

# Metal Organic Frameworks as Versatile Materials for Energy Storage, Environmental Remediation, and Catalytic Applications

Manisha Singhal, Seema Jangid, Deepak Singh Rajawat

Department of Chemistry, IIS (Deemed to be University), Jaipur, Rajasthan, India. Email: manishasinghal007@gmail.com

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REVIEW

**Abstract:** Metal organic Framework is a family of 2D transition-metal carbides and nitrides, and has emerged as promising materials for a wide range of applications, particularly in electro- and photocatalytic water splitting for hydrogen generation. Their unique structure, large surface area, metallic conductivity, and surface terminations offer numerous advantages in enhancing catalytic activity. Metal organic framework compounds are also called MXene. This review provides a detailed examination of the organic framework of metals and their properties, including their synthesis methods, structural features, and surface chemistry. Recent advances in MXene-based composites, especially MXene-TiO<sub>2</sub> and MXene/metal composites, are also discussed for improved water splitting efficiency. Challenges such as weak environmental stability, limited intrinsic catalytic activity, and charge recombination are highlighted along with strategies for overcoming these limitations. Finally, the future outlook of MXene-based materials for scalable, sustainable hydrogen production is presented. This review summarizes the most recent breakthroughs and predicts the prospects of MOFs for heterojunctions, composites, doping, and other technologies that enhance their capabilities. This review provides a comprehensive overview of the present state of research on MOFs and emphasizes their prospective applications in materials science, energy science, environmental science, photoelectrochemistry, and photoelectronic devices.

**Keywords:** metal-organic frameworks, heterojunction, composite, doping, photoelectrochemistry, photoelectronic devices, and applications

## INTRODUCTION

The ever-growing global energy demand and environmental concerns related to fossil fuels have spurred significant interest in alternative energy sources. Among these, hydrogen energy stands out as one of the most promising solutions due to its high-energy content and environmentally friendly combustion by-product, water. Electrocatalytic and photocatalytic water splitting has been identified as an efficient method to generate hydrogen, but the challenge lies in the development of catalysts that exhibit high efficiency, long-term stability, and low cost (Mikolasek et al., 2019; Ronchi et al., 2019).

Transition-metal carbides and nitrides, collectively known as MXenes, are a family of two-dimensional (2D) materials that have garnered considerable attention for their unique properties. These materials possess large specific surface areas, excellent metallic conductivity, hydrophilicity, and tunable surface chemistry, making them ideal candidates for applications in catalysis, especially water splitting (Carson et al., 2012; Fasano et al., 2021). MXenes can be synthesized from layered transition metal carbides, nitrides, or carbonitrides, which are selectively exfoliated into their 2D forms.

Researchers began to examine the characteristics and manufacturing of these innovative materials in the late 1990s, which marked the beginning of the history of metal-organic frameworks (MOFs) (Guo et al., 2023; Lin et al., 2021). The following are some significant developments and turning points in MOF history. In coordination chemistry research, MOFs were initially presented when organic ligands connected metal ions or clusters to form longer networks (Guidelines for drinking water quality, 2017; Lv et al., 2017). In the 1990s, researchers first investigated the possibility of employing these materials in gas separation and storage processes. Groundbreaking work by Naguib et al. at the University of California, Los Angeles and the University of Michigan revealed that the first highly porous MOF, MOF-5 or IRMOF-1, was synthesized in 1999 (Bueken et al., 2017; Podgorski & Berg, 2020). This groundbreaking achievement demonstrated how to fabricate porous materials with large surface areas and highly adjustable characteristics. Since the synthesis of MOF-5, research on new MOFs with various structures and functions has expanded rapidly. Scientists have started to create new synthetic techniques, describe MOFs and investigate their possible use in gas storage, catalysis, and sensing (Guo et al., 2023; Lv et al., 2017). Concerns such as production scalability, stability in real-world settings, and practical usefulness in industrial and environmental applications are being addressed as MOFs have become more popular. The integration of MOFs with cutting-edge technology to offer environmentally friendly and sustainable energy solutions has also been studied (Carson et al., 2012; Guo et al., 2023; Lin et al., 2021). Ligands, often referred to as linkers, and metals found in various salts such as nitrates, chlorates, perchlorates, and sulfates, are the two primary components required to make MOFs. The s-block, p-block, transition metals and rare earth metals may be among these (Guidelines for drinking water quality, 2017).

\*Corresponding Author: Deepak Singh Rajawat, Department of Chemistry, IIS (Deemed to be University), Jaipur, Rajasthan, India. E-mail: drdeepaksr@gmail.com

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The generation of 1, 2, and 3 D MOFs is directly influenced by the metal used for the synthesis, specifically its oxidation state and the geometries it can acquire. Linear, T- or Y-shaped, tetrahedral, square-planar, square-pyramidal, trigonal-bipyramidal, octahedral, trigonal-prismatic, and pentagonal-bipyramidal are among the coordination numbers and geometries preferred by certain metal ions. As an illustration, Cu(II) ions prefer tetrahedral and square-planar geometries, although they also have varying coordination numbers based on the solvent and ligand(s) employed (Liu et al., 2013; Zhu et al., 2009).

Different metals exhibit preferred coordination geometries, which influence the connectivity and overall structure of MOFs. Some common geometries include

- **Linear (Coordination Number 2):** Common for Ag(I) and Au(I) ions, leading to 1D chain-like structures.
- **T-Shaped & Y-Shaped (Coordination Number 3):** It is found in some transition metals like Cu(I), leading to branching structures.
- **Tetrahedral (Coordination Number 4):** Preferred by Zn(II), Co(II), and Cu(II), which often form 3D frameworks.
- **Square Planar (Coordination Number 4):** Typical for Ni(II), Pt(II), and Pd(II), influencing 2D layered structures.
- **Square-Pyramidal & Trigonal-Bipyramidal (Coordination Number 5):** Found in Mn(II) and Fe(III), leading to complex frameworks.
- **Octahedral (Coordination Number 6):** Common for Fe(III), Co(III), and Al(III), favoring 3D porous MOFs.
- **Trigonal-Prismatic & Pentagonal-Bipyramidal:** Found in some rare-earth and high-oxidation-state metals, enabling highly porous structures.

The field of metal–organic framework development has been dynamic and rapidly evolving, with significant advances in material synthesis, characterization, and application development since its inception (Bueken et al., 2017; Hou et al., 2020; Podgorski & Berg, 2020). Given the unique properties of these versatile materials, further research on MOFs may address significant issues in energy, environmental sustainability, and other areas.

MOFs are porous materials composed of metal ions or clusters connected by organic ligands. There is a lot of interest in MOFs due to their variable porosity, large surface area, and diverse chemical activities (Guidelines for drinking water quality, 2017; Bueken et al., 2017; Lin et al., 2021; Podgorski & Berg, 2020). MOFs are a new type of porous material composed of metal-containing nodes, also known as organic linkers and secondary building units. Porous coordination polymers are another type of polymer. Because MOFs can be tuned structurally and functionally, this field has grown rapidly in recent years. MOF research has contributed to five developments (Bueken et al., 2017; Hou et al., 2020; Liu et al., 2013; Saha et al., 1999).

1. Development of Cluster Chemistry
2. Preparing ligands and postsynthesis modifications associated with organic synthesis maturation
3. Improving structure determination, particularly through the use of X-ray crystallography, and developing gear and software for evaluating sorption qualities.
4. Multidisciplinary growth of MOF research in related domains
5. Countless potential uses

This review focuses on the advancements in MXenes as catalysts for water splitting, particularly for hydrogen evolution reactions. It provides insights into the synthesis of MXenes, their structural characteristics, surface chemistry, and strategies used to enhance their catalytic activity. Furthermore, the challenges and future directions for MXene-based materials in practical applications are discussed.

## **MXENES: STRUCTURE, SYNTHESIS, AND PROPERTIES**

### **Structure and Composition**

MXenes are typically synthesized by selectively etching the layer 'A' from their parent MAX phases, which consist of transition metals (M), elements such as carbon or nitrogen (X), and an element in the 'A' group such as aluminum or silicon (Lu et al., 2022; Song et al., 2018). The general formula for MXenes is  $M_n X_n T_x$ , where n represents the number of metal layers in the structure and T represents surface termination groups such as -OH, O or F.

MXenes possess a unique layered structure, similar to that of graphene, which allows them to be exfoliated into thin 2D nanosheets. These materials exhibit metallic conductivity, high surface area, and exceptional mechanical properties, which make them ideal candidates for various energy and environmental applications, particularly catalysis.

## Properties of MOF

There are many 2D materials accessible, but the reason we require 2D MOF is that they provide a palette of 2D materials, most of which are semiconductors, semimetals, or dielectrics, with metallic electrical conductivity, a property that 2D sheets lack (Liu et al., 2013; Song et al., 2018; Wu et al., 2020).

It also offers scalable solution synthesis, biocompatibility, aqueous solution processing without surfactants, sufficient environmental stability for a variety of applications, greater strength and stiffness than other solution-processed 2D materials, and reported conductivity values up to 20,000 S/cm (Lin et al., 2021; Lv et al., 2017; Mikolasek et al., 2019; Podgorski & Berg, 2020). They are interesting because of their unique qualities, which arise from the uncommon fusion of metallic and ceramic behaviors. Metallic materials have similar electrical and thermal conductivities and good machinability.

The major bonds are responsible for these revolutionary properties: M-A bonds are completely metallic, whereas M-X bonds mix ionic, metallic, and covalent contributions (Bueken et al., 2017; Hou et al., 2020; Liu et al., 2013; Saha et al., 1999; Zhu et al., 2009). Because of this, MAX phases have strong connections that make them resistant to breakage by shearing or other mechanical methods, in contrast to other 3D layered materials, such as graphite and transition-metal dichalcogenides, which are joined by weak Vanderwaals interactions.

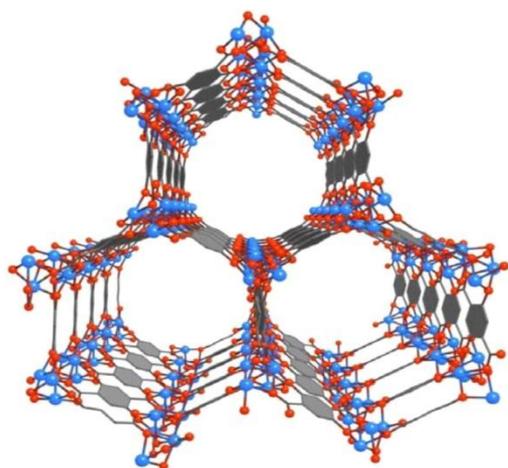
## Creation of MOFs

MXenes are primarily synthesized through a top-down approach, where the MAX phase is subjected to selective etching using a fluoride-containing acidic solution (such as HF or a mixture of hydrochloric acid and fluoride salts). The etching process removes the 'A' layer, creating the desired 2D MXene sheets. Alternative etching techniques, including electrochemical and molten salt methods, have also been explored to enhance control over the morphology and surface terminations of MXenes.

Synthesis conditions, such as the etching time, temperature, and choice of fluoride salts, play a critical role in determining the properties of MXenes, including their surface chemistry, layer spacing, and structural integrity. Post-synthesis treatments, such as annealing or functionalization, can further tailor the properties of MXenes to suit specific applications.

MOF synthesis requires two primary elements, and the solvent is typically used as the reaction medium. MOFs are primarily composed of inorganic and organic linkers (Gurusamy et al., 2021; Li et al., 2012; Li et al., 2023; Ramanayaka et al., 2019; Wu et al., 2020). Examples of commonly used inorganic metal precursors include trivalent oxidation states such as Fe<sup>3+</sup>, Cr<sup>3+</sup> and Al<sup>3+</sup>, as well as divalent atoms such as Zn<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Ru<sup>2+</sup>, and Zr<sup>2+</sup>. Additionally, the lanthanide series with Li, B and Ca ions along with La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb have attracted attention (Karimi et al., 2021; Ratnaike, 2003). Solvent evaporation is the most frequently used method for MOF syntheses. Additional synthetic techniques include diffusion, hydrothermal, solvothermal, microwave, electrochemical, mechanochemical, and ultrasonic processes.

MOFs have several useful uses, including sensors, storage, medicine, separation, and catalysis. Metal ions and organic components self-assemble to form inorganic–organic hybrid compounds. The Zn-MOF/COF was prepared via hydrothermal synthesis. When used without a solvent, the produced Zn-MOF/COF is a very good heterogeneous catalyst for the Knoevenagel process. The catalyst exhibited remarkable activity and was reused eight times without significantly decreasing activity (Federal Register, ATSDR, substance priority list resource, 2019).



**Figure 1.** Mg-MOF-74 is an open metal-organic framework (MOF) site (National Academy of Sciences).

Jianglog et al. 2019 (Miao et al., 2020) created new 0D / 2D SnO<sub>2</sub> / SnS<sub>2</sub> step-scheme heterojunctions (S-scheme) were created by Jianglog et al. 2019 (Miao et al., 2020) using oxidation and solvothermal methods by regulating the temperature in N<sub>2</sub>/H<sub>2</sub>. The photocurrent density 0.33 mA/cm<sup>2</sup> at 1.23 V was highest in SnS<sub>2</sub> nanosheets annealed at 400 °C, which was greater than that of SnS<sub>2</sub> annealed at 300 and 500 °C. These evolution rates were 5.5 μmol for hydrogen and 2.7 μmol for oxygen cm<sup>-2</sup> h<sup>-1</sup>. The proper quantity of 0 D SnO<sub>2</sub> nanoparticles formed on the surface and edge of the SnS<sub>2</sub> nanosheets, which regulates the recombination rate and encourages charge separation, is why SnS<sub>2</sub> 400 shows strong photocatalytic activity. For photoelectrochemical (PEC) water splitting, Qiong et al. (2014) (Tong et al., 2019) created a 2D ZnIn<sub>2</sub>S<sub>4</sub> nanosheet/1D TiO<sub>2</sub> nanorod heterojunction as a photoelectrode. When the 2D ZnIn<sub>2</sub>S<sub>4</sub> nanosheet/1D TiO<sub>2</sub> was used as the electrode, the electron hole separation was quick, the charge transfer was good, and the current density was 1.2 mA/cm<sup>2</sup>

Ghosh et al. (2020) created a hexagonal microwell on P-GaN as a photocathode for PEC water splitting, and GaN was then modified with 2D MoS<sub>2</sub>. In addition to demonstrating the greatest applied bias photon to the current conversion efficiency of 3.18 % with a hydrogen evolution rate of 89.56 μmol/hr at 0.3 V against reversible hydrogen electrode (RHE), 2D MoS<sub>2</sub>/P-GaN demonstrated greater stability during PEC performance.

In 2019, Seo et al. (Dhaka et al., 2019) successfully fabricated centimeter-scale multi-TMD thin films composed of MoS<sub>2</sub>/WS<sub>2</sub>/WSe<sub>2</sub> and MoS<sub>2</sub>/WSe<sub>2</sub> using sequential pulsed laser deposition, an in situ growth approach. Using conventional deposition procedures to produce large-scale Vanderwaals multiheterojunction transition metal dichalcogenides in situ has proven challenging. Making a fire. In several applications, including PEC hydrogen evolution, MoS<sub>2</sub>/WS<sub>2</sub>/WSe<sub>2</sub> effectively transfers photogenerated electrons from p-Si to the electrolyte through a p-Si photocathode thin film catalyst. Overall, the PEC performance was improved by the metal dichalcogenides.

Ye et al. (2021) (Ye et al., 2021) reported the synthesis of MOF 2D Ti<sub>3</sub>C<sub>2</sub> materials using a simple hydrothermal method and applied it to the surface of α-Fe<sub>2</sub>O<sub>3</sub>. The use of an electrode based on MOF material boosted stability and improved the PEC performance by seven times. The Ti source in this material suppresses charge recombination and promotes bulk electron transfer, thereby increasing the overall PEC performance. The photocurrent density was seven times higher than that of the virgin Fe<sub>2</sub>O<sub>3</sub>.

A p-type NiO nanocluster on an n-type cubic silicon carbide (3C-SiC) photoanode was developed by Jingxin Jian et al. in 2013 (Zhou et al., 2012), which exhibited a notable decrease in the onset potential and a significant increase in photovoltage and photocurrent. Under AM 1.5 G 100 mW / cm<sup>2</sup> illumination, the 3C-SiC photoanode with NiO coating exhibits a high fill factor of 57% for PEC water splitting, a very low onset potential of 0.20 V RHE, and a photocurrent density of 1.01 mA/cm<sup>2</sup> at 0.55 V versus RHE.

The 3C-SiC/NiO photoanode displays the maximum recorded photovoltaic value of 1.0 V. Measurements of impedance measurements show that 3C-SiC/NiO improves the charge transfer for water oxidation. This heterojunction increased solar water splitting by promoting the separation of photogenerated carriers and reducing carrier recombination.

For solar water splitting, Jian and Jokubavicius (2021) developed a straightforward anodization method to create nanoporous 3C-SiC photoanodes connected to a Ni: FeOOH cocatalyst. 3.3 times higher than its planar counterpart, the optimized nanoporous 3C-SiC photoanode achieved a high photocurrent density of 2.30 mA/cm<sup>2</sup> at 1.23 V RHE under one solar irradiation. This study proposes a process to generate 3C-SiC for solar hydrogen synthesis. The construction of indirect bandgap semiconductors for solar energy conversion is possible using this technique.

Researchers described the manufacturing and characterization of structures based on amorphous silicon carbide (a-SiC:H) for PEC water splitting. The PEC photocurrent increased as CH<sub>4</sub> flow decreased during the deposition phase. The bandgap closing and increased light absorption in a-SiC:H were linked to this increase in the photocurrent. A photocurrent of 50 mA/cm<sup>2</sup> is achieved for the PEC structure formed with the least flow of CH<sub>4</sub> during the deposition process. A silicon heterojunction structure ITO/a-SiC:H/Si was developed to supply extra voltage and produce a hybrid PEC-PV system. The basic photovoltaic cell (PV) formed by this configuration has an efficiency of 9.66%. An ASA simulation showed that a hybrid PEC-PV structure with five PVs connected in series could produce a solar-to-hydrogen efficiency of 0.76% and a photocurrent of 0.62 mA/cm<sup>2</sup> (Alguacil & Escudero, 2022; Liu & Tang, 2013).

Direct hydrogen production from water using sunlight and an integrated 'hybrid' PEC cell with amorphous silicon carbide (a-SiC:H) as the photoelectrode. Using a gas mixture of SiH<sub>4</sub>, H<sub>2</sub> and CH<sub>4</sub>, high-quality a-SiC:H thin films with a band gap of 42.0 eV were produced. Carbon was added to the a-SiH layer to increase the band gap and the electrolyte's resilience to corrosion. The DOS in the films decreased when H<sub>2</sub> was added during the production process. As of the testing, the a-SiC:H(p)/aSiC:H(i) structure demonstrated exceptional power for up to 100 hr; however, following that time, the photocurrent rose and its onset varied anodically. It was also discovered that a-SiC:H formed a SiO<sub>x</sub> layer in the presence of air, resulting in a cathodically shifting photocurrent onset and a drop in the photocurrent. Water splitting may be accomplished by arranging an a-Si:H tandem (or 'micromorph') / a-SiC:H structure (PV/PEC), which increases the photovoltaic (potential) required. The potential use of a-SiC:H as a photoelectrode to increase the efficiency of solar-to-hydrogen conversion was finally demonstrated through simulations (Liu et al., 2020; Ramanayaka et al., 2019; Xie et al., 2017). A BiVO<sub>4</sub> film generated on a FTO substrate was spin-

coated with small Ti<sub>3</sub>C<sub>2</sub>TX (MXene) flakes to create a new Ti<sub>3</sub>C<sub>2</sub>TX / BiVO<sub>4</sub> composite photoanode. Reannealing bare BiVO<sub>4</sub>/FTO photoanodes in argon significantly increased the photocurrent density from 2.1 to 2.95 mA/cm<sup>2</sup>. This indicates that the BiVO<sub>4</sub> layer and FTO can improve their contact and reduce interfacial charge recombination. When thin Ti<sub>3</sub>C<sub>2</sub>TX flakes are added to the BiVO<sub>4</sub> film, the photocurrent density would increase to 3.45 mA/cm<sup>2</sup>. Under the light of one sun, this photocurrent density was evaluated at 1.23 V versus a RHE and demonstrated a surface charge separation efficiency of 73% and a photoconversion efficiency of 0.78% (Furukawa et al., 2013; Ren et al., 2023).

Well-designed two-dimensional exfoliated titanium carbide (2D TiC) multilayers were fabricated and anchored on two-dimensional hierarchical g-C<sub>3</sub>N<sub>4</sub> (2D HCN) nanosheets to enhance H<sub>2</sub> production under visible light. Changing the etching time from 24 to 96 h directly affected the Ti<sub>3</sub>C<sub>2</sub> efficiency. The highest H<sub>2</sub> yield of 182.5 mol grams<sup>1</sup> h<sup>1</sup> was achieved using optimized 2D TiC multilayers embedded with TiO<sub>2</sub> (anatase) with an initial time of 48 h. This results in a higher production rate than when employing etchant times of 24, 72, and 96 h because heterojunction formation improves the charge carrier separation efficiency. Due to efficient migration and transportation of charge carriers, hierarchical g-C<sub>3</sub>N<sub>4</sub> showed a 1.26-fold higher H<sub>2</sub> yield than bulk g-C<sub>3</sub>N<sub>4</sub>.

The rate of H<sub>2</sub> generation in this heterojunction was 310 mol grams<sup>1</sup> h<sup>1</sup>. This effective hydrogen synthesis was caused by faster electron transit from HCN to TiC-MXene, which resulted from increased conductivity and formation of a heterojunction between HCN and TiO<sub>2</sub>, which had synergistic effects. The benefits of the 2D/2D heterojunction and the function of the hierarchical MXene compound were proven by the continuous synthesis of H<sub>2</sub> with recyclability, both of which are beneficial for solar energy (Sharma et al., 2021; Sun et al., 2019; Wang et al., 2015).

In 2022, Rafiee et al. investigated the hydrothermal synthesis of new Zn-based nanoporous microspheres through the reaction of an amine, thiol and pyrimidine functional group that contains 4,6-Diamino-2-pyrimidinethiol with a salt of zinc nitrate hexahydrate. Additionally, we discovered that Zn-MOFs could be utilized as quick catalysts to produce high-yield polyhydroquinolines. This is a novel approach to rapid and safe synthesis of asymmetrical dihydropyridine (Rafiee, 2021).

In 2018, Lv et al. built a Zn(II)-based metal-organic framework (Zn-MOF) that demonstrated exceptional selectivity, sensitivity, and rapid response time to Fe (III) and Cr(VI) ions. Furthermore, the other ions did not affect the quenching effect of the Fe(III) and Cr(VI) ions on the Zn-MOF luminescence. Furthermore, the Eu<sup>3+</sup>@Zn-MOF was obtained.

Additionally, combining Zn-MOF and Eu<sup>3+</sup>@Zn-MOF allowed us to distinguish between the Fe(III) and Cr(VI) ions. More significantly, this is the first instance of a MOF-based luminescent sensor that uses a fluorescence mechanism to distinguish between Fe(III) and Cr(VI) ions. The potential use of Zn-MOFs for the selective detection and discrimination of Fe(III) and Cr(VI) ions is demonstrated in this work, which also offers a new, simple method for creating functional MOFs as fluorescence sensors. However, the issue of how to increase MOF utilization efficiency is still pressing (Lv et al., 2017).

The rapid synthesis of Ni-MOF via a mechanical ball milling technique was reported by Zhang et al. in 2018. In approximately 1 min, Ni-MOF was produced without bulk solvent, additives, or pretreatment, and the shape and structure of Ni-MOF were verified by scanning electron microscopy and powder X-ray diffraction. Within 1 min, Ni-MOF was created by rapid crystallization; even after 180 min, there was no discernible decrease in yield or crystallinity.

A systematic investigation was conducted on the effects of milling duration, mechano-frequency, helper liquid type, and assistant water quantity. At a current density of 1 A/g, the Ni-MOFs produced exhibited a high capacitance of up to 640 F/g. This is the first instance of an ultra-fast synthesized Ni-MOF using ball milling (Zhang et al., 2018).

Using a straightforward solvothermal technique, Chen et al. fabricated ultrathin 2D Ni-MOF nanosheets in 2018. The ultrahigh specific surface area and many active sites of the nanosheet allowed the nanosheet to exhibit amazing peroxidase-like activity. The Ni-MOF nanosheets that were produced had good stability and dispersion, and to create colorimetric detection, the Ni-MOF nanosheet was employed as a peroxidase mimic. In the presence of H<sub>2</sub>O<sub>2</sub>, Ni-MOF nanosheets can rapidly catalyze the oxidation of 3,3',5,5'-tetramethylbenzidine (TMB) into a visible blue product. A high affinity for the peroxidase substrate (TMB) was observed for Ni-MOF nanosheets. High selectivity and good sensitivity were demonstrated using a straightforward colorimetric platform based on Ni-MOF nanosheets for the measurement of H<sub>2</sub>O<sub>2</sub>. The colorimetric approach also showed promising results when used to measure H<sub>2</sub>O<sub>2</sub> levels in disinfectant samples and human serum, indicating its great potential for future biocatalysis and bioassays (Chen et al., 2018).

The compound Ti<sub>3</sub>C<sub>2</sub> of the MXene family was successfully developed as a precursor for the production of C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalysts without the need for additional carbon. The photocatalysts prepared using this method exhibited markedly increased photocatalytic hydrogen generation activity.

When the mass ratio of Ti<sub>3</sub>C<sub>2</sub> to g-C<sub>3</sub>N<sub>4</sub> in the compound was 10% by weight, the composite photocatalyst C-TiO<sub>2</sub> / g-C<sub>3</sub>N<sub>4</sub> showed the highest photocatalytic H<sub>2</sub> production activity of up to 1,409 mol / hour / g, which is approximately 8 and 24 times higher than those of pure g-C<sub>3</sub>N<sub>4</sub> and C-TiO<sub>2</sub>, respectively.

The photocatalytic hydrogen production activity of C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalysts under visible light was greatly enhanced by the formation of an intimate heterojunction between Ti<sub>3</sub>C<sub>2</sub> MXene-derived C-doped TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>, which facilitated effective photogenerated charge transfer and prevented hole and electronic recombination (Xu et al., 2021).

Through the in situ synthesis of TiO<sub>2</sub> nanosheets on Ti<sub>3</sub>C<sub>2</sub> MXene and PtO deposition, this review effectively created an efficient photocatalyst of PtO @ Ti<sub>3</sub>C<sub>2</sub> / TiO<sub>2</sub>. At up to 2.54 mmol g<sup>-1</sup> hr<sup>-1</sup>, the generated PtO @ Ti<sub>3</sub>C<sub>2</sub> / TiO<sub>2</sub> compound exhibited remarkable photocatalytic hydrogen evolution activity.

Jin et al. (Lu et al., 2022) designed a 2D layered V<sub>0.2</sub>Mo<sub>0.8</sub>N<sub>1.2</sub> material for the PEC splitting of water with high H<sub>2</sub> production efficiency. DFT-based calculations confirmed that MXene V<sub>0.2</sub>Mo<sub>0.8</sub>N<sub>1.2</sub> has the potential for high-rate hydrogen production. It is a clean energy source with low-cost materials and excellent electrocatalytic stability. In V<sub>0.2</sub>Mo<sub>0.8</sub>N<sub>1.2</sub>, material electrons move from the V to Mo sites for energy production and suppress the rate of recombination of charge carriers (Ren et al., 2022).

Photogenerated electrons and holes flow in the opposite direction, increasing the separation efficiency and suppressing the unfavorable hydrogen back reaction. This results in higher photogenerated carrier separation and transmission efficiency. This work introduces a novel approach to enhance the photocatalytic efficiency for hydrogen production by simultaneously enhancing charge separation and inhibiting hydrogen backreaction (Li et al., 2023).

Table 1 provides a comprehensive overview of different metal-organic framework (MOF) synthesis methods, highlighting their key characteristics, benefits, limitations, and notable examples for each approach.

Table – 1 : Comprehensive Overview of Different Metal-Organic Framework (MOF)

Synthesis Method	Description	Advantages	Disadvantages	Examples of MOFs
Solvothermal	Reaction occurs in a sealed vessel under heat & pressure	High crystallinity, large pore volume	High energy consumption, long reaction time	MOF-5, MIL-101, UiO-66
Hydrothermal	Uses water as a solvent under high temperature & pressure	Environmentally friendly, good for water-stable MOFs	Limited control over morphology	Fe-MOF, Cu-BTC, ZIF-8
Microwave-Assisted	Uses microwave irradiation for rapid heating	Fast synthesis, uniform particle size	Requires specialized equipment.	HKUST-1, MIL-53
Mechanochemical	Solid-state reaction through grinding/milling	Solvent-free, eco-friendly, and scalable	Poor crystallinity requires post-treatment	ZIF-8, Ni-MOF
Electrochemical	Uses applied voltage to generate MOFs	High purity and precise control over morphology	Limited scalability, requires conductive metal ions.	Fe-BTC, Ni-ZIF
Sonochemical	Uses ultrasound waves for rapid synthesis	Short reaction time, fine control over particle size	Requires high-power ultrasound	MIL-88, MOF-74
Post-Synthetic Modification (PSM)	Functionalizing presynthesized MOFs	Tunable properties enhances stability.	Additional processing steps required	UiO-66-NH <sub>2</sub> , MIL-101-SO <sub>3</sub> H

## Recent Progress and Challenges in MOFs for Electrocatalysis and Energy Storage

Organic “linker” molecules encircle a regular array of positively charged metal ions to form MOFs, which are hybrid organic-inorganic crystalline porous materials (Zhu et al., 2009). The metal ions formed a repeating cage-like structure by joining the arms of the linkers. MOFs have a very large surface area, with an inertial surface area of more than 7,800 m<sup>2</sup> / g. We may demonstrate this, for example, saying that a football field’s worth of surface area would be available in a teaspoon of this substance (approximately 1 g of solid) (Pan et al., 2018). MOFs are distinguished by their diversity, homogeneous pore topologies, atomic-level structural homogeneity, programmable porosity, and flexibility in size, shape, and chemical usefulness. MOFs with intriguing structures and abundant coordination centers have been widely exploited as precursors for synthesizing functional materials because of their large surface areas, ultrahigh porosities, and compositional flexibilities. However, before most pure MOF materials can be used directly as electrocatalysts, some problems must be addressed, such as weak water

stability, low electrical conductivity, and little exposure to active metal centers (Ikreedeegh & Tahir, 2021; Lu et al., 2022; Song et al., 2018).).

In 2021, Lin et al. reported a variety of active materials generated from MOFs. Before being directly used in electrocatalysts and utilized as long-lasting, efficient electrocatalysts for oxygen evolution reaction (OER), these problems must be addressed. These problems include low exposure to active metal centers, poor electrical conductivity, low water stability, and the most pristine MOF materials. Although these MOF-based materials perform extraordinarily well, they still need to improve their electrocatalytic activity to reach OER in alkaline solutions (Wang et al., 2019; Yang et al., 2021).

A useful method for regulating the surface electronic structure of catalysts has been thought to be to incorporate heteroatom ions into the host material. This can improve charge carrier mobility and electrocatalytic kinetics, ultimately increasing the catalytic properties. Recently, the doping of ruthenium (Ru.) of OER catalysts has attracted much interest (Ramish et al., 2022). Ru, the least expensive metal in the platinum group, has a hydrogen binding strength similar to that of Pt (about 65 kcal/mol) and can adsorb intermediates that include hydrogen and oxygen (Ronchi et al., 2019; Wang et al., 2022). One example is the synthesis of Ru-doped NiCoP on nickel foam (Ru-NiCoP/NF) by Mu et al. using the Co zeolitic imidazolate framework (Co ZIF-L).26 Doping of the NiCoP surface of Ru atoms may accelerate electron transfer and increase the number of accessible active sites, which would have an increasing effect on OER processes, based on the relevant calculations of the functional density theory (Wu et al., 2020).).

MOFs are porous crystalline materials composed of both organic and inorganic components in a rigid periodic network structure (Ramanayaka et al., 2019). Their unique structural design and tunability are difficult to access with conventional porous materials such as purely inorganic zeolites. A new class of porous solids, MOFs or porous coordination polymers, has emerged in the last 10 years. These porous materials are distinguished by their extraordinary and unique properties, including their large known pore volumes and surface areas (Li et al., 2023).

Metal–organic frameworks are grouped based on attributes such as comparable symmetry and discovery sites. The most well-known MOF groups include LIC, MIL, HKUST, UiO, IRMOF, and LIC. Temporal branching occurred in these cohorts. The MOF structure HKUST-1 is well known (Lu et al., 2022; Pan et al., 2018; Saha et al., 1999).

Cu-BTC (copper benzene-1,3,5-tricarboxylate) is another common name for it. MOF structures are known for their high surface areas, pore volumes, tenabilities, and adsorption capacities; this material is an example of these properties (Ramish et al., 2022; Ronchi et al., 2019; Wang et al., 2022; Yang et al., 2021). Nevertheless, various features, such as mechanical, optical, and magnetic properties, can be incorporated into MOFs. Numerous synthesis and construction methods can be used to obtain these properties. Metal–organic frameworks (MOFs) have been widely used as precursors or templates to prepare metal oxides / metal sulfides, bimetal oxides / metal sulfides, porous carbons and corresponding nanocomposites for high-performance electrode materials in supercapacitors. The morphologies of the MOF-derived nanostructures were determined at the nanometer scale. Enhancing our understanding of the connection between morphology and energy storage performance is crucial (10, 18, 24).

MOF-derived porous nanostructured electrodes exhibit exceptional electrochemical stability, high surface area, and strong electrical conductivity (Gurusamy et al., 2021; Li et al., 2012; Li et al., 2023).

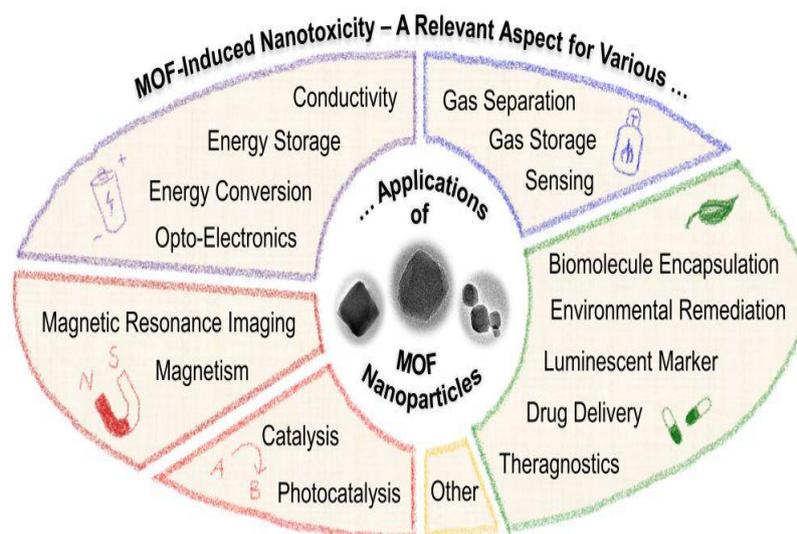
The complex production procedure and unstable structure in highly corrosive electrolytes continue to plague the products developed from MOFs. Developing electrode materials for next-generation asymmetrical supercapacitors using porous nanocomposites produced from MOFs has recently received considerable interest (Li et al., 2012).

## APPLICATIONS

MOFs have many different applications. Composite MOFs have other possible applications in addition to pure MOF structures. Composites using MOFs are made of various materials, including polymers, active species, metal nanoparticles, quantum dots, carbon nanotubes, graphene, and enzymes. The large surface area of MOF structures, porous structure, thermal conductivity, electrical conductivity, and surface activity are all useful in real world applications (Huang et al., 2020).

Carbonaceous materials are gaining considerable attention because of their wide use in medication administration, imaging, batteries, fuel cells, adsorption, catalysis, and supercapacitors. In addition, some sensors also have important applications for carbonaceous materials because they are closely related to human health (Samimi et al., 2022).

MOFs have been frequently used as photocatalysts for the hydrogen evolution reaction using sacrificial agents with UV–vis or visible-light irradiation. MOFs have many uses, including as catalysts, sensors, drug delivery agents, and storage and separation systems. Nontoxic, drug-carrying, nontoxic nano-MOFs with customized surfaces and cores can be nanodrug carriers for anti-HIV and anticancer medications. Compared with MOFs bearing conventional organic linkers, MOFs containing biomolecules as organic linkers are still at the nursery stage. Lithium-ion batteries have excellent qualities, including high energy density, low weight, and minimal pollution, they are widely used in robotics, laptop computers, mobile phones, and other portable electronic equipment (Chen et al., 2018; Lv et al., 2017; Ren et al., 2022; Xu et al., 2021; Zhang et al., 2018).).



**Figure 2.** Application of metal–organic frameworks (MOFs) in various fields (Ettliger et al., 2022)

Numerous applications have been developed for the adaptability of MXene. On the contrary, chemical stability, ion intercalation, and adjustable band gaps indicate catalysis and energy storage applications, such as fuel cells, hydrogen storage, and lithium-ion batteries. Composites are attractive for these materials due to their high Young's modulus, good electrical conductivity, and surface chemistry alteration. Promising outcomes have been obtained in many fields, including biological and environmental, as well as opto-spintronics and flexible/wearable electronic devices (Li et al., 2023; Liu et al., 2013; Mikolasek et al., 2019; Rahman & Haseen, 2015; Sharma et al., 2021).

## CONCLUSIONS

In summary, ongoing research into the doping and heterostructuring of MOFs holds great promise for creating next-generation materials that address critical issues in energy, the environment, and health. As we continue to unlock the potential of these versatile frameworks, we pave the way for transformative advances across multiple scientific domains. Overall, the strategic manipulation of doping and heterostructuring in MOFs presents exciting opportunities for advancing materials science and engineering. Continued research in this field is essential to unlock the full potential of MOFs in energy storage, environmental remediation, drug delivery, and beyond. Future studies should focus on understanding the underlying mechanisms that govern the behavior of doped and heterostructured MOFs to facilitate the design of next-generation materials tailored for specific applications. Finally, interdisciplinary collaboration will be vital in advancing this field. By integrating insights from chemistry, materials science, engineering, and environmental science, researchers can develop innovative solutions that take advantage of the unique properties of MOFs for real-world challenges.

## FUTURE SCOPE

In summary, the future of metal–organic frameworks is bright, with opportunities for innovation across various fields. As research continues to evolve, MOFs are likely to play a pivotal role in addressing some of the most pressing challenges in energy, environment, healthcare, and beyond. Future research should focus on optimizing the synthesis and functionalization of MOFs to enhance their performance and expand their applicability in emerging fields such as renewable energy and advanced environmental technologies. The future of MOFs is promising, with several key areas poised for significant development and innovation.

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