Supplementary information for

HKUST-1 MOF Nanoparticles: Non-classical Crystallization Route in Supercritical CO_2

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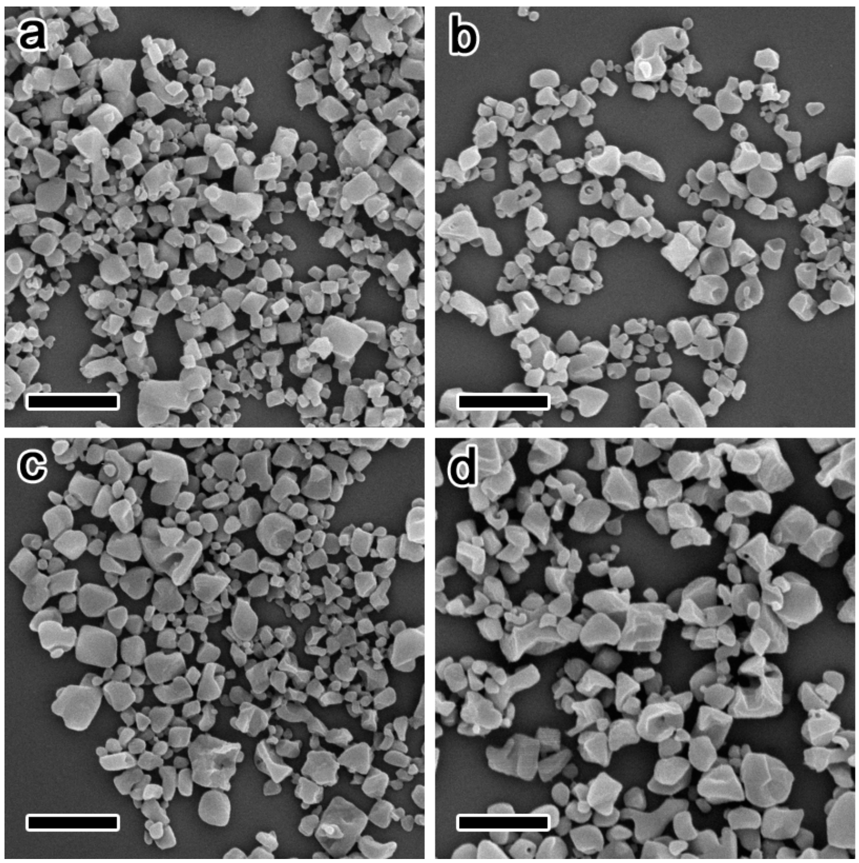

Fig. S1. SEM images of products obtained with different concentrations of $Cu(NO_3)_2$: 0.05 M (a), 0.1 M (b), 0.2 M (c) and 0.3 M. The scale bars are 500 nm. The synthesis was done in a mixture of ethanol and $scCO_2$ (X_{EtOH} = 0.1). The temperature and pressure were 75 °C and 10 MPa.

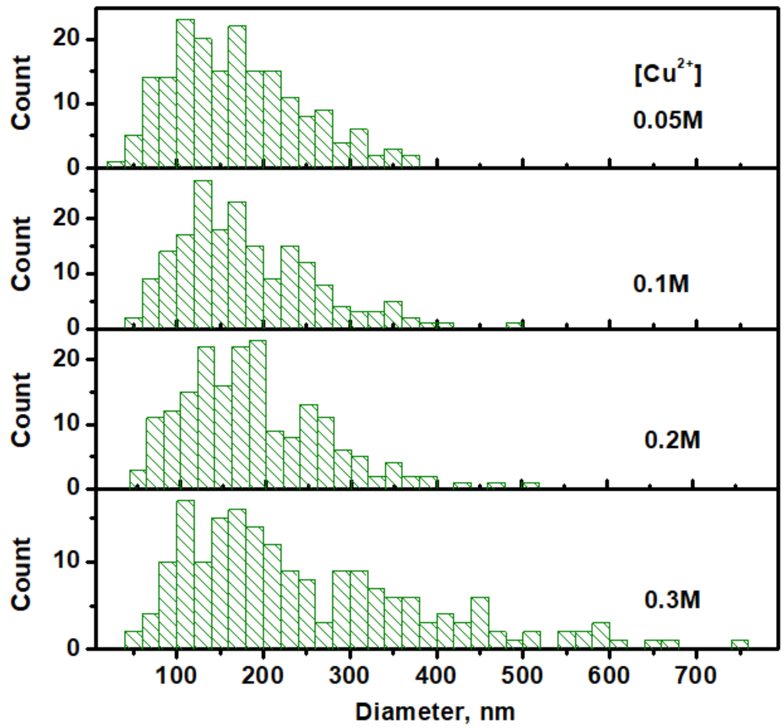

Fig. S2. Particle size distribution observed with $Cu(NO_3)_2$ concentrations ranging from 0.05 M to 0.3 M. The synthesis was done in a mixture of ethanol and $scCO_2$ (X_{EtOH} = 0.1). The temperature and pressure were 75 °C and 10 MPa.

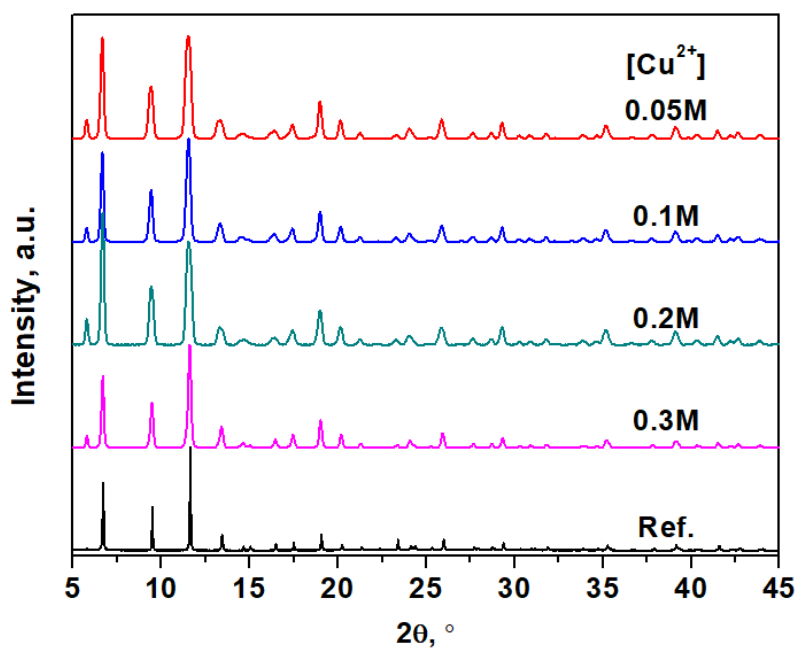

Fig. S3. XRD patterns of products obtained using $Cu(NO_3)_2$ concentrations ranging from 0.05 M to 0.3 M. The synthesis was done in a mixture of ethanol and $scCO_2$ (X_{EtOH} = 0.1). The temperature and pressure were 75 °C and 10 MPa.

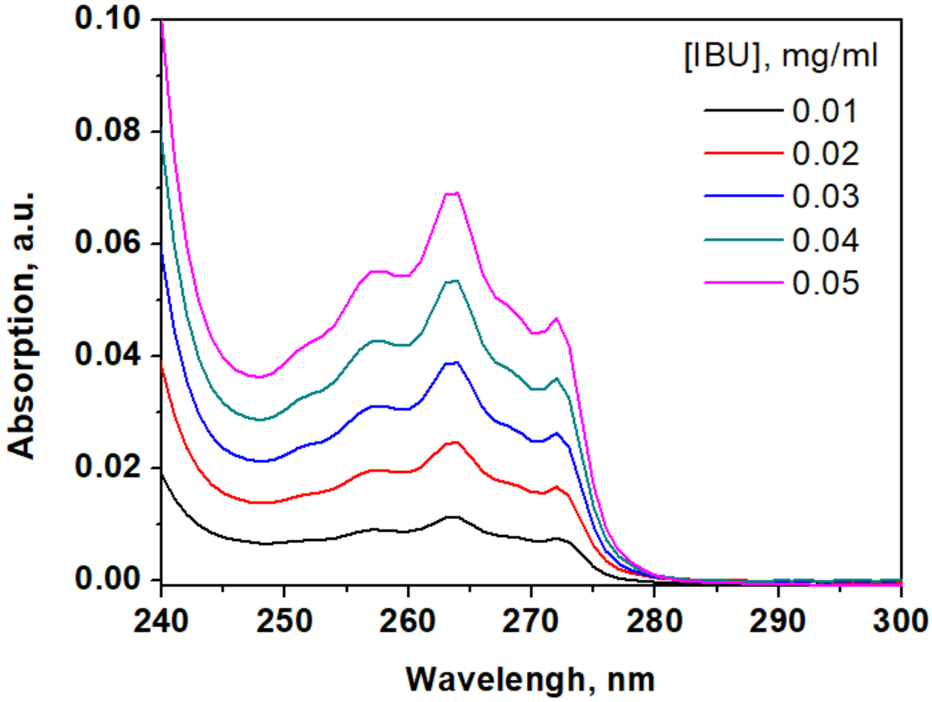

Fig. S4. UV-vis spectra of IBU for the preparation of calibration curve.

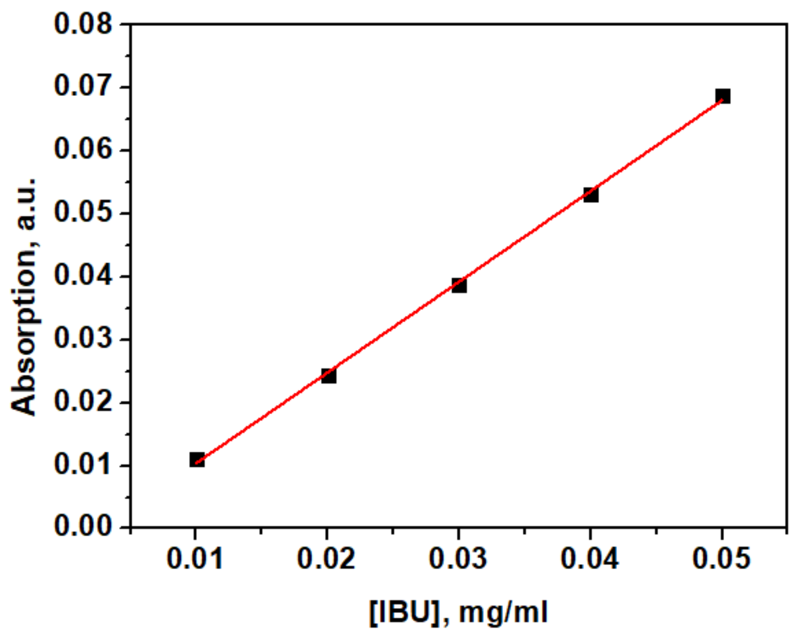

Fig. S5. Calibration curve for ibuprofen (IBU) plotted using the absorption intensity at 263 nm from the UV-vis spectra. The linear fit is described by the equation: A = 1.44194*[IBU]−0.004, with an R^2 value of 0.99878.

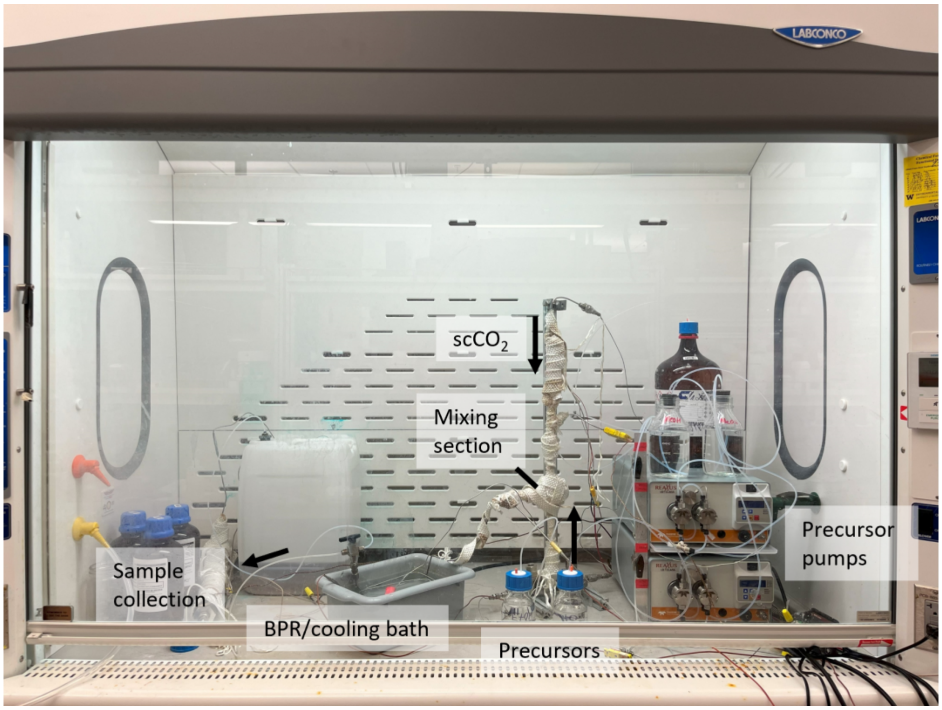

Fig. S6. Photo of our reactor setup.

Table S1. Summary of particle size analysis for the $scCO_2$ assisted synthesis at 75 °C and 10 MPa.

	0.05 M	0.1 M	0.2 M	0.3 M
$r1^a$, nm	84.40	90.13	93.29	125.72
$r3^b$, nm	98.99	106.38	111.14	161.78
rh^c, nm	67.80	74.52	76.10	91.18
μ_1	1.46	1.43	1.46	1.77
μ_3	0.85	0.85	0.84	0.78

$^a r_1 = \sum r_i / N$; $^b r_3 = \sqrt[3]{\sum r_i^3 / N}$; $^c r_h = N / \sum (1/r_i)$.

Table S2. Summary of gas adsorption analysis.

$[Cu^{2+}]$, M	Temperature, °C	Pressure, MPa	BET surface area, m^2/g
0.05	75	10	1613
0.1	75	10	1785
0.2	75	10	1856
0.3	75	10	1694
35	35	10	1887
115	115	10	1750

Table S3. Adsorption capacity of HKUST-1 for Ibuprofen (IBU) at equilibrium, with a constant IBU volume of 3 mL in all cases.

Sample	IBU initial concentration, mg/ml	Activated	Averaged adsorption capacity, mg/g	Standard deviation, mg/g
CF 5mg	0.5	No	43	5
CF 25mg	0.5	No	39	0.4
CF 50mg	0.5	No	24	0.6
Mix 50 mg	0.5	No	6	1
CF 5mg	5	Yes	619	20
CF 12.5 mg	5	Yes	401	30
CF 25 mg	5	Yes	327	8
CF 40 mg	5	Yes	267	3
CF 50 mg	5	Yes	257	2

Table S4. Continuous synthesis for the production of HKUST-1 with reactor volume, particle size, solvent, residence time (τ_{res}), space-time yield (STY), surface area (SA), and surface area production rate (SAPR) included.

Method	Reactor volume, ml	Particle size, μm	Solvents	τ_{res}	STY, $kgm^{-3}d^{-1}$	SAPR, $m^2m^{-3}d^{-1}$	SA, m^2g^{-1}	Ref
Continuous flow	100	-	Ethanol	1.5h	1479	$1.3*10^9$	911	1
Continuous flow, microwave	25	-	Ethanol	13s	$4*10^5$	$2.4*10^{11}$	600	1
Microfluidic synthesis	0.24	5-15	DMF/H_2O/ethanol/oil	6min	5.8	$1.1*10^7$	1911	2
Continuous flow	108	0.2	Ethanol	1.2min	4533	$9.3*10^9$	2046	3
Continuous flow	-	5-10	H_2O 300°C, 25MPa	-	-	-	1950	4
Microfluidic synthesis	6.12	14	DMF/H_2O/ethanol/oil	13min	1122	$1.8*10^9$	1615	5
Our work	3.22	0.11-0.25	Ethanol/$scCO_2$	10s	5668	$1.0*10^{10}$	1610-1890	

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