Electronic Supplementary Material (ESI) for Nanoscale.

Cobalt-Doped SnS_2 Nanosheets towards High-Performance Anode for Sodium Ion Batteries

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Experiment

Prepare of Co-doping SnS_2/CC

All the chemical reagents were purchased directly and used without purification, carbon cloth was purchased from Tsukuba Materials Information Laboratory. Co-doping SnS_2/CC sample was prepared by one-step hydrothermal method according to our previous report [1].Typically, a piece of CC was oxidized by H_2O_2 at 45 °C for 12 h and ultrasonic washed by acetone and ethanol for 2 h, then dried and slowly put it into Teflon-lined autoclave along the wall. 1 mmol $SnCl_4$•$5H_2O$ (0.3506 g), 2 mmol thioacetamide (TAA 0.1503 g) and a certain amount of $CoCl_2$•$6H_2O$ were dissolved into 10 ml isopropanol and continuously stirred for 30 min, then transfer to above autoclave and sealed and maintained 160 °C for 16 h. After the reactor cool naturally to room temperature, the CC was took out and gently cleaned by deionized water and absolute ethanol for several times. After dried in 80 °C oven for overnight, then cut into small rounds with diameter of 10 mm. The weight of active material on every small round is calculated to be 1-1.5 mg.

According to the mass ratio of Co to SnS_2 ((xg/0.1827g)*100% = 0, 1%, 2%, 3%, 4%, 5% and 6%) the corresponding samples are referred to as SnS_2/CC, 1Co-SnS_2/CC, 2Co-SnS_2/CC, 3Co-SnS_2/CC, 4Co-SnS_2/CC, 5Co-SnS_2/CC and 6Co-SnS_2/CC, respectively. The contrastive specific capacities of Co doping with different concentrations of SnS_2/CC samples are measured at a current density of 0.2 A g^{-1} with the voltage of 0.01-2.5 V and shown in Fig. S7.

Co-doping SnS_2 nanoflower was prepared via same synthetic method without CC support.

Prepare of CoS_2 particles

2 mmol $Co(CH_3COO)_2$•$4H_2O$ (0.498 g) was dissloved into 35 ml deionized water and stirred for 10 min. Then added 0.5 mL ethylenediamine and continue to stir for 20 min, when the colour of solvent from red to grayish green and added 0.8 mL CS_2. After stirred for 30 min, the solvent transfer to 50 mL Teflon-autoclave and reaction at 180 ^oC for 12 h. Finally, the autoclave naturally cool to room temperature and washed by deionized water and absolute ethyl alcohol for several times and then dried to obstain CoS_2 particles.

Structural characterization

X-ray diffraction (XRD) measurements were performed to characterize the crystal phase and crystallinity of the composite on PANalytical X-pert diffractometer (Netherlands) with standard Cu-Kα radiation (λ=0.15418 nm), the scanning range from 20^o to 80^o with per step of 0.02^o. The morphology of samples were investigated by Field Emission Scanning Electron Microscopy (FE-SEM) on Hitachi S-4800

analyzer with energy-dispersive X-ray spectroscopy (EDS, EDAX, PW9900) instrument. And the microstructures were observed by High Resolution Transmission Electron Microscopy (HRTEM, JSM-2100F) using 200 kV operating voltage. The valence states of elements were studied by X-ray photoelectron spectroscopy (XPS) employing PHI Quanteral II analyzer with Al Kα source (1486.6 eV).

Electrochemical Measurements

The 2025 coin cells were assembled in the high purity argon-filled glove box with the concentrations of O_2 and H_2O were limited below 0.1 ppm. 1 M $NaClO_4$ dissolved in dimethyl carbonate (DMC) and ethylene carbonate (EC) with volume ratio of 1:1 as electrolyte, and the glass fiber was used as the separator. The as-prepared Co-doping SnS_2/CC was directly as the working electrode without any binder or conductive agent, and metallic Na be used as counter electrode. The mass density of active material anchored on CC was 1.27-1.91 mg•cm^{-2}. Besides, the contrast electrodes of Co-doping SnS_2 nanoflower and CoS_2 nanoparticle were prepared by coating slurry. For working eletrode was consisted of active material, super P and polyvinylidene fluoride (PVDF) in N-Methyl-2-pyrrolidone (NMP) with the mass ratio of 7:2:1. Cyclic voltammetry (CV) curves were tested by Electrochemical Workstation (CHI 660E, Chen-hua) with voltage ranging from 0.01 to 2.5 V and the scan speed was 0.1-1 mV s^{-1}. Galvanostatic charge/discharge measurements, rate tests and long-term cycling performances were measured count on a Land battery system (LAND CT2001A). Electrochemical impedance spectroscopy (EIS) was carried out by potentiostat at a frequency range of 10^{-2}-10^5 Hz with applicable AC voltage

amplitude of 5 mV.

Results and discussion

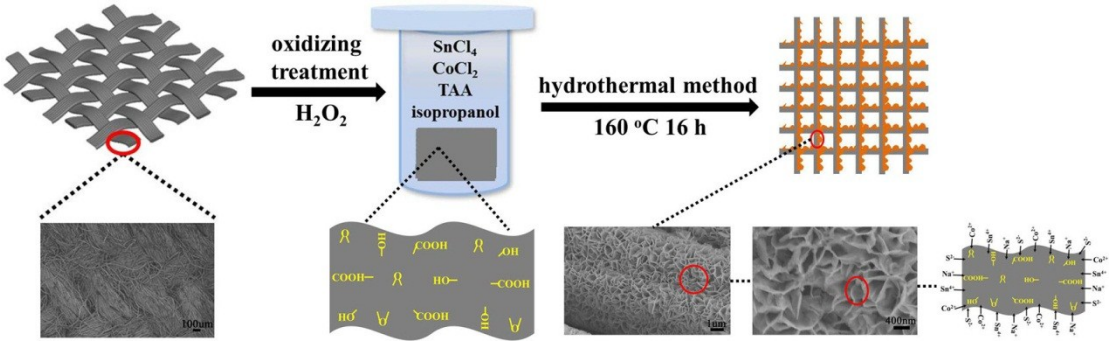

Fig. S1 The typical synthesis principles of Co-SnS_2/CC anode material.

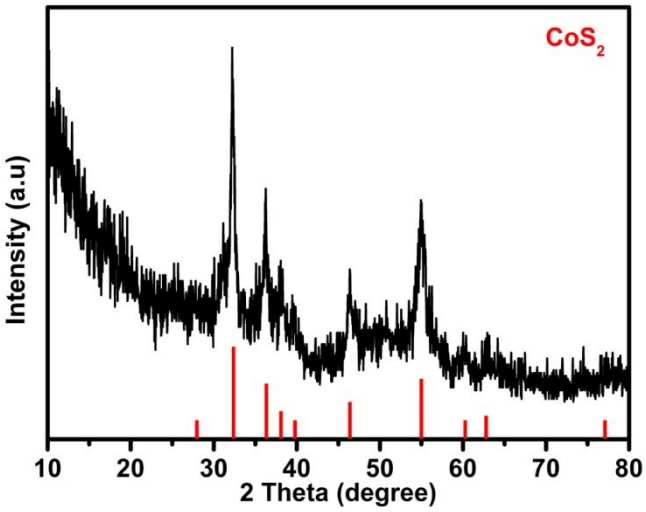

Fig. S2 XRD pattern of as-obtained CoS_2.

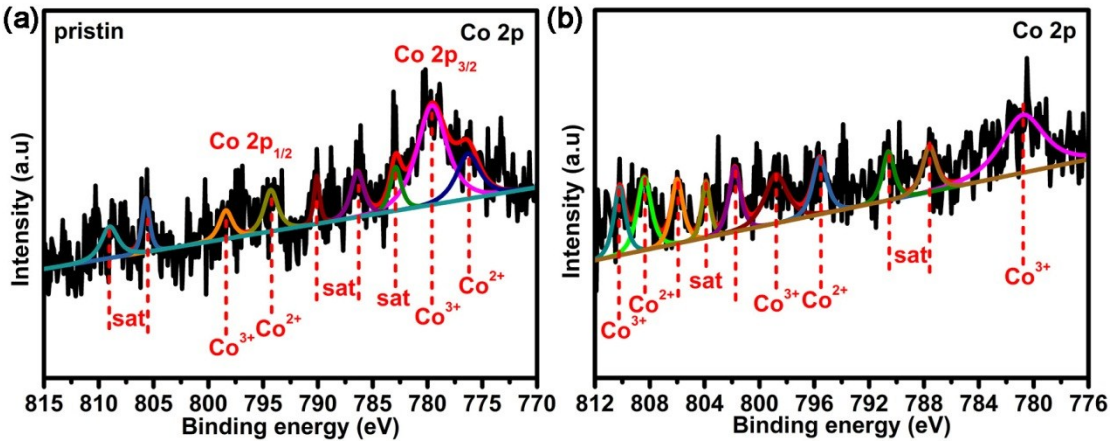

Fig. S3 XPS spectra of the Co 2p in Co-SnS_2/CC sample (a) pristin and (b) after 100 cycles at charge state.

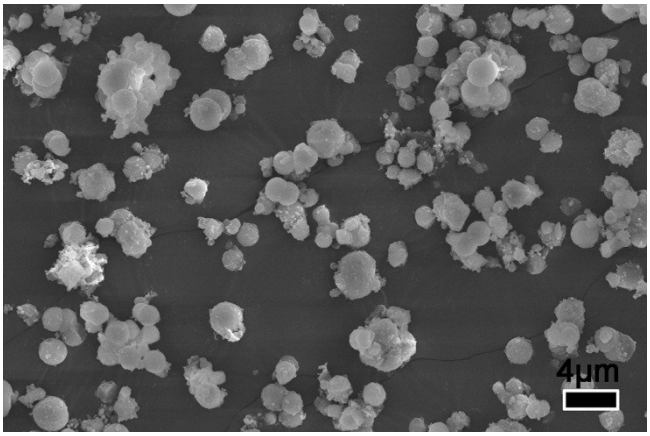

Fig. S4 SEM image of as-obtained CoS_2 nanoparticles.

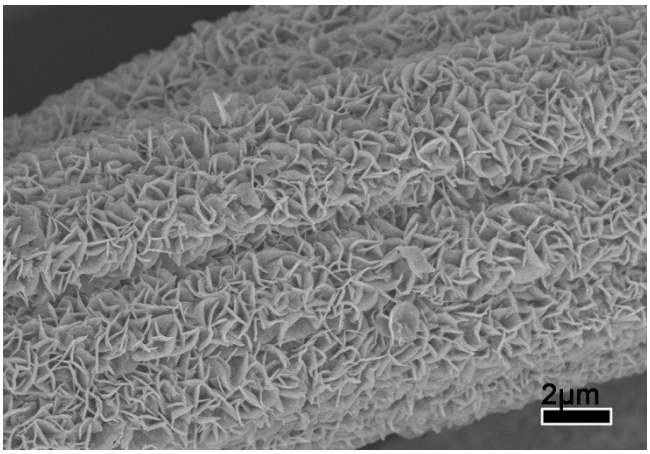

Fig. S5 SEM image of as-obtained SnS_2/CC sample.

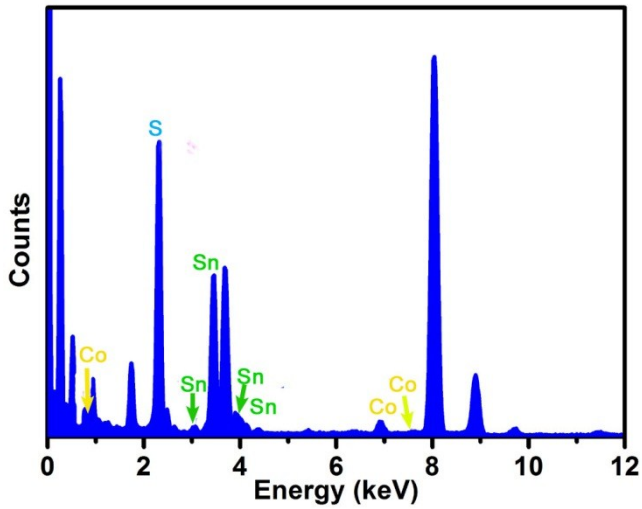

Fig. S6 Energy disperse spectroscopy (EDS) of Co-SnS_2 sample.

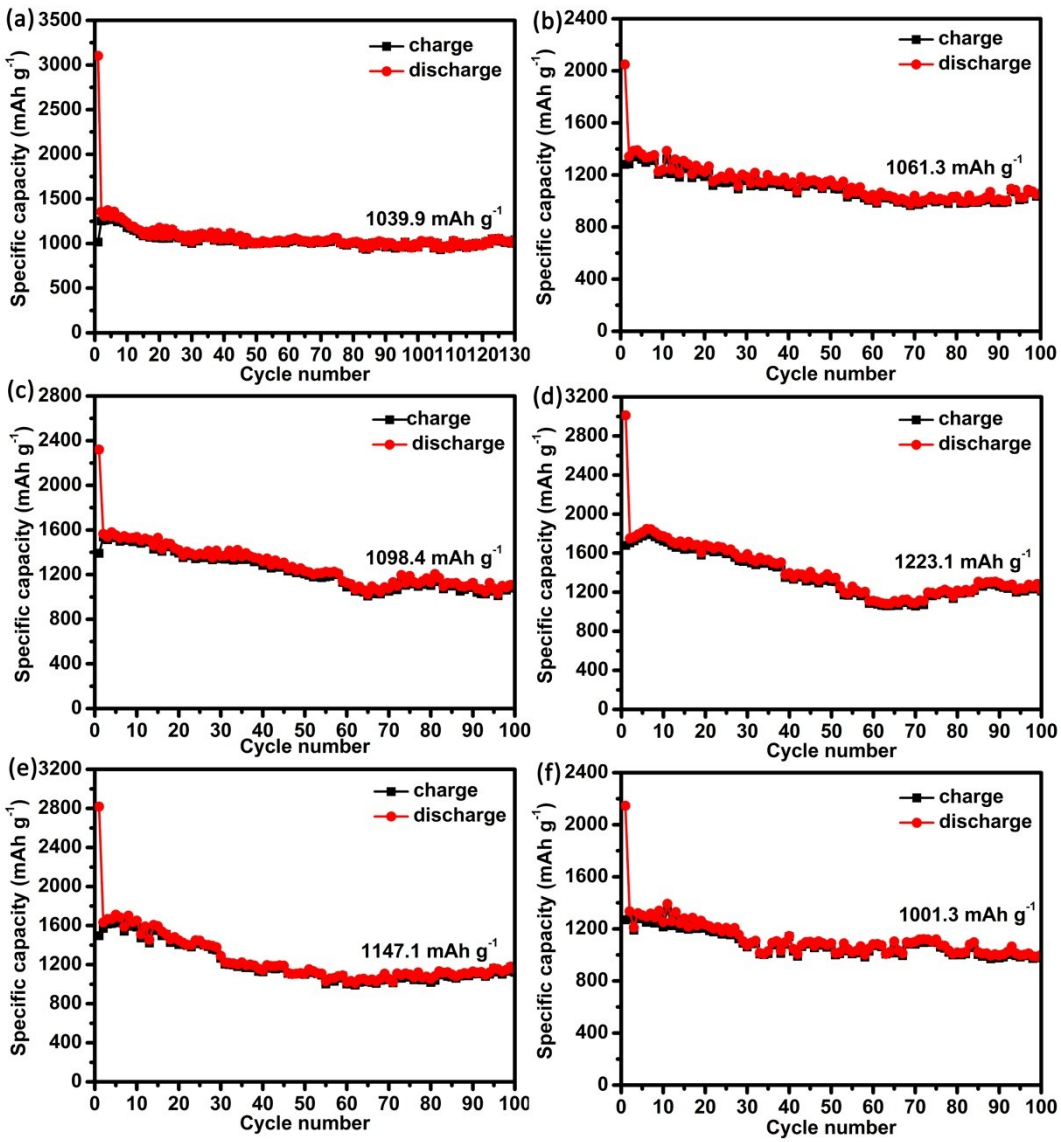

Fig. S7 The contrastive specific capacities of (a) SnS_2/CC[1], (b) 1Co-SnS_2/CC, (c) 2Co-SnS_2/CC, (d) 3Co-SnS_2/CC, (e) 5Co-SnS_2/CC and (f) 6Co-SnS_2/CC at 0.2 A g^{-1} of 0.01-2.5 V.

Table S1 The capacity comparison of SnS_2-based materials for sodium storage capacity.

materials	current density (A g^{-1})	cycle number	specific capacity (mAh g^{-1})	references
Co-SnS_2/CC	0.2	100	1288	our work
Co-SnS_2/CC	2	200	800.4	our work
SnS_2@N,S-GA	0.05	100	360.5	2
SnS_2 NS⊂HTSs	0.05	50	414	3
SnS_2/C	0.05	100	600	4
SnS_2@C	0.05	150	631	5
SnS_2/S-rGO	0.1	85	530	6
SSC@SnS_2	0.1	100	564	7

SnS_2-C	0.1	100	587	8
CNT/SnS_2@C	0.1	200	605	9
SnS_2@C	0.1	100	690	10
MoS_2/SnS_2-GS	0.15	100	655	11
SnS_2-NGS	0.2	100	450	12
SnS_2/rGO	0.2	300	509	13
SnS_2-rGO	0.2	100	627	14
SnS_2-RGO	0.2	100	630	15
SnS_2 NC/EDA-RGO	0.2	100	680	16
c-SnS_2 NSA	0.5	100	420	17
SnS_2/NGS	0.5	200	453	18
SnS_2 NWAs	0.5	100	510	19
SnS_2-RGONRP	1	100	418	20
SnS_2@3DRGO	2	500	521.8	21
SnS_2/GN sheets	2.5	150	338	22

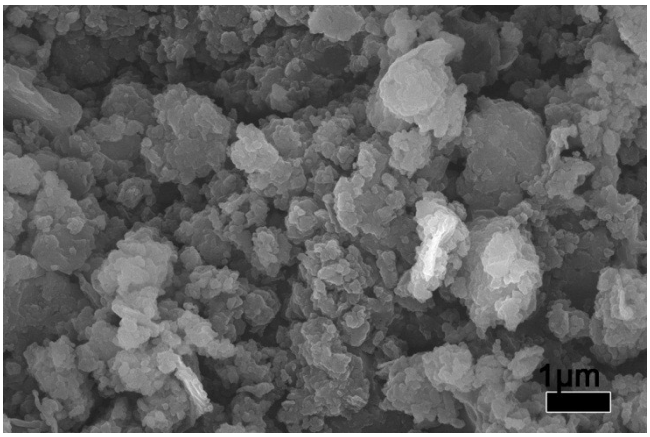

Fig. S8 SEM image of SnS_2 without CC substrate after 100 cyles.

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