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Significance of Copper Benzene 1,3,5-tricarboxylate Metal Organic Framework: Environmental and Biomedical Applications

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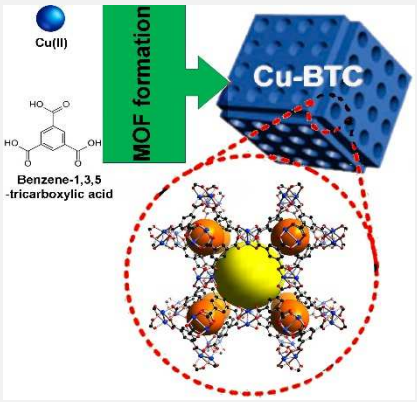
ABSTRACT

Copper benzene 1,3,5-tri carboxylates are widely used in research due to their numerous advantages. With abundant resources, excellent catalytic activity, and relatively simple synthetic procedures, Cu MOFs are ideal for activating starting materials and creating complex structural designs. The tunable conditions promote useful reactions such as oxidation, click chemistry, and Friedel-Crafts alkylation. All these properties make Cu MOFs an excellent choice for scientific research. This review provides an overview of this rapidly evolving research field, highlighting novel $Cu_3(BTC)_2$ synthesis strategies and $Cu_3(BTC)_2$ applications such as electrochemical sensing and metal ion extraction, energy storage, drug delivery, and its role as a catalyst.

Keywords: Copper catalyst, heterogenous catalysis, metal-organic frameworks, sensors, energy storage, drug delivery



1. Introduction

Copper benzene 1,3,5-tricarboxylate (commonly known as HKUST-1 or MOF-199). Its high porosity and high surface area make it an ideal material for these applications. Additionally, HKUST-1 is very stable and can be synthesized in various shapes and sizes. Therefore, it is a highly versatile material that can be used for various applications. HKUST-1 is a powerful electron transfer agent widely used as an oxidizing agent in chemical synthesis reactions such as oxidation and dehydrogenation. It is also useful in photochemical processes and organic synthesis. This compound can also catalyze various organic transformations, such as polymerization and Suzuki-Miyaura coupling reactions. It is also used as a catalyst for organic reactions and as a support for other catalysts. It is an acid catalyst commonly used in many organic synthesis reactions. This catalyst is important because it stabilizes reactive intermediates such as aryl halides formed in organic synthesis reactions and also helps facilitate atom and group transfer reactions. $Cu_3(BTC)_2$ is particularly useful in the synthesis of polymers and other macromolecules, as it can facilitate the coupling of two different reactants. Furthermore, $Cu_3(BTC)_2$ is inexpensive and easy to use, making it an attractive option for organic synthesis.

In environmental science, HKUST-1 is expected to be an efficient adsorbent of carbon dioxide, an important greenhouse gas that causes global warming[1]. Solid adsorption is an environmentally friendly, simple, and energy-efficient method for long-term CO_2 capture, emphasizing the importance of novel adsorbents like Cu-BTC. A combination of Cu-BTC and graphene oxide effectively adsorbed methane for potential clean energy gas applications. The composite formed uniform, integrated pellets without needing a binder[2,3]. MOFs are also used for energy storage. For example, they have been synthesized in mixed phases as electrode materials for supercapacitors. The manufactured product has significantly improved specific capacitance compared to other electrodes, suggesting suitability for supercapacitor applications[4].Regarding gas storage, Cu-BTC was combined with carbon aerogels to

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increase pressure resistance. One of the most promising materials for gas storage applications, MOFs can adsorb large amounts of methane, the main component of natural gas[5].Cu-BTC has been investigated as an electrode in lithium-ion batteries (LIB) for energy conversion[6]. CuO's size and content were meticulously regulated to optimize the electrochemical performance of the Cu-BTC structure. These factors were crucial in facilitating efficient ion transport and high electrical conductivity, which directly influenced the overall performance and longevity of the lithium-ion batteries. Further studies are underway to fully comprehend and exploit the potential of this promising nanostructure[7].Finally, this review provides a comprehensive overview of various applications of Cu-BTC, focusing on the synthesis, reactivity, and applications of $Cu_3(BTC)_2$.

2. Advantages and disadvantages of Cu MOFs compared to traditional nanomaterials

Copper-based metal-organic frameworks (Cu-MOFs) are nanoporous materials that can be used in various applications due to their unique properties. They differ from conventional nanomaterials in several respects and thus have their advantages and disadvantages. Advantages of Cu-MOFs: High Surface Area: MOFs, including Cu-MOFs, typically have a very high surface area, which makes them excellent for applications such as gas storage and separation, catalysis, and sensing[8]. Tunability: The properties of MOFs can be easily tuned by varying the metal ion (in this case, Cu) and the organic ligand used to form the MOF. This allows for a wide range of possible structures and properties. Pore Size Control: The pore size of MOFs can be controlled at the molecular level, which can be beneficial for applications such as selective gas adsorption[8]. Functionalization: MOFs can be easily functionalized with different organic groups, further expanding their potential uses.

Disadvantages of Cu-MOFs: Stability: MOFs, including Cu-MOFs, are often less stable than traditional nanomaterials. They can degrade under certain conditions, such as high temperatures or in the presence of certain chemicals[9]. Complex Synthesis: The synthesis of MOFs can be more complex and time-consuming than that of traditional nanomaterials. The need for specific precursors and controlled reaction conditions can also make MOF synthesis more expensive[10]. Low Conductivity: Compared to traditional metallic nanoparticles, MOFs generally have lower electrical and thermal conductivities. This property could limit their use in applications where high conductivity is needed. Reproducibility Issues: Due to the complexity of their synthesis, achieving reproducibility in the structure and properties of MOFs can be challenging[10].

3. Recent synthesis of $Cu_3(BTC)_2$

Many techniques have been documented in published works for synthesizing $Cu_3(BTC)_2$. Here, we summarize recent studies showcasing various methods and their respective findings. Zhao et al. developed millimeter-scale poly(ether sulfone) composite beads loaded with porous Cu-BTC [$Cu_3(BTC)_2$, BTC = 1,3,5-benzenetricarboxylate] (Cu-BTC@PES) using a phase inversion method for the removal of volatile iodine. Three types of Cu-BTC@PES composite beads with different Cu-BTC contents (48.6%, 60.2%, and 71.9%) were obtained. These composite beads maintained crystallinity and exhibited higher I_2 vapor adsorption capacity (639 mg/g) in the form of iodine molecules (**Figure 1**) [11].

Figure 1. Millimeter-scale poly(ether sulfone) composite beads loaded with porous Cu-BTC[$Cu_3(BTC)_2$. Reprinted with permission from ref [11].

Pirzadeh et al. studied the electrochemical synthesis of $Cu_3(BTC)_2$, for CO_2 capture and separation from N_2. The Taguchi method was employed to optimize key synthesis parameters, determining the optimum conditions: 1 g of ligand, an applied voltage of 25 V, a synthesis time of 2 h, and electrode length of 3 cm. The synthesized microstructure $Cu_3(BTC)_2$ exhibited a significant single gas sorption capacity for CO_2 (4.40 mmol·g^{-1} at 298 K and 1bar)[12].
In another study by Irandoost et al., preparing the copper-based $Cu_3(BTC)_2$ in aqueous media was attempted as a green method (**Figure 2**) [13].

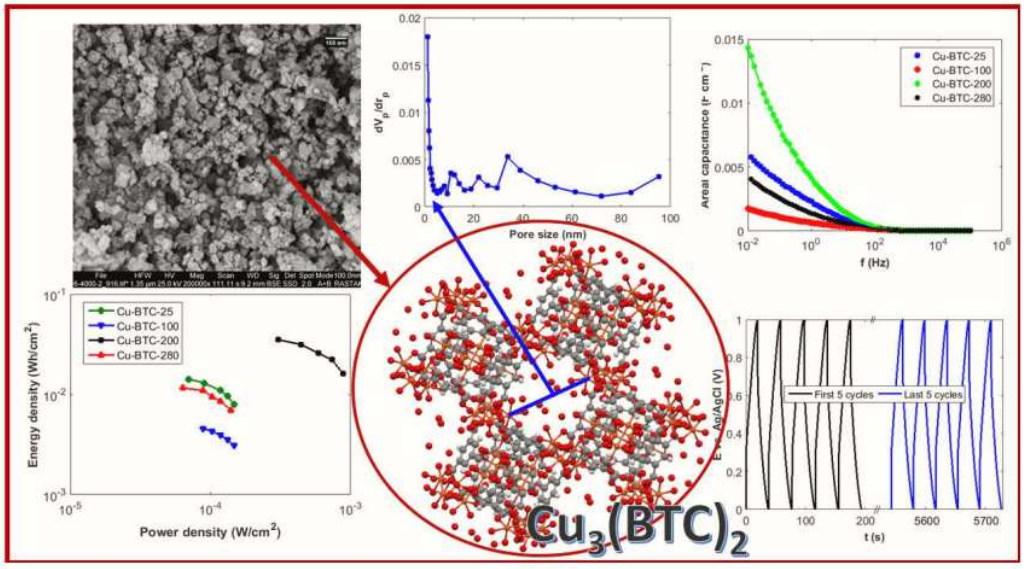

Figure 2. Electrochemical synthesis of $Cu_3(BTC)_2$, for CO_2 capture and separation from N_2. Reprinted with permission from ref [13].

Furthermore, a research team demonstrated the synthesis of $Cu_3(BTC)_2$ nanoflakes using a binary solvent of ionic liquid (IL) and water. This novel MOF architecture exhibited a high surface area and abundant unsaturated coordination metal sites, making it attractive for adsorption and catalysis. $Cu_3(BTC)_2$ nanoflakes displayed superior catalytic performance in the oxidation reactions of various alcohols compared to $Cu_3(BTC)_2$ microparticles synthesized in a conventional solvent. The team discovered that the IL accelerated the crystallization of $Cu_3(BTC)_2$ while facilitating the early-stage stripping of $Cu_3(BTC)_2$ blocks with water assistance. This in situ crystallization-exfoliation process using an IL/water solvent provides a new approach to producing low-dimensional MOFs with improved properties compared to their 3D counterparts[14].

Agbaje et al. developed a cost-effective and green synthesis method for $Cu_3(BTC)_2$ metal-organic framework (MOF) in crystalline powder form, utilizing a copper mesh as the metal source without additional metal precursors. The resulting MOF exhibited high crystallinity, small size (~2 μm), uniform crystal morphology, and mesoporosity. The CO_2 adsorption capacity of the MOF at various temperatures surpassed that of HKUST-1 synthesized through conventional methods, with higher CO_2/N_2 adsorptive selectivity and faster adsorption kinetics. Notably, the CO_2 uptake (~5.2 mmol/g at 1 bar and 25 °C) was among the highest reported for this MOF. Furthermore, this synthesis procedure demonstrated a high yield (up to 85%), reduced chemical requirements, and minimized waste generation compared to the solvothermal approach, making it suitable for scale-up production (**Figure 3**)[15].

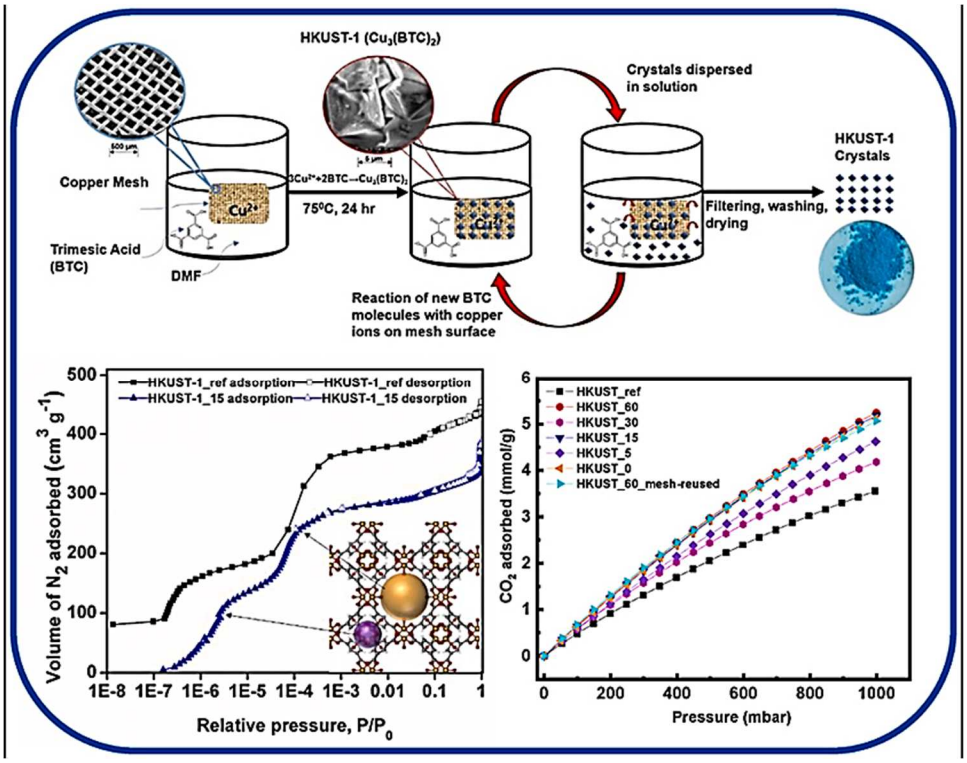

Figure 3. Green synthesis method for $Cu_3(BTC)_2$ metal-organic framework (MOF) in crystalline powder form. Reprinted with permission from ref [15].

Aqueous system synthesis of $Cu_3(BTC)_2$ with small crystal sizes was achieved by regulating Polyvinylpyrrolidone (PVP). It was observed that this molecule contributed to forming a hierarchical porous structure and functioned as a nucleating, coordination, and template agent. Furthermore, PVP helped to reduce the sizes of crystals for $Cu_3(BTC)_2$[16]. These studies explore techniques for synthesizing $Cu_3(BTC)_2$ and investigate its properties and applications in areas such as iodine removal, CO_2 capture, catalysis, and capacitive properties. These findings contribute to the understanding and development $Cu_3(BTC)_2$ -based materials for diverse applications (**Figure 4**)[16].

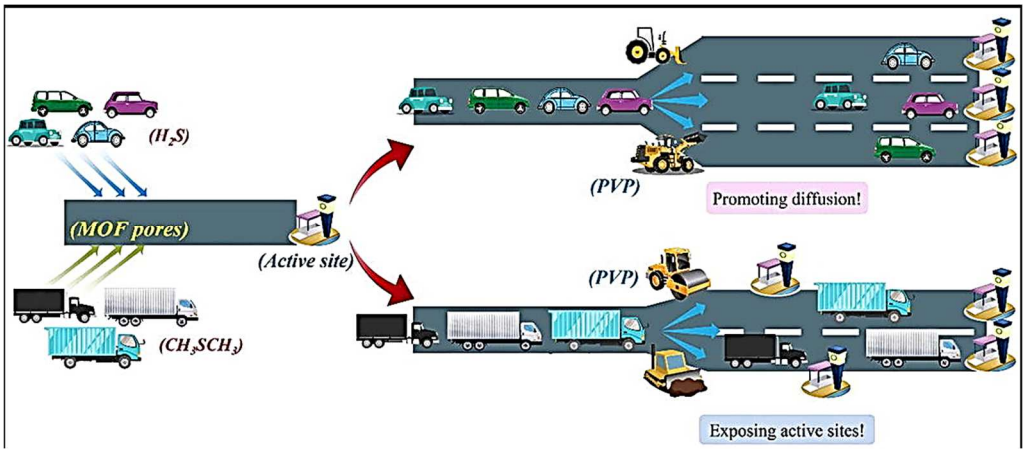

Figure 4. Aqueous system synthesis of $Cu_3(BTC)_2$ with small crystal sizes. Reprinted with permission from ref [16].

These mentioned studies demonstrate the versatility and applicability of $Cu_3(BTC)_2$ in numerous scientific fields, by employing various synthesis methods. Each method not only produced $Cu_3(BTC)_2$ with unique properties but

also expanded the potential applications of this MOF. It is noteworthy that all the mentioned methods can control the physical and chemical properties of $Cu_3(BTC)_2$, such as its porosity, crystallinity, particle size, and morphology, which can be tuned according to the specific application.

4. Applications

4.1. As Electrochemical sensors

Metal–organic frameworks (MOFs) have been investigated as electrode materials for developing electrochemical sensors. They have usually been reported to suffer from poor conductivity and improvement in the conductivity of MOFs is still a great challenge. There are some reports the fabrication of an electrochemical sensor based on the in situ growth of framework HKUST-1 on conductive fibres. A carbon dioxide (CO_2) sensor coated with HKUST-1, has been developed using an optical fibre long period grating (LPG). In-situ crystallization and layer by layer (LbL) techniques of HKUST-1 thin film synthesis were compared in terms of the feasibility of the deposition procedure (time and cost efficiency) and the sensitivity of the film to CO_2. The sensing mechanism is based on the measurement of the change of the refractive index (RI) of the coating that is induced by the penetration of CO_2 molecules into the HKUST-1 pores. Through scanning electron microscopy, the HKUST-1 film was characterized for thickness and RI using ellipsometry. Results indicated that an LPG modified with 10, 20 and 40 layers of HKUST-1 films using LbL method had good sensitivity to CO_2 in the range of 500 ppm to 40,000 ppm. The film containing 40 layers showed the highest sensitivity to CO_2 with an obtained detection limit of 401 ppm[17].

In another research, the performance of two distinct forms of HKUST-1- octahedral and ultrathin nanosheets, were studied for their application to humidity sensing. Compared to the octahedral structures, the HKUST-1 nanosheets demonstrated a broader and lower detectable humidity range with a faster response. It was revealed that hydrophilic ligands exposed on the surface of HKUST-1 nanosheets improve the adsorption capacity for humidity detection. In addition, the ultra-thin structure of HKUST-1 nanosheets enabled rapid proton transfer and water molecule movement. To further enhance the sensor's sensitivity, composites of black phosphorus quantum dots and HKUST-1 nanosheets were prepared, resulting in a one-order magnitude improvement compared to HKUST-1 alone. Thus, this study has shed light on the morphology–activity relationship of the HKUST-1 sensor for humidity sensing[18].

A team of researchers has developed a new high-performance electrochemical sensing platform for sensitive and selective detection of isoproturon herbicide made from a molecularly imprinted polymer (MIP) capped Au@HKUST– 1 nanocapsules. The electrode displayed a linear relationship spanning 0.0010 - 45 µM with an ultra-low detection limit of 0.45 nM and a relative standard deviation of fewer than four percent when tested in water samples. Furthermore, the sensing specificity for isoproturon yielded recoveries in the range of 99.07 - 105.8% (**Figure 5**) [19].

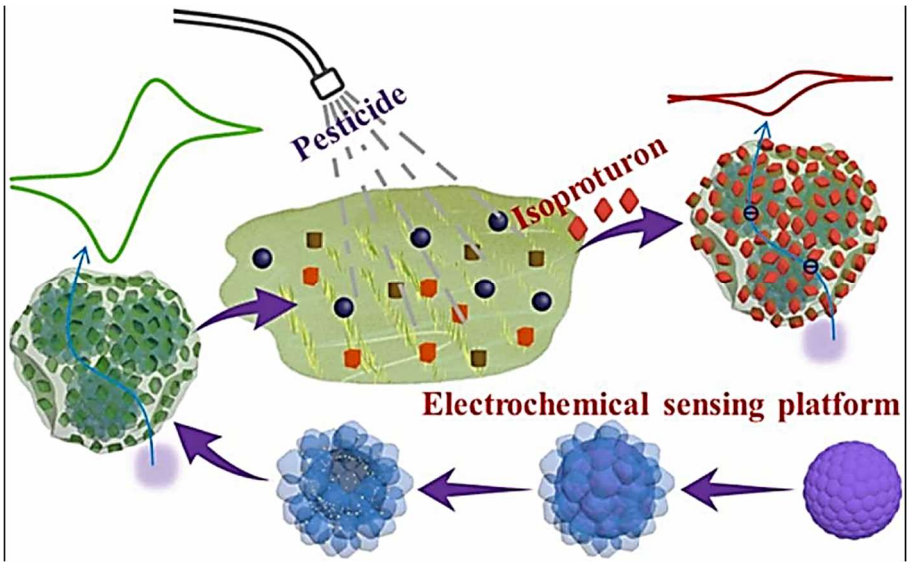

Figure 5. High-performance electrochemical sensing platform for sensitive and selective detection of isoproturon herbicide. Reprinted with permission from ref [19].

Researchers have developed a sensitive modified carbon paste electrode (CPE/$CoFe_2O_4$@SiO_2@HKUST-1) for the determination of azaperone (AZN) via a multi-step self-assembly technique. The results showed that this electrode had an impressive electrocatalytic effect on AZN oxidation, with a wide linear range (0.05 to 10000 nM) and a trace detection limit of 0.01 nM. Additionally, the study found that the modified CPE had good selectivity and precision for AZN determination with an accuracy of 85% to 103.4% relative recovery in standard and real samples such as ostrich meat and rat blood serum (**Figure 6**)[20].

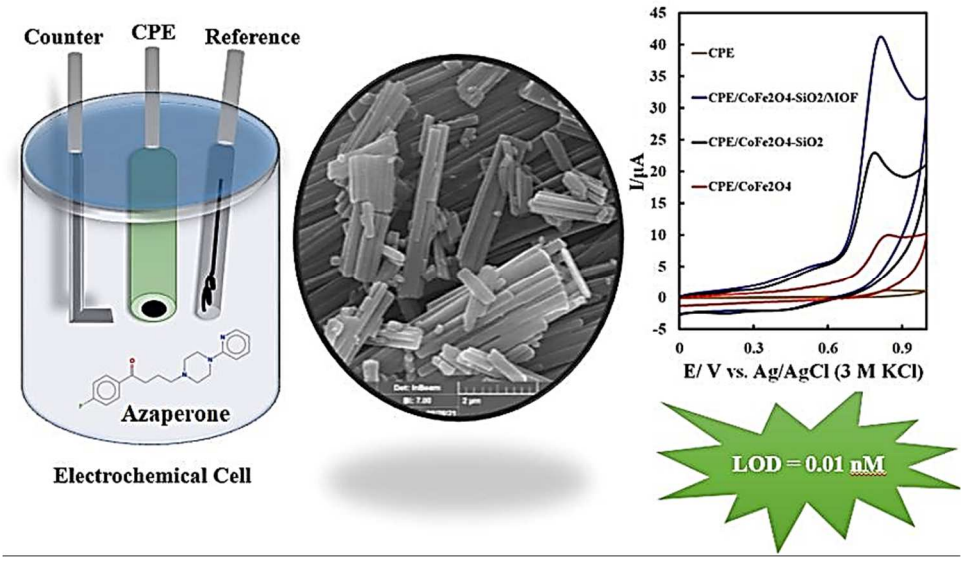

Figure 6. Sensitive modified carbon paste electrode (CPE/$CoFe_2O_4$@SiO_2@HKUST-1). Reprinted with permission from ref [20].

In a different work, a composite hydrogel consisting of halloysite nanotubes and HKUST-1 was developed as human motion detection sensors with antibacterial property. It was found to have high tensile strain properties (elongation at break of 912.5% and tensile strength of 22.4 kPa), a recyclable composition, excellent sensitivity,

and rapid responses. Moreover, including Cu^{2+} in HKUST-1 provided excellent conductivity and antibacterial properties to the composite. These properties make the composite hydrogel highly suitable for use as a flexible material to monitor movements of the human body in real-time and also prevents microbial infection, showing great potential in terms of wearable strain sensors (**Figure 7)** [21].

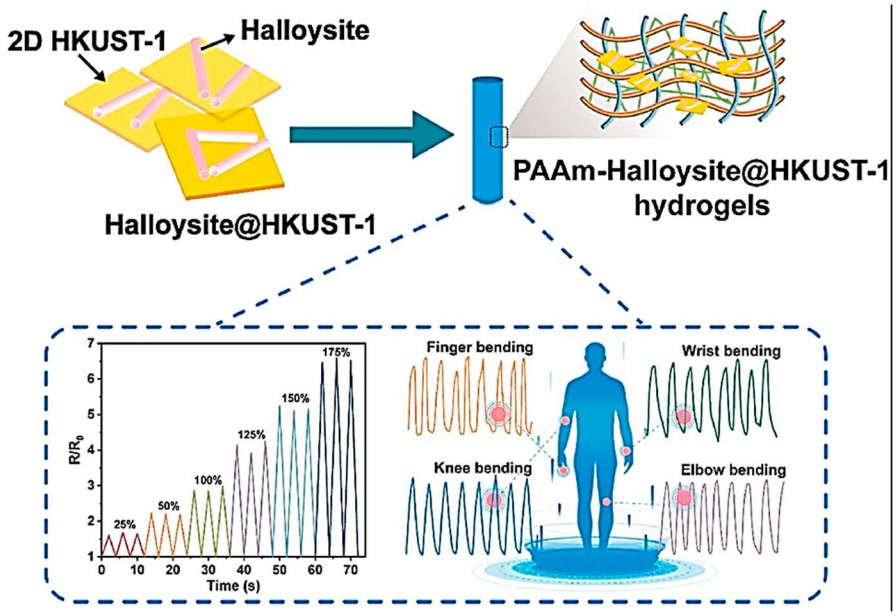

Figure 7. Composite hydrogel consisting of halloysite nanotubes and HKUST-1 was developed as human motion detection sensors with antibacterial properties. Reprinted with permission from ref [21].

These works have successfully demonstrated various methods for improving the conductivity of MOFs, which has been a critical challenge in their application as electrode materials. They also highlight the importance of the controlled fabrication and design of the MOFs, such as controlling their morphology and integrating them with other materials, to enhance their sensing performance.

4.2. Extraction of metal ions with $Cu_3(BTC)_2$

HKUST-1 was found to have a high affinity and selectivity for the adsorptive recovery of rare earth ions (Ce^{3+} and La^{3+}) in aqueous solutions. The examination of the adsorption process shows that the MOF was tested to have an adsorption capacity of 234 mg/g for Ce^{3+} and 203 mg/g for La^{3+} at a pH of 6, with a selectivity of 87% against other metal ions. The isotherm and kinetics of this process were further analyzed and found well-fitted by the Freundlich and pseudo-second-order models, respectively. The selective nature of the adsorption process was attributed to the different bonding abilities of metal ions with the adsorbent, potentially due to ion exchange and covalent bonding. Thus, the adsorptive recovery of rare earth ions from wastewater using the HKUST-1 MOF holds the potential for using precious resources[22].

A recent study investigated the effects of doping iron into HKUST-1 on hydrostability. It was found that substituting as low as 5 mol% of Fe into the MOF enhanced its hydrostability drastically, where the structure remained intact for up to 10 hours even when the MOF came in contact with water. In addition, this substitution also caused a 53% reduction in the amount of Cu leaching from the MOF. Additionally, the Fe doped HKUST-1 MOF showed promising results in environmental remediation applications, such as selective Pb(II) removal with an efficiency of over 90% and an adsorption capacity of 565 mg g^{-1}. This study demonstrates the potential for doping to significantly enhance the hydrostability of metal-organic frameworks, thereby widening its application in environmental remediation (**Figure 8**)[23].

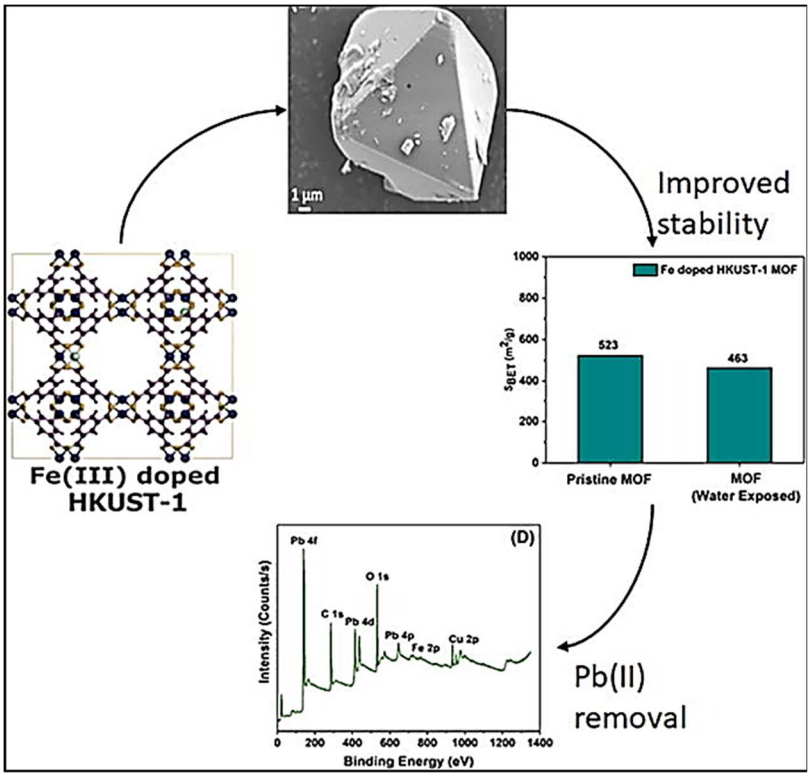

Figure 8. The effects of doping iron into HKUST-1 on its hydrostability. Reprinted with permission from ref [23].

These part provide intriguing insights into the potential applications of HKUST-1 in environmental remediation, specifically in the recovery of rare earth ions from wastewater and in the removal of toxic lead ions. Overall, these findings highlight the tuneable nature of MOFs, like HKUST-1, and their potential in applications requiring specificity and stability, such as environmental remediation.

4.3. Energy storage

This part highlight the tremendous potential of Metal-Organic Frameworks (MOFs), specifically HKUST-1, in the realm of energy storage, both in terms of hydrogen storage and as an electrode material for energy storage devices. In a paper, Madden D G, et al. said they are witnessing the emergence of the hydrogen (H_2) economy, where H_2 is expected to become a primary fuel for heating, transportation, and long-term energy storage. H_2 can be stored as a pressurized gas, a cryogenic liquid, or adsorbed onto porous materials as a solid fuel. Among these options, metal-organic frameworks (MOFs) have emerged as highly promising adsorbent materials, offering the highest theoretical H_2 storage densities in terms of volume and weight. However, the practical application of MOFs as transportation fuel has been hindered by the lack of densification methods that can shape MOFs into usable forms while maintaining their adsorptive performance. In this study, They conducted a comprehensive high-throughput screening and in-depth analysis of a MOF database to identify optimal materials. Subsequently, They synthesized, characterized, and evaluated the performance of an optimal monolithic MOF (mono MOF) for H_2 storage. After densification, this monoMOF achieved a storage capacity of 46 g H_2 per liter at 50 bar and 77 K (**Figure 9**)[24].

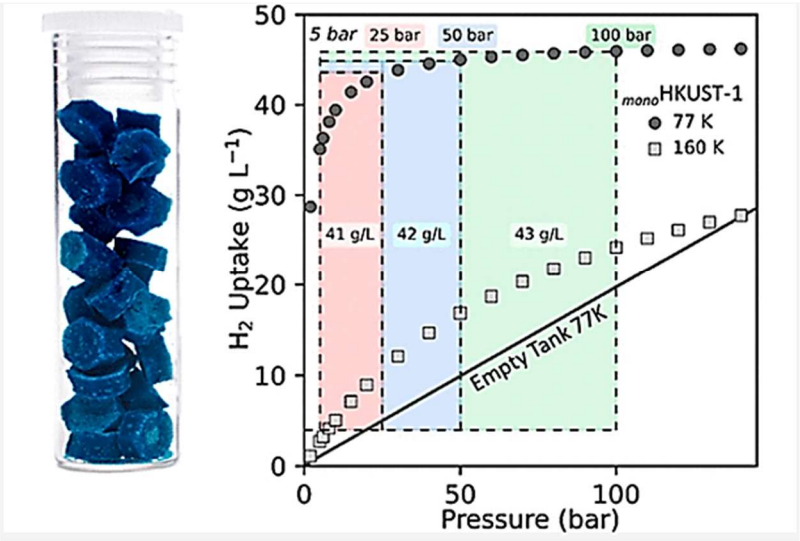

Figure 9. Densified HKUST-1 Monoliths as a route to high volumetric and gravimetric hydrogen storage capacity. Reprinted with permission from ref [24].

Moreover, it delivered 41 g H_2 per liter at an operating pressure of 25 bar and 42 g H_2 per liter at 50 bar, when utilized in a combined temperature-pressure swing gas delivery system (25-50 bar/77 K → 5 bar/160 K). These results indicate an impressive 80% reduction in the operating pressure requirements for H_2 gas delivery compared to benchmark materials and an 83% reduction compared to compressed H_2 gas. This study represents a significant advancement in the practical application of high-density materials for volumetric H_2 storage.

As said above, metal-organic frameworks (MOFs) are gaining recognition as potential electrode materials for future energy storage devices.

In work by Sundriyal, Shashank et al., TCNQ (tetracyanoquinodimethane) was introduced to HKUST-1, resulting in the synthesis of an efficient energy storage electrode material with high surface area and excellent electrical conductivity. The TCNQ@HKUST-1 electrode exhibited a remarkable specific capacity of 208.8 mAh/g (751 C/g) at a current density of 2 A/g. An all-solid-state symmetrical device utilizing a polymer gel electrolyte was constructed, demonstrating energy and power densities of 70.5 Wh/kg and 0.83 kW/kg, respectively. Furthermore, the device achieved a maximum energy efficiency of 58.6% and maintained a cycle life of 96% over 5000 successive charging-discharging cycles. The TCNQ@HKUST-1 system exhibited superior energy storage performance compared to previously reported MOF-based electrodes (**Figure 10**)[25].

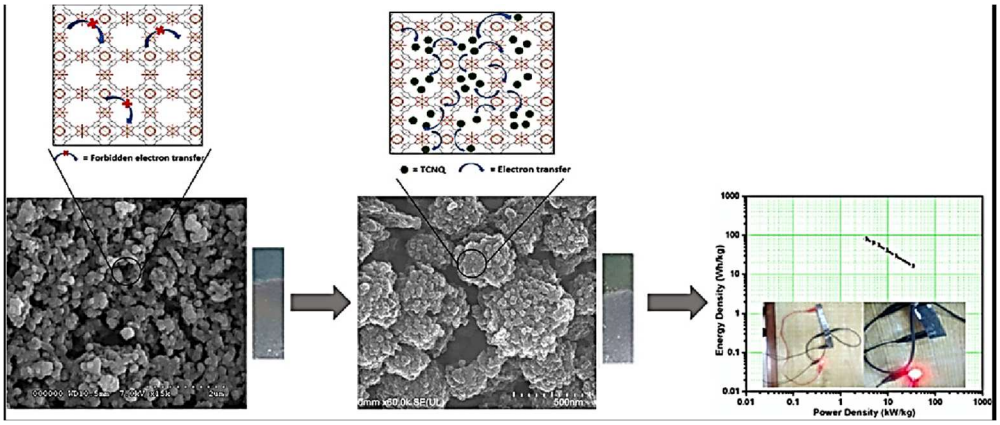

Figure 10. TCNQ@HKUST-1 electrode synthesis. Reprinted with permission from ref [25].

4.3.Drug delivery

Magnetic drug delivery has emerged as a highly effective approach to delivering drugs directly to specific organs and target sites in the body. This method uses a magnetically responsive material coated with a matrix loaded with the drug of interest. Koryakina I G et al. demonstrate the directed synthesis of HKUST-1 microcrystals with surface defects by a one-step microfluidic method. The synthesis process has been optimized to obtain the desired His MOFs, resulting in increased molecular (fluorochrome) loading on the surface compared to solvothermal synthesized MOFs. Under continuous wave laser irradiation (532 nm), dye loading and high beam emission were detected. Furthermore, they tested the toxicity of the obtained MOFs and their interaction with mouse melanoma cells. Therefore, the potential to design and synthesize MOFs with desirable physicochemical properties and twice the loading capacity of solvothermal-synthesized MOFs by using microfluidic approaches has implications for developing improved drug delivery platforms (**Figure 11**)[26].

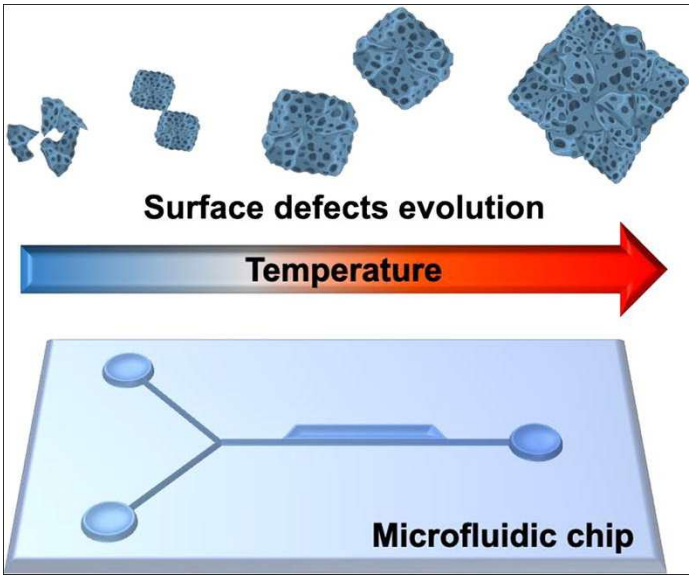

Figure 11. HKUST-1 microcrystals with surface defects by a one-step microfluidic method Reprinted with permission from ref [26].

Nabipour et al. conducted a study focusing on the solvothermal preparation of a copper-metal organic framework to load baclofen as a model drug. The objective was to enhance the controllability of drug release in a bio-polymeric carboxymethyl cellulose (CMC) hydrogel within the gastrointestinal tract (GIT) by incorporating baclofen-HKUST-1. In vitro drug delivery and kinetic evaluations, they demonstrated that the CMC/baclofen-HKUST-1 bio-nanocomposite exhibited improved performance in the face of stomach pH, resulting in enhanced release uniformity and effective drug delivery within GIT conditions. Furthermore, cytotoxicity assessments using the MTT assay revealed significant toxicity against human colon cells associated with the CMC/baclofen-HKUST-1 bio-nanocomposite. Based on the findings of these assessments, it can be concluded that the CMC/baclofen-HKUST-1 bio-nanocomposite holds promise for applications in drug administration[27].

Djahaniani et al. present the synthesis and characterization of a hybrid polymer/HKUST-1 composite designed for oral drug delivery applications. A green and efficient one-pot approach was employed to synthesize the modified metal-organic frameworks (MOFs) composite, utilizing alkali lignin as a novel biopolymer carrier with pH-responsive properties for simulated oral delivery systems. The drug loading capacity and controlled release behavior of HKUST-1 and lignin/HKUST-1 composites were investigated using ibuprofen (IBU) as a model oral drug. The lignin/HKUST-1 composite exhibited pH-controlled drug release behavior, thereby ensuring drug stability under low pH conditions such as the gastric medium and facilitating controlled drug release within the pH range of 6.8–7.4, which mimics the

intestinal pH environment. Based on the results, the lignin/HKUST-1 composite demonstrates great potential as a promising candidate for oral medication delivery (**Figure 12**)[28].

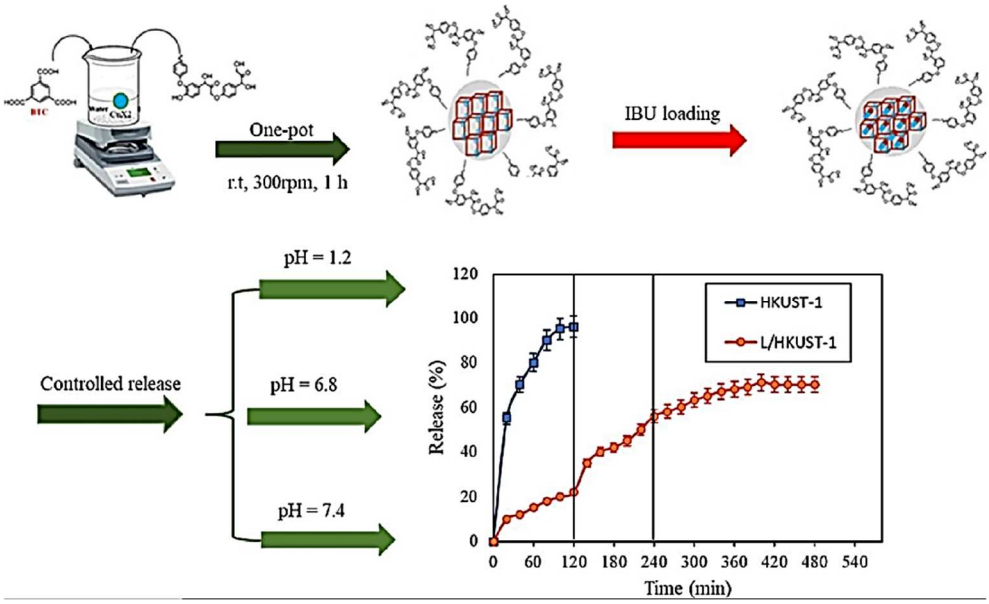

Figure 12. Hybrid polymer/HKUST-1 composite synthesis for oral drug delivery applications. Reprinted with permission from ref [28].

In sum, these studies provide significant insights into the potential of HKUST-1 MOFs in targeted drug delivery, with implications for a range of therapeutic applications.

4.4. Optical devices

HKUST-1 has various potential applications, one of which is optical devices. These optical applications can leverage the unique properties of MOFs, such as their porosity, high surface area, structural flexibility, and tunable chemical functionality. Optical devices using Copper BTC can take advantage of these characteristics in several ways. Below are some potential applications:

Photonic Devices: The controlled porosity of Copper BTC can be used to trap specific wavelengths of light, creating photonic band gaps. This makes it an exciting material for photonic devices that manage, generate, or manipulate light, including optical telecommunications and data storage[29].

Optical Sensors: Due to its high surface area and tunable chemical functionality, Copper BTC can be used to create optical sensors. By introducing various target-responsive groups into the framework, Copper BTC-based optical sensors could respond to changes in the local environment by changing their optical properties, such as fluorescence[30].

Nonlinear Optics: MOFs have been identified as promising materials in the field of nonlinear optics, where the response of a material to incident light changes with the intensity of the light. Copper BTC, with its copper ions and organic ligands, could show significant third-order nonlinear optical responses, which are useful in devices like optical limiters, switches, and modulators[31].

Luminescent Devices: Copper BTC can be used to create luminescent devices. Luminescence of MOFs can be tuned through the appropriate selection of metal ions and organic ligands, and so by controlling the preparation conditions and components, Copper BTC can be used to produce light-emitting diodes (LEDs) and other luminescent devices[32]. Kulachenkov et al. present a study of an all-optical switch utilizing stimuli-responsive and photochromic-free HKUST-1. By utilizing ultrafast near-infrared laser pulses, the researchers observe a reversible 0.4 eV blue shift in the absorption band of HKUST-1. This shift is attributed to the dehydration and concurrent contraction of the structure-forming $[Cu_2C_4O_8]$ cages within HKUST-1, occurring at a remarkable rate of up to 200 s^{-1}. The light-induced

switching phenomenon enables remote modulation of photoluminescence intensities in single crystals of HKUST-1, as well as the manipulation of visible radiation passing through the crystal, achieving a two-order-of-magnitude change. These findings indicate the potential of utilizing stimuli-responsive metal-organic frameworks (MOFs) for the development of all-optical data processing devices[33].

4.5. As a catalyst

4.5.1. Friedel-Crafts alkylation

$Cu_3(BTC)_2$ was used to examine a Friedel-Crafts alkylation reaction of indole with β-nitrostyrene under mild reaction conditions. This catalyst was selected from a screening of different catalysts due to its higher activity and the absence of leaching of active sites. It was then used to synthesize a series of heterocyclic compounds with different indole and β-nitrostyrene derivatives in moderate to high yields. Additionally, the catalyst was found to be reusable for 4 cycles with minimal loss of activity. The catalytic system demonstrated similar activity to recent reports but offers the advantage of not needing any post-functionalization and being readily synthesized, providing promising prospects for the synthesis of heterocyclic compounds with high biological interest (**Figure 13**)[34].

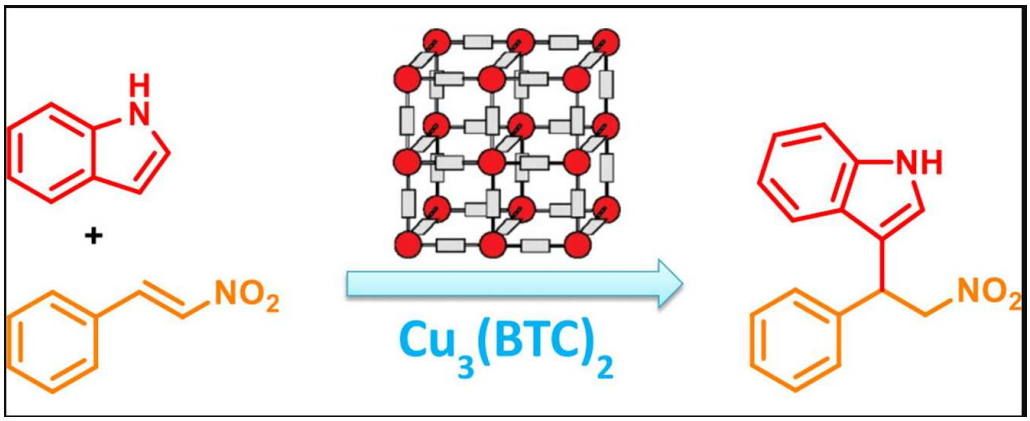

Figure 13. Friedel-Crafts alkylation reaction of indole with β-nitrostyrene under mild reaction conditions with $Cu_3(BTC)_2$. Reprinted with permission from ref [34].

4.5.2. $Cu_3(BTC)_2$ in click chemistry

Research has found that Cu-MOFs are highly recyclable, giving them a greater appeal than other metal catalysts. Furthermore, their ability to coordinate with both hard and soft donor ligands makes them a versatile option for different kinds of ligand interactions. This makes Cu-MOFs a superior choice compared to other metal catalysts[35].

The nanocomposite AC/HKUST-1, made from activated carbon from the Cortaderia Selloana flower and copper-based metal-organic framework (HKUST-1) produced through a single-step solvothermal method, was tested for the removal of lead ions from aqueous solution through adsorption. After being characterized, it was found to contain octahedral crystals. Further study of different factors affecting adsorption processes, such as solution pH, contact time, adsorbent dose, and initial metal pollution concentration, resulted in a Freundlich and Langmuir model solving the experimental data on adsorption of lead ion. The nanocomposite was found to have an excellent adsorption capacity at 249.4 mg g−1 for 15 min at pH 6.1. These findings suggest the nanocomposites have considerable potential for use as a functional material in the ink formulation of lead sensors[36].

The synthesis of a new type of HKUST-1 variety using a defect engineering (DE) technique was reported. The introduction of truncated pyridine-3,5-dicarboxylate (PyDC) as the parent linker allowed for the formation of mixed-valence Cu(I)-Cu(II) paddlewheels (PWs) in the DE-CuBTC structure, leading to an improvement in its catalytic performance for the click reaction of azide–alkyne cycloaddition. The A^3 coupling reaction of phenylacetylene, paraformaldehyde, and piperidine was also studied, further demonstrating the enhanced activity of DE -CuBTC due to its defect engineering method. This study showed that defect engineering provides the excellent potential to create tailored catalytic active sites in catalysts (**Figure 14**)[37].

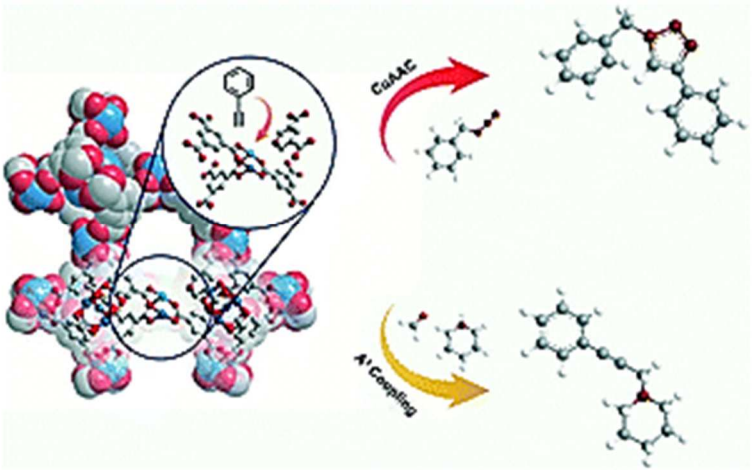

Figure 14. The synthesis of a new type of HKUST-1 variety using a defect engineering (DE) technique. Reprinted with permission from ref 37.

4.5.3.Oxidation reaction

Fan, Sh et al. reported the synthesis of Cu-$CuFe_2O_4$@HKUST-1 heterostructures, which demonstrates high activity in the selective oxidation of benzylic C–H bonds under mild conditions. This high activity is attributed to the multifunctional design of this heterostructure, providing multiple active sites and attracting and preconcentrating molecular oxygen. Under optimized reaction conditions, the catalyst was able to convert fluorene to fluorenone with greater than 99% conversion and selectivity. Additionally, the catalyst displayed excellent stability as it was easily recovered by magnetic separation and reused for up to 10 cycles without significant losses in catalytic activity (**Figure 15**)[38].

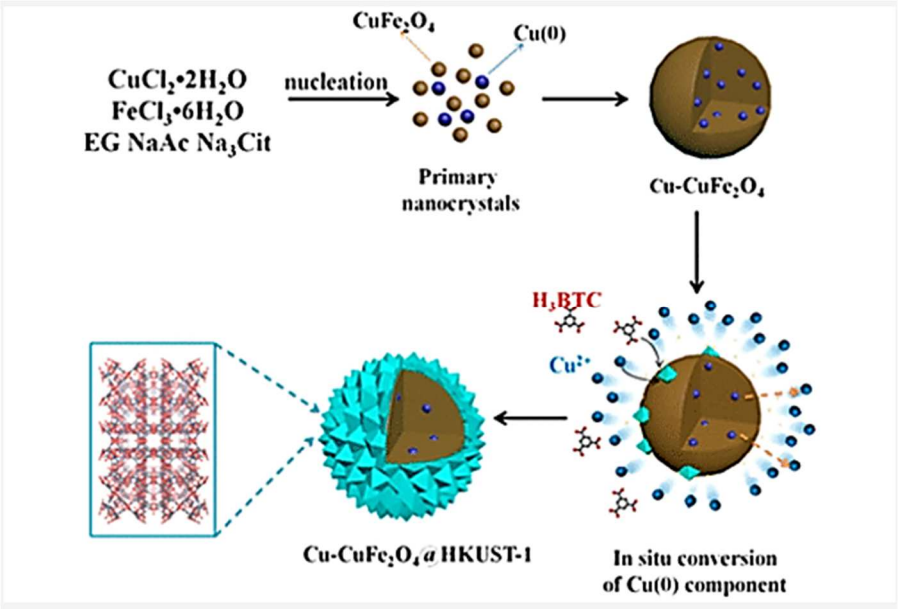

Figure 15. The synthesis of Cu-$CuFe_2O_4$@HKUST-1 heterostructures. Reprinted with permission from ref [38].

It has been discovered that metal-organic frameworks (MOFs) featuring isolated coordinatively unsaturated metal sites (CUS) have great potential as single-site catalysts. In order to explore the unique catalytic properties of mixed-metal MOFs, a thorough fundamental study was conducted on CuPd-HKUST-1 ($[Cu_3–xPdx(BTC)_2]n$. The two-step synthesis, characterization, and catalytic performance were evaluated, and the findings showed that the incorporation

of Pd can alter the chemical properties of HKUST-1–CUS into the framework, leading to the formation of new Cu–Pd and/or Pd–Pd dimers. The introduced Pd occurred exclusively at the metal nodes and retained structural integrity. Further catalytic performance evaluation showcased the superior activity and selectivity of these mixed-metal CuPd-MOFs in the aerobic oxidation of benzyl alcohol to benzaldehyde, with the doped Pd^{2+}–CUS species as the isolated single-active sites[39].

5. Conclusion

In conclusion, the significance of Copper Benzene 1,3,5-tricarboxylate Metal Organic Framework (Cu MOFs) is evident from its wide range of applications and advantages over traditional nanomaterials. Cu MOFs, such as $Cu_3(BTC)_2$ (also known as HKUST-1 or MOF-199), exhibit excellent catalytic activity, simple synthetic procedures, and abundant resources, making them ideal for activating starting materials and creating complex structural designs. The tunable conditions of Cu MOFs enable useful reactions, including oxidation, click chemistry, and Friedel-Crafts alkylation. Their versatility, coupled with their advantageous properties, makes them valuable for catalysis, drug delivery, energy storage, environmental applications, and optical devices. Continued research and exploration of Cu MOFs will undoubtedly contribute to further advancements and innovations in these fields.

Authors' contributions

All authors contributed to drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

Declaration of competing interest

The authors declare no competing interest.

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Data availability

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References

[1] Y. Liu, P. Ghimire, M. Jaroniec, Copper benzene-1, 3, 5-tricarboxylate (Cu-BTC) metal-organic framework (MOF) and porous carbon composites as efficient carbon dioxide adsorbents, J. Colloid Interface Sci. 535 (2019) 122-132.

[2] A. Domán, J. Madarász, G. Sáfrán, Y. Wang, K. László, Copper benzene-1, 3, 5-tricarboxylate (HKUST-1)–graphene oxide pellets for methane adsorption, Microporous Mesoporous Mater. 316 (2021) 110948.

[3] A. Domán, S. Klébert, J. Madarász, G. Sáfrán, Y. Wang, K. László, Graphene oxide protected copper benzene-1, 3, 5-tricarboxylate for clean energy gas adsorption, Nanomaterials 10(6) (2020) 1182.

[4] R. Ramachandran, C. Zhao, D. Luo, K. Wang, F. Wang, Synthesis of copper benzene-1, 3, 5-tricarboxylate metal organic frameworks with mixed phases as the electrode material for supercapacitor applications, Appl. Surf. Sci. 460 (2018) 33-39.

[5] A. Domán, B. Nagy, L.P. Nichele, D. Srankó, J. Madarász, K. László, Pressure resistance of copper benzene-1, 3, 5-tricarboxylate–carbon aerogel composites, Appl. Surf. Sci. 434 (2018) 1300-1310.

[6] P. Hu, C. Meng, Y. Cai, P. Wang, H. Zhou, X. Li, A. Yuan, Supernano crystals boost the initial coulombic efficiency and capacity of copper benzene-1, 3, 5-tricarboxylate for Li-Ion batteries, Energy & Fuels 37(4) (2023) 3134-3141.

[7] P. Wang, M. Shen, H. Zhou, C. Meng, A. Yuan, MOF-derived CuS@Cu-BTC composites as high-performance anodes for lithium-ion batteries, Small 15(47) (2019) 1903522.

[8] L. Jiao, J.Y.R. Seow, W.S. Skinner, Z.U. Wang, H.-L. Jiang, Metal–organic frameworks: Structures and functional applications, Mater. Today 27 (2019) 43-68.

[9] X. Zhang, S. Zhang, Y. Tang, X. Huang, H. Pang, Recent advances and challenges of metal–organic framework/graphene-based composites, Compos. B: Eng 230 (2022) 109532.
[10] N. Baig, I. Kammakakam, W. Falath, Nanomaterials: A review of synthesis methods, properties, recent progress, and challenges, Mater. Adv. 2(6) (2021) 1821-1871.
[11] Q. Zhao, L. Zhu, G. Lin, G. Chen, B. Liu, L. Zhang, T. Duan, J. Lei, Controllable synthesis of porous Cu-BTC@ polymer composite beads for iodine capture, ACS Appl. Mater. Interfaces 11(45) (2019) 42635-42645.
[12] K. Pirzadeh, A.A. Ghoreyshi, M. Rahimnejad, M. Mohammadi, Optimization of electrochemically synthesized $Cu_3(BTC)_2$ by Taguchi method for CO_2/N_2 separation and data validation through artificial neural network modeling, Front. Chem. Sci. Eng. 14 (2020) 233-247.
[13] E. Irandoost, H. Farsi, A. Farrokhi, Effects of water content on electrochemical capacitive behavior of nanostructured Cu3 (BTC) 2 MOF prepared in aqueous solution, Electrochim. Acta 368 (2021) 137616.
[14] Z. Su, Jianling Zhang, Bingxing Zhang, Xiuyan Cheng, Mingzhao Xu, Yufei Sha, Yanyue Wang, Jingyang Hu, Lirong Zheng, and Buxing Han, Cu 3 (BTC) 2 nanoflakes synthesized in an ionic liquid/water binary solvent and their catalytic properties, Soft Matter 18(32) 6009-6014.
[15] T.A. Agbaje, S. Singh, K.S.K. Reddy, K. Polychronopoulou, L.F. Vega, M. Khaleel, K. Wang, G.N. Karanikolos, Salt-free synthesis of Cu-BTC metal-organic framework exhibiting mesoporosity and enhanced carbon dioxide adsorption, Microporous and Mesoporous Mater. 324 (2021) 111265.
[16] Y. Wang, C. Yang, C. Zhang, M. Duan, H. Wang, H. Fan, Y. Li, J. Shangguan, J. Lin, Hierarchical Porous MOF-199 Regulated by PVP for Desulfurization at Ambient Conditions, Available at SSRN 3994498.
[17] J. Hromadka, B. Tokay, R. Correia, S.P. Morgan, S. Korposh, Carbon dioxide measurements using long period grating optical fibre sensor coated with metal organic framework HKUST-1, Sens. Actuators B: Chem. 255 (2018) 2483-2494.
[18] Q. Wang, M. Lian, X. Zhu, X. Chen, Excellent humidity sensor based on ultrathin HKUST-1 nanosheets, RSC Adv. 11(1) (2021) 192-197.
[19] X. Liu, L. Chen, Y. Gao, J. Li, J. Sun, T. Gan, Molecularly imprinted polymer capped Au@ HKUST− 1 nanocapsules-based electrochemical sensing platform for monitoring isoproturon herbicide in water at sub− nanomole level, J. Environ. Chem. Eng. 10(3) (2022) 107661.
[20] M. Ghalkhani, M. Gharagozlou, E. Sohouli, E.M. Khosrowshahi, Preparation of an electrochemical sensor based on a HKUST-1/CoFe2O4/SiO2-modified carbon paste electrode for determination of azaperone, Microchem. J. 175 (2022) 107199.
[21] W. Zhao, Y. Long, Y. He, J. Cai, M. Liu, HNTs@ HKUST-1 strengthened PAAm hydrogel for strain sensing and antibacterial application, Microporous and Mesoporous Mater. 344 (2022) 112207.
[22] L. Zhao, X. Duan, M.R. Azhar, H. Sun, X. Fang, S. Wang, Selective adsorption of rare earth ions from aqueous solution on metal-organic framework HKUST-1, Chem. Eng. J. Adv. 1 (2020) 100009.
[23] P. Goyal, A. Paruthi, D. Menon, R. Behara, A. Jaiswal, V. Keerthy, A. Kumar, V. Krishnan, S.K. Misra, Fe doped bimetallic HKUST-1 MOF with enhanced water stability for trapping Pb (II) with high adsorption capacity, Chem. Eng. J. 430 (2022) 133088.
[24] D.G. Madden, D. O'Nolan, N. Rampal, R. Babu, C. Çamur, A.N. Al Shakhs, S.-Y. Zhang, G.A. Rance, J. Perez, N.P. Maria Casati, Densified HKUST-1 Monoliths as a Route to High Volumetric and Gravimetric Hydrogen Storage Capacity, J. Am. Chem. Soc. 144(30) (2022) 13729-13739.
[25] S. Sundriyal, V. Shrivastav, S.K. Bhardwaj, S. Mishra, A. Deep, Tetracyanoquinodimethane doped copper-organic framework electrode with excellent electrochemical performance for energy storage applications, Electrochim. Acta 380 (2021) 138229.
[26] I.G. Koryakina, S.V. Bachinin, E.N. Gerasimova, M.V. Timofeeva, S.A. Shipilovskikh, A.S. Bukatin, A. Sakhatskii, A.S. Timin, V.A. Milichko, M.V. Zyuzin, Microfluidic synthesis of metal-organic framework crystals with surface defects for enhanced molecular loading, Chem. Eng. J. 452 (2023) 139450.
[27] H. Nabipour, M. Mansoorianfar, Y. Hu, Carboxymethyl cellulose-coated HKUST-1 for baclofen drug delivery in vitro, Chem. Pap. 76(10) (2022) 6557-6566.
[28] H. Djahaniani, N. Ghavidel, H. Kazemian, Green and facile synthesis of lignin/HKUST-1 as a novel hybrid biopolymer metal-organic-framework for a pH-controlled drug release system, Int. J. Biol. Macromol. 242 (2023) 124627.
[29] Y. Zhao, W. Wang, X. Li, H. Lu, Z. Shi, Y. Wang, C. Zhang, J. Hu, G. Shan, Functional porous MOF-derived CuO octahedra for harmonic soliton molecule pulses generation, Acs Photonics 7(9) (2020) 2440-2447.
[30] S.-I. Ohira, N. Nakamura, M. Endo, Y. Miki, Y. Hirose, K. Toda, Ultra-sensitive Trace-Water Optical Sensor with In situ-synthesized Metal-Organic Framework in Glass Paper, Anal Sci. 34(4) (2018) 495-500.
[31] T.N. Nguyen, F.M. Ebrahim, K.C. Stylianou, Photoluminescent, upconversion luminescent and nonlinear optical metal-organic frameworks: From fundamental photophysics to potential applications, Coord. Chem. Rev. 377 (2018) 259-306.
[32] Y. Cui, Y. Yue, G. Qian, B. Chen, Luminescent functional metal–organic frameworks, Chem. Rev. 112(2) (2012) 1126-1162.

[33] N.K. Kulachenkov, D. Sun, Y.A. Mezenov, A.N. Yankin, S. Rzhevskiy, V. Dyachuk, A. Nominé, G. Medjahdi, E.A. Pidko, V.A. Milichko, Photochromic free MOF-based near-infrared optical switch, Angew. Chem., Int. Ed. Engl. 59(36) (2020) 15522-15526.
[34] A. Nagaraj, D. Amarajothi, Cu3 (BTC) 2 as a viable heterogeneous solid catalyst for Friedel-Crafts alkylation of indoles with nitroalkenes, J. Colloid Interface Sci. 494 (2017) 282-289.
[35] M. Meldal, C.W. Tornøe, Cu-catalyzed azide– alkyne cycloaddition, Chem. reviews 108(8) (2008) 2952-3015.
[36] P.S. Abhari, F. Manteghi, Z. Tehrani, Adsorption of lead ions by a green AC/HKUST-1 nanocomposite, Nanomaterials 10(9) (2020) 1647.
[37] Z. Fan, Z. Wang, M. Cokoja, R.A. Fischer, Defect engineering: an effective tool for enhancing the catalytic performance of copper-MOFs for the click reaction and the A 3 coupling, Catal. Sci. Technol. 11(7) (2021) 2396-2402.
[38] S. Fan, W. Dong, X. Huang, H. Gao, J. Wang, Z. Jin, J. Tang, G. Wang, In situ-induced synthesis of magnetic Cu-$CuFe_2O_4$@HKUST-1 heterostructures with enhanced catalytic performance for selective aerobic benzylic C–H oxidation, Acs Catalysis 7(1) (2017) 243-249.
[39] P. Guo, C. Froese, Q. Fu, Y.-T. Chen, B. Peng, W. Kleist, R.A. Fischer, M. Muhler, Y. Wang, CuPd mixed-metal HKUST-1 as a catalyst for aerobic alcohol oxidation, J. Phys. Chem. C 122(37) (2018) 21433-21440.

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