid) were isotropically and anisotropically grown on a microMIL-68. The isotropic growth of MIL-68–Br on the MIL-68 template led to the production of the core–shell-type MIL-68@MIL-68–Br.42 The atypical lopsided core–shell of MIL-88B@MIL-88A has also been constructed via the unbalanced growth of an MOF-on-MOF hybrid. Although MIL-88A and MIL-88B had a large overall mismatch in their cell parameters because of the introduction of diverse organic linkers, the abnormal anisotropic MOF-on-MOF hybrid was obtained due to the analogous ab plane in the core and shell. Initially, nano-scale hexagonal MIL-88B rods were prepared, which then acted as a template to achieve the MIL-88B@MIL-88A hybrid by growing MIL-88A.49 The MOF hybrid of the MIL-88B or MIL-88C structure was similarly gained via the isotropic or anisotropic preparation method because these two MOFs possessed different components and/or cell lattices. Ga–MIL-88B was isotropically grown on the Fe–MIL-88B core, showing well-matched cell lattices and different components. Fe–MIL-88C was also grown on MIL-88B with mismatched cell lattices and diverse structures, resulting in single-shelled Fe–MIL-88B@Fe–MIL-88C and double-shelled Fe–MIL-88B@Ga–MIL-88B@Fe–MIL-88C hybrids.50 However, to date, the isotropic and anisotropic growth methods have only been used to prepare a series of MIL-based MOFs. Wide varieties of MOF@MOF heterostructures should be constructed in the near future.

3.1.2.2 Internal and epitaxial growth. To date, only a few core–shell MOF@MOF heterostructures have been obtained via the epitaxial growth method due to the picky designs of more than two MOFs with analogous crystal structures in one nanoparticle. Gu et al. used the internally extended growth method to prepare hierarchical MOF composites and overcome the restriction of the lattice matching. NH2–Uio-66(Zr) and NH2–MIL-125(Ti) were integrated to form the MOF-on-MOF heterostructure by implementing the internally extended growth method. NH2–Uio-66(Zr) was interacted with the NH2–MIL-125(Ti) precursors with the help of PVP. Consequently, the NH2–MIL-125(Ti) nuclei were assembled with NH2–Uio-66(Zr) to produce the hybrid.78 Kim’s group constructed MOF@MOF hybrids with matched interface configurations (Fig. 14b).55 The results showed a MOF-5 crystal that had grown on the [111] planes of the octahedral HKUST-1, thus forming the HKUST1@MOF-5 hybrid. Zhang’s group developed a novel MIL-88B-on-Uio-66 hybrid using the heteroepitaxial growth method.33 Accordingly, coordination occurred between the linear linkers and coordinate unsaturated metal modes, giving a layer of coordinately unsaturated ligands by epitaxial growth.

3.1.2.3 van der Waals force method. As is known, van der Waals force can be freely used to combine different materials, differing from chemical bonding at the interface between two diverse materials. For instance, Cu-TCPP layers were deposited on semiconductive Cu-HHTP layers using van der Waals forces, forming oriented MOF-on-MOF thin films, which can overcome the lattice mismatching issue (Fig. 14c). Consequently, Cu-TCPP-on-Cu-HHTP thin films were obtained.41

3.2 MOF@COF heterostructures

Besides MOF-on-MOF heterostructures, integrating MOFs with COFs also can overcome the limitations of each component. A few methods have been explored for the hybridization of COFs and MOFs and showed extensive applications in diverse fields. The preparation methods of MOF@COF hybrids include interfacial design strategy, one-step synthesis method, modular synthesis strategy, and coordination-induced interlinked hybrid strategy, which will be discussed below.

3.2.1 Interfacial design strategy. The interfacial design strategy involves coating COF layers on size-selective MOF cores to construct MOF@COF hybrids.79 Zhang’s group developed core–shell NH2–MIL-68@TPA-COF hybrid materials by controlling the synthesis of TPA-COF on NH2–MIL-68 (Fig. 15a). The prepared NH2–MIL-68 was functionalized with TFPA for the formation of NH2–MIL-68(CHO). TPA-COF was then in situ formed on the NH2–MIL-68(CHO) surface by covalent connection with TFPA and TAPA via condensation reaction. Hence, the
NH₂-MIL-68@TPA-COF hybrid was prepared. The NH₂–UiO-66/TPPA-1-COF hybrid also was gained by combining NH₂–UiO-66 with TPPA-1-COF. For this preparation system, NH₂–UiO-66 was modified with slightly extra Tp and used as a template for the synthesis of TPPA-COF. Furthermore, the size-selective MOF cores were coated with COF layers via an interfacial design strategy to improve the polymer-filler compatibility. For this, the UiO-66–NH₂ crystals were applied as the MOF component, and TPPA-1 was prepared via aldehyde–amine Schiff base reaction and irreversible enol-to-keto tautomerization. For the synthesis of these MOF@COF hybrids, the amino-functional MOFs afforded efficient interface for binding the COF layer to fabricate excellent MOF@COF heterostructures.

3.2.2 One-step synthesis method. As mentioned in Section 3.1.1.3, integrating multiple functionalities into one system can lead to the generation of porous heterostructures. Yaghi’s group prepared a crystalline 2D MOF@COF nanohybrid using a one-step synthesis strategy (Fig. 15b). Ti₆O₆(OCH₃)₆(AB)₆ (AB prepared a crystalline 2D MOF@COF nanohybrid using a one-pot synthesis method via a modular synthesis strategy. COF-303, which was synthesized by growing NUT–COF–1@NH₂–MIL101(Fe) heterostructure was prepared via the reaction of 1,3,5-triformylbenzene with PDA, while ACOF-1 with high-crystallinity was synthesized by reacting TFB with hydrazine hydrate. Owing to the feasible preparation of COF-LZU1 via TFB and PDA, the COF-LZU1-ACOF-1 bilayer was easily synthesized through a facile temperature-swing solvothermal synthesis. Furthermore, the functionality of MOFs is essential for the preparation of MOF@MOF hybrids using ligands with similar lattices. The one-pot synthesis method and epitaxially/internally extended growth method are beneficial for the preparation of MOF@MOF hybrids using different ligands. The isotropic and anisotropic growth methods are helpful for MOF-on-MOF hybrids that use ligands with a matched lattice. Furthermore, the functionality of MOFs is essential for the construction of various types of MOF-on-MOF and MOF@COF heterostructures. For instance, the seed-mediated growth method is suitable for the synthesis of core–shell MOF@MOF hybrids using ligands with similar lattices. The one-pot synthesis method and epitaxially/internally extended growth method are beneficial for the preparation of MOF@MOF hybrids using different ligands. The isotropic and anisotropic growth methods are helpful for MOF-on-MOF hybrids that use ligands with a matched lattice. Furthermore, the functionality of MOFs is essential for the construction of various types of MOF-on-MOF and MOF@COF heterostructures.
fabrication of MOF@COF to bind different layers into an integrated system. Choosing a suitable preparation approach is essential for the development diverse MOF/COF-based hybrids with different nanostructures. The utilization of surfactants is a feasible way to control the formation mechanism and behavior of MOF/COF hybrids.

4. Applications of MOF/COF-based heterostructures

Due to the efficient integration of different types of MOFs and COFs, the formed diverse MOF-on-MOF, MOF@COF, and COF-to-COF heterostructures often exhibit excellent crystal and structural performances, such as extended skeletons, large specific surface area, excellently electrochemical activity, and synergistic effect among their different components. Therefore, these MOF/COF-based heterostructures show practical applications in different fields, including catalysis, gas adsorption/separation, biosensing and biomedicine.

4.1 Catalysis

Various MOF/COF-based heterostructures have been developed as multifunctional catalysts, such as electrocatalysts, photocatalysts, photodegradation catalysts for pollutants and heavy metal ions, and molecular catalysts. According to their application field, these MOF/COF-based heterostructures are mainly classified into three categories, including photocatalysts for energy transfer, photodegradation catalysts, and molecular catalysts for organic synthesis (Fig. 17). In this section, the extensive and promising applications of these heterostructures will be highlighted and discussed.

4.1.1 Photocatalysts for energy transfer. Various photocatalysts such as MOFs, COFs, noble metals, carbon-based dots, g-C3N4, and Bi-based compounds have been developed and used for energy transfer. Compared with conventional photocatalysts, MOFs and MOF-based hybrids exhibit some excellent merits, such as well-defined topology and porous nanostructure, which can greatly boost the transfer and diffusion of molecules and benefit the photo-induced reaction. Because of porous nanostructure and large surface area of MOFs, large amounts of active catalytic sites are exposed and enhanced for catalytic reactions. Concurrently, COFs and their related composites have also been utilized as efficient photocatalysts for driving diverse reactions, such as water splitting, organic reactions, hydrogen production, and water oxidation. Compared with traditional semiconductors, COFs often demonstrate some advantages, such as designable nanostructure, large surface area, high chemical and thermal stability, and extended π–π conjugated structures in-plane and in the stacking direction. To date, various MOF/COF hybrids have been used to modulate their structure and functionalities, reserving their large surface area and high porosity and crystallinity, and thus showing vast applications in diverse catalytic fields.

MOF@COF hybrids inherit the advantages of their parent components, and thereby have wide potential applications as photocatalysts for driving diverse reactions. Therefore, the good photoconductivity and/or fast charge transfer features of COFs can remedy the poor conductivity of MOFs. Owing to the tunable features of both MOFs and COFs, chemical interactions can occur between them, thus leading to some specific functionalities. This operation can avoid the removal of COF layers and result in a homogeneous integration, which can be
explored as diverse photocatalysts. Lan’s group provided an integrated porous NH2–UiO-66/TpPa-1-COF hybrid with superior photocatalytic H2 evolution under visible light (Fig. 18a–d). After modulation of its basic performances, the NH2–UiO-66/TpPa-1-COF (4:6) hybrid displayed a high photocatalytic H2 evolution rate of 23.41 mmol g\(^{-1}\) h\(^{-1}\), 20-times higher than that of TpPa-1-COF. Because of its outstanding light absorbance ability, TpPa-1-COF in NH2–UiO-66/TpPa-1-COF played a light-harvesting role upon visible light irradiation. The photogenerated electrons of TpPa-1-COF transferred from the valence-band (VB) to conduction-band (CB), which then further rapidly migrated to the CB of NH2–UiO-66 via covalent bonding interaction, ensuring that the photogenerated electrons oppositely moved to holes. The efficiently separation of electrons in the CB of NH2–UiO-66 reduced H\(^+\) in the presence of a Pt cocatalyst.\(^{115}\) Li et al. presented the hierarchical NH2–MIL-125(Ti)/B-CTF-1 (15TBC), which displayed superior photocatalytic ability for hydrogen production, with a transfer rate over 15 wt% (15TBC) and maximum photocatalytic activity of 360 \(\mu\)mol h\(^{-1}\) g\(^{-1}\) under visible light irradiation (Fig. 18e–h). The good photocatalytic ability of the MOF/COF hybrids was attributed to the large amounts of amide bonds formed between B-CTF-1 and MOFs. These functional groups are essential for both the enhancement of charge separation and the improvement of photocatalysis stability. For this novel photocatalysis system, electrons and holes were generated from both NH2–UiO-66 and B-CTF-1, providing a new photocatalysis strategy based on an MOF/COF hybrid.\(^{77}\) Similarly, the NH2–UiO-66@TFPT–DETH nanohybrid exhibited a high hydrogen evolution rate of 7178 mmol g\(^{-1}\) h\(^{-1}\), which was 3-fold higher than that of TFPT–DETH. Electron–hole pairs were produced from both NH2–UiO-66 and TFPT–DETH under visible light illumination (Fig. 18i–l). For this system, photogenerated electrons migrated rapidly from NH2–UiO-66 CB to TFPT–DETH CB, while holes transferred in the opposite direction. The enhanced photocatalytic activity of the core–shell NH2–UiO-66@TFPT–DETH heterostructure was mainly due to the synergistic effect originated from the NH2–UiO-66@TFPT–DETH heterostructure, such as the extension of light absorption, the improvement in exaction dissolution and transfer, and high porous structures.\(^{44}\)

Beside the exploration of photocatalysts for H2 evolution based on MOF@COF, Guo reported core–shell ZIF-67@MOF (MOF = Co-MOF-74, Co-BDC, Co–NH2BDC and Co-BTC) catalysts for driving water oxidation reaction under visible light. They revealed that the core–shell ZIF-67@Co-MOF-74 with an MOF shell of 50 nm showed the oxygen evolution production of 15 \(\mu\)mol after 8 min, while that of ZIF-67 and Co-MOF-74 was 9.8 and 11.8 \(\mu\)mol, respectively. The core–shell ZIF-67@Co-MOF-74 hybrid showed enhanced catalytic activity due to the following factors: (i) abundant crystal defects formed on the rough surface of the core–shell MOFs substantially improved the exposed metal centers and their sufficient contact; (ii) abundant OH and –COO groups on the core–shell surface were helpful for adsorbing water molecules, leading to overall water splitting to produce oxygen; and (iii) the interface of the core–shell MOFs exhibited high conductivity, further boosting the electron transport and resulting in the separation of electrons and holes, which greatly inhibited charge recombination.\(^{122}\)

Additionally, Lu et al. used the NH2–MIL-125@TAPB-PDA hybrid as a good photocatalyst for selectively oxidizing alcohols. The results demonstrated that the addition of an appropriate content of COF greatly facilitated the electronic and optical performances, and thus improved the photocatalytic ability distinctly. The NH2–MIL-125@TAPB-PDA-3 composite with a 20 nm-thick COF shell had the highest production (94.7%) of benzaldehyde, which was 2.5- and 15.5-times higher than that of NH2–MIL-125 and COF, respectively. The excellent photocatalytic ability of the NH2–MIL-125@TAPB-PDA-3 hybrid was ascribed to the boosted charge transfer between the two parts.\(^{127}\) Based on the above discussion about the photocatalytic activity of MOF@COF heterostructures, it can be deduced that combining the two components of MOFs and COFs can greatly enhance their catalytic performance.

### 4.1.2 Photodegradation catalysts

Wastewater always contains some hazard components, which are toxic to human beings and cannot be completely degraded by conventional biochemical processes.\(^{128}\) Thus, it is essential to develop the efficient techniques for treating wastewater, such as photocatalysis under visible-light.\(^{129}\) Photocatalysis is usually used for degrading these compounds because of its low-cost and high efficiency.\(^{130}\) In the photocatalysis technique, the key factor is the use of a photocatalyst, which can efficiently transfer solar energy into chemical energy, thus resulting in the degradation of pollutants.\(^{131}\) Currently, different photocatalysts have been developed for degrading or removing pollutants from the aqueous environment such as TiO2 and its composites, transition metal compounds, carbon nitrides, noble metals, and porous-organic frameworks.\(^{106,133-134}\) Among them, the advantages of MOFs can endow them with superior photocatalytic performances.\(^{135}\) MOFs not only can increase the reaction activity near by the catalytic active sites by selectively adsorbing molecules, but also can participate in the charge transfer process by modifying them with functional groups,\(^{136,137}\) as well as being used as carriers for supplying photocatalytic active sites.\(^{138}\) Currently, different types of MOFs and MOF-based composites have been developed for the photocatalytic treatment of pollutants and antibiotics.\(^{138-141}\) However, some disadvantages of pure MOFs, such as their poor photosensitivity, low separation ability of electron–holes and photocorrosion problems, as well as their hydrophilic property can remarkably reduce their catalytic activity and reduce their structural stability in a humid environment.\(^{142}\) Thus, these shortcomings of pure MOFs limit their further practical application for degrading pollutants. Although plenty of work has been devoted to the construction of MOF composites, their limited classes and complex preparations restrict their applications as photocatalysts. As previously mentioned, integrating various MOFs can combine the functionalities of different MOFs, thus enhancing their interfacial properties. The synergistic effect in different MOFs is helpful for enhancing target functions. Different MOF-on-MOF or MOF@COF heterostructures have been fabricated and utilized as the efficient photocatalysts for
degrading various pollutants, such as heavy metal ions and organic dyes (Table 1).

4.1.2.1 Removal and photodegradation of heavy metal ions. Heavy metal ions (Cu(II), Cd(II), Cr(VI), and Pb(II)) in water bodies are seriously harmful to human beings. The high accumulation of heavy metal ions not only can remarkably destroy the natural ecosystem but also can lead to serious damage to human beings. Recently, Zhang et al. reported core–shell NH2-MIL-101(Al)/ZIF-8 nanohybrids and explored their use as an adsorbent for Cu(II) (Fig. 19a). Considering the high binding of the imidazole nitrogen in ZIF-8 with Cu(II), the proposed NH2-MIL-101(Al)/ZIF-8 hybrid exhibited a high adsorption efficiency (526.74 mg g\(^{-1}\)) toward Cu(II). In addition, the fluorescence performance of NH2-MIL-101(Al) demonstrated a Cu(II)-dependent change, resulting in a superior selective/sensitive sensing performance in a broad linear range (1.5–625 mM), showing a low detection of limit (LOD) of 0.17 mM for Cu(II) (Fig. 19b and c). Additionally, it is essential to adsorb Cr(III) from wastewater due to its high toxicity toward organisms. Kitagawa’s group proposed a novel MIL-101(Cr)@NH2–MIL-125(Ti) heterostructure (Fig. 19d), where the synergy between the two pure MOFs was beneficial for enhancing the degradation of Cr(III). The MIL-101(Cr)@NH2–MIL-125(Ti) exhibited an adsorption capacity for Cr(III) of 3.16 mg g\(^{-1}\). Apparently, the presence of MIL-101(Cr) supplied additional mesoporous channels for boosting the adsorption of Cr(III) in the internal microporous NH2-MIL-125(Ti) (Fig. 19e). However, Cr(III) was not degraded by the single MIL-101(Cr). As shown in Fig. 19f, 72% of Cr(III) was dislodged from the solution by MIL-101(Cr)@NH2–MIL-125(Ti) after 120 min under visible light irradiation, while only 47% of Cr(III) was removed by NH2–MIL-125(Ti). It also displayed the band-gap energy of MIL-101(Cr)@NH2–MIL-125(Ti) was identical to that of the pure NH2–MIL-125(Ti).

4.1.2.2 Adsorption and photodegradation of organic pollutants. Organic dyes have been vastly applied in diverse industrial production fields. Also, water containing organic dyes is released to the aquatic environment, resulting in severe pollution. Thus, the removal and treatment procedures of organic dyes from water systems are extremely significant for protecting

<table>
<thead>
<tr>
<th>Materials</th>
<th>Contaminant</th>
<th>Irradiation time (min)</th>
<th>Initial concentration (mg L(^{-1}))</th>
<th>Removal%</th>
<th>Adsorption capacity</th>
<th>Ref.</th>
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<tr>
<td>NH2-MIL-101(Al)/ZIF-8</td>
<td>Cu(II)</td>
<td>—</td>
<td>10–250</td>
<td>—</td>
<td>526.74 mg g(^{-1})</td>
<td>59</td>
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<tr>
<td>MIL-101@NH2–MIL-125</td>
<td>Cr(III)</td>
<td>120</td>
<td>10</td>
<td>72</td>
<td>—</td>
<td>70</td>
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<tr>
<td>Fe(_2)O(_3)@HKUST-1/MIL-100(Fe)</td>
<td>MB</td>
<td>180</td>
<td>20</td>
<td>&gt;90</td>
<td>—</td>
<td>144</td>
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<tr>
<td>MIL-125@ZIF-8</td>
<td>Orange II</td>
<td>120</td>
<td>50</td>
<td>97.3</td>
<td>—</td>
<td>69</td>
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<tr>
<td>NH2-MIL-68@TPA-COF</td>
<td>RhB</td>
<td>40</td>
<td>20</td>
<td>—</td>
<td>—</td>
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<tr>
<td>NH2-MIL-125(Ti)/TTB-TTA</td>
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<td>20</td>
<td>10</td>
<td>&gt;90</td>
<td>—</td>
<td>89</td>
</tr>
<tr>
<td>MOF-5/COF (MSC)</td>
<td>AO and RhB</td>
<td>8</td>
<td>5</td>
<td>&gt;90</td>
<td>—</td>
<td>145</td>
</tr>
</tbody>
</table>

Fig. 19 (a) SEM image of NH2–MIL-101(Al)/ZIF-8 core–shell nanoflower. (b) Fluorescence emission spectra of NH2–MIL-101(Al)/ZIF-8 suspension (0.047 mM) upon the addition of various concentrations of Cu(II) under excitation at 325 nm. (c) Corresponding Stern–Volmer linear fitting curves of NH2–MIL-101(Al)/ZIF-8 toward Cu(II) in a high concentration range. Reproduced from ref. 59 with permission from The Royal Society of Chemistry, Copyright 2018. (d) SEM image of typical MIL-101@NH2–MIL-125 heterostructured hybrid crystal. (e) Pore width distribution based on the NLDFT model of MIL-101, NH2–MIL-125, and MIL-101@NH2–MIL-125. (f) Adsorption and photocatalytic degradation toward Cr(III) with MIL-101, NH2–MIL-125, and MIL-101@NH2–MIL-125. Reproduced from ref. 70 with permission from Wiley, Copyright 2017.

Fig. 20 (a) SEM and TEM images of the obtained Fe\(_2\)O\(_3\)@HKUST-1/MIL-100(Fe) (1 : 1) particles. (b) MB removal efficiency as a function of time with different types of hybrid materials. The shadowed area represents the experiments conducted in a dark environment. Reproduced from ref. 144 with permission from the American Chemical Society, Copyright 2019. (c) SEM images of MIL-125@ZIF-8. (d) Degradation efficiency of ZIF-8, MIL-125, MIL-125@ZIF-8, MIL-125/ZIF-8, MIL-125@ZIF-8, MIL-125@ZIF-8 and MIL-125@ZIF-8. Reproduced from ref. 69 with permission from The Royal Society of Chemistry, Copyright 2020.
the environment and life.48 Chen’s group reported a series of hierarchically sandwiched Fe3O4@HKUST-1/MIL-100(Fe) hybrid materials and their application as photocatalysts to degrade methylene blue (MB) under visible light (Fig. 20a). In comparison with the individual or pristine MOFs, the obtained MOF-on-MOF hybrid demonstrated a substantially improved specific surface and small interior pore size. Meanwhile, the removal efficiency of MB by Fe3O4@HKUST-1/MIL-100(Fe) hybrid was comparable with pure Fe3O4@MIL-100(Fe) but with only half the layers (Fig. 20b).49 Further, Liu et al. developed MIL-125@ZIF-8 heterostructures, where the high adsorption ability of ZIF-8 and the photocatalytic performance of MIL-125 were integrated (Fig. 20c). The developed MIL-125@ZIF-8 hybrid displayed a faster degradation rate of Orange II with a removal rate of 97.3% within 2 h under visible light irradiation, much higher than that of MIL-125 (54.6%) (Fig. 20d). The physically mixed ZIF-8/MIL-125 exhibited a much lower degradation efficiency in comparison to that of the MIL-125@ZIF-8 heterostructure, revealing the synergistic effect between MIL-125 and ZIF-8. These results verified that control over the site of ZIF-8 growth is vital for modulating the photocatalytic activity of MOF-on-MOF heterostructures.49

Besides the superior catalytic ability of MOF@MOF hybrids, there are many reports on the application of MOF@COF nanohybrids for the photodegradation of different pollutants. Zhang’s group prepared a core–shell NH2–MIL-68@TTA-COF hybrid material and employed it as an efficient photocatalyst for the visible-light driven degradation of rhodamine B (RhB) (Fig. 21a and b). Given that NH2–MIL-68 possesses photocatalytic activity, NH2–MIL-68@TTA-COF displayed a photocatalysis rate constant of 0.077 min⁻¹, 1.4-times higher than that of NH2–MIL-68 (Fig. 21c and d). The detailed discussion on the basic characterization of the NH2–MIL-68@TTA-COF nanohybrid revealed that the improved photocatalytic property of NH2–MIL-68@TTA-COF was mainly ascribed to its large Brunauer-Emmett-Teller (BET) surface area and small band gap.74 Further, He et al. prepared an NH2–MIL-125(Ti)/TTA-TTA hybrid with outstanding photocatalytic activity. Specifically, NH2–MIL-53(Al), NH2–MIL-125(Ti) and NH2–UiO-66(Zr) were utilized for doping TTA-TTA for the production of heterogeneous photocatalysts (Fig. 21e–g). Considering the well-matching band gaps between NH2–MIL-125(Ti) and TTA-TTA, the obtained NH2–MIL-125(Ti)/TTA-TTA hybrid illustrated remarkably photocatalytic activity for degrading methyl orange (MO) dye and colorless phenol under visible light irradiation owing to its intrinsic features of large surface area, porous nanostructure and high crystallinity. The self-photoysis of MO was very slight under visible light exposure in the absence of NH2–MIL-125(Ti)/TTA-TTA, while the NH2–MIL-125(Ti)/TTA-TTA catalyst showed a high photodegradation capacity toward MO (Fig. 21h and i). However, the photocatalytic activity of a physical mixture of NH2–MIL-125(Ti) and TTA-TTA was inferior to that of NH2–MIL-125(Ti)/TTA-TTA. This was mainly ascribed to the prominent role of the covalent binding in the NH2–MIL-125(Ti)/TTA-TTA hybrid, which greatly enhances the transfer of photogenerated electrons.88 An MOF-5/COF (M5C) hybrid was prepared via the hybridization of a zinc-based MOF and melamine-terephthaldehyde (Fig. 21j and k) and applied as a good sorbent to quickly and efficiently remove auramine O (AO) and RhB cationic dyes from aqueous media due to its combined forces. The obtained MOF-5/COF adsorbent displayed an adsorption efficiency of 17.95 and 16.18 mg g⁻¹ for AO and RhB dyes, respectively, at pH 9.5. The results showed that AO and RhB molecules were planar, which were easily adsorbed by the MOF-5/COF hybrid via physisorption forces besides the MOF-5/COF cavities. Also, the AO and RB dyes were encapsulated in the cavities of MOF-5/COF and bound to MOF-5/COF through electrostatic interaction, hydrogen bonding, and van der Waals forces, as well as host–guest interactions with the MOF-5/COF cavities (Fig. 21l).85

Based on the above discussion, it can be deduced that only limited MOFs or COFs can be explored as photocatalysts for degrading pollutants or adsorbing the organic dyes or heavy metal ions. MIL-101(Cr), NH2–MIL-125(Ti), NH2–MIL-125(Ti), and MIL-100(Fe) are often integrated with other types of MOFs or COFs, showing improved photocatalytic activity. Thus, to further broaden the range of degradable pollutants, it is significant to develop some novel heterostructures based MOFs or COFs.

4.1.3 Molecular catalysis. Some noble metal catalysts, such as Au, Pt, Pd, and Ru, can be embedded within the pores of different MOFs and COFs, which can avoid the aggregation of these catalysts and improve their catalytic activity.49 As mentioned previously, MOF-on-MOF and MOF@COF hybrids

Fig. 21 SEM image of (a) NH2–MIL-68 and (b) NH2–MIL-68@TTA-COF. (c) UV-vis absorption spectra of RhB in the presence of NH2–MIL-68 and NH2–MIL-68@TTA-COF. Reproduced from ref. 74 with permission from Wiley. Copyright 2018. TEM images of (e) NH2–MIL-53(Al)/TTA-TTA, (f) NH2–MIL-125(Ti)/TTA-TTA and (g) NH2–UiO-66(Zr)/TTA-TTA. (h) Photocatalytic degradation of MO (10 mg L⁻¹) over as-prepared photocatalysts under visible light irradiation. (i) Photocatalytic degradation of phenol (10 mg L⁻¹) over TTA-TTA, NH2–MIL-53(Al)/TTA-TTA, NH2–MIL-125(Ti)/TTA-TTA, NH2–UiO-66(Zr)/TTA-TTA, and a physical mixture of NH2–MIL-125(Ti) and TTA-TTA (NH2–MIL-125(Ti) + TTA-TTA). Reproduced from ref. 89 with permission from Elsevier. Copyright 2019. (j) and (k) SEM images of MSC. (l) Interactions of the dyes with the adsorbent and proposed mechanism. Reproduced from ref. 145 with permission from the American Chemical Society. Copyright 2020.
exhibit comprehensive performances, which can combine the advantages of different frameworks. Thereby, it can be expected that these heterogeneous systems will display extensive applications in the molecular catalysis field (Table 2). Tsung’s group prepared a homogeneous Pd–UiO-NH₂@ZIF-8 hybrid, where UiO-66–NH₂ served as the core MOF for the entrapment of Pd NPs, while ZIF-8 was conformally overgrown as the shell. Different hybrids, including Pd–UiO-NH₂ (before ZIF-8 overgrowth), Pd–UiO-NH₂@ZIF-8 (conformal shell), Pd–UiO-NH₂@ZIF-8 (fractured shell), and Pd–UiO-NH₂@ZIF-8 (synthesized in methanol in the presence of PVP) loading with Pd NPs (0.14 mg) were applied to analyze the catalytic activities for ethylene hydrogenation. The four samples showed comparable catalytic performances because ethylene molecule only had a small kinetic diameter of 2.5 Å, allowing ethylene to easily diffuse through UiO-66–NH₂ and ZIF-8. Afterward, the ethylene molecule was accessible to Pd owing to its smaller kinetic diameter than the aperture size of ZIF-8 (3.4 Å) and UiO-66 (6.0 Å). High catalytic efficiency was observed for Pd–UiO-NH₂ when cyclohexene hydrogenation was carried out. On the contrary, only negligibly catalytic activities of Pd–UiO-NH₂@ZIF-8 (conformal shell) and Pd–UiO-NH₂@ZIF-8 (fractured shell), and Pd–UiO-NH₂@ZIF-8 (synthesized in methanol in the presence of PVP) loading with Pd NPs (0.14 mg) were further observed for smaller olefins. This was owing to the fact that the kinetic diameter of cyclohexene (5.5 Å) was larger than that of ZIF-8. Thereby, the cyclohexene molecules could not penetrate the conformal ZIF-8 crystalline shell or large ZIF-8 microcrystals. However, substantial cyclohexene hydrogenation activity was achieved for Pd–UiO-NH₂@ZIF-8 (fractured shell), which was mainly ascribed to the potential diffusion pathway through the ZIF-8 shell of cyclohexene molecules caused by the boundaries between adjacent ZIF-8 crystallites.44

Given that epoxides are extensively applied in the production of diverse chemical raw materials and intermediates in many organic reactions, olefin epoxidation is a vital reaction.150 However, although many transition-metal catalysts have been developed for catalytic epoxidation reactions, it is difficult to separate the product from the catalyst.151 Recently, Zhou’s group explored the preparation of PCN-222@Zr-BPDC hybrids with mismatching lattices, followed by their application as size-selective catalysts for olefin epoxidation, where the high porosity of the MOFs remarkably boosted the selectivity toward shape and size. In the case of the core–shell PCN-222@Zr-BPDC hybrid, the Fe-porphyrin moieties on PCN-222 served as the active centers for the epoxidation reaction toward olefin, whereas the selectivity of the substrates was dependent on the tunable shell. Olefins with different molecular sizes were transformed into the corresponding epoxides, showing different conversion ratios, where the small olefins demonstrated ideal conversions. The PCN-222@Zr-BPDC hybrid exhibited high accessibility and catalytic activity given that the size of the olefin was smaller than the pore size of Zr-BPDC ( UiO-67), affording fast and efficient diffusion of the substrate. The catalytic results displayed that the olefin conversion decreased with an increase in the size of the olefins. Conversely, the decreasing trend of olefin conversion was not further observed for smaller olefins obtained under analogous preparation conditions. This revealed that olefins with large sizes were blocked by the shell, limiting the diffusion rates and hampering the accessibility of these molecules to the catalytic centers. Consequently, this catalytic system showed high size selectivity.49 Similarly, Han’s group proposed the core–shell PCN-222-Co@TpPa-1, which integrated the advantages of PCN-222-Co and TpPa-1. Due to the Lewis acid active sites present in PCN-222-Co, active Brønsted base sites in TpPa-1 (imine groups), and efficient interaction between the reactants and the PCN-222-Co@TpPa-1 hybrid, the PCN-222-Co@TpPa-1 heterostructure demonstrated an efficient bifunctional catalysis performance for the one-pot cascade decatetralization–Knoevenagel condensation reaction. Two sequential steps occurred in the catalytic reaction, including the reaction of benzaldehyde dimethylacetal to benzaldehyde by catalyzing with the unsaturated Zr(iv) and Co(ii) centers and production of 2-benzylidenemalononitrile via the Knoevenagel condensation reaction by catalyzing with the imine groups in TpPa-1, giving a high yield of 99.3%.71 Considering that it is difficult to separate and recover the catalyst used for Knoevenagel condensation, consequently generating a large amount of waste,152 it is vital to develop heterogeneous catalysts, which illustrate evident advantages such as less side reactions, feasible separation step, low corrosiveness and good reusability. Gong et al. reported a UiO-67–BPY@UiO-66 shell-structure. Combining the high stability of UiO-66 and active Lewis basic sites of the bipyrindyl linker, the UiO-67–BPY@UiO-66 hybrid was then explored as a heterogeneous catalyst for catalyzing the Knoevenagel condensation. The outstanding catalytic efficiency was mainly attributed to the

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Substrate</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Time</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd@H–Zn/Co-ZIF</td>
<td>Ethylene hydrogenation</td>
<td>&gt;80</td>
<td>&gt;80</td>
<td>10 h</td>
<td>105</td>
</tr>
<tr>
<td>PCN-222(Fe)@Zr-BPDC</td>
<td>Epoxidation of alkenes</td>
<td>&gt;99</td>
<td>—</td>
<td>12 h</td>
<td>30</td>
</tr>
<tr>
<td>PCN-222-Co@TpPa-1</td>
<td>Deacetalization-Knoevenagel condensation</td>
<td>99.3</td>
<td>—</td>
<td>10 h</td>
<td>71</td>
</tr>
<tr>
<td>UiO-67-BPY@UiO-66</td>
<td>Benzaldehyde</td>
<td>98</td>
<td>—</td>
<td>1 h</td>
<td>67</td>
</tr>
<tr>
<td>MOF-901</td>
<td>Polymerization of methyl methacrylate</td>
<td>87</td>
<td>—</td>
<td>18 h</td>
<td>116</td>
</tr>
<tr>
<td>UiO-66–NH₂@COP@[2.34%]Pd</td>
<td>Deacatalization-Knoevenagel condensation</td>
<td>99.6</td>
<td>99.6</td>
<td>12 h</td>
<td>79</td>
</tr>
<tr>
<td>MIL@NTU-1</td>
<td>Styrene oxidation</td>
<td>32</td>
<td>84</td>
<td>12 h</td>
<td>153</td>
</tr>
<tr>
<td>UiO-66–NH₂@COP@[2.34%]Pd</td>
<td>Hydrogenation of nitrobenzene</td>
<td>100</td>
<td>99.9</td>
<td>30 min</td>
<td>84</td>
</tr>
<tr>
<td>Ti-MOF@Pt@DM-LZU1</td>
<td>Hydrogenation of styrene</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>40 min</td>
<td>85</td>
</tr>
</tbody>
</table>

Table 2 Molecular catalysis by MOF/COF-based hybrids
homogeneous distribution of active sites (Lewis basic) present in the external layer of the UiO-67–BPY@UiO-66 heterostructure.67

Besides MOF-on-MOF hybrids, diverse MOF@COF hybrids have also been constructed for application in heterogeneous catalysis and organic transformation. Cordova’s group developed a 2D MOF-901, involving Ti-MOF modified with benzene-1,4-dialdehyde through imine condensation reactions. The incorporation of Ti(n) units endowed MOF-901 with efficient photocatalysis ability by coating poly(methyl methacrylate) (polyMMA), which showed a high-number-average molar mass (26 850 g mol⁻¹).118 Furthermore, Kim’s group developed a Pd/TiATA@LZU composite as an excellent photocatalyst toward tandem dehydrogenation and hydrogenation reactions, where these reactions were carried out in a continuous-flow microreactor.68 Further, Wu et al. presented a UiO-66@SNW-1 photocatalyst for tandem decarboxylation–Knoevenagel condensation reaction. Owing to the fact that UiO-66@SNW-1 was comprised of Lewis acid sites (Zr clusters in UiO-66) and Bronsted base sites (amino groups in SNW-1), the UiO-66@SNW-1 catalyst exhibited remarkably higher catalysis ability than that of its UiO-66, SNW-1, and UiO-66–NH₂ parents. Moreover, Li’s group prepared a core–shell MOF@COF composite with enhanced catalytic efficiency and fast transfer procedure. The prepared NH₂–MIL-101(Fe)@NTU-COF hybrid displayed good selectivity toward benzaldehyde, indicating that the catalytic selectivity was remarkably improved by the NTU-COF shell.69 Zhu et al. constructed a UiO-66–NH₂@COF@Pd heterostructure as an efficient catalyst for reducing 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). The results verified that BH₄⁻ and 4-NP were adsorbed on the surface of UiO-66–NH₂@COF@(2.34%)Pd via π–π stacking interaction. Afterward, the donor BH₄⁻ transferred electrons to the acceptor 4-NP, together with the reaction of BH₄⁻ with H₂O, affording NaBO₂ and H₂. Additionally, Pd nanoclusters prompted H₂ to dissociate into H–H bonds. Subsequently, the activated H atoms escaped from the Pd sites to catalyze 4-NP, further efficiently transferring to 4-AP and desorbing from the UiO-66–NH₂@COF@(2.34%)Pd surface.64 As aforementioned, the NH₂–MIL-125(Ti) MOF has been explored as an excellent photocatalyst for degrading pollutants and photocatalytic hydrogen evolution.114 It also has great promise for application as a molecule catalyst. Sun et al. proposed a core–shell NH₂–MIL-125(Ti)@DM-LZU heterostructure and loaded Pt NPs. The prepared Ti-MOFs@Pt@DM-LZU hybrid was used as a photocatalyst for site-selective hydrogenation reactions. Accordingly, the Pt NPs remarkably promoted the charge separation in Ti-MOFs to produce electron-rich Pt NPs, while the reactant and diffusion around the active Pt NPs were remarkably boosted owing to the high hydrophobicity and porosity of the COF shell.65

Owing to the fact that MOF-based heterogeneous catalysts are composed of organic and inorganic segments, multiple active sites can be integrated in MOF-on-MOF and MOF@COF heterostructures for synergistic and/or cascade organic catalysis and photocatalysis. However, aiming at the improvement of the catalytic activity and selectivity, the poor acid stability of these nanomaterials, which cannot withstand harsh conditions, have to be overcome. Moreover, given that COFs have superior catalytic activity to many MOFs, further work is needed to develop much more MOF@COF heterostructures and exploit them in the field of organic catalysis.

4.2 Gas sorption and separation

As reported, MOFs and COFs have been vastly explored as excellent adsorbents for gas adsorption and separation. In this part, the applications of MOF-on-MOF and MOF@COF heterostructures in the field of gas adsorption/separation are highlighted and discussed in detail.

4.2.1 Gas sorption or storage. Among the different energy sources, hydrogen has aroused great attention owing to its

Table 3  Some representative materials for gas sorption

<table>
<thead>
<tr>
<th>Materials</th>
<th>S_BET (m² g⁻¹)</th>
<th>Adsorbate</th>
<th>Gas uptake (mmol g⁻¹)</th>
<th>Uptake pressure (bar)</th>
<th>Uptake temp. (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-101@UiO-66</td>
<td>2772</td>
<td>H₂</td>
<td>2.4 wt%</td>
<td>1</td>
<td>-196</td>
<td>18</td>
</tr>
<tr>
<td>MIL-101</td>
<td>1716</td>
<td>H₂</td>
<td>1.9 wt%</td>
<td>1</td>
<td>-196</td>
<td>157</td>
</tr>
<tr>
<td>UIO-66</td>
<td>1186</td>
<td>H₂</td>
<td>1.5 wt%</td>
<td>25</td>
<td>-196</td>
<td>157</td>
</tr>
<tr>
<td>IRMOF-2@MOF-5</td>
<td>610</td>
<td>H₂</td>
<td>1.9 wt%</td>
<td>2.78 wt%</td>
<td>5.02 wt%</td>
<td>157</td>
</tr>
<tr>
<td>IRMOF-2</td>
<td>1700</td>
<td>H₂</td>
<td>1.5 wt%</td>
<td>2.78 wt%</td>
<td>5.02 wt%</td>
<td>157</td>
</tr>
<tr>
<td>MOF-5</td>
<td>3340</td>
<td>H₂</td>
<td>2.03 wt%</td>
<td>1</td>
<td>-196</td>
<td>158</td>
</tr>
<tr>
<td>ZIF-8@ZIF-67</td>
<td>1402.15</td>
<td>H₂</td>
<td>1.43 wt%</td>
<td>1</td>
<td>-196</td>
<td>158</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>1323.62</td>
<td>CH₄</td>
<td>1.53 wt%</td>
<td>197 mg g⁻¹</td>
<td>80</td>
<td>66</td>
</tr>
<tr>
<td>ZIF-67</td>
<td>1392.30</td>
<td>H₂</td>
<td>0.39 g g⁻¹</td>
<td>80</td>
<td>25</td>
<td>17</td>
</tr>
<tr>
<td>nHKUST-1 C MOF-5</td>
<td>1470</td>
<td>H₂</td>
<td>0.43 g g⁻¹</td>
<td>0.9 P/P₀</td>
<td>—</td>
<td>17</td>
</tr>
<tr>
<td>nHKUST-1</td>
<td>—</td>
<td>H₂</td>
<td>0.20 g g⁻¹</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>MOF-5</td>
<td>—</td>
<td>H₂</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>UiO-66–NH₂@COF-TAPB-BTCA</td>
<td>1153</td>
<td>H₂</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>UiO-66–NH₂</td>
<td>1151</td>
<td>H₂</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>COF-TAPB-BTCA</td>
<td>319</td>
<td>H₂</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* BET specific surface area.
substantial advantages such as non-toxicity, abundance, and easy preparation. However, there are still some challenges in the large-scale production of H₂. Diverse adsorbent materials, such as porous materials, are used for the adsorption H₂, where among them, MOFs and COFs are superior candidates for adsorbing H₂. Therefore, it is expected that diverse MOF-on-MOF and MOF@COF hybrids will be developed as promising H₂ storage nanomaterials (Table 3).

Ren et al. developed the MIL-101(Cr)@UiO-66(Zr) heterostructure as an efficient H₂ adsorbent (Fig. 22a and b). Basic characterizations verified that the MIL-101@UiO-66 sample displayed an enhanced surface area and large pore volume, indicating the introduction of UiO-66 in the MIL-101 framework (Fig. 22c). The enhanced hydrogen uptake capacity of MIL-101@UiO-66 was higher than that of MIL-101 by 26% and that of UiO-66 by 60% (Fig. 22d). Additionally, the Janus IRMOF-2@MOF-5 heterostructure was proposed and developed as a hydrogen adsorbent. The hydrogen-storage capacity of the Janus particles was similar to that of a physical mixture of the two components. Janus particles seem to maintain their interconnected pore structures, making them good candidates for gas separation. Moreover, two types of ZIF-8@ZIF-67 and ZIF-67@ZIF-8 heterostructures were prepared. The H₂ storage ability of the two core-shell ZIFs was superior to that of Co/Zn-ZIF and a physical mixture of ZIF-8 and ZIF-67 owing to their unique structures and element diversity. The “nHKUST-1 ⊂ MOF-5” heterostructure was developed for adsorbing fuel molecules (Fig. 22e). Differing from the pure MOF-5 or nHKUST-1 framework, the gravimetric uptake capacity of nHKUST-1 ⊂ MOF-5 for CH₄ illustrated high volumetric fuel storage capacity and reversible CH₄ uptake efficiency (Fig. 22f–h).

Besides the exploration of adsorbents based on MOF-on-MOF nanohybrids, the MOF@COF heterostructure also demonstrates a synergistic enhancement in gas adsorption. Maspoch’s group presented the UiO-66–NH₂@COF-TAPB-BTCA nanohybrid (Fig. 22i). Because of its large surface area, UiO-66–NH₂@COF-TAPB BTCA displayed higher adsorption ability for water at the same P/P₀ than that of the pristine COF pores, displaying enhanced water uptake. The N₂ and H₂O adsorption isotherms of the UiO-66–NH₂@COF-TAPB-BTCA cores both exhibited around 3-fold higher S_{het} and 2-fold higher q_{max} values due to the additional pores at the MOF/COF interface (Fig. 22j and k). Further, Wang et al. proposed an novel COF-MOF co-assembly strategy by combining [M₃(OH)₁₋₃(OH)₃(CO)₅]MOF-type and [B₃O₃(py)₃]COF-type trimers. At 1 bar and 273 K, the CO₂ uptake capacity was 3.96 to 6.32 mmol g⁻¹ in tpb-pacs. The C₂H₂ uptake of the COF-MOF was enhanced from 5.61 to 10.45 mmol g⁻¹, which was ascribed to tpb. This investigation demonstrated the introduction of C₃-symmetric fragments present in COFs in COF-MOF structures. However, in comparison with the conventional MOF and COF materials, the limited types of MOF@MOF and MOF@COF hybrids restrict their applications in gas adsorption.

### 4.2.2 Gas separation
Owing to the fact that high adsorption selectivity and the removal of CO₂ from CH₄, N₂, and H₂ play an important role in the purification of natural gas and biogas, it is significant to develop advanced methods for the efficient separation of CO₂. The membrane separation approach has been used extensively owing to its merits, such as low cost, energy efficiency, feasible operation, and reliability. However, although considerable efforts have been devoted to the development of MOFs and COFs for membrane-based gas separation, the advancement of heterostructured nanohybrids based on MOFs and COFs has only recently attracted attention from researchers (Table 4). Qiù’s group constructed a series of MOF@COF composites and developed them as separation membranes for H₂/CO₂ gas mixtures, which was ascribed to the chemical bonds produced between the MOF and COF of the membrane. Furthermore, due to the formation of an amorphous MOF in MOF@COF and the hermetically sealed space between the COF crystals, the obtained [COF-300]₃[ZIF-8] had a high membrane selectivity toward H₂/CO₂ gas mixtures. This finding hinted the synergetic effect between the different molecular sieve materials, which endowed the COF-MOF a substantially enhanced performance as a membrane. Recently, Webley’s group developed a polymorphous core–shell MOF-S@MOF-C (Fig. 23a and b), which exhibited high adsorptive selectivity/capacity for CO₂ and N₂ simultaneously. The core–shell MOF-S@MOF-C hybrid with combined features showed superior gas separation ability. The 4-day exchanged MOF-S@MOF-C composite had a CO₂ adsorption capacity that was higher than that of the pure MOF-S, and higher CO₂/N₂ selectivity than that of the pristine MOF-C (Fig. 23c and d).
Table 4  Some representative materials for gas separation

<table>
<thead>
<tr>
<th>Materials</th>
<th>Pore size (nm)</th>
<th>$S_{\text{BET}}^d$ (m$^2$ g$^{-1}$)</th>
<th>Gas separation</th>
<th>Capacity (mmol g$^{-1}$, 1 bar)</th>
<th>Selectivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF@COF composite</td>
<td></td>
<td></td>
<td>$\text{H}_2/\text{CO}_2$</td>
<td>13.5</td>
<td>6.0</td>
<td>93</td>
</tr>
<tr>
<td>MOF-S@MOF-C</td>
<td></td>
<td></td>
<td>$\text{CO}_2/\text{N}_2$</td>
<td>2.3</td>
<td>32.7</td>
<td>162</td>
</tr>
<tr>
<td>PSF-ZIF@MOF</td>
<td>0.6/0.4</td>
<td></td>
<td>$\text{CO}_2/\text{N}_2$</td>
<td>2.33</td>
<td>39</td>
<td>58</td>
</tr>
<tr>
<td>MOF@COF-based MMMs</td>
<td></td>
<td></td>
<td>$\text{N}_2/\text{CO}_2$</td>
<td>93</td>
<td>46.7</td>
<td>78</td>
</tr>
<tr>
<td>COF-LZU1-ACOF-1</td>
<td>0.3–0.5</td>
<td></td>
<td>$\text{H}_2/\text{CH}_4$</td>
<td>95</td>
<td>15</td>
<td>96</td>
</tr>
<tr>
<td>TpEBr@TpPa-SO$_3$Na iCON</td>
<td>0.4</td>
<td></td>
<td>$\text{H}_2/\text{CO}_2$</td>
<td>386</td>
<td>26</td>
<td>79</td>
</tr>
<tr>
<td>FeNi-M’ MOF</td>
<td>0.4</td>
<td></td>
<td>$\text{C}_2\text{H}_2/\text{CO}_2$</td>
<td>4.29</td>
<td>24</td>
<td>163</td>
</tr>
</tbody>
</table>

$^d$ BET specific surface area.

Song et al. reported a core–shell PSF-ZIF@MOF (PSF: polysulfone) crystalline structure and developed it as a separation membrane for $\text{CO}_2/\text{N}_2$ gas mixtures (Fig. 23e and f). In comparison with conventional fillers, the developed ZIF-8@UiO-66–NH$_2$ demonstrated some intrinsic advantages originating from each component. The large pores of the UiO-66–NH$_2$ MOF greatly improved molecular transport through the membrane. Further, the small pores or even smaller pores of the thin ZIF-8 shells also enhanced the molecular sieving, thus distinguishing $\text{N}_2$ molecules from smaller $\text{CO}_2$ molecules. The integrated ZIF-8@UiO-66–NH$_2$ hybrid membrane (40 wt% loading) exhibited enhanced hydrophobicity and substantial $\text{CO}_2$ separation capacity through both improved $\text{CO}_2$ permeability and $\text{CO}_2/\text{N}_2$ selectivity (Fig. 23g and h).  

Considering the outstanding separation performance toward mixed gases by MOFs and COFs, combined frameworks based on MOF@COF and COF@COF have also been explored as separation membranes toward gas mixtures. For instance, Chen et al. reported UiO-66–NH$_2$@TpPa-1 hybrids by combining the size selectivity of MOF fillers with the high stability of COF, which were explored as fillers in mixed matrix membranes (MMMs) for separating mixtures of $\text{CO}_2/\text{CH}_4$. Especially, the large pores of TpPa-1 COF efficiently prevented the blockage of the MOF pores, thus improving the gas permeation. Because of the high binding interaction between the coated COF layers and PSF, the developed UiO-66–NH$_2$@TpPa-1-based MMM acted as a polymer and filler. Significantly, the synergism caused by the size selectivity of the MOF pores and rigid modification of the polymer chains permitted the excellent permeation of $\text{CO}_2$ over $\text{CH}_4$ through the obtained MMMs. Moreover, Fan et al. developed a COF-LZU1-ACOF-1 membrane with a suitable size range for gas molecules (Fig. 23i and j). Its separation selectivity toward gas mixtures of $\text{H}_2/\text{CO}_2$, $\text{H}_2/\text{N}_2$, and $\text{H}_2/\text{CH}_4$ outperformed that of the COF-LZU1 and ACOF-1 membranes because of its interlaced pore networks (Fig. 23k and l). Notably, the prepared membrane not only showed high permeability and selectivity but also surpassed the latest Robeson upper bounds. Its high permeability was ascribed to its thin COF-to-COF layer with a thickness of about 1 μm.  

Ying et al. proposed a TpEBr@TpPa-SO$_3$Na iCON hybrid and employed it for the gas separation of an $\text{H}_2/\text{CO}_2$ mixture (Fig. 23m and n). The
TpEBr@TpPa-SO₃Na iCON hybrid demonstrated superior separation capacity, showing a high separation factor of 22.6, higher than that of the TpEBr nanosheet membrane and TpPaSO₃Na membrane (Fig. 23o). Notably, the TpEBr@TpPa-SO₃Na iCON membrane had a good separation performance with H₂ and an H₂/CO₂ separation factor of 22.6 (Fig. 23p). This high separation factor of the TpEBr@TpPa-SO₃Na iCON was mainly ascribed to the reduced pore size caused by the staggered stacking of iCONs and the compact dense membrane structures.

Although the extensive applications of MOFs and COFs have been investigated in the field of gas separation, their disadvantages such as high cost and poor stability in some organic solvents hinder their extensive industrial applications. Thus, rapid development and many efforts should be focused on the construction of diverse MO-on-MOF, MOF@COF and COF-to-COF hybrids, which meet some requirements such as low cost, high aqueous and chemical stability, and high separation efficiency.

4.3 Biosensing and biomedical fields

Compared to traditional nanomaterials applied in the fields of biosensors and biomedicine, nano-sized MOFs exhibit the superior biological activity, high chemical and colloidal stability, efficient surface modification, and improved biological distribution. However, most MOFs and COFs suffer from a lack of multi-functional performance and unsatisfactory stability in various environments such as acidic and alkaline media or the physiological environment. Chemical stability and biocompatibility are crucial for the sensing performances and effective treatment. The stability of MOFs is governed by multiple factors, including their ligand structure, the oxidation state and the ionic radius of their metal ions, metal–ligand coordination geometry, and hydrophobicity of their pore surface. Among them, the metal–ligand bond strength is critical to obtain labile coordination bonds, further controlling the stability of MOFs in different sensing systems. Theoretically, the stability of the metal–ligand bond can be simply predicted using the hard/soft acid/base (HSAB) principle. Another concern in the biosensing and biomedical fields is biocompatibility, and therefore metal ions and ligands or monomers with low toxicity should be adopted for the synthesis of MOF/COF hybrids. To achieve the desired functions such as light harvesting, monomers with specific structures such as phthalocyanines and porphyrin are required. Diverse MOFs or COFs have been explored as platforms for biosensors or as drug delivery systems and nanocatalytic drugs. Thus, to extend the application range of these porous materials, some MOF@COF conjugations were prepared and have demonstrated promise in the biomedical field.

4.3.1 Biosensing strategies. As aforementioned, MOFs possess some advantages of adjustable structures, large surface area and porosity, abundant exposed active sites, and excellent biocompatibility. Moreover, due to the presence of functional groups of –NH₂ or –COOH on MOFs, MOFs have been used as great potential platforms with boosted immobilization ability toward antibiotics and biomolecules such as glucose, antibodies and aptamers. Similarly, COFs demonstrate the advantages of unique structural properties, high specific area, and chemical and physical stability, which are comprised of strong covalent bonds and show superior biosensing performances toward different targets, together with extensive applications in the biomedical field. Recently, many biosensors based on diverse MOFs (Zr-MOF, Al-MOF, Fe-MOF, Zn-MOF, etc.) and COFs have been developed for detecting diverse targets, such as small biomolecules (H₂O₂, dopamine, and ascorbic acid (AA)), antibiotics, biomarkers, heavy metal ions, proteins, and living cancer cells, via different determination techniques, including electrochemical methods, fluorescence approaches, electrochemical luminescence, surface plasmon resonance,

<table>
<thead>
<tr>
<th>Material</th>
<th>Target</th>
<th>Detection method</th>
<th>Linear range</th>
<th>LOD</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-67@Ni-MOF</td>
<td>Glucose</td>
<td>Amperometric</td>
<td>5–3.9 mM</td>
<td>0.98 mM</td>
<td>189</td>
</tr>
<tr>
<td>Zn-MOF-on-Zr-MOF</td>
<td>PTK7</td>
<td>EIS</td>
<td>1 x 10⁻³ to 1 ng mL⁻¹</td>
<td>0.84 pg mL⁻¹</td>
<td>45</td>
</tr>
<tr>
<td>Tb-MOF-on-Fe-MOF</td>
<td>CA125</td>
<td>EIS</td>
<td>0.1–200 U mL⁻¹</td>
<td>58 μU mL⁻¹</td>
<td>46</td>
</tr>
<tr>
<td>AgNCs/Apt@CuFe@FeFe</td>
<td>MCF-7 cells</td>
<td>EIS</td>
<td>1 x 10⁻⁶ to 1 x 10⁻³ cell per mL</td>
<td>19 cell per mL</td>
<td>95</td>
</tr>
<tr>
<td>Ce-MOF@g-COF</td>
<td>OTC</td>
<td>EIS</td>
<td>1 x 10⁻⁴ to 0.1 pg mL⁻¹</td>
<td>0.0082 fg mL⁻¹</td>
<td>94</td>
</tr>
<tr>
<td>Co-MOF@TPN-COF</td>
<td>AMP</td>
<td>EIS</td>
<td>1 x 10⁻⁶ to 2 ng mL⁻¹</td>
<td>0.217 fg mL⁻¹</td>
<td>94</td>
</tr>
<tr>
<td>UiO@COF</td>
<td>ATP</td>
<td>Ratiometric fluorescence</td>
<td>0–10 μM</td>
<td>0.067 μM</td>
<td>80</td>
</tr>
<tr>
<td>Cr-MOF@CoPc</td>
<td>CT26</td>
<td>EIS</td>
<td>0–30 μM</td>
<td>0.038 μM</td>
<td>193</td>
</tr>
<tr>
<td>CDs@ZrHf-MOF</td>
<td>HER2</td>
<td>EIS</td>
<td>50–1 x 10⁷ cells per mL</td>
<td>36 cells per mL</td>
<td>194</td>
</tr>
<tr>
<td>Pb NPs/CMC-COF-LZU1</td>
<td>HeLa cells</td>
<td>Colorimetric</td>
<td>1 x 10⁻³–1 x 10⁻⁷ cell per mL</td>
<td>19 fg mL⁻¹</td>
<td>174</td>
</tr>
</tbody>
</table>

* PTK7: protein tyrosine kinase 7; EIS: electrochemical impedance spectroscopy; CA125: carbohydrate antigen 125; MCF-7 cells: human breast adenocarcinoma cells; BLM: bleomycin; OTC: oxetrenacycline; AMP: ampicillin; ATP: adenosine triphosphate; CT26 cells: colorectal cancer cells; DPV: differential pulse voltammetry; SWV: square wave voltammetry; HER2: human epidermal growth factor receptor 2; miRNA-21: microRNA 21; and PSA: prostate specific antigen.
colorimetric method,\textsuperscript{180} microfluidic impedance\textsuperscript{181} and chemiluminescence.\textsuperscript{182} Among them, the electrochemical method is an efficient technique for the detection of biomolecules in the biological field. In the case of most individual components of MOFs and COFs, some shortcomings such as poor electrochemical activity, low stability, and narrow linear concentration range of targets greatly restrict their application as electrochemical biosensors. Thus, other components such as inorganic NPs,\textsuperscript{183} conducting polymers,\textsuperscript{184} quantum dots,\textsuperscript{185} carbon nanomaterials,\textsuperscript{186} biomolecules,\textsuperscript{187} and other types of MOFs\textsuperscript{188} have been combined with MOFs and COFs to overcome their disadvantages. By integrating one MOF within or on another MOF or COF layer, chemical, physical, and structural advantages of MOF-on-MOF or MOF@COF nanohybrids can be obtained, together with some unexpected synergistic effects (Table 5). Based on the electrocatalytic ability of Ni-MOF, Lu et al. fabricated the UiO-67@Ni-MOF composite and used it for the detection of glucose (Fig. 24a and b). Accordingly, the large specific area and highly electrocatalytic ability of UiO-67 greatly improved the electron transfer in UiO-67@Ni-MOF, while Ni-MOF showed high electrochemical catalytic ability for glucose (Fig. 24c and d). Thus, the constructed electrochemical biosensor displayed a fast response, wide detection range, and low LOD (Fig. 24e and f).\textsuperscript{189}

Considering the immobilization interaction between aptamer strands and MOF or COF networks such as π–π stacking, van der Waals force, hydrogen bonds, and possible coordination networks,\textsuperscript{186} MOFs or COFs can be employed as a sensitive layer for the development of biosensors. These biosensors can be further used to detect the corresponding targets of the aptamers or antibodies (biomarkers, antibiotics, or heavy metal ions).\textsuperscript{174} By integrating the advantages of diverse MOFs and COFs, MOF-on-MOF and MOF@COF heterostructures can lead to superior sensing performances compared to their individual components. In our previous work, we developed two novel types of scaffolds for binding the PTK7-targeted aptamer (PTK7: protein tyrosine kinase 7), followed by the detection of PTK7. The Zr-MOF component remarkably enhanced the anchoring of the aptamer, while the Zn-MOF part greatly stabilized the formed G-quadruplex of the ZnZr-based MOFs (Fig. 25a–f) developed between the aptamer strands and PTK7 because of the specific recognition (Fig. 25g and h).

Compared with the Zr-MOF-on-Zn-MOF-based aptasensor, the Zn-MOF-on-Zr-MOF-based aptasensor had higher sensing ability, an ultralow detection limit of 0.84 pg mL\textsuperscript{−1} within a wide linear PTK7 concentration (Fig. 25i and j) and comprehensive excellent sensing performances. Moreover, Tb-MOF exhibited remarkable fluorescence, while both Fe-MOF and Tb-MOF displayed outstanding detection performances, excellent electrochemical activity, and good biocompatibility.\textsuperscript{45} Hence, our group synthesized two types of heterostructured bimetallic TbFe-MOF, \textit{i.e.}, Tb-MOF-on-Fe-MOF and Fe-MOF-on-Tb-MOF (Fig. 25k–p). After the CA125-targeted aptamer (CA125: carbohydrate antigen 125) was anchored, the obtained bimetallic MOF-based aptasensor was effectively used to sensitively determine CA125 and cancer cells. The Tb-MOF-on-Fe-MOF-based biosensor displayed higher stabilization ability toward the formed G-quadruplex than that of the Fe-MOF-on-Tb-MOF-based biosensor because of the strong immobilization of aptamer over the Tb-MOF-on-Fe-MOF substrate. Hence, the fabricated biosensor showed a very low LOD for analyzing...
CA125 and cancer cells (Fig. 25q-t) owing to its superior biocompatibility and good endocytosis.86

Diverse aptamers have been applied to construct various aptasensors that sensitively and selectively determine antibiotics in the aqueous environment owing to the high bioaffinity between aptamers and antibiotics.193 Thus, by anchoring aptamers on MOFs and COFs, different types of biosensors based on these porous frameworks have been developed and used to detect antibiotics.94 In our previous work, core–shell heterostructured PBA nanospheres embedded in Ag NCS (Fig. 26a–f) were prepared and employed as a sensitive layer to immobilize bleomycin (BLM)-targeted aptamer, following by the detection of BLM. Ag nanoclusters were prepared using an aptamer that for other aptasensors for the detection of antibiotics.

The electrochemical results showed that the developed aptasensor, combining Fe(II) ions of CuFe@FeFe PBA and BLM led to the irreversible cleavage of the heterostructured PBA nanospheres embedded in Ag NCs/Apt@CuFe@FeFe PBAs. (g) EIS Nyquist plots of the OTC detection procedures using the electrochemical aptasensors based on Ce-MOF@MCA500 in 5 mM [Fe(CN)6]3−/4− containing 0.1 M KCl. (d) Corresponding variations in the Rct values of the five types of aptasensors for detecting OTC. (e) EIS Nyquist plots for the detection of different concentrations of OTC using the Ce-MOF@MCA500-based aptasensor. (f) Corresponding calibration curves between ∆Rct and OTC concentrations (inset: the linear fit plot of ∆Rct as a function of the logarithm of OTC concentration). Reproduced from ref. 95 with permission from Elsevier, Copyright 2019. (g) and (h) Low- and high-magnification FE-SEM images of Co-MOF@TPN-COF. (i, j, and k) TEM and HR-TEM images of Co-MOF@TPN-COF. (l) EIS responses of the Co-MOF@TPN-COF-based aptasensor with different AMP concentrations. (m) Dependence of ∆Rct on the concentration of AMP. The linear parts of the calibration curves are shown in the inset of (l). Reproduced from ref. 94 with permission from Elsevier, Copyright 2019.

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Significant work has been done on combining COFs and MOFs because MOF@COF hybrids possess the merits of each component. Our group developed a series of Ce-MOF and COF nanohybrids and exploited them as novel platforms for an oxytetracycline (OTC) aptasensor (Fig. 27a and b). Integrating the excellent sensing properties of Ce-MOF and good electrochemical activity of MCA, the Ce-MOF@MCA-based biosensor exhibited a very low LOD for detecting OTC and other good sensing ability in aqueous solution (Fig. 27c–f).95 Recently, our group prepared a Co-MOF@TPN-COF nanoarchitecture and used it as a platform after immobilizing the AMP-targeted aptamer (AMP: ampicillin) (Fig. 27g–k). Given that a large number of aptamer molecules were anchored on the Co-MOF@TPN-COF nanosheets via complex interaction, the developed Co-MOF@TPN-COF-based biosensor showed a low LOD of 0.217 fg ml−1 (Fig. 27l and m).94 The Ce-MOF@MCA and Co-MOF@TPN-COF heterostructures exhibited common features, as follows: (i) abundant nitrogen-functional groups in the COF component, which can greatly facilitate the adsorption of the aptamer species; (ii) the conjugation of the COF and the electrochemically active Ce-MOF or Co-MOF can outstandingly amplify the electrochemical signal; and (iii) the porous nanostructures and large cavities in the heterostructures can allow the aptamer to adsorb onto the heterostructure and permeate its interior, thus boosting the sensing ability and enhancing the G-quadruplex stability. Although great efforts have been dedicated to exploring new porous MOF@COF hybrids and to developing their applications in diverse fields, these materials are still in the early stage of advancement in the biosensing field.

In addition to their application as electrochemical biosensors, MOF-on-MOF and MOF@COF heterostructures have been used as fluorescence biosensors because of their remarkable fluorescence performances. Wang et al.194 proposed an MOF@COF to remove aggregation-caused quenching and to enhance the emission intensity of COFs (Fig. 28a and b). The abundant

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Zr⁴⁺ ions present in UiO-66 led to high binding affinity with the phosphate group to enhance the sensing selectivity, while the organic linker, BDC-NH₂, which made the UiO-66 surface rich in amino groups, bound with the COF shell by covalent bonds. The multi-emission of the UiO@COF hybrids exhibited remarkable ratiometric sensing abilities toward PO₄³⁻ in the concentration range of 0–30 μM. Fluorescence spectra (λex = 270 nm) of 0.1 mg mL⁻¹ (c) UiO@COF1 and (d) UiO@COF2 upon the addition of PO₄³⁻ in the concentration range of 0–10 μM. Reproduced from ref. 80 with permission from the American Chemical Society. Copyright 2020.

4.3.2 Cancer therapy and wound healing. Cancer has become a major global problem with extremely high mortality.¹⁹ MOFs and COFs have recently attracted attention in cancer therapy because of their unique advantages, including regular pore structure, high specific surface area/porosity, low density, adjustable pore size, easy surface modification, and chemical structure design (Table 6).¹⁹⁶ The exquisitely designed nanoMOFs and COFs with small sizes [approximately 200–300 nm] exhibit good biocompatibility and biodegradability, thus showing potential applications in cancer therapy.¹⁹⁷ Different types of MOFs containing metal ions or organic ligands with catalytic performances, such as Cu-MOF,¹⁹⁸,¹⁹⁹ NH₃–MIL-88B (Fe),²⁰⁰,²⁰¹ Mn-MOF,²⁰²,²⁰³ UiO-66/Zr-MOF,²⁰⁴–²⁰⁷ and porphyrin-based MOFs,²⁰⁸–²¹⁰ have been explored not only as anticancer drug carriers but also as catalysts for chemodynamic therapy (CDT) and photodynamic therapy (PDT). COFs have unique advantages, such as high crystallinity, inherent pores, and large specific surface areas, which remarkably improve their loading ability toward different cancer drugs such as ibuprofen,²¹¹ 5-fluorouracil,²¹² captopril,²¹³ and curcumin,²¹⁵–²¹⁷ as well as near infrared (NIR) dyes.²¹⁸ Most importantly, structure and function modularity can be realized by logically selecting functional monomers, which endow COFs with different functionality, such as photosensitizers for PDT and photothermal therapy (PTT).²¹⁹,²²⁰ Therefore, COFs have been explored as multifunctional cancer therapeutic reagents for tumor hypoxia relief and PDT,²²¹,²²² chemo-PTT,²²³ and PT/PDT²²⁴ owing to their good aqueous dispersion, excellent biodegradability, strong light conversion, and efficient reactive oxygen species (ROS) generation ability.²²⁵

ZIF-8 is often used as a promising drug carrier owing to its nontoxicity and remarkable biocompatibility.²²⁶ This MOF displays high pH-responsiveness as a drug-loading carrier in the acidic tumor microenvironment (pH 5.7–7.8) and high stability under normal physiological conditions. Therefore, combining PB and ZIF-8 can form a core–shell dual MOF with potential application as a drug delivery system with dual-mode-responsive abilities. Wang et al. reported a PB/ZIF-8 hybrid using PB as the core (Fig. 29a–c), which showed excellent chemo-PTT cancer therapy performances under NIR light. The ZIF-8 shell was then degraded and removed from the PB core. The inner PB particles were then irradiated by NIR light, generating heat to kill cancer cells. The results revealed its higher efficacy toward HeLa cancer cell lines than that of the single therapy mode (Fig. 29d). Thus, the obtained PB/ZIF-8 hybrid therapy system attained synergistic chemo-PTT therapy efficacy (Fig. 29e and f). The anti-tumor efficiency of CSD-MOFs@DOX + NIR was much higher than that of single mode

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therapy.\textsuperscript{62} The core–shell Mn$_3$[Co(CN)$_6$]$_2$@MIL-100(Fe) (CS-MOFs) hybrid was prepared and utilized for the synchronous co-delivery of artesunate (AS) and ferric ions for cancer therapy. Owing to the fact that the Mn$_3$[Co(CN)$_6$]$_2$@MIL-100(Fe) hybrid had a mesoporous nanostructure and high binding interaction with organic linkers, it exhibited a high loading capacity toward the two therapeutic agents. \textsuperscript{63} Furthermore, the COFs had a mesoporous nanostructure and high binding interaction with organic linkers, and could thus exhibit a high loading capacity toward the two therapeutic agents. Therefore, the CS-MOFs@AS system demonstrated remarkably improved tumor delivery specificity, which was 5.79-times higher than that of free AS.\textsuperscript{227}

As discussed above, the surface morphologies and sizes of MOF/COF hybrids can be modulated using the template strategy and surfactant-assisted emulsion approach.\textsuperscript{228} Zheng et al. reported a novel H$_2$P-MOF@UiO-AM hybrid, where the photoactive porphyrin-MOF (H$_2$P-MOF) was in situ grown on the outer UiO-AM–NH$_2$ surface. The formed hybrid had a nanosize, which was smaller than 200 nm, showing the ability to be internalized by cancer cells (Fig. 30a and b). O$_2$ species were generated by irradiating the H$_2$P-MOF@UiO-AM hybrid, thus showing potential application in PDT (Fig. 30c–f).\textsuperscript{77} Zheng et al. obtained the Hf-UiO-AM@HUC-PEG hybrid (Fig. 30g and h), where its small particle size afforded improved uptake ability toward cancer cells. After endocytosis, the Hf-UiO-AM@HUC-PEG hybrid also produced cytotoxic \textsuperscript{1}O$_2$ for PDT \textit{in vitro}. Nevertheless, the porphyrin displayed a short excitation wavelength and low molar extinction coefficient, remarkably inhibiting the \textit{in vivo} application of this hybrid. Tetratopic chlorin-doped Hf-Uio-66 showed spatial arrangement-dependent photochemical behavior, and thus potential application in PDT and PTT (Fig. 30i and j). Owing to the features of the Hf element, the proposed Hf-Uio-AM@HUC-PEG hybrid demonstrated computed tomography/photothermal imaging functionalization (Fig. 30k and l).\textsuperscript{82} In 2020, Zhang and co-workers proposed a novel MIL-88B-on-UiO-66 hybrid as a bifunctional drug delivery nanosystem. The \textit{in vitro} anticancer effect of the prepared MIL-88B-on-UIO-66 was probed against MCF-7 breast cancer cells, and the results revealed its synergistic effect for 5-fluoracil (5-Fu) and alendronate (AL). This successful controlled drug release can provide a novel drug delivery nanosystem for combined cancer therapy.\textsuperscript{52}

Owing to the fact that some MOFs with peroxidase features can generate ROS, which play an important role in the eradication of bacteria by catalyzing the conversion of H$_2$O$_2$ into the highly toxic hydroxyl radical (‘OH), they show great potential as antibacterial agents. Qu’ group reported a novel MOF@COF nanozyme as a high-efficiency peroxidase mimic, which exhibited enhanced bacterial inhibition.\textsuperscript{83} For the synthesis of this MOF@COF nanozyme, the superficial COF$_{TP-TTA}$ was prepared on the surface of NH$_2$–MIL-88B(Fe) using weak acidic (phenol) and basic functional (triazine) groups as building blocks to achieve a high pore volume and surface area. The obtained MOF@COF hybrid was further functionalized with azido-functional 1,4-benzenedicarboxylic acid (3-azido benzene-1,4-dicarboxylic acid), which was used as a bioconjugation handle to link the COF with a targeting ligand.\textsuperscript{83} The MOF@COF nanozyme was successfully conjugated with a targeting monoclonal antibody (Moc18) via a click reaction, and the conjugate displayed cytotoxic effects against Gram-negative bacteria \textit{in vitro}. The MOF@COF nanozyme also demonstrated controlled drug release and \textit{in vivo} antibacterial activity against Gram-negative bacteria, showing potential for the design of multifunctional nanocomposites with enhanced antibacterial efficacy.\textsuperscript{83}

Fig. 29 (a–c) TEM images of DOX@CSD-MOFs after drug release at pH = 7.4, 6.2 and 5.0, respectively. Error bars are based on triplicate measurements. (d) Photographs of tumors harvested from mice receiving different therapeutic treatments. (e) Relative viability of HeLa cells incubated with free DOX, CSD-MOFs@DOX, CSD-MOFs and CSD-MOFs@DOX with or without laser irradiation (1.6 W cm$^{-2}$, 5 min). (f) Tumor growth curves of the corresponding group. Reproduced from ref. 62 with permission from Ivspring International Publisher. Copyright 2017. (g–j) Corresponding TEM images of CS-MOFs nanocubes in PBS solution with different pH values (pH 7.4 (panel (g)), pH 6.5 (panel (h)), and pH 5.0 (panel (i)) after the Fe(III) release process. (j) \textit{In vitro} therapeutic efficacy. (k) Tumor growth curves of different mice groups at day 17 after treatment and (m) biodistribution of CS–MOFs in HeLa tumor-bearing mice at 24 h after IV injection. Reproduced from ref. 227 with permission from the American Chemical Society, Copyright 2017.

Fig. 30 TEM images and hydrodynamic size distribution (inset) of (a) UIO-AM and (b) UNM. (c) Time-dependent UV absorption spectra of ICG at 778 nm with UNM in PBS after irradiation with a 450 nm lamp from 0 to 180 s. (d) Comparison of the decay rate of ICG alone (black), UIO-AM (red), UNM in the dark (blue), and UNM upon irradiation with (green) or without (pink) the vitamin C scavenger, respectively. \textit{In vitro} photocytotoxicity of MOF@COF nanocomposites at different laser intensities, irradiation times, and PS concentrations against (e) HePG2 cells and (f) HeLa cells. Reproduced from ref. 77 with permission from the American Chemical Society. Copyright 2017. TEM images and corresponding DLS profiles of (g) Hf-Uio-AM and (h) HUC-PEG. Cell viability of (i) HeLa cells and (j) HepG2 cells after incubation with HUC-PEG with or without 671 nm light illumination. (k) Relative tumor volume changes of mice treated with PBS, PBS + laser, only HUC-PEG, and HUC-PEG by intravenous and intratumoral injection + laser. (l) Representative tumor photographs. Reproduced from ref. 82 with permission from Elsevier, Copyright 2020.
blocks. Due to its hierarchical nanocavities with tailored surface functional groups, COF\textsubscript{TP-TTA} served as enzyme binding pockets for the formation of a specific pore microenvironment around the active sites. The TEM image showed that a sparse and dendritic COF\textsubscript{TP-TTA} skin grew on the surface of NH\textsubscript{2}-MIL-88B(Fe)-CHO. The NH\textsubscript{2}-MIL-88B(Fe)@COF\textsubscript{TP-TTA} (denoted as NMC\textsubscript{TP-TTA}) nanozyme efficiently captured bacteria tightly via multivalent topological interactions, eventually leading to the death of the bacteria by the generated ROS. Both the \textit{in vitro} and \textit{in vivo} studies revealed its satisfactory catalytic microbicidal efficacy, which enabled a wound to become red quickly, displaying a nature-inspired strategy that can remarkably facilitate the design and construction of versatile enzyme mimics. To date, only five samples of MOF-on-MOF and MOF@COF hybrids have been applied as delivery systems of anticancer drugs and photosensitizers for cancer therapy. Although rapid progress has been achieved in the application of MOFs/COFs in cancer therapy, the use of MOF-on-MOF and MOF@COF conjugations as nanocatalytic medicine is still in the early stage. Most studies have concentrated on the preparation approaches of nano-scale MOF-on-MOF for different therapeutic fields, and the degradation behavior and \textit{in vivo} chronic toxicity of these MOF-based conjugations have been rarely reported.

5. Conclusions and future outlook

Great efforts have been devoted to exploring the types, formation mechanism of heterostructures, and basic characteristics of new MOFs and COFs and their applications. Synthesizing diverse MOF/COF-based heterostructures with specific morphologies and shapes, new features, and synergistic effects is essential for the further development of advanced materials. To ameliorate the inferior electrochemical activities of most MOFs and COFs, their lack of multi-functional performances, and unsatisfactory stability in various environments, such as acidic and alkaline media or the physiological environment, hybrids or composites have been developed using various techniques to improve their potential applications. The integration of MOFs or MOFs and COFs, such as MOF-on-MOF, MOF@COF, and COF-to-COF hybrids, has been achieved by synthesizing guest MOFs or COFs on preformed host MOFs or COFs to overcome the above-mentioned disadvantages. These strategies provide much more possibilities for the development of novel MOF hybrids or MOF/COF heterostructures with new structural diversities and enhanced properties. Compared with the individual MOFs or COFs, the MOF/COF heterostructures normally exhibit the following fantastic properties due to their synergistic effects.

(i) MOF/COF-based hybrid nanomaterials present intensive applications in photocatalysis, sorption or separation, molecular recognition, and drug delivery.

(ii) The integration of MOF and COF components can complement each other. For example, MOFs usually demonstrate poor stability due to their reversible coordination bond in water and other physiological environments, while COFs are more stable because of their strong covalent bond. Therefore, the hybridization of MOFs and COFs results in increased stability in water and other physiological environments. Also, by combining with conductive COFs, the electrochemical properties of MOF/COF-based hybrids such as electrochemical catalytic ability and electrochemical sensing ability can be improved.

(iii) Excellent synergistic properties are introduced, such as irregular morphologies, micro- and mesopores at the MOF/COF interface, and strong multi-emission property. The synergism of different components in MOF/COF-based composites is of great significance for the improvement of their application-related performances, such as irregular morphology for catalytic selectivity, gas sieving, ratiometric sensing, and enhanced drug delivery and cancer synergistic therapy.

Most pristine MOF/COF-based heterostructures exhibit potential applications in gas separation/adsorption, biosensing and biomedical fields, photocatalysis, and molecular catalysis. However, research on these materials is still in its infancy and needs to be expanded and improved.

(i) Together with the development of the state-of-art of hybrid materials, fabricating ternary or even multicomponent MOF/COF-based heterostructures is urgent for their diverse applications in the near future. Therefore, to overcome the inherent restrictions of structures, new construction approaches and formation mechanisms should be proposed.

(ii) It is a great challenge to explain the functions of each component since the structure–function relationship of hybrids become more sophisticated. Complicated experiments are usually required; thus, computational simulation can give scope to reduce the amount of work and help explain the specific mechanism in complicated applications.

(iii) Although the performances of MOF/COF hybrids are enhanced, their applications in diverse scopes such as catalysis, energy storage, and cancer diagnosis and therapy are greatly restricted due to their low content of catalytic sites, absence of excellent electrochemical activity, and complicated preparation procedures. Thus, it is still urgent to explore new types of MOF-on-MOF, MOF@COF, and COF-to-COF heterostructures with remarkable electroconductivity and superior catalytic activity. The combination of MOF/COF hybrids with the currently active frontier of single-atom catalysts (SACs) is a promising field.

Together with the development of synthetic chemistry, MOFs or COFs with diverse structures and functionality will be proliferated, leading to the booming development of MOF/COF-based heterostructures. The fast-emerging synthetic strategies also pave the way for the rational design and synthesis of novel MOF/COF-based heterostructures, showing great potential for expanding the practical application of MOF materials.
Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references