Mechanically stable, hierarchically porous Cu_3(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 structuralization. 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 macro-mesoporous 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/oxyhydroxide 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 macro pores have been reported by this procedure.

In the case of PCPs, though monolithic materials with additional macro pores 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 macro-porous metal oxide/hydroxide/oxyhydroxide 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

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properties of final PCP monoliths, thus extending application forms of PCPs.

Using the copper hydroxide (Cu(OH)$_2$)-based monolith$^{24}$ as an example, we herein show the direct conversion into a corresponding PCP monolith by an acid–base reaction: $3\text{Cu(OH)}_2 + 2\text{H}_3\text{btc} \rightarrow \text{Cu}_3(\text{btc})_2 + 6\text{H}_2\text{O}$ (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 Cu$_3$(btc)$_2$, also known as HKUST-1, is one of the most studied forms of PCPs.

As aforementioned, we have recently demonstrated a facile protocol for the synthesis of hierarchically porous copper hydroxide-based monoliths (amorphous), in which the microstructure and macropore size can be controlled.$^{24}$ Copper chloride and propylene oxide ($\pm$) were used as the metal source and acid scavenger, respectively.$^{27-29}$ The starting compositions for the synthesis of Cu(OH)$_2$-based monoliths are described in Table 1. The role of PAAM ($M_w = 10\,000$ Da) in the reaction mixture is not only controlling phase separation but also supporting the scaffold of Cu(OH)$_2$ by chelating the copper ions with nitrogen in the amide groups of PAAM, which is responsible for low crystallinity in the as-dried gels. Indeed, the precipitate was obtained when the reaction was conducted without the presence of PAAM (sample Cu-00). The addition of $0.30$ g of PAAM (Cu-03, Fig. 2a) in the reaction mixture results in the formation of a monolithic gel. However, the gel morphology consists of aggregated particles due to high phase separation tendency. The increase in the amount of PAAM to $0.60$ g (Cu-06, Fig. 2b) leads to the decreased phase separation tendency and a change in the gel morphology from aggregated particles to co-continuous structures with the macropore size of approximately $3$ μm. The further increase in the amount of PAAM to $1.00$ g (Cu-10, Fig. 2c) leads to a further decrease in phase separation tendency and the macropore size reduces to $0.5$ μm.

The replication of the Cu(OH)$_2$ monolith to Cu$_3$(btc)$_2$ monolith was performed by immersing the as-synthesized Cu-06 in a solution containing $0.5$ M H$_3$btc 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 crystallizes 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 Cu$_3$(btc)$_2$. In order to observe the course of conversion, we have optimized the reaction conditions by immersing $200$ mg of as-dried Cu-06 in $5$ mL of the $0.5$ M H$_3$btc 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 Cu$_3$(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

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>PAAM/g</th>
<th>$a_{BET}$/m$^2$ g$^{-1}$</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-00</td>
<td>0</td>
<td>N.A.</td>
<td>Precipitation</td>
</tr>
<tr>
<td>Cu-03</td>
<td>0.30</td>
<td>212</td>
<td>Particle aggregates</td>
</tr>
<tr>
<td>Cu-06</td>
<td>0.60</td>
<td>146</td>
<td>Co-continuous</td>
</tr>
<tr>
<td>Cu-10</td>
<td>1.00</td>
<td>97</td>
<td>Co-continuous</td>
</tr>
</tbody>
</table>

* In all the cases, $1.53$ g of CuCl$_2\cdot2$H$_2$O, $1.10$ mL of water, $0.30$ mL of ethanol, $2.40$ mL of glycerol and $1.47$ mL of propylene oxide ($\pm$) were used for gel synthesis.
the parent co-continuous macroporous structure. After a reaction
time of 6 min, densely packed crystals with the parent macroporous
architecture were obtained. This is also supported by the XRD
results, which demonstrate the appearance of a highly crystalline
Cu₃(btc)₂ phase. The highly crystalline and porous daughter phase
causes a decrease in the macropore size. The progress of the reaction
stopped at this stage and the total specific surface area reaches
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 chromato-
graphy (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 compres-
sive 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
supported by 4 wt% of polyvinyl alcohol.5 Although other reported
MOF–polymer composites35–37 may show higher mechanical stabi-
lity 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,

Fig. 3  SEM images of the conversion of Cu-06 to Cu₃(btc)₂ with 1 minute
time intervals, showing the growth of polyhedral crystallites with the
preservation of the co-continuous macroporous gel structure. All the
images are in the identical magnification.

Fig. 4  (a) XRD patterns (Cu Kα) of Cu-06 in the course of coordination
replication recorded at 1 minute time intervals. A simulated pattern is also
shown at the bottom; (b) nitrogen adsorption–desorption isotherms of the
same samples; (c) BJH pore size distribution of the samples; (d) TG-DTA
results of the samples before (Cu-06) and after conversion (6 min),
showing an increase in the organic content.

Fig. 5  (a) Photographs of as-dried Cu-06 monolith (i) before and (ii) after
conversion to the Cu₃(btc)₂ monolith, (iii) cross-section of the Cu₃(btc)₂
monolith shows uniform replication throughout the monolith (the scale
bars correspond to 1 cm); (b) stress–strain curves of Cu-06, after conver-
sion to Cu₃(btc)₂ (6 min), and a macroporous silica monolith with SBA-15-
like periodic mesopores.
(HKUST-1) monoliths by coordination replication in the presence of H$_3$btc as the ligand with complete preservation of the macroporous 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.

Notes and references