Supporting Information

Rationally Design Hierarchical SnO_2/1T-MoS_2 Nanoarray Electrode for Ultralong-life Li-S Batteries

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Experimental Section

Synthesis of C@SnO_2/TMS. C@SnS_2 nanosheets precursor were prepared by a one-step hydrothermal method. Typically, 400 mg $SnCl_4$, 400 mg Thioacetamide (TAA) and 20 mL isopropanol were stirred together for 30 min at room temperature, and then one piece of carbon cloth (2 cm * 2 cm) was put into above solution. Then transferred to a 100 mL Taflon-lined stainless autoclave. Subsequently, the autoclave was sealed and heated at 180 ℃ for 24 h. Waiting for the autoclave cool to room temperature naturally, the carbon cloth was taken out and washed with water for three times. Then dried at 70 ℃ overnight and the C@SnS_2 nanosheets precursor was obtained. Porous C@SnS_2 nanosheets was fabricated via a high-temperature calcination method. Typically, the C@SnS_2 nanosheets was placed in a porcelain, and then transferred into a tube furnace. After annealed at 500 °C in air for 4 h, the porous C@SnO_2 nanosheets were prepared. Next, 92 mg $Na_2MoO_4 \cdot 2H_2O$, 152 mg L-cysteine, 56 mg $NaBH_4$, 42 mL DMF and 28 mL deionized water were stirred for 30 min and then transferred into 100 mL Taflon-lined stainless autoclave. Then the C@SnO_2 was placed into the autoclave and sealed and heated at 200 ℃ for 12 h. After it cooling to room temperature, the carbon cloth was taken out and washed with water for at least 5 times. After dried at 70 ℃ for 6 h, the hierarchical porous C@SnO_2/TMS nanosheets were obtained. The C@1T-MoS_2 was prepared in a similar procedure by using carbon cloth instead of C@SnO_2. ***Synthesis of C@SnO_2/TMS/S.*** The C@SnO_2/TMS/S were prepared by a previously reported method. Briefly, 0.4 g sulfur was dissolve in 2 mL of CS_2. Dry C@SnO_2/TMS (φ = 1 cm) composite was completely soaked in the CS_2 solution for 5 min, and then dried out at 40 ℃ for 12 h. Finally, the C@SnO_2/TMS/S composite placed in an autoclave and heated at 155 ℃ for 24 h with an average sulfur mass loading about 2.75 mg cm^{-2}. The control groups of C@S, C@SnO_2/S and C@1T-MoS_2/S were prepared by the same method. In addition, the C@SnO_2/TMS/S with a high sulfur loading 5.0 mg cm^{-2} was prepared in a similar procedure by using 1.0 g sulfur instead of 0.3 g sulfur.

Synthesis of Li_2S_x solution. Li_2S_x solution was prepared by mixing Li_2S and sulfur, and then dissolve into the solution of volume ratio 1:1 of 1,2-dimethoxyethane (DME)

and 1,3-dioxolane (DOL) with 0.1 mol/L lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) stirred for various hours to fabricate the concentration of 1.0 mg mL^{-1} Li_2S_x solution.

Materials characterization. SEM (Hitachi, SU8010) and HRTEM (G2 F20FEI Tecnai G2 F20 microscope at 200 kV) were utilized to characterize the microstructure of the samples. And the element mapping was recorded by EDX spectroscope attached with TEM. The X-ray diffraction (PANalytical X'Pert PRO, monochromated Cu Kα radiation 40 mA, 40 kV) was used to determine the crystal phases of samples. XPS analysis was performed at room temperature to analyze the compositions and contents of element. The energy resolution is 0.5 eV and the step size is 0.1 eV. The ASAP 2020 (Micromeritics) was used to investigated the specific surface area and N_2 adsorption/desorption isotherms. The thermogravimetric analysis (TGA, Shimadzu DRG-60) was used to determine the component contents of the sample.

Electrochemical Measurements. The C@SnO_2/TMS/S was used as the electrode without additional conductive additive and insulating binder. Celgard 3501 sheets as the separator and the 2025 coin cells were assembled in a glovebox filled with Ar with the Li metal disc as the counter electrode. The electrolyte was composed of 1 mol/L lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) in a solvent of 1, 3-dioxolane (DOL) and dimethoxymethane (DME) (1:1 ratio by volume) with 2% $LiNO_3$ addition. The Neware battery test system was used to carry out the charge-discharge performance, and the voltage windows is 1.7-2.8 V. The CV measurements were recorded with a CHI600D electrochemical workstation form 1.7 to 2.8 V. The EIS measurements was investigated by PARSTAT 2273 advanced electrochemical system, and the frequency range from 1 MHz to 1 Hz. In addition, the measurement time is about 24 h after cell assembly.

Theoretical Computation. The first principle calculations were conducted, using spin-polarized Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional in the framework of CASTEP in Materials Studio of Accelrys Inc. The CI-NEB is applied for computing diffusion, which is an improved algorithm of the traditional NEB method and is more efficient in obtaining the minimum energy path between the

given initial and final positions with linear interpolation of the diffusion coordinates

Results

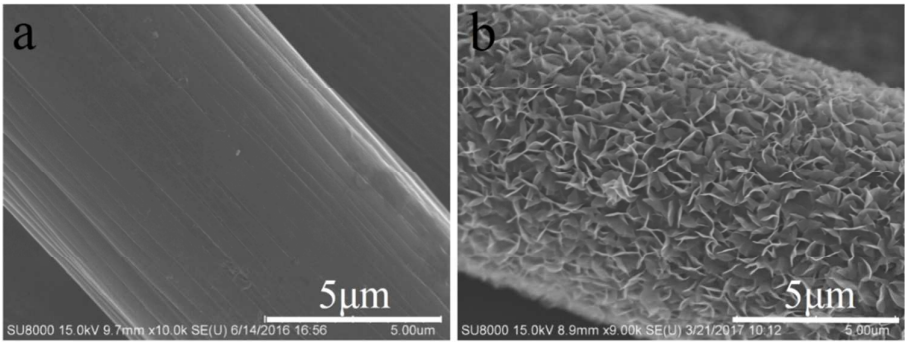

Figure S1. SEM images of a) Carbon cloth and b) C@SnS_2.

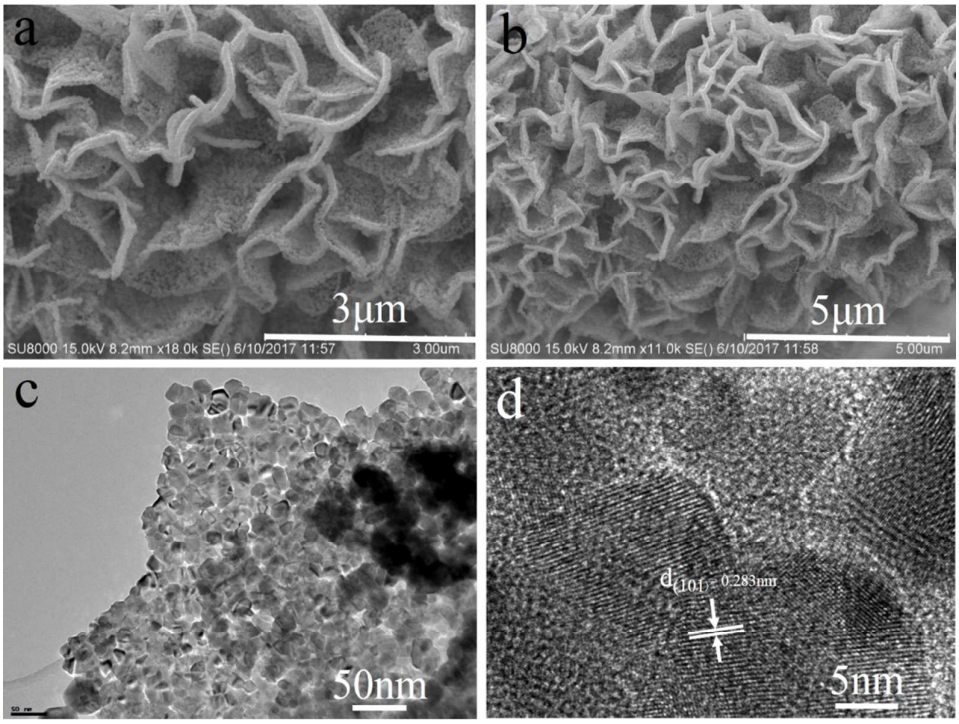

Figure S2. SEM images of C@SnO_2 porous nanosheets. a) 3μm； b) 5 μm. c) TEM image of SnO_2; d) HRTEM of SnO_2.

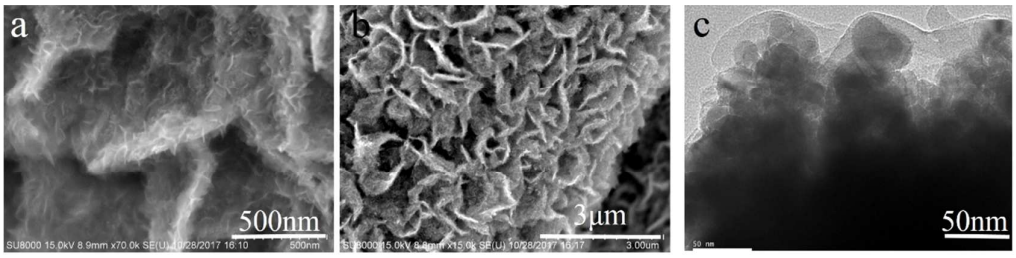

Figure S3. a, b) SEM images of C@SnO_2/TMS nanosheets and c) TEM image of SnO_2/TMS.

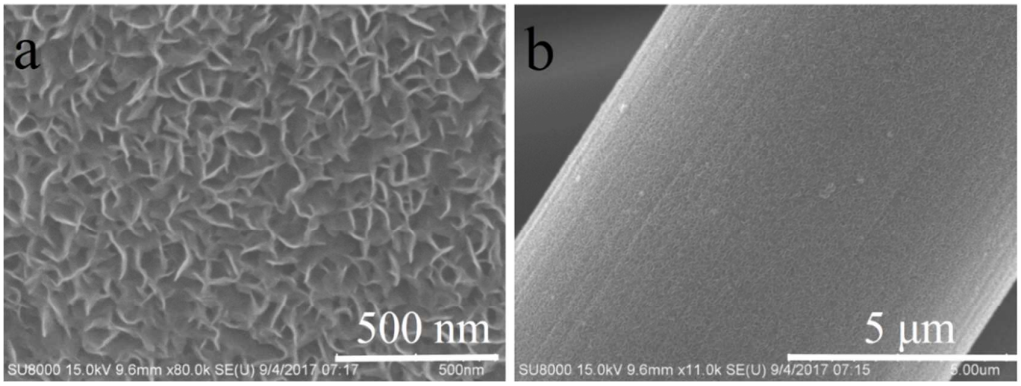

Figure S4. SEM images of C@MoS_2 nanosheets. a) 500 nm; b) 5 μm.

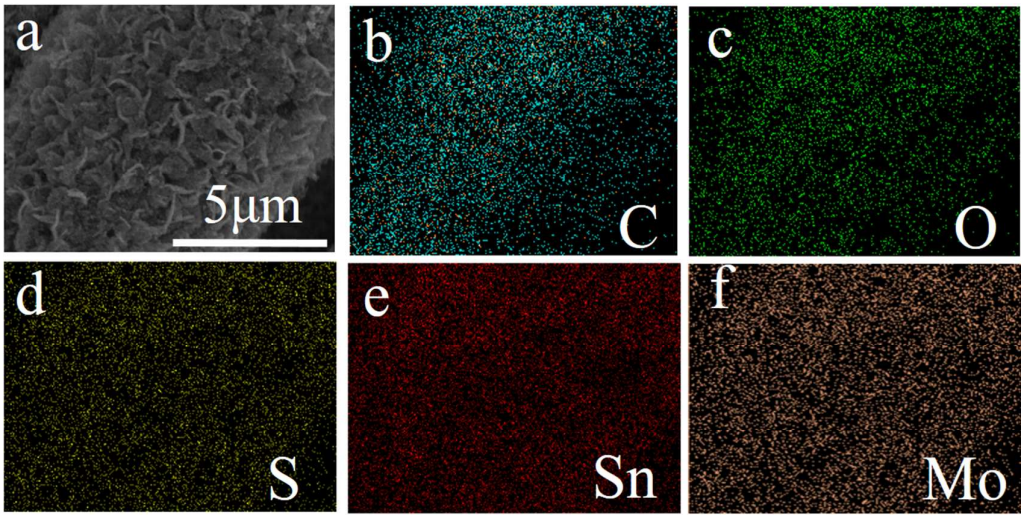

Figure S5. a) SEM image and corresponding EDS mapping of C@SnO_2/TMS sample b) C; c) O; d) S; e) Sn; f) Mo.

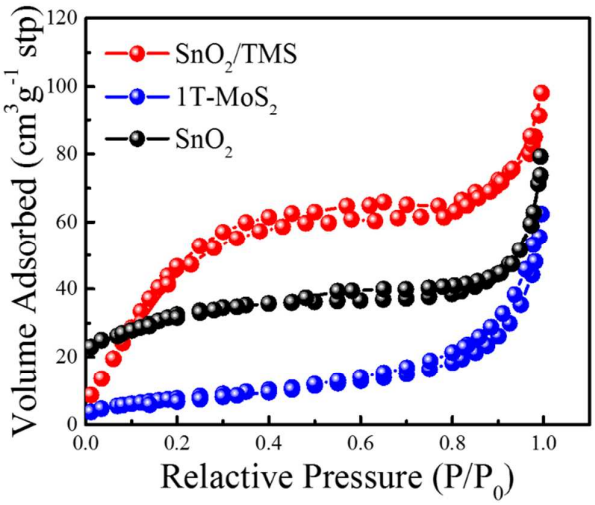

Figure S6. The N_2 isothermal adsorption and desorption curves of SnO_2, 1T-MoS_2 and

SnO_2/TMS composites.

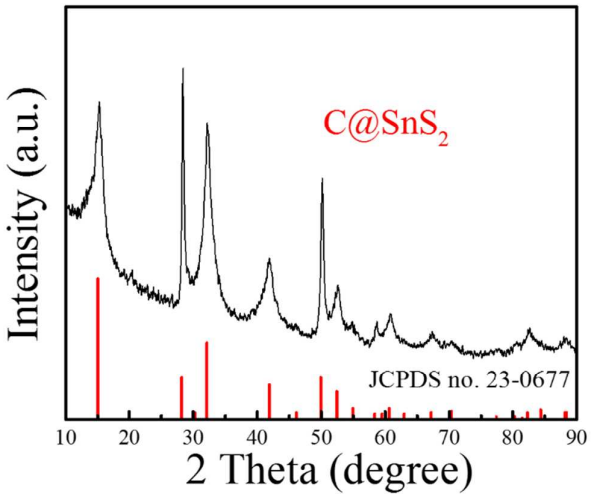

Figure S7. XRD pattern of C@SnS_2 sample.

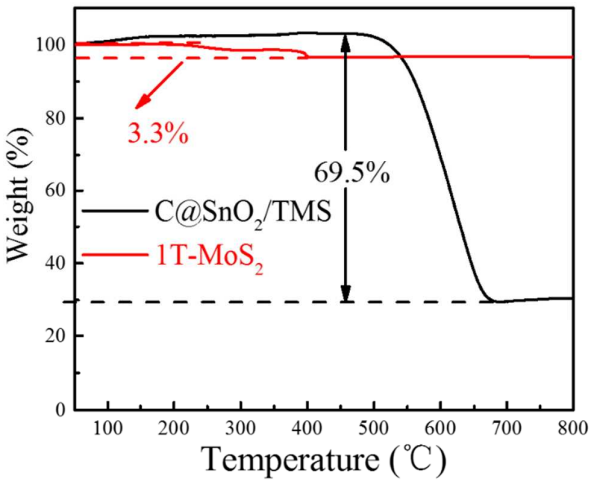

Figure S8. The TGA curves of C@SnO_2/TMS and 1T-MoS_2 in Air with a rate of 2°C/min.

Table S1. Element content of C@SnO_2/TMS materials by XPS results.

Name	C	Sn	O	Mo	S
Atomic ratio (%)	32.48	14.85	32.83	6.52	13.32

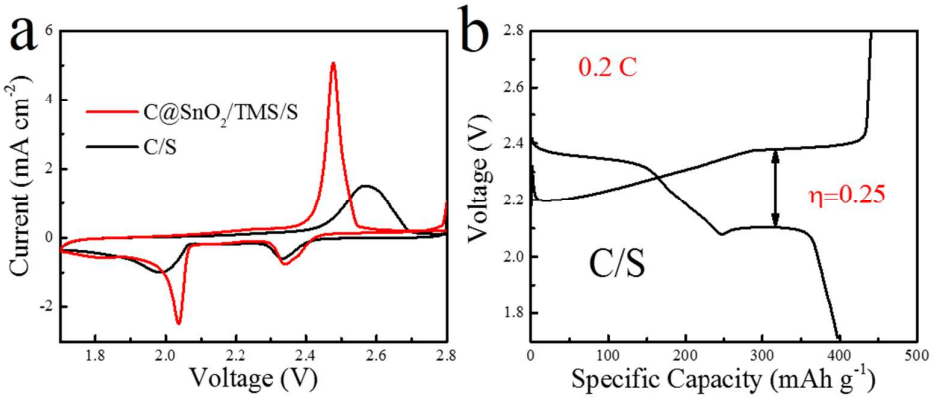

Figure S9. a) The CV profiles recorded at 0.1 mV s^{-1} from 1.7 V to 2.8 V of C@SnO_2/TMS/S and C/S. b) Representative charge–discharge voltage profiles at 0.2 C of C/S.

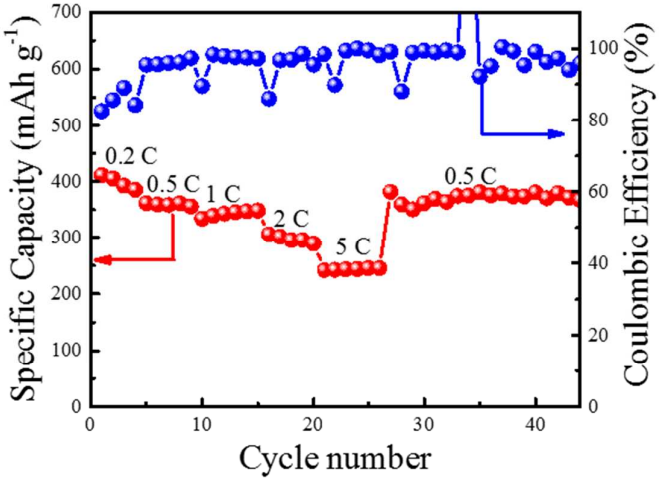

Figure S10. The rate performance of C/S from 0.2 C to 5 C.

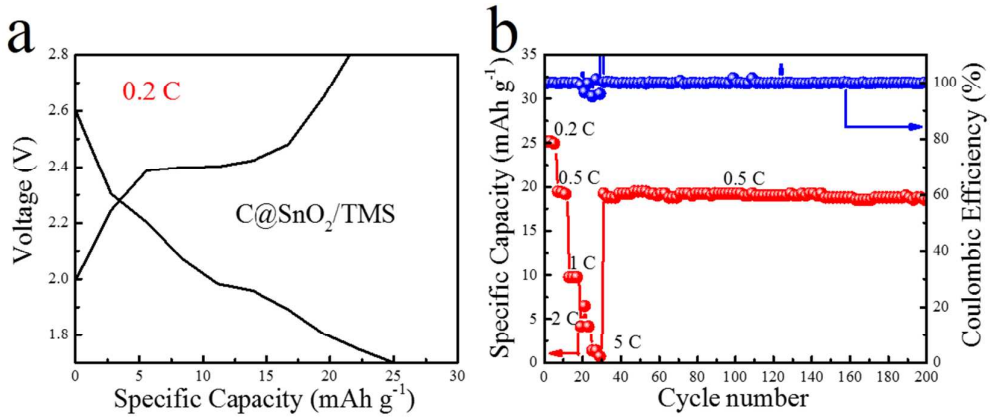

Figure S11. a) Representative charge–discharge voltage profiles of C@SnO_2/TMS as the Li-ion batteries in the Li-S system at 0.2 C. b) The rate performance of C@SnO_2/TMS from 0.2 C to 5 C in the Li-S system.

Table S2. A brief summary of the typical array electrode materials for Li–S batteries

Materials Type	Rate	Sulfur loading (mg/cm^2)	Initial Capacity (mAh/g)	Cycle Number	Cycled Capacity (mAh/g)	Decay Per Cycle	Ref.
C@SnO_2/TMS	0.5 C	2.75	1261	200	1175	0.034%	This work
	5 C	2.75	710	4000	448	0.009%	
C@WS_2	0.5 C	1.5	1200	200	1000	0.08%	1
Polymer	0.5 C	2.1	1050	200	860	0.09%	2
ReS_2	0.5 C	2.0	920	200	800	0.063%	3
MnO_2	0.2 C	2.4	1000	100	900	0.1%	4
TiO_2	1 C	1.5-2.0	871	700	608	0.045%	5

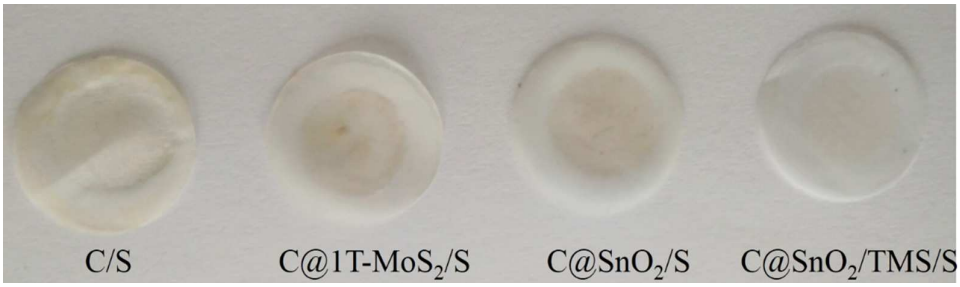

Figure S12. Photograph images of the separators of C/S, C@1T-MoS_2/S, C@SnO_2/S and C@SnO_2/TMS/S electrodes after 200 cycles at 0.5 C.

References

1. Lei, T.; Chen, W.; Huang, J.; Yan, C.; Sun, H.; Wang, C.; Zhang, W.; Li, Y.; Xiong, J., Multi-Functional Layered WS_2 Nanosheets for Enhancing the Performance of Lithium-Sulfur Batteries. *Adv. Energy Mater.* **2017**, *7*, 1601843.
2. Wu, F.; Zhao, E.; Gordon, D.; Xiao, Y.; Hu, C.; Yushin, G., Infiltrated Porous Polymer Sheets as Free-Standing Flexible Lithium-Sulfur Battery Electrodes. *Adv. Mater.* **2016**, *28*, 6365-6371.
3. Gao, J.; Li, L.; Tan, J.; Sun, H.; Li, B.; Idrobo, J. C.; Singh, C. V.; Lu, T. M.; Koratkar, N., Vertically Oriented Arrays of ReS_2 Nanosheets for Electrochemical Energy Storage and Electrocatalysis. *Nano lett.* **2016**, *16*, 3780-3787.
4. Xu, H.; Qie, L.; Manthiram, A., An Integrally-Designed, Flexible Polysulfide Host for High-Performance Lithium-Sulfur Batteries with Stabilized Lithium-Metal Anode. *Nano Energy* **2016**, *26*, 224-232.
5. Lei, T.; Xie, Y.; Wang, X.; Miao, S.; Xiong, J.; Yan, C., TiO_2 Feather Duster as Effective Polysulfides Restrictor for Enhanced Electrochemical Kinetics in Lithium-Sulfur Batteries. *Small* **2017**, 13, 1701013.