Electronic Supplementary Information

Thiostannate Coordination Transformation-Induced Self-crosslinking Chalcogenide Aerogel with Local Coordination Control and Effective Cs^+ Remediation Functionality

Yeo Kyung Kang,‡[a] Heehyeon Lee,‡[bc] Thanh Duy Cam Ha,[d] Jong Kook Won,[a] Hongil Jo,[e] Kang Min Ok,[e] Sangdoo Ahn,[a] Byungman Kang,[f] Kyunghan Ahn,[d] Youngtak Oh,*[b] and Myung-Gil Kim*[d]

[a] Department of Chemistry, Chung-Ang University, Seoul 06974, Republic of Korea
[b] Center for Environment, Health, and Welfare, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea
[c] Department of Materials Science and Engineering, Korea University, Seoul 02841, Republic of Korea
[d] School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 16419, Republic of Korea
[e] Department of Chemistry, Sogang University, Seoul, 04107, Republic of Korea
[f] Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Daejeon 34057, Republic of Korea

‡Y. K. Kang and H. Lee contributed equally to this work
Email of corresponding (*) authors: ytoh@kist.re.kr and myunggil@skku.edu

Single crystal X-ray diffraction analysis of $Na_4Sn_2S_6 \cdot 5H_2O$

The crystal was grown by slow diffusion of methanol into 100 mg/ml aqueous solution of $Na_4Sn_2S_6 \cdot 5H_2O$ at room temperature. Single crystal X-ray diffraction data for the $Na_4Sn_2S_6 \cdot 5H_2O$ were collected at room temperature using a Bruker D8 QEUST diffractometer equipped with a graphite-monochromated Mo Kα radiation. Colorless octahedron-like crystal with the size of 0.376 mm × 0.443 mm × 0.464 mm was selected to data collection. The data were integrated using the program SAINT,[1] and the absorption correction was made through the program SADABS.[2] An initial structure solution was obtained using SHELXS-2013[3] and further refinement was performed via SHELXL-2013,[4] implemented in the program WinGX-2014.[5] The crystallographic information and selected bond lengths for $Na_4Sn_2S_6 \cdot 5H_2O$ are listed in Tables S1–S2, respectively.

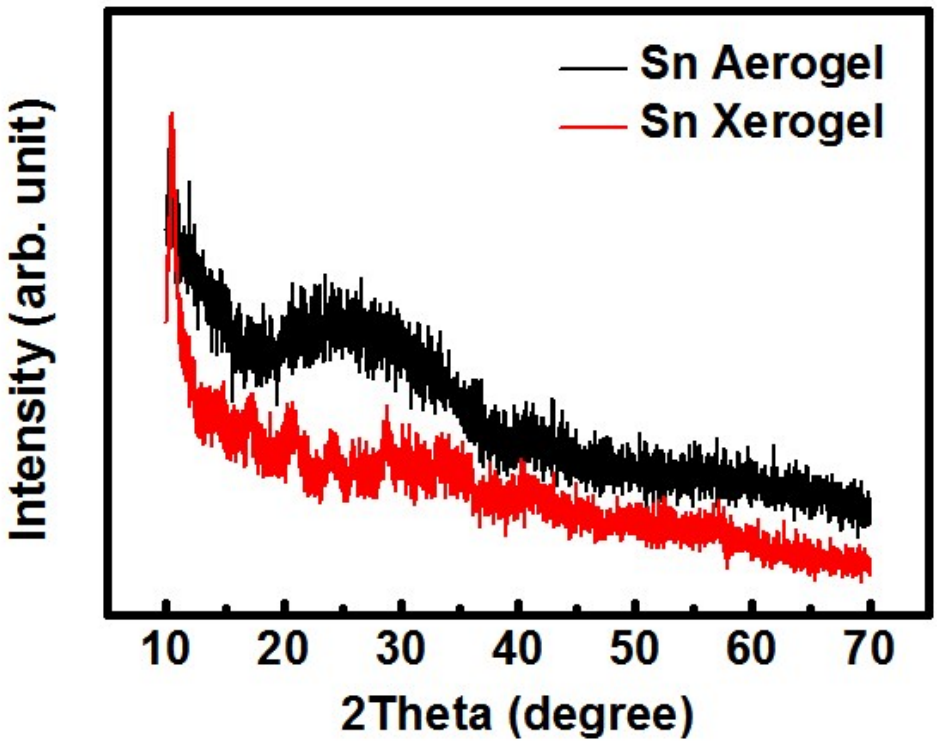

Figure S1. PXRD analysis of TAC-1 and its Xerogel counterpart.

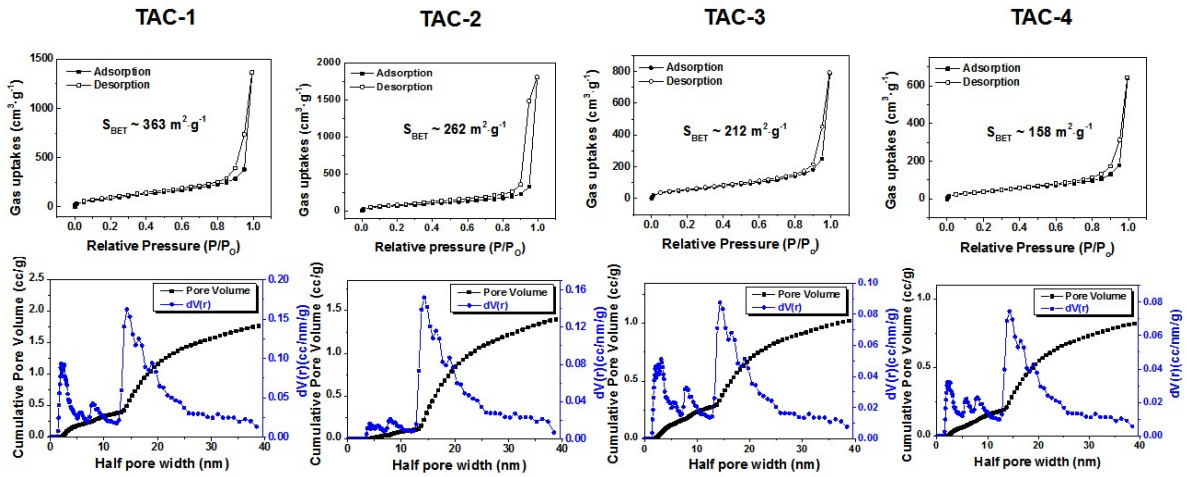

Figure S2. BET surface area measurement and BJH pore size distribution of TAC-1, TAC-2, TAC-3, and TAC-4.

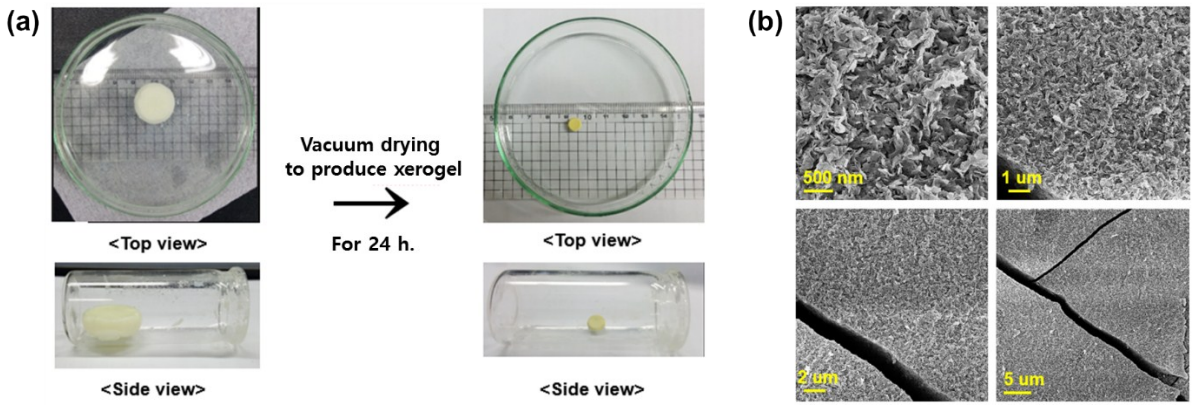

Figure S3. Effect of surface tension (vacuum drying) on macrostructure of TAC-1. (a) volume shrinkage of gel (b) FE-SEM analysis of TAC-1 xerogel.

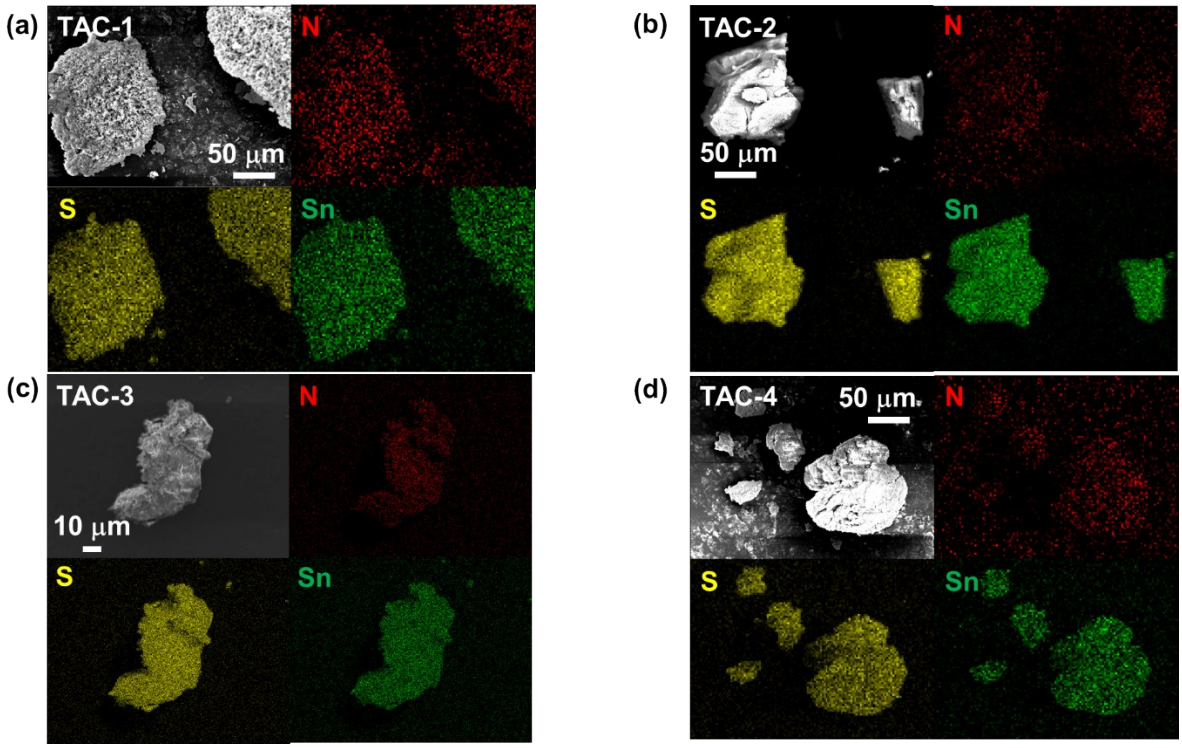

Figure S4. EDS mapping analysis of (a) TAC-1 (b) TAC-2 (c) TAC-3 (d) TAC-4.

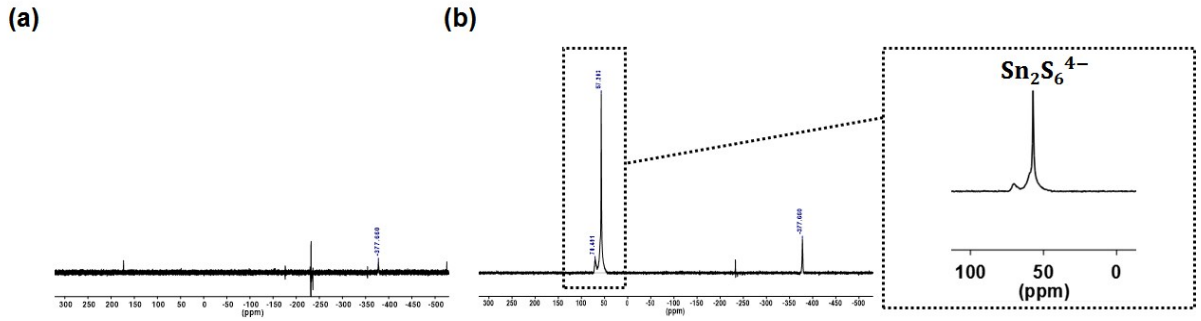

Figure S5. ^{119}Sn NMR analysis of (a) $SnCl_2$ in DMSO-*d*6 / deionized water, (b) $Na_4Sn_2S_6{\cdot}5H_2O$ in deionized water.

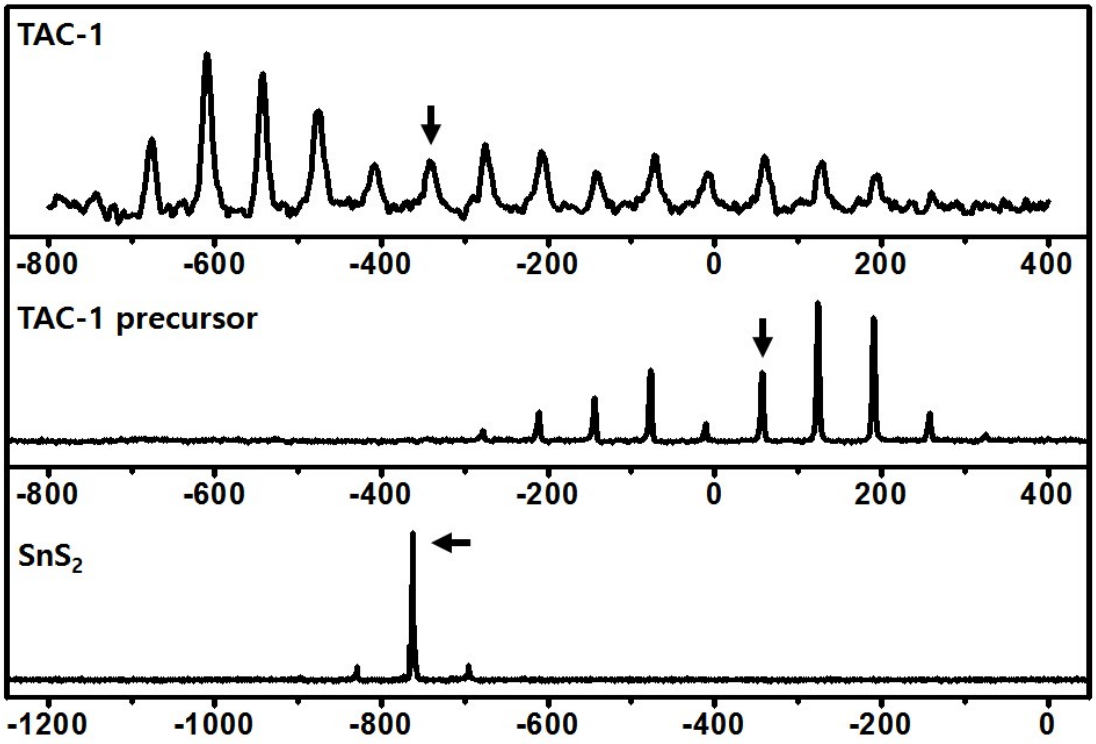

Figure S6. Solid state ^{119}Sn NMR of TAC-1, TAC-1 precursor, and SnS_2 reference material.

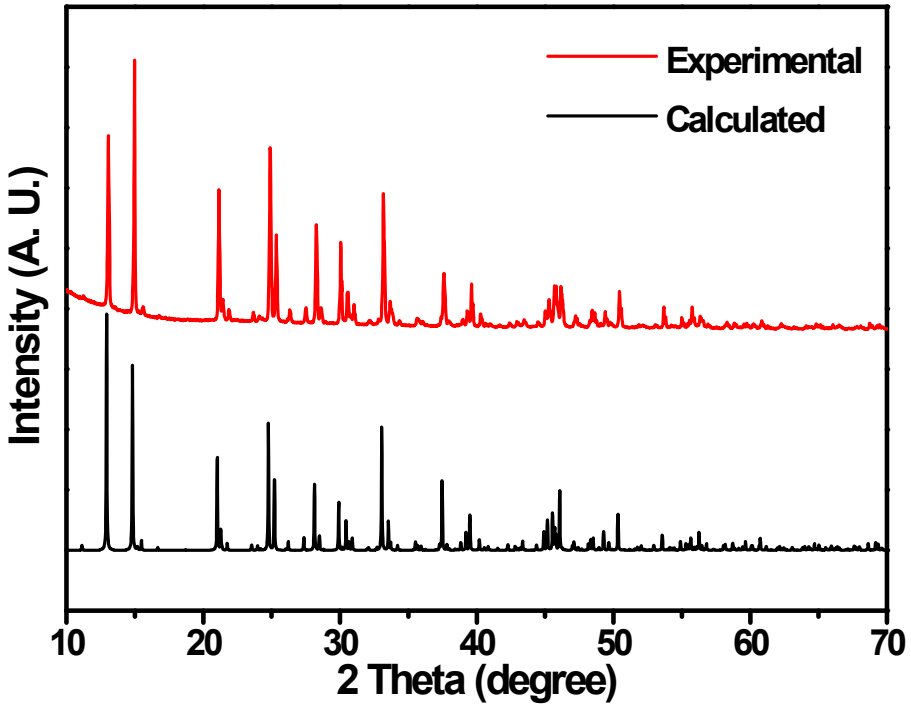

Figure S7. Calculated and experimental powder X-ray diffraction patterns for $Na_4Sn_2S_6{\cdot}5H_2O$.

Table S1. Stoichiometric ratio of TACs through pyrolytic elemental analysis (EA)* and energy dispersive x-ray spectroscopy (EDS)

		Sn	S	N	C
TAC-1	EA	1.0	2.3	0.6	2.8
	EDS	1.0	1.9	-	-
TAC-2	EA	1.0	2.4	0.6	1.5
	EDS	1.0	1.8	-	-
TAC-3	EA	1.0	2.4	0.6	1.1
	EDS	1.0	1.7	-	-
TAC-4	EA	1.0	2.3	0.4	N/A
	EDS	1.0	1.9	-	-

*the weight % of Sn was evaluated based on the sum of all other elements (S, N, C, H, and O) in chalcogel through pyrolytic elemental analysis

Table S2. Crystal data and structure refinement for $Na_4Sn_2S_6{\cdot}5H_2O$

Formula weight	611.78
Temperature	300(2) K
Wavelength	0.71073 A
Crystal system, space group	Tetragonal, P 4_12_12
Unit cell dimensions	a = 8.44260(10) Å α = 90° b = 8.44260(10) Å β = 90° c = 23.3145(5) Å γ = 90°
Volume	1661.80(5) Å^3
Z, Calculated density	4, 2.445 g/cm^3
Absorption coefficient	3.862 mm^{-1}
F(000)	1160
Crystal size	0.464 x 0.443 x 0.376 mm
Theta range for data collection	2.566 to 28.329°
Limiting indices	-11<=h<=11, -11<=k<=11, -31<=l<=31
Reflections collected / unique	45537 / 2069 [R(int) = 0.0266]
Completeness to theta = 25.242	99.70%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2069 / 8 / 100
Goodness-of-fit on F^2	1.351
Final R indices [I>2sigma(I)]	R_1 = 0.0113, wR_2 = 0.0279
R indices (all data)	R_1 = 0.0113, wR_2 = 0.0279
Absolute structure parameter	0.016(5)
Extinction coefficient	0.0157(3)
Largest diff. peak and hole	0.463 and -0.359 e Å^{-3}

Table S3. Selected bond lengths (Å) for $Na_4Sn_2S_6 \cdot 5H_2O$

Sn(1)–S(3)	2.3355(6)
Sn(1)–S(1)	2.3504(6)
Sn(1)–S(2)	2.4435(6)
Sn(1)–S(4)	2.4560(6)
Na(1)–O(1)	2.306(3)
Na(1)–O(2)	2.342(3)
Na(1)–S(3)#1	2.8392(17)
Na(1)–S(1)	2.8663(16)
Na(1)–S(4)#2	3.2434(17)
Na(2)–O(1)	2.378(3)
Na(2)–O(2)	2.414(3)
Na(2)–O(3)	2.542(2)
Na(2)–S(3)#3	2.9731(15)
Na(2)–S(3)#2	2.9949(16)
Na(2)–S(2)#4	3.1439(16)

Symmetry transformations used to generate equivalent atoms:
#1 *x*+1/2,-*y*+1/2,-*z*+3/4 #2 -*y*+3/2,*x*+1/2,*z*+1/4 #3 *y*+1,*x*,-*z*+1 #4 -*y*+3/2,*x*-1/2,*z*+1/4

Table S4. ICP-MS analysis of TAC-3 in Cs^+ solution before and after Cs^+ adsorption

	Cs	Sn
	ppm	ppm
The solution before Cs+ adsorption	79.8	-
The solution after Cs+ adsorption	46.8	-

– below detection limit (<0.1ppm)

References

1. *SAINT: Area-Detector Integration Software*, Siemens Industrial Automation, Inc.; Madison: 1996.
2. *SADABS: Area-Detector Absorption Correction*, Siemens Industrial Automation, Inc.: Madison: 1995.
3. Sheldrick, G. M., *SHELXS-2013—A Program for Automatic Solution of Crystal Structures*. University of Göttingen: Göttingen, Germany: 2013.
4. Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Cryst.* **2015,** *71*, 3-8.
5. Farrugia, L. J., WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **2012,** *45*, 849-854.