Journal of nanoporous Systems

Review Paper

Green Synthesis Strategies for Nanoporous HKUST-1 (MOF199)

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Article history
Received: 11 June 2026
Revised: 14 July 2026
Accepted: 17 Guly 2026

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Abstract: HKUST-1 is known as an important copper-based metal–organic frameworks because of its high specific surface area, permanent microporosity, accessible open Cu sites, and broad applicability in various fields. However, conventional solvothermal preparation of HKUST-1 commonly relies on large quantities of organic solvents, extensive washing and activation steps, and poorly recyclable mother liquors that limit its compatibility with green chemistry principles and large-scale production. This review critically explains recent progress in sustainable and function-oriented synthetic strategies for HKUST-1, with emphasis on solvent decrease or elimination, precursor efficiency, process circularity, defect engineering, metal doping, monolithic shaping, and composite integration. These studies demonstrate that greener synthesis can be coupled with competitive or enhanced properties, including high BET surface areas, large pore volumes, controlled defect densities, and improved accessibility of active sites. In addition, future advances will require synthesis protocols that are not only environmentally benign and resource-efficient, but also reproducible, scalable, and compatible with practical device or process architectures.

Keywords: Green synthesis, HKUST-1; MOF199, catalysis; metal-organic framework

Introduction

The versatile family of crystalline nanoporous materials known as metal-organic frameworks (MOFs) has drawn a lot of interest due to characteristics including tunable pore diameters, high surface areas, and permanent porosity [1]. MOFs can be used in a variety of fields, including adsorption [2-4], gas storage and separation [5-7], catalysis [4, 8, 9], sensing [4, 10, 11], and biomedical technologies [12, 13], due to these structural characteristics. A lot of works have been done over the last 20 years to create a variety of MOF designs by carefully choosing metal nodes and organic linkers.

The copper-containing metal–organic framework HKUST-1 (also known as MOF 199) is a representative of dinuclear Cu paddlewheel secondary building units connected by benzene 1,3,5 tricarboxylate (BTC) linkers (Figure 1). This arrangement results in a 3D crystalline nanoporous network with accessible pore channels and defined metal sites. Each Cu center is axially coordinated by a water molecule in its hydrated state, usually as a result of exposure to ambient moisture [14]. These water molecules can be removed via thermal or vacuum activation to create coordinatively unsaturated Cu sites, also known as open metal sites. Such sites are crucial for the strong interaction of HKUST-1 with guest molecules and largely determine the adsorption and catalytic properties of the material.

The field of MOFs is growing rapidly, and this is making the development of simple, sustainable, and scalable synthetic routes increasingly important. For benchmarks such as HKUST-1, the challenge is to maintain crystallinity and porosity while reducing solvent consumption, energy demand, and downstream waste. Now, MOF synthesis is characterized by both material performance and process sustainability.

Although, HKUST-1 is widely used in adsorption [15], catalysis [16-18], separation [19, 20], sensing [21, 22] and environmental remediation [23-25], there is still a clear sustainability gap between its intended applications and conventional preparation routes.

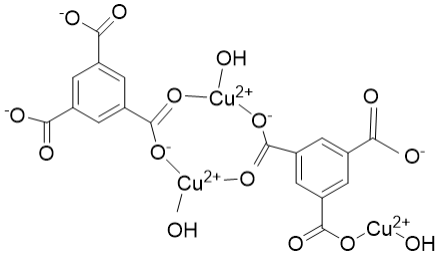

Fig. 1. Structure of HKUST-1.

HKUST-1 is a functional nanoporous material of interest for environmentally relevant processes, featured in many studies, but its synthesis still relies on solvent intensive solvothermal methods, long heating times and multi-step washing or solvent-exchange procedures. Moreover, activation treatments required to remove coordinated or trapped solvent molecules and to create accessible porosity and open Cu sites, can further increase solvent use and energy demand.

Therefore the environmental impact of HKUST-1 production should not be evaluated on the crystallization step alone, but over the entire preparation workflow including synthesis, purification, solvent exchange, drying and activation.

HKUST-1 has been synthesized by a number of routes ranging from conventional solvothermal methods to more sustainable and intensified approaches. The synthetic route is of crucial importance for the phase purity and crystallinity of the framework, as well as for its nanoporous properties, including specific surface area, pore volume, pore accessibility, particle morphology, and the generation of open Cu sites upon activation. The synthesis of HKUST-1 should therefore not be regarded only as a way to obtain a crystalline product, but also as a processing step defining the final porous architecture and practical performance of the material.

This review addresses the mentioned issue via a porosity-oriented and metric-driven analysis of green synthesis strategies of HKUST-1. Unlike reviews mainly focusing on MOF structures or application performance, we provide insight into the effect of greener preparation routes on key nanoporous properties of HKUST-1, including crystallinity, specific surface area, pore accessibility, defect formation, and availability of open Cu sites. Special focus is on downstream processing, which is usually overlooked but plays an important role in waste production and energy consumption. This review aims to provide a more consistent framework for evaluating the sustainability of HKUST-1 synthesis routes.

Green Synthetic Routes

Solvothermal synthesis

The typical synthesis of HKUST-1 has been mainly solvothermal or hydrothermal, which involves the reaction of copper salts and trimesic acid (H_3BTC) in polar solvent systems at high temperature and autogenous pressure.

These methods are commonly used because they usually provide good crystallinity, relatively high surface area and reproducible framework formation. In most cases, mixed organic solvents such as ethanol, methanol, or dimethylformamide, often mixed with water, are used for precursor dissolution and crystal growth. Conventional synthetic routes, albeit efficient, are often associated with high solvent consumption, energy demanding processing, post-synthetic washing and waste generation that have inspired the development of greener and more sustainable alternatives.

Chui and co-workers reported the synthesis of a highly porous copper–trimesate coordination polymer by solvothermal chemistry with an isolated yield of about 80 % in the copper trimesate system. The work presented here showed that higher temperature synthesis is beneficial for the formation of higher-dimensional coordination framework, leading to a 3D nanoporous structure with square pores, large hexagonal windows and extremely high accessible porosity. With pore apertures around 1 nm and accessible porosity of ~40% and surface area 692.2 m2g-1 after activation [26]. Importantly, the article also demonstrated the critical role of post-synthetic activation in determining the accessible nanoporous state of HKUST-1, since vacuum heating or thermal dehydration at 100 °C is necessary to remove coordinated water and access the full porosity of the framework.

The room-temperature synthesis of HKUST-1 is a prime example of the ways in which phase control and solvent engineering can help to relieve the energetic cost of MOF-199 production without sacrificing crystallinity and microporosity. The study showed that HKUST-1 can be prepared in full at room temperature without any need to prior nucleation-induction steps in mixed solvent systems of DMF/EtOH/H_2O or EtOH/H_2O with a small amount of diethylamine added. The authors show that the ratio of H_2O/EtOH is critical for phase purity: inappropriate solvent combinations led to competing side phases, while optimized formulations produced pure HKUST-1. Although DMF was observed to suppress the formation of side-phases, it is desirable to remove it from a sustainability point of view due to its poor health and environmental profile.

Significantly, the substitution of DMF by a small amount of Et_2NH allowed the direct deprotonation of trimesic acid and led to the instant formation of phase pure HKUST-1 at room temperature. This method was

reported to be efficient as the crystallization was quantitative and no copper was detected in the filtrate. Importantly the final material still contained significant microporosity with the Et_2NH assisted sample showing a BET surface area of ~940 $m^2.g^{-1}$ and a micropore volume of 0.33 cm^3g^{-1}. Therefore, this synthesis route is a major step towards greener HKUST-1 production as it combines ambient temperature crystallization, reduced reaction time, enhanced metal utilization and partial replacement of troublesome polar aprotic solvents [27].

Another study describes a modified solvothermal procedure for the synthesis of mesoporous HKUST-1 by mixing copper(II) nitrate trihydrate and benzene 1,3,5 tricarboxylic acid in ethanol/DMF/water system at 100 ◦C for 10 h, using cetyltrimethylammonium bromide (CTAB) as a soft template and acetic acid as a modulator. The authors show that CTAB is essential for the formation of mesopores while the amount of acetic acid needs to be carefully optimized as a large addition suppresses crystallinity and decreases textural properties.

The synthesized solids were then subjected to soaking in DMF and washing with methanol to remove CTAB as evidenced by FTIR . They were activated by degassing at 150 ∘C for 8 h under vacuum prior to adsorption analysis. Among the prepared materials, CuBTC(S0.3) showed the best textural performance with a BET surface area of 1010 m^2g^{-1}, pore volume of 0.61 cm^3g^{-1} and pore diameter of 9.2 nm, with the type IV nitrogen sorption isotherms and H3 hysteresis loops indicating mesoporous slit-like pores. The work does not explicitly show the results in the context of green chemistry, but it is relevant to the design of sustainable MOFs, as it shows how template- and modulator-assisted processing can enlarge the pore architecture of HKUST-1 while maintaining the framework integrity and high porosity [28].

In the work of Kareem and co-workers, MOF-199 was prepared by a solvothermal route where the synthesis time, reaction temperature and ethanol: water ratio was systematically varied to study their influence on porosity development and crystallinity. Reaction times of 24–48 h were investigated at 85 and 100 °C with ethanol: water mixtures of 1:1 to 1:2 and all products were subjected to a common activation protocol of 21 h at 60 °C. The best condition was 100 °C for 48 h with a ratio ethanol:water of 1:1, under which the material presented a BET surface area of 5518 m^2g^{-1}, a specific pore volume of 0.693 cm^3g^{-1}, pore size of 11.8 Å and a crystallinity value of 103. These results show that the fine-tuning of solvothermal parameters is crucial for the optimal textural quality of MOF-199, although the process is still dependent on high temperature and long thermal treatment times, which are important considerations in any sustainability assessment [29].

Hydrothermal synthesis of MOF-199 using palm-oil-derived fatty alcohols as renewable templates is an interesting sustainability-oriented strategy towards the morphology control. Copper(II) nitrate trihydrate and 1,3,5-benzenetricarboxylic acid were used as metal source and linker, respectively. Ethanol was used as the solvent. The materials showed good octahedral single particle morphologies with sizes of 15-60 μm. Nitrogen adsorption studies indicated a specific surface area of 400-1100 m^2g^{-1} and pore volumes of 0.17-0.43 cm^3g^{-1} depending on the template chain length. As the chain length of the fatty alcohol increased, the surface area and pore volume decreased (Table 3), which is likely due to the lower mobility of the chain. This work is important from a green-synthesis point of view as it replaces conventional templating agents by renewable, palm-oil-based surfactants [30].

Pham et al. (2023) reported a green hydrothermal synthesis of MOF-199 using a mixed solvent system of water, ethanol and polyethylene glycol (PEG). The synthesized material showed well defined octahedral morphology with particle size of 5-8 μm. Specific surface area was determined to be 1360.76 m^2g^{-1} by BET analysis. Thermal stability studies (TGA) indicate that the framework is stable up to 310 °C and then decomposes to CuO.

The synthesized MOF-199 has shown a great potential for environmental applications, especially for the adsorption of volatile organic compounds (VOCs). The maximum adsorption capacities were calculated as 104.50 mg/g for butyl acetate and 99.50 mg/g for ethanol with retention of >90% of its performance after seven regeneration cycles [31].

Chen et al. reported the synthesis of HKUST-1 via the hydrothermal strategy under relatively mild conditions, which realized the rapid formation of high-quality with strong textural performance. The optimized protocol was to mix the precursors at 50 °C for 3 h followed by methanol reflux activation which gave a highly crystalline product with a BET surface area of 1615 $m^2g^{-1}$and an isolated yield of 84.1 (Figure 2). This study is relevant as an example of process optimization towards milder and more efficient HKUST-1 synthesis as opposed to the conventional high temperature high pressure autoclave routes [32] although not completely free of solvent.

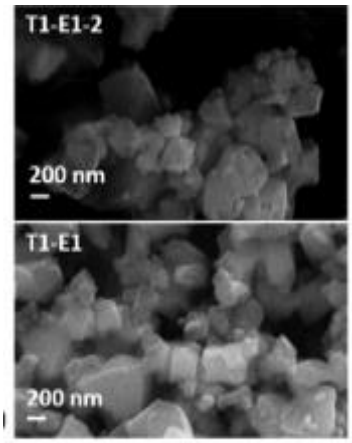

Fig. 2. SEM images of the samples synthesized under different reaction conditions (Reproduced from [32] under the Creative Commons Attribution (CC-BY-NC-ND) license).

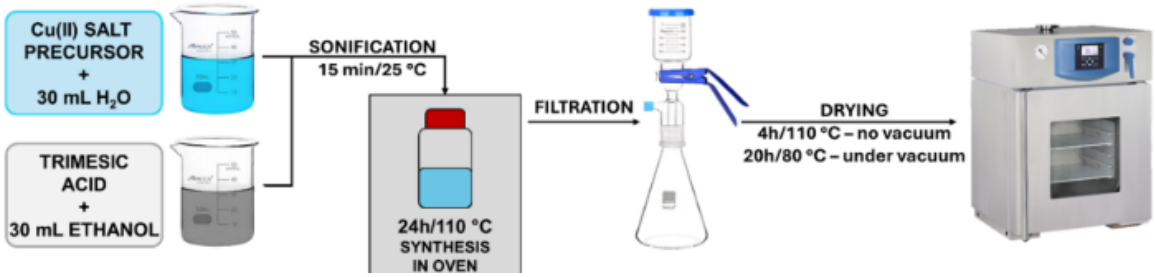

Fig. 3. Synthesis scheme of HKUST-1 (Reproduced from [34] under the Creative Commons Attribution (CC BY) license).

The synthesis of copper (II) trimesinate coordination polymers was explored by three different approaches, i.e., slow evaporation, solvothermal synthesis with PEG-1500 as a modulator and green synthesis in water by Dzhardimalieva et al.

The study showed that the structure and adsorption capacity of the obtained MOF materials depend on the synthetic pathway and reaction conditions. The samples obtained showed permanent microporosity, high surface areas and type-I nitrogen adsorption behavior. Kinetic, isotherm and thermodynamic analyses were performed to study the adsorption performances towards organic dyes such as methylene blue, Congo red and methyl violet. Moreover, thermolysis of copper trimesinate produced high purity Cu@C carbon materials, underlining the dual functionality of this material as an adsorbent and a precursor for nanostructured carbon-based composites [33].

Klęba et al. investigated the effect of various Cu(II) salt precursors on the morphology and physicochemical properties of HKUST-1 obtained by a DMF-free solvothermal route (Figure 3). The authors compared copper nitrate, sulfate, acetate and chloride and demonstrated that the choice of precursor plays a critical role in yield, phase composition, surface area, pore volume, thermal stability and morphology. Samples of HKUST-1 were obtained with BET surface areas of 1153, 937 and 553 m^2g^{-1} for the nitrate-, sulfate- and acetate-derived materials respectively. No product was formed from copper(II) chloride. The study highlights the role of precursor identity in controlling the HKUST-1 crystallization and illustrates a greener synthetic route to the conventional DMF-based protocols [34].

Abou-Elyazed et al. reported a solvent-free synthesis of HKUST-1, which, either deliberately or spontaneously, generated a large number of defect sites compared to its solvothermal counterpart. The material was synthesized by heating a ground mixture of copper nitrate trihydrate and BTC. The BET surface area and pore volume were high, 1671 m^2g^{-1} and 0.8 cm^3/g, respectively. TGA and potentiometric acid–base titration supported the defect formation, suggesting an increased missing-linker density in the solvent-free sample. Interestingly, the defect-rich HKUST-1 exhibited good catalytic activity for the esterification of oleic acid, producing 91 % methyl oleate against 70 % of the solvothermal reference, and was also found to be reusable as a heterogeneous catalyst. Solvent-free

synthesis is highlighted as an effective route for defect engineering in HKUST-1 with prominent catalytic benefits [35].

Sakai et al. demonstrated a one-pot hydrothermal conversion of a Cu monolith to a HKUST-1 monolith without the use of an external metal precursor. The authors showed that the crystallization rate can be controlled by using BTC in a water/ethanol medium with nitric acid as a dissolution promoter, and that the crystallization can be tuned from powder formation to monolith preservation.

The optimized monolith synthesized at 373K for 8 h in the presence of 130 mM HNO_3 preserved the macroporous architecture of the parent Cu monolith, exhibited HKUST-1 octahedral crystals of about 20 μm, and revealed a BET surface area of 1307 m^2g^{-1} with a micropore volume of 532 $cm^3(STP)g^{-1}$ MOF. Importantly, the monolith showed a CO_2 uptake of 118 $cm^3(STP)g^{-1}$ MOF MOF at 298 K and 100 kPa, which is on par with commercial HKUST-1 powder (Basolite C300), thus demonstrating the potential of direct monolithic conversion for gas adsorption applications [36].

Mechanochemical synthesis

Mechanochemical synthesis has emerged as an attractive green alternative in the preparation of HKUST-1 as it allows the formation of the framework by mechanical energy instead of the conventional solvent-mediated crystallization. In this approach, copper precursors and trimesic acid are typically mixed and activated via grinding, milling or ball-milling processes that favor coordination between Cu^{2+} centers and BTC linkers under solvent-free or minimal-solvent conditions.

Compared to conventional solvothermal synthesis, mechanochemical synthesis can greatly reduce the consumption of organic solvent, shorten the reaction time, reduce the amount of waste, and improve the process efficiency. These advantages make mechanochemical synthesis a particularly relevant pathway for the sustainable and scalable production of HKUST-1. However, parameters such as milling time, frequency, precursor type, liquid-assisted grinding conditions and post-synthetic activation strongly affect crystallinity, particle morphology, porosity and accessibility of open copper sites. Thus, careful optimization is needed to obtain HKUST-1 with high structural quality and appropriate performance for applications like gas adsorption, catalysis and sensing.

Mechanochemical synthesis offers an attractive solvent-free route to the formation of HKUST-1 ($Cu_3(BTC)_2$) and other metal-organic frameworks. Klimakow et al. synthesized HKUST-1 by ball milling as a solid-state reaction (Figure 4). The materials obtained showed a quantitative conversion and a specific surface area of 1713 m^2g^{-1}. The authors emphasized mechanochemistry as a rapid and simple alternative to conventional solvothermal routes, especially as it avoids solvent intensive processing and reduces the need for expensive activation and post-synthetic treatment. From a sustainability point of view, this work is remarkable because it combines solvent elimination, fast synthesis and high porosity, showing that green processing can still be compatible with high-performance MOF formation [37].

Stolar et al. have shown that the mechanosynthesis of HKUST-1 can be precisely controlled by the choice of the liquid additive in liquid-assisted grinding conditions. The authors used $Cu(OAc)_2.H_2O$ and H_3btc as precursors and monitored the reaction by in situ synchrotron powder X-ray diffraction. They identified additive-dependent reaction pathways for the formation of HKUST-1 via previously undetected copper-containing intermediates.

Thestudy demonstrated that low levels of protic and aprotic additives can strongly modulate milling reactivity while retaining a solvent-minimized route to a highly porous product with a specific surface area of 1713 m^2g^{-1}. From sustainability point of view, this work shows the efficiency of the mechanochemistry as

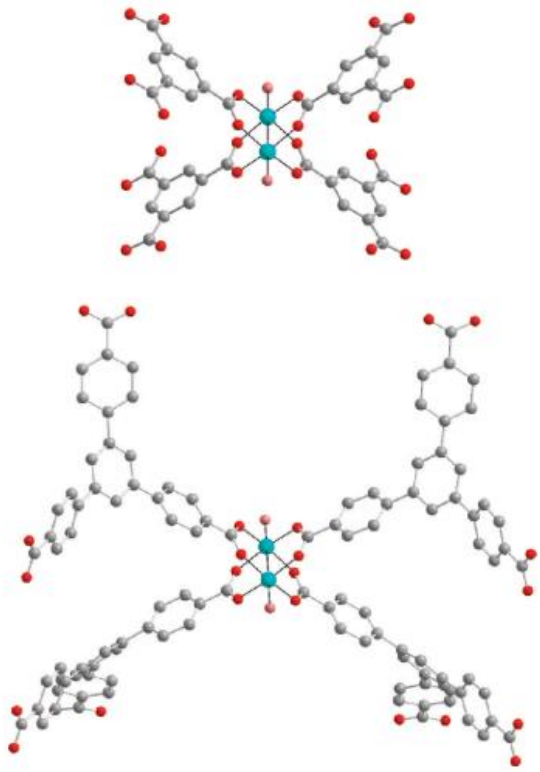

Fig. 4. Coordination environment around the dimeric copper unit (Reproduced from [37] under the Creative Commons Attribution (CC BY) license).

a promising approach to decrease the solvent consumption, the synthesis time and to improve the reaction efficiency in the preparation of MOFs [38].

Tran et al. developed an ethanol-assisted mechanochemical method to synthesize MOF-199 from $Cu(NO_3)_2.3H_2O$ and H_3BTC precursors. In this method, the reactants were hand-ground for 30 min in an agate mortar and pestle with only 0.1 mL of anhydrous ethanol, then heated at 120 °C for 4 h under nitrogen atmosphere.

The resultant MOF-199 showed a type-I N_2 adsorption isotherm, characteristic of microporous structure, with a BET surface area of 845 m^2g^{-1}. SEM analysis showed well defined octahedral crystals of the size of about 15–25 μm. The BET surface area obtained is lower than that of some solvothermally synthesized HKUST-1, but the method provides a greener and solvent minimized alternative to synthesize crystalline MOF-199, which can be a suitable precursor for CuOx/carbon composites in photo-enhanced Fenton-like dye degradation [39].

Zelenka et al. (2024) studied the effects of hand grinding and mechanical activation on the stability, particle size, textural properties and CO_2 sorption behavior of HKUST-1 (Figure 5) and MOF 76. While the study did not address the de novo synthesis of HKUST-1 (also known as MOF 199 or Cu BTC), it provided important insight into post-synthetic mechanical processing as a route to tuning adsorption performance. Hand grinding significantly increased the CO_2 uptake of HKUST-1 from 25.70 wt.% (5.84 mmol g^{-1}) to 41.37 wt.% (9.40 mmol g^{-1}) (~38%) while high-energy ball milling resulted in a decrease of the adsorption performance. This work showed that the sorption properties of HKUST-1 can be enhanced by mild mechanical treatment without re-synthesis, which is relevant for sustainable post-synthetic processing and performance enhancement of Cu BTC based materials [40].

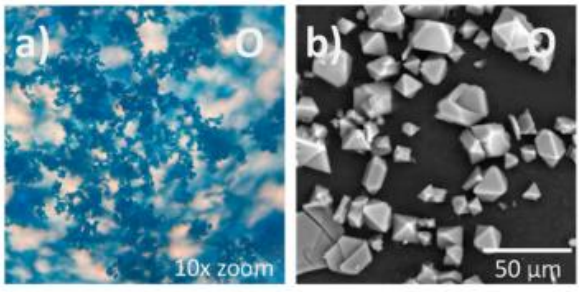

Fig. 5. (a) Optical (10 × zoom) and (b) SEM image of the original HKUST-1 (O) (Reproduced from [40] under the Creative Commons Attribution (CC BY) license).

Sondermann and co-workers reported a green mechanochemical route for the synthesis of mixed-metal Cu-Ru HKUST-1 (CuxRu-BTC) frameworks by liquid-assisted grinding explicitly based on the HKUST-1/MOF-199 scaffold. The synthesis was carried out in a planetary ball mill with methanol as a minimal amount of liquid additive (400 μL per vial), ZnO balls and 60 min milling time at 30 Hz. The successful synthesis of crystalline HKUST-1-type frameworks with homogeneous Cu/Ru distribution and microporous structure was verified by structural characterization. The mechanochemically synthesized HKUST-1 possessed a large BET surface area (1027 m^2g^{-1}) and also the mixed-metal analogues still showed significant porosity. Notably, the $Cu_{10}Ru$-BTC-based catalyst exhibited electrocatalytic oxygen evolution activity comparable to RuO_2 with an overpotential of 314 mV at 10 mA cm^{-2}, a Tafel slope of 55 mV dec^{-1} and low charge-transfer resistance of 13.6 Ω. This work is highly relevant as a case study of sustainable mechanochemical HKUST-1 synthesis and subsequent functional derivatization towards electrocatalysis [41].

Reaction-diffusion framework (RDF) in agar gel was used to achieve room-temperature synthesis of MTV-MOF-199, which allowed the controlled addition to the HKUST-1 scaffold in the presence of BTC. The mixed-linker frameworks obtained were crystalline MOF-199 topology, with the morphology evolution, tunable porosity and different surface areas as a function of the linker ratio. Interestingly, the 1:3 OH-BDC: BTC sample had a BET surface area of 900 m^2g^{-1}, whereas the functionalized samples with a 1:1 ratio exhibited lower surface areas of about 420 m^2g^{-1} and 410 $m^2g^{-1}$for the OH- and NH_2-based systems, respectively. The selective adsorption of methylene blue and rhodamine B by these materials highlights the advantage of linker engineering in HKUST-1-derived adsorbents [42].

Microwave-assisted synthesis

Microwave-assisted synthesis has been widely explored as an efficient alternative pathway for the preparation of HKUST-1, providing quick and uniform heating in contrast to the conventional solvothermal methods. In this approach, microwave irradiation directly interacts with polar solvents and reactive species leading to a faster nucleation and crystal growth of Cu-BTC framework in much shorter reaction times. The fast energy transfer can increase the synthesis efficiency, reduce thermal gradients and in some cases allow a better control of the particle size, morphology and crystallinity. From the green chemistry point of view, the microwave-assisted synthesis is attractive, as it can decrease the reaction time, the consumption of energy and the long high-temperature treatment. However, the final properties of HKUST-1 are highly dependent on parameters such as microwave power, irradiation time, solvent composition, precursor concentration and post-synthetic activation. Thus, systematic optimization is

necessary to obtain highly crystalline and porous HKUST-1 with available open copper sites for gas adsorption, catalysis, separation and sensing.

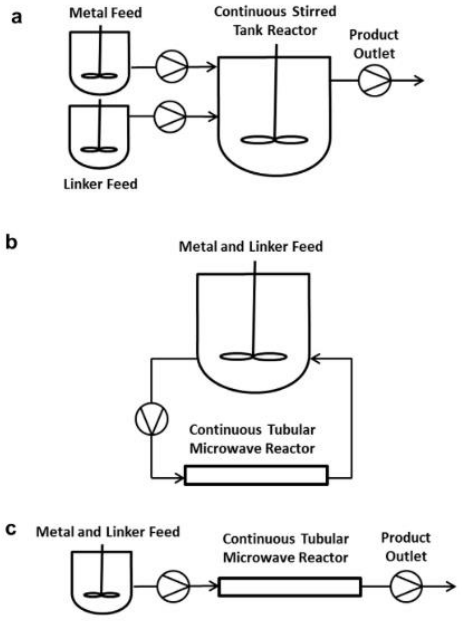

Fig. 6. Layouts of the continuous HKUST-1 synthesis systems used in this study. a: A CSTR used with conventional heating. b: A multi-pass continuous microwave assisted synthesis. c: A single-pass continuous microwave assisted synthesis (Reproduced from [46] under the Creative Commons Attribution (CC BY) license).

Seo et al. studied an early microwave-assisted synthesis of HKUST-1from a Cu(II)-trimesate mixture and proved that microwave irradiation can significantly accelerate crystallization in comparison with conventional hydrothermal processing. The study demonstrated a strong temperature dependence of the phase formation, solvent, reactant concentration and reaction time as well as the formation of additional Cu-BTC related phases under specific conditions. This work is particularly pertinent as it demonstrated microwave synthesis as a rapid and potentially greener way to make HKUST-1, and also compared the synthetic efficiency and quality of the product with traditional methods [43].

Tran Thanh Minh et al. reported microwave-assisted synthesis of HKUST-1 and its application as electrode modifier for simultaneous voltammetric determination of paracetamol and caffeine. The use of microwave irradiation led to a considerable decrease in crystallization time and an increase in yield compared to conventional hydrothermal synthesis, but without affecting the characteristic crystalline structure of HKUST-1. The study also showed the accurate simultaneous determination of both analysts at the MOF-199/Nafion-modified glassy carbon electrode in agreement with HPLC measurements, adding to the synthetic and functional value of this rapid preparation route [44].

In another study, direct comparison of microwave-assisted and solvothermal synthesis of HKUST-1 was studied. The use of a domestic microwave source under ambient atmosphere led to rapid formation of crystalline MOF-199 by microwave irradiation in only 30 min with a yield of 77.2 %, whereas the solvothermal route required much longer reaction times for comparable conversion. Both products were purified by several washes with DMF and dried at 180 °C. The present study is of interest as it shows that the microwave synthesis is a fast and efficient way to prepare HKUST-1 [45].

McKinstry et al. described a highly relevant and process-oriented approach for the scalable continuous production of high quality HKUST-1 employing conventional as well as microwave assisted heating. This work aimed at transferring the production of Cu BTC towards a more industrially relevant continuous process, in contrast to many laboratory-scale batch syntheses of HKUST-1 (Figure 6). The authors highlighted that ethanol was the only solvent used, which is significant in terms of sustainability and manufacturing, as it is less problematic than the commonly used solvents, DMF, and can be easily recovered and recycled. A significant contribution of the work was the development of a continuous microwave-assisted recycle-loop configuration, where the microwave irradiation and the overall reaction/residence time were more independently controlled than in a simple batch microwave system. The design enabled fast crystallization with good product quality, making the method attractive for process intensification. The paper reported a very high space–time yield for HKUST-1 production. The authors claimed that the reported space–time yield was higher than previously reported production rates for HKUST-1 and was about 17 times higher than the best previously reported ethanol-only systems. [46].

In 2017 Blanita et al. showed a very efficient microwave-assisted non-solvothermal synthesis of HKUST-1 at atmospheric pressure with a high yield of about 90% (including recovery of mother liquor) in just 10 min. The parameters optimization as the solvent composition ($EtOH/H_2O/DMF$), the temperature and the microwave exposure time were systematically performed. Interestingly, the BET surface areas of the optimized samples were more than 1700 m^2g^{-1}, close to the theoretical limits for Cu-BTC. However, the authors noticed a substantial decrease in porosity when the microwave irradiation was prolonged (15 min) or the temperature was increased to 80 °C, implying a narrow window for optimal rapid synthesis. Thermal

analysis (TGA) confirmed the structural stability of the microwave-derived HKUST-1 up to ~300 °C where the framework decomposition occurs. This fast method is a big step towards a scalable and energy-efficient synthesis of high-quality MOF-199 without the need for high-pressure solvothermal conditions [47].

Xue et al. developed a dual copper source strategy for the green synthesis of HKUST-1 with $Cu(NO_3)_2 \cdot 3H_2O$ and $Cu(OH)_2$ in the system of ethanol/water, achieving zero-discharge operation by reusing the mother-liquor. Under the optimized conditions (1:1 $Cu(OH)_2/Cu(NO_3)_2.3H_2O$, 383 K, 12 h, 4 mL solvent), the BET surface area, pore volume, and CO_2 uptake of MOF-199-50 at 196 K and 1 bar were 1902 $m^2.g^{-1}$, 0.82 $cm^3.g^{-1}$, and 341.01 $cm^3.g^{-1}$, respectively. The reused mother liquor product MOF-199-100R retained a high surface area of 1872 $m^2.g^{-1}$, supporting the feasibility of a closed-loop and environmentally benign synthesis route for HKUST-1 [48].

Sonochemical synthesis

Sonochemical synthesis is a fast and energy efficient method for the preparation of HKUST-1, where ultrasonic irradiation is used to promote the formation of the framework under mild conditions. The collapse of acoustic cavitation bubbles leads to the creation of localized hotspots with very high temperature and pressure for very short times, which improves the precursor mixing, accelerates the nucleation and facilitates the growth of Cu-BTC crystals. Compared with the conventional solvothermal synthesis, the sonochemical method can save reaction time, energy input and in some cases the amount of solvent used, and therefore it is an attractive approach from a green chemistry viewpoint. Furthermore, ultrasound-assisted synthesis can result in smaller particles, narrower size distributions and increased surface accessibility, which can be beneficial for adsorption, catalysis and sensing applications. However, the quality of the obtained HKUST-1 is strongly dependent on parameters such as ultrasound frequency, power, irradiation time, solvent system and precursor concentration, which need to be carefully optimized for high crystallinity and structural stability.

Armstrong et al. (2017) studied the sonochemical synthesis of HKUST-1 focusing on the particle-size evolution and crystallization mechanisms under ultrasonic irradiation. HKUST-1 was prepared using copper(II) nitrate and BTC in a DMF/water mixture with a QSonica Q500 sonicator (20 kHz, 500 W maximum power) at 60% amplitude for 30 min, followed by washing with acetone and drying in air overnight. The product obtained was confirmed by PXRD to be in agreement with the simulated pattern of HKUST-1 . Nitrogen adsorption at 77 K revealed a Type I isotherm and a BET surface area of approximately 850 $m^2.g^{-1}$, indicating the preservation of microporosity under sonochemical conditions. Importantly, the study proposed a mechanistic framework involving crystal nucleation, growth, and ultrasound-induced sonofragmentation in hot-spot, shockwave, and bulk fluid regions, which is a valuable reference for morphology-controlled and scalable HKUST-1 synthesis [49].

Electrochemical synthesis

Electrochemical synthesis is a promising and relatively clean route to prepare HKUST-1 where metal ions are generated in situ from a sacrificial copper electrode and then coordinated with trimesic acid linkers to construct the Cu-BTC framework. Electrochemical methods can reduce the dependence on metal-salt precursors, minimize counter-ion contamination and provide better control over crystal nucleation by applied voltage or current, in contrast to traditional solvothermal routes that often rely on soluble copper salts and large amounts of organic solvents. The method is also attractive for direct production of HKUST-1 films or coatings on conductive substrates, which is particularly useful for sensing, membranes, and device-integrated applications. Electrochemical synthesis has green chemistry benefits including mild reaction conditions, tunable reaction rates, reduced reagent waste, and possible compatibility with continuous or scalable production systems. However, the final crystallinity, morphology, adhesion, porosity and surface coverage of HKUST-1 are very dependent on parameters like electrolyte composition, applied potential, current density, electrode material, linker concentration, reaction time and solvent system. Therefore, careful optimization of the electrochemical conditions is required to obtain phase-pure, porous and structurally stable HKUST-1 materials for practical applications.

A rapid electrochemical route was reported for the fabrication of HKUST-1 films on indium tin oxide (ITO) substrates. The approach was two-step, the first one was the electrodeposition of copper on ITO from an aqueous electrolyte followed by anodic conversion of the deposited Cu layer to HKUST-1 in an ethanol/water medium containing BTC and TBAP. The process produced octahedral HKUST-1 crystals directly anchored on the conductive substrate under an applied potential of 1.5 V for 100 s. XRD analysis demonstrated the nearly complete conversion of metallic Cu to the MOF phase as evidenced by the disappearance of Cu reflections and the appearance of the characteristic HKUST-1 peak at 11.6°. Overall, the

study presents a substrate-compatible and time-efficient approach to prepare HKUST-1 films with potential relevance to sensing and electrochemical device integration [50].

Van Assche et al. reported an electrochemical route for the synthesis of thin HKUST-1 layers on porous copper mesh, representing an early example of structured-support growth of CuBTC rather than conventional bulk powder production. In this approach, the copper mesh served simultaneously as the substrate and the copper source, enabling direct electrochemical oxidation in an ethanol/water medium containing BTC (16 mg/mL). The influence of solvent composition, particularly the water fraction (10–50 wt.%), and temperature was systematically examined, revealing that homogeneous HKUST-1 coatings could be obtained under suitable conditions, whereas higher water contents led to the formation of additional structures [51].

In another work, Nguyen et al. reported an applied-current electrochemical synthesis of HKUST-1 from H_3BTC and copper in the presence of $NaNO_3$ electrolyte and methanol. By systematically varying current intensity, electrolyte concentration, synthesis time, and hydrate treatment, the authors demonstrated that the crystallographic phase and morphology of the product are highly condition-dependent, with CuBTC being obtainable in 1D or 3D forms. The optimal condition for the 3D phase was 100 mA in 0.05 M $NaNO_3$ for 10 min. BET analysis showed a marked increase in surface area from 79 to 617 $m^2.g^{-1}$ after a short hydrate process, whereas prolonged hydration damaged the structure. This study highlights the strong sensitivity of electrochemically synthesized HKUST-1 to synthesis and post-treatment conditions [52].

Under optimized conditions, the authors obtained a high yield of 97.51% with respect to copper anode dissolution. The resulting material was highly porous with cubic morphology consisting of primary particles of 10-20 nm size and network-like aggregates of 0.2-0.5 um. The formation of phase-pure $Cu_3(BTC)_2$ was confirmed by structural. The material exhibited a type-I N_2 sorption isotherm, with a BET surface area of 1308 $m^2.g^{-1}$, pore volume of 0.61 $cm^3.g^{-1}$, and pore size of 13.2 Å. In a model catalytic reduction of p-nitrophenol by $NaBH_4$, the electro synthesized MOF showed excellent activity with an apparent rate, which demonstrated the strong dependence of catalytic performance on the electrochemical synthesis conditions, nanostructure and porosity [53].

Recently, Araújo-Cordero et al. (2023) demonstrated an advanced direct electrochemical conversion pathway to fabricate core-shell architectures, i.e. $Cu_2O@Cu_3(BTC)_2$. Conformal MOF shell growth was achieved via controlled anodic dissolution of copper microstructures on ITO substrates at room temperature (Figure 7). This is in contrast to conventional bulk powder electrosynthesis because here spatial control over the MOF formation is obtained, which leads to an increase in the dimensions of the initial copper-based microcubes of ~38.7 %. The structural integrity and coordination were confirmed by Raman spectroscopy and XRD indicating the potential of this method for integrated electronic and sensing applications where it is essential to have a thin film MOF coverage [54].

Supercritical CO_2 synthesis

Taking the advantage of peculiar physicochemical properties of carbon dioxide in the supercritical state, the synthetic method of HKUST-1 in supercritical CO_2 has been developed as an environment-friendly method. In its supercritical state, CO_2 has gas-like diffusivity and liquid-like density, allowing for efficient mass transfer, better penetration into porous media, and improved removal of reaction byproducts and residual solvents. These features can help the crystal formation and at the same time reduce the use of common organic solvents making the process in

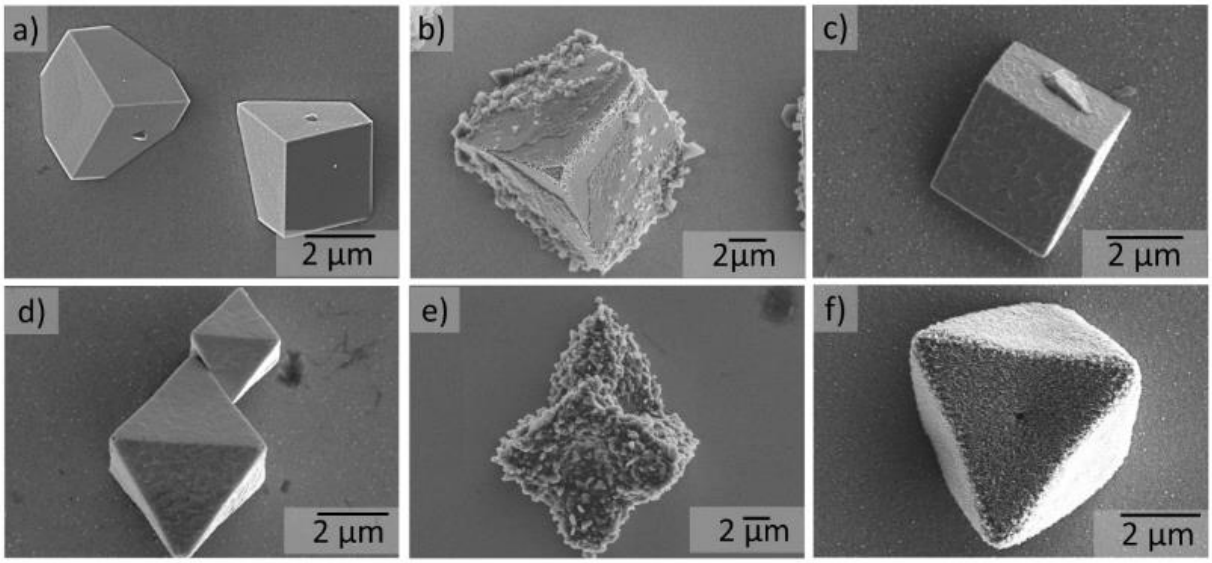

Fig. 7. a–c) SEM images of Cu_2O c) Cu(TCPP). d–f) Cu_2O cubes with exposed [100] planes a) before and b, c) after electrochemical conversion into either b) $Cu_3(BTC)_2$ octahedra with exposed [111] planes d) before and e, f) after electrochemical conversion into either e) $Cu_3(BTC)_2$ or f) Cu(TCPP) (Reproduced from [54] under the Creative Commons Attribution (CC BY-NC-ND) license).

accordance with green chemistry principles. Supercritical CO_2 can be used to aid activation and drying procedures, where it is important to preserve the microporous structure, as in the case of HKUST-1, while reducing surface tension effects and minimizing pore collapse. But the success of this method is highly dependent on parameters like pressure, temperature, co-solvent usage, solubility of the precursor and reaction time. Therefore, the operating conditions should be carefully controlled to obtain highly crystalline HKUST-1 with desired porosity, morphology and functional performance for applications in gas adsorption, catalysis and sensing.

A new route for HKUST-1 was reported by systematically changing pressure (8-10 MPa), $scCO_2$ injection temperature (80-180 °C), CO_2 mol fraction (0.392-0.720) and residence time (70-170 s), the authors demonstrated robust formation of high-quality HKUST-1 under all the conditions studied. The obtained particles possessed sizes of 55–300 nm (average 135 nm) and high BET surface areas between 1374 and 2389 $m^2.g^{-1}$. The long residence times favored the particle growth and the morphology change from spherical to octahedral, while the pressure in the supercritical regime had little effect on the material properties. Of particular interest was the strong negative correlation between the temperature of the reactor section and particle size ($r = -0.86$, $p = 0.04$), which highlights the dominant role of thermal history in controlling HKUST-1 nucleation and growth [55].

Feng et al. reported a continuous-flow supercritical CO_2 process for the rapid synthesis of HKUST-1 nanoparticles. The synthesis took less than 10 s using a $scCO_2$/ethanol (9:1 co-solvent system) at 75 °C and 13 MPa with a 0.1 M Cu precursor. The obtained HKUST-1 particles had median sizes of 110–250 nm, BET surface areas of 1610–1890 m^2/g, and a typical dry yield of 53.7 wt%, which gave a space-time yield of 5668 $kg \cdot m^{-3} \cdot d^{-1}$. Mechanistic analysis showed a non-classical crystallization pathway where aggregation of nascent aerosolized structures contributes to particle growth. This work is unique in process intensification, high throughput and potential solvent/precursor recycling for scalable HKUST-1 production. [56].

Doan and co-workers studied sophisticated route for the synthesis of hierarchical HKUST-1 by using CO_2 -expanded solvent (CXL) systems (Figure 8). The crystallization process was controlled by using a 1:1 DMSO/MeOH precursor solution at a mild temperature of 40 °C and pressures from 40 to 100 bar. One of the main findings was that $scCO_2$ drives a post-crystallization etching mechanism that results in the formation of hierarchical porosity. The conventional methanol-precipitated HKUST-1 had a high surface area of ~2032 $m^2.g^{-1}$, but the CO_2-processed samples showed tunable porosities. For example, at 70 bar and 24 h, a surface area of 1693 $m^2.g^{-1}$ and a total pore volume of 0.794 cm^3.g-1 were obtained. This CXL approach provides a material-efficient and green alternative to the conventional solvothermal methods

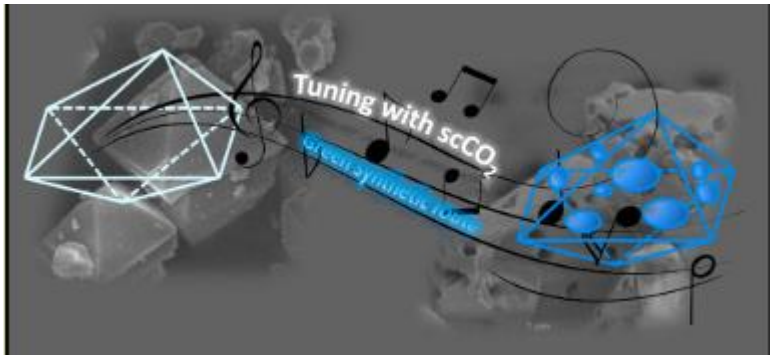

Fig. 8. Controlled Formation of HKUST-1Using CO_2-Expanded Solvent Systems (Reproduced from [57] under the Creative Commons Attribution (CC BY) license).

and offers the possibility to tailor pore architectures, which is essential in mass transport applications [57].

Comparative perspective on green synthesis strategies for HKUST-1

Because of its distinct paddlewheel secondary building units, accessible pore network, and open metal sites following activation, HKUST-1 has long been used as a benchmark copper-based metal-organic framework. It is widely used in adsorption, gas storage and separation, catalysis, and sensing because of these structural characteristics. However, the conventional solvothermal synthesis of HKUST-1 typically relies on high-energy input, solvent-consuming procedures, and downstream purification stages, all of which are increasingly at odds with the concepts of sustainable manufacturing and green chemistry. Because of this, a lot of work has gone into creating synthetic pathways that maintain porosity and crystallinity while lowering waste, solvent consumption, and process complexity.

Table 1 summarizes the main green synthesis routes reported for HKUST-1, highlighting the trade-off between process design, structural quality and sustainability metrics. Among these, the dual copper source strategy, one of the examples of the process circularity, is especially instructive: Xue et al. prepared a high-quality product with a BET surface area of 1902 $m^2.g^{-1}$, a pore volume of 0.82 $cm^3.g^{-1}$ and a yield of 98.1% in an ethanol/water medium, while mother-liquor reuse and zero-discharge operation were also enabled. In parallel, solvent-free mechanochemical routes have shown that HKUST-1 can be synthesized in the absence of bulk solvent, often giving rise to defect-rich frameworks with promising catalytic activity. Microwave- and ultrasound-assisted methods also reduce reaction time and energy demand, while CO_2-assisted and aqueous/ethanol/PEG-based routes are other attempts to minimize environmental burden by medium engineering.

The two approaches, though very different in chemistry and reactor design, have a common goal, moving the HKUST-1 synthesis from a purely preparative exercise to a scalable, resource-efficient and application-oriented manufacturing process. Importantly, the synthesis route affects not only the yield and surface area but also the particle morphology, defect density, hierarchical porosity and ultimately the performance of HKUST-1 in adsorption, catalysis and sensing. This requires the comparative analysis of green synthesis strategies to identify routes that optimize sustainability and functional performance.

Challenges and Future Perspectives

Despite significant advances in the green and functional synthesis of HKUST-1, there still exist several scientific and technological challenges limiting its wider practical implementation. One of the key challenges is that it is hard to achieve high crystallinity, large surface area, controlled defect density and environmentally benign processing conditions simultaneously. In many cases, greener routes such as solvent-free or low-solvent synthesis can be used to reduce solvent consumption and waste generation, but may also influence the uniformity of the crystals, accessibility of the pores, phase purity, or reproducibility. Therefore, a major challenge is to optimize sustainable synthesis protocols without affecting the structural quality of the final material and its performance.

Another major problem is the poor scalability of many synthesis methods at laboratory scale. Many promising hydrothermal, sonochemical, mechanochemical and solvent-free routes for HKUST-1 preparation have been reported in the literature. Nevertheless, many of these routes are still difficult to apply to industrial production due to issues relating to heat

and mass transfer, batch-to-batch variability, activation efficiency and process control. In addition, the use of pure high purity reagents, lengthy reaction times and post-synthetic purification steps may mask the overall economic and environmental advantages of the proposed green methods. Thus, the development of scalable, reproducible and cost-effective synthesis platforms is still a significant goal.

A different problem is the stability of HKUST-1 under realistic conditions of use. HKUST-1 shows good porosity and accessible open metal sites, but its moisture sensitivity and structural degradation in humid environments restrict some applications, in particular gas separation, catalysis and sensing under ambient conditions. This limitation is even more significant when defect engineering or metal substitution is introduced, as these modifications may improve functionality but can also change framework stability. Hence, future studies should focus more on the relationship between green synthesis conditions, defect formation, metal-site chemistry and long-term structural durability.

Further, research on HKUST-1 synthesis should target a more integrated design strategy, whereby sustainability, structural control and application performance are all optimized together. More systematic studies are required to develop clear correlations between synthesis parameters and final framework properties such as particle size, morphology, porosity, defect concentration, and accessibility of active sites. In particular, advanced in situ and operando characterization techniques may give valuable insight into nucleation, crystal growth, defect generation, and solvent or modulator effects during synthesis.

Moreover, the future progress will much rely on the use of quantitative sustainability metrics. Many reports classify a method as “green” primarily based on decreased solvent use or lower temperature, but more rigorous evaluation is required by metrics such as atom economy, E-factor, energy consumption, solvent recyclability and life-cycle assessment. These investigations would enable more realistic comparisons of synthetic routes and the identification of the most practical strategies for large-scale implementation.

Table 1. Comparative overview of green synthesis strategies for HKUST-1.

Synthesis route	Ref.	BET (m^2/g)	Yield (%)
Conventional solvothermal	Literatures	1500–1900	70–95
Mechanochemical	[39]	845	-
Mechanochemical (Cu–Ru HKUST-1)	[41]	1027	-
Microwave-assisted	[45]	-	77.2
Microwave-assisted optimized	[47]	>1700	~90
Continuous microwave process	[46]	-	N.R.
Electrochemical	[53]	1308	97.5
Sonochemical	[49]	850	-
Dual copper source	[48]	1902	98.1
Continuous $scCO_2$	[55]	1374–2389	-
$scCO_2$/EtOH continuous	[56]	1610–1890	53.7

The development of shaped, composite and device-compatible HKUST-1 materials is another promising direction. Monolithic architectures, membrane-supported growth, conductive hybrids and binder-free structured forms may be a path from powder synthesis to real technological applications. At the same time, continuous-flow, semi-continuous and electrochemical synthesis methods could provide more controllable and scalable alternatives to conventional batch processes. Machine learning in combination with data-driven optimization may also enable rapid identification of optimal green synthesis windows for targeted applications.

The future of HKUST-1 research is not only in more sustainable preparation of the material, but also in understanding how synthesis governs functionality at multiple scales. A successful next-generation synthesis strategy for HKUST-1 must be environmentally responsible, economically viable, structurally reproducible, and directly relevant to the demands of practical applications such as carbon capture, hydrogen storage, catalysis and electrochemical sensing.

Conclusion

HKUST-1 is one of the most important and widely investigated metal-organic frameworks for its high surface area, permanent porosity, accessible open copper sites, and versatile performance in the fields of gas adsorption, catalysis, sensing and energy-related applications. However, HKUST-1 is troubled by the

traditional synthetic route, which takes a long time, uses a lot of solvent, requires energy-intensive activation, and produces waste. These drawbacks have encouraged the development of more eco-friendly, more efficient and application-oriented strategies for the synthesis.

Recent developments show that sustainable synthesis of HKUST-1 is no longer limited to replacing toxic solvents or lowering the reaction temperature. Rather, green synthesis has evolved to a more holistic design concept including solvent minimization, precursor efficiency, waste reduction, process circularity, morphology control, defect engineering and metal doping and composite formation. Methods such as solvent-free synthesis, hydrothermal synthesis with recycling of the mother liquor, modulated one-step synthesis, monolithic conversion and in situ growth on conductive carbon supports demonstrate that environmentally friendly routes can still generate HKUST-1 with high crystallinity, large BET surface area, tunable pore structure and improved functional performance.

Additionally, the properties of HKUST-1 are directly influenced by the synthesis route. Crystal size, defect density, porosity, morphology and accessibility of active Cu sites depend on parameters such as solvent, copper source, modulator, reaction temperature, aging time and post-synthetic activation. These structural features then determine the performance of HKUST-1 in practical applications such as CO_2 capture, hydrogen storage, heterogeneous catalysis and electrochemical sensing. Future development of HKUST-1 should therefore not only focus on high surface area, but also on the balance of structural quality, environmental sustainability, scalability, reproducibility and application-specific functionality.

In general, green synthesis strategies offer a promising route for the practical and sustainable synthesis of HKUST-1. Further progress will require systematic life-cycle assessment, a better understanding of the mechanisms of defect formation, optimization of solvent-free and low-solvent routes, and development of scalable continuous or semi-continuous processes. The combination of the green chemistry principles and the exact control of the framework structure and morphology is a promising approach to bring HKUST-1 closer to large scale implementation in environmentally and industrially relevant technologies.

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