

Uniformly dispersing Sb_2Se_3 nanoparticles in porous carbon as anode material for enhancing sodium storage

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Experimental section

Chemicals

Terephthalic acid ($C_8H_6O_4$, AR) and anhydrous ethanol (C_2H_5OH , AR) were procured from Sinopharm Group Co., Ltd. Antimony trichloride ($SbCl_3$, AR), Selenium powder (Se, AR), methanol (CH_3OH , AR) and dimethylformamide (C_3H_7NO , AR) were obtained from Shanghai Aladdin Biochemical Co., Ltd. All chemicals were utilized as received without requiring any further purification procedures. Deionized water was prepared in the laboratory.

Preparation of Sb/C composite

0.8 mmol of $SbCl_3$ was added to 50 mL methanol solution, which was stirred until complete dissolution to obtain solution A. Subsequently, 0.4 mmol of terephthalic acid (TPA) was added to 50 mL deionized water, and 1 mol L^{-1} KOH was gradually added dropwise until the pH became neutral as solution B. Then solution A was added dropwise to solution B under stirring, and the solution was centrifuged after stirring for 24 h. The obtained white precipitate was washed with ethanol and deionized water before being collected. The white precipitate was transferred to a freeze dryer at $-60\text{ }^\circ\text{C}$ for 12 h to obtain the Sb/C precursor. Finally, the prepared Sb/C precursor was placed in a tube furnace under hydrogen-argon mixed atmosphere ($H_2/Ar=5/95$) and heated to $650\text{ }^\circ\text{C}$ at a heating rate of $3\text{ }^\circ\text{C min}^{-1}$ for 4 h to prepare Sb/C composite.

Preparation of Sb_2Se_3/C composite

The obtained Sb/C composite and selenium powder were placed downstream and upstream of a ceramic boat, respectively, with a mass ratio of 1:2. Under an Ar atmosphere, the system was heated to $350\text{ }^\circ\text{C}$ at a rate of $2\text{ }^\circ\text{C min}^{-1}$ for solid-phase selenization for 2 h, followed by heating to $500\text{ }^\circ\text{C}$ at the same rate for 90 minutes to obtain Sb_2Se_3/C composite.

Characterization

The phase structure of the samples was investigated using X-ray diffractometer (XRD, Smart Lab 9 KW, Cu target, scan speed $10\text{ }^\circ\text{min}^{-1}$). The morphology and internal particle

distribution of the samples were observed using scanning electron microscope (SEM, XL30) and transmission electron microscope (TEM, JEM2100F). The graphitization and defect level of the materials were analyzed using laser confocal Raman spectrometer (Edinburgh RM5, $\lambda=514$ nm). The surface chemical composition of the materials was detected using X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific Escalab-250 Xi). The content of Sb_2Se_3 and C in $\text{Sb}_2\text{Se}_3/\text{C}$ composite was determined by thermogravimetric analyzer (TGA, TA Instruments, Q50). The calculation process for the Sb_2Se_3 content is shown below.

Determine the molar masses:

Molar mass of Sb_2Se_3 :

$$M_{\text{Sb}_2\text{Se}_3} = 480.4 \text{ g/mol}$$

Molar mass of Sb_2O_4 :

$$M_{\text{Sb}_2\text{O}_4} = 307.52 \text{ g/mol}$$

Molar mass ratio of Sb_2Se_3 to Sb_2O_4 :

$$M_{\text{Sb}_2\text{Se}_3}/M_{\text{Sb}_2\text{O}_4} \approx 1.562$$

Calculate the mass fraction of Sb_2Se_3 :

Since the mass of Sb_2O_4 after the reaction is 52.4%, we can calculate the mass fraction of Sb_2Se_3 in the original sample:

$$m_{\text{Sb}_2\text{Se}_3} = m_{\text{Sb}_2\text{O}_4} \times 1.562 / (100\% - 3.5\%)$$

Substituting the value for $m_{\text{Sb}_2\text{O}_4} = 0.524$ (52.4%):

So, the mass fraction of Sb_2Se_3 in the original sample is approximately 84.8%.

Electrochemical measurements

The electrochemical performance of anode materials was conducted by assembling CR2032-type half-cells. The electrode was prepared by mixing the active material (e.g., $\text{Sb}_2\text{Se}_3\text{-C}$), carbon black (Super P), and carboxymethyl cellulose (CMC) with a mass ratio of 7:1.5:1.5, then ground in an agate mortar for 30 minutes. The obtained mixture was transferred to a stirring bottle, and an appropriate amount of deionized water was added using a pipette. The mixture was stirred for 12 h to form homogeneous slurry. Using a doctor blade, the uniform slurry was coated onto copper foil, which was pre-dried at 25 °C

for 30 minutes and further dried at 70 °C in a vacuum drying oven for 12 h. The dried copper foil was cut into circular pieces with a diameter of 12 mm, controlling the loading of the active material to be 1.0-1.2 mg per single piece. Sodium foil and glass fiber filter paper (Whatman GF/F) were used as the counter electrode and separator, respectively. The 1.0 mol L⁻¹ NaPF₆ in propylene carbonate was served as the electrolyte. The cell assembly was performed in an Ar-filled glovebox with water and oxygen concentrations both below 0.1 ppm. For comparison, Sb/C material without solid-phase selenization was directly used as the anode material, and a similar cell assembly method was employed.

The charge/discharge profiles and cycling performances were conducted from 0.01 to 3.0 V on LAND battery testing system (LAND CT2001A) within a voltage range of 0.01-3.0 V. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a Chenhua Instruments workstation (CHI760E) within a voltage window of 0.01-2.0 V. The scan rate for CV was set between 0.1-1.0 mV s⁻¹, and the frequency range for EIS was 0.1-100 kHz.

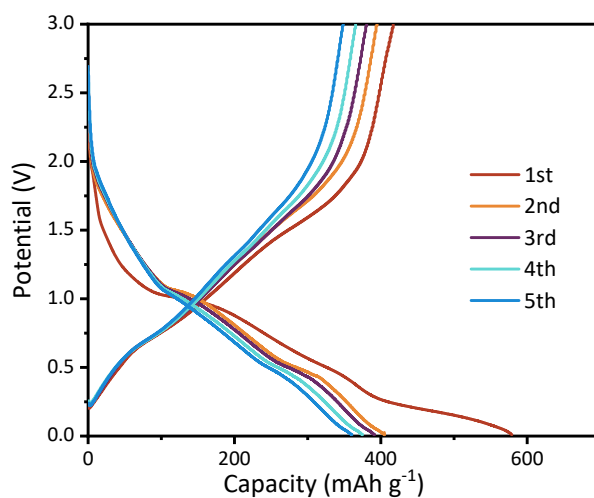


Fig. S1 Charge-discharge curves of Sb/C anode at 0.1 A g⁻¹.

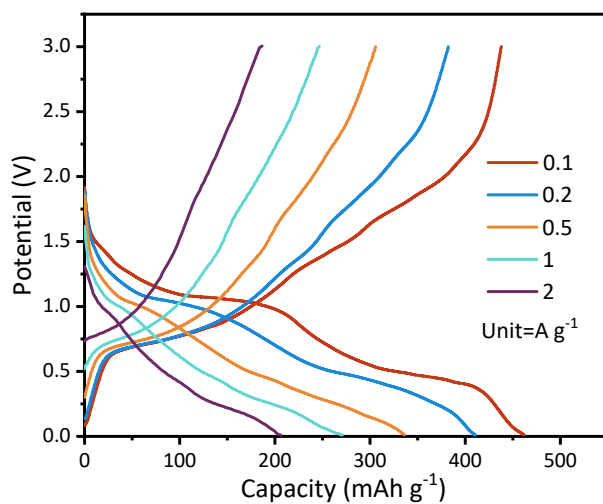


Fig. S2 Charge-discharge curves at various current densities.

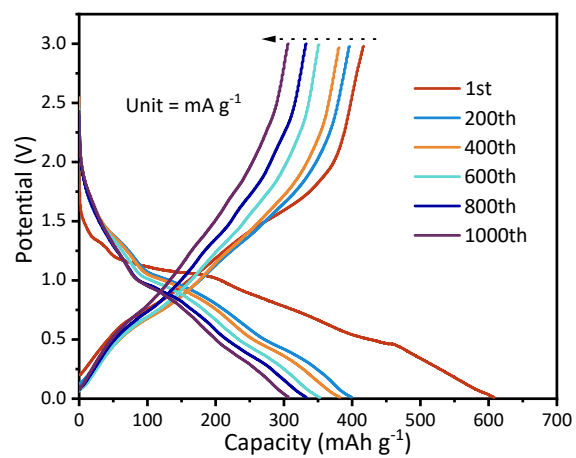


Fig. S3 Long cycle charge-discharge curves of Sb₂Se₃/C anode at 0.1 A g⁻¹.

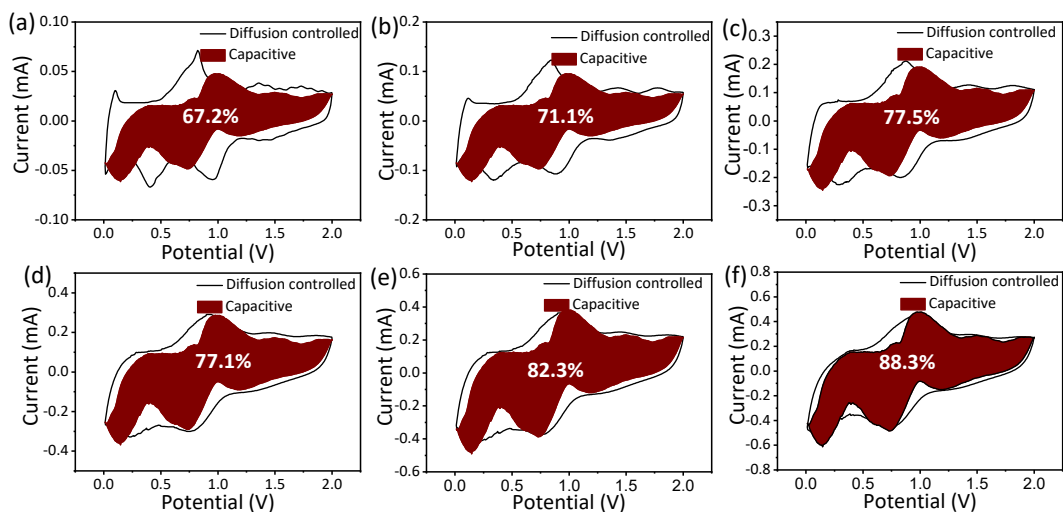


Fig S4. Contribution of the capacitive-driven process of $\text{Sb}_2\text{Se}_3/\text{C}$ anode: (a) 0.1 mV s^{-1} ; (b) 0.2 mV s^{-1} ; (c) 0.4 mV s^{-1} ; (d) 0.6 mV s^{-1} ; (e) 0.8 mV s^{-1} ; (f) 1.0 mV s^{-1} .

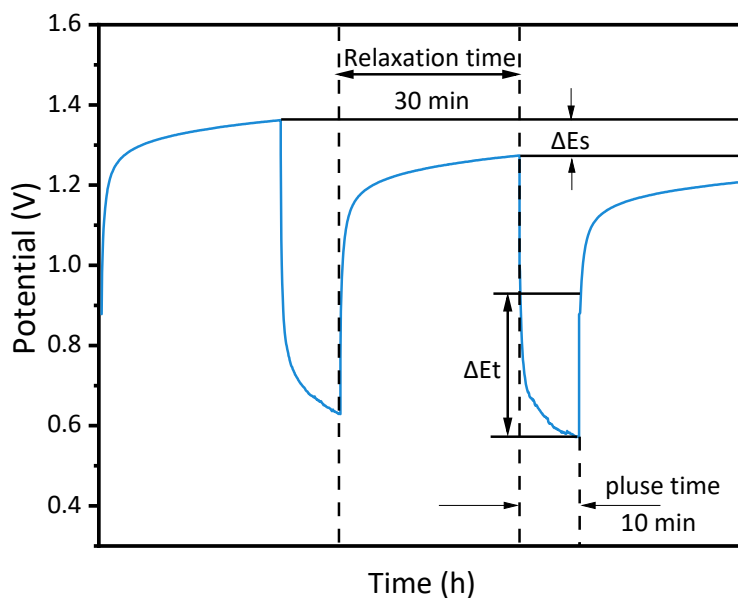


Fig S5. E vs. t curves of $\text{Sb}_2\text{Se}_3/\text{C}$ anode.

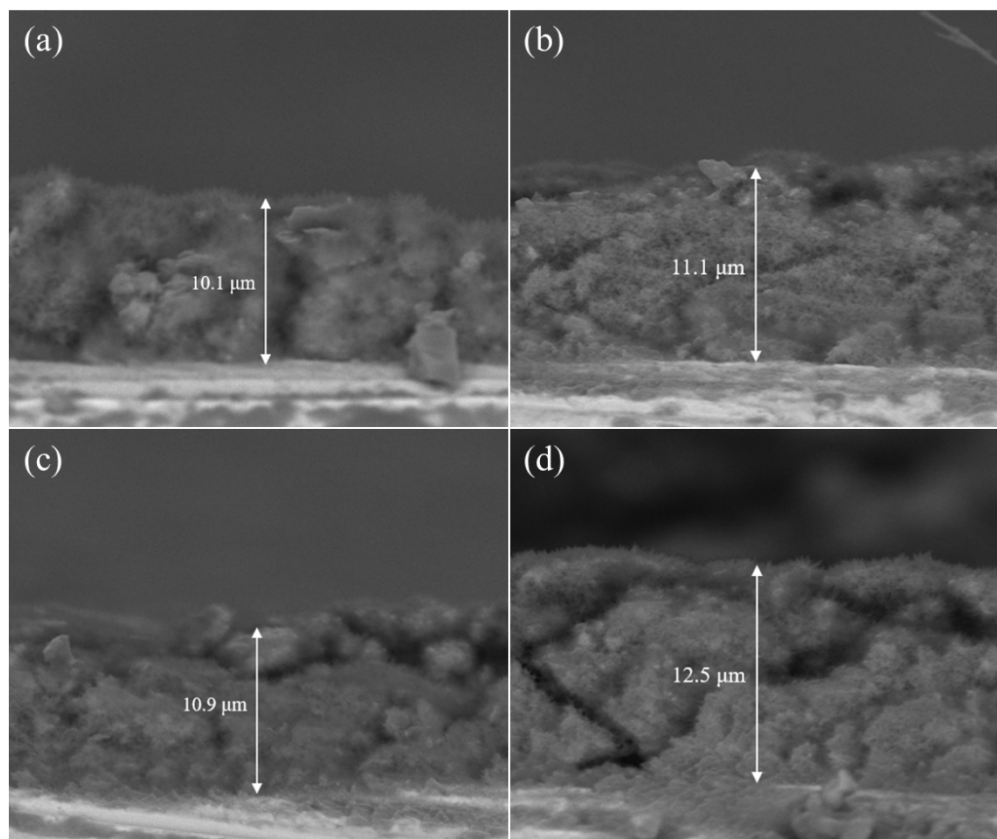


Fig S6. SEM images of cross section: (a) $\text{Sb}_2\text{Se}_3/\text{C}$ anode before cycle; (b) $\text{Sb}_2\text{Se}_3/\text{C}$ anode after 100 cycles; (c) Sb/C anode before cycle; (d) Sb/C anode after 100 cycles.

Table S1. Comparison of cycling performance and rate capability of Sb₂Se₃-based anodes.

Anode materials	Cycling performance			Rate capability		Refs
	Capacity (mA h g ⁻¹)	Current density (A g ⁻¹)	Cycle number	Capacity (mA h g ⁻¹ , 0.1 A g ⁻¹)	Capacity (mA h g ⁻¹ , 1 A g ⁻¹)	
Sn _{0.2} Sb _{1.8} Se ₃	428	0.1	100	510	307	1
CoSe ₂ /Sb ₂ Se ₃ @C@C/NF	406	0.2	200	484	369	2
CoSb ₂ Se ₄ @Sb ₂ Se ₃	231	0.1	120	415	296	3
Sb ₂ Se ₃ /Ti ₃ C ₂ Tx	304	1	100	553	504	4
Sb ₂ Se ₃ /CTP6	231	0.1	150	336	288	5
Sb ₂ Se ₃ @g-C ₃ N ₄	165.3	1	600	376	336	6
Sb ₂ Se ₃ ultralong nanowire	289	0.1	50	618		7
Sb@C@TiO ₂ TSNBs	420	0.1	150	452	354	8
CoSe ₂ /Sb ₂ Se ₃ @C	413	0.1	100	461	355	9
Sb ₂ Se ₃ @rGO@NC	288.5	0.1	100	273	181	10
Sb ₂ Se ₃ /C	334	1	100	443	306	This work
	339	0.1	1000			

References

- 1 S.-u. Islam, K. Majid, and M. Wahid, ACS Appl. Energy Mater., 2023, 6, 170–180.
- 2 Y. Li, X. Gao, L. Zhang, M. Wei, C. Jiang, Z. Li, and M. Wu, J. Alloys Compd., 2024, 999, 175014.
- 3 Y. F. Guo, X. Z. Li, Z. X. Li, P. F. Wang, J. H. Zhang, M. C. Han, and T. F. Yi, Ceram. Int., 2024, 50, 14959–14967.

- 4 J. Yang, J. Li, J. Lu, X. Sheng, Y. Liu, T. Wang, and C. Wang, *J. Colloid Interface Sci.*, 2023, 649, 234–244.
- 5 X. Z. Li, S. H. Tian, Z. C. Lv, P. F. Wang, and T. F. Yi, *Ceram. Int.*, 2023, 49, 7414–7423.
- 6 X. Z. Li, Y. F. Guo, S. Zhao, P. F. Wang, Z. L. Liu, J. Shu, J. H. Zhang, and T. F. Yi, *Surf. Interfaces*, 2024, 48, 104275.
- 7 W. Luo, A. Calas, C. Tang, F. Li, L. Zhou, and L. Mai, *ACS Appl. Mater. Interfaces*, 2016, 8, 35219–35226.
- 8 M. Kong, Y. Liu, B. Zhou, K. Yang, J. Tang, P. Zhang, and W. Zhang, *Small*, 2020, 16, 2001976.
- 9 G. Li, M. Song, X. Zhang, Y. Sun, and J. Guo, *Dalton Trans.*, 2023, 52, 4973–4979.
- 10 S. Chong, M. Ma, L. Yuan, S. Qiao, S. Dong, H. Liu, and S. Dou, *Energy Environ. Mater.*, 2023, 6, e12458