

Supporting Information

Hierarchical Mesoporous SnO₂ Nanosheets on Carbon Nanofibers toward Enhancing the Polysulfides Redox for Lithium-Sulfur batteries

Maoxu Wang,^a Lishuang Fan,^{ b} Xian Wu,^a Da Tian,^a Junhan Cheng,^a Yue Qiu,^a*

*Hexian Wu,^a Bin Guan,^a Naiqing Zhang,^{*b,c} Kening Sun^{b,c}, and Yan Wang^c*

a. School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China

b. State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150001, China

c. Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin 150001, China

Experiment

Synthesis of C@SnS₂: Thioacetamide (0.064 g) and SnCl₄ (0.064g) were added to a 100 mL Teflon-lined stainless steel autoclave containing 40 mL isopropanol and sonicated until all the materials were dissolved. Afterwards, a piece of carbon cloth (Φ =1 cm) was inserted into the autoclave and heated at 180 °C for 24 h. After cooling to room temperature naturally, the carbon cloth was taken out by a tweezer, rinsed with water and ethanol for at least 5 times and then dried in the oven at 80 °C overnight.

Synthesis of C@SnO₂: The as-prepared C@SnS₂ was placed in a quartz boat, and calcined at 500 °C for 2 h in a furnace under the air atmosphere. After cooling to room temperature, C@SnO₂ was obtained. The mass loading of SnO₂ on CNFs was about 1.24 mg cm⁻².

Synthesis of the C@SnS₂/S and C@SnO₂/S: To uniformly distribute sulfur in the C@SnS₂ composite, 0.1 g of sulfur was dissolved in 2 mL of CS₂. Dry C@SnS₂ composite was completely soaked in the CS₂ solution for 5 min, and then dried out at 40 °C for 12 h. Finally, the C@SnS₂/S composite was placed in an autoclave and heated at 155 °C for 24 h to obtain the uniform C@SnS₂/S composite, with an average sulfur mass loading between 1.2 and 1.4 mg cm⁻². The C@SnO₂/S was prepared by the same method. And the average sulfur mass loading for C@SnO₂/S was between 1.2 and 1.4 mg cm⁻² too.

Visualized adsorption test

Li₂S₄ solution was prepared by adding Li₂S and sulfur at a molar ratio of 1:3 in DME followed by vigorous magnetic stirring. Solutions with Li₂S₄ concentration of 10 mmol L⁻¹ (1.4 mg mL⁻¹) were used for adsorption test. Typically, 15 mg of CNFs, C@SnS₂ and C@SnO₂ composites were added to 3.0 mL of Li₂S₄/DME solutions separately, and the mixtures were vigorously stirred to realize thorough adsorption. 3.0 mL Li₂S₄/DME solution was used as a comparison.

Material Characterization: The morphology and microstructure characterization for C@SnS₂ and C@SnO₂ was conducted using a SEM (Hitachi, SU8010)¹ and HRTEM (G2 F20FEI Tecnai G2 F20 microscope at 200 kV).² Elemental mapping was performed with SEM. The crystal structure was characterized by X-ray diffraction (PANalytical X'Pert PRO, monochromated Cu K α radiation 40 mA, 40 kV).³ The method used in the paper is flat sample stage. Step size is 0.013°, scan range from 5° to 90° with a scan rate 1°/min. The sulfur content in the composite was tested by TG thermogravimetric

analyzer system. The specific surface area, pore volume and N₂ adsorption/desorption isotherms were measured by using an ASAP 2020 (Micromeritics). X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-Alpha XPS (Fisher Scientific Ltd, Nepean, ON)^{4, 5}. The energy resolution is 0.5 eV and the step size is 0.1 eV.

Electrochemical Measurements: The C@SnO₂/S composite was incorporated into 2025 coin-type cells. The C@ SnO₂/S material was employed as the cathode without any polymer binder; lithium foil was used as the anode, and Celgard 3501 sheets as the separator. The 2025 coin cells were assembled with Li metal disc as anode in a glovebox filled with Ar. The electrolyte was composed of 1mol/L lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) in a solvent of 1, 3-dioxolane (DOL) and dimethoxymethane (DME) (1:1 ratio by volume) with 2% LiNO₃ addition. CV test was recorded on a CHI 660D electrochemical workstation between 1.5 and 3.0 V. The charge transfer kinetics was investigated by EIS measurements using a PARSTAT 2273 advanced electrochemical system, the frequency range was set between 1 MHz and 1Hz and the amplitude is 10 mV with an ac signal. And the measurement time is about 24 h after cell assembly for the cell which was before discharging. The measurement time is about 5 min for the cell which was after 1000th cycles. A Neware battery test system is used to perform charge/discharge measurements, the voltage window is 1.7–2.8 V for various current rates (1 C is equivalent to 1675 mA/g).

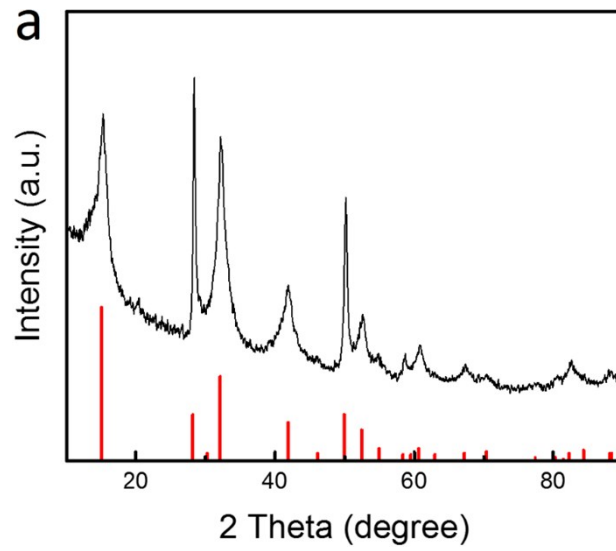


Figure S1. XRD patterns of the C@ SnS₂.

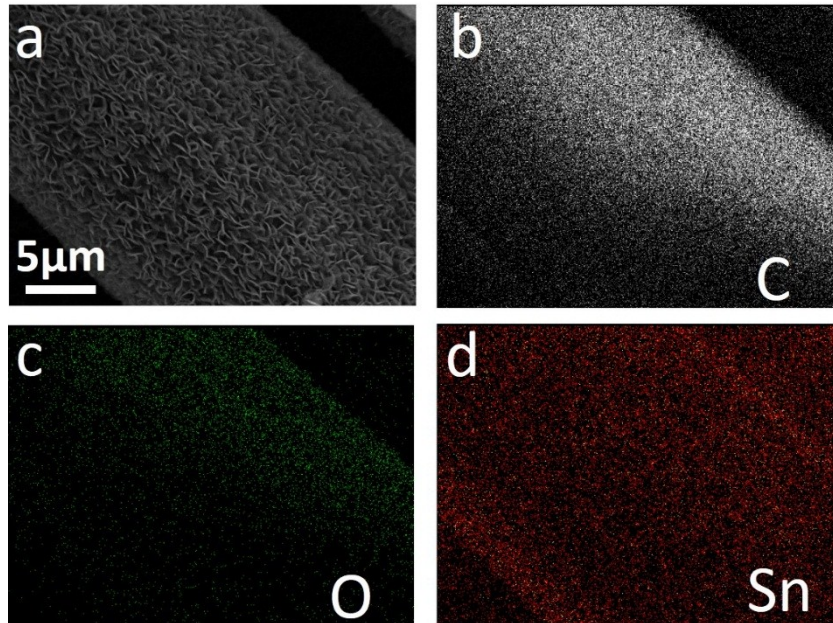


Figure S2. a) SEM image of the C@SnO₂. b-d) EDS element mapping images of b) C, c) O, d) Sn in the selected regions.

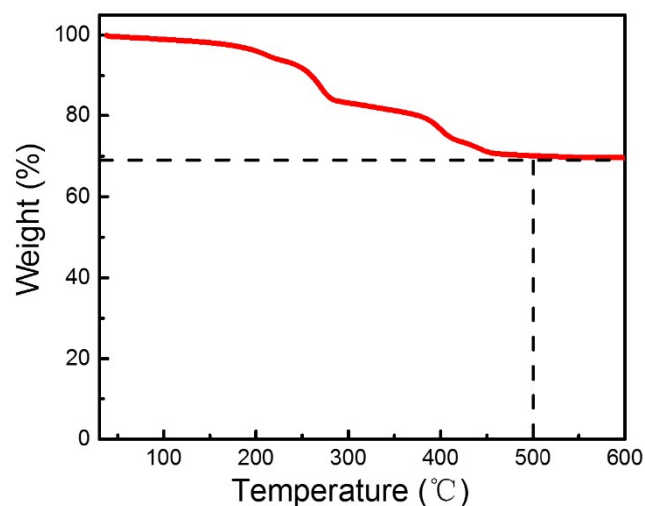


Figure S3. a) Thermal gravity analysis (TGA) curve of SnS_2 materials. There is no obvious phase transformation when temperature over $500\text{ }^\circ\text{C}$, which indicated SnS_2 have been converted to SnO_2 when the temperature reach $500\text{ }^\circ\text{C}$.

Table 1. Element content of SnO_2 materials

Name	C	Sn	O
Atomic ratio (%)	19.96	26.35	52.69

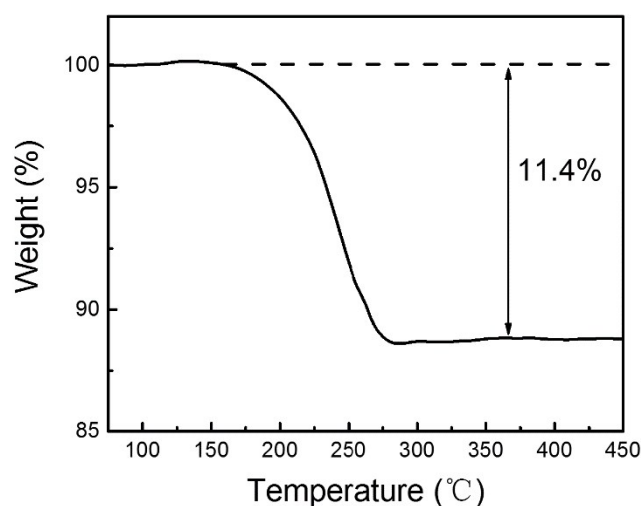


Figure S4. Thermal gravity analysis (TGA) curve of $\text{C@SnO}_2/\text{S}$ composites.

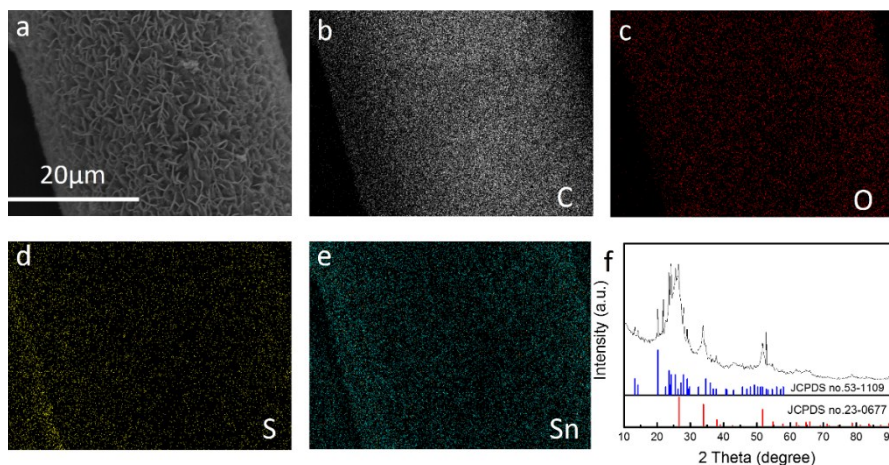
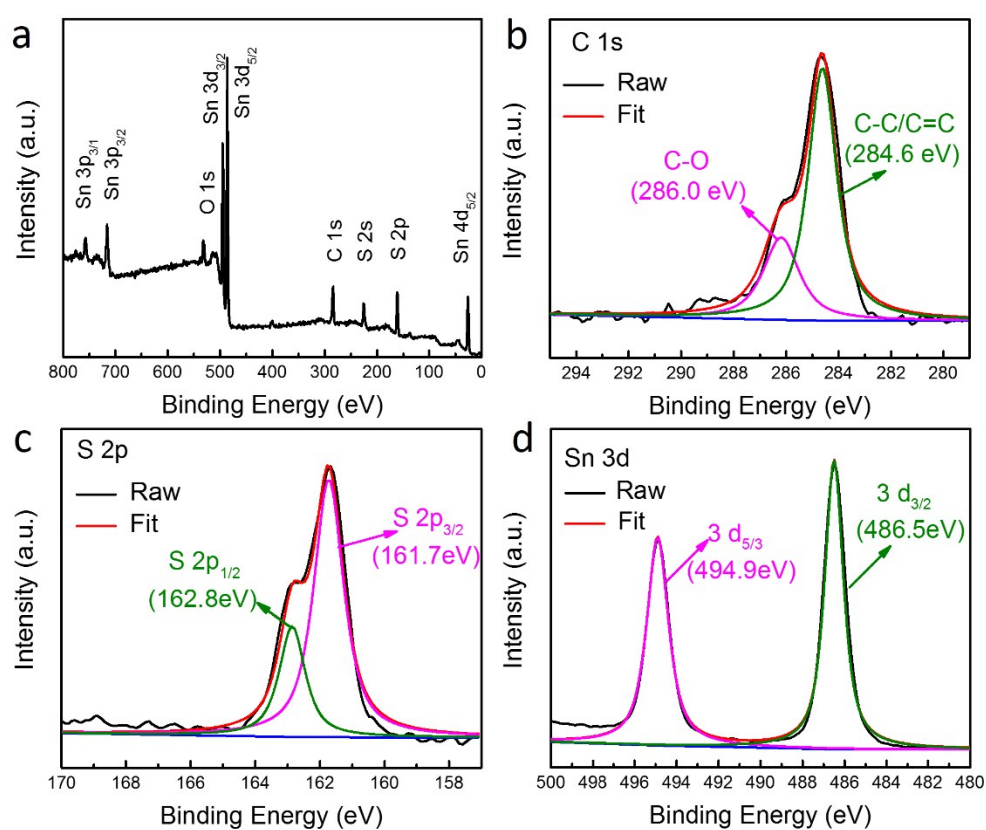


Figure S5. a) SEM image of the $\text{C@SnO}_2/\text{S}$. b-e) EDS element mapping images of b) C, c) O, d) S, e) Sn in the selected regions and the XRD patterns of $\text{C@SnO}_2/\text{S}$.

Table 2. Electrochemical performance of Li-S cells basing on different self-standing materials

Materials type	Rate	Initial Capacity (mAh/g)	Cycled capacity (mAh/g)	decay per cycle	Ref.
MWCNT	0.2C	1446	962 (50th)	0.66%	6
N-doped graphene papers	0.2 C	1300	1000 (100th)	0.23%	7
CNT/ACNF@MnO ₂	0.5C	822	618 (300th)	0.11%	8
VN/G	2 C	1128	917 (200th)	0.09%	9
WS ₂ /CCI	0.05 C	1500	1201 (100th)	0.2%	10
C@SnO ₂	0.2 C	1228	1101 (100th)	0.1%	This work
	1C	883	754 (500th)	0.029%	
	2 C	745	564 (1000th)	0.024%	

**Figure S6.** a) Wide-scan survey XPS spectrum of C@SnS₂. b–d) Elemental XPS spectra of C@SnS₂: C 1s (b), S 2p (c), and Sn 3d (d). This data was used to identify the bonding characteristics and to obtain an accurate surface composition of the as-synthesized SnS₂ composites.

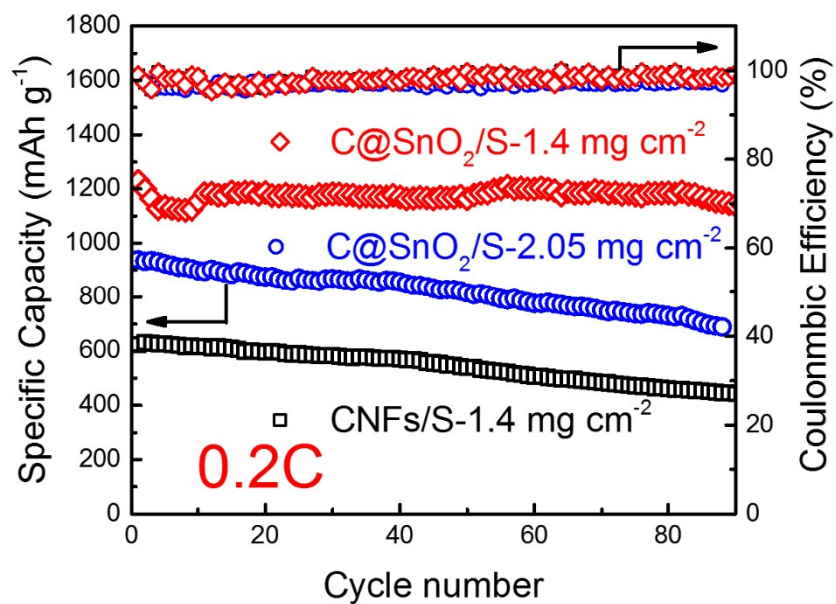


Figure S7. Cycling at 0.2C over 88 cycles of C@SnO₂/S and CNFs/S with the different mass loading.

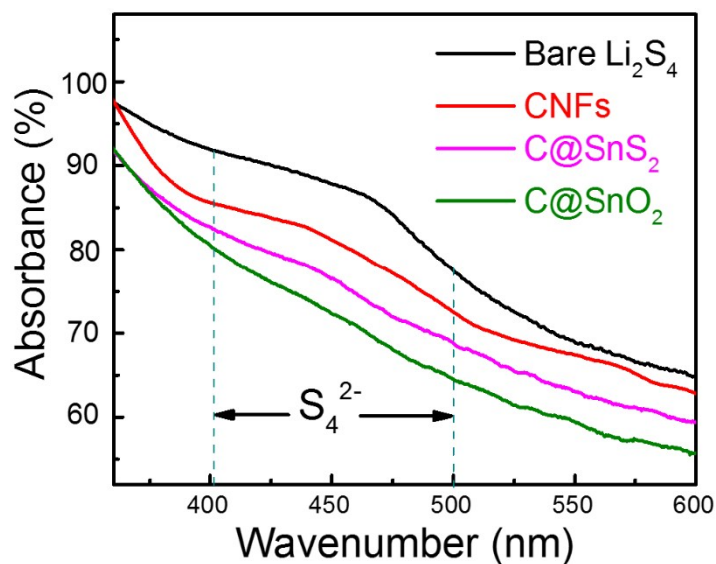


Figure S8. UV-vis spectra of the Li₂S₄ solution exposure to CNFs, C@SnS₂ and C@SnO₂ materials.

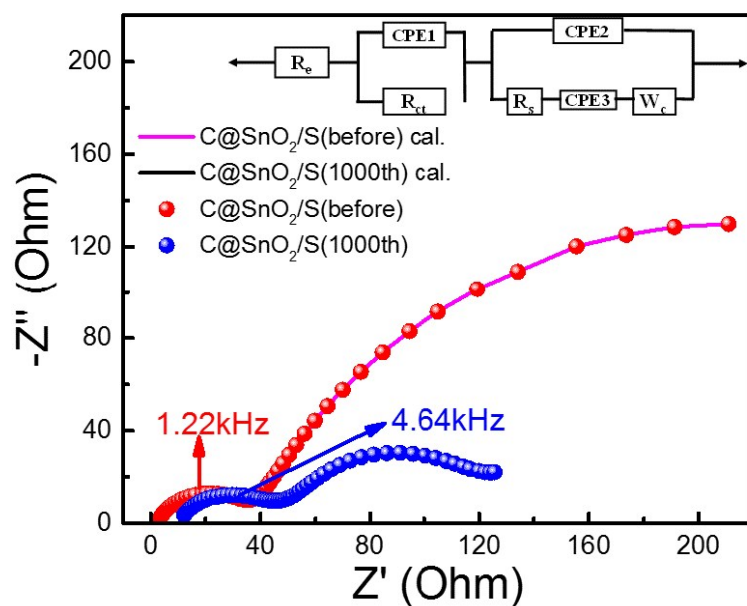


Figure S9. Electrochemical impedance spectra of before discharged and after 1000th discharged C@SnO₂/S composites. R_e is the impedance contributed by the resistance of the electrolyte, R_{ct} represents the charge transfer resistance between the electrolyte and sulfur electrode, R_s is the deposit diffusion resistance of SEI film, and W_c is the Warburg impedance owing to the diffusion of the polysulfides within the cathode.

Table 3. Impedance parameters simulated from the equivalent circuits

Cycle number	$R_e(\Omega)$	$R_{ct}(\Omega)$	$R_s(\Omega)$
Before discharge	3.06	41.49	-
After 1000th cycles	11.09	44.91	61.42

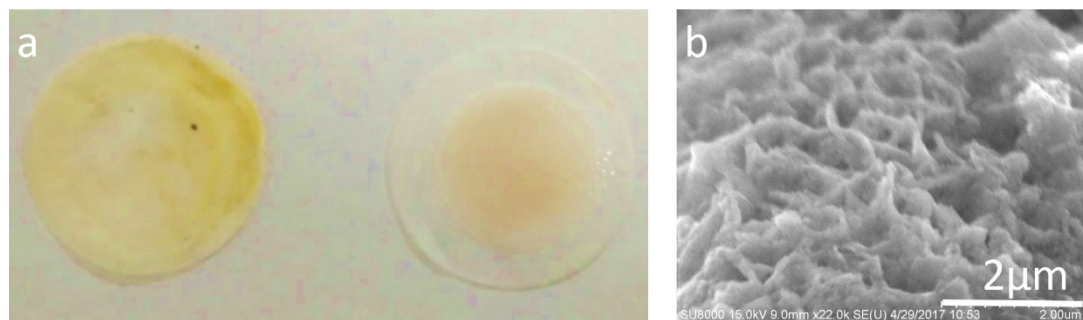


Figure S10. a) Photographs of the separators in the cells with C@SnS₂/S electrode (left) and with (right) C@SnO₂/S electrode after 1000th discharge at 2C rate. b) SEM image of the C@SnO₂/S electrode discharged at 2C after 1000th cycles.

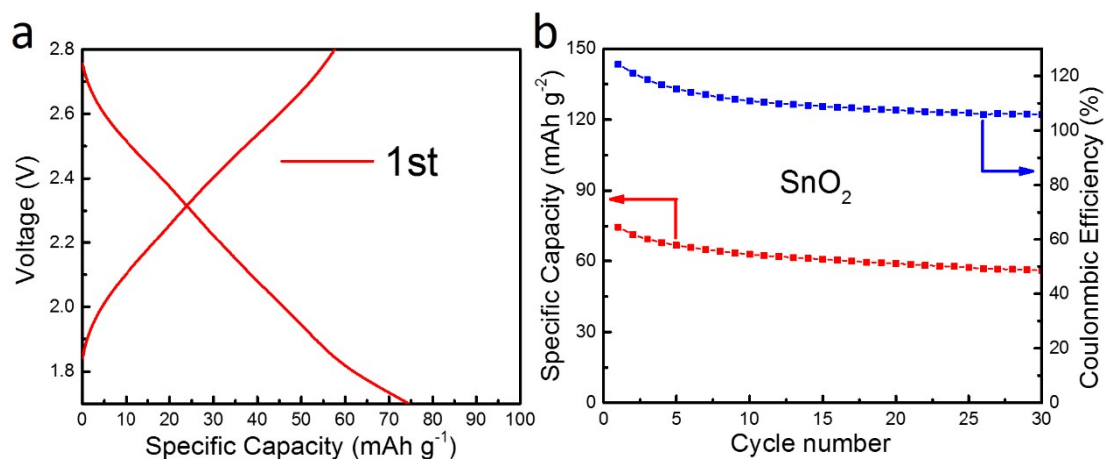


Figure S11. a) Representative charge–discharge voltage profiles at 0.2 C for SnO₂. b) Cycling at 0.2 C over 30 cycles of SnO₂. (0.2 C is based on the 1.4 mg/cm² of sulfur where 1C = 1675 mA/g).

Table 4. Electrochemical performance of Li–S cells basing on SnO₂ materials

Materials type	Rate	Initial Capacity (mAh/g)	Cycled capacity (mAh/g)	decay per cycle	Ref.
C@SnO ₂ /s	0.2 C	1228	1101 (100th)	0.1%	This work
	1C	883	754 (500th)	0.029%	
	2 C	745	564 (1000th)	0.024%	
S/SnO ₂ @C	0.12 C	1473	764 (100th)	0.48%	11
	0.24C	989	781 (100th)	0.21%	
	1.91 C	644	616 (100th)	0.043%	
S/SnO ₂	0.8 C	700	500 (100th)	0.28%	12

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