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Review Article

Metal-Organic Frameworks (MOFs): Recent Advances in Synthetic Methodologies and Some Applications

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ABSTRACT

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MOFs Synthesis Methodologies Applications The pursuit of rapid development in the area of catalysis, solar energy, environmental remediation, wastewater treatment and other aspects of ecological and sustainable chemistry has prompted substantial research by material chemists, physicists, academics and other scientists for the development of porous material. A lot of energy had been invested in this course by scientist, research organizations and public sector agencies from antiquity, but the resulting solution has been somewhat undesirable until two decades ago when Metal-Organic Frameworks (MOFs) appears to offer a glimpse of solution to those challenging issues. The adaptability, flexibility, uniqueness and usability of the metal-organic frameworks material, and its suitability to every facet of scientific and technological advancement has since triggered an incredible upsurge in studies aimed at uncovering more of the inherent influential properties of the materials, and its improvement for the betterment of material science and research world. This review is aimed at investigating some of the recent advancements/ frameworks. breakthrough in metal-organic synthetic methodologies and impending applications.

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Graphical Abstract



Introduction

Owing to considerable porosity, inherent surface area and versatility in properties of the materials involved in the formation of Metal-Organic Frameworks (MOFs) [1-7], they have wide applications in areas such as; storage of gases, heterogeneous catalysis, solar energy, super-capacitors, chemical sensing and therapeutic and diagnostics in biomedicine [8-10]. Regardless of the foreseeable applications of these MOFs in various areas of research, there has not been a consensus as regards to the uniformity in its definition. MOFs, to some researchers, are porous polymers and coordination polymers. Whichever way the definition is depicted; Metal-Organic Frameworks or rather MOFs in short form, since have been understood to be porous coordination polymers, formed from the bonding between different organic linkers and metal-based node.

Historically, MOFs and its branches could be traced to the famous field of zeolite/coordination chemistry [11]. This particularly research area had gained attention since 1964 [12], a lot of people were mostly interested in exploring every facets of Hofmann clathrates and Prussian blue compounds because of what their complexes possesses in terms of properties; "irreversible sorption and other wonderful properties". This was the main focus until around 1989 [13]-1990 [14], when Robson and Hoskins came up with a visionary hints as regards to the formation of a crystal-based porous materials whose catalytic, sorption and ion exchange properties promotes further enhancement of its functional groups after synthesis [15, 16], then this work gave birth to

MOFs, and since then a lot of energy has been channeled towards the improvement in this area of research.

There are several routes involved in the synthesis, assembling and formulation of these influential materials and the type of methods involved has a huge influence on the properties and applicability of the formed MOFs material. Figure 1. shows how organic linkers and the secondary building units assemble to form the much anticipated Metal-Organic Frameworks and Figure 2 shows regular secondary assembly units of different central metal atoms. The central metal atoms as shown in the image play a significant role in stabilizing the formed MOFs and its suitability to certain applications.

Some of the known methods involved in the synthesis of MOFs are as follows: Solvo-thermal and Non solvo-thermal synthesis, electrochemical synthesis, microwave synthesis, mechano-chemical synthesis, sono-chemical synthesis. Many studies revealed that the stability of MOFs is dependent to the fortification of its organic linkers; hence, more techniques are emerging towards the enhancement of the organic linkers with different functional groups after synthesis [12]. The essence of the post-synthetic enhancement is to increase the stability, versatility and intending applicability of the formed MOFs.



Figure 1. Examples of different existing MOFs. Excerpted from [131], copyright 2013. Korean Journal of Chemical Engineers

There are several methods of post-synthetic enhancement of MOFs but the most commonly used method is the covalent modification techniques in which the organic linkers are functionalized with amino and other functional groups like; -Br, -OC₃H₇, -OC₅H₁₁, -C₂H₄ and -C₄H₄ etc. Organic linkers with amino acids functional group are quite compatible with lots of MOFs. For example; 'Amino terephthalate' for MIL-101(Al, Cr, and Fe), MIL-53(Al, Cr, and Fe), CAU-1 [24-27]. Other sublime methods have also proven to be effective in the enhancement of organic linkers. Examples are the dative methods of MOFs metalation after synthesis [28], further incorporation of ligands to coordinately unsaturated metal sites of MOFs [29, 30].

Figure 2. Building blocks of Metal-Organic Frameworks. Excerpted from [132] Copyright 2014, American Chemical Society

Figure 2. shows a pictorial difference between the components of MOFs and their interconnectedness and Figure 3 showed few examples of some different existing MOFs and some that you might likely get know in the course of the article.

Recent advancements in the field of MOFs have yielded an estimable solution to the challenges facing a lot of areas as stated in forgoing paragraphs. Areas like waste water treatment [17, 18, 19], degradation of insoluble substances in aqueous medium, capturing or adsorption and separation of some interfering gases in biofuel production and gas storage [20, 21], biological processing and proper control of some therapeutic and biocompatible medicine [22], sensing and removing antibiotics and other unwanted explosives in water [23], and most importantly in every facet of photo-catalytic reactions [31, 32, 33, 34]. Examples of some of the areas of photo-catalytic reactions

where MOFs have recently shown great potentials include: redox catalytically inclined reactions [38], Lewis and Brownsted acid catalysis (cyanosilylation of aldehyde [39], Friedel-Craft reactions [40], cycloaddition of CO₂ and epoxides [41, 42] and Hetero-Diels-Alder reaction [43]), and Electro-catalytically inspired reactions [44-48].

Figure 3. Regular Secondary Assembly Units of different Central Atom. Excerpted from [132], copyright 2014

Methodologies involved in metal-organic framework synthesis

As for the formation or breakage of bonds energy is required, this same phenomena is also applicable for MOFs synthesis because it involves the bonding of metal oxides and organic linkers. Generally, Metal-Organic Frameworks and likes compounds are synthesized at temperature ranges -273.15 °C to 273.15 °C. Heat energy or change in temperature is synthetically important in MOFs synthesis, and any form of appliances that can generate a controllable amount of heat will do the job amicably. For instance, heat can be generated and transferred from sources such as microwaves, oven, electrical heating appliances or electric potentials, ultrasound, radiations from electromagnetic waves, mechanical [49] and the sources or types of heat energy has a great impact on the nature of the Metal-Organic Frameworks formed. In the synthesis of MOFs, multiple synthetic routes are important because every synthetic method leads to diverse properties of the MOFs during synthesis will indicate a MOF with different properties, and those parameters will in turn play a massive role in the usability or applicability of the formed MOFs. So, in a nutshell the

porosity of the formed MOFs is a function of the heat sources and the type of induced heat energy during its synthesis.

As highlighted in the introductory note of this review, there are several methodologies involved in the synthesis of Metal-Organic Frameworks like Solvo-thermal and non solvo-thermal synthesis, electrochemical synthesis, microwave synthesis, mechano-chemical synthesis, sono-chemical synthesis.

SOLVO-THERMAL/HYDRO-THERMAL AND NON SOLVO-THERMAL SYNTHESIS

According to Rabenau [50], a reaction that occurs in tightly closed vessels, under an autogenous pressure above the boiling point of its solvent is called a solvo-thermal reaction while a nonsolvo-thermal reaction takes place below or at the boiling point under room temperature [16]. There are terms indicating the rangesin temperature, and has been the focal point in determining the kind of reaction path that must be ensued during MOFs synthesis.

Figure 1. Solvo-thermal Synthesis of Metal-Organic Frameworks. Excerpted from [131], copyright 2013. Korean Journal of Chemical Engineers

A lot of MOFs has been synthesized by this process because of its low-temperature dependency [51], and the choice it provides for the modification of the reaction condition (rate nucleation and crystal growth) [16]. To attain a clear crystal, a gap must be bridged between the concentration of the reactant and critical nucleation of creation, in a manner that allows the critical nucleation concentration to exceed the concentration of the reactants. This is achievable by simply devising a means of evaporating the solvents or altering the reaction temperature [51]. The gradient of the reacting temperature supports the formation of MOFs, and some other methods that have a great impact on the temperature gradient include: diffusion of the reactant slowly, layering of the solutions and evaporation of the solution of the reactants. Alteration in the reaction temperature

has a great impact on the synthesized MOFs and it will results in the formation of dense-structure MOFs [52, 53]. The morphology of the crystals of the formed MOFs is a function of the formed MOF [54], and prolongation of the reaction time will have a negative impact on the MOFs; the crystals are most likely going to be degraded and the pores weakened [55]. Examples of some of the MOFs that have successfully been formed through these methods include: MOF-5, MOF-74, MOF-177, ZIP-8 [56-58].

MICROWAVE SYNTHESIS

Microwave is one of the famous synthetic routes toward Metal-Organic Framework synthesis that could be traced to organic [59, 60] and synthetic [61], as well as zeolite chemistry [7]; the grandparent of MOFs. Its proven successes in those fields of research especially in zeolite chemistry were the main conviction and rationale behind its deployment in nonporous coordination polymers and metal-organic frameworks [61].

Figure 2. Microwave Assisted Synthesis of Metal-Organic Frameworks. Excerpted from [131], copyright 2013. Korean Journal of Chemical Engineers

The main principle is that the energy obtained through the irradiations from microwave is used to activate an interaction between electromagnetic waves and mobile electric charges of different polarity in a solid or liquid state. In the liquid state, molecules of different polarity are arranged in an oscillatory fashion within an electromagnetic spectrum, with the sole aim of permanently altering the configuration of the molecules involved. This alteration provides a platform for a decisive increment in the temperature of the system whenever the forces of collision are introduced.

Microwave assisted synthesis has proven to be one of the best way of synthesizing MOFs because of its energy and cost effectiveness, and the privilege it offers in the regulations of reaction conditions during synthesis. Regardless of the advantages and freedom, the methodology posed over other routes, efforts are currently on to improve the crystallinity, purity and kinetics of crystal and nucleation growth of the topical compounds. To achieve this, some scientists have incorporated this methodology to a ball milling machine, with the objectives to catalyze the reaction rates and efficiency of the methods [41-47]. Here, the starting materials (Organic linkers and metal ion sources), a stainless steel ball washed with deionized water are placed in a miller of a certain diameter, height and volume, irradiations from microwave are introduced and the miller is stirred concurrently at constant speed. The solution is observed after about 30-50 minutes and filtered thoroughly. The filtrate then placed in an ethanol solution and stirred in a magnetic stirrer. After about 2-3 hours, the precipitates filtered under suction and dry then the product is ready for analysis.

SONO-CHEMICAL SYNTHESIS

The term "Sono", linked with ultrasound, and the processes whereby an ultrasound of considerable amount of energy is/are exerted on a reaction which is called a sono-chemical process. This process or mechanism has also been adopted in recent times by researchers to synthesize Metal-Organic Frameworks of specific characteristics. Sono-chemical process was came into existence from the desire to make MOF synthesis which is easily reachable, cost and energy effective, and eco-friendly and those that occurs through the homogeneous and accelerated nucleation has a greater chance of reducing the crystallization time and also reducing the particles size [62, 63]. This is important because of the potential application of the synthesized MOF, since fastness of the process has a great role to play in scaling up MOFs. Bang et al. and Mason et al., in their various books, have given an explicit explanations of the mechanistic protocols involved in the uses of this wonderful methods for the synthesis of different kind of material of needs [64, 65].

Figure 3. Sono-chemical Synthesis of MOFs. .Excerpted from [131], copyright 2013. Korean Journal of Chemical Engineers

A lot of notable MOFs have been synthesized through this process, and the first reactions in this context were aimed at investigating the synthesis of Zn carboxylates [66]. Others include HUSK-1, MOF-5, Mg-MOF-74, PCN-6/PCN-6', IRMOF-9/IRMOF-10 [67-69]. The reaction times of all the MOFs that were synthesized by this process were short. Figure 6 is a typical representative of a Sonochemical process of MOF synthesis.

ELECTROCHEMICAL SYNTHESIS

As more synthetic methodologies are evolving, researchers are keen on solving the issues that could aid easy commercialization of every process. Perhaps, the history of electrochemical synthesis of Metal-Organic Frameworks could be dated back to 2005 when researchers at BASF [70] worked assiduously with a foresight to improve on the productivity of a certain MOF, HKUST-1. For better explanations, a typical setup for the electrochemical synthesis of MOF contains a battery cell, an anode and cathode plates immersed in an electrochemical bath (medium) containing a metal salts and organic linkers as shown in Figure 7.

Figure 7. Electrochemical synthetic setup for MOF synthesis, Excerpted from [131], copyright 2013. Korean Journal of Chemical Engineers

Here the metal ions were provided unceasingly via the anodic dissolution to the electrochemical bath (reaction medium) against the normal conventional ways of using metal salts. The metal deposition on the cathode is avoided by using protic solvents, but in the process Hydrogen (H₂) gas is produced [71]. Recent advancement in this process has yielded commendable recommendations from all research work based on these, as lots of MOFs were successfully synthesized *via* the same processes that were evoked by those BASF researchers. Examples of some the recently synthesized MOFs includes HKUST-1, ZIF-8, Al-MIL-100, Al-MIL-53, and Al-MIL-53-NH₂ [72]. After the synthesis, all the reaction parameters are normally recorded for further calculations and the formed MOF will be subjected to characterization. Some examples of the reaction parameters are as follows: solvent,

electrolyte, voltage-current density, and temperature on the synthesis yield and textural properties and many more. The apparatus for characterization includes by X-ray diffraction, gas adsorption, atomic force microscopy, diffuse reflectance infrared Fourier transform spectroscopy, and scanning electron microscopy.

MECHANO-CHEMICAL PROCESS

As the name implies, mechano-chemical process is the combination of both mechanical and chemical processes for the synthesis of Metal-Organic Frameworks. The mechanical aspect of the process involves the breaking of intra-molecular bonds while the chemical path of the process involves the transformation that follow suit [73]. Historically, mechano-chemical synthesis has had a fairly large share in synthetic chemistry [74], for the synthesis of different synthetic materials. Further advancement has seen mechano-chemical processes being adopted widely in areas ranging from pharmaceutical, organic, inorganic, solid states, polymers and many other like this [75-77].

Figure 8. Mechano-chemical setup for MOF synthesis. Excerpted from [131], copyright 2013. Korean Journal of Chemical Engineers

Mechano-chemical processes made its imminent mark in the field of Metal-Organic Frameworks in the early 2006 and the data were recently collated by Friscics [78]. The major inspiration behind this synthesis of mechanically activated MOFs is the issues relating to the environments, and the opportunity to conduct reactions without any stresses, at room temperatures and under a solvent free scenario [73]. In this case, a relatively short reaction time might be achieved, which has a great impact on the yield and particle size. A lot of MOFs with wonderful properties has been synthesized through this process and more are currently under reviews. Examples HKUST-1 as reported [79, 80-83] and imidazolate-based compounds as reported [84, 85] respectively.

IONO-THERMAL PROCESS

Iono-thermal synthesis is another evolving method where MOFs are synthesized in ionic liquid medium instead of the normal conventional water/organic solvent medium [86, 87]. Ionic liquids being used as solvents in chemical synthesis has scientifically proven to have an excellent solvating properties, recyclability, high thermal stability and zero vapour pressure [88, 89].

Figure 9. Iono-thermal setup for MOFs synthesis.Excerpted from [131], copyright 2013. Korean Journal of Chemical Engineers

One of the known MOF that was synthesized by this process is the famous HUSK-1, where, choline chloride/dimethyl urea was used as solvent [88].

MICROFLUIDIC PROCESS

The search for suitable, cost effective and efficient methods of MOF synthesis is earnestly on the high, as various scientists in the field are on a look for a better and improved methodologies with a prospect for higher yield of MOFs. This is exactly what microfluidic processes stand at addressing [91].

Figure 10. Microfluidic Setup for MOF synthesis. Excerpted from [131], copyright 2013. Korean Journal of Chemical Engineers

Recent advancement in this path has seen thorough research of HKUST-1 with the help of a microfluidic device [92, 93]. Further details about the process could be found in [91-93].

Applications of metal organic frameworks

As earlier stated, Metal-Organic Frameworks has important applications in areas such as; storage of gases, heterogeneous catalysis, solar energy, super-capacitors, chemical sensing, therapeutic and diagnostics in biomedicine [8-10], owing to its considerable porosity and inherent surface area, and versatility in properties of the materials involved in its formation. Few of the applications are discussed here in this review.

Catalysis

MOFs have found a great niche in every facet of catalysis and catalytic reactions, ranging from photo-catalysis, electro-catalysis, redox catalysis, bronsted acid catalysis, Lewis acid catalysis etc. In the spirit of candor, MOFs incorporation to catalyze has made catalysis a more interesting field of research and widened its scopes of applicability. A lot of new MOFs are synthesized by green chemistry and they are and as well in the future will be useful in the biological aspects to retrieve some environmental issues with highly efficient recyclable capability of catalyst [136]. Some new and novel synthesis techniques were also been done for the synthesis of symmetrical and unsymmetrical compounds/MOFs from stable halides and other components like ethyl potassium xanthogenate. Their catalytic yield for some compounds is greater than 80% that showed a profound increment in MOF industry [137].

Electrocatalysts

The importance of platinum based catalyst in electro-catalytic reactions cannot be overemphasized but the main hindrance of this widely used compound is its scarcity and cost inefficiencies. So, substitution of Pt-group metals with a cost effective and abundant compound like MOF has a great potential for the future of green devices and energy generation. MOFs have shown promising results in electro-catalytic reactions because of their versatility and usability. For examples; Yang and his co-workers in one of their research on the electrochemical reduction of CO_2 , introduced a thin films of nanosized MOFs as atomically derived, nanoscopic catalyst for the electrochemical reduction of CO_2 in aqueous medium [94]. Also in trying to simulate MOFs with efficient electrocatalytic properties for Oxygen evolution, Zang, Li and their team of researchers employed an alkaline stable, metal hydroxide [MOF-X27-OH]([$Co_2(\mu-OH)_2(BBTA)$]) for the successful evolution of Oxygen [95]. MAF-X27-OH was obtained by postsynthetic ion exchange of MAF-X27-Cl ([$Co_2(\mu-OH)_2(BBTA)$]) Cl)₂(BBTA)]), which possesses open metal sites on its pore surface. After the hydroxide functionalization of MAF-X27-Cl, the electro-catalytic activity of MAF-X27-OH for the oxygen evolution reaction (**OER**) was drastically improved (an overpotential of 292 mV at 10.0 mA.cm⁻² in 1.0 M KOH solution). In addition, isotope tracing experiments confirmed that the hydroxide ligands are involved in the **OER** process to provide a low energy intra framework coupling pathway.

Figure 11. 3D Coordination network and pore surface structures of MAF-X27-OH. Local coordination environments of b) water-appended MAFX27-Cl, c) guest-free MAF-X27-Cl, d) water-appended MAF-X27-OH, and e) guest-free MAF-X27-OH. f) Solid–liquid coupling pathway for MAF-X27-Cl.g) Intra framework coupling pathway for MAF-X27-OH. Excerpt X.F. LU and co [95] Copyright 2016, American Chemical Society

Redox catalysis

Incorporation redox catalyst to the cavity of various MOFs has shown a great potentials application in energy conversion storage, drug delivery, chemical production and environmental remediation [96, 97]. A lot of MOFs has been used for several purposes within this context and also the linkers of various MOFs have been functionalized by some researchers for the epoxidation of Olefins in Chemical Industries. And in a similar vein, functionalization of MOFs with MO (IV) has proven to be very effective in lots of epoxidation reaction; posing about 99% conversion rate.

Recent advancement in this area has seen MOFs being functionalized with metal and metal oxides nanoparticles with the aim of simulating the famous $Cu/ZnO/Al_2O_3$ ternary catalyst used in industries for the seamless catalytic hydrogenation of CO_2 into methanol [98].

After the initial synthesis of a bpy functionalized Zr-MOF, UiO-bpy, Cu^{2+} was made to be metallated into the active and free sites of bpy, then, a Zn^{2+} ion was introduced reacting with ZnEt2 and μ_3 -OH sites on the $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4(COO)_{12}]$ cluster. The resulting Cu/ZnOx nanoparticles which were generated through in situ means in the presence of H₂ at a controlled temperature of 250 °C were in situ generated. The catalyst obtained aftermath, Cu/ZnOx@MOF showed a great potential for high activity and 100% selectivity for CO₂ hydrogenation to methanol.

Figure 12. Synthesis of CuZn@UiO-bpy via in situ reduction of postsyntheticallymetalatedUiO-bpy.Excerpt from. [98] Copyright 2017, American Chemical Society

Photocatalysis

Photo-catalysis is a promising field of study that's focused on the conversion of solar to chemical energy for various uses [99]. MOFs have found an excellent application in research that's connected to photo-catalysts owing to the presumable photo-responsiveness of some of it components. The absorption of light by the metal centers, organic linkers and other components of Metal-Organic Frameworks rendered it very useful in photo-catalytic reactions. Through photo-catalytic processes, various MOFs have been used for the generation of Hydrogen [100, 101], reduction of CO₂ [102], Oxidation of alcohol and water [103], degradation of toxins in water [104] and reduction of Cr(vi) [105]. Also functionalized MOFs are utilized in the visible-light driven for the evolution of

hydrogen and Oxygen from water [106, 107]. Research have also shown the versatility and usability of MOFs for the photo-catalytic degradation of Organic dyes and antibiotics [108, 109], oxidation of alcohol [110] and evolution of hydrogen [111] when the photo-responsive sites of MOFs are modified [112] and molecular catalysts are encapsulated into one another [113-116]. A lot has been done in and more research are ongoing to improve of the tenability and flexibility of MOFs in photocatalytic reactions. As shown in Figure 13 above, substitution of Zr in NH₂-Uio-66(Zr) partially by post-synthetic exchange (**PSE**) method using Ti moieties lead to the mixed metal NH₂-Uio-66(Zr/Ti) with improved photo-catalytic performance for CO₂ reduction under visible light irradiations. The experiment proved beyond reasonable doubt that NNU-28 is highly efficient for visible-light-driven CO₂ reduction with a formate formation rate of 183.3 mmol.h⁻¹.mmol MOF⁻¹¹³⁵

Figure 13. Dual photo-catalytic routes for visible-light driven CO₂ reduction in NNU-28. Excerpted from [134]. Copyright 2016, Journal of Material Chemistry

Biological application and drug delivery

MOFs have been very useful in various biological application and drug manufacturing processes since its discovery. It has been conversed before in the above section that a new type of MOFs which are efficiently reusable catalyst. The benefits which are eco-friendly can be used for biological practice like $Zn_3(BTC)_2$ MOF a novel, recyclable and porous catalyst [138]. The reusability, high isolated yield of the catalyst, ethanol as a reaction medium (green solvent) serve as a beneficial pros for these kinds of features. A lot of nontoxic metal-based MOFs are used in drug delivery systems because of their biocompatibility and high stability in biological environments [117]. Recent advancements in metal organic frameworks has given industrial researchers and pharmaceutical scientists the impetus and freedom to effectively control the release of drugs in a highly organized manner, this is due to the flexibility and multivariate nature of MOFs [118]. The stability and tenability of MOFs has garnered it more potential uses in pharmaceutical and medicinal industries as nanocarriers in the delivery of synthetic medicines.

Sensing, adsorption and seperation

In chemical sensing, MOFs has been used in various capacities for the detection of ketonic compounds in aqueous solution, recent advancement has shown a great potentials for the compounds being used in the detection and possible removal of several antibiotics, toxins and explosives in water [119]. Moreso, looking at Figure 14 critically, A fumarate-based RE-fcu-MOF if manufactured as thin film and grown to electrodes has shown by researchers to convert stimuli directly to electronic signals and will show a very considerable amount of sensitivity towards H₂S gas [120]. This particular kind of MOFs are built on **fcu** topology, which is iso-structural to the Zrbased MOF-801. It normally offers a selective H₂S detection to concentrations as low as 100 ppb with a detection limit of 5.4 ppb. In the same vein, Owing to the porosity of MOFs, it has been used and currently being used in various gas storage and separation technologies. A lot has been done to investigate the retention and uptake ability of a certain MOF, PCN-250-(FeM), and the result was superbly positive [121]. In the production processes of thermal batteries, delivery of drinking water in dry areas and various dehumidification processes, adsorption of water is very important [122-126], and the hydro stability of MOFs made it one of the best compound for this purpose. This is not enough, in the areas of air pollution and because of its tunability it has also been used for removal of toxic gases from the atmosphere [127-130].

Figure 14. Schematic representation of the preparation the fumarate based cfcu-MOF thin film on the interdigitated electrode. Excerpt from [120] Copyright 2016, Wiley-VCH

Conclusion

With the increasing research in the field of Metal-Organic Frameworks for various scientific endeavors, there is an urgent need for a better understanding for most of the main synthetic routes towards its synthesis and directives on their applications. In the course of the review, all the known MOFs synthetic routes were highlighted and their applications in various scientific fields were discussed in detail.

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