Advances and challenges of MOF derived carbon-based electrocatalysts and photocatalyst for water splitting: A review

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Abstract   Environmental pollution and energy shortage are substantial fears to the modern world's long-term sustainability. Water splitting is an essential technique for eco - friendly and sustainable energy storage, as well as a pollution-free method to produce hydrogen. In this regards Metal–organic frameworks have emerged as the most competent multifunctional materials in recent times, due to its large surface areas, adjustable permeability, easy compositional alteration, and capability for usage as precursors with a wide range of morphological forms. Further, MOF-derived carbon-based nanomaterials also offer significant benefits in terms of tunable morphological features and hierarchical permeability, as well as ease of functionalization, making them extremely effective as catalysts or catalysts supports for a wide variety of important reactions. Recent developments in carbon-based MOFs as catalysts for overall water splitting are discussed in this review. We explore how MOFs and carbon-based MOFs might well be beneficial, as well as which methods should be explored for future development. We divided our review into two sections: photocatalytic and electrocatalytic water splitting, and we gathered published literature on carbon-based MOFs materials for their outstanding activity, offers helpful methods for catalysts design and analysis, as well as difficulties This study highlights the developments in MOF derived materials as photo and electro catalysts by explaining respective approaches for their use in overall water splitting.

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Contents

1. Introduction

Continuous economic expansion and an ever-growing world population at a pace of approximately 1.05 % annually, demand a consistent rise in energy consumption (Ager and Lapkin, 2018). The present energy sector's reliance on fossil fuels, oil, and natural gas puts our long-term development at risk due to finite reserves. Furthermore, the detrimental impact of fossil fuel consumption has been adequately shown by its disastrous impact on our planet's environment, climate, and overall health (Ahmad et al., 2015). Hence, conventional fossil fuel reserves depletion and the environmental hazards associated with their use, have necessitated the development of clean, renewable and sustainable energy sources as an alternate energy source (Xu et al., 2018; Zhang and Guan, 2021).

Sustainable energy sources often generate energy sporadically, demanding the storage of energy for future use (Mousazade et al., 2020; Wen et al., 2020). Therefore, much research has been directed toward the use of hydrogen (H_2) as an environmentally preferable energy carrier in a post-fossil fuel era. At the moment, it is widely accepted that H_2 may be the optimal solution for addressing the triple threat of fatigue, pollution, and climate change consequences (Acar and Dincer, 2015). It is possible to produce hydrogen from water by dividing it into its constituent components. A variety of energy sources can be used to split an H-O-H bond, including electricity, heat, and light. Electrolysis, thermolysis, and photolysis are the most common types of energy sources used in water splitting operations, with electrolysis and thermolysis being the most common (Rizvi et al., 2020). Overall water splitting is a chemical process that converts water to oxygen and hydrogen:

$$2H_2O \rightarrow 2H_2 + O_2$$
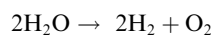
Here water is split into gaseous oxygen, together with protons and electrons, at the anode. The protons and electrons recombine to form hydrogen gas at the cathode (Yaqoob et al., 2021). By far, the energy conversion technology has piqued the interest of many people owing to its high conversion efficiency, low environmental impact, and potentially broad variety of applications (Li and Li, 2017). Electrocatalytic and photocatalytic hydrogen generation using water have already been examined as potential approaches for storing renewable energy in the form of chemical bonds to overcome the intermittent character of renewable energy sources such as solar irradiation (Liu et al., 2021; Anantharaj et al., 2016; Chen et al., 2022).

One of the strategies for producing hydrogen is photocatalytic water splitting as illustrated in Fig. 1, which utilizes photonic energy, the most abundant source of energy on the planet. According to previous studies, solar-based H_2 production via photocatalysis produces almost no global warming or air pollution and is stored safely (Dubey et al., 2014). As a result, H_2 is being evaluated as a potential
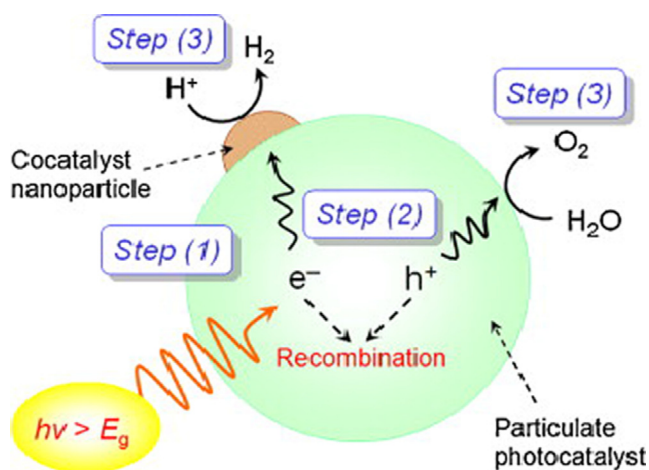
Fig. 1 Schematic representation of steps involve in water splitting via photocatalyst (Maeda, 2011). Exclusive rights 2011 Elsevier.

significant energy source in the future, as it is toxic-free and can generate significant amounts of energy from natural sources such as light energy and water, which are both clean, long-lasting, and renewable sources of energy (Tee et al., 2017).

Another strategy of hydrogen production is electrocatalytic water splitting, has been proposed as a viable solution to the renewable energy intermittency problem as an electrical current is used to split water electrolytically, and the electrical energy is converted to chemical energy at the electrode-solution junction via charge transfer processes in a device known an electrolyze. At the anode, water interacts to create oxygen and protons, however at the cathode, hydrogen is evolved (Yaqoob et al., 2020; Mei et al., 2021). Besides, it is estimated that electrolysis can provide just 3.9 % of the world's hydrogen consumption (Matheu et al., 2019). In comparison to conventional SMR, electrolytic water splitting is described as having "zero" CO_2 emissions (since oxygen will be the only by-product) (Hunter et al., 2016). However, as electrolysis are usually electrically powered, which would be primarily produced through the ignition of coal and natural gas and carbon dioxide is released as a by-product as an outcome. The electrochemical/catalytic water-splitting reaction is now being driven by sustainable harvesting technologies (such as wind generators or photovoltaic cells), and this is progressively becoming the focus of study in the current era. Using photochemical or photocatalytic water splitting to produce hydrogen is a potential alternative for hydrogen generation that is aimed toward reducing CO_2-emissions and making use of sustainable resources like water and sunshine (Albonetti et al., 2019; Wang et al., 2020).

On top of that, water electrolysis has a significant history and is often considered to become the most appealing and convenient way to generate hydrogen and oxygen. At the moment, the majority of commercial uses for water splitting catalysts are limited due to their high cost and scarcity of earth-scarce metals. There have thus been considerable efforts to substitute these precious metals and utilize more plentiful, robust, active, and cost-effective transition electrocatalyst (Walter et al., 2010). Recent advances in developing materials for water splitting. Long-term operating stability is a significant concern and materials are therefore needed, which play a protective function and characteristically stable in acute conditions (acid, base, lighting, heat) (Buriak et al., 2018). For electrocatalytic water splitting the development of efficient electrocatalysts that may efficiently accelerate slow kinetic processes and allow for both water reduction and oxidation at low overpotentials is crucial to ongoing research efforts (Hanif et al., 2019).

In this regards, a novel class of porous materials known as metal organic frameworks stand out as a promising water splitting candidate (Voitic and Hacker, 2016) as they are distinguished by a high degree of crystallinity, porosity, and pore size that significantly exceeds that of other porous materials, and the development of MOF as a catalyst has piqued the interest of researchers over the last decade (Yaqoob et al., 2019; Noor et al., 2019). As MOFs will draw a lot of attention in the future for catalytic applications like water splitting owing to their wide variety of inorganic and organic constituents and following are some of the most common benefits of MOFs and MOFs based composites for using as catalyst: (i) All of the building units, such as metal nodes, organic ligands, and channels, could be modified, resulting in a variety of frameworks, morphologies, sizes, and functional areas; (ii) organic ligands and metal nodes, including both are employed as catalytic centers and light-harvesting centers, to increase active surface area and shorten the photo-generated charges transmission distance; (iii) The porosity of the structure allows encapsulation of additional functional elements in order to create a novel composites and achieve synergetic catalysis; (iv) nanopores may provide the substratum with a unique chemical environment that is able, like the secondary structure of the active site, to interact with the catalytic active site and further enhances its activities and selectivity; (v) The simulation at molecular level of the natural photosynthesis system and single-site catalysts loading can be carried out over certain control of the contact between metal and ligand; (vi) MOFs to create particular functional metal complexes might be utilized as a precursor to get new structures which cannot be achieved using conventional techniques.

Despite considerable success in using MOF-based composites as electro /photocatalysts, additional effort is needed to address the subsequent challenges. such as, MOFs' quantum efficiency of hydrogen generation is poor, demanding further research into the complex chemistry of MOFs for photocatalytic and electrocatalytic applications.

The moisture sensitivity and excellent stability in aqueous environments over a wide pH range of some MOFs has long been regarded as a crucial issue that restricts their applicability (Noor et al., 2019; Noor et al., 2021; Yaqoob et al., 2021). Additionally, the inclusion of noble metals, which are scarce and costly and are not economically desired for large-scale use, improved the efficacy of most reported MOF-based catalysts. Furthermore, certain MOFs' organic linkers are complicated and costly, posing a challenge for their use. Therefore, development of mixed organic linkers, exploration of mixed-organic linkers and transition metal-based catalysts and use of carbon-based co-catalysts including graphene may be an interesting approach in the future to minimize the cost of MOF-based catalysts (Wen et al., 2020; Huang et al., 2022). Further as photocatalyst, several MOF have a limited light harvesting capability by nature, which is a major hindrance to high photocatalytic performance (Gao et al., 2022). MOF materials' soft structures can collapse during the photo water splitting reaction, prompting concerns about their stability. Furthermore, the charge carrier separation and transfer are limited by the intrinsic weak conductivity of MOF material. Therefore, subsequent techniques can be considered in order to address these issues. To begin, more conductive MOF materials must be explored and developed in order to increase electron–hole separation and transmission in a photocatalysts system. For constructing MOF-based solar-driven water splitting, a thorough knowledge of charge transport across the interfaces of MOF based composites is essential. Further, in situ spectroscopic and structural studies of the reaction intermediates, charge transfer, and products, as well as advanced characterization techniques, can give significant information. Additionally, to explain the unclear water splitting process on MOF-based materials, it is required to integrate experimental and theoretical techniques (Li et al., 2021).

Despite these problems, catalytic water splitting over MOFs-based catalysts has a promising future due to its distinct attributes such as large surface area, tunable pore volume, size, 3D structure, and rich coordinating chemistry (Nguyen, 2021) and the synergistic impact of MOFs framework and porous characteristics has provided a new set

of possibilities for these MOFs in a wide variety of zones, notably in catalysis (Zhang et al., 2020; Sarwar et al., 2018). The outer coordinating sphere impacts of MOFs-based catalyst, such as hydrogen bonding and proton transfer transmission, must be noted. This tends to imply that MOF catalytic sites may be approached by designing of its framework through integrating different active ligands and metal components, and therefore can exhibit extremely amazing synergic effect, resulting in significantly enhanced catalytic performance (Ipadeola and Ozoemena, 2020; Noor et al., 2020).

Furthermore, carbon materials have been proven to be active materials for OER and HER throughout the last decade. Carbon compounds as an effective material and will also act as catalyst supports have both been actively researched in recent years for overall water splitting, with benefits in both structural characteristics and intrinsic activity (Liu et al., 2021) and can be employed as multifunctional supports to promote charge and mass transport when combined with a metal organic framework. Likewise, carbon products derived from MOFs have superior features such as a large surface area, a variable pore size, high porosity, high conductivity, and stability (Yang et al., 2021). Further, graphene sheets have been demonstrated as a component in the fabrication of new heterojunctions with various MOFs for water splitting. The graphene oxides (GO), reduced graphene oxide (rGO) were chosen for their textural and electrical features.

In the design and synthesis of cost-effective high-activity electro/ photocatalysts for the water splitting system, MOFs are commonly used as templates to fabricate variety of carbon based catalysts such as carbon based materials composited with metal, metal oxides and metal carbides. Chen et al. prepared Co@N-CNTs@rGO by a new and efficient method for producing ultrafine Co nanoparticles enclosed in nitrogen-doped carbon nanotubes (N-CNTs) mounted onto rGO. Pyrolysis of coreshell ZIF-67@ZIF-8 evenly attached on graphene oxide yielded hybrid composites with 3D hierarchical structure (GO). Organic ligands derived from core-shell ZIF-67@ZIF-8 crystals were gradually changed into N-doped carbon nanotubes during carbonization due to the catalytic activity of the Co species, resulting in tightly linked Co cores and NCNTs shells. Simultaneously, the graphene oxide was thermally reduced to rGO. It revealed that integrating Co nanoparticles, N-CNTs, and graphene sheets into a 3D hierarchical design resulted in highly exposed active sites and increased diffusion kinetics and mass transfer, owing to the catalyst's synergistic interactions, large interfacial area, and plentiful porosity (Chen et al., 2018).

Above and beyond, the shortage of pure water, hydrogen generation from saltwater electrolysis is becoming more appealing. If saltwater is directly electrolyzed rather than pure water, it may not only store clean energy but also create fresh drinking water, which is very useful in desert regions. According to statistics, seawater comprises for > 97 % of earth's water resources over 1.33 billion cubic kilometers. Further, the effective implementation of seawater splitting will be extremely beneficial to the growth of the sustainable society (Mohammed-Ibrahim and Moussab, 2020). Additionally, given the availability of saltwater on the planet, using actual seawater for the creation of hydrogen to generate energy will effectively tackle the problems of fossil energy scarcity and pollution. Because of the numerous advantages of seawater splitting, more and more attention is being paid to seawater electrolysis research (Wang et al., 2021) and much improvement has already been achieved in seawater electrolysis research. The development of suitable electrode catalysts with selective and constant electrocatalytic efficiency in seawater is a critical step in the implementation of seawater electrolysis. Electrocatalysts with inherent corrosion resistance or selective surface chemistry are being suggested as promising solutions for improving the long-term stability of electrocatalysts in seawater (Huang et al., 2019). However, high overpotential, poor stability and low activity remain issues with the developed electrocatalyst. Furthermore, as sodium chloride is present in saltwater, a significant overpotential will result in a major unfavorable reaction of chlorine evolution and electrode degradation. Furthermore, it is well understood that saltwater is a complex solution containing up to 3.5 % different salts, in which multiple competing redox processes and dramatic pH swings result in catalyst deterioration and biofouling (Wang et al., 2022).

A large number of strategies for preparing electro catalysts for sea water splitting have recently been reported. Through structural and morphological engineering of various catalysts the electro catalyst performance in seawater splitting is improved. In addition, carbon-based electro catalysts have recently been discovered to have large surface area and elevated surface activity, allowing them to widen the interfacial interaction between the electrode and electrolyte and thus improve electron, ion, and reactions product transfer (Liu et al., 2020). As a consequence, most carbon-based catalysts may be capable of achieving the efficiency of seawater splitting, and appropriate materials as precursors are required for the creation of carbon-based electro catalysts. A suitable precursor can aid to boost the catalyst's effectiveness and broaden its range of applicability. Amongst several precursors, zeolite imidazolate frameworks which are built by coordinating metal ions with imidazole linkers, have received a lot of attention because of metal ions, that are distributed equally as catalytic active centers and the particular frame structure can be preserved after heating treatment. The overall conductivity and stability of ZIF-derived materials, however, limit their use in electro catalysts. Mixing with a durable and conducting substrate has been shown to be a successful solution to this problem (Khan et al., 2021). Zhang et al. reported the carbonization of a composite material made up of ZIF and carbon paper (ZIF-L-Co@CP) to produce a novel multifunctional catalyst (Co/ Co_3O_4@C). Surprisingly, the OER property of Co/Co_3O_4@C seems to be much superior in real seawater than in 1 M KOH. The ability of Co/Co_3-O_4@C (1.929 V) to achieve a current density of 10 mA/cm^2 is significantly lower than that of ZIFL-Co@CP, though there is still a small difference when compared to IrO_2 (1.858 V). Co/Co_3O_4@C also shows good catalytic activity for HER in seawater. Overall, Co/ Co_3O_4@C displays excellent HER and OER catalytic activities in seawater, which can be used to enhance the electrophilic adsorption and OH$^-$ oxidation during the oxygen evaluation reaction (Zhang et al., 2020). To our understanding, the majority of carbon-based catalysts reported have excellent water splitting ability in alkaline electrolytes, but only a few have been used in actual seawater.

The purpose of this article is to discuss the current advancement of MOF-based materials for photocatalytic and electrocatalytic water splitting processes. Numerous key variables affecting the activity of water splitting reactions are reviewed, and techniques for catalyst design are highlighted. The authors emphasize significant problems in the domains of photocatalytic and electrocatalytic water splitting and provide some insights on current developments in the production of MOF-based catalysts. Future research directions are indeed discussed, with a particular emphasis on obtaining the required MOF functionality and developing framework correlations in order to discover and explain the variables that affect catalytic activity. This article will offer an overview of current developments in this dynamic sector, and also some suggestions for the future development of highly effective photocatalysts and electrocatalysts for water splitting based on MOFs.

1.1. Stability challenges and its solutions of MOFs during water splitting

An entirely new family of porous materials, known as metal–organic frameworks, has been created by combining metal ions and organic ligands. They have been widely used in a wide range of fields due to the various of functions they can perform owing to its regular and well-defined structures and relatively high surface areas as well as its capacity to be tailored in many different ways (Gong et al., 2021). However, according to the latest findings, majority of MOF types are unstable when exposed to water and losing their structural integrity. Because of metal and oxygen connections inside the frameworks are rather weak, they are rapidly targeted by molecules of water and thus it loses its structure, preventing their operability in water splitting

either by electro catalytic way or photo catalytically. Further, the charge and mass transmission may be hampered by the intrinsically poor conductivity and tiny pore size, which is difficult to compensate for even if a much more permeable and conducting support is used. Likewise, majority of metal active sites are firmly encircled by organic ligands, rendering them unable to participate to the reaction. In addition, sustaining the MOF structure during the harsh oxidative conditions of the OER process is also difficult (Fan et al., 2017).

To address these problems, researchers have worked hard to create a variety of ways to improve MOF stability. In general, the stability of MOFs is governed primarily by the metal and ligand bond strength when it come in contact with water. For improving stability Pearson's hard/soft acid/base (HSAB) concept may be used to estimate the strength of metal–ligand coordination bonds. Stable MOFs may be made via the de novo synthesis approach by linking high-valent metal ions (hard acids) with carboxylate-based ligands (hard bases). UiO-66 and MIL-101 are some well-known examples for water splitting photo catalytically (Luo et al., 2020). Similarly, stable MOFs may be made by combining low-valent metal ions (soft acids) with azolate ligands (soft bases), such as $Ni_3(BTP)_2$, ZIF-8, and PCN-602, among others (Gao et al., 2021). Another way to improve the stability of MOF based catalysts for water splitting is by the introduction of rigid and hydrophobic linkers utilization during MOF synthesis. High-connected metal clusters are usually linked with rigid organic linkers that are generally very stable. This typically leads to dense and rigid frameworks. Because some isostructural MOFs have organic linkers that get longer, this can make the framework less stable. On the other hand, making low permeability or interfaces by adding hydrophobic groups to the linkers can also make MOFs more stable.

Fortunately, the insertion of hydrophobic functional groups inside the frameworks has the potential to significantly strengthen the M−O bonds, thereby significantly increasing the water resistance of the MOFs. For example, inserting a CH_3 functional group inside the framework may improve its water/moisture stability. In this regards, Liu et al. reported Cu-MOFs complexes for oxygen evaluation reaction. He suggested, the incorporation of hydrophobic functional groups (methyl) on the ligands attributes to the stability of Cu-MOF significantly, which plays key role in better electrocatalytic activity for oxygen evaluation reaction during water splitting in an alkaline media by showing high electrocatalytic activity with lower overpotential values such as 1.54 V and low Tafel slope value i.e., 122 mV/dec. Lastly, via introduction of hydrophobic layer on the surface. Aside from the internal elements mentioned above, the outer surface of MOFs, has also an impact on MOF stability. The surface wettability of MOFs can be changed by coating hydrophobic substances on the exterior of water - soluble MOFs or by heating them after they've been made, which makes them more stable. With the above methods, a lot of stable MOF materials were prepared for oxygen evaluation reaction either thru photocatalytic and or electrocatalytic way of water splitting (Zhu et al., 2018).

2. Photocatalytic water splitting

A number of studies is focusing on photocatalytic water splitting to produce oxygen and hydrogen as a possible source of renewable energy generation which is not dependent on fossil fuels and emits no carbon dioxide. Photocatalytic water splitting is termed as an artificial photosynthesis, since it is comparable to photosynthesis process in green plants by utilizing solar energy (Abe, 2010; Shi et al., 2014). In addition, hydrogen production from organic precursors from wastewater possibly will achieved with photocatalytic processes by utilizing sun energy that hit the surface of earth each day (Clarizia et al., 2014). The photocatalyst-assisted water splitting technology has received considerable recognition because to its ecologically friendly conversion of solar energy to clean and storable chemical energy. The ideal and ultimate objective for practical applications is to split the water without requiring a sacrificial reagent. Unfortunately, photocatalytic water splitting confronts number of challenges due to thermodynamic and kinetics limitations as water splitting is an uphill process with a Gibbs free energy of 237 kJ/mol (Xu et al., 2018). Generally, the oxygen evolution half-reaction, which has several stages and a high activation barrier, limits the total water-splitting process. A photocatalyst must not only have a proper band structure with adequate redox power, but also have a high separation efficiency of photogenerated carriers and a sufficient quantity of active sites to provide a desirable total water splitting efficiency. Rarely a photocatalyst meet all of the above cited criteria.

For photo-catalytically splitting of water, there are more than one methods are presented (Yang et al., 2021). One method is to split water into oxygen and hydrogen using a single visible-light-responsive photocatalyst with enough capability to accomplish total water splitting. In such system the photocatalyst must have an appropriate thermodynamic potential for water splitting i.e., a relatively low band gap to collect visible photons, and a high level of durability over photo corrosion. These strict criteria mean that the range of photocatalysts that can reliably split water in a single process is restricted (Srinivas et al., 2021).

Therefore, various techniques, such as doping, metal loading, heterojunction construction, and others, have been researched to improve the photoconversion efficiency of photocatalysts throughout last few decades. Among these proposed solutions, combining two semiconductors to make a type-II heterojunction photocatalyst is one of the simplest ways to improve photocatalytic activities, owing to its efficacy in spatially isolating photogenerated electron–hole pairs via the band gaps of two semiconductors. In a typical type-II heterojunction, semiconductor A conduction band and valence band are both greater than those of semiconductor B. (Fig. 3a). As a consequence of band alignment, photogenerated electrons in semiconductor A conduction band will migrate to semiconductor B conduction band upon light irradiation. Consequently, photogenerated holes in semiconductor B valence band will move to semiconductor A valance band. As photogenerated holes and electrons collect on semiconductor A and semiconductor B, a type-II heterojunction photocatalyst can accomplish spatial separation of the electrons and holes to improve photocatalytic activity. However, there are a number of issues that prevent type-II heterojunction photocatalysts from being widely used (Lu et al., 2022). More in detail, type-II heterojunction photocatalysts' reduction and oxidation reactions occur for semiconductor B with a relatively low reduction potential and semiconductor A with a lower oxidation potential, respectively. As a result, type-II heterojunction photocatalysts' redox capacity will be considerably diminished. Additionally, electrons in semiconductor A and holes in semiconductor B have a lot of difficulty during migration to the electron-rich conduction band and hole-rich valance band regions of semiconductor B and A, respectively, due to electrostatic repulsion between hole–hole and electron–electron. To overcome these issues, new heterostructure photocatalytic systems are desperately needed (Xu et al., 2020).

Alternatively, the second method is the use of two distinct photocatalysts in a two-step excitation method, inspired by the Z-scheme (a natural photosynthesis of green plants), and

in 2013, Yu et al. came up with the idea of a direct Z-scheme photocatalyst to explain why the TiO$_2$/g-C$_3$N$_4$ composite had a high photocatalytic formaldehyde (HCHO) degradation rate. In recent times, the Z-scheme configuration in photocatalytic based systems is one of the most up to date strategies to enhance the performance of catalyst in contrast to single semiconductor photocatalyst utilizations. Usually, Z-scheme systems are classified with redox intermediates, without intermediaries of electrons, and with solid state electron intermediaries (Li et al., 2016). Generally, reactants, photocatalyst, photoreactor and light for the emission of hydrogen are required in a photocatalytic system. Water act a reactant, for photocatalyst, it must be functioning with light, either visible or UV light. Absorbing light in the visible range might be an assurance to capture considerable part of the energy evolved by the sunlight (Tahir and Amin, 2013). Photocatalytic reaction starts with light irradiation equal to the band gap of photocatalyst may excite the electron from valance band to conduction band. Generated electron and hole pair is separated and use it for reduction and oxidation (Acar et al., 2014).

Compared to the one-step water splitting system, developing a direct Z-scheme photocatalyst significantly suppresses electron–hole recombination and isolates the photocatalytic reaction oxidation and reduction sites. As a result, numerous direct Z-scheme photocatalysts have now been investigated in order to maximize the effectiveness of photocatalytic hydrogen production (Li et al., 2021; Lu et al., 2019). Further, Z-scheme water splitting system has the benefit of a broader spectrum of visible light that's because the Gibbs free energy needed to drive a photocatalyst may be lowered, as well as

the separation of hydrogen and oxygen is also possible (Nasir et al., 2020; Nishioka et al., 2019), following one step and two step photocatalysis of water splitting is shown in Fig. 2.

Further, the structure of a direct Z-scheme photocatalyst is identical to that of a type-II heterojunction photocatalyst (Fig. 3a,b), but the mechanism of charge carrier migration is different. In a typical direct Z-scheme system, the charge-carrier migration pathway resembles the letter "Z". During the photocatalytic reaction, the photogenerated in semiconductor B with lower reduction ability recombine with the photogenerated holes in semiconductor A with lower oxidation ability. As a result, the direct Z-scheme photocatalyst's redox capability can be improved. It should also be noted that charge-carrier migration in direct Z-scheme photocatalysts is physically more feasible than in type-II heterojunction photocatalysts, because the migration of photogenerated electrons from semiconductor B conduction band to semiconductor A photogenerated hole-rich valance band is preferred owing to the electrostatic attraction between the hole and the electron (Low et al., 2017).

Furthermore, the performance of photocatalytic water splitting may be determined by analyzing the efficiencies of total water splitting in the absence of sacrificial reagents. H$_2$ and O$_2$ are created simultaneously in a 2:1 stoichiometric ratio during total water splitting (eq. 1–2). To explore the kinetics of the proton reduction or water oxidation half reactions, sacrificial reagents are used to rapidly consume the photo - induced holes or electrons, thereby rendering the related half reaction as rate determining step. For instance, lactic acid, methanol,
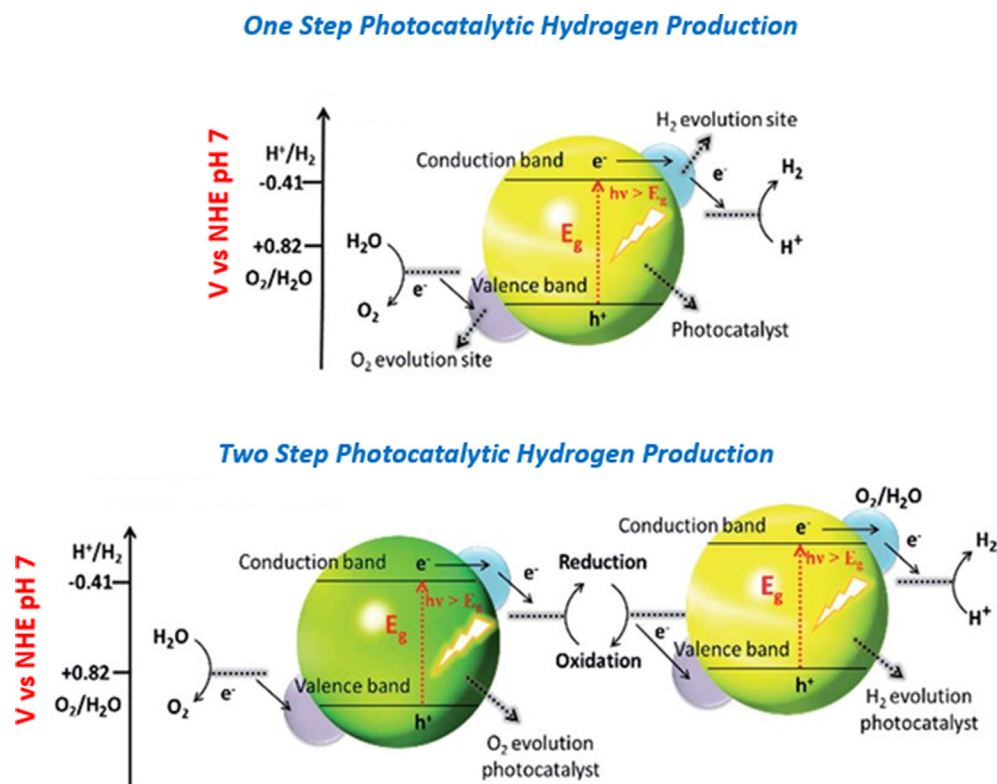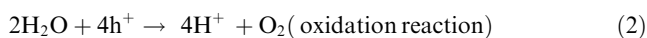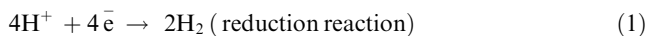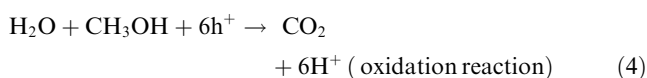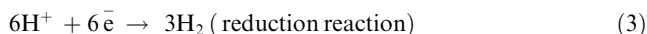

Fig. 2 Representation of one step and two step photocatalytic hydrogen production through a photocatalysts for water splitting (Maeda and Domen, 2010). Exclusive rights 2010 American Chemical Society.
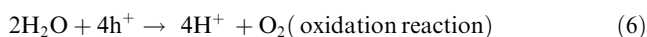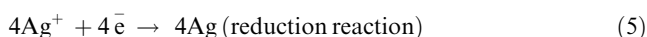
or triethanolamine are often employed as hole scavengers in the H_2 generation half reaction (eq. 3–4), whereas Ag^+, Fe^{3+} or IO_3 are typically utilized as electron scavengers in the O_2 evolution half reaction (eq. 5–6) (Li and Li, 2017). The overall photocatalytic water splitting mechanism for Hydrogen production is demonstrated in below equations (Fajrina and Tahir, 2019).

$$4H^+ + 4\bar{e} \rightarrow 2H_2 \,(\text{reduction reaction}) \tag{1}$$

$$2H_2O + 4h^+ \rightarrow 4H^+ + O_2 (\text{oxidation reaction}) \tag{2}$$

H_2 production half reaction in the presence of sacrificail reagent, taking CH_3OH as an example :

$$6H^+ + 6\bar{e} \rightarrow 3H_2 \,(\text{reduction reaction}) \tag{3}$$

$$H_2O + CH_3OH + 6h^+ \rightarrow CO_2 \\ + 6H^+ \,(\text{oxidation reaction}) \tag{4}$$

O_2 evoltion half reaction in the presence of sacrificail reagent, taking Ag as an example :

$$4Ag^+ + 4\bar{e} \rightarrow 4Ag \,(\text{reduction reaction}) \tag{5}$$

$$2H_2O + 4h^+ \rightarrow 4H^+ + O_2 (\text{oxidation reaction}) \tag{6}$$

Photocatalysis is a potential way to convert solar energy into chemical energy, various co-catalysts are frequently utilized to increase charge carrier separation at the semiconductor-electrolyte interface, hence enhancing the charge transport kinetics of the holes for water oxidation. Unfortunately, noble metal co-catalysts such as Pt, Au, and Ag nanoparticles are exceedingly costly. This necessitates the fabrication of photocatalysts that are cost effective (Wang et al., 2022). In this regard metal–organic frameworks have subsequently emerged as novel photocatalysts, due to their intrinsic structural properties of having a high specific surface area with a high porosity (Li et al., 2016). In comparison to conventional photocatalysts, MOFs exhibit a number of significant benefits in photo-induced reactions. MOFs, for example, can facilitate the exchange and dissemination of molecules due

to their desired topology and varied pore structure, which inherits the benefits of porous materials like zeolite, carbon nanomaterials and covalent organic frameworks (COFs). Additionally, numerous catalytic active sites are accessible as a result of the porous nature and large surface area of MOFs (Limwichean et al., 2021). The most unique characteristic of MOFs is their chemical and physical features, which can be augmented through careful design and tuning of their structure and composition; consequently, numerous reports have indeed been devoted to identifying the appropriate modification strategy for MOF photocatalysts for particular photo-induced applications. Numerous studies on the use of MOFs in photocatalytic water splitting have already been published in recent years as illustrated in Fig. 4.

2.1. Fabrication strategies for MOF derived photocatalysts

Many studies have shown that MOF-based photocatalysts with a porous structure can give various benefits during the photocatalytic activity, including abundant carrier charge transfer pathways, many reaction active sites, and excessive adsorption and desorption channels. In comparison to other semiconductor-based photocatalysts, MOF-based photocatalysts have the following advantages: i) the organic and inorganic constituents in MOFs contributes to enhance the structural stability; ii) the adjustable structure of MOFs promotes carrier charge separation and transfer rate. iii) MOFs with a high porosity may efficiently supply a large number of light absorption sites, resulting in enhanced light absorption capabilities (Sun et al., 2021). Such as Bag et al. reported CdS@NU-1000 and CdS@NU-10001% rGO composites for water splitting reaction under the irradiation of visible light exhibits 12.1 time more than CdS, due to its high surface area provided by rGO substrate and porosity is provided by MOF structure (Bag et al., 2017). Further, many researchers are inspired by these benefits, and they try to synthesize various types of MOFs and their composite as photocatalysts using variety of strategies, such as hydrothermal reaction method, solvothermal method, solution precipitation route, sonication method, microwave strategy, oil bath
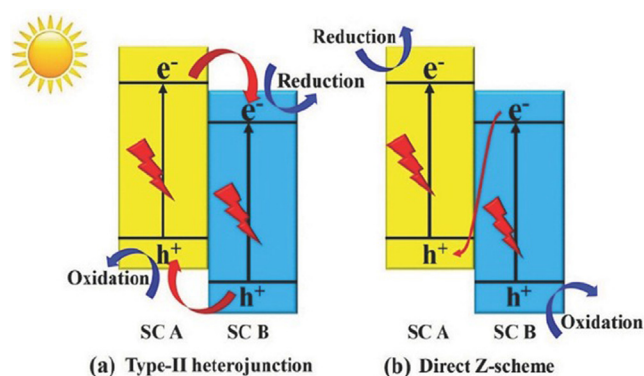

Fig. 3 Charge-carrier separation mechanisms on (a) type-II heterojunction and (b) direct Z-scheme for water splitting via two distinct photocatalysts (Low et al., 2017). Exclusive rights 2017 Wiley Online Library.
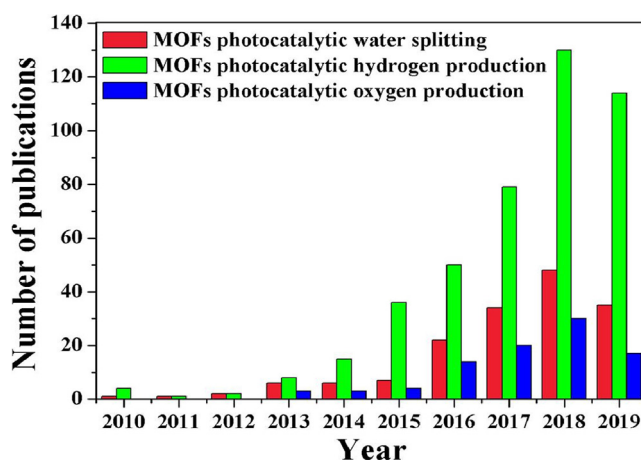

Fig. 4 The latest study advances in photocatalytic water splitting using metal–organic frameworks (Luo et al., 2020). Exclusive rights 2020 Elsevier.
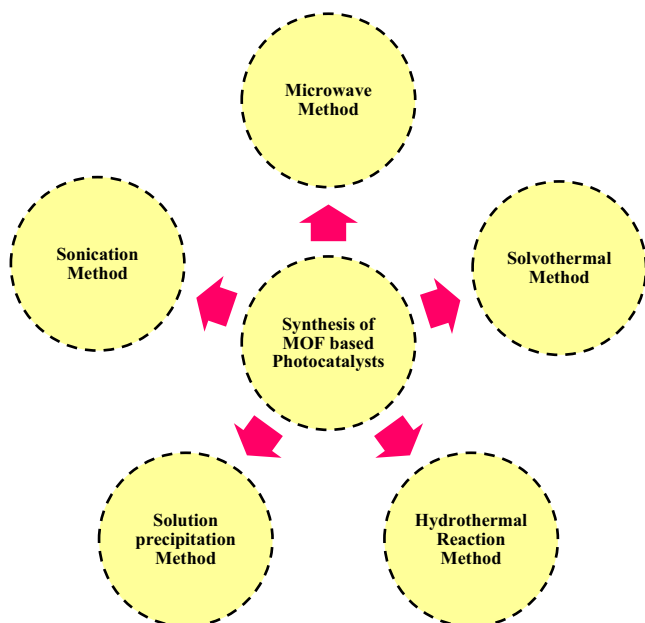
Fig. 5 synthetic routes of MOF based photocatalysts.

approach, template method, and so on (as shown in Fig. 5) (Su et al., 2018; Qian et al., 2021).

2.1.1. Solvothermal method

To synthesize MOFs and their composites as photocatalysts, the solvothermal approach is preferred because of its high yield, ease of use, low pressure and low temperature but selecting a suitable organic solvent is crucial points as organic solvents serve as both a structure-directing agent and a synthesis medium throughout the synthesis process. Various organic solvents, such as N,N-dimethylformamide, dimethyl sulfoxide, N,N-dimethylformamide and toluene, have been widely used to fabricate MOFs and their composites up to now. Among above mentioned organic solvents the DMF is most often selecting for the synthesis of MOF and its composites, due to its high boiling point and solubility, for instance, Ye et al. reported $rGO/ZnIn_2S_4$ nanocomposites were synthesized by utilizing a one-pot solvothermal technique from $InCl_3$, $ZnCl_2$, and TAA in the presence of varying amounts of GO in a 1:1 mixture of DMF and EG. To make $rGO/ZnIn_2S_4$ nanocomposites with a sheet-on-sheet morphology, a simple one-pot solvothermal process was established (Ye et al., 2014). Further, Huang et al. reported a MOF (PCN-624) was effectively prepared in the presence of DMF at 120 °C for 72 h through the solvothermal technique. Specifically, by incorporating the 12-connected nodes such as $[Ni_8(OH)_4(H_2-O)_2Pz_{12}]$ into PCN-624 during the solvothermal process, the as-prepared sample demonstrated significantly increased photocatalytic stability under a variability of conditions, including organic solvents, strong acid, and base solutions (Huang et al., 2018). Besides, numerous reports illustrated that MOFs and its carbon based composites were also synthesized in a variety of sizes and morphologies via the solvothermal method, for example, the polyhedral $PCN-250-Fe_3$ with a size of 13 m, UiO-68-TZDC over sizes ranging from 10 to 20 m, and the octahedral UiO-68.

Though the solvothermal approach has been widely applied to manufacture MOFs and their composite-based photocatalysts, the organic solvents' toxicity and environmental unfriendliness significantly limit their widespread deployment. Additionally, it is difficult to eliminate organic solvents afterwards the synthesis. Thus, it is critical to create green, safe, and environmentally acceptable solvents for the solvothermal approach of fabricating MOFs and their composite-based photocatalysts in the near future.

2.1.2. Hydrothermal method

Hydrothermal reactions can also be used to prepare MOFs and their composite-based photocatalysts. The reaction parameters, including the reaction temperature, solvents, pH, solvents, precursors, and reaction time, may be adjusted flexibly during the hydrothermal reaction process. MOFs and their composites with adjustable size and structure may be readily created by carefully controlling the synthesis conditions. Several research groups took use of the benefits of the hydrothermal reaction approach to manufacture high-performance MOFs and composite-based photocatalysts. Karthik et al in 2018 reported a reduced graphene oxide based MOF i.e., NH_2– MIL-125(Ti)/rGO photocatalyst for water splitting, prepared via hydrothermal method at 150 °C for 48 h. The strong $\pi - \pi$ connection was generated by combining NH_2-MIL-125(Ti) MOF with rGO and as a result of this interaction an enhanced photocatalytic hydrogen production ~9.1-fold is measured in contrast to NH_2-MIL-125(Ti) MOF.

Even though the hydrothermal reaction approach is an effective method for preparing MOFs and composite-based photocatalysts with adjustable size and shape, it still has significant drawbacks, such as low yield and extended reaction times. Furthermore, the creation mechanism of MOFs and their composites during the hydrothermal reaction phase remains unknown.

2.1.3. Solution precipitation method

Solution precipitation has been a frequently utilized approach for the fabrication of inorganic nanomaterials during the last several years. Since the cations are precipitating simultaneously, this technique is also known as the "co-precipitation method." In comparison to hydrothermal reaction, the solution precipitation technique is more simple and quicker for the synthesis of MOFs and their composites due to the ease of control and mild experimental conditions. Numerous research groups have taken use of these advantages to synthesize MOFs and their composites for use as photocatalysts. For instance, in 2021, Peng et al. synthesized Zn-ZIF-L composites by a one-step solution precipitation approach. In this study, $Zn(NO_3)_2 \cdot 3H_2O$ and MIM were combined in ultrapure water and then stirred at a low speed for > 4 h to create white precipitates. After that, the prepared Zn-ZIF-L was employed as a precursor to produce the two-dimensional (2D NC) N-doped nano porous carbon composites. Due to their high porosity and large surface area, these 2D NC composites exhibit a quick activity.

Apparently, the one-step solution precipitation approach is an easily manageable procedure for fabricating MOFs and their composites. Additionally, by carefully controlling the synthesis parameters, like stirring speed, reaction duration, and temperature, homogeneous morphology MOFs and their

composites may be obtained. We expect that this approach will attract more interest in the near future for the fabrication of MOFs and their composites.

2.1.4. Sonication method

The sonication approach has been established and developed as an efficient method for fabricating MOFs and their composites. In general, energy is transferred during sonication synthesis by acoustic cavitation, which would be the production, growth, and implosion of bubbles within the solvent. A sonication procedure like this, along with the produced high pressure and energy, can produce novel chemical effects and make it easier to construct a new structure. Numerous studies have been published so far employing the sonication approach to synthesis MOFs and composite-based photocatalysts. For instance, Abazari et al. reported g-C3N4/ Ti-MIL125-NH$_2$ composite photocatalysts via sonication method. To make the g-C$_3$N$_4$/Ti-MIL125-NH$_2$ composites, the g-C$_3$N$_4$ powder was first disseminated in a combination of methanol and DMF; the TPOT and 2-ATA were then added to the aforesaid solution and sonicated for 20 min. The as-fabricated g-C$_3$N$_4$ based Ti-MIL125-NH$_2$ composites have a wide surface area and strong light absorption capabilities (Li et al., 2018).

Besides, the tremendous energy and high pressure created during the sonication process help to create a stable structure. Because of these features, the sonication process has a lot of potential for producing high-quality, large-scale, and long-lasting MOFs based photocatalyst composites at quite a low cost.

2.1.5. Microwave method

The microwave approach has recently been recognized as a strong approach for generating functional materials. Throughout the reaction progression, the frequency of electromagnetic irradiation typically varies from 0.2 to 300 GHz, and energy may be transmitted quickly from the electromagnetic irradiation to the reaction precursor. The microwave technique is safer and quicker than the hydrothermal and solvothermal methods. Many research groups used this strategy to synthesize MOFs and their composite photocatalysts, fascinated by the benefits listed above.

For instance, Zhu et al. reported rGO based composites with MOF derived ZnO, synthesized via microwave assisted method. In summary, 16 mg of MOF-derived ZnO was introduced to a 20 mL graphene oxide solution, which was subsequently treated for 10 min at 150 °C with a microwave irradiation strength of 150 W using an automatic focused microwave system (Zhu et al., 2017). Though the microwave technique has been effective in fabricating MOFs and their composite photocatalysts, there are still major drawbacks in controlling the shape and size.

2.2. Basics of photocatalytic water splitting

The capability of photocatalyst to generate e$^-$/h$^+$ for the water splitting depends on number of factors that comprises of; (i) it should have greater capability to absorb wide range spectrum light to confirm the conversion of maximum photons in to charge carriers i.e., e$^-$ and h$^+$. (ii) The photocatalyst's band gap should be large enough i.e., 1.23 eV to fulfill the thermodynamic requirement of the overall water splitting process

(Ullah et al., 2018): (iii) The photocatalyst's conduction band edge must be relatively negative to the H$^+$/H$_2$ redox potential (0.0 V vs. NHE), while the valence band edge must be relatively positive to the O$_2$/H$_2$O redox potential (1.23 V vs. NHE). Furthermore, for oxygen and hydrogen generation the redox potential is dependent on the electrolyte pH (Ni et al., 2007): (iv) Another most important factor is the lifetime of the charges that must be protracted enough to participate in a particular redox process. This means photogenerated charges must reach the surface reaction sites before their recombination (Luo et al., 2020).

After the photocatalytic tests, TOC analysis was performed on the solutions to determine the degradation of organic sacrificial agents in the solutions. TOC values have been correlated with the overall concentration of organics in the solution (Kumaravel et al., 2019).

2.3. Challenges of photocatalytic water splitting

The rapid recombination process, poor absorption capacity, redox potential variance, and high diffusion barrier for charge transfer in successful catalysis processes are the main challenges that need to be focused. Additional difficulties connected with water splitting catalysts include poor absorption capability, structural degradation owing to photo corrosion, and recombination of rapid charge carriers (e$^-$/h$^+$). In addition to many other materials investigated over the past decades, MOFs are developing materials with the ability to solve the related problems owing to its intrinsic catalytic capability and tunable characteristics (Li et al., 2021). Some of the other challenges are:

2.3.1. Light absorption

In order to mollify the thermodynamic requirement of 1.23 V for photocatalytic water splitting, light absorbing materials with a sufficient band gap are required. To overcome kinetic limitations and successfully release molecular products, some overpotential is needed. The greater the overpotential, the quicker the electron transport to the catalytic site for accelerating the redox process. However, significant overpotential limits the choice of photocatalyst to broad band gap materials that exclusively use UV light. Various methods have been used to optimize photocatalytic material absorption ranges while considering thermodynamic and kinetic limitations (Kato et al., 2003; Marcus, 1957).

2.3.2. Charge separation

After generating (e$^-$/h$^+$) pairs, their isolation must be sustained until they can be used effectively in specific redox processes. Unfortunately, the majority of charge carriers recombine prior to participating in redox reactions due to its relatively limited survival time (nanoseconds) in comparison to water reduction (milliseconds) and oxidation (seconds) processes. Numerous methods have been developed to extend the lifespan of charge carriers in order to solve this challenge (Tang et al., 2008; Huang et al., 2018).

2.3.3. Effective charge utilization

In the photo-assisted water splitting process, the interfacial charges (e$^-$/h$^+$) are transferred to the adsorbate molecules

$(OH_2/H^+/OH)$, resulting in the formation of redox products (H_2/O_2), which is the rate determining factor. Usually, just one reaction, presumably oxidation or reduction, occurs to effectively generate the required product, while the remaining half of the reaction is scavenged by the sacrificial agents. During the reduction half reaction (HER), reductive sacrificial agents such as triethanolamine and many other are used to scavenge the holes. In comparison, during the oxidation half reaction (OER), electron acceptor scavengers (e.g., $Na_2S_2O_8$) are employed to obstruct the HER reaction. But the sacrificial agent's redox potential has to be greater than that of the photocatalyst, which may be fine-tuned through pH modification (Ullah et al., 2021).

2.4. Key strategies for improving MOF-Based photocatalyst water splitting performance

Many strategies have been developed to optimize the desirable characteristics of photocatalysts while also resolving related difficulties in order to increase the total photon to hydrogen conversion efficiency. Therefore, motivated by the aforementioned structural characteristics, photocatalysts of the MOF type have lately been extensively studied and categorized in to two subdivision, MOFs and MOF based compounds. Though, MOFs as photocatalysts face certain bottlenecks such as their low quantum efficiency. There are certain key strategies that has been adopted for improving the MOF-Based photocatalyst water splitting performance it includes:

- By band gap engineering
- By active sites engineering
- By coupling of metal organic framework with other functional materials

2.4.1. By band gap engineering

Due to the fact that photocatalytic activity is largely reliant on the photocatalyst's electronic structure, it is critical to modify the bandgap in order to use the maximum amount of visible photons and reach the goal of 10% solar to fuel conversion efficiency and by integrating the benefits of inorganic and organic chemistry, metal–organic frameworks (MOFs) offer a flexible platform for photocatalysts (Wang et al., 2018).

The majority of MOFs may be thought of as an assembly of semiconductor quantum dots that are dispersed uniformly across the structures and separated through tunable organic linkers. Both organic linkers and inorganic metal nodes may be readily tailored for light harvesting via the use of appropriate organic linkers, metal nodes, and their adjustable coordination modes (Li et al., 2021). Researchers have published large number of publications utilizing MOFs for photocatalysis across the globe in recent decades, but only a few dozens of papers concentrate on the engineering of band gaps from a theoretical and experimental standpoint. The band gap modulation of MOFs was addressed in fewer review papers (Guo et al., 2021).

according to Lu et al., band gaps may be reduced, via increasing the degree of linker conjugation, selecting electron-rich metal nodes and organic molecules, and decorating linkers with nitro and amino groups. The modifying photoelectronic performance of MOFs for premium

photocatalysis was summarized by Duan et al. in 2019. Based on the categorization of energy photocatalysis. Many researchers presented various methods for band gap engineering of semiconductor-type MOFs (Zhan et al., 2019).

Furthermore, Volkmer et al. suggested a number of alternative methods for lowering the band gap energy, such as (i) by increasing the degree of conjugation of the linker to achieve VB at a higher energy level, (ii) choosing a metal with diffuse and partially unoccupied d-orbitals as the node to lower the CB energy level, and (iii) by putting rich electronic fragments into the nodes of MOFs to lower the CB energy level (Kondo et al., 2021). In addition, Allendorf et al. suggested three broad strategies for modifying MOF electrical properties, such as (i) by changing the metal ion, (ii) by altering the organic linker, and (iii) by introducing specific organic groups into the frameworks (Yao et al., 2021). A series of MOF photocatalysts were produced by Wang and Huang et al via a Schiff-base reaction involving aldehyde[2/3/3- pyridine carboxaldehyde (2/3/4-PA)] and NH_2 in the NH_2-MIL-125 MOF groups as shown in Fig. 6a. XPS valence band spectrum and Mott-Schottky plots correspondingly have been used to evaluate CB and VB potential of heterocycle grafted NH_2-MIL-125 and the experimental findings show that the decrease of the bandwidth of implanted MIL-125 is positive with the aromatic heterocycle's electron donating ability as illustrated in Fig. 6b. The limited capacity to absorb light and the challenging recombination of semiconducting MOFs restrict artificial photosynthesis (Karthik et al., 2020). The insertion via simple postsynthetic coordination of metal ions into MOFs may not only increase optical absorption but also enhance the solar-to-fuel transformation. Moreover, the effective incorporation of transition metal ions (Ti^{2+}, Ni^{2+}, Co^{2+} or Cu^{2+}), via coordinating with $-NH_2$ Group, by means of a post-synthetic change into NH_2-MIL-125 and referred as Ni-MOF, Co-MOF, Ti-MOF, and Cu-MOF and illustrated in Fig. 6c. The UV–Visible tests reveals, absorption changes into the visible area as a result of the d-d transitions of coordinated M^{2+} ions. The band gaps of Ni-MOF, Cu-MOF, Co-MOF and Ti-MOF, compared to Mott-Schottky and Tauc plots, are 1.9 V, 1.7 V, 2.2 V, and 2.7 V correspondingly (Fig. 4b). Based on the coordination of M^{2+}, the VB potential of all M−me MOF are lower than the pure Ti-MOF since it only interacts with organic linkers (Huang et al., 2021).

2.4.2. By active sites engineering

Recently, a wide range of MOFs have been developed and manufactured, with the variability owing to the wide range of metal nodes and organic ligands. Metal nodes are, in general, the most important component in catalytic performance, and they may be purposefully chosen to create MOFs with the best activity (Wang et al., 2021). Using MOFs as carriers for photo catalytically active species is a more advanced way to employ them for photocatalysis. This technique has been extensively used for the encapsulation of a range of active sites, ranging from semiconductor nanoparticles to molecular catalysts and overall based on transition metal complexes. In this context, the MOF may either serve as a passive container or take part in the process of charge transfer (Hu et al., 2021). One of the most appealing aspects of employing MOFs to sustain active species is that these groups covalently linked to the framework or enclosed in its cavities. This method has been
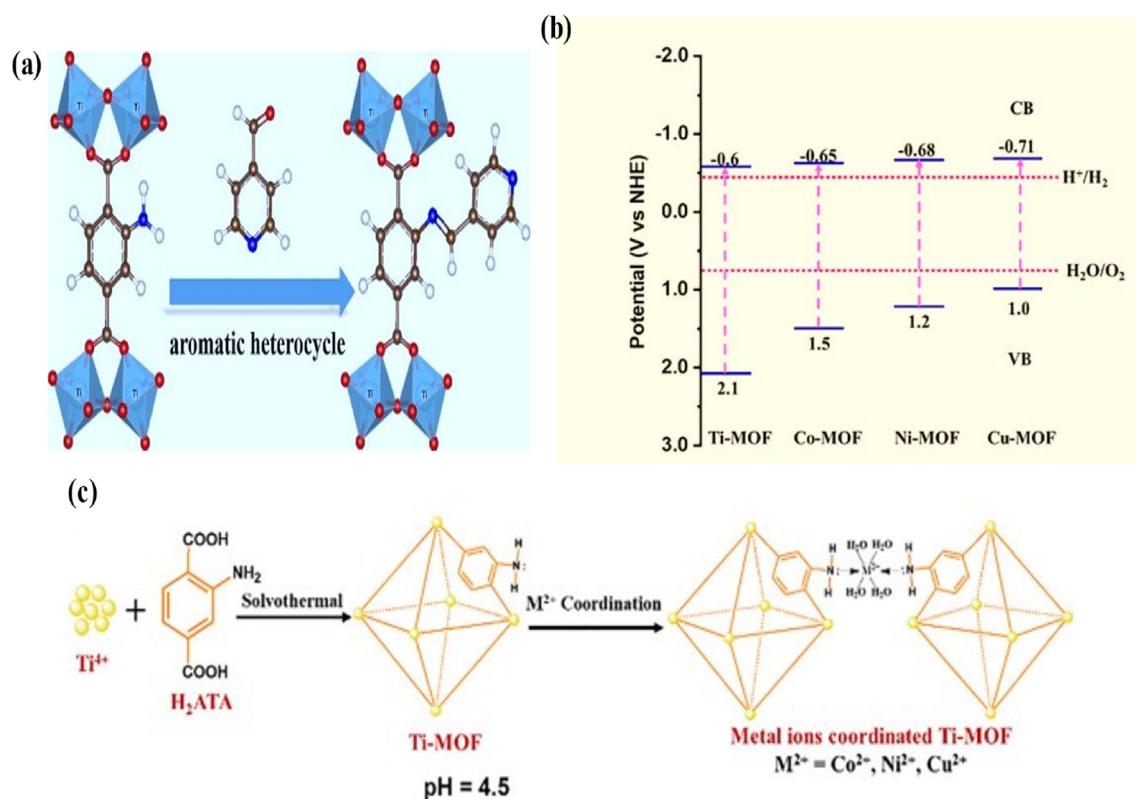
Fig. 6 (a) Schematic of NH_2-MIL-125 post-synthetic grafting with aromatic heterocycles; (b) Band levels of Ti-MOF, Co-MOF, Ni-MOF and Cu-MOF(c) Schematic depiction of M^{2+} ions covalently linked to NH_2-MIL-125 (Guo et al., 2021). Exclusive rights 2021 Elsevier.

shown to avoid the discharge of homogeneous catalysts, which are typically made up of precious metals and are soluble under certain reaction conditions (Hu et al., 2021). In 2011 Lin and colleagues published a variety of UiO-67(Zr) materials doped with Re-, Ir- and Ru- complexes, which were used for water oxidation, respectively. The photocatalytic activity of the solids is similar to that of homogenous counterparts. Furthermore, the catalysts' recyclable status was verified, demonstrating their heterogeneous character (Karthik and Neppolian, 2021).

2.5. Carbon based MOFs as photocatalysts in water splitting

It is well understood that MOFs alone exhibit low electrical conductivity. This constraint prevents them from demonstrating their full potential in the electrochemical sector. While conductive MOFs have been discovered lately, they are not yet frequently used owing to numerous restrictions. Apart from their low conductivity, MOFs suffer structural instability due to the weak coordinated connection between organic ligand and metal node, as well as a high moisture vulnerability, that further restricts their commercial use. Some functional carbon additives have been incorporated into MOF catalysts to improve the capacity to transfer charges. Graphene (2D polyaromatic carbon allotrope) has attracted great attention in the field of hydrogen production from water splitting because of its high theoretical surface area, outstanding electro chemical stability, superior electrostatic conductivity with few addi-

tional exclusive chemical and physical proprieties, it may be rolled into a 0D, 1D, 3D structure of carbon atoms known as fullerenes, carbon nanotube and a graphite assembly. Another derivative of graphene is reduced-graphene oxide (rGO), is formed by the reduction graphene oxide by number of synthetic approaches. It offers number of substantial characteristics when it is utilized as photocatalyst for the splitting of water as it offer more active sites, increase the separation of charges, and suppress the recombination of charges. Furthermore, availability of oxygenated functional groups just like GO have also been increase the number of active sites for water splitting. In addition, with band gap of 11.69 eV it also creates a heterojunction when it mixes with other light absorbing substances, and further improves the separation of charges and suppressing the recombination of charges thus overall, it plays a significant role in water splitting (Xie et al., 2013). Furthermore, for various photocatalysts graphene is a good support material due to its large surface area. Besides, the presence of defective sites serve as a nucleation site for the metal oxide part of the MOFs. Likewise, reduced graphene oxide (rGO) with a negatively charged surface, is a desirable adsorbent for metal oxides as well. And among them the presence of attractive forces will avoid the agglomeration of following nanoparticles improving the photocatalyst's stability and reusability (Fadlalla and Babu, 2019).

The use of MOF structures to decorate a graphene sheet reduces charge recombination while simultaneously facilitating charge carrier separation and transfer. Karthik et al in 2018 reported a photo catalyst i.e., NH_2-MIL-125(Ti) MOF and

reduced graphene oxide based NH_2-MIL-125(Ti) MOF composite for hydrogen production via water splitting. The strong $\pi - \pi$ connection was generated by combining NH_2-MIL-125 (Ti) MOF with rGO, and as a result of this interaction an enhanced photocatalytic hydrogen production $\sim$9.1-fold is observed in contrast to NH_2-MIL-125(Ti) MOF. Overall mechanism involve in hydrogen production is illustrated in Fig. 7.

In photocatalytic activity of water splitting following steps are included; (i) visible light is absorbed by a linker 2-amino terephthalic acid, (ii) an electron excitation occurred from the organic linker's HOMO to the LUMO, (iii) following photoexcited electron was then transported to the titanium-oxo cluster of MOF through the ligand to cluster charge transfer mechanism (LCCT), (iv) finally this photogenerated electrons are swiftly transported to rGO via $\pi - \pi$ interactions. The transfer of electron through rGO is then engaged in the H^+ ions reduction into H_2 and the photogenerated holes oxidise the TEOA (triethanolamine a sacrificial reagent) and form TEOA $+$ ions (Karthik et al., 2018).

Bag et al. in 2012 reported CdS@NU-1000 and CdS@NU-10001% RGO composites for water splitting reaction under the irradiation of visible light. Theses Zr(IV) based MOF i.e., NU-1000 with CdS and rGO based photocatalysts are prepared via using CdS, RGO, and NU-1000 in various proportions, a ternary composite was created: CdS@NU-1000/ RGO. The hydrogen production performance of CdS was enhanced by the combination of NU-1000 and rGO, i.e., ternary composite, because of availability of high catalytic sites and reaction centers created by avoiding the agglomeration of CdS nanoparticles caused by NU-1000's large pore size and minimal charge carrier recombination. Using visible light, CdS@NU-1000 has 9.35 times the photocatalytic activity of commercial CdS whereas CdS@NU-1000/1% rGO has 12.1 times the photocatalytic activity, overall comparison is shown in Fig. 8.
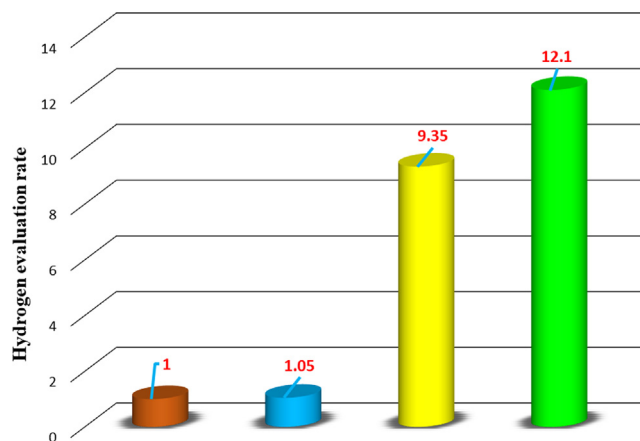
Fig. 8 Hydrogen evolution rate under visible light from photocatalyst.

Further, following ternary composites overall water splitting process mechanism, where CdS's lowest conduction band potential and reduced graphene oxide's fermi level are –0.65 V and –0.08 V against NHE, correspondingly, photogenerated electrons from CdS might be transported to NU-1000 and subsequently transferred to RGO sheets. To determine if the holes in CdS could oxidise the NU-1000, the ternary composite was irradiated in aqueous solution without the addition of sacrificial agents to preserve the direct contact between the holes in CdS and the pyrene tetracarboxilic acid fragments of MOF. Thus, this research shows unequivocally the benefit of MOF-supported CdS nanoparticles for improving photocatalytic H_2 evolution activity while maintaining high stability (Bag et al., 2017).

Zhang et al. in 2018 reported composites of NH_2-UiO-66/g-C_3N_4 and CD@NH_2-UiO-66/g-C_3N_4 with g-C_3N_4 and Car-

Fig. 7 Schematic mechanism for photocatalytic H_2 production under visible-light irradiation (Karthik et al., 2018). Exclusive rights 2018 American Chemical Society.

bon nanodots for photocatalytic water splitting. CDs were incorporated into the pores of NH_2-UiO-66 to create a ternary composite. The inclusion of CDs efficiently enhance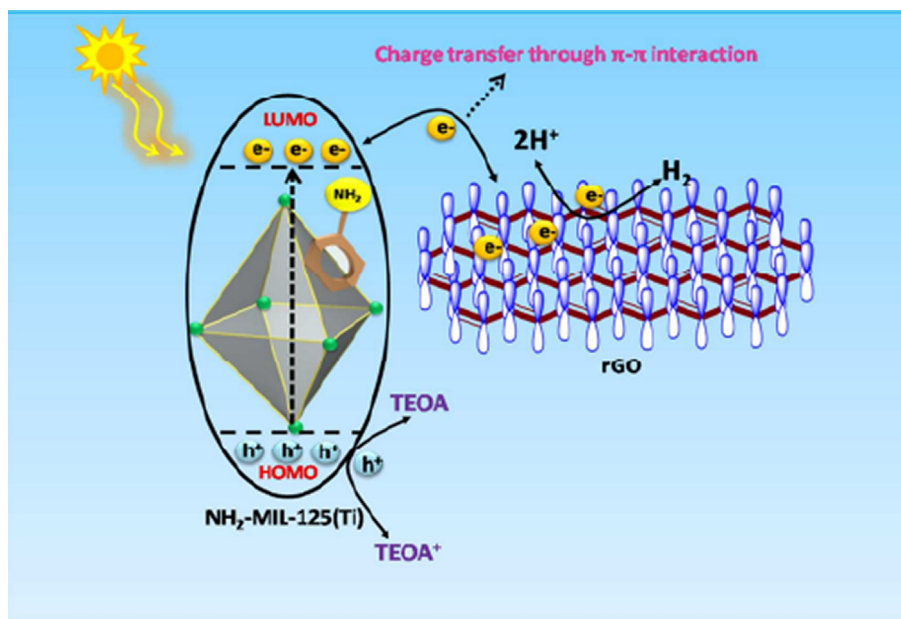s visible light absorption areas, improves charge carrier lifespan, and reduces charge carrier recombination. As a result, CD@NH_2-UiO-66/g-C_3N_4 had better photocatalytic performance for visible-light-driven hydrogen production (> 420 nm), with a hydrogen evolution rate of 2.930 mmolg-1 h^{-1}, which is 32.4, 38.6, and 17.5 times greater than g-C_3N_4, NH_2-UiO-66, and NH_2-UiO-66/g-C_3N_4, correspondingly. The substantial enhancement of photocatalytic capabilities in the ternary composite may be attributed primarily to the ability of CDs as cocatalysts to efficiently increase electron interfacial charge transfer in the composite system, resulting in a reduction in photo - generated charge recombination. Further, g-C_3N_4 and NH_2-UiO-66 have comparable light absorption, g-C_3N_4 has a substantially higher CB than NH_2-UiO-66, which implies that from g-C_3N_4 even more photogenerated electrons may move to NH_2-UiO-66's CB and from the CB of NH_2-UiO-66 the photogenerated electrons is then readily transferred to CDs and then further reduce H^+ into H_2, whereas the holes restricted in g-C_3N_4 and NH_2-UiO-66 allow the electron donor sodium ascorbate to be oxidized, Furthermore, including CDs into NH_2-UiO-66 improves the material's light absorption capacity, perhaps leading to an increase in H_2 generation (Zhang et al., 2018).

Further, for the optimization of the NH_2-UiO-66 photocatalyst Zhang et al. in 2020 reported a Pt@NH_2-UiO-66@MnOx (PUM) heterostructure photocatalyst using Pt and MnOx as cocatalysts is constructed as illustrated in Fig. 9a. The PUM sample produces the most hydrogen when compared to the pristine NH_2-UiO-66, NH_2-UiO-66@MnO_x (UM) and Pt@NH_2-UiO-66 (PU) samples. Pt prefers to capture electrons as a cocatalyst, whereas MnO_x prefers to accumulate holes. Electrons and holes move within and outside of the MOF based photocatalyst after being generated from NH_2-UiO-66, collecting on the matching cocatalysts, and then participating in the redox processes as illustrated in Fig. 9b. The lifespan of photogenerated electrons and holes is enhanced by the PUM photocatalyst, which favors electron–hole separation. In addition, the PUM sample can help with overall water splitting even when there are no sacrificial agents, which shows that it could be used to change MOF-type semiconductors so that the overall water-splitting reaction can happen.

Fig. 9c shows the hydrogen production capability of PUM, UM and PU, in the absence of sacrificial agents only the UM, PUM, and UPM can catalyze the splitting of water into hydrogen and oxygen. Despite the fact that the PUM samples hydrogen and oxygen generation rates is just 19.6 μmol / g/ h and 10.1 mol/ g/ h, are substantially lower than those achieved in the presence of sacrificial agents as illustrated in Fig. 9d (Zhang et al., 2020).

Table 1 and 2 illustrates comparison study from literature by carbon based MOFs as photocatalysts for OER and HER.

In summary, one of the most important processes in the emerging renewable energy industry is the conversion of solar energy to chemical energy. Photocatalytic water splitting is an excellent way for hydrogen production because it is simple and

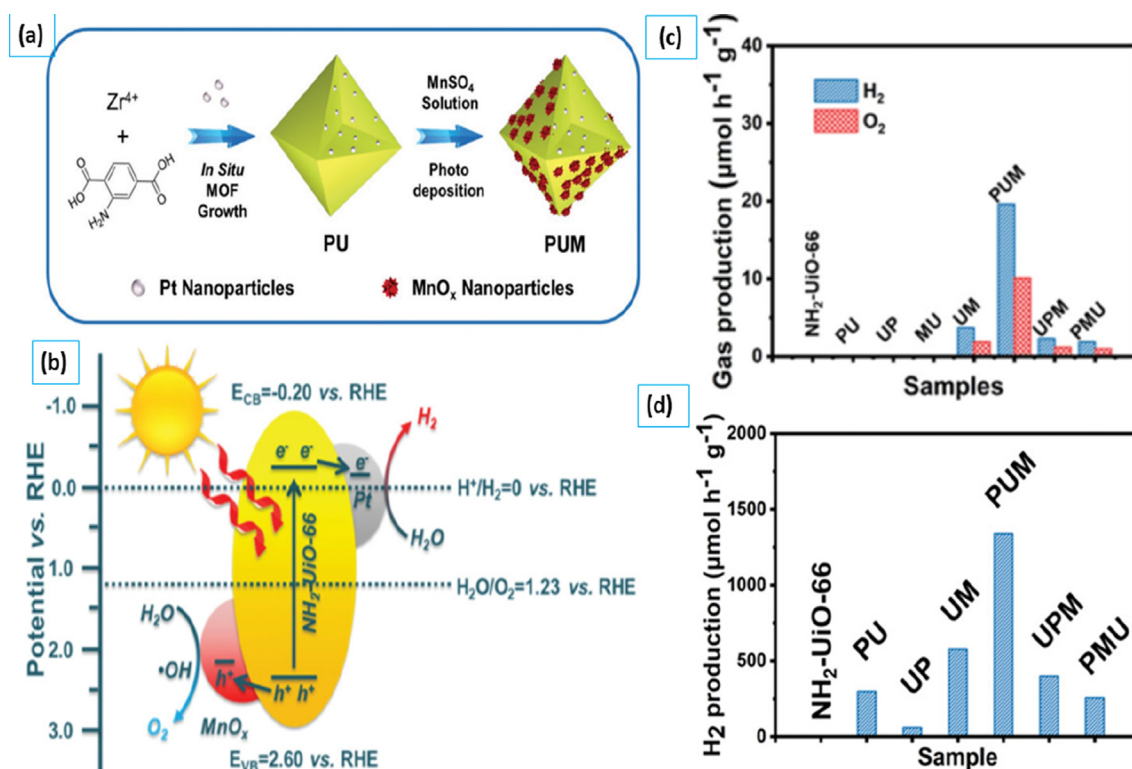**Fig. 9** (a) Schematic of Pt@NH_2-UiO-66@MnOx preparation; (b) Schematic diagram for overall water splitting by Pt@NH_2-UiO-66@MnOx (c) Hydrogen production rates in the absence of sacrificial agent (d) Hydrogen production rates in the presence of sacrificial agent (Zhang et al., 2020). Exclusive rights 2020 Wiley Online Library.

Table 1 MOF based photocatalysts for OER.

MOF-based Photocatalyst	Sacrificial reagents	Illumination (nm)	Activity (μmol h^{-1} g^{-1})	Activity (mmol g^{-1}h^{-1})	Ref.
Bi-based MOF	$AgNO_3$	/	$\approx$180	-	(Wang et al., 2015)
ZnIn$_2$S$_4$@NH$_2$-MIL-125(Ti)	Na$_2$S and Na$_2$SO$_3$	> 420 nm	–	2.204	(Nasalevich et al., 2015)
2.6 wt% CoO$_x$ NPs-MIL-101	[Ru(bpy)$_3$]$^{2+}$–Na$_2$S$_2$O$_8$	/	$\approx$11,000	-	(Han et al., 2015)
3.9 wt% CoO$_x$ NPs-MIL-101	[Ru(bpy)$_3$]$^{2+}$–Na$_2$S$_2$O$_8$	/	$\approx$15,000	-	(Han et al., 2015)
4.9 wt% CoO$_x$ NPs-MIL-101	[Ru(bpy)$_3$]$^{2+}$–Na$_2$S$_2$O$_8$	/	$\approx$13,000	-	(Han et al., 2015)
MnTD/MIL-101	Ceric ammonium nitrate	520 nm	2,250	-	(Hansen et al., 2014)
MIL-101	Ceric ammonium nitrate	520 nm	125	-	(Hansen et al., 2014)
Porous Co$_3$O$_4$ nanocages	[Ru(bpy)$_3$]$^{2+}$–Na$_2$S$_2$O$_8$	–	$\approx$7,900	-	(Wei et al., 2015)
Porous Mn$_x$Co$_{3-x}$O$_4$ nanocages	[Ru(bpy)$_3$]$^{2+}$–Na$_2$S$_2$O$_8$	–	$\approx$4,900	-	(Wei et al., 2015)
Porous Fe$_x$Co$_{3-x}$O$_4$ nanocages	[Ru(bpy)$_3$]$^{2+}$–Na$_2$S$_2$O$_8$	–	4,000	-	(Wei et al., 2015)

clean. Just the photocatalyst, water and sunlight are needed to make hydrogen at room temperature. Even though this method of converting solar energy into usable energy has a lot of benefits, making hydrogen via photocatalytic water splitting is really not ready for use so far. This is mostly because the photocatalysts have a very high rate of electron–hole recombination. overall water splitting comprises of both HER and OER reactions. In comparison to HER, OER is slow in terms of kinetics, owing to the elevated overpotential values, with high energy barrier, and also the rate-determining step which involve multiple electrons. Therefore, relative to HER in photocatalytic water splitting, OER growth is limited.

Numerous semiconductor-based photo - catalysts have already been explored and used to produce photocatalytic hydrogen, but MOFs are a new type of photocatalyst because they have high surface area, evident active sites, and can be changed in structure. Innate pores and high specific surface areas make it easier for reactant molecules to adsorb to the active sites. Further, concise active sites are good for studying the photocatalytic reaction mechanism, and number of strategies are reported for the fabrication of various MOF derived photocatalysts where ligand and metal active sites are controlled by varying reaction conditions and using various solvents makes it easier to investigate the effects of different metal water splitting capabilities (Feng et al., 2019).

3. Electrocatalytic water splitting

Electrochemical water splitting has long been regarded as a viable and effective method of transforming water into renewable hydrogen and oxygen. Electrocatalytic water splitting comprises of two half-reactions and might be represented in several ways depending on the reaction considerations (Huang et al., 2018). Further, during the electrocatalytic water splitting process, both the hydrogen evolution reaction and the oxygen evolution reaction are significant half-reactions. Noble metal oxides like platinum for HER and RuO_2 for OER have been utilized as potential catalysts, but they have two drawbacks: (i) the high cost and scarcity of materials, which preclude large-scale deployment; and (ii) the loading of catalysts onto glassy carbon, which necessitates the use of binders and additives, which raises contact resistance and degrades electrocatalytic performance. Direct fabrication of non-noble metal compounds, including transition metal complexes, on conductive interfaces, is one typical strategy for overcoming the aforementioned challenges (i.e., copper foams, nickel foams, carbon cloths) (Yang et al., 2021).

Moreover, transition-metal oxides or hydroxides and their derivatives are often the most important active species, resulting in comparatively higher activity and better durability. For electrochemical water splitting a potential of 1.23 V is needed under normal circumstances, equating to an energy input of G = 237.1 kJ/mol (Baig et al., 2021). But to achieve a significant current density, large overpotentials are needed, due to the slow kinetics of the hydrogen evolution reaction and the oxygen evolution reaction and thus results in poor energy conversion efficiencies (Zaman et al., 2021). Consequently, in real electrolyzers, the input potential for water splitting is considerably higher than 1.23 V, therefore high activity suffers from poor explication and the creation of an O = O bond

Table 2 MOF based photocatalysts for HER.

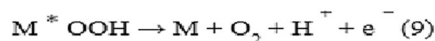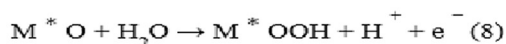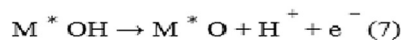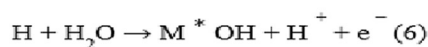| MOF-based Photocatalyst	Sacrificial reagents (vol%)	Illumination (nm)	Activity (μmol h^{-1} g^{-1})	Activity (Mmol g^{-1}h^{-1})	Ref.
UiO-66	Na$_2$S, Na$_2$SO$_3$	/	0	-	(Zhou et al., 2015)
UiO-66/CdS	Na$_2$S, Na$_2$SO$_3$	/	1,700	-	(Zhou et al., 2015)
UiO-66/CdS/1% rGO	Na$_2$S, Na$_2$SO$_3$	/	2,100	-	(Zhou et al., 2015)
UiO-66/CdS/1% rGO	Na$_2$S and Na$_2$SO$_3$	> 420 nm	–	2.100	(Yuan et al., 2015)
UiO-66/CdS/rGO	Na$_2$S and Na$_2$SO$_3$	> 420 nm	–	2.09	(Yuan et al., 2015)
UiO-66/CdS	Lactic acid	420 nm	1,250	-	(Shen et al., 2015)
UiO-66	Lactic acid	420 nm	0	-	(Shen et al., 2015)
g-C$_3$N$_4$/UiO-66 (1:1, w/w)	Lactic acid	420 nm	1,141	-	(Shen et al., 2015)
Ti-MOF-Ru(tpy)$_2$	TEOA	500 nm	≈200	-	(Zhou et al., 2013)
Pt based MOF-253	CH$_3$CN	440 nm	≈58,000		(Zhou et al., 2013)
Pt@UiO-66	TEOA	> 420 nm	3.9		(He et al., 2014)
2.54 mg g^{-1} of RhB/Pt@UiO-66	TEOA	> 420 nm	5.6	-	(He et al., 2014)
11.92 mg g^{-1} of RhB/Pt@UiO-66	TEOA	> 420 nm	≈100	-	(He et al., 2014)
ErB dye-sensitized Pt/UiO-66 octahedrons	Methanol	420 nm	460	-	(Yuan et al., 2015)
Hollow Fe$_2$O$_3$-TiO$_2$-PtO$_x$	Lactic acid		1,100		(Pham et al., 2013)
Co$_3$O$_4$/TiO$_2$ p–n heterojunction	Methanol		7,000	-	(Bala et al., 2015)
UiO-66/g-C$_3$N$_4$	Ascorbic acid	420 nm	14.11	-	(Wang et al., 2015)
CdS@MIL-101(Cr)	Lactic acid	> 420 nm	14.66	-	(Meng et al., 2019)
CD@NH$_2$-UiO-66/g-C$_3$N$_4$	Sodium ascorbate	> 420 nm	–	2.930	(Zhang et al., 2018)
rGO/MOF/Co–Mo–S	TEOA	> 420 nm		0.678	(Liu et al., 2017)
CFB/NH$_2$-MIL-125(Ti)	Triethanolamine	> 420 nm	–	1.123	(Song et al., 2019)
Ni NPs based MOF-5	TEOA	520 nm	3,022	-	(Zhen et al., 2016)

and the loss of four electrons and four protons, resulting in slow kinetics, thermodynamics, and a high overpotential, which is a major bottleneck in the entire water splitting process. Additionally, OER can also be used to generate electrons for carbon dioxide reduction processes for fuel generation. OER is a laborious, two-step process that results in a double bond between two oxygen atoms (O = O), which is hard to activate and sluggish to move (Liu et al., 2018; Anwar et al., 2020).

Different assessment criteria may be used to assess the activity of a water-splitting catalyst. The slope of the Tafel is an essential metric in determining the activity of a catalyst. It's a graph that shows the relationship between the current produced in an electrochemical cell and the electrode potential of a particular metal. In basic terms, the Tafel plot shows an electrode's ability to generate current in accordance with a potential change given to it. It has a relationship between the response rate and the overpotential. Because a lower overpotential is needed to get a large current when the Tafel slope (mV/decade) is low, a lower overpotential is needed to acquire a high current. The Tafel slope for the Pt/C electrode is stated to be 30.3 mV/dec in 0.5 M H_2SO_4, while the Tafel slope for RuO_2 is said to be 89 mV/dec in 1.0 M KOH (Noor et al., 2021).

Overpotential is another important consideration for evaluating a catalyst's potential for water splitting. Overpotential is defined as the potential provided to start the reaction and liberate the entity at the electrodes that is larger than that of the equilibrium voltage. To split water into its constituents, a voltage of at least 1.23 V is necessary, although owing to the com-

In acidic electrolyte:

$$H + H_2O \rightarrow M^*OH + H^+ + e^- \quad (6)$$

$$M^*OH \rightarrow M^*O + H^+ + e^- \quad (7)$$

$$M^*O + H_2O \rightarrow M^*OOH + H^+ + e^- \quad (8)$$

$$M^*OOH \rightarrow M + O_2 + H^+ + e^- \quad (9)$$

In alkaline electrolyte:

$$M + OH^- \rightarrow M^*OH + e^- \quad (10)$$

$$M^*OH + OH^- \rightarrow M^*O + H_2O + e^- \quad (11)$$

$$M^*O + OH^- \rightarrow M^*OOH + e^- \quad (12)$$

$$M^*OOH + OH^- \rightarrow M + O_2 + H_2O + e^- \quad (13)$$
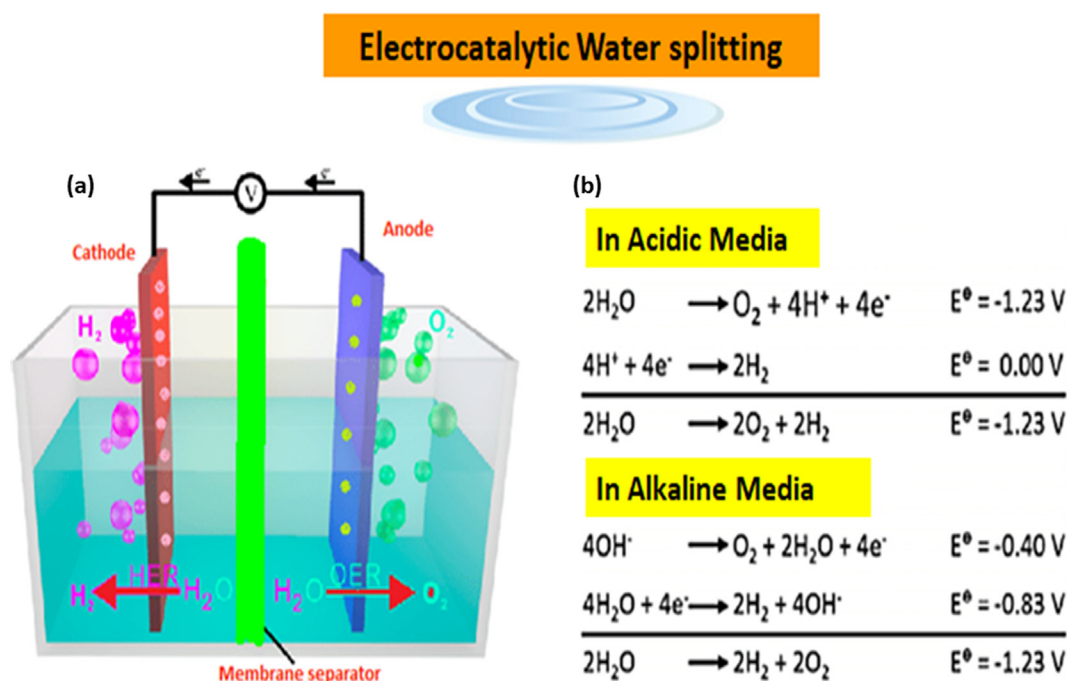
Fig. 10 (a) Electrocatalytically splitting of water in cell (b) water splitting reactions in acidic and alkaline media. Exclusive rights 2020 American Chemical Society.

plicated reaction kinetics, a significant overpotential is usually required. An ideal catalyst for water splitting must have a low Tafel slope and a large current density. The crystallinity, size, and dimensionality of a catalyst have a big impact on electron transport, which affects the Tafel slope and water-splitting overpotential. As a result, the MOF catalysts have a favorable impact on these assessment criteria. The inclusion of metal centers strengthens the charge transfer characteristics of MOFs (Salahuddin et al., 2021).

Farther, in contrast to HER, OER is strongly dependent on the electrolyte solution pH value and show comparatively different mechanism in alkaline and acidic media (Xiong et al., 2021). As hydrogen and oxygen are generated in acidic medium by oxidizing two water molecules at a potential of 0.404 V. In an alkaline medium, the OH group is converted to oxygen and water at a cost of 1.230 V (vs RHE). As a result of the preceding, it can be concluded that the process operates more efficiently in an alkaline conditions than in an acidic one.

Moreover, one of the primary goals in developing an efficient and cost-effective electrocatalysts for water splitting that substitutes the most active but most expensive noble Pt electrocatalyst (Hu et al., 2019). A variety of non-noble metal- based and carbon-based electrocatalysts have been created based on their outstanding activity, low cost, and abundant availability on the earth, with an emphasis on modifying the aforementioned characteristics, the metallicity of an electrocatalyst is another critical app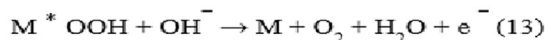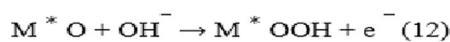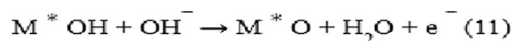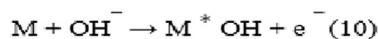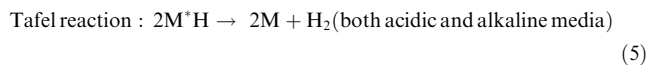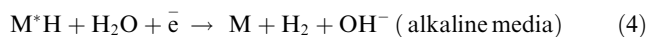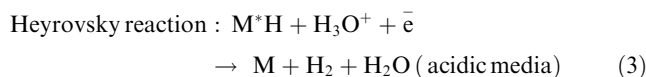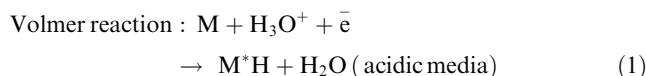roach that affects the electron density, electrical conductivity, and electron transit between the adsorbate and the catalyst surface (Hu et al., 2020). Therefore, in electrocatalytic water splitting, the goal of using electrocatalysts is to decrease the reaction overpotential and increase the rate of the reaction as often as feasible, thus lowering total amount of energy needed. for alkaline media, transition metal-based catalysts i.e., nickel electrodes for HER and stainless steel composites for OER are usually employed. Besides, for acidic media, noble metal-based catalysts such as platinum for hydrogen evaluation reaction and RuO_2 for oxygen evaluation reaction are often required. Further, precious metal-based electrocatalysts and noble metal-free electrocatalysts are prohibitively expensive for large-scale H_2 generation from electrolysis of water due to their high cost, limited supply, and low stability (Guan et al., 2017).

The catalyst activity may be efficiently increased by a process known as synergetic interaction between various kinds of materials. It is defined as two or more active components in sequential or supplementary form showing nonlinear cumulative effects of their distinct characteristics. Synergetic effect is defined as the creation of hybrids/composites with enhanced activity and increased accessible active sites as a consequence of combining catalytic material and/or conductive support in the development of water-splitting catalyst. MOF-based catalysts have a greater potential for creating synergetic effects that enhance catalytic activity as it exists among MOF and conducting substrates provide more active sites. One of the key elements influencing the performance of MOF-based composite catalysts and may be engineered for operation at various functioning levels as well. Intra-molecular synergistic effects

might be seen in various metal groups of a multi-metallic MOF (Yaqoob et al., 2020).

3.1. Mechanism for HER and OER on MOF-derived electrocatalysts

Currently, electrocatalytic water splitting can be done via MOF derived electrocatalysts in an acidic or alkaline electrolyte as shown in Fig. 10. Overall water splitting comprises of two reactions hydrogen evaluation reaction and oxygen evaluation reaction, HER is considered to be a two-electron transfer process including three probable reaction steps such as Volmer, Heyrovsky, and Tafel reaction and two alternative mechanisms such as Volmer-Heyrovsky or Volmer-Tafel mechanism are involved in acidic or alkaline electrolytes. The potential step reactions are represented by the subsequent equations 1–5, where M denotes electro catalyst active sites. whereas, * denotes reaction intermediates adsorbed on the catalysis sites. Clearly, the way HER works in acidic electrolytes is different from the way it works in alkaline electrolytes. In acidic media, the abundance of protons may facilitate the synthesis of H * during the Volmer reaction, whereas in alkaline media, H * is generated by the adsorption and dissociation of water molecules on catalytic active sites. After then, the adsorbed H * would be either joined with another produced H * to produce H_2 molecule by Tafel reaction or an electron transfer reaction with a proton or water molecule to form an H_2 via Heyrovsky reaction. Overall, the binding strength between the catalytic site and the electrode is important for the best HER electrocatalysts.

$$\text{Volmer reaction}: M + H_3O^+ + \bar{e}$$
$$\rightarrow M^*H + H_2O \,(\text{acidic media}) \tag{1}$$

$$M + H_2O + e^- \rightarrow M^*H + OH^- \,(\text{alkaline media}) \tag{2}$$

$$\text{Heyrovsky reaction}: M^*H + H_3O^+ + \bar{e}$$
$$\rightarrow M + H_2 + H_2O \,(\text{acidic media}) \tag{3}$$

$$M^*H + H_2O + \bar{e} \rightarrow M + H_2 + OH^- \,(\text{alkaline media}) \tag{4}$$

$$\text{Tafel reaction}: 2M^*H \rightarrow 2M + H_2 (\text{both acidic and alkaline media})$$
$$\tag{5}$$

The OER mechanism is of more intricate than that of HER, comprising a four-electron transferring. As illustrated in equations 6–13, in acidic and alkaline or acidic media, hydroxyl ions or water molecules are employed as oxygen-containing reactants. The water molecules or hydroxyl ions are progressively oxidized to oxygen-containing intermediates of *OOH, *OH and *O after being adsorbed on the MOF derived electro catalysts active sites, with an electron transfer occurring at each step reaction. Finally, *OOH is oxidized further and converted into an oxygen molecule. The above four sequential proton and electron transport stages are thermodynamically advantageous during the oxidation process, which involves a variety of intermediates formation such as *OH, *O, and *OOH. The step with the largest energy barrier deter-

mines the reaction rate. Due to the large activation energy necessary to break the energy barrier, the OER is kinetically slow. To optimize OER activity, the bonding strength between MOF derived catalysts containing oxygen-based species should be mediated in a systematic manner (Zhang et al., 2020).

In acidic electrolyte:

$$H + H_2O \rightarrow M^*OH + H^+ + e^- \tag{6}$$

$$M^*OH \rightarrow M^*O + H^+ + e^- \tag{7}$$

$$M^*O + H_2O \rightarrow M^*OOH + H^+ + e^- \tag{8}$$

$$M^*OOH \rightarrow M + O_2 + H^+ + e^- \tag{9}$$

In alkaline electrolyte:

$$M + OH^- \rightarrow M^*OH + e^- \tag{10}$$

$$M^*OH + OH^- \rightarrow M^*O + H_2O + e^- \tag{11}$$

$$M^*O + OH^- \rightarrow M^*OOH + e^- \tag{12}$$

$$M^*OOH + OH^- \rightarrow M + O_2 + H_2O + e^- \tag{13}$$
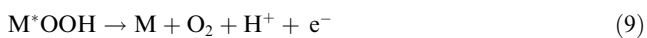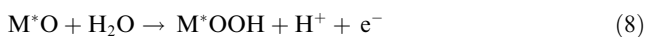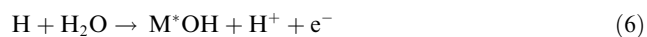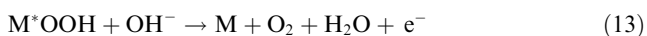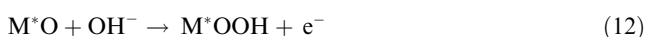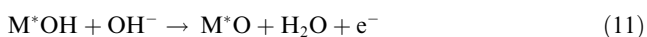
3.2. Challenges for electrocatalytic water splitting

For electrocatalytic water splitting there are number of challenges that need to be focus such as, (i) HER and OER electrocatalysts are often produced under distinct circumstances, and the current methods for nonprecious catalyst synthesis frequently result in incompatible or complex integration. (ii) hydrogen and oxygen evaluation reactions are tightly linked in traditional water electrolysis, which may result in the production of explosive hydrogen and oxygen gas blends. Not only does the gas crossover create safety concerns, but it also decreases energy proficiency by converting O_2 back to water on the cathode side. Meanwhile, the sharing of gas mixtures and electrocatalysts may result in the formation of reactive oxygen species, which can damage the membrane and result in premature device failure. (iii) Due to the fact that OER is a four-electron reaction, it needs a much greater overpotential than HER in order to maintain the same current density, contrary to expectations, the product O_2 is not a very useful component of OER. (iv) It remains challenging to procure cost-effective H_2 storage and transportation systems utilize on-demand. (v) Hydrogen production from HER in an alkaline medium is the water splitting phase (i.e., the breakage of the strong H–OH bond), which needs extra energy to generate H* intermediates (Xiong et al., 2022).

3.3. Fabrication of MOF derived electrocatalysts

There are several important issues that must be addressed in order to better understand MOF and MOF-derived electrocatalysts water splitting activity. Currently, a number of MOF precursors have been studied individually, generally in distinct dimensions (i.e., 1D, 2D, and 3D). It is broadly accepted that a three-dimensional MOF demonstrates greater stability in terms of shape and structure due to its high porosity but has
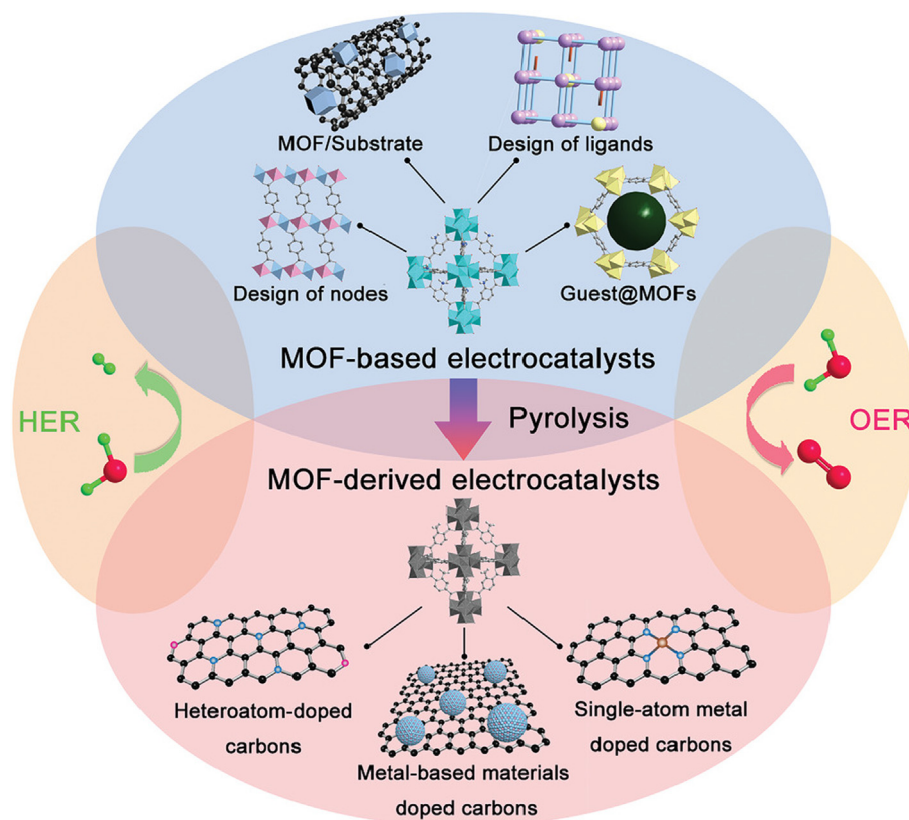

Fig. 11 Schematic diagram for possible ways to fabricate and tailor MOFs and MOF-based materials for overall water splitting (Zhang et al., 2021) Exclusive rights 2021 Wiley Online Library.

a lower active site usage. In comparison to the 3D MOFs, other 1D/2D MOF has a higher usage of active sites but is less stable in terms of structure and morphology with low porosity (Li et al., 2021). As a result, combining the benefits of the 3D MOF with those of the 1D/2D MOF is very desirable, although it remains a difficult task for researchers (Aneeshkumar et al., 2021; Tang et al., 2022). Second, MOF and MOF-based composites work better as an electrocatalyst for water splitting, they are readily collapsed, fused, and aggregated at high temperatures, reducing the accessibility of the catalyst active sites, and reducing its mass transfer capacities. As a consequence, their electrocatalytic performance deteriorates.

In order to address these difficulties, a lower temperature treatment is essential, but low temperature carbonization treatment, will result in poor electrical conductivity owing to the low degree of graphitization of the composite. As a result, finding the right temperature to achieve an optimal balance among particle distribution, graphitization degree and surface assembly in MOF-based composite systems remains a challenge (Zaman et al., 2021). Besides, most papers seldom explore the stability of MOF-based catalysts in real-world applications and disregard the degradation process. As a result, a concerted effort must be made to understand the foundations of degrading activity, as well as the development of MOF-based electrocatalysts that display high electrocatalytic activity

and long-term stability across a variety of working conditions (Song et al., 2019).

In this regards, various MOF-derived catalysts have already been reported recently, including transition metal oxides, sulphides, selenides, phosphides, carbides, and more. During the fabrication of MOF derived electrocatalysts, MOFs are always used as sacrificial templates; when they're pyrolyzed, many different types of carbon nanostructure, metal oxides, metal composites, and metal carbides and nitrides can be formed and can be functionalized during, before, or after pyrolysis (Bavykina et al., 2020). It has also been noticed that heteroatom doping with nitrogen (N), phosphorous (P), boron (B), etc., increases catalytic responsiveness exponentially in carbon-based metal-free and non-precious M/C hybrid electrocatalyst systems. These MOF derivatives greatly outperform direct-MOF electrocatalysts in terms of application, avoiding some major limitations. By and large, prepared MOFs have limited robustness in strongly acidic or alkaline aqueous electrolytes, which are commonly used in electrochemical systems, whereas derivatives of MOFs exhibit significantly greater robustness under severe working conditions (Huang et al., 2019).

Further, from earlier studies general fabrication procedures can be divided into three categories: (i) in situ nitrogen doping, using MOFs containing nitrogen such as zeolitic imidazolate frameworks (ZIFs); (ii) ex situ nitrogen doping using a gas
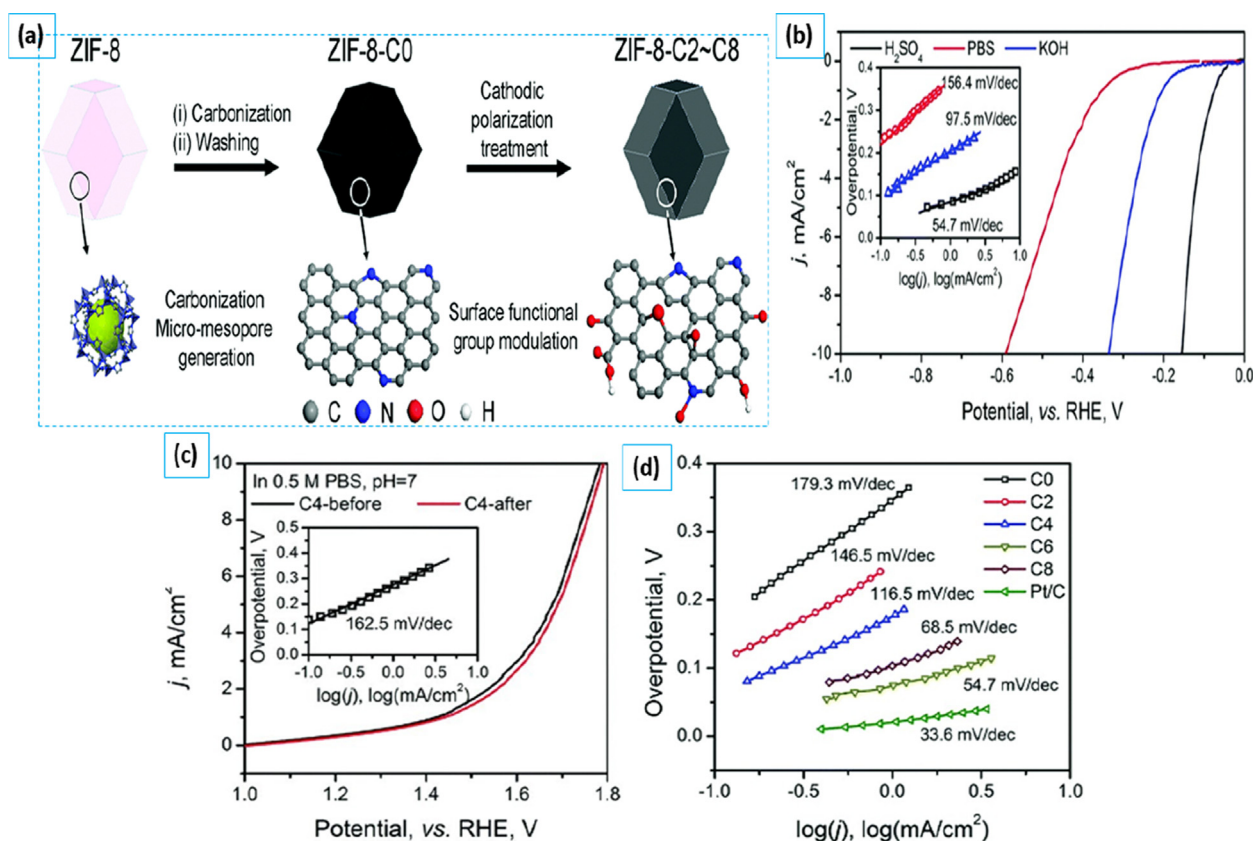

Fig. 12 (a) schematic illustration of carbon electrocatalyst preparation from ZIF-8 (b) electrochemical testing in 0.5 M H_2SO_4 for HER and (c, d) electrochemical testing in 0.1 M KOH for OER (Zhang et al., 2021) Exclusive rights 2021 Wiley Online Library.

guest molecule, such as ammonia; and (iii) using a second solid material as a nitrogen source mixed with MOFs. Further, metal organic frameworks can also be used as an immediate precursor to make heteroatom-doped porous carbon electrocatalysts, also used as templates and nitrogen-doped carbon can be synthesized during the structural precursor transition for MOFs carrying nitrogen (Zhou et al., 2015; Wang et al., 2020). So, accessibility of homogeneous dispersed catalytic centers and dense active sites it can be employed as an effective precursors for carbon-based catalysts and number of ways are reported in literature discussed as follows:

3.3.1. Fabrication of MOF derived electrocatalysts via pyrolysis

MOFs used as sacrificial precursors is a common method for obtaining carbon based substances by pyrolyzing MOFs in gaseous environment. During pyrolysis organic ligands of MOFs can be transformed into carbon based materials such as amorphous carbon, or carbon nanotubes in the final composite electrocatalysts and the relevant metal-based nanoparticles such as metals, alloys, or metal-based compounds can be formed from metal nodes. The obtained carbon substrate can inhibit metal-based nanoparticles from further aggregating (Zhang et al., 2020). Further, adjusting MOFs and pyrolysis conditions can influence the electrocatalytic performance of pyrolysis products. The porous structure of the original MOFs can be partially inherited by the MOF-derived catalyst. Although the specific surface area and pore volume of the

derivatives may be compromised during the reaction as the porous structure get collapsed, they can still perform well as catalysts. Likewise, researchers may also regulate the morphology and size of the resulting catalysts using this approach, making it possible to analyze the active regions of as-prepared catalysts (Han et al., 2021). In addition, bimetallic MOF materials have also been used as a successful approach to create effective catalysts via direct carbonization, to circumvent the atom type limitation of a MOF precursor. Because of the synergetic impact of bimetal doping, the efficiency of bimetallic MOF electrocatalysts is usually substantially higher than that of single atom MOF-derived ones (Radwan et al., 2021; Guan et al., 2021).

3.3.2. Fabrication of heteroatom dopped MOF derived electrocatalysts via pyrolysis

Another way of fabricating MOF derived electrocatalysts is doping with outside heteroatom such as nonmetal sources (N, P, S, and C) and/or metal sources are used as external heteroatom doping sources (Fe, Co, Cu, etc.), might be created strategically that act as an additional heteroatom resource into MOFs as precursors (Yang et al., 2012). Besides, thiourea, urea, cyanamide, dimethyl sulfoxide, melamine, and others are among the secondary nonmetal dopants. Furthermore, the charge density of carbon materials can also be successfully adapted by combining it with highly different electronegativity nonmetal atoms inside carbon frameworks. Thus metal doping
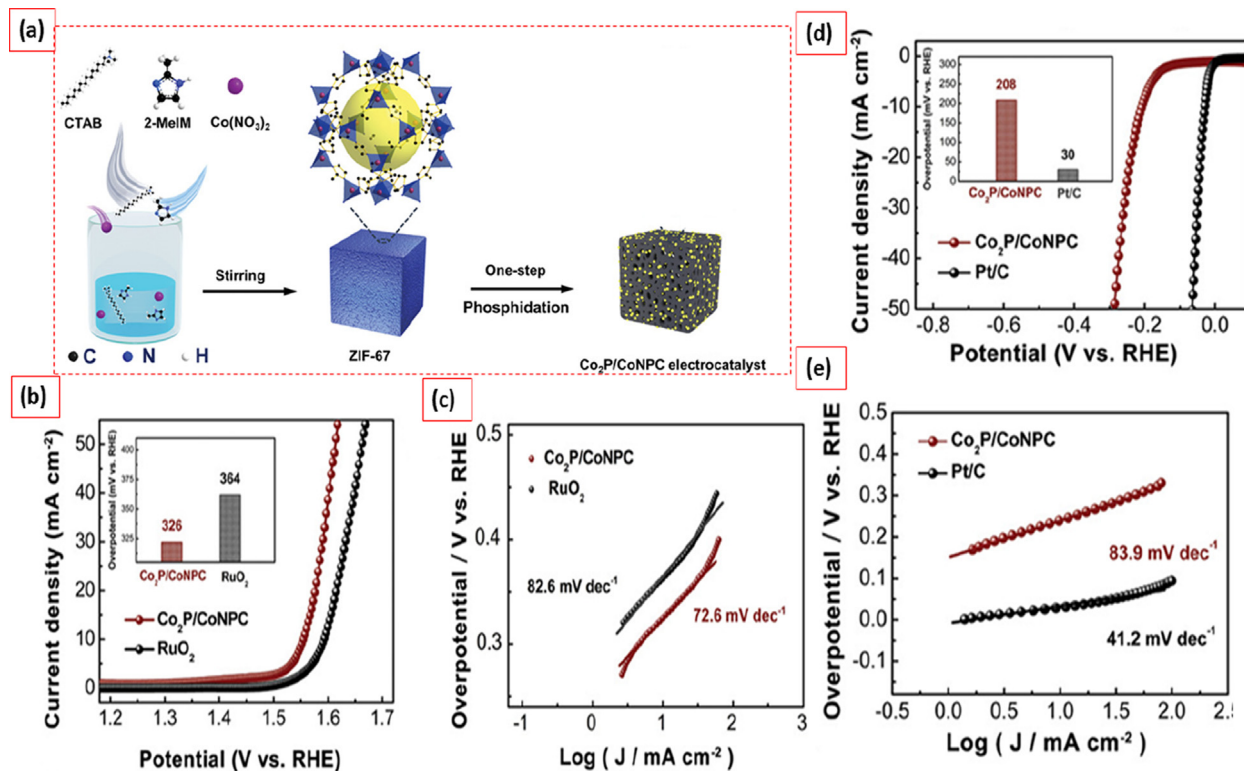

Fig. 13 (a) schematic illustration of phosphorous based carbon electrocatalyst preparation from ZIF-67 (b, c) electrochemical testing in 0.1 M KOH for OER and (c, d) electrochemical testing in 0.1 M KOH for HER (Liu et al., 2020) Exclusive rights 2021 Wiley Online Library.

would result in a bare active site that is free of aggregation, accordingly enhance the overall catalytic activity (Choi et al., 2012).

3.3.3. Fabrication of MOF derived electrocatalysts from MOF based carbon composites via pyrolysis

Carbon electrocatalysts derived from MOF precursors at an elevated temperatures are well known for having variety of problems such as skeleton distortion and porosity loss occur at temperatures equal or above than 700 °C. Surprisingly, the composites made from MOF-based precursors, such as MOF/carbon nanotubes and MOF/graphene, can overcome the challenges of producing highly effective catalysts and could effectively prevent the MOF skeleton material from breaking down, implying that porous carbon composite catalysts derived from MOF can preserve high surface area and porosity, resulting in an improved conductivity and graphitization degree of the produced materials. As a result, this approach considerably improves the catalysts' catalytic efficiency (Yang et al., 2018; Gong et al., 2009). Fig. 11 shows the possible ways to fabricate and tailor MOFs and MOF-based materials for overall water splitting.

3.4. MOF derived carbon based electrocatalysts for water splitting

Abundant research work have now been acknowledged for developing many forms of micro and mesoporous materials; among them, MOFs outperformed other materials in terms of structure, surface morphology, and electrical characteristics. Additionally, it exhibits exceptional cycling and thermal stability, enabling them to precisely regulate the porous structure and nanostructure shape of their nanoparticles. All of these physicochemical features have received considerable interest over the last two decades due to their potential utility in a broad variety of electrochemical applications. MOFs are compelling options because they are well-suited to the requirements of next-generation energy storage systems as they have a substantially larger specific surface area (SSA) than conventional nanomaterials, over 10,000 m^2 g^{-1}.

When contrasted to certain other electrocatalysts, MOFs offers number of benefits such as i) MOFs exhibit both heterogeneous and homogeneous catalytic characteristics and considered as an attractive platforms for studying catalytic processes because of their perfect crystalline structure at molecular level and highly porous state. ii) It also exhibits superior catalytic performance, improved chemical stability, and simpler recyclability than other electro catalysts due to overall active sites availability for catalytic action, hence boosting the electrocatalytic efficiency. iii) Metal ion dopants or functionalizing an organic ligands may readily change the optical and electrical structure of MOFs without modifying their crystalline structure. iv) Further, MOFs can have many functional sites, that can be used for electrocatalytic overall water splitting (Sun et al., 2022; Tong et al., 2020). v) MOFs have adjustable porous structure and pore environment, allowing for improved selectivity of intended products, particularly in catalytic organic fabrication processes. vi) MOFs may readily be combined with other nanomaterials in enlarged pores or even on the surface. Further, MOF based composites offer the benefit of large intrinsic activity, improved conductivity and charge

transport mechanism, reduced nanoparticle aggregation, and a potential synergistic interfacial impact to boost catalytic activity in comparison to every component (Huang et al., 2021).

As MOFs have shown to be good sacrificial templates for MOF-derived materials due to its unique structural and compositional properties. Various carbon–metal, nanostructured porous carbons and metal-oxide composites can be made by varying the synthesis conditions during MOF transformation which are extensively studied in electrochemical water splitting, subsequently certain particular components in them are excellent electrocatalysts for HER and OER. Furthermore, creating unique morphologies (nano cubes, nanorods, nanotubes, nanosheets) and growing them directly on conductive precursors (Ti foil, Ni Foam, carbon paper, Cu Foam, carbon clothes, and so on) can dramatically improve conductivity and charge/mass transfer efficiency, thereby improving water splitting efficiency. However, the process of converting MOFs to MOF-derived materials is still unknown, and the mechanism of MOFs for water splitting is seldom addressed since researchers work to simplify models into useful catalysts that have already been well investigated.

Noticeably, for researchers to develop and manufacture cost-effective high-activity, MOF-derived catalysts for overall water splitting is a crucial challenge. Unfortunately, an efficient HER catalyst may not be able to effectively catalyze OER and vice versa in an acidic/alkaline electrolyte, in spite of the comparable essential parameters used to assess the water splitting performance of those catalysts are similar to those used to evaluate the performance of HER or OER.

3.4.1. MOF-derived carbon materials

A wide range of practices are possible for carbon based materials with various astonishing properties such as high specific surface area, electrical conductivity, and chemical stability. Chemical stability and superior conductivity are typically found in doped carbon materials derived from MOFs with diverse nanostructures. Some MOFs with nitrogen-containing ligands, such as zeolitic imidazolate frameworks, can be annealed in inert gases to produce N-doped carbons (Chen et al., 2021; Chai et al., 2019).

In recent years, carbon materials with heteroatomic dopants (i.e., boron or nitrogen or phosphorous or sulphur), exhibits high conductivity are considered as good at catalysis and have been getting more attention day by day. Recently, MOFs have been considered as good templates for generating carbon nanomaterials due to its huge surface area, good electrical conductivity, and low cost strategy (Wang et al., 2019). Heteroatom-containing MOFs can be exploited as precursors to create metal-free carbon-based electrocatalysts through carbonization. Lei et al. revealed that MOF derived N and O doped carbon materials might be exploited for the electrochemical splitting of water (Lei et al., 2018). This bifunctional catalyst was produced by calcinating the ZIF-8 precursor, accompanied by the catalytic sites electrochemical activation. Among all prepared series of carbon materials such as (ZIF-8 C2-C8) Six hours CPT (C6) carbon catalysts exhibits an astonishing HER activity in 0.5 M H$_2$SO$_4$ electrolyte and display current density of 0.063 mA/cm^2 with overpotential of 155 mV and Tafel slope of 54.7 mV/dec as demonstrated in Fig. 12 (b, e). Further, four hours CPT (C4) carbon catalysts

exhibits a surprising OER activity in 0.1 M KOH electrolyte and display overpotential of 476 mV and Tafel slope of 78.5 mV/dec as demonstrated in Fig. 12 (c, d).

Calcination of MOFs with particular atmospheres, such as NH_3, PH_3 and H_2S gases, can also be used to make carbonaceous materials with heteroatomic dopant. Liu et al. reported an electrocatalyst ($Co_2P/CoNPC$) with N- and P-doping produced by calcining MOF precursors in a PH_3 atmosphere. $Co_2P/CoNPC$ exhibits an improved OER activity in 1 M KOH electrolyte display overpotential of 326 mV at current density of 10 mA/cm^2 and Tafel slope of 72.6 mV/dec as demonstrated in Fig. 13 (b, c). Further, $Co_2P/CoNPC$ also exhibits an improved HER activity in 0.1 M KOH electrolyte display overpotential of 208 mV and Tafel slope of 83.9 mV/dec as demonstrated in Fig. 13 (c, d) (Liu et al., 2020).

In recent years, novel three-dimensional carbon structures derived from ZIFs such as hollow polyhedrons, carbon nanotube polyhedrons, and carbon nanotube have been reported, resulting in increased surface area, rapid charge and mass movement, and enhanced water splitting electrocatalytic activity. Pan et al. reported a new water splitting electrocatalyst NCNHP (N-doped carbon nanotube hollow

polyhedron) and CoP/NCNHP (CoP nanoparticles embedded in an N-doped carbon nanotube hollow polyhedron) produced from core-shell ZIF-8@ZIF-67 and it exhibits overpotentials of 310 mV and −115 mV at 10 mA cm^{-2} and Tafel slopes of 70 mV dec^{-1} and −66 mV dec^{-1} for OER and HER in 1 M KOH, accordingly, the catalyst demonstrated outstanding bifunctional electrocatalytic efficacy. It was ascribed to the NCNHP matrix, and the synergistic impact between CoP and NCNHP, which increased the charge and mass transfer efficiency, and electrolyte stability and achieved a current density of 10 mA cm^{-2} at 1.64 V, exceeding the majority of reported non-noble-metal electrocatalysts, and displayed remarkable stability for at least 36 h as illustrated in Fig. 14 (Pan et al., 2018).

3.4.2. MOF-derived single-atom materials

Single-atom catalysts have been getting a lot of consideration in the field of catalysis because of their extraordinary catalytic activity, ability to use the most metal atoms and specific selectivity (Mitchell et al., 2018; Zhang and Guan, 2022). However, due to the high surface energy of monatomic catalysts, single atoms may easily move and aggregate into nanoparticles under
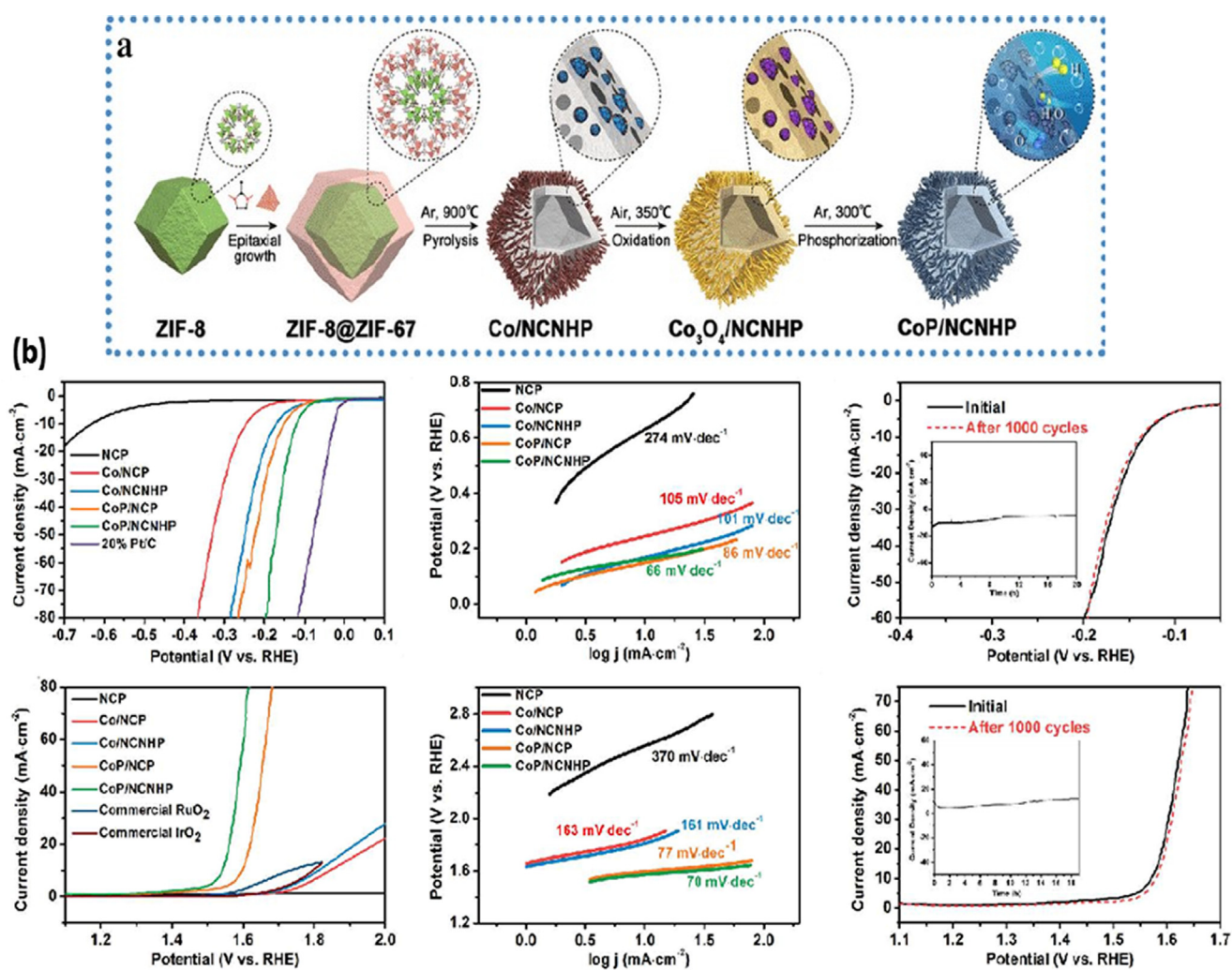

Fig. 14 (a) Two step synthesis of CoP/NCNHP and (b) its electrochemical results for overall water splitting (Pan et al., 2018)Exclusive rights 2018 ACS publications.

actual reaction circumstances. To solve this problem, MOFs have become a promising precursor for developing SACs because of their porous structure and availability of different components from which it can be made exactly how they should be. Direct pyrolysis of MOFs is a simple way to make SACs (Yang et al., 2018; Zhang et al., 2019). Further, the N-doped carbon also obtained from the MOF pyrolysis is a good scaffold for metal ions to be absorbed. Li et al. reported a simple way to make atom-distributed Fe–N$_4$ active sites that are embedded in carbon phases that are made by carbonizing ZIF-8 precursors (Li et al., 2019).

Further, Fan et al. recently reported Ni-based SACs (A-Ni-C). Fig. 15a shows schematic illustration for the synthesis of A-Ni-C, where the carbonization of a Ni-MOF was followed by HCl etching and then electrochemical activation led to the formation of A-Ni-C. single atom catalyst such as A-Ni-C exhibits a surprising HER activity in 0.5 M H$_2$SO$_4$ electrolyte display current density of 10 mA/cm^2, overpotential of −34 mV and Tafel slope of 41 mV/dec as demonstrated in Fig. 15 (b, c) (Fan et al., 2016). Furthermore, selecting appropriate MOF precursors is a familiar strategy for controlling the chemical properties of MOF derivatives. Controlling the chemical composition of the electrocatalysts can also be done by manipulating the conversion conditions and adding additional components. In most of the cases, these approaches are used in combination to obtain effective electrocatalytic activity and stability.

Zeolitic imidazolate frameworks are the best scaffolds that can be used to make different types of water splitting electro-catalysts by trying to control morphology structures and chemical constituents. In 2015, you et al. reported porous Co-P/NC nano-polyhedrons made of nanoparticles of CoPx (a mixture of CoP and Co2P) that were integrated in N-doped carbon by direct carbonizing ZIF-67 and then phosphating them. These nanoparticles were used as electrocatalysts for overall water splitting. These nano-polyhedrons had a surface area of 183 m^2 g^{-1} and large mesopores in which CoPx (about 33 nm) particles were dispersed and encased in carbon matrixes, as shown in the Fig. 16. CoP/NC nano poly-hedrons with the precise number of pores were very good electrocatalysts for both HER and OER in 1.0 M KOH. They had low overpotentials, which meant they could get 10 mA cm^{-2} at low overpotentials for OER and HER, respectively. It also worked better than the Pt/IrO$_2$ couple (165 mA cm^{-2} at 2.0 V) and was very stable over 24 h of electrolysis (You et al., 2015).

3.4.3. MOF-derived composites

Fabrication of MOF derived composites is an alternative efficient approach for improving MOF overall electrocatalytic performance, mechanical characteristics, and stability. Although pure MOFs have a broad variety of structural capabilities, but its composites with other carbon based materials such as graphene oxide reduced graphene oxides and etc. resulting in a distinctive electrochemical activity of the resulting electrocatalysts due to a potential synergic effect. Further, it lowers the aggregation in chemical reactions, increased structural stability with much more catalyst active sites and im-
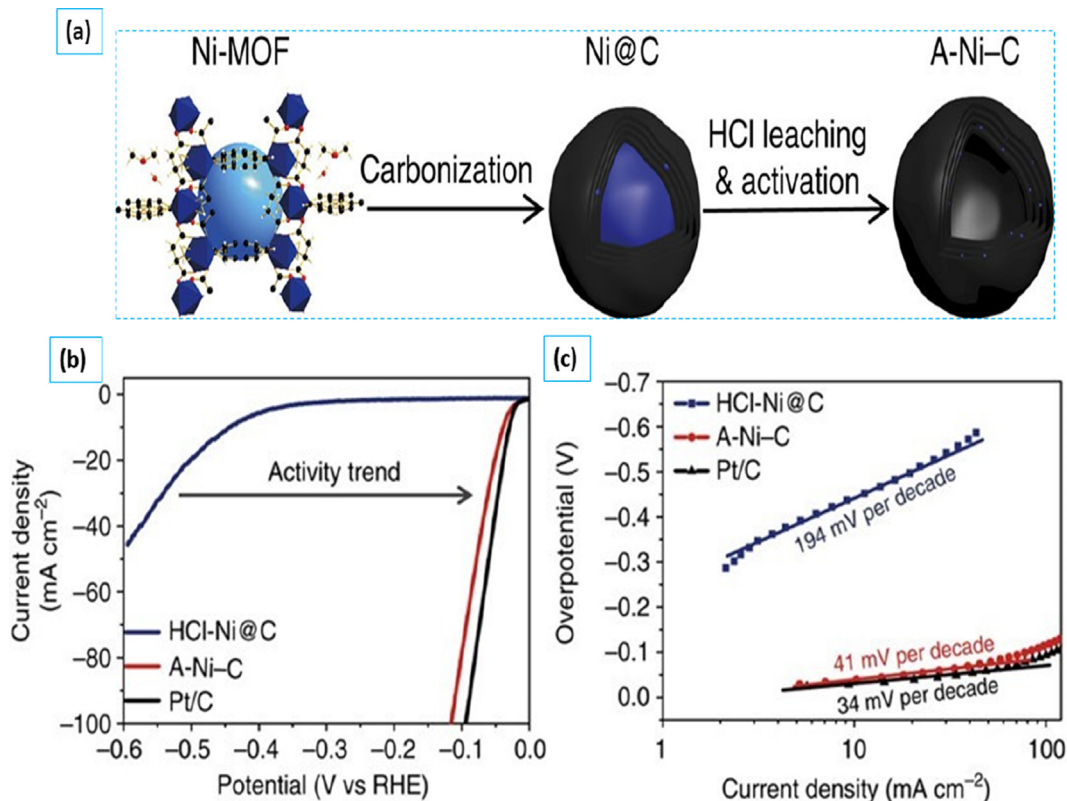

Fig. 15 (a) schematic illustration of single atom electrocatalyst (A-Ni-C) preparation from Ni-MOF (b, c) electrochemical testing in 0.5 M H$_2$SO$_4$ for HER (Fan et al., 2016) Exclusive rights 2016 Springer Nature.
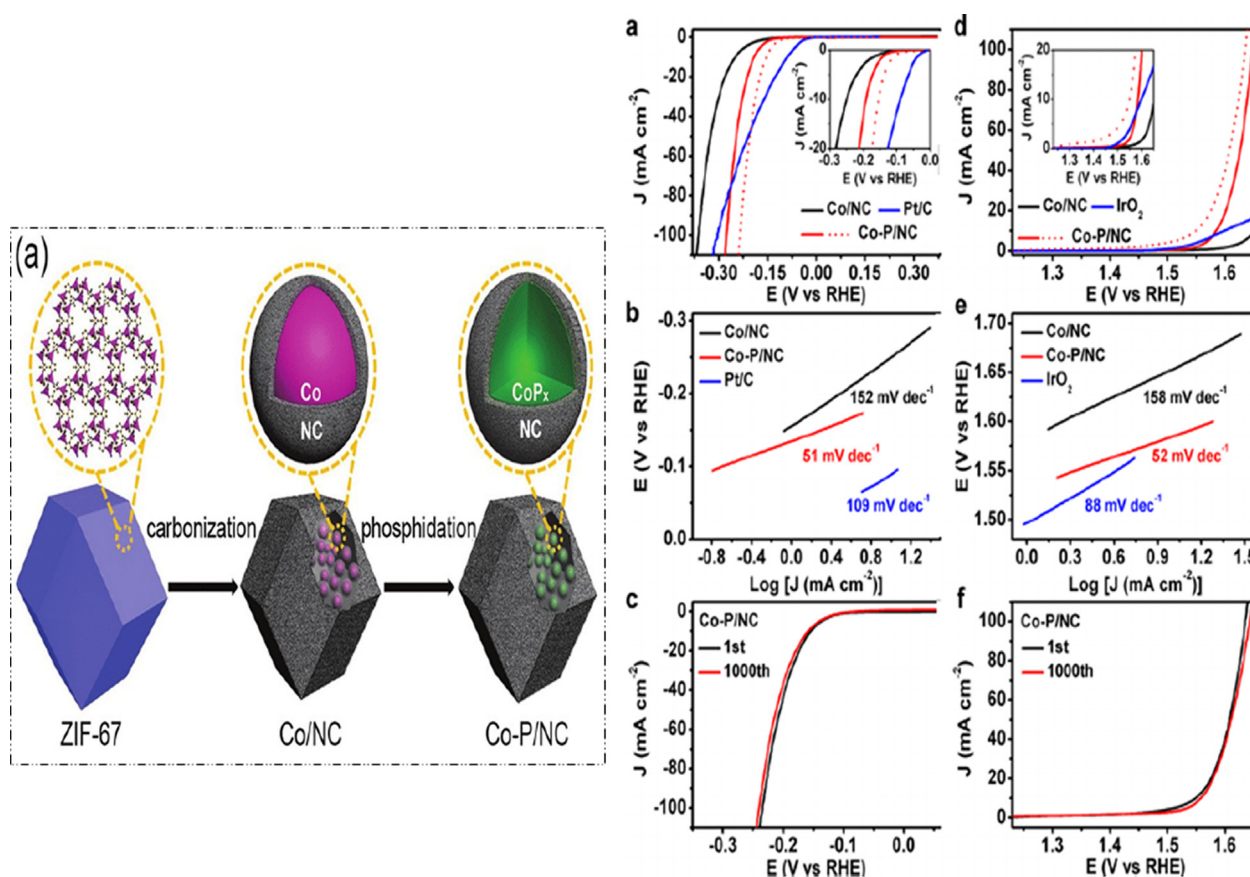
Fig. 16 (a) Synthetic scheme of Co-P/NC, (b) Tafel Plots comparison (You et al., 2015). Exclusive rights 2015 American Chemical Society.

proved mass transfer are all benefits of MOF-based composite materials (Zhou et al., 2022).

Gopi et al. in 2021 reported an efficient bifunctional electrocatalyst for water splitting, such as graphene oxide based V dopped Ni_x Fe_y MOF/GO composites with different ratio of Ni and Fe i.e., V-$Ni_{0.06}$ $Fe_{0.03}$ MOF/GO, V-$Ni_{0.06}$ $Fe_{0.06}$ MOF/GO, V-$Ni_{0.06}$ $Fe_{0.09}$ MOF/GO. Among them, V-$Ni_{0.06}Fe_{0.06}$ MOF/GO showed superb electrocatalysis for both oxygen and hydrogen evaluation reactions and exhibited superior durability in alkaline, and acidic media. In case of OER, the catalyst V-$Ni_{0.06}$ $Fe_{0.06}$ MOF/GO exhibits excellent electrocatalytic activity in 1.0 M KOH i.e., show current density of 579 mA/cm^2 with overpotential value of 210 mV, in addition, it exhibits the lowest onset potential value (i.e.,1.44 mV) with smaller value of Tafel slope 97 mV/dec, in comparison to all other prepared V doped V-Ni_x Fe_y MOF/GO these values are higher as shown in Fig. 17 a, b. Moreover, for HER the electrocatalytic study is performed in acidic media (0.5 M H_2SO_4), Like OER the catalyst V-$Ni_{0.06}$ $Fe_{0.06}$ MOF/GO shows an admirable performance as well i.e., show current density of 208 mA/ cm^2, onset potential of 90 mV to reach stable current density of 10 mA/cm^2, and over potential is 130 mV, with smaller Tafel slop value 150 mV/dec. Furthermore, Fig. 17 c shows the comparison of Tafel slope and over potential values, and Fig. 17 d illustrates the overall water splitting by corresponding electrocatalysts (Gopi et al., 2021).

In addition, Hu et al. in 2019 reported Co/CoN/Co_2P-NPC a ternary metallic carbon based composites for electrocatalytic

water splitting and for comparison an electrocatalyst i.e., Co/CoN-NC is also studied. The resulting Co/CoN/ Co_2P-NPC exhibits good OER and HER electrocatalytic activity in alkaline solution due to high carbon content of MOFs precursors. A standard three-electrode setup in 1.0 M KOH electrolyte was used to evaluate the electrocatalytic performance of the corresponding prepared catalysts. In comparison to Co/CoN-NC, Co/CoN/ Co_2P-NPC exhibits astonishing HER and OER performance. As shown in Fig. 18a LSV results for OER shows the overpotential 272 mV is needed to achieve the current density of 10 mA/ cm^2 for Co/CoN/Co_2P-NPC in contrast to Co/CoN-NC needed 306 mV of over potential. Further, Tafel slope value of 62 mV/dec for Co/CoN/Co_2P-NPC is lower than Co/CoN-NC (i.e., 76 mV/dec) as illustrated in Fig. 18b. While, for HER LSV results from Fig. 18 a Co/CoN/Co_2P-NPC show the lower value of overpotential 99 mV is needed to achieve the current density of 10 mA/ cm^2 and in case of Co/CoN-NC needs higher overpotential value of 143 mV. Further, for HER the Tafel slope value of 51 mV/dec for Co/CoN/Co_2P-NPC is lower than Co/CoN-NC (i.e., 55 mV/dec) as shown in Fig. 18c (Hu et al., 2019).

Table 3 and 4 shows comparison study of MOF based electrocatalysts for HER and OER.

In summary, electrocatalytic water splitting comprises of hydrogen evolution reaction and the oxygen evolution reaction of water electrolysis produce hydrogen and oxygen from water. Water is split into gaseous oxygen, together with protons and electrons, at the anode. The protons and electrons

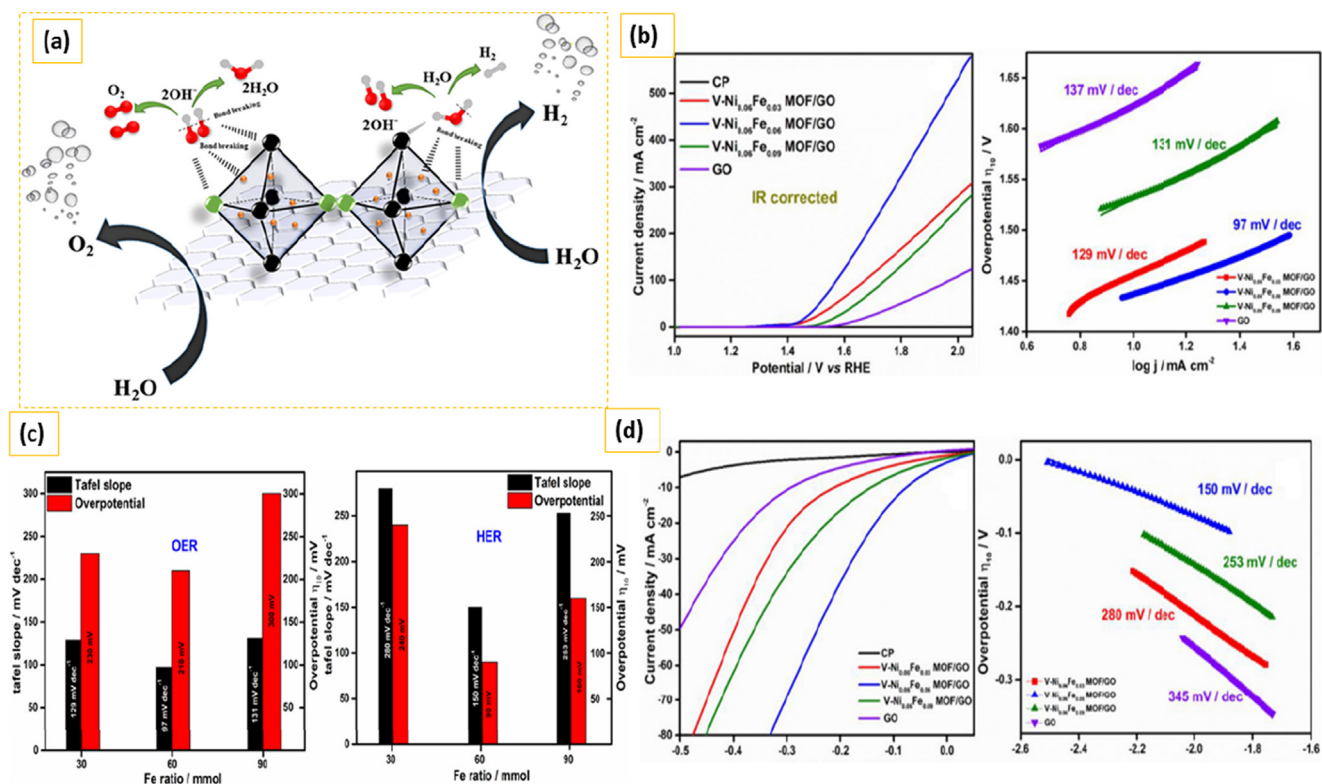**Fig. 17** (a) OER LSV and Tafel slopes (b) HER LSV and Tafel slopes (c) comparison of Tafel slope and over potential values, (d) overall water splitting by corresponding electrocatalysts (Gopi et al., 2021). Exclusive rights 2021 ELSEVIER.
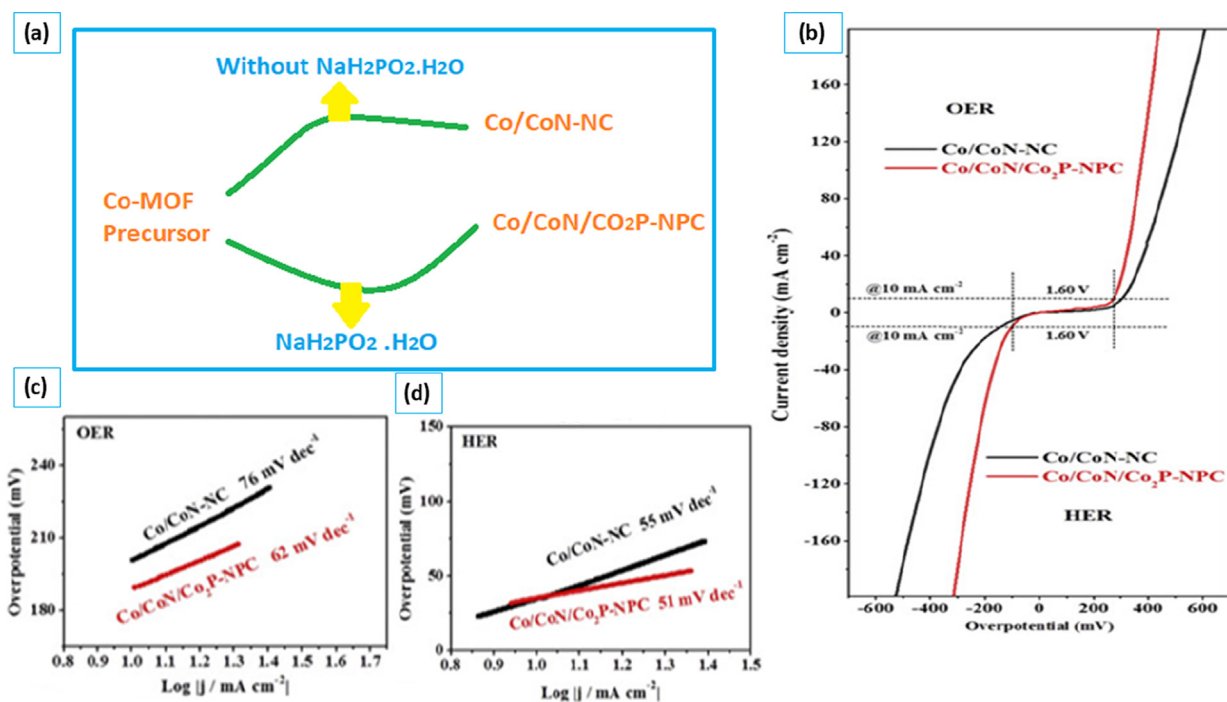

Fig. 18 Co/CoN-NC and Co/CoN/Co2P-NPC (a) LSV curves for HER and OER, (b) Tafel plots for OER and (c) Tafel plots for HER (Hu et al., 2019). Exclusive rights 2019 ELSEVIER.

Table 3 MOF based electrocatalysts for HER.

Electrocatalysts	Electrolyte	Tafel slope (mV dec^{-1})	Overpotential (mv)	Ref.
CTGU-5	0.5 M H$_2$SO$_4$	−125	−388	(Wu et al., 2017)
CoP/rGO-400	1 M KOH	−38	−150	(Jiao et al., 2016)
Co-Ni-Se/C/NF	1 M KOH	−81	−90	(Ming et al., 2016)
CTGU-6	0.5 M H$_2$SO$_4$	−176	−425	(Wu et al., 2017)
PNC/Co	1 M KOH	−131	−298	(Li et al., 2016)
AB&CTGU-5	0.5 M H$_2$SO$_4$	−45	−44	(Wu et al., 2017)
UiO-66-NH$_2$-Mo-5	0.5 M H$_2$SO$_4$	−59	−200	(Dai et al., 2016)
CoSe$_2$@C cages	0.5 M H$_2$SO$_4$	−51	−43	(Kwak et al., 2016)
NENU-500	0.5 M H$_2$SO$_4$	−96	−237	(Qin et al., 2015)
NENU-501	0.5 M H$_2$SO$_4$	−137	−392	(Qin et al., 2015)
Co$_{0.85}$Se@NC	1 M KOH	−125	−230	(Meng et al., 2017)
HUST-201	0.5 M H$_2$SO$_4$	−79	−192	(Zhang et al., 2018)
Mo-N/C@MoS$_2$	1 M KOH	−64	−117	(Amiinu et al., 2017)
HUST-200	0.5 M H$_2$SO$_4$	−51	−131	(Zhang et al., 2018)
(GO 8 wt%) Cu-MOF composite		84	209	(Jahan et al., 2013)
ZIF@LDH@NF-600	1 M KOH	−109	−106	(Jadhav et al., 2021)
Zn$_{0.30}$Co$_{2.70}$S$_4$ polyhedra	0.5 M H$_2$SO$_4$	47.5	80	(Huang et al., 2016)
Y − S Co$_{0.85}$Se/CFP	1 M KOH	−72	−250	(Ao et al., 2018)
CoP CPHs	0.5 M H$_2$SO$_4$	51	133	(Xu et al., 2015)
3D-CNTA	1 M KOH	−135	−185	(Ren et al., 2021)
MoC$_x$ nano-octahedrons	0.5 M H$_2$SO$_4$	53	142	(Wu et al., 2015)
NF@Fe$_2$-Ni$_2$P/C	1 M KOH	30	−39	(Cai et al., 2022)
MoS$_2$/3D-NPC	0.5 M H$_2$SO$_4$	51	210	(Liu et al., 2015)
Cu0.3Co2.7P/NC	1 M KOH	−120	−220	(Song et al., 2017)
Au@Zn − Fe − C	0.5 M H$_2$SO$_4$	130	123	(Lu et al., 2016)
Layered CoP/rGO composite	0.5 M H$_2$SO$_4$	50	105	(Jiao et al., 2016)
Ni-Fe-P@C NRs	1 M KOH	−93	−79	(Ahn and Manthiram, 2017)
Ni@graphene	1 M KOH	−120	−240	(Kakaei and Ostadi, 2020)
NiFeP	1.0 M KOH	−69	−178	(Du et al., 2019)
Fe$_3$C/Mo$_2$C@NPGC	0.5 M H$_2$SO$_4$	−45	−98	(Li et al., 2016)
Ni@CoO@CoNC	1 M KOH	−98	−190	(Li et al., 2022)
Cu$_3$P@NPPC-650	0.5 M H$_2$SO$_4$	−76	−89	(Wang et al., 2018)
MoS$_2$/3D-NPC	0.5 M H$_2$SO$_4$	−51	−210	(Liu et al., 2015)
Ni$_2$P/C	0.5 M H$_2$SO$_4$	−113	−198	(He et al., 2018)
Cu-Co$_9$S$_8$	1 M KOH	−132	−62	(Du et al., 2019)
CoP-CNTs	0.5 M H$_2$SO$_4$	−52	−139	(Wu et al., 2017)
Ni-MoCx -C (HC800)	1.0 M KOH	−83	−123	(Sun et al., 2017)
CoS$_2$ NTA/CC	1 M KOH	−88	−193	(Lu et al., 2020)
Mo$_2$C/C	1.0 M KOH	−64	−165	(Qamar et al., 2016)
Co/Co$_9$S$_8$@ SNGS1000	0.1 M KOH	−96	−350	(Zhang et al., 2016)
A-Ni-C	0.5 M H$_2$SO$_4$	−41	−34	(Fan et al., 2016)
Zn$_{0.1}$Co$_{0.9}$Se$_2$	0.5 M H$_2$SO$_4$	−50	−140	(Wang et al., 2017)
Cr$_{0.6}$Ru$_{0.4}$O$_2$	0.5 M H$_2$SO$_4$	58	178	(Lin et al., 2019)
NGO/Ni$_7$S$_6$	1 M KOH	−146	−370	(Jayaramulu et al., 2017)
CoP@BCN-1	1.0 M KOH	−52	−215	(Tabassum et al., 2017)
Co@NCNT	0.5 M H$_2$SO$_4$	−93	−210	(Tang et al., 2021)
CuCo@NC	0.5 M H$_2$SO$_4$	−79	−145	(Kuang et al., 2017)
Cu$_3$P@NPPC-650	0.5 M H$_2$SO$_4$	−76	−89	(Wang et al., 2018)
Co-NC/CNT-800	1 M KOH	−125	−203	(Zhang et al., 2016)
Ni foam, SS mesh	1 M KOH	130, 51	1.74 V, 0.277	(Hu et al., 2019)
NSPC −1000	0.5 M H$_2$SO$_4$		172	(Liu et al., 2019)
CoSe$_2$/CF	1 M KOH	−52	−95	(Ma et al., 2018)

recombine to form hydrogen gas at the cathode. By far, the energy conversion technology has piqued the interest of many people owing to its high conversion efficiency, low environmental impact, and potentially broad variety of applications (Yagi and Kaneko, 2001). Various MOF based/ derived electrocatalysts are fabricated for electrocatalytic water splitting, include encapsulating metal NPs in carbon nanotubes or carbon shells. As a precursor to the fabrication of core–shell structured hybrid electrocatalysts, MOFs might be used as a latest research path to create effective water splitting MOF-based catalysts. Since we know even less about the transformation process, it is difficult to regulate exactly how these materials will change morphology. Clarity on this problem is critical for the development of large surface area, regular pore structure, and adjustable composition MOF nanostructures for electrochemical water splitting processes (Wang et al., 2017). Table 5 shows the comparison of MOF and MOF derived electrocatalysts for overall water splitting.

Table 4 MOF based electrocatalysts for OER.

Electrocatalyst	Electrolyte	OER		Ref.
		Tafel mV/ dec	Overpotential (η_{10}) mV	
Fe:2D-Co-NS@Ni	0.1 M KOH	46	211	(Chen et al., 2021)
NiFe-NFF	1 M KOH	38.9	227	(Qin et al., 2021)
CoP/rGO-400	1 M KOH	66	340	(Jiao et al., 2016)
$CoSe_2$	1 M KOH	79	330	(Liu et al., 2017)
PNC/Co	1 M KOH	76	370	(Li et al., 2016)
Co-Ni-Se/C/NF	1 M KOH	63	275	(Ming et al., 2016)
CeO_x/CoS	1 M KOH	50	269	(Xu et al., 2019)
NCNTFs	1 M KOH	93	370.	(Wang et al., 2017)
$CoSe_2$/CF	1 M KOH	41	297	(Ma et al., 2018)
Fe_3-Co_2	0.1 M KOH	48	225	(Li et al., 2021)
Co-NC/CNT-800	1 M KOH	78	314	(Zhang et al., 2016)
Co@NCNT	1 M KOH OER	116	429	(Tang et al., 2021)
Co/Co_9S_8@ SNGS1000	0.1 M KOH	80	290	(Zhang et al., 2016)
Ni MOF	1 M KOH	64	346	(Maruthapandian et al., 2018)
$Cu-Co_9S_8$	1 M KOH	50	260	(Du et al., 2019)
Ni-Fe-P@C NRs	1 M KOH	40	217	(Ahn and Manthiram, 2017)
Ni-MOF@Fe-MOF	1 M KOH	82	265	(Cheng et al., 2021)
$NF@Fe_2-Ni_2P$/C	1 M KOH	52	205	(Cai et al., 2022)
Ni@graphene	1 M KOH	66	370	(Kakaei and Ostadi, 2020)
Co_3S_4/EC-MOF	1 M KOH	120	226	(Liu et al., 2019)
$Mo-N/C@MoS_2$	0.1 M KOH	72	390	(Amiinu et al., 2017)
Cu-doped RuO_2	0.5 M H_2SO_4	43.96	188	(Li et al., 2021)
Ni@CoO@CoNC	1 M KOH	53	309	(Li et al., 2022)
$CoSe_2$@C cages	1 M KOH	83	200	(Kwak et al., 2016)
FeCoNi	1 M KOH	60	325	(Xu et al., 2018)
CoS_2 NTA/CC	1 M KOH	81	276	(Lu et al., 2020)
$Cr_{0.6}Ru_{0.4}O_2$	0.5 M H_2SO_4	58	178	(Li et al., 2021)
NGO/Ni_7S_6	0.1 M KOH	45	380	(Jayaramulu et al., 2017)
CoFe-MOF-OH	1 M KOH	44	310	(Zou et al., 2019)
$Co_{0.85}$Se@NC	1 M KOH	75	320	(Meng et al., 2017)
NGO/Ni_7S_6	0.1 M KOH	45.4	380	(Stelmachowski et al., 2021)
$Cu_{0.3} Co_{2.7}P$/NC	1 M KOH	44	190	(Song et al., 2017)
$Ni_xCo_{3-x} O_{4-y}$	1 M KOH	53	320	(Antony et al., 2016)
ZIF@LDH@NF-600	1 M KOH	97	318	(Jadhav et al., 2021)
3D-CNTA	1 M KOH	89	360	(Ren et al., 2021)
NiFe MOF/OM-NFH	1 M KOH	123	270	(Li et al., 2019)
$Zn_{0.1}Co_{0.9}Se_2$	1 M KOH	43	340	(Wang et al., 2017)
Ni-Fe-MOF NSs	1 M KOH	56.0	221	(Li et al., 2019)
$Y - S Co_{0.85}Se$/CFP	1 M KOH	87	300	(Ao et al., 2018)

4. Conclusion and future perspectives

Hydrogen production using electrocatalysis and photocatalysis is intended to address a variety of environmental and energy-related issues. The formation of an affordable, easily available, and unique catalysts is a critical challenge for achieving effective water splitting. In this regard, MOF derived carbon catalysts may provide various benefits over traditional catalysts due to their distinctive morphologies, superior optical, electrical, and catalytic capabilities, high porosity, crystallinity, structural adjustability, and increased surface area. Beginning with the principles, procedure, and evaluation aspects, and detailed research of MOFs as direct new catalysts, precursors for derived catalysts, and MOF based composites for electrocatalytic and photocatalytic water splitting, various noteworthy outcomes are reported.

We reviewed significant achievements in recent research on fabricating MOF derived carbon based catalysts for effective electro and photo catalytic water splitting. Various MOF derived carbon based materials with high water splitting performance have been developed by exploiting the vast surface area, customizable chemical components, controllable pore structure, programmable topology, and quite well surface functionality. This review highlights a variety of novel synthetic strategies for improving the chemical composition and structural functionalization of catalytic sites in order to enhance their electro/photo catalytic activity, particularly at the atomic scales and for tailoring nanoarchitectures and combinations. The morphological characteristics of MOFs require more comprehensive experimental analysis or theoretical research (Yang et al., 2014). Along with shape, electro/photo catalyst interactions or synergistic effects have a significant impact on the catalytic performance of carbon based MOFs, necessitating more focus on the application of MOF-based electro and photocatalysts for water splitting processes (Jiao et al., 2016). The rapid advancements in catalytic activity, the identification of highly active sites and basic processes contribute to the hydrogen generation industrially (Wang et al., 2017).

This review also summarized the current challenges in the use of carbon based MOFs as photocatalysts for water splitting, with a focus on several important methods for developing high-performance photocatalysts that significantly influenced by its sunlight absorption capacity (i.e., band gap), the charge separation/transfer efficiency, and the number of active sites (Liang et al., 2015). The inclusion of active sites, like Pt nanoparticles, into MOFs was revealed to significantly improve

Table 5 MOF based electrocatalysts for overall splitting of water.

Catalyst	Electrolyte	OER		HER		Ref.
		Tafel mV/dec	Overpotential (η_{10}) mV	Tafel mV/dec	Overpotential (η_{10}) mV	
V-Ni$_{0.06}$Fe$_{0.06}$ MOF/GO	1 M KOH	97	210	150	90	(Zhang et al., 2021)
CoP/rGO	1 M KOH	66	272	46	107	(Zhang et al., 2021)
NiFeP/CC	1 M KOH	147	425	112	109	(Roger et al., 2017)
Co$_{5.47}$N NP@N-PC	1 M KOH	54	248	86	149	(Chen et al., 2018)
CoP-NS/C	–	64	292	59	140	(Liu et al., 2017)
CoP NA/CC	–	58	52	58	52	(Liu et al., 2017)
Ni$_{0.9}$Fe$_{0.1}$/NC	1 M KOH	45	330	111	231	(Du et al., 2018)
CO$_2$P/CNT	–	68	292	103	132	(Lu et al., 2021)
FeNi@N-CNT (OER)Ni-NPs@NC (HER)	1 M KOH	47.7	300	68	77	(Tao et al., 2016)
Ni$_2$P-CoP	–	64–69	320	64	105	(Liang et al., 2017)
Ni$_2$P/rGO	–	62	142	58	260	(Liang et al., 2017)
NiCOP/CC	–	64	242	68	62	(Du et al., 2017)
Fe-Ni@NC-CNT	1 M KOH	45.47	274	113	202	(Anantharaj et al., 2016)
Co-NCNTFs//NF	1 M KOH	–	141	–	230	(Yuan et al., 2019)
Co$_3$ZnC/Co-NCCP	1 M KOH	188	70	108	295	(Yu et al., 2018)
Co$_9$S$_8$ − NSC@Mo$_2$C	1 M KOH	59.7	89	69.3	293	(Luo et al., 2018)
NiCoFeP/C		65	270	108	149	(Wei et al., 2019)
Co/NBC-900	1 M KOH	70	302	247	117	(Liu et al., 2018)
Co$_3$O$_4$@CuCAT	1 M KOH	75	267	59	100	(Hu et al., 2019)
Co$_3$S$_4$/EC-MOF	1 M KOH	120	226	82	84	(Liu et al., 2019)
NiFe-MOF	0.1 M KOH	34	240	N/A	134	(Duan et al., 2017)
MFN-MOFs	1 M KOH	55.4	294 at 500 mA/cm^2	30.1	234 at 500 mA/cm^2	(Raja et al., 2019)
NFN-MOF/NF	1 M KOH	58.8	240	35.2	87	(Senthil Raja et al., 2018)
FeNi(BDC)(DMF,F)/NF	1 M KOH	37.4	227 at 60 mA/cm^2	96.2	234 at 60 mA/cm^2	(Lin et al., 2019)
NiFeZn-MNS/NF	1 M KOH	49	350 at 50 mA/cm^2	N/A	180	(Wei et al., 2019)
Cu$_3$(PO$_4$)$_2$/Cu-BDC150-6 foam	1 M KOH	76	241	N/A	145	(Rong et al., 2019)
Ni-ZIF/NieB@NF	1 M KOH	57	234	108	67	(Xu et al., 2020)

photocatalytic activity. Unfortunately, platinum's limited supplies and expensive cost make it inappropriate for widespread use. Recently, it was shown that extremely effective, small-sized Ni particles implanted in MOF-5 as co-catalysts with negligible overpotential for photocatalytic HER under visible light. This photocatalyst had a low overpotential of 0.37 V, which was similar to Pt@MOF-5.

Although great progress has been made in the field of MOF-based catalysts for electrocatalyst and photocatalytic water-splitting, major work has to be done to make hydrogen production processes practicable and completely economical at an industrial scale. In the future, greater emphasis will be paid for the creation of non-precious metal NPs from MOFs to improve catalytic activity. For this, various research approaches on MOFs for water-splitting may be investigated, along with (i) Researching novel forms of MOFs with design and active sites has a broad scope because only a few are presently used (MIL, UiO, and ZIFs). (ii) As MOFs have a hybrid structure, adjusting the charge transfer capacities of MOFs by fine-tuning the coordination arrangement of metal nodes with organic linkers is an appealing option. (iii) Charge transfer attributes inside different components of MOF derived photo/electrocatalysts are largely unknown; a thorough knowledge of the mechanisms underlying elementary reactions for hydrogen production, light collecting, and electron transfer reactions between the interfaces could result in a rise in hydrogen production efficiency. (iv) So, because exact structure of the majority of MOF based carbon catalysts is still unknown, limitations in comprehending structure-catalysis correlations exist; hence, further extensive study on the morphology of MOF based carbon catalysts should be conducted. (v) Improved stability, direct application of MOF catalysts to a surface of the electrode without the need of binders, and the fabrication of new MOFs are other highly wanted future research subjects (Pham et al., 2014; Toyao et al., 2013).

CRediT authorship contribution statement

Neelam Zaman: Data curation, Writing – original draft. **Naseem Iqbal:** Conceptualization, Methodology, Supervision. **Tayyaba Noor:** Writing – review & editing, Supervision.

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.

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