Supporting Information for:

A versatile, industrially relevant, aqueous room temperature synthesis of HKUST-1 with high space-time yield

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Section S1: Materials and methods.

All chemicals used in this work were purchased from Sigma Aldrich and used as received without further purification. Ultrapure Milli-Q water (Milli-Q System, Millipore, Billerica, MA) was used in all experiments.

Scanning electron microscopy (SEM) measurements were made on a JEOL JSM 6500F field-emission scanning electron microscope at an accelerating voltage of 10 kV. The sample for SEM measurements was prepared by firstly placing a drop of microsphere suspension in absolute ethanol on a carbon paste attached on an aluminum substrate, being dried under vacuum overnight, then sputter-coated with a thin conductive gold layer. The particle size distribution was estimated from relative SEM images using Nano Measurer version 1.2.5. Transmission electron microscopy (TEM) measurements were made on a FEI Tecnai G2 Spirit BioTWIN transmission electron microscope operated at an accelerating voltage of 120 kV. The samples for TEM characterization were prepared by placing a drop of particle suspension in absolute ethanol on a carbon-coated Cu grid and being dried at room temperature under air. Powder diffraction patterns were collected on a Bruker D2 phaser in the angular range $2\theta = 5-40^{\circ}$ employing a Ni K β filter (detector side) producing Cu (K α 1/K α 2) radiation. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer STA6000 Simultaneous Thermal Analyzer and the sample was heated from room temperature to 800 °C at a rate of 10 °C min⁻¹ under an Argon atmosphere.

 N_2 adsorption/desorption isotherm was measured at 77 K using a Micromeritics 3-Flex Surface Characterization Analyzer after the sample was first degassed at 100 °C overnight. Surface areas were determined by the BET method in an appropriate pressure range, and total pore volume was determined using the adsorption branch of N_2 isotherm curve at the P/P0 = 0.99 single point. Pore size distribution was determined using the adsorption branch of N_2 isotherms. Micropore size distribution analysis was carried out using the Horvath-Kawazoe method. The mesopore size distribution was calculated using the Barrett-Joyner-Haelnda (BJH) method.

Section S2: Synthetic details.

Synthesis of HKUST-1 nanomaterials:

In a typical synthesis, a suspension of 0.126 g of H_3BTC (0.6 mmol) in 6 ml water was added rapidly into a solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.07g, 0.3 mmol) in 6 ml water with strong stirring (1200 rpm) for 60 min at room temperature. The nanoparticles were collected by repeated sonication with ethanol and centrifugation (9000 rpm, 12 min) for three times, and dried at 100 °C under vacuum overnight. Yield = 35.0 %.

Synthesis of hierarchically porous HKUST-1:

Typically, a suspension of 0.126 g of H_3BTC (0.6 mmol) in 6 ml water was added rapidly into a solution of $Cu(OAc)_2 \cdot H_2O$ (0.06g, 0.3 mmol) in 6 ml water with strong stirring (1200 rpm) for 60 min at room temperature. The products were collected by repeated sonication with ethanol and centrifugation (9000

rpm, 12 min) for three times, and dried at 100 $^{\circ}$ C under vacuum overnight. Yield = 90.0 %.

Synthesis of HKUST-1 microparticles:

Typically, a suspension of 0.126 g of H_3BTC (0.6 mmol) in 6 ml water was added rapidly into a solution of $Cu(OAc)_2 \cdot H_2O$ (0.06g, 0.3 mmol) in 6 ml water with strong stirring (1200 rpm) for 24 h at room temperature. The products were collected by repeated sonication with ethanol and centrifugation (9000 rpm, 12 min) for three times, and dried at 100 °C under vacuum overnight. Yield = 96.5 %

20 times scaled-up synthesis of HKUST-1 nanoparticles:

Typically, a suspension of 2.52 g of H₃BTC (12 mmol) in 120 ml water (sonicated for 5 min) was added rapidly into a solution of Cu(NO₃)₂·2.5H₂O (1.4 g, 6 mmol) in 120 ml water with strong stirring (1200 rpm) for 60 min at room temperature. The nanoparticles were collected by repeated sonication with ethanol and centrifugation (9000 rpm, 12 min) for three times and were dried at 100 °C under vacuum overnight. Yield = 34.2 %.

20 times scaled-up synthesis of hierarchically porous HKUST-1:

Typically, a suspension of 2.52 g of H₃BTC (12 mmol) in 120 ml water (sonicated for 5 min) was added rapidly into a solution of $Cu(OAc)_2 \cdot H_2O$ (1.2 g, 6 mmol) in 120 ml water with strong stirring (1200 rpm) for 60 min at room temperature. The product was collected by repeated sonication with ethanol and centrifugation (9000 rpm, 12 min) for three times, and dried at 100 °C under vacuum overnight. Yield = 90.8 %.

20 times scaled-up of HKUST-1 microparticles:

Typically, a suspension of 2.52 g of H₃BTC (12 mmol) in 120 ml water (sonicated for 5 min) was added rapidly into a solution of $Cu(OAc)_2 \cdot H_2O$ (1.2 g, 6 mmol) in 120 ml water with strong stirring (1200 rpm) for 24 h at room temperature. The product was collected by repeated sonication with ethanol and centrifugation (9000 rpm, 12 min) for three times, and dried at 100 °C under vacuum overnight. Yield = 100 %.

Scaled-up synthesis of HKUST-1 by mixing of Cu(OAc)₂·H₂O and H₃BTC at 20 times concentration:

Typically, 24 ml of water was added into a mixture of 3.36 g of H_3BTC (8 mmol) and 2.4 g Cu(OAc)₂·H₂O (12 mmol) with strong stirring (1200 rpm) for 1 h at room temperature. The product was collected by repeated sonication with ethanol and centrifugation (9000 rpm, 12 min) for three times, and dried at 100 °C under vacuum overnight. Yield = 84.8 %.

Large scale aqueous synthesis of HKUST-1

Typically, 1.2 L of water was added into a mixture of 252 g of H₃BTC (1.2 mol) and 120 g Cu(OAc)₂·H₂O

(0.6 mol) with strong stirring using an overhead stirrer for 1 h at room temperature. The product was collected by repeated sonication with ethanol and centrifugation (9000 rpm, 12 min) three times, and dried at 100 $^{\circ}$ C under vacuum overnight. Yield = 74.6 %.

Samples	Copper source	Time (h)	Yield (%)	Surface area (m ² /g)
1	Cu(NO ₃) ₂ .2.5H ₂ O	1	35.0	1346
2	Cu(NO ₃) ₂ .2.5H ₂ O	2	50.0	
3	Cu(NO ₃) ₂ .2.5H ₂ O	24	75.0	
4	Cu(OAc) ₂ .H ₂ O	1	90.0	989
5	Cu(OAc) ₂ .H ₂ O	24	96.5	1376
6	CuCl ₂ .2H ₂ O	1	n.d.	
7	CuCl ₂ .2H ₂ O	6	8.5	
8	CuSO ₄ .H ₂ O	1	16.3	
9	CuSO ₄ .H ₂ O	24	38.3	
10(20S)	Cu(NO ₃) ₂ .2.5H ₂ O	1	34.2	1403
11(20S)	Cu(OAc) ₂ .H ₂ O	1	90.8	1436
12(20S)	Cu(OAc) ₂ .H ₂ O	24	100	1514
13(20C-dm)	Cu(OAc) ₂ .H ₂ O	1	84.8	1763
14(LS-dm)	Cu(OAc) ₂ .H ₂ O	1	74.6	1560

Table S1. % yields of all aqueous HKUST-1 reactions*

* 20S = 20 times scaled-up synthesis; 20C = scaled-up synthesis at 20 times concentration, LS = large scale aqueous synthesis, and dm = direct mixing of Cu(OAc)₂.H₂O and H₃BTC; n.d. indicates the yield was too low to be determined.

Table S2. Variation in particle size and porosity vs. stirring speed for HKUST-1 prepared from Cu(OAc)2 for a reaction time of 1 hr.

Stirrer speed (rpm)	Particle size (nm) ^a	BET area (m2g-1)	V _{micro} : V _{meso}
1200	40	989	1:1
250	167	1474	2.4:1
0	279	1529	2.5:1
Cu(NO ₃) ₂ data for comparison	74	1346	2.2:1

^a Particle sizes are average determined by SEM, except for entry 1 which was determined from the PXRD data.

Section S3: Supplementary figures and data



Figure S1. EtOH redispersion of HKUST-1 nanoparticles prepared in water for 1 hr from a $Cu(NO_3)_2$ precursor demonstrate a clear Tyndall effect when laser light is passed through the colloidal solution.



Figure S2. (a) Low and (b) high magnification SEM images for HKUST-1 prepared from $Cu(NO_3)_2$ and H_3BTC in water after stirring for 30 min only.



Figure S3. (a and d) Low and (b and e) high magnification SEM images and (c and f) size distribution histograms for HKUST-1 prepared from $Cu(NO_3)_2$ and H_3BTC in water for 2 h (a-c) and 24 h (d-f).



Figure S4. Typical TGA profile of HKUST-1 nanoparticles prepared from $Cu(NO_3)_2$ and H_3BTC in water for 1h.



Figure S5. PXRD pattern of HKUST-1 (prepared from $Cu(OAc)_2$) after standing in the aqueous synthesis mixture for 1 week, revealing crystallinity and phase integrity are maintained.



Figure S6. Nitrogen adsorption isotherm (77 K) of HKUST-1 prepared from $Cu(OAc)_2$ after standing in the aqueous synthesis mixture for 1 week. No loss of porosity is observed, and the apparent BET surface area is 1445 m²g⁻¹ and is comparable to microcrystals formed under the same conditions after 24 hr (see fig S14).



Figure S7. PXRD data of HKUST-1 microparticles formed from the aqueous synthesis using $Cu(NO_3)_2$ following isolation and soaking in water for 2 (middle) and 24 (top) hrs. vs. the simulated pattern for HKUST-1 (bottom).



Figure S8. SEM images of HKUST-1 microparticles formed from the aqueous synthesis using $Cu(NO_3)_2$ following isolation and soaking in water for 2 (left) and 24 (right) hrs.



Figure S9. PXRD data and SEM (inset) of HKUST-1 prepared in aqueous solution from CuCl₂ for 6 h.



Figure S10. PXRD data and SEM (inset) of HKUST-1 prepared in aqueous solution from CuSO₄ for 24 h.



Figure S11. Experimental (i) and simulated (ii) PXRD patterns of HKUST-1 prepared from $Cu(OAc)_2$ and H₃BTC in water for 1h.



Figure S12. TGA graph of hierarchically porous HKUST-1 prepared from Cu(OAc)₂ and H₃BTC in water for 1h.



Figure S13. PXRD and SEM data for mesoporous HKUST-1 aggregates formed from Cu(OAc)2, following soaking in water for 2 hrs.



Figure S14. SEM images of HKUST-1 micromaterials prepared from $Cu(OAc)_2$ after stirring in water for 24 hrs.



Figure S15. Experimental (i) and simulated (ii) PXRD patterns of HKUST-1 micromaterials prepared from $Cu(OAc)_2$ and H_3BTC in water for 24h.



Figure S16. TGA graph of HKUST-1 micromaterials prepared from $Cu(OAc)_2$ and H_3BTC in water for 24 h.



Figure S17. N₂ isotherms (77 K) of HKUST-1 micromaterials prepared from $Cu(OAc)_2$ and H_3BTC in water for 24h. The BET surface area is 1376 m²g⁻¹.



Figure S18. (a) Low and (b) high magnification SEM images and (c) size distribution histogram for the 20x scaled-up HKUST-1 prepared from $Cu(NO_3)_2$ and H_3BTC in water for 1 h. The size distribution is slightly larger than that obtained during the small scale batch synthesis.



Figure S19. Experimental (i) and simulated (ii) PXRD patterns of the 20x scaled-up HKUST-1 prepared from $Cu(NO_3)_2$ and H_3BTC in water for 1 h.



Figure S20. N₂ isotherm of the scaled-up HKUST-1 prepared from $Cu(NO_3)_2$ and H₃BTC in water for 1 h. The BET surface area is 1403 m²g⁻¹.



Figure S21. (a) Low and (b) high magnification SEM images for the 20x scaled-up HKUST-1 prepared from $Cu(OAc)_2$ and H_3BTC in water for 1 h, demonstrating that hierarchically porous materials are still accessible as the reaction scale is increased.



Figure S22. Experimental (i) and simulated (ii) PXRD patterns of the 20x scaled-up HKUST-1 prepared from $Cu(OAc)_2$ and H_3BTC in water for 1 h.



Figure S23. (a) N_2 isotherm and (b) BJH mesopore size distribution of the 20x scaled-up HKUST-1 prepared from Cu(OAc)₂ and H₃BTC in water for 1 h, demonstrating that hierarchically porous materials are still accessible as the reaction scale is increased. The BET surface area is 1436 m²g⁻¹.



Figure S24. TGA graph of the 20x scaled-up HKUST-1 prepared from Cu(OAc)₂ and H₃BTC in water for 1 h.



Figure S25. (a) Low and (b) high magnification SEM images for the 20x scaled-up HKUST-1 prepared from $Cu(OAc)_2$ and H_3BTC in water for 24 h.



Figure S26. Experimental (i) and simulated (ii) PXRD patterns of the 20x scaled-up HKUST-1 prepared from $Cu(OAc)_2$ and H_3BTC in water for 24 h.



Figure S27. N₂ isotherm (77 K) of the microcrystals from the 20x scaled-up HKUST-1 prepared from $Cu(OAc)_2$ and H₃BTC in water for 24 h. The BET surface area is 1514 m²g⁻¹.



Figure S28. (a) Low and (b) high magnification SEM images for the scaled-up HKUST-1 prepared from direct mixing of $Cu(OAc)_2$ and H_3BTC in water for 1 h.



Figure S29. Experimental (i) and simulated (ii) PXRD patterns of the scaled-up HKUST-1 prepared from direct mixing of $Cu(OAc)_2$ and H_3BTC in water for 1 hr.



Figure S30. (a) N_2 isotherm and (b) meso/macropore size distribution of the 20x scaled-up HKUST-1 prepared from direct mixing of Cu(OAc)₂ and H₃BTC in water for 1 h. The BET surface area is 1763 m²g⁻¹.



Figure S31. TGA graph of the scaled-up HKUST-1 prepared from direct mixing of $Cu(OAc)_2$ and H_3BTC in water for 1 hr.



Figure S32. SEM images of HKUST-1 crystals formed from $Cu(OAc)_2$ after 1 hr without stirring (top) and with stirring at 250 rpm (bottom). These are clearly not as small or aggregated as those shown in manuscript figure 3, where the stirring speed is 1200 rpm. Without stirring, the results are comparable to those obtained with $Cu(NO_3)_2$.



Figure S33. N₂ isotherm and BJH pore size distribution (inset) of HKUST-1 crystals formed from $Cu(OAc)_2$ after 1 hr without stirring. The BET area is 1530 m²g⁻¹, and is comparable to that formed from $Cu(NO_3)_2$ under identical conditions.



Figure S34. N₂ isotherm and BJH pore size distribution (inset) of HKUST-1 crystals formed from $Cu(OAc)_2$ after 1 hr stirring at 250 rpm. The BET area is 1474 m²g⁻¹.



Figure S35. Digital images of the scaled-up aqueous synthesis of HKUST-1 (1.2 L) using the direct mixing method.



Figure S36. Experimental (i) and simulated (ii) PXRD patterns of HKUST-1 prepared at the 1.2 L scale using the direct mixing method for 1 hr.



Figure S37. N₂ adsorption data of HKUST-1 prepared at the 1.2 L scale using the direct mixing method for 1 hr. The apparent BET surface area is $1560 \text{ m}^2\text{g}^{-1}$.