

Recent advances in metal-loaded MOFs photocatalysts: From single atom, cluster to nanoparticle

Shenglan Zhou^a, Haijian Li^{b,*}, Hongyi Gao^{a,c,*}, Ang Li^{d,*}, Tian Li^a, Shanshan Cheng^a, Jingjing Wang^a, Jitti Kasemchainan^e, Jianhua Yi^b, Fengqi Zhao^b, Wengang Qu^b

^a Advanced Innovation Center for Materials Genome Engineering, Beijing Key Laboratory of Function Materials for Molecule & Structure Construction, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

^b National Key Laboratory of Energetic Materials, Xi'an Modern Chemistry Research Institute, Xi'an 710065, China

^c Shunde Innovation School, University of Science and Technology Beijing, Shunde 528399, China

^d School of Materials Science and Engineering, Suzhou University of Science and Technology, Suzhou 215009, China

^e Department of Chemical Technology, Chulalongkorn University, Bangkok 10330, Thailand

ARTICLE INFO

Article history:

Received 4 March 2024

Revised 16 June 2024

Accepted 19 June 2024

Available online 20 June 2024

Keywords:

Metal-loaded MOFs

Photocatalysis

Single atom catalysts

Nanoclusters

Nanoparticles

ABSTRACT

Photocatalysis is widely regarded as a highly promising sustainable technique for addressing the challenges posed by environmental pollution and energy provision. In recent years, metal-loaded MOFs has become a rising star within the domain of photocatalysis due to its high specific surface area and porosity, adjustable structure, diverse and abundant catalytic components, which has exhibited excellent photocatalytic activity and exhibit great potential in a range of disciplines. In this paper, the principles for evaluating the photocatalytic performance of MOFs-based materials were firstly introduced, and some typical examples were also listed accordingly. Along with this, particular emphasis is paid to the main factors affecting the photocatalytic performance of metal-loaded MOFs. Then the synthesis and design strategies of MOFs loaded metal entities of varying sizes (single atoms, nanoclusters, and nanoparticles), and their applications in photocatalytic CO₂ reduction, hydrogen production, photooxidation and photocatalytic hydrogenation were summarized and discussed. Finally, the opportunities and challenges faced in this kind of MOFs-based composites were analyzed from different perspectives. This report is expected to help researchers design and develop high-performance MOFs-based photocatalytic materials.

© 2024 Published by Elsevier B.V. on behalf of Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences.

1. Introduction

Environmental pollution and energy scarcity have gradually become key constraints on the development of human society, which have forced mankind to look for sustainable and clean energy sources [1–3]. Among the various types of alternative energy resources, solar energy stands out for its ubiquity, accessibility, inexhaustible supply, and environmental sustainability. Photocatalysis is one of the most important methods of solar photochemical conversion, which is considered to be a promising technology for addressing energy supply and environmental degradation. Over the past few decades, significant efforts have been made in multiple photocatalysis domains (including hydrolytic hydrogen production, CO₂ reduction, etc.), resulting in noteworthy accomplishments.

The photocatalyst is essential for capturing solar energy and enabling the generation and transfer of photo-induced electrons, thereby directly impacting the catalytic activity and extent of the photocatalytic reaction. More and more researchers have paid great attention to developing high-performance photocatalysts. Inorganic semiconductors such as TiO₂ [4–10] have long been studied and used within the domain of photocatalysis. Nevertheless, these semiconductors are constrained by their wide band gap, rapid recombination of photo-generated charge carriers, and limited gas adsorption capabilities. As a result, it remains essential and extremely advantageous to create high-efficiency photocatalysts to overcome the aforementioned limitations of the semiconductor photocatalysts.

Metal-organic frameworks (MOFs) are a new type of crystalline porous organic-inorganic hybrid materials, which are composed of metal or metal cluster nodes and organic ligands [11–15]. Compared with traditional semiconductor photocatalyst, MOFs shows the favorable aspects of large specific surface area, strong structure

* Corresponding authors.

E-mail addresses: h.j.li@outlook.com (H. Li), hygao@ustb.edu.cn (H. Gao), angli@usts.edu.cn (A. Li).

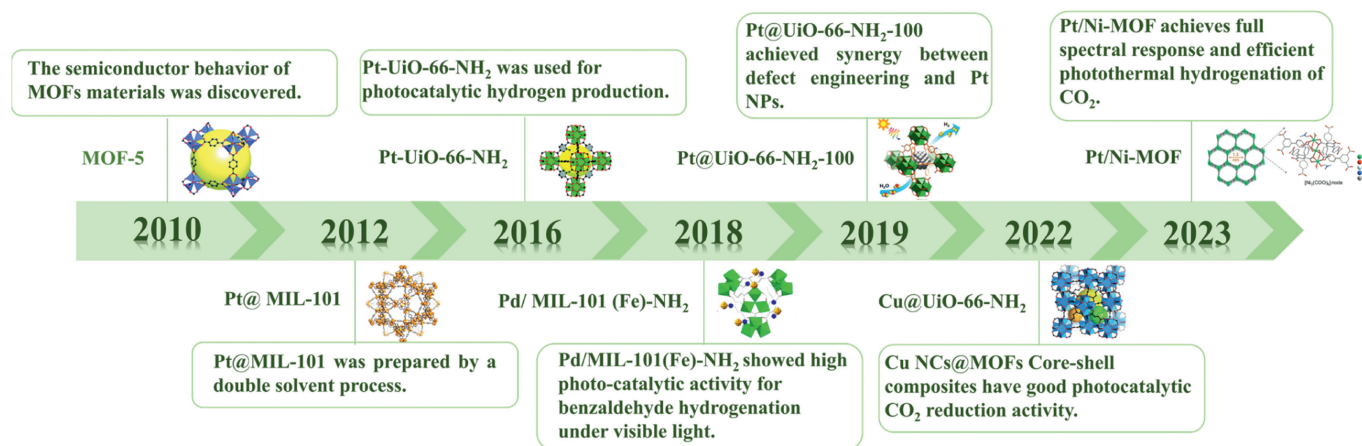


Fig. 1. Recent research progress of metal-loaded MOFs photocatalysts.

designability and performance adjustability, which have been extensively adopted for adsorption and separation [16–19], gas storage [20,21] and catalytic reactions [22–33] (including thermocatalysis, electrocatalysis and photocatalysis [34]). In particular, MOFs have been found everywhere within the domain of photocatalytic hydrolysis for hydrogen production [35–39], CO₂ reduction [40–44] and photooxidation [45,46]. However, many MOFs cannot meet the needs of practical applications due to their insufficient light absorption capacity and photogenerated carrier separation rate. Therefore, various active metal species have been introduced into MOFs hosts to prepare metal loaded-MOFs composites, which have exhibited excellent photocatalytic performance.

The difference between metal particles with sizes ranging from metal single atoms (SAs, 0.1–0.2 nm), nanoclusters (NCs, <1 nm), and nanoparticles (NPs, >1 nm) leads to differences in the electronic and geometric structure of metal-loaded MOFs, thus resulting in different catalytic behaviors in various heterogeneous catalytic reactions [47,48]. Notably, these precisely defined metal entities can contribute to the enhancement of photocatalytic activity by broadening the spectral absorption range or facilitating charge separation [49–51]. However, the surface free energy of these metal entities is so high that they can easily aggregate to form large-sized particles [52,53]. Therefore, a class of carriers with sufficient anchor points is required to stabilize them. MOFs are just an ideal host, which can not only prevent their aggregation by providing abundant anchoring sites, but also cooperate with them to jointly improve the catalytic activity [54–57]. Metal-loaded MOFs have received increasing attention. Since Pt/MIL-101 was prepared by the double-solvent method in 2012 [58], this kind of MOFs-based photocatalytic material has gradually become the focus of researchers. For example, Xiao *et al.* [59] also selected Pt NPs as a co-catalyst to support MOFs and studied its photolysis performance for hydrogen production from water. Studies on Pd/MIL-101(Fe)-NH₂ within the domain of photocatalytic hydrogen production were also reported in the following two years [60]. In late years, metal-loaded MOFs photocatalysts have been reported in a wide variety of designs. Some MOFs have been inserted into *N*-heterocyclic carbene (NHC) groups to form strong Au-NHC covalent bonds to more effectively fix Au NCs, and some MOFs have been synthesized with Cu NCs outside to prepare core-shell type photocatalysts [61,62]. As reported this year, a class of MOFs has realized a response to the infrared light region and efficient photothermal conversion of CO₂ after loading Pt [63]. MOFs have been designed in different ways. The general idea is to make the metal entities uniformly dispersed on the surface/interior of MOFs in order to achieve a synergistic effect to facilitate the catalytic process (Fig. 1).

There are increasing reports on metal-loaded MOFs materials in the last decades. At present, the research on MOFs-based composites within the domain of photocatalysis has been relatively mature, and many excellent reviews have been reported [49,64–67], but there is few review focused on metal single atom catalysts (SACs), metal NCs and NPs loaded MOFs within the domain of photocatalysis. Therefore, a comprehensive and timely review of the metal loaded MOFs recently applied in photocatalysis is considered to be very necessary, which will help the rational design and efficient preparation of MOFs-based photocatalysts, and inspire some new ideas. In this paper, the factors affecting the photocatalytic performance were listed and discussed to help achieve deeper understanding of the reaction principle. Secondly, the synthesis strategies of various metal-loaded MOFs and related studies were summarized and listed. In addition, the applications of these metal entities loaded MOFs in different photocatalytic aspects were briefly discussed. Finally, we also draw a brief conclusion and discussed the prospects and challenges of this kind of composite material within the domain of photocatalysis.

2. Evaluation principle for photocatalytic performance of MOFs-based materials

The metrics here are mainly based on the structure of the MOFs-based material, involving various steps of the photocatalytic reaction process. In MOFs, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are present on organic ligands and metal nodes/clusters, respectively (Fig. 2). When exposed to light, the HOMO of MOFs is photoexcited to produce electrons that have enough energy to transfer. In the interior of MOFs, there are typically two types of charge transfer effects: Ligand-to-metal charge transfer (LMCT) [68] and charge transfer within the ligand (LLCT) [69,70]. The resulting electrons and holes can then participate in the subsequent reduction and oxidation processes, respectively.

2.1. Spectral absorption range

Spectral absorption range is an important indicator of the photocatalytic performance of materials. MOFs-based materials with a wide range of spectral absorption (e.g., involving visible light) are better able to absorb sunlight and excite more photogenerated charges, which means that there are more opportunities to subsequently participate in the catalytic conversion process of the substrate. It has been reported that it is possible to introduce metal entities into MOFs or to modulate their ligands for the purpose

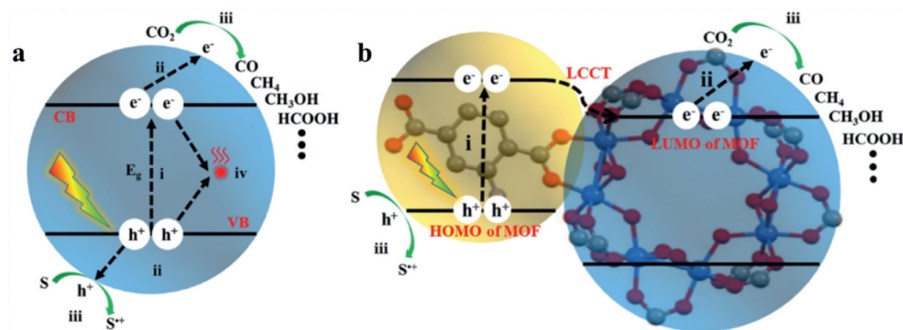


Fig. 2. Schematic illustration of the photocatalytic CO_2 reduction process of semiconductors (a) and MOF-based materials (b) (S: substrate; S^+ : oxidized substrate). Reproduced with permission [70]. Copyright 2020, Elsevier.

of increasing the absorbance. For instance, Sun *et al.* [71] demonstrated that it is the interband excitation of Pt NPs that causes the wider spectral absorption range (200–800 nm) of MOFs (ZIF-8, UiO-66 and MIL-125). Cu SAs and Cu NPs were introduced into UiO-66- NH_2 by Wang *et al.* [43], respectively. Diffuse reflectance spectra (DRS) show that Cu SAs and Cu NPs can enhance the spectral absorption of MOFs, which can broaden the light absorption range of UiO-66- NH_2 up to 450–800 nm. In addition, Ma *et al.* [63] developed a Pt/Ni-MOF by loading Pt into Ni-MOF that is also responsive under infrared light irradiation. UV-vis-NIR absorption spectra indicate that the absorbance range of the sample extends up to 1400 nm, which achieves an ultra-high full solar spectral utilisation. There are other examples of enhancement of the spectral absorption of MOFs by modulation of ligands. Fu and colleagues [3] expanded the visible absorption spectrum of NH_2 -MIL-125(Ti) to 550 nm through the use of an amino-containing ligand exchange technique, which was linked to the reduction of the band gap resulting from the presence of the $-\text{NH}_2$ group (from 3.6 eV to 2.46 eV). Subsequent broadening of the spectral absorption range of MOFs is achieved upon substitution of the $-\text{NH}_2$ group with a dye group featuring enhanced para-conjugated moieties. NTU-9 prepared by introducing two $-\text{OH}$ groups in MIL-125(Ti) has an energy band gap of 1.72 eV and exhibits enhanced light trapping ability.

2.2. Band-edge position

The redox capacity of MOFs-based photocatalyst is greatly affected by LUMO and HOMO position. Specifically, the edge position directly reflects the redox potential of MOFs-based photocatalyst. The level of the edge position determines the possibility of the reaction process and the selectivity of the product. In general, the more negative the LUMO potential of MOFs-based photocatalysts, the stronger their reduction ability; while the more positive the HOMO potential, the more significant their oxidation ability. As an efficient photocatalyst, MOFs-based materials can simulate photosynthesis and effectively convert solar energy into chemical energy. However, depending on the type of photocatalytic redox reaction (such as photocatalytic decomposition of aquatic hydrogen, CO_2 reduction), there are different requirements for the edge position of MOFs-based materials. The edge position is not only the basis of the absorption of light radiation, but also the prerequisite for the subsequent redox reaction. Taking photocatalytic water decomposition as an example, in theory, to achieve water decomposition, the LUMO potential of MOFs-based photocatalyst should be more negative than $E(\text{H}^+/\text{H}_2)$, the HOMO potential should be more corrected than $E(\text{O}_2/\text{H}_2\text{O})$, and its band gap should be no less than 1.23 eV. Similarly, selective reduction of CO_2 to CO in photocatalytic CO_2 reduction requires that the LUMO potential of the MOFs be more negative than -0.53 V (Fig. 3), which helps the excited elec-

trons migrate more easily to the metal center. Therefore, in order to achieve good redox ability of MOFs, it is very important to adjust the edge position reasonably.

2.3. Stability

Stability as another measure usually includes: chemical, thermal and mechanical stability. The former generally refers to the ability of MOFs materials to withstand a variety of hostile environments (e.g., acids, alkalis, and water), whereas the latter two are mainly concerned with evaluating the ability of MOFs to maintain their structural integrity after treatment in harsh environments (e.g., at high temperatures, vacuums, and high pressures) [72]. The above stability is expressed as a quantitative indicator that if a material can maintain no significant decrease in photocatalytic activity (usually not more than 10%) and intact morphology and structure after several (≥ 3) cyclic reactions, it indicates that its stability is good. However, most MOFs materials are often limited by their poor relative stability. Therefore, the design and development of MOFs-based materials with good stability is still worth studying. The main strategies to improve the stability of MOFs materials include constructing MOFs composed of metal ions that can form strong coordination bonds with ligands (such as high-priced metal ions and carboxylic acid linkers or low-priced metal ions and azole linkers), doping to prepare mixed-metal MOFs and dividing pore spaces [72]. In addition to these methods, ligands with rigid structures can also be selected for MOFs (Text S1 in Supporting information).

2.4. Conversion rate and selectivity

The most intuitive and important indicators to measure the photocatalytic activity of MOFs materials are conversion and selectivity. Almost most reports are based on these two indicators to measure the photocatalytic activity of materials. It is worth noting that differences in reaction conditions and catalysts lead to inconsistencies in the measurements, which is the reason why most of them are based on changes in conversion and selectivity before and after modification. Preparation of metal-loaded MOFs is a feasible strategy to improve photocatalytic conversion and selectivity. For instance, Zuo *et al.* [73] loaded 6.0 wt% Co SACs on ultrathin MOF nanosheets to achieve an extremely high conversion rate ($7041 \mu\text{mol g}^{-1} \text{ h}^{-1}$) and selectivity (86%) of CO_2 to CO conversion. This report provides a new way to construct high-load metal SACs, and also proves the great potential of ultra-thin MOF nanosheets for photocatalytic CO_2 reduction. Other studies have integrated approaches to enhance the stability of MOFs by incorporating metal entities. For instance, Liu *et al.* [74] created two types of Pt/Eu-MOF-Ru(cptpy) $_2$ and Pt/Pr-MOF-Ru(cptpy) $_2$ with a

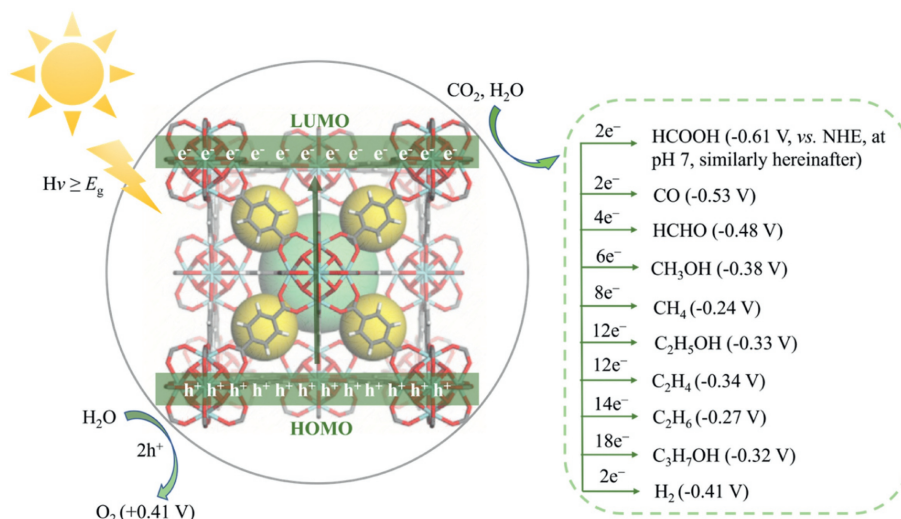


Fig. 3. Schematic diagram of reduction potentials (E) of different products during photoreduction of CO_2 and oxidation of H_2O to O_2 in aqueous solution at pH 7 and 1 atm relative to normal hydrogen electrode (NHE).

photoactive mixed-metal MOF as the catalyst and Pt as the co-catalyst. They investigated the impact of Pt loading capacity and the type of sacrificial agent on photocatalytic activity. 0.5% Pt/Eu-MOF-Ru(cptpy) $_2$ showed the maximum hydrogen production (up to 4373 $\mu\text{mol g}^{-1} \text{h}^{-1}$) in the presence of ascorbic acid for 3 h and the catalytic activity did not decrease significantly after 3 cycles. In addition, Che *et al.* [75] introduced ultra-small Ag NPs into MOFs by photoreduction and prepared a series of Ag/MOF-n by regulating the irradiation time (expressed as n in minutes). The results of photocatalytic cross dehydrogenation coupling (CDC) showed that the CDC yield of methanol photocatalyzed by Ag/MOF-10 under optimized conditions reached 94%. There are many other such reports, which are not listed here. The improvement of photocatalytic activity of metal-loaded MOFs depends on the joint action of metal entities and MOFs, so the research on this subject is still of great significance.

3. Factors affecting the photocatalytic performance of metal-loaded MOFs

In this review, the factors that affect the photocatalytic performance of metal-loaded MOFs are discussed from the following three aspects (Fig. 4).

3.1. Metal type

The introduction of the metal entities can enhance mass diffusion, optimize charge separation, and minimize charge transfer resistance by lowering the free energy of proton reduction. The Gibbs free energy (ΔG_{H^*}) is used here to measure the free energy barrier required for proton reduction. Taking photocatalytic hydrogen production as an example, ΔG_{H^*} is a core part of this reaction process. When the absolute value of ΔG_{H^*} of metal-loaded MOFs material is close to 0 eV, it indicates that the load of the metal entities is conducive to the enhancement of the photocatalytic hydrogen production activity of the material. A very low ΔG_{H^*} value not only promotes the combination of electrons and protons to form H^* , but also ensures the rapid desorption of H_2 , thus improving the efficiency of the entire photocatalytic process. For example, M1/MOFs has a ΔG_{H^*} of -0.50 eV, while M2/MOFs has a ΔG_{H^*} of -0.22 eV. This means that the free energy barrier of M2/MOFs in the process of photocatalytic hydrogen production is lower than that of M1/MOFs. Therefore, compared with M1, M2 load shows superior performance in photocatalytic hydrogen production [76]. For metals SAs is also reflected in the maximum utilization of metal atoms. After consulting relevant reports, it is found that Pt has a strong advantage in photocatalytic hydrogen production. There have been

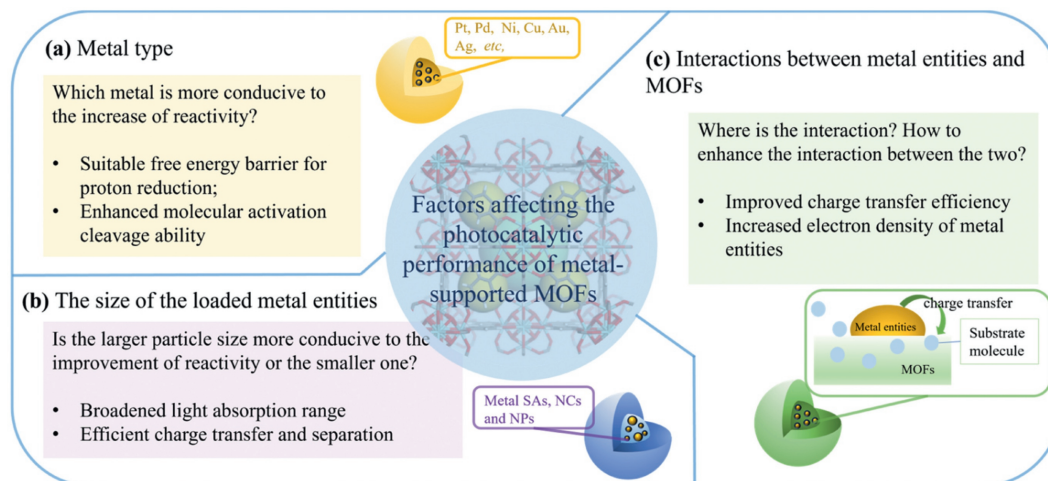


Fig. 4. Summary of factors affecting the photocatalytic activity of metal-loaded MOFs.

many reports showing the strong advantages of Pt in photocatalytic hydrogen production (Text S2 in Supporting information). Therefore, when designing and selecting the type of second phase metal, we should focus on the following two aspects. Firstly, the ΔG_{H^+} of the target metal-supported MOFs can be predicted with the help of density functional theory (DFT) calculations. Through this method, we can preliminarily determine whether the loading of the metal entity helps to improve the photocatalytic activity, so as to provide a strong theoretical support for the subsequent experiments. Secondly, when the loading of a single metal entity cannot achieve the expected photocatalytic activity enhancement effect, we can consider introducing two or more metal entities for loading. However, in this process, the role of each metal entity must be clearly analyzed and evaluated to ensure that the synergies between them can achieve the best photocatalytic performance improvement. Through this design strategy, we can more effectively screen out metal-loaded MOFs materials suitable for specific photocatalytic reactions, and promote the further development of photocatalytic technology.

3.2. The size of the loaded metal entities

The impact of particle size on the catalytic activity of metal-loaded MOFs cannot be ignored. The loading of these three types of metal entities can be used as cocatalysts to promote the activity of MOFs photocatalysts by promoting photogenerated charge transfer. According to the reported studies on the loading of metal SAs and metal NPs of the same metal species, it can be seen that the metal SAs with the smallest particle size has more advantages for the enhancement of the photocatalytic activity of MOFs due to its significant dispersion and high atomic utilization. There are several reasons for this enhancement: (1) Enhancing the spectral absorption capacity. The introduction of SAs into MOFs can enhance their light absorption range by adjusting the electronic structure and reducing the energy gap due to the electronic interaction between SAs and MOFs frameworks. For example, Sui *et al.* [76] showed that Pt₁/SnO₂/UiO-66-NH₂ loaded with Pt SAs has a stronger light absorption capacity than the original MOFs due to changes in the electronic structural environment, and the introduction of Pt SAs leads to a lower absolute value of ΔG_{H^+} than that loaded with Pt NPs, which is also the reason why its photocatalytic hydrogen production activity is the best. (2) Accelerating charge transfer. The easily accessible and atomically dispersed metal SAs is closer to the electronic level in MOFs, which facilitates effective charge transfer and separation between metal SAs and MOFs frameworks. For example, Ma *et al.* [38] demonstrated that Ni₁-X/MOF promotes a significant increase in photocatalytic hydrogen production activity compared to the same MOFs material loaded with Ni NPs due to the highest atomic availability and close proximity to the photosensitive unit, which gives Ni SAs the best charge separation efficiency and the lowest proton activation barrier. Similarly, Zuo *et al.* [77] also showed that the introduction of Pt SAs causes more electrons to be transferred from the porphyrin ring to Pt SAs, thus facilitating charge transfer and separation. (3) Promoting the formation of important intermediates. The coordination interaction between metal SAs and organic linkers can further enhance the catalytic activity of MOFs. Using DFT calculations, Wang *et al.* [43] revealed the reaction mechanism of photocatalytic reduction of CO₂ to methanol and ethanol by Cu SAs/UiO-66-NH₂ materials: Cu SAs and two neighboring amino groups formed a planar bicoordination configuration, which changed the state density and band structure of MOFs. Specifically, the introduction of Cu SAs causes the band gap of MOFs to narrow and the conduction band to move down to Fermi level, which is conducive to electron enrichment on Cu SAs/UiO-66-NH₂, creating conditions for the multi-electron process of CO₂ reduction. In addition, due to the redistribution of the state

density of Cu SAs and its coordination with amino groups, this contributes to the formation of CO* and CHO* as intermediates, which in turn promotes the activity and selectivity of CO₂ conversion to methanol and ethanol. The conclusions obtained from these reports not only open up a way for the synthesis of metal SAs-loaded MOFs, provide a deep understanding of the electron transfer mechanism of metal SAs involved in MOFs, but also promote further research on the development of more efficient visible light response MOFs photocatalysts.

3.3. Interactions between metal entities and MOFs

The interaction between metal entities and MOFs is also critical for the improvement of photocatalytic performance of MOFs-based materials. On the one hand, the presence of metal entities can alter the charge transfer efficiency with MOFs. On the other hand, MOFs can affect the electron density of the metal entities by modulating the microenvironment around them. For example, unsaturated Co sites were introduced into MOF-525 by Zhang and colleagues [78]. The improved photogenerated electron-hole pair separation efficiency on MOF-525-Co compared to MOF-525 was attributed to the directional migration of photogenerated excitons from the porphyrin to the electron capture site achieved by the injected Co SACs. Jiang *et al.* [61] efficiently immobilized the Au NCs through the introduction of NHCs into the MOFs. The test results confirmed that it was the localized surface plasmon resonance (LSPR) of Au NCs that facilitated the transfer of photogenerated electrons and thus improved the photocatalytic activity. Moreover, the Cu nodes within the PtSA-MNS, as prepared by Zuo *et al.* [77], enhance the transfer of photogenerated charges. Simultaneously, the Pt SAs capture electrons and function as active sites for proton reduction. The synergistic effect of the two leads to a higher rate of hydrogen production. Similarly, experimental results obtained by Chen *et al.* after fixing the reaction temperature (16 °C) corroborate the existence of charge transfer between Pt NCs and PCN-224(M) (M: Zn, Ni, Co, Mn) [79]. Wang *et al.* [80] demonstrated that moderate amounts of Pd NCs embedded in MIL-125-NH₂ were favourable for the enhancement of photo-oxidative benzylamine activity. The appropriate amount of Pd NCs plays two main roles in the MOFs: (1) Providing more active sites for the catalysts enabling the composites to have a higher molecular activation capacity, which results in the production of more $\cdot O_2^-$ and $^1O_2$; and (2) facilitating the photogenerated charge transfer and segregation, which contributes to the enhancement of the photocatalytic activity. These reports all focus on the analysis of charge transfer between metal entities and MOFs. Overall, the level of charge transfer efficiency determines the rate at which the photocatalytic reaction proceeds. Therefore, the design and preparation of metal-loaded MOFs with synergistic effects remains a hot research topic.

4. Synthesis strategy of metal-loaded MOFs photocatalyst

There are mainly four methods to prepare metal SAs and NCs/NPs loaded MOFs (Table S1 in Supporting information). The first method is the "ship in a bottle" method, which is generally suitable for preparing composite materials with metal SAs or NCs/NPs loaded on the surface of MOFs. The dual solvent method of this type of method can be used to obtain composite materials with metal SAs or NCs/NPs encapsulated in the holes of MOFs. The main step of the "ship in a bottle" method is to mix the prepared MOFs with a precursor solution containing the target metal ions, which is then converted into metal SAs, NCs, or NPs loaded on the MOFs through a subsequent reduction step. This method requires that MOFs should have considerable stability to ensure that the structure will not be destroyed in the subsequent restoration process. The second method is the "bottle around ship" method.

Contrary to the "ship in a bottle" method, the metal NCs/NPs is first prepared, then mixed with the precursor solution of MOFs, and finally operated according to the operation flow of synthesizing MOFs. The metal NCs/NPs prepared by this method are usually encapsulated in MOFs, and their morphology and size are relatively easy to control [64]. However, the high interfacial energy between the two materials can sometimes hinder the growth of MOFs [80]. The third method, known as the "one-pot" approach, is simple to operate, involving the preparation by mixing all necessary precursor solutions, but it is difficult to control the nucleation and simultaneous growth of SAs, NCs, or NPs. The fourth method is an improvement or combination of the first two methods, such as the sandwich strategy. The methods employed are varied, but the principle is the same. For example, supercritical CO₂ can be used to immerse metal ions in MOFs, and then the subsequent reduction operation is carried out. Although it is not operated as the typical dipping method but by other means, it still falls under the category of ship in a bottle method. Furthermore, the sandwich strategy is to prepare core-shell composite catalysts with two layers of MOFs and one layer of metal NCs/NPs in the middle by using the ship in a bottle method and then the ship around a bottle method. The application scenarios and specific examples of the above four methods will be introduced respectively from the types of loaded metal entities.

4.1. Synthesis of metal SAs-loaded MOFs

As the name suggests, SAs are a class of catalysts that with isolated metal atoms fixed into a solid substrate. Due to the difference in the number of clustered atoms, SAs have many characteristics that are different from NPs, such as maximum atomic utilization and metal-carrier interface. Because metal SAs are easy to agglomerate, so it is not suitable to prepare this kind of composite catalyst by bottle around ship method. Lately, the ship in a bottle method has been widely reported for the preparation of such composites. For instance, Zhang *et al.* [78] mixed cobalt nitrate and zinc nitrate with DMF solution of MOF-525 respectively, then replaced DMF with acetone, and finally heated at high temperature under vacuum (120 °C, 48 h) to obtain MOF-525-Co. A general synthetic strategy on the two-step microwave-assisted modification method for the preparation of MOFs loaded with different SACs has been reported by Ma *et al.* [38] and Sui *et al.* [76] (Text S3 in Supporting information). In addition, photoinduced methods (PIMs) have also been developed for the synthesis of metal-loaded MOFs. After immersion, Wang *et al.* [43] used H₂ produced by the decomposition of water under visible light to convert Cu²⁺ into Cu SAs and anchored it to UiO-66-NH₂. Finally, Cu-SAs/UiO-66-NH₂ is prepared. Experimental and theoretical studies have shown that Cu SAs as active species can significantly promote the photoreduction of CO₂ to liquid fuels (such as methanol and ethanol) under visible light (Fig. 5).

4.2. Synthesis of metal NCs-loaded MOFs

Metal NCs, which typically consist of several to a few hundred metal atoms, have a distinct atomic composition and structure compared to NPs. This gives metal NCs powerful quantum size effects, electronic and optical properties. There are various methods for loading metal NCs, all of which can be prepared by the four methods mentioned above. Here, it is explained in the order of the above three methods (Fig. 6).

(1) Ship in a bottle method

For instance, Ishida *et al.* [81] used solid grinding method to deposit Au NCs in narrow size distribution on a variety of MOFs (including MOF-5), and found that such samples can catalyze the aerobic oxidation of alcohols efficiently.

Using the dual-solvent method and photoreduction process, Sun *et al.* [82] prepared Pd²⁺@NH₂-UiO-66(Zr) with hexane as the hydrophobic solvent and palladium nitrate as the metal precursor, followed by photoreduction to Pd@NH₂-UiO-66(Zr) in degassed ethylene glycol. Through the successful coupling of MOFs and Pd NCs, the ultra-small active Pd NCs encapsulated in MOFs were prepared. This work demonstrates an efficient and gentle way to encapsulate metal nanoclusters in MOF cavities. Similarly, Zheng *et al.* [83] used MOF-74 as a template to fix tiny Pd NCs in pores by a two-solvent method and applied the composite to electrocatalytic hydrogen evolution and oxygen reduction reactions. In this method, anhydrous n-hexane was used as a hydrophobic agent, and the metal precursor solution (PdCl₂ aqueous solution) was introduced into the pore of MOFs through capillary action. After vacuum drying, it was reduced by hydrazine hydrate (N₂H₄·H₂O) solution to obtain Pd@MOF-74-M (Co, Zn, Ni) with different loading capacities of Pd NCs.

(2) Bottle around ship method

In addition, the bottle around ship method can also be used to prepare metal NCs loaded MOFs. Using this method, Yang *et al.* [84] elucidated the synthesis strategy for Pd-NCs involving the reduction of K₂PdCl₄ with L-ascorbic acid, while employing PVP and KBr as the stabilizer and capping agent, respectively. Pd NCs@ZIF-8 composite was designed and manufactured by self-assembly method using ZIF-8 as the carrier, and was applied to selective catalytic hydrogenation of olefin under visible light irradiation. Different from the previous study, the size of Pd particles prepared in this study is large (7 ± 3 nm), which is suitable for MOFs with mesoporous or even macroporous as carriers. For more examples of these two synthesis methods, please see Text S4 (Supporting information).

(3) Sandwich strategy

Yun *et al.* [85] reported a coordinated assisted self-assembly method for the design and fabrication of novel sandwich composites ZIF-8@Au₂₅@ZIF-67[tkn] and ZIF-8@Au₂₅@ZIF-8[tkn] [tkn = shell thickness]. The attributes of the composite sandwich catalyst can be readily modulated through the manipulation of the shell thickness. It can be seen that the synthesis strategies of metal NCs-loaded MOFs are easier and more diversified than those of metal SACs-loaded MOFs. The preparation of metal NPs-loaded MOFs with smaller size limitations is discussed in the next section.

4.3. Synthesis of metal NPs-loaded MOFs

Unlike metal SAs and NCs, metal NPs have been extensively reported. Here are some representative reports of relevant methods (Fig. 7).

(1) Adsorption strategy

The most direct and convenient method to synthesize metal nanoparticle loaded MOFs is adsorption. For instance, Jorge Becerra *et al.* [86] synthesized Au_x@ZIF-67 by depositing presynthesized Au NPs on the surface of ZIF-67 using an adsorption strategy. The author first synthesized PVP blocked Au NPs and ZIF-67 nanocrystals in the size range of 30–40 nm. Subsequently, Au NPs and ZIF-67 were mixed in methanol for 24 h. After centrifuge washing, Au_x@ZIF-67 composite material was obtained. The composite can efficiently convert CO₂ to methanol and ethanol under sunlight, and the total yield is higher than that reported in other studies. The implication here is that plasmonic gold nanoparticles (PNPs) sized between 30 nm and 40 nm are

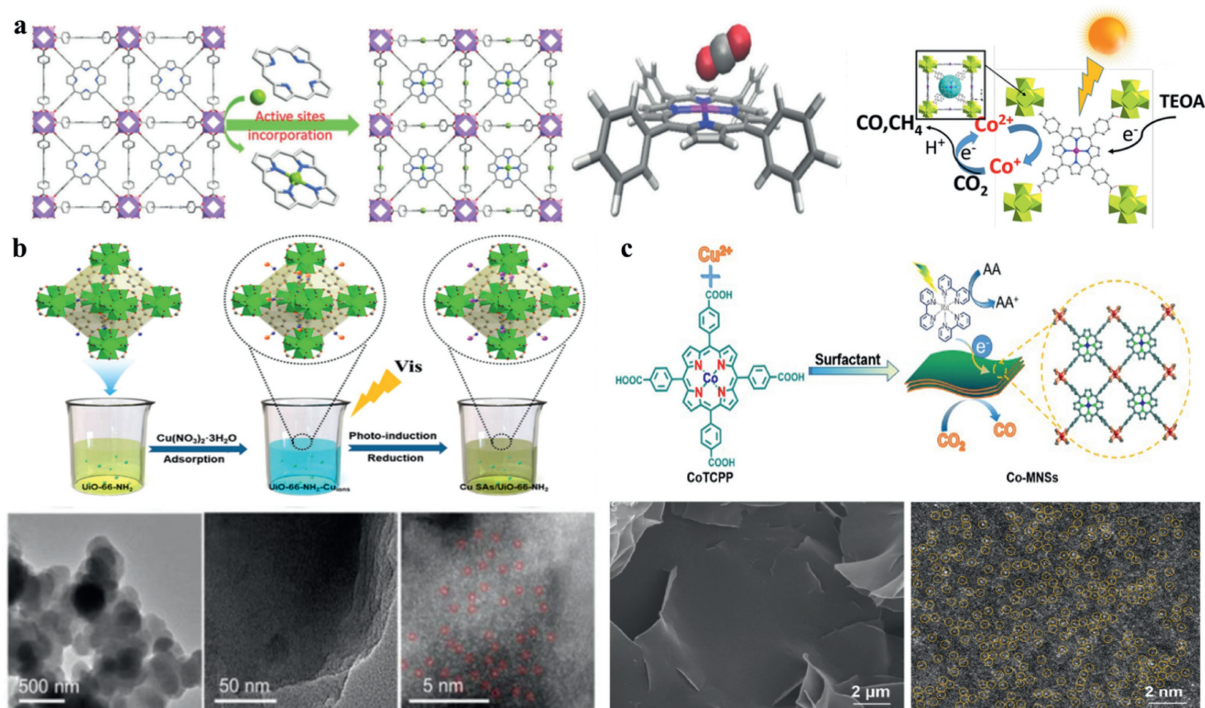


Fig. 5. (a) The schematic diagram of the structure of MOF-525-Co, the optimized structure for CO₂ adsorption on a porphyrin-Co unit, and mechanisms underlying the photoexcited dynamics involved in MOF-525-Co. Reproduced with permission [78]. Copyright 2016, Wiley. (b) Synthesis process of the Cu SAs/Uio-66-NH₂ photocatalyst (C (gray), O (red), Zr–O clusters (green), N (blue), Cu ions (orange), and Cu SAs (purple)), TEM and HRTEM of Cu SAs/Uio-66-NH₂, aberration-corrected STEM images of Cu SAs/Uio-66-NH₂. Reproduced with permission [43]. Copyright 2020, American Chemical Society. (c) Synthesis of Co-MNSs and schematic diagram of their photocatalytic conversion of CO₂. Reproduced with permission [73]. Copyright 2023, Springer Nature.

pivotal in augmenting light absorption, as well as promoting effective charge separation and selectivity.

(2) Ship in a bottle method

The impregnation strategy and the double solvent method are used more than the adsorption strategy, which is mainly reflected in the uniformity and size of the particle size. Arshad Aijaz and coworkers [58] documented a direct two-solvent technique that allows for the easy introduction of metal precursors into the voids of MOFs, thereby precisely controlling the formation of ultrafine metal nanoparticles. The authors chose MIL-101 because of its high stability in water, large surface area and pores into which metal precursors can be diffused. Metal precursors whose volume does not exceed the volume of the MIL-101 pore enter the MIL-101 pore due to capillary action. The prepared Pt@MIL-101 showed excellent catalytic performance in the process of ammonia-boron hydrolysis, ammonia-boron thermal dehydrogenation and CO oxidation. Similarly, in 2018, The two-solvent method was used by Chen *et al.* [87] to synthesize Ag@HKUST-1 composites encapsulated with ultrafine Ag NPs. The cage structure of HKUST-1 can not only effectively limit the growth of Ag NPs, but also prevent the entry of olefin with molecular size larger than 5.0 Å. The catalyst showed high catalytic activity and cycle stability in the hydrogenation of various olefins. In the same year, Sun *et al.* [88] synthesized a three-layer core-shell composite catalyst using the double solvent method, involving the reduction of Cu²⁺ ions to form Cu NPs as cores, followed by the precipitation of Co NPs as middle shells facilitated by intermediate Cu-H species, and subsequent reduction of Ni²⁺ to produce Ni NPs shells by the resulting Co-H species. Finally, ammonia borane was hydrolyzed to obtain Cu@Co@Ni/MIL-101 catalyst. The research on this kind of multilayer metal NPs is relatively few and new, which can provide researchers with

a way of thinking. Nevertheless, the investigation into the catalytic mechanism remains insufficiently elucidated.

(3) Bottle around ship method

There are also a few reports on the preparation of metal NPs-loaded MOFs materials by bottle around ship method (Text S5 in Supporting information).

(4) One-pot method

Because of the uncontrollability of the reaction process, there are few researches on the preparation of metal NPs-loaded MOFs by one-pot method. Here is just one example. Chen *et al.* [89] reported a simple and straightforward programmed temperature control strategy that can incorporate metal nanoparticles into MOFs in one step. The metal precursor is first incorporated *in situ* at a low temperature (e.g., 80 °C), which allows the palladium precursor to be evenly distributed in the pore of the MOFs. The temperature was then raised to 130 °C to allow the solvent DMF to reduce Pd²⁺ to Pd NPs (1.5 ± 0.3 nm) dispersed in Uio-67. In the absence of an external reducing agent, the synthetic route is greatly simplified and helps to confine the tiny Pd NPs to the MOFs pore.

(5) Sandwich strategy

Details can be found in Text S5.

In summary, the synthesis strategy of metal solid-loaded MOFs materials can be selected based on specific applications. The aforementioned preparation methods each possess their own set of advantages and drawbacks, such as the “bottle in a ship” method, which can obtain composite materials with excellent catalytic activity and selectivity. But its cycling stability may not be satisfactory, as the metal entities loaded on the surface of MOFs may be washed off before the next cycling operation. Furthermore, in the absence of regulation of the reduction process, the metal entities' particle size may be sufficiently large to induce aggregation. The

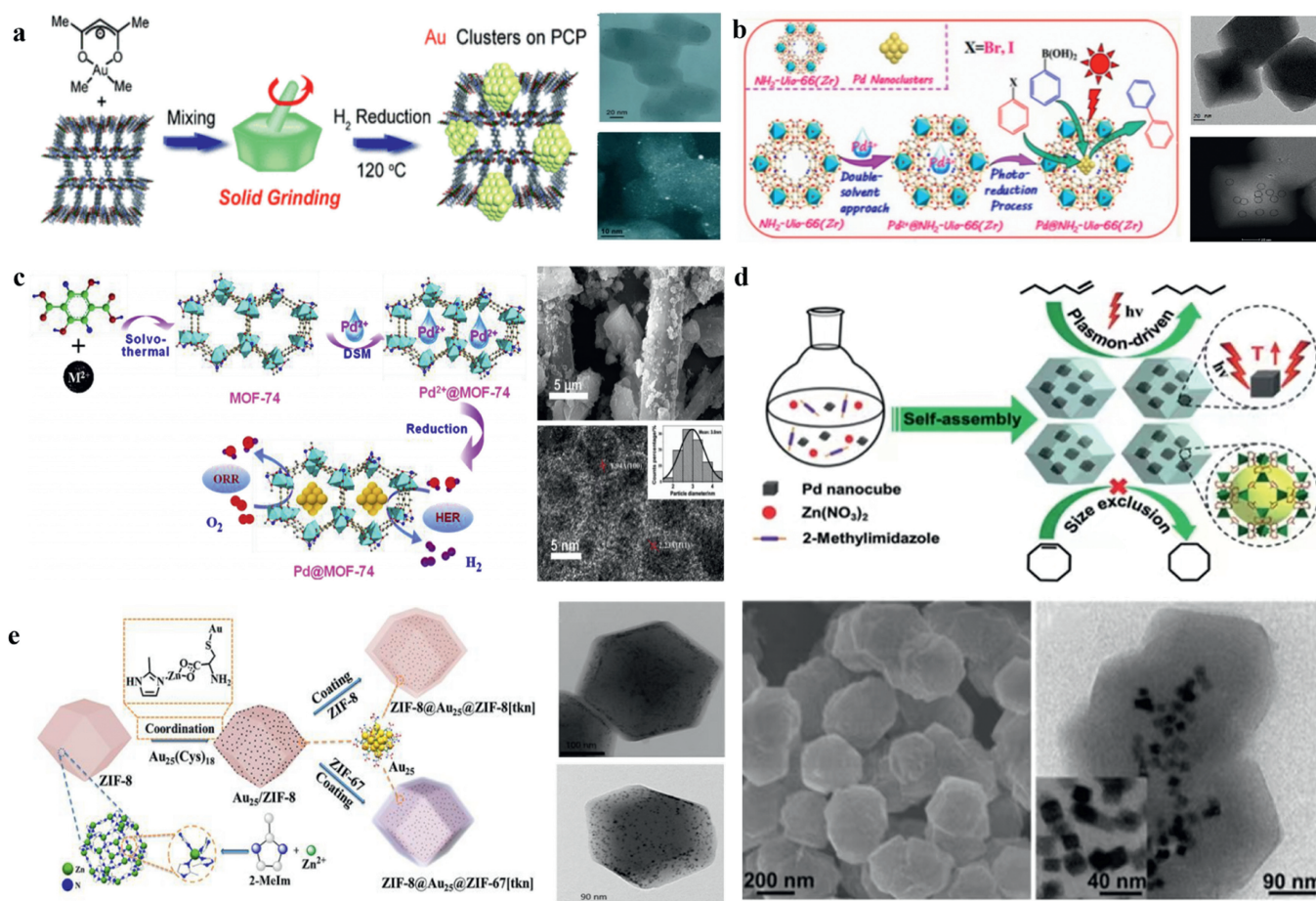


Fig. 6. (a) Scheme of synthesis of Au clusters loaded PCP composite by the solid grinding method, TEM image of Au/CPL-2 and HAADF-STEM image of Au/MIL-53 prepared by the solid grinding method. Reproduced with permission [81]. Copyright 2008, Wiley. (b) Schematic synthesis, TEM and HAADF-STEM images of Pd@NH₂-Uio-66(Zr). Reproduced with permission [82]. Copyright 2016, American Chemical Society. (c) Schematic synthesis of Pd@MOF-74, SEM and TEM images of Pd@MOF-74-Co. Reproduced with permission [83]. Copyright 2019, Elsevier. (d) Photocatalytic hydrogenation schematic, SEM and TEM images of Pd NCs@ZIF-8. Reproduced with permission [84]. Copyright 2016, Wiley. (e) Scheme of synthesis of ZIF-8@Au₂₅@ZIF-8 or ZIF-8@Au₂₅@ZIF-67 via a coordination assisted sandwich strategy, typical TEM image of single ZIF-8@Au₂₅@ZIF-67 with shell thickness of 8 nm, and TEM images of the sandwich ZIF-8@Au₂₅@ZIF-67. Reproduced with permission [85]. Copyright 2020, American Chemical Society.

“bottle around ship” method often requires the use of encapsulation agents and stabilizers to encapsulate and control the size of the metal entities. While the “one pot” method is simple, the micro process is challenging to regulate. The sandwich strategy is difficult to explain. Therefore, the design and selection of synthesis methods for metal-loaded MOFs depend more on the reaction mechanism and its application fields.

5. Application and performance of metal-loaded MOFs photocatalysts

In recent years, metal SAs, NCs and NPs-loaded MOFs have been applied by many researchers within the domain of photocatalysis, including CO₂ reduction, decomposition of aquatic hydrogen, photooxidation, photocatalytic hydrogenation, photodegradation of organic pollutants and photocatalytic sterilization, due to their advantages of good light absorption capacity, large specific surface area and abundant active sites. This chapter will center its attention on the advancement of these loaded MOFs materials in the initial four domains.

5.1. Photoreduction of CO₂

The massive emission of CO₂ has become one of the biggest environmental problems in the world. Among the various CO₂ utilization technologies, the electrochemical CO₂ reduction reaction

(CO₂RR) has garnered significant attention due to its utilization of clean energy and production of high value-added fuels [90,91]. In contrast to electrocatalysis, photocatalytic technology boasts numerous advantages, including the ability to harness solar energy efficiently and operate under mild reaction conditions. Therefore, the conversion of CO₂ into other high value-added chemicals by MOFs-based photocatalysts is a viable option for reducing CO₂ emissions and promoting carbon neutrality [92,93]. Reaction processes and principles and examples of studies are detailed in Texts S6 and S7 (Supporting information).

(1) Metal SAs-loaded MOFs

Previous studies have shown that because the local alkaline environment created by -NH₂ groups is conducive to the adsorption of CO₂, MOFs with ligands of -NH₂ groups can be selected as carriers. Strategies combined with defect engineering can also be used. In 2021, Hao *et al.* [94] introduced metal SAs (such as Ir and Pd) into NH₂-Uio-66 (labeled A-aUiO) with structural defects. SA/A-aUiO was deposited on PTFE film after dipping and annealing to form a breathable film. In the traditional particle solution (PiS) mode, HCOOH yield was highest (0.51 mmol g⁻¹ h⁻¹) when the Ir SAs load was 1.4 wt%, which was the result of the synergistic effect of MOFs and Ir SAs. In the gas-film-gas (GMG) mode, the HCOOH yield of Ir₁/A-aUiO films was 3.38 mmol g⁻¹ h⁻¹, which was higher than that of Ir₁/A-aUiO particles. This is

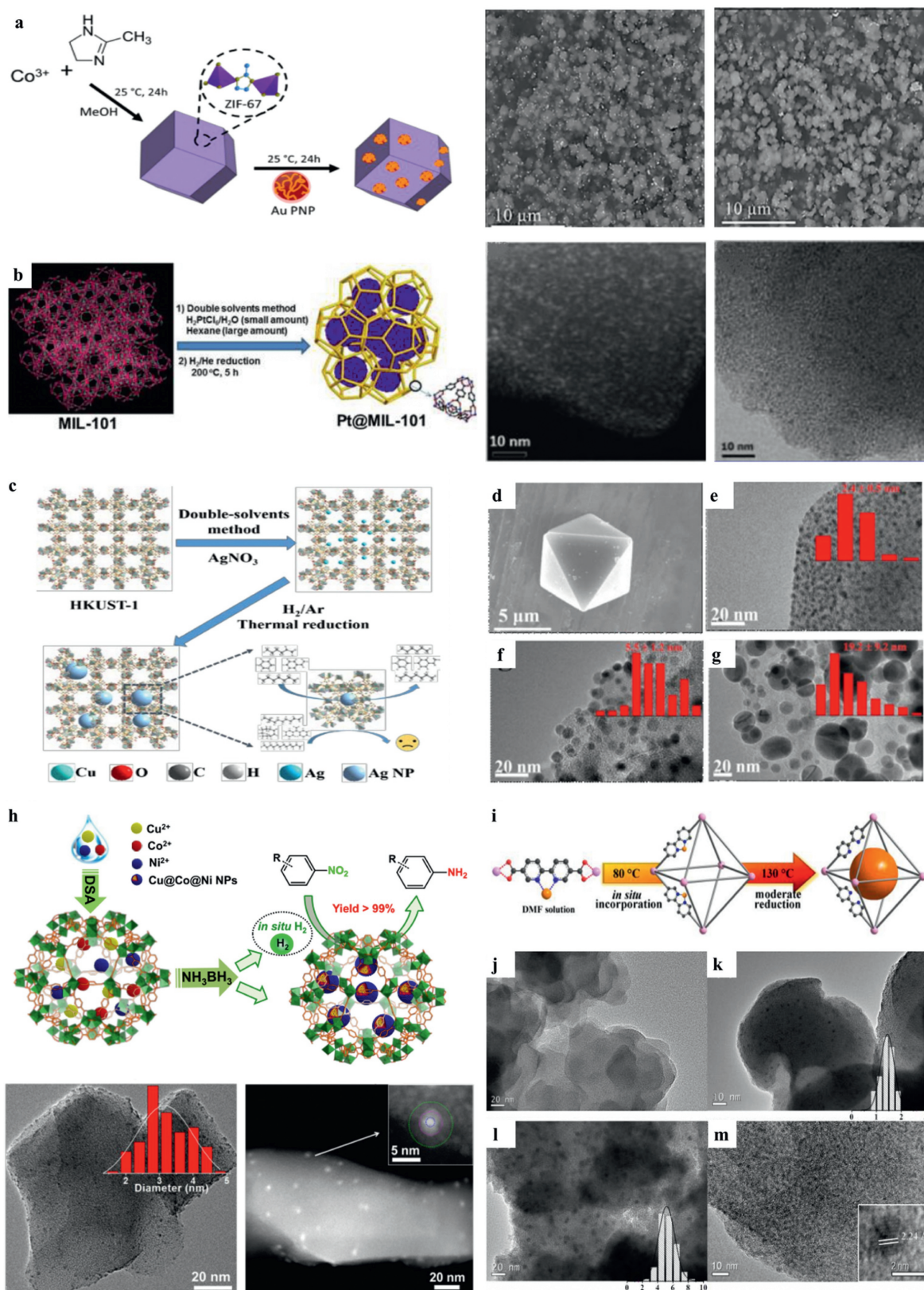


Fig. 7. (a) The schematic illustration of the synthesis of Aux@ZIF-67, SEM images for the Aux@ZIF-67 samples with 10 wt% and 20 wt% Au loadings. Reproduced with permission [86]. Copyright 2020, American Chemical Society. (b) Scheme of synthesis of Pt@MIL-101 by the double-solvent method, HADDF-STEM image and tomographic reconstruction image of as-synthesized Pt@MIL-101. Reproduced with permission [58]. Copyright 2012, American Chemical Society. (c) Structure and synthetic schematic of Ag@HKUST-1. (d) SEM images of 0.1 mmol Ag@HKUST-1. (e) TEM images of 0.1 mmol Ag@HKUST-1 (e), 0.2 mmol Ag@HKUST-1 (f), and 0.1 mmol Ag@HKUST-1 (g). Reproduced with permission [87]. Copyright 2018, Wiley. (h) Schematic of the preparation and catalytic principle of Cu@Co@Ni/MIL-101, TEM image (size distribution of Cu@Co@Ni NPs in the interior) and HAADF-STEM image of metal NPs. Reproduced with permission [88]. Copyright 2019, American Chemical Society. (i) Scheme of synthesis of Pd@UiO-67 composites via the one-pot strategy. TEM images of (j) PdII-in-UiO-67, (k) Pd-in-UiO-67, (l) Pd@UiO-67, and (m) ultrathin cuts from Pd-in-UiO-67. The insets of (k) and (l) are the particle size distributions of Pd NPs. The inset of (m) is the corresponding HRTEM image. Reproduced with permission [89]. Copyright 2015, Royal Society of Chemistry.

due to the reduction of CO₂ diffusion distance and the increase of resistance. MOFs play a crucial role in this composite, and the authors innovatively use the GMG model to enhance activity.

(2) Metal NCs-loaded MOFs

For metal NCs supported-MOFs, metal NCs are often stabilized by the formation of coordination. Fixation of metal NCs by regulatory structures has also been reported. Dai *et al.* [62] synthesized Cu NCs@MOFs core-shell composites with unique CO₂ photoreduction capability. The main products of Cu NCs@MOF-801 are HCOOH (64.9%) and CO (22.5%), and the conversion rates are 32 and 94 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively. The formic acid selectivity and yield of core-shell Cu NCs@UiO-66-NH₂ are higher than Cu NCs@MOF-801, reaching 86% and 128 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively. The reason for this difference may be their different affinity for CO₂. The -NH₂ group exhibits stronger host-guest interaction with formic acid. In addition, the Cu^I site at the interface between Cu NCs and MOFs carrier was the active site to promote the catalytic activity. The two composites are well stabilized as evidenced by the post-reaction PXRD. This core-shell strategy is useful for designing and constructing efficient MOFs-based catalysts.

(3) Metal NPs-loaded MOFs

Due to the large particle size of metal NPs, it is easy to cause particle aggregation, which affects the catalytic activity of MOFs. Recently, Lu *et al.* [95] constructed 2D Zn-MOF-NH₂/Cu heterojunction by loading Cu NPs onto 2D Zn-MOF-NH₂ using a simple photodeposition method. The lower Fermi level of Cu serves the purpose of electron collection from MOFs into the CB, effectively minimizing the recombination of photogenerated carriers. In the absence of any sacrifice agent, The CO yields of 2D Zn-MOF-NH₂/Cu (0.5 wt%), 2D Zn-MOF-NH₂/Cu (1 wt%) and 2D Zn-MOF-NH₂/Cu (2.5 wt%) were 0.48, 0.76 and 0.55 $\mu\text{mol/h}$, respectively. The CO yield of 2D Zn-MOF-NH₂/Cu (1 wt%) with the best photocatalytic activity is 2.7 times and 16.2 times that of 2D Zn-MOF-NH₂ and bulk Zn-MOF-NH₂, respectively. This report has some implications for the preparation of 2D MOFs composite photocatalysts. (Table S2 in Supporting information)

5.2. Photolysis of water for hydrogen production

Garcia and his colleagues began exploring the semiconductor behavior of MOFs in 2007 [96,97], and in 2010 they applied UiO-66 to photocatalytic hydrogen production under ultraviolet light, based on its excellent structural stability in water. This was a prelude to the application of MOFs in photocatalytic water decomposition (Table S3 in Supporting information). Please see Texts S8 and S9 (Supporting information) for the principle and examples of research.

(1) Metal SAs-loaded MOFs

In recent years, Xu and colleagues [98] have prepared PVP blocked Pt (Pt_{PVP}), partially PVP removed Pt (Pt_{rPVP}) and PVP-free Pt (Pt) by modulating the microenvironment of metal-assisted catalysts and encapsulated them in UiO-66-NH₂, respectively. In addition, the authors also introduced ferrocene carboxylic acid (Fc) to prepare Pt-Fc@UiO-66-NH₂. The photogenerated charge separation of PtPVP@UiO-66-NH₂ was intermediate among all samples. This suggests that PVP impedes charge transfer and does not facilitate the enhancement of conductivity. The hydrogen evolution activity of PtPVP@UiO-66-NH₂ (242.7 $\mu\text{mol g}^{-1} \text{h}^{-1}$) surpasses that of PtPVP@UiO-66-NH₂, and exhibits the capability to increase to 375.9 $\mu\text{mol g}^{-1} \text{h}^{-1}$ with varying immersion times

in Meerwein salt solution. Pt@UiO-66-NH₂ showed higher H₂ yield (400.7 $\mu\text{mol g}^{-1} \text{h}^{-1}$). At present, there have been too many reports that Pt and UiO-66-NH₂ have been selected as objects for research within the domain of photocatalysis and other metal-loaded substances and MOFs can be appropriately expanded for related research.

(2) Metal NCs-loaded MOFs

The Pt(x)/MIL-125-NH-CH₂OH prepared by Huang *et al.* [99] was able to exhibit excellent hydrogen production activity under visible light (>420 nm). In this investigation, the optimal Pt loading was determined to be 1.43 wt%, resulting in a remarkable 31-fold increase in hydrogen production activity compared to pure MOFs, reaching 4496.4 $\mu\text{mol g}^{-1} \text{h}^{-1}$. This enhancement can be attributed to the synergistic interplay between highly dispersed Pt clusters and MOFs, which facilitates charge transfer and separation. The photocatalytic activity of MOFs was significantly enhanced by Pt NCs loading.

(3) Metal NPs-loaded MOFs

There are many studies on loading metal NPs onto MOFs. For example, Toyao *et al.* [100] used photodeposition to deposit Pt on Ti-MOF-NH₂. The improvement of photocatalytic performance is mainly attributed to the fact that the deposited Pt NPs can effectively improve the separation rate of photo-generated electron-hole pairs.

5.3. Photooxidation

Photooxidation processes require the selective oxidation of organic matter into other intermediate products or derivatives with the assistance of reactive oxygen species (ROS). Please see Texts S10 and S11 (Supporting information) for the principle and examples of studies. Similar to the line taken by other reports, Kondo *et al.* [101] selected Hf-UiO-66-NH₂ with good water stability, combined with acetic acid synthesis and the introduction of metallic SAs, and the SAs/MOF prepared by this method was used for photocatalytic production of hydrogen peroxide. In Ni/Hf-0.5, defects inhibit non-radiative relaxation and H₂O₂ decomposition, while Ni SA prevents electron hole recombination. In visible light, Ni/Hf-0.5 produces 6.3 times more H₂O₂ than the original Hf-UiO-66-NH₂ within 3 h. Different from other studies focusing on the LMCT effect in MOFs, the authors chose MOFs without this effect, which is innovative.

In addition, photocatalytic hydrogen production and organic oxidation conversion reactions can be combined. Liu *et al.* [102] first reported the implementation of this coupling strategy with MOFs-based catalysts (Pt/PCN-777 and Pt/MOF-808). This process entails the reduction of water to H₂ and the simultaneous oxidation of benzylamine to *n*-benzylidene-diamine. In the presence of TEOA, the H₂ yield of Pt/PPCN-777 reaches a remarkable 586 $\mu\text{mol g}^{-1} \text{h}^{-1}$. Substituting TEOA with an equivalent amount of benzylamine results in a decreased H₂ yield (332 $\mu\text{mol g}^{-1} \text{h}^{-1}$) and a highly selective conversion of benzylamine (>99%, 486 $\mu\text{mol g}^{-1} \text{h}^{-1}$). On the contrary, the catalytic activity of Pt/MOF-808 was much lower than that of Pt/PCN-777. This is mainly due to the promotion of charge separation by elongated conjugated ligands in PPCN-777. Therefore, in addition to the regulation of ligand functionalization of MOFs, MOFs composed of different ligands can also be selected as carriers to study their catalytic properties.

5.4. Photo-hydrogenation

Photocatalytic hydrogenation has also become an important branch in the field of photocatalysis, the principles of which are

detailed in Text S12 (Supporting information). For instance, ultra-fine Pd₃Cu NPs are limited by Ling *et al.* for CO₂ hydrogenation in UiO-66 [103]. The results show that the role of solar energy cannot be ignored. Under the same conditions (200 °C, 1.25 MPa H₂), the methanol yield (340 μmol g⁻¹ h⁻¹) of Pd₃Cu@UiO-66 under light condition is 5.6-fold greater than that under dark condition. The transfer of photogenerated electrons from MOF to the antibonding orbital of CO₂* promotes the activation of CO₂ and the formation of HCOO*. In addition, Pd₃Cu microenvironment plays a key role in CO₂ hydrogenation.

From the results reported above, it can be seen that such metal-loaded MOFs are widely used within the domain of photocatalysis at present. However, the significant improvement in the performance of the vast majority of catalysts depends on the supporting of precious metals. Therefore, it is worth studying how to regulate the catalytic activity of materials loaded with precious metals by non-precious metal or pure MOFs. For other examples of coverage, please see Text S13 (Supporting information).

6. Conclusion and outlook

In conclusion, this paper provides a comprehensive review of the advancements in research related to MOFs loaded with metal entities of diverse sizes (single atoms, nanoclusters, and nanoparticles) is reviewed in this paper. Based on the factors affecting the photocatalytic performance, the design principle, synthesis method and application of metal-loaded MOFs photocatalysts photocatalysis were summarized. In addition, many relevant studies were listed for readers' reference. For example, from the perspective of structural regulation of MOFs, a variety of metal-loaded MOFs materials with various structures can be designed and prepared by combining the crystal growth law, defect engineering, ligand exchange and functionalization theories. In general, the role of MOFs carrier should not be ignored in the design of metal-loaded MOFs, but should be highlighted to the greatest extent. We also deliberate on the prospects and hurdles associated with these photocatalysts:

- (1) Maximizing the advantages of MOFs
Materials is still worth studying. Numerous reports frequently overlook the benefits of MOFs subsequent to the preparation of metal-loaded MOFs, including their flexible and adaptable structure, substantial specific surface area and pore structure, exploitable unsaturated active sites and adjustable solar response range. However, many MOFs materials still confront with the problems such as poor stability and low electronic conductivity. The structural collapse of MOFs is challenging to circumvent during the loading process, underscoring the critical importance of carefully selecting a suitable MOFs carrier and designing and preparing a composite photocatalyst based on MOFs with exceptional stability.
- (2) There is still a certain distance to achieve industrial production and application. Compared with the industrial production process, the preparation process of metal-loaded MOFs is complex and the yield is low. The preparation process of different types of metal-loaded MOFs materials is often different. In addition, many photocatalytic applications are still in the laboratory research stage, and these reaction conditions and yields are difficult to meet the requirements of practical industrial applications. In addition, costs due to the load of the precious metal entity and the complex composition of the ligand need to be considered. However, with the continuous deepening of research, we believe that these problems will be solved in the near future. In addition, the metal-loaded MOFs photocatalysts reported so far have been used in many fields such as photocatalytic CO₂

reduction, photocatalytic hydrogen production, photooxidation and photocatalytic hydrogenation, which are of great significance for energy conservation and sustainable development. Therefore, after the subsequent exploration of reaction mechanisms in other fields, such photocatalysts are expected to be applied in more fields.

- (3) Many reports lack in-depth study on the mechanism of the photocatalytic reaction process, which leads to the reason why the enhanced photocatalytic performance of many metal-loaded MOFs remains unexplained clearly. Therefore, further exploration of its mechanism is necessary through a variety of characterizations, testing methods, and theoretical calculations. Based on the above discussion, we believe that the metal-loaded MOFs described in this paper are promising photocatalysts due to their extremely high photocatalytic activity increased by their interactions and will become more dazzling in future studies. We hope that this review will bring insight and inspiration to the readers.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Shenglan Zhou: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Haijian Li:** Supervision. **Hongyi Gao:** Validation, Supervision, Investigation, Funding acquisition. **Ang Li:** Supervision, Investigation. **Tian Li:** Supervision. **Shanshan Cheng:** Visualization. **Jingjing Wang:** Supervision. **Jitti Kasemchainan:** Supervision. **Jianhua Yi:** Supervision. **Fengqi Zhao:** Supervision. **Wengang Qu:** Supervision.

Acknowledgments

This work was supported by the Beijing Natural Science Foundation (No. L233011), Guangdong Province Natural Science Foundation (No. 2022A1515011918), USTB Research Center for International People-to-People Exchange in Science, Technology and Civilization (No. 2023KFYB003).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2024.110142.

References

- [1] M. Mastalerz, M.W. Schneider, I.M. Opper, O. Presly, *Angew. Chem. Int. Ed.* 50 (2011) 1046–1051.
- [2] D.M. D'Alessandro, B. Smit, J.R. Long, *Angew. Chem. Int. Ed.* 49 (2010) 6058–6082.
- [3] Q. Wang, Q. Gao, A.M. Al-Enizi, A. Nafady, S. Ma, *Inorg. Chem. Front.* 7 (2020) 300–339.
- [4] T. Zhao, Y. Ren, J. Yang, et al., *J. Mater. Chem. A* 4 (2016) 16446–16453.
- [5] F. Shiraishi, M. Iwanaga, N. Kitagawa, F. Miyazaki, *J. Chem. Technol. Biotechnol.* 95 (2020) 2034–2044.
- [6] A. Samokhvalov, *Renew. Sustain. Energy Rev.* 72 (2017) 981–1000.
- [7] M. Ruokolainen, E. Ollikainen, T. Sikanen, T. Kotiaho, R. Kostianen, *J. Am. Chem. Soc.* 138 (2016) 7452–7455.
- [8] K. Wang, E. Kowalska, *Front. Chem.* 10 (2022) 972494.
- [9] M. Nasr, C. Eid, R. Habchi, P. Miele, M. Bechelany, *ChemSusChem* 11 (2018) 3023–3047.
- [10] A. Fujishima, K. Honda, *Nature* 238 (1972) 37–38.
- [11] A.J. Howarth, Y. Liu, P. Li, et al., *Nat. Rev. Mater.* 1 (2016) 15018.
- [12] Z.J. Lin, J. Lü, M. Hong, R. Cao, *Chem. Soc. Rev.* 43 (2014) 5867–5895.
- [13] A. Bavykina, N. Kolobov, I.S. Khan, et al., *Chem. Rev.* 120 (2020) 8468–8535.

- [14] Q. Pang, B. Tu, Q. Li, *Coord. Chem. Rev.* 388 (2019) 107–125.
- [15] H. Furukawa, K.E. Cordova, M. O’Keeffe, O.M. Yaghi, *Science* 341 (2013) 1230444.
- [16] X. Wang, X. Wang, X. Zhang, et al., *Cryst. Growth Des.* 20 (2020) 5670–5675.
- [17] Z. Li, K. Shi, L. Zhai, et al., *Sep. Purif. Technol.* 307 (2023) 122725.
- [18] Z. Li, P. Liu, C. Ou, X. Dong, *ACS Sustain. Chem. Eng.* 8 (2020) 15378–15404.
- [19] P. Brandt, S.H. Xing, J. Liang, et al., *ACS Appl. Mater. Interfaces* 13 (2021) 29137–29149.
- [20] K. Suresh, D. Aulakh, J. Purewal, et al., *J. Am. Chem. Soc.* 143 (2021) 10727–10734.
- [21] T. Jia, Y. Gu, F. Li, *J. Environ. Chem. Eng.* 10 (2022) 108300.
- [22] Z.B. Fang, T.T. Liu, J. Liu, et al., *J. Am. Chem. Soc.* 142 (2020) 12515–12523.
- [23] C. Zhang, C. Xie, Y. Gao, et al., *Angew. Chem. Int. Ed.* 61 (2022) e202204108.
- [24] Y. Zhu, J. Zheng, J. Ye, et al., *Nat. Commun.* 11 (2020) 5849.
- [25] Y. Liu, X. Yang, R. Guo, Z. Yao, *Int. J. Hydrog. Energy* 47 (2022) 39001–39017.
- [26] X. Kong, T. He, J. Zhou, et al., *Small* 17 (2021) 2005357.
- [27] E.S. Gutterød, S.H. Pulumati, G. Kaur, et al., *J. Am. Chem. Soc.* 142 (2020) 17105–17118.
- [28] J. Zhang, B. An, Z. Li, et al., *J. Am. Chem. Soc.* 143 (2021) 8829–8837.
- [29] M. Nie, H. Sun, D. Lei, et al., *Mater. Chem. Phys.* 254 (2020) 123481.
- [30] T. Stolar, A. Prašnikar, V. Martinez, et al., *ACS Appl. Mater. Interfaces* 13 (2021) 3070–3077.
- [31] X. Wang, Y. Zhu, H. Li, et al., *Small Methods* 6 (2022) 2200413.
- [32] J. Di, Y. Li, Y. Zhang, et al., *Trans. Tianjin Univ.* 29 (2023) 235–245.
- [33] Q. Lan, S. Jin, B. Yang, et al., *Trans. Tianjin Univ.* 28 (2022) 214–225.
- [34] X. Liang, L. Zhang, L. Chen, C.Y. Su, *Chin. Sci. Bull.* 63 (2018) 248–265.
- [35] Y. Wang, L. Ling, W. Zhang, et al., *ChemSusChem* 11 (2018) 666–671.
- [36] H. Chang, Y. Li, X. Jia, et al., *Mater. Sci. Semicond. Process.* 150 (2022) 106914.
- [37] J.D. Xiao, L. Han, J. Luo, S.H. Yu, H.L. Jiang, *Angew. Chem. Int. Ed.* 57 (2018) 1103–1107.
- [38] X. Ma, H. Liu, W. Yang, et al., *J. Am. Chem. Soc.* 143 (2021) 12220–12229.
- [39] D. Li, S.H. Yu, H.L. Jiang, *Adv. Mater.* 30 (2018) 1707377.
- [40] S. Payra, S. Roy, *J. Phys. Chem. C* 125 (2021) 8497–8507.
- [41] Y.C. Hao, L.W. Chen, J. Li, Y. Guo, et al., *Nat. Commun.* 12 (2021) 2682.
- [42] X. Feng, Y. Pi, Y. Song, et al., *J. Am. Chem. Soc.* 142 (2020) 690–695.
- [43] G. Wang, C.T. He, R. Huang, et al., *J. Am. Chem. Soc.* 142 (2020) 19339–19345.
- [44] Y. Fu, J. Wu, R. Du, et al., *RSC Adv.* 9 (2019) 37733–37738.
- [45] H. Wei, Z. Guo, X. Liang, et al., *ACS Appl. Mater. Interfaces* 11 (2019) 3016–3023.
- [46] X. Qiu, Y. Zhu, X. Zhang, et al., *Sol. RRL* 4 (2020) 1900449.
- [47] L. Liu, A. Corma, *Chem. Rev.* 118 (2018) 4981–5079.
- [48] L. Zhang, M. Zhou, A. Wang, T. Zhang, *Chem. Rev.* 120 (2020) 683–733.
- [49] J. Mao, J. Iocozzia, J. Huang, et al., *Energy Environ. Sci.* 11 (2018) 772–799.
- [50] Z. Zeng, Y. Su, X. Quan, et al., *Nano Energy* 69 (2020) 104409.
- [51] P. Zhou, F. Lv, N. Li, et al., *Nano Energy* 56 (2019) 127–137.
- [52] T.E. James, S.L. Hemmingson, C. Campbell, *ACS Catal.* 5 (2015) 5673–5678.
- [53] A. Corma, P. Concepción, M. Boronat, et al., *Nat. Chem.* 5 (2013) 775–781.
- [54] Q. Yang, Q. Xu, H.L. Jiang, *Chem. Soc. Rev.* 46 (2017) 4774–4808.
- [55] N. Cheng, L. Zhang, K. Doyle-Davis, X. Sun, *Energy Rev.* 2 (2019) 539–573.
- [56] K.L. Kollmannsberger, L. Kronthaler, J.R. Jinschek, R.A. Fischer, *Chem. Soc. Rev.* 51 (2022) 9933–9959.
- [57] H. Liu, M. Cheng, Y. Liu, et al., *Energy Environ. Sci.* 15 (2022) 3722–3749.
- [58] A. Aijaz, A. Karkamkar, Y.J. Choi, et al., *Am. Chem. Soc.* 134 (2012) 13926–13929.
- [59] J.D. Xiao, Q.C. Shang, Y.J. Xiong, *Angew. Chem. Int. Ed.* 55 (2016) 9389–9393.
- [60] S. Dong, Z. Liu, R. Liu, et al., *ACS Appl. Nano Mater.* 1 (2018) 4247–4257.
- [61] Y. Jiang, Y. Yu, X. Zhang, et al., *Angew. Chem. Int. Ed.* 60 (2021) 17388–17393.
- [62] S. Dai, T. Kajiwara, M. Ikeda, et al., *Angew. Chem. Int. Ed.* 61 (2022) e202211848.
- [63] W. Ma, J. Sun, S. Yao, et al., *Angew. Chem. Int. Ed.* 62 (2023) e202313784.
- [64] Y. Liu, Z. Liu, D. Huang, et al., *Coord. Chem. Rev.* 388 (2019) 63–78.
- [65] M. Wen, Y. Kuwahara, K. Mori, H. Yamashita, *Nanometal-loaded metal-organic-framework photocatalysts, Nanostructured Photocatalysts in: H. Yamashita, H. Li (Eds.), Springer International Publishing, Cham, 2016, pp. 507–522.*
- [66] J. Guo, Y. Wan, Y. Zhu, M. Zhao, Z. Tang, *Nano Res.* 14 (2021) 2037–2052.
- [67] Y. Shi, A.F. Yang, C.S. Cao, B. Zhao, *Coord. Chem. Rev.* 390 (2019) 50–75.
- [68] M. Alvaro, E. Carbonell, B. Ferrer, F.X. Llabrés i Xamena, H. Garcia, *Chem. Eur. J.* 13 (2007) 5106–5112.
- [69] Y. Cui, Y. Yue, G. Qian, B. Chen, *Chem. Rev.* 112 (2012) 1126–1162.
- [70] X. Li, Q.L. Zhu, *Energy Chem.* 2 (2020) 100033.
- [71] Z. Sun, K. Sun, M. Gao, Ö. Metin, H. Jiang, *Angew. Chem. Int. Ed.* 61 (2022) e202206108.
- [72] M. Ding, X. Cai, H.L. Jiang, *Chem. Sci.* 10 (2019) 10209–10230.
- [73] Q. Zuo, R. Cui, L. Wang, et al., *Sci. China Chem.* 66 (2023) 570–577.
- [74] W. Liu, S. Zhang, B. Wu, et al., *ACS Appl. Nano Mater.* 6 (2023) 16826–16836.
- [75] Y. Che, X. Liu, M. Li, et al., *Appl. Surf. Sci.* 634 (2023) 157699.
- [76] J. Sui, H. Liu, S. Hu, et al., *Adv. Mater.* 34 (2022) 2109203.
- [77] Q. Zuo, T. Liu, C. Chen, et al., *Angew. Chem. Int. Ed.* 58 (2019) 10198–10203.
- [78] H. Zhang, J. Wei, J. Dong, et al., *Angew. Chem. Int. Ed.* 55 (2016) 14310–14314.
- [79] Y.Z. Cheng, Z.U. Wang, H. Wang, et al., *J. Am. Chem. Soc.* 139 (2017) 2035–2044.
- [80] T. Wang, X. Tao, Y. Xiao, et al., *Catal. Sci. Technol.* 10 (2020) 138–146.
- [81] T. Ishida, M. Nagaoka, T. Akita, M. Haruta, *Chem. Eur. J.* 14 (2008) 8456–8460.
- [82] D. Sun, Z. Li, *J. Phys. Chem. C* 120 (2016) 19744–19750.
- [83] F. Zheng, C. Zhang, X. Gao, et al., *Electrochim. Acta* 306 (2019) 627–634.
- [84] Q. Yang, Q. Xu, S.H. Yu, H.L. Jiang, *Angew. Chem. Int. Ed.* 128 (2016) 3749–3753.
- [85] Y. Yun, H. Sheng, K. Bao, et al., *J. Am. Chem. Soc.* 142 (2020) 4126–4130.
- [86] J. Becerra, D.T. Nguyen, V.N. Gopalakrishnan, *ACS Appl. Energy Mater.* 3 (2020) 7659–7665.
- [87] W.J. Chen, B.H. Cheng, Q.T. Sun, H. Jiang, *ChemCatChem* 10 (2018) 3659–3665.
- [88] J.L. Sun, Y.Z. Chen, B.D. Ge, J.H. Li, G.M. Wang, *ACS Appl. Mater. Interfaces* 11 (2019) 940–947.
- [89] L. Chen, X. Chen, H. Liu, C. Bai, Y. Li, *J. Mater. Chem. A* 3 (2015) 15259–15264.
- [90] M. Liu, L. Zhan, Y. Wang, et al., *J. Mater. Sci. Technol.* 165 (2023) 235–243.
- [91] L. Zhan, Y. Wang, M. Liu, et al., *Chin. Chem. Lett.* (2024), doi:10.1016/j.ccllet.2024.109695.
- [92] J. Liu, C. Chen, K. Zhang, L. Zhang, *Chin. Chem. Lett.* 32 (2021) 649–659.
- [93] Q. Huang, R. Wang, X. Li, et al., *Chin. Chem. Lett.* 34 (2023) 108517.
- [94] Y.C. Hao, *Nat. Commun.* 12 (2021) 2682.
- [95] J. Lu, S. Wang, Y. Zhao, et al., *Catal. Commun.* 175 (2023) 106613.
- [96] F.X. Llabrés i Xamena, A. Corma, H. Garcia, *J. Phys. Chem. C* 111 (2007) 80–85.
- [97] C.G. Silva, A. Corma, H. García, *J. Mater. Chem.* 20 (2010) 3141–3156.
- [98] M. Xu, D. Li, K. Sun, et al., *Angew. Chem. Int. Ed.* 60 (2021) 16372–16376.
- [99] X. Huang, X. Li, Q. Luan, et al., *Nano Res.* 14 (2021) 4250–4257.
- [100] T. Toyao, M. Saito, Y. Horiuchi, et al., *Catal. Sci. Technol.* 3 (2013) 2092.
- [101] Y. Kondo, K. Honda, Y. Kuwahara, et al., *ACS Catal.* 12 (2022) 14825–14835.
- [102] H. Liu, C. Xu, D. Li, H. Jiang, *Angew. Chem. Int. Ed.* 57 (2018) 5379–5383.
- [103] L. Ling, W. Yang, P. Yan, M. Wang, H. Jiang, *Angew. Chem. Int. Ed.* 61 (2022) e202116396.