Electronic Supporting Information for

A Hierarchical Supra-nanostructure of HKUST-1 Featuring Enhanced H_2 Adsorption Enthalpy and Higher Mesoporosity

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Experimental Sections

Preparations

All the reagents and solvents were commercially available and used as received. A hierarchical supra-nanostructure of HKUST-1 was prepared by the following process. A solution of H_3BTC (0.210g, 1.0mmol) in 10mL of ethanol was quickly poured into a solution of $Cu(OAc)_2 \cdot H_2O$ (0.300g, 1.5mmol) in a bimodal solvents (H_2O, 10ml and acetic acid, 1mL) under vigorous stirring at room temperature, instantaneously a turquoise suspension developed. Further stirring one hour, the product was collected by centrifugation from the reaction mixture, rinsed with ethanol several times via successive centrifugation-redispersion cycles, and followed by rinsing with fresh acetone several times, and finally desiccated at 80℃ for 4 hours.

Measurements

The wide-angle powder x-ray diffraction (PXRD) measurement in the 2θ range of 5-50° was recorded on a Bruker axs D8 Advance 40kV, 40mA for CuKα (θ = 1.5418 Å) with a scan rate of 0.2 s/deg at room temperature. Simulation of the PXRD pattern was obtained by the single-crystal data and diffraction-crystal module of the *Mercury* program.

The morphology of the product was performed by FE-SEM using Hitachi S4800 operating at 10kV, TEM and HR-TEM images were performed with JEOL JEM-2100 at an accelerating voltage of 200kV.

Gas sorption isotherms of product. N_2 (77K) and H_2 (77 and 87K) isotherms were measured using a liquid nitrogen bath (77K) or liquid argon bath (87K) respectively, employing a Micromeritics ASAP 2020 system after the samples were degassed at 130 ℃ for 10 hours. Based on the N_2 sorption data at 77K, the average mesopore diameter is calculated from BJH method and the whole meso/macropore size distribution is calculated from DFT model in the Micromeritics ASAP 2020 software package.

The thermogravimetric analysis was performed on a Universal V3.9A TA Instruments from room temperature to 600°C with a heating rate of 10 °C/min under a flowing nitrogen.

Calculation of H_2 adsorption enthalpy

The hydrogen adsorption isotherms of SNHKUST-1 at 77 and 87K were described and analyzed using the following virial-type[1] equation:

$$\ln p = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} a_i N^i$$

$$\mathrm{Ln(P)} = \mathrm{Ln(N)} + (a_0 + a_1 * N + a_2 * N^{\wedge 2} + a_3 * N^{\wedge 3} + a_4 * N^{\wedge 4})/T + b_0 + b_1 * N + b_2 * N^{\wedge 2}$$

where p is the pressure in mmHg, N is the amount adsorbed in mmol/g, T is the temperature in K, α_i and b_i are adjustable

parameters, and m and n represent the order of polynomials that required to adequately describe the isotherms. The coverage-dependent H_2 adsorption enthalpy, Q_{st}, was calculated according to the following expression:

$$Q_{st}(N) = -R\sum_{i=1}^{m} a_i N^i$$

$$Q_{st} = - 8.314*(a_0+a_1*N+a_2*N^2+a_3*N^3+a_4* N^4)/1000$$

where R is the universal gas constant.

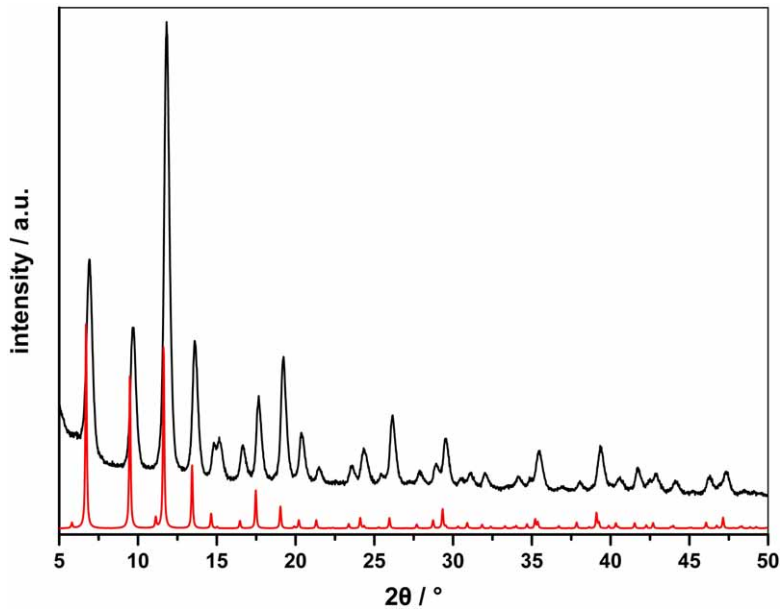

Fig. S1 The patterns of PXRD, as synthesized, black line and the simulated,[2] red line.

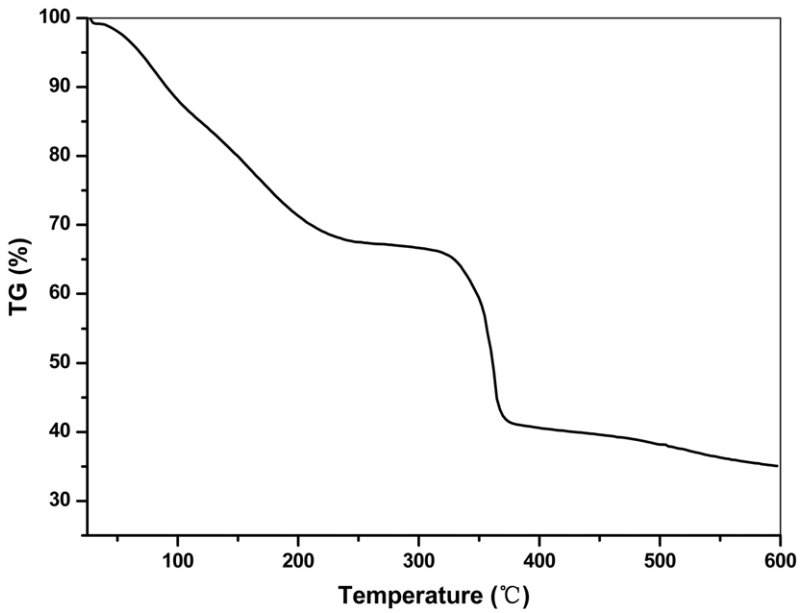

Fig. S2 TGA diagram for SNHKUST-1.

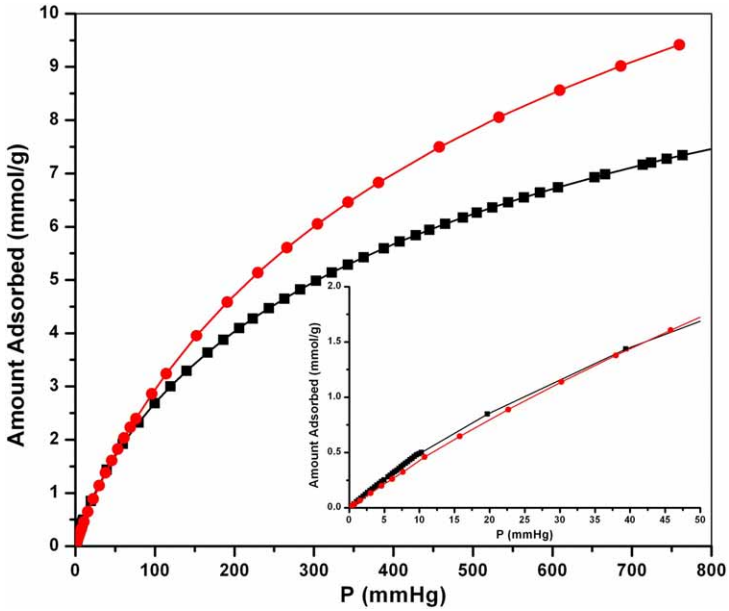

Fig. S3 A comparison of H_2 adsorption data from the literature and the result in this work at 87K, 0 < P < 1atm. Red circles , Rowsell et al.[5]; black squares, this work (SNHKUST-1).

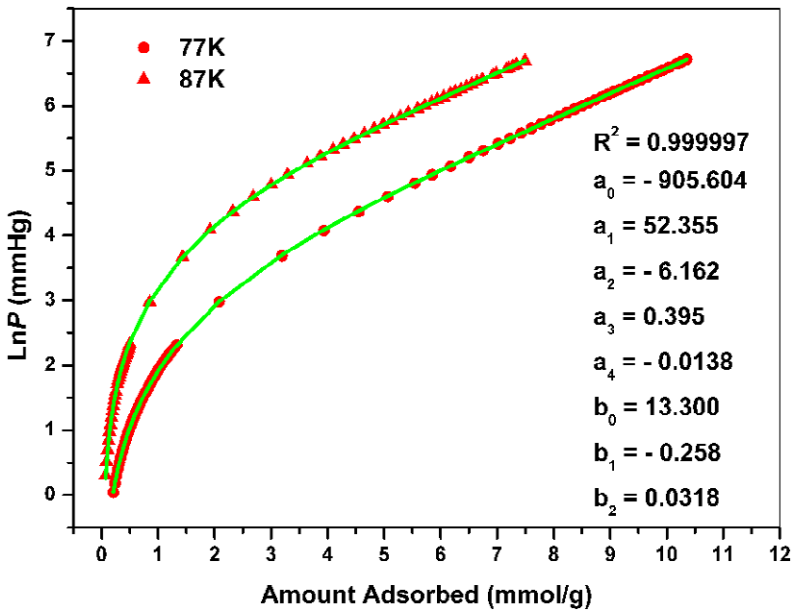

Fig. S4 The virial equation fits (lines) for SNHKUST-1.

Table S1 A comparison of BET surface area, pore volume and H_2 uptake for different HKUST-1 samples under 1atm at 77K.

References	$SSA_{BET}(m^2/g)$	$V_p(cm^3/g)$	$N_{H2}(mg/g)$	H_2 wt%
3	1239 (P/P_0 = 0.3)	0.62 (P/P_0 = 0.2)	21.6	2.16
4	1944 (P/P_0 = 0.02-0.1)			
5	1507 (P/P_0 = 0.02-0.3)	0.75	26.7	2.67
6	1482 (P/P_0 = 0.1-0.3)	0.828 (P/P_0 = 0.995)	25.3	
SNHKUST-1	1444 (P/P_0 = 0.001-0.08)	1.288 (P/P_0 = 0.994)	20.2	2.02

Table S2 N_2 Sorption Data for SNHKUST-1.

P/P_0	N (cm^3/g)	P/P_0	N (cm^3/g)
1.71445e-006	15.1658	0.993894	832.781
1.55421e-006	30.1918	0.984187	825.785
1.58134e-006	45.2277	0.979869	797.67
1.66637e-006	60.2731	0.965939	617.211
1.79771e-006	75.3051	0.930669	477.841
1.99499e-006	90.3103	0.914747	460.43
2.18253e-006	105.475	0.89156	446.702
2.55524e-006	120.639	0.866083	437.757
3.36722e-006	135.8	0.839999	431.619
6.08698e-006	150.948	0.814399	427.248
1.49649e-005	166.05	0.776522	422.158
2.9623e-005	181.081	0.726436	416.761
4.52586e-005	196.044	0.67629	412.384
5.78995e-005	210.958	0.626146	408.592
6.81655e-005	225.835	0.575435	404.997
7.86103e-005	240.671	0.525352	401.629
9.34104e-005	255.443	0.475254	398.3
0.000124825	270.064	0.424737	395.037
0.000205215	284.267	0.37501	391.741
0.00036197	297.677	0.325005	388.212
0.000784113	308.428	0.274998	384.432
0.00304305	320.003	0.225109	380.172
0.00777453	327.518	0.150393	372.051
0.0138529	332.421		
0.0310857	340.882		
0.048365	347.428		
0.0791198	357.45		
0.0954444	361.09		
0.118884	365.917		
0.139055	369.168		
0.158977	371.897		
0.178912	374.29		
0.199075	376.547		
0.249105	381.327		
0.300839	385.653		
0.354363	389.692		
0.400273	392.886		
0.450238	396.122		
0.500247	399.314		
0.550228	402.527		
0.600242	405.815		
0.650285	409.317		
0.70029	413.195		
0.750174	417.668		
0.800135	423.144		
0.820532	426.059		
0.850495	430.823		
0.875099	435.802		
0.899961	442.7		
0.924824	452.676		
0.948373	470.799		
0.969586	515.013		
0.976904	559.696		
0.984326	706.174		
0.993894	832.781		

Table S3. H_2 adsorption Data for SNHKUST-1 at 77 and 87K.

77K		87K	
P (mmHg)	N (mmol/g)	P (mmHg)	N (mmol/g)
0.065796	0.01187	0.078280	0.00088
0.195118	0.04029	0.401638	0.01879
0.327160	0.06824	0.720878	0.03606
0.462275	0.09590	1.045542	0.05362
0.604137	0.12414	1.356834	0.07026
0.759402	0.15423	1.681589	0.08742
0.900530	0.18090	2.007400	0.10451
1.042227	0.20745	2.332962	0.12135
1.204380	0.23687	2.659912	0.13813
1.350419	0.26267	2.987649	0.15488
1.497853	0.28827	3.313675	0.17123
1.647064	0.31362	3.640240	0.18751
1.798279	0.33880	3.969250	0.20378
1.950211	0.36369	4.298667	0.21992
2.104199	0.38843	4.627899	0.23585
2.260200	0.41304	4.957000	0.25173
2.416572	0.43733	5.539453	0.27873
2.575706	0.46151	5.859418	0.29375
2.735702	0.48537	6.164641	0.31045
2.896770	0.50910	6.482018	0.32513
3.059250	0.53264	6.807563	0.33875
3.222353	0.55624	7.099833	0.35607
3.387662	0.57946	7.407946	0.37188
3.578768	0.60593	7.726515	0.38659
3.770521	0.63215	8.039409	0.40172
3.965209	0.65821	8.352800	0.41730
4.144566	0.68210	8.668383	0.43284
4.353164	0.70921	9.001497	0.44629
4.527316	0.73172	9.309709	0.46229
4.728260	0.75708	9.621805	0.47687
4.929883	0.78222	9.971953	0.48679
5.311697	0.82982	10.301384	0.49947
5.525672	0.85536	19.691858	0.84774
5.754987	0.87886	39.415470	1.43475
5.816351	0.88638	59.768749	1.92039
6.047657	0.90952	79.567383	2.32187
6.257150	0.93514	99.727493	2.68234
6.491147	0.95848	119.716782	3.00070
6.709605	0.98346	139.707169	3.29110
6.941809	1.00696	166.129822	3.63684
7.017417	1.01251	186.047104	3.87489
7.250218	1.03616	205.970245	4.09687
7.478238	1.05977	223.161499	4.27482
7.545878	1.06677	243.199005	4.46928
7.767821	1.09119	262.890533	4.65099
7.996140	1.11438	282.876678	4.82342
8.213105	1.13904	302.722351	4.98544
8.440328	1.16312	322.642181	5.13962
8.670938	1.18637	342.706573	5.28645
8.902643	1.21063	362.548248	5.42539
9.115522	1.23595	387.970642	5.59464
9.191529	1.24178	407.867371	5.71940
9.421640	1.26451	428.034241	5.84039
9.654046	1.28693	445.283997	5.94076
9.897207	1.30828	465.035645	6.05225
10.136982	1.32996	487.550537	6.17242
19.811958	2.08414	504.845367	6.26253
40.054272	3.19184	524.572021	6.36056
58.971691	3.93540	544.314026	6.45607
78.932098	4.55026	564.194153	6.54930
99.442375	5.06486	584.528442	6.64068
122.548424	5.54600	607.022583	6.73757
139.495850	5.85067	653.058716	6.92788
159.750122	6.17569	666.428345	6.98418
182.796585	6.50117	713.714478	7.16259
202.677887	6.75430	724.112366	7.20250
225.391281	7.01633	743.746094	7.27297
245.244904	7.22767	763.433167	7.34065
265.372314	7.42460	809.044739	7.49193

285.453186	7.60711
305.387360	7.77638
324.961395	7.93587
345.202209	8.08881
364.876801	8.23220
385.195221	8.37077
404.791321	8.49877
424.889069	8.62307
444.635590	8.74153
464.846924	8.85612
484.494720	8.96338
504.101074	9.06646
524.626526	9.17214
544.773376	9.26969
564.018799	9.35930
583.994751	9.44947
603.454834	9.53462
634.766541	9.66577
669.298096	9.80169
694.572876	9.89952
703.339966	9.93293
733.978882	10.04220
770.456909	10.16855
794.794312	10.25110
828.003784	10.35606

References

1. L. Czepirski, J. Jagiello, *Chem. Eng. Sci.* 1989, **44**, 797.
2. S. Chui, S. Lo, J. Charmant, A. Orpen and I. Williams, *Science*, 1999, **283**, 1148.
3. P. Krawiec, M. Kramer, M. Sabo, R. Kunschke, H. Fröde and S. Kaskel, *Adv. Eng. Mater.,* 2006, **8**, 293.
4. A. G. Wong-Foy, A. J. Matzger and O. M. Yaghi, *J. Am. Chem. Soc.,* 2006, **128**, 3494.
5. J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.,* 2006, **128**, 1304.
6. J. Liu, J. T. Culp, S. Natesakhawat, B. C. Bockrath, B. Zande, S. G. Sankar, G. Garberoglio and J. K. Johnson, *J. Phys. Chem. C,* 2007, **111**, 9305.