



# Synthesis of Metal-Organic Frameworks (MOFs) and Their Biological, Catalytic and Energetic Applications: A Mini Review

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## Abstract

Metal–organic frameworks (MOFs) have emerged as a new category of porous hybrid materials that have fascinating structures and diverse applications. These are also called porous coordination polymers. It has become increasingly more important to synthesize new MOFs, to reveal their structure–property relationships for the purpose of rationally designing novel frameworks with expected properties. At present, much research has been conducted to develop and rationalize the design and synthesis of MOFs. Currently, MOFs or/and MOF-based materials have been studied to look at their applications such as gas storage, gas separation, heterogeneous catalysis, energy production, sensing, drug delivery, electronics, bioreactor, optics, etc. This review depicts advances in both synthetic methods of MOFs and their structure analysis. Additionally, several applications of MOFs for different purposes such as medical and biological applications, removal of absorption and separation of toxic substances from gas and liquid, catalysts, storage of clean energies and environmental applications has been accounted for.

**Keywords:** Metal–organic frameworks (MOFs); Synthetic methods; Drug delivery; Toxic Pollution; Catalysis; Electrochemical charge storage.

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## 1. Introduction

Owing to considerable porosity, inherent surface area and versatility in properties of the materials involved in the formation of Metal-Organic Frameworks (MOFs),<sup>[1-9]</sup> attracted the attention of material scientists and researchers. Because of the high demand of materials in human daily life, the modern technologies are extremely welcome. Constructed with metal clusters connected by organic ligands, MOFs are classified as porous inorganic-organic hybrid constituents. The structures of MOFs have both organic linkers called organic SBU (Secondary Building Unit) which act as ‘strut’, and metal centers called inorganic SBU which act as ‘joints’ in MOFs structures. There are total three important parameters of MOFs,

*i.e.*, topology of framework, inorganic metal centers, and organic ligands. Large pore size of zeolites is obtained by addition of expanded zeolite topology. The pore diameter and porosity depends on the length of organic ligands. Large pore volume and specific surface area of MOFs are recognized as an excellent platform for immobilizing molecular catalysts on conductive substrates, leading to increased selectivity. Typically, MOF emergence is recognized as an approach to imitate inorganic constituents (e.g., zeolites). Zeolites do not allow a close control of the functionalization, shape, and size of pores, giving added advantage to MOFs.<sup>[10,11]</sup> Those materials/compounds that can be simply made, have consistency, and are easily applied are recognized as the ideal/best constituents.

This review depicts advances in synthetic methods of MOFs and structure analysis. Improving the synthetic conditions to scale up the synthetic process for commercial application is a major challenge for this study. Moreover, several applications of MOFs such as medical and biological applications, the removal of absorption and separation of toxic substances from gas and liquid, catalysts, storage of clean energies and environmental applications is also major area of research.

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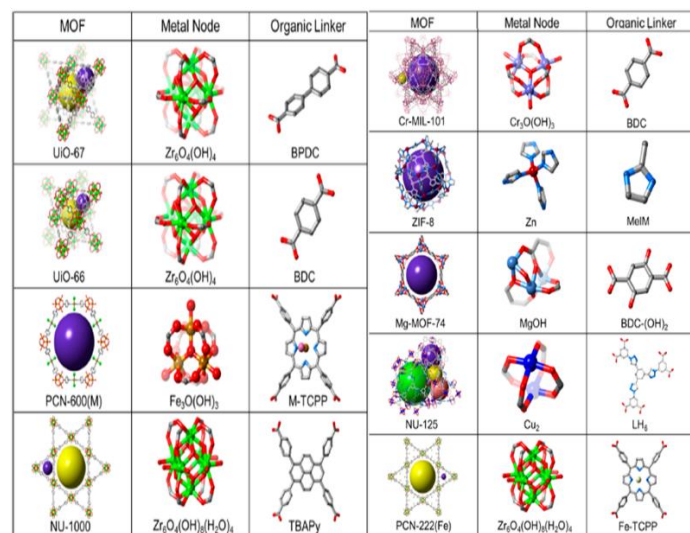
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## 2. Categories and name of metal organic frameworks

MOFs are generally classified by ordinal numbers (Fig. 1). The designed framework MOF structures with desired properties are grouped into a family of MOFs with the same symmetry IRMOF-1–IRMOF-16 (isoreticular metal-organic frameworks),<sup>[12,13]</sup> Russian<sup>[14,15]</sup> and Chinese<sup>[16,17]</sup> researchers used the term ‘metalorganic coordination polymers’ with specified composition. Some MOFs are named based on their discovery place such as UiO, MIL, HKUST, LIC, etc. There is another large family of MOFs, abbreviated as ZIF (zeolite imidazolate framework) having zeolite topology. Metal ions such as Fe, Co, Cu, Zn, etc. are surrounded by tetrahedra made of nitrogen atoms and are connected through imidazole rings, which can have different functionalities. The name of MOFs can be designed using a number and sometimes it varies with different research groups' such as CPL, F-MOF-1, and MOP-1, *etc.*

## 3. Synthesis of metal organic frameworks

The porous compound MOFs are most recognized due to their specific functional and structural properties. These frameworks are synthesized by using organic linkers and metal ion clusters and metal ions. The resulting structures and features of the MOFs synthesized, depends of synthetic methods and parameters involved such as temperature, reaction time, pressure, pH, and solvent., By considering those parameters several synthetic methods are involved, including slow diffusion,<sup>[18-21]</sup> hydrothermal (solvothermal),<sup>[22-24]</sup> electrochemical,<sup>[25,26]</sup> mechanochemical,<sup>[27-29]</sup> microwave assisted<sup>[30-33]</sup> heating and ultrasound.<sup>[34-36]</sup>



**Fig. 1** Representations of MOF Structures and the Corresponding Node and Linker Constituents (Zr: green; Fe: yellow; Cr: light purple; Zn: dark red; Mg: blue; Cu: royal blue; C: grey; O: red; N: light blue; Cl: pink, reproduced with the permission from [37].

### 3.1 Diffusion method

The standard diffusion method is liquid liquid diffusion, where solvents form two layers due to difference of densities, one

being the precipitant solvent and the other one encompassing the product. In this method, crystal growth happens after gradual diffusion of the precipitant solvent into the separate layer; or the reactants in two vials with various sizes are gradually diffused by diving them with physical barriers. Moreover, in some cases to reduce the pace of diffusion and to prevent the bulk material's precipitation, gels are applied as crystallization and diffusion media. Rather than non- or polycrystalline products, single crystals of poor soluble materials are appropriate for X-ray diffraction analysis, these crystals are expected from the diffusion technique.<sup>[38-40]</sup>

### 3.2 Hydro (solvo) thermal method

One of most used method is hydro (solvo) thermal technique, where MOFs form by self-assembly of soluble precursors. In this process inside a sealed space (autoclave), autogenous pressure is created, and generally the operational temperature ranges from 80to 260 °C, which can be cooled with a programmed speed rate when the reaction ends. In some cases, long reaction periods are required (many days to many weeks).<sup>[41]</sup>

### 3.3 Microwave method

For small scale synthesis of small metal and oxide particles, microwave method is highly appreciated. In this procedure, temperature of the solution might be raised for an hour or more to create nanosized crystals. Generally this method is not applied regularly to produce crystalline MOFs. More importantly, by this method, syntheses of materials occur at high speed and shape and size of the resulting particles can be controlled. The microwave technique typically cannot produce crystals for single X-ray analysis. However, the cycle of synthesis for several operations can be greatly shortened and control the crystals' shape and size.<sup>[42]</sup> Only under suitable circumstances, such as the method of solvent evaporation, the saturated solutions and improvement of solubility with temperature results in formation of crystals during the cooling phase.<sup>[43]</sup>

### 3.4 Electrochemical method

Large scale synthesis of MOF powders are manufactured by applying electrochemical technique. The advantage of this methods are avoiding anions such as nitrates from metal salts, lower temperatures of reaction and extremely quick synthesis. The drawback is in the bulk crystallization step, due to production of the metal ions *in situ* near the support surface, which decreases unfavorable accumulation of crystals during the synthesis of membrane. Moreover, milder temperatures are useful to reduce thermally-induced cracking in cooling process (as compared to solvothermal synthesis). This cracking is due to inappropriate thermal growth coefficients between the different support structure and the MOF. In this respect, MOF shows a negative thermal expansion coefficient.<sup>[44,45]</sup> So, electrochemical synthesis methods are useful for fine tuning due to the simple adjustment of the

voltage or imposing particular signals than solvothermal techniques.

### 3.5 Mechanochemical method

Some chemical reactions and also several physical phenomena can be conducted by the mechanical chemical transformation, which reveals mechanical breakage of intramolecular bonds.<sup>[46,47]</sup> Now a days, mechanochemistry is applied in synthetic chemistry and also in multicomponent (binary and higher) reactions to establish co-crystals, inorganic solid-state chemistry, polymer science, and many others. For the syntheses of MOFs too, this method is highly adopted for several reasons. First, environmental issues; the reactions can be performed without organic solvents reactions at ambient temperature. Second, quantitative yields of products can be obtained in a short durations of reaction (10-16 min).<sup>[48,49]</sup> Third, as side product water is produced in some case of metal salts. Besides this, the reactions of low solubility of metal oxides face solubility issues. Metal acetates or carbonates can produce well-crystalline compounds with byproduct acetic acid and carbon dioxide existing in pores; these can easily be extracted through thermal activation.<sup>[50]</sup> Mechanochemical method with small amounts of solvents is known as liquid-assisted grinding (LAG). The solvents may accelerate the mechanochemical reactions possibly through intensification in the reactants' mobility at the molecular level. Recently, ion- and liquid assisted grinding (ILAG) showed high efficient technique for selective production of pillared-layered MOFs, depict that ions and solvents have a structure directing influence.<sup>[51]</sup>

### 3.6 Sonochemistry method

Generally sonochemistry deals with high-energy ultrasound (cyclic mechanical vibration) exposure to a reaction mixture with frequency range 10 MHz - 20 kHz. By this strong vibrations, activation is created on the solid surface in the form of microjets that are able to corrode, activate, and clean the surface with the dispersion of smaller particles agglomerations. In a homogeneous liquid with strong shear forces, reactions can occur in the cavity at the interface or in the bulk media. The sonochemistry is widely applied to organic and nanomaterials' syntheses. In MOF synthesis, the sonochemical method is helpful to design a quick method at ambient temperature, environmentally friendly, energy-efficient, and easy to use. In the future it can be potentially useful for scaling up synthesis of MOF within quick reactions time.<sup>[52]</sup>

## 4. Application of metal organic frameworks

### 4.1 Adsorption in aqua solutions

Metal-organic frameworks (MOFs) are class of compounds consisting of metal ions or clusters coordinated to organic ligands to form one-, two-, or three-dimensional structures, are novel enhanced hybrid crystal substance. In addition, various soluble, insoluble and inorganic, organic and biological compounds can be eliminated from different water systems by

this method.<sup>[53,54]</sup> MOFs are of high adsorption capacity, large specific surface area, structurally flexible, porous, customizable, and photometric, which make them useful in multiple areas including chemical recognition and separation.<sup>[55,56]</sup>

### 4.1.1 Biological compounds

Pan *et al.* synthesized a magnetic metal-organic framework composite and it worked as an adsorbent by using self-assembly approach. It showed excellent capability towards adsorption of glufosinate, bialaphos, and glyphosate, as well as their major metabolites (3-methylphosphinopropionic acid and aminomethylphosphonic acid). Combining with magnetic solid-phase withdrawal technique using UHPLC-HRMS, five target mixtures were determined in environmental waters with recoveries in 86.2-104.6% range with relative standard deviations below 10%. The linearity range was 1.0-100.0 mg/L for five target analytes, respectively with recognition limit range of 0.01-0.03 mg/L.<sup>[57]</sup>

MG@MIL-100-B nanoparticles were prepared using MLFC approach by inserting functionalized mesopores into MOFs by He *et al.* Using this composite materials norepinephrine, epinephrine, and dopamine from rat plasma were removed. The detection limits (S/N = 3) for epinephrine and dopamine's were as low as 0.005 ng mL<sup>-1</sup>, whereas for norepinephrine was estimated at 0.02 ng mL<sup>-1</sup>. The inter- and intra-day accuracy were 5.70-11.44% (N = 6) and 2.84-6.63% (N = 6), respectively. Now this method is applied for sample pre-treatment in clinical therapy and study.<sup>[58]</sup>

One magnetic framework composites with core-shell structure (Fe<sub>3</sub>O<sub>4</sub>@TMU-21) was prepared by Yamini *et al.* It was used as an efficient adsorbent to remove magnetic solid-phase (MSPE) of trace pyrethroid residues from samples of fruit juice. Optimal linearity was achieved in the range of 0.5-250 mg L<sup>-1</sup> (R<sup>2</sup> = 0.99), where the range of 0.1-0.05 mg L<sup>-1</sup> was the limit of recognition (based on S/N = 3). The range of 3.1-4.4% was reported for accuracy of the technique articulated as a relative standard deviation (RSD) for removing and determining the 100 mg L<sup>-1</sup> pyrethroid residues in the samples solution.<sup>[59]</sup>

### 4.1.2 Antibiotics

MOFs are also applicable to extract antibiotics. A combination of two conventional antibiotics, namely oxytetracycline hydrochloride and tetracycline were extracted by Li *et al.* using Zeolite Imidazole Framework-8 (ZIF-8). Interestingly ZIF-8 was capable of simultaneously removing 82.5% of oxytetracycline hydrochloride and 90.7% of tetracycline with the rates of 312.5 mg g<sup>-1</sup> and 303.0 mg g<sup>-1</sup> as the maximum adsorption capacities for the same, respectively. The antibiotics' adsorption is pseudo-second-order kinetics and nicely fit the Langmuir adsorption model with values R<sup>2</sup> of 0.963 and 0.981, for tetracycline and oxytetracycline hydrochloride at 303 K, respectively.<sup>[60]</sup>

Another excellent result on ciprofloxacin antibiotic

remediation extraction using mesoporous carbon-embedded zero-valent Fe sites from the metal organic framework MIL-53 (Fe) was reported by Tran *et al.* The embedded material showed high chemical stability and reusability up to 5 cycles. The adsorption capacity was 90.9 mg/g in leaching test, where mesoporous carbon derived from MIL-53 could be an efficient adsorbent for aquatic antibiotic treatment.<sup>[61]</sup>

#### 4.1.3 Drug delivery systems

In biomedical fields, metal-organic frameworks find applications as delivery vehicles for therapeutic agents and bioactive gases. Recently, lots of efforts have been dedicated to produce novel techniques for innovative drug delivery systems with controlled release of drug.<sup>[62,63]</sup>

In this application, Javanbakht *et al.* designed composed carboxymethylcellulose (CMC) biopolymer graphene oxide (GO) with MOF-5 (Zinc-based MOF). They reported the drug loading and releasing tests by doxorubicin's effective loading on and leasing from of the CMC/MOF-5/GO nanocomposite. For this purpose they used K562 cells and distinguished cytotoxicity by DOX@CMC/MOF-5/GO by the MTT assay. CMC/MOF-5/GO show these features due to its water solubility and positively charge characteristics. So it proved to be a great choice for targeted delivery and managed release of drug for cancer treatment.<sup>[64]</sup>

For meticulous drug release, an *insitu* approach was introduced by Azizi vahed *et al.* They synthesized a composite material with imidazole Zn-based metal-organic framework (ZIF-8 MOF) with sodium alginate and coated. It was prepared by green one-pot solvent free mechanochemical ballmilling of the MOF components and sodium alginate powder, (ZIF-8@alginate NPs). Metformin (an oral anti hyperglycemic agent to cure type II diabetes) was trapped inside the alginate-coated ZIF-8 pores. Due to the presence of consistent porosity and zinc ions, efficiency and controlled release of metformin can be achieved.<sup>[65]</sup>

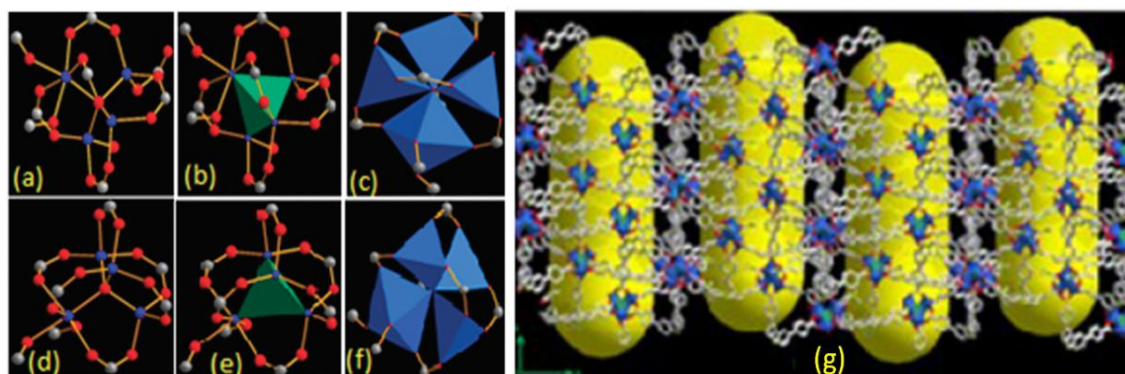
Sun *et al.* fabricated a ketone functionalized 1D, robust

microporous Gd(III)-MOF by applying one-pot solvothermal reaction of  $[\text{Gd}(\text{NO}_3)_3](\text{H}_2\text{O})_6$  and  $\text{H}_3\text{BCB}$  ligand,. Around 36.4 wt% of the the anticancer drug 5-Fu could be incorporated into the activated functionalized MOF; the drug delivery test showed very promising results, leading to release of drug in an extremely progressive and controlled manner, in phosphate buffer saline at two various pH values. In the present study, MTT assay was used to explain the cytotoxicity of 5-Fu@1a towards human liver cancer cells HCC, which shows evident anticancer activity.<sup>[66]</sup>

A robust highly water stable (up to 3 weeks) microporous MOF (1),  $[\text{Zn}_8(\text{O})_2(\text{CDDDB})_6(\text{DMF})_4(\text{H}_2\text{O})]$  {where CDDDB= 4,4'-(9-H carbazole-3,6-diyl)dibenzoic acid}, was synthesized based on an open N–H site (Fig. 2).. Interestingly, it exhibited an outstanding loading capacity (around 53.3 wt%) and satisfactory release capability (64.9% and 81.9%) for 5-fluorouracil, constituting a negligible cytotoxicity effect.<sup>[67]</sup>

Under solvothermal conditions, Guo *et al.* synthesized a porous Dy(III)-based MOF,  $[\text{Dy}(\text{HABA})(\text{ABA})](\text{DMA})_4$  (1, H2ABA = 4,4'-azanediylidibenzoic acid, DMA = N,N-dimethylacetamide) with open N donor sites, fabricated by applying a bent polycarboxylic acid linker. The activated 1 was used for loading of anticancer drug 5-Fu within functionalized 1D channels and proper window size. It showed pH-dependent drug-release behavior and high drug loading. Additionally, the MTT assay confirmed the anticancer activity of this drug/MOF composite against human osteosarcoma cell lines MG63.<sup>[68]</sup>

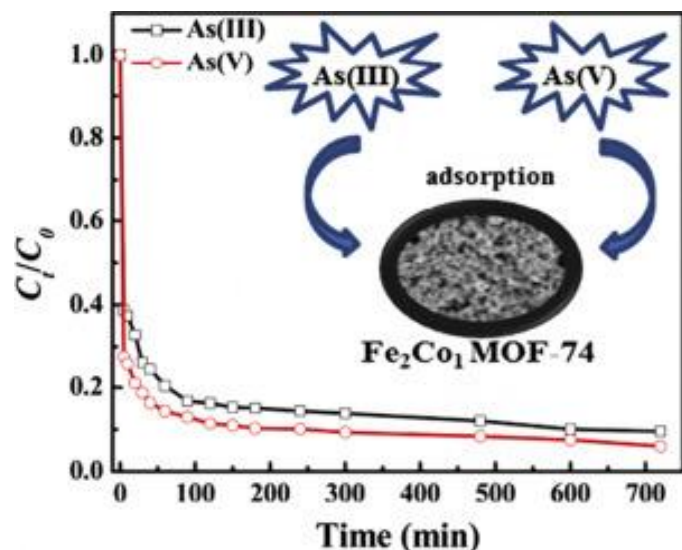
Javanbakht *et al.* loaded ibuprofen into the 2D tunnels and empty face centered cubic cubes of Cu-MOF porous via immersion in the drug solution. They present the pH-sensitive biopolymeric gelatin microsphere protected Cu-Based metalorganic framework/ibuprofen nanohybrid (Cu-MOF/IBU). Additionally, Cu-MOF/IBU microsphere (Cu-MOF/IBU@GM) was encapsulated by gelatin. The MTT assay confirmed low toxicity of the Cu-MOF/IBU@GM against Caco-2 cells.<sup>[69]</sup>



**Fig. 2** Construction of the framework of 1. (a) The  $\text{Zn}_4(\text{O})(\text{CO}_2)_6(\text{DMF})_2(\text{O})$  and (d) the  $\text{Zn}_4(\text{O})(\text{CO}_2)_6(\text{DMF})_2$  cluster as a ball and stick model (Zn, blue; O, red; C, grey). (b and e) The same with the  $\text{Zn}_4(\text{O})$  tetrahedron indicated in green. (c and f) The same but now with the  $\text{ZnO}_4$  tetrahedra indicated in blue. (g) Side view of 1D channel through a-axis having size  $28.1 \text{ \AA} \times 23.17 \text{ \AA}$ , indicated by a yellow cylinder, formed by double interpenetrating 2-fold 2D network, reproduced with the permission from [67].

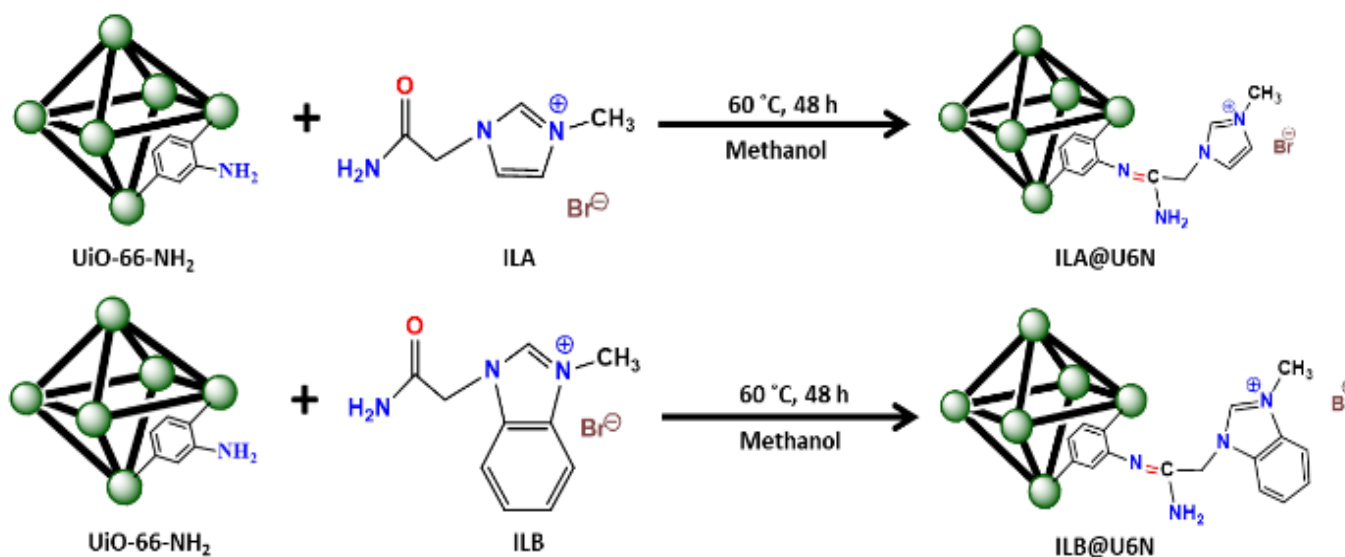
#### 4.1.4 Toxic pollution

Due to toxic materials, pollution has been increasing progressively. MOFs can play a major role to curb this. In this regard, a nanostructured Fe-Co based metal organic framework (MOF-74) adsorbent was synthesized by Sun *et al.* to extract arsenic from water (Fig. 3). The optimal adsorption molar ratio of Fe/Co on the adsorbent was 2:1, indicating  $\text{Fe}_2\text{Co}_1$  composition with MOF-74 nanoparticle diameter 60-80 nm of through different methods with surface area 147.82  $\text{m}^2/\text{g}$ . The maximum adsorption capacities toward As (V) and As (III) are 292.29 and 266.52  $\text{mg}/\text{g}$ , respectively.<sup>[70]</sup>



**Fig. 3** The adsorption capacities of  $\text{Fe}_2\text{Co}_1\text{MOF-74}$  toward As (V) and As (III), reproduced with the permission from [70].

Yin *et al.* produced hierarchical porous UIO-66 (HP-UIO-66) materials which showed an excellent adsorption behavior



**Fig. 4** Synthesis of ILA@U6N and ILB@U6N by the post impregnation method, reproduced with the permission from [81].

of uranium. Ideal values for adsorption were observed in alkaline conditions and the process was pseudo second-order rate equation and based on Langmuir isotherm model. The maximum value of the saturated adsorption capacity is 1217  $\text{mg}/\text{g}$ .<sup>[71]</sup>

Benzothiophene is a toxic material present in liquid fuel. To remove this, Ullah *et al.* prepared an adsorbent by modification of a highly porous MOF, a bicomponent zirconium (IV) benzene-tricarboxylate Zr (BTC) postsynthetically with dodeca-tungstophosphoric acid (HPW/Zr) (Fig. 4). The maximum predicted adsorption capacities were to be 238  $\text{mg}/\text{g}$  for Zr(BTC) and 290  $\text{mg}\cdot\text{g}^{-1}$  for HPW (1.5)/Zr(BTC). The DFT calculations were predicted a desirable adsorption of benzothiophene with estimated binding energies of  $-47.3 \text{ kJ}\cdot\text{mol}^{-1}$  for Zr(BTC) and  $-140.2 \text{ kJ}\cdot\text{mol}^{-1}$  and HPW (1.5)/Zr(BTC).<sup>[72]</sup>

To elimination of malachite green (MG) and methyl red (MR) from wastewaters Hamedi *et al.* proposed an adsorbent by using an eco-friendly and effective binder tinny film of 3, 4-dihydroxy-L phenylalanine (L-Dopa), MIL-101(Fe) and  $\text{Fe}_3\text{O}_4$  particles, a magnetic MOF composite material MIL-101(Fe)@PDopa@ $\text{Fe}_3\text{O}_4$ . The perfect capacity of adsorption for MG was 833.33 and that for MR was 1250  $\text{mg}/\text{g}$ , respectively. This adsorbent can efficient to eliminate industrial colors from real textile wastewater.<sup>[73]</sup>

Jarrah *et al.* synthesized a composite nanohybrid of Dowson-type polyoxometalate with MIL-101(Cr) abbreviated as P2W18@MIL-101(Cr) having surface area of 1167.4  $\text{m}^2/\text{g}$ . Interestingly P2W18@MIL-101(Cr) eliminated methyl orange (MO), Rhodamine B (RhB), and methylene blue (MB) organic dyes from aqueous solutions, indicating towards the compound's usefulness to treat toxic organic pollutants in the colored wastewater.<sup>[74]</sup>

## 4.2 Catalysts

A MOF can enhance its stability and catalytic activity by incorporating the catalytically active but unstable nanoparticles within its porous cavity/channel. Oxygen reduction reaction (ORR) is one important factor in proton exchange membrane fuel cells. To accelerate the reaction in the inactive kinetics of ORR, high loading of Pt catalysts is required, which enhances the cost and encumber the large-scale commercialization of fuel cells. MOFs can play the role of templates and precursors to prepare hierarchical porous structured metal nanoparticles/carbon composites through pyrolysis in inert atmosphere.<sup>[75,76]</sup> For shape-selective and bifunctional catalysis, the compositions of MOFs and pore structure can control the performance of catalyst, even though intensive research is needed to identify catalytic sites, quantify mechanism in MOFs and determine catalytic reaction rates. Since, it is very difficult to know the heterogeneity of MOFs and the defect by X-ray diffraction, optimization of synthesis is important. Moreover, the node-linker bonds in MOF can break during catalysis which is another challenge to the stability and regeneration of MOFs.

MIL-101-NH<sub>2</sub> supported well-dispersed and ultrafine CrPd NPs were designed by Gao *et al.* by wet-chemical approach. The synthesized Cr<sub>0.4</sub>Pd<sub>0.6</sub>/MIL-101-NH<sub>2</sub> catalyst showed effective catalytic activity for creation of hydrogen from aqueous solutions of formic acid with primary turn over of approximately 2009 mol H<sub>2</sub> mol/Pd/h at 323 K.<sup>[77]</sup>

Yang *et al.* synthesized NaOH-assisted metal-organic framework (MOF) and encapsulated  $\gamma$ -Fe nanoparticles into the porous N-doped carbon matrix. There is a major involvement of Fe atoms doped in the creation of constant g-Fe. Doping of Fe atoms in the MOF structure showed good catalytic activity with the four-electron transfer pathway for ORR in alkaline solution.<sup>[78]</sup>

One highly thermal stable (~550 °C) MOF composite of MIL-53(Al) (Al (OH)-[O<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>]) was designed by Sun *et al.*, used for Fischer-Tropsch synthesis. By immobilizing Co NPs on the MIL-53(Al) support, it showed efficient activity of Fischer-Tropsch synthesis.<sup>[79]</sup>

Wu *et al.* synthesized a series of heterogenized ruthenium MOFs, Ru<sub>x</sub>-NHC-MOF (x = 1, 2, 3; NHC = N-heterocyclic carbene) by immobilization of ruthenium complexes RuCl<sub>3</sub>, [RuCp\*Cl<sub>2</sub>]<sub>2</sub> (Cp\* = pentamethylcyclopentadienyl) and [Ru(C<sub>6</sub>Me<sub>6</sub>)Cl<sub>2</sub>]<sub>2</sub> (C<sub>6</sub>Me<sub>6</sub> = hexamethylbenzene) into azolium based MOF via post-synthetic metalation. The catalytic hydrogenation of CO<sub>2</sub> to formic acid was carried out after retrieving the heterogenized catalysts. High electron-donating capability of C<sub>6</sub>Me<sub>6</sub> of [Ru(C<sub>6</sub>Me<sub>6</sub>)Cl<sub>2</sub>]<sub>2</sub> complex revealed the highest activity for Ru<sub>3</sub>-NHC-MOF catalyst, which was desirable for hydrogenation of CO<sub>2</sub> to formic acid. With K<sub>2</sub>CO<sub>3</sub> additive, it also showed a high turnover number (TON) value up to 3803 at 120 °C under 8 MPa pressure (H<sub>2</sub>/CO<sub>2</sub> = 1) for two hours in N,N-Dimethylformamide solvent with negligible loss of catalytic activity. Additionally, the heterogenized Ru<sub>3</sub>-NHC-MOF catalyst was efficiently

recovered by filtration.<sup>[80]</sup>

Kurisingal *et al.* prepared Zr-based UiO-66-NH<sub>2</sub> with two IL-binded heterogeneous catalysts by a post-impregnation technique. Fig. 4 shows the incorporation of the ILs into MOFs following the creation of MOFs. The coupling of an epoxides and CO<sub>2</sub> received the synthesized heterogeneous catalysts. The introduction of IL units into the UiO-66-NH<sub>2</sub> framework resulted in ILB@U6N and ILA@U6N by introducing the methylbenzimidazolium (ILB) and methylimidazolium (ILA), respectively. The porous structure and high surface area of UiO-66-NH<sub>2</sub> enhanced the efficiency of the catalyst and availability of the ILs.<sup>[81]</sup>

By Post Synthetic Method (PSM) approach a new shape-selective catalyst was created by immobilization of the ionic liquid (IL) into metal-organic framework MIL-101-NH<sub>2</sub>, by Chong *et al.*. The catalytically active groups BmimOAc were grafted onto the amino groups of MIL-101-NH<sub>2</sub> via acylamino groups. Shape-selective catalytic features are confined to microenvironment of IL (OAc-)-MIL-101-NH<sub>2</sub> catalyst for the diversity of substrates. Synthesis of 3-aryl-2-oxazolidinones was proposed, to exploit its properties of wide range of substrate, simple recovery, and recyclability of the catalyst for a minimum of six times negligible loss of activity.<sup>[82]</sup>

### 4.2.1 Electrochemical charge storage

To reduce the non-renewable resources, ability of electrochemical energy storage systems can be improved and applied to the intermittent energy from green sources. With increasing human population, demand of energy also increases. This can be optimized by increasing the accessible renewable energy demand with proper procedures and appropriate storing for better future.

In this regards, some novel applications of MOFs or MOF related materials as electrochemical capacitors, and electrocatalytic generation of fuels cell and electrode materials for rechargeable batteries. The rechargeable and long durable Zn-Ag<sub>2</sub>O battery having binder-free electrodes was created by Li *et al.* with a considerable energy density of 14.4 mWh/cm<sup>2</sup>, a high capacity of 1.03 mAh/cm<sup>2</sup>. However, the main drawbacks are, its weak cyclic performance and energy density, low loading of active substances and Ag ion migration. This was overcome by application of Ag<sub>2</sub>O on MOF derived N-doped carbonnanosheet arrays (NC) with a poly (3, 4-ethylenedioxythiophenepoly (styrenesulfonate)) (PEDOT:PSS) buffer layer as cathode and resulted quasisolid-state fiber-shaped battery.<sup>[83]</sup>

Nanoflowers of layered double hydroxide (NiCo-LDH) was composited with conductive two-dimensional metal-organic framework (Ni-CAT) nanocones by Li *et al.* The composite MOF structure showed specific capacitance of 882 F g<sup>-1</sup> at a current density of 1 A/g, high energy density of 23.5 Wh/kg at power density of 394.6 W/kg and long-term cycling stability up to 82% after 10,000 cycles.<sup>[84]</sup>

Bunzen *et al.* prepared one proton conducting iron (II)-MOF [Fe(C<sub>6</sub>N<sub>6</sub>O<sub>2</sub>)(H<sub>2</sub>O)<sub>4</sub>] 5H<sub>2</sub>O of an unusual structure

where iron (II) cations coordinated with four axially water molecules and forms chains of alternating bistriazolate-p-benzoquinone anions. The 3D grid-type network has channel pores occupied by water molecules and the chains gathered between the aromatic units held by p-p stacking. The proton conductivity is  $3.3 \times 10^{-3}$  S/cm at 94% relative humidity and temperature of 22 °C, which can be used as membrane materials in proton-exchange membrane fuel cells.<sup>[85]</sup>

## 5. Conclusions

Nowadays, in material chemistry, different types of materials are incorporated. Among them, MOFs are considered as a new and emerging member of porous materials. It is acceptable that due to the presence of big pore and large surface area, MOFs will be an important future of porous compounds having extraordinary advantages in comparison with other traditional porous materials. So both the application and the manufacturing of the techniques of MOFs have to be developed. Among several methods, mechano, sono, electrochemical and microwave-assisted syntheses are being developed as synthetic tools. Usually these methods are conducted under milder reaction conditions, which lead to the production of compounds with various features and particles sizes. Specifically, it can be considered that these techniques can be used for the reproduction of popular materials. So that MOFs can be prepared in simple, easy, green and low-cost ways which fulfill large scale preparation of MOFs. Moreover, the use of MOFs in biological, energy based, and its catalytic applications are discussed here. This review mainly depicts the challenges of continual expansion interest and the bright future of MOF chemistry.

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## Supporting information

Not applicable

## Conflict of interest

There are no conflicts to declare.

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