

Support information

Bifunctional Structure Modulation of Sb-Based Sulfide for Boosting Fast and Large Sodium Storage

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Experimental section

- *Preparation of CrSbS₃ and Sb₂S₃-C*

CrSbS₃ was synthesized through solid state reaction. 1 mmol Cr (99.999%, Alfa Aesar Puratronic), 1 mmol Sb (99.999%, Alfa Aesar Puratronic), 3 mmol S were mixed uniformly and loaded in pre-evacuated quartz tube. Then the tube was kept at 650 °C for 12 h and cooled down to room temperature to obtain the rod like sample. Sb₂S₃-C was synthesized through high-energy ball milling of Sb₂S₃ (99.999%, Alfa Aesar Puratronic) and graphene (weight ratio: 7:3).

- *Material Characterization*

X-ray diffraction patterns of CrSbS₃ samples were collected on a Bruker D8 Advance diffractometer equipped with mirror-monochromatic Cu K α radiation ($\lambda = 0.15406$ nm). The XRD patterns were collected at a scan rate of 2° min⁻¹ with 2θ from 5° to 80°. Simulated patterns were calculated through the mercury program and CIF file downloaded from the ICSD. The *in-situ* XRD measurement was conducted on a live discharge/charge process in a cell purchased from Beijing Scistar Technology Co. Ltd. The morphology was investigated by a JEOL (JSM6510) scanning electron microscope equipped with energy dispersive X-ray spectroscopy (EDXS, Oxford Instruments) and aberration-corrected field transmission electron microscopy (FEI Tecnai F20, USA). Temperature dependent conductivity was obtained from standard four-probe technique with the resistivity model and collected on physical properties measurement system (PPMS, Quantum Design). For the electric property tests, powders of CrSbS₃ were

pressed into square disc, and silver paste was used as the contact electrode. Raman spectroscopy was conducted on a Jobin-Yvon LabRAM HR-800 spectrometer with a laser excitation at 532 nm. The surface chemistry was probed by X-ray photoelectron spectrometer (XPS, Thermo Scientific, ESCALAB 250, USA).

- *Electrochemical Characterization*

The electrodes were prepared through mixing the active materials powder (70 wt%), Super P (20 wt%) and Carboxymethylcellulose sodium (CMC-Na) binder (10 wt%) homogeneously in deionized water to get a slurry. Then the slurry was coated evenly on a copper foil using a blade with mass loading of $\approx 0.7\text{--}1.2\text{ mg cm}^{-2}$. The electrode was then dried at 80 °C for 8 h before final assembling. The half cells were assembled in coin-type cells (MTI corporation-CR2032) within an Ar filled glove box. A piece of sodium was employed as counter electrode. The electrolyte is composed of 1 M NaPF₆ in Diglyme solution. Glass fiber is used as a separator. For the full battery, cathode was developed by mixing Na_{0.44}MnO₂(80 wt%), Super P (10 wt%) and polyvinylidene fluoride (PVDF) binder (10 wt%) homogeneously in N-methyl pyrrolidinone (NMP) solvent to get a slurry. Then the slurry was coated evenly on an aluminum foil. The anode was made through the same process for half-cell. The N:P ratio of full cell and the area of the electrodes were 1.05: 1 and 1.1 cm². A Land CT2001A tester (Wuhan, China) was applied to get the galvanostatic cycling performance of the assembled cells with a cutoff voltage between 2.5 V and 0.01 V at room temperature. A CHI1760e electrochemical workstation was applied for the cyclic voltammetry tests with a potential range between 2.5 V and 0.01 V at different scan rates.

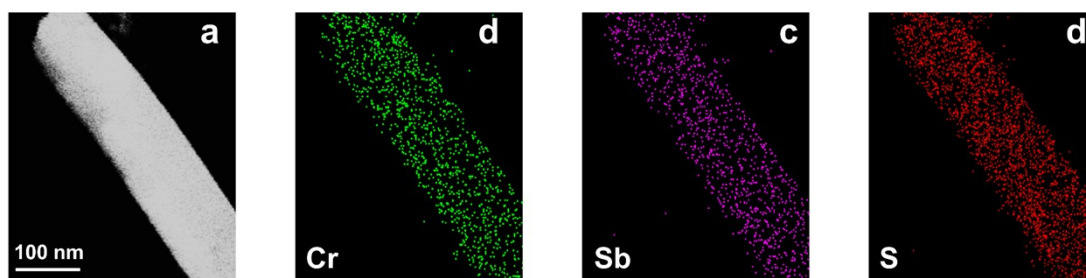


Figure S1. a) HAADF-STEM image of CrSbS_3 and b-d) EDX mapping of Cr, Sb and S elements

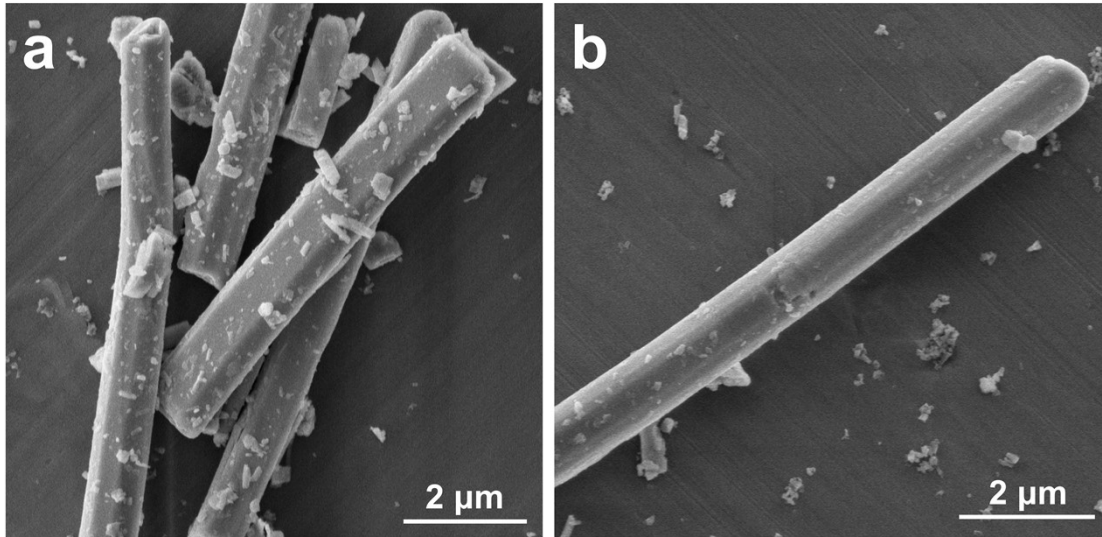


Figure S2. SEM images of CrSbS₃.

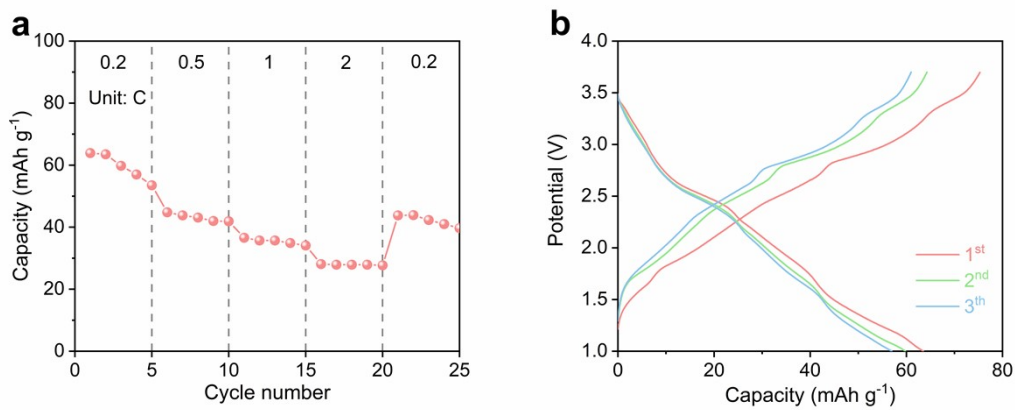


Figure S3. Electrochemical performances of CrSbS₃//Na_{0.44}MnO₂ full cells. (a) rate capability at various current densities. (b) galvanostatic discharge/charge curves of the initial three cycles.

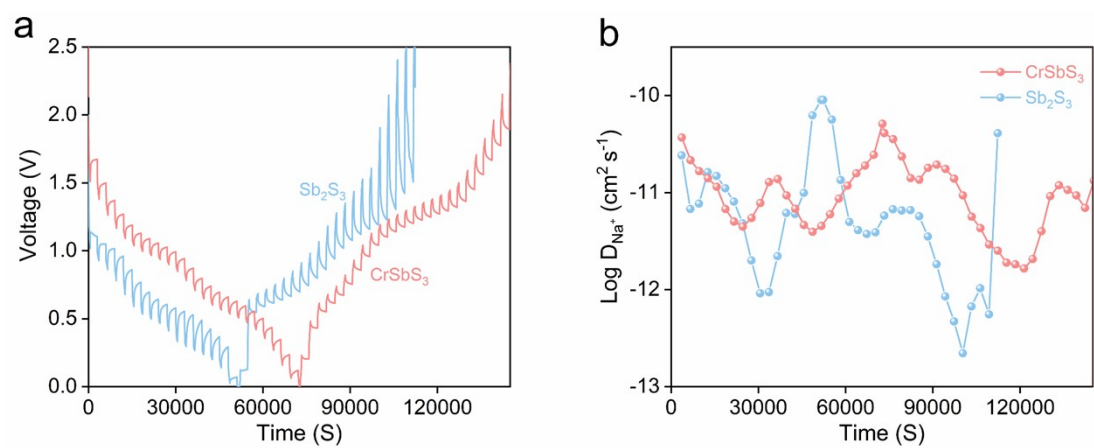


Figure S4. (a) GITT potential profiles in the second cycle. (b) Diffusion coefficients of Na⁺ calculated from the GITT tests for CrSbS₃ and Sb₂S₃.

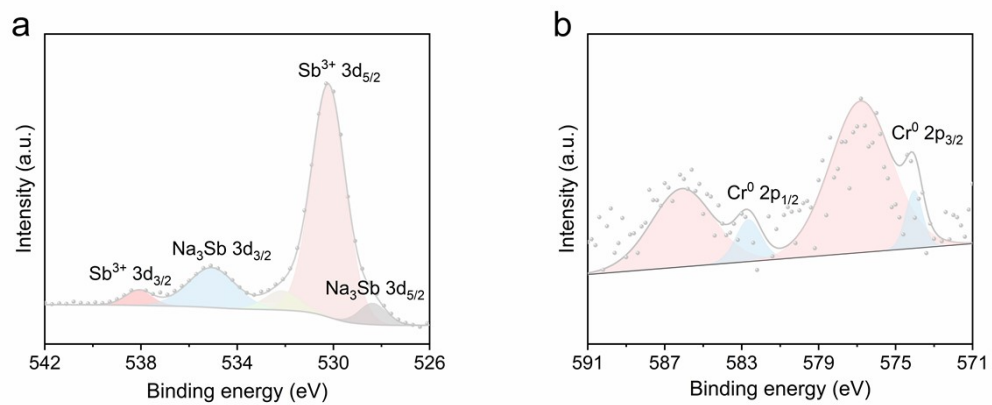


Figure S5. High-resolution XPS spectra of (a) Sb 3d and (b) Cr 2p after discharging into 0.01 V

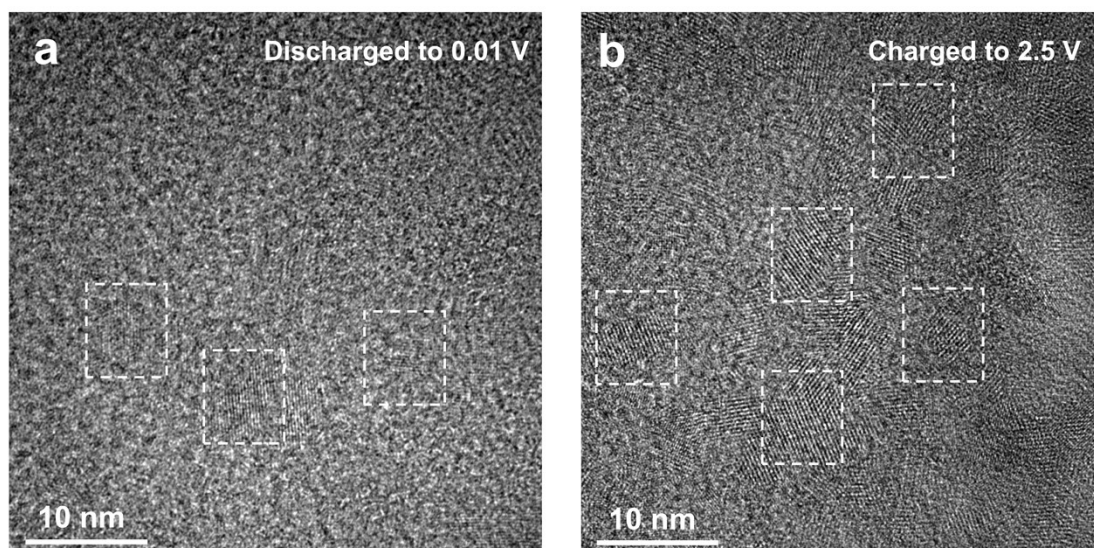


Figure S6. Ex situ HRTEM images of CrSbS₃ (a) after discharge at 0.01 V and (b) recharge at 2.5 V.