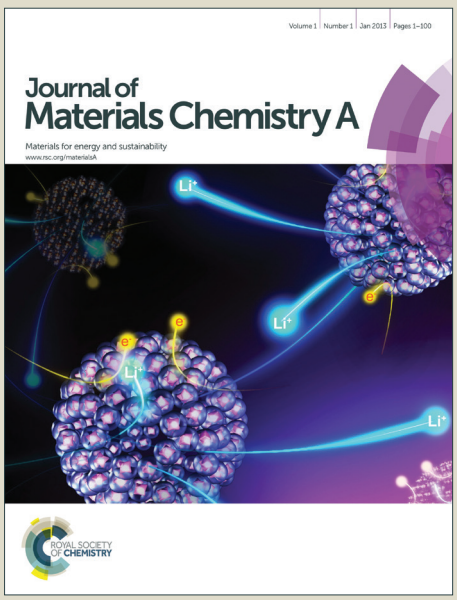
Journal of Materials Chemistry A

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsA

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Macroporous metal-organic framework microparticles with improved liquid phase separation

Adham Ahmed,[a] Nicola Hodgson,[a] Michael Barrow,[a] Rob Clowes,[a] Craig M. Robertson,[a] Alexander Steiner,[a] Paul McKeown,[a] Darren Bradshaw,[b] Peter Myers[a] and Haifei Zhang*[a]

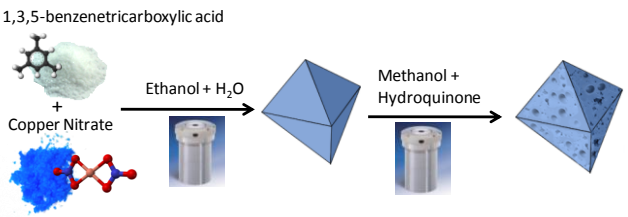
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Typically, metal-organic frameworks (MOFs) exhibit ordered micropores (< 2nm). Control of pore shape, surface functionality and high surface area, which comes with the variety of metal ions and enormously available organic ligands, has rendered a wide range of applications for MOF materials. Due to the limited mass transport of micropores, various approaches have been developed to produce mesoporous MOFs. However, the preparation of macroporous MOFs (with macropores in addition to the micropores) has been scarce, despite this type of materials can considerably facilitate applications such as separation and catalysis. Here, we report the solvothermal modification of HKUST-1 microparticles with hydroquinone. An etching mechanism is suggested for the formation of macroporous HKUST-1 particles, which presents high surface area and high macropore volume with HKUST-1 characteristic pattern. Single x-ray diffraction data shows a cubic unit cell eight times the size of the HKUST-1 unit cell, as a result of slight distortions to the framework. The modified macroporous HKUST-1 particles are further packed into a column, showing fast and improved separation of ethylbenzene and styrene by high performance liquid chromatography.

Introduction

Metal-organic frameworks (MOFs) are regarded as a type of porous coordinated polymeric materials. MOFs are formed from metal ions linked together by organic bridging ligands.[1] The typical feature of MOFs is the presence of ordered and well-defined (pore size & pore shape) micropores (< 2nm). This leads to the unique advantage for applications in gas storage and gas separation.[2] The variety of metal ions and the nearly unlimited organic ligands provide the opportunities for synthesis of new MOFs and engineering of pore surface functionalities.[3] The capability of generating MOFs to bridge pore size gap between zeolites and common mesoporous materials and also via biomimetic design has found extensive applications in catalysis,[4] biomedicine,[5] and liquid phase separation.[6]

For a number of applications such as separation and catalysis, particularly when liquid phase is involved, the small micropores can be a significant issue in limiting mass transport to and from the active surface sites. Introducing large pores such as mesopores into MOFs are thus highly desirable. Different methods have been used to produce mesoporous MOFs,[7] including ligand extension & ligand exchange,[8-11] surfactant templating,[12-14] and some other approaches (*e.g.*, mechanochemical synthesis,[15] gelation to generate aerogels,[16,17] and solvent etching[18]). It should be mentioned that in the surfactant templating approach, the mesopores are present in addition to the micropores, while the ligand approach is to



Scheme 1. Schematic representation for the preparation of HKUST-1 particles and the subsequent modification to produce macroporous HKUST-1 particles.

enlarge the micropores to mesopores. The former is a type of hierarchically porous materials (materials containing pores at different length scales) although macropores (> 50 nm) are normally present in hierarchically porous materials. The presence of macropores may be particularly useful in improving mass transport for a wide range of applications.[19]

MOF topology and morphology synthesis has been mostly focused on particles engineering, thin films, membranes and composites.[20] Reports on fabrication of macroporous MOFs are rather limited although macroporosity is observed in MOF aerogel or mechanochemical-synthesized MOFs.[15-17] With the studies reported so far, the macroporous MOF structures are mostly prepared by a bottom-up approach from the precursors and ligands, *e.g.*, formation of capsules by interfacial synthesis around emulsion droplets,[21] hollow superstructures by spray freezing,[22] sponge structure by adding monofunctional ligand in

the synthesis,[23] ordered macroporous structure via colloidal templating,[24] hollow microspheres by synthesis with and the subsequent removal of microsphere template[25], MOF-polymer composite microcapsules derived from Pickering emulsions,[26], and colloidosomes constructed of MOF cubes via an one-step emulsion approach.[27] Modification of pre-formed crystalline MOF particles is another route to producing macroporous MOFs. However, there is no report of macroporous MOFs with distinct microporosity & macroporosity and the use of such materials for enhanced separation.[28-30] Herein, we report a simple solvothermal modification of HKUST-1 (as a model MOF) with hydroquinone for the formation of macroporous MOF particles (Scheme 1). The macroporous HKUST-1 particles are packed into a column and evaluated for high performance liquid chromatography (HPLC) separation of styrene and ethylbenzene.

Experimental

Chemicals and Reagents

1,3,5-benzenetricarboxylic acid (BTC, 95%), styrene (≥ 99%), hydroquinone (≥ 99.0%), boric acid (98.0%), HCl solution, sodium chloride, Basolite C300, $Cu(NO_3)_2.3H_2O$, absolute ethanol, methanol, tetramethylethylene diamine (TMEDA, 99%), and all the solvents were purchased from Sigma-Aldrich and used as received. The HPLC grade solvents were used for HPLC tests.

Preparation of HKUST-1 ($Cu_3(BTC)_2$)

The method was an adaptation of a previously published solvothermal synthesis.[31] $Cu(NO_3)_2.3H_2O$ (146mg, 0.6mmol) and BTC (280mg, 1.3mmol) were mixed together in a 1:1 ethanol/H_2O solution (4 cm^3 volume), in a small glass reaction vessel which was fitted into a Teflon liner within a bomb (Parr Teflon Lined Acid Digestion Vessels, general purpose bomb with safety blow protection, purchased from Scientific & Medical Products Ltd) (this procedure was always used to avoid possible contamination by directly using Teflon liner to contain the solution). The resulting cloudy blue solution was heated in a sealed autoclave at 120 ^oC, under autogenous pressure, for 16 hours. Once cooled, the turquoise materials were washed with fresh ethanol and initially dried under vacuum, at 25 ^oC for 16 hours, resulting in turquoise crystals. Further drying under vacuum at 80 ^oC for 16 hours produced dehydrated purple particles.

Solvothermal modification of pre-formed HKUST-1 particles

Preformed HKUST-1 (20 mg), methanol (2 cm^3) and hydroquinone (100 mg) were mixed together in a small glass vessel. Once hydroquinone was completely dissolved, the mixture was heated in a sealed autoclave at 150 ^oC under autogenous pressure for 16 hours. After the autoclave cooled to room temperature, the resulting dark turquoise materials were collected and washed with fresh methanol and dried under vacuum at 80 ^oC for 16 hours, resulting in dark green particles. Control experiments with H_2O (2 cm^3) under the same solvothermal conditions with and without hydroquinone (100 mg) were also performed. For the particles packed column for HPLC, commercial Basolite C300 particles were modified with the same procedure and used. The modification of HKUST-1 particles was also carried out similarly at 180 ^oC for 16 hours and 150 ^oC for 72 hours.

Column packing and HPLC assessment

To pack the HPLC column, 0.12 g as-purchased or modified Basolite C300 crystals were suspended in 15 cm^3 methanol by ultrasonication for 2 minutes (sonication bath, Fisherbrand FB11021). The slurry was poured into a 15 cm^3 reservoir and packed into a 4.6 mm (I.D.) x 50 mm (L) stainless steel column using the in-house packing method at 400 bars with Knauer K-1900. The column was flushed with heptane before testing.

For the HPLC tests, the columns were fitted into an Agilent 1200 series HPLC, comprising of a vacuum degasser, quaternary pump, ALS auto-sampler, heated column compartment and UV-Vis detector. All the tests were carried out at 25 ^oC unless otherwise stated. All signals were UV detected at 254 nm. Data analysis was performed using Agilent Chemstation software, version B.02.01 (Agilent Technologies, USA).

Characterizations

The morphologies were observed by a Hitachi S-4800 scanning electron microscope (SEM). The samples were coated with gold using a sputter-coater (EMITECH K550X) for 2 minutes at 25 mA before imaging. The Brunauer-Emmett-Teller (BET) surface area and pore size by N_2 sorption at 77 K were measured using a Micromeritics ASAP 2420 adsorption analyzer. The micropore size distributions were calculated by the non-local density functional theory (NLDFT) method which is typically used for micropores. Samples were degassed for 10 h at 120 °C before N_2 sorption analysis. The pore volume and macroporosity of the solvothermally modified HKUST-1 materials were determined using Hg intrusion porosimetry (Micromeritics Autopore IV 9500) in the pressure range of 0.10- 60000 psia. The by-product solution was characterized using ^1H NMR (Bruker Avance 400 MHz) in deuterated methanol. The samples characterised by inductive coupling plasma (ICP) microanalysis were diluted 10-fold with Milli-Q H_2O to prevent plasma extinguish during the analysis and recorded on a Specto Ciros Charged Coupled Devise using Inductively Coupled Plasma -Optical Emission Spectrometry -Side on Plasma. The high vapour pressure of organic solvents, even at room temperature, can disrupt or even extinguish the plasma. In addition to diluting the methanol solution with water, a cooling chamber was also used to avoid plasma extinguishing and allow the accurate analysis of Cu ion concentrations. The measurements were performed in triplicates and the average values were used. Powder X-ray diffraction (PXRD) data were collected on a Panalytical X'Pert Pro Multi-Purpose Diffractometer in high-throughput transmission geometry. Cu anode was operated at 40 kV and 40 mA. Samples were pressed into the well of aluminium plate. The PXRD patterns were collected over 5-50° 2θ with a scan time of 40 minutes.

Single crystal data of modified HKUST-1 were collected on a Bruker Photon100 diffractometer using MoKα radiation (λ = 0.71073 Å). The crystal structure was refined with SHELX by full-matrix least squares against F2 using all data.[32] All non-hydrogen atoms of the framework were refined anisotropically. H- atoms were constrained geometrically to parent C-atoms. High residual electron density peaks found in the voids were refined as

partially occupied Cu sites (labeled Cu?T in CIF-file), others (labeled C?T) were refined with a scattering factor of carbon. "?" represents a certain number, *e.g.*, Cu1T, Cu2T, C1T, C2T, *etc.* Cubic space group Fm-3c, T = 100 K, a = 52.5078(17) Å, V = 144768(8) Å3, 2θmax = 50°, 3261 unique reflections, Rint = 0.056, R1 (I > 2σ(I)) = 0.105, wR2 (all data) = 0.394. Crystallographic data in CIF format (CCDC 987873) can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html.

Results and discussion

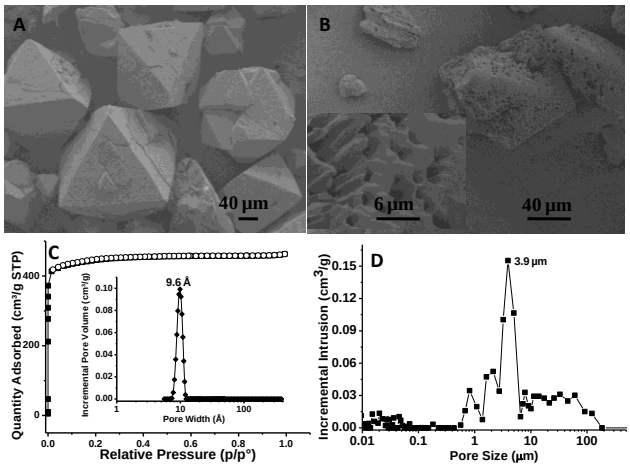


Figure 1. (A) The HKUST-1 microparticles prepared by solvothermal synthesis with water:ethanol (1:1 v/v). (B) The SEM image shows the marcoporous microparticles and the close view of the macropores on the modified HKUST-1 particle (the inset image) with hydroquinone at 150 °C for 16 hours. (C) The isothermal curve and pore size distribution calculated by the NLDFT method from N_2 sorption data for the modified sample. (D) The macropore size distribution as measured by Hg intrusion porosimetry, with an intrusion pore volume 2.65 cm^3 g^{-1}, for the modified HKUST-1 particles.

Large crystalline HKUST-1 microparticles (50 – 300 µm) were produced from ethanol-water (1:1 v/v) mixture using $Cu(NO_3)_2.3H_2O$ and BTC by solvothermal synthesis at 120 °C (Figure 1A).[31] PXRD analysis showed the formation of pure phase HKUST-1. Nitrogen sorption measurements of the HKUST-1 revealed a type I isotherm, commensurate with a highly microporous system, with a surface area of 1670 m^2 g^{-1}, a sharp pore size distribution around 1 nm (similar to the original HKUST-1)[33] and a micropore volume of 0.709 cm^3 g^{-1} (Figure S1). These crystalline HKUST-1 particles were modified with hydroquinone in methanol in an autoclave at 150 °C for 16 hours. After modification, the octahedral shape of the crystalline particles was unchanged. Interestingly, the formation of microchannel-like macropores was observed on the particles (Figure 1B). The N_2 sorption isotherm is of a type I shape, with sharp micropore sizes around 9.6 Å (0.96 nm), a surface area of 1616 m^2 g^{-1} and a micropore volume of 0.71 cm^3 g^{-1} (Figure 1C), very similar to the synthesized HKUST-1 particles before modification. CO_2 adsorption was performed on these HKUST-1 particles. The total CO_2 uptake of the modified HKUST-1 (8.73 mmol g^{-1}) is similar to the HKUST-1 particles (9.02 mmol g^{-1}) (Figure S2). It should be noted that macropores contribute little to the uptake of the gaseous molecules due to the smaller exposed surface area. This suggests that CO_2 sorption capability is not affected after the modification. As measured by Hg intrusion porosimetry, the macropores are mainly in the range of 500 nm – 10 µm, peaking around 3.9 µm (Figure 1D), which agrees with the channel sizes observed from the SEM image (Figure 1B inset). The larger pore sizes (in the region of 100 – 200 µm) are likely to arise from the interparticle voids during Hg intrusion measurement.

Both reaction temperature and reaction time were further investigated for the modification reactions. At 180 °C, highly macroporous particles were produced (Figure 2A). The SEM image at a higher magnification (Figure 2A inset) shows a rough and porous surface. Macropores on the particles are in the range of 5-10 µm, with an accessible open structure. The reaction was also studied at 120 °C, yielding a reduced degree of macropores on the surface (both the number and size of the macropores, Figure S3). With increased reaction time (72 hours at 150 °C), the macroporous channels were formed across the microparticles (Figure 2B & 2C). Compared to Figure 1B, the channel size is increased and the pore wall becomes thinner.

All the modified HKUST-1 particles exhibited BET surface areas in the region of 1600 m^2 g^{-1}, indicating a microporous material (but with macroporosity) similar to the original HKUST-1. The PXRD patterns of the modified samples display intense and sharp peaks (Figure 2D), suggesting the crystalline structure retained. A general trend is noticed that higher reaction temperature or longer reaction time could produce highly macroporous materials.

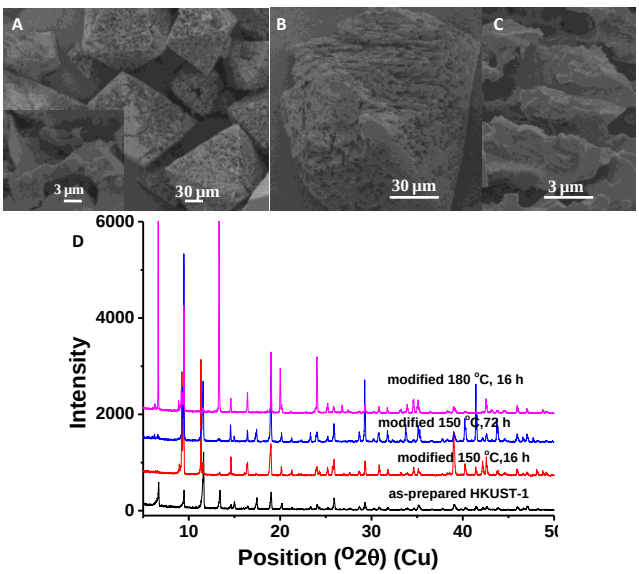


Figure 2. (A) The structure of HKUST-1 particles and the closer view (the inset image) after treatment with hydroquinone at 180 °C for 16 hours. (B&C) The structures of HKUST-1 particles at different magnifications after treatment with hydroquinone at 150 °C for 72 hours. (D) Overlap of the PXRD patterns of as-prepared

HKUST-1 and the modified HKUST-1 particles prepared under different conditions.

The PXRD patterns are similar to the HKUST-1 structure albeit small variations in peak intensities are observed after modification. Single crystal XRD pattern of the modified crystals revealed additional weak reflections. The cell indexed as a cubic F-centred unit cell (space group Fm-3c, a = 52.509(2) Å) eight times the volume of the unit cell of the standard HKUST-1.[33] In comparison to the high symmetry framework of the latter (space group Fm-3m), which contains one crystallographically independent Cu site and two unique void sites of high symmetry (point group m-3m), the framework of the modified crystals is slightly distorted (Figure 3). It exhibits three independent Cu sites and four distinct voids, one of which (Wyckoff site 8a) contains residual peaks of high electron density that indicate the presence of heavier elements, most probably due to Cu deposits generated during the modification process. The deposits in the micropores may also explain the cause of the small variations compared to the PXRD pattern of the pure HKUST-1 phase. However, the nature of these Cu residues, which are highly disordered due to the high symmetry of the void site, needs to be investigated further in more details. As from Figure 1 and Figure 2, the modification of the crystals does not alter the morphology of the majority of crystals in the samples. Indeed, the diffraction patterns of the modified crystals are characteristic of single crystals with varying degrees of mosaicity. The indexing of the single X-ray data shows that the modified crystals maintain the HKUST-1 structure. The small additional peaks in Figure 2D are highly likely from the low level of framework distortion rather than other impurity phases.

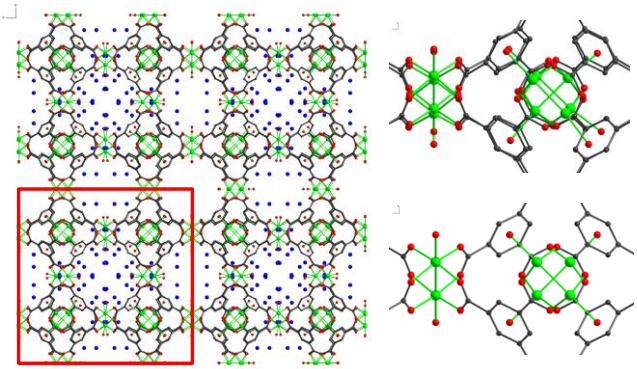


Figure 3. Left: The unit cell of the modified crystal of HKUST-1 (green: Cu, red: O, dark grey: C, blue: high residual electron density due to possible Cu deposits in micropores). The red frame indicates the size of the smaller cell of standard HKUST-1. Right: Comparison of the distorted structure of the modified crystals viewed along [1 0 0] (top) with the high-symmetry structure of the standard HKUST-1 (bottom).

As seen from the SEM images in Figure 1 and Figure 2, it appears that an etching-like process occurs from the top surface which then penetrates into the crystal. After modification, a colour change was observed - blue crystals turned dark turquoise. When no hydroquinone was added into the reactions, the HKUST-1 particles were mainly stable, *i.e.*, no macropores formed (Figure S4). The presence of hydroquinone thus played a crucial role in modifying HKUST-1 into the macroporous crystalline particles. ICP analysis was employed to monitor how the content of Cu ions changed in the methanol solution during the reactions. 9.96 ppm of Cu was detected in the modifying reaction with hydroquinone while a very small amount of Cu (1.48 ppm) was found for the reaction without hydroquinone (Figure S5). This supports the suggestion of the etching of HKUST-1 by selective removal of Cu(II) ions from the framework into the solution.

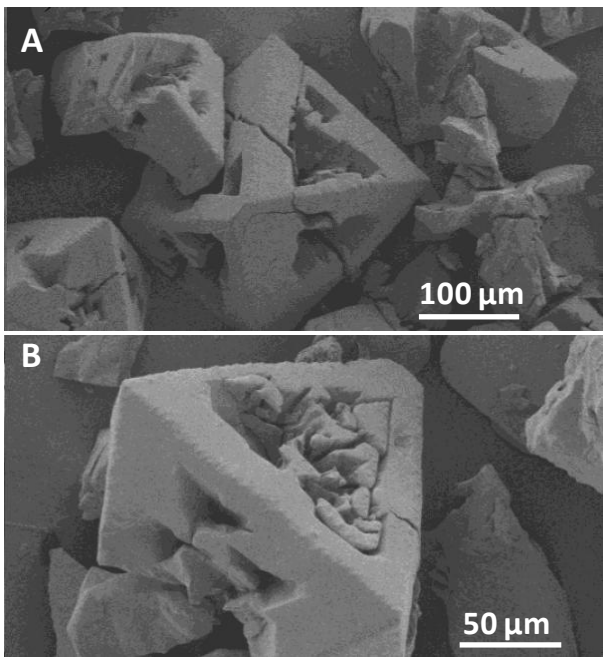


Figure 4. The SEM images show the morphology of HKUST-1 particles modified in methanol with other reagents under solvothermal conditions. (A) modified by addition of 50 µL 1N boric acid aqueous solution at 150 ^{o}C for 16 hours; (B) modified by addition of 50 µL 1N NaCl aqueous solution at 150 ^{o}C for 16 hours.

It was reported previously that, when treated in a NaCl solution, smooth crystals of a Cu-MOF can be turned into hairy surface features, yielding more contact areas for protein binding.[28] Also it is known that MOFs are generally unstable under acidic condition. Some MOFs could also be modified in the presence of a base, *e.g.*, IRMOF-3 modified with cyanuric chloride in the presence of tetraethylamine.[29] In order to see how other reagents could be used to modify HKUST-1, we tried different reagents, by adding 50 µL of 1 N of H_3BO_3, 1 N NaCl aqueous solution or 50 µL TMEDA into the modification reactions, replacing hydroquinone. The use of both H_3BO_3 and NaCl resulted in large etched holes from the centre of the HKUST-1 particles while some nanopores (around 500 nm) were observed on the edge surface (Figure 4A & 4B, Figure S6 & S7). This morphology is similar to the microcages of squarate based metal-organic coordination framework formed by selective anion etching.[30] However, the porosity data was not reported and the morphology is considerably different from what we have shown

in Figure 1 & Figure 2. When TMEDA was employed in the reaction, microparticles with hairy surface features were formed (Figure S8), similar to the morphology as reported recently.[28] However, the hairy or spiky structure is only observed on the surface and there are no macropores extending into the particles Although these modified particles are still crystalline, the PXRD. pattern shows it is not of HKUST-1 structure (Figure S8C). As previously reported, etching of MOFs typically involves ionic interaction/reaction to disintegrate the frameworks via Na^+,[28] H^+,[29] or OH^-.[30] We hypothesize that hydroquinone acted as a weak acid (pKa = 9.85 in water) and interacted with exposed Cu^{2+} co-ordinated with BTC in HKUST-1. While strong acid can destroy HKUST-1 completely, weak acid etching may generate porous particles. Compared to the etching with H_3BO_3 and NaCl, the use of hydroquinone appeared to allow faster initiation reactions in methanol on various sites across the crystal surface. Once initiated, the etching reaction could undergo deeper into the crystals and create microchannels, a mechanism maybe similar to the etching of zeolites.[34]

HKUST-1 is classified as water unstable (structure decomposition and/or transformation) although it can maintain structural integrity in the presence of small amounts of water.[35] The modification of HKUST-1 particles was also performed in water with (Figure S9) and without hydroquinone (Figure S10). In both cases, macroporous particles with crystalline nanofibers were obtained. The presence of hydroquinone seemed to slow down the transformation (or decomposition) of HKUST-1 particles. However, no hollow particles were formed. The XRD pattern showed that the modified structure is not of HKUST-1 nature (Figure S9C), also with low surface area around 20 m^2/g. Therefore, although HKUST-1 may be modified in water to produce highly macroporous structures, the modified materials do not exhibit the original MOF properties any more. The stability of HKUST-1 and the hydroquinone-modified HKUST-1 particles was assessed by soaking in water at room temperature for 16 hours. As a result, the HKUST-1 in water completely turned into nanofibers (Figure S11). While for the hydroquinone-modified HKUST-1, in spite of the structure being etched and made more porous, the shaped microparticles were largely maintained (Figure S12). This increased stability in water with modified HKUST-1 particles is an interesting observation. Further study is required to investigate this observation.

One of the emerging applications is to use MOFs as stationary phase for liquid chromatography.[36] The small pore sizes and low efficient packing of MOF particles often lead to high back pressure and collapse of packed MOF particles. In the previous effort to address this problem, the column packed with silica-HKUST-1 composite microspheres showed highly efficient and fast separation for HPLC.[37] Alternatively, introducing macropores into MOF particles could considerably improve mass transport particularly when liquid phases are involved. This would be highly beneficial for HPLC separation. Thus, we further investigated how the macroporous HKUST-1 particles could be used for HPLC separation.

For the HPLC study, the commercially available HKUST-1 particles (Basolite C300) and their modified particles were evaluated for separation of styrene and ethylbenzene (Figure 5) When the column packed with Basolite C300 particles was used, only one broad peak and a small shoulder were observed from the elution. It took about 10 minutes for the elution of the peak. However, when the modified macroporous particles were employed, the baseline separation of styrene and ethylbenzene was realized in 3 minutes. A trail from peak 2 was observed. This could be attributed to the dead volume (due to large interparticles space and shape of the particles) and dichloromethane (DCM) in the mobile phase (presence of DCM could enhance the interaction of styrene with HKUST-1).[37] The differences between these two columns (fast separation at 3 minutes with low back pressure of 13 bars for the modified HKUST-1 particles and non-separated peaks in 10 minutes with a back pressure of 21 bars for Basolite C300) demonstrated the advantage of macroporous MOF particles. The improved HPLC separation is resulted from the presence of macropores in the modified particles. For liquid phase chromatographic separation, the minimal pore sizes required are > 7 nm.[38] The pore sizes of HKUST-1 are around 1 nm, too small for liquid chromatography. The separation thus occurs on the surface of the HKUST-1 particles, other than inside the micropores, due to the fast flow dynamics of the mobile phase in the column. The macropores in the modified particles can increase the exposed surface which interact and partition the analytes in the mobile phase, resulting in more efficient separation. In addition to this, macroporosity provided faster mass transfer kinetics to reduce the chance of the analytes to redisperse in the column. The column packed with the modified particles showed good reproducibility and stability (tests for over one week with different composition of mobile phases). The low operating pressure, due to the larger size of the crystalline particles and the macropores within the particles, could reduce the chance of deformation of the stationary phase, *i.e.*, making the column more stable.

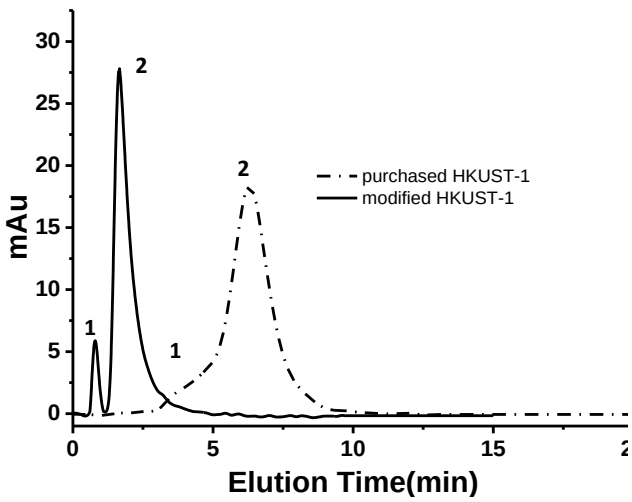


Figure 5. Comparison of the columns packed with the purchased Basolite C300 particles and the correspondingly modified macroporous particles for the HPLC separation of ethylbenzene (1), and styrene (2). Conditions: injection volume 1μL, flow rate 1 cm^3 min^{-1}, heptane:dichloromethane 98:2 v/v as the mobile phase.

Conclusions

In summary, we have demonstrated the preparation of macroporous MOF microparticles (with HKUST-1 as the model MOF) via the solvothermal modification of pre-formed HKUST-1 particles. An etching mechanism was suggested for the formation of macroporous channels across the HKUST-1 particles. PXRD patterns confirmed that the HKUST-1 crystalline structure was retained with slight distortion. Single x-ray diffraction data showed a cubic unit cell eight times the size of the standard HKUST-1 unit cell, as a result of slight distortions to the framework. The macroporous HKUST-1 particles exhibited high surface area (from the micropores by N_2 sorption) and high pore volume (from the macropores). The column packed with the modified macroporous HKUST-1 particles gave a fast separation of styrene and ethylbenzene with low back pressure. The improved mass transport and separation efficiency with the presence of macropores within MOF particles may be advantageous for other potential applications, for example, catalysis and controlled release.

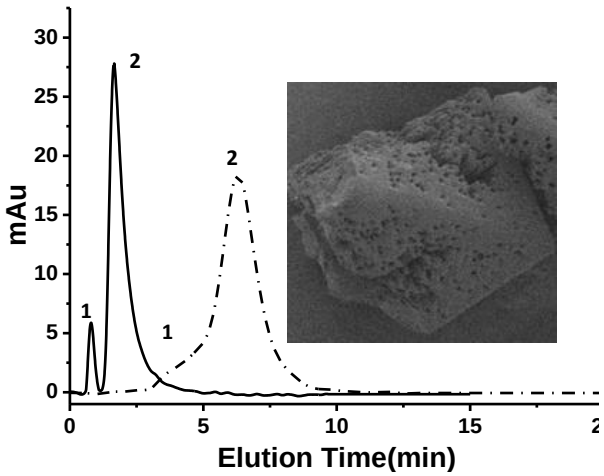
Notes and references

[a] *Department of Chemistry, University of Liverpool, Oxford Street, Liverpool, L69 7ZD, UK. Fax: +44 151 7943588; Tel: +44 151 7943545; E-mail: zhanghf@liv.ac.uk*
[b] *Department of Chemistry, University of Southampton, Highfield, Southampton, SO17, 1BJ, UK.*

† Electronic Supplementary Information (ESI) available: additional N_2 sorption, SEM, ICP and PXRD data. See DOI: 10.1039/b000000x/

1 S. L. James, *Chem. Soc. Rev.* 2003, **32**, 276.
2 M. P. Suh, H. J. Park, T. K. Prasad, D.-W. Lim, *Chem. Rev.* 2012, **112**, 782; K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* 2012, **112**, 724; J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.* 2012, **112**, 869.
3 D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, *Acc. Chem. Res.* 2005, **38**, 273; J. R. Long, O. M. Yaghi, *Chem. Soc. Rev.* 2009, **38**, 10 1213.
4 D. Farrusseng, S. Aguado, C. Pinel, *Angew. Chem. Int. Ed.* 2009, **48**, 7502.
5 P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris, C. Serre, *Chem. Rev.* 2012, **112**, 1232.
6 K. A. Cychosz, R. Ahmad, A. J. Matzger, *Chem. Sci.* 2010, **1**, 293.
7 W. Xuan, C. Zhu, Y. Liu, Y. Cui, *Chem. Soc. Rev.* 2012, **41**, 1677.
8 X.-S. Wang, S. Ma, D. Sun, S. Parkin, H.-C. Zhou, *J. Am. Chem. Soc.* 2006, **128**, 16474.
9 N. Klein, I. Senkovska, K. Gedrich, U. Stoeck, A. Henshel, U. Mueller, S. Kaskel, *Angew. Chem. Int. Ed.* 2009, **48**, 9954.
10 T. Li, M. T. Kozlowski, E. A. Doud, M. N. Blakely, N. L. Rosi, *J. Am. Chem. Soc.* 2013, **135**, 11688.
11 H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'Keeffe, O. Terasaki, J. F. Stoddart, O. M. Yaghi, *Science* 2012, **336**, 1018.
12 L.-G. Qiu, T. Xu, Z.-Q. Li, W. Wang, Y. Wu, X. Jiang, X.-Y. Tian, L.-D. Zhang, *Angew. Chem. Int. Ed.* 2008, **47**, 9487.
13 M.-H. Pham, G.-T. Vuong, F.-G. Fontaine, T.-O. Do, *Cryst. Growth Des.* 2012, **12**, 1008.
14 Y. Zhao, J. Zhang, B. Han, J. Song, J. Li, Q. Wang, *Angew. Chem. Int. Ed.* 2011, **50**, 636.
15 M. Klimakow, P. Klobes, A. F. Thünemann, K. Rademann, F. Emmerling, *Chem. Mater.* 2010, **22**, 5216.
16 L. Li, S. Xiang, S. Cao, J. Zhang, G. Ouyang, L. Chen, C.-Y. Su, *Nature Commun.* 2013, **4**, 1774.
17 M. R. Lohe, M. Rose, S. Kaskel, *Chem. Commun.* 2009, 6056.
18 Y. Yue, Z.-A. Qiao, P. F. Fulvio, A. J. Binder, C. Tian, J. Chen, K. M. Nelson, X. Zhu, S. Dai, *J. Am. Chem. Soc.* 2013, **135**, 9572.
19 Y. Li, Z. Fu , B. Su, *Adv. Funct. Mater.* 2012, **22**, 4634.
20 D. Bradshaw, A. Garai, J. Huo, *Chem. Soc. Rev.* 2012, **41**, 2344; N. Stock, S. Biswas, *Chem. Rev.* 2012, **112**, 933.
21 R. Ameloot, F. Vermoortele, W. Vanhove, M. B. J. Roeffaers, B. F. Sels, D. E. De Vos, *Nature Chem.* 2011, **3**, 382.
22 A. Carné-Sánchez, I. Imaz, M. Cano-Sarabia, D. Maspoch, *Nature Chem.* 2013, **5**, 203.
23 K. M. Choi, J. J. Jeon, J. K. Kang, O. M. Yaghi, *J. Am. Chem. Soc.* 2011, **133**, 11920.
24 Y.Wu, F. Li, W. Zhu, J. Cui, C. Tao, C. Lin, P. M. Hannam, G. Li, *Angew. Chem. Int. Ed.* 2011, **50**, 12518.
25 H. J. Lee, W. Cho, M. Oh, *Chem. Commun.* 2012, **48**, 221.
26 J. Huo, M. Marcello, A. Garai, D. Bradshaw, *Adv. Mater.* 2013, **25**, 2717.
27 M. Pang, A. J. Cairns, Y. Liu, Y. Belmabkhout, H. C. Zeng, M. Eddaoudi, *J. Am. Chem. Soc.* **2013**, 135, 10234.
28 G. Wang, Z. Xu, Z. Chen, W. Niu, Y. Zhou, J. Guo, L. Tan, *Chem. Commun.* 2013, **49**, 6641.
29 Y. Yooa, H.-K. Jeonga, *Chem. Eng. J.* 2012, **181– 182**, 740.
30 K. Jayaramulu, K. S. Krishna, S. J. George, M. Eswaramoorthy, T. K. Maji, *Chem. Commun.* 2013, **49**, 3937.
31 L. D. O'Neill, H. Zhang, D. Bradshaw, *J. Mater. Chem.* 2010, **20**, 5720.
32 G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112.
33 S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* 1999, **283**, 1148; Y. Wu, A. Kobayashi, G. J. Halder, V. K. Peterson, K. W. Chapman, N. Lock, P. D. Southon, C. J. Kepert, *Angew. Chem. Int. Ed.* 2008, **47**, 8929.
34 Z. Qin, L. Lakiss, J.-P. Gilson, K. Thomas, J.-M. Goupil, C. Fernandez, V. Valtchev, *Chem. Mater.* 2013, **25**, 2759.
35 K. A. Cychosz, A. J. Matzger, *Langmuir* 2010, **26**, 17198.
36 Z. Gu, C. Yang, N. Chang, X. Yan, *Acc. Chem. Res.* 2012, **45**, 734.
37 A. Ahmed, M. Forster, R. Clowes, D. Bradshaw, P. Myers, H. Zhang, *J. Mater. Chem. A* 2013, **1**, 3276.
38 K. K. Unger, R. Skudas, M. M. Schulte, *J. Chromatogr. A* 2008, **1184**, 393.

TOC figure



Macroporous HKUST-1 crystalline particles are prepared by solvothermal modification and exhibit improved liquid chromatographic separation.