Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.
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Supporting Information

Characterization

Using X-ray diffraction (XRD) to ascertain the crystal phase of composition at 10° to 80° by Bruker D8 diffractometer. The surface morphology and internal crystal structure of samples were observed by SEM (Hitachi 8100) and TEM (FEI F20 S-TWIN). The thermogravimetric analysis (TGA) was conducted to measure the compound by TA-SDT Q600 analyzer. The heating rate in the atmosphere was 10 ºC min^{-1}. The attribute of chemical bonds was determined by Raman spectroscopy (DXR2xi) of a 532 nm laser. The surface property of the composition was researched by X-ray photoelectron spectroscopy (XPS).

Electrochemical measurements

For SIBs, the anode electrode was formed by blending the active component, super P and carboxymethyl cellulose (CMC) in a proportion of 8: 1: 1 in deionized water. Each active material loaded in the anode electrodes is closed to 1.5-2.5 mg cm^{-2} for SIBs tests system. The solution was fixed to copper foil and dried at 80°C overnight under vacuum. In the half sodium-ion batteries, 1 M $NaClO_4$ in 1:1 (weight ratio) EC/DMC with 5% fluoroethylene carbonate (FEC) additives and whatman glass fiber were conducted as electrolyte and separator, respectively. In the half-cells, sodium metal was served as the counter electrode. For full SIBs, the capacity ratio of WS_2-SPAN-2 anode and NVP cathode was optimized to 1: 1.2. The WS_2-SPAN-2 anode was pre-cycled for three times before assembling full cells and before measuring the high and low temperature performance.

As for PIBs half-battery, the anode was fabricated by admixing the active materials (WS_2-SPAN-2, 80 wt.%) with super P (10 wt.%) and CMC (10 wt.%) in deionized water. Every active material loaded in active materials in the anode electrodes is closed to 1.5-2.5 mg cm^{-2} for PIBs tests. In addition, 3.0 M potassium bis(fluorosulfonyl)imide (KFSI) in DME (100% *Vol*%) was employed as electrolyte. The counter electrode was made up of sheet potassium metal. Notably, all the assembly work was carried out in a glove box filled with high pure argon.

Electrochemical characterization

Galvanostatic charge/discharge tests and the galvanostatic intermittent titration technique (GITT) of the electrode materials were tested on Land CT 2001A tester between 0.01 to 3 V. The cyclic voltammetry (CV) tests were conducted by an Ivium-n-Stat electrochemical workstation at diverse scan rates (vs. Na/Na^+ or K/K^+).

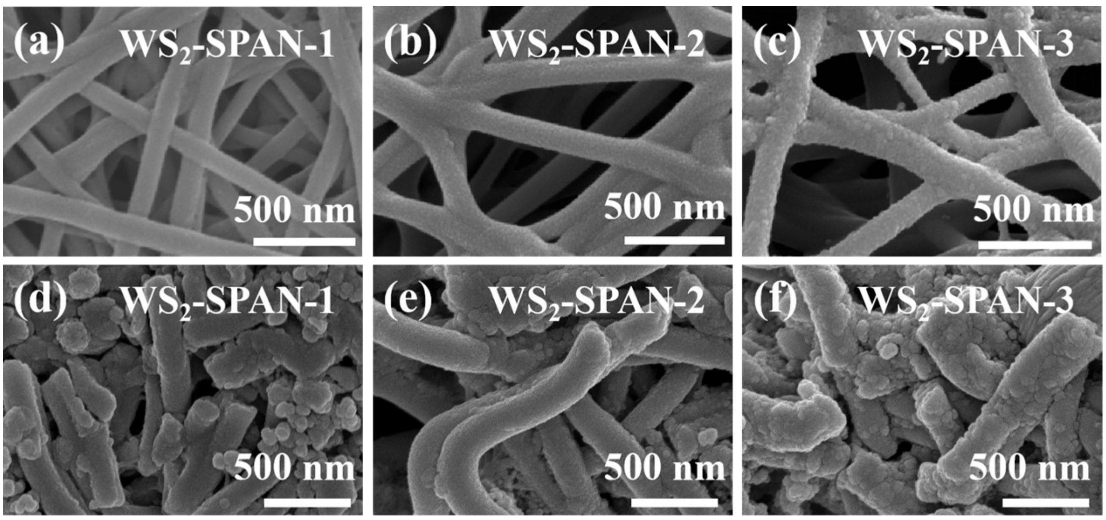

Fig. S1 SEM images before (a-c) and after cycling (d-f) of WS_2-SPAN-1, WS_2-SPAN-2 and WS_2-SPAN-3 electrodes.

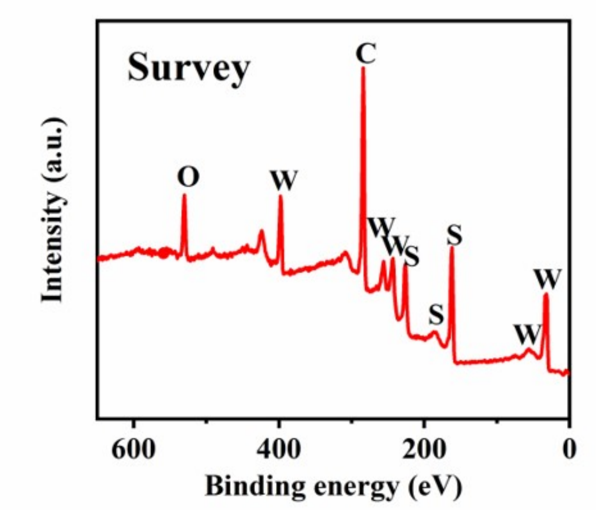

Fig. S2 Survey spectrum of WS_2-SPAN-2 sample.

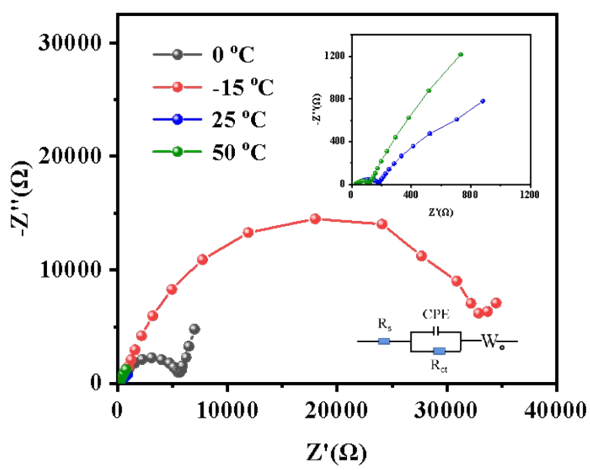

Fig. S3 Electrochemical impedance spectra (EIS) of WS_2-SPAN-2 electrodes at different temperatures in SIBs.

Table S1 Impedance values fitted from an equivalent circuit model.

Temperature	Rs (Ω)	Rct (Ω)
-15 °C	139.8	42294
0 °C	74.5	6875
25 °C	30.8	170.3
50 °C	23.7	122.9

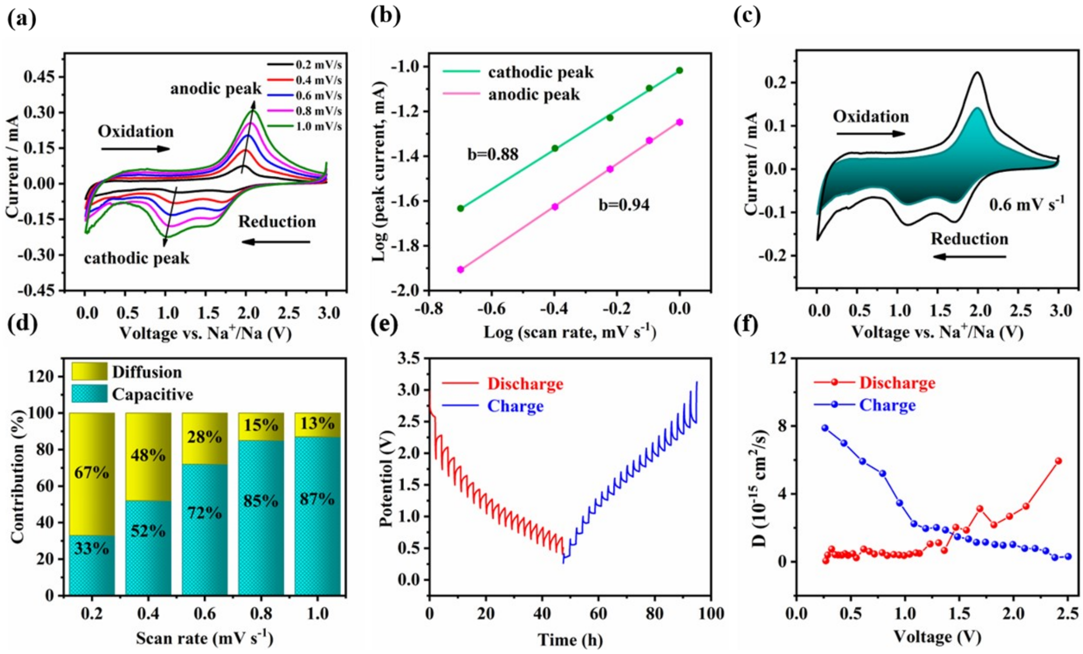

Fig. S4 (a) Cyclic voltammetry curves of WS_2-SPAN-2 electrode at different scan rates from 0.2 to 1.0 $mV{\cdot}s^{-1}$. (b) log (i) versus log (v) plots at different oxidation and reduction peaks. (c) Capacitive contribution (green area) of WS_2-SPAN-2 at 0.6 $mV{\cdot}s^{-1}$. (d) The diffusion controlled (yellow) and capacitive (blue) capacities of WS_2-SPAN-2 at different scan rates. (e) GITT charge/discharge profile, (f) Na^+ diffusion coefficients and reaction resistance for the WS_2-SPAN-2 anode of SIBs.

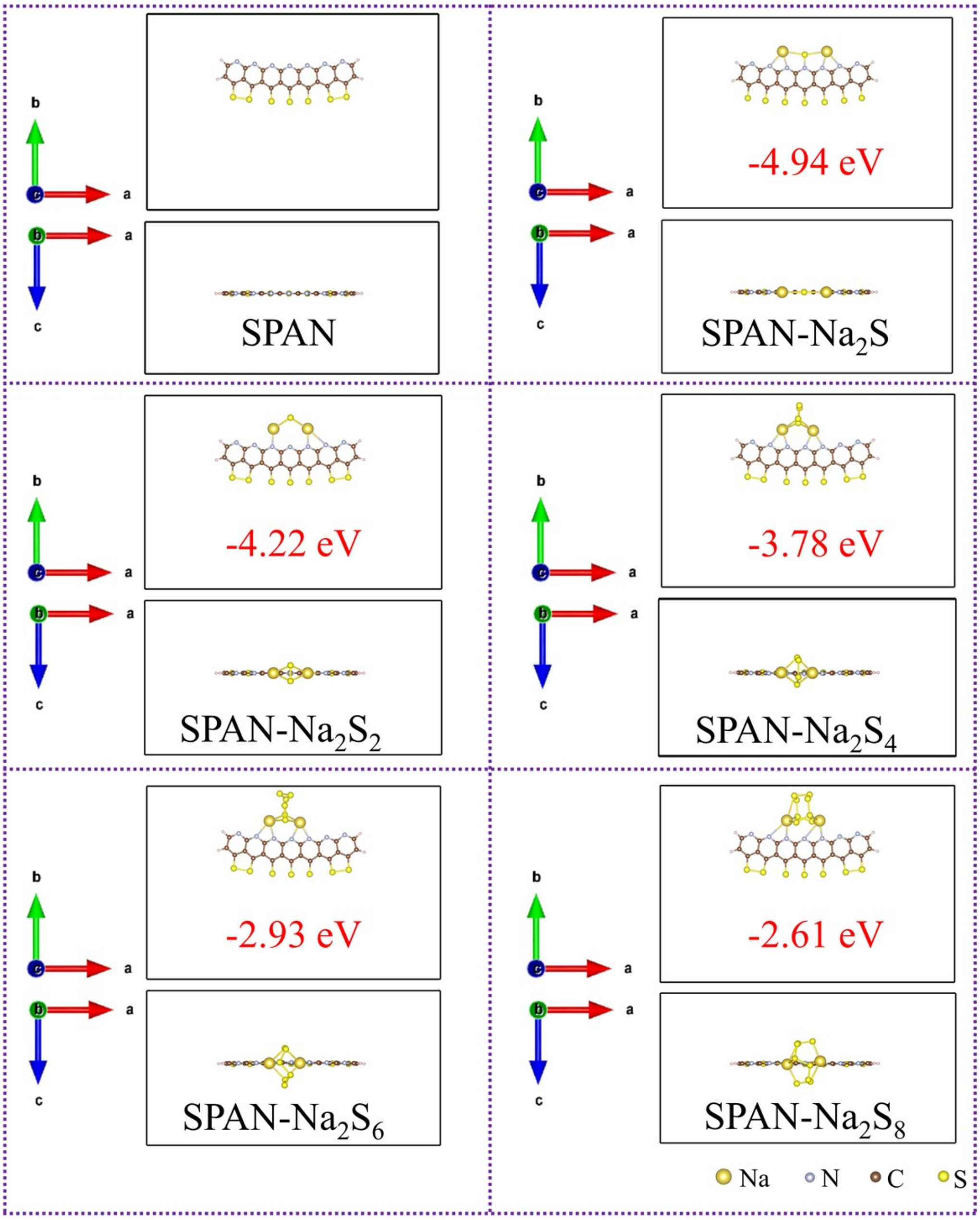

Fig. S5 Front and top views of optimized configurations of sodium polysulfide Na_2S_n (n= 1, 2, 4, 6 and 8) clusters adsorbed on SPAN.

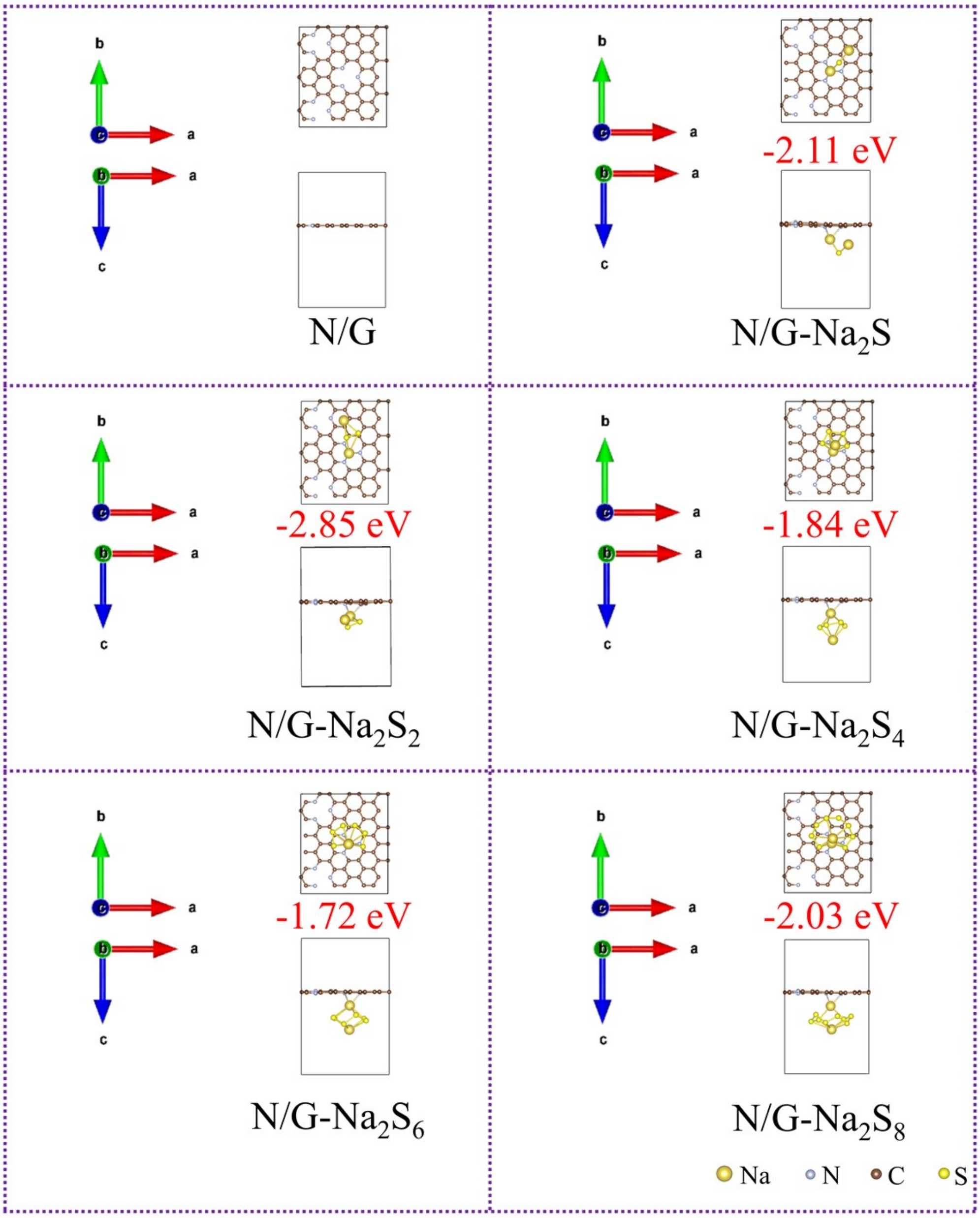

Fig. S6 Front and top views of optimized configurations of sodium polysulfide Na_2S_n (n= 1, 2, 4, 6 and 8) clusters adsorbed on N/G.

Table S2 Cycling performance of the WS_2-SPAN-2 electrode and newly reported WS_2 based and other anodes for SIBs/PIBs.

Electrode materials	fields	Cycling capacity (mAh g^{-1})	Current density (A g^{-1})	Cycle numbers	Ref.
WS_2-SPAN-2	SIBs	464 354 190 129	0.5 2 5 10	450 1400 12000 18000	This work
WS_2-SPAN-2	-15 °C 0 °C 25 °C 50 °C	307/210 402/266 457/382 245/228	0.5/1	200/500	This work
WS_2-SPAN-2	PIBs	362 278	0.1 1	100 3000	This work
WS_2	SIBs	471 240	0.2 5	300 250	3
WS_2@NC	SIBs	384 151	1 5	200 500	11
H-WS_2@NC	SIBs	468 375	0.1 1	200 1000	14
WS_2/CNT-rGO	SIBs	311 252	0.1 0.2	100 100	18
Co_9S_8/WS_2@NC	SIBs	405 354	1 2	100 120	25
$FeSe_2$/rGO	-40 °C 60 °C	217 422	1 5	200	37
WS_2@S/N-C	SIBs	321 175	0.1 5	100 1000	44
C-WS_2@CNFs	PIBs	247 168	0.5 2	300	61
WS_2@rGO-HC	SIBs	522 190	0.1 1	70 200	S1
WS_2	PIBs	103	0.1	100	S2
FeS_2/WS_2-CNFs	SIBs	423 308	0.5 4	500 1000	S3
WS_2 hollow spheres	SIBs	353 285	0.2 2	80 2000	S4

WS_2-MWCNTs	SIBs	289	1	60	S5
NGQDs-WS_2/3DCF	SIBs	268	2	1000	S6
HB WS_2@CNFs	SIBs	381 130	0.2 2	100 300	S7

Refs:

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