Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Anchoring Atomic Antimony in an Intercalative Mo–S Framework via Soft Covalent Bonding for Fast-charging and Longevous Sodium Ion Battery

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Experimental section

Synthesis of Mo_2SbS_2: Mo_2SbS_2 was synthesized through typical solid state reaction. 2 mmol Mo (99.999%, Alfa Aesar Puratronic), 1 mmol Sb (99.999%, Alfa Aesar Puratronic) and 2 mmol S (99.999%, Alfa Aesar Puratronic) were grinded and mixed uniformly and put into a pre-evacuated quartz tube. Then the quartz tube was sealed by hydrogen flame and putted into a muffle furnace with temperature of 1173 K for 12 hours. After cooling down to room temperature naturally, the micro sphere Mo_2SbS_2 sample stacked by nano rods was obtained. The as obtained sample was directly used to fabricate electrode slurry.

Synthesis of $NaNi_{0.5}Mn_{0.5}O_2$: Stoichiometric amounts of Na_2CO_3, NiO, and Mn_2O_3 were ball milled for 2 h and pressed into pellet. Then the pellet was annealed at 1173 K in a muffle furnace for 24 h. After cooling to room temperature, the black $NaNi_{0.5}Mn_{0.5}O_2$ powder was obtained.

Material characterization: X-ray diffraction patterns of Mo_2SbS_2 samples were obtained on a Bruker D8 Advance diffractometer equipped with mirror-monochromatic Cu Kα radiation (λ = 0.15406 nm) at a scan rate of 12˚ min^{-1} with 2θ from 5˚ to 80˚. The *in-situ* XRD spectra were obtained on a live discharge/charge process in a cell purchased from Bejing Scistar Technology *Co. Ltd.* The morphology of Mo_2SbS_2 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). Raman spectra was

obtained from a Jobin-Yvon LabRAM HR-800 spectrometer with a laser excitation at 532 nm. Electrical conductivity test was conducted on a physical properties measurement system (PPMS, Quantum Design). The High resolution XPS spectra were obtained from an X-ray photoelectron spectrometer (XPS, Thermo Scientific, ESCALAB 250, USA).

Electrochemical characterization: The composite electrodes were fabricated from the active materials Mo_2SbS_2 powder (80 wt%), super P (10 wt%) and sodium alginate (SA) binder, and deionized water was utilized as solvent to get a slurry. Then the slurry was coated evenly on a copper foil using a blade with mass loading of ~1.5 mg cm^{-2}. The electrode was then dried at a vacuum oven at 80 °C for 8 h. The half cells were assembled in coin-type cells (MTI corporation-CR2032) within an Ar gas filled glove box. A piece of sodium was utilized as counter electrode. For the full battery, cathode was prepared by mixing $NaNi_{0.5}Mn_{0.5}O_2$ (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 on an aluminum foil. The anode was made through the same process for half-cell. The N : P ratio of full cell is 1.1 : 1. The electrolyte is composed of 1 M $NaPF_6$ in DME solution. Glass fiber is utilized as a separator.

A CHI1760e electrochemical workstation was used for the cyclic voltammetry (CV) tests with a potential range between 3 V and 0.01 V at different scan rates. A Land CT2001A tester (Wuhan, China) was applied to get the galvanostatic cycling performance and the GITT voltage profile of the assembled cells with a cutoff voltage

between 3 V and 0.01 V at room temperature. Electrochemical impedance spectroscopy (EIS) was also tested with a CHI1760e electrochemical workstation at the frequency of 0.1 to 10000 Hz.

Theoretical capacity calculation: The electrode reactions in Mo_2SbS_2 anode based on our results are summarized as following:

$$Mo_2SbS_2 + 5Na^+ + 5e^- \rightarrow (Na_3Sb)Na_2Mo_2S_2$$

The theoretical capacity (C_t = 355mA h g^{-1}) is calculated according to equation:

$$C_t = nF/3.6M_r \quad (1)$$

where, n is the number of transferred electrons, F is Faraday constant (96485 C mol^{-1}), M_r is the molar mass of Mo_2SbS_2 (378 g mol^{-1}).

Density functional theory (DFT) calculation details: The Vienna initio simulation package (VASP) code with the projector augmented wave (PAW) method were used to perform our DFT calculation. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used in our calculations. The kinetic energy cutoff is set to be 300 eV for the expanding the wave functions into a plane-wave basis. For the structure optimizations, 5×10×4 k-points were used for the conventional cell. The internal atomic positions were relaxed until the force is less than 0.01 eV/Å. The energy convergence criterion was 10^{-5} eV. For the band structure calculation, high-symmetry points in the Brillouin zone (G, Z, D, B, G, A, E, Z, C, Y and G corresponding to (0, 0, 0), (0, 0.5, 0), (0, 0.5, 0.5), (0, 0, 0.5), (0, 0, 0), (-0.5, 0, 0.5), (-0.5, 0.5, 0.5), (0, 0.5, 0), (-0.5, 0.5, 0), (-0.5, 0, 0) and (0, 0, 0) points) were utilized.

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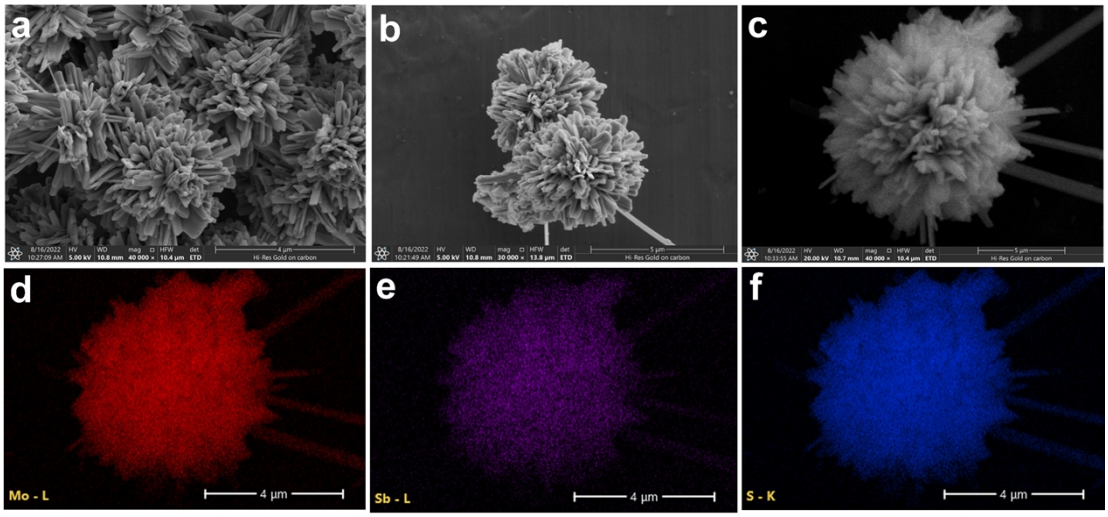

Figure S1. a, b) SEM images of Mo_2SbS_2 micro sphere; c-f) element mapping images of Mo, Sb and S.

Table R1. Relative intensities of the top five XRD peaks of Mo_2SbS_2.

	Observed	Standard
(001)	62	79
(100)	100	100
(012)	71	89
(20-3)	70	68
(112)	97	82

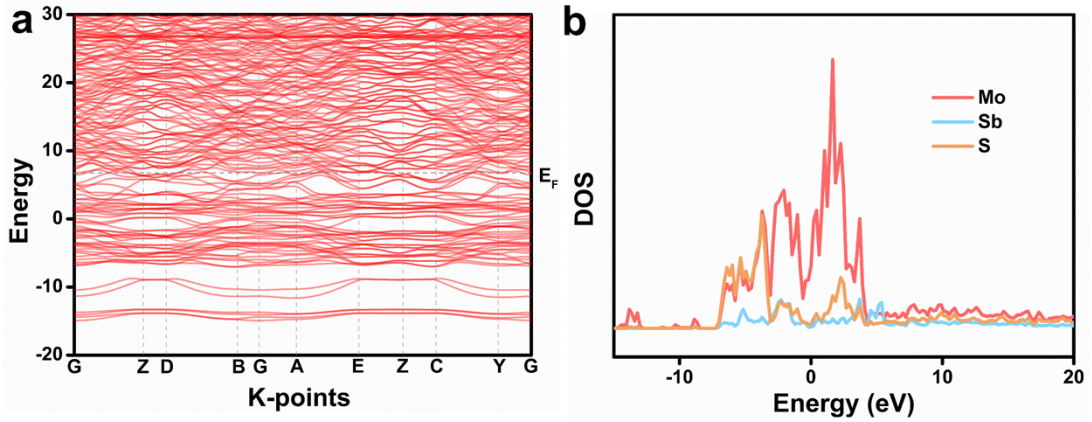

Figure S2. a) Band structure of Mo_2SbS_2; b) PDOS of Mo, Sb and S.

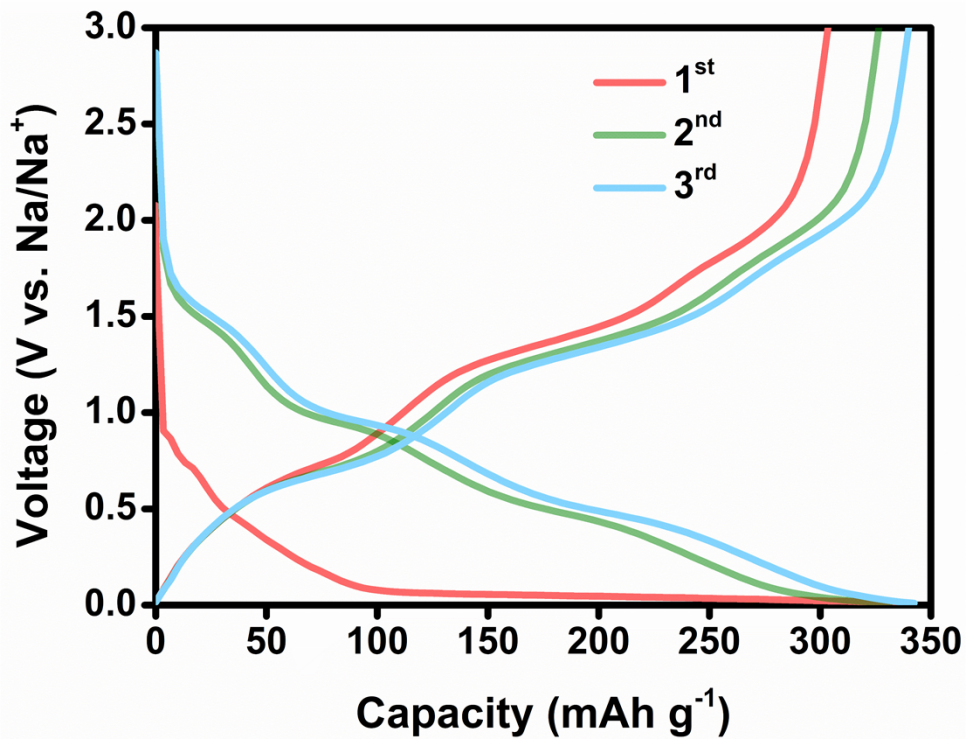

Figure S3. GCD profiles of Mo_2SbS_2 anode at initial 3 cycles.

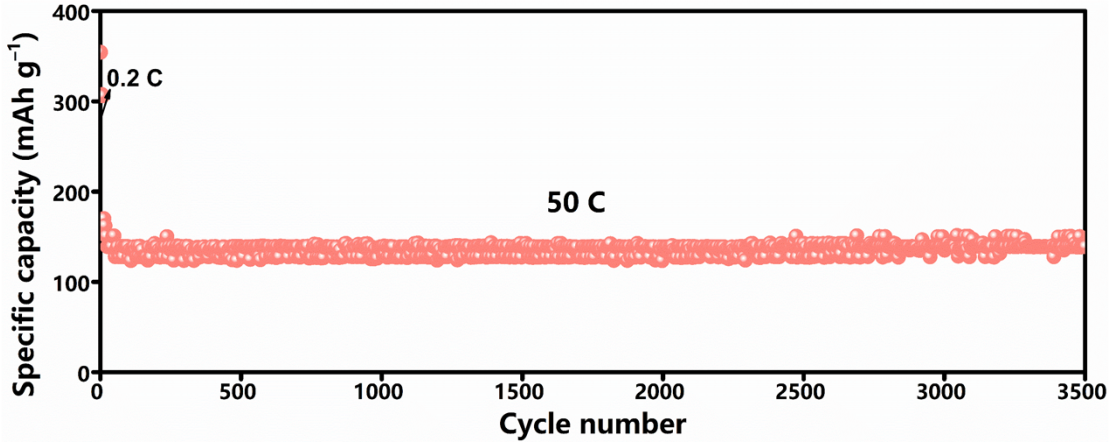

Figure S4. Cycling performance of Mo_2SbS_2 anode at current density of 50 C.

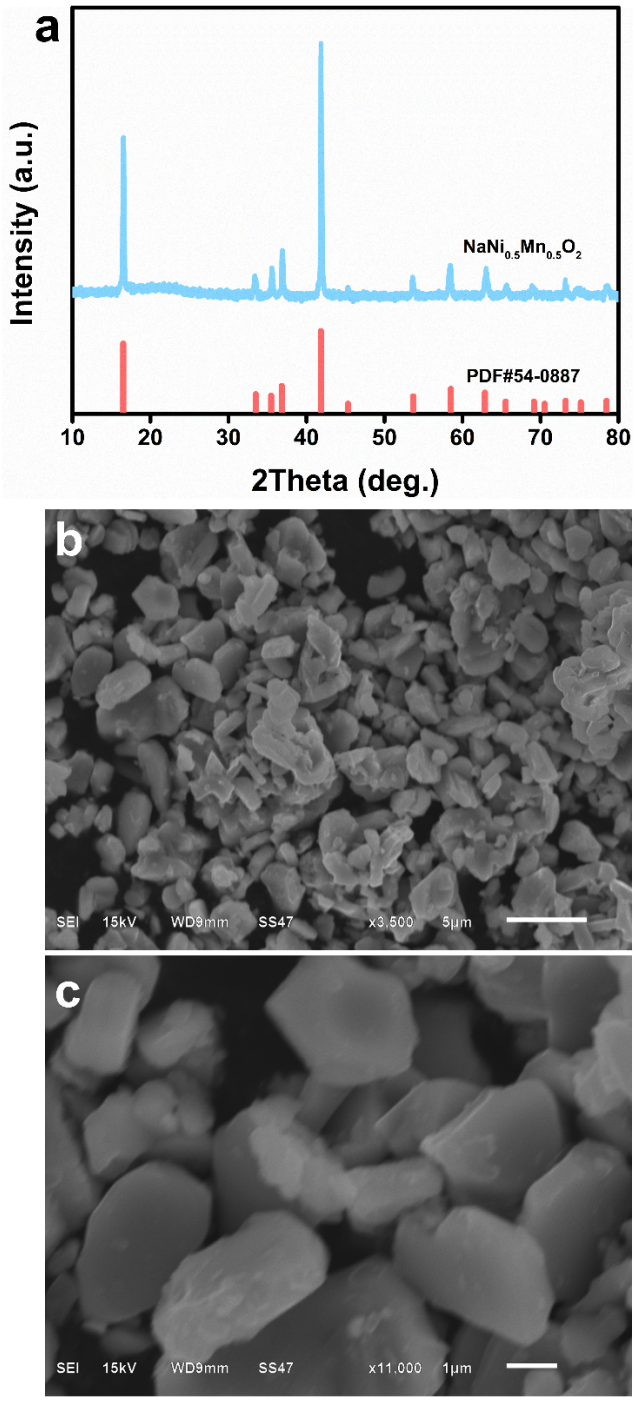

Figure S5. a) XRD pattern of $NaNi_{0.5}Mn_{0.5}O_2$; b-c) SEM images of $NaNi_{0.5}Mn_{0.5}O_2$ at different resolution.