

Review

Metal–Organic Frameworks and Their Derivatives for Photocatalytic Water Splitting

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Abstract: Amongst many strategies for renewable energy conversion, light-driven water splitting to produce clean H₂ represents a promising approach and has attracted increasing attention in recent years. Owing to the multi-electron/multi-proton transfer nature of water splitting, low-cost and competent catalysts are needed. Along the rapid development of metal–organic frameworks (MOFs) during the last two decades or so, MOFs have been recognized as an interesting group of catalysts or catalyst supports for photocatalytic water splitting. The modular synthesis, intrinsically high surface area, tunable porosity, and diverse metal nodes and organic struts of MOFs render them excellent catalyst candidates for photocatalytic water splitting. To date, the application of MOFs and their derivatives as photocatalysts for water splitting has become a burgeoning field. Herein, we showcase several representative MOF-based photocatalytic systems for both H₂ and O₂ evolution reactions (HER, OER). The design principle of each catalytic system is specifically discussed. The current challenges and opportunities of utilizing MOFs for photocatalytic water splitting are discussed in the end.

Keywords: metal–organic framework; photocatalysis; water splitting

1. Introduction

The ever-increasing global energy demand, depletion of fossil fuel reserves, together with the climate change resulting from fossil fuel consumption all motivate the exploration of alternative energy solutions, which are preferably based on renewable and environmentally friendly energy sources [1–6]. The transformation from fossil fuel-based economy to renewable energy-driven economy calls for the development of low-cost and competent catalysts for the capture and storage of intermittent renewable energy sources, like solar and wind. Among various green energy carrier candidates, dihydrogen (H₂) is particularly attractive, not only because of its high gravimetric energy density (120 kJ·g^{−1}, by comparison the gravimetric energy density of petroleum is 44 kJ·g^{−1}) [7–9], but also because of its clean nature (the sole product of H₂ combustion is water). The current industrial approaches for H₂ production, such as steam methane reforming and coal gasification, are very energy intensive and rely highly on fossil fuels [10–19]. Therefore, it remains a great necessity to develop alternative low-cost methods to produce H₂, ideally driven by renewable energy sources. Within this context, photocatalytic water splitting emerged as a very appealing method in producing H₂ from solar energy and water [20,21]. Since the pioneering work of Fujishima and Honda in 1972 that TiO₂ was able to catalyze water splitting to produce H₂ and O₂ under ultraviolet light irradiation, the last four-and-a-half decades have witnessed a tremendous growth in developing various competent photocatalytic systems for light-driven water splitting [22–28]. A large number of light-absorbing materials (semiconductors) and complexes (photosensitizers), as well as photocatalysts have been

developed, albeit the quantum yield of H₂ production and solar energy conversion efficiency both require further improvement for large-scale applications.

During the last two decades, a new type of inorganic–organic hybrid and crystalline materials of high porosity, named metal–organic frameworks (MOFs), have attracted intense academic interest because of the following reasons [29–37]. MOFs are constructed by connecting metal and metal cluster nodes with organic bridging ligands in three-dimensional space. Therefore, a rich library of metal cations and organic ligands are available for the formation of diverse MOFs, enabling facile modulation of each component in MOFs. In addition, the intrinsically high surface area and regular pores and channels allow efficient interaction between substrates and reaction sites, beneficial to the overall catalytic performance. Table 1 summarizes the physical properties of representative MOFs discussed herein. Finally, MOFs are solid materials which might be able to be separated from reaction mixture for recycling utilization. Besides directly acting as photocatalysts for water splitting, carbonization of appropriate MOFs will result in metal/metal oxide nanoparticles embedded in highly porous carbon matrices resulting from the original organic ligands. In this case, the original MOFs not only provide the metal and carbon sources but also act as the sacrificial templates. The final hybrid composites can also be utilized for various photocatalytic applications including water splitting [38–40]. Owing to the aforementioned advantages, MOFs and their derivatives have been widely employed as photocatalysts for H₂ production through water splitting [41]. In this short review, we do not intend to present a comprehensive overview of MOF-based photocatalytic systems for water splitting. Instead, we will introduce several representative MOF or MOF-derived photocatalysts and highlight their designing principle in order to achieve enhanced performance relative to their homogeneous/heterogeneous counterparts. It is our hope that this mini review will provide the audience with a flavor of the burgeoning field of photocatalytic water splitting utilizing MOFs and their derivatives.

2. Photocatalytic H₂ Evolution Utilizing MOF-based Photocatalysts

Photocatalytic water splitting consists of two half-reactions: photocatalytic H₂ and O₂ evolution reactions (HER and OER). Each half-reaction involves the transfer of multiple protons and multiple electrons with slow kinetics under ambient conditions. Consequently, competent photocatalysts are desired for both HER and OER. In this section, we will first introduce the application of MOF-based photocatalytic systems for H₂ production.

The first example of a MOF-based catalyst for photocatalytic H₂ evolution was reported by Mori et al. in 2009 [42]. A Ru-MOF constructed with paddlewheel diruthenium cores ([Ru₂(*p*-BDC)₂]_{*n*}, *p*-BDC = 1,4-benzenedicarboxylate) could act as active sites for water reduction to H₂ in the presence of [Ru(bpy)₃]²⁺ (bpy = 2,2'-dipyridyl), MV²⁺ (methyl viologen, *N,N'*-dimethyl-4,4'-bipyridinium dichloride), and EDTA-2Na (ethylenediaminetetraacetic acid disodium salt), each of which played the role of photosensitizer, electron relay, and sacrificial electron donor, respectively (Figure 1). Control experiments without photosensitizer or electron relay did not produce any H₂ under visible light irradiation, which indicated that [Ru₂(*p*-BDC)₂]_{*n*} itself did not exhibit effective light absorption for photocatalysis. Compared with the molecular counterpart Ru₂(CH₃COO)₄BF₄, [Ru₂(*p*-BDC)₂]_{*n*} was far more superior in photocatalyzing H₂ production, resulting in a nearly 10 times higher turnover number (TON) during the first hour of visible light irradiation (λ = 420 nm). It is believed that almost all of the catalytic reaction occurred on [Ru₂(*p*-BDC)₂]_{*n*} surface and in the inner pore space near to the surface, because the pore size of [Ru₂(*p*-BDC)₂]_{*n*} is small and does not allow MV²⁺ to enter the pores freely. However, the overall turnover number based on Ru-MOF (TON = 8.16, Table 2) was mediocre and the quantum yield (4.82%) required further improvement. In addition, expensive photosensitizer [Ru(bpy)₃]²⁺ was required for the production of H₂. Following this work, Mori's group also reported a series of similar Ru-MOFs [43] and Rh-MOFs [44] as photocatalysts for H₂ evolution from water under visible light irradiation.

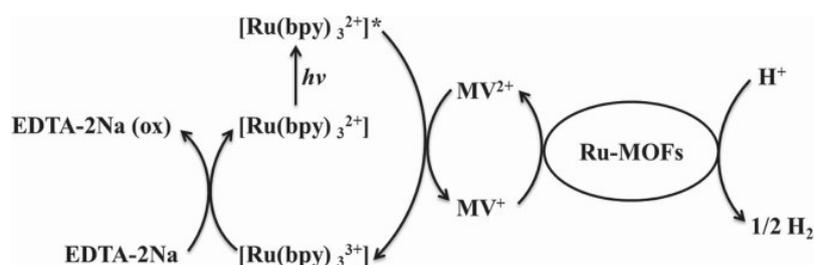


Figure 1. The reaction scheme of photochemical H_2 production from water using Ru-MOFs in the presence of $\text{Ru}(\text{bpy})_3^{2+}$, MV^{2+} , and EDTA-2Na. Reproduced with permission from ref. [42], Royal Society of Chemistry.

Besides acting as the direct catalyst for photocatalytic H_2 generation, MOFs can also be utilized as photosensitizers. For instance, Garcia and co-workers reported two highly water-stable Zr-based MOFs in 2010, UiO-66 ($\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_{12}$, where BDC = 1,4-benzenedicarboxylate) and UiO-66(NH_2) ($\text{Zr}_6\text{O}_4(\text{OH})_4(\text{ATA})_{12}$, where ATA = 2-aminoterephthalate), which were able to show appreciable light absorption depending on organic ligand modification [45]. The two MOFs are isorecticular and they both contain hexameric Zr_6O_{32} units as the metal clusters linked by 12 bridging ligands (BDC or ATA). The remarkable water stability of these two Zr-based MOFs enabled their application for photocatalysis applications, including water splitting. Even more exciting is that by tuning the bridging ligand, amending an amino group on the benzene ring of BDC, a significant bathochromic shift in the absorbance spectrum was obtained for UiO-66(NH_2) as shown in Figure 2a. An intense absorption band between 300 and 400 nm with an absorption maximum at 360 nm was achieved for UiO-66(NH_2). Such a ligand modification did not compromise the crystallinity and water stability of UiO-66(NH_2) compared to the parent UiO-66. Even though these Zr-based MOFs did not exhibit appreciable H_2 production by themselves under visible light irradiation, decent amounts of H_2 were generated when Pt nanoparticles were introduced as cocatalysts, which could accelerate charge separation and reduce the reaction barriers towards H_2 formation. Figure 2b compares the H_2 evolution performance of four samples. It is apparent that the presence of Pt substantially increased the activity towards photocatalytic H_2 production and UiO-66(NH_2) was more active than UiO-66. Thanks to the modular synthesis of MOFs, this work vividly demonstrates how to take advantage of ligand modification to achieve enhanced photocatalytic activities of MOF-based catalysts.

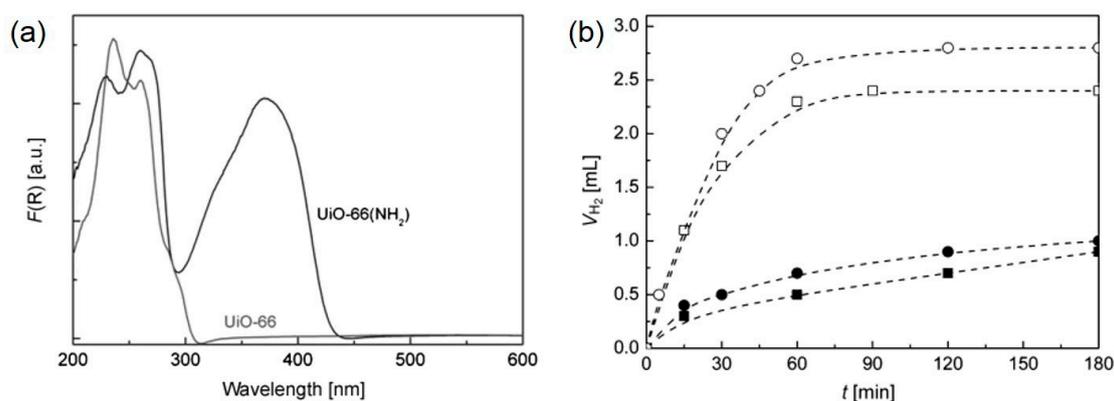


Figure 2. (a) UV-vis spectra of UiO-66 and UiO-66(NH_2) MOFs; (b) Volume of H_2 evolved during the photocatalytic reactions using UiO-66 (solid square), UiO-66/Pt (hollow square), UiO-66(NH_2) (solid dot) and UiO-66(NH_2)/Pt (hollow dot). Reproduced with permission from ref. [45], Wiley-VCH.

The aforementioned photocatalytic systems proceeded through the ligand-to-cluster charge transfer mechanism for H_2 production. It was reasoned that an alternative titanium-oxo cluster would

possess a more positive-lying conduction band than that of the zirconium counterpart. Therefore, more efficient charge transfer from the excited organic linkers to the metal clusters would be realized together with a higher yield of photocatalytic H₂ production. Following this rationale, Matsuoka et al. prepared an amino-functionalized Ti (IV) MOF (Ti-MOF-NH₂) which utilized the same organic linker 2-amino-1,4-benzenedicarboxylic acid [46]. In contrast to its counterpart Ti-MOF with the conventional 1,4-benzenedicarboxylic acid linker (MIL-125), Ti-MOF-NH₂ indeed exhibited intense absorption in the visible region with its absorption tail beyond 500 nm (Figure 3a). When Pt nanoparticles were photodeposited into the MOF pores and triethanolamine (TEOA) was utilized as the sacrificial electron donor, light-to-cluster charge transfer took place for Ti-MOF-NH₂ under visible light irradiation. As schematically displayed in Figure 3b, photogenerated electrons were transferred from the excited BDC-NH₂ group to the conduction band of the titanium-oxo cluster, followed by migration to Pt cocatalysts for eventual proton reduction to H₂. Similar strategy has been adopted by the Yamashita group to synthesize an amine-functionalized MIL-101(Cr) photocatalyst for photocatalytic H₂ production [47]. These works demonstrated that modifying the metal clusters while keeping the same organic ligands would also lead to various photocatalytic activities for water splitting, highlighting the beauty of the modular synthesis of MOFs for catalysis applications.

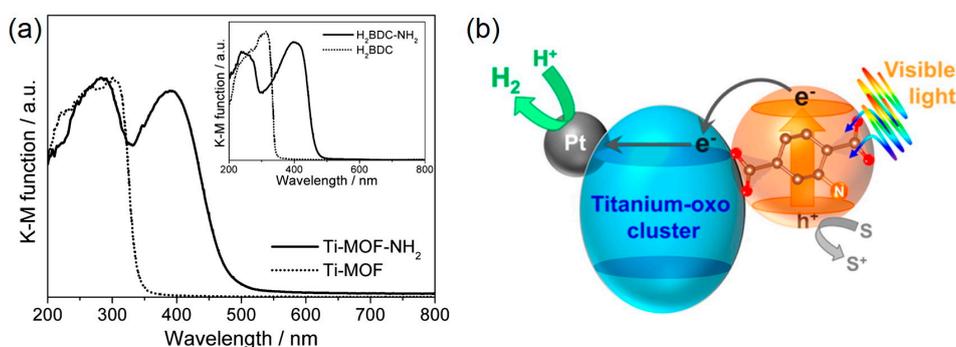


Figure 3. (a) Diffuse reflectance UV-vis (DRUV-vis) spectra of Ti-MOF (dotted line) and Ti-MOF-NH₂ (solid line). Inset shows the DRUV-vis spectra of H₂BDC (dotted line) and H₂BDC-NH₂ (solid line); (b) Schematic illustration of photocatalytic H₂ production reaction over Pt-supported Ti-MOF-NH₂. Reproduced with permission from ref. [46], American Chemical Society.

Another interesting and also widely studied organic species for visible light absorption is porphyrin and its derivatives. Following the same strategy described above, Rosseinsky and coworkers explored the photocatalytic H₂ production performance of porphyrin-incorporated MOFs: H₂TCPP[Al(OH)₂(DMF₃(H₂O)₂)₂] (Al-MOF, where H₂TCPP = *meso*-tetra(4-carboxy-phenyl)porphyrin) and the zinc metalated ZnTCPP[Al(OH)₂] (Al/Zn-MOF) [48]. Owing to the presence of porphyrin as the organic linker, the absorption spectrum of Al-MOF showed a strong Soret band at 415 nm and four Q bands between 500 and 600 nm (Figure 4a). When a zinc cation was metalated into the porphyrin core of Al-MOF, the resulting Al/Zn-MOF presented a slightly red-shifted Soret band at 425 nm and only two Q bands between 550 and 650 nm due to the higher symmetry of the metalated compound. Both Al-MOF and Al/Zn-MOF were employed as photosensitizers to produce H₂ under visible light irradiation in the presence of colloidal platinum and sacrificial EDTA. The authors also attempted to employ MV²⁺ cations as electron acceptors/mediators to facilitate the reaction rate. Unfortunately, a rather low quantum yield (less than 0.01%) of H₂ production was obtained after 15 h photoirradiation. It was postulated that such a poor activity was mainly due to the limited diffusion of MV²⁺ within the MOF pores. Nevertheless, a second approach with no MV²⁺ but higher concentration of platinum was adopted to conduct the photocatalysis of H₂ production catalyzed by both Al-MOF and Al/Zn-MOF (Figure 4b). Both MOFs showed decent photocatalytic performance in producing H₂, reaching a rate of 100 and 200 μmol·g⁻¹·h⁻¹ for Al/Zn-MOF and Al-MOF, respectively. Control experiments of removing all the solid components for photocatalysis were also carried out to prove

that indeed H_2 was produced from the heterogeneous MOF-based photocatalytic systems rather than some unknown homogeneous species.

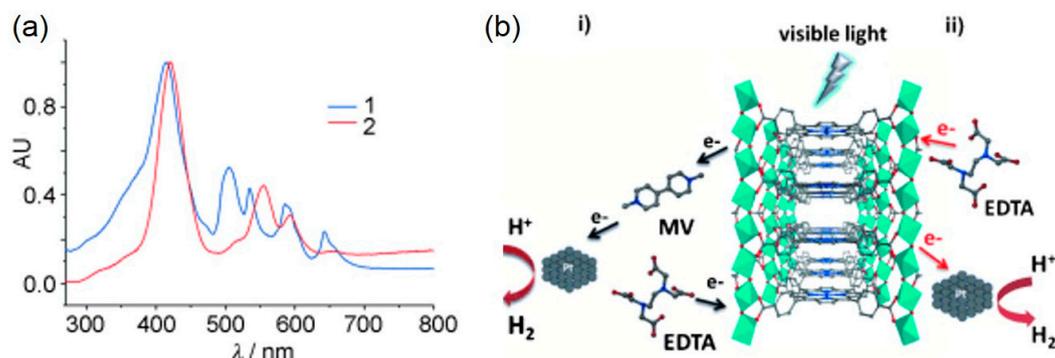


Figure 4. (a) UV/Vis solid-state absorption spectra of **1** and **2**; (b) The photocatalytic reaction using Al/Zn-MOF. (i) Reaction involving Al/Zn-MOF, MV, colloidal Pt, and EDTA. (ii) Reaction involving Al/Zn-MOF, colloidal Pt, and EDTA. Reproduced with permission from ref. [48], Wiley-VCH.

In addition to simply mixing MOFs and Pt nanoparticles for photocatalysis, the tunable cavities of MOFs can be purposely designed to encapsulate platinum nanoparticles for intimate interaction between light-absorbing sites and H_2 -evolving sites. In 2012, Lin and co-workers reported the synthesis of UiO-type MOFs (**1** and **2**) with diethyl (2,2'-bipyridine)-5,5'-dicarboxylate (**1**) and dimethyl (2,2'-bipyridine)-5,5'-dibenzoate (**2**) bridging ligands which were able to coordinate $Ir(ppy)_2$ ($ppy = 2\text{-phenylpyridine}$) units as phosphors for light absorption [49]. In situ photoreduction of K_2PtCl_4 resulted in the incorporation of Pt nanoparticles into the cavities of MOF **1** and **2**. Figure 5a presents the schematic diagram for light-induced H_2 evolution: excited iridium chromophores are reductively quenched by the sacrificial electron donor triethylamine (TEA) and subsequently promotes electron transfer to the encapsulated Pt nanoparticles where proton reduction to H_2 takes place. Under visible light irradiation ($> 420\text{ nm}$), it was found that Pt@**2** showed the highest H_2 evolution activity, achieving a TON of 7000 based on Ir content after a 48 h photolysis (shown in Table 2). Such a high activity was nearly five times that of its homogeneous control sample (Figure 5b). This work demonstrates that in addition to organic ligands as light-absorbing units, highly photoactive inorganic complexes can be incorporated into the linkers of MOFs for photocatalytic H_2 production, further highlighting the design flexibility of MOFs for photocatalytic applications. Following this work, UiO-66/CdS/1% reduced graphene oxide (RGO) [50] and RhB-sensitized Pt@UiO-66 [51] were also prepared and these MOF-based photocatalytic systems both showed enhanced catalytic performance for H_2 generation compared to their homogeneous counterparts.

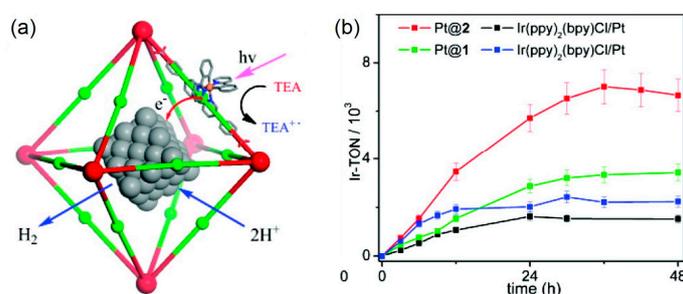


Figure 5. (a) A schematic diagram depicts the steps of photoinjection of electrons from MOF frameworks under light irradiation into Pt nanoparticles for the photocatalytic H_2 evolution. Red: $Zr_6(O)_4(OH)_4(\text{carboxylate})_{12}$ cores; green: Ir-phosphor ligand; (b) Time-dependent H_2 evolution curves of Pt@**1** (green), Pt@**2** (red), and homogeneous control $[Ir(ppy)_2(bpy)]Cl/K_2PtCl_4$ (blue: Pt/Ir: 86.0; black: Pt/Ir 24.2). Reproduced with permission from ref. [49], American Chemical Society.

Besides Pt nanoparticles, Pt coordination complexes can also be utilized as H₂ evolution catalysts. Recently, Xu and co-workers developed a new MOF material (MOF-253-Pt) by immobilizing Pt²⁺ into MOF-253 with 2,2-bipyridine-based linkers following a post-synthesis modification strategy (Figure 6a) [52]. The resultant MOF-253-Pt served both as a photosensitizer and a photocatalyst for H₂ evolution under visible light irradiation. After the introduction of Pt, an obvious red-shift in its absorption was observed (Figure 6b). The low-energy absorption in Pt-MOF-253 was due to the metal-to-ligand (Pt^{II}/bipyridine) charge transfer transition. The photocatalytic H₂ generation rate was highly dependent on pH values. The optimum pH was found to be 8.5. At lower pH values, the protonated TEOA was a weak electron donor, while at higher pH values, TEOA was not able to form the hydride-diplatinum (II, III) species (a postulated reaction intermediate) and hence the driving force for H₂ formation was diminished. Compared to the bare MOF-253 and the molecular Pt(bpydc)Cl₂ (bpydc = 2,2'-bipyridine-5,5'-dicarboxylic acid) complex, the hybrid Pt-MOF-253 photocatalytic system exhibited significantly improved photocatalytic activity for H₂ evolution under visible light irradiation. The enhanced activity of Pt-MOF-253 was due to the short spacing between Pt...Pt, which was beneficial to the formation of the critical intermediate hydride-diplatinum (II, III), more efficient electron transfer within the MOF structure, and the slowed decomposition of the anchored Pt(bpy)Cl₂ units in Pt-MOF-253. The overall photocatalytic cycle was schematically pictured in Figure 6c.

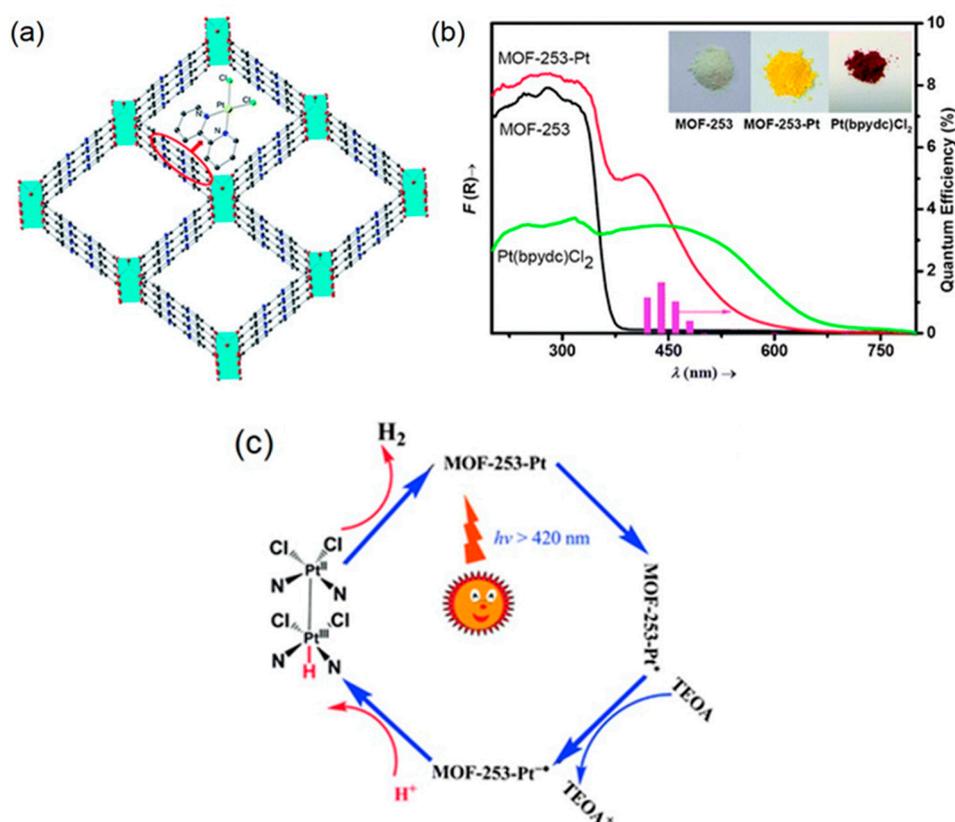


Figure 6. (a) Model structure of MOF-253-Pt, through post-synthetic modification of MOF-253 with PtCl₂; (b) UV-vis absorption spectra of MOF-253, Pt-MOF-253, and Pt(bpydc)Cl₂ together with H₂ evolution quantum efficiencies of Pt-MOF-253 at different wavelengths. The color of three samples are shown in the inset; (c) A proposed mechanistic diagram of H₂ evolution photocatalyzed by Pt-MOF-253. Reproduced with permission from ref. [52], Royal Society of Chemistry.

In order to develop cost-effective catalysts for future water splitting on an industrial scale, it is imperative to explore noble metal-free catalysts for H₂ production from water. Such a trend has been well manifested in the electrocatalysis field which has witnessed the emergence of 1st-row

transition metal-based complexes [53] and solid-state materials [54–59] as competent electrocatalysts for water splitting. One of those well-established molecular electrocatalysts for H₂ evolution is cobaloxime complex. Recently, Gascon and co-workers introduced cobaloxime into the pores of NH₂-MIL-125(Ti) following a “ship-in-the-bottle” strategy [60]. As shown in Figure 7a, the size selection of the pores in NH₂-MIL-125(Ti) was crucial to the successful formation of the cobaloxime complex inside the MOF cavities. For instance, the intact cobaloxime complex was too large to diffuse into and out from the NH₂-MIL-125(Ti) pore windows. However, the free ligand (DOH)₂pn (*N*²,*N*^{2'}-propanediylbis(2,3-butanedione 2-imine 3-oxime)) was able to migrate into the internal channels of NH₂-MIL-125(Ti). Upon the addition of CoBr₂ as the cobalt source under aerobic conditions, cobaloxime was assembled inside the MOF pores. Such a strategy would minimize the exclusion of the H₂ catalyst from the MOF cavities. Varying the initial amounts of the free ligand and CoBr₂ could facilitate tune the catalyst loading within the MOF structure. The pristine NH₂-MIL-125(Ti) possessed a pore volume of 0.58 cm³·g⁻¹. After the loading of cobaloxime, the resulting Co@MOF exhibited an expected smaller pore volume of 0.46 cm³·g⁻¹. Figure 7b presented the evolved H₂ amount over 25 h photolysis under visible light irradiation (λ > 408 nm). The cobaloxime-encapsulated Co@MOF clearly displayed a markedly improved photocatalytic performance for H₂ evolution with nearly 20-fold higher H₂ production rate compared to the pristine MOF. More importantly, Co@MOF possessed a high stability with a turnover frequency of 0.8 h⁻¹ even after operating for 65 h. Furthermore, the system could be recycled several times without any loss of activity (Figure 7c). Even though remarkable photocatalytic H₂ evolution performance was achieved by this hybrid Co@MOF systems solely consisting of earth-abundant elements, the exact structure of the cobalt catalyst within the MOF pores remained unknown. However, it still strongly demonstrates that the modular design and synthesis of multicomponent MOF systems opens a new window to develop low-cost photocatalytic composites for H₂ production from water.

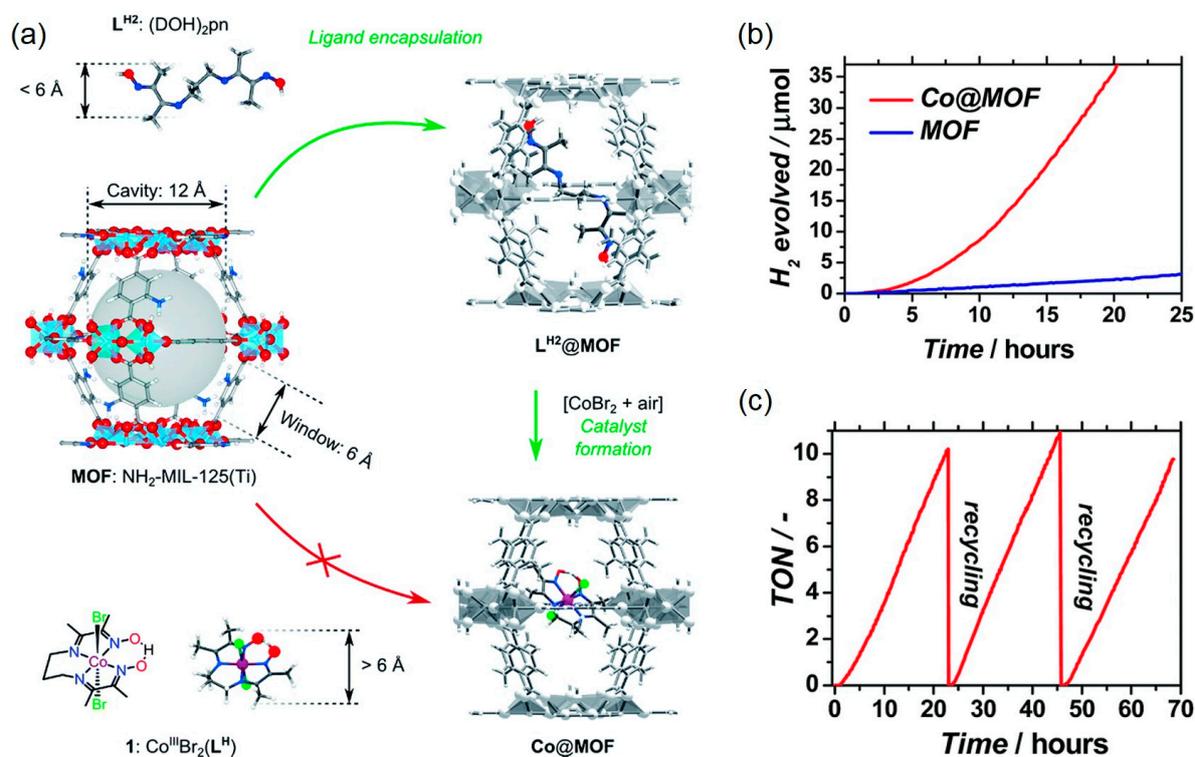


Figure 7. (a) “Ship-in-a-bottle” synthetic strategy for the preparation of Co@MOF; (b) Photocatalytic proton reduction using MOF and Co@MOF; (c) Recycling tests on Co@MOF bearing medium cobalt loading. Reproduced with permission from ref. [60], Royal Society of Chemistry.

3. O₂ Evolution Catalyzed by MOF-based Hybrid Systems

In contrast to the large number of MOF-based photocatalytic systems for H₂ evolution, much fewer studies have been reported for the other half-reaction of water splitting, the O₂ evolution reaction, utilizing MOF-based catalysts. This might be attributed to the harsh oxidizing condition of O₂ evolution where most MOFs could not survive [61–63]. Nevertheless, a few MOF systems have still been reported with promising O₂ evolution performance. The first work of MOF-based catalysts for water oxidation was reported by Lin et al. in 2011 [64]. Highly robust and porous Zr₆O₄(OH)₄(bpdc)₆ (UiO-67, bpdc = *para*-biphenyldicarboxylic acid) framework was employed as a heterogeneous support to incorporate a variety of iridium and other complexes for various applications, including water oxidation. Following a mix-and-match synthetic strategies, three iridium complexes, [Cp*Ir^{III}(dcppy)Cl] (MOF-1; Cp* = pentamethylcyclopentadienyl, dcppy = 2-phenylpyridine-5,4'-dicarboxylic acid), [Cp*Ir^{III}(dcbpy)Cl]Cl (MOF-2; dcbpy = 2,2'-bipyridine-5,5'-dicarboxylic acid), and [Ir^{III}(dcppy)₂(H₂O)₂]OTf (MOF-3), were bound into UiO-67. The synthetic route and the corresponding molecular structures of the three iridium units are included in Figure 8. The water oxidation performance of MOF 1–3 was examined with Ce⁴⁺ as the chemical oxidant (Figure 9a). All the Ir-incorporated MOFs were effective water oxidation catalysts with TON values as high as 4.8 (Table 2) (MOF 1). Repeated catalytic cycles demonstrated robust stability of these MOFs for elongated water oxidation (Figure 9b). Control experiments confirmed that the observed water oxidation activities were originated from the heterogeneous MOFs. However, compared to their homogeneous counterparts, MOF 1–3 exhibited lower turnover frequencies (only 6.4–12.9% of the homogeneous catalyst activities). Such a decreased performance was rationalized by the fact that only those iridium complexes exposed on the MOF surfaces were involved in water oxidation, since the cerium nitrate anions were too bulky to enter the MOF channels. Therefore, in order to increase catalytic activity, Lin and co-workers further prepared two other Zr-based MOFs with larger channels using two elongated dicarboxylate ligands [65]. These new MOFs showed enhanced water oxidation activity when using cerium nitrate as the oxidant. Although their instability and partial decomposition of the iridium complexes were observed under the water oxidation condition, these works presented the possibility of incorporating molecular active sites in MOFs structures for water oxidation, complementary to those homogeneous O₂ evolution studies.

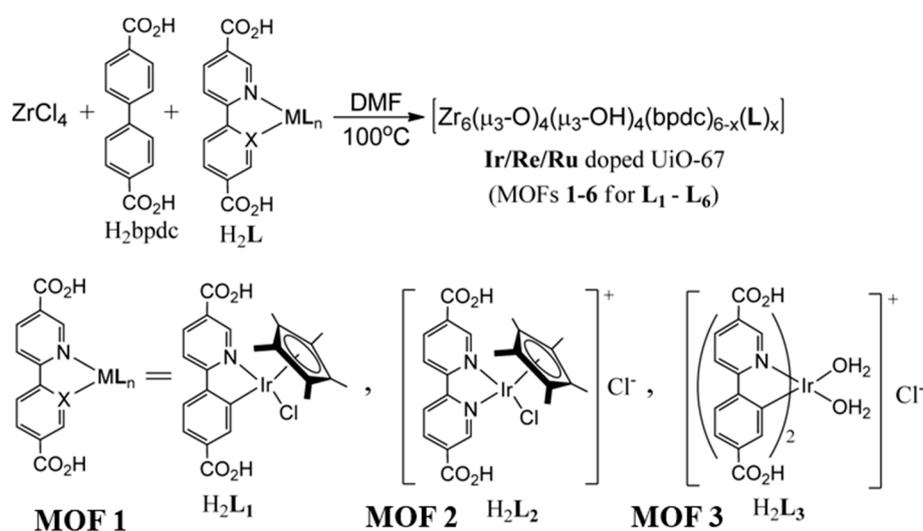


Figure 8. Synthesis of Zr/Ir MOFs incorporating varying iridium catalysts for water oxidation. Reproduced with permission from ref. [64], American Chemical Society.

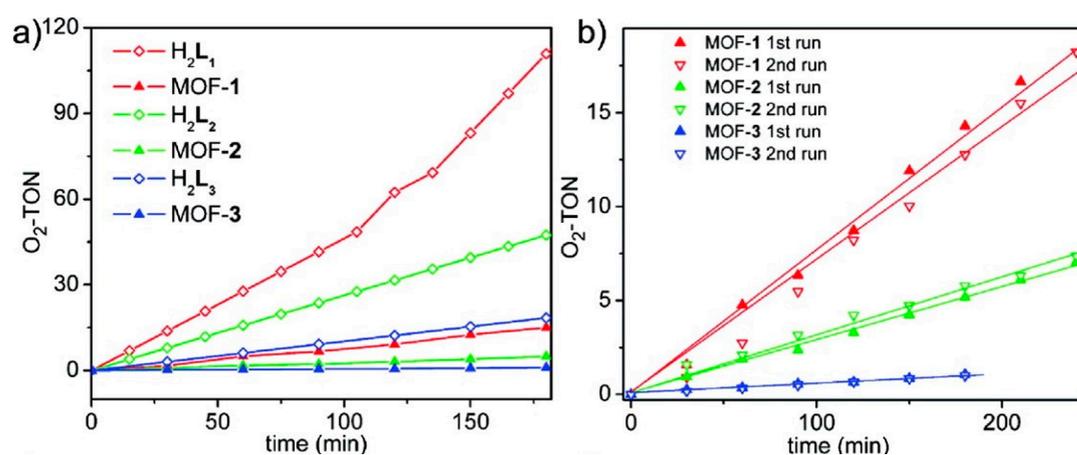


Figure 9. (a) Plots of O₂ evolving turnover number (O₂-TON) vs. time for MOFs 1–3 and the homogeneous complexes; (b) Plots of O₂-TON vs. time for reuse experiments of MOFs 1–3. Reproduced with permission from ref. [64], American Chemical Society.

4. Photocatalytic Water Splitting Utilizing MOF-derived Photocatalysts

Metal–organic frameworks not only represent attractive scaffolds for the incorporation of diverse components (phosphors, active sites, etc.) for photocatalytic water splitting, but also can act as sacrificial templates to produce a variety of highly porous carbon materials. Under certain conditions, multiple beneficial components for photocatalysis, including nonmetals, metals, and metal oxides, are embedded in those MOF-derived carbon composites. In fact, MOF-derived hybrid materials have been successfully employed in many fields, ranging from catalysis [66–71], supercapacitors [72], to batteries [73–75]. For photocatalytic water splitting, several representative MOF-derived systems are introduced herein. Following the MIL-101 structure, Lin and co-workers utilized microwave treatment to synthesize a MOF material with the formula of Fe₃OCl(H₂O)(BDC)₃ (BDC = benzene dicarboxylate) [76]. Subsequently, the Fe-based MIL-101 particles were coated with an amorphous layer of TiO₂ by acid-catalyzed hydrolysis and TALH (titanium (IV) bis(ammonium lactate)dihydroxide) condensation in water. The obtained core–shell particles were then calcined at 550 °C in air to form iron oxide covered with a shell of TiO₂ (Fe₂O₃@TiO₂). Pt particles were deposited on the surface of Fe₂O₃@TiO₂ for photocatalytic H₂ evolution. The overall synthetic scheme is outlined in Figure 10a. Compared to Fe₂O₃, TiO₂, or their mixtures, the MOF-derived Fe₂O₃@TiO₂ showed superior photocatalytic performance for H₂ generation under visible light irradiation ($\lambda > 420$ nm) with triethylamine (TEA) as the sacrificial electron donor (Figure 10b). The amount of H₂ produced increased linearly during the 48 h photolysis (Figure 10b inset). The MOF-derived photocatalyst also possessed high stability with nearly no decrease in activity for three photolysis cycles. Analogous strategies were adopted to prepare other MOF-derived hollow Fe₂O₃-TiO₂-PtO_x systems employing MIL-88B as a sacrificial MOF template [77]. Promising photocatalytic H₂ evolution rate was obtained from the Fe₂O₃-TiO₂-PtO_x system as well.

Photocatalytic H₂ evolution could also be realized by MOF-derived hybrid composites without noble-metal cocatalysts. For instance, Qiu et al. reported a magnetic photocatalyst derived from an iron MOF [78]. The magnetic nature of this photocatalyst enabled its easy separation from the reaction media for repeated use. In 2015, a cobalt-based MOF was utilized as a sacrificial template to prepare Co₃O₄/TiO₂ for photocatalytic H₂ production from water [79]. After calcination, Co₃O₄ and TiO₂ were well dispersed throughout the composite. It was found that the close heterojunction between Co₃O₄ and TiO₂ and the co-catalytic role of Co₃O₄ both resulted in fast interfacial charge transfer and efficient electron-hole separation, contributing to the overall photocatalytic performance. Very recently, a new mesoporous p–n heterojunction semiconductor nanocomposite, Cu₂O@C₃N, was prepared

by pyrolysis of a copper-based MOF, $\text{Cu}_3(\text{BTC})_2$ (BTC = 1,3,5-benzenetricarboxylate) together with urea [80]. The obtained $\text{Cu}_2\text{O}@C_3\text{N}$ nanocomposite exhibited a lower band gap energy in comparison with bulk carbon nitride and Cu_2O , as well as dramatically enhanced photocatalytic activity for H_2 production from water.

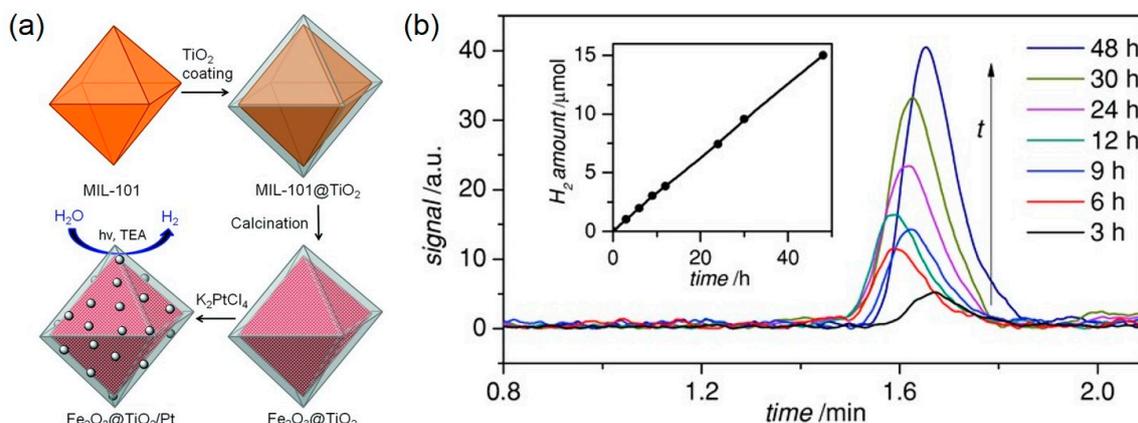


Figure 10. (a) MOF-templated synthesis of $\text{Fe}_2\text{O}_3@\text{TiO}_2$ by coating MIL-101 with TiO_2 followed by calcination, and its use for photocatalytic H_2 production after functionalized with Pt particles; (b) H_2 produced by $\text{Fe}_2\text{O}_3@\text{TiO}_2$ in 20/1 v/v $\text{H}_2\text{O}/\text{TEA}$ at various time points over 48 h, with a 420 nm filter. The inset shows the amount of H_2 produced over this time period. Reproduced with permission from ref. [76], Wiley-VCH.

Table 1. The porosity properties of the representative metal–organic frameworks (MOFs).

MOF	Surface Area ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore Volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Space Groups	Reference
Ru-MOF	516.5	0.26	<i>P213</i>	[42]
Ti-MOF	1202		<i>I4/mmm</i>	[46]
Ti-MOF- NH_2	1101		<i>I4/mmm</i>	[46]
MIL-101- NH_2	1436	0.98	<i>Fd-3m:2</i>	[47]
Al-MOF	1400	0.62	<i>Cmmm</i>	[48]
Al/Zn-MOF	1200		<i>Cmm2</i>	[48]
Zr-MOF	1194		<i>F23</i>	[49]
UiO-66	972		<i>Fm-3m</i>	[50]
Co@ NH_2 MIL-125		0.46	<i>I4/mmm</i>	[60]
Doped-UiO-67 (1)	1254			[64]
Doped-UiO-67 (2)	1947			[64]
Doped-UiO-67 (3)	1410			[64]
Co-MOF	520		<i>C2/c</i>	[79]
Cu-MOF	1182		<i>Fm3 m</i>	[80]

Table 2. Comparison of photocatalytic properties of various photocatalysts.

Catalyst	TON	Time (h)	Photocatalytic Reactions	Ref.
Ru-MOF	8.16	4	HER	[42]
Pt/ NH_2 -MIL-101	110	6	HER	[47]
Pt/Zr-MOF	7000	48	HER	[49]
Doped-UiO-67 (1)	15	3	OER	[64]
Doped-UiO-67 (2)	6	3	OER	[64]
Doped-UiO-67 (3)	2	3	OER	[64]
Zr/Ir MOF	4	1	OER	[65]

5. Conclusions

The last decade has witnessed the rapid advance in photocatalytic water splitting utilizing MOF-based and/or derived catalytic systems. This brief review has presented quite a few number of

representative examples in this field. It is apparent that by taking advantage of the modular synthesis and rich diversity in the selection of inorganic and organic components, MOFs and their derivatives will certainly attract even more attention in the foreseeable future for catalytic applications, including water splitting. Even though a great progress has been achieved in producing H₂ under visible light irradiation catalyzed by MOF-based composites, several challenges remain to be addressed. First of all, very few systems have been reported for photocatalytic O₂ evolution from water. Since H₂ production is only one of the two half-reactions of water splitting, it is equally if not more important to develop competent water oxidation catalysts, in order to realize water splitting for practical applications. More efforts need to be devoted to exploring the rich chemistry of MOFs and their derivatives in preparing highly robust and active photocatalytic systems for water oxidation under visible light irradiation. Secondly, most of those reported MOF-based photocatalysts require noble metal co-catalysts for the efficient production of H₂, which is not economically attractive for industrial application. Economically competitive systems solely consisting of earth-abundant elements are highly desirable. In addition, complex and expensive organic linkers for some MOFs also seem to be problematic. A mixed-linker strategy with low-cost organic linkers might be a promising alternative to reduce the cost of desirable MOFs, which should deserve more attention in the future. More efforts should be shifted towards exploring mixed-organic linkers and 1st-row transition metal-based catalysts derived from MOFs for photocatalytic water splitting. Finally, the intrinsic activity and density of active sites of the photocatalysts should be further improved to meet the requirements of practical application. TONs ought to be >1000 for small-scale and high-value products, but it is better to be >50,000 for industrial applications. Currently, the reported activities (TON < 7000) of most MOF-based photocatalytic systems are still below the expectation for industrial application. Therefore, the unique features of MOFs, including large surface area, tunable pore volume and size, rich coordination chemistry, high crystallinity, and diverse three-dimensional structure, should be wisely utilized to maximize the overall catalytic performance. Molecular approaches of catalyst design coupled with materials science strategies in the development of MOF-based catalysts will undoubtedly lead to a very bright future for photocatalytic water splitting.

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