

Supplementary Information

Amorphous Sb₂S₃ Embedded in Graphite: A High-rate, Long-life Anode Material for Sodium-ion Batteries

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Experimental Section

Material preparation: Micrometer-sized Sb₂S₃-wire was prepared by a hydrothermal reaction.

In a typical synthesis, 0.28 mmol of SbCl₃ was dissolved in 1.1 mL of HCl (37 wt. %), followed by the addition of 17 mmol citric acid into the beaker. 40 mL of H₂O (18 MΩ·cm at 25 °C) was slowly poured into the beaker under magnetic stirring, forming a transparent colorless solution. Then, 11 mmol of thioacetamine was added into the solution and the color gradually changed to orange. The solution was transferred into a 100 mL Teflon-lined autoclave and heated at 200 °C for 24 h in an oven. After the hydrothermal reaction, the sample was collected, washed with water, and dried in a vacuum oven. Sb₂S₃-Graphite was prepared by high energy mechanical milling (HEMM). 1.6 g of the as-prepared Sb₂S₃ micrometer-sized wire and 0.4 g of natural graphite flake (200 mesh) was mixed in a hardened steel chamber with steel balls in an argon-filled glovebox. The chamber was then mounted in a Fritsch Pulverisette 6 planetary mill and rotated for 48 h at 500 rpm. The Sb₂S₃ wire (crystalline)-Graphite sample was prepared by manual grinding of 1.6 g micrometer-sized Sb₂S₃-wire and 0.4 g graphite in a mortar and pestle.

Electrochemical characterization: The slurry for electrode casing was prepared by mixing 280 mg of Sb₂S₃-Graphite, 80 mg of Super P conductive carbon black, 40 mg of sodium carboxymethyl cellulose (M_w ~70,000) and 3.1 mL of H₂O in a glass vial. The slurry was magnetically stirred overnight and then casted onto a copper foil by the doctor blade method. The film was dried, roll-pressed, and cut into electrodes. The mass of the active materials

(Sb₂S₃-Graphite) is *ca.* 1.5 mg per electrode. The electrochemical performance of the electrodes was assessed within CR2032 coin cells with glass fiber as the separator and sodium metal as the counter/reference electrode. The coin cells were assembled in an Argon-filled glovebox (O₂ and H₂O level: 0.1 ppm). The electrolyte was composed of 1 M NaClO₄ in ethylene carbonate (EC)/propylene carbonate (PC) (1: 1 v/v) containing 5 (wt.) % fluoroethylene carbonate (FEC) as additive. Charge/discharge performance was assessed with an Arbin battery cycler under galvanostatic condition in the voltage window of 0.01 - 2.8 V (*vs.* Na⁺/Na).

Characterization: SEM-EDS analysis was carried out with a Hitachi S5500 SEM. TEM images were obtained with a JEOL 2010F transmission electron microscope. X-ray diffraction (XRD) data were collected with a Rigaku Mini-Flex X-ray diffractometer with Cu K α radiation. Cyclic voltammetry scan was conducted with a VoltaLab PGZ402 potentiostat at a scan rate of 0.05 mV s⁻¹ at the voltage window of 0.01 and 2.8 V. XPS was conducted on a Kratos X-ray Photoelectron Spectrometer – Axis Ultra DLD.

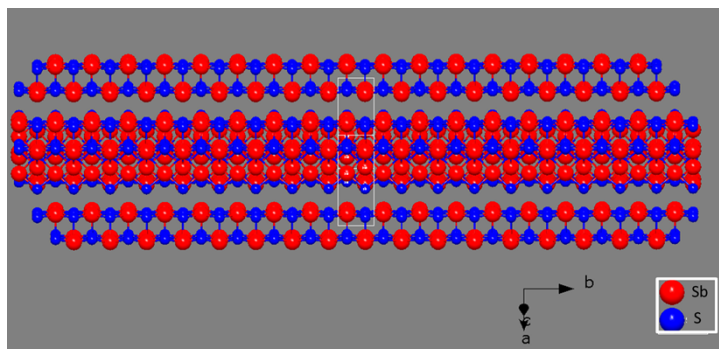


Figure S1. Scheme of the atomic arrangement of the Sb_2S_3 crystals showing the layered structure.

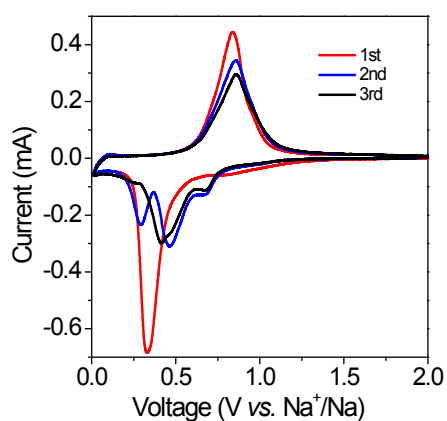


Figure S2. Cyclic voltammetry (CV) scan of Sb/C electrode with sodium as the counter electrode/reference electrode at a scan rate of 0.05 mV s^{-1} . The Sb/C sample is the mechanical mixture of Sb metal powder and acetylene black.

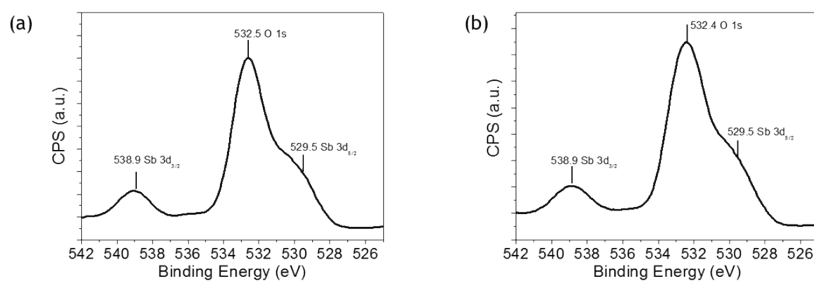


Figure S3. XPS characterization of the Sb_2S_3 -Graphite electrode (a) before and after (b) discharge/charge cycle.

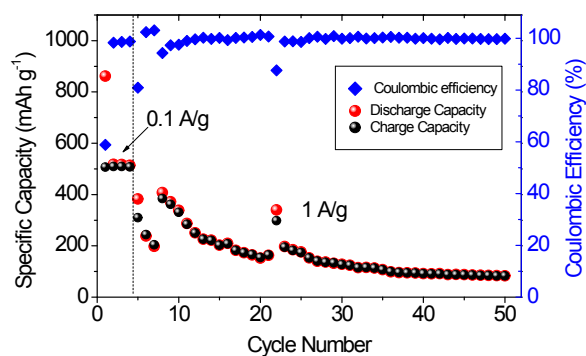


Figure S4. Cycle performance of the Sb_2S_3 -wire-Graphite electrode at galvanostatic condition with a current density of 1 A g^{-1} in sodium-ion battery.

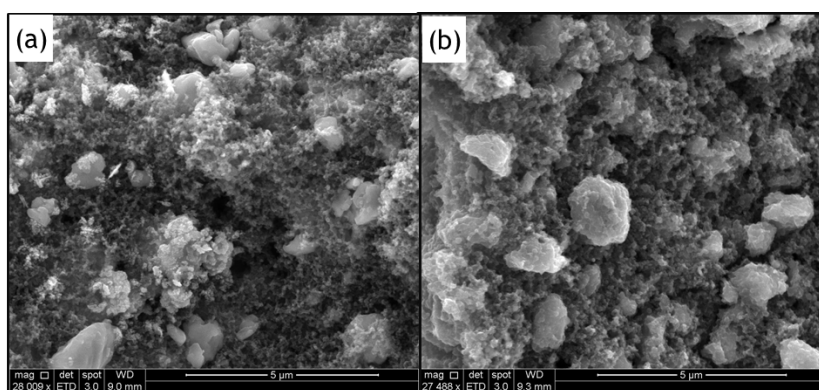


Figure S5. SEM images of the Sb_2S_3 -Graphite electrode: (a) pristine electrode surface and (b) electrode after 100 cycles at a current density of 1 A/g .

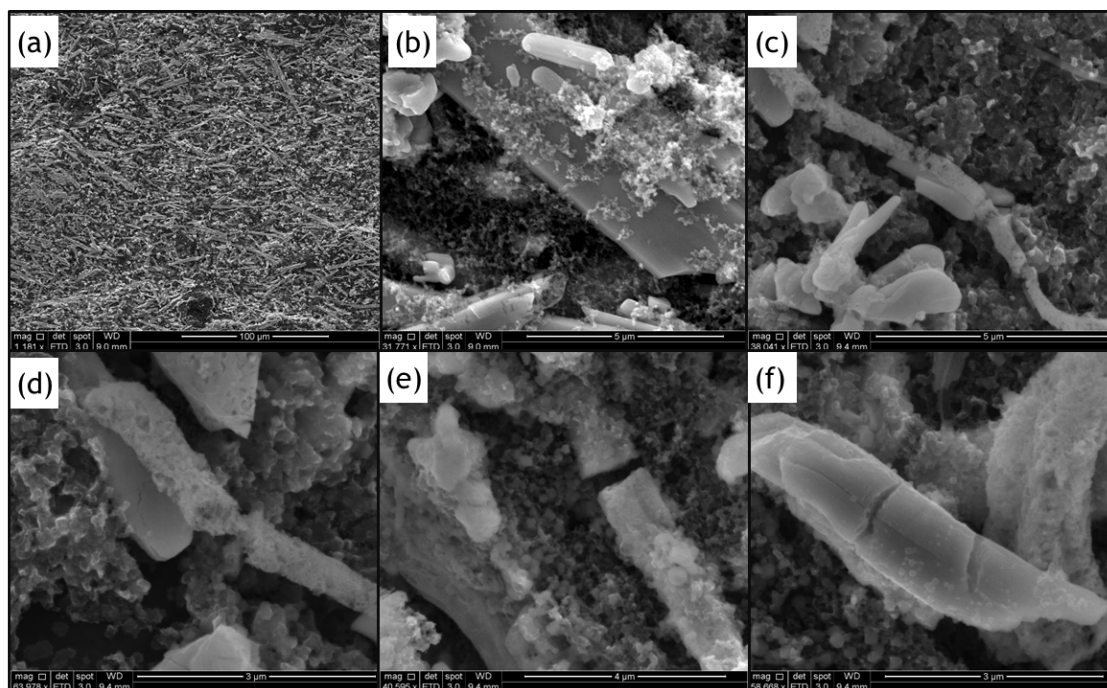


Figure S6. SEM images of the Sb_2S_3 wire-Graphite electrode: (a and b) pristine electrode surface and (c-f) electrode after 50 cycles at a current density of 1 A/g .

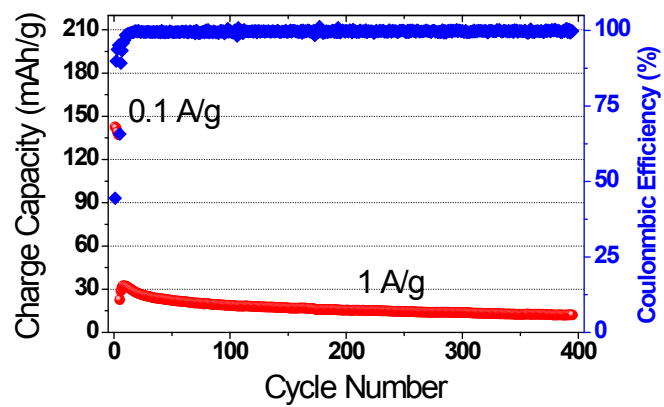


Figure S7. Charge capacity and coulombic efficiency of the graphite electrode in NIB.