Metal-Organic Framework for Energy Application

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SUBMITTED BY

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CANDIDATE'S DECLARTION

We Sachin Kumar (2K21/MSCCHE/39) and Aizak (2K21/MSCCHE/03) students of M.Sc (Chemistry) hereby declare that the project Dissertation titled " Metal-Organic Framework for Energy Application " which is submitted by us to the Department of Applied Chemistry, Delhi Technological University, Delhi in the partial fulfillment of the requirement for the award of the degree of Master of Science, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma, Associate-ship. Fellowship or other similar title or recognition.

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CERTIFICATE

We hereby certify that the Project Dissertation titled " Metal-Organic Framework for Energy Application " which is submitted by Sachin Kumar (2K21/MSCCHE/39) & Aizak(2K21/MSCCHE/03), Department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the Master of Science, is a record of the project work carried out by the student under my supervision. To the best of my/our knowledge this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

Place: Delhi

Date: 23/05/2023 **Dr. Raminder Kaur**
(Supervisor)

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Sachin Kumar & Aizak

Abstract

Researchers are frantically looking for clean, alternative energy sources to replace fossil fuels because of the rising pollution levels and the continuously growing need for energy. Therefore, it is crucial to produce carriers that can be used for storing energy or for the promotion of mass and electron transfer in storing and conversion of energy. New opportunities for the conversion, storage, and use of renewable energy have been created by the continued progress in the field of metal-organic frameworks (MOF). The exceptional characteristics of MOFs, their composites, and related compounds have prompted to be intriguing and hence, an increase in investment, leading to the development of unique and innovatory materials for use in the energy sector. The following project presents a summary of latest advancements in the field of storing and conversion of energy using MOFs and their composition, with a focus on the link between structure, composition, and function.

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1. Introduction

Recently, our attention has been on the creation of sustainable and clean energy storage to combat environmental degradation. Thus, the development of energy carriers or energy transportation is crucial. Because of its intrinsic benefits, including structural diversity, functionality, and various other useful applications, the metal-organic framework (MOF) chemistry is well suited for such purposes [1]. Moreover, metal-organic frameworks (MOFs) combine organic-inorganic entities and provide a highly porous structure, uniform arrangement of constituents, variable pore size, topologies, and multi-functionality.

Because of its properties and the present-day development of MOFs, this led to the conventional energy application. MOFs also have excellent gas storage capacity. The remarkable capabilities of these frameworks and related compounds have sparked the development of novel materials for use in the energy sector. Along with a current assessment of their multiple energy uses, the following is a summary of the configurations, components, and distinctive qualities of these frameworks which are favourable for converting and storing energy, namely, fuel storage; photo-induced H_2 evolution; and reduction of carbon dioxide. Fuel and solar cells, supercapacitors, Li- batteries, fuel cells, and water electrolysis are among the other technologies.

2. ABOUT METAL-ORGANIC FRAMEWORKS

2.1 What are metal-organic frameworks?

Recent advances in metal-organic frameworks (MOFs) in materials chemistry are very intriguing. These materials are crystalline, and constructed from metal-containing nodes and organic linkers.

They can be structured in varying pore sizes with high surface areas of up to 10,000 m^2/g as compared to activated carbon and zeolites which have surface areas of 3500 m2/g and 1000 m^2/g respectively [2].

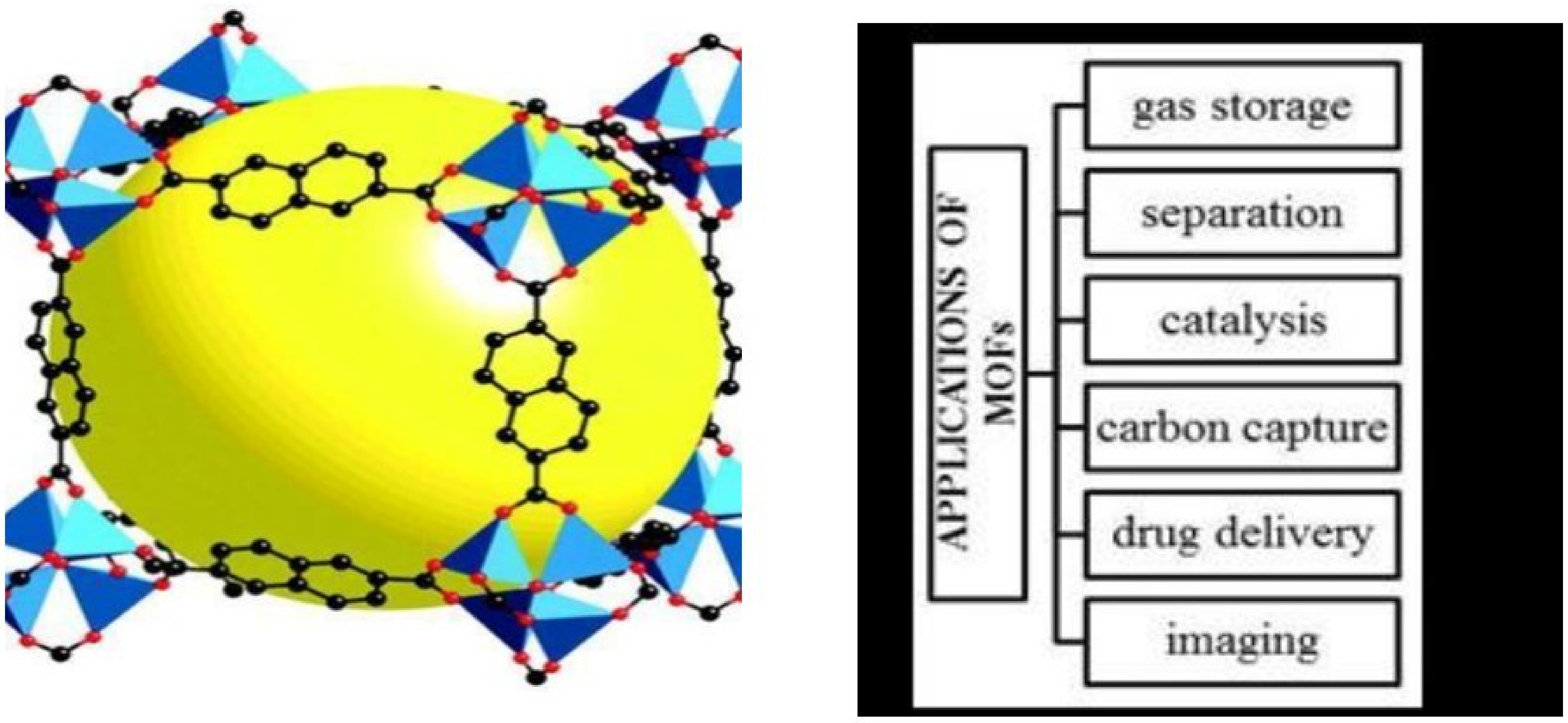


Fig 1: Crystal Structures in metal-organic frameworks (a) MOF-5. (b) Application of MOFs.

An MOF is described as "a transition metal bonded to an oxygen or nitrogen atom via polymeric bond" (CSD, Cambridge Structural Database) [4], where the term "polymeric bond" refers to bonds between several monomer units. This definition, however, has two significant flaws.

First, it limits to only transition metal ions, excluding alkali, alkaline-earth metal ions and metalloids.

Second, the organic linkers may not always be oxygen or nitrogen.

A coordination polymer is a coordination compound that extends continuously in 1, 2, and 3 dimensions and is connected by coordinate bonds [3]. The current IUPAC definition, which incorporates these two recommendations, is "a coordination polymer (or coordination network) with an open framework containing potential voids."

MOFs can be understood as a class of hybrid materials where a single-phase crystalline material is formed from inorganic and organic counterparts. Porosity is an important characteristic which results from organic frameworks playing the role of linkers between metal nodes, popularly known as porous coordination polymers or PCPs.

Scientists and engineers have shown a keen interest in MOF structures materials because of the structural and functional tuning of these materials, as well as their versatile application scope. They have been carefully studied for prospective commercial applications such as gas storage and separation, heterogeneous catalysis, chemical sensing, biomedical applications, and proton conduction, in addition to academic uses including intermediate trapping and energy transfer.

Due to their unique construction, and a wide choice of components they can be used to create alterable properties, i.e., crystalline, high porosity and a large specific area, depending on the application of interest.

The seven MOF building-block requirements may be defined by various connections between the two main building blocks of MOFs, the metal units and organic linkers (Fig. 2).

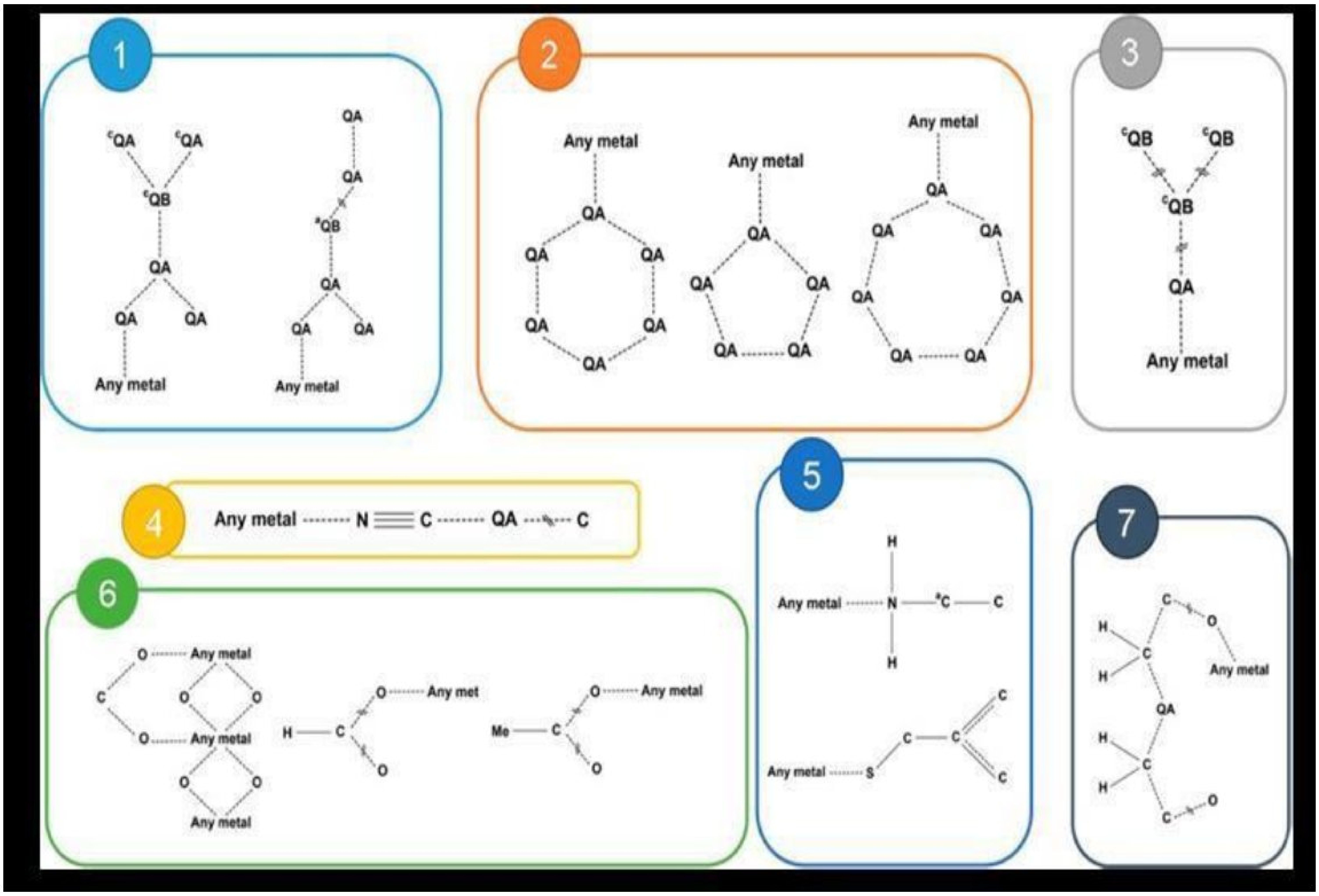


Fig 2. The seven criteria that were used to create the CSD MOF subset, where QA = O, N, P, C, B, and S. Superscripts "c" and "a" force the corresponding atoms to be "cyclic" or "acyclic," respectively, in the equation QB = N, P, B, S, and C. Me stands for methyl groups. Any of the bond types (single, double, triple, quadruple, aromatic, polymeric, delocalized, and pi) that are stored in the CSD are represented by the dotted line. A variable bond type, which includes two or more of the possibilities above, is shown by the dotted line with two lines through it. The variable type in these scenarios might be single, double, or delocalized.

(Ref- 4.P. Z. Moghadam, A. Li, S. B. Wiggin, A. Tao, A. G. P. Maloney, P. A. Wood, S. C. Ward and D. Fairen-Jimenez, Chem. Mater., 2017, 29, 2618-2625)

2.2 Synthesis

An important circumstance for MOF synthesis is the formation of a stable metal-ligand bond, but these bonds should not be so stable that it inhibits the propagation of structures. To allow propagation these bonds should be able to break and reform at the same time. This kind of dynamic bonding pattern is the key to forming the orderly arranged crystalline materials so that any irregularity in bonding can be fixed to avoid disorders or premature termination (5).

SOLVOTHERMAL SYNTHESIS:

The most popular technique for creating MOFs is solvothermal synthesis. A high-boiling solvent, such as DMF, DMSO, or DEF, is used to combine a metal salt with an organic linker. After that, the mixture is cooked for 12 to 48 hours in an oven.

By varying parameters like pH, temperature, time, concentrations and nature of reagents used properties of the synthesised MOFs can be altered. These factors affect the size, pore structure and purity of the material. For instance, a metal chloride when mixed with a linker of carboxylic acid will release a large amount of HCl in which the MOF may be dissolved which leads to very slow crystallization, but if metal acetylacetonate (M(acac)x) derivative is used, then a milder by-product, acetylacetone is obtained which does not affect the crystallization process.

The following are a few essential requirements for synthesis:

(i) The metal salt and organic linker must be soluble at reaction temperature.

(ii) The balanced chemical equation of the synthesis must be known.

(iii) Sufficient space in the reaction vessel must be left empty to allow for the potential build-up of pressure during the course of the reaction.

Taking an example of Zr based MOFs in which strong bonds of Zr(IV) and O are present, non-structural modulators like hydrochloric, benzoic, or acetic acids can be made use of in order to avoid rapid precipitation and to increase crystallization time to compete with metal coordination sites.

An alternate synthesis method involves the construction of secondary building units (SBUs) having metals and then mixing them with a linker in presence of a modulator for the synthesis of MOF. By forming metal-SBUs separately, optimization of surface area and phase purity is done. For instance, by synthesising and keeping the metal cluster nodes isolated [Fe3O(OOCCH3)6OH], a series of MOFs of metalloporphyrin containing nodes of Fe3, PCN-600(M), were created. These node clusters were then combined with a modulator and a linker made from a porphyrin derivative. DMF is heated in an oven over night after adding acid. In-situ generation of metal-clusters nodes before adding structural organic linkers is also a variation of this method.

Electrochemical, mechanochemical, sonochemical and microwave-assisted methods are also some strategies for MOF synthesis. Liquid phase epitaxial growth, layer-by-layer deposition or development from seeds on a protected substrate are some methods that can be used to create MOF thin films.

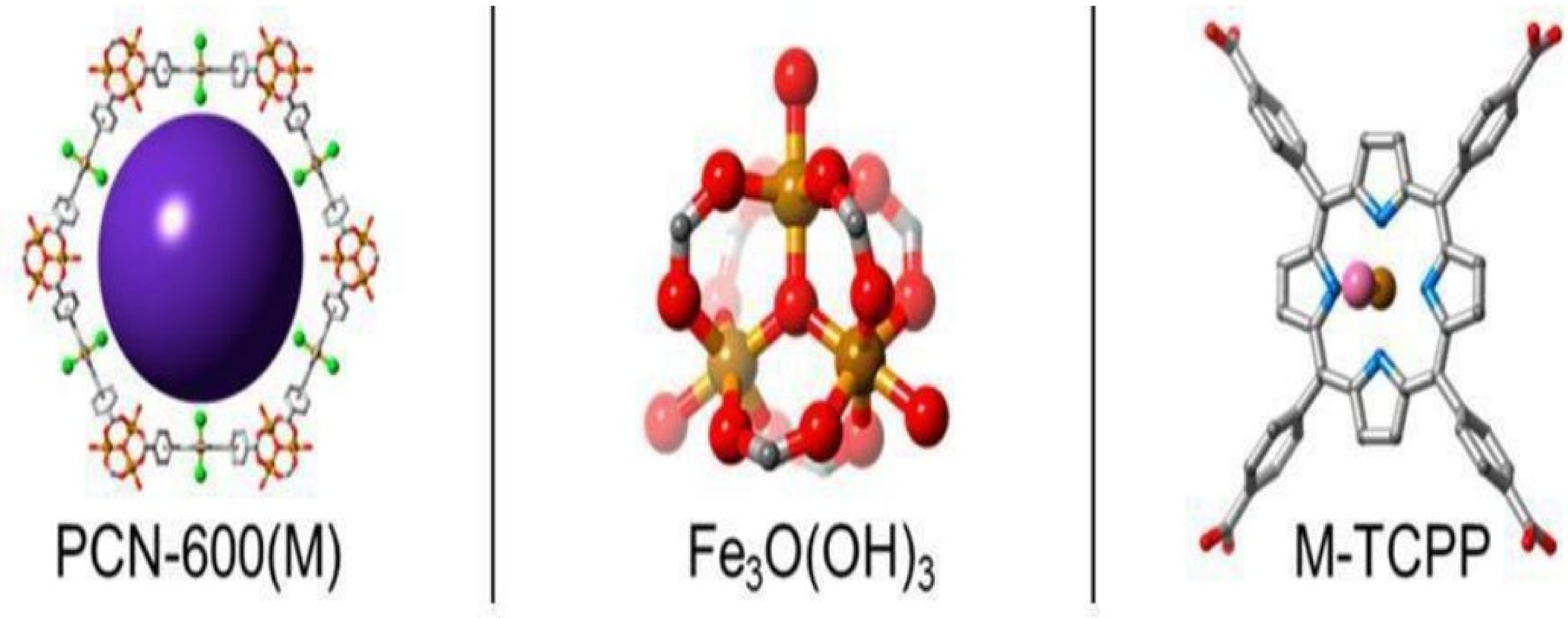


Fig. 3 PCN-600(M) MOF with $Fe_3O(OH)_3$ metal cluster; Fe: yellow, O: red, C: grey Ref-5

3. H_2 and CH_4 storage:

3.1 Storage by Physical Adsorption Process:

H_2 storage :

Although H_2 is a non-polluting energy source, it is also very combustible, which makes H_2 storage materials with large volumetric densities crucial in real-world applications. Since MOFs are highly porous, they have attracted as the H_2 adsorbent. In 2003, MOF-5 (fig 4a) was the first discovered MOF with H_2 storage ability. With the greatest surface area and the maximum H_2 storage capacity to far, MOF-210, which possesses net H_2 gravimetric absorption of 17.6% (w/w) at 79 and 77, atm and K respectively, is one example of the remarkable developments made in the field thus far. By introducing alkaline or alkaline earth metal ions (such as Li^+ and Mg^{2+}), metal nanoparticles, and small pores in the MOFs their H_2 performance can be significantly improved. Even if these MOF-based adsorbents are capable of storing the necessary amount of H_2 at very less temperatures, it is still difficult to fulfil the industrial H_2 storage aim at room temperature. [6]

CH_4 storage :

CH_4, which is frequently referred to as natural gas, is the hydrocarbon with the highest H to C ratio (4 out of every hydrocarbon compounds) and the highest octane number (107). Because they are porous, metal-organic frameworks are employed in adsorbed natural gas (ANG) technology. Also, its properties such as pore volume and Brunauer-Emmett-Teller (BET) surface area are well known. As a result, its most important application is the physical adsorption of CH4. Under high pressure, the total amount of gas adsorption by MOFs is directly proportional to the above-mentioned properties viz. p0re volume and BET surface area however, when the benzene ring of one such MOF is switched out for the pyrimidine ring, an unanticipated rise in volumetric absorption is seen. [7]. While other porous adsorbent materials' capacity to store CH4 is superior to MOF in using volumetric or gravimetric methods, MOF mediums' ability to adsorb CH4 is much superior. But a lot of work and advancement is required to get desired adsorbents before they can be made commercially available for ANG technology and related applications.

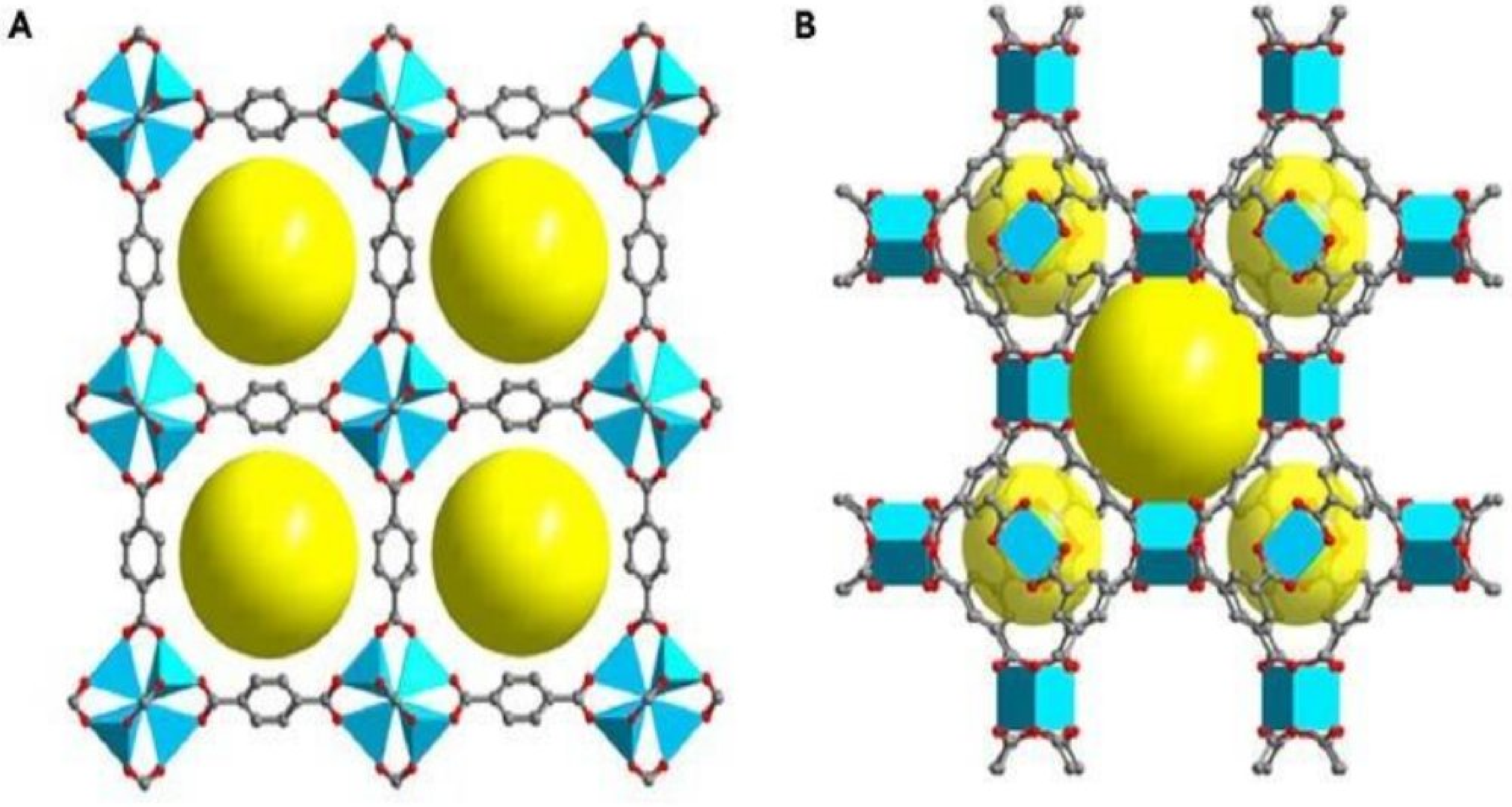


Figure (4) : (a) MOF-5 (b) HKUST-1.

Ref.6 Rosi, N.L., Eckert, J., Eddaoudi, M., Vodak, D.T., Kim, J., O'Keeffe, M., and Yaghi, O.M. (2003). Hydrogen storage in microporous metal–organic frameworks. Science 300, 1127–1129.

3.2 Chemical hydrogen storage

Researchers and scientists are working to increase the density and reduce the cost of currently available hydrogen storage systems, and also working in the direction to develop new technologies which can exceed or at least match the conventional gasoline systems in terms of performance and cost characteristics. The term "chemical hydrogen storage" refers to storage technologies in which

(i) hydrogen gas is liberated by a chemical reaction and

(ii) hydrogen is absorbed again into the system by a chemical reaction for fuel cells.

It is a secure and cost-effective alternative to physical hydrogen storage. MOFs can hold such compounds like chemical hydrides in their nanopores, out of which hydrogen gas can be released later under mild conditions. Furthermore, the rate of release of hydrogen from chemical hydrides in the liquid phase is improved by incorporating MOF-supported metal nanoparticles as catalysts in the system.

Confinement of chemical hydride nanoparticles:

Due to two factors, the confinement of hydrides nanoparticles in the MOF pores is frequently exploited in hydrogen storage:

(i) It changes the thermodynamic properties of chemical hydrides.

(ii) It improves dehydrogenation rates while suppressing the release of other unwanted gaseous by-products.

Numerous light-weight hydrides incorporating metals (Li, Na, Mg, and Ca) and inorganic elements (B, Al, and N) have been utilised to create them due to their high volumetric and gravimetric energy densities. It is first attempted with HKUST-1(fig-4b) [8] confined in solid $NaAlH_4$. The obtained HKUST-1 $NaAlH_4$ MOF showed a dehydrogenation temperature of 343 K which is much lower than 523 K in the case of $NaAlH_4$ alone. This temperature difference is due to a change in the process's thermodynamics and accelerated hydrogen desorption kinetics when chemical hydrides confined in nonporous materials are used. To confine ammonia boron and increase the hydrogen desorption kinetics while decreasing the liberation of other volatile by-product formations in the process, Pt@MIL-101 was used, which is a MOF embedded with a metal nanoparticle.

4. Solar energy conversion:

Solar energy, a clean and unlimited source, comes into the picture whenever clean energy and environmental issues are addressed. Solar energy-based photocatalysis is an efficient method of converting solar energy into fuel energy and could offer a significant contribution to preventing environmental and energy crises. Additionally, solar energy may be used to power an electrochemical cell's chemical capacitance or the Nernst potential of electrolytes.

4.1 Hydrogen production by MOF-based photocatalysis:

Hydrogen has currently proven to be an ideal alternative to fossil fuels which can be obtained from water in the presence of photocatalysts. In the presence of [Ru(bpy)3]2+

photosensitizer, the ruthenium-based MOF complex [Ru2(1,4-benzene dicarboxylic acid)2]n) was employed in 2009 to degrade water [9]. Its turnover number and quantum yield were reported to be 8.16 and 4.28% respectively.

MOF combined with noble metal results in more efficient hydrogen production. An alternate method involves the incorporation of organic ligands derivatized from $[Ru(bpy)_3]^{2+}$ or $[Ir (ppy)_2(bpy)]^+$ into photosensitizer-based photocatalytic MOF systems. Many molecules like amorphous C_3N_4, metal, metal oxide and polyoxometalate. can be integrated with MOF to synthesize photocatalysis sensitizer material for the photocatalysis reaction (Fig5).

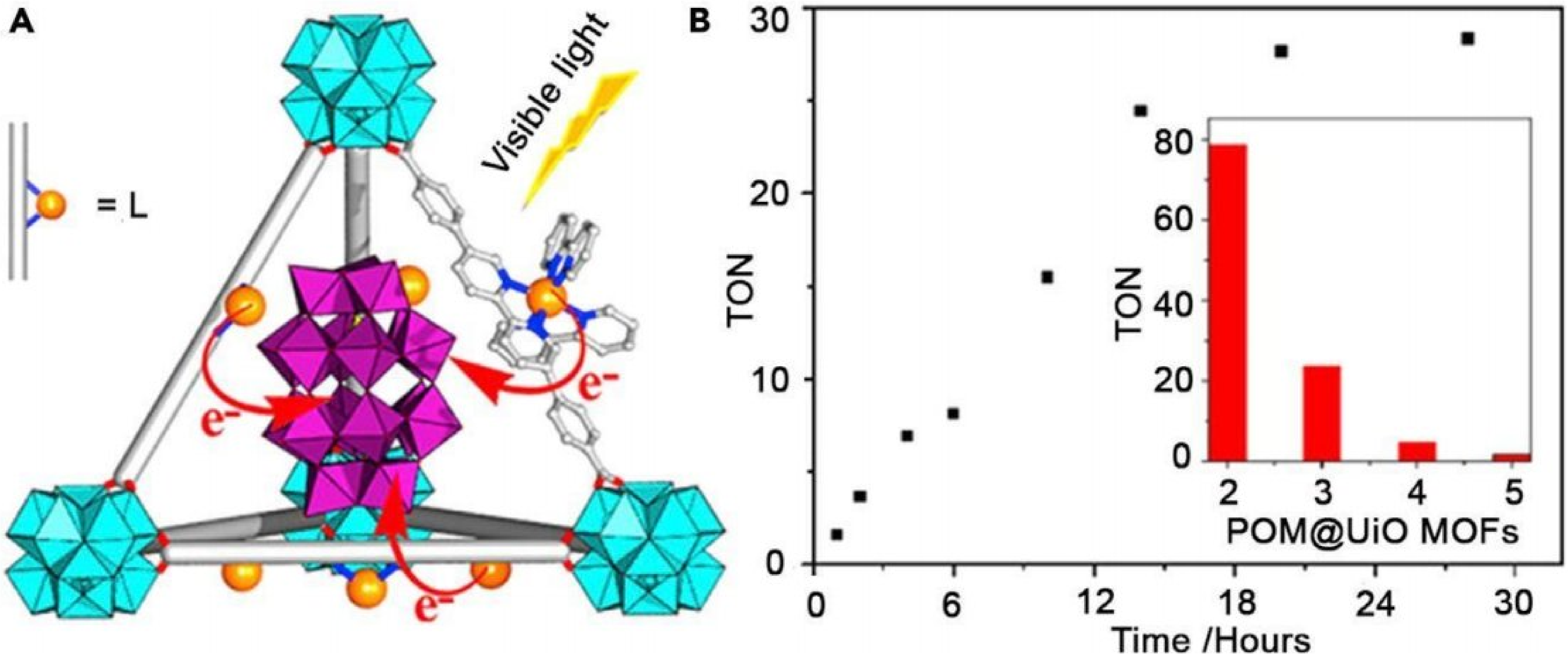


Figure 5 shows evolution of H_2 by photocatalysis over a MOF catalyst with POM implantation.

A. Diagram demonstrating the visible-light stimulation of the MOF framework and the absorption of electrons in the POM system.

B. Methanol serving as the sacrificed electron donor in a MOF catalyst with time-dependent HER TONs.

Ref-10

In an intriguing system, Wells-Dawson polyoxometalate (WD-POM) [P2W18O62]6- cluster which is anionic in nature may be absorbed by a [Ru(bpy)3]2+ based framework (soluble in water) named SMOF-1 (supramolecular MOF), increasing the kinetics of H2 photoliberation.

4.2 Carbon dioxide reduction by MOF-based photocatalysis:

CO_2 which is one of the elements in the greenhouse gases which pose a threat to the ozone layer and the environment. Hence, the reduction of CO_2 has posed to be an important issue to be dealt with and scientists and researchers have been working on it for quite some time now. Also, the restoration of CO_2 back as a fuel gives a solution to the problems due to high CO_2 emission. Because of the benefits of cost, improved efficiency, and increased recyclability, photosynthesizing simple organic compounds like formic acid, formaldehyde, methanol and methane is an ideal strategy for reducing and consuming excess CO_2. In general, natural photosynthesis consists of the following three steps:

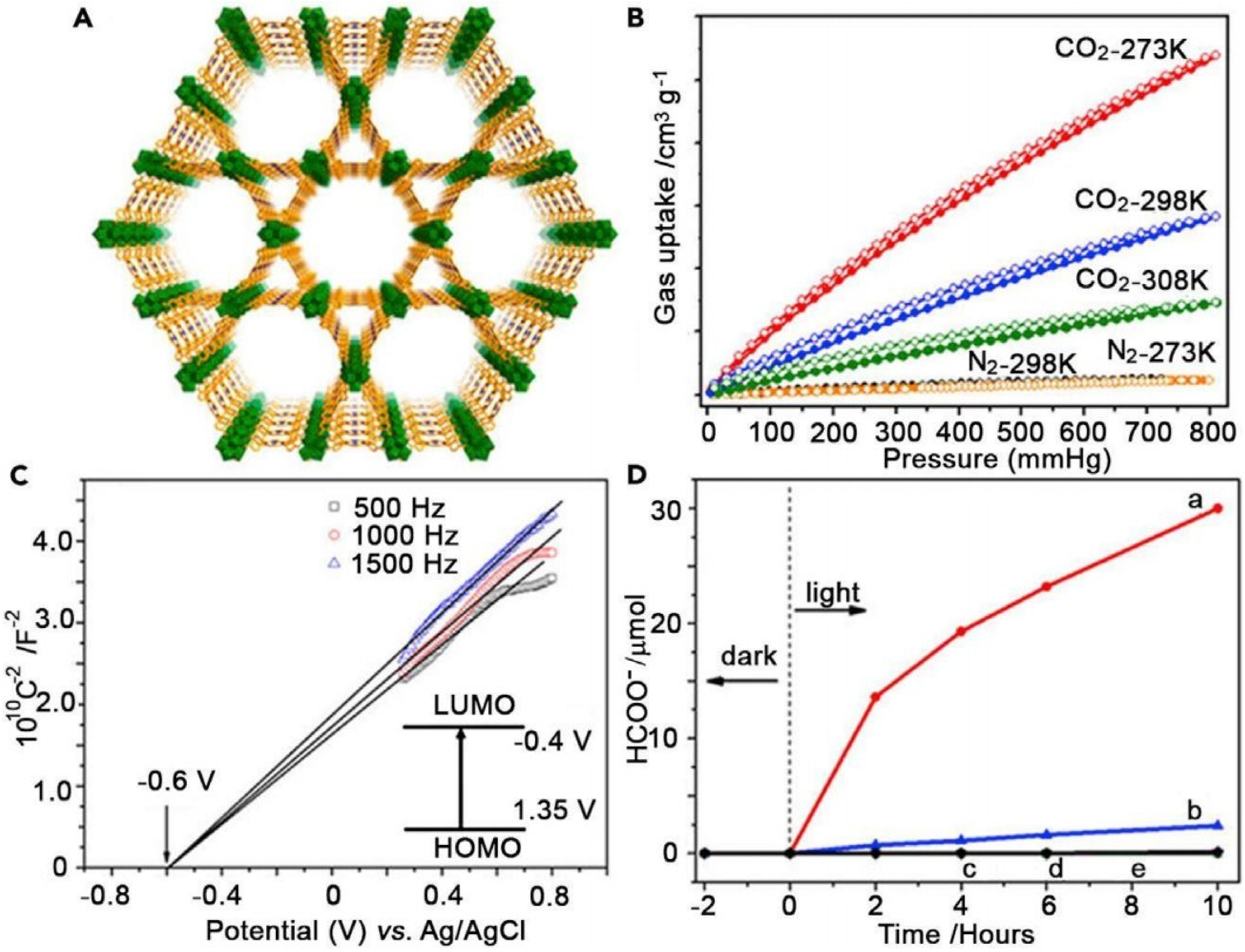
(i) Light adsorption in photosystems

(ii) Transfer of charges

(iii) Conversion by photocatalysis and desorption (CO2 adsorption and conversion).

The idea is to use solar energy to activate CO2 and MOF-based catalysts to transform it into fuels. The first photocatalytic MOF-based catalyst that could decrease CO2 was created by incorporating [ReI(CO)3(dcbpy)Cl] (dcbpy = 2,2′-bipyridyl-5,5′-dicarboxylic acid) as a catalytic component into a very stable and porous MOF (UiO-67). The equal distribution of [ReI(CO)3(dcbpy)Cl] in active MOF sites led to a unimolecular mechanism for CO2 reduction by photocatalytic MOF. Excellent for reducing CO2 is PCN-222, a porphyrin-based MOF photocatalyst that operates in the visible spectrum (fig 6).

However, the photoactivities of MOF photocatalysts for CO_2 reduction are still far from the photoactivities of conventional semiconductor species. A clever strategy is the combination of MOFs with inorganic semiconductors to improve charge separation and charge gathering efficiencies. Furthermore, by varying the density of MOF (increasing repetitive units i.e., increasing ‘n’ number) in the framework peak photocatalytic activity of Re_3MOF was obtained. Moreover, photocatalytic MOF units can be exposed to a high electromagnetic field in less volume. This improves activity for visible radiation-induced photoreduction of CO_2.



CO_2 Reduction via Photo-Induced Over a MOF Catalyst
(A) Showing the PCN-222 3-Dimensional structure.
(B) Showing the PCN-222 gas sorption isotherms.
(C) Showing PCN-222 plot created by Mott-Schottky.
(D) Time-dependent amount of HCOO under visible-light irradiation. (Ref 11)

4.3 Photoelectric Conversion:

A solar cell, also known as a photovoltaic cell, is an electrical device that converts light energy directly into electric energy by the application of photovoltaic effect, which is a physiochemical phenomenon. This is another application of MOFs. A thin, crystalline, porphyric-based MOF sheet with a high porosity Zn-SURMOF2 was produced with high conductivity substrate using the liquid phase epitoxy technique [12]. The current-voltage or the I-V curve properties for the photovoltaic cell and MOF-modified version are given in the table below:

	Short Circuit Current (I_{SC}) (mA cm^{-2})	Open Circuit Voltage (V_{OC}) (V)	Efficiency (η)
Photovoltaic cell	0.45	0.57	0.20 %
Photovoltaic cell with immobilized Pd (II) ions	0.71	0.70	0.45 %

Thus, the photophysical activities of the cell are highly improved because of the prevention of direct electron-hole recombination.

5. ENERGY STORAGE BY ELECTRICITY AND ITS CONVERSION:

5.1 Fuel Cells :

We can describe fuel cell as an electrochemical cell which, through an electrochemical reaction, generates electrical energy from the fuel i.e., combustion energy is converted to electric energy. Hydrogen gas (H_2) and oxygen gas (O_2) are passed through a conductive porous membrane usually a proton exchange membrane. The products of the redox reaction in the fuel cell are water, electricity, and heat. This is another clean energy option that can be used for various purposes. After all fuel cells are costly, less efficient and do not last for long. So, fuel cells can be combined with MOFs and their derivatives to reduce costs and improve efficiencies.

5.2 Proton Conduction:

Scientists are interested in PEMFCs because they have interesting onboard uses. PEMFC is an abbreviation for polymer electrolyte membrane fuel cells. The well-known fluoropolymer called Nafion, created by DuPont, is used as a PEM material due to good conductive nature of proton i.e., proton conductivity, stable chemically and thermally. It is a crucial link for the development of novel electrolyte materials having better proton conductivity. Newly developed MOFs with very good proton conductivities and affordable synthesis methods are favourable for future developments in the field of fuel cell electrolytes. MOFs are able to support low and humid temperatures below 100 degrees in Celsius and also in dry circumstances above 100 degrees in Celsius.

The first proton-conducting MOF that operates in low temperature ranges, [(NH4)2(adp)Zn2(ox)3], was published in 2009.3H2O-n, whose performance is equivalent to that of nafion (fig. 7a), where adp denotes adipic acid and ox denotes oxalic acid. This MOF's proton conductivity was measured at 298 K and a relative humidity (RH) of 98%, and it was determined to be 8x103 S cm-1.

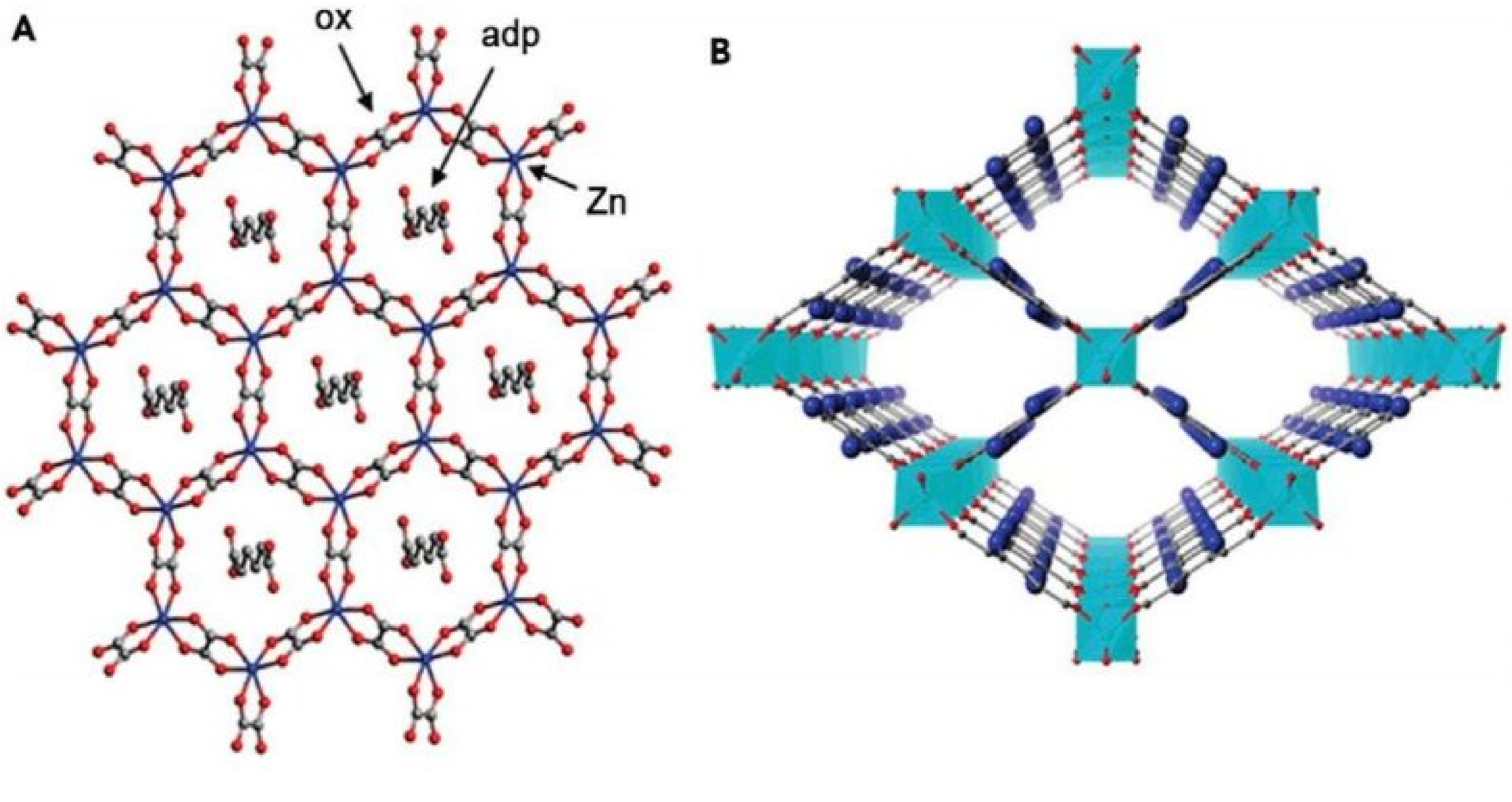


Figure 7. Proton Conductors based on MOF

(A) $\{(NH_4)_2(adp)[Zn_2(ox)_3].3H_2O\}_n$ structure excluding ammonium ions (Honeycomb layer) ref 13

(B) MIL-53 crystal structure. Functional groups are represented by the light blue C atoms, red O atoms, and blue atoms. (–NH2, –OH, or –COOH).

Using Cr-Au electrodes, a highly orientated MOF nanofilm of [Cu(TCPP)]n was created, where TCPP stands for 5,10,15,20-tetrakis (4- carboxyphenyl)porphyrin. The nanostructured sample was placed on a Si wafer (SiO_2 with 300 nm thickness) and placed between the electrodes. (Figure 8). This nanofilm was found to be having a conductivity of 3.93103 S cm^{-1} which is unusually high at 98% RH. This might be due to the numerous hanging groups on the nanosheet surface, including non-coordinated carboxyl groups, acidic coordinated water, as well as thin films.

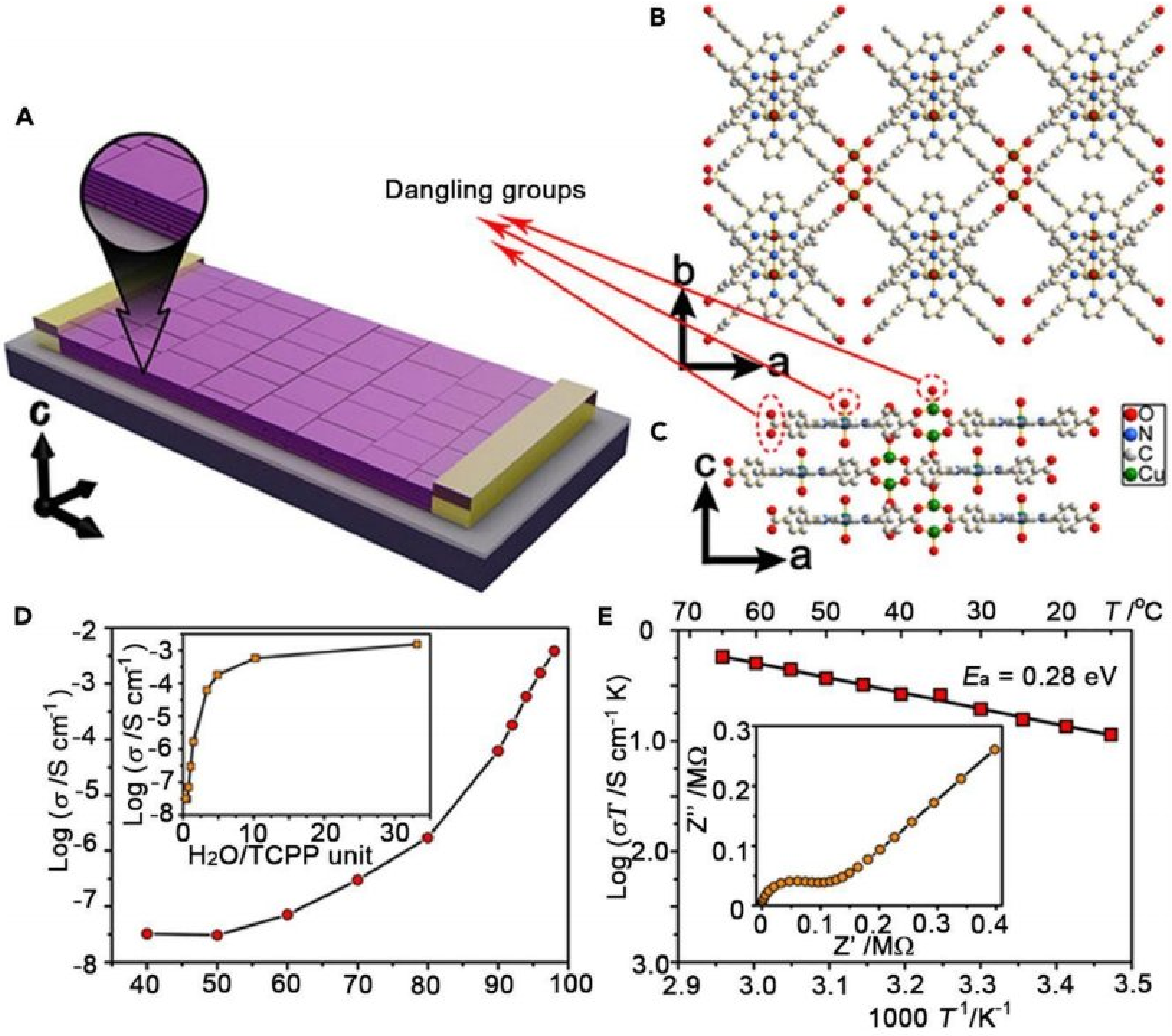


Figure 8. Proton Conducting MOF film

(A) MOF nanofilm made of nanosheet.

(B, C) Showing a MOF nanofilm schematic model.

(D) Showing MOF nanofilms' proton conductivities at different conditions of RH. Comparison of MOF film proton conductivities to adsorbed water at 95% RH is shown in the inset.

(E) Using a solid line, least-squares fitting is displayed. The inset shows a MOF nanofilm

Nyquist curve observed at room temperature and 98% relative humidity. ref 15

In case of high-temperature range proton conductors, the introduction of non-volatile agents like triazole, imidazole, histamine, and benzimidazole is also a very effective technique even acids like H_2SO_4 and H_3PO_4 can be used for the pores of MOFs to provide simple proton movement channels in order to enhance conduction of proton at temperatures as high as above 373 K in dry circumstances. [16]

5.3 Supercapacitors:

Supercapacitors (SC) or ultracapacitors, are high-capacity capacitors having substantially larger capacitance values than conventional capacitors but low voltage limits., Because of their high-power density, fast charge/discharge rates, extended lifecycle, and environmental friendliness, these supercapacitors, also known as electrochemical capacitors, have piqued the interest of many researchers.

Pure MOF SCs, even though they have great porosity, typically have less specific capacitance because of weak conductivity. In order to improve SC performance, MOFs can be combined with graphene and polymers with good conductivity. Investigation of a wide range of nanocrystalline MOFs with various metals, ligands, architectures, and pore volumes has been done. Supercapacitors based on $\{Zr_6O_4(OH)_4(bpydc)_6\}_n$ (bpydc=2,2'-bipyridine-5,5'-dicarboxylate) nanocrystals show the highest SC performance with a stack capacitance value of 0.64 mF cm^{-2} and areal capacitance of 5.09 mF cm^{-2} (in fig9). Recently, an MOF with a very good conductive nature, [Ni3(hitp)2]n (where hitp is abbreviated for 2,3,6,7,10,11-hexaiminotriphenylene), is claimed to have been evaluated for EDLC.

A newly developed MOF was used as a single electrode material in a MOF-based SC that was created without the need of any organic binders or conductive fillers; its discharge rates and gravimetric capacitance are greater than those of carbon nanotubes with values of 0.05 A g-1 and 111 F g-1, respectively. This MOF-based SC has a very high surface area, 18 mF cm^{-2} normalized capacitance and its capacity remains intact even after 10,000 cycles, better than the majority of carbon-based products except some materials. Bipolar operating flexibility, fast charge and discharge rates and low weights, among other benefits of carbon SCs, encourage the use of nonporous carbons generated from MOFs in capacitive applications. An innovative method was used in 2008 to create NPCs utilising FA as a secondary carbon source and MOF-5 as a precursor template. 204 Fg1 of capacitance and a 5 mVs-1 sweep rate was shown by these NPCs.

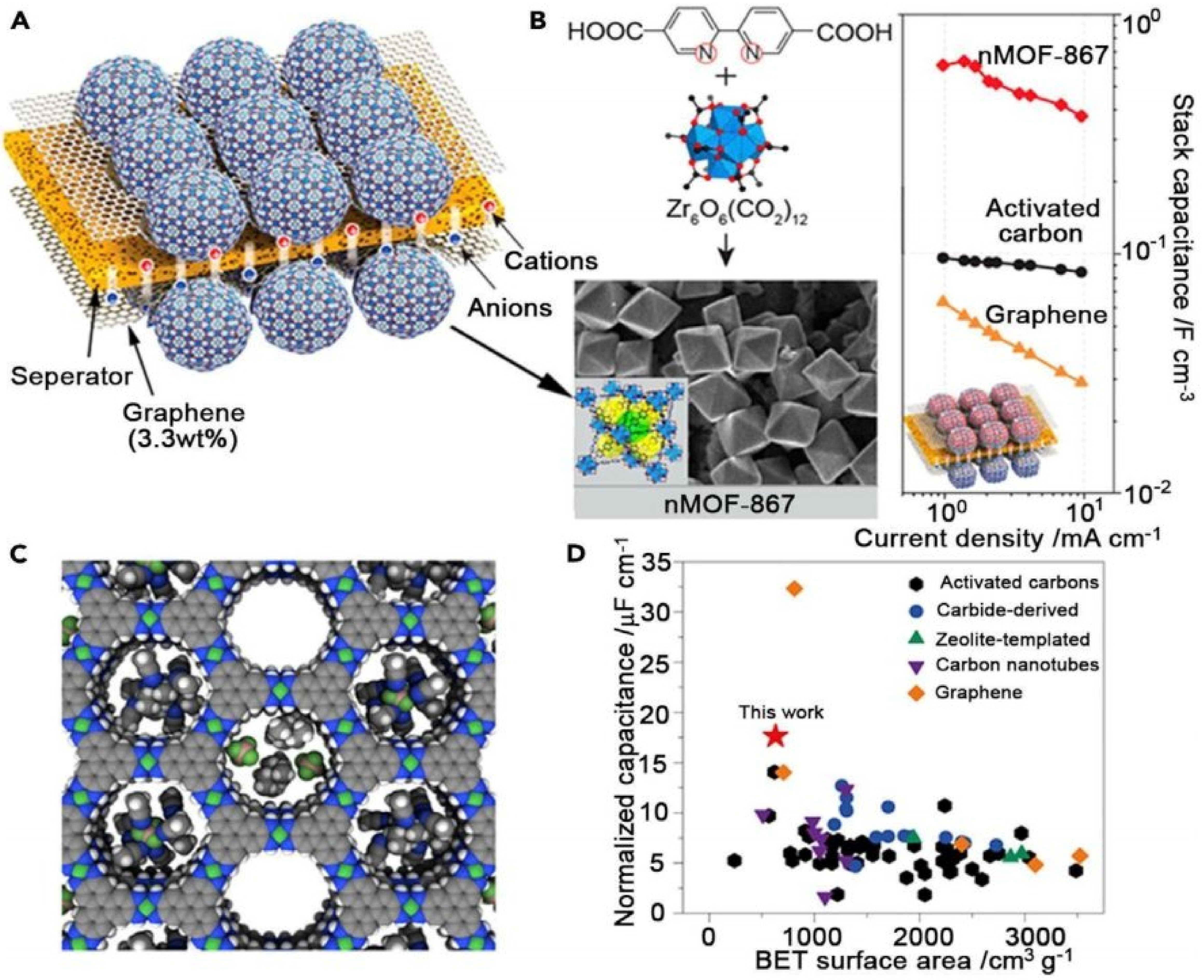


Figure 9. MOF-Based Supercapacitors

(A) Illustrative diagram for nMOF-based supercapacitors.

(B) Structure of nMOF-867 and the morphology of its nanocrystals.

(C) An idealised diagram of Ni3(hitp)2 is shown in (C). (Where C atoms, grey; B atoms, brown; H atoms, white; Ni atoms, green; N atoms, blue; F atoms, lime).9

(D) Areal capacitance as per normalized BET-surface-area and comparison of different EDLC materials. Ref 17

In a publication published a few years back, investigations were also conducted into the [Ni3(hitp)2]n MOF's EDLC behaviour (hitp = 2,3,6,7,10,11- hexaiminotriphenylene). (Figure 9).

SCs are classified into two categories based on their energy storage mechanism:

(i) Electric double layer capacitance (EDLC)

(ii) pseudo-capacitance.

The first carbonization of MOFs for use as SCs was reported in 2008, with outstanding electrochemical performance.

Using amorphous coordination polymer shells and a fast thermal oxidation technique, seven-layered nanostructures of anions of Ni-Co oxides were created in 2017.

There are some benefits to the carbon-based SCs which motivate capacitive uses of MOF-derived nonporous carbons, such as low weight, quick charging-discharging rates, and operating bipolar flexibility.

In 2018, a 2D MOF was used as a high-performance electrode which was built of ultra-tiny hexamine benzene (HAB), it was used in aqueous acid and alkaline. [18] A higher volumetric capacitances (760 F cm3), good areal capacitances (over 20 F cm2), and highly reversible redox behaviours shown by MOFs' multilayer porous structure and high packing density qualities, were caused by the HAB's tiny size.

Figure 10: Systematic diagram for MOFs application as Lithium-ion batteries and Supercapacitors.

5.4 Lithium Batteries:

In the early 1990s, lithium-ion batteries (LIBs) were marketed. Since then, LIBs have grown fast in popularity because of their high energy density and inexpensive cost, development of LIBs also received a Nobel prize in 2019. Graphite is an anode (negatively charged electrode) while layered oxides are used as the cathode (positively charged electrode). Oxides commonly used for cathode are ($Li[Ni_xCo_yMn_z]O_2$), $LiFePO_4$, and $LiMn_2O_4$. [19]

MOFs having a wide surface area and a high porosity can provide additional reaction sites and a conduit for charge carriers to diffuse. MOFs are so employed as electrodes (both positive and negative), electrolyte, matrix, and precursor materials in LIBs, as well as in supercapacitors in form of electrode and precursor materials.

Because of their low cycling capacity, reversible Li^+ ion movement was not supported by MOF-177 and Zn-based MOFs such as Mn-LCP (manganese layered coordination polymer). Because of their high discharge capacities of MOFs, the development of novel LIB anode materials is also a scope for the future. An intercalated MOF (abbreviated as iMOF) comprised of 2,6-naphthalene dicarboxylate was discovered as a potential anode material for the intercalation of Li+ ions in 2014.[20]

The first MOF-based cell, which showed high - (i)cell voltage, (ii)specific power, (iii)specific energy, and (iv)excellent cyclability, was made using iMOF at anode and LiNi0.5Mn1 at cathode. This shows that MOFs can be utilised as anode components in LIBs.

The challenge now is to produce reversible ion creation and generation for improved performance. In laboratories, a number of experiments were run for this. After 50 cycles, a graphene-based MOF (derived from ZIF-8) with nitrogen doping achieved a reversible specific capacitance of 2.13 Ahg-1 with 0.1 Ag-1 current density(Figure 11). This shows promise for highly efficient anode materials in LIBs.

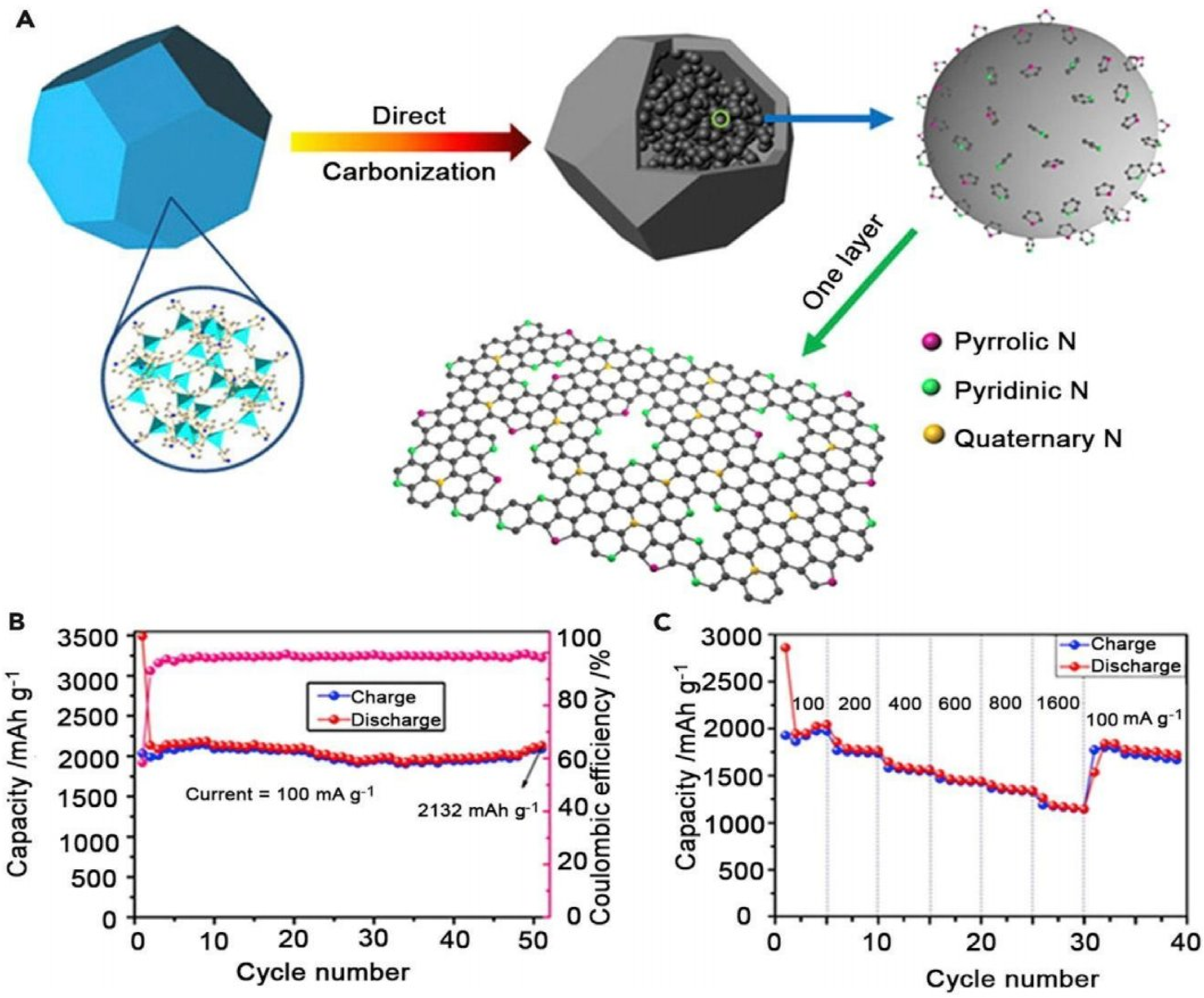


Figure 11. As a LIB Anode, MOF Derivative and Corresponding Behaviour

(A) Diagram of the process for creating analogues of graphene (N-doped) and a model showing the N-doping.

(B) Showing implementation of cycling process at a 100 mAg-1 current density.
(C) A graph showing capacity against cycle number with coulombic efficiency is shown. This graph shows its behaviour at various current densities between 100 and 1,600 Ag-1.

Alternately, a Fe_2O_3 based fibrous material has been derived by a pyrolysis strategy in a two-step process, it was derived from MIL-88-Fe. [22] In comparison to pure metal oxides, these MOF-doped metal oxides typically exhibit poor cyclability. One proposed option is to cover or envelop metal oxides with a carbon-based nanostructure that is porous in nature. Thus, NiO/Ni/graphene mixed composite structure gives 1.14 Ahg-1, a high reversible specific capacity, and outstanding cyclability (capacity retention of almost 100% after 1,000 cycles).

Since 2007, the development of MOF-derived electrode materials and LIBs-based MOFs has escalated quickly. A Li-based electrochemical cell with a cathode made of MIL-53(Fe) desolvation and 15% conductive carbon was constructed. Until now, it has been challenging to solve issues like low capacity and capacity retention. Additionally, standard cathode materials have been modified using compounds made from MOFs.

Next generation LIBs :

The initial MOF-based Li-O2 batteries were created in 2014. Li-O2 Batteries are the next-generation LIBs; Li-O_2 has an energy density of 3500 $Whkg^{-1}$ and Li-S has an energy density of 2500 $Whkg^{-1}$ which is higher than the usual LIBs.

Li-O2 LIBs were created using metal anodes, electrolyte-soaked separators, and cathodic active material. The disadvantages of Li-O2 LIBs' inefficiencies are as follows:

a) The electrode pores were sealed and air flow was impeded by the accumulation of by-products which are insoluble on the anode and cathode surfaces.

b) The multi-phase ORR/OER at the air cathode is slower than the anode reaction.

c) Non-uniform deposition, dendritic development, and change of shape in metal anodes were brought on by the dissolution and deposition of metal. [23]

The development of Li-O2 LIBs has been aided by MOFs, MOF composites, and its derivatives, such as Li-air batteries. Air batteries come in a variety of forms, including Al-air batteries, Na-air batteries and Zn-air batteries.

Challenges in Metal-Sulphur Batteries (MSBs):

a) The inability to manage the metal-electrolyte interaction

b) The insulating properties of sulphur and the solid reduction products create poor electrode recharge rate capability.

c) The decrease in capacity due to movement caused by numerous dissolvable polysulphide intermediates of polysulphides between the cathode and anode.

In order to solve these problems, MSBs were developed, which may provide microchannels for ion transport while simultaneously separating the cathode and anode to prevent short circuits. Co9S8-Celgard was an effective barrier for LiPSs in Li-S batteries created in 2018. (LiPSs = Lithium Polysulphides)

6. Electrolysis of Water:

Water is electrolysed into oxygen and hydrogen gas by passing an electric current.

This process can be used to create hydrogen gas, a key clean fuel, and breathing oxygen gas, these two can be combined to create oxyhydrogen, which can also be used as fuel but it is more volatile and dangerous.

Also known as water splitting. To split water, an EMF of 1.23 volts is ideal. Effective energy conversion technologies include electrolysis cells, metal-air batteries, fuel cells and electrolysis by water splitting. These technologies rely on the following three key electrochemical reactions namely, HER, OER, and ORR. (OER= Oxygen Evolution Process, HER= Hydrogen Evolution Reaction, ORR= Oxygen Reduction Process)

Thanks to the employment of MOFs, their composites, and their derivatives as potential electrocatalysts, the electrolysis of water has advanced quickly.

Hydrogen evolution reaction (HER):

H_2 gas production by electrical decomposition of water is a highly efficient way to get this fuel. We need a costly Noble metal-based agent to catalyse this reaction. MOFs, their derivatives, and their composites have been developed as HER catalysts in recent years due to their appropriate properties; yet, they must increase their catalytic activity and long-term stability. N- doped carbon produced from UiO- 66-NH 2 MOF had high hydrogen evolution reaction (HER) activity and stability as well.

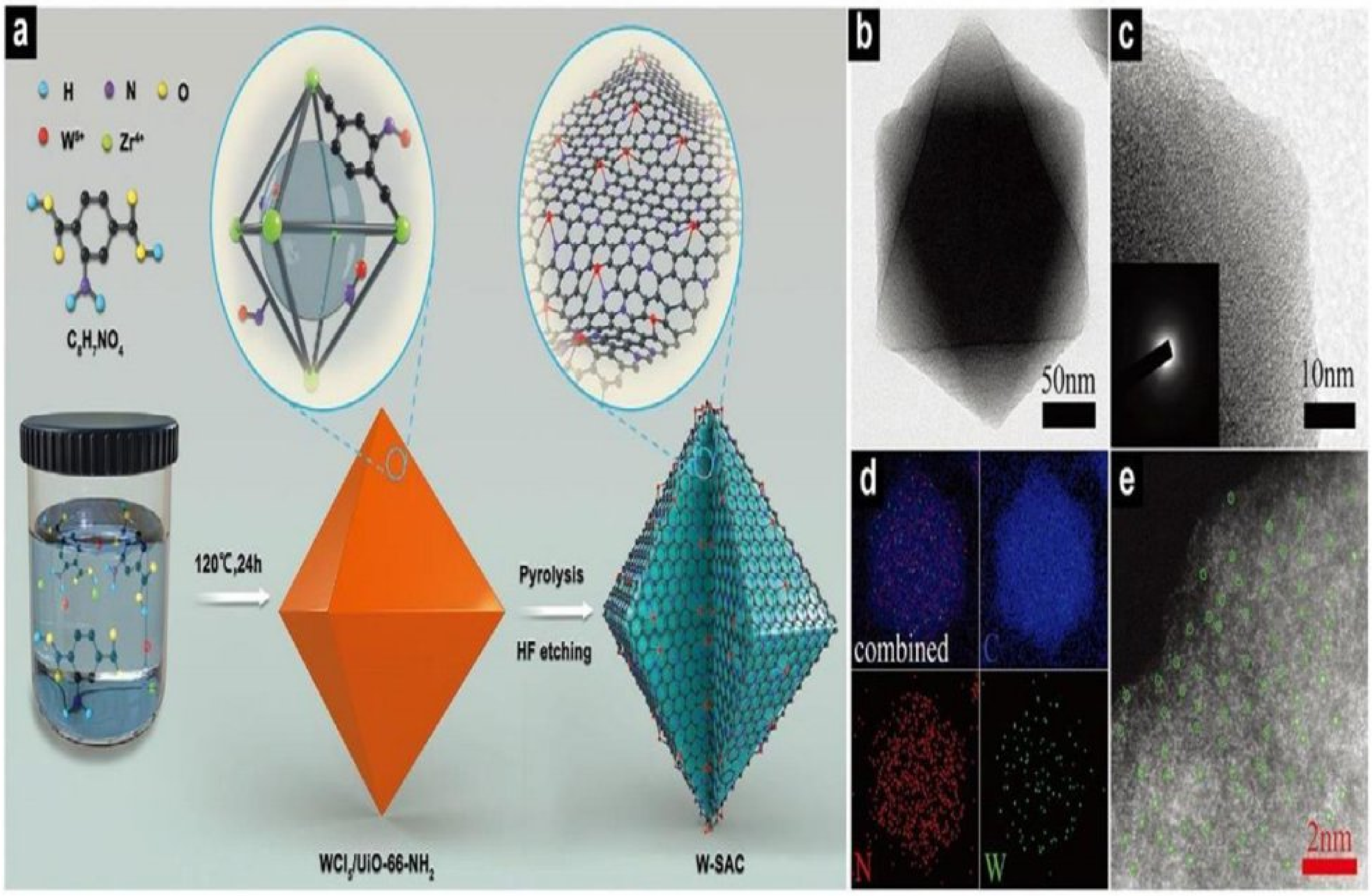


Fig. 12. a) Schematic diagram for the formation of W-SAC; b, c) Characterizations of the W-SAC at different magnifications using TEM; d) Mapping of the W- SAC using EDS; e) The HAADF-STEM image of the W-SAC. Ref 24

Oxygen evolution reaction (OER) :

Reaction involved

$H_2O \rightarrow 1/2O_2 + 2H^+$

The poor kinetics process and multistep proton-coupled electron transfer impede this reaction. Metal oxides, metal phosphides, and metal sulphides, which are MOF derivates, are desirable electrocatalysts for OER because of their high conductivity, abundance of metal active sites, excellent electron transport, and speedy mass transfer.

To increase OER, a hybrid CeOx/CoS (Fig. 13 a) made of hollow CoS generated from ZIF-67 and embellished with CeOx NPs was recently developed.

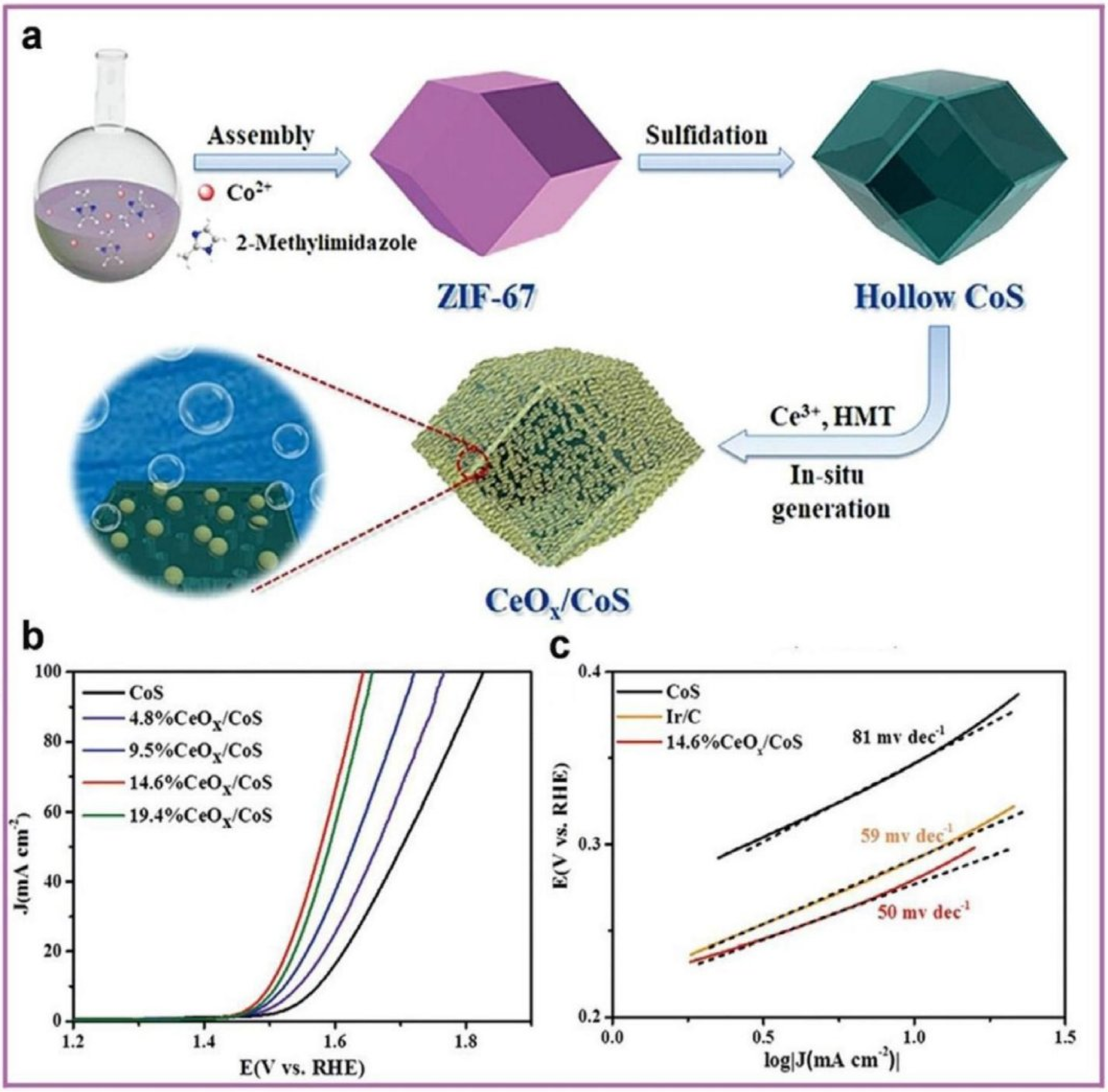


Fig. 13. a) Showing the method used to create the hybrid CeOx/CoS nanostructure.

b) Showing the OER's CoS and CeOx/CoS LSV curves.

c) Depicting the OER Tafel plots (adapted by approval)Ref 25

Ultrathin nanosheets of Ni, Bi, Co mounted on copper foam was employed as an Oxygen Evolution Reaction catalyst in 2016.

In situ formation of nanosheet of NiFe-based MOF (MIL-53) on Ni foam was reported in 2018 using a one-step solvothermal technique.

Oxygen Reduction Reaction or ORR:

Only on the cathode of electrochemical devices that convert energy does the ORR, a reaction that determines rate, take place. The ORR may be improved by substituting metal atoms and porous carbons with N-atoms, according to recent study. By employing MOFs as sacrificial templates, numerous N-doped and carbons loaded with single metal atom with substantial surface areas have been produced during thermal transformation.

The coupling of carbon nanotubes with MOF results in materials with strong electrocatalytic activity and rapid mass movement. These materials also have a large specific surface area, an acceptable distribution of pore size, sufficient doping, internal voids, and robust frameworks.

In order to produce ORR catalysts with metal that was slightly less costly and N-doping, covalent organic polymers that were synthesised in situ in the pores of crystalline metal organic frameworks were thermally treated in the year 2017.

7. Future Approach:

Since MOF is a rich ongoing research field and has plenty of applications in various aspects like environmental remedies, catalytic activity, photo catalysation and other energy-related applications.

Hence, there are many scopes in the application and the field of research as well.

1. MOFs are highly porous, in acidic and basic mediums and also at a high temperature, they tend to be the least stable and also least conductive. Additional attempts at improving MOF stability and conductivity are envisaged.

2. Despite significant recent progress in the precise control of microstructure nanomaterials derived from MOFs, including di-atoms, single atoms and metal cluster catalysts, continuous work is needed to make this strategy workable in real-world applications.

8. Conclusions:

In recent decades, there have been several attempts to build metallic-organic frameworks (MOFs) to achieve suitable renewable energy conversion, usage, and storage, along with the constant study on establishing novel ideas and methods of renewable energy application. Some of the examples addressed. Examples from this study help to clarify the workings and characteristics of MOFs as well as some of its uses in energy-related fields.

We have come to the conclusion that, as a means of gas molecule storage, enhancing gas diffusion, aiding mass, electron, and charge transportation, cultivating exoteric energy, facilitating reactant activation, enhancing conductivity and durability, etc., MOFs, composites, and derivatives play significant roles in the storage and conversion of photo and electrochemical energy.

When converting and storing electrical energy, MOF derivatives can boost material cyclability and quicken reaction kinetics. This study describes recent developments in the use of all sorts of MOFs for energy-related uses.

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