Electronic Supplementary Information

Thermal conversion of a tailored metal-organic framework into lithium silicate with an unusual morphology for efficient CO_2 capture

Jae Hwa Lee,[a] Byoungnam Moon,[a] Tae Kyung Kim,[a] Sungeun Jeoung,[a] and Hoi Ri Moon*[a]

[a] Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 689-798, Republic of Korea. E-mail: hoirimoon@unist.ac.kr

Experimental section

All chemicals and solvents used in the synthesis were of reagent grade and those were used without further purification. Tetrakis(4-carboxyphenyl)silane (TCS) was prepared by the method reported in the previous study.[S1] Infrared spectra were recorded with a ThermoFisher Scientific iS10 FT-IR spectrometer. Elemental analyses were performed at the Ulsan National Institute of Science and Technology (UNIST) Central Research Facilities by using a Thermo Scientific Flash 2000 series CHNS/O analyzer. Thermogravimetric analysis (TGA) was performed under a N_2 (g) atmosphere at a scan rate of 5 ^oC min^{-1} using Q50 from TA instruments. X-ray powder diffraction (XRPD) data were recorded on a Bruker D2 phaser diffractometer at 30 kV and 10 mA for Cu Kα (λ = 1.541 Å), with a step size of 0.02° in 2θ. Scanning electron microscope (SEM) images were taken using a Quanta 200 microscope (FEI) operating at 18 kV. Transmission electron microscope (TEM) images and energy dispersive X-ray spectra were obtained with a JEOL JEM-2100F microscope. The nitrogen adsorption-desorption isotherms were measured at 77 K using liquid nitrogen on a BELsorp-MAX. Prior to adsorption measurement the samples were evacuated at 250 ^oC under vacuum ($p < 10^{-4}$ bar) for 6 h.

Synthesis of LiTCS, $[Li_4(TCS)\cdot 2DEF\cdot 1EtOH]\cdot 0.25EtOH\cdot 1H_2O$

TCS (40 mg, 0.078 mmol) was dissolved in DEF (4 mL) and added to an EtOH solution (2 mL) of $LiNO_3\bullet 6H_2O$ (25 mg, 0.31 mmol). The mixture was placed in a Teflon vessel within the autoclave, and heated and kept at 120 ^oC for 24 h. The solution was cooled to room temperature. Pale-yellow crystals formed, which were filtered off and washed briefly with the mother liquor. Yield: 69%. FTIR (KBr, cm^{-1}): 3449 (O-H, coordinated EtOH), 3059 (Ar-H), 2976 (C-H, DEF), 2880 (C-H, aldehyde in DEF), 1660 (C=O amide in DEF), 1611 (asymmetric O-C=O, carboxylate), 1414 (symmetric O-C=O, carboxylate), 1100, 730 (Si–Ph). Anal. Calcd for $C_{40.5}H_{47.5}Li_4N_2O_{12.25}Si_1$: C, 59.75; H, 5.88; N, 3.44. Found: C, 59.10; H, 5.13; N, 3.41.

Synthesis of Li_4SiO_4 by a conversion reaction of LiTCS MOF

Grinded LiTCS crystals were heated at 5 ^oC min^{-1} under a nitrogen flow of 250 mL min^{-1}. After reaching the target temperature of 700 ^oC, it was maintained for 6 h, then cooled to room temperature. As the next step, the resultant black powder was heated in a box furnace (ambient air environment) at 10 ^oC min^{-1}. After reaching the target temperature of 650 ^oC, the material was maintained at that temperature for 2 h. After cooling to room temperature, white solid was acquired.

Synthesis of Li_4SiO_4 by a conventional method for comparison

A mixture of lithium hydroxide monohydrate and fumed silica in water with a Li/Si molar ratio of 4.1:1 was stirred and heated at 70 ºC until the precursors were dissolved in water. Then, the solution was heated at 105 ºC to evaporate the water and the resulting powder was calcined at 700 ºC for 4 h in tube furnace under a nitrogen flow of 500 mL/min.

Single-crystal X-ray crystallography

A single-crystal of LiTCS was coated with paratone-*N* oil, and the diffraction data were measured at 100 K with synchrotron radiation (λ = 0.64999 Å) on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Republic of Korea. The ADSC Q210 ADX program[S2] was used for

data collection, and HKL3000sm (Ver. 703r)[S3] was used for cell refinement, reduction, and absorption correction. The crystal structures were solved by direct methods and refined by full-matrix least-squares calculations with the SHELXL computer program.[S4] The positions of all non−hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were positioned geometrically using a riding model. The crystallographic data and selected bond lengths and angles of LiTCS are summarized in Tables S1 and S2.

References

S1. H. Yu, M. Tian, C. Shen and Z. Wang, Polymer Chemistry, 2013, **4**, 961-968.

S2. A. J. Arvai, C. Nielsen, *ADSC Quantum-210 ADX Program*, Area Detector System Corporation; Poway, CA, USA, **1983**.

S3. Z. Otwinowski, W. Minor, Methods in Enzymology, Part A. In *Macromolecular Crystallography*; Carter Jr., C. W., Sweet, R. M., Eds.;, Academic Press: New York, **1997**; Vol. 276, pp 307-326.

S4. G. M. Sheldrick, *Acta Crtst, Section C*, 2015, **71**, 3.

Table S1. X-ray crystallographic data of LiTCS.

Compound	LiTCS
Empirical formula	C40 H44 Li4 N2 O11 Si
Formula weight	784.62
Temperature, K	100(2)
Wavelength. Å	0.64999
Crystal system	Triclinic
Space group	P -1
a, Å	13.725(3)
b, Å	14.074(3)
c, Å	14.187(3)
α, deg	114.15(3)
β, deg	114.20(3)
γ, deg	98.24(3)
Volume, Å^3	2115.7(10)
Z	2
Density (calculated), g cm^{-3}	1.232
Absorption coefficient, mm^{-1}	0.091
F(000)	824
Theta range for data collection, deg	1.563 to 24.347
Index ranges	-17<=h<=17, -17<=k<=17, -17<=l<=17
Reflections collected	16681
Independent reflections	8489 [R(int) = 0.0198]
Completeness to theta = 22.954°	94.4 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8489 / 12 / 552
Goodness-of-fit on F^2	1.075
Final R indices [I>2sigma(I)]	R1 = 0.0577, wR2 = 0.1731
R indices (all data)	R1 = 0.0663, wR2 = 0.1816
Largest diff. peak and hole, eÅ^{-3}	0.983 and -0.499

[a] $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR(F^2) = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$ where $w = 1/[\sigma^2(Fo^2) + (0.1155P)^2 + (1.4119)P]$, $P = (Fo^2 + 2Fc^2)/3$.

Table S2. Selected bond distances (Å) and angles (deg.) of LiTCS.

Li(1)-O(1)	1.902(4)	Li(1)-O(9)	1.908(4)
Li(1)-O(8)#1	1.946(4)	Li(1)-O(10)	1.972(5)
Li(1)-Li(4)#1	2.831(5)	Li(2)-O(3)#2	1.907(4)
Li(2)-O(2)#3	1.915(4)	Li(2)-O(2)	1.939(4)
Li(2)-O(11)	1.945(5)	Li(2)-Li(2)#3	2.719(8)
Li(3)-O(6)#4	1.879(4)	Li(3)-O(4)#5	1.908(4)
Li(3)-O(7)	1.949(4)	Li(3)-O(7)#6	1.951(4)
Li(3)-Li(3)#6	2.716(7)	Li(4)-O(5)#4	1.974(4)
Li(4)-O(3)#5	2.019(4)	Li(4)-O(1)#7	2.037(4)
Li(4)-O(8)	2.060(4)	Li(4)-Li(1)#7	2.830(5)
O(1)-Li(1)-O(9)	116.2(2)	O(1)-Li(1)-O(8)#1	90.84(17)
O(9)-Li(1)-O(8)#1	120.5(2)	O(1)-Li(1)-O(10)	109.7(2)
O(9)-Li(1)-O(10)	115.9(2)	O(8)#1-Li(1)-O(10)	100.29(19)
O(3)#2-Li(2)-O(2)#3	126.9(2)	O(3)#2-Li(2)-O(2)	100.95(17)
O(2)#3-Li(2)-O(2)	90.17(17)	O(3)#2-Li(2)-O(11)	122.3(2)
O(2)#3-Li(2)-O(11)	100.82(17)	O(2)-Li(2)-O(11)	110.24(19)
O(6)#4-Li(3)-O(4)#5	109.21(18)	O(6)#4-Li(3)-O(7)	109.49(19)
O(4)#5-Li(3)-O(7)	109.33(18)	O(6)#4-Li(3)-O(7)#6	122.2(2)
O(4)#5-Li(3)-O(7)#6	113.12(19)	O(7)-Li(3)-O(7)#6	91.69(16)
O(5)#4-Li(4)-O(3)#5	109.34(16)	O(5)#4-Li(4)-O(1)#7	114.01(17)
O(3)#5-Li(4)-O(1)#7	106.21(17)	O(5)#4-Li(4)-O(8)	115.33(17)
O(3)#5-Li(4)-O(8)	124.75(18)	O(1)#7-Li(4)-O(8)	83.93(13)

Symmetry transformations used to generate equivalent atoms:
#1 x,y-1,z #2 x-1,y-1,z-1 #3 -x,-y,-z+1 #4 x,y,z-1
#5 x-1,y,z-1 #6 -x,-y+1,-z+1 #7 x,y+1,z #8 x+1,y+1,z+1
#9 x+1,y,z+1 #10 x,y,z+1

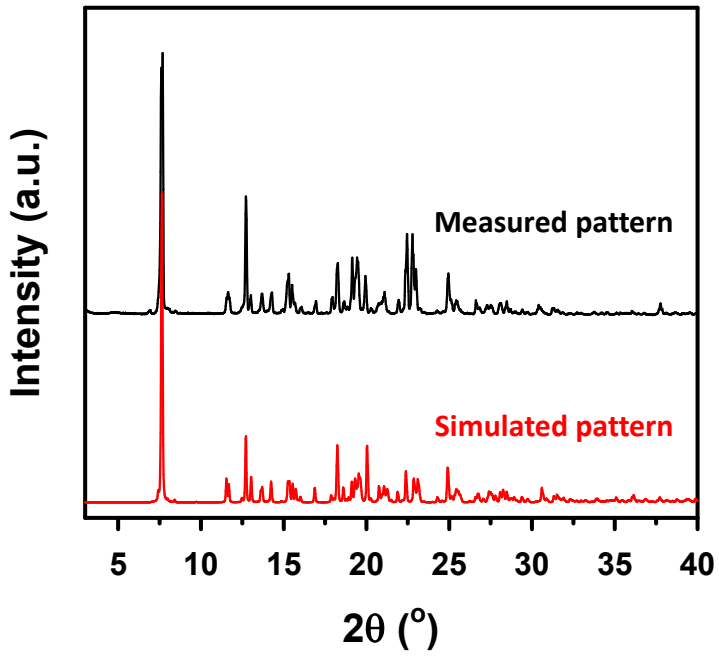

Fig. S1 XRPD patterns of LiTCS: (a) measured pattern of as-synthesized LiTCS and (b) simulated pattern from the single-crystal X-ray diffraction data.

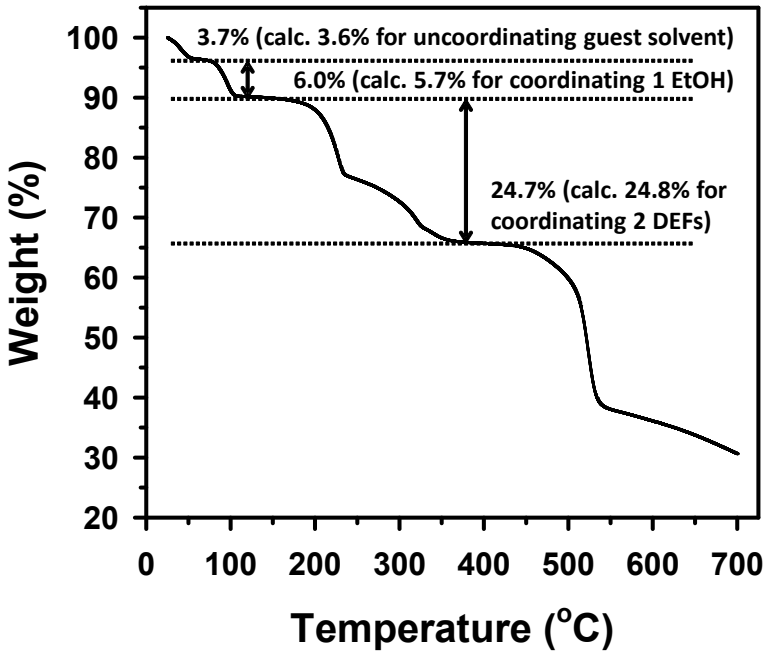

Fig. S2 TGA trace of LiTCS, measured under nitrogen atmosphere with 5 °C/min ramping rate. The result indicates 3.7% weight loss under 55 °C for uncoordinating guest solvent molecules (calc. 3.6%), 6.0% at 70–110 °C for one coordinating EtOH (calc. 5.7%), and 24.7% at 170–370 °C for two coordinating DEFs (calc. 24.8%).

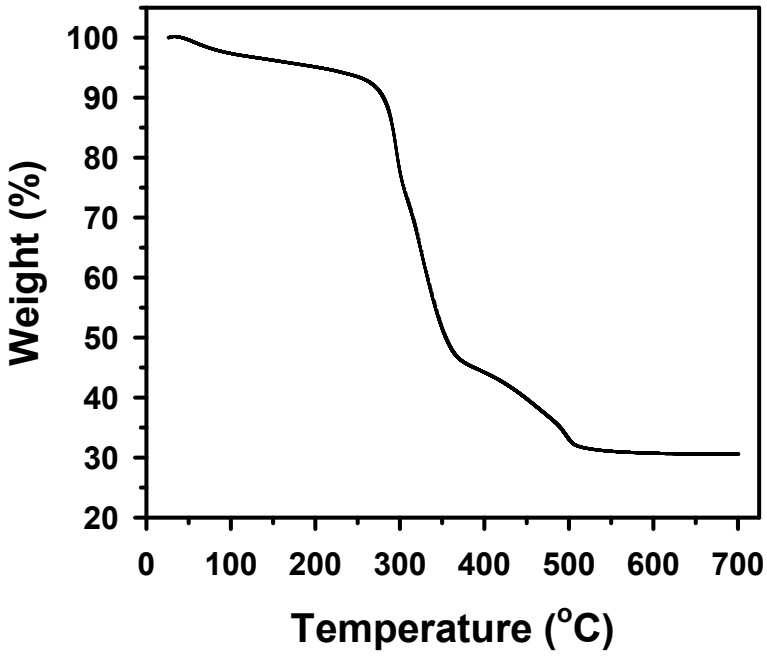

Fig. S3 TGA trace of black power Li_4SiO_4, measured under oxygen atmosphere with 3 ^oC/min. The result indicates 70% weight loss until 550 ^oC, corresponding to decomposition of carbon residue and further progress of incomplete reaction.

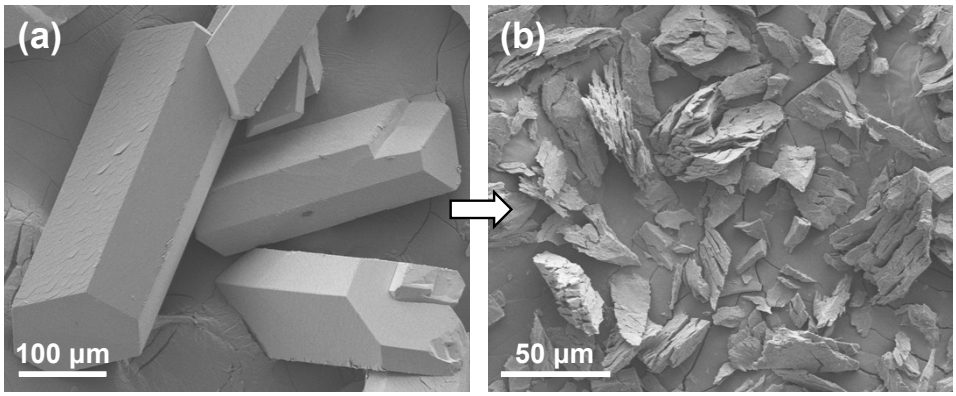

Fig. S4 SEM images of (a) LiTCS and (b) the as-synthesized Li_4SiO_4, synthesized and measured without any grinding to observe morphological change of LiTCS during the thermal conversion.

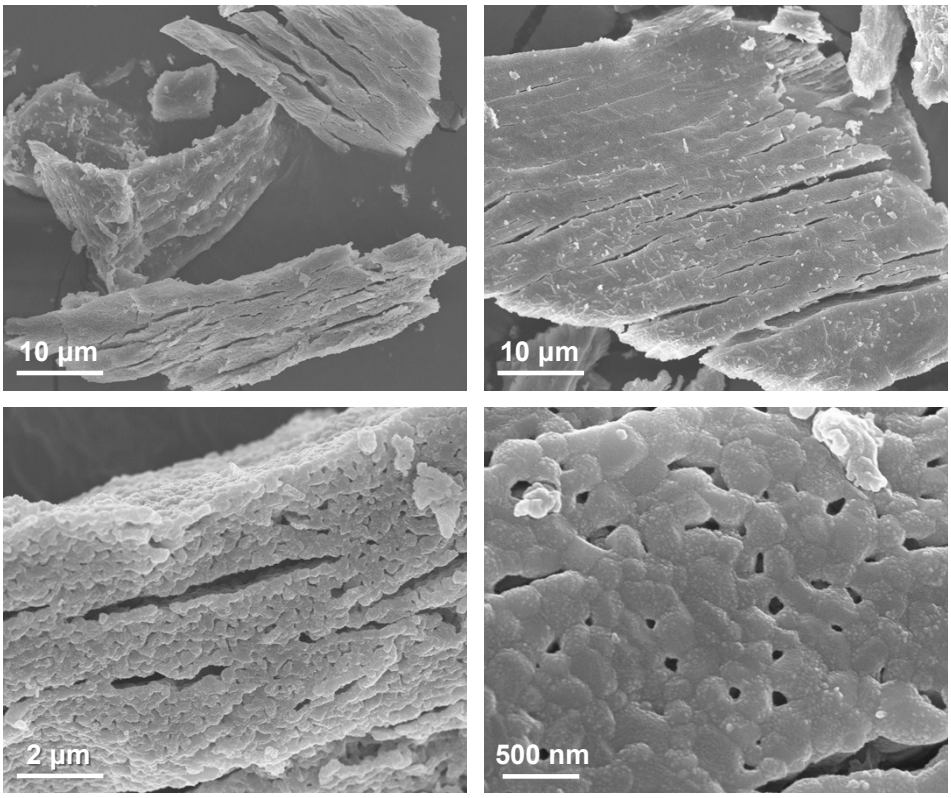

Fig. S5 SEM images of the as-synthesized Li_4SiO_4.

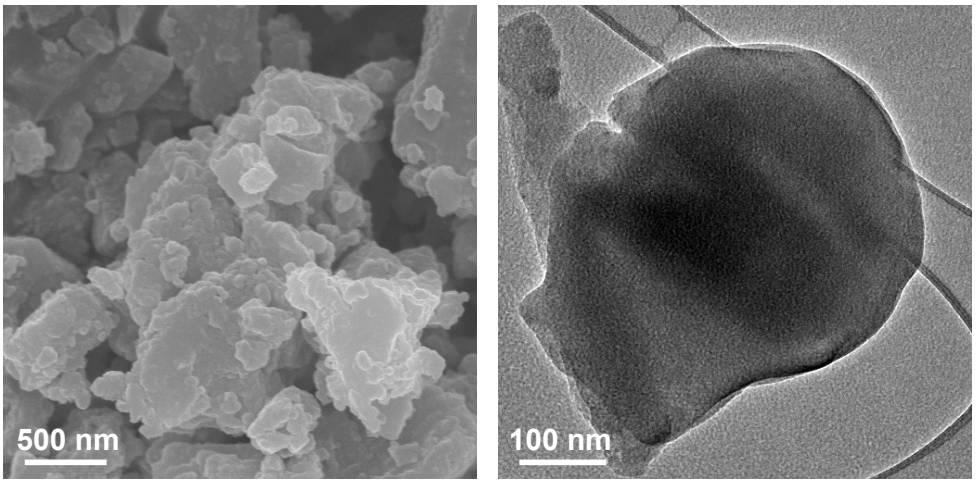

Fig. S6 SEM and TEM images of the rock-like Li_4SiO_4 synthesized conventionally.

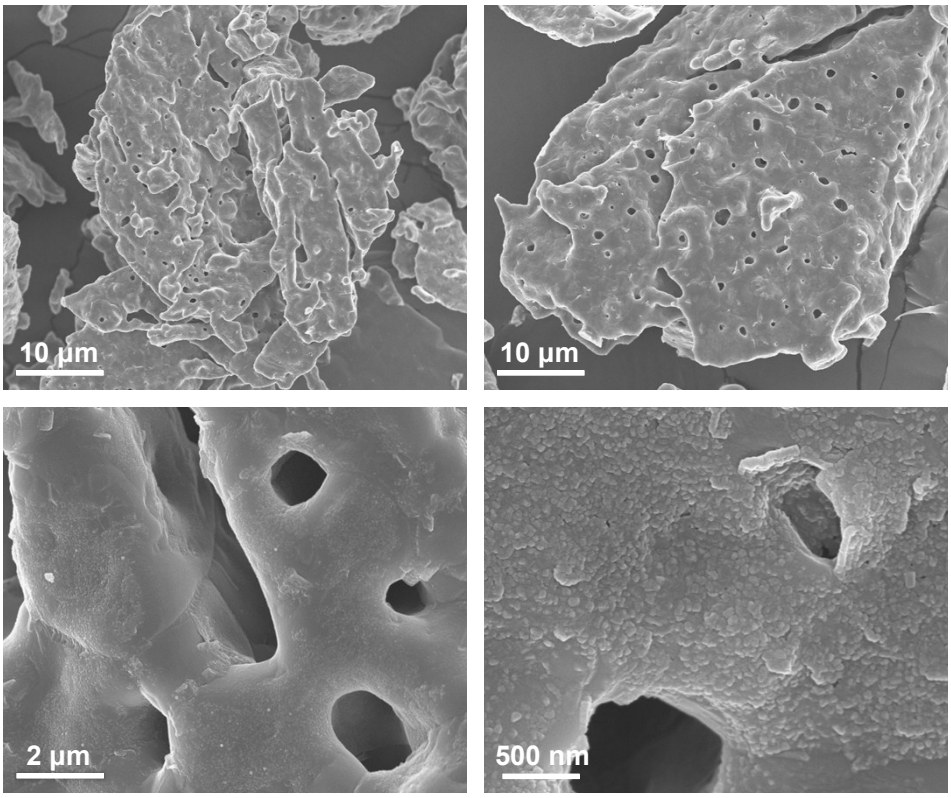

Fig. S7 SEM images of the Li_4SiO_4 absorbent after twenty five absorption-desorption cycles.