1. Introduction

The rapid growth of energy consumption is making irreversible changes to the climate, which may threaten the survival on the earth in the near future. Among the many renewable and sustainable approaches currently being explored to solve these energy and environmental problems, solar fuels, from the nearly infinite solar energy, are receiving significant attention. Similar to other energy sources, solar fuels should be affordable, but unfortunately, they still cost more than fossil fuels. Considering this perspective, it is highly necessary to produce solar fuels in a cost-effective way by the rational design of photocatalytic (PC) and photoelectrochemical (PEC) reactions.

PC and PEC splitting of H₂O into H₂ (g) + ½ O₂ (g) [3] and reduction of CO₂ [4] into value-added chemicals involves redox reactions (Figure 1) assisted by the photo-generation, transport, and surface reaction of charge carriers. In this procedure, a negative conduction band relative to the reduction potential of H₂ (or CO₂) and a positive valence band relative to the oxidation potential of O₂ are necessary for the photocatalytic reactions. Therefore, under illumination, electrons can transfer from the conduction band to H⁺ (or CO₂), and the holes can transfer from the valence band to H₂O. For the effective PC and PEC reactions, it is required to design the photoactive materials with many distinctive properties such as a proper bandgap, favorable band-edge position, long lifetime and high mobility of charge carriers, catalytic activity, porosity for smooth diffusion of electrolyte toward reaction sites, abundant reaction sites at the surface, uniform dispersion of nanoscale co-catalysts, product selectivity, cost-effectiveness, and stability. Although materials such as transition metal oxides and metal chalcogenides have been intensively investigated as photoactive materials, it remains challenging to design the photoactive materials that fulfill all the above requirements. This is because many key parameters to determine PC and PEC reactions, such as energy band structures, charge separation and transport, catalytic activity, and product selectivity, are closely associated with the intrinsic properties of materials. Accordingly, the formation of hybrids, which are the heterostructures or nanocomposites between two or more different materials, has been explored to complement the limitation of using photoactive materials. The formation of heterostructures with a suitable bandgap enhances the harvesting of visible light. The establishment of charge-funneling energy band structures suppresses the recombination of charge carriers, and the incorporation of nanoscale co-catalysts promotes redox reactions at the surface. Unlike most hybrids or composites for other applications, which exhibit the average characteristics of two components, the majority of hybrids for PC and PEC reactions have demonstrated unprecedented enhancement of solar-fuel production.
genuinely demonstrating the synergistic enhancement of functional performance.

Metal organic frameworks (MOFs) consisting of metal ions (or clusters) and organic ligands are a new class of porous crystalline materials with extremely high surface area, well-defined and tunable porosity, diverse crystal structures, compositional controllability, versatile functionalization, and the capability to accommodate nanoscale catalysts. In the early stage of research, MOFs have been used in the applications of gas separation, gas adsorption, catalysts, and water treatment. With the recent progress in the design of conducting/semiconducting and photo-responsive MOFs, the application of MOFs has expanded to more diverse fields including chemical sensors, electrochemical energy storage, and PC and PEC production of solar fuels. Furthermore, various inorganic materials, such as oxides, chalcogenides, and phosphides, with unique morphology, porosity, and high surface area can be prepared by MOF-derived synthesis. In addition to the properties inherited from MOFs, the decomposition of organic components establishes hollow or reactant-accessible structures, and the controlled carbonization of organic components enables hybrids with conducting carbon. Finally, nanoscale composites with uniform cation mixing can be prepared from bimetallic MOFs. It should be pointed out that the MOF-derived materials provide distinctive structural and physicochemical properties as well as compositional uniformity that cannot be accomplished using other conventional synthetic routes.

In this perspective, the MOFs and MOF-derived materials have been considered good photocatalysts, and there have been reviews on the MOF photocatalysts for solar fuel production, CO₂ reduction, environmental remediation, and water purification, and MOF-derived semiconductor photocatalysts. Furthermore, there have been review and research articles on the various hybrid photocatalysts among oxides, chalcogenides, phosphides, noble metals, carbon-based materials (e.g., graphene, graphene oxide (GO), and graphitic carbon nitrides (g-C₃N₄)). However, the rational design of hybrid photocatalysts by synergistic combinations between MOF-based materials (MOFs or their derived materials) and other materials for solar fuel production has been barely reviewed. It should be noted that most of the distinctive features of MOFs and their derived materials match well with the requirements of photoactive materials for PC and PEC reactions, which can enhance solar fuel production significantly via well-designed hybridization with other materials. Moreover, recent progress on the fabrication, assembly, and postsynthetic modification of MOF-based materials enables a myriad of new hybrids for enhancing PC and PEC reactions. Therefore, it is worth understanding, discussing, and overviewing the key issues in the design of MOF-based hybrids for PC and PEC reactions.

2. Why MOF Hybrids?

The key parameters for determining the PC and PEC reactions in MOF-based hybrids are summarized in Figure 2. When MOFs are used as photoactive materials in hybrids, it is important to control the bandgap of the MOF, band alignment of the hybrids, charge transport within the MOFs and across the hybrid interfaces, porosity of the MOFs, and co-catalyst incorporation. These issues in the rational design of MOFs as a component of hybrid photocatalysts will be discussed in Section 2.1. In hybrid photocatalysts prepared from or using MOF-derived materials, the tailored control of size, morphology, and composition as well as the contacting configuration of the hybrid photocatalysts becomes more important. This will be covered in Section 2.2.
2.1. Rational Design of MOFs for Hybrid Photocatalysts

2.1.1. Energy Band Structures of MOFs

Energy bandgap and energy band-edge positions are two key parameters in determining PC and PEC reactions. For the absorption of visible light, the energy bandgap ($E_g$) of 1.5–3.2 eV is advantageous. In addition, the conduction band minimum (CBM) should be located above the hydrogen reduction potential ($H^+/H_2$) and the valence band maximum (VBM) should be below the water oxidation potential ($H_2O/O_2$). Accordingly, to optimize MOFs for optoelectronic applications, considerable effort has been devoted in controlling the energy band structures. In MOFs, the energy bandgap and energy band-edge position can be manipulated by choosing MOFs with different topological structures, modifying organic linkers, and controlling composition at metal nodes.

Butler et al.\textsuperscript{[19]} suggested that the electrostatic potentials at the center of MOF pores calculated by density functional theory

Figure 2. Key parameters to determine the PC and PEC reactions in MOF-based hybrids.
(DFT) can provide the reference vacuum level. Using this approach, they calculated the energy band diagrams of MOF-5(Zn), CPO-27(Mg), HKUST-1(Cu), COF-1M (covalent organic framework (COF)-1M), ZIF-8(Zn) (zeolitic imidazolate framework-8(Zn)), and MIL-125(Ti) (Figure 3a). This work demonstrates that most MOFs exhibit a relatively high bandgap (\(E_g > 3.0\) eV); \(E_g\) CBM, and VBM differ significantly depending on the topological structures and metal nodes in MOFs.

The organic linkers can be modified to engineer the energy bandgap as well as the band-edge position. Three key approaches used to alter the energy band structure without the changing framework topology are the elongation, functionalization, and mixed design of organic linkers. Civalleri et al.\cite{20} predicted that the bandgap of MOF-5(Zn) would decrease if its benzene-1,4-dicarboxylate linkers were exchanged with larger molecules. Gascon et al.\cite{21} verified this suggestion by measuring the bandgap of the isoreticular MOFs with different organic linkers (terephthalic acid, 2-bromoterephthalic acid, 2,5-dibromoterephthalic acid, biphenyl-4,4′-dicarboxylic acid, 1,4-naphthalenedicarboxylic acid and 2,6-naphthalenedicarboxylic acid) (Figure 3b). The decrease in the energy bandgap by the elongation of organic linkers in MOFs is analogous to substituting a larger anion with a smaller isovalent anion in compounds semiconductors. That is, the isoreticular expansion of MOFs can be used to narrow the bandgap. However, there is a limitation to the bandgap control because excessively long organic linkers often make MOFs unstable.\cite{22}

Li et al.\cite{23} calculated the energy band structures of MIL-125(Ti), in which the 1,4-benzendicarboxylate (BDC) linkers were functionalized by NH\(_2\), OH, and NO\(_2\) (Figure 3c). The work suggests that \(E_g\), CBM, and VBM can be modulated by the functionalization of organic linkers. These results are feasible, considering that the delocalization of electrons is associated with the electrostatic potential in MOF crystals. In particular, it is interesting that \(E_g\) of MIL-125(Ti)-NH\(_2\) (2.68 eV) is smaller than that of MIL-125(Ti) (4.08 eV), and the \(E_g\) can be further narrowed down to 1.48 eV by increasing the amount of NH\(_2\) groups. The upward shift of the VBM in amine-functionalized MIL-125(Ti) emanates from the lone pair electrons of nitrogen atoms, which facilitates the absorption of visible light. It is also reported that the calculated energy bandgap of UiO-66(Zr) and Zn\(_6\)(BTC)\(_2\) significantly decreased by the functionalization of BDC(benzendicarboxylate) linkers with –NH\(_2\) groups,\cite{24} demonstrating that amine functionalization can be a general pathway to narrow the bandgap. Halogen atoms have also been considered as functional groups to modify the bandgap. Pham et al.\cite{25} reported a calculation demonstrating that the introduction of halogen atoms (X) into the aromatic rings in IRMOF-2X is effective in decreasing the \(E_g\) and raising the VBM position. Additionally, the bandgap was shown to decrease from 3.80 eV to the visible range (2.69 eV) through the partial exchange (20%) of BDC ligands in MIL-125(Ti) with BDC-(SCH\(_2\))\(_2\).\cite{26} These results demonstrate that energy band structures can be modulated by the diverse strategies of ligand functionalization.

The two aforementioned approaches hint that the energy band structures of MOFs can be tuned further by the tailored design of organic linkers. Grau-Crespo et al.\cite{27} calculated the energy band structures of ZIFs with 12 different imidazole-based organic linkers (Figure 3d-1). Despite the same sodalite (SOD) topology, the ZIFs showed significantly different band structures (Figure 3d-2). Furthermore, the energy band structures best-fitted to PC and PEC reactions could be designed by optimized mixing between two different organic linkers (Figure 3d-3). Although this calculation needs experimental confirmation, it provides an elegant approach to tailor the band structures of MOFs for photocatalytic applications.

The modification of metal ions in MOFs has also been explored for controlling the energy band structures. Fuentes-Cabrera et al.\cite{28} predicted that the energy bandgap of MOF-2(Zr) would not change, regardless of the substitution of group IIA metal ions (Be, Mg, Ca, Zn, and Cd) with the d\(^{10}\) configuration. However, if the metal–ligand interaction of MOFs depends closely on the metal species, the band structures can be controlled by a partial or complete replacement of metals within the metal nodes. For example, Syzgantseva et al.\cite{29} reported that the bandgaps of Sn-, V-, Nb-, and W-doped MIL-125(Ti)-NH\(_2\) and Ta-, Y-, Nb-, and W-doped Uio-66(Zr)-NH\(_2\) are substantially different from those of MIL-125(Ti)-NH\(_2\) and Uio-66(Zr)-NH\(_2\), respectively, and suggested the possibility to modulate the energy bandgap by partial doping of the metals.

Aziz et al.\cite{30} calculated the energy band structures of porphyrin-based MOFs with an octahedral metal center containing trivalent ions (Al\(^{3+}\), Fe\(^{3+}\), Al\(^{3+}/Fe^{3+}\)) and a porphyrin center containing divalent ions (Zn\(^{2+}\), Fe\(^{2+}\)). The Fe\(^{3+}\) at the octahedral metal node significantly lowered the CBM due to the empty Fe 3d orbital with low energy levels, whereas Fe\(^{2+}\) at the porphyrin center raised the VBM. Moreover, the mixed MOFs with 50% Al and 50% Fe at the octahedral sites exhibited nearly ideal bandgap and band-edge positions for water splitting. These results deliver a few important points. The doping of multivalent Fe is an effective tool for modulating the energy band structures. Additionally, the porphyrin-based MOFs with two different metal sites provide higher controllability of the CBM and VBM. Furthermore, the controlled mixing of two different cations can provide further tuning of energy band structures.

Both organic linkers and metal cations can be simultaneously adopted to tailor the band structures. As shown in Figure 3d-4, Grau-Crespo et al.\cite{27} incorporated Co and Cu into the tetrahedral sites of the mIm/mIm(mIm: methyl functionalized imidazolate, nIm: nitro functionalized imidazolate) mixed ZIF and revealed that Cu with a relatively low empty three-band-edge is effective in lowering the CBM. The calculated band structure can slightly differ from the real samples owing to the variation in surface termination and the presence of defects and impurities. However, the calculation also enables the assessment of band structures with varying organic linkers and metal clusters without the fluctuation of extrinsic properties.

2.1.2. Charge Transport in MOFs

In the previous section, it was demonstrated that the bandgap of MOFs can be modulated to absorb visible light. However, the photogeneration of electrons and holes in MOFs does not always guarantee rapid charge transport, while less-mobile charge carriers are prone to recombination. Accordingly, the charge carriers in MOFs should be migrated effectively
Figure 3. a) Calculated valence and conduction band energy levels of the five MOFs, which are aligned through the Hartree potential in the center of their pores. b) Bandgap values observed for the different MOFs arranged in decreasing order with the structures of the linker groups shown. c) Calculated edge positions of the VBM and CBM with respect to the vacuum level of different MIL-125(Ti). The values of bandgaps were calculated with hybrid HSE06 exchange correlation functional. d-1) List of linkers (X) in the ZIF structures with composition ZnX₂. d-2) Positions of the highest occupied energy levels (blue) and lowest unoccupied energy levels (red) of the ZnX₂ crystal structures (lines), and of the isolated HX molecules (crosses). d-3) Equivalent plot for the mixed ZIF structures created by combining nlm with mlm or fclm linkers; the crosses represent the higher HOMO (blue) and the lower LUMO (red) among the two mixed linkers. d-4) Equivalent plot for mixed mlm/nlm ZIF structures with Co or Cu centers. a) Reproduced with permission.[19] Copyright 2014, American Chemical Society. b) Reproduced with permission.[21] Copyright 2008, Wiley. c) Reproduced with permission.[23] Copyright 2018, American Institute of Physics. d) Reproduced with permission.[27] Copyright 2016, Wiley.
Electronic conduction in MOFs can occur through bond, through space, and by the mediation of guest molecules. In particular, the 1D (–Fe–N–N–)∞ chains of Fe–azolate frameworks are known to enhance conductivity when the multivalency (FeII/FeIII) is properly controlled. The Fe–azolate frameworks can also offer 3D-network-containing (–Fe–N–N–)∞ chains, which enable isotropic conduction. Several C-MOFs have been prepared by the partial oxidation of FeII (into FeIII) in Fe(1,2,3-triazolate)2 by I2 (σ: 1.0×10−3 S cm−1)[33] or by BF3− (σ: 0.31 S cm−1 at RT, increase ≈108 times),[34] the gradual oxidation of FeII in Fe2(BDT)3 (BDT: benzene-1,4-ditertrazolate) (σ: 1.8 S cm−1 at RT, increase ≈6×104 times)[35] and partial reduction of FeIII (into FeII) in Fe2(BDP)3 (BDP = benzene-1,4-dipyrrozolate) using K+ (σ: 0.025 S cm−1 at RT, increase ≈7×105 times; mobility: 0.84 cm2 V−1 s−1, increases by 420 times).[36] The concentrations of redox pairs (e.g., [FeII] and [FeIII]) should be high and comparable with each other to increase the neighboring probability of redox pairs. The control of the [FeII]/[FeIII] ratio either by redox reaction or by additives to balance the valence control offers convenient modulation of conductivity. However, the stability of MOFs can be affected by pH, ions, and additives of the electrolyte solution during solar fuel production. At this moment, although Fe is known as the most effective multivalent metal for enhancing electronic conductivity, more investigation into other MOFs and bimetallic MOFs containing multivalent metal ions can provide opportunities to design new C-MOFs. For this, the standard reduction potential for redox reactions and the interaction between metal ions and neighboring organic linkers should be taken into account. In addition, the redox pair of organic linkers can also enhance the conduction. For instance, (NBu4)2FeIII2(dhbq)3 (dhbq: 2,5-dioxido-1,4-benzoquinone) showed a conductivity of 0.16 ± 0.01 S cm−1 at 298 K[37] and (Me2NH2)2[Fe2L3]·2H2O·6DMF (LH2 = 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) exhibited the conductivity of 14.7 × 10−2 S cm−1 at ambient temperature,[38] both of which were attributed to the mixed valence of the ligand.

Conduction can occur through space when the organic linkers show π–π interactions (Figure 4b).[32] The conductivity depends closely on the stacking distance between the ligands. Park et al.[39] demonstrated that the conductivity of single crystalline M4(TTFTB) (M = Cd, Mn, Co, and Zn) (TTFTB: tetrafluorvalene tetrabenzoxaole) samples increases with decreasing the shortest S···S spacing (Figure 4c). Thus, the conductivity can be tuned by the incorporation of metal ions with different sizes and the variation of stacking motifs in the ligands.[40] Representative MOFs with π–π interaction are TTF(tetrafluorvalene),[41] naphthalene-, anthracene-, and naphthalenediimide-based MOFs. As expected from the directionality of π–π interactions, the anisotropy of through-space conductivity in MOFs is unavoidable.[39] This suggests that the aligned growth of C-MOFs on other materials may be necessary to facilitate conduction across the interfaces of C-MOF-based hybrids. Lastly, the introduction of electroactive guest materials such as I2 (or poliodide) and TCNQ[42] (Figure 4d) can increase the conductivity of MOFs. The charge transfer through guest–guest or guest–framework is responsible for conduction. This is convenient but can decrease the number

toward the surface of the MOFs or the adjacent materials of the MOF-based hybrids for their participation in PC and PEC reactions. The former requires charge transport within the MOF, and the latter involves transport across the heterointerfaces. Long-range charge transport in most MOFs is generally known to be difficult, because the conducting metallic ions are linked to insulating organic linkers. In addition, the extremely porous MOF structures also hamper the electronic conduction. Thus, the charge transport in MOFs for PC and PEC reactions has been one of the most challenging issues. Nevertheless, the promising potential of hybrid photocatalysts assisted by conductive MOFs (C-MOFs) should not be underestimated because significant progress has been achieved in designing C-MOFs and understanding the relevant conduction mechanisms in recent years. Both ion-conducting and electron-conducting MOFs are available. However, in the present section, only electronic conduction of MOFs in close relation with PC and PEC reactions will be discussed.

Many excellent reviews have compiled various C-MOFs and their conduction mechanisms in detail.[31] Thus, this section covers representative C-MOFs and the possible strategies to enhance PC and PEC reactions using C-MOF-based hybrids. Electronic conduction in MOFs can occur through bond, through space, and by the mediation of guest molecules. In conduction through bond (Figure 4a),[32] the bonding nature is an important parameter to determine the conduction. For instance, the ionic bonding characteristics between metals and carboxylate linkers usually do not establish substantial orbital overlap for conduction, whereas the interaction between metals and azolate linkers (pyrazolate, triazole, and tetrazolate) provides more favorable orbital overlap. In particular, the 1D (–Fe–N–N–)∞ chains of Fe–azolate frameworks are known to enhance conductivity when the multivalency (FeII/FeIII) is properly controlled. The Fe–azolate frameworks can also offer 3D-network-containing (–Fe–N–N–)∞ chains, which enable isotropic conduction. Several C-MOFs have been prepared by the partial oxidation of FeII (into FeIII) in Fe(1,2,3-triazolate)2 by I2 (σ: 1.0×10−3 S cm−1)[33] or by BF3− (σ: 0.31 S cm−1 at RT, increase ≈108 times),[34] the gradual oxidation of FeII in Fe2(BDT)3 (BDT: benzene-1,4-ditertrazolate) (σ: 1.8 S cm−1 at RT, increase ≈6×104 times)[35] and partial reduction of FeIII (into FeII) in Fe2(BDP)3 (BDP = benzene-1,4-dipyrrozolate) using K+ (σ: 0.025 S cm−1 at RT, increase ≈7×105 times; mobility: 0.84 cm2 V−1 s−1, increases by 420 times).[36] The concentrations of redox pairs (e.g., [FeII] and [FeIII]) should be high and comparable with each other to increase the neighboring probability of redox pairs. The control of the [FeII]/[FeIII] ratio either by redox reaction or by additives to balance the valence control offers convenient modulation of conductivity. However, the stability of MOFs can be affected by pH, ions, and additives of the electrolyte solution during solar fuel production. At this moment, although Fe is known as the most effective multivalent metal for enhancing electronic conductivity, more investigation into other MOFs and bimetallic MOFs containing multivalent metal ions can provide opportunities to design new C-MOFs. For this, the standard reduction potential for redox reactions and the interaction between metal ions and neighboring organic linkers should be taken into account. In addition, the redox pair of organic linkers can also enhance the conduction. For instance, (NBu4)2FeII2(dhbq)3 (dhbq: 2,5-dioxido-1,4-benzoquinone/1,2-dioxido-4,5-semiquinone) showed a conductivity of 0.16 ± 0.01 S cm−1 at 298 K[37] and (Me2NH2)2[Fe2L3]·2H2O·6DMF (LH2 = 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) exhibited the conductivity of 14.7 × 10−2 S cm−1 at ambient temperature,[38] both of which were attributed to the mixed valence of the ligand.

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Figure 4. a,b) Orbital representations of potential charge transport pathways operative in MOFs. a) The through-bond pathway involves orbitals from the metal and ligand functional groups. b) The through-space pathway involves π–π stacking of organic moieties. c) Correlation between S···S distance and electrical conductivity in M2(TTFTB). d) TCNQ – TCNQ stacking of organic moieties. c) Correlation between S···S distance and electrical conductivity in M2(TTFTB). d) TCNQ – TCNQ stacking of organic moieties. c) Correlation between S···S distance and electrical conductivity in M2(TTFTB). d) TCNQ – TCNQ stacking of organic moieties.
of available micropores at the excessive introduction of electroactive guests.

C-MOFs are generally designed to be used in ambient atmosphere. However, for PC and PEC reactions, the photoactive properties and stability in liquid electrolyte solution are also important. Although C-MOFs do not always satisfy all the requirements, many C-MOFs with a high stability in aqueous environments have been reported.\(^\text{[43]}\) Additionally, a number of C-MOFs are actively being designed; thus, more C-MOFs will be available in the near future. Accordingly, the design of water-stable C-MOFs is expected to significantly contribute to the photocatalytic performance. The detailed stability issues of MOFs in aqueous environments will be discussed in Section 2.1.5.

Although the conductivity of MOFs are not high but moderate, MOF-based hybrids can be useful since the charge transport length can be shortened by decreasing the size (or thickness) of the MOFs. Furthermore, in most MOFs, the photogenerated electrons need not migrate a long distance for surface redox reactions because highly porous structures facilitate the transport of electrolytes to the entire region of the MOFs. Thus, the design of MOF-based nanocomposites\(^\text{[44]}\) or the coating of a MOF thin film on another substrate\(^\text{[45]}\) is effective. Furthermore, thin MOFs are also advantageous for effective light penetration.

C-MOFs without photogeneration can also contribute to photocatalytic reaction via the formation of hybrids. Various MOFs exhibit abundant redox pairs through metal and/or organic linkers, wide surface redox reaction sites, and porous structures. From these results, C-MOFs appear to be excellent candidates for cost-effective co-catalysts to promote PC and PEC reactions. These conclusions are supported by the recent reports that the conductive Ni\(_3\)(HITP)\(_2\) (HITP=2, 3, 6, 7, 10, 11-hexaiminotriphenylene) MOF can be used as an excellent oxygen reduction electrocatalyst in alkaline solution\(^\text{[46]}\) and co-catalyst for photocatalytic CO\(_2\) reduction.\(^\text{[47]}\) Furthermore, C-MOFs are effective in separating the charges generated in adjacent photoactive materials. For example, if hybrids between C-MOFs and CdS are formed, the photogenerated charge carriers in CdS can be easily transferred to conductive MOFs, which suppress the charge recombination and photocorrosion in CdS. Charge transport in MOFs is generally the rate-determining step in photocatalytic reaction and thus should be enhanced further by rational material design.

2.1.3. Porosity of MOFs

MOFs exhibit extremely high surface area and porosity owing to the distinctive combination between metal ions and organic links. The structural diversity of MOFs provides a wide size range of micropores (<2 nm), as summarized in Figure 5a.\(^\text{[48]}\) Accordingly, MOFs can be chosen depending on the type of application, such as gas adsorption, gas separation, catalyst, photocatalyst, and gas sensors. Furthermore, various methods have been suggested to tune the microporosity (<2 nm) in MOFs. The methods include the synthesis of isoreticular MOFs with the same framework topology but with the different length of organic chains (Figure 5b).\(^\text{[49]}\) postsynthetic linker reinstallation to tune the lattice size,\(^\text{[50]}\) and the interpenetration of MOFs (Figure 5c).\(^\text{[51]}\) In general, micropores smaller than 0.5 nm are used for gas separation and gas adsorption.
However, from the viewpoint of PC and PEC reactions, the micropores of MOFs are often extremely small to transport the large reactants from the liquid electrolyte to the surface redox sites and reaction products toward the counter direction. Notably, the development of mesopores by isoreticular expansion is difficult because excessively long organic linkers are unstable and often lead to interpenetration. In this perspective, hierarchical porosity covering micro- (size < 2 nm), meso- (size 2–50 nm), and macropores (size > 50 nm) has been developed in MOFs using various routes. The simplest approach to develop mesopores within MOFs is the partial removal of organic linkers. Two organic linkers with different stability against chemicals, light, and high temperature are generally used, and a more liable linker is removed by ozonolysis (Figure 5d),[52] acid treatment,[53] laser photolysis (Figure 5e),[54] and thermolysis (Figure 5f),[55] respectively. The size of mesopores can be modulated by controlling the mixing ratio of liable and stable linkers as well as the amount of exposure to ozone, acid, laser, and high temperature. The difference in linker stability and the variation of MOF stability can be utilized to develop mesoporosity within MOFs. For example, Huang et al.[56] prepared a hierarchical MOF containing mesopores using acid-sensitive and thus liable MOF nanoparticles (NPs) as templates (Figure 5g). It is worth noting that the final MOFs with mesoporosity consist of only stable linkers/MOFs, and the templates with liable linkers/MOFs are removed. The surfactants or block copolymers have also been used as the supramolecular templates to develop the mesopores in MOFs,[57] and the agent to induce the swelling of templates can facilitate the tuning of pore sizes.[58] Moreover, postsynthetic treatment of MOFs provides a convenient tool to modify MOFs. Accordingly, a myriad of combinations between different linkers and MOFs offer diversified designs of stable and mesoporous MOFs and MOF-based hybrids for PC and PEC solar fuel production.

When the size or thickness of MOFs becomes significantly larger than the mesopores, the mesopores can be insufficient for effective diffusion of reactants/products, and the mass transport can be the rate-determining step for PC and PEC reactions. Accordingly, various routes have been suggested to develop macroporosity in MOFs,[59] which includes templating using polystyrene (PS) (Figure 6a),[59] SiO2,[60] and block co-oligomers,[61] the addition of H2O2 during MOF synthesis,[62] postsolvothermal modification of MOFs,[63] phase separation due to self-assembly of MOFs,[64] and the replacement of MOF-stabilized high-internal-phase emulsion using supercritical CO2 (Figure 6b).[65] In particular, ordered macromicroporous MOF single crystals can be prepared by the controlled reaction of precursor of ZIF-8(Zn)@PS monolith with CH3OH/NH3·H2O mixed solutions. This is encouraging since the high performance of single crystalline materials can be synergistically combined with macroporosity.[59] Additionally, not only the size of macropores, but also high interconnectivity is required for effective mass transport for PC and PEC reactions, and special care must be taken during template removal to minimize the damage to MOFs. In general, trimodal porosity with micro-, meso-, and macropores is advantageous for achieving rapid mass transport without compromising high surface area, which should be tuned depending on the MOF size and the requirements of MOF-based hybrids.

Figure 6. a) Schematic diagram to prepare SOM-ZIF-8(Zn) (SOM: single-crystal ordered macropore, PS: polystyrene, THF: tetrahydrofuran, Cryst.: crystallization), representative SEM image of SOM-ZIF-8(Zn), and SEM images of individual crystals taken from four different directions. b) Diagram illustrating the MOF-stabilized high-internal-phase emulsion (HIPE) and derivation of MOA from HIPE. a) Adapted with permission.[59] Copyright 2018, AAAS. b) Adapted with permission.[65] Copyright 2016, Springer Nature.

2.1.4. Immobilization of Co-Catalysts within MOFs

MOFs with periodic, tunable, and abundant micropores are ideal scaffolds for encapsulating various atomic-scale/nanoscale co-catalysts such as metals, metal complexes, and catalytic oxides without aggregation. Since the electrons photogenerated in MOFs can be moved readily to adjacent co-catalysts, photocatalytic performance can be enhanced significantly. Moreover, co-catalysts confined within the crystal lattice of MOFs are stable against dissolution and corrosion. Finally, wide range of different topologies, metal ions, and organic linkers of MOFs as well as their combinations with various nanostructures enable the design of diversified hybrids structures. Thus, the hybrids between MOFs and nanoscale co-catalysts can provide new opportunities to maximize catalytic sites and minimize the degradation of catalysts.

Metal NPs are generally immobilized within MOFs by post-synthetic routes involving the in-diffusion of metal sources through the pores of MOFs and the subsequent reduction by physico-chemical methods. The pore windows in MOFs should be wide enough for the in-diffusion of metal ions, source compounds, and reducing agents. The minimum opening of the pores, rather than the maximum pore diameter available, is more important. Liquid impregnation, chemical vapor deposition,[66] and atomic layer deposition (ALD)[67] have been suggested for providing metal sources within MOFs. Metallic sources are generally reduced to metal NPs by annealing in H2, solution reduction, or photoreduction.[68]

Overall, the complete filling of every available pore by the metallic NPs seems to be effective for photocatalytic
performance. However, it is technically challenging and not always beneficial, since the mass transport of both reactants and products can be blocked. This is feasible considering the decrease of surface area mostly with the incorporation of metallic NPs.\(^6[^0]\) Moreover, if the metallic NPs become larger than the available pore size, the structure of the MOF can be distorted or degraded\(^6[^8,^7]\), which may deteriorate the photocatalytic performance. Accordingly, the size and number density of metal NPs should be carefully controlled depending on the nanocages of the MOFs and functionality of the hybrids.

The size and shape of the metallic NPs are constrained by the pores in the MOFs.\(^6[^8]\) For a synergistic effect between the catalytic promotion and mass transportation of reactant/product, the incorporation of metallic NPs that are smaller than the available pores in the MOFs would lead to the optimal configuration of the hybrids. Partial filling of the pores with smaller and size-tunable metal NPs can be achieved by controlling the concentration of metal sources or reducing agents\(^6[^2]\) as well as the use of double solvents (one with a metal source and the other without).\(^7[^1,^2]\) The hybrids can be further diversified by the immobilization of binary metal NPs such as AuNi,\(^7[^1]\) Pd@Ag,\(^7[^3]\) and Pd@Co.\(^7[^4]\) Additionally, the size of metal co-catalysts can be decreased to the atomic scale. For example, the porphyrin rings in Al-TCPP\(^7[^5]\) are known to accommodate single Pt atoms, which can establish MOF–metal hybrids without changing the crystallinity and structure.

Non-noble metal NPs have also been incorporated into MOFs\(^6[^6]\) and oxidized by thermal annealing in an oxygen-containing atmosphere, leading to MOF-oxide NP hybrids. For instance, Han et al.\(^7[^6]\) prepared cobalt-oxide-incorporated MIL-101(Cr) by the solution-based impregnation of Co\(^2+\) in the cavity and a subsequent two-step annealing at 250 °C in Ar and at 150 °C in air. Sources of non-noble metals can also be incorporated within nanocages by gas-phase adsorption. Müller et al.\(^7[^7]\) prepared MOF-5(Zn) loaded with Cu and/or ZnO by vapor phase adsorption of volatile metal precursors and subsequent photostimulated thermolysis or hydrolysis/oxidation. When the metal oxide NPs are immobilized within MOFs in a postsynthetic manner, a relatively low annealing temperature (<300 °C) is generally used to avoid the oxidation and destruction of MOFs. Accordingly, there can be a limitation to the incorporation of highly crystalline oxide NPs within MOFs. Extremely small and well-dispersed non-noble metal NPs incorporated within MOFs provide enhanced photocatalytic performance; this can be a cost-effective alternative for replacing expensive noble metal co-catalysts.

Catalytic organometallic compounds or metal complexes have been also incorporated into MOFs. Representative examples are Fe-complex doped UiO-66(Zr)\(^7[^8]\) and zirconium-porphyrin based MOFs.\(^8[^0]\) Ir, Re, and Ru-complex doped UiO-67(Zr),\(^8[^1]\) Ru-complex doped Ti-MOF,\(^8[^2]\) and Co-complex doped MIL-125(Ti)-NH\(_2\).\(^8[^3]\) Unlike the formation of separate metal NPs within nanocages of MOFs, the incorporation of organometallic compounds or metal complexes generally does not destroy but retains MOF structures. Notably metal complexes can be used either as co-catalysts or as photosensitizers.

Extremely porous structures of MOFs enable the postsynthetic incorporation of nanoscale co-catalysts, providing tailored control of the size, composition, and configuration of catalysts.

Furthermore, the organic linkers of MOFs provide a strategy for the linker-assisted loading of atomic scale metal catalysts, as well as the doping of functional metal complexes. Accordingly, superior photocatalytic properties can be uniquely achieved using MOF-co-catalyst hybrids, which minimize the use of expensive noble metal co-catalysts and enable the use of non-noble metal co-catalysts.

### 2.1.5. Stability of MOFs in Solvents and during Activation

Due to high porosity and high surface area, MOFs in the early stage of research have been utilized for gas storage and gas separation. However, during the process, the MOFs are structurally decomposed by moisture-driven damage.\(^8[^4]\) For example, HKUST-1(Cu), a hydrophilic MOF, is prone to structural collapse when exposed to water because the water molecules bind strongly to the unsaturated metal sites, thus eventually breaking the metal–ligand bonding.\(^8[^5]\) Likewise, MOF-5(Zn) undergoes lattice distortion and framework collapse when the water content is higher than 3.9% by mass.\(^8[^6]\) The water stability of various MOFs has been investigated because water damage is the greatest challenge to overcome for stable application of MOFs in hydro-related fields. Typically, MOF stability is tested by examining the crystal structure after soaking the MOFs in a room-temperature or heated solution for a long duration. For instance, 12 ZIFs were studied for their thermal and chemical stability; among them, ZIF-8(Zn) and ZIF-11(Zn) revealed to have remarkable stability in boiling alkaline water and organic solvents.\(^8[^7]\)

As PC and PEC reactions take place in an aqueous medium, the applied MOFs should have high durability in water. Reviews on this topic were published by Burch et al. in 2014 and Wang et al. in 2016.\(^8[^8]\) Wang et al. proposed three features of water stable MOFs. First, MOFs built from high-valence metal ions with high charge density could have a stronger coordination bond toward the ligands. Secondly, azolate ligands, such as imidazolates, pyrazolates, triazolates, and tetrazoles, can be utilized for building water-stable MOFs. Lastly, MOFs could be modified for steric hindrance to sustain the crystallinity in an aqueous medium. To date, several MOFs are reported to have water stability, for example, Al-PMOF,\(^8[^9]\) UiO-66(Zr),\(^8[^10]\) UiO-67(Zr),\(^8[^11]\) UiO-66(Zr)-NH\(_2\),\(^8[^12]\) MIL-100(Cr),\(^8[^13]\) MIL-101(Al and Cr),\(^8[^14]\) MIL-53(Al and Cr),\(^8[^15]\) MIL-125(Ti),\(^8[^16]\) and ZIF-8(Zn).\(^8[^17]\) Among them, UiO-66(Zr), UiO-67(Zr), MIL-101(Al and Cr), MIL-125(Ti), and ZIF-8(Zn) showed excellent performance in photocatalytic H\(_2\) production.

In addition to water stability, pH stability is another crucial factor that needs to be considered for PEC H\(_2\) production. Typically, when MOFs are hybridized with other materials such as metal oxides for PEC H\(_2\) production, both materials should be stable in the same pH range so that they can be activated for water oxidation and H\(_2\) production. For example, WO\(_3\) is unstable in highly alkaline conditions (pH > 11) but stable in acidic conditions.\(^8[^18]\) ZnO is stable in the pH range of 9 to 13.\(^8[^19]\) Thus, the MOFs for PC and PEC reactions should be chosen considering the components of hybrid materials used in the aqueous environment. Figure 7 summarizes the pH stability of various types of MOFs reported to date. Some MOFs are stable...
in acidic solution whereas other MOFs show stability in alkaline solutions.⁹⁹ For example, MIL-100(Fe) and MIL-53(Fe) decomposed in water with pH 7 but retained a relatively stable structure in weakly acidic conditions.¹⁰⁸ Moreover, the pH of the electrolyte changes as the PEC reaction proceeds; therefore, it would be beneficial to apply MOFs that are stable over a broad pH range.

The stability of porous channel structures during the activation of MOFs is also important. The solvents or chemicals can remain within MOFs during the synthesis or PC and PEC reactions, which should be removed for the regeneration of MOFs via the collapse of MOFs, which include the use of a solvent with low surface tension,¹⁰¹ supercritical CO₂ activation,¹⁰² ligand rigidity,¹⁰³ and the introduction of polymer guests.¹⁰⁶

To date, the stability of MOFs in aqueous medium has been studied intensively. However, many cases of solar fuel production occur in solutions containing organic molecules that act as hole-sacrificial agents. In photocatalytic reaction, hole-sacrificial agents prevent the fast recombination of charge carriers by attracting the hole at the surface;⁶⁷ thus, they can balance the surface charges of the MOFs to retain structural stability.¹⁴ Various types of organic solvents or weak acids, such as methanol, ascorbic acid, and triethanolamine (TEOA), are involved in the reactions of hole scavengers.¹⁰⁸ As the hole-sacrificial agents dominate the efficiency of the solar fuel production,¹⁰⁹ the long-term interactions between the hole scavengers and the MOFs should be taken into account. Furthermore, organic solvents such as acetonitrile and dimethylacetamide are often used in photocatalytic CO₂ reduction.¹¹⁰ Thus there have been several studies to report the stability of MOFs in organic solutions. Chiong et al.¹¹¹ reported that Fe-HAF-1 is stable in ammonium hydroxide, trimethylamine, pyridine, methanol, acetic acid, acetonitrile, and acetone for 1 week. Hu et al. found that the USTC-7(Zn) retained its structural stability after the soaking of MOFs in ethanol, ethyl acetate, toluene, and hexane for 12 h.¹¹² The stability of NKU-105 in boiling acetonitrile, chloromethane, DMF, and methanol is reported,¹¹¹ and [Zn₄O(3,5-dimethyl-4-carboxypyrazolato)]₄ is also known as a stable MOF in boiling benzene and methanol.¹¹¹ Park et al.⁶⁷ showed that the ZIF-8 and ZIF-11 maintained the crystallinity in boiling methanol and benzene for 7 days. The chemical stability of MOFs in water and various organic solvents is summarized in Ding’s review.¹¹⁵ Note that some organic solvents can distort the crystalline structure of MOFs,¹¹⁶ which should be avoided when designing MOF-based hybrids for photocatalytic applications

### 2.1.6. Product Selectivity of MOFs for CO₂ Reduction Reactions

Product selectivity is a key parameter in photocatalytic CO₂ reduction reactions. Based on the standard reduction potentials for CO₂ reduction reactions (Table 1),⁶⁶ CO₂ can be reduced to various products such as formate, CO, CH₃OH, and CH₄ in a similar range of standard potentials. Accordingly, selective reduction of CO₂ to an on-demand product is an important issue for practical applications.⁶⁶,¹¹⁷ In addition, when CO₂ is reduced in aqueous media, hydrogen evolution reaction may occur, which is a side reaction in this case. Therefore, the hydrogen evolution reaction should be prevented, and only the CO₂ reduction reactions should proceed. Although various CO₂ reduction reactions are possible, most studies have focused on the reduction of CO₂ to CO or formic acid that are more facile for reaction and advantageous for commercial use. Since only two electrons participate in the reduction to CO or formate, the reaction is kinetically easier than other reduction reactions. Furthermore, CO and formic acid are promising fuels in practical applications. CO can be used for syngas, which is a critical C₁ feedstock for the Fischer-Tropsch synthesis,¹¹⁸ methanol synthesis, and syngas fermentation,¹¹⁹ while formic acid is a promising candidate fuel for low-temperature fuel cells as well as a variety of traditional industrial uses.¹²⁰

In the electrochemical reduction of CO₂ in aqueous electrolytes, a wide range of metal cathodes have been studied.⁴,¹²¹ Figure 8 shows the categorized periodic table based on the main products produced by each element in the electrochemical reduction of CO₂. CO is mainly produced from Au, Ag, Zn, and Pd metal cathodes, and formic acid is produced from metal cathodes such as Si, Sn, and In. Based on this preferred selectivity depending on metal cathodes, Hwang and coworkers reported that the enhanced faradaic efficiency and the lowered overpotential for selective reduction of CO₂ to CO were achieved using immobilized Ag NPs supported on carbon electrodes.¹²² Additionally, Zn NPs,¹²³ Bi nanotubes,¹²⁴ and SnO₂

Table 1. Redox potentials for various CO₂ reduction reactions in aqueous media at neutral pH 7.⁶⁶

| Reaction                                                                 | Redox Potential (V vs. NHE) |
|------------------------------------------------------------------------|-----------------------------|
| CO₂ + e⁻ → CO₂⁻                                                        | −1.85                       |
| CO₂ + H₂O + 2e⁻ → HCOO⁻ + OH⁻                                          | −0.665                      |
| CO₂ + H₂O + 2e⁻ → CO + 2OH⁻                                            | −0.521                      |
| 2H₂O + 2e⁻ → H₂ + 2OH⁻                                                 | −0.414                      |
| CO₂ + 5H₂O + 6e⁻ → CH₄OH + 6OH⁻                                        | −0.399                      |
| CO₂ + 6H₂O + 8e⁻ → CH₄ + 8OH⁻                                          | −0.246                      |
nanoclusters\textsuperscript{[125]} have been introduced into noncatalytic silicon or carbon electrodes to improve the catalytic activity and selectivity of the \textit{CO$_2$} reduction reaction to CO or formic acid. Co-catalytic NPs have also been applied on MOF photocatalysts for promoting the reduction to CO. Deng et al. synthesized Ag NPs on hollow structural Co-MOF-74 and reported the enhancement of performance for photocatalytic \textit{CO$_2$} reduction to CO.\textsuperscript{[126]} When Ag NPs were also decorated on other MOFs such as ZIF-9\textsuperscript{[127]} and UiO-67,\textsuperscript{[128]} the photocatalytic activity and selectivity for \textit{CO$_2$} reduction reactions were increased. The above results show that the metal centers in MOFs play a key role in product selectivity. Thus it is essential to select appropriate elements for the metal centers for the desired product. In particular, the bimetallic MOFs can be a promising solution to control the product selectivity\textsuperscript{[129]} since the synergistic combination of catalytic activity can promote a specific intermediate reaction.

2.2. Rational Design of MOF-Derived Materials for Hybrid Photocatalysts

In Section 2.1, the key parameters to determine the photocatalytic properties of hybrids consisting of MOFs in their unmodified forms have been discussed. When oxides, chalcogenides, and phosphides are prepared from MOF templates, distinctive properties can be inherited from the MOFs. Furthermore, the carbonization of organic linkers provides additional strategies for designing hybrid catalysts. This section will discuss the key parameters for designing MOF-derived materials for high performance hybrid photocatalysts as well as new strategies to enhance the PC and PEC reactions using MOF-derived hybrids.

2.2.1. Compositional Tuning in MOF-Derived Hybrids

A key requirement for achieving high photocatalytic performance using hybrid structures is the control of composition. Diverse MOFs and their derived photocatalysts and co-catalysts have been reported in the literature, which suggests that nearly every photocatalytic material, including oxides, sulfides, and phosphides, can be prepared from MOFs.\textsuperscript{[130]} Furthermore, the MOF-mediated synthetic routes enable many unique designs of hybrids that cannot be achieved by other conventional synthetic routes.

The coating of thin MOFs on 1D, 2D, and 3D inorganic materials and subsequent converting of MOFs into oxides, sulfides, and phosphides are viable strategies for establishing MOF-derived hybrids, which will be covered in the morphological design section. In the present section, the design of hybrids derived from compositionally controlled bimetallic and core–shell MOFs is mainly discussed. Bimetallic MOFs have been prepared either by using two different metal precursors or by postsynthetic cation modification. In particular, postsynthetic cation exchange is a unique route to modify the composition of MOFs\textsuperscript{[131]} as well as to design new MOFs. The extremely porous structure of MOFs enables the cation exchange of the entire structure at low or mild temperature, whereas the postsynthetic compositional modification in other dense inorganic solids often limits exchange to the surface region or requires high reaction temperatures. Accordingly, it is possible to achieve atomic scale uniformity of cation distribution and high tunability of composition in MOFs, leading to the tailored design of highly porous MOF-derived inorganic materials.

Bimetallic MOFs can be converted to various forms of inorganic materials such as oxides, chalcogenides, and phosphides.\textsuperscript{[132]} The conversion of AB-MOFs (A: cation 1, B: cation 2) depends on various parameters. When AX$_a$ (X: oxygen, chalcogen, or phosphine) and BX$_b$ are mutually insoluble, AX$_a$–BX$_b$ hetero–nanostructures are formed.\textsuperscript{[133]} If AX$_{a}$–BX$_{b}$ hybrids exhibit favorable band structures for photoexcitation and charge separation, the use of smaller AX$_a$–BX$_b$ hetero–nanostructures is more advantageous to shorten the charge transport path. The organic linkers suppress the coarsening of AX$_a$ and BX$_b$ particles during annealing, and the MOFs with homogeneous

*Figure 8. Periodic table showing the primary products from \textit{CO$_2$} reduction reactions on metal and carbon electrodes in aqueous electrolytes. (based on data from Hori et al.\textsuperscript{[121]}) Adapted with permission.\textsuperscript{[4a]} Copyright 2015, American Chemical Society.*
mixing of two metallic ions facilitate the formation of nanoscale heterostructures. When $A_X$ and $B_X$ are soluble with each other, doped structures and solid solutions (e.g., $A_bB_aX$ or $A_{1-a}B_bX$) are formed. Doping of a small concentration can be used to enhance the electronic conductivity, while compositional control over a wide concentration range offers bandgap engineering. Furthermore, new compounds (e.g., $AB_3$ and $AB_2X_4$) can be formed from AB-MOF templates.[134] MOFs with uniform distribution of two cations can facilitate the formation of compounds at low processing temperature with minimal unreacted second phase. Moreover, binary–ternary hybrids such as $AX_{1-a}AB_2X_4$ or $ABX_YB_{2-a}X_4$ can also be designed from the AB-MOF templates. Again, the uniform mixing of cations and the presence of organic linkers facilitate the formation of nanoscale hybrids.

MOF-based synthesis also offers the formation of nanohybrids between oxides and sulfides. For example, the sulfuration of MOF-5(Zn) into ZnS, carbonation of ZnS into ZnS@C by annealing in nitrogen, and subsequent partial oxidation have been reported for preparing ZnS/ZnO hetero–nanostructures.[135] The carbon components evolving from the organic linkers of MOFs suppressed the coarsening of particles and enabled the controlled oxidation of ZnS. Lastly, MOFs with a core–shell configuration have been established when two precursors with significantly different reactivity were used for MOF formation,[136] postsynthetic compositional modification was applied only to the surface region of MOFs,[137] or the different MOF layers were heteroepitaxially grown on inner MOF.[138] These MOF@MOF structures can be converted into various hybrids such as core–shell oxides, sulfides, and phosphides. The above clearly demonstrates that various MOF-derived hybrids with different cations/anions and spatial variation of composition can be rationally designed for high-performance photocatalysts.

### 2.2.2. Morphology of MOF-Derived Hybrids

The photogeneration of charge carriers, charge transport across the interfaces, and surface redox reaction are all involved in the photocatalytic reaction of MOF-derived hybrid materials and are closely dependent upon the size and morphology of the materials inherited from the MOFs. Accordingly, the MOF-mediated morphological control of hybrid photocatalysts is crucial.

For photocatalysts suspended in liquid, high surface area, abundant porosity, good dispersion, and reactant accessible structures are advantageous. Monodisperse MOF nanocrystals can be prepared at a large scale using a facile solution-based reaction. MOF nanocrystals dispersed in liquid solvent are excellent substrates for the tailored coating of metal precursors and the following thermal annealing leads to the formation of core–shell hybrid catalysts.[139] The size of MOF crystals can be controlled by the concentration of reactants (i.e., supersaturation) (Figure 9a),[140] facilitating the dispersion and recycling of photocatalysts. The morphologies of MOFs are primarily associated with the crystal structures determined by the combination of metal clusters and organic linkers, which can be tuned further using surfactants[141] (Figure 9b) or coordination modulators[142] (Figure 9c) that hinder/promote the growth of specific crystal planes. If two different ligands were involved in MOF growth toward achieving different crystallographic orientations, it would be possible to control the aspect ratio of the MOF crystals by regulating the relative portions of the two ligands.[143] In addition, the choice of solvents can be an alternative option for tailoring the morphology and size of the MOF crystals.[144] The photocatalytic activity of MIL-125(Ti)-NH$_2$ is known to be closely dependent on the crystal facets,[145] and well-developed facets can be maintained even after the oxidation of MOFs.[146] Since various shapes of MOFs (rods, cubes, dodecahedrons, and sheets) are retained after carbonization, oxidation, sulfidation, and phosphidation, the MOFs with highly tunable morphology and size are excellent templates for the rational design of well-defined hybrid photocatalysts.

The 2D MOFs are also promising for designing hybrid-type photocatalysts. Since the photocatalytic effect of hybrid materials largely depends on the intimate contacts between two materials, 2D/2D hybrids are advantageous for maximizing the contact area for charge transport. Furthermore, many 2D materials with extraordinary photocatalytic performances are available, and can be used as components within hybrid-type photocatalysts.[147] To date, various 2D/2D hybrids have exhibited enhanced photocatalytic performances, which include Fe$_2$O$_3$/g-C$_3$N$_4$, WO$_3$/g-C$_3$N$_4$, C$_3$N$_4$/MnO$_2$, Ti$_2$C/C/Bi$_2$WO$_6$, MoS$_2$/rGO (reduced graphene oxide) and MoS$_2$/COF. Note that 2D MOF (or thin MOF) template layer can be coated on other 2D materials such as $g$-C$_3$N$_4$, rGO, and MXenes (2D metal carbides or nitrides), which can be converted into thin oxide or sulfide layers. Thus, MOF-mediated synthesis will offer a facile route to prepare 2D/2D hybrid photocatalysts in the near future.

In the photoanodes for PEC reaction, nanorod arrays (NRAs) have been generally used to maximize the reaction area on the
surface and to facilitate charge transport along the nanorods. Hybrids with photoactive materials (MOFs, oxides, and chalcogenides) can significantly enhance the PEC reaction. First, the photoactive MOFs can be coated on the NRA photoanode. It is reported that the photocurrent density is significantly enhanced by the formation of hybrids such as Ti-doped Fe3O4 NRA@MIL-101(Fe)-NH2[155] and TiO2 NRA@MIL-125(Ti)-NH2[156] demonstrating the validity of the charge funneling design of MOF/oxide for PEC reaction. For this, it is necessary to achieve a conformal coating of MOF with high stability in liquid electrolyte, good cohesion between two layers, and electronic conduction within the MOF as well as across the interface. Secondly, the MOF layer coated on oxide NRAs can be converted into oxides or chalcogenides, forming oxide–oxide or oxide–chalcogenide hybrid photoanodes. The hybrid photoanodes of TiO2 NRA@Co3O4 and ZnO NRA@ZnS/CoS have been prepared from TiO2 NRA@ZIF-67(Co) and ZnO NRA@ZnCo-ZIF, respectively.[157] The MOF-mediated formation of overlayers enables the control of thickness, composition, porosity, and hierarchical morphology of overlay in the photoanodes.

The hierarchical structures of MOFs are also attractive for preparing similar structures of photocatalysts. The hierarchical nanostructures assembled from nanoparticles, nanorods, and nanosheets as well as hollow nanostructures are known to be advantageous for increasing light absorption due to enhanced light scattering.[158] Furthermore, hierarchical structures with macro-, meso-, and microporosity provide effective and rapid mass transport toward all reaction sites through highly interconnected pores. Accordingly, photocatalysts with hierarchical structures have been investigated intensively.[159] Hierarchical structures of MOFs have been prepared by various solution-based synthetic routes, and the conversion of hierarchical MOFs is more advantageous for acquiring a high surface area for PC and PEC reactions than for the direct synthesis. Representative hybrid photocatalysts and photoanodes prepared from hierarchical MOFs are CdS/MoS2 nanoflowers,[160] CuS/ZnS porous microspheres,[161] CoS3@ZnIn2S4 nanocages,[162] MoS2/TiO2,[163] and CoO4/TiO2.[157a]

2.2.3. Hybrids with Carbon-Based Materials

The recombination of photogenerated charge carriers prior to the surface redox reaction significantly deteriorates the photocatalytic performances. The formation of hybrids between photoactive semiconductors and conducting carbon-based phases can be a solution to enhance charge transport to the surface reaction sites. Note that the organic linkers in MOFs are ideal precursors to form carbon-related phases, and the metallic clusters can be converted into semiconducting oxides, chalcogenides, and phosphides. Accordingly, MOF-derived synthesis provides the unique design of carbon-containing hybrids. For this synthesis method, the MOFs are generally carbonized at higher temperature and then oxidized, chalcogenized, and phosphidated at a lower temperature to retain the carbon phase during the second annealing.[164] The key benefit of the carbon-related phase is the high electronic conductivity.[165] Depending on the composition of the organic linkers, carbons or nitrogen-doped carbons can be formed.[166] Furthermore, when the favorable catalytic component (i.e., Co) is present, both carbon and carbon nanotubes (CNTs) are often co-developed, which synergistically enhance the electronic conduction.[167] In addition, the carbonization of the organic linkers in the MOFs blocks the densification and coarsening of semiconductors, enabling the preparation of reactant-accessible porous hybrids.[168] Furthermore, carbon doping in ZnO is possible by controlled thermal annealing of MOF-8(Zn), which can be used to control the bandgap.[169] Lastly, the carbon and nitrogen sources in MOFs can be used as precursors to form highly photoactive materials such as g-C3N4.[170] All of the above results demonstrate that MOFs are unique precursors for hybrid photocatalysts with porous structures for effective mass transport and rapid charge transport to suppress charge recombination.

3. MOF Hybrids for Hydrogen Production

3.1. MOF/Oxide Hybrids

Metal oxide semiconductors have been intensively studied as photocatalysts and photoelectrodes for solar hydrogen production over the last few decades[171] owing to their distinctive advantages such as suitable bandgap, low cost, photochemical stability, and nontoxicity. Typically, TiO2, WO3, α-Fe2O3, and BiVO4 are used for designing photoactive materials. The relatively wide energy bandgaps of oxides provide excellent photochemical stability but low visible-light absorption efficiency. In addition, the short hole-diffusion length of metal oxides often hampers the charge separation and charge transfer. Accordingly, it remains challenging to design metal oxide photocatalysts/photoanodes with both high photochemical stability and high hydrogen production rate.

The formation of hybrids between oxides and MOFs is a viable option for complementing the limitations of oxide-based photoactive materials. MOFs offer versatile structures and various functionalizations; they can be grown or attached on the surface of oxides. In particular, the semiconducting MOFs with a tunable bandgap, band-edge position, and electrical properties are advantageous for modulating light absorption and enhancing the charge separation/transfer through the formation of MOF/oxide hybrids. In this section, several synthetic strategies of MOF/oxide hybrids for PC and PEC water splitting and the mechanisms underlying the enhanced photocatalytic performance are explained.

3.1.1. Synthetic Strategies for MOF/Oxide Hybrids

Slurry coating is a relatively simple route for preparing MOF/oxide hybrids, which includes spin coating and screen printing (Figure 10a). Screen printing is rarely used to coat MOFs on oxides because it involves the use of binders and surfactants that need to be removed by thermal annealing at elevated temperature (≈400 °C), which might oxidize/decompose the MOFs. In contrast, spin coating uses volatile solvents that can be easily evaporated at relatively low temperatures and does not limit the coating materials. Diverse MOF/oxide hybrids can be fabricated if MOFs are uniformly dispersed in a solvent. For instance,
Hu et al.\textsuperscript{[172]} prepared TiO\textsubscript{2}/MOF multilayered hybrids by the alternative spin coating of TiO\textsubscript{2} sol and MIL-88B(Fe)-NH\textsubscript{2} alcoholic suspension on a silicon wafer (Figure 10b). Zhang et al.\textsuperscript{[173]} spin coated a MIL-100(Fe) alcoholic suspension on nanoporous Mo-doped BiVO\textsubscript{4} (Figure 10c) and Jiao et al.\textsuperscript{[174]} spin coated MIL-100(Fe) NPs on Fe/W co-doped BiVO\textsubscript{4} photoanodes. These confirm the general validity of spin coating. Spin coating is a cost-effective route for coating diverse MOFs on large-area oxide films. However, the bonding/cohesion between the MOF and oxide is generally not strong, and rapid evaporation of the solvents often causes the development of surface cracks. In addition, it is difficult to achieve a conformal coating of MOF on oxides with complex surface morphologies.

If MOF particles or nanostructures exhibit surface charge, the electrostatic assembly of MOF and oxide in the slurry can be used to form oxide/MOF hybrids (Figure 10d). In aqueous suspension, the oxide surface is positively charged at low pH (potential determining ion: H\textsubscript{3}O\textsuperscript{+}), and it becomes negatively charged at high pH (potential determining ion: OH\textsuperscript{−}). The isoelectric points (IEPs) of oxide particles in the water solvent depend on the acid-base properties of the oxides. Similarly, the surface charge of the MOF particles dispersed in the water-based slurry can also be controlled by modulating the pH. The IEP values of various MOFs reported in the literature are summarized in Figure 11a.\textsuperscript{[175]} A wide range of IEPs demonstrates the controllability of the self-assembly reaction in slurry solutions at different pH values. If the pH of a slurry solution is higher than IEPoxide but lower than IEPMOF, the positively charged MOF nanostructures will be spontaneously assembled onto the negatively charged oxide surfaces. Accordingly, the pH value of the aqueous slurry solution should be located between IEPoxide and IEPMOF (Figure 10e). For example, Shi et al.\textsuperscript{[176]} coupled Cu-BTC (zeta potential −4.06 mV) and ZnO/OGO (zeta potential 33.4 mV) by electrostatic self-assembly in water-based solvents (Figure 10f).

The surface charge of MOFs can also be developed in non-water-based slurry (Figure 11b).

When MOFs are charged, the deposition of MOFs on a wide substrate can be facilitated/accelerated by applying an electric field (Figure 10g). Hod et al. demonstrated that diverse MOFs such as HKUST-1(Cu), MIL-53(Al), UiO-66(Zr), and NU-1000(Zr)\textsuperscript{[181]} dispersed in toluene can be coated on positively charged fluorine-doped tin oxide (FTO) electrodes by electrophoretic deposition (EPD) (Figure 10h). They suggested the

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Figure 10. Schematic diagrams and SEM images demonstrating various methods to prepare MOF/oxide hybrids. a) MOF slurry coating on oxide. b) Cross-sectional SEM image of TiO\textsubscript{2}/MIL-88B(Fe)-NH\textsubscript{2} multilayered hybrid prepared by alternative spin coating of TiO\textsubscript{2} sol and MIL-88B(Fe)-NH\textsubscript{2} alcoholic suspension. c) Cross-sectional image of Mo-doped BiVO\textsubscript{4}/MIL-53(Fe) hybrids prepared by solution spinning. d) Electrostatic self-assembly of MOF/oxide hybrids. e) The pH window for electrostatic self-assembly. f) TEM image of hybrids between ZnO/OGO and Cu-BTC. g) Electrophoretic deposition of MOF on oxide. h) SEM images of Nu-1000(Zr) film on fluo-

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surface defects in MOFs as a possible origin for the surface charge, although a further systematic investigation is necessary to confirm this. To date, various MOFs have been coated by EPD, which include MOF-525(Fe) (in toluene),[182] HKUST-1(Cu) (in water:ethanol),[183] ZIF-8(Zn) (in water:ethanol),[183] and Ln/UiO-66(Zr) hybrid (in CH2Cl2 solvent).[184] The EPD is a general and facile route to prepare MOF/oxide hybrids. For electrostatic self-assembly, the surface charge should be carefully controlled either by modulating pH or by the selection of solvents. In contrast, once MOF shows a substantial surface charge, the coating process in EPD can be conveniently manipulated and accelerated by controlling the strength and polarity of the electric field, and the patterned coating of MOFs using photore sist masks is also possible (Figure 10i).[181]

Since the metal cations are positively charged (ex: Zn2+, Ti4+) and the organic ligands have negative charges on the functional groups (ex: –OH, –COOH), a conformal coating of MOF layers on the support can be achieved through a layer-by-layer (LbL) method, a sequential coating of the materials with positive and negative charges (Figure 10j).[185] This technique offers the design of diverse MOF/oxide hybrids by combining various metal ions or ligands, which has been demonstrated through the coating of MOFs on various substrates such as silica foam,[186] nanofiber@Al2O3 (Figure 10k),[187] Si/SiO2,[188] sapphire,[188] and glass.[188] For facilitating the growth of the first layer, the substrates are often functionalized with a self-assembled monolayer or –OH radical.[189] Although the multistep process takes a relatively long time for coating, it promises uniform thickness, smooth surface morphology, and high homogeneity. The key advantage of the LbL process is excellent tunability of a nanoscale (a few nanometers) coating thickness by controlling the growth cycles. For designing high performance MOF/oxide hybrid photoelectrodes, the coated MOF layer should be thin because the charge transfer path is required to be shortened to compromise with the low electronic conductivity of most MOFs. When the growth process is well-controlled using the LbL process, highly crystalline and well-oriented MOF films can be coated. For instance, Yao et al.[188] grew electronically conductive 2D Cu3(HHTP)2 hexagonal layers by a spray Lbl method on various substrates (Figure 10l). The growth of highly oriented and crystalline MOF films is advantageous for achieving high electronic conductivity, which can provide various new opportunities in PC and PEC water splitting. Moreover, through the LbL process, two or more layers of different MOFs can be coated on the surface to form metal oxide/MOF/MOF heterostructures. Thus, the LbL process offers versatile combinations of MOF/oxide hybrids for fabricating highly efficient photoelectrodes.

The hydrothermal/solvothermal growth of MOFs on the surface of oxides has been widely utilized to prepare MOF/oxide hybrids (Figure 10m). It allows a facile metal ion/ligand modification, thus offering diverse hybrid combinations between MOFs and oxides. Zhan et al. reported the growth of a Zn-based MOF (ZIF-8(Zn)) on ZnO nanorods.[191] They introduced only the ligand (2-methylimidazole) because the Zn2+ ions for MOF growth are released from the surface of pre-fabricated ZnO nanorods. That is, the surface region of ZnO nanorods played the role of self-templates. Uniform growth of ZIF-8(Zn) on ZnO nanorods was achieved, and the thickness of ZIF-8(Zn) could be tuned by controlling the growth time (Figure 10n), suggesting that the outward diffusion of Zn2+ ions through the ZIF-8(Zn) layer is the rate-determining step for the growth of ZIF-8(Zn) layer. ZnO is a typical amphoteric oxide that is easily dissolved either in acidic or basic aqueous solutions to release Zn2+ ions and can be used as an excellent template. However, not all oxides can induce self-templated growth of MOFs on the surface with only ligands. Accordingly, the surface of the solid to be coated is modified with functional groups and surfactants to achieve surface cohesion between the MOFs and oxides. Zhang et al. reported the solvothermal
growth of three Ti-based MOFs with different ligands on TiO$_2$ nanowires (NWs).$^{[392]}$ For the uniform growth of MOF and strong binding between MOF and oxide, they modified the TiO$_2$ surface with –COOH functional groups. In another work, MIL-101(Fe) was coated on Fe$_2$O$_3$:Ti nanorods with polyvinylpyrrolidone (PVP) molecules as the bridging agent.$^{[135]}$ The PVP molecules adsorbed on Fe$_2$O$_3$ provide the nucleation sites for Fe$^{3+}$ adsorption and the following growth of coordinated MOF. For photocatalysts suspended in a solvent, homogeneous nucleation of monodisperse MOF polyhedrons is advantageous for enhancing PC reactions. In contrast, to coat a thin MOF layer on oxide photoanodes, the homogenous growth of MOF particles within slurry solution should be suppressed by surface modification or controlled growth of MOF. Although the metal oxide and MOF with the same cations are more advantageous for strengthening the binding at the interfaces of hybrids by anchoring, surface modification can be used to achieve diverse combinations between oxides and MOFs for hybrid design.

Lattice matching between the oxide and MOF is an important parameter for binding. The heteroepitaxial growth of MOF on oxide provides a high quality of hybrid with intimate contact at interfaces that is advantageous for photocatalytic applications. Because both oxides and MOFs are crystalline materials, a few requirements should be satisfied for the heteroepitaxial growth of MOFs. First, the lattice mismatch between the MOF and oxide should be negligible. Generally, crystalline MOFs prefer homogeneous nucleation and growth because of the lattice mismatch between the MOFs and metal oxides.$^{[393]}$ Bristow et al.$^{[394]}$ suggested that the lattice mismatch should be lower than 8%, even when considering the relatively soft nature of MOFs containing organic linkers. There is an optimal coupling between inorganic materials (oxides, chalcogenides, phosphides, and nitrides) and MOFs, considering both lattice mismatch and lattice strain. Higher lattice strain tends to form more defects at the interface, which eventually deteriorates the charge transport across the interfaces. Accordingly, the specific planes of oxide and MOF should be well-coupled to form a heteroepitaxial layer. Second, for strong anchoring of MOFs on oxides, there should be favorable bonding between the metal ion in the oxide and the ligands in the MOF. For example, the (110) surface of rutile TiO$_2$ is known to bind tightly with BDC ligands within MOF-5,$^{[195]}$ enabling the formation of a hybrid between TiO$_2$ and MOF-5(Zn). Lastly, the pore topology and thermal expansion coefficient of the MOF also determines the compatibility of the two materials. The above consideration is based on a single crystalline oxide substrate. However, most oxide substrates are polycrystalline and thus consist of various crystalline planes, which can make the fabrication of heteroepitaxial MOF/oxide hybrids difficult.

MOF/oxide hybrids can also be fabricated by the partial oxidation of MOFs (Figure 10o). Zhang et al. synthesized MIL-125(Ti)-NH$_2$@TiO$_2$ core–shell particles by a two-step solvothermal method. Solvothermally prepared MIL-125(Ti)-NH$_2$ was oxidized by a two-step solvothermal reaction in a thiocetamide ethanolic solution (Figure 10p)$^{[196]}$ The thiocetamide broke the bridging linker of the MOF to oxidize the surface, and the types of solvents (ethanol, methanol, and propanol) played a significant role in developing different pore sizes in the composite. The solution-based oxidation provides the tunability of thickness and porosity in the outer oxide layer in MOF/oxide hybrids. Oxygen plasma has also been used for partial oxidation of MOFs. Dou et al. demonstrated that atomic-scale CoO$_x$ (0.2–0.3 nm) can be formed within the MOF by the partial oxidation of ZIF-67(Co) via O$_2$ plasma treatment (Figure 10q)$^{[197]}$ Rapid formation of a uniform oxide phase on MOFs with high surface area is advantageous for enhancing catalytic promotion. However, the accompanying change of MOF structures by O$_2$ plasma treatment should be also considered when using this process for designing photoactive materials.

Compared with the slurry coating method, electrostatic self-assembly and EPD offer a stronger binding between MOF and oxide. Hydrothermal/solvothermal methods and the LbL process allow the oxides to be thoroughly soaked by metal ions/ligands and can therefore provide conformal growth sites for MOF formation and facilitate the formation of robust interfaces. Furthermore, these methods also exhibit high tunability of MOF thickness, which enables the on-demand design of MOF/oxide hybrids for PC and PEC water splitting.

### 3.1.2. MOF/Oxide Hybrids for Solar Hydrogen Production

Designing MOF/oxide hybrids is a promising way to enhance the efficiency of both PC and PEC hydrogen production. In general, the hybrids are in the form of MOF@oxide core–shell, oxide@MOF core–shell, and oxide/MOF heterojunction. Zhang et al. prepared MIL-125(Ti)-NH$_2$@TiO$_2$ core–shell particles by a simple post-solvothermal method for PC hydrogen production (Figure 12a)$^{[196]}$ A hydrogen production rate of 496 µmol g$^{-1}$ h$^{-1}$ was achieved, which was 70 times higher than that of the pure MOF. In this study, the hybridization of MOF and oxide played a significant role in enhancing the light absorption and increasing the conductivity.

Similarly, the coating of MOF on oxide photoanodes has been used to enhance the absorption of visible light and to facilitate the charge funneling. Zhang et al.$^{[192]}$ grew three different Ti-based MOFs (MIL-125(Ti), MIL-125(Ti)-NH$_2$, and MIL-125(Ti)-NH$_3$) on TiO$_2$ photoanodes. The MOFs are in the same family but exhibit different light absorption properties depending on the types of ligands, as discussed in Section 2.1.1. MIL-125(Ti) has a bandgap of 3.6 eV, whereas MIL-125(Ti)-NH$_2$ has a bandgap of 2.6 eV, indicating amine-modified ligands are responsible for reducing the bandgap.$^{[198]}$ Indeed, the coating of MIL-125(Ti)-NH$_2$ on TiO$_2$ NWs increased the photocurrent density from 10 to 20 µA cm$^{-2}$ at a potential of 0.75 V versus reversible hydrogen electrode (RHE) under visible light illumination, whereas the coating of MIL-125(Ti) did not show any remarkable enhancement. This is attributed to the formation of a type-II heterojunction between TiO$_2$ and the reduced bandgap of MIL-125(Ti)-NH$_2$ that facilitates the photogenerated electrons in $E_c$(MIL-125(Ti)-NH$_2$) to transfer to $E_c$(TiO$_2$) and holes in $E_v$(TiO$_2$) to transfer to $E_v$(MIL-125(Ti)-NH$_2$). Under this band configuration, the charge recombination rate is slowed, and charge separation becomes more effective, which improves the PEC performance. The present authors$^{[196]}$ experimentally verified the establishment of type-II interfaces between MIL-125(Ti)-NH$_2$ and TiO$_2$, as well as the remarkably increased
Moreover, it was suggested that the optimum thickness of the MIL-125(Ti)-NH₂ overlayer is around 5–10 nm for the highest photocurrent density. It is worth noting that the outer MOF layer should not be excessively thick because the poor electron transport properties in most MOFs might lead to significant charge recombination within the MOF.[199]

The hybrids between bimetallic MOFs and oxides have been developed to promote the oxygen evolution reaction (OER) in the photoanode. Peng et al.[200] designed a ZnO NWs@ZnNi MOF NW array for solar hydrogen production. The photocurrent density of ZnO NW@MOF-5(Zn) was about 1.6 times higher than that of ZnO NWs@ZnNi MOF NW array for solar hydrogen production. The photocurrent density of ZnO NW@ZnNi MOF (1.40 mA cm⁻²) was about 1.6 times higher than that of ZnO NWs@ZnNi MOF (0.87 mA cm⁻²). This was attributed to the redox process of Ni²⁺/Ni³⁺/Ni⁴⁺ that can reduce the energy barrier of the water oxidation reaction by photogenerated holes. The photogenerated holes in ZnO can be trapped in the ZnNi MOF and can oxidize the Ni²⁺ into higher valence Ni³⁺/Ni⁴⁺, which are responsible for promoting the water oxidation reaction (Figure 12c).

In order to enhance the hydrogen production rate further, the co-catalyst incorporated MOFs have been coated on the surface of oxides. Han et al.[201] designed nitrogen-doped carbon dot (N-CD) incorporated ZIF-8(Zn) that anchored onto ZnO nanotubes for effective PEC water splitting. The onset potential of the ZnO/N-CD@ZIF-8(Zn) exhibited an ≈100 mV cathodic shift compared with the pristine ZnO and ZnO/ZIF-8(Zn) nanotubes (Figure 12d). Moreover, the photocurrent density increased significantly (133% at 0.23 V vs Ag/AgCl) with the coating of N-CD embedded ZIF-8(Zn) on ZnO nanotubes. This is attributed to the higher light-harvesting rate in the visible range and enhanced charge separation by ZIF-8(Zn) encapsulating the conductive N-CDs. Recently, Yang et al.[202] reported that the coating of cobalt-incorporated Zr-MOF improving the PEC performance of TiO₂ nanorods by 180% when compared...
with TiO2@bare Zr-MOF, which was explained by the enhanced charge separation. In addition, the further increase in photocurrent due to the incorporation of Co(II) into the MOF was attributed to the enhanced charge mobility. The incorporation of co-catalysts with high electronic conductivity is a favorable strategy to improve the charge transfer efficiency in MOFs.

The surface plasmon resonance (SPR) effect of Au NPs has been used to enhance the light harvesting capability. Dou et al.\[202\] reported that the photocurrent of ZnO@Au@ZIF-67(Co) reached 1.93 mA cm−2 at 0.6 V versus saturated calomel electrode (SCE), which was five times higher than pristine ZnO.

Furthermore, the coating of Au-incorporated ZIF-67(Co) significantly improves the charge separation of the ZnO photoanode while the MOF overlayer prevents the leaching of Au with SPR. This demonstrates the protective role of MOFs to increase the stability of photoanodes.

The MOF/oxide hybrids provide various irreplaceable advantages including light absorption in the visible range, enhancement of charge transport/separation by establishing type-II interfaces, promotion of OER by bimetallic MOF, incorporation of co-catalysts, and enhancement of SPR using noble metal catalysts.

### 3.2. MOF/Chalcogenide Hybrids

Metal chalcogenides have relatively smaller bandgaps than most metal oxides,\[203\] which are attractive as visible-light-activated photocatalysts.\[204\] For instance, CdS has been intensively investigated for PC and PEC hydrogen production because of its narrow bandgap (≈2.4 eV) and suitable band position for the water oxidation reaction.\[205\] However, the rapid charge recombination and redox instability makes CdS vulnerable to photocorrosion. Although metal sulfide photocatalysts in the nanometer-scale have been explored to enlarge the catalytic sites and avoid charge recombination via shortening the diffusion path, the aggregation between sulfide NPs due to van der Waals attraction deteriorates the PC and PEC H2 evolution activity. Furthermore, its sulfide anion is often oxidized to soluble sulfate, leading to further deterioration of the PC and PEC activity.\[206\] Accordingly, the stable dispersion of metal sulfide nanostructures in special support for preventing charge recombination and photocorrosion is of crucial importance in solar fuel production. The MOF is an excellent and ideal scaffold for immobilizing metal sulfides and can mitigate the aggregation and photocorrosion of metal sulfide NPs. Owing to these attractive properties, the formation of hybrids between MOFs and metal sulfides is receiving attention for the purpose of enhancing PC and PEC performance.

#### 3.2.1. Synthetic Strategies for MOF/Chalcogenide Hybrids

Hydrothermal reaction, solvothermal reaction, and precipitation are three facile solution-based routes to establish MOF/sulfide hybrids. These include in-situ growth of metal sulfides on MOF and vice versa, which have shown promising potential and versatility for the preparation of diverse MOF/sulfide hybrids.\[207\] Xu et al.\[208\] uniformly decorated UiO-66(Zr) with CdS NPs by the solvothermal reaction (Figure 13a). The MOF supports played the role of preventing the aggregation of CdS NPs and the amounts of CdS NPs could be tuned by controlling the Cd concentration during the solvothermal process. The solution-based method has been adopted to synthesize bimetallic MOF/sulfide hybrids. Zhao et al.\[209\] combined bimetallic ZIFs such as ZnNi-ZIF, ZnCu-ZIF, and ZnCo-ZIF with CdS nanorods by a simple room-temperature precipitation. Doping Ni, Cu, and Co in ZIF-8(Zn) did not affect the morphology of the heterostructures, and the elemental mapping showed all the components were uniformly distributed, demonstrating that solution-based methods provide efficient and facile pathways for fabricating hybrids between chalcogenides and diverse compositions of MOFs.

Photodeposition has also been used to synthesize MOF/sulfide hybrids. It offers uniform coverage of metal sulfide quantum dots (QDs) and intimate cohesion between QDs and MOFs. Typically, metal sulfides are photodeposited on the MOFs by the illumination of UV−vis light to the slurry solution containing the MOF, metal ions, and sulfuric acid. During the light illumination, the MOFs absorb UV−vis light to form the electron trapping sites, which later provide adsorption and nucleation sites for metal sulfide QDs (Figure 13b). Wang et al.\[209\] successfully demonstrated the photodeposition of AgxS, CdS, CuS, and MoS2 NPs with a size of 10 nm on the surface of MIL-125(Ti) via in-situ photodeposition (Figure 13c). The formation of Ti4+ with strong reducing ability through light illumination was responsible for the reduction to metals of the metal precursors (Ag+, Cd2+, Cu2+, and Mo4+) adsorbed on MIL-125(Ti), which eventually promoted the formation of metal sulfide NPs. Similarly, a trace amount of MoS2 was synthesized on UiO-66(Zr)/CdS through photodeposition.\[210\] Although the morphology of MoS2/CdS was maintained after the deposition of MoS2, the MoS2 showed poor crystallinity due to the synthesis at low temperature. This indicates that synthesis at elevated temperatures is necessary to obtain highly crystalline metal sulfides by photodeposition. It is also required to optimize the UV−vis irradiation intensity, as the strong light energy might damage the MOF structures.

Vapor-phase deposition techniques, such as ALD, are suitable alternatives for installing cluster-scale metal sulfide into the MOFs. This process offers exceptional manipulation of the size and composition of the incorporated metal sulfides. Peters et al.\[211\] synthesized NiS2 incorporated NU-1000(Zr) through ALD (Figure 13d). Unlike other deposition methods that decrease the surface area of the MOF next to the incorporation of second components, the Brunauer−Emmett−Teller (BET) surface area of NiS2/NU-1000(Zr) remained significantly high even after NiS2 deposition. The incorporation of atomicscale metal sulfides without the sacrifice of surface reaction sites is promising for designing high performance MOF/sulfide hybrids for solar hydrogen production.

#### 3.2.2. MOF/Chalcogenide Hybrids for Photocatalytic Hydrogen Production

Metal sulfides and metal selenides are incorporated into MOFs for improving both H2 production and photochemical
stability. With excellent visible light response and efficient charge separation, MOF/chalcogenide hybrids exhibit a promising potential in photocatalytic H₂ evolution. Similar to MOF/oxide hybrids, the construction of a charge-funneling band alignment between the MOF and chalcogenide can increase the H₂ production rate by enhancing the light absorption and charge separation efficiency. In general, metal sulfides with a relatively small bandgap match well with MOFs of a comparable bandgap. For instance, amine-functionalized MOF groups are often chosen for designing MOF/sulfide hybrids because they exhibit a small bandgap enough to absorb visible light. Su et al. reported that the Cd₃Zn₉S₄@UiO-66(Zr)-NH₂ composites showed a twice-higher rate of H₂ evolution compared to pristine Cd₃Zn₉S₄.

A remarkably decreased photoluminescence (PL) intensity in Cd₃Zn₉S₄@UiO-66(Zr)-NH₂ composites suggested a decreased charge recombination rate, indicating that the photoinduced charges can be efficiently separated by establishing a heterojunction with the MOF. In this case, the hybrid had established a type-I heterojunction that allowed the holes to migrate easily to the surface of the material, so that they could participate in the oxidation reaction (Figure 13e). The H₂ evolution rate was also enhanced by type-II band alignment between the UiO-66(Zr) and CdS. Liu et al. reported that ZnIn₂S₄@MIL-125(Ti)-NH₂ with a type-II interface exhibited a six times higher H₂ production rate than the pristine ZnIn₂S₄. These studies confirm that MOF/sulfide hybrids with favorable band alignment and an intimately

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**Figure 13.** a) Synthetic process for CdS/UiO-66(Zr) Composites. b) Schematic diagram to show photodeposition of metal sulfides on MOF. c) SEM images of photodeposited MIL-125(Ti)/Ag₂S, MIL-125(Ti)/CdS, MIL-125(Ti)/CuS, and MIL-125(Ti)/MoS₂. d) Idealized representation of NU-1000(Zr) after imparting NiSₓ functionality via ALD. e) Schematic diagram of the photogenerated electrons and holes transfer in the Cd₃Zn₉S₄@UiO-66(Zr)-NH₂ composite and the mechanism of photocatalytic H₂ production under visible light irradiation. f) Recycling test for the photocatalytic H₂ production of pure CdS and MoS₂/UiO-66(Zr)/CdS. a) Adapted with permission. Copyright 2018, American Chemical Society. c) Adapted with permission. Copyright 2015, The Royal Society of Chemistry. d) Adapted with permission. Copyright 2016, American Chemical Society. e) Adapted with permission. Copyright 2017, Elsevier. f) Adapted with permission. Copyright 2015, Elsevier.
contacting interface lead to effective separation and transfer of the photogenerated charge carriers, eventually improving the PC performance.

During photocatalytic reactions, metal chalcogenide photocatalysts are prone to photocorrosion, where the metal chalcogenides are oxidized by the photogenerated holes.\(^{216}\) The photocorrosion of metal chalcogenides can be reduced by increasing the charge separation efficiency of the photogenerated carriers at the surface. To this end, MOFs are often coupled with metal chalcogenides to enhance photochemical stability. Shen et al.\(^{210}\) prepared a MoS\(_2\)/UiO-66(Zr)/CdS composite for photocatalytic H\(_2\) evolution. Two different metal sulfides were introduced for enhancing the performance and achieving photochemical stability (Figure 13f). Only a trace amount of Cd\(^{2+}\) leached out from the MoS\(_2\)/ UiO-66(Zr)/CdS composite after the photocatalytic reaction, whereas 30% of the Cd\(^{2+}\) leached from the pure CdS. This is consistent with the literature results, demonstrating that the photocorrosion of metal sulfides is generally suppressed by improving the charge separation.\(^{227}\) In another work, He et al. reported a CdS-embedded MIL-101(Cr) hybrid for stable photocatalytic H\(_2\) production.\(^{207b}\) Unlike the CdS NPs, which generally undergo significant aggregation and phase transformation after photocatalytic reactions, CdS/MIL-101(Cr) retained a relatively stable and unchanged structure even after use. This is attributed to the prevention of CdS aggregation due to the supporting MOFs. The hybridization of sulfides with MOFs provides abundant photocatalytic reaction sites, efficient charge separation/transfer, and the stability of sulfides against photocorrosion.

3.3. MOF/Metal NP Hybrids

Noble metal NPs are excellent co-catalysts that significantly promote HER and OER reactions at the surface of photocatalysts. It is evident that smaller metal NPs with a wider surface area are more advantageous for achieving a higher catalytic activity. However, unfortunately, most metal NPs are vulnerable to aggregation due to strong van der Waals forces, which significantly deteriorates their PC and PEC performance.\(^{218}\) Accordingly, the stable and uniform dispersion of metallic NPs is crucial in the design of photocatalysts. MOFs with highly periodic and tunable porosity are ideal platforms for loading single-atom-scale or nanoscale noble metal catalysts. Thus, the researchers tried to load, impregnate, and incorporate metals into MOFs to maximize the catalytic promotion, to minimize the use of expensive materials, and to stabilize the nanoscale catalysts. In this section, several synthetic strategies to prepare MOF/metal NP hybrids are discussed along with the mechanisms underlying enhanced PC and PEC reactions.

3.3.1. Synthetic Strategies of MOF/Metal NP Hybrids

Photodeposition provides a facile process to uniformly incorporate metal NPs in a nanometer scale into MOF scaffolds. In general, the as-prepared MOF photocatalysts are dispersed in a solution containing metal cations. Subsequently, electrons generated by UV–vis light illumination reduce the metal cations, leading to the formation of MOF/metal NP hybrids. Remiro-Buenamañana et al.\(^{219}\) synthesized metal or metal oxide NPs (Pt, CoO\(_x\), and RuO\(_2\)) on MIL-125(Ti)-NH\(_2\) by a photodeposition method. The sizes of these catalytic NPs are around 1–3 nm and are well distributed in the MOFs. Liang et al.\(^{220}\) synthesized Au@MIL-100(Fe), Pd@MIL-100(Fe), and Pt@MIL-100(Fe) through room-temperature photo deposition. The average diameters of the Au, Pd, and Pt NPs dispersed on the MOF were 15, 12, and 2 nm, respectively. In addition, the crystalline structure of the MIL-100(Fe) remained undamaged after the photodeposition. However, the UV–vis light irradiation should be tuned carefully because weak irradiation can be insufficient for the reduction of metal ions, whereas excessively strong irradiation may lead to structural damage of the MOF as well as aggregation of the metal NPs.\(^{222}\)

The impregnation method is a convenient route for preparing MOF/metal NP hybrids. Zhen et al.\(^{76}\) prepared Ni/MOF-5(Zn) by the addition of MOF-5(Zn) to a Ni(acac)\(_2\)/ethanol solution (60 °C) and subsequent reduction of the Ni\(^{2+}\) ions with hydrazine into Ni NPs (9 nm diameter). In the impregnation method, the contents of the metal NPs are controlled by the concentration of the metal salt.\(^{222}\) This is a critical point, as metal NPs start aggregating into larger secondary particles when the loading content exceeds an optimum range. However, under different conditions, the size of metallic NPs can be decreased further down to the atomic scale. Fang et al.\(^{221}\) successfully demonstrated the incorporation of single Pt atoms into an aluminum-based MOF (Al-TCPP) through simple impregnation of Pt(II) into the center of porphyrin linkers, followed by reduction to Pt at 180 °C in H\(_2\) atmosphere (Figure 14a). The single atomic configuration of the Pt atoms was confirmed by the dominant Pt–N peak contribution seen in extended X-ray absorption fine structure (EXAFS) analysis as well as the scarce Pt clusters shown in diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). As another method to incorporate metal NPs into MOFs, functional organic linkers have been modified by metal coordination before the formation of the MOFs. In this process, Pt atoms were coordinated with porphyrin rings to form PtTCPP units, and then they were coordinated with Cu\(_x\)(COO)\(_x\) paddle-wheel metal nodes to form MOF structures (Figure 14b).\(^{224}\) In the resulting product, Pt particles of 0.1–0.2 nm were observed in the form of isolated single atoms. These studies indicate that the impregnation method allows metal NPs to be effectively incorporated into MOFs with high surface area, which can prevent aggregation of the NPs, maximize photocatalytic activity, and improve photochemical stability.

The Ship-in-a-bottle (SIB) method is a process that incorporates metal complexes, rather than pure metals, into the MOF cavities. This process has been commonly adopted in the field of zeolite/metal complex hybrids to prevent leaching of the metal guest molecules, by confining the metal complexes within the small pores of the zeolites. Owing to the topological diversity and tunability of porous structures, MOFs have become promising supports for accommodating metal complexes through the SIB process. Generally, the encapsulation of metal compounds in MOFs through the SIB method is carried out by the introduction of a flexible ligand.\(^{225}\) Flexible ligands can be incorporated freely into the MOF pores and
thus eventually allow metal ions to be immobilized inside the cages. Nasalevich et al. demonstrated a synthetic protocol for designing Co@MOF by the SIB method (Figure 14c).\textsuperscript{[226]} The flexible ligand, N\textsubscript{2},N\textsuperscript{′}-propanediylbis(2,3-butanedione 2-imine 3-oxime), was incorporated into the pores of MIL-125(Ti)-NH\textsubscript{2}, and then CoBr\textsubscript{2} was added for Co encapsulation within the MOF. In another study, instead of employing flexible ligands before the metal incorporation, metal salts were pre-adsorbed into the MOF, followed by the coordination of desirable metal ions and ligands.\textsuperscript{[227]} Through this process, Cu complexes were successfully encapsulated in MIL-100(Al) without structural distortion of the MOF. The pre-incorporation of flexible ligands or metal salts into MOFs enables the encapsulation of metal complexes, diversifying the chemical routes available to incorporate single atom catalysts (SACs) into MOFs. However, it remains challenging to tailor the shape and composition of the metal NPs in the MOFs with the SIB process.

3.3.2. MOF/Metal NP Hybrids for Photocatalytic Hydrogen Production

MOF/metal hybrids are novel composites for solar hydrogen generation that promise efficient charge transfer between the metal guest-molecule and photoactive MOF structure. In addition, the MOF provides an ideal matrix for metal NP encapsulation and prevents aggregation during the catalytic reaction. Xiao et al.\textsuperscript{[228]} reported that the hydrogen production rate of Pt NPs encapsulated by MOF (Pt@UiO-66(Zr)-NH\textsubscript{2}) (257.38 \textmu mol g\textsuperscript{−1} h\textsuperscript{−1}) is five times higher than that of Pt NPs surface-coated onto MOF (Pt/UiO-66(Zr)-NH\textsubscript{2}) (Figure 15a).

Furthermore, Pt/UiO-66(Zr)-NH\textsubscript{2} suffered from deterioration of the catalytic activity due to leaching or aggregation of the Pt NPs. The study suggests that the encapsulation of Pt NPs using MOF suppresses charge recombination by shortening the electron transport path and prevents aggregation and leaching of the Pt NPs.

The localized surface plasmon resonance (LSPR) effect increases when the metallic particle size reaches the nanoscale. This can enhance the photocatalytic activity of MOF/metal NP hybrids. In particular, Au is well-known for the strong absorption of visible light. Wen et al.\textsuperscript{[229]} combined Au@Pd NPs with Ti-Zr-MOF to perform hydrogen production from formic acid. The bimetallic Ti-Zr-MOF provided good photoreactive support and allowed the efficient harvesting of light assisted by the LSPR effect. Indeed, Au@Pd NPs in MOFs was able to significantly improve the H\textsubscript{2} production rate compared to monometallic Au NPs or Pd NPs in MOFs. Nanoscale metallic NPs uniformly dispersed within MOFs is an ideal platform for utilizing high catalytic activity, strong LSPR effect, and the synergistic combination between the two.

In addition to the encapsulation of noble metal NPs in MOFs, cost-effective transition metal catalysts such as cobalt and nickel\textsuperscript{[230]} have also been introduced for use in MOF/metal NP hybrids. Nasalevich et al.\textsuperscript{[226]} used a cobalt catalyst in a MOF for solar hydrogen production. The Co@MIL-125(Ti)-NH\textsubscript{2} employed in the study exhibited remarkably enhanced photocatalytic performance, with up to 20 times higher H\textsubscript{2} generation rate compared to the pristine MOF (Figure 15b), and demonstrated high photochemical stability without Co leaching. They proposed that the photoinduced electrons in the MOF linkers were transferred to the Co complex, providing an efficient
charge-transfer path and facilitating charge separation at the same time. After Nasalevich's work, a few related papers postulated that the Co species in the MOF cages were responsible for accumulating the electrons needed for reducing protons to H₂.[231] The Ni NPs have also been incorporated in MOF-5(Zn) for effective photocatalytic H₂ production.[76] Before the photocatalytic reaction, a metal complex photosensitizer, Eosin Y (EY), was added on Ni@MOF-5(Zn) to extend the light absorbance spectrum. EY-Ni@MOF-5(Zn) exhibited 302.2 μmol of H₂ evolution in 2 h, which is 6.06 times higher than that of EY-Ni (Figure 15c). This was attributed to the superior π-conjugated scaffold of MOF-5(Zn), which offers a facilitated path for electron transfer from the EY to the anchored Ni NPs throughout the framework. The long-term stability of EY-Ni@MOF-5(Zn) reveals that the MOF played an important role in preventing the Ni complexes from aggregating. These MOF/metal hybrids are attractive platforms for creating an efficient path for charge carriers and for providing a scaffold to stabilize the metal species.

Figure 15. a) Schematic illustration for the synthesis of Pt@UIO-66(Zr)-NH₂ and Pt/UIO-66(Zr)-NH₂, with the photocatalytic hydrogen production process over Pt@UIO-66(Zr)-NH₂ being highlighted, and H₂ production rate of UIO-66(Zr)-NH₂. Pt NPs encapsulated MOF (Pt@UIO-66(Zr)-NH₂), and Pt NPs surface-coated MOF (Pt/UIO-66(Zr)-NH₂). b) Photocatalytic proton reduction using MOF and Co@MOF and steady state H₂ evolution rate plotted against the average number of cobalt atoms inside each MOF cavity. c) Photocatalytic mechanism for H₂ evolution over the EY sensitized Ni@MOF-5(Zn) with triethanolamine (TEOA) as a sacrificial donor under visible light irradiation and The hydrogen evolution of EY-Ni, EY-MOF-5(Zn), EY-Pt@MOF-5(Zn), and Ni@MOF-5(Zn) photocatalysts in 100 mL 10% (v/v) TEOA aqueous solution (pH 11) under visible light irradiation (λ ≥ 420 nm). a) Adapted with permission.[228] Copyright 2016, Wiley. b) Reproduced with permission.[226] Copyright 2015, The Royal Society of Chemistry. c) Reproduced with permission.[76] Copyright 2016, Elsevier.
3.4. MOF/Carbonaceous Material (CM) Hybrids

CMs have gained considerable attention because of their visible-light response, environmental compatibility, cost-effectiveness, and earth abundance. Due to their unique characteristics and properties, they can replace expensive noble metal catalysts in solar hydrogen production. Unfortunately, most carbonaceous materials exhibit rapid electron–hole recombination and low surface area, limiting their solar-to-hydrogen conversion applications. Accordingly, the PC and PEC performance can be enhanced by forming MOF/CM hybrids that can promote charge separation/transfer or increase the surface area. Furthermore, hybridization of CMs with MOFs can provide a higher surface area to increase the number of reaction centers for photocatalytic activities.

3.4.1. Synthetic Strategies for MOF/CM Hybrids

The hydrothermal/solvothermal, electrostatic self-assembly, and thermal annealing processes have been used to synthesize MOF/CM hybrids. Hydrothermal and solvothermal methods are the simpler processes for preparing MOF/CM hybrids. They provide a facile metal ion/ligand modification, thus offering diverse hybrid combinations between MOFs and carbonaceous materials such as g-C₃N₄, GO, and rGO.[51] For instance, Li et al. synthesized MIL-88B(Fe)-NH₂/g-C₃N₄ hybrids via a solvothermal reaction.[234] The strong bonding that formed between the MOF and g-C₃N₄ is known to be responsible for efficient charge transfer. However, achieving a uniform coating of MOF on carbonaceous material can become difficult when carbonaceous materials such as g-C₃N₄ and GO become aggregated in the slurry solution.[234] Therefore, it is essential to disperse the carbonaceous material prior to the solvothermal reaction.

Electrostatic self-assembly is another facile process for establishing a stable MOF/CM hybrid. Two oppositely charged materials are required to promote coupling by mutual electrostatic attraction in the suspension.[235] Liang et al.[175b] prepared MIL-53(Fe)/rGO by an electrostatic self-assembly of negatively charged rGO and positively charged MIL-53(Fe). Intimate interfacial contact was achieved through uniform stacking of the heterointerfaces. Alternatively stacked 2D GO/Co-MOF multilayer hybrids have also been prepared by electrostatic self-assembly.[236] The opposing surface charges on the two different 2D nanosheets are responsible for preventing the self-stacking of the same 2D nanosheets.

The MOFs and carbonaceous materials can also be coupled by thermal annealing. Wang et al.[236] coated g-C₃N₄ on UiO-66(Zr) by thermal annealing in Ar atmosphere. Intimate contact between UiO-66(Zr) and g-C₃N₄ nanosheets were observed, and the morphology of the MOF remained unchanged after the annealing process, leading to high stability and reusability for photocatalytic activities.[236] However, the annealing temperature should be carefully optimized as most MOFs decompose at temperatures higher than 400 °C.[51]

3.4.2. MOF/CM Hybrids for Photocatalytic Hydrogen Production

MOF/CM hybrids have received considerable attention as a class of photocatalysts that are free of noble metals. For MOF/CM hybrid photocatalysts to be effectively used for solar-hydrogen evolution, efficient charge separation/transfer, and high stability should be achieved. One possible approach is the formation of a robust π–π interaction between the MOF and the carbonaceous material. As most MOFs and CMs contain aromatic rings,[235] the π–π stacking interaction can be effectively formed between them. For example, in Karthik’s work,[240] MIL-125(Ti)-NH₂/rGO hybrids exhibited a significantly enhanced H₂ production rate compared to the pristine MOF (Figure 16a).

Figure 16. a) Mechanism for π–π interaction between rGO and MIL-125(Ti)-NH₂ MOF and photocatalytic production of H₂ using different MIL-125(Ti)-NH₂/rGO-based MOFs under visible-light illumination. b) Schematic of the possible mechanism for H₂ evolution using the g-C₃N₄/MIL-53(Fe) composite and H₂ evolution rate of photocatalysts under visible light irradiation (g-C₃N₄/MIL-53(Fe)-0.25 sample: weight ratio of g-C₃N₄/MIL-53(Fe) is 0.25). c) The photocatalytic H₂ evolution activities and the photocatalytic stability of UiO-66(Zr)-NH₂/TpPa-1-COF (4:6). d) Photocatalytic mechanism of the charge transfer for hydrogen evolution over the 15TBC (15 wt% MIL-125(Ti)-NH₂/B-CTF-1) under visible light irradiation and rate of hydrogen evolution over the different samples under visible light irradiation (15T/C: 15 wt%MIL-125(Ti)-NH₂/B-CTF-1, 15T/BC: 15 wt%MIL-125(Ti)-NH₂/B-CTF-1, 15ZBC: 15 wt%MIL-125(Ti)-NH₂/B-CTF-1).

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The $\pi-\pi$ interaction between the MIL-125(Ti)-NH$_2$ and rGO was responsible for facilitating charge separation/transfer by providing a direct transport path for electrons to migrate from the MIL-125(Ti)-NH$_2$ to the rGO, which significantly enhanced the H$_2$ production rate.

Constructing a type-II band alignment between the MOF/CM photocatalysts is another approach. Cao et al. fabricated hybrids between ultrathin 2D Ni MOFs and 2D g-C$_3$N$_4$ by electrostatic self-assembly.[176] They suggested that the 2D MOF has an excellent band position for g-C$_3$N$_4$ to promote electron/hole transfer and separation at the interface. Similarly, a composite between g-C$_3$N$_4$ and MIL-53(Fe) was used to promote photocatalytic H$_2$ evolution by constructing a type-II heterojunction (Figure 16b).[243] The H$_2$ production rate of the MOF/g-C$_3$N$_4$ hybrid was remarkably increased when compared with pristine MOF and pristine g-C$_3$N$_4$. This enhancement was attributed to the increase in the number of active sites upon incorporating g-C$_3$N$_4$ into MIL-53(Fe) and the accelerated charge separation through the type-II band alignment. However, the H$_2$ production rate substantially decreased after three cycles, probably due to the photochemical instability of the MOF in the solution. Accordingly, it is essential to achieve photochemical stability of the MOF for the design of reusable and long-term stable MOF/CM hybrids.

3.5. MOF/COF Hybrids

Similar to MOF, COFs are another class of porous crystalline materials with a high surface area and semiconducting properties, which have recently emerged as a new molecular platform for designing photocatalysts.[242] The COFs generally possess small bandgaps because of the strong $\pi$-conjugation in the organic linkers. Due to their structural and bandgap tunability, forming a heterojunction with MOFs can offer synergistic effects in photocatalysts by improving the visible light absorption and charge separation/transfer efficiencies. Moreover, the hierarchical and discrete pore structures of both MOFs and COFs can be synergistically combined to achieve a higher surface area. MOF/COF hybrids for solar hydrogen production have not been systematically explored yet, but they have significant potential for photocatalytic applications.

3.5.1. Synthetic Strategies for MOF/COF Hybrids

Condensation reactions have been widely used for synthesizing MOF/COF hybrids. The process is generally based on Schiff’s base chemistry, which is a stepwise reaction that involves surface functionalization on the MOF followed by interfacial growth of the COF. As both MOFs and COFs have organic linkers that can be functionalized by functional groups, Schiff’s base-type linkages, such as imine, hydrazine, azine, enamine, and phenazine, can be formed at the initial stage to induce the growth.[243] Various types of MOFs and COFs have been hybridized through a simple condensation reaction.[234]

In 2017, Peng et al.[245] proposed MIL-68(In)-NH$_2$@TPA-COF, a new type of MOF/COF core–shell hybrid material, through a convenient condensation reaction. During the synthesis, the aldehyde-functionalized groups on the surface of the MOF induced the growth of the COF. Additionally, the hybridization of the MOF and COF showed a significantly higher surface area and discrete porosity, indicating that the formation of MOF/COF hybrids can provide abundant reaction sites for photocatalytic activities. In another work, highly crystalline MIL-125(Ti)-NH$_2$@TAPB-PDA was obtained by the condensation reaction.[246] The strong covalent bonds formed by the Schiff’s base-type linkages were able to extend the visible-light absorption range and improve structural stability during the photocatalytic reaction. The types of ligands, solvent combinations, and temperatures are key parameters that should be considered for ensuring high crystallinity of the MOF/COF hybrids.

3.5.2. MOF/COF Hybrids for Photocatalytic Hydrogen Production

As MOFs share similar structural features with COFs, the hybridization of the two materials can ensure high crystallinity and the surface area for photocatalytic reaction. Strong covalent bonding between the MOF and COF is beneficial for the formation of stable hybrids. Zhang et al.[247] reported a UiO-66(Zr)-NH$_2$/TpPa-1-COF hybrid for efficient photocatalytic H$_2$ production. The H$_2$ evolution rate of TpPa-1-COF increased by 20 times when UiO-66(Zr)-NH$_2$ was integrated (Figure 16c). This was attributed to the increase in surface area upon incorporating MOF on the COF, as well as the strong covalent bonds between them. In another work, Li et al.[248] proposed incorporating MIL-125(Ti)-NH$_2$ onto B-CTF-1 to enhance the photocatalytic performance. The H$_2$ evolution rate of TpPa-1-COF hybrid constructed a type-II heterojunction, which acted as an efficient charge-carrier path for improved photocatalytic performance. In another work, Li et al.[249] proposed incorporating MIL-125(Ti)-NH$_2$ onto B-CTF-1 to enhance the photocatalytic H$_2$ evolution rate of the pristine COF (Figure 16d). The 15 wt% MIL-125(Ti)-NH$_2$/B-CTF-1 (15 TBC) hybrid showed improved photochemical stability compared to the bare COF. These results demonstrate that MOF/COF hybrids are excellent photocatalysts because they exhibit similar and compatible porous networks, high structural tunability, and suitable bandgaps. However, MOF/COF hybrids for photocatalytic H$_2$ production are at an early stage of development, with great possibilities still left to explore.

3.6. Enhanced Solar Hydrogen Production Using MOF Hybrids

The enhancement of the hydrogen production rate in PC reaction and photocurrent density in PEC reaction by forming hybrids between MOFs and other materials in the literature is summarized (Figure 17).[155, 157, 163, 175, 177, 190a, c, d, 192, 196, 200–202, 207b, c, 210, 212–215, 219, 224, 226, 236, 240, 241, 242–249] Compared to the single component counterparts, MOF hybrid photocatalysts led to the ~2–28 000 times higher solar hydrogen production efficiency, clearly confirming that the hybrid formation is one of the most promising strategies to design high-performance photocatalysts.

To date, TiO$_2$ and ZnO have been widely applied to design MOF/oxide hybrids.[177, 190a, c, d, 200–202, 207b, c, 210, 249a–c] Thus, it is necessary to enhance the solar hydrogen production using hybrids between MOFs and other binary and ternary oxides. On the
The distinctive advantages of MOFs, such as high surface area, abundant porosity, compositional tunability, and the ability to incorporate atomic scale catalysts, can be maintained even after the conversion of MOFs into oxides, chalcogenides, and phosphides. Moreover, their organic linkers, which mainly consist of carbon and nitrogen, provide new opportunities for fabricating inorganic semiconductor-carbon nanohybrids that can facilitate charge transfer. Since the MOF-derived synthesis provides versatile controllability of inorganic materials, MOFs and MOF-derived hybrids are promising platforms for PC and PEC hydrogen production. This section covers the synthetic strategies for MOF-derived photocatalytic hybrids and the mechanisms underlying their enhancement of hydrogen production.

### 4. MOF-Derived Hybrids for Hydrogen Production

The distinctive advantages of MOFs, such as high surface area, abundant porosity, compositional tunability, and the ability to incorporate atomic scale catalysts, can be maintained even after the conversion of MOFs into oxides, chalcogenides, and phosphides. Moreover, their organic linkers, which mainly consist of carbon and nitrogen, provide new opportunities for fabricating inorganic semiconductor-carbon nanohybrids that can facilitate charge transfer. Since the MOF-derived synthesis provides versatile controllability of inorganic materials, MOFs and MOF-derived hybrids are promising platforms for PC and PEC hydrogen production. This section covers the synthetic strategies for MOF-derived photocatalytic hybrids and the mechanisms underlying their enhancement of hydrogen production.

#### 4.1. Hybrids between MOF-Derived Oxides (Oxide\textsubscript{MOF}) and Other Materials

##### 4.1.1. Synthetic Strategies for Oxide\textsubscript{MOF}/Other Material Hybrids

In addition to the energy band structure and electronic properties, structural parameters of photoactive materials, such as size, surface area, porosity, morphology, and aggregation, should be tailored carefully to maximize the PC and PEC reactions. MOF-derived preparation of oxide nanostructures provides an excellent tunability of size, morphology, and surface area of the photocatalysts and offers diverse synthetic strategies for designing hybrids between oxides and other materials. The choice of metallic cation in MOF templates enables the compositional control of transition metal oxides after oxidation, and the use of bimetallic/multi-metallic MOF templates provides synthetic routes for fabricating well-defined nanocomposites. In addition, the post-synthetic cation exchange in MOFs and the reaction of MOFs with other materials offer new pathways for designing diverse oxide\textsubscript{MOF}-based hybrid photocatalysts. Furthermore, oxide nanostructures encapsulating nanoscale noble-metal catalysts can be prepared from...
the noble-metal-incorporated MOFs. Finally, the carbonization of MOFs in reducing atmospheres enables the preparation of (oxide/CM)MOF hybrids in a nonaggregated configuration, which facilitates the transport of photogenerated carriers and increases the number of reaction sites.

Thermal annealing of MOFs is the most convenient route for preparing oxideMOF nanostructures. There are several MOFs with different morphologies that consist of diverse metal cations and organic ligands. However, for understanding the general mechanisms underlying the key strategies toward the MOF-derived design of oxides, oxide synthesis using ZIF-67(Co) templates are mainly discussed in this section (Figure 18). When the ZIF-67(Co) dodecahedrons are annealed at >400 °C in an oxidizing atmosphere such as air or oxygen, the organic linkers are oxidized into gaseous CO2, H2O, and NO2, while the Co metals are converted into Co3O4. With the increase in temperature, the heating starts from the outer part of the polyhedrons; thus, a thin shell-layer of Co3O4 begins to form while the core-part oxidizes afterward. The Co source is not abundant owing to van der Waals forces, the nanoparticles of several hundred nanometers are less likely to aggregate with each other, which makes their separation and recycling convenient.[251] Moreover, the hollow morphology is advantageous for enhancing light scattering. Thus, the MOF-derived oxide nanocages can be a viable solution to implement as photocatalysts.

The temperature, atmosphere, and heating rate of thermal annealing are three principal parameters for determining the appropriate oxidation of MOFs, nanocage morphology, residual amount of carbon/nitrogen, coarsening of the oxide NPs, and densification of the nanocages. Jiang et al.[256a] prepared Co3O4 nanocages (modal pore size: ~26 nm), collapsed nanocages (modal pore size: ~20 nm), and NPs by heat treatment of ZIF-67(Co) rhombic dodecahedrons at 350, 500, and 700 °C in air, respectively (Figure 18b). This demonstrates that the size of mesopores and crystallites, as well as the nanocage morphology can be manipulated by regulating the annealing temperature.

The (oxide/CM)MOF hybrids can be prepared by carbonization of the organic linkers at high temperature in a reducing atmosphere, followed by the oxidation of the metals in an oxygen-containing atmosphere at a lower temperature. Zhang et al. prepared (CoOx/C)MOF hybrids by the carbonization of ZIF-67(Co) in Ar at 500–900 °C with subsequent oxidation of Co into Co3O4 by thermal annealing in air at 200 °C (Figure 18c).[168] The presence of porous C or N-doped C with high electric conductivity can enhance the PC and PEC properties by facilitating charge transport[165c,252] while the relative content of residual N and C after carbonization can be controlled by the selection of the organic linkers in the MOFs.

Chemical reaction with the MOF templates can further modify the morphology or composition of postannealed oxides. Jo et al.[140] prepared hollow hierarchical cobalt layered double hydroxides (Co LDH) nanocages by solvothermal reaction of ZIF-67(Co) dodecahedra and converted those into hollow
hierarchical (Co3O4)MOF nanocages ((Co3O4)MOF HHNs) by thermal annealing (Figure 18d). The size and monodispersity of (Co3O4)MOF HHNs was controlled in the stage of preparing the ZIF-67(Co) dodecahedra, while the surface area was maximized by growing numerous Co LDH nanosheets, both of which can provide excellent control of the catalytic properties. Moreover, atomic or nanoscale noble metal catalysts can be incorporated within the MOFs and metal-loaded MOFs can be used as valuable templates for preparing oxide nanostructures uniformly loaded with nanocatalysts, as shown by the Pd-loaded (Co3O4)MOF nanocages in Figure 18e.[250b]

Hybrids between two different oxides have been prepared using MOF templates to harvest their synergistic effects. The hybrid photocatalysts can be classified into two categories: nanocomposites and core–shell heterostructures. It is advantageous to form small-size nanocomposites with intimate contact at the interface for charge transfer/separation when the type-II interface is established. To this end, uniform mixing between two different metal cations using MOF templates is effective. Bala et al.[253] mixed four different types of Co-MOFs with Ti-isopropoxide, gradually hydrolyzed the suspensions, and converted the products into (Co3O4)MOF/TiO2 nanocomposites by thermal annealing. The rapid charge transfer across the interfaces of the (Co3O4)MOF/TiO2 nanocomposite and consequent charge separation are responsible for the high photocatalytic performance observed in the study, which was achieved by uniform mixing of the MOF template and Ti source. Bimetallic MOFs with a uniform distribution of two cations provides another pathway for preparing nanocomposites. For instance, Xu et al.[254] synthesized composite (Co3O4/TiO2)MOF hollow polyhedrons by thermal annealing of Ti4+–exchanged ZIF-67(Co) polyhedrons (Figure 18f), and Lan et al.[131b] prepared (ZnO/Co3O4)MOF nanocomposites from co-precipitated ZnCo-ZIFs. It should be noted that the bimetallic/multi-metallic compositions can be developed either during preparation of the MOFs or by the posttreatment of the MOFs.

The yolk–shell or core–shell hybrid configurations have also been adopted for designing high-performance photocatalysts or battery electrodes. To this end, a chemical reaction occurs at the outer part of the MOF particles, which is followed by thermal annealing. Hu et al.[255] prepared (Co3O4@NiCo2O4)MOF yolk–shell nanocages by the reaction of ZIF-67(Co) with Ni-nitrate in ethanol, followed by thermal oxidation to Co3O4/NiCo LHD dodecahedra (Figure 18g). Various yolk–shell or core–shell hybrids have been fabricated using this strategy, which includes hexagonal (Co3O4@MnCo2O4)MOF yolk–shell nanocubes from ZIF-67/Mn-Co LDH nanocubes,[256] (ZnO@ZnCo2O4)MOF nanocages from ZIF-8(Zn)/Co-Zn hydroxides,[257] and (NiF2O4)MOF@(Fe2O3)MOF nanotubes from FeNi MIL-88/Fe MIL88 nanorods.[258] In a sufficient reaction time, nanocages with a homogeneous distribution of two cations (nanocomposites) can be developed, as demonstrated by the (CoO/MoO3)MOF nanocages in Figure 18h.[250] Likewise, Zou et al.[260] reported the preparation of (ZnO/ZnFe2O4/C)MOF nanocages by thermal annealing of Fe-modified MOF-5(Zn) in N2 atmosphere, demonstrating that the concurrent control of bimetallic composition and residual carbon is possible.

In the photoanodes using hybrids between oxides and other materials, the co-catalytic effect, charge funneling by establishing type-II interfaces, and maximization of surface reaction sites are required. Cardenas-Morcoso et al.[261] prepared BiVO4 photoanodes that were uniformly decorated with a co-catalyst of porous (Co3O4)MOF polyhedrons. This was done by coating ZIF-67(Co) polyhedrons on BiVO4 surfaces modified by H3BTC, followed by heat treatment (Figure 18i). The high surface area, porosity, and catalytic activity of the porous Co3O4 polyhedrons were obtained from the distinctive properties of the MOFs. Shi et al.[262] prepared mixed-phase (TiO2)MOF (anatase and rutile) nanopolyhedrons from MIL-125(Ti)-NH2 and prepared a hybrid with CdSe@CdS QDs by electrodeposition (Figure 18j). The mixed TiO2 phase facilitated charge separation due to the formation of a type-II heterojunction between the anatase and rutile. Furthermore, the hybrid formation with the CdSe@CdS co-catalyst provided another type-II heterojunction and enhanced visible light absorption, which maximized the PEC performances. The MOF-derived synthesis allowed for the preparation of highly dispersed TiO2 MOF octahedrons with monodispersity, which facilitated the formation of well-defined hybrids with CdSe@CdS QDs by electrodeposition. This suggests that MOFs are suitable templates for hybrid formation.

The growth of MOFs on photoanodes can also significantly increase the number of reaction sites. Tang et al.[157a] hydrothermally grew ZIF-67(Co) nanosheets on TiO2 NRAs after depositing a Co(OH)2 seed layer and converting it into hybrid (Co3O4)MOF/TiO2 by heat treatment (Figure 18k). In addition to the type-II heterojunction between the TiO2 and Co3O4 promoting charge separation, the synergistic combination of TiO2 nanorods for charge transfer and Co3O4 nanosheets for high reactivity significantly enhanced the water splitting. The high porosity, surface area, and unique morphology of the Co3O4 nanostructures was designed into the material during the stage of MOF growth, while the Co(OH)2 seed layer was a suitable mediator for combining the MOF and oxide with different cations. Furthermore, the heat treatment used to oxidize the MOF had the potential to strengthen the bonding between the two oxides. However, as a different method, the second oxide layer may be directly grown onto oxide NRAs by hydrothermal/solvothermal reaction. In general, MOF-derived oxides can provide a much higher surface area as well as beneficial porosity properties and thus are more advantageous for designing high-performance photoanodes.

The above results clearly demonstrate that MOF templating provides various irreplaceable advantages for synthesizing oxide/oxide hybrid photocatalysts, such as high controllability of the size, porosity, monodispersity, morphology, surface area, and composition of photoactive materials, formation of uniform oxide/oxide or oxide/CMs nanocomposites, tailored design of core–shell (or yolk–shell) nanostructures, and intimate contact between the two contacting phases.

4.1.2. OxideMOF/Other Material Hybrids for Photocatalytic Hydrogen Production

For suspension-type photocatalysts, monodisperse, well-dispersed, porous, and small particles are advantageous for maximizing the PC reaction, which can be best achieved by MOF-templated synthesis. deKrafft et al. coated a thin,
amorphous TiO$_2$ layer on Fe-MOF octahedrons by hydrolysis reaction and then converted it into Fe-doped anatase octahedral nanoshells encapsulating Fe$_2$O$_3$ NPs ([Fe$_2$O$_3$]$_{MOF}$/TiO$_2$) by subsequent calcination (Figure 19a). The [Fe$_2$O$_3$]$_{MOF}$/TiO$_2$ produced large amounts of H$_2$ (light filter: 420 nm), whereas no hydrogen was produced by Fe$_2$O$_3$, TiO$_2$, or the mixture of [Fe$_2$O$_3$]$_{MOF}$ and TiO$_2$ (Figure 19b). Photocatalytic hydrogen production using visible light is explained by band narrowing due to Fe doping of TiO$_2$. This work demonstrates some of the various advantages of MOF templating, such as monodispersity of the photocatalysts, doping of photocatalysts for bandgap engineering, and the development of abundant reaction sites using unique nanocage morphology. Since the size, morphology, and composition of MOFs are controllable, the thermal oxidation of MOF particles coated with other materials provides a diverse synthetic route for fabricating high-performance hybrids for PC and PEC reactions.

Chen et al. prepared hollow (Cu-TiO$_2$)/$C_{MOF}$ composites by coating a thin Cu-MOF layer (HKUST-1(Cu)) and Ti-precursors on SiO$_2$ spheres and converted them into a hollow (Cu-TiO$_2$)/$C_{MOF}$ hybrid by calcination in N$_2$ atmosphere and subsequent etching of the spherical SiO$_2$ template (Figure 19c). The high hydrogen evolution rate of (Cu-TiO$_2$)/$C_{MOF}$ composites (Figure 19d) is associated with their thin shell morphology with a high accessibility of reaction sites, type-II interfaces between Cu$_2$O and TiO$_2$ for effective separation of charge carriers, and enhanced charge transport along conductive carbons. This work shows that templates other than MOFs can also be used to enhance the accessibility of reactants, confirming that MOF-derived synthesis enables uniform and porous nanocomposites with many different materials such as Cu$_2$O, TiO$_2$, and conducting carbon.

Zhang et al. prepared (CoO$_x$/C)$_{MOF}$ hybrids by heat-treating ZIF-67(Co) at 700°C in Ar and at 200°C in air (Figure 19e). The CoO$_x$ particles, uniformly distributed in a porous carbon matrix, showed high photocatalytic properties for water oxidation. In particular, (CoO$_x$/C)$_{MOF}$ hybrids exhibited superior oxygen yields compared to a physical mixture between Co$_3$O$_4$ MOF and C or pure Co$_3$O$_4$MOF (Figure 19f). This verifies that the oxid$_{MOF}$/C composites offer various advantages such as the uniform mixing of oxide and C, effective charge transport, high surface area, and porous structure, all of which enhance photocatalytic performance.

Furthermore, the above strategies to design oxide-based photocatalysts can be combined synergistically. Huang et al. synthesized (NiFe$_2$O$_4$)$_{MOF}$/(Fe$_2$O$_3$)$_{MOF}$ hybrid nanotubes by coating Fe MIL-88 shell onto the surface of Fe$_3$Ni MIL-88 nanorods, followed by heat treatment. That is, two different MOF templates were used to form oxide-oxide hybrids with a complex composition; this demonstrated that various hybrids can be designed by the combination of monometallic, bimetallic, and multi-metallic MOFs. Therefore, the oxidation of MOF templates provides a simple route to prepare oxide-based photocatalysts with highly tunable size, shape, morphology, porosity, composition, and carbon content.

**4.2. Hybrids between MOF-Derived Chalcogenides (Chalcogenide$_{MOF}$) and Other Materials**

Transition-metal chalcogenides have been widely investigated as promising photocatalysts with favorable visible light absorption and earth-abundance. In spite of their high potential for photocatalytic activity, several drawbacks, such as aggregation, poor charge separation, and low tunability of size and morphology, limit their performance. Accordingly, it is important to develop a facile method for synthesizing metal chalcogenide nanostructures with high specific surface area and small particle sizes in a highly dispersed manner. Similar
to oxide\textsubscript{MOF}, chalcogenide\textsubscript{MOF}s offer large surface area, pore controllability, and compositional tenability\cite{264}, and can function as excellent photocatalysts compared to those prepared by conventional synthetic routes. In addition, the photocatalytic performance of metal chalcogenides can be enhanced further by forming hybrids with other materials. In this section, the synthetic methods and photocatalytic performance of chalcogenide\textsubscript{MOF}/other material hybrids are discussed.

### 4.2.1. Synthetic Strategies for Chalcogenide\textsubscript{MOF}/Other Material Hybrids

Solution-based and vapor-phase reactions have been used to synthesize chalcogenides from MOF templates. MOFs can be converted into metal chalcogenides by solution-based routes such as hydrothermal, solvothermal, and microwave-assisted reactions. In liquid-phase chalcogenization, thioacetamide, thiourea, sodium sulfide, and Se powder have been used as chalcogen sources. For instance, cubic pyrite nickel disulfide ([NiS\textsubscript{2}]\textsubscript{MOF}) hollow microspheres (HMS) were prepared from spheres consisting of Ni-BTC (benzene-1,3,5-tricarboxylic acid) via microwave treatment in a thioacetamide ethylene glycol solution (Figure 20a).\cite{265} Flower-like nanostructures consisting of Cd-MOFs have also been converted into a similar morphology of [Cd\textsubscript{5}S\textsubscript{8}]\textsubscript{MOF} nanostructures via solvothermal reaction using Na\textsubscript{2}S$\cdot$9H\textsubscript{2}O\cite{160} as the sulfurization source (Figure 20b), while solution-based sulfidation was used to convert (Co\textsubscript{2}O\textsubscript{3})\textsubscript{MOF} spheres into (Co\textsubscript{2}S\textsubscript{3})\textsubscript{MOF} spheres.\cite{266} These studies demonstrate that metal sulfides can be prepared from either MOFs or oxide\textsubscript{MOF}s and that the morphology of metal chalcogenides can be designed during the formation stage of the MOF templates.

Solution-based sulfurization has been also adopted to prepare metal chalcogenide polyhedrons from MOF templates. Lan et al.\cite{132b} prepared (ZnS/CoS)\textsubscript{MOF} hollow dodecahedrons by sulfurization of ZnCo-ZIF dodecahedrons in a solution containing thioacetamides (Figure 20c). Wang et al.\cite{267} prepared diverse compositions of binuclear ZIF (Zn\textsubscript{2}Co\textsubscript{2}−xZIFs, Ni\textsubscript{2}Co\textsubscript{2}−xZIFs, and Cu\textsubscript{2}Co\textsubscript{2}−xZIFs) dodecahedrons by co-precipitation and then converted those into (Zn\textsubscript{2}Co\textsubscript{1−x}Se\textsubscript{x})\textsubscript{MOF}, (Ni\textsubscript{2}Co\textsubscript{1−x}Se\textsubscript{x})\textsubscript{MOF}, and (Cu\textsubscript{2}Co\textsubscript{1−x}Se\textsubscript{x})\textsubscript{MOF} nanocages, respectively, through solution-based selenization (Figure 20d). The composition of sulfide\textsubscript{MOF}s can be tuned further by the reaction of MOFs with other materials. Yu et al. synthesized Ni-Co incorporated MoS\textsubscript{2} nanoboxes by the solvothermal reaction of nickel cobalt Prussian blue analog (Ni-Co PBA) with ammonium thiomolybdate (Figure 20e).\cite{268} Inheritance of the polyhedral morphology from the MOF templates allows for the morphological control of photocatalysts. The preceding results confirm that the use of binuclear MOFs with various combinations of cations, as well as the postsynthetic reaction of MOFs with other materials, enables the preparation of diverse chalcogenide-based hybrids with uniform cation mixing, tunable energy bandgaps, and high catalytic activity. The solution-based synthesis of chalcogenides from MOF templates exhibits various distinctive advantages, such as uniform products, short reaction times, moderate synthetic conditions, and scalable processes.

Vapor-phase chalcogenization has also been utilized for the MOF-derived synthesis of metal chalcogenides. In general, as-synthesized MOFs are placed in a vacuum chamber, followed by chalcogenization at elevated temperature in an S or Se atmosphere, which leads to the formation of thermodynamically stable chalcogenides. Huang et al.\cite{269} prepared coral-like (NiSe/N-doped carbon(NC))\textsubscript{MOF} hybrids by the selenization of Ni-MOFs (Ni(HBTC)(4,4′-bipy)-3DMF). Ming et al. prepared Co-doped nickel selenide ([NiSe\textsubscript{2}+NiSe\textsubscript{4}]\textsubscript{MOF}) hybrid structures on Ni foam by vapor phase selenization of ZIF-67(Co)-derived NiCo LDH templates (Figure 20f).\cite{270} Wu et al. synthesized (Fe-doped CoSe@NC)\textsubscript{MOF} hybrids by vapor phase selenization of Co−Fe ZIF-67 (Figure 20g).\cite{271} It is worth noting that the oxygen partial pressure during chalcogenization must be low to prevent oxidation, and the temperature in vapor phase reactions is relatively higher than that in solvothermal reactions. Accordingly, the residual carbon or N-doped carbon is often derived from organic linkers of MOFs during chalcogenization at low oxygen partial pressure. Furthermore, other carbon-based phases such as CNTs can grow when favorable catalytic materials (e.g., Co or Ni) are included in the MOF. For example, Wu et al. prepared hybrids of (Co@PCP(polyhedral)/CNTs)\textsubscript{MOF} by the vapor-phase sulfidation of ZIF-67(Co).\cite{267} Yu et al. prepared (Zn\textsubscript{0.97}Co\textsubscript{0.03}S/CoS\textsubscript{2} embedded in N,S-co-doped CNT/nanopolyhedra)\textsubscript{MOF} by annealing bimetallic ZnCo-ZIFs in Ar with subsequent vapor-phase sulfidation (Figure 20h).\cite{272} The carbon-based materials provide protection to the chalcogenides from harsh environments as well as conductive pathways for charge transfer, thus enhancing the photocatalytic performance.\cite{273} Accordingly, the formation and control of conductive carbon-based phases is a distinctive merit of vapor phase chalcogenization.

### 4.2.2. Chalcogenide\textsubscript{MOF}/Other Material Hybrids for Photocatalytic Hydrogen Production

The formation of hybrids between oxides and metal chalcogenides increases visible-light absorption as well as charge funneling by tailoring the band structures. In addition, the rapid charge recombination in pure metal-chalcogenides can be suppressed by forming hybrids between chalcogenides and conducting phases such as carbon or N-doped carbon. Furthermore, in addition to the above merits, the hybrid formation of MOF-derived chalcogenides provides higher surface area, abundant porosity, and compositional/structural tunability, which can enhance the PC and PEC performance. MOF templating enables the design of nanostructures with high surface area and abundant porosity. Kumar et al. prepared onion-type hollow Co\textsubscript{3}S\textsubscript{4} structures with embedded CdS by the solution-based sulfurization of (Co\textsubscript{3}O\textsubscript{4})\textsubscript{MOF} and subsequent impregnation of CdS NPs.\cite{266} The CdS/(Co\textsubscript{3}S\textsubscript{4})\textsubscript{MOF} hybrid demonstrated a high H\textsubscript{2} production rate of 12 360 μmol h\textsuperscript{−1} cm\textsuperscript{−2} under simulated sunlight, which is much higher than that of pristine CdS NPs. This was attributed to the abundant active sites on the surface of the onion-type Co\textsubscript{3}O\textsubscript{4} nanostructures that were developed by the substantial contraction of Co-MOF templates during thermal annealing and the improved charge separation through the formation of type-II heterojunctions between (Co\textsubscript{3}S\textsubscript{4})\textsubscript{MOF} and CdS.

Although the impregnation method is convenient for fabricating hybrids, it often leads to poor cohesion at the interfaces...
and does not offer the preparation of nanoscale hybrids. To overcome these problems, the in-situ growth of MOFs on oxide surfaces and subsequent transformation into chalcogenides has been proposed. Zhou et al. fabricated the hybrid of ZnO@(ZnS/CoS)MOF through the chemical growth of ZnCo-ZIF on the surface of ZnO nanorods and subsequent sulfuration (Figure 21a). The final ZnO@(ZnS/CoS)MOF hybrid exhibited excellent photocurrent density (2.46 mA cm⁻² under full spectrum illumination) (Figure 21b) due to the MOF-derived wide surface area for active photocatalytic reaction, porous structures for enhanced light absorption, and improved interface adhesion. Furthermore, the uniform formation of type-II heterojunctions at ZnO@(ZnS)MOF interfaces facilitated charge separation, while the CoS played the role of the co-catalyst. A thin configuration of ZnS overlayer is advantageous for effective charge transfer and separation. All of these features can be best harvested through thin bimetallic MOF templates with uniform distribution of Zn and Co.

Yilmaz et al. prepared nickel iron Prussian blue analog (NiFe-PBA) on carbon fiber (CC) and converted it into a (NiFeSe@NiSe|CC)MOF/CC hybrid through vapor phase selenization (Figure 21c). The resulting chalcogenide MOF acquired a highly interconnected porous conductive network and a high surface area, which enhanced the catalytic activity, while the

Figure 20. a1) Schematic procedure to prepare (NiS₂)MOF hollow microspheres (HMS) by solution-based sulfurization. a2) SEM image of (NiS₂)MOF HMS. b1) Schematic procedure to prepare flower-like (CdS)MOF structures. b2) SEM image of flower-like (CdS)MOF. c1) Schematic illustration of the fabrication of (ZnS/CoS)MOF photocatalysts. c2) TEM image of (ZnS/CoS)MOF. d1) Schematic of the fabrication process of (M₄CoₓSe₂)MOF catalyst. d2) EDS elemental mapping image of (M₄CoₓSe₂)MOF catalyst. e) Schematic illustration and TEM image show the converting of NiCo-PBA (Prussian blue analog) into NiCo-MoS₂ nanoboxes (NBs). f1) Schematic illustration of the synthetic route to prepare NiCo LDH(layered double hydroxide)/C/NF(nickel foam) and Co-Ni-Se/NF. f2) TEM image of Co-Ni-Se/NF. g1) Schematic illustration of the synthesis process for (ZnCoS@NSCNT(N,S-codoped carbon nanotube)/NP(nanopolyhedra))MOF. h2) TEM images of (ZnCoS@NSCNT/NP)MOF.

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carbon fiber provided a conducting path which could accelerate electron transfer, both of which significantly enhanced the PEC performance (Figure 21d). This demonstrates the promising potential of hybridization between MOF-derived chalcogenides and conducting carbon nanofibers.

MOF templates also offer the fabrication of composites with different anions. Zhao et al. prepared a nanoscale (ZnO/ZnS)MOF heterostructure through a series of processes: beginning with solution-based sulfurization of MOF-5(Zn), subsequent thermal annealing in N₂, followed by partial oxidation of the (ZnS@C)MOF in ambient atmosphere (Figure 21e).[135] The relative amounts of ZnO-MOF and ZnS-MOF were controlled by altering the heat-treatment temperature or time. The main advantage of this procedure is the design of nanoscale oxide/sulfide hybrid structures in a highly uniform manner, which significantly increases the interfacial catalytic active sites for light absorption and facilitates the intimate formation of type-II heterojunctions between the ZnOMOF and ZnS-MOF for efficient charge separation. The photocatalytic hydrogen production (415.3 µmol g⁻¹ h⁻¹) of the hybrid ZnOS-MOF is significantly

Figure 21. a) Schematic illustration for the fabrication of cellular ZnO@(ZnS/CoS)MOF. b) J–V curves at a potential of 0.6 V (vs SCE) under chopped light illumination. c) Schematic illustration for the synthesis strategy of NiCH/CC, NiFe-PBA@NiCH/CC, and (NiFeSe@NiSeO)MOF/CC. d) Chronoamperometric i–t curve of the Si, NiSeO-Si, and (NiFeSe@NiSeO)MOF-Si at a bias potential of −0.4 V (vs RHE) under chopped illumination. e) Schematic illustration of the synthetic procedure of (ZnO/ZnS)MOF heterostructures. f) Comparison of photocatalytic HER of (ZnS/ZnO)MOF mixture, (ZnS)MOF and (ZnOS-n)MOF under visible-light irradiation. (n: the time (minutes) for calcining (ZnS@C)MOF at 550 °C in air to produce (ZnOS)MOF). g) Schematic illustration of the synthetic procedure for (NiS/ZnCd₁−ₓS)MOF. h) Comparison of photocatalytic HER rates of (NiS/ZnCd₁−ₓS)MOF under visible-light irradiation. i) Schematic illustration of the synthesis process of the sandwich-shelled (ZnCdS/ZnO/ZnCdS)MOF cages. j) H₂ production activity comparison of the sandwich-shelled (Zn₀.₅Cd₀.₅S/ZnO/Zn₀.₅Cd₀.₅S)MOF cages with (Zn₀.₅Cd₀.₅S)MOF solid, single-shelled (Zn₀.₅Cd₀.₅S)MOF cages, physical mixture of the sandwich-shelled (Zn₀.₅Cd₀.₅S/ZnO/Zn₀.₅Cd₀.₅S)MOF and (CdS/ZnO/CdS)MOF cages, physical mixture of single-shelled (ZnCdS)MOF and (ZnO)MOF. a,b) Adapted with permission.[157b] Copyright 2016, Elsevier. c,d) Adapted with permission.[274] Copyright 2019, Wiley. e,f) Adapted with permission.[135] Copyright 2018, Wiley. g,h) Adapted with permission.[275] Copyright 2018, Wiley. i,j) Adapted with permission.[276] Copyright 2018, The Royal Society of Chemistry.
higher than that (24.1 μmol g⁻¹ h⁻¹) of the (ZnO/ZnS)MOF mixture (Figure 21f). Additionally, the carbon species formed from the carbonization of the MOF block the coarsening of ZnS particles during thermal annealing, playing a key role in the preparation of uniform (ZnO/ZnS)MOF hetero–nanostructures. The MOF-derived synthesis of metal sulfide-carbon composites follows by partial oxidation provides a unique strategy for preparing nanoscale oxide/sulfide hybrid structures for high-performance photocatalysts.

The tailored design of metal cations in MOFs provides more opportunities to create diverse hybrid materials. Zhao et al. prepared (NiS/ZnₐCdₐS)MOF hybrids by solution-based sulfurization of Ni-ZnₓCdₓSₓ-C-α-MOFs (x = 0, 0.25, 0.5, 0.75, and 1.0) (Figure 21g). The compositional control of Zn and Cd enabled engineering of the bandgap from 2.08 to 3.01 eV, while the catalytic activity of the Ni promoted the dissociation of water. The (NiS/Zn⁰.₅Cd⁰.₅S)MOF hybrid showed the highest HER rate (16.78 mmol g⁻¹ h⁻¹) (Figure 21h). The relatively low HER rate of the ZnS emanated from the reduced visible light absorption due to the large bandgap, whereas the low HER rate of the CdS was associated with the lower conduction band position for hydrogen production. These results clearly demonstrate that the templates of bimetallic or multi-metallic MOFs allow for the preparation of diverse compositions of chalcogenides with tunable bandgaps and band-edge positions, as well as synergistic catalytic promotion.

The oxide/sulfide hybrid nanocages can be also prepared from MOF polyhedrons. Chen et al. prepared yolk–shell ZIF-8(Zn) polyhedral cages by etching ZIF-8(Zn) and converted them into (ZnS/ZnO/ZnS)MOF cages by solution-based sulfurization (Figure 21i). Afterward, the (Zn₁₋ₓCdₓSₓ/ZnO/Zn₁₋ₓCdₓSₓ)MOF cages were prepared by a cation exchange reaction. Similar to the previous Ni-ZnₓCdₓSₓ compound, the sandwich-shelled (Zn₀.₅Cd₀.₅Sₓ/ZnO/Zn₀.₅Cd₀.₅Sₓ)MOF showed the highest photocatalytic hydrogen evolution and a superior HER rate when compared to other counterparts with solid and single-shelled structures. This can be attributed to the engineering of the bandgap and band position, abundant specific surface area, shortened charge diffusion distance, enhanced charge separation, compositional control, and intimate type-II heterojunctions at ZnCdS/ZnO interfaces. In addition, the ~700 nm diameter polyhedrons inherited from the MOF enabled efficient dispersion of the photocatalysts while the sandwiched yolk–shell morphology maximized the reaction sites. The above results suggest that the MOF-derived hybrid design between chalcogenides and other materials provides various irreplaceable advantages, such as a high surface area for active catalytic reaction, thin and conformal coating of sulfides, excellent cohesion at interfaces, nanoscale heterostructures, compositional control of cations and anions, band-structure engineering using multinary chalcogenides, and dispersive polyhedral morphology.

**4.3. Hybrids between MOF-Derived Phosphides (PhosphideMOFs) and Other Materials**

Recently, transition metal phosphides (TMPs) have emerged as effective co-catalysts to promote water splitting and CO₂ reduction. The TMPs consist of earth-abundant materials and are stable over a wide range of pH in water and can be used as cost-effective and reliable photocatalysts to substitute noble-metal catalysts. The mechanisms regarding the co-catalytic properties of TMPs for PC and PEC water splitting can be found in the relevant review article. The representative TMP-based photocatalysts are Ni₃P, CoP, MoP, FeP, and Cu₃P, while the hybrids between TMPs and transition metal chalcogenides (TMCs) are generally used to maximize hydrogen production. In the hybrids, TMCs generally absorb visible light, and TMPs facilitate the charge separation/transport of TMCs. Accordingly, uniform nanoscale hybrids with TMPs and TMCs with intimate contacts are necessary, moreover, it is advantageous to use TMPs with tunable energy bandgaps, surface areas, porosity, and conducting pathways. These desired properties can be best achieved through MOF-derived synthesis.

**4.3.1. Synthetic Strategies for PhosphideMOF/Other Material Hybrids**

Thermally annealing a mixture of MOF (or MOF-derived materials) and sodium hypophosphite (NaH₂PO₂) at ~300 °C in Ar or nitrogen has been generally used as a route for MOF-derived synthesis of metal phosphides. Similar to chalcogenideMOFs, the conducting C or NC(N-doped C) phase can be developed by carbonization at elevated temperatures. For instance, You et al. prepared a (CoP₂/NC)MOF hybrid by the carbonization of ZIF-67(Co) and subsequent phosphidation after mixing with NaH₂PO₂. The monodisperse (CoP₂/NC)MOF polyhedrons with a high surface area (183 m² g⁻¹) and pore volume (0.276 cm³ g⁻¹) could be prepared using MOF templates (Figure 22a,b). The phosphideMOF exhibited abundant reaction sites, water accessible pore structures, and highly conducting pathways.

The morphology of phosphides can be designed by coating MOFs onto well-designed nanoarchitectures and subsequent conversion into phosphides. Wang et al. prepared porous (Ni₃P)MOF nanosheets by annealing a mixture of NiO nanosheet/MOF-74(Ni) and NaH₂PO₂ at 350 °C (Figure 22c,d). The MOF-74(Ni) layer was coated onto the NiO nanosheets to create electrolyte-accessible Ni₃P structures while minimizing the aggregation of Ni₃P. This hints that various reactant-accessible morphologies of metal phosphides with a high surface area and well-defined porosity can be fabricated by the mediation of MOF templates. Bimetallic or multi-metallic MOFs are also used for the compositional tuning of phosphides to enhance the photocatalytic properties. Song et al. prepared a (Cu₉₈Co₂₇P/NC)MOF hybrid by the carbonization of CuCo-ZIF and subsequent phosphidation (Figure 22e,f). In addition to the conducting NC phase developed by the organic linkers of the MOF, uniform doping of Cu during the formation of the MOF also played a role in enhancing the electrical conductivity. Li et al. also demonstrated that photocatalytic H₂ and O₂ generation using (Fe–Ni–P)MOF nanotubes can be bolstered by the compositional control of Fe–Ni MIL-88 templates. Considering these results, it can be noted that phosphideMOFs provide advantages for designing hybrid photocatalysts of more diverse compositions.
4.3.2. PhosphideMOF/Other Material Hybrids for Photocatalytic Hydrogen Production

PhosphideMOFs have also been hybridized with light-absorbing CdS nanostructures. Kumar et al.[288] prepared hybrids between CdS NPs and Ni-BTC derived Ni$_2$P$_x$MOF NPs (Figure 22g). The H$_2$ production rate of 2 at% Ni$_2$P$_x$MOF/CdS hybrids (33480 µmol h$^{-1}$ g$^{-1}$) using a hole scavenger (lactic acid) was 112, 62, and 2.6 times higher than those for pure Ni$_2$P, CdS, and Pt/CdS NPs, respectively (Figure 22h), which verified the...
beneficial effect of hybrid formation. The Ni$_2$P$_3$MOF NPs scavenge the photogenerated electrons in the CdS, which produce hydrogen by reaction with protons. Thus, the hybridization of light-absorbing CdS with electron-consuming Ni$_2$P$_3$MOF effectively suppresses charge recombination of the CdS. Furthermore, the H$_2$ production of the Ni$_2$P$_3$MOF/CdS hybrid was superior to that of Pt/CdS, demonstrating that phosphides are excellent and cost-effective co-catalysts that can replace noble metals. The formation of hybrids between CoP and g-C$_3$N$_4$ was also investigated to enhance the H$_2$ production rate. Sun et al.[289] reported that the CoP$_{x}$MOF/g-C$_3$N$_4$ hybrid prepared by phosphidation of a mixture of ZIF-67(Co) polyhedrons and g-C$_3$N$_4$ exhibited a ≈23 times higher H$_2$ production rate (201.5 mmol g$^{-1}$ h$^{-1}$ under light irradiation, $\lambda > 320$ nm) when compared to that of g-C$_3$N$_4$. Similarly, the role of CoP in the hybrid is the production of hydrogen through the scavenging of photogenerated electrons from g-C$_3$N$_4$.

A MOF-derived conformal coating of thin phosphate layers on the complex shapes of photoanodes or photocathodes has also been investigated. Weng et al.[290] electrochemically deposited a thin Co(OH)$_2$ layer on TiO$_2$ NW arrays and Si NW arrays; the Co(OH)$_2$ layer then converted into ZIF-67(Co) by a solution reaction. It is worth noting that thin and conformal MOF layers can be coated onto various oxide or inorganic NWs using a sacrificial Co(OH)$_2$ layer. The carbonization and subsequent phosphidation led to the formation of a TiO$_2$ NW@(CoP/NC)$_{x}$MOF photoanode and a p-type Si NWs@(CoP/NC)$_{x}$MOF photocathode (Figure 22i). The hybrid photoanode and photocathode significantly promoted electrochemical water splitting (Figure 22j). The NC derived from the MOF ligands significantly enhanced the stability of embedded CoP NPs while the MOF-driven conformal coating of the CoP with its lower bandgap (1.71 eV) facilitated light absorption as well as charge transport across the interfaces.

MOF-derived synthesis has been also used to prepare hybrids with two different phosphides. Lan et al.[132b] prepared (ZnO/Co$_3$O$_4$)$_{x}$MOF nanocages by annealing ZnCo-ZIF and converting it into a (Zn$_2$P$_3$/CoP)$_{x}$MOF hybrid by vapor-phase phosphidation and converting it into a (Zn$_2$P$_3$/CoP)$_{x}$MOF hybrid by vapor-phase phosphidation. Unlike other phosphide/chalcogenide hybrids, both Zn$_2$P$_3$ and CoP played the role of light absorption, and their contacts generated type-II interfaces. The high H$_2$ production rate of the (Zn$_2$P$_3$/CoP)$_{x}$MOF hybrid was explained by its charge-funneling band structure and enhanced light scattering due to porous structures. Notably, the uniform mixing of the Zn and Co cations in the MOF facilitated the nanocomposite formation between Zn$_2$P$_3$ and CoP.

Hybridization between multi-component metal phosphides and other materials assisted by MOF templating can be used to further tune the photocatalytic properties. For this, multi-component transition metal phosphides (MCTMPs) containing Co, Ni, and Mo were prepared by reacting ZIF-67(Co) with Ni and Mo components, followed by phosphidation, and then loaded onto ZnS nanorods for hybridization. The H$_2$ production rate of the (CdS/MCTMPs)$_{x}$MOF was 4.37 times higher than that of Pt/CdS nanorods, confirming the promising potential of phosphide-based co-catalysts. The use of MCTMPs can alter the charge transport/separation and enable bandgap engineering. This suggests that MOF-derived synthesis is a promising tool for designing multinary phosphides with high functionality.

For maximizing H$_2$ production using phosphide-based hybrids, the following properties are desired: a) small phosphides with a high surface area, b) intimate contact between the phosphides and light-absorbing materials, c) favorable band-edge position to scavenge photogenerated electrons, d) compositional uniformity and tunability, and e) cost-effectiveness and stability. MOF-derived synthesis enables a simple and cost-effective preparation of various phosphides with abundant reaction sites at a large scale, offering various practical designs of hybrids for catalytic application.

### 4.4. Enhanced Solar Hydrogen Production Using MOF-Derived Hybrids

The enhancement of the hydrogen production rate or photocurrent density by forming hybrids between MOF-derived materials and other materials in the literature is summarized (Figure 23). The MOF-derived hybrid photocatalysts showed ≈2–62 times higher solar hydrogen production efficiency than the single component counterparts. Although the research on the design of MOF-derived hybrids is in the beginning stage, diverse strategies on the MOF-driven synthesis of materials will substantially progress in this field. Overall, the MOF/chalcogenide or

![Figure 23. Summary of the photocatalytic and photoelectrochemical activity of MOF-derived hybrids over single components in the literature. (PC: Rate of H$_2$ production ($R_{\text{hybrid}}/R_{\text{single}}$) (%)) or PEC: Photocurrent density ($J_{\text{hybrid}}/J_{\text{single}}$) (%))][32b,157b,160,165c,261,262,266,288–290]

![Figure 23. Summary of the photocatalytic and photoelectrochemical activity of MOF-derived hybrids over single components in the literature. (PC: Rate of H$_2$ production ($R_{\text{hybrid}}/R_{\text{single}}$) (%)) or PEC: Photocurrent density ($J_{\text{hybrid}}/J_{\text{single}}$) (%))][32b,157b,160,165c,261,262,266,288–290]
MOF/phosphide hybrids show a higher efficiency compared to MOF/oxide hybrids, which can be explained by the superior catalytic characteristics of chalcogenides and phosphides to OER reaction. The main advantages of MOF-derived hybrids are the facile synthesis of hybrids with intimate cohesion of two different materials via various routes such as partial oxidation, sulfidation, phosphidation, and postsynthetic compositional control. In this perspective, diverse hybrids structures composed of MOF-inherited structures can be a promising material platform for PC and PEC reactions.

5. MOFs and MOF-Derived Hybrids for CO2 Reduction

5.1. Brief Introduction to Photocatalytic Reduction of CO2

Using solar energy, the PC and PEC reduction of CO2 can lower the concentration of CO2 in the atmosphere and produce valuable carbon-based fuels and chemicals, making it a viable option for environmental and energy-related issues.[292] The PC and PEC reduction of CO2 is similar to water splitting. Although the photocatalytic CO2 reduction performance of MOF-derived hybrids is lower than that of O2, it is highly stable owing to its strong C=O bond (750 kJ mol−1).[292] Therefore, proton-coupled electron transfer generally proceeds, which is electron transfer to CO2, together with proton transfer. In the process, the hydrogen evolution reaction due to protons may occur, which is an unwanted side reaction and must be hampered. Secondly, various fuels such as CO, formic acid, and hydrocarbons can be produced from the photocatalytic CO2 reduction reaction. To practically utilize the products from the photocatalytic CO2 reduction reaction. The main advantages of MOF-derived hybrids are the facile synthesis of hybrids with intimate cohesion of two different materials via various routes such as partial oxidation, sulfidation, phosphidation, and postsynthetic compositional control. In this perspective, diverse hybrids structures composed of MOF-inherited structures can be a promising material platform for PC and PEC reactions.

5.2. MOFs for Photocatalytic Reduction of CO2

For the first time in 2012, the photocatalytic reduction of CO2 to HCOO− on MOF photocatalysts was demonstrated by Fu et al.[293] They synthesized amine-functionalized titanium MOF photocatalyst TiO4(OH)2(bdc-NH2)6 (MIL-125(Ti)-NH2) using 2-amino-terephthalic acid as an organic linker and measured the photocatalytic performance of the photocatalyst in acetonitrile electrolytes with TEOA under visible light irradiation. After comparing the photocatalytic CO2 reduction of MIL-125(Ti)-NH2 and MIL-125(Ti), they confirmed that the amino functionality promoted photocatalytic activity for the CO2 reduction reaction. Although the photocatalytic CO2 reduction performance of MIL-125(Ti)-NH2 was very low, producing only 8.14 μmol of HCOO− in 10 h, they proved the possibility that MOF photocatalysts can be applied to photocatalytic CO2 reduction by the rational design of organic linkers. In addition, catalytic activity for the CO2 reduction reaction can be improved further by modulating the composition and structure of the MOFs. Thus, several studies on photocatalytic CO2 reduction using various forms of MOFs have been conducted.

5.2.1. Engineering of Organic Linkers of MOFs

The most important property in photocatalytic reduction of CO2 using MOFs is that the MOF photocatalysts must absorb light to generate charge carriers. In the study by Fu et al. mentioned previously, the photoactive reaction was determined by the presence of NH3 functional groups in the MIL-125(Ti) MOFs.[293] Therefore, the first step for the photocatalytic reduction of CO2 is the synthesis of MOFs using the appropriate organic linkers for promoting light absorption. To date, various organic linkers have been used to modulate the bandgap of MOF photocatalysts, which includes porphyrin-based, metal complex-functionalized, and amine-functionalized organic linkers.[294] Porphyrin-based MOFs are suitable for photocatalytic CO2 reduction because they can effectively absorb visible light and generate charge carriers.[294] Xu et al. synthesized porphyrin-based MOF photocatalysts that can reduce CO2 under visible light irradiation.[294] They demonstrated that the porphyrin-based ligands in the PCN-222(Zr) MOF act as a visible-light-harvesting unit, inheriting the feature of the tetras(is-carboxyphenyl) porphyrin (H2TCPP) ligand, as shown in Figure 24a. Furthermore, Mott–Schottky measurements confirmed the semiconducting characteristics of PCN-222(Zr). In Figure 24b, the edges of the conduction band and the valence band in PCN-222(Zr) are −0.40 and 1.35 V versus normal hydrogen electrode (NHE), respectively, indicating that the photocatalytic CO2 reduction reaction is feasible on the PCN-222(Zr) MOF. The PCN-222(Zr) MOF with catalytic Zr6 centers was able to selectively reduce CO2 to 30 μmol of formate over 10 h in CH3CN solvent under visible light irradiation.

Another way to utilize MOFs for photocatalytic CO2 reduction is to synthesize MOFs consisting of ligands functionalized with metal complexes that can function as photosensitizers, and even act as catalytic active sites.[296] Deng et al. used MOF-253(Al) as a platform for the construction of photocatalysts for the CO2 reduction reaction.[296] MOF-253(Al)-Ru(dcbpy)2 was synthesized by the reaction of MOF-253(Al) with Ru(dcbpy)2Cl2 in anhydrous DMF using a solvolothermal method. Owing to the Ru complex in the MOF-253(Al)-Ru(dcbpy)2, the performance of MOF-253(Al)-Ru(dcbpy)2 was similar to that of MOF-253(Al) alone. The performance of MOF-253(Al)-Ru(dcbpy)2 for photocatalytic CO2 reduction was measured in acetonitrile solvent with THIQ(1,2,3,4-tetrahydroisoquinoline), where MOF-253(Al)-Ru(dcbpy)2 produced 52.8 μmol of formic acid and 11.3 μmol of CO after 5 days (Figure 24c). The Ru complexes on the MOF-253(Al)- Ru(dcbpy)2 photocatalysts remained stable without degradation. As described, the photocatalytic properties of MOFs can be enhanced by the synergistic combination of metal complexes. Liu et al. synthesized the (Co/Ru)2-CuO-67(bpydc) MOF, which
is the UiO-67(bpydc) MOF functionalized with Co- and Ru-complexes. The Ru and Co complexes enabled the absorption of a broad range of visible light (≈400–600 nm) by the (Co/Ru)2.4-UiO-67(bpydc) MOF, as displayed in Figure 24d. The (Co/Ru)2.4-UiO-67(bpydc) photocatalysts were capable of producing syngas at the rate of 13,600 µmol g⁻¹ with a 2:1 ratio of H₂ and CO for 16 h in CH₃CN/H₂O solvent with TEOA. In addition, the (Co/Ru)2.4-UiO-67(bpydc) photocatalysts exhibited highly stable photocatalytic activity over three cycles (Figure 24e). X-ray diffraction (XRD) and scanning electron microscopic (SEM) measurements after three cycles showed no obvious changes of structure and shape. The authors postulated that the performance of (Co/Ru)2.4-UiO-67(bpydc) for photocatalytic reduction of CO₂ was improved by integrating the photosensitive Ru complex and the catalytically active Co complex, through the proposed mechanism in Figure 24f.

5.2.2. Engineering of Metal Centers of MOFs

To improve the photocatalytic properties of MOFs, the metal centers as well as the organic linkers in the MOFs can be modulated. Since the catalytically active sites of MOFs are generally the metal centers, the performance for photocatalytic reduction of CO₂ mainly depends on the composition of the metal centers. Wang et al. designed three isostructural MOFs, each containing of Cu, Co, and Ni metal elements (Figure 25a), and compared the photocatalytic performance of the synthesized MOFs, as shown in Figure 25b. The Ni-MOF exhibited the highest selectivity of 97.7% for CO among the three MOFs. The reasons for the different photocatalytic activity in the three MOFs can be found from the differences in the charge separation efficiency and the binding energy between CO₂ and the three metal sites. Photocurrent measurements were conducted, and the photo-generated charge carriers were found to be more efficiently separated in Ni-MOF and Co-MOF than in Cu-MOF, under the same conditions. Furthermore, through DFT calculations, they revealed that Ni formed strong bonding with CO₂, resulting in a short distance of 2.4 Å, whereas Co and Cu bonded with CO₂ over a long distance of 3.6 Å owing to weak interactions (Figure 25c,d). The Ni-MOF photocatalyst can produce CO at a rate of 371.6 µmol g⁻¹ h⁻¹ in a acetonitrile/H₂O solution with triisopropanolamine as an electron donor, while the H₂ production rate is only 8.3 µmol g⁻¹ h⁻¹, as shown in Figure 25e.

The metal center of the MOF has a great influence on the photocatalytic reduction of CO₂, and it is reported that the photocatalytic activity has been improved by changing the composition of metal centers. The Fe₂Zn cluster-based MOF (NNU-31(Zn)) photocatalysts were demonstrated to successfully achieve artificial photosynthetic full reaction without adding additional photosensitizers and sacrificial agents. They described that the 4,4',4″-tricarboxytriphenylamine ligand and heterometallic Fe₂Zn cluster absorbed visible light, while the catalytic sites of high-valent Fe³⁺ and low-valent Zn²⁺ ions oxidized H₂O and reduced CO₂, respectively (Figure 25f). The NNU-31(Zn) photocatalysts could produce HCOOH at a rate of 26.3 µmol g⁻¹ h⁻¹ in a acetonitrile/H₂O solution with triisopropanolamine as an electron donor, while the H₂ production rate is only 8.3 µmol g⁻¹ h⁻¹, as shown in Figure 25g.
MOFs are used. This can be attributed to the low conductivity and insufficient light absorption of MOFs. Therefore, for practical use of MOFs for photocatalytic CO₂ reduction, the MOFs with higher conductivity and photoactivity should be designed.

5.3. Hybrids between MOFs and Other Materials for Photocatalytic Reduction of CO₂

To date, diverse MOF photocatalysts for CO₂ reduction have been studied, but MOFs still have the limitations of low charge transfer efficiency and insufficient light absorption. To improve these weak points, combining metal or oxide NPs and carbon-based materials with MOFs can be an effective solution.[126,299]

Ma et al. successfully synthesized hierarchical porous-structured UiO-66(Zr) decorated with ultrafine TiO₂ NPs.[299b] The TiO₂ NPs were loaded onto the UiO-66(Zr) at 81.3 wt% of the MOF. The specific surface area of TiO₂/UiO-66(Zr) was as low as 35% of that of pristine UiO-66(Zr). However, as can be seen in Figure 26a, the CO₂ uptake of TiO₂/UiO-66(Zr) was reduced only by 20% compared to the pristine UiO-66(Zr), due to the porous structure of UiO-66(Zr). The photocatalytic performances of the TiO₂/UiO-66(Zr) were measured in a gas–solid reaction system. The best-performing TiO₂/UiO-66(Zr) photocatalyst could produce CH₄ at the rate of 17.8 µmol g⁻¹ h⁻¹ and exhibited selectivity for CH₄ that was as high as 90% (Figure 26b).
mechanism shown in Figure 26c, the authors explained that the absorption of light on both TiO$_2$ and UiO-66(Zr) and the fast charge separation at the TiO$_2$/UiO-66(Zr) interface due to a well-matched bandgap led to enhanced photocatalytic performance. As a result, UiO-66(Zr) and TiO$_2$ could be combined to improve the photocatalytic performance while maintaining high CO$_2$ uptake. Zhou et al. fabricated MOF/oxide hybrid photocatalysts using leaf-like ZIF-L and branch-like TiO$_2$/C nanofibers. The fabricated MOF/oxide hybrid photocatalysts have synergistic effects; they exhibited efficient light absorption, high CO$_2$ adsorption capability, and abundant catalytically active sites. Additionally, the well-matched band structure between ZIF-L and TiO$_2$ can facilitate effective charge separation to prevent fast charge recombination. Based on these advantages, the TiO$_2$/C@ZIF-L hybrid photocatalysts exhibited a remarkable CO conversion yield of 28.6 µmol g$^{-1}$ h$^{-1}$ and a selectivity of 99%, without the use of photosensitizers or sacrificial reagents.

5.3.2. MOF/Metal NP Hybrids for Photocatalytic Reduction of CO$_2$

Despite the advantages of MOFs for photocatalysts, MOFs still have low energy transfer efficiency and catalytic activity for the photocatalytic CO$_2$ reduction reaction. Metal NPs, the most effective catalytic species, are attractive materials that can form composites with MOFs to enhance the energy transfer efficiency, catalytic activity, and product selectivity. Furthermore, light absorption can also be increased by LSPR.

Guo et al. synthesized MIL-101(Cr) decorated with Ag NPs and reported that the photocatalytic activity of the hybrid photocatalysts was improved due to the Ag NPs. The MIL-101(Cr) was synthesized at sizes of 80, 150, 400, and 800 nm (Figure 26d–g), followed by deposition of Ag NPs on the surface of the MIL-101(Cr). For the Ag/MIL-101(Cr), additional light absorption was observed at the near-IR region in UV–vis near-IR spectra, which was attributed to the localized surface plasmon band of the Ag NPs. The photoresponse capability of
the synthesized Ag/MIL-101(Cr) in various sizes was analyzed, and the 80 nm sized Ag/MIL-101(Cr) photocatalyst exhibited the highest photoresponse capability (Figure 26h). The photocatalytic CO₂ reduction reaction on the Ag/MIL-101(Cr) and bare MIL-101(Cr) photocatalysts were conducted in TEOA solvent. The Ag/MIL-101(Cr) at 80 nm showed the highest production rates of CO, CH₄, and H₂ at 808.2, 427.5, and 82.1 µmol g⁻¹ h⁻¹, respectively (Figure 26i). The smallest size of MIL-101(Cr) showed the highest catalytic activity, due to the higher density of unit cells on the edges and corner sites, which facilitated more efficient charge transfer. Coupling of MOFs to plasmonic metal NPs can provide an effective approach for designing photocatalysts to improve photocatalytic activity. Choi et al. fabricated a Re₁-MOF decorated with Ag nanocube photocatalysts for a plasmon-enhanced photocatalytic CO₂ reduction reaction. Under light irradiation, the surface of the Ag nanocubes produce intensified electric fields, while photoactive Re centers on the Re₁-MOF layer are localized to the intensified electric fields, thus improving the photocatalytic CO₂ reduction reaction. As a result, the photocatalytic behavior for CO₂ reduction was enhanced and the stability was improved, demonstrating that the synergistic effects obtained from combining MOFs and plasmonic metal NPs can enhance the photocatalytic activity of hybrid photocatalysts.

5.3.3. MOF/CM Hybrids for Photocatalytic Reduction of CO₂

CMs, such as carbon nitride, can also be used in photocatalytic reduction of CO₂ by forming hybrids with MOFs. The hybridization between the MOFs and CMs improve the charge transport/separation and facilitate the photocatalytic CO₂ reduction reaction. 0D carbon nitride QDs (g-CNQDs) have been reported to enhance the photocatalytic activity for the reduction of CO₂, when combined with 2D porphyrin MOFs (PMOFs). A 2D PMOF was synthesized by reacting TCPP with cobalt nitrate using benzoic acid as a modulator. Subsequently, the g-CNQDs were strongly adsorbed onto the PMOF by strong interactions with the TCPP ligands. The coordination of g-CNQDs to Co centers in the PMOF facilitated the migration of photogenerated charge carriers from the g-CNQDs to the Co active centers. The large decrease of strong emission at 441 nm in the PL spectrum after the formation of the g-CNQDs/PMOF hybrids (Figure 26j) verified the suppressed charge recombination and efficient charge transport from g-CNQDs to PMOF. Based on these properties of the g-CNQD/PMOF hybrids, the photocatalytic activity for the CO₂ reduction reaction of g-CNQD/PMOF hybrids was largely enhanced to produce CH₄ and CO with the production rates of 6.86 and 16.1 µmol g⁻¹ h⁻¹, respectively (Figure 26k,l).

In addition to the hybrids mentioned, MOFs can form complexes with a number of materials to achieve excellent synergistic effects for photocatalytic activity. The formation of hybrids with other materials is an effective approach to complement the insufficient light absorption or low charge transfer efficiency of MOFs.

5.4. MOF-Derived Catalysts for Photocatalytic Reduction of CO₂

Another way to utilize MOFs for photocatalytic reduction of CO₂ is to make metal oxide photocatalysts using a MOF as a template. When metal oxide NPs are prepared from MOF templates, the large surface area and tunable porosity can be inherited from the MOF. Wang et al. fabricated hollow multi-shelled structured (Co₃O₄)MOF photocatalysts using ZIF-67(Co) as a template. Figure 27a showed the “Genetic Inheritance” from the ZIF-67(Co) to the (Co₃O₄)MOF HoMS through the sequential templating approach. In the process, the organic linkers are removed and Co₃O₄ nanocrystals are formed by oxidation of the Co atoms. Core-shell (CS), double-shell (DS), triple-shell (TS), and quadruple-shell (QS) Co₃O₄ structures were designed by controlling the oxygen partial pressure and the heating rate, as shown in Figure 27b–g. These SEM and TEM images also indicate that a hollow multi-shelled morphology was inherited from the MOFs. The XRD patterns showed that the intensity of the (111) facets increased with the increasing shell number. Since the (111) facets of Co₃O₄ are known to have excellent catalytic activity for the CO₂ reduction reaction, the superior performances of the (QS-Co₃O₄)MOF photocatalysts were expected. The (QS-Co₃O₄)MOF showed the highest photocatalytic activity for CO₂ reduction reaction, as expected (Figure 27h), as the CO production rate of the (QS-Co₃O₄)MOF was 46.3 µmol g⁻¹ h⁻¹ in a gas-solid system. Furthermore, no changes in the morphology and crystal structure of the (QS-Co₃O₄)MOF or degradation of the performance were observed (Figure 27i), demonstrating the excellent catalytic stability of (QS-Co₃O₄)MOF photocatalysts. This method, of making porous metal oxide nanostructures using MOFs as a template, is currently attracting attention, and it is considered to have great potential for contribution to the study of photocatalytic CO₂ reduction.

6. Remaining Challenges in Solar Fuel Production Using MOF-Based Hybrids

There has been rapid progress in MOF-based hybrids for photocatalytic applications. Nevertheless, much work remains unsolved in the design of MOFs, MOF-derived materials, and MOF-based hybrids to enhance PC and PEC reactions further. Particular attention should be paid to the following key challenges in MOF-based hybrids for bolstering solar fuel production.

1) Energy band alignment: The MOFs and MOF-derived materials offer various energy bandgaps, energy band-edge positions, and work functions. Accordingly, the on-demand design of energy band alignment in MOF-based hybrid photocatalysts can enhance the photoexcitation, charge separation, and redox power. To date, MOF-based hybrid photocatalysts are mostly designed based on the type-II band alignment. In the future, the direct Z-scheme[303] or S-scheme[304] band alignment with the merit of high redox power should also be investigated to design hybrid photocatalysts.

2) High and isotropic electronic conductivity: MOFs with high electron conductivity for PC and PEC solar fuel production are still insufficient. For the rational design of conductive MOFs, an in-depth investigation of the charge carriers, electron mobility, and conduction mechanism is necessary. To date, high electron conductivity is frequently observed.
in 1D and 2D structured MOFs. Accordingly, the strategies to assemble the 1D/2D MOFs and other materials along the preferred direction should be established to facilitate the conduction across the heterointerfaces. For enhanced PC and PEC reactions irrespective of the crystallographic direction of MOFs, it is essential to design more conductive 3D MOFs with isotropic conductivity.

3) Morphology and composition: The morphology of photocatalysts determines the surface reaction sites, the transport and recombination of charge carriers, and mass transport of reactants/products in PC and PEC reactions.\[305\] However, the morphological design of MOF-based hybrid photocatalysts is still in the nascent stage and thus should be investigated further. The compositional control is also a promising strategy to design photocatalytic materials. The diversification of MOF-based hybrids using the MOFs with mixed metals, mixed or functionalized organic linkers, and mixed co-catalysts can shed new light on the tailored control of energy band structure, catalytic promotion, charge transport, and product selectivity.\[306\]

4) Chemical stability: The PC and PEC reactions occur mostly in liquid electrolytes, and the solution can contain various sacrificial agents to consume holes at the surface of photocatalysts.\[309,307\] In addition, diverse solution-based routes have been adopted to prepare or modify MOFs as well as to form MOF-based hybrids. For instance, organic solvents are used for solution-based coating processes such as EPD, and chemicals such as reducing agents (NaBH\(_4\)) are utilized for immobilizing the metallic co-catalysts. From this viewpoint, the chemical stability of MOFs and MOF-based hybrids during postsynthetic modification as well as photocatalytic reaction should be achieved. The chemical stability of MOFs is usually investigated by the change of XRD, surface area, and pore size distribution after the exposure to chemicals. However, the variation of defect concentration, electronic conductivity, and energy band structures of MOFs as well as the structural change of interfaces between MOFs and other materials should also be investigated in detail to optimize the PC and PEC reactions further.

5) Photostability and thermal stability: For solar fuel production, MOFs are exposed to strong sunlight for an extended time. Thus, MOFs should be stable against the high-intensity irradiation of visible as well as UV light. Mateo et al.\[308\] reported the substantial photodecarboxylation of BDC linkers in various dry MOFs powders of UiO-66(Zr), UiO-66(Zr)-NO\(_2\), MIL-101(Fe), MIL-125(Ti)-NH\(_2\), and MIL-101(Cr) upon UV/vis irradiance (Xe lamp: 300 W) under Ar atmosphere for 19 days, whereas no decarboxylation was observed in ZIF-8 with imidazole based linkers. It is worth noting that photodegradation rate differs depending on metal nodes, ligands, and node-ligand interactions. This hints the design strategy of photostable MOFs. However, the research on long-term stability of MOFs under simulated or natural sunlight is still at a nascent stage and thus needs further in-depth analysis with varying MOFs and their surroundings (oxygen gas or water solvent). In addition, the thermal stability of MOFs must be considered when hybrid photocatalysts are designed by postsynthetic annealing.

6) Mechanical cohesion with other materials (oxides, chalcogenides, phosphides, and carbon-based materials): Single...
crystalline MOFs can be grown on other materials that have the form of planar highly crystalline inorganic substrates. However, substrates with complex surface morphology are frequently used to maximize reaction sites. Moreover, hybridization with diverse materials is highly required for the on-demand design of photocatalysts. Additionally, the substrate materials can exhibit different surface chemistries. Accordingly, new strategies to form mechanically strong bonding between MOFs and diversified substrates with different crystalline structure, surface morphology, material, and surface chemistry should be further explored.

7) Electronic conduction across the interface: Conduction across the interface between the MOF and other materials is a critical step for charge separation through charge funnelling. In addition to the bandgap and band-edge position, the correlation between the bonding nature (or contacting configuration) of interfaces and electronic conduction should be revealed for controlling the charge transport across the interface.

8) Cost-effectiveness: For real applications, a facile, cost-effective, and large-area fabrication of MOF-based hybrids is necessary. At this moment, except for highly popular and commercially available MOFs such as ZIF-8(Zn), HKUST-1(Cu), and MIL-100(Fe), most MOFs are not cost-effective, most likely because MOFs often need a multistep synthesis for ligand design.\[309\] Moreover, although the immobilization of atomic-scale co-catalysts within MOFs can decrease the usage of expensive noble metals, more effort is required to decrease the material cost. Additionally, large-scale processes for real implementation of solar fuel production will need to be established.

9) Recycling: For PC applications, the smaller hybrids are more advantageous for increasing the surface area and decreasing the charge-transfer distance. However, they hamper the recycling of photocatalysts because the filtering of NPs is difficult. One possible solution may be the use of MOFs or MOF-derived materials with magnetic properties. For example, MOFs can be coated on magnetic NPs\[310\] or converted into hybrids with magnetic properties.\[311\] This is a reasonable approach, considering that MOFs frequently contain diverse transition metals that can be converted into magnetic materials.

10) Product selectivity: Considering the photocatalytic CO\textsubscript{2} reduction reaction of MOF and MOF-hybrid photocatalysts, most studies are focused only on the conversion of CO\textsubscript{2} into CO or formic acid, which are C\textsubscript{1} species. To date, product selectivity has been lacking in reduction reactions for C\textsubscript{2} or C\textsubscript{3} species, which have a high energy density and market price.\[312\] Therefore, it is important to study the mechanism of reduction reactions to C\textsubscript{2} or C\textsubscript{3} species, which will increase the product selectivity for valuable chemicals such as ethanol and ethylene.

7. Conclusions

Solar fuel production is a sustainable solution for energy and environmental problems but requires the rational design of many parameters such as the energy band structure, electronic conduction, catalytic activity, morphology, production selectivity, and water-stability of photoactive materials. The MOFs are ideal platforms for designing hybrid photocatalysts that can complement the limitations of a single photocatalytic material, as they have many irreplaceable advantages such as exceptionally high surface area and porosity, diverse topology, high crystallinity, post-synthetic modification of metals and organic linkers, capability to immobilize nanoscale co-catalysts, and compositional tunability. Furthermore, the formation of new hybrids via MOF-derived synthesis enables the harvesting of numerous MOF-inherited merits that cannot be achieved using other conventional routes. Recent studies have confirmed the remarkable synergistic effect of MOF-based hybrids photocatalysts but further progress is needed to enhance the electronic conductivity and stability of MOFs. The chemical diversity and structural tunability of MOFs and their derived materials will provide the solutions for the rational design of tailored MOF-based hybrids, thereby offering new opportunities toward the practical and efficient production of solar fuels.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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