Mechanically stable, hierarchically porous Cu₃(btc)₂ (HKUST-1) monoliths via direct conversion of copper(II) hydroxide-based monoliths.
Mechanically stable, hierarchically porous Cu$_3$(btc)$_2$ (HKUST-1) monoliths via direct conversion of copper(II) hydroxide-based monoliths†

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The synthesis of highly crystalline macro-meso-microporous monolithic Cu$_3$(btc)$_2$ (HKUST-1; btc$^{3^-}$ = benzene-1,3,5-tricarboxylate) is demonstrated by direct conversion of Cu(OH)$_2$-based monoliths while preserving the characteristic macroporous structure. The high mechanical strength of the monoliths is promising for possible applications to continuous flow reactors.

Porous coordination polymers 1,2 (PCPs) or metal–organic frameworks (MOFs) assembled from metal ions with organic bridging units are of tremendous importance because of their possible applications in areas including gas storage, separation, catalysis, sensing, drug delivery, proton conduction, optics, biomedicine and microelectronics. 3 In order to maximize the performance of PCPs in such a diverse host of applications, it is necessary for fabrication techniques that deliver these materials in an appropriate material form to be developed. In recent years, there has been an increasing number of studies directed toward the structuralization of PCP crystallites into various material forms, such as hollow spheres, 4,5 core shell particles, 6 thin-films, 7 membranes, 8 patterns on surfaces, 9 coatings on monoliths, 10 and aerogels. 11 Many of these are achieved through synthetic strategies that result in the preferential deposition of PCPs at an appropriately functionalized surface, 12 and can be combined with techniques such as liquid-phase epitaxial growth, 13 seeding, 14 evaporation deposition 15 and electrochemistry for the preparation of high-quality PCP thin films, composites and crystal arrangements. 16 Despite the significant advances made in this regard, there is still a critical need for the development of fast and inexpensive methods that facilitate a greater control over material structur-alization. In particular, porous materials that simultaneously offer a high effective surface area and efficient transport of fluids are crucial for the applications of PCPs in separation and catalysis.

Three-dimensional silica gel monoliths with a hierarchically macroporous structure are some of such porous materials and of high particular importance for real-world applications. 17,18 These monolithic silica materials are directly prepared through the alkoxysilane-derived sol–gel process accompanied by phase separation. In addition to the well-defined pore structure of the monoliths, their high enough mechanical strength is crucial to withstand the pressure of the fluids, which reaches 1 MPa at the linear velocity of 1 mm s$^{-1}$ in the case of 100 mm length monolithic silica columns. 19 Recent developments in the synthesis strategy of the epoxide-mediated sol–gel accompanied by phase separation 20–24 have opened a pathway to transition metal hydroxide/oxhydroxide monolithic gels, which otherwise end up with the crystalline precipitations. Syntheses of aluminum, 20 iron, 21 nickel, 22 chromium, 23 and copper 24 (oxy)hydroxide monoliths with well-defined macropores have been reported by this procedure.

In the case of PCPs, though monolithic materials with additional macropores would exhibit a high potential for enhancing their applicative domains, the direct synthesis has been still challenging because of the high tendency of PCP crystallites to precipitate as powders rather than to be integrated into a homogeneous monolithic form. Recently, the coordination replication technique, which allows the direct conversion of preformed three-dimensional macroporous metal oxide/oxhydroxide/oxhydroxide monoliths into their corresponding PCP monoliths, was shown to be an alternative way to synthesize porous monolithic PCPs. Although promising, the scope of this technique has so far been limited to Al$_2$O$_3$ and V$_2$O$_5$. 25,26 The mechanical properties of the resultant PCP monoliths are, however, not satisfactory because of weak linkage between the PCP crystallites that constitute the macroporous framework. In the above cases of iron, 21 nickel, 22 chromium, 23 and copper 24 (oxy)hydroxide monoliths, polyacrylamide (PAAm), which is employed in the starting solution to induce phase separation, is found to take an additional part of “gluing” the (oxy)hydroxide colloidal constituents in the monolithic structure. The presence of PAAm in the original (oxy)hydroxide network may give a positive effect on the mechanical
properties of final PCP monoliths, thus extending application forms of PCPs.

Using the copper hydroxide (Cu(OH)₂)-based monolith as an example, we herein show the direct conversion into a corresponding PCP monolith by an acid–base reaction: 3Cu(OH)₂ + 2H₃btc → Cu₃(btc)₂ + 6H₂O (btc = benzene-1,3,5-tricarboxylate), while preserving the well-defined co-continuous macroporous structure and monolithicity in the original gels (Fig. 1). The resultant Cu₃(btc)₂, also known as HKUST-1, is one of the most studied forms of PCPs.

Table 1 Starting compositions and BET surface area (a_{BET}) values of the samples

| Entry | PAAm/g | a_{BET}/m² g⁻¹ | Morphology              |
|-------|--------|----------------|------------------------|
| Cu-00 | 0      | N.A.           | Precipitation          |
| Cu-03 | 0.30   | 212            | Particle aggregates    |
| Cu-06 | 0.60   | 146            | Co-continuous          |
| Cu-10 | 1.00   | 97             |                        |

CuCl₂ Sol-Gel with Phase Separation Macroporous Cu(OH)₂ Monolith Hierarchically Porous Cu₃(btc)₂ Monolith

![Fig. 1 Schematic representation of the synthesis of a Cu(OH)₂-based monolith and its coordination replication to a Cu₃(btc)₂ monolith in the presence of H₂btc with preserved macropores.](image)

In all the cases, 1.53 g of CuCl₂, 2H₂O, 1.10 mL of water, 0.30 mL of ethanol, 2.40 mL of glycerol and 1.47 mL of propylene oxide (±) were used as the metal source and acid scavenger, respectively. The starting compositions (Table 1) were selected by immersing 200 mg of as-synthesized Cu-06 in 5 mL of the 0.5 M H₃btc solution in N,N-dimethylformamide (DMF) and ethanol (1:1 by volume) at 80 °C. The progress of conversion with time was monitored by scanning electron microscopy (SEM, Fig. 3, and Fig. S2 in the ESI† at lower magnification), XRD (Fig. 4a), and nitrogen adsorption–desorption (Fig. 4b and c) of the samples at different time intervals.

The replication of the Cu(OH)₂ monolith to Cu₃(btc)₂ monolith was performed by immersing the as-synthesized Cu-06 in a solution containing 0.5 M H₂btc at 80 °C. We have screened out Cu-03 and Cu-10, since the precursor gel has low mechanical properties due to the low connectivity of macropore skeletons and too small macropores that easily collapse when the PCP crystallites develop with the reaction time, respectively. An immediate change in the color of the gel from green to blue with the preservation of the monolithic form indicates successful progression of conversion. The powder X-ray diffraction (XRD) of the dried gel unambiguously confirms the formation of Cu₃(btc)₂. In order to observe the course of conversion, we have optimized the reaction conditions by immersing 200 mg of as-synthesized Cu-06 in 5 mL of the 0.5 M H₂btc solution in N,N-dimethylformamide (DMF) and ethanol (1:1 by volume) at 80 °C. The progress of conversion with time was monitored by scanning electron microscopy (SEM, Fig. 3, and Fig. S2 in the ESI† at lower magnification), XRD (Fig. 4a), and nitrogen adsorption–desorption (Fig. 4b and c) of the samples at different time intervals.

The PCP daughter phase derived from the Cu(OH)₂-based monolith was observed by SEM after an immersion time of 2 min by roughening of the smooth parent surface, because of the surface-directed growth of small ill-defined nuclei of sub-100 nm. The XRD of the gel after 2 min also indicated the change from amorphous to slightly crystalline in the gel; these observations are supported by an increase in the surface area contributed mostly by the increased microporosity of Cu₃(btc)₂. Upon increasing the reaction time to 3 and 6 min, the population of well-defined sub-micrometer-sized PCP crystals and the microporosity were further increased with the preservation of...
stopped at this stage and the total specific surface area reaches ca. 1315 m² g⁻¹ (Table S1, ESI†), which is comparable to the Cu(OH)₂ derived Cu₃(btc)₂ powders³⁰ and remains almost constant even after a reaction time of 24 h, indicating the total possible conversion of Cu(OH)₂ monoliths. The extension of the mesopore size is attributed to the interstitial pores formed in-between the Cu₃(btc)₂ crystallites in the macropore skeletons. An increase in the incorporation of H₃btc in the gel network was confirmed by thermogravimetry-differential thermal analysis (TG-DTA), which shows a sharp weight loss at around 375 °C (Fig. 4d). In all the cases, crack-free monoliths were obtained after solvent exchange with ethanol and drying at 40 °C for 1 d. It is noteworthy that the kinetics of coordination replication depends also on the dimension of the monolith. The increase in the replication time with increasing dimension of the monolith is attributed to the extended time required for diffusion of the ligand inside the monolith. It took 30 min for complete replication when using a cylinder-shaped monolith with a diameter of 1 cm and a height of 0.5 cm (Fig. 5a).

The monoliths were then subjected to mechanical measurement by uniaxial compression. For this study, a macroporous silica monolith with SBA-15-type periodic mesoporosity,³¹ which has been used as a stationary phase for high-performance liquid chromatography (HPLC),³² has been used as a reference to compare the mechanical properties of as-dried Cu-06 and the Cu₃(btc)₂ monolith (reacted for 6 min). Although a decrease in strength (stress values at catastrophic failure) is found from ~2.5 MPa for Cu(OH)₂ to ~1.5 MPa for Cu₃(btc)₂ as shown in Fig. 5b, the value is still well comparable to that of the periodic mesoporous silica monolith (strength ~1.5 MPa). This result promises the uses under liquid flow by pumping such as chromatography columns and continuous flow reactors.³³,³⁴ The decrease in Young’s modulus and compressive strength is probably due to the lowered connectivity between the Cu₃(btc)₂ crystallites formed by the transformation; however, the presence of a small amount of PAAm in the skeletons should enhance the binding of each crystallite to increase the toughness of the monolith just as in the case of Cu₃(btc)₂-based hollow capsules.³⁵ Although other reported MOF–polymer composites³⁶–³⁷ may show higher mechanical stability because they consist mostly of the polymer, their accessible surface area is limited to around 500 m² g⁻¹ or less, which is lower than 1315 m² g⁻¹ in our case.

In summary, we have demonstrated the direct conversion of hierarchically porous Cu(OH)₂-based monoliths to Cu₃(btc)₂...
(HKUST-1) monoliths by coordination replication in the presence of H$_2$btc as the ligand with complete preservation of the macro-porous structure. After 6 min of the conversion treatment, the resulting Cu$_3$(btc)$_2$ monolith shows high crystallinity, a high surface area of 1315 m$^2$ g$^{-1}$, and high enough mechanical properties. These properties make this material attractive for future applications as the heterogeneous monolithic catalyst that can be used in the continuous flow mode.

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