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Review Article

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Metal-organic-frameworks (MOFs) advanced synthetic strategies and applications, including light emitting diodes, solar cells and photodetectors

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Abstract: Several synthetic approaches, such as solvothermal, microwave-assisted, electrochemical, and mechanochemical techniques, are used in the creation of metal-organic frameworks (MOFs). The resulting MOFs can be tailored for particular purposes by utilizing the distinct benefits that each of these approaches offers in terms of managing their size, shape, and functional qualities. The most recent developments in MOF synthesis are examined in this study along with how they are being used in optoelectronic devices such as photodiodes, solar cells, and light-emitting diodes (LEDs). MOFs are potential candidates for these applications because of their special qualities, which include their capacity to host light-emitting guest molecules, promote charge transport, and improve light absorption. MOFs effectively house luminescent centers in LEDs, improving brightness and color purity. MOFs improve charge separation and light collecting efficiency in solar cells. The customizable band gaps of MOFs, which may be designed to maximize their performance in photodetection, are advantageous to photodiodes. Advances in MOFs could revolutionize future optoelectronics. Finally, MOFs are based on the ongoing development of advanced synthetic methods that allow for the fabrication of LEDs, solar cells and photodetectors at higher levels of technological innovation and application. Additionally, MOFs in photodetectors, are thought to be active material and their special capacity to interact at various wavelengths may pave the way for more sensitive and adaptable application-specific sensors in a range of areas, including high-speed communication technologies and environmental monitoring.

Keywords: MOFs; nanoporous; light emitting diodes; visible light communication; white light emitting diodes; solar cells

1 Introduction

Metal-organic frameworks, or MOFs, have garnered a lot of interest in the last 20 years due to their remarkable versatility. These frameworks are composed of inorganic nodes and organic linkers.[1–3] MOFs have distinct morphological properties, including as large surface areas, pore diameters that may be adjusted, and organized crystalline structures. These characteristics offer a great deal of design flexibility for creating unique setups. These features increase the versatility of MOFs by allowing them to be customized for a range of uses, such as sophisticated gas storage, effective catalytic reactions, and selective separation procedures.[4,5] They differ from several conventional porous materials, including zeolite, porous silica, and carbon, due to these properties. Zeolite is a mineral of aluminosilicate and have 3D crystalline structure with high porosity but lake flexibility in structure which limitized its use, porous silica is an highly porous form of silicon dioxide, but its lacks modular metal organic linkage, that's why it differ from MOFs and carbon activated material irregular pore distribution and amorphous structure limit their applications.[6,7] Furthermore, customized MOF frameworks with desired topological structures, pore shapes/sizes, and chemical affinities suited

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to particular activities can be produced by carefully choosing metal ions and organic linkers, as well as by using the proper synthetic techniques or post-synthetic modifications.[8–10] MOFs are often made in laboratories on a milligram scale using costly organic solvents and multi-day reaction durations. Successful synthesis often requires a narrow range of reaction conditions since their synthesis frequently involves the balance of several opposing forces that can result in a variety of kinetic and thermodynamic products.[11–14] It is now critically important to develop effective and adaptable methods of mass generating MOFs due to the significant discrepancy between production in laboratories and that needed for commercial applications. The development of scale-up manufacturing methods has led to the importance of parameters in determining their feasibility.[15–20] The space-time yield (STY), one of the parameters used to assess MOF production, is extremely significant. As an indicator of process efficiency, it quantifies the amount of MOF produced daily per unit reactor volume. Furthermore, while evaluating total production rates and process viability, scientists stress the importance of the absolute amount in grams per hour (g/h). There is a possibility that the computed STY will be over-extrapolated because many contemporary production processes are still in their early stages of development. A further important factor is the yield, particle size control, process flexibility, surface area and phase purity measurements of the product.[21–26] The applications of MOFs in various fields such as light emitting diodes, solar cells and photodiodes future manufacturing techniques discussed in this review will be described using these standards. The majority of potential scale-up techniques have the same difficulties:

- Utilizing solvents that are organic. Their expense, toxicity, and sometimes flammability become major problems when they grow in volume.
- The accumulation of anion. As precursor molecules, metal salts are typically used. Both anions, like chlorides, and nitrates pose a safety risk when present in large quantities. It is better to use precursors of hydroxide and oxide metals.
- Accessibility of Ligand. Specific organic ligands are needed for a lot of MOFs. Ongoing research is being done on production techniques that could also yield these raw elements.
- Management of particle size. Particles the size of nanometers are needed for applications like membranes, but not for storage. To prevent unintentional MOF particle movement, larger particles are preferred. It's crucial to have control of this.
- Starting the process. Unreacted starting materials and non-volatile solvents must be extracted from the pores of MOFs. This is an important consideration on a large scale.
- In order to use the manufactured MOF powders in actual industrial applications, they must also be shaped.

In contrast to zeolites, which are often simpler to synthesize, the manufacture of MOF families is more complex due to specific challenges that each family encounters in spite of their high porosity. These challenges are particular to each MOF family and require unique conditions. Various methods have been explored in recent times to tackle these difficulties, such as hydro/solvothermal, sonochemical in addition to electrochemical, microwave, and mechanochemical synthesis.[27–31] With the use of metal electrodes as metal sources, BASF's first goal in developing the electrochemical synthesis of MOF was to eliminate anions. The utilization and production of MOFs by companies has increased recently due to the swift advancement of these techniques. With direct feedback from these companies, this evaluation aims to give an update on their progress.[32,33] Mostly for use in vehicle natural gas storage, BASF invented large-scale, customized solvothermal processes. In the wake of this, spin-out companies have emerged, frequently founded on cutting-edge response techniques that were initially created in a research place.[34–38] Consequently, a novel class of multifunctional crystalline porous materials, referred to as MOFs, has come to light, exhibiting exceptional performance in a range of applications. Applications of MOFs in a variety of fields, including photodiodes, solar cells, and light emitting diodes, are described in this review article.[39–41]

2 Synthetic strategies of MOFs synthesis

In the past several years, there has been a lot of interest in the development of metal-organic frameworks (MOFs) because of their intriguing and varied architectures. This interest is a result of their possible uses in a number of industries, including as catalysis, storage, and separation. These structures have great promise for a range of porous material applications. Among the synthesis methods that can be used are hydrothermal and solvothermal synthesis, electrochemical synthesis, mechanochemical synthesis, sonochemical synthesis, and microwave-assisted synthesis Figure 1.

2.1 Microwave assisted methods

Metal-organic frameworks (MOFs) and other multidimensional coordination polymers have recently been

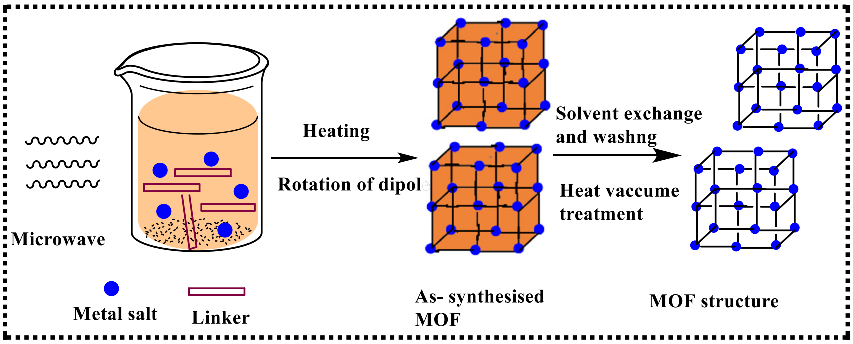

Figure 1: Microwave assisted solvothermal synthesis of MOFs. Redrawn on ChemDraw Ultra 21.0 from source.[42]

prepared using microwave heating, a technology that was previously mainly used in organic chemistry. Higher yields of the intended MOF products can be produced at quicker reaction times thanks to this method's acceleration of crystal nucleation and growth kinetics. By minimizing the time needed for synthesis and decreasing the production of byproducts, microwave heating improves efficiency and streamlines the procedure. These enhancements are made possible by the technique's capacity to quickly and evenly heat the reaction mixture, which presents a viable method for the synthesis of complex MOFs with lower complexity and greater purity.[43–45] The most common methods for achieving fast crystallization of MOF are ultrasound (US) and microwave (MW) approaches, which have been extensively researched as a substitute for conventional heating.[46] Particle size distributions become more homogeneous as a result of a quick and steady nucleation process brought about by the creation of localized super-hot patches and quick heat transfer made possible by MW.[46] As shown in Figure 2b, Gholami et al. improved the performance of PES membranes by synthesizing TMU-5 particles by the use of ultrasonic radiation. These particles were then used as fillers.[47–49] One benefit of the ultrasonic approach for uniform coating of tiny nanostructures is its narrow size dispersion.[50,51]

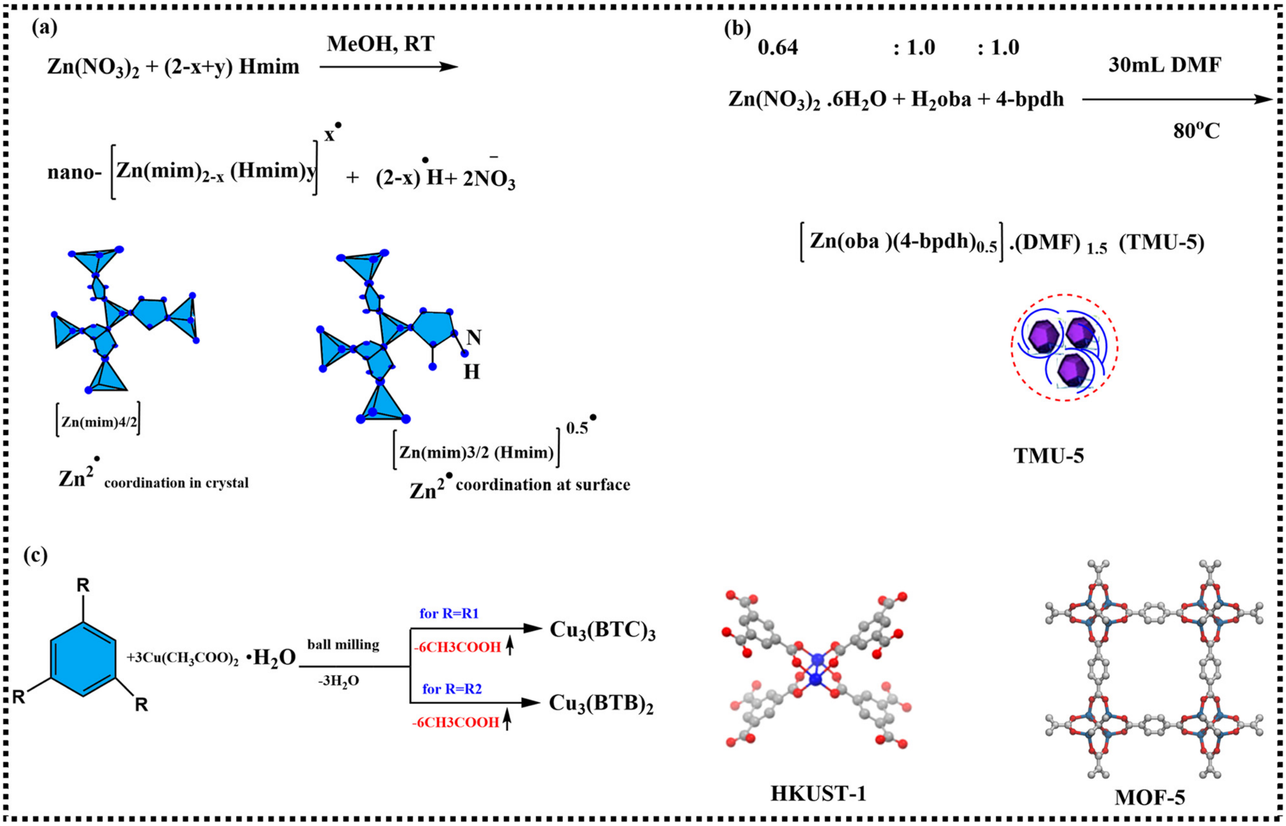

Figure 2: Different methods of MOFs preparation are shown in Figure (a), (b) using a microwave to prepare TMU (c) mechanochemical synthesis of MOF-14 and HKUST-1.[52]

By using microwave heating, Jamshidifard and associates were able to improve the structural and functional characteristics of a polyacrylonitrile (PAN), chitosan, and UiO-66-NH_2 MOF composite membrane.[53] The synthesis of UiO-66-NH_2 was achieved with efficiency and consistency by the reaction of $ZrCl_4$, DMF, BDC-NH_2, and hydrochloric acid by microwave heating. It is possible to accurately adjust the size and crystallinity of MOF particles by adding modulators during the nucleation process. By improving crystallite formation, this modification enables customized MOF characteristics for a range of applications. In order to prepare UiO-66-$NHCOCH_3$, Lin et al. used UiO-66-NH_2 as their raw material after employing post-synthesis modification for defect technology.[54,55] The resultant MOF's comparatively narrow pore size is used to eliminate minor compounds.[56] Modification by structural defects is also carried out in this way. A microwave-assisted technique is widely used for the fast hydrothermal synthesis of MOF different types of MOFs synthesized by different methods are shown in Figure 2a–c. This method is used to obtain small metal and oxides.[42,43,57] When mobile solvent charges, like polar molecules or ions, combine with electromagnetic waves, they efficiently produce heat and cause a rapid heating process. This technique, which has been well researched and used in organic chemistry, makes it easier to produce oxides at the nanoscale. Particle formation and reaction speeds are accelerated by the interaction of solvent charges and waves, providing fine control over the synthesis of nanomaterials and improving their characteristics for a range of applications.[58–60]

For a minimum of 24 h, microwaves were utilized to increase the temperature of solution and form metal nanosized crystals. Teflon vessel is filled with the substrate combination and the proper solvent. It is then closed and sealed, and the microwave is used to preheat and cook the mixture for the desired amount of time.[61–63] In a microwave, the energy from electromagnetic is converted to thermal energy. As seen in Figure 1, this mechanism raises the temperature of the mixture by lining up the applied electric field with the permanent dipole moments of the molecules.

By placing themselves in oscillatory and electromagnetic fields, the polar molecules in the base mixture irreversibly alter their orientation. Applying the proper frequency causes more collisions between the molecules, which raises the system's temperature and kinetic energy.[64–67] It is an easy and energy efficient technology because of the direct interaction between the electromagnetic radiations and solution. Achieving homogeneous nanocrystals requires careful consideration of the solvent to use and the precise energy input. Better purity products are produced for polymorph synthesis using microwave-assisted MOF synthesis. Its two main traits are the fabrication of nanoscale goods and fast crystallization.[11,18,60,68–70]

2.2 Hydro/solvothermal synthesis

As one of the most popular, effective, and widely utilized techniques for preparing MOF in different sizes, solvothermal is the most widely used course.[71,72] Because of its high yield, simplicity, ease of use, and crystallinity, this approach is the most preferred and widely used one. In a closed container, the reaction in the solvothermal synthesis process occurs at an autogenous pressure higher than the solvent's boiling point. The most important stage in solvothermal synthesis is choosing the chemical modulator. Varying modulator concentrations may result in different crystallite sizes by influencing the availability of nucleation sites through the competition for metal binding sites.[18,73] The choice of modulator can sometimes end up in modulator moieties replacing the ligands and creating structural flaws in the crystals.[74,75] Metal salts and organic ligands are combined using the solvothermal process, which uses protic or aprotic solvents with formamide functionality. Protic solvents such as methanol, ethanol and aprotic solvents include DMA, NMP, DEF, DMSO, DMF, acetonitrile, and toluene are often used. The solvothermal approach is better than other reactions, but it needs to be carefully regulated in terms of both temperature and time, as alterations to either could cause MOF particles to degrade.[76,77] To address the problem of the original components' significant solubility, a complex mixture of solvents is used; if water is used as the solvent in the solvothermal process, this approach is referred to as the Hydrothermal Synthesis Method. Teflon-lined stainless-steel autoclaves are used for reactions that need temperatures higher than 400 K because of their capacity to withstand high temperatures and pressures. Glass vials work well for lower temperatures. The mixture is put into a sealed vessel and exposed to high pressure and temperature during the reaction. This configuration provides the best possible circumstances for the creation of the product by guaranteeing that the reaction continues smoothly over a time span of several hours to a day.[78]

The temperature of the closed vessel is raised above the boiling point of an aprotic or protic solvent in order to achieve a higher pressure.[17,79,80] Temperature is a key factor in the solvothermal synthesis reaction. Reactions fall into two categories: non-solvothermal reactions, which happen at or below the solvent's boiling point when the solvent is at room temperature, and solvothermal reactions, which happen in a sealed vessel at temperatures above the solvent's boiling point and generate autogenous pressure.

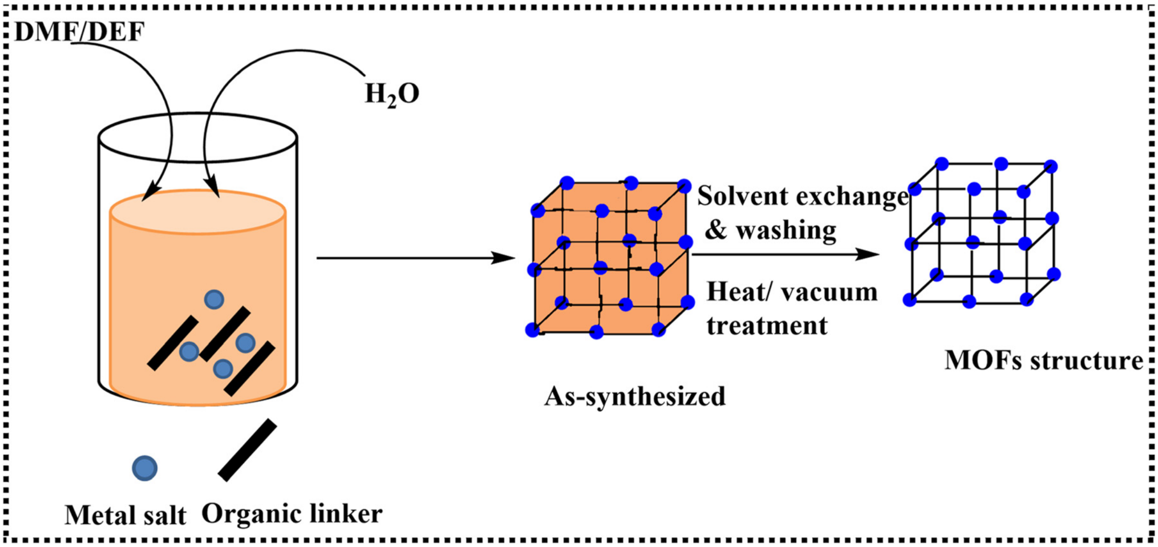

Figure 3: Solvo/hydrothermal synthesis of MOFs. Redrawn on ChemDraw Ultra 21.0 from source.[42]

Standard conditions are used in the former, while high temperatures and pressures are used in the latter to accelerate processes that would otherwise be unfeasible or slow.[18,81] Because of the high pressure, the temperature rises over the solvent's boiling point, causing the salt to melt and aiding in the process. As a result of the increased pressure, the temperature rises over the solvent's boiling point, melting the salt and facilitating the process. In order for the solution to crystallize slowly and form a large crystal with a high interior surface area. MOF-5 and Ag@MOF-5 were successfully produced by solvothermal synthesis and to improve resistance to fouling bacteria and inhibit clustering they were then joined with a PVDF matrix. Using the *in situ* solvothermal synthesis approach porous α-Al_2O_3 substrates PVP-activated were used to build continuous polycrystalline MOF-808 membranes.[82,83] A wood/MIL-100(Fe) membrane with super hydrophilic characteristics was developed, improving its performance in separating oil from water with improved flow rates and efficacy. This allowed for outstanding separation efficiency and high flux for oil-in-water emulsions. Following the hydrothermal treatment, the membrane's surface uniformized as a result of the production of more compact MOF nanoparticles see Figure 3.[84–87]

2.3 Sonochemical method

Sonochemical approaches allow for homogenous and fast nucleation in contrast to typical solvothermal synthesis, which leads to shorter crystallization durations and much smaller particle sizes. During synthesis, this method improves efficiency and control over particle diameters.[44,71,88–90] A horn-type Pyrex reactor with an adjustable power output and sonicator bar is shown in Figure 4. It is intended to process a mixture of substrate solutions for a particular MOF structure without the need for external cooling. Acoustic cavitation, in which bubbles develop and burst inside the fluid, happens during sonication. Very high local temperatures – roughly 5,000 K and 1,000 bar of pressure are produced by this process. These extreme circumstances speed up the MOF particle's nucleation and development, greatly improving the synthesis process by fostering the production of desirable structures in a highly reactive environment.[91,92] Moreover, sonochemical synthesis produces heating and cooling rates that are much faster than $>10^{10}$ K/s, which promotes the creation of fine crystallites. This approach effectively produced high-quality MOF-5 crystals in the 5–25 μm range in less than 30 min using NMP (1-methyl-2-pyrrolidone) as the solvent. After thorough evaluation, the crystals' physical characteristics were found to be similar to those of samples that are regularly manufactured. In addition, HKUST-1 was created by immersing a mixture of DMF, ethanol, and water in an ultrasonic bath. This method shows how versatile and effective sonochemical techniques are in creating high-quality MOFs with regulated properties in a much shorter amount of time.[93–95] The product crystallized into a 10–40 nm nanocrystalline powder in 5 min and longer reaction times produced bigger crystals (between 50 and 200 nm). Substantially greater yields however, additional reaction caused them to partially decompose. Using a sonochemical technique, high-quality Mg-MOF-74 crystals were produced in 1 h with triethylamine (TEA) as a reducing agent. With a BET surface area of 1,640 m^2/g and particle sizes of about 0.6 μm, these crystals showed excellent performance and efficient synthesis.

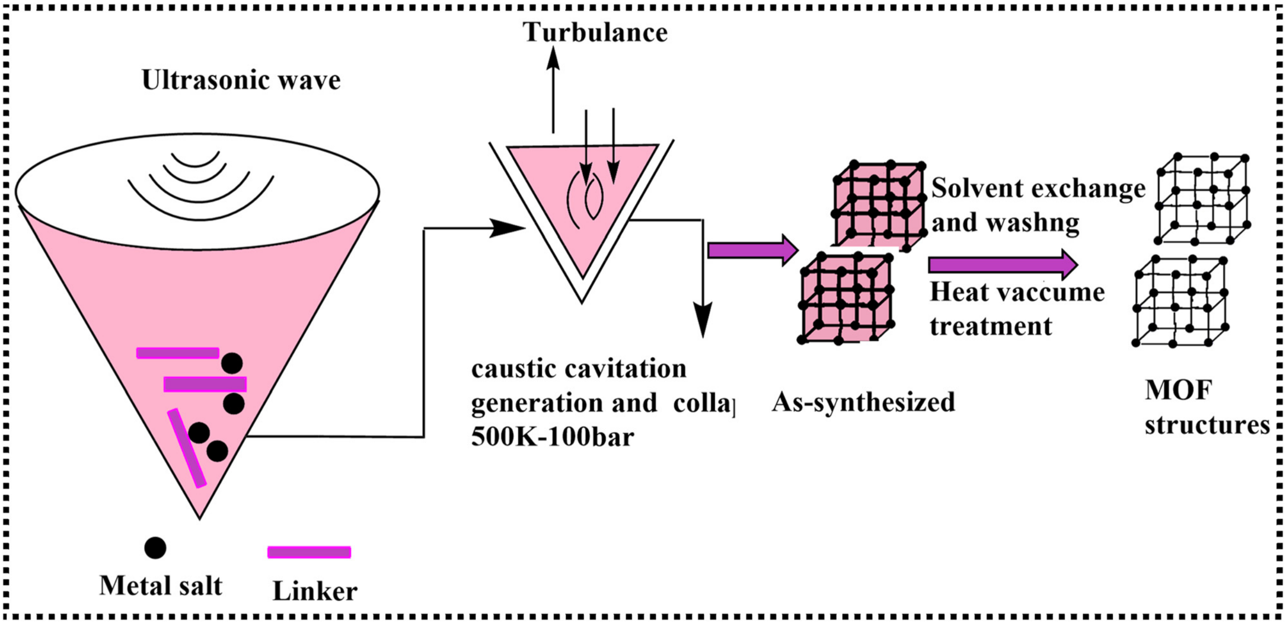

Figure 4: Schematic synthesis of MOFs by sonochemical method. Redrawn on ChemDraw Ultra 21.0 from source.[42]

Mesopores were generated, which is interesting, and is likely the result of TEA's competitive binding to Mg^{2+} ions.[15,96–98] Sonochemical synthesis allows for the straightforward regulation of ultrasonic power levels to synthesize both interpenetrated and non-interpenetrated MOF structures, such as PCN-6/PCN-6′ and IRMOF-9/IRMOF-10.[60,99] PCN-6 and IRMOF-10 are examples of non-interpenetrated structures that were created at lower power levels; mixes were produced at intermediate power levels; and phase-pure interpenetrated structures of the comparable MOF were produced at higher power levels (PCN-6, IRMOF-9).[100]

2.4 Electrochemical method

In this process, the anode is provided by metal ions, while the linker molecule dissolves in the electrolyte and reaction vessel. MOFs can be produced by electrochemical synthesis indefinitely. Mainly consist of cathode and anode, which dipped into the solution. Figure 5a–c illustrates how the addition of protonic solvents to the reaction mixture keeps metal ions from the anode from accumulating on the cathode.[89,101–104] $Cu_3(BTC)_2$ phases with pore volumes and surface areas nearly comparable to those of HKUST-1 MOFs were produced via hydrothermal, non-solvothermal, and electrochemical techniques. Using this method, several anode combinations between metals (zinc, copper, magnesium, and cobalt) and linkers (1,3,5-H_3BTC, 1,2,3-H_3BTC, H_2BDC, and H_2BDC-$(OH)_2$) were created.[11,105–108]

High porosity compounds based on zinc and copper were produced by these combinations. In conjunction with MOF and porous nanoparticles, other MOF architectures have also been studied. Films and coatings with patterns were produced using HKUST-1. Careful control of the

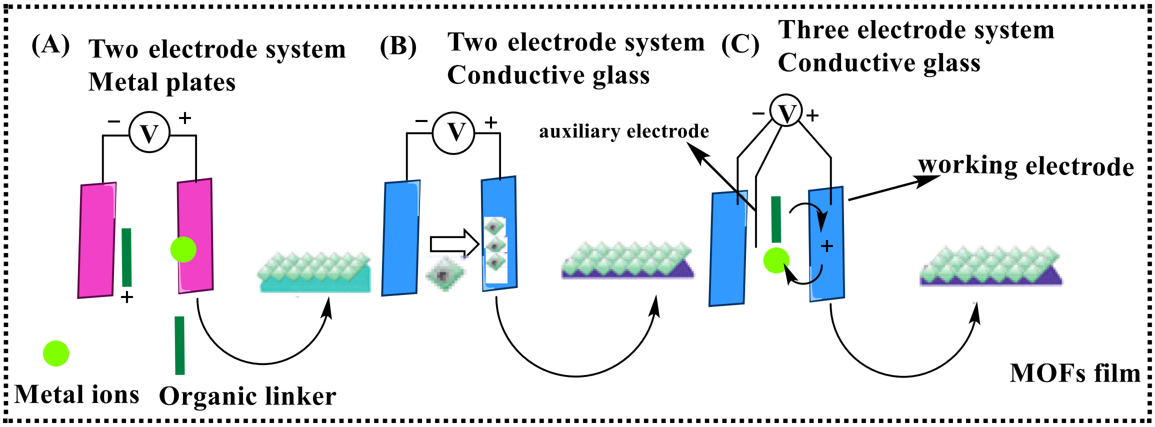

Figure 5: Schematic of the processes utilized in the electrochemical synthesis of MOF thin films Redrawn on ChemDraw from source.[109]

production parameters made it easier for the movie to develop.[110–113] The conventional electrochemical method was substituted with a galvanic substitution technique to create MOFs. By applying metallic Cu to the glass plate, tiny octahedral crystallites with particle sizes between 100 and 200 nm were covered. Octahedral HKUST-1 crystallites were produced as a result of silver ions oxidizing copper during the spin-coating of H_3BTC, DMSO, and $AgNO_3$ on a Cu-coated glass slide.[18,114–116] Metal nanoparticles with pores, such as platinum and its basic alloys, have been produced in the past using electrochemical synthesis techniques. Using poriferous metal nanoparticles with this MOF-making technique, a novel type of porous core–shell MOF with potential applications in drug administration and catalysis could be created.[117–122]

2.5 Mechanochemical method

In recent decades, mechanosynthesis has quickly spread into several branches of chemistry, including pharmaceutical synthesis, inorganic chemistry and catalysis. In the fields of metallurgy and mineral processing, it is a widely recognized technology.[123–127] By milling or grinding materials without utilizing solvents or with very little of them, the main idea behind this synthetic process is to encourage chemical reactions. Instead of the conventional solvothermal MOF reactors, this approach uses a mechanical process with an automated ball mill or a mortar and pestle. Because it guarantees batch-to-bath reproducibility, mechanosynthesis generally requires more energy as shown in Figure 6. In addition to enabling the synthesis of MOFs in solvent-free conditions, this approach also makes it possible to use MOF precursors with low solubility, such as hydroxides, oxides and carbonates. It also makes the process faster and more efficient. Upscaling the process is the primary constraint of mechanosynthesis, which is primarily a batch processing technology with a limited production rate.[15,128–130]

Furthermore, keep in mind that purification can still be necessary and might need for a solvent even in cases when the synthesis is "solvent-free". The most environmentally friendly way to produce MOFs is by this synthetic process, which could result in significantly cheaper production costs. When creating MOFs, three different mechanochemical techniques are employed: Ion-and-Liquid Assisted Grinding (ILAG), which exploits a catalytic liquid with traces of salt additives to speed up MOF formation; Liquid-Assisted Grinding (LAG), which is more adaptable and faster than Solvent-Free Grinding (SFG) because it uses catalytic amounts of liquid phases to increase reagent mobility.[128,131,132] It has been shown that practically all families of MOFs may be synthesized using these methods. Using acetic acid and water molecules occluded in the pores, James et al.'s created copper(II) isonicotinate MOF using the SFG method. Isonicotinic acid (Hina) powder and dry copper acetate were combined and ground for 10 min (see Figure 7a). James and colleagues demonstrated that the synthesis might be expedited by pre-processing small volumes of liquid byproducts produced by the SFG method. By adding small amounts of acetic acid to the precursor mixtures, $Cu(INA)_2$ MOF production was considerably enhanced; however, no improvement was found for HKUST-1 due to the reduced solubility of the trimesic acid. By employing X-ray diffraction the same group (2010) examined the structural properties of $[Zn_2(fma)_2(bipy)]$, where fma is for fumaric acid and bipy is for 4,4-bipyridine, which is created by

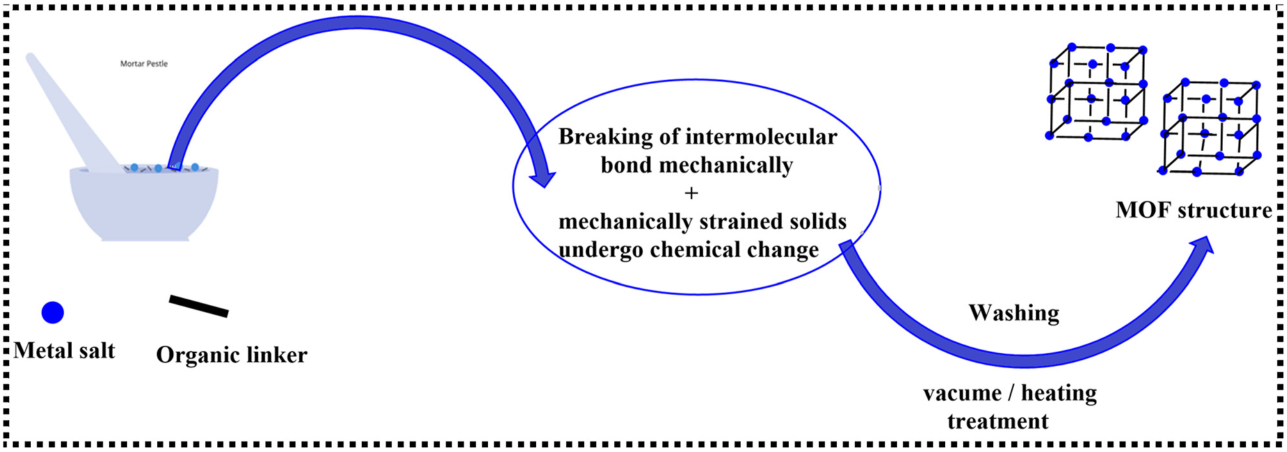

Figure 6: Schematic synthetic procedure of MOFs by mechanical process. Re-drawn on ChemDraw Ultra 21.0 from source.[77]

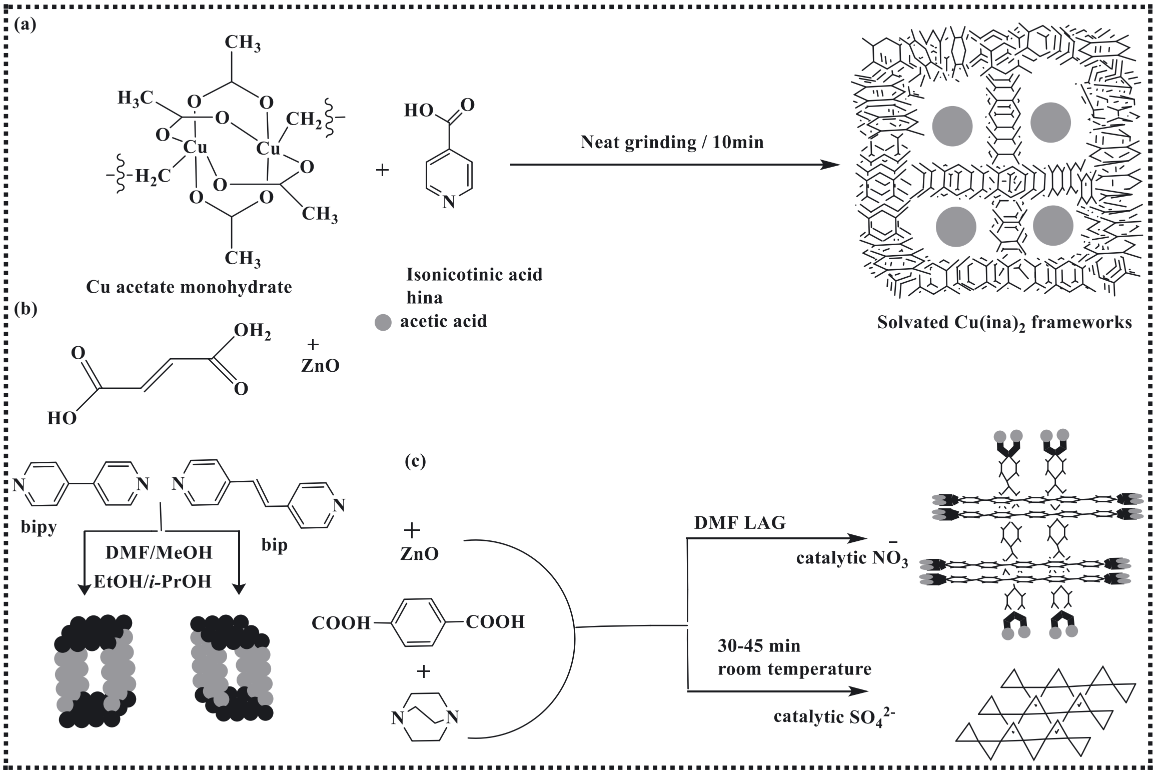

Figure 7: Synthesis of porous MOFs by mechanochemical means (a) by liquid-assisted grinding (b) by neat grinding; and (c) by ion- and liquid-assisted grinding, which takes use of the nitrate and sulfate catalytic effect. Porous MOFs and their characteristics and how MOF synthesized by this approach show performance in photovoltaic devices. Used with permission from source.[133] Re-drawn on ChemDraw Ultra 21.0, omission and errors are possible. See the citation for more details.

mechanosynthesis as showned in Figure 7b. In order to remove the acetic acid and H_2O byproducts that had trapped in the pores heat treatment was applied to remove the trapped byproducts and refine the interpenetrated structure.[133] Xu et al. recently reported synthesizing MIL-101-Cr without the need for hydrofluoric acid or solvent. After 30 min of grinding at room temperature, the chromium salt and terephthalic acid were placed in an autoclave set at 220 °C for 4 h. This process yielded a material with a BET (Brunauer–Emmett–Telle) surface area of 3,517 m^2/g and a smaller particle size than the batch procedure.[134–136]

It was shown that the pillared-layered MOFs may be synthesized with great efficiency using the third mechanochemical approach, ILAG. The mixture was supplemented with catalytic quantities of an alkali metal or ammonium nitrate salt based on terephthalic acid and dabco (1,4-diazabicyclooctane), after 45 min of reaction to synthesize the zinc pillared substance Figure 7c. With the same starting ingredients, a hexagonal grid with the same pillared-layered structure was produced by substituting sulphates for ammonium nitrate.[137–139]

3 Applications of MOFs

MOFs are excellent options for membranes, biomedical imaging, light emitting diodes, solar cells, photodiodes, gas storage and separation, catalysis and luminescence-based sensing and lighting, because of these exceptional qualities. Because of their structural predictability, multifunctionality, nanoscale processability, and well-defined habitats for luminophores in crystalline forms, MOFs in particular provide a special platform for the production of luminous materials. This paper covers a detailed description of solar cells, photodiodes, and light-emitting diodes.

3.1 Role of MOFs in light emitting diodes

Luminosity in metal-organic frameworks can be attributed to many factors, including metal ions, organic ligands, includes charge transfers between metal and ligand, ligand and ligand and metal and metal. Additionally, some of the guests that are added to MOFs through supramolecular interactions have the capacity to emit or induce luminescence, and with innovative structure design and appropriate guest selection white light can be created with ease.[140,141] Thus, it is not surprising that there has been conjecture regarding MOFs possible use in WLEDs given these diverse effects. The earliest known attempt to use MOFs to produce white light was made in 2007.[142] Consequently, white light has been produced by MOFs by adding various conjugated organic ligands, color-emitting lanthanide metals and guest species like quantum dots and dye molecules and. Obtaining MOFs with different luminescence emissions is easy with the encapsulation of emissive organic dye.[143,144] Organic dyes are certainly the most commonly utilized fluorescent materials because of their wide excitation spectrum, high absorption coefficient, moderate-to-high quantum yields, short luminous lifespan, and ease of access.[145,146] When using organic dyes directly in WLEDs, there are two main problems. First problem is aggregation caused quenching (ACQ) effect, which is brought about by the organic dyes stacking interactions and causes the fluorescence intensity in solid states to be lower than in brilliant solution forms. Second is the organic dyes photo and thermal-stability.[147] MOFs are the ideal supporting substances to prevent the solid-state aggregation of organic dyes, because of their high porosity, which allows them to enclose molecular dyes in small pores. This prevents quenching caused by aggregation and limits internal molecular motions, which inhibits nonradiative relaxation.[148–150] If organic dyes and fluorescent linkers are chosen appropriately, to transfer energy to the dyes MOFs play crucial role. To alter the emissions from encapsulated dyes, the dyes' composition and content can be easily modified. Furthermore, by designing interactions between the elements of MOFs and dyes, a variety of luminescence qualities can be obtained. Consequently, it is commonly recommended to use. In white light emitting diodes by encasing dyes inside of them, MOFs act as phosphor converter.[151–153] Encasing organic dyes in MOFs can be done in three main ways. The first approach involves a two-step synthesis process wherein the pristine MOF is first created and subsequently submerged in a fluorescent dye solution. This process is simple, but it cannot be widely employed because of the size disparities between the metal-organic frame works aperture and organic dyes, which restricts the variety of colors that may be used and causes guest leakage.[111,154–156]

The second approach involves the introduction of dyes during the crystal formation process, known as *in situ* encapsulation. Despite the fact that this method works well for creating fluorescent MOFs with a consistent fluorescent dye dispersion other aspects, such as MOF structures, pore windows, and size need be taken into account for the desired organic dyes.[151,157,158] The last technique involves using fluorescent linkers that are integrated into the MOF frame. This allows for the easy acquisition of persistent fluorescence, however bulky ligands often create steric hindrance, which decreases the yield of luminous material in MOFs. In practice, dual emissions are often produced by the combination of fluorescent ligands and dyes. Fluorescent ligands are frequently used in conjunction with dyes to produce dual emissions in practice. The excitation energy can be adjusted to regulate the energy transfer process between the ligand and the dye.[159–161]

3.2 Role of MOFs in solar cells

Solar cell technology provides a sustainable and ecologically beneficial way to directly convert optical information, like sunshine, into electrical circuits. Because of the important optoelectronic qualities of the perovskite materials, PSCs, or hybrid organic-inorganic perovskite solar cells, are regarded as one of the most promising options for the next generation of photovoltaic devices. The power conversion efficiency of PSCs was significantly increased by the Miyasaka group's 2009 research, going from 3.8 % to 25.7 %. This represents a significant improvement in the performance of perovskite solar cells.[162–164] See Figure 8a for the perovskite crystal structure, which is ABX3. The massive cation Methylammonium (MA^+) or formamidinium (FA^+) ions make up the A site, halide anion species like I^-, Br^-, or Cl^- make up the small cation B site, and divalent metals like Pb^{2+} or Sn^{2+} make up the X site. Large-cavity porous coordination polymers make up MOF compounds. The MOF materials consist of organic ligands connected to metal cations Figure 8b.[165–167] Their principal attributes include distinct crystallinity, large distinct surface area (up to 7,000 $m^2 g^{-1}$), interconnected porosity, and a wide range of functionalities. Recently, a lot of study has been done on MOFs in solar technology. MOFs can be more stable when used in a variety of solution settings if suitable metal ions and ligands are selected to increase the coordination bonds inside the frameworks. Due to the distinct physical, electrical and optical features of MOFs, solar cells composed of MOF materials such as dye-sensitized solar cells, organic-inorganic PSCs, and organic solar cells display increased efficacy and stability.[97,168–170] There are following advantages of MOFs in solar cell technology. For guest compounds that may be incorporated into or joined to the framework (Table 1),

1) MOFs function as supports in solar cell systems and offer high porosity, stability and linked spaces.
2) MOFs can be processed and analyzed with reasonable ease.

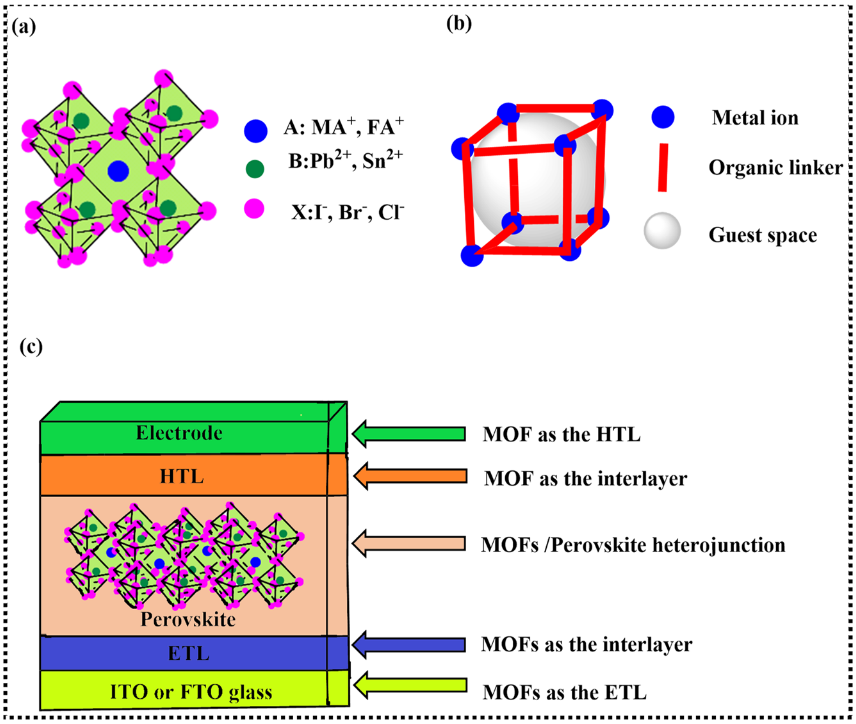

Figure 8: Metal-halide perovskites' crystal structure shown in Figure (a), (b) MOF model in which the blue cylinders represent organic linkers and the orange polyhedrons represent metallic clusters and (c) the application of MOFs across each PSC functional layer. Redrawn on ChemDraw Ultra 21.0 from source[175] errors and omissions are possible.

Table 1: Represent the use of metal organic framework and covelent organic framework (metal free framework) in solar cells with improved efficiencies.

	Material	Device structure	PCE %	References
MOFs	nTi-MOF	ITO/nTin MOF/PCBM/perovskite/spiro OMeTAD/Au	18.94	[173]
	MOF-derived ZnO	FTO/c-TiO_2/MOF-derived ZnO/perovskite/spiro-OMeTAD/Au	18.1	[174]
	ZIF-8 derived porous carbon	FTO/ZIF-8-derived porous carbon layer/TiO_2/perovskite/spiro-OMeTAD/Au	17.32	[175]
COFs	COFs	FTO/c-TiO_2/perovskite with COFs/carbon	14.35	[176]
	Amine–COF	FTO/SnO_2/perovskite with amine-COF/spiro-OMeTAD/MoO_3/Ag	22.13	[177]
	HS-COFs	FTO/c-TiO_2/HS-COFs/perovskite/HS COFs/spiro-OMeTAD/Au	24.26	[178]
	TFPPy-ETTA	ITO/PTAA/TFPPyETTA/perovskite/PCBM/BCP/Ag	19.72	[179]

3) By utilizing components such as organics and metal salts optoelectronic properties can be carefully controlled. Microporous films can be produced by spin-coating the nanoscale distributed MOFs with additional precursors. It is also simple to modify MOFs physical characteristics at the nanoscale level to permit a variety of capabilities in solar-cell devices, including as size, surface area, and porosity.[164,171,172] It's becoming more and more popular to use MOFs in PSCs to improve long-term stability and device efficiency through sensible composition engineering.

To control the formation of perovskite layers, MOFs often build a microporous scaffold. This increases the perovskites quality and crystallinity. Additionally, the conductivity of (cataluminescence) CTLs and the band-alignment in PSCs can also be enhanced by blending MOFs into CTLs. Most recent developments in the use of MOFs at every PSC functional layer are mentioned in Figure 8c. An outline of the major advancements in the discipline is provided below, MOFs perform the following functions:

1) They create a hybrid MOF/perovskite heterojunction layer by combining with the perovskite.
2) They integrate into the CTL or serve as the CTL.
3) They serve as the layer of interface between the perovskite interface and the CTL.
4) They recycle lead from halide perovskites and modules or reduce lead leakage.[163,180]

3.3 Role of MOFs in photodetectors

Because of their special blend of large surface area, adjustable porosity, and varied chemical activity MOFs have become a potential new class of materials for photodetectors. They are great options for improving the functionality of photodetectors because of their crystalline structure, which facilitates effective charge transport and interaction with light.[181–183] The ability of MOFs to be designed to absorb particular light wavelengths is essential for maximizing detection sensitivity in a variety of applications, such as imaging systems and environmental monitoring. Furthermore, MOFs can be made to incorporate various metal centers and functional groups, further customizing their optical and electrical characteristics due to their adaptability. To further enhance photodetector response times and dependability, high stability MOFs with regulated pore environments can be produced. MOFs are expected to improve the capabilities of photodetection technology in a major way as research continues.[184–186]

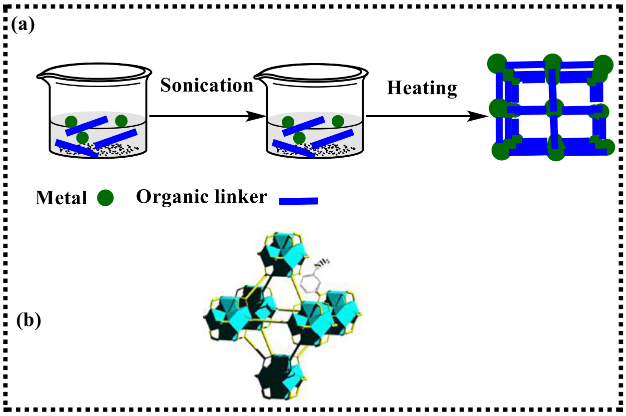

Figure 9: Schematic method to synthesize MOFs single crystals are shown in Figure (a), (b) UiO-66-NH2 crystal formations. Redrawn on ChemDraw ultra 21.0 and errors are expected for more detsils please see citation.[198]

3.3.1 Categorization of MOF-based photodetectors

MOF-based photodetectors are composed of three main types of MOF: MOF single crystals MOF composites, MOF thin films.

3.3.2 MOF single crystals

Their ideal characteristics that influence the materials' intrinsic conductivity and crystalline structure with no grain boundaries make them desirable, single crystals make excellent candidates for optoelectronic devices.[181,187] The solvothermal approach, slow diffusion, hydrothermal, electrochemical, mechanochemical, microwave-assisted heating, ultrasound, and other methods can all be utilized to produce MOF single crystal used in photodiodes. At the moment, the hydro/solvothermal approach is largely employed to synthesis MOF single crystals, which are used to create photodetectors.[40,188–190] The MOF crystals created using the solvent/hydrothermal technique are of high quality and appropriate for structural analysis see Figure 9a. By using a hydrothermal process with benzoic acid present, Wang et al. produced nanosized MOF UiO-66-NH_2 used in photodetectors Figure 9b. They then employed UiO-66-NH_2 as a self-calibration nanoprobe to selectively detect and image hypochlorite biologically. When ClO^- group is added, under 400 nm excitation, UiO-66-NH_2 displays a new luminescence at 533 nm and a luminescence at 432 nm. The emission intensity at 533 nm increases with increasing ClO^- concentration.

3.3.3 MOF thin film

For the purpose of incorporating conductive MOF into optoelectronic devices, thin-film high-performance samples are a suitable option. According to Lu et al., thin film production, contact construction, and circuit design are thought to be the primary issues with semiconductor MOF integration in active devices.[192] A range of recently developed methods have made it possible to build MOF films on substrates. Large specific surface area and continuous density are two advantages of MOF in thin film form over powder or crystal MOF materials. This allows MOF to uniformly cover a wider region and has greater practical utility.[193–195] In photodetection MOFs thin film have attracted considerable attention due the unique tunable characteristics like high porosity, tunable band gaps, and tunable pore size Such properties allow MOFs to improve spectral selectivity which is required for selective detection of certain wavelengths of light, and becomes critical in multi-spectral photodetectors. Moreover, the highly-ordered nature of MOF thin films can also enhance charge transport kinetics for accelerated photoresponse and diminished recombination rates. Such structural benefit boost the sensitivity of photodetectors, realizing the detection of signals with lower intensity, and upgrading the efficiency and performance of photodetectors in operational use for optoelectronic applications that are attracted to developers of optoelectronic applications. That is the reason behind the discovery of diverse synthetic methods for MOF thin films and the four most often employed approaches are.

3.3.3.1 Interfacial synthesis of MOFs thin film

The development of MOF thin films can be controlled by liquid/liquid or liquid/air contact by interfacial technique. MOF nucleation and growth can be precisely controlled due to the interaction that occurs at the solvent-solvent interface. Liquid/air interface synthesis makes fine control over the thickness of MOF thin films possible by taking use of the better dispersion of organic ligands at the liquid surface. This process yields thin films of superior quality because it offers a regulated environment for the consistent growth and deposition of MOF layers. Liquid/air interface synthesis has been a popular method for producing MOF thin films due to its ability to precisely control film thickness and homogeneity, proving its usefulness in the creation of innovative materials.[196–198] In order to efficiently create 2D Ni MOF nanosheets with controlled molar ratios of metal precursors and organic linkers (RM/L), with regulated molar ratios of organic linkers and metal precursors, 2D Ni MOF nanosheets can be produced with good efficiency, Huang and colleagues introduced a mild liquid–liquid interfacial reaction approach.[198] These NSs demonstrate their great catalytic performance by acting as dependable and effective electrocatalysts for oxygen reduction reaction (ORR) in alkaline solutions, which is a two-electron transfer mechanism.[197,199] The process of creating Ni MOF NSs through interface reaction is shown in Figure 10a.[200]

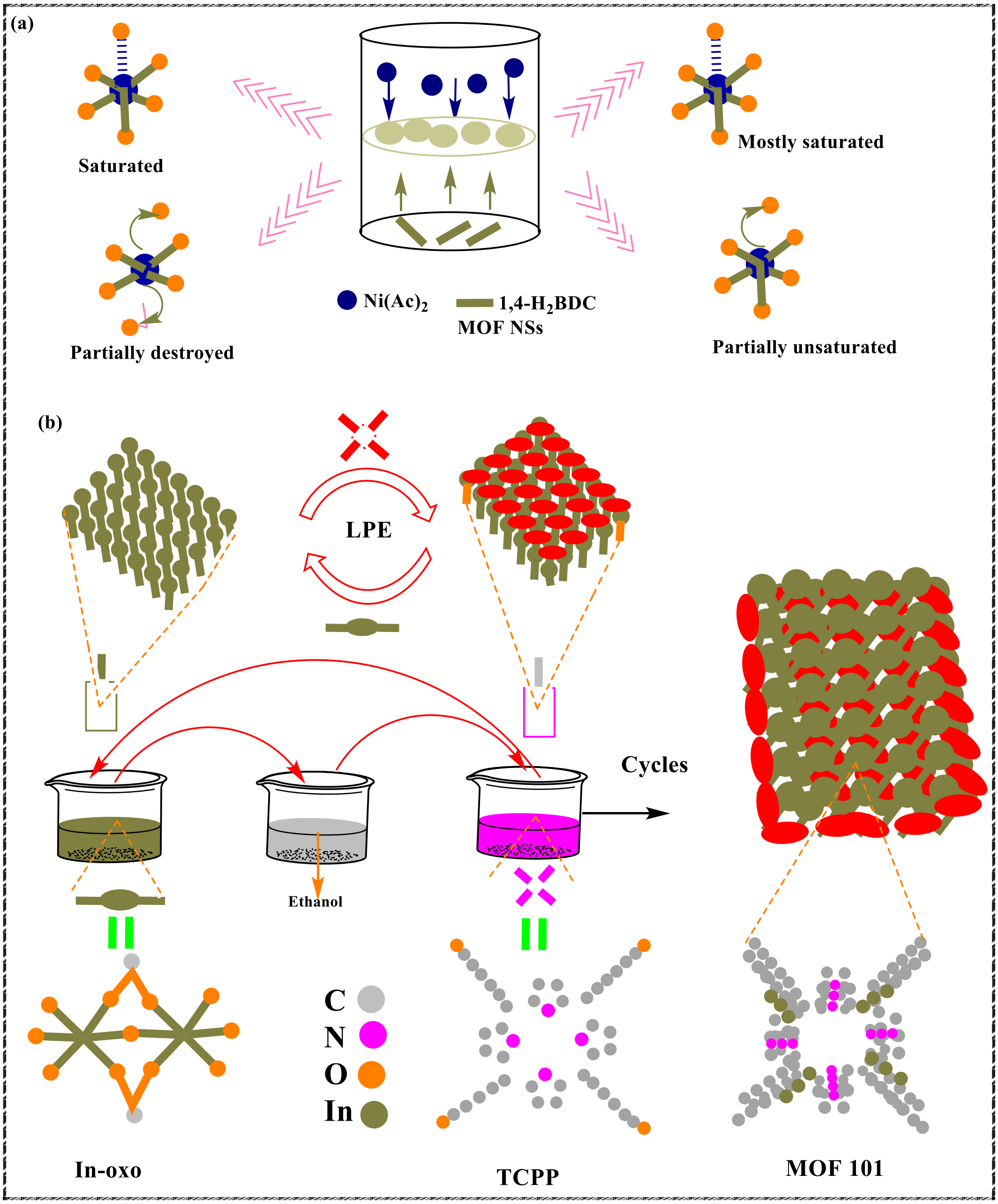

Figure 10: Example of interfacial reaction-based Ni MOF NS preparation process are shown in Figure (a),[200] (b) schematic representation of MOF produced utilizing the layer-by-layer dipping approach on a functionalized substrate.[201] Redrawn on Chem Draw Ultra 21.0 and errors are possible.

3.3.3.2 Semiconductor photodetectors produced by powder deposition method

Using this method, MOF thin films are produced from MOF powder dropcasting in a constant stream. When MOF is deposited onto suitable substrates or prepatterned metal electrodes, deposition is facilitated. In order to create a porous MOF thin film, Kazemzad et al. chose zeolite imidazolium frameworks (ZIF) and filled them with porous silicon (PS). Semiconductor photodetectors are made using ZIF/PS MOF thin films. It is discovered that the photocurrent is temperature-dependent and that, at low temperatures, it is significantly photosensitive to UV rays.[116,183,202,203]

3.3.3.3 MOFs produced from layer by layer method for use as photodetectors

Xu et al. utilized a spray LPE approach for developing chemically resistant sensors with a conducting MOF, improving the robustness and performance of these sensors in different conditions.[202] An EC-MOF thin film with low roughness, ultra-thinness, and high orientation was developed and shown to be a useful interlayer material for varying the height of the Schottky barrier. Using $Cu_3(HHTT)_2$ thin film, Yan and associates created a flexible photodetector that showed a consistent light response at room temperature in the ultraviolet to mid-infrared wavelength range.[204–206] Compared to the broadband photodetectors that were previously disclosed, this is substantially wider. Recently, using the layer-by-layer (LBL) method of liquid phase epitaxy (LPE) on SiO_2/Si substrates, generated In-TCPP films illustrated in Figure 10b and then constructed photodetectors. With a maximum detectivity (D^*) of 7.28×10^{14} Jones and a quick rise/fall duration of 0.07/0.04 s the photoelectric detector performs better in terms of light detection.[207–210]

3.3.3.4 Chemical vapor deposition (CVD)

Thin film growth is achieved by depositing vaporized solid materials on a variety of surfaces using a top-down method known as CVD. The molecular oxide layer that was previously formed transforms into the appropriate MOF structure when ligands are CVD-deposited, enabling the vapor-phase development of MOF thin films. CVD method may produce solvent-insensitive thin films that are of excellent quality and directionally produced low porosity coatings with uniform thickness on a variety of substrates. This provides new opportunities for the incorporation of semiconductor MOFs into useful devices. This was established by Park et al. by synthesizing highly orientated, large-area, two-dimensional conductive MOF films ($Cu_3(C_6O_6)_2$) via the CVD technique. They afterward produced thin-film microchips using electron beam lithography, attaining remarkable conductivities of 92.95 S cm^{-1}. This development opens the door for MOFs to be used in technology on a larger scale by highlighting their potential in the creation of high-performance electrical devices and components.[211–213]

3.3.4 MOFs composites

A flexible MOF's highly changeable optical characteristics are attributed to an intrinsic multiple charge transfer process between the metal and the ligand. Large porosity, low conductivity, and inadequate crystallinity, however, continue to hinder its commercialization. Composites with improved performance can be created by combining MOF with other materials.[143,144,155] MOF thin films are often grown using ZnO and graphene composite materials in order to create MOF composites. Recently, Xue et al. improved photodetection performance with a self-powered photodetector that merged a Si heterojunction with a ZIF-8@ZnO core–shell nanorod array[214] to solve the unpredictable responses to visible light and sluggish sensing caused by flaws on the ZnO surface.[145,213,215] The ZnO and MOF composites' production process is depicted in Figure 11. After that, a Schottky junction was integrated with the ZIF-8/Si top electrode to build a photodetector. With a five-fold increase in response rate over the original ZnO nanorod array/Si heterojunction photodetector, this design offers a significant performance boost. Hydrogenation and the ZIF-8 treatment work together to maximize the efficiency of the photodetector, leading to improved performance. The photodetector has significantly better photoresponse characteristics. Photodetector exhibits a high detection rate and a high response rate of roughly 7.07×10^4 mA W^{-1} at about 2.14×10^{16} Jones. Comparable to self-powered photodetectors, it can be found in both two and zero dimensional materials. Through post-processing methods, this strategy offers a wide range of application possibilities for creating high-performance, self-powered photodetectors.[40,216]

4 Challenges and future priorities

Before MOF manufacture becomes a fully developed commercial technology, a few challenges need to be resolved. The approaches that have the best chance of being both environmentally and economically viable for large-scale production are water-based synthesis and solvent-free approaches. A crucial issue is subsequent processing, in addition to the creation of synthetic pathways, since large production rates are not well suited for the traditional downstream techniques employed in laboratories. Therefore, the commercial availability of MOFs and, consequently, the sustainability of the synthesis process will probably limit the large-scale application of MOFs unless these approaches

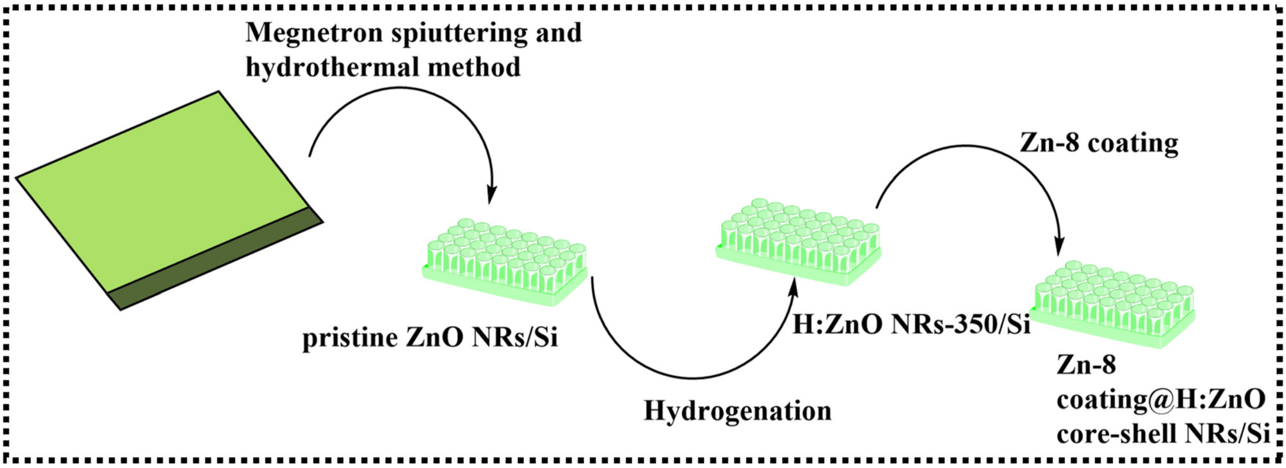

Figure 11: Shows the ZIF-8@H:ZnO NRs/p-Si heterojunction preparation process. Redrawn on ChemDraw Ultra 21.0 and errors are possible, for more detail please see citation.[214]

are significantly improved. The utilization of metal-organic materials for actual practical applications will undoubtedly be introduced by this next research, which will bring together experts from a wide range of sectors. Because of their superior electrical properties, customizable architectures, and variety of functions or MOFs have shown great promise in the field of photodetectors, solar cells and LEDs. MOFs provide better color purity and efficiency in LEDs, and they also help with better light harvesting and charge separation in solar cells. MOFs offer a flexible foundation that helps photodetectors achieve great selectivity and sensitivity. Still, there are a number of obstacles in the way of these encouraging developments. To enable the actual use of MOF-based devices in commercial technologies, future research should concentrate on enhancing the devices' scalability and stability. It is also essential to comprehend how MOFs function over the long run in various operational environments, including those that involve light, moisture, and temperature changes. A viable approach to improving MOFs' characteristics and capabilities even further would be to combine them with other materials to produce hybrid systems. Collaborative cooperation between chemists, materials scientists, and engineers will be crucial to achieving the full potential of MOFs in various applications. By resolving these issues, MOFs may be essential to the development of optoelectronic devices in the future, providing effective and sustainable methods of managing light and energy conversion.

5 Conclusions

In summary, metal-organic frameworks, are a potentially useful starting point for porous crystalline materials. They are made up of an organic linker and a metal atom and they can be utilized to create a wide range of complex functional materials that have the necessary morphology, structure, composition and properties. They consist of a metal atom and an organic linker. They have a wide range of uses, particularly in the fields of fuels, batteries, cells, and superconductors, which are involved in energy conversion and storage. In this review article we looked at the several methods for creating porous crystalline MOFs. In the last few decades, scientists have employed a variety of techniques to synthesize a range of MOFs by altering their structural and electrical characteristics. Hydrothermal treatment bombs, heating materials to extremely high temperatures, and a discussion of their many geometries can all be used to synthesis these MOFs in a lab setting. The possibility of adjusting the ratios of metal to organic ions to modify the shape of MOFs has also been explored. Because of their varied properties, different kinds of MOFs can be created and applied in different ways. This review covered the developments in a number of synthetic techniques. These advanced synthetic methods offer unusual ranges of control over the reaction conditions, enhancing consistency and allowing for greater control over the shape and size of the particles between batches. Reaction rates and improved yields through rapid heating can be improved by use of microwave, electrochemical method use electrical energy to start reaction, which minimize waste and enable selective transformation, ultrasonic waves used to drive the chemical reaction which results in unique reaction pathway and improved product quality. Microwave assisted, electrochemical and ultrasonic methods might be more suitable due to the reason that the MOFs prepared by these methods have large porosity, high efficiency, cost effectiveness, scalability and structural control.

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Informed consent: Not applicable.

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