Recent progress on metal-organic frameworks based- and derived- photocatalysts for water splitting

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Abstract

Since the global energy demand and consumption increased sharply, photocatalytic water splitting becomes a promising solution to provide continuous and sustainable energy resources. However, exploring photocatalysts that could meet energy needs and put into industrial manufacture still remains a challenging task. Metalorganic frameworks (MOFs), as a class of porous crystalline materials with tailorable structure and ultrahigh surface area, are regarded as an ideal candidate for photocatalysis application. Recently, its peculiar employment ocatalytic water splitting aroused tremendous interests. Although this topic early stage, recent advanced experiments results have certified its potential for future application. This review starts with the fundamentals of photoca al water splitting, and subsequently summarizes and exemplifies recent developments of MOFs based- and derivedng water-splitting half reaction and overall photocatalysts for water splitting water splitting. Particularly two strategies to enhance photocatalytic performance of asiled, namely functional modification and surface or pore MOFs are specific emi decoration. Finally, his review identifies the scarcities of MOFs based- and derivedphotocatalysts and proposes pertinent suggestions for further improvement, whilst also highlights a green future for photocatalytic water splitting.

Key words: Metal-organic frameworks; Derivatives; Photocatalysts; Water splitting

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1. Introduction

The rapid development of industrialization has promoted the prosperity of the global economy [1], but also brought severe energy and environmental issues [2, 3], such as greenhouse effect, water pollution [4, 5] and concealable soil contamination [6]. It is unambiguous that continuing utilize of traditional fossil fuels will exacerbate these problems. Recently the global energy consumption and climate changes have stimulated researchers to exploit renewable and sustainable energy sources [7]. Solar energy which represents an enormous and sustainable resour om natural has the largest potential to provide powers for energy conversion ction. In this regard, photocatalytic water splitting into hydrogen and o sources has been recognized yge applicable and eco-friendly technology en has been expected to replace traditional fossil fuels due to its clean toxic byproducts and storable characteristics. lution reaction (HER) rate has become a hot Accordingly, how to enhance hy topic in this field. The In more sluggish and challenging half reaction, i.e. OER), has also developed rapidly because its impact on oxygen evolution overall water splitting rate.

Although pioneer research on solar energy to chemical energy conversion was reported in 1972 by Honda and Fujishima [9], there are few photocatalysts that can meet actual energy demand at present. In fact, it is unrealistic to rely on materials with only unitary property to gain optimal photocatalytic performance [10]. For example, inorganic semiconductors TiO₂, which generally possess excellent stability during photocatalytic reaction [11], own wide band gap (3.2 eV) [12] and poor quantum yield [13]. On the contrary, the photoactivity of organic photocatalysts could be well tuned by introducing functional groups [14], but their stability in solution still remains a severe problem [15]. Despite researchers have applied various methods to improve energy conversion efficiency of traditional photocatalyst [16], more efforts should be put into the development of alternative photocatalyst.

Metal-organic frameworks (MOFs), constructed by metal nodes (metal clusters or ions) and organic linkers, have attracted widespread attention owing to its structural diversity and tailorability, ultrahigh surface area and crystalli 17]. It has been applied in many applications, such as CO₂ reduction [18], water plitting [19], organic pollutants degradation [20], adsorption [21, 22], c is [23] and sensing [24]. It is tary noteworthy that there has been a group and a group of the second se est in the use of metal-organic frameworks as photocatalysts for o itting and water-splitting half reaction. e in Clarivate analytics (Fig. 1), more and According to the data from W eworks have emerged in a few years from the start more papers on metal growth. The number of publications further indicating the of the studies to a high importance and tremendous research interests in this area.



Fig. 1. The current research trends of metal-organic frameworks in photocatalytic water splitting (the data from Web of Science).

Compared with traditional photog have several outstanding 10Fs advantages in photo-induced reaction nstance, the desirable topology and multiple porous structure of MOFs can substrate molecules transfer and diffusion [25], which inherited es of porous materials such as zeolite [26], carbon alent organic frameworks (COFs) [29] and DNA hydrogels nanomaterials [2] [30]. Additionally, abundant active sites for catalytic reaction are exposed which succeed to the porous property and high surface area of MOFs [17]. Most outstanding merit is the physical and chemical properties of MOFs which could be enhanced by sensible designing and tuning the composition and structure, thus considerable reports have devoted to pursue the optimal modification strategy of MOFs photocatalysts for specific photo-induced application [31]. Actually, several reviews related to MOFs in photocatalytic water splitting have been published. For instance, Wang and co-workers summarized the application of MOFs based composites in photocatalytic and electrocatalytic water splitting [32]. Recently, Shi et al. discussed the photocatalytic application of MOFs based composites and MOFs derivatives for hydrogen production from water [33]. These works reflected the rapid development of MOFs in photocatalytic water splitting. However, the bottlenecks of overall water splitting and water-splitting half reaction for practical application are still unrevealed. Additionally, the functionalization and decoration strategies of MOFs for further improvement in photocatalytic water splitting application are urgently required to charified.

Herein, recent progress of MOFs based photocatalysts and MOFs derivatives for water splitting, i.e. oxygen evolution reaction (OEIc) and hydrogen evolution reaction (HER), is exemplified and summarized. These stratces of MOFs based photocatalysts are clarified into two types according to the mode of modification, i.e. functional modification and surface or portedeoration. As a supplementary, the developments of MOFs derivatives which obtained by pyrolyzation are also concluded. Finally, the critical challenges and harmers of this field are presented and the potential solutions are proposed.

2. Fundamentals of photocatalytic water splitting

Photocatalytic water splitting mechanism includes following steps [34]: First, after activated by light irradiation, the electrons of photocatalyst transfer from valence band (VB) to conduction band (CB) while the holes of photocatalyst are left in the VB, thus creating electron-hole pairs. The photogenerated electrons and holes subsequently

migrate to the surface of the photocatalyst while some of them recombined in this process. Finally, electrons and holes on the surface of photocatalyst react with water molecules to generate hydrogen and oxygen, respectively. Corresponding to the three steps some requirements are highlighted to enhance catalytic performance of photocatalysts (Fig. 2). In terms of light harvesting efficiency, there are three compositions in sunlight and can be divided by wavelength: infrared rays (λ >800nm), visible light (400nm< λ <800nm) and ultraviolet rays (λ <400nm). However, ultraviolet ray accounts for a small fraction (about 4%) of the entire s while visible light (about 53%) and infrared light (about 43%) holds great proortion [35]. Owing to larger proportion that visible light occupied, hary visible light is essential for Sth improving energy conversion efficiency. Parti , some advanced semiconductors even accept near-infrared (NIR) Water splitting [36, 37]. Secondly, the or photocatalytic performance is epended on the separation efficiency of electrons and holes. Str ch as constructing heterojunction to prolong charges ze to reduce the distance that electrons reach to the surface, lifetime, shrinking adding sacrificial agents to consume electrons or holes provide avenues for suppress recombination [38]. Lastly, high surface area and massive active sites can increase the contact area between photocatalyst and substrate, i.e. water molecules, thus improving the rate of water splitting reaction.



Fig. 2. Main processes in photocatalytic water splitting and corresponding strategies to enhance photocatalytic performance.

In thermodynamically, overall water splitting (1)) is an uphill reaction (ΔG^0 Lqs. appresed of two half reactions, i.e. OER = 237 kJ/mol correspond to 1.23 eV), and it is c (Eqs. (2)) and HER (Eqs. (4)). Unli ater reduction reaction, water oxidation is a sluggish reaction [13]. Hence, a mber of holes accumulate on the surface of photocatalyst during of er splitting process. However, promoting excessive sult in competition with hydrogen for electrons and oxygen evolution subsequently generate superoxide radicals [37]. Consequently, it is essential to properly control the rate of oxygen evolution in overall water splitting. Besides, the CB and VB edges of photocatalysts must be suitable to trigger overall water splitting. In other words, the CB edge of photocatalysts should be relatively negative than the redox potential of H^+/H_2 (0.0 V vs. NHE), while the VB edge should be relatively positive than the redox potential of O₂/H₂O (1.23 V vs. NHE) [39].

Overall water splitting

$$H_2 O \rightarrow H_2 + 1/2 O_2 \tag{1}$$

Water oxidation half reaction (oxygen evolution dominate)

$$4h^+ + 2H_2O \rightarrow O_2 + 4H^+ \tag{2}$$

$$A+e^{-} \rightarrow A^{-}$$
 (A is an electron acceptor) (3)

Proton reduction half reaction (hydrogen evolution dominate)

$$2H^+ + 2e^- \rightarrow H_2 \tag{4}$$

$$D+h^+ \rightarrow D^+$$
 (D is an electron donor) (5)

To meet specific industrial needs, water-splitting helf cachon gained the popularity in recent years due to its less difficulty in gas secaration. In some cases, sacrificial electron donors or electron acceptors are added to consume holes or electrons and accelerate water-splitting half reaction (1.e., (f)) and (5)) [40]. In recent years, several reports also suggested combine plue-added chemicals oxidation reaction with H₂-producing half reaction [41], which increasing overall reaction rate and saving costs. Compare with overall proceeding, the lower restrictive band gap requirement of water-splitting half reaction also broaden the choice of photocatalysts.

With regard to photocatalysts, two properties are essential to induce photocatalytic water splitting reaction, i.e. catalytic property and photosensitivity [42]. MOFs have unique advantages in these two properties. When it comes to catalytic property of MOFs, some MOFs have been considered as microporous semiconductor as it undergoes electrons and holes separation under light irradiation [43]. Nevertheless, most MOFs are gradually accepted as poor electrical conductivity [44], which is ascribe to the symmetry mismatch of ligand and orbital as well as their energy-level alignment

inadequacy [45]. It is the porosity of MOFs that compensate this drawback, which can be explained to the short distance between redox sites and the evolution position of photogenerated carriers. Moreover, these pores also allow efficient diffusion of the reactants and intimate contact with active sites. As for photosensitivity, some MOFs, such as MIL-101, MIL-100, MIL-53 (MIL, Materials of Institut Lavoisier), possess excellent photoactivity and even respond in the visible light range. Moreover, due to its high designability, components functionalization can be utilized as efficient strategy to strengthen MOFs visible light and even NIR light respo a reflected the superiority of MOFs over traditional semiconductor such as CdS and TiO_2 [46]. For example, the introduction of amino group into merganic ligands of Ti-MOF can shift the band as they devote 2p electrons to are atil linker [47]. Besides, the pore size of MOFs is positively correlated with length of organic ligands, which is beneficial to decorate functional substance ent sizes as needed.

MOFs have been proved to be applied in photocatalytic water splitting. Several pristine MOFs show ood photocatalytic activity for water splitting without doing further post-modification. For example, Shi et al. [48] synthesized Cu-I-bpy (bpy=4,4'-bipyridine) without additional photosensitizers and cocatalysts, which showed good photocatalytic hydrogen production rate (7.09 mmol $g^{-1} h^{-1}$). In addition, the method for combining with photosensitizing units and MOFs is also beneficial for highly photocatalytic activity for hydrogen production, such as some well-known molecular dyes (Ru(bpy)₃Cl₂ and less expensive porphyrines, etc) as photosensitizing linkers [49]. However, some pristine MOFs are still restricted by limited visible light response and

short life time of excited carriers, etc. On the other hand, development of novel MOFs with above mentioned merits still remains a challenge task. On the basis of existing pristine MOFs, it is sensible to employ effective modification or decoration strategies to make it possess better photocatalytic property. In this regard, two typical strategies are emphasized in this review: functional modification refers to the integration of foreign groups or ions into metal center or organic ligand of MOFs, while surface or pore decoration refers to the decoration of foreign functional substances on surface or pores of MOFs.

- 3. MOFs based composites as photocatalysts
- 3.1 Functionalization modification of MQFs

Characteristic properties of MOEs nostly depend on their composition, which will further have an effect on their proportativic performance. Hence, it is extraordinary important to modify organic inform and metal centers of MOEs for expected chemical and physical properties, which leads to two ways of functionalization: functional groups modification and metal doping. The photocatalytic water splitting performance of MOEs by functional modification are concluded in **Table 1**.

3.1.1 Functional groups modification

Decoration of the organic linkers of MOFs can decrease the band gap energy to some extent. According to the formula: λg (nm) = 1240/Eg (eV), the light absorption edge could expand to the visible light or even NIR light region. For instance, functional groups such as amino and porphyrins [50] can be insert into organic linkers to decrease

the band gap energy and expand the light absorption edge of MOFs. Not only decrease the band gap energy, some reports manifested that metal complex can even expand the choice of sacrificial agents of water splitting system [51].

Amino groups have been insert into organic linker to expand the light absorption edge of MOFs. For example, UiO family have been favourite by researchers of solar energy conversion [52]. Owing the highly water-stable property [49], UiO have an attractive prospect for photocatalytic water splitting. Sliva et al. compared the photocatalytic performance of UiO-66 and ATA modified U for HER [53], and the results suggested that introducing amino to BDC li to red shift of the adsorption from 300 to 440 nm without changing t cture of MOFs. Similarly, the photocatalytic hydrogen production of ncionalized MIL-101(Cr) has been explored by Wen and co-workers [5 ous hydrogen generation of pure NH₂rhodamine B (RhB) photosensitizer. From MIL-101 was observed in the atant solutions, the intensity and position of the the UV-visible spectra not change, which means that Pt/NH₂-MIL-101 possesses absorption peak c high chemical stability. Since the photocatalytic activities of various Fe-based MOFs (MIL-101(Fe), MIL-126(Fe), MIL-100(Fe), MIL-88(Fe) and MIL-53(Fe)) for water oxidation have been investigated in visible light [55], Chi and co-workers also have explored the photocatalytic water oxidation capacity of different iron-based MOFs (i.e. MIL-53(Fe), MIL-88(Fe) and MIL-101(Fe)) as well as their amino functionalized counterparts under visible light [56].

Except amino group, porphyrins are also used to enhance the photosensitivity of

MOFs. Recently, a PMOF which consist of Ti-oxo clusters and porphyrin has been synthesized [57], and the light adsorption range have been enlarged to 700 nm. Benefiting from this, it exhibits excellent photocatalytic hydrogen production rate (8.52 mmol•g⁻¹•h⁻¹). In addition to being introduced into MOFs as an organic ligands, porphyrin molecules can also improve the performance of photocatalysts by metallization. For example, He et al. not only synthesized zirconium–porphyrinic hollow nanotubes MOF (denoted as HNTM) but immobilized single noble-metal atom (Pd, Ru, Pt, Au, Ir) on porphyrinic linker by solvothermal performance for protocatalytic hydrogen generation (201.9 μ mol h⁻¹ g⁻¹), in which porphyrine-it units served as catalysts and porphyrinic-Ir units acted as photosensitizers.

Other photosensitizers also have been infroduced into MOFs as organic linkers. For example, Hou and co-workets encapsulated a Ru-based molecular photosensitizer and a Pt-based molecular an lyst into UiO-67 by mix-and-match approach [58]. In this case, the excited Pureseer molecular photosensitizer transfers electrons to Pt-based catalyst after light irradiation, then water was reduced to hydrogen in Pt-catalytic center of MOFs. Finally, the excited state of Ru-based molecular photosensitizer back to the ground state by sacrificial electron donor, i.e. EDTA-2Na. Kim et al. have embedded a Pt(II) molecular catalyst and an Ir(III)-based photosensitizer into bipyridine-embedded UiO-67 MOF (BUiO) [59], and the as-synthesized MOF was termed as self-healing system that spontaneously repair the catalyst and photosensitizer during HER by controlling the ratio of 2,2'-bipyridine-5,5'-dicarboxylate to Pt. Cd-based MOFs also have been functionalized by photosensitizer for photocatalytic water splitting. For instance, the photoactivity of Cd-based MOFs have been enhanced by embedding ecofriendly dye, i.e. Eosin Y (EY), into linker [60], and the as-synthesized Cd-EY1 photosensitizer cooperated with co-catalyst $[Co(bpy)_3]Cl_2$ (bpy = 2,2'-bipyridine) to facilitate electron transmission and improve hydrogen production rate. Additionally, in the case of the same organic linker, Cd-based MOF has been compared with Cu-based MOF [61]. The spectra response range of Cu-based MOF was wider than Cd-based MOF, and it also could induce hydrogen evolution under the nyth irradiation. Furthermore, without any cocatalyst and photosensitizer, two nytel Cu-based MOFs have been reported to catalyze photocatalytic hydrogen production half reaction under visible light or even NIR light irradiation. [62].

In recent works, the metal con ysts are introduced into MOFs which len and co-workers prepared UiO-66serve as superior supports [FeFe](dcbdt)(CO)₆ (d -dicarboxylbenzene-2,3-dithiolate) MOF by PSE MOF provided a platform to improve UiO-66 strategy [64]. [FeFe](dcbdt)(CO)₆ moiety structural stability. The as-synthesized MOF exhibited excellent hydrogen production rate in water at pH=5. Likely, molecular catalysts [Fe₂(cbdt)(CO)₆] ([FeFe], cbdt =3-carboxybenzene-1,2-dithiolate) have been covalently incorporated into amino-functionalized MIL-101(Cr) (denoted as MIL-101-NH-[FeFe]) [65], and the MIL-101-NH-[FeFe] with different catalysts concentration all displayed better catalytic capacity for hydrogen production than pure MIL-101-NH₂. Similar research also has been reported by Sasan et.al, they incorporated

photosensitizer porphyrin and active catalyst sites biomimetic [Fe₂S₂] into Zr based MOF [66]. Recently, four Rh- and Ru- based molecular complexes was created and encapsulated into UiO-67 by exchange with the original dicarboxylate bpdc ligands [67], namely RuCl@UiO, RuOH₂@UiO, RhOH₂@UiO and RhCl@UiO (Fig. 3a). The optical band gap of UiO-67 (~3.5 eV) rapidly reduced to around 2.4 eV after PSE process while there was no significant change in structure and particles size (Fig. 3b), and RuCl@UiO, RuOH₂@UiO, RhCl@UiO, RhOH₂@UiO MOFs were all responsive to visible light (400 ~ 500 nm). Moreover, photocatalytic t of hydrogen production indicated that RhOH2@UiO perform best, which over number (TON) was 125.0 and the turnover frequency (TOF) was (Fig. 3c). A well crystalline MIL-125(Ti) was first reported in 2009 consist of titanium-oxo-hydroxo clusters and terephthalate acid (H2H However, the optical band gap energy of MIL-125(Ti) is 3.6 eV [69 cates its poor photoactivity in visible light range. Horiuchi et al. s in amino-functionalized Ti(IV) based MOF (denoted as visible light adsorption ($\lambda > 500$ nm) and then Pt as NH₂-MIL-12 nanoparticles (NPs) were loaded by photodeposition method [70]. As a result, the photocatalytic activity of Pt/NH2-MIL-125 for hydrogen production was improved. Moreover, this group proposed that the optimized amount of Pt NPs deposition was 1.5 wt% [71]. The Pt(1.5)/Ti-MOF-NH₂ had no significant loss of photocatalytic activities after three cycles of experiments. In addition, from XRD and FT-IR measurements, the diffraction peaks corresponding to the MIL-125 structure were unchanged. This means the organic linker with amino group stably exist during the reaction. Owing to the fact

that this system was limited by available longest light wavelength and irreplaceable sacrificial electron donor (i.e. TEOA, triethanolamine), Ru complex was employed as organic linker by solvothermal method with Ru(tpy)2, methanol, DMF and tetrapropyl orthotitanate (TPOT) as raw materials [51]. In this case, Ti-MOF-Ru(tpy)₂ not only achieve excellent stability and steady hydrogen production after three cycles, but its structure remains the unchanged, which can be confirmed by XRD. Ultimately the visible light adsorption wavelength for hydrogen production was up to 620 nm and the choice of sacrificial agent was also expanded. Moreover, mo lt (Co) catalyst also have been encapsulated into a photoactive NH₂ (denoted as Co@MOF) by 'ship-in-the-bottle' approach (Fig. [2], and the Co complex was a) connected to the Ti oxo-cluster of MOF, as eneficial for well dispersed of Co molecules in MOF cavities (Fig. 4b lower catalytic potential of Co@NH₂-MIL-125(Ti) than the lowest molecular orbital (LUMO) of NH₂-MILons of organic linkers rapidly transfer to Co species 125(Ti), the photogene sacrificial electron donor. Consequently, the Co@MOF while the holes of showed excellent photocatalytic activity with higher to 20-fold hydrogen production rate than pristine Co-free MOF. Moreover, after recycling tests, the activity of Co@MOF remained unchanged and its internal cobalt did not leach, indicating that the composite is stable in water. Through the several cycles of experiments, the Co@MOF retained the catalytic activity very well and the active substance was not detected in the solution. This means that the Co@MOF is very stable in solution. It can be inferred that its crystallinity has unchanged in the solution. Furthermore, Iglesias-Juez et al.

illuminated the structure and property of photocatalytic Co@NH₂-MIL-125(Ti) for hydrogen production by Electron Paramagnetic Resonance (EPR) and X-ray absorption spectroscopy (XAS) analysis [73].



Fig. 3. (a) Installation of heterogeneous MOFs catalysts through PSE method. (b) SEM of the assynthesized UiO-67, and RuCl@UiO, RuOH₂@UiO, PLCLUIC, RhOH₂@UiO MOFs. (c) Results for RuCl@UiO, RuOH₂@UiO, RhCl@UiO and thOH₂@UiO under optimized condition for shortterm (3 h) photocatalytic hydrogen evolution. Reprinted with the permission from Ref. [67].



Fig. 4. (a) 'Ship-in-the-bottle' synthetic strategy followed for assembling of Co@MOF. (b)-(e) TEM

of pristine NH₂-MIL-125(Ti) (200 nm-b; 100 nm-c) and Co@MOF (200 nm-d;100 nm-e). Reprinted with the permission from Ref. [72]. Copyright 2015 Royal Society of Chemistry.

3.1.2 Metal doping

Metal doping is regarded as an efficient method to improve photocatalytic performance of MOFs. The affluent coordination sites in MOFs afford spaces for stabilizing foreign metals. The doped metals serve as mediators to facilitate electron transfer, greatly boosting the photocatalytic activity. Inspired by the application of metal doping in semiconductor, Sun et al. employed a post-(PSE) method to prepare a Ti-replaced NH₂-UiO-66(Zr/Ti) [74 functional theory (DFT) and electron spin resonance (ESR) were em to unveil the path of electron ATA) ligand transfer electrons to transmission: The excited 2-aminotereph Ti⁴⁺ (larger probably to Ti⁴⁺ rathe and the reduced Ti³⁺ acts as electron mediator that donate electrons the efficient charge transfer result in higher photocatalytic activity O-66(Zr/Ti) as the amount of hydrogen production of pristine NH₂-UiO-66(Zr). Besides, since the previous was equivalent to work that water-stable $Zn_{0.986(12)}TCPP-[AlOH]_2$ composed of Al^{3+} ions as metal center and porphyrin metallized by zinc as a linker has been reported [75], Aziz et al. overcame the shortcomings of Zn_{0.986(12)}TCPP-[AlOH]₂ that slightly wide band gap and low efficiency of spatial charge separation by partial substitution Al by Fe at metal centers [76]. Therefore the band gap (1.9 eV) has been well tuned and effective suppressed the electron-hole recombination.

Except functional groups modification and metal doping, other factors also have

impact on the photocatalytic performance of MOFs. For instance, Owing chemical/thermal stability and easy-controlled synthesis advantages, ZIF-8(Zn) become one of the most typical MOFs materials. Nevertheless, the photocatalytic application of ZIF-8(Zn) has restricted by its large band gap energy (5.1eV) and poor visible light response. The band edge position of ZIF-8(Zn) has been adjusted by linker mix-and-match approach [77], which indicated that the band position could be well tuned by mixing linkers of low-lying conduction edge with high-lying valence edge.

In summary, benefiting from its design flexibility, the usters and the organic ligands of MOF can be easily functionalized, such tial substitution of metal center and introduction of functional group organic ligands. Besides, the 100 stability of MOFs in photocatalytic proce d ake into consideration, especially in water splitting system which the ueous solution fluctuate. According to previous research [78, 79], MOFs based photocatalysts could retain eak acid and base, such as UiO-66, MIL-100, MILcrystallinity and activi 53, ZIF-8 and etc orts also have been devoted to strengthen the stability of novel MOFs. For example, a novel MOF consisted of 9-phenylcarbazole-3,6dicarboxylic acid (H₂PDA) and Zn(NO₃)₂ 6H₂O have been synthesized[80]. Because pure Zn–PDA₂ was easily decomposed, thus the hydrogen production of pure Zn–PDA₂ is reduced by half after one cycle. From ICP-MS analysis of the supernatant solution, about half of the Zn leaks into the solution. However, for PDMS-coated Zn-PDA₂, only 3% of Zn leached in solution after 5 cycles (PDMS=polydimethylsiloxane). From the PXRD images of the PDMS@Zn-PDA₂ soaked in water or alkaline solution (PH=10)

for five days, they found the sample still remains intact.

Accepted

Functional	MOFs	Metal clusters/core	Ligands	Sacrificial	Target	Production rate	Recycle	Recycle Ref. d times
modification				reagent	reaction		d times	
Functional groups	Pt/NH ₂ -MIL-101(Cr)	Cr-O cluster	ATA	TEC	HER	0.6 mmol•h ⁻¹ •g ⁻¹	5	[54]
modification	HNTM-Ir/Pt	Zr-O cluster	porphyrin	TEOA	HER	0.2 mmol•h ⁻¹ •g ⁻¹		[50]
	Co@MOF	Ti-O cluster	ATA, L ^H	TEA	HER	22.5 mmol•h ⁻¹ •g ⁻¹	3	[72]
	MIL-101(Fe)-NH ₂	Fe-O cluster	PDC-NN	$Na_2S_2O_8$	OER	61.8 mmol•h ⁻¹ •g ⁻¹		[56]
	PMOF	Ti-O cluster	pophyrin	ascorbic acid	HER	8.52 mmol•h ⁻¹ •g ⁻¹	3	[57]
	Pt/Cd-MOFs	Cd-O-slutter	H ₂ DSPTP	TEOA	LIED	1.2 mmol•h ⁻¹ •g ⁻¹	5	[61]
	Pt/Cu-MOFs	C O craster			ΠĽΚ	7.3 mmol•h ⁻¹ •g ⁻¹	8	
	RhOH ₂ @UiO	Zr-O cluster	BPDC	TEOA	HER	10.4 mmol•h ⁻¹ •g ⁻¹		[67]
	Pt(1.5)/Ti-MOF-NH ₂	Ti-O cluster	ATA	TEOA	HER	$\approx 0.4 \text{ mmol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$	3	[71]

 Table 1. Photocatalytic water splitting performance of MOFs by functional modification.



3.2 Surface or pore decoration of MOFs

Even though functional modification is beneficial to improve the photocatalysis property of MOFs to some extent, further enhance photocatalytic performance should rely on more efficient strategy, i.e. surface or pore decoration [81]. The superiority of surface or pore decoration compared with functional modification is reflected in the following aspects: Firstly, the band gap of MOFs could be well tuned when combine with other typical photoactive substances, therefore enlarge light and even NIR light adsorption scope of these composites. In some dual-excitation of typical photoactive substances and MOFs is be ial to boost quantum yield. nen Secondly, surface or pore decoration could eff interparate electrons and holes pairs spatially. Besides, the intimate con etween MOFs and photoactive substances osition CB electrons and higher-position VB could induce the recombination higher-position CB electrons and lower-position VB holes, promoting the se or pore decoration can equip MOFs with more active sites holes. Additional for catalytic reaction. The photocatalytic performance of MOFs based photocatalysts for water splitting are concluded in Table 2.

3.2.1 Corporation with semiconductor

Except judicious construct metal center and organic linker of MOFs, there is a facile solution of assemble MOF with semiconductor to narrow the band gap of MOF. There are two merits of this heterogeneous photocatalysts: one is to enlarge light adsorption edge to visible or even NIR light region and another is to realize efficient

separation of electron and holes.

Graphitic carbon nitride $(g-C_3N_4)$ has received great concerns in recent years [82]. As a typical metal-free polymeric semiconductor [83], g-C₃N₄ is mainly composed of C, H and N, and it has been applied in photocatalytic reaction due to its high chemical and thermal stability [84], low economic cost and excellent visible-light capacity [85]. To improve the photocatalytic activities of UiO-66 with wide band gap (3.5 eV), Wang et al. synthesized several hybrids that were consist of g-C₃N₄ and UiO-66 MOF with different ratios by annealing the mixture of them at Ar atmosp Fig. 5a). Along with mass fraction of g-C₃N₄ in hybrids increases the surfa this hybrid became rough and uneven till fully coated (Fig. 5b-d). Ow the flexible layered structure ng and narrow band gap (2.7 eV) of g-C₃N wrap or anchor on UiO-66 MOF that and transfer electrons to UiO-66 MO photocatalytic hydrogen production amount of these hybrids increased as fraction of g-C₃N₄ (below 50%) in hybrid nount of hydrogen generation dropped significantly increase (Fig. 5e). Ho 4 in hybrid was 70%, which was ascribed to the "covering when mass fractio effect". Recently, ultrathin two-dimensional meta-organic framework (UMOF) nanosheets have aroused numerous attentions. Cao et al. have attempted to assemble 2 dimentional (2D) g-C₃N₄ nanosheets and 2D Ni-based MOF nanosheets together by self-assembly process [87]. Benefiting from the ultrathin thickness of 2D structure, the electrons transfer more efficiently and further boost the photocatalytic efficiency. In addition to changing the morphology of the composite, employing organic acids as an electronic mediator can also strengthen the photocatalytic performance. For instance,

NH₂-MIL-125(Ti) MOF have been combined with benzoic acid functionalized graphitic carbon nitride (g-C₃N₄) to build a Z-scheme heterojunction photocatalyst for HER [88], in which semiconductor and MOF were connected by covalent bonds as the carboxylate groups of the functionalized g-C₃N₄ are coordinated with the Ti ions of MOF. More than promote suitable heterojunction formed, the benzoic acid also acts as electron mediator to induce recombination of holes in MOF and electrons in g-C₃N₄ (Fig. 6b), leading to high hydrogen generation rate of 1.123 mmol $h^{-1} g^{-1}$ that equivalent to 6 times of pristine NH₂-MIL-125(Ti) MOF (I er four cycles, the photocatalytic H₂ evolution rate of 10wt%g-C₃N₄/MO arkedly reduced by 0.1 mmol \cdot h⁻¹ \cdot g⁻¹. In contrast, the photocatalyt volution rate of novel MOFs nearly became unchanged. This explain novel Z-scheme heterostructured catalysts linked by covalent bonds water stability than the conventional 10wt%g-C₃N₄/MOFs linked b aals force. Moreover, the amine group of g-C₃N₄ makes it possible hor metal nanoparticles [89]. Bimetal nanoparticles NiPd mto MOF/g-C₃N₄ photocatalytic systems as co-catalyst [90]. NPs were also intr The strong light-harvesting abilities of NiPd NPs were beneficial to improve photocatalytic performance of MOF/g-C₃N₄. As a result, the photocatalytic hydrogen production rate of NH₂-MIL-125(Ti)/0.75g-C₃N₄/Ni_{15.8}Pd_{2.1} was about 322 times than that of NH₂-MIL-125(Ti)/0.75g-C₃N₄.



Fig. 5. (a) Schematic illustration of decorating g-C₃N₄ on UiO-66 octahedrons through annealing process. SEM images of (b) UiO-66, (c) UG-10 and (d) UG-50. (e) T histogram showing the hydrogen production rate over pristine UiO-66, g-C₃N₄ and UO 10, 30, and 50), the inset shows the long term hydrogen production over UG-50 sample (UG-x means UiO-66 and g-C₃N₄ composites and x is the mass content of g-C hri s). Reprinted with the permission from Ref. [86]. Copyright 2015 Wiley. (b) Potential vs NHE **(a)** 1 NH_-MIL-125 5CFBM -2.0 10CFBM 15CFBM H2O/H+ -1.0 MOF 0 H, 1.0 h+* 2.0 hν h Oxidation 0.0 Samples

Fig. 6. (a) The rate of hydrogen evolution of NH₂-MIL-125, 5CFBM, 10CFBM and 15CFBM under visible light irradiation. (b) Photocatalytic mechanism of the charge transfer for hydrogen evolution over the 10CFBM under visible light irradiation. Reprinted with the permission from Ref. [88]. Copyright 2018 Elsevier.

Owing to its ideal band gap (2.4eV) and excellent photoelectric properties [91],

CdS NPs also have been encapsulated into MOFs, such as MIL-101(Cr) [92] and UiO-66 [93], to provide extra active sites. However, these composites also bring some severe challenges, for example, the photogenerated electrons and holes are easily recombined. To solve this problem, a ternary complex Au@CdS/MIL-101 has been synthesized by deposited Au nanoparticles on the MIL-101 and CdS coated on Au nanoparticles subsequently [94], and the outstanding catalytic capacity of the as-synthesized ternary complex (hydrogen production rate: 25 mmol $h^{-1} g^{-1}$) could ascribe to two aspects: (i) Au accelerate charge transition and enlarge the visible light n ectrum of CdS. (ii) MOF not only serve as support to disperse nanoparticles generate electrons under light irradiation. Recently, carbon nanodots (Ds particles have been introduced into MIL-101@CdS system for further promotion g charge transfer efficiency [95]. The prolonged lifetime of electrons of dSMIL-101 also contribute to enhance photocatalytic hydrogen evolution ty. Additionally, be endowed with higher nary metal sulfide Cd_{0.5}Zn_{0.5}S aroused numerous photoactivity than pur ice, Cd_{0.5}Zn_{0.5}S has been introduced into UiO@g-C₃N₄ attention [96]. (denoted as UCN) system to construct a ternary heterojunction (Fig. 7d) [97], and the photocurrent intensity improved from 0.20 μ A cm⁻² of UCN to 0.82 μ A cm⁻² of $Cd_{0.5}Zn_{0.5}S@UCN$ (Fig. 7a), which demonstrated more photoelectrons generation of UCN after Cd_{0.5}Zn_{0.5}S decoration. Meanwhile, the electrochemical impedance spectra (EIS) Nyquist plots proved higher electrical conductivity of Cd_{0.5}Zn_{0.5}S@UCN than UCN as the arc radius of Cd_{0.5}Zn_{0.5}S@UCN was smaller (Fig. 7b). Accordingly, the hydrogen production activity of Cd_{0.5}Zn_{0.5}S@UCN enhanced significantly than other counterparts (Fig. 7c).



Fig. 7. (a) Transient photocurrent response of the of $0.66@g-C_3N_4$, ZnS@UiO- $66@g-C_3N_4$, CdS@UiO- $66@g-C_3N_4$ and Cd_{0.5}Zn_{0.5}S@UiO- $66@g-C_3N_4$ under visible-light irradiation. (b) The EIS Nyquist plots of the UiO- $66@g-C_3N_4$ and Cd_{0.5}Zn_{0.5}S@UiO- $66@g-C_3N_4$ composites. (c) Photocatalytic hydrogen exclusion rate under visible light irradiation over the as-prepared samples (Na₂S and Na₂SO₃ wave and as the hole scavenger without noble metal co-catalysts). (d) Schematic of photocatalytic hydrogen evolution over the Cd_{0.5}Zn_{0.5}S@UiO- $66@g-C_3N_4$ under visible light irradiation. Reprinted with the permission from Ref. [97]. Copyright 2018 Royal Society of Chemistry.

Likewise, other semiconductors such as MoS₂ and Cu₂O also have been explored for combination with MOFs. MoS₂ composed of a layered structure has been widely investigated because of its high activity for solar hydrogen production [98]. For example, MoS₂ has coupled with UiO-66/CdS system and serves as one kind of noble-

metal-free co-catalyst for HER in visible light [99]. Since the well-matched band structures of three components, the ternary heterojunction presented remarkable hydrogen production rate, i.e. 32.5 mmol h⁻¹ g⁻¹, which is better than the ternary heterojunction that Pt as co-catalyst. Besides, as an economical and sustainable semiconductor, Cu₂O has also been applied in photocatalytic hydrogen evolution by post-synthetic encapsulation into NH2-MIL-125(Ti) [100]. Specifically, the Ti⁴⁺ of NH₂-MIL-125(Ti) partially reduced to Ti^{3+} during post-synthetic encapsulation, and the increased hydrogen evolution could be ascribed to the efficiency charge separation between Cu₂O and Ti³⁺. More recently, traditional semico ductor TiO₂ hollow nanospheres (TiO2 HNPs) have been created through template method and then decorated by ZIF-8 MOFs [101], the photocata vac performance of this heterogeneous photocatalyst promoted greatly beca he shell of TiO₂ HNPs enlarged the surface area.

3.2.2 Decoration of graph

Graphene is a sequence carbon atom-plane material which is stripped from graphite materials [102]. It shows superior thermal and electrical conductivity, high chemical stability. Especially graphene oxide (GO) and reduced GO (rGO) are widely studied and applied [103]. GO can facilitate charges transfer and surface-adsorbed amount of chemical molecules through π - π interactions. MOFs could potentially evolve into highly efficient photocatalysts when incorporated into graphene decorated system. In the photocatalytic system, the GO serves as electron-transfer mediator, provides more active sites and leads to significantly improvement of the photo-

generated charge separation efficiency [104]. Wang et al. introduced GO to UiO-66-NH₂ by applying three incorporation methods respectively, i.e. random mixing, singleface interaction and multiple-face interaction [105], and the results manifested that every face of UiO-66-NH₂ MOF was covered by GO and reached high hydrogen production rate (41.4 mmol $h^{-1}g^{-1}$) when employed the multiple-face interaction approach, which can be explained by the efficient charge transmission between UiO-66-NH₂ MOF and GO. Furthermore, Liu et al. not only prepared UiO-66/rGO by solvothermal method but introduced Ni₄S₃ into UiO-66/rGO hermal method to construct rGO/MOF/Ni₄S₃ photocatalytic system [106], expected, the light adsorption edge of rGO/MOF/Ni₄S₃ has showed cant red shift. Moreover, the hydrogen amount of EY-sensitized rGO photocatalyst produced about 185 times than the pure rGO/MOF phot Besides, Shi et al. demonstrated that Cucould act as microcontainer which benzene-1,3,5-tricarboxylate)F radicals during photocatalytic reaction by electron encapsulate and stabili alysis [107], and they incorporated it into ZnO/GO by spin resonance (electrostatic interaction for increasing the possibilities of H• radical recombination. Finally the photocatalytic hydrogen production amount was increased by about 9 times. Moreover, UiO-66/CdS/RGO composite has been designed to inhibit the electron-hole pairs recombination and increase more catalytic sites of CdS [108]. Likewise, the synergistic effect of GO and MoS₂ quantum dots on the photocatalytic hydrogen production of MOF also has been proved [109]. To be specific, the hydrogen generation amount of MoS₂/UiO-66-NH₂/GO reached 186.37 µmol while the UiO-66-NH₂/MoS₂ and the UiO-66-NH₂/GO was 75.1 µmol and 1.98 µmol, respectively.

3.2.3 Metal nanoparticles loading

Nanotechnology has developed rapidly and is widely used in medicine, biology and biochemical engineering in recent years [110, 111]. Also, the inherent advantages of nanomaterials such as various morphologies and abundant surface states make a new path for the use of renewable energy [112, 113]. Metal nanoparticles (MNPs) is a kind of excellent catalyst compared with the bulk noble metals, which reflected in its high ratio of surface area to volume [114]. When the size of the m es is reduced to the order of nanometers, the catalytic performance of MNPs mprove significantly [115, 116]. However, MNPs is tended to aggrega th each other in solution and greatly suppressed its catalytic property prevent this phenomenon, stable supports such as MOFs are utilized dispersion, meanwhile MNPs serve as NP co-catalyst for efficient spatial c ration.

Noble MNPs have accord numerous attention in catalysis due to their outstanding catalysis havior [118]. Notably, Pt NPs have been frequently applied with MOF for photocatalytic water splitting. Wen et al. constructed a Pt NPs loaded and RhB sensitized NH₂-MIL-101(Cr) for HER, significantly improved the efficiency of electron-hole separation [54]. Moreover, the influence of different Pt NPs spatial position on the photocatalytic activity of UiO-66-NH₂ also have been investigated [119], and the results indicated that UiO-66-NH₂ encapsulated Pt NPs into pores showed higher efficiency of charge separation than UiO-66-NH₂ that supported Pt NPs on the surface. Besides, Pt NPs confined in pores are less likely to leak or aggregate than

deposited on the surface. Recently, a novel Cd-based MOFs (denoted as Cd-TBAPy) has been reported [120], the novel Cd-TBAPy possess excellent solvent and thermal stability and ideal band gap of 2.15 eV for visible light adsorption as well as sufficient potential of both VB and CB for water oxidation and reduction (Fig. 8), simultaneously realized effective HER and OER after loading Pt and CoPi co-catalyst. Particularly, a novel approach has been reported that through a redox reaction between oxidative metal salt and reductive Ti³⁺-MIL-125(Ti) to decorate MIL-125(Ti) with noble M (Pt, Pd and Au NPs) [121]. The as-synthesized Pt/MIL-125(Ti) showed a drogen amount (38.68 µmol) than the Pt/MIL-125(Ti) (about 20 µmol) pre by photodeposition method. Au NPs with excellent catalytic properties so be applied in photocatalysis. an a Interestingly, Jiang et al. have extended the s response range of MOFs to NIR light by constructing core-shell stru UCMPs-Pt@MOF/Au composites (UCNPs denote NaYF4:Yb, Tm, Er) [12 composite, UCNPs could accept NIR light and convert it into ultra visible light that could be further utilized by MOF NPs-Pt@MOF/Au showed excellent catalysis activity for and Au NPs. In th hydrogen evolution under stimulated solar light.



Fig. 8. The proposed mechanism for visible-light-driven photocatal via flydrogen and oxygen evolution over Cd-TBAPy. Reprinted with the permission rom Ref. [120]. Copyright 2018 Wiley.

In recent work, noble metal nanoparticle ave been replaced or partial replaced by earth-abundant metals for clean technology. Nickel (Ni) based co-catalyst received tremendous of its excellent catalysis activity for attentior photocatalytic applicat stance, Ni has been incorporated with noble metal NiPd co-catalyst for hydrogen production [90]. Ni₂P NPs palladium (Pd) to are also inserted into g-C₃N₄/UiO-66 system to inhibit recombination of electrons and holes (Fig. 9) [123]. Accordingly, the hydrogen evolution rate of g-C₃N₄/UiO-66/Ni₂P is higher than g-C₃N₄/UiO-66. Additionally, the photocatalytic performance of NH₂-MIL-125(Ti)/Ni₂P and NH₂-MIL-125(Ti)/Pt has been compared for HER in visible light [124]. The photocurrent response and the photoluminescence spectrum (PL) showed that NH₂-MIL-125(Ti)/Ni₂P performed higher efficient electron transfer and lower possibility of recombination than Pt/NH₂-MIL-125(Ti). Recently, p-type semiconductor NiO co-catalyst, which worked as collector of photogenerated electrons, has been embedded in UiO-66-NH₂ and this composite showed enhanced hydrogen production rate of 2561.32 μ mol h⁻¹ g⁻¹ [125].



Fig. 9. Schematic for the mechanism of $g-C_3N_4/UiO$ -CONER photocatalytic hydrogen production. Reprinted with the permission from Ref. [123]. Copyright 2018 Elsevier.

3.2.4 Sensitization

Besides loading metri nanoparticles, dye-sensitization is another appealing approach to boost the protocitalytic efficiency. Dye-sensitization has been widely used in the field of semiconductors, and has been gradually regarded as an effective strategy to enhance the photocatalytic performance of MOFs for water splitting. Between MOF and organic dye, various forces (such as π - π interaction and Van der Waals force) could effectively suppress the recombination of photogenerated electrons and holes, which benefit for photocatalytic reaction [125]. RhB has been combined with MOF for hydrogen production [54]. Nevertheless, RhB is not a suitable photosensitizer since its poor stability for photocatalytic application [126]. Conversely, erythrosin B (ErB) is a

kind of relatively stable dye and has been used for improving the photocatalytic performance of MOF. Liu et al. applied ErB as photosensitizer to sensitize MIL-101 which loaded Ni/NiO_x NPs [127]. The results unveiled that moderate amount of ErB dye could effectively facilitate hydrogen generation, but excessive amount lead to competition between ErB dyes and resulted in low hydrogen evolution rate. Similarly, Yuan et al. employed UiO-66 which was sensitized by ErB dye and deposited by Pt NPs for hydrogen production in visible light [128]. As for dye and MOF combination system, efficient electron transfer and high hydrogen product ostly depended on the stability of dye and MOF binding. For instance, a alixarene-based dye (denoted as Calix-3) has been used as light absorbing anonna of UiO-66-NH₂/Pt system for HER [129]. Except from Van der Waals ce and π - π stacking, hydrogen bond among Calix-3 dye and UiO-66-NH also have influence on their stability. It was indicated that small amount of UiO-66-NH₂ has strong binding with -COOH moieties of Cal d lead to higher hydrogen production rate. Recently, and simple manner for constructing a photoactive MIL-101(Cr) Li et al. reported a with polyoxometalates (POMs) loaded and $[Ru(bpy)_3]^{2+}$ sensitized [130], i.e. introduced the anionic POMs into cationic MOF that could overcompensated the charge of MIL-101(Cr), and then the anionic MIL-101(Cr)@POM composites absorbed cationic $[Ru(bpy)_3]^{2+}$ from solution (Fig. 10a). It has been proved that MOF@P₂W₁₅V₃ POM showed better light adsorption activity than isolated MIL-101(Cr) (Fig. 10b and c). Therefore, the performance of photocatalytic hydrogen production of MIL-101(Cr) corporated with different POMs was higher than homogeneous photocatalytic system
(Fig. 10d and e).



Fig. 10. (a) Scheme view for constructing POM@MOF and POM@Photosensitizer@MOF composite materials. UV–vis spectra of $[Ru(bpy)_3]^{2+}$ (48 µvf) solution in the presence of 10 mg (b) isolated MIL-101 and (c) MIL-101 and 80mg P₂W₁₅W (d) Linetics of hydrogen production in the photocatalytic system with different catalyse. (e) Kinetics of hydrogen production in the photocatalytic system with Mo₂S₁₂. Repented with the permission from Ref. [130]. Copyright 2018 Elsevier.

3.2.5 Incorporation of polyoxometalates (POM)

Polyoxometalates (POM) is a class of inorganic polyatomic clusters formed by linking transition metal atoms with oxygen atoms. POM owns excellent redox ability, various structural characteristics and highly negative charges, playing a vital role in catalytic reaction. Particularly, POM has been widely utilized in water-splitting half reaction as it could maintain its structure during intricate electron transfer [131]. However, POM also restrict its catalytic application by small surface area and low stability in aqueous solution [132]. Immobilization of POMs into MOFs has been demonstrated to be a promising approach to optimize the catalytic performance and the structure stability of MOFs. The interactions between the function group of MOFs and POMs dramatically improved catalytic activity. The synergistic effect enhances the stability of both components mutually. For instance, POM (H₃PW₁₂O₄₀) and Pt NPs have been encapsulated into NH₂-MIL-53 [133], in which POM not only stabilized Pt NPs onto the surface of NH₂-MIL-53 MOF but promoted photocatalytic water reduction. At the same time, a polycationic supramolecular MOF (SMOF-1) has been fabricated, and SMOF-1 which adsorbed anionic Wellspe POM also exhibited efficient hydrogen production rate [134]. Co-based which contain earth abundant element has well catalytic properties for ate oxidation. As one of the most typical Co-based POM, [Co₄(H₂O)₂(P has been introduced into MIL-101(Cr) by an ion exchange method The synergistic effect between MIL-101(Cr) and Co-POM enhanced the ph of this composite than single-component. However, due to the lan v sizes of MIL-101(Cr), the Co-POM in the pores of ay and lost its activity. Accordingly, a more appropriate host MIL-101(Cr) will lea MIL-100(Fe) MOF has been investigated to immobilize $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10^-}$ POM and further applied in water oxidation reaction [136]. The results suggested that the TOF and oxygen yield of MIL-100(Fe)/Co-POM ($9.2 \times 10^{-3} \text{ s}^{-1}$; 72%) were higher than MIL-101(Cr)/Co-POM ($7.3 \times 10^{-3} \text{s}^{-1}$; 66%). MOF-545 which consisted of Zrbased clusters and TCPP-H₂ linker has been fabricated [137] (Fig. 11a and b). Different from previous studies that used noble metal composites as photosensitizer, MOF-545 inherited photoactivity from the TCCP-H₂ linker which could adjust the valence band.

After encapsulated $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10^-}$ POM into channels, MOF-545 also possessed Co-POM as catalyst for efficient water oxidation (**Fig. 11c**). Besides, Kong et al. embedded $[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10^-}$ POM into $[Ir(ppy)_2(bpy)]^+$ -derived (ppy = 2phenylpyridine) and $[Ru(bpy)^3]^{2+}$ -derived UiO-MOF (**Fig. 12a-d**), respectively [138], which indicated that Ir-based UiO-MOF exhibited highly photocatalytic performance for HER than the Ru-based UiO-MOF, and the mechanism was similar to Co-POM/MOF for OER (**Fig. 12e**).





Fig. 12. (a) Chemical structures of [Ir(ppy)₂(bpy)]⁺-derived dicarboxylic acid and [Ru(bpy)₃]²⁺-V₉O₃₄)₂]¹⁰⁻ POM. derived dicarboxylic acid. (b) Polyhedral view of the structure of [N (c) Structural model of $[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ POM@MOF as view ng the [1,1,1] direction. (d) Structural model showing unoccupied cavities the central tetr and near $[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ POM-loaded octahedral ca) Schematic showing the injection of upor photoexcitation of the MOF framework to electrons to the [Ni₄(H₂O)₂(PW₉O₃₄)₂]¹⁰⁻ enable proton reduction. Reprinted with more nission from Ref. [138]. Copyright 2016 Wiley.

	MOF	1.4.11	Target	Sacrificial	Production rate	Recycled	Dí
Strategies	photocatalysts	details	reaction	reagent	$(\text{mmol } h^{-1} g^{-1})$	times	Ker.
Corporation	UiO-66	g-C ₃ N ₄	HER	ascerbic raid	$\approx 1 \text{ mmol } h^{-1} \text{ g}^{-1}$		[86]
with	NH ₂ -MIL-125(Ti)	NH ₂ -MIL-125(Ti) g-C ₃ N ₄ , Ni _{15.8} Pd _{2.1} NPs		TEOA	8.7 mmol h ⁻¹ g ⁻¹	3	[90]
semiconductor	NH ₂ -MIL-125(Ti)	g-C ₃ N ₄	HER		$\approx 0.027 \text{ mmol } \text{h}^{-1} \text{ g}^{-1}$		
	UNiMOF (2D)	g-C ₃ N ₄ nanosheets	IER	TEOA	0.4006 mmol h ⁻¹ g ⁻¹	3	[87]
	MIL-101(Cr)	CdS	HER	lactic acid	\approx 7.5 mmol h ⁻¹ g ⁻¹	4	[92]
	MIL-101(Cr)	Au, Cdf	HER	Na ₂ S and NaSO ₃	25 mmol h ⁻¹ g ⁻¹	4	[94]
	MIL-101(Cr)	CDs, CdS	HER	lactic acid	0.488 mmol h ⁻¹ g ⁻¹	4	[95]
	UiO-66	$Cd_{0.5}Zn_{0.5}S$, g- C_3N_4	HER	Na_2S	1.2811 mmol h ⁻¹ g ⁻¹	3	[97]

 Table 2. Photocatalytic performance of MOFs decorated by different substances.



	MIL 101(Cr)	CdS NPs, bromoacetic	UED	Na_2S	30.1 mmol h-l go w-l		
	MIL-101(Cr)	functionalized PTC	пек	and NaSO ₃	39.1 minor n * gcds *		
	MIL-101(Cr)	CdS NPs, benzoic functionalized	HED	Na ₂ S	53.3 mmol h^{-1} gaus ⁻¹		
		РТС		an Nales	55.5 minor nº gcas		
	MIL-101(Cr)	CdS NPs, isonicotinic		Na ₂ S	61.8 mmol h^{-1} g _{cds} ⁻¹		
		functionalized PTC	C	rid NaSO ₃			
	UiO-66-NH ₂	Cd _{0.2} Zn _{0.8} S NPs	HE	Na_2S	5.8465 mmol h ⁻¹ g ⁻¹	4	[96]
			2	and NaSO ₃			
Decoration of	UiO-66-NH ₂	Graphene(50 wtw)	HER	TEOA	41.4 mmol h ⁻¹ g ⁻¹	4	[105]
graphene	UiO-66	graphene, Ni4 ¹ 3(20)/t%)	HER	TEOA	\approx 2.8 mmol h ⁻¹ g ⁻¹		[106]
	UiO-66	griphene	HER	TEOA	\approx 0.015 mmol h ⁻¹ g ⁻¹		
	Cu-BTC	electrostatic interaction assembly	HER	methanol	0.191 mmol h ⁻¹ g ⁻¹		[107]



	MIL-125(Ti)	Pt NPs (photodeposition method)	HER	TEOA	$\approx 0.08 \text{ mmol h}^{-1} \text{ g}^{-1}$		
	NH ₂ -MIL-125(Ti)	Ni _{15.8} Pd _{2.1} NPs	HER	TEOA	8.7 mmol h ⁻¹ g ⁻¹	3	[90]
	UiO-66	Ni ₂ P NPs	HER	TEOA	2 mmol h ⁻¹ g ⁻¹	4	[123]
	NH ₂ -MIL-125(Ti)	Ni ₂ P NPs	HER	TEAL	0.894 mmol h ⁻¹ g ⁻¹	7	[124]
	NH ₂ -MIL-125(Ti)	Pt NPs	HER	TEA	\approx 0.269 mmol h ⁻¹ g ⁻¹		
	UiO-66-NH ₂	NiO NPs	HER	ТЕОА	2.56132 mmol h ⁻¹ g ⁻¹	3	[125]
	UCNPs-		XC)			
	Pt@MOF/Au	UCNPs, Pt NPs, Au NPs	HER	TEOA	0.280 mmol h ⁻¹ g ⁻¹	4	[122]
	(under NIR light)						
	Cd-TBAPy	Pt NRs	HER	TEOA	0.086 mmol h ⁻¹ g ⁻¹		[120]
	Cd-TBAPy	CoPi NPs	OER	AgNO ₃	1.634 mmol h ⁻¹ g ⁻¹		
Sensitization	MIL-101(Cr),	Erythrosin B	HER	TEOA	6.25 mmol h ⁻¹ g ⁻¹		[127]

	UiO-66	Erythrosin B(30 mg)	HER	l-ascorbic acid	0.46 mmol h ⁻¹ g ⁻¹	3	[128]
	LEO 66 NH	cone-calixarene-based dye(200		UED modernel	1.520	2	[120]
	010-00-11112	ppm CHCl ₃ solution)	HEK		1.528 mmor n g	5	[129]
	MIL-101(Cr)	$[Ru(bpy)_3]^{2+}$	HER	FEOL	25.578 mmol h ⁻¹ g ⁻¹		[130]
	MIL-101(Fe)	$[Ru(bpy)_3]^{2+}$	HER	TEOA	21.732 mmol h ⁻¹ g ⁻¹		
	MIL-101(Al)	$[Ru(bpy)_3]^{2+}$	HER	ТЕОА	27.082 mmol h ⁻¹ g ⁻¹		
Incorporation	SMOF-1	Wells-Dawson-type POM	VIER	methanol	3.353 mmol h ⁻¹ g ⁻¹		[134]
of	MIL-101(Cr)	$[Co_4(H_2O)_2(PW_9O_{34})_2]^{10^-}$ POM	OER	$Na_2S_2O_8$	\approx 6.7 mmol h ⁻¹ g ⁻¹		[135]
polyoxometalat	MIL-100(Fe)	[Co ₄ (H ₂ O) ₂ (PW ₉ O ₃₄) ₂) PON	OER	$Na_2S_2O_8$	\approx 7.5 mmol h ⁻¹ g ⁻¹		[136]
es (POM)	MOF-545	[Co ₄ (H ₂ O) ₂ (PW ₉ Q ₃₄) ₂] [↑] POM	OER	$Na_2S_2O_8$	\approx 4 mmol h ⁻¹ g ⁻¹	3	[137]
	[Ir(ppy) ₂ (bpy)] ⁺ -		UED	methanol	$4.4 \text{ mmol } \text{h}^{-1} \text{ a}^{-1}$	2	[129]
	derived UiO-MOF	[1914(112O)2(F 99034)2] FOIM	ΠĽΚ	methanoi	4.4 IIIII0I II g	J	[130]

* If not stated, the light source of photocatalyst refers to visible light.

4. MOF derivatives as photocatalysts

As a highly ordered porous crystalline catalyst with periodical structure, MOFs have been widely employed as sacrificial template or precursor to prepare porous materials (such as porous carbon and metal oxides) by calcination process [140, 141]. The resulting derivatives can largely maintain the initial structures and typologies feature of parent MOFs, and possess dispersed nanoscale subunits, rich active sites and high surface area [142]. These merits have motivated the attempt to utilize MOFs derivatives for photocatalytic application, and the recent decomposition of MOFs derivatives for HER and OER are summarized in Table 3.

4.1 Metal oxides

Among various MOF materials, ZIFs e een explored widely due to its excellent thermal stability and water rance. There are many researches on metal IF as precursors. For example, Au/ZnO oxides which are obtained by nanoparticles ained the calcination of have by glutathione-Au nd the enhanced photocatalytic performance result from the nanoclusters/ZIFefficient charge transfer of Au/ZnO NPs and the surface plasmon resonance (SPR) of Au NPs. Another porous Co₃O₄/CuO also has been constructed by the calcination of ZIF-67/Cu(NO₃)₂•6H₂O at 360 °C [144]. The porous Co₃O₄/CuO catalysts showed excellent water oxidation performance when both photosensitizer ($[Ru(bpy)_3]^{2+}$) and electron acceptor (Na₂S₂O₈) were added (Fig. 13a). It can be ascribe to the heterojunction formed and the sufficient potential of the valence band of Co₃O₄/CuO to drive OER (Fig. 13b). Besides, Lan and co-workers fabricated the porous Pt-doping

ZnO-Co₃O₄ heterojunctions by calcinating the bimetallic ZnCo-ZIF MOFs and depositing Pt NPs [145]. The scanning electron microscope (SEM) and transmission electron microscope (TEM) demonstrated that ZnO-Co₃O₄ maintained the polyhedral morphology of parent ZnCo-ZIF MOF even after doping Pt NPs (Fig. 14a-c). Moreover, owing to the porous structure that inherited from ZnCo-ZIF precursor and the suitable band-structure matching between ZnO (2.7 eV) and Co₃O₄ (2.52 eV) (Fig. 14e), Pt-ZnO-Co₃O₄ also exhibited better photocatalytic performance than individual Co₃O₄ (hydrogen evolution rate: 0.19 mmol $h^{-1} g^{-1}$) and ZnO (hydrogen evolution rate) (hydroge volution rate: 0.22 mmol h^{-1} g⁻¹) (**Fig. 14d**). Furthermore, Su et al. synthesized ternary composites ZnO/rGO/carbon sponge by the carbonization of ZrF-SGO/melamine foam at 350 °C [146], and the ZIF-8 derivatives have been doned with C and N during pyrolyzation process. Hence its adsorption edge ifted to visible light region. This ternary composite possesses porous structure in rited from ZnO and carbon sponge, and the efficient charge transfe ZnO and rGO also make the porous composites capable of degrad taminants and hydrogen evolution.



Fig. 13. (a) Photocatalytic water oxidation cycle in the presence of Co₃O₄/CuO catalyst,

photosensitizer ($[Ru(bpy)_3]^{2+}$) and electron acceptor (Na₂S₂O₈). (b) Band diagram and mechanism of charge separation for Co₃O₄/CuO heterojunctions. Reprinted with the permission from Ref. [144].



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Fig. 14. (a) SEM and (b) TEM images $O(Zn0-Co_3O_4)$. (c) TEM images of Pt-ZnO-Co₃O₄. (d) Photocatalytic hydrogen generation as the function of reaction time over ZnO, Co₃O₄, ZnO-Co₃O₄, and Pt-ZnO-Co₃O₄. (e) Schematic illustration of photoexcited electron transfer and hydrogen generation over the Pt-InO-Co₃O₄. Reprinted with the permission from Ref. [145]. Copyright 2017 Elsevier.

Metal oxides derive from other MOFs also have been explored for photocatalytic applications. For instance, NH₂-MIL-125(Ti) has been used as precursor to prepare hierarchical TiO₂ with exposed active sites and large special surface area [147]. Likewise, the hierarchical TiO₂ also preserved regular structure feature of NH₂-MIL-125(Ti) precursor, and the photocatalytic performance of hierarchical TiO₂ for hydrogen evolution can be enhanced by loading Pd NPs as co-catalyst. Besides, iron oxide nanomaterials could show better visible light adsorption than TiO_2 which has wider band gap [148]. Confined by the undesirable conduction band, Fe_2O_3 derived from MIL-88B(Fe) also has been explored to incorporate with rGO [149], and the synergistic effect between them reflected in the adjustment of conduction band of Fe_2O_3 and the efficient charges separation.

4.2 Porous carbonaceous materials

Except precursors for metal oxides, MOFs could ale as sacrificial templates to construct porous carbonaceous materials. Carb anomaterials derived from MOFs have been regarded as a promising caralys for photocatalytic application ed inder 800 °C, 900 °C and 1000 °C [150, 151]. For example, ZIF-8 has been calcin [152], respectively, and the forme doped graphene analogs almost retained sis temperature was 1000 °C the derivative unbroken structure of ZIF-8. W exhibited the highest p tic efficiency for hydrogen evolution. This may be t of graphitic nitrogen, which maintains the high mobility ascribed to its his of charges. Similarly, He et al. developed a C-ZIF/g-C₃N₄ composite by pyrolysis the mixture of ZIF-8 and melamine at 650 °C [153], and the ZIF-8 derived carbon (denoted as C-ZIF) served as co-catalyst in C-ZIF/g-C₃N₄ system for photocatalytic hydrogen production. Moreover, Zhang et al. applied an in situ calcination method to prepare porous CoO_x-carbon hybrids [154], a series of products have been fabricated by different thermal treatment of ZIF-67. Under near neutral circumstance (pH=8.5) and $[Ru(bpy)_3]^{2+}$ -S₂O₈²⁻ system, CoO_x-carbon hybrids calcinated at 700 °C performed the best photocatalytic activity for OER.

4.3 Others

Templating method also could be used as effective method to prepare other porous materials. Confined by easy recombination of electrons and holes, cadmium sulfde (CdS) has been fabricated by pyrolyzation of MOFs to increase surface area. For example, Xiao et al. selected MIL-53(Al) which loaded Cd(NO₃)₂•4H₂O as sacrificial template to prepare hierarchically porous CdS [155], further enlarged the BET surface area (119 m² g⁻¹), weakened the PL intensity, therefore imp th photocatalytic performance of CdS for hydrogen production. Besides, et al. synthesized NiS/Zn_xCd_{1-x}S catalyst by taking Cd-MOF as temp. te (Fig. 15a) [156], and the elements of the prepared NiS/Zn_{0.5}Cd_{0.5}S homogeneously dispersed over the nanoparticles (Fig. 15b). It unveiled t ifferent ratio of Zn to Cd resulted in different photocatalytic activity of NiS/Z atalyst for hydrogen evolution (Fig. 15c). In this regard, NiS/Zn_{0.5}Co ved a good balance between ZnS which has reduction lution and CdS which has visible light response. ability for hydro



Fig. 15. (a) Schematic illustration of the synthetic procedure for NiS/ZKCGC_xS. (b) EELS elemental mapping images of NiS/Zn_{0.5}Cd_{0.5}S. (c) Comparison of phytocatalytic HER rates of NiS/Zn_xCd_{1-x}S under visible-light irradiation. Reprinted with the paralision from Ref. [156]. Copyright 2018 Wiley.

Moreover, MOFs derivatives derivatives and could act as co-catalyst to replace some noble metals. Containing early-annuant metal clusters, NH₂-MIL-101(Fe) has been cooperated with NiCOD₂ NPs as precursors for boosting the photocatalytic efficiency of g-C₃N₄ [157]. Besides, Ni₂P has been fabricated by the calcination of Ni-BTC and NaH₂PO₂ at 275 °C [158], and it could serve as co-catalyst for CdS photocatalytic system to suppress charge carrier recombination and provide active sites for proton reduction.

Table 3. Photocatalytic performance of MOFs derivatives.



C-ZIF/g-C ₃ N ₄	ZIF-8 (melamine)	650 °C	HER	TEOA	0.0326 mmol h ⁻¹ g ⁻¹	4	[153]
ZnO/rGO/carb	ZIF-						
on sponge	8/GO/melamine	350 °C	HER	methanol	0.0146 mmol h ⁻¹ g ⁻¹	3	[146]
on sponge	foam		•				
ZnO/carbon	ZIF/melamine foam	350 °C	HER	methanol	0.0134 mmol h ⁻¹ g ⁻¹		
sponge							
Hierarchical	NH2-MIL-125(Ti)	400 °C	HER	methanol	48.985 mmol h ⁻¹ g ⁻		[147]
TiO ₂		∂X ∂	~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~		¹ (UV-vis light)		
CN/FeNiP	NH ₂ -MIL-		HER	TEOA	13.81 mmol h ⁻¹ g ⁻¹	5	[157]
(co-catalyst)	101(Fe)/Ni(OH) ₂						
CN/FeP (co-	NH ₂ -MIL-101(Fe)	▼ 350 °C	HER	TEOA	2.73 mmol h ⁻¹ g ⁻¹		
catalyst)					-		



* If not stated, the light source of photocatalyst refers to visible light

5. Conclusions and outlooks

Photocatalytic water splitting, including overall water spitting and water-splitting half reaction, has attracted considerable attention in energy conversion field, and it is regarded as a promising solution of energy crisis. Owning coordination-unsaturated metal sites, uniform and tailorable structure, MOFs are supposed to be an ideal photocatalysts candidate for water splitting. In this review, recent developments of MOFs based- and derived- photocatalysts for water splitting have been summarized, and modification and decoration strategies of MOFs sts have been specifically emphasized. However, compare with other the-art non-MOF photocatalysts for HER/OER (Table 4), we could that MOF based- and derivedphotocatalysts still have space for furth ment. To be closer to industrial application, some critical issues that l er the employment of MOFs should be taken uld focus on removing these obstacles: into consideration, and future re (1) Only few MOFs ow the mal and chemical stability, such as UiO-66 and MILlost MOFs will decompose under light irradiation and the 101. Organic link structure of MOFs will collapse simultaneously, which leads to poor photocatalytic performance. Besides, since the rate of oxygen generation and hydrogen evolution is different, the pH values of aqueous photocatalytic system will fluctuate in a wide range. Consequently, it is prominent to strengthen the durability and stability of MOFs photocatalysts in acid/alkaline environment.

	photocatalyst	HER	OER	Turnover	Ref
				frequency	
MOF-based	PTC ^a / CdS / MIL-101	94.9 mmol (g _{Cds} h) ⁻¹			[139]
photocatalysts	Au@CdS / MIL-101	25 mmol h ⁻¹ g ⁻¹			[94]
	RCGO / U6N ^b	41.4 mmol h^{-1} g ⁻¹		161.7h ⁻¹	[105]
	Mo ₂ S ₁₂ @MIL-101(Al)	27.082 mmol $g^{-1} h^{-1}$	$\mathbf{\hat{\mathbf{A}}}$	31.25 h ⁻¹	[130]
	MoS_2 / UiO-66 / CdS	32.5 mmol $g^{-1} h^{-1}$			[99]
MOF-derived			0.01244 μmol (0.2 g L ⁻¹		
photocatalysts	Co_3O_4 / CuO HPNCs ^c / (ZIF-67 / Cu(NO ₃) ₂ •6H ₂ O)		catalyst after 11 min	$4.9 \times 10^{-3} \text{ s}^{-1}$	[144]
			photoirradiation)		
		48. 85 m hol $g^{-1} h^{-1}$ (UV-			
	$Pd / TiO_2 / (NH_2-MIL-125(Ti))$	vis light)		40.3 h^{-1}	[147]
	Ni ₂ P/CdS / (Ni-BTC MOF)	$33.48 \text{ mmol g}^{-1} \text{ h}^{-1}$			[158]
	NiS / Zn _{0.5} Cd _{0.5} S / (Ni-Zn _x Cd _{1-x}				
	-MOF)	16.78 mmol $g^{-1} h^{-1}$			[156]

Table 4. Comparison of photocatalytic performance of non-MOF photocatalysts, MOFs based- and derived- photocatalysts.

	Pt-ZnO-Co ₃ O ₄ / (ZnCo-ZIF)	7.80 mmol $g^{-1} h^{-1}$		[145]
	HP-CdS _d / (MIL-53(Al) / CdO)	$0.63 \text{ mmol g}^{-1} \text{ h}^{-1}$		[155]
The state-of-the-art	CdS@NiMoS	185.4 mmol $g^{-1} h^{-1}$		[159]
non-MOF	EY ^e /1T-MoSe ₂	75.00 mmol $g^{-1} h^{-1}$	19 h ⁻¹	[160]
photocatalysts	CoP/CdS	254 mmol $g^{-1} h^{-1}$		[161]
	Ni ₂ P/CdS	1200 mmol $g^{-1} h^{-1}$	36 400 h ⁻¹ (for Ni ₂ P)	[162]
	Cring-C ₃ N ₄ ^f	$0.371 \text{ mmol g}^{-1} \text{ h}^{-1}$	nmol $g^{-1} h^{-1}$	[163]
	Pt/Calix-3-TiO ₂	2444 mmol g^{-1} h ⁻¹ for Pt mat ()	498.4 h ⁻¹ (for Pt)	[164]
	8			

(2) Although surface and pore decoration strategies have greatly improved the photocatalytic performance of MOFs photocatalysts and widely applied in experiments of laboratory, there are still exist some barrier block their future industrial application. Firstly, noble metal particles co-catalysts are restricted by excessively high-cost and low recovery rate. There is still lack of research on economical and recyclable cocatalyst. Secondly, the stability of sensitized MOF by organic dye after a long operation should be given enough attention. Specifically, the type and strength of bonds between organic dyes and MOFs should discuss following routines zation. Finally. although post-synthesize modification and decoration have ap in many researches, complicated synthesize process and harsh reaction condition make it lose its competitiveness compared to one-step meth Further exploitation of facile and effective synthesize method is also the us of future researches.

(3) Water-splitting half reaction has been employed widely due to its less band confinement to photocartiys. It most cases, sacrificial agents have been added into this system to construct electrons or holes, which is neither eco-friendly to water resources nor sustainable for practical application. Several researches have combined water-splitting half reaction with high-value chemicals generation by selective oxidation or reduction process to solve this problem. Reports on simultaneously generation of gas product and degradation of refractory contaminants are rare. Hence, replacing sacrificial agent with a refractory contaminant or a precursor of valuable chemical product should stimulate future works in this field.

(4) As mentioned above, sluggish oxygen evolution reaction will hamper the rate of

overall water splitting. Recent reports of electrocatalysis [165, 166] have replaced oxygen evolution reaction by diligent anodic reactions, which could accelerate hydrogen production rate. This also provides a solution for photocatalytic water splitting. Besides, although co-catalyst such as Pt NPs have been frequently used in water splitting system, their weak durability and high-cost make them lost competitiveness. Future works should focus on developing economical and durable cocatalysts [167]. Moreover, MOFs also have good performance in electrocatalytic energy conversion application [168], but few reports have approved MOFs in photoelectrocatalysis water splitting.

(5) Although the photocatalytic mechanism of other protocatalysts have been clearly uncovered [169], the detailed photocatalytic wave splitting mechanism of MOFs is still unclear, which limited the exploration of effective MOFs photocatalysts. Therefore, rigorous experimental design and theoremsal calculations are essential to fill this gap.

In summary, photoetal sticewater splitting has been regarded as the realizable solution to energy provision. As a class of emerging porous crystalline materials with metal clusters and organic linkers, MOFs provide possibility for modification or decoration with particular property for photocatalytic application. Despite there are still exist barriers of MOFs based- and derived- photocatalysts for water splitting application, it is expected that the recent progress will simulate more research on this field and exploit more advanced MOFs for energy conversion application.

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