# Recent advances of Zr based metal organic frameworks photocatalysis: Energy production and environmental remediation

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### Abstract

Recently, Zirconium (Zr) based metal organic frameworks (Zr-MOFs) materials have gathered increasing interest in the field of photocatalysis. Zr-MOFs not only have the large surface area, orderly porous structure, and tunable organic bridging linker/metal clusters as other MOFs, but also possess higher thermal stability and excellent watertolerant than most of other MOFs. In this review, the Zr-MOFs with excellent photocatalytic properties reported in recent years are reviewed. Moreover, the strategies of improving the photocatalytic activity of Zr-MOFs and their applications in water splitting for hydrogen production, carbon dioxide reduction, removal of organic pollutants and Cr(VI) reduction are discussed, in addition, the mechanisms of these processes are also described in detail. Finally, the future developments and challenges of Zr-MOFs photocatalyst are also prospected.

**Keywords:** Metal-organic frameworks; Zr-MOFs; Photocatalysis; Energy production; Environmental remediation.

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# Content

# **1. Introduction**

With the progress of social development and the continuous improvement of industrialization, the serious environmental pollution and energy shortage have become an urgent hindrance need human being to solve [1-4]. Scientists invested heavily in exploring renewable and clean energy in recent decades. Among all kinds of renewable energy, solar energy as a clean and abundant energy has attracted great attention of researchers [5-9]. Photocatalyst has become the most attractive way of solar energy utilization because of its simple synthetic method, low consumption, high photocatalytic efficiency, and has made great progress in recent years [10]. However, photocatalytic performance is still below par for the industrial viability due to low specific surface area, poor response for visible-light and fast recombination of photogenerated electron holes of photocatalysis [11-13]. Therefore, further exploration of new photocatalysts with more effectively and stably is an interesting and significant field.

As an emergent three-dimensional microporous material, metal organic frameworks (MOFs) with considerable surface adsorption capacity, adjustable aperture and numerous catalytically active sites have a great vogue in various fields [14-17]. Among these applications fields, the most classical is to utilize the high adsorption capacity and regulable pore of MOFs, regarding MOFs as microporous materials focused on storage of gases such as  $H_2$ ,  $CH_4$  and  $CO_2$  [18]. Typically, MOFs are designed via the self-assembly of metal ions center and organic linkers, the existence of different metal centers and acid binders allows the pore size, hydro- and/or thermal stability of MOFs to be customized to achieve the desired properties. In recent years, through reasonable selection of metal ions with photosensitive organic ligand, MOFs widely studied as promising photocatalysts for  $H_2$  production [19, 20],  $CO_2$  reduction [21, 22], degradation of organic pollutants [23-25] and heavy metal removal [26, 27]. However, most of current results are considered conceptual, because the over idealized experimental requirements and economical inapplicability can't ensure the suitability

of the materials. In addition, the limited light absorption and low stability in aqueous solution also restrict the application of MOFs in photocatalysis.

In all reported MOFs, Zr-MOFs have shown excellent stability due to the strong Zrcarboxylate interactions as well as the high connection number of the secondary building units (SBUs) [28]. For most reported MOFs, the thermal stability is limited among 350–400 °C, while UiO-66 (UiO = University of Oslo), a type of Zr-MOF, exhibits relatively high thermal stability at the decomposition temperature of 540 °C due to strong Zr-O bonds [29]. This excellent chemical and thermal stability make Zr-MOFs extensively applied to thermal catalysis, encapsulation and drug delivery [30-32]. In addition, Zr-MOFs have been proved that they show excellent water-tolerant across a wide pH range in aqueous media which makes them as prospective materials for the photocatalysis process [33]. Lillerud et al. [34] designed Zr-MOFs for the first time in 2008, which named as UiO-66(Zr). Due to the outstanding structural stability in aqueous solution, the development of UiO-66(Zr) based photocatalysts has attracted wide publicity. Silva et al. [35] first used UiO-66(Zr) as photocatalyst for H<sub>2</sub> production under ultraviolet (UV) light. From then on, Zr-based MOF has been widely reported as a photocatalyst (Table 1).

However, further research have shown that Zr-MOFs exist some inherent weaknesses which limited the application in photocatalysis, such as the Zr-MOFs have suffered from poor photoactivity because of the unsatisfactory exciton productivity and charge migration rate as well as the inconformity between adsorption and catalytic sites [36]. Therefore, it is obliged to design new Zr-MOFs materials according to the targeted requirements [37]. As far as we know, many reviews of MOFs in the field of photocatalysis have been published. However, there are few specific reviews of Zr-MOF in the field of photocatalysis. At the same time, much attention has been concentrated on the research progress of only UiO series Zr-MOFs [38, 39]. In this review, we concentrate on the various Zr-MOFs with excellent photocatalytic properties reported in recent years, not limited to the UiO series. It includes photosensitive Zr-MOFs by direct synthesis, post synthesis modified (PSM) photosensitive Zr-MOFs and the composite of Zr-MOF with other photoactive materials. Furthermore, the strategies

of improving photocatalytic activity of Zr-MOFs and their application in H<sub>2</sub> evolution, CO<sub>2</sub> reduction, removal of organic pollutants and Cr(VI) reduction are discussed systematically. Additionally, the mechanisms of these processes are also described in detail. This review aims to focus on the research progress of the whole Zr-MOFs in the field of photocatalysis and provide suggestions for the future development direction.

#### Table 1

Materials	Ligand	Zr cluster/core	BET (m <sup>2</sup> g <sup>-1</sup> )	Light absorbing edge (nm)	Application	Ref.
UiO-66	BDC	Zr <sub>6</sub> (µ <sub>3</sub> -O) <sub>4</sub> (µ <sub>3</sub> -OH) <sub>4</sub>	NA	300	Hydrogen generation	[35]
			NA	440	Hydrogen generation	[35]
UiO-66-NH <sub>2</sub>	ATA	Zr <sub>6</sub> (µ <sub>3</sub> -O) <sub>4</sub> (µ <sub>3</sub> -OH) <sub>4</sub>	832	450	Aerobic organic transformations	[40]
			756	450	Cr (VI) reduction	[41]
UiO-66-OH	OH-BDC	$Zr_6(\mu_3-O)_4(\mu_3-OH)_4$	788	420	Cr (VI) reduction	[42]
UiO-66-(OH) <sub>2</sub>	(OH) <sub>2</sub> -BDC	$Zr_6(\mu_3-O)_4(\mu_3-OH)_4$	562	490	Cr (VI) reduction	[42]
UiO-66(AN)	AN	$Zr_6(\mu_3-O)_4(\mu_3-OH)_4$	627	510	Degradation of methyl orange	[43]
UiO-66(NA)	NA	Zr <sub>6</sub> (µ <sub>3</sub> -O) <sub>4</sub> (µ <sub>3</sub> -OH) <sub>4</sub>	757	440	Degradation of methyl orange	[43]
UiO-66-NO <sub>2</sub>	NO <sub>2</sub> -BDC	$Zr_6(\mu_3-O)_4(\mu_3-OH)_4$	465	400	Oxidation of As (III)	[44]
Zr-SDCA-NH <sub>2</sub>	NH <sub>2</sub> -H <sub>2</sub> SDCA	Zr <sub>6</sub> (µ <sub>3</sub> -O) <sub>4</sub> (µ <sub>3</sub> -OH) <sub>4</sub>	2546	600	CO <sub>2</sub> reduction	[45]

The Zr-MOFs has been used in the field of photocatalysis in recent few years.

Zn-MOF-74	H <sub>4</sub> DOBDC	$Zr_6(\mu_3-O)_4(\mu_3-OH)_4$	826	594	Removement of glyphosate	[46]
NU-1000	TBAPy	Zr <sub>6</sub> (µ <sub>3</sub> -OH) <sub>8</sub>	2260	500	Nitrate Conversion	[47]
NU-400	Py-DCA	$Zr_6(\mu_3-O)_4(\mu_3-OH)_4$	1325	400	Degradation of organic pollutants	[48]
AUBM-4	Ru(cptpy) <sub>2</sub>	$ZrO_8$	50	660	CO <sub>2</sub> reduction	[49]
DUT-67	H <sub>2</sub> TDC	$Zr_6(\mu_3-O)_4(\mu_3-OH)_4$	723	330	Conversion of thioanisole	[50]
MOF-801	FUM	Zr <sub>6</sub> (µ <sub>3</sub> -O) <sub>4</sub> (µ <sub>3</sub> -OH) <sub>4</sub>	710	NA	Methyl violet 2B decolorization	[51]
MOF-808	BTC	Zr <sub>6</sub> (µ <sub>3</sub> -O) <sub>4</sub> (µ <sub>3</sub> -OH) <sub>4</sub>	1205	300	Hydrogen generation	[52]
NNU-28	ADBEB	$Zr_6(\mu_3-O)_4(\mu_3-OH)_4$	1490	650	CO <sub>2</sub> reduction	[22]
MOF-525	ТСРР	$Zr_6(\mu_3-O)_4(\mu_3-OH)_4$	1485	750	Degradation of arylboronic acids	[53]
Rh-PMOF-1(Zr)	Rh(TCPP)Cl	Zr <sub>6</sub> (µ <sub>3</sub> -O) <sub>8</sub>	3015	750	CO <sub>2</sub> reduction	[54]
PCN-134	[BTB] <sub>2</sub> [TCPP]	$Zr_6(\mu_3-O)_4(\mu_3-OH)_4$	756	NA	Diclofenac reduction	[55]
PCN-222	H <sub>2</sub> TCPP	Zr <sub>6</sub> (µ <sub>3</sub> -OH) <sub>8</sub>	1728	708	CO <sub>2</sub> reduction	[56]
JLU-MOF60	H <sub>4</sub> TCPP	$Zr_6(\mu_3-O)_4(\mu_3-OH)_4$	1553	500	Cr (VI) reduction	[57]

BDC=1,4-benzenedicarboxylate; ATA=2-aminoterephthalate; ANDC=anthracene-9,10-dicarboxylic acid; NADC=naphthalene-1,4-dicarboxylic acid; NO<sub>2</sub>-BDC= NO<sub>2</sub>-1,4-benzenedicarboxylate; H<sub>2</sub>SDCA-NH<sub>2</sub>= 2,2'-diamino-4,4'-stilbenedicarboxylic acid; H<sub>4</sub>DOBDC= 2,5dihydroxyterephtalic acid; TBAPy= tetraphenyl-carboxylated pyrene units; Py-DCA = pyrene-2,7-dicarboxylic acid ; AUBM=American University of Beirut Materials; Ru(cptpy)<sub>2</sub>= 4'-(4-Methoxycarbonylphenyl)2.2':6',2''terpyridine; DUT= Dresden University of Technology; NDC=2,6-naphthalenedicarboxylic acid; H<sub>2</sub>TDC= 2,5-thiophene

dicarboxylic acid; TCPP= tetrakis (4-carboxyphenyl)porphyrin; FUM= fumarate; BTC= 1,3,5-trimesic acid; NNU= Northeast Normal University; ADBEB =4,4'-(anthracene-9,10-diylbis(ethyne-2,1-diyl)) dibenzoic acid; PCN= porous coordination network; BTB= 4,4',4'',-Benzene1,3,5-triyl-tris; H<sub>2</sub>TCPP= tetrakis (4-carboxyphenyl)porphyrin; H<sub>4</sub>TCPP= 2,3,5,6-tetrakis (4-carboxyphenyl)pyrazine.

# 2. Photosensitive Zr-MOFs

# 2.1 Direct synthesis of photosensitive Zr-MOFs

Most of the reported Zr-MOFs were prepared by the reaction of Zr metal precursor, organic ligand and modulator under specific experimental conditions via a direct onestep synthesis. Particularly, stable Zr-MOF photocatalytic materials can be constructed by designing organic ligands with excellent light absorption ability and combining with Zr-clusters according Zr–O bonds. Organic ligand is the primary factor to determine the photocatalytic performance of Zr-MOFs. In this section, visible light driven Zr-MOFs by direct synthesis in recent years are introduced (Fig. 1), according to different types of organic ligands, they can basically be divided into Zr-carboxylate MOFs, Zr-Porphyrin MOFs and Zr-Pyridine MOFs. In addition, Zr-MOFs synthesized by other ligands for photocatalysis are also summarized in Table 1.



**Fig. 1.** (a) Direct synthesis of Zr-MOF photocatalysts; (b) the common ligands for synthesis of Zr-carboxylate MOF (BDC=1,4-benzene-dicarboxylate; BPDC=4,4' biphenyl-dicarboxylate; TPDC= terphenyl dicarboxylate); (c) the common ligand for synthesis of Zr-Porphyrin MOF (TCPP=tetrakis (4-carboxyphenyl) porphyrin); (d) the common ligand that contain pyridine motifs for synthesis of Zr-Pyridine MOF (BPY=bipyridine; TPY=terpyridine, Q=quinoline).

#### 2.1.1 Zr-carboxylate MOFs

The typical Zr-carboxylate MOF is Face-centered cubic (**fcu**) UiO-66  $(Zr_6O_4(OH)_4(CO_2)_{12})$ , which is formed via the assembly of 6 Zr atoms with 8  $\mu_3$ -O or  $\mu_3$ -OH bridged oxygen atoms connect with 12 BDC (1,4-benzene-dicarboxylate) linkers. A representation of this structure is shown in Fig. 2a. The robust coordination interlinkage between the Zr-O cluster and carboxylate ligand lead to the outstanding chemical and thermal stabilities of UiO-66. Subsequently, a series of Zr-carboxylate MOFs were reported by changing different carboxylate-based ligands, such as UiO-67 and UiO-68 (Fig.2b and c) with 4,4' biphenyl-dicarboxylate (BPDC) and terphenyl dicarboxylate (TPDC) as linker, respectively.



**Fig. 2.** The structure of (a) UiO-66; (b) UiO-67; (c) UiO-68. Zirconium, oxygen, carbon, and hydrogen atoms are red, blue, gray, and white, respectively. Reproduced with permission from Ref. [34]. Copyright 2008 American Chemical Society.

Normally, the surface properties of the UiO-66(Zr) can be regulated by selecting organic ligands with different functional groups such as amines, hydroxyls, halogens, alkyls, nitro, etc. [58]. In addition, though functionalizing the matrix structure of UiO-66(Zr), extra catalytic active sites could be introduced into MOFs, which can artificially

adjusted band gap of Zr-MOFs, so that Zr-MOFs can also show photocatalytic activity under visible light. The most typical functional group is -NH<sub>2</sub> which has been demonstrated to be the most efficient component to narrow the raw band gap of UiO-66 framework compare with other UiO-66-X Zr-MOFs (e. g. UiO-66-OH, UiO-66-NO<sub>2</sub> UiO-66-Cl, UiO-66-Br) [44, 59, 60]. Researches showed that the improvement of visible-light utilization was mainly attribute to the conjugated  $\Pi$  electron diversion from the amine-containing chromophores to the Zr center and creating Lewis-basic sites in the structure. For this reason, absorption band-edge of UiO-66-NH<sub>2</sub> could reached 450 nm [40], the corresponding band gap energy (Eg) is 2.72 eV. Due to its narrowed band gap (compared with UiO-66(Zr), 4.13 eV) with more efficient light absorption ability and electron donor properties, UiO-66-NH<sub>2</sub> widely studied as an outstanding photocatalyst for H<sub>2</sub> evolution [35], CO<sub>2</sub> reduction [61], degradation of organic pollution [40] and reduction of heavy metal [41].

In previous researches, the improvement of photocatalytic activity of Zr-MOFs is mostly described the wide visible absorption range, so that the researches of UiO-66-NH<sub>2</sub> in photocatalysis are more common than others UiO-66-X. However, Mu et al [62]. constructed a series of UiO-66-X (X=H, Br, NH<sub>2</sub>, (OH)<sub>2</sub>) and investigating their photodegradability for Rhodamine B (Rh B). Surprisingly, the result showed that UiO-66-(OH)<sub>2</sub> and UiO-66-NH<sub>2</sub> which had relatively narrow bandgaps (the Eg of UiO-66-(OH)<sub>2</sub>=2.69 eV and the Eg of UiO-66-NH<sub>2</sub>=2.83 eV,) did not presented higher photodegradability compared to UiO-66 (Eg=3.91eV) and UiO-66-Br (3.69 eV. Mott-Schottky plots and photocurrent spectra were performed to defined the band potential of UiO-66-X and elucidated the surprising phenomenon. The result showed that the V<sub>CB</sub> of UiO-66 and UiO-66-Br (-0.72 V and -0.76 V vs. NHE) were more positive than the potential of the excited Rh B (Rh B\*, -1.09 V vs. NHE) which made the electron transfer from the Rh B\* to the CB of UiO-66 or UiO-66-Br was thermodynamically advantageous. However, the V<sub>CB</sub> of UiO-66-NH<sub>2</sub> and UiO-66-(OH)<sub>2</sub> (-1.01 V and -1.06 V vs. NHE) were very close to Rh B\*. Therefore, the transfer of electrons between Rh B\* and Zr-MOF was limited. This leaded to the rapid recombination of photogenerated carriers, while the Rh B\* also easily go back to the unexcited state.

Combined with the above analyses, compared with the band gap of photocatalyst, the efficient and rapid electronic transfer and dye sensitization effect were more important element for photodegrade Rh B.

To further explore the mechanism of functional groups on the photocatalytic process of Zr-MOFs, Chen et al. [63] constructed a variety of UiO-66-X<sub>2</sub> (X=SO<sub>3</sub>H, SH and SCH<sub>3</sub>) (Fig. 3a). The UV–vis spectra illustrated that the band edges of UiO-66-(SCH<sub>3</sub>)<sub>2</sub>, UiO-66-(SH)<sub>2</sub> and UiO-66-(SO<sub>3</sub>H)<sub>2</sub> were reached 470, 440 and 425 nm, the corresponding Eg was 2.8 eV, 3.0 eV and 3.2 eV, respectively (Fig. 3b). With platinum (Pt) (1.5 wt%) as co-catalyst, the H<sub>2</sub> production value of Pt/UiO-66(SCH<sub>3</sub>)<sub>2</sub>, Pt/UiO-66-(SH)<sub>2</sub> and Pt/UiO-66-(SO<sub>3</sub>H)<sub>2</sub> after 60 min were 6.96, 2.97 and 0 µmol/g, respectively (Fig. 3c). Surprisingly, the Eg of UiO-66-NH<sub>2</sub> (2.72 eV) was similar to UiO-66-(SCH<sub>3</sub>)<sub>2</sub> (2.80 eV), while UiO-66-NH<sub>2</sub> had no photocatalytic activity for H<sub>2</sub> production even with Pt as co-catalyst under the same conditions [64]. This difference in photocatalytic effect can be explained by the different effects of -NH<sub>2</sub> and -SCH<sub>3</sub> on the aromatic ring of terephthalate linker in UiO-66(Zr).



**Fig. 3.** (a) Synthesis of UiO-66-X (X=SO<sub>3</sub>H, SH and SCH<sub>3</sub>); (b) UV–vis absorption spectra of UiO-66-X; (c) H<sub>2</sub> generation efficiency of Pt/UiO-66-X<sub>2</sub>. Reprinted with permission from Ref. [63]. Copyright 2019 Applied Catalysis B: Environmental.

Therefore, these facts suggest that Eg is not the only element determining the photocatalytic performance of functional group modified Zr-carboxylate MOFs. Different molecule sizes and geometries of functional group display different influence on the aromatic ring of the terephthalate bonds of Zr-MOFs. In addition, the potential relationship between contaminants and Zr-MOFs were significant to be considered.

#### 2.1.2 Zr-Porphyrin MOFs

Because of the broad range of light response range, porphyrins as a type of photosensitizers have shown outstanding long lifetime of the triplet excited state [65]. Furthermore, Zr-porphyrin MOFs which composed of Zr center and porphyrins or metallo porphyrin-based linkers have drew wide attention due to their excellent textural property, tunable functionalities and chemical stability [33]. The porphyrins-based ligand in Zr-MOF behaves as a light-harvesting group, which reacts with pollutants or gases adsorbed on the surface of Zr-MOF, thereby enhancing the photocatalytic efficiency [56]. In 2012, Morris et al. [66] successfully synthesized two Zr-porphyrins MOFs, MOF-525 and MOF-545 (Fig. 4). The synthesized MOFs had great BET surface proportion with 2620 and 2260 m<sup>2</sup>/g respectively. Because of the incorporation of Zr-O bonds, this two Zr-MOFs possessed exceptional chemical stability which maintaining their three-dimensional structure under aqueous and organic phases. These characteristics indicated that MOF-525 and MOF-545 could be used as materials with excellent adsorption capacity and high stability. The photocatalytic performance of MOF-525 and MOF-545 had been studied by Toyao's group [53] and Xu'group [56], respectively. UV-vis absorption spectra illustrated that MOF-525 and MOF-545 inherited the feature of the porphyrin ligand, which showed a wide and intense absorption in the region of 350-750 nm and 200-800 nm respectively. This was a huge improvement compared with UiO series Zr-MOFs, which was also reflected in their photocatalytic performance. MOF-525 presented a higher visible light driven catalytic efficiency and stability for arylboronic acid degradation than the corresponding homogeneous catalyst H<sub>4</sub>TCPP. In addition, they found a special electron trapped state in MOF-525 which effectively restricted the rapid electron-hole recombination. Therefore, MOF-525 supplied long-lifetime electrons for the photoreduction.



**Fig. 4.** Crystal structures of MOF-525 and MOF-545. Pores in the frameworks are illustrated by yellow spheres. Atom colors: zirconium, green; carbon, black; nitrogen, dark green; oxygen, red. Hydrogen atoms are omitted. Reprinted with permission from Ref. [67]. Copyright 2012 Inorganic Chemistry.

Porphyrin-based linkers could be metallized by artificially synthesize. Compared with nonmetal porphyrin, the lifetime of excited-states molecules which formed by metalloporphyrin under visible light is longer [68]. For example, a Zr-porphyrin (Rh) MOF (RhPMOF-1(Zr)) was synthesized directly by a metallized porphyrin ligand (Rh(TCPP)Cl) with Zr<sub>6</sub> center [54] (Fig. 5a). The new Zr-MOF contained 3D channels and the Rh-porphyrin groups were exposed in the cavities (Fig. 5(b-e)). The solid-state UV–vis absorption spectra indicated Rh-PMOF-1 exhibited outstanding optical characteristics with extended absorption boundary reached 750 nm (Fig. 5(f-g)). Rh-PMOF-1(Zr) displayed obviously better catalytic activity towards CO<sub>2</sub> reduction which up to 99% selectivity compared to pure PCN-224 (Fig. 5h). The reason for the enhancement of photocatalytic performance of Rh-PMOF-1(Zr) could be concluded as follows: (1) The compound possibility of electron-hole pairs descended when the Rh-porphyrin group was integrated. (2) The long-lived excited-states of Rh-PMOF-1 (207

µs under vacuum) is important for an efficient photocatalyst.



**Fig. 5.** (a) Syntheses of Rh-PMOF-1; (b-e) Crystal structures of Rh-PMOF-1(Zr): (b) 6connecting  $Zr_6O_8$  cluster; (c) Rh(TCPP)Cl; (d, e) 3D views (the axil Cl atom are omitted for clarity). Rh (brown), N (blue), O (red), Cl (bright green) and C (gray); (f) The steady-state UV-vis spectra of Rh(TCPP)Cl, Rh-PMOF-1 and PCN-224; (g) Photoluminescence spectra of Rh(TCPP)Cl and Rh-PMOF-1 excited at 376 nm; (h) The amount of HCOO<sup>-1</sup> (µmol/µmolcat) produced in different reaction time. Reprinted with permission from Ref. [54], copyright 2018 Applied Catalysis B: Environmental.

Recently, Boyer et al. [69] synthesized a series Zr-porphyrins (Zn) MOFs (MOF-525(Zn), MOF-545(Zn), PCN-223(Zn) and PCN-224(Zn)) as heterogeneous photocatalysts (Fig. 6a). Fig. 6b confirmed that MOF-525 had minimum size (0.18  $\mu$ m x 0.18  $\mu$ m) compared with other Zr-porphyrins (Zn) MOFs (PCN-223 (Zn), 0.32  $\mu$ m x 0.52  $\mu$ m; MOF-545 (Zn), 0.19  $\mu$ m x 0.58  $\mu$ m; PCN-224 (Zn), 0.69  $\mu$ m x 0.69  $\mu$ m). Polymerization kinetics (Fig. 6(c-e)) were studied to investigate the photocatalytic activity of mediated polymerization of methyl acrylate (MA) by using these Zrporphyrins (Zn) MOFs as photocatalysts under visible light irradiation. MOF-525 (Zn) exhibited superior performance compared with other Zr-MOFs (Zn) due to its small size and Fig. 6g confirmed that the polymerization was controlled by photomediated. Furthermore, Zr-porphyrins (Zn) MOFs displayed better polymerization efficiency and reusability compared to non-metallated Zr-porphyrins MOFs (MOF-525) (Fig. 6f and Fig. 6h).



**Fig. 6.** (a) Crystal structures of porphyrinic Zr-MOFs (Zn); (b) TEM micrographs of porphyrinic Zr-MOFs (Zn) (scare bar = 0.5  $\mu$ m); (c-e) The kinetic plot of ln([M]0/[M]t) vs exposure time, (c) without TEA in nitrogen (d) with TEA in nitrogen (e) with TEA in oxygen; (f) Kinetics of MA were performed under LED light irradiation ( $\lambda$ max= 565 nm, 9 mW/cm<sup>2</sup>) with a ratio of [MA]: [BTPA]: [TEA] = 200: 1: 1 using MOF-525 and MOF-525 (Zn) as photocatalysts (0.5 mg/mL); (g) Kinetics of MOF-525 (Zn) catalysed PET-RAFT polymerization with the light ON/OFF periods; (h) The recycling test of MOF-525 (Zn); PET-RAFT polymerization. Reprinted with permission from Ref. [69]. Copyright 2020 Angewandte Chemie-International Edition.

In conclusion, porphyrins are frequently applied to constructed MOF photocatalysts. It is attribute to the excellent textural property, broad visible light response range and long lifetime of excited state of porphyrin ligands. In addition, porphyrins are generally devoid of cytotoxicity in the absence of light, which is important in environmental applications. Therefore, the combination of water stability, high porosity, relatively large pore size environment friendly and photoactivity makes Zr-porphyrin MOFs act attractive photocatalyst material.

#### 2.1.3 Zr-Pyridine MOFs

Because of their excellent redox ability and long lifetime of photoexcited molecule, the incorporation of pyridine and its derivatives (e.g. bipyridine (bpy), terpyridine (tpy), quinoline and metallized pyridine.) in the ligands of MOFs has been proved an useful method to intensify the light absorption properties of the Zr-MOFs [70]. Zr<sup>4+</sup> framework is a significant member in stabilizing the catalytic species and boosting the photocatalytic activity of pyridine ligands. Zr-MOFs modified by pyridine ligands serve as versatile platform can effectively couple these functional components, achieving the conversion of solar energy to energy products. Therefore, pyridine functionalized Zr-MOFs, due to their plasticity of ligands and the stability of Zr-O framework, encourage researchers to explored this type of materials with better photocatalytic performance.

For example, by the incorporation of Ru and Co-based photosensitizer (PS) into UiO-67(bpy), the single-site MOF system Co-Ru-UiO-67(bpy) was synthesized directly [19]. The absorption edge of Co-Ru-UiO-67(bpy) extended to 750 nm compared to UiO-67(Zr) due to the incorporation of 2,2-bipyridine-5,5-dicarboxylic acid ligands in CO and Ru complexes. The photocatalytic activity and stability of Co-Ru-UiO-67(bpy) for H<sub>2</sub> evolution was studied. Under the illumination of visible light, Co-Ru-UiO-67(bpy) reached 27 853 mol H<sub>2</sub>/g after 40 h and displayed constant activity for at least three runs during the recycling experiments. In 2019, by the incorporation of the photoactive Ru(cptpy)<sub>2</sub> ligand into ZrO<sub>8</sub> cluster, Elcheikh Mahmoud et al. [49] successfully synthesized a new chemically stable Zr-MOFs, which named AUBM-4 (Fig. 7a and Fig. 7b). The optical band gap of this new Zr-MOF was calculated to be 1.88 eV, corresponding to the 660 nm absorption edge (Fig. 7c(I)). The excellent light absorption ability made AUBM-4 possessed great ability for photocatalytic CO<sub>2</sub> reduction. The HCOO<sup>-</sup> production increased linearly and the average rate of formation was 366  $\mu$ mol·g<sup>-1</sup>·h<sup>-1</sup> under the visible light (Fig. 7c(II)). The outstanding efficiency of this catalytic photoreduction could be explained that the long launch lifetime of the photosensitive Ru based ligands in AUBM-4. In addition, the authors speculated that the fast metal to ligands charge migration between ruthenium and cptpy generated cptpy<sup>-</sup>. Finally, CO<sub>2</sub> coordinated with Zr metal center which promoted the charge transfer from the cptpy<sup>--</sup> to the coordinated CO<sub>2</sub> (Fig. 7d).



**Fig. 7**. (a) Synthesis of Ru(cptpy)<sub>2</sub> linker and AUBM-4 Crystals; (b) Crystal structure of AUBM-4: view along x axis (I), selected adjacent chains showing the  $\pi$ - $\pi$  interactions (II), the four chains are in different colors (III), Zr–Ru–Zr chain of AUBM-4 (Ru: gold; Zr: green; C: black; O: red; N: blue) (IV), side view of two of the adjacent linear chains presented in cyan and turquoise (V); (c) Photoluminescence spectra of Ru(cptpy)<sub>2</sub> and AUBM-4 (I), time resolved luminescence traces at 520 nm of AUBM-4 crystals suspended in acetonitrile (red) and for Ru(cptpy)<sub>2</sub> suspended in chloroform (black) or dissolved in acetonitrile (blue) (II); (d) Proposed mechanism for CO<sub>2</sub> photoreduction over AUBM-4 under visible light irradiation. Reprinted with permission from Ref. [49], copyright 2019 Journal of the American Chemical Society.

Zr-pyridine MOFs can adsorb a large amount of  $CO_2$  and photocatalytic degradation of  $CO_2$  in situ because of the excellent surface adsorption. In this case, the photocatalytic effect of Zr-pyridine MOFs mainly focused on the reduction of  $CO_2$ . Recently, researchers are exploring its performance in photocatalytic removal of organic pollutants. Wei et al [71]. synthesized three high stable Ir-Zr MOFs (Zr<sub>6</sub>-Irphen, Zr<sub>6</sub>-IrbpyOMe and Zr<sub>6</sub>-Irbpy) by using bipyridine-Ir(III) complexes methyl-2-phenylquinoline-4-carboxylate; ([Ir(pqcMe)<sub>2</sub>L]Cl; pqcMe= L=Irbpy, IrbpyOMe and Irphen) as organic linkers (Fig. 8) and tested the visible photocatalytic effects for the conversion of sulfide to sulfoxide. [Ir(pqcMe)<sub>2</sub>L]Cl consisted with cyclometalated Ir(III) complexes and 2-phenylquinoline (pq). Cyclometalated Ir(III) complexes had excellent intersystem-crossing ability and long excited triplet lifetimes [72], 2-phenylquinoline as a derivative of pyridine was an excellent ligand which had been demonstrated the triplet lifetime of  $[Ir(pq)_2(proline)]$  [73]. Therefore,  $Zr_6$ -Irphen displayed the optimum photocatalytic performance for sulfide-sulfoxide conversion. With the addition of polar protic solvent, the photocatalytic sulfoxidation reaction reached 100% yield within 6 h. This example showed that pyridine and its derivatives could form new ligands by anchoring specific components and synthesizing new Zr-MOF, which displayed efficient photocatalytic effect for degradation of refractory organic pollutants.



**Fig. 8**. (a) Synthesis of [Ir(pqcMe)<sub>2</sub>Cl]<sub>2</sub> dimer precursor; (b) synthesis of [Ir(pqcMe)<sub>2</sub>L]Cl linkers; (c) single-crystal structures of [Ir(pqcMe)<sub>2</sub>L]<sup>+</sup> linkers (the length are measured between the C atoms

from both of the carboxylate); (d) construction of Ir(III)–Zr MOFs. Reprinted with permission from Ref. [71]. Copyright 2019 ACS Appl. Mater. Interfaces.

# 2.2 Post synthesis modified of photosensitive Zr-MOFs

PSM is an important method to produce new functionalized MOFs. The presynthesized functional units (metal center or organic ligands) lead into the synthetic tunability and modularity of MOFs might result in interesting structures with the desired characteristics. In particular, the ability to encapsulate photo-active molecules and catalytically active molecular species within the confined nano spaces of MOFs affords the opportunity to construct powerful solar energy conversion systems [74]. In addition, the stability of these new MOF materials in aqueous solution and high temperature environment is an important factor to be considered. In this case, it has been widely reported that new photocatalytic materials prepared by post synthetic modification of photoactive molecules embedded in Zr-MOFs. According to the different synthetic sites on Zr-MOF, it can be divided into three types: covalent linking of functional groups, postsynthetic photoactive ligands and postsynthetic exchange of metal center (Fig. 9).



**Fig. 9.** Post synthesis of Zr-MOF (take  $Zr_6$  center as an example), (a) Covalent linking of functional groups; (b) postsynthetic photoactive ligands; (c) postsynthetic exchange of metal center.

# 2.2.1 Covalent linking of functional groups

The reaction based on the covalent Linking with pendant functional groups of Zr-MOFs has been widely reported by PSM method (Fig. 8a), such as amine groups, azide groups and sulfonic acid groups [75]. In this pendant groups, the amine groups of UiO-66-NH<sub>2</sub> with the wealth of chemical transformations possible and had been extensively studied. In 2012, the covalent synthesis modifications for -NH<sub>2</sub> functional group of UiO-66-NH<sub>2</sub> by vapor method was reported for the first time. In the next few years, by covalently linking with the amine group of UiO-66-NH<sub>2</sub>, many novel Zr-MOFs had been prepared and applied in many fields such as heterogeneous catalyst [76, 77], adsorption [78, 79] and anticancer [80].

Recently, the researchers found that covalently linking the photosensitive materials with the functional groups of Zr-MOFs can improved the photocatalytic efficiency of Zr-MOFs without losing the stability and large specific surface area of Zr-MOFs. For example, in 2020, PIU (PI-UiO) were prepared by an amidation reaction between UiO-66-NH<sub>2</sub> and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) [81]. Considering -NH<sub>2</sub> pendant spread on the surface of UiO-66-NH<sub>2</sub>, the PTCDA molecule and -NH<sub>2</sub> pendant of UiO-66-NH<sub>2</sub> to form PI by amidation reaction (Fig. 10a). The TEM and SEM images showed that the morphology of PIU unchanged with the increase of PTCDA content (Fig. 10(b-e)). The covalently linking PTCDA with UiO-66-NH<sub>2</sub> broadens the response wavelength range to 700 nm. Moreover, the PI was a system conjugated planar which displayed sustained electronic affinity and great efficient separation of electron and hole. For the above reasons, PIU exhibited excellent performance for TC photocatalytic degradation and remained good catalytic stability after three cycles.



**Fig. 10.** (a) The synthetic route of PIU; (b,c) SEM and TEM images of UiO. (d,e) SEM and TEM images of PIU. Reprinted with permission from Ref. [81], copyright 2020 Journal of Photochemistry & Photobiology A: Chemistry.

Kumar and coworkers [82] reported a new Zr-MOF by utilizing PSM of an amine functionalized UiO-66(Zr) formed amide linkage with EOSIN-Y. EOSIN-Y is one of organo-photo redox dyes with high efficiency photocatalytic ability. However, the difficulty of separation and toxicity limit its further development. In this work, the post modified EY@UiO-66-NH<sub>2</sub> avoided the difficulty of homogeneous catalytic separation and the adverse effects of toxic organic dye on the environment had been controlled. Furthermore, UiO-68-Fe-bpy (Fig. 11a) was synthesized by amine–aldehyde condensation between UiO-68-NH<sub>2</sub> and 4'methyl-[2,2'-bipyridine]-4-carbaldehyde [83]. Compared with pure UiO-68, the visible absorption boundary of UiO-68-Fe-bpy was extended to 750 nm. UiO-68-Fe-bpy exhibited outstanding photocatalytic performance for CO<sub>2</sub> reduction (about 10 times that of UiO-68-NH<sub>2</sub>), suggesting that the incorporated Fe(bpy)Cl<sub>3</sub> played an important role in photocatalytic process (Fig. 11b). Additionally, the recycling experiments showed that UiO-68-Fe-bpy remained good catalytic stability during the three runs (Fig. 11c).



**Fig. 11.** (a) Synthesis of UiO-68-Fe-bpy; (b) Photocatalytic CO evolution of UiO-68-NH<sub>2</sub>, TPDC-Fe-bpy and UiO-68-Fe-bpy; (c) Recycling performance of UiO-68-NH<sub>2</sub> and UiO-68-Fe-bpy. Reprinted with permission from Ref. [83], copyright 2021 Dalton Transactions.

The above work proved that the covalent linkage of functional groups is an efficient method for the modification of Zr-MOF on the premise of retaining the original morphology and structural. Although this strategy has been explored less as photocatalysis, the research results in recent years are encouraging. Compared with the incorporation of another catalytically materials (especially those containing precious metal) into Zr-MOFs, the covalent linking with functional groups of Zr-MOFs is simpler, lower cost and effectively avoid the separation of heterogeneous catalyst.

#### 2.2.2 Postsynthetic photoactive ligands

By incorporation of metal complex-based photosensitizers into the organic ligands of pre-synthesised Zr-MOF has been considered an effective strategy to prepare novel photocatalysts. Compared to the metal ions embedded in Zr-MOF by direct synthesis, the PSM increase the conversion rate of metal ions thus providing more active sites for catalytic reaction [84]. For example, UiO-67-Co and UiO-67-Re was constructed though a post metallization strategy [85]. The exchange capacity of Co and Re was determined by inductively coupled plasma massspectrometry (ICP-MS). The result displayed 53% and 82% of the original ligands had been functionalized with Re and Co respectively, therefore, UiO-67-Co showed superior photocatalytic efficiency for CO<sub>2</sub> reduction compared with UiO-67-Re. Furthermore, the introduction of photosensitive contained organic ligands into pre-synthesized Zr-MOFs could significantly improve the absorption capacity for visible light. UiO-67 is a representative Zr-MOF, the poor visible light absorption capacity limits its development as a photocatalyst. Recently, four Ru- or Rh- based visible light responsive organic ligands were incorporated into pre-synthesized UiO-67 as metal linkers by PSM to exchange the original dicarboxylate bpdc ligands [86]. The light absorption boundary of these post synthesized Zr-MOFs reached 500 nm. Therefore, the optical absorption range of UiO-67 was successfully extended to visible light.

Zr-MOFs can be used as a platform for connecting metal photosensitizers and catalytic active centers. In this case, the integration of photosensitizers and catalytic active centers in a molecular platform was achieved, which could enhanced the charge transfer between antennas and catalytic active centers [87]. For instance, Karmakar et al. [74] synthesized a train of Zr-MOFs (Zr-MBA-MOF, Zr-MBA-MOF(Ru), Zr-MBA-MOF(Re) and Zr-MBA-MOF(Re/Ru)) via post-synthetic ligand exchange. Zr-MBA-MOF(Re/Ru) was synthesized by using Ru<sup>II</sup>-based clusters ([Ru(bpy)<sub>2</sub>]<sup>2+</sup>) as photosensitizer and Re<sup>I</sup>-based group ([Re(CO)<sub>5</sub>Cl]) as molecular catalyst. Zr-MBA-MOF(Re) and Zr-MBA-MOF(Ru) was prepared by the same method when only Re<sup>I</sup>-based molecular catalyst or Ru<sup>II</sup>-based photosensitizer was added (Fig. 12). Finally, the

author tested the photocatalytic CO<sub>2</sub> reduction of Zr-MBA-MOF(Ru), Zr-MBA-MOF(Re) and Zr-MBA-MOF(Re/Ru) in aqueous solution with no sacrificial electron donor added. The results indicated that Zr-MBA-MOF(Re/Ru) displayed highly efficient conversion of CO<sub>2</sub>-to-CO with an optimum yield rate of 440 mmol g<sup>-1</sup> h<sup>-1</sup> while only a few CO<sub>2</sub> reduced product was obtained by using Zr-MBA-MOF(Re) and Zr-MBA-MOF(Ru) as the photocatalyst. In addition, the rate of CO<sub>2</sub> reduction with Zr-MBA-MOF(Re/Ru) heterogeneous catalyst was 53 times higher than [MBA-Ru(bpy)<sub>2</sub>]Cl<sub>2</sub> and [MBA-Re(CO)<sub>3</sub>Cl] homogeneous catalysts.

In summary, postsynthetic metalation of organic ligands of pre-synthesised Zr-MOF has been determined as an effective strategy to synthesize new Zr-MOFs with excellent photocatalytic ability. This new heterogeneous photocatalyst combines the advantages of Zr-MOF and photosensitive molecular complexes, and display a higher photocatalytic performance than the original homogeneous catalyst. However, molecular polymers contained noble metals such as Pt, Ru and Ir incorporated into Zr-MOFs are most reported, the economic problem of material synthesis hinders its development. In the future development, looking for suitable molecular complexes based on abundant elements in earth is necessary. Furthermore, the purpose and performance of these photocatalyst need to be further improved, and the photocatalytic mechanism needs to be further implemented.



**Fig. 12.** Schematic for the construction of Zr-MBA-MOF(Ru), Zr-MBA-MOF(Re) and Zr-MBA-MOF(Re/Ru) via post-synthetic linker exchange and immobilization of the molecular photosensitizer and catalyst toward CO<sub>2</sub> reduction. Reprinted with permission from Ref. [74], copyright 2021 Energy & Environmental Science.

#### 2.2.3 Postsynthetic exchange of metal center

Completely or selectively exchanging metal centers is another way of PSM to promote the light capture capability of Zr-MOF. UiO-66(Zr) is the most reported Zr-MOF for metal center exchange and Ti<sup>4+</sup> is a common ion exchanged with Zr<sup>4+</sup> in UiO-66(Zr) [88]. Partial substitution of Zr by Ti can effectively increase light absorption range though the introduction of intra band gap states into frameworks. The pioneering research of Ti<sup>4+</sup> introduced into the metal center of Zr-MOF through PAM to form Zr/Ti-MOF was proposed by Lee et al. [89], and its photocatalytic performance under illumination of visible light was also studied. As is illustrated in Fig. 13, UiO-66(Zr/Ti)-NH<sub>2</sub> and **1**(Zr/Ti) (Zr<sub>4.3</sub>Ti<sub>1.7</sub>O<sub>4</sub>(OH)<sub>4</sub>(C<sub>8</sub>H<sub>7</sub>O<sub>4</sub>N)<sub>5.17</sub>(C<sub>8</sub>H<sub>8</sub>O<sub>4</sub>N<sub>2</sub>)<sub>0.83</sub>) were synthesized

via two steps facile hydrothermal reaction. The diffuse reflectance spectra showed that two band edges were obtained for 1(Zr/Ti) at 503 nm and 748 nm. It was indicated that a new energy level was introduced into 1(Zr/Ti), which made 1(Zr/Ti) showed great photocatalytic efficiency and stability for carbon dioxide reduction.



**Fig. 13.** Synthesis of mixed-ligand MOFs 1(Zr/Ti) and UiO-66(Zr/Ti)-NH<sub>2</sub>. Reprinted with permission from Ref. [89], copyright 2015 Chem Commun.

The previously reported solvothermal approach usually takes several days. In order to shorten the preparation time, Tu et al. [90] developed a microwave-assisted method to introduce Ti into the UiO-66(Zr) which was completed within a few hours. Specifically, TiCp<sub>2</sub>Cl<sub>2</sub> and UiO-66(Zr) were thoroughly mixed in 60 mL DMF, then the mixture was transferred to microwave reactor, incubated at 120 °C, finally, UiO-66(Zr/Ti)-M (synthesized though microwave assisted) were successfully prepared after filtration and rinsing. The results showed the exchange rate of UiO-66(Zr/Ti)-M rose to 50% after only 4 h. For comparison, UiO-66(Zr/Ti)-S displayed (designed via a solvothermal method) only about 35% exchange rate after 2 days and still less than 60% after 8 days. This developed method greatly shortened the synthesis time compared with the traditional method previously reported, which was very promising in practical utility. He et al. [91] proposed the incorporation of Ti in Zr-porphyrins MOFs (PCN-224) via a simple PSM process (Fig. 14a). After cation exchange for 48 h, the Ti-Zr exchange rate reached 33.7%. UV-vis spectra (Fig. 14b) illustrated the introduction of Ti shortened the band gap of original PCN-224. Mott-Schottky plot (Fig. 14d and Fig. 14e) indicated the replacement of Ti made significant effect to the V<sub>CB</sub> which improved charge transfer efficiency between TCPP and oxo-clusters thus transformed more adsorbed  $O_2$  into  $O_2^-$  (Fig. 14c). Therefore, the photocatalytic efficiency of PCN-224(Zr/Ti) for MB degradation and Se(VI) reduction was outstanding which obviously higher than ZrO<sub>2</sub>, TiO<sub>2</sub>, and other reported MOFs (Fig. 14(f-g)). As we all known, the incorporation of precious metal to porphyrinic core could improve the photocatalytic activities of Zr-porphyrins MOFs, however, it requires high cost for amplification production. Fortunately, this study provided a replaceable suggestion for the improvement of photocatalytic efficiency of Zr-porphyrins MOFs.



**Fig. 14.** (a) Synthesis of PCN-224(Zr/Ti) via PSM based on cation exchange; (b) Diffuse reflectance UV-vis spectra of PCN-224 and PCN-224(Zr/Ti); (c) the proposed mechanism involving a band structure for the enhancement of photo-redox catalytic properties of PCN-224 based on Ti incorporation; (d-e) Mott-Schottky plot of PCN-224 (d) and PCN-224 (Zr/Ti) (e); (f) concentration ratio of MB evolved during the photodegradation process by using various photocatalysts; (g) AFS signal intensity of SeH<sub>2</sub> generated via the photo-reduction of Se(VI) by using various catalysts. Reprinted with permission from Ref. [91], copyright 2018 Chem Commun.

Except for Ti, the complete or partial metal substitutions with Cerium (Ce), hafnium (Hf), Thorium (Th) and Uranium (U) in the  $Zr_6O_4(OH)_4$  nodes have become feasible as well [92]. Among these new UiO-66 frameworks, only UiO-66(Ce) is favorable for ligand-to-metal charge transfer (LMCT) because the low-lying nature of the empty 4f

orbitals of  $Ce^{4+}$  leads to a negative  $E_{LMCT}$ . Therefore, the incorporation of  $Ce^{4+}$  into the metal center of MOFs is considered to be a promising strategy to stabilize the excited state of LMCT and improve the photocatalytic activity [93]. Inspired by this conclusion, Melillo et al. [94] constructed a series of UiO-66(M) (M: Zr, Ce, Zr/Ti, Zr/Ce and Zr/Ce/Ti) by partially or completely replacing Zr in UiO-66(Zr). The absorption spectrum showed that the introduction of Ti<sup>4+</sup> resulted in the red shift of original UiO-66(Zr) and the absorption band of UiO-66(Zr/Ce/Ti) expanded up to 600 nm (Fig. 15b). The photocatalytic performance of these MOFs for overall water splitting was studied. Comparison of Fig. 15c and Fig. 15d showed that UiO-66 only showed photocatalytic activity in the UV region. UiO-66(Ce) remained almost unchanged photocatalytic activity when it was under the the UV-vis or visible light, which means that the light response of UiO-66(Ce) was mainly from visible light. UiO-66(Zr/Ce/Ti) showed the best photocatalytic performance for water splitting, no matter under the irradiation of UV-vis or visible light. It was worth noting that UiO-66(Ce) displayed highest visible absorption capacity, but it was much less active than UiO-66(Zr/Ce/Ti) indicated that polymetallic composition played an important role. The emission spectra of acetonitrile suspensions of sample illustrated that UiO-66(Zr/Ce/Ti) showed lower emission intensity, which meant that the possibility of charge recombination was lower than other samples (Fig. 15e). Therefore, the polymetallic composition was conducive to higher charge separation, which improved the photocatalytic efficiency of the material. In addition, Ti was acting as a mediator in the charge transfer, which enhanced the separation and migration of photogenerated exciton and thus resulting in overall water splitting.



**Fig. 15.** (a) SEM image and elemental EDX mapping for UiO-66(Zr/Ce/Ti); (b) Diffuse reflectance UV–vis spectra of a) UiO-66(Zr), b) UiO-66 (Zr/Ti), c) UiO-66(Zr/Ce), d) UiO-66(Zr/Ce/Ti), e) UiO-66(Ce). The inset (at right) corresponds to a magnification of the 400-650 nm region for plots a, b, c and d; (c-d) Photocatalytic gas evolution using different UiO-66 as photocatalysts upon irradiation with UV–vis light (c) or exclusively with visible light (d); (e) Emission spectra ([exc=266 nm) of acetonitrile suspensions of a) UiO66(Zr), b) UiO-66(Zr/Ti), c) UiO-66(Zr/Ce), d) UiO-66(Zr/Ce/Ti), and e) UiO-66(Ce). Reprinted with permission from Ref. [94], copyright 2020 Applied Catalysis B: Environmental.

In a word, the mixed metals MOFs can effectively improve the photocatalytic efficiency through adding intra band gap states to narrow the band gap of original MOF. In addition, multimetallic center can also promote the photocatalytic performance by improving the possibility of charge separation and the survival time of excited state Specifically, for Zr-MOF, the CB and VB are dominated by organic linker, the metal center is the most important factor that restricts its photocatalytic efficiency.

# 3. Doping of Zr-MOF photocatalyst

The photocatalytic activity of Zr-MOFs or other light-harvesting materials in

photocatalytic process is intensely related to the efficient generation of e<sup>-</sup> and h<sup>+</sup>, fast transmission path, and as many reactive active site as possible [95]. However, almost no Zr-MOF monomer meets all the above requirements. As a result, the selection of appropriate co-catalysts or other light-harvesting materials for doping with Zr-MOF has raised concern [96]. The Zr-MOF based heterogeneous photocatalysts could exhibit obvious superiority than the original MOFs due to the synergistic effect [97-99]. In this section, the heterogeneous photocatalytic systems by doping co-catalyst or light-harvesting materials in Zr-MOFs in recent years are introduced, including Zr-MOFs/metal NPs, Zr-MOFs/metal oxide, Zr-MOFs/metal sulfides, Zr-MOFs/metal halides, Zr-MOFs/metal free semiconductors and Zr-MOFs/polyoxometalates. Normally, co-catalyst or light-harvesting materials are usually compounded with Zr MOF in three ways: on the surface, in the pore and as membranes loaded with Zr-MOF (Fig. 16). Additionally, the photocatalytic mechanisms of these heterogeneous structure will be described in detail.



**Fig. 16.** The Zr-MOF based heterogeneous photocatalytic systems. (a) photoactive materials on the surface of Zr-MOF; (b) photoactive materials in the pore of Zr-MOF; (c) photoactive materials

as membranes loaded with Zr-MOF.

#### 3.1 Zr-MOFs/metal NPs

Because of high fermi energy levels, metal nano particles (NPs) are expected to be use as co-catalyst to achieve the efficient photocatalytic process. Normally, metal NPs doped Zr-MOFs can improve the visible light response range compared with the pure Zr-MOFs. In the last decade, UiO-66(Zr) was the most commonly used Zr-MOF as the carriers of doped metal NPs, and the most commonly used metal NPs are precious metal such as Au, Ag, Pt and Pd [100-104]. Furthermore, the bimetallic alloys doped Zr-MOFs were also reported recently. For example, AgPd@UIO-66-NH<sub>2</sub> was constructed presented excellent activity for H<sub>2</sub> evolution from formic acid without any additives [105]. Yin et al. [106] successfully synthesized Au/Pd@UiO-66-NH<sub>2</sub> composite though a facile absorption/reduction process [107]. By comparing the conversion of benzaldehyde under the same reaction, Au/Pd@UiO-66-NH<sub>2</sub> composites showed high catalyst activity for the removal of benzaldehyde (100%). Furthermore, Parida et al. [108] tested the visible light driven liquid-phase Suzuki–Miyaura coupling (SMC) reaction of Au/Pd@UiO-66-NH<sub>2</sub> [108].

Not only UiO series Zr-MOFs, but also other Zr-MOFs doped with metal NPs have been reported recently. For example, MOF-808  $(Zr_6O_4(OH)_4(BTC)_2(HCOO)_6,$ BTC=1,3,5-trimesic acid) showed strong adsorption capacity, good chemical stability, reusable and other excellent characteristics which had been widely studied for hydrolysis [109], catalytic [110], heavy metal removal [111] and so on. However, the broad band gap (3.9 eV) restricted the application of MOF-808 for photocatalyst. Recently, Xu et al. [52] successfully synthesized two kinds Pd@MOF-808(Pd@MOF-808-a and Pd@MOF-808-b) by simple solution method (Fig. 17). After introducing Pd NPs of MOF-808, because of the strong conductivity of Pd NPs, its enriched photoelectrons and improved the absorptivity and light utilization of MOF-808 materials. In addition, the band gap of Pd@MOF-808 decreased and its photocatalytic activity was enhanced. Photocatalytic H<sub>2</sub> production experiments displayed the optimum productivity of Pd@MOF-808 was up to 236  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>, while MOF-808 presented no H<sub>2</sub> production capacity under the same conditions.



**Fig. 17.** Schematic illustration for synthesizing Pd@MOF-808-a (a) and Pd@MOF-808-b (b). Reprinted with permission from Ref. [52], copyright 2019 Journal of Materials Science.

Another example was NNU-28(Zr) (Table 1), which was first synthesized in 2016 [22]. Recently, Xing et al. [112] explored the photocatalytic H<sub>2</sub> production performance of NNU-28 by loading Pt NPs on the surface of NNU-28. The optimum visible light driven H<sub>2</sub> evolution of Pt/NNU-28 (1.0 wt% Pt loaded) reached 0.70 mmol·h<sup>-1</sup>·g<sup>-1</sup>, it was 220 times higher than original NNU-28 under same condition. because of the  $\pi$ - $\pi$ \* transitions [113] of the ADBEB ligand (Table 1), NNU-28 presented broad absorption bands in 300–580 nm region. The band edge kept almost unchanged demonstrated the introduction of Pt NPs did not changed the band gap of NNU-28 (Fig. 18b). Photoluminescence (PL) spectrum (Fig. 18c) illustrated that Pt NPs was effective to inhibit the recombination of the e<sup>-</sup> and h<sup>+</sup>. However, the PL spectra of NNU-28 with different Pt NPs loaded were similar, their photocatalytic performance was quite different. It was suggested the limited recombination of e<sup>-</sup> and h<sup>+</sup> by Pt loaded was not the key reasons for the improved photocatalytic activity of NNU-28. The mechanism of enhanced H<sub>2</sub> evolution was further studied by surface photovoltage (SPV) technique.

As shown in Fig. 18d, the SPV response of either the pristine NNU-28 or the Pt/NNU-28 was negative value, which indicated the downward band bending toward surface/interfaces [114, 115]. In this case, the photogenerated charge carriers transfered from NNU-28 to Pt NPs so that the photocatalytic efficiency was improved (Fig. 18e).



**Fig. 18.** (a) Scanning electron microscopy (SEM) image of the resulting NNU-28; (b) diffuse reflectance UV–Vis spectra of the NNU-28 decorated with different amount of Pt NPs; (c) PL spectra of the NNU-28 decorated with different amount of Pt NPs catalysts; (d) SPV spectra of the NNU-28 decorated by different amount of Pt NPs catalysts: (e) Schematic representation of the band structure and the proposed mechanism for immigration of the photogenerated electrons to the catalyst to contribute to the visible light driven H<sub>2</sub> evolution, in which L-ascorbic acid (LAA) is
used as the electronic sacrificial agent, and dehydroascorbic acid (dHA) represents the oxidation product of LAA. Reprinted with permission from Ref. [112], copyright 2020 Applied Surface Science.

Zr-MOFs/metal NPs photocatalytic system has been widely studied and reported in recent ten years. In early studies, Zr-MOFs/metal NPs has been proved to have excellent photocatalytic ability and stability [100, 116]. However, high expense of metal nanoparticles and the fussy synthesis process limit the application of Zr-MOFs combined with metal nanoparticles. In recent years, researchers focus on finding efficient methods to prepare efficient and economic Zr-MOFs/metal NPs photocatalytic system. Recently, Yin and coworkers [117] made delightful achievements by depositing and encapsulating non-precious metals (Cu) on UiO-66(Zr). As shown in Fig. 19, Cu@UiO-66(Zr) was constructed by traditional double-solvent process. In this case, Cu quantum dots (QDs) only to be covered in the cavities of Zr-MOF. Through an advanced double-solvent process, Cu/Cu@UiO-66 were synthesized by the incorporation of Cu QDs into the cavities while load Cu NPs onto the surface of MOF. Cu/Cu@UiO-66 displayed optimum photocatalytic efficiency for oxidation of aromatic alcohols. This phenomenon was the result of synergism between Cu-MOF Schottky junction and Cu plasmon resonance. Considering that Cu/Cu@UiO-66 was composed of UiO-66 and nonprecious metal Cu, this was a significant breakthrough of this study.



Fig. 19. Schematic for the synthesis of Cu@UiO-66 and Cu/Cu@UiO-66 via double-solvent

process and advanced double-solvent process, respectively. Reprinted with permission from Ref. [117], copyright 2019 Applied Catalysis B: Environmental.

#### 3.2 Zr-MOFs/metal oxide

Metal oxide semiconductors have been widely used and considered as an effective photocatalytic material due to their excellent structure-directing effect with the modifiable and tunable energy band structures that exhibit novel physical and chemical properties [118]. However, the short carrier lifetime, low carrier mobility and uncontrollable particle size are seriously restricted the photocatalytic activity of metal oxide semiconductors [119]. The combination of Zr-MOFs and metal oxide semiconductors can absorb the characteristics of both sides and make up for their shortcomings. Specifically, the well-distributed nanopores in Zr-MOFs provide a fixed microenvironments for the restricted growth of metal oxide semiconductors, and the organic ligands of Zr-MOF can be used as anchors to stabilize these nanoclusters. Furthermore, Zr-MOFs exhibits high chemical, thermal stability and high structural stability which can improve the application range and stability of metal oxide semiconductors. On the other hand, metal oxides semiconductors make up for the low visible light utilization of Zr-MOFs. For example, α-Fe<sub>2</sub>O<sub>3</sub>@UiO-66(Zr) composites was constructed through an absorption and transformation process [120]. UiO-66(Zr) was enlarged the pore diameters by thermally treated to remove a part of the functional group, then the neutral iron acetylacetonate was encapsulated into the UiO-66(Zr) and formed  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoclusters by a thermal conversion (Fig. 20a). The diameter of the prepared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was effectively controlled at 3 nm, which restricted the recombination of photoinduced  $e^-$  and  $h^+$  (Fig. 20(b-e)). Additionally, the band gap of UiO-66 decreases from 3.90 eV to 2.07 eV after the introduction of aFe<sub>2</sub>O<sub>3</sub> nanoclusters. Other Zr-MOFs/metal oxide semiconductors composites with similar mechanism were also been reported such as UiO-66/BiVO<sub>4</sub> [121], ZnO/Zr-MOF(bpy) [122], UiO-66/Ag<sub>3</sub>PO<sub>4</sub> [123] UiO-66/Bi<sub>2</sub>MoO<sub>6</sub> [23] and so on. All these researches indicated that Zr-MOFs/metal oxide semiconductors composites were promising photocatalytic materials.



**Fig. 20.** (a) Scheme of preparation process of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@UiO-66 heterostructure; (b-c) dark-field (b) and bright-field (c) TEM images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@UiO-66; (d) the high-magnification TEM images of local region, the responding structure scheme inserted in the (d); (e) high-resolution TEM image images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@UiO-66 calcined at 700 °C in air atmosphere. Reprinted with permission from Ref. [120], copyright 2019 Applied Surface Science.

Furthermore, Zr-MOFs can exhibit photocatalytic activity upon visible light by ligand modification, which has been described above. In this case, Zr-MOFs doped

metal oxides can form typical heterojunction to improve the effectively generation and transfer of photogenerated carriers. Normally, the common heterostructures reported including Type I, Type II, Schottky junction, p-n heterojunction and Z-scheme heterojunction [124]. For instance, Subudhi et al. [125] constructed a p-n junction architecture of CoTiO<sub>3</sub> integrated UiO-66-NH<sub>2</sub> via hydrothermal method. CoTiO<sub>3</sub> was p-type semiconductors, while UiO-66-NH<sub>2</sub> acted as typical n-type semiconductors. Under the irradiation of sun light, they were excited to produce  $e^{-}$  and  $h^{+}$ . Subsequently, the hole will divert from CoTiO3 to the Zr-MOF while the electrons shift from Zr-MOF to the CoTiO<sub>3</sub>. In the end, an electric field was formed at the heterointerface between Zr-MOF and CoTiO<sub>3</sub>. The photoinduced electron and hole will be effective separated by electric field assist. Fig. 21a illustrated the HRTEM of the composite (1:1) CoTiO<sub>3</sub>/ UiO-66-NH2 showed a distinct different boundary slices verified the formation of heterojunction and SAED pattern confirmed the intimate contact of CoTiO<sub>3</sub> with UiO-66-NH<sub>2</sub> (Fig. 21b and Fig. 21c). Fig. 21d showed a smaller circle indicated the recombination probability of electron-hole pairs was reduced by electric field assist, which led to an improvement of electrical conductivity of the composites. Additionally, compared to original Zr-MOF, CoTiO<sub>3</sub>/ UiO-66-NH<sub>2</sub> (1:1) showed higher transient current which indicated the lifetime of charge carriers was improved (Fig. 21f).



**Fig. 21.** (a) Fringe of (1:1) CoTiO<sub>3</sub>/UiO-66-NH<sub>2</sub> (b) SAED pattern of UiO-66-NH<sub>2</sub> (c) SAED pattern of (1:1) CoTiO<sub>3</sub>/UiO-66-NH<sub>2</sub>; (d) EIS representation of UiO-66-NH<sub>2</sub>, CoTiO<sub>3</sub> and CoTiO<sub>3</sub>/UiO-66-NH<sub>2</sub> (1:1); (e) Schematic representation of proposed p-n heterojunction mechanism for NFX photodegradation; (f) transient current representation of UiO-66-NH<sub>2</sub> and (1:1) CoTiO<sub>3</sub>/UiO-66-NH<sub>2</sub>. Reprinted with permission from Ref. [119]. Copyright 2020 Journal of Colloid and Interface Science.

Recently, a novel oxygen-defective Z-scheme photocatalyst, UiO-66-NH<sub>2</sub>/O-ZnO, was synthesized [126]. The formation of HCOOH and Mott–Schottky plots determined the formation of Z-scheme heterojunction (Fig. 22a and Fig. 22b). Commonly, the V<sub>CB</sub> of O-ZnO (-0.39 V vs NHE) was more positive than the potential of CO<sub>2</sub>/HCOOH (-0.61 V vs NHE), the formation of HCOOH was thermodynamically unavailable. In this case, Z-Scheme heterojunction could be considered (Fig. 22c). Both O-ZnO and UiO-66-NH<sub>2</sub> generated electron and hole under the sun light, subsequently, the e<sup>-</sup> and h<sup>+</sup> deposited in the CB of UiO-66-NH<sub>2</sub> and VB of O-ZnO because of effect of internal electric field. Therefore, the lifetime of photogenerated e<sup>-</sup> and h<sup>+</sup> was extended. The results of photocatalytic reduction of CO<sub>2</sub> further proved that Z-scheme O-ZnO/UiO-66-NH<sub>2</sub> had excellent photo reductive activity, with the yields of HCOOH and CH<sub>3</sub>OH reaches 6.40 and 34.85 µmol g<sup>-1</sup>h<sup>-1</sup>. It is significantly superior than type II O-ZnO/UiO-66-NH<sub>2</sub>.



**Fig. 22.** Mott–Schottky plots of (a) O-ZnO and (b) UiO-66-NH<sub>2</sub> and (c) Z-scheme mechanism. Reprinted with permission from Ref. [126]. Copyright 2019 ACS Applied Materials & Interfaces.

#### 3.3 Zr-MOFs/metal sulfide

Great progress has been made in photocatalytic removal of organic pollutants by Zr-MOFs/metal oxides systems. However, most of these composites are large band gap and low conduction band which restricted their application for energy production [127]. To solve this problem, metal sulfides, one of traditional semiconductor materials such as CdS, In<sub>2</sub>S<sub>3</sub>, ZnIn<sub>2</sub>S<sub>4</sub> etc, has attracted widespread attention owing to their superior photoelectric properties [128, 129]. Furthermore, due to the adjustable structure and thermochemical stability of Zr-MOFs, metal sulfides combined with Zr-MOFs can synthesize new photocatalytic materials with higher catalysis properties and stability [119].

So far, many Zr-MOFs/metal sulfide heterogeneous materials have been of great

significance for photocatalytic environmental remediation and energy production under visible light irradiation [130-142]. Most of them presented the performance of photocatalytic energy production (H<sub>2</sub> evolution and CO<sub>2</sub> reduction), which is one aspect that Zr-MOFs/metal sulfides are better than Zr-MOFs/metal oxides. For example, MoS<sub>2</sub> nanosheets modified UiO-66-(COOH)<sub>2</sub>/ZnIn<sub>2</sub>S<sub>4</sub> heterogeneous materials was designed by a simple hydrothermal methods [134] (Fig. 23f). The pristine ZnIn<sub>2</sub>S<sub>4</sub> exhibited as flower-like microspheres (Fig. 23a), and the structure had no apparent change after the incorporation of MoS<sub>2</sub> and UiO-66-(COOH)<sub>2</sub> (Fig. 23(b-d)). Among the reported Zr-MOF/metal sulfides, this composite presented the highest photocatalytic efficiency for 138, 139, 141, 142]. The  $H_2$ evolution [133, optimized UiO-66-(COOH)<sub>2</sub>/MoS<sub>2</sub>/ZnIn<sub>2</sub>S<sub>4</sub> showed the maximum H<sub>2</sub> evolution rate of 18.794 mmol h<sup>-1</sup>  $g^{-1}$ . The remarkable improvement of photocatalytic activity could be due to the formation of Z-scheme heterojunction improved the redox ability and separation efficiency of e<sup>-</sup> and h<sup>-</sup>. In addition, the large surface area of UiO-66-(COOH)<sub>2</sub> provided more active sites to adsorbed reactants (Fig. 23g).



Fig. 23. (a-c) FESEM image of ZnIn<sub>2</sub>S<sub>4</sub> (a), FESEM image of MoS<sub>2</sub>/ZnIn<sub>2</sub>S<sub>4</sub> (b) and UiO-66-

(COOH)<sub>2</sub>/MoS<sub>2</sub>/ZnIn<sub>2</sub>S<sub>4</sub> (c); (d) TEM image of UiO-66-(COOH)<sub>2</sub>/MoS<sub>2</sub>/ZnIn<sub>2</sub>S<sub>4</sub>; (e) Elemental mapping images of UiO-66-(COOH)<sub>2</sub>/MoS<sub>2</sub>/ZnIn<sub>2</sub>S<sub>4</sub>; (f) schematic illustration of the synthesis of 3D hierarchical UiO-66-(COOH)<sub>2</sub>/ZnIn<sub>2</sub>S<sub>4</sub> decorated with cocatalyst MoS<sub>2</sub> nanosheets; (g) the proposed Z-scheme photocatalytic mechanism. Reprinted with permission from Ref. [134]. Copyright 2020 Chemical Engineering Journal.

Overall water splitting has always been a bottleneck in the field of photocatalysis. Photocatalyst should not only be stable in aqueous solution, but also fulfill the thermodynamic requirements of water splitting. In 2020, the photocatalytic water splitting efficiency of Zr-MOF/metal sulfide was studied by Subudhi et al. [135]. The UiO-66-NH<sub>2</sub>/MoS<sub>2</sub> composite was prepared through a facile hydrothermal technique, the fabrication of MoS<sub>2</sub> on exposed surface of MOF. The p-n junction heterojunction of UiO-66-NH<sub>2</sub>/MoS<sub>2</sub> was confirmed by UV-DRS and Mott–Schottky analyses. Therefore, the internal electric field generation caused effective separation of H<sub>2</sub> and O<sub>2</sub> evolution reached 513 µmol/h and 264 µmol/h respectively. These results showed that Zr-MOFs has a broad prospect for photocatalytic energy production by compounding with metal sulfides.

#### 3.4 Zr-MOFs/metal halides

Metal halide semiconductors have aroused considerable concern because of their excellent light capture capability. Most notably, silver halides AgX (e. g., AgCl, AgBr, AgI) often forms metallic Ag on its surface which produced surface plasmon resonance (SPR) effect. In addition, the emergence of small amount metallic Ag bringing about the transformation from AgX/Zr-MOF type II heterojunction to AgX/Ag/Zr-MOF Z-scheme heterojunction. For instance, Pan et al. [143] constructed AgI/UiO-66-NH<sub>2</sub> photocatalyst by an facile ion exchange strategy (Fig. 24a). Through the immobilized of AgI on the surface of UiO-66-NH<sub>2</sub>, the photocatalytic tetracycline (TC) degradation of composite enhanced obviously compared to pure UiO-66-NH<sub>2</sub>. Considering the presence of a small amount of Ag and great photocorrosion inhibition performance of

AgI/UiO-66-NH<sub>2</sub>, the Z-scheme mechanism was suitable in elucidating the charge transfer mechanism (Fig. 24b). The tiny amounts of Ag could be used as the charge transfer bridge of Z-scheme heterojunction and bring SPR effect thus improving the separation efficiency of photogenerated carriers [144]. Other AgX/Zr-MOF, such as AgBr/UiO-66-NH<sub>2</sub> [145], AgCl/UiO-66-NH<sub>2</sub> [146] were also constructed and they also had similar Z-scheme heterostructures. These works illustrated the great application potential of AgX/Zr-MOF heterogeneous photocatalyst in environment remediation.



**Fig. 24.** (a) Formation mechanism of AgI/UiO-66-NH<sub>2</sub> composites; (b) Schematic illustration of the charge pathway and degradation mechanism in AgI/UiO-66-NH<sub>2</sub>. Reprinted with permission from Ref. [143]. Copyright 2020 Chemical Engineering Journal.

#### 3.5 Zr-MOFs/metal free semiconductors

As a low cost, easy synthesis, environment friendly nonmetallic semiconductor, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has been the focus of intense interest in the field of materials in recent years [147-149]. Because of the narrow band gap and  $\pi$ - $\pi$ conjugated structures, g-C<sub>3</sub>N<sub>4</sub> has also aroused a lot of interest for photocatalysis [150]. However, the photocatalytic activity of pure g-C<sub>3</sub>N<sub>4</sub> is strictly restricted due to its weak surface adsorption capacity and low light utilization [151]. Zr-MOF has been considered to an ideal material to solved these deficiencies of g-C<sub>3</sub>N<sub>4</sub> due to its strong adsorption. For instance, Zhang et al. [152] designed g-C<sub>3</sub>N<sub>4</sub>/UiO-66 nanohybrid via a facile hydrothermal strategy. The visible light driven photodegradation efficiency of the heterogeneous photocatalyst for Rh B was 6.0 and 3.3 times faster than pure g-C<sub>3</sub>N<sub>4</sub> and UiO-66 respectively. The composite displayed strong photocurrent response caused efficient transmission of optically excited electrons between UiO-66 and g-C<sub>3</sub>N<sub>4</sub>. Recently, some studies have further explored the photocatalysis of other Zr-MOF/ g-C<sub>3</sub>N<sub>4</sub>. In 2020, UiO-66-NH-BT@g-C<sub>3</sub>N<sub>4</sub> heterogeneous materials were synthesized by the benzothiadiazole functionalized Zr-MOF doped with g-C<sub>3</sub>N<sub>4</sub> through a facile stepby-step assembly strategy [153]. Fig. 25a showed that UiO-66-NH-BT and UiO-66-NH-BT@g-C<sub>3</sub>N<sub>4</sub> possessed an improved absorption for visible light. The photocurrent measurements further determined that benzothiadiazole could efficiently promote the transmission of photogenerated carrier (Fig. 25b). The result of photocatalytic removal of sulfamethoxazole (SMZ) showed the heterogeneous photocatalyst had an excellent degradation efficiency (97.6%) compared with pure UiO-66-NH<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> also verified the above optical properties. Additionally, the production of an n-n heterojunction boundary between UiO-66-NH-BT and g-C<sub>3</sub>N<sub>4</sub> further enhanced the efficiency of charge transfer (Fig. 25c).



**Fig. 25.** (a) UV-vis diffuse reflectance spectra of the as-prepared photocatalysts; (b) the transient photocurrent response of the as-prepared photocatalysts; (c) Schematic diagram for the photocatalytic degradation mechanism of contaminants over UiO-66-NH-BT@g-C<sub>3</sub>N<sub>4</sub> under visible light irradiation. Reprinted with permission from Ref. [153], copyright 2020 Catalysis Science & Technology.

In addition to g-C<sub>3</sub>N<sub>4</sub>, the heterojunction interaction between other metal free semiconductors and Zr-MOFs has also been reported in recent years. For example, The UIO-66-NH<sub>2</sub>/GR (graphene) was designed in situ assembly by a microwave-assisted synthesis route. This method made UIO-66-NH<sub>2</sub> nanocrystals highly dispersed on GR surface which resulted in highly improved the interaction between GR and UiO-66-NH<sub>2</sub> and allowed more active surface for visible light absorption [21]. Zhang et al. [20] prepared a g-C<sub>3</sub>N<sub>4</sub>/UiO-66-NH<sub>2</sub>@CDs ternary photocatalyst by incorporating CDs (Carbon nanodots) into the pores of UiO-66-NH<sub>2</sub>. This ternary photocatalyst displayed a H<sub>2</sub> production rate of 2.930 mmol·g<sup>-1</sup>·h<sup>-1</sup> which was 32 and 39 times higher than that of pure g-C<sub>3</sub>N<sub>4</sub> and UiO-66-NH<sub>2</sub>, respectively. By combining VB<sub>2</sub> (vitamin B<sub>2</sub>) and UiO-66, the VB<sub>2</sub>@UiO-66 was prepared though one-step synthesis strategy and displayed highly activity for visible light transformation of benzyl alcohol to benzaldehyde [154].

#### **3.6 Zr-MOFs/Polyoxometalates**

Polyoxometalates (POMs) are soluble anionic metal oxide clusters of d-block transition metals in high oxidation states (e. g.  $W^{6+}$ ,  $Mo^{5+}$ ,  $Mo^{6+}$ ,  $V^{4+}$ ,  $V^{5+}$ ) exhibiting specific properties in different fields [155, 156]. POMs possess efficient redox characteristics and reversible multi-electrons transformation. However, the low specific area and self-aggregation in solution greatly hindered the catalytic efficiency of original POMs. Researchers around the world are committed to resolve these shortcomings, among which the incorporation of POMs to heterogeneous photocatalysts was widely studied [157, 158]. Recently, the successful incorporation of POM into Zr-MOF cavities had been reported. These materials integrated the advantages of Zr-MOF and POM, which has been confirmed to be a novel efficient photocatalyst [159-163]. For example, Parida et al.[160] constructed HPW@UiO-66 composites via a hydrothermal strategy. The composite exhibited outstanding photocatalytic activity of H<sub>2</sub> evolution and antibiotic tetracycline hydrochloride degradation which might be attributed to the interaction of Zr–O–W between the metal nodes of UiO-66 and PW<sub>12</sub>O<sub>40</sub><sup>-3</sup>, resulting in effective exciton splitting.

Furthermore, by introducing a POM ( $[(PW_9O_{34})_2Co_4(H_2O)_2]^{10-}$ ) into the cavities of a Zr-porphyrins MOF (MOF-545), a noble metal-free heterogeneous photosystem, named P<sub>2</sub>W<sub>18</sub>Co<sub>4</sub>@MOF-545 had been constructed [159]. As is shown in Fig. 26a and Fig. 26b, the side and top views of P<sub>2</sub>W<sub>18</sub>Co<sub>4</sub>@MOF-545 reflected the POM was encapsulated in two Zr<sub>6</sub> clusters linked by two porphyrin linkers. The composite was immobilized by a tight hydrogen bonds meshwork on the POM–MOF interface (Fig. 26c). These results determined that the successful combination of the two components. Furthermore, the photocatalytic water oxidation performance of P<sub>2</sub>W<sub>18</sub>Co<sub>4</sub>@MOF-545 was evaluated. The result revealed that the composite displayed excellent activity with a turnover number (per POM) of 70 after 60 min reaction. For comparison, pure MOF-545 did not showed any  $O_2$  evolution under same condition (Fig. 26d). The reaction mechanism illustrated in Figure. 26e, the excited TCPP-MOF was produced in the existence of sun light and sacrificial reagents, then the singer electron redox occurred on POMs. After accumulation of this oxidizing essential factors on the POM, water was oxidized to  $O_2$ .



**Fig. 26.** (a-c) Computed position of the  $P_2W_{18}Co_4$  POM in MOF-545, "Side" (a) and "top" (b) views of the POM positioned between two Zr<sub>6</sub>-clusters and two porphyrins; detailed lateral view of the POM–MOF interface and the hydrogen-bond network (c); (d) amount of O<sub>2</sub> produced against time under irradiation: black: 0.5 mg of  $P_2W_{18}Co_4@MOF-545$ , red: no  $P_2W_{18}Co_4@MOF-545$ , blue: no irradiation, pink: 0.5 mg of MOF-545; (e) schematic representation of the proposed mechanism for the light-driven OER by  $P_2W_{18}Co_4@MOF-545$ . Reprinted with permission from Ref. [159]. Copyright 2018 Journal of Materials Science.

## 4. Photocatalysis application of Zr-MOFs

#### 4.1 H<sub>2</sub> evolution

Photocatalytic hydrogen production has been demonstrated as an alternative environmentally method, because it can get clean H<sub>2</sub> from water splitting by using solar energy [164]. However, the production of highly active and economic photocatalyst still has some limitations [36]. To date, various light-harvesting materials for hydrogen production have been reported, for example, metal sulfide, metal oxide and nitride semiconductors. Recently, because of its excellent surface adsorption properties, modified crystalline structures, tunable band-gap, and controlled chemistry and functionality, MOFs have been studied for photocatalytic H<sub>2</sub> evolution [165-167]. However, due to the weak visible light utilization, instability in aqueous solution and high recombination possibility of electron and hole for most of MOFs, the H<sub>2</sub> production efficiency remains low. It's even harder to build an effective structure on MOFs to overcome the shortcoming and improve the H<sub>2</sub> production activities. Despite some water stable MOFs such as Zr-MOFs was constructed and several functional ligands or dye sensitizing system were introduced to enhance the light visible adsorption of MOFs, the first two problems were solved to some extent. However, the recombination of photogenerated  $e^-$  and  $h^+$  still remain as a big obstacle to the development of Zr-MOFs for H<sub>2</sub> evolution. Since Silva open the door that use Zr-MOF applied to the field of H<sub>2</sub> evolution under the UV light, more and more researchers are looking for methods expand the light range from UV to visible region. Herein, the photocatalytic H<sub>2</sub> production activity of Zr-MOFs based systems are summarized in Table 2.

It is important to note that the H<sub>2</sub> evolution ability of pure Zr-MOFs are poor due to their broad bandgap [168]. However, Zr-MOFs can be combined with other components with high photocatalytic efficiency by synergistic effect. In addition, Zr-MOFs display excellent stability could improve the stability and recovery of the composites. Among the reported methods, Zr-MOF/noble metal NPs showed excellent photocatalytic performance for H<sub>2</sub> evolution (Table 2). However, because of exorbitant cost and scarcity, the production and application of metal NPs are limited. Recently, metal sulfides have been considered as qualified substitutions of precious metals owing to their outstanding light absorption capacity and electrical properties. As illustrated in table 2, the productivity of Zr-MOF/metal sulfide for H<sub>2</sub> evolution is close to that of Zr-MOF/metal NPs. Furthermore, the ternary light harvesting system also attracted the attention. For example, Hao et al. [169] constructed MoS<sub>2</sub> QDs/UiO-66-NH<sub>2</sub>/Graphene composite though a simple solvothermal method and the optimum visible light driven activity of MoS<sub>2</sub> QDs/UiO-66-NH<sub>2</sub>/Graphene for H<sub>2</sub> evolution reached 62.1 µmol h<sup>-1</sup>. The excellent catalytic performance was attributed to the high specific surface area of UiO-66-NH<sub>2</sub>/Graphene which supported the formation of MoS<sub>2</sub> QDs. The introduction of MoS<sub>2</sub> QDs increased the generation and migration efficiency of photogenerated carriers. Hou et al. [170] successfully fricated UiO-66-NH<sub>2</sub>@Au@CdS photocatalyst via a hydrothermal process. By comparing the production of H<sub>2</sub>, Z-scheme UiO-66-NH<sub>2</sub>@Au@CdS exhibited higher photocatalytic activity for H<sub>2</sub> production with the rate rose to 39.5 µmol h<sup>-1</sup>.

In the photocatalyst system based on Zr-MOFs, Zr-MOFs provides attachment space for active components and effectively reducing the particle size and increasing the dispersion of this components. In addition, the formation of heterojunction in Zr-MOF photocatalyst system successfully extended the lifetime of photogenerated charge carriers and improved the utilization of visible light of Zr-MOFs. Photogenerated electrons are collected to decreased the adsorbed H to evolved H<sub>2</sub>, finally, the yield of H<sub>2</sub> increased significantly (Fig. 27).



Fig. 27 The mechanism of photocatalytic H<sub>2</sub> evolution by Zr-MOF based composites.

## Table 2

Materials	Light wavelength	Sacrificial reagent	$H_2$ evolution rate (µmol h <sup>-1</sup> g <sup>-1</sup> )	Cycles/Activity	Ref.
Pd/EY/UiO-66	$\lambda \ge 420 \text{ nm}$	TEOA	2280	3/55%	[101]
Au/UiO-66-NH <sub>2</sub>	$\lambda \ge 420 \text{ nm}$	methanol	19350	NA	[102]
Au@UiO-66@ZnIn <sub>2</sub> S <sub>4</sub>	$\lambda \ge 420 \text{ nm}$	Na <sub>2</sub> S and Na <sub>2</sub> SO <sub>3</sub> 39160		6/>90%	[132]
Pt/Au@UiO-66-NH2@CdS	$\lambda \ge 420 \text{ nm}$	L-ascorbic acid	39500	NA	[170]
GOWPt@UiO-66-NH2	$\lambda \ge 420 \text{ nm}$	TEOA	18150	6/>70%	[171]
UiOS-Cu-CdS/ZnS QDs	$\lambda \ge 320 \text{ nm}$	Na <sub>2</sub> S and Na <sub>2</sub> SO <sub>3</sub>	42550	7/>90%	[172]
ZnIn <sub>2</sub> S <sub>4</sub> /UiO-66-NH <sub>2</sub>	$\lambda \ge 420 \text{ nm}$	Na <sub>2</sub> S and Na <sub>2</sub> SO <sub>3</sub>	2199	4/76%	[141]
EY/MoS2 QDs/UiO-66-NH2/G	$\lambda \ge 420 \text{ nm}$	TEOA	4142	2/<30%	[169]
UiO-66-(COOH) <sub>2</sub> /MoS <sub>2</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	$\lambda \ge 420 \text{ nm}$	Na <sub>2</sub> S and Na <sub>2</sub> SO <sub>3</sub>	18794	4/96%	[134]
UiO-66/CdS/WP	$\lambda \ge 420 \text{ nm}$	lactic acid	5266.7	4/>85%	[142]
EY/rGO/UiO-66/Ni <sub>4</sub> S <sub>3</sub>	$\lambda \ge 420 \text{ nm}$	TEOA	5600	NA	[139]
Cd <sub>0.5</sub> Zn <sub>0.5</sub> S/UIO-66@g-C <sub>3</sub> N <sub>4</sub>	$\lambda \ge 420 \text{ nm}$	Na <sub>2</sub> S and Na <sub>2</sub> SO <sub>3</sub>	1281.1	3/>90%	[138]
Cd <sub>0.2</sub> Zn <sub>0.8</sub> S/UiO-66-NH <sub>2</sub>	$\lambda \ge 420 \text{ nm}$	Na <sub>2</sub> S and Na <sub>2</sub> SO <sub>3</sub>	5846.5	4/>90%	[133]

Summary of the photocatalytic performance of Zr-MOF based photocatalysts system toward H<sub>2</sub> evolution reaction.

$Ti_3C_2/TiO_2/UiO\text{-}66\text{-}NH_2$	$\lambda \ge 420 \text{ nm}$	Na <sub>2</sub> S and Na <sub>2</sub> SO <sub>3</sub>	1980	3/>60%	[173]
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EY=Eosin-Y; TEOA=triethanolamine; NA=not available

### 4.2 CO<sub>2</sub> reduction

Excessive carbon dioxide (CO<sub>2</sub>) emissions caused numerous environment issues such as seawater acidification and greenhouse effect. Photocatalytic reduction of CO<sub>2</sub> to carbon-based supplies (e.g., CO, CH<sub>4</sub>, CH<sub>3</sub>OH, etc.) is one of crucial way to resolve energy shortage as well as a strategy of alleviation the increasing amount of CO<sub>2</sub> [22, 174, 175]. In particular, the conversion of CO<sub>2</sub> by solar energy obtained great attention due to the economy and renewability [176]. So far, some studies have focused on CO<sub>2</sub> photoreduction, including homogeneous transition metal-based complexes and semiconductor materials. However, due to the high cost, these method are still challenging [56]. Zr-MOFs could be an ideal candidate due to their structural adaptivity, flexibility and high CO<sub>2</sub> capture capacity [177-180]. On the one hand, they can act as photocatalysts themselves, using open metal sites, unsaturated metal centers and organic ligands with visible light photocatalytic activity. Furthermore, Zr-MOFs can behave as semiconductors to form heterojunction by doping other semiconductors. The recent significant progresses of Zr-MOF based systems in the photocatalytic CO<sub>2</sub> reduction have been summarized in this section and Table 3.

By introducing appropriate light harvested components, Zr-MOFs can adjust their photochemical properties to achieve light capture. Furthermore, Zr-MOF has been determined a promising material due to its high CO<sub>2</sub> capture capacity and semiconductor-like behaviors with many reactive metal sites [21, 181]. Table 3 has presented the Zr-MOFs with good photocatalytic CO<sub>2</sub> reduction effect reported in recent years. For example, in 2020, Cheng and co-workers [182] designed UiO-66-NH<sub>2</sub>-tpy catalyst for photocatalytic CO<sub>2</sub> reduction. 2,4,6tris(4-pyridyl)pyridine (tpy) possessed great electron donating ability and promoted the conversion of CO<sub>2</sub>, The tpy modified NH<sub>2</sub>-UiO-66 exhibited great enhanced visible light driven photocatalytic CO<sub>2</sub> revolution (184.03  $\mu$ mol·g<sup>-1</sup>·h<sup>-1</sup>) which was 5 times higher than pure Zr-MOF. Liu et al. [56] designed a novel Zr-porphyrin MOF (Rh-PMOF-1(Zr)) by self-assembly of Rh(TCPP)Cl ligand with ZrCl4 (Table 1). Without the addition of photosensitizer, RhPMOF-1 significantly catalyzed CO<sub>2</sub> conversion into formate anion with up to 99% selectivity. In the reported Zr-MOFs in this paper, AUBM-4 showed highest conversion rate for CO<sub>2</sub> to HCOOH which reached 366  $\mu$ mol·g<sup>-1</sup>·h<sup>-1</sup> due to the long lifetime of excited Ru(cptpy)<sub>2</sub> group and the fast charge transfer between metal and ligands [49]. Normally, photosensitive organic ligands generate excited state elements and photogenerated electrons under visible light. The excited ligands could directly convert CO<sub>2</sub> to carbon-based fuel while the photogenerated electrons sensitize the Zr-O cluster and reduced CO<sub>2</sub> near the Zr-O cluster (Fig. 28).





Another way to enhance the light driven CO<sub>2</sub> reduction rate of Zr-MOFs is to form heterojunction by hybridizing with other semiconductors. For example, Wang et al. [183] constructed Cu<sub>2</sub>O@Cu@UiO-66-NH<sub>2</sub> heterogeneous photocatalyst through a facile hydrothermal method for efficient CO<sub>2</sub> conversion. Benefiting from the p–n junctions of the heterogeneous photocatalyst, the yields of CH<sub>4</sub> and CO reached to 8.3 and 20.9  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>. GR/UiO-66-NH<sub>2</sub> was prepared though a microwave-assisted strategy [21]. The results showed that the HCOOH evolution rate of heterogeneous catalyst reached 443.75  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>, it was 11 times higher than that of pure Zr-MOF.

## Table 3

Sample	Light wavelength	Sacrificial agent	Production	Evolution rate ( $\mu$ mol h <sup>-1</sup> g <sup>-1</sup> )	Cycle/activity	Ref
PCN-222	$\lambda \ge 420 \text{ nm}$	TEOA	НСООН	60	NA	[56]
Zr-SDCA-NH <sub>2</sub>	$\lambda \ge 420 \text{ nm}$	TEOA	НСООН	39.17	NA	[45]
AUBM-4	$\lambda \ge 420 \text{ nm}$	TEOA	НСООН	366	4/>90%	[49]
NH <sub>2</sub> -UiO-66-tpy	$\lambda \ge 350 \text{ nm}$	TEOA	СО	184.03	NA	[182]
NNU-28	$\lambda \geq 420 \text{ nm}$	TEOA	НСООН	52.8	3/>90%	[22]
O-ZnO/rGO/UiO-66-NH <sub>2</sub>	$\lambda \ge 420 \text{ nm}$	-	CH <sub>3</sub> OH and HCOOH	34.83 / 6.41	6/>90%	[126]
Cu <sub>2</sub> O@Cu@UiO-66-NH <sub>2</sub>	$\lambda \ge 400 \text{ nm}$	TEOA	CO / CH <sub>4</sub>	20.9 / 8.3	3/>90%	[183]
CuTCPP & UiO-66/TiO <sub>2</sub>	$\lambda \ge 300 \text{ nm}$	TEOA	СО	31.32	4/>90%	[184]
UIO-66-NH <sub>2</sub> /GR	$\lambda \geq 410 \text{ nm}$	TEOA	НСООН	443.75	8/>90%	[21]

Summary of the photocatalytic performance of Zr-MOF based photocatalysts toward CO<sub>2</sub> reduction.

TEOA= triethanolamine; NA= not available.

## 4.3 Removal of organic pollutants

Recently, researchers have done a lot of researches on removal of organic pollutants and pointed out that photocatalytic process is an effective strategy [12, 185-189]. Since Garcia et al. [190] firstly determined that MOF-5 served as a photocatalyst with outstanding activity in the removal of organic pollutants, more and more MOF materials have been used in photocatalysis (e.g., MIL-53, MIL-68, TMU and JUC-138) [191-194]. Zr-MOFs exhibit superior thermal and chemical stability to water, which make it as an ideal material for photocatalytic removal of organic pollutants. Herein, the photocatalytic removal of organic pollutants of Zr-MOF systems was summarized in Table 4.

In recent years, pure Zr-MOF has been extensively reported as a visible light driven photocatalyst for organic pollutants removal. For example, DUT-67(Zr) was constructed for selective oxidation of thioanisole [50]. He et al. [91] proposed the incorporation of Ti in Zr-porphyrins MOFs via a simple PSM process and used as a photocatalyst for the removal of MB. Although Zr-MOFs has been determined to be capable of degrading organic pollutants, the degradation efficiency is still very low. Recently, the preparation of Zr-MOF based composites has made significant progress for the removal of organic pollutants (Table 4). For example, Tong et al. [25] successfully synthesized the BiOCl/UiO-66 composite to degrade RhB by simple hydrothermal method. Under visible light irradiation, compared with pure BiOCl(28.31%) and UiO-66(14.55%), the hybrid material displayed obviously higher photocatalytic activity on Rh B degradation with the degradation rate of 97.34% after 2 h under LED light irradiation. The reason was explained as that, the two materials were bonded together by chemical bonds(C-Cl), due to these changes, the composite had good adsorption of RhB and could realize effective electron transfer in hybrid materials. Ding et al. [23] constructed UiO-66/Bi<sub>2</sub>MoO<sub>6</sub> photocatalyst for degradation of RhB by a self-assembly method. The participation of Bi2MoO6 improved the response range of visible light and the existence of UiO-66 promote the adsorption and diffusion of RhB on it. The results of photocatalytic experiment showed that the Bi<sub>2</sub>MoO<sub>6</sub>/UiO-66 composites displayed enhanced photodegradation efficiency.

In addition to organic dyes, there are some studies on the removal of other organic substances in water by Zr-MOFs system. For example, Yao et al. [24] prepared TiO<sub>2</sub>@MOF nanocomposites by the introduction of TiO<sub>2</sub> within UiO-66-NH<sub>2</sub> and applied to VOCs (volatile organic compounds) purification. The removal rate of VOCs reached 90% in 80 min. Li et al. [195] synthesized a series of UiO-66/BiOI heterojunction photocatalysts via a simple hydrothermal process and applied to the photodegradation of salicylic acid. The degradation efficiency up to 90% in 2 h under the irradiation of visible light. Wang and co-workers [196] constructed AgI/UiO-66 mixture and made great progress in degradation of sulfamethoxazole under LED light irradiation. Within 20 min, the contamination was almost completely removed.

## Table 4

Materials	Light wavelength	Contaminants (concentration)	Efficiency/time (min)	Mechanism	Cycles/activity	Ref.
ZnIn <sub>2</sub> S <sub>4</sub> /UiO-66-(SH) <sub>2</sub>	$\lambda \geq 400 \text{ nm}$	Rh B (20 mg/L)	96% / 60	$\cdot O_2^- \cdot OH$	NA	[137]
Ag <sub>3</sub> PO <sub>4</sub> /UiO-66	$\lambda \geq 420 \text{ nm}$	Rh B (20 mg/L)	100% / 18	$\cdot O_2^-  h^+ \cdot OH$	5/99%	[123]
CdS/UiO-66-NH <sub>2</sub>	$\lambda \geq 420 \text{ nm}$	Rh B (10 mg/L)	92.5% / 40	$\cdot O_2^- h^+$	4/90%	[140]
ZnIn <sub>2</sub> S <sub>4</sub> @PCN-224	$\lambda \geq 420 \text{ nm}$	TC (20 mg/L)	99.9% / 60	$\cdot O_2^-$	3/95%	[197]
TiO <sub>2</sub> @UiO-66-NH <sub>2</sub>	$\lambda \geq 400 \text{ nm}$	TC (20 mg/L)	75% / 60	$\mathbf{h}^+$	4/70%	[118]
AgI/UiO-66-NH <sub>2</sub>	$\lambda \geq 420 \text{ nm}$	TC (10 mg/L)	80.7% / 40	$\cdot O_2^- h^+$	4/86%	[143]
Ag/AgBr@UIO-66-NH <sub>2</sub>	$\lambda \geq 420 \text{ nm}$	MO (12.5 mg/L)	92.1% / 65	$\cdot O_2^-$	5/85%	[198]
rGO@In2S3@UiO-66	$\lambda \geq 420 \text{ nm}$	MO (15 mg/L)	98.1% / 60	$\cdot O_2 h^+$	5/94.2%	[199]
Cd <sub>0.5</sub> Zn <sub>0.5</sub> S@UIO-66@g-C <sub>3</sub> N <sub>4</sub>	$\lambda \geq 420 \text{ nm}$	MO (20 mg/L)	82% / 120	$\cdot O_2 h^+$	NA	[138]
ZnIn <sub>2</sub> S <sub>4</sub> /UiO-66-NH <sub>2</sub>	$\lambda \geq 420 \text{ nm}$	MG (10 mg/L)	98% / 120	·OH	4/76%	[141]
α-Fe <sub>2</sub> O <sub>3</sub> @UiO-66	$\lambda \geq 420 \text{ nm}$	MB ( $4 \times 10^{-5} \text{ mol }/\text{L}$ )	100% / 50	NA	3/99%	[120]
CoTiO <sub>3</sub> /UiO-66-NH <sub>2</sub>	sun light	NFX (20 mg/L)	90.13% / 60	·OH	NA	[125]
BiOI/UiO-66	$\lambda \geq 420 \text{ nm}$	SA (10 mg/L)	90% / 120	$\cdot O_2^-$	5/85%	[195]

Summary of the photocatalytic performance of Zr-MOF based photocatalysts toward degradation of organic pollutants.

TiO <sub>2</sub> @UiO-66-NH <sub>2</sub>	$\lambda \geq 420 \text{ nm}$	VOCs (35 mL/min)	90% / 80	NA	NA	[24]
AgI/UiO-66	$\lambda \geq 400 \text{ nm}$	SMZ (5 mg/L)	99.6% / 20	$\cdot O_2^- \cdot OH$	4/99%	[196]

Rh B= Rhodamine B; PC= 2-pyridinecarboxaldehyde; TC= tetracycline hydrochloride; MG= malachite green; MO= methyl orange; SA= salicylic acid; NFX= norfloxacin; SMZ= sulfamethoxazole; TCH= tetracycline hydrochloride; NA= not available.

### 4.4 Hexavalent chromium reduction

Hexavalent chromium (Cr (VI)) has been widely applied in many fields such as leather tanning, paint, paper, printing and electroplate [200-202]. However, Cr (VI) mainly discharged into the environment through industrial wastewater which is a serious threat to human beings due to its carcinogenicity and mutagenicity [203]. Therefore, the efficient degradation of Cr from high toxicity hexavalent chromium form to low valent chromium with low toxicity is extremely crucial for environmental protection. Due to the high porosity, tunable surface functionalities and chemical stability, Zr-MOF materials are extremely important to eliminate Cr (VI) from wastewater. Recent examples of Zr-MOF and its complexes for the removal of Cr (VI) are given in Table 5 and the applications of Zr-MOFs based system for hexavalent chromium reduction are introduced in this chapter.

The pure Zr-MOFs possess absorb and remove ability for Cr (VI) because of their adsorption and semiconductor properties [204]. Under visible light, Zr–O clusters acted as catalytic active sites for Cr(VI) reduction, organic ligands were excited to produce photogenerated electrons and adsorb the generated Cr(III) (Fig. 29). The redox reaction occurred as follows:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
 (1)

$$2H_2O + 2h^+ \rightarrow H_2O_2 + 2H^+$$
<sup>(2)</sup>

For instance, Wang et al. [205] prepared UiO-66-OH and UiO-66-(OH)<sub>2</sub> for removal of Cr(VI) via a modified solvothermal approach. The -OH functional group in Zr-MOF are not only a reductive site for efficient Cr(VI) removal, but also serve as pivot point for capturing Cr(III). The electrostatic attraction between Cr(VI) and organic ligands of MOFs played an important role. Du et al. [206] constructed UiO-66-NH<sub>2</sub>(Zr/Hf) membrane through a reactive seeding method. The membrane exhibited excellent photocatalytic activity to reduce Cr(VI) and easily separate them from the treated wastewater under visible light irradiation. After 20 cycles, the membrane still maintained over 94% degradation efficiency due to its excellent chemical stability and

water stability. Liu et al. [57] synthesized a new Zr-porphyrin MOF, JLU-MOF60  $([Zr_6O_4(OH)_8(H_2O)_4(TCPP)_4] \cdot 9DMF \cdot 3.5H_2O)$  by a facile hydrothermal reaction (Table 1). This new framework displayed excellent photodegradation performance for Cr(VI), the degradation efficiency reached 98% under the irradiation of visible light. Additionally, The Zr-MOF based heterogeneous photocatalyst also exhibited great photocatalytic degradation performance for Cr(VI), and these complexes were listed in Table 5.



Fig. 29. The mechanism of photocatalytic Cr (VI) reduction by Zr-MOF.

## Table 5

Materials	pН	Concentration (ppm)	Band gap	Time (min)	Removal efficiency	Cycles/activity	Ref
UiO-66-(OH) <sub>2</sub>	6.0	8	2.8 eV	10	100%	NA	[42]
JLU-MOF60	6.0	80	2.5 eV	70	98%	5 />95%	[57]
UiO-66-NH <sub>2</sub> (Zr/Hf)	2.0	5	2.7 eV	120	98%	20 / 94%	[206]
ZnIn <sub>2</sub> S <sub>4</sub> /UiO-66	NA	80	1.8 eV	60	99%	3 />90%	[131]
UiO-66-	NT A	50	25-34		09.40/	4 / > 000/	[124]
(COOH) <sub>2</sub> /MoS <sub>2</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	NA	50	2.3 ev	00	90.470	4/~90%	[134]
Ag/AgCl/ UiO-66-NH <sub>2</sub>	2.0	20	2.8 eV	150	74.2%	3 />90%	[146]
UiO-66-NH <sub>2</sub> /BiOBr	2.0	10	NA	360	88%	NA	[207]
CFs/MoS <sub>2</sub> /UiO-66-NH <sub>2</sub>	NA	50	2.6 eV	120	98.4%	NA	[208]

Summary of the photocatalytic performance of Zr-MOF based photocatalysts toward Cr(VI) reduction.

NA= not available.

# 5. Summary and perspective

As an emerging material, MOFs with considerable surface adsorption capacity, adjustable aperture and numerous catalytically active sites have a great vogue in various fields. In these MOFs, Zr-MOFs show an excellent stability due to the strong Zr–O cluster interactions as well as the high connection number of the secondary building units. In addition, Zr-MOF has been proved that it shows excellent water-tolerant across a wide pH range in aqueous media which makes it as a promising candidate for the photocatalysis process. In this review, we introduced the research progress of Zr-MOFs in the field of photocatalysis in recent years and summarized their applications in H<sub>2</sub> evolution, CO<sub>2</sub> reduction, organic pollution degradation and hexavalent chromium reduction. Although existing studies have indicated that Zr-MOFs has a bright future in improving the performance and stability of photocatalysts, the following problems still need to be solved in the further application:

(1) At present, UiO series MOFs are the most widely reported Zr-MOFs in photocatalytic field. However, there are many kinds of Zr-MOFs reported in recent years. Whether other Zr-MOFs can also make progress in the field of photocatalysis is the future research direction.

(2) The photocatalytic activity of Zr-MOFs can be improved effectively by the incorporation of noble metal and metal semiconductors. However, due to the valuableness and environmental pollution, the practical application of these compound materials is limited. Recently, metal free semiconductor such as graphene and carbon nitride were welcomed by researchers due to their low cost and tunable structure. In addition, large number of studies have shown that doping metal-free semiconductor in MOFs could improve the utilization rate of visible light. Compared with other MOFs, Zr-MOFs have excellent stability in water. Thus, the construction of Zr-MOF/metal free semiconductor system will provide a new direction for photocatalytic treatment of pollutants in water.

(3) Zr is one of hexa-nuclear metal (e.g., Zr, Ce, U, and Hf). The exceptional thermal and chemical stability of MOFs composed of composed of hexa-nuclear metal makes Zr-MOF as an ideal photocatalyst. However, compared with Zr-MOF, other hexanuclear metal is still in its infant stage in the field of photocatalysis due to some intrinsic defects. It is necessary to explore the mechanism as photocatalysis of other hexanuclear MOFs.

(4) Most Zr-MOF based photocatalysts are studied in powder systems, which cause challenges in large-scale process associated with catalyst recovery efficiency and cost. In addition, Zr-MOF usually needs the participation of sacrificing reagents to show good photocatalytic performance, the photocatalytic performance of Zr MOF still needs to be improved without sacrificing reagents. Therefore, we should focus on finding innovative methods to prepare efficient and economic Zr-MOFs based photocatalytic system to shift it from laboratory phase to practical application.

(5) Even though there are still many deficiencies in Zr-MOFs based photocatalyst systems, the broad prospects of Zr-MOFs as photocatalyst with excellent water stability and thermal stability in environmental remediation and energy production cannot be ignored. In addition, Zr-MOF is effective in enhancing the stability of other photocatalysts. By looking for new materials and methods to compound with Zr-MOF, we can draw on the advantages of both to prepare photocatalysts with both high efficiency and sustainable utilization.

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