Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Cobalt-Doped Hollow ZnS Polyhedrons@Porous Carbon Shell Composite Anode for High-Rate Sodium-Ion Batteries

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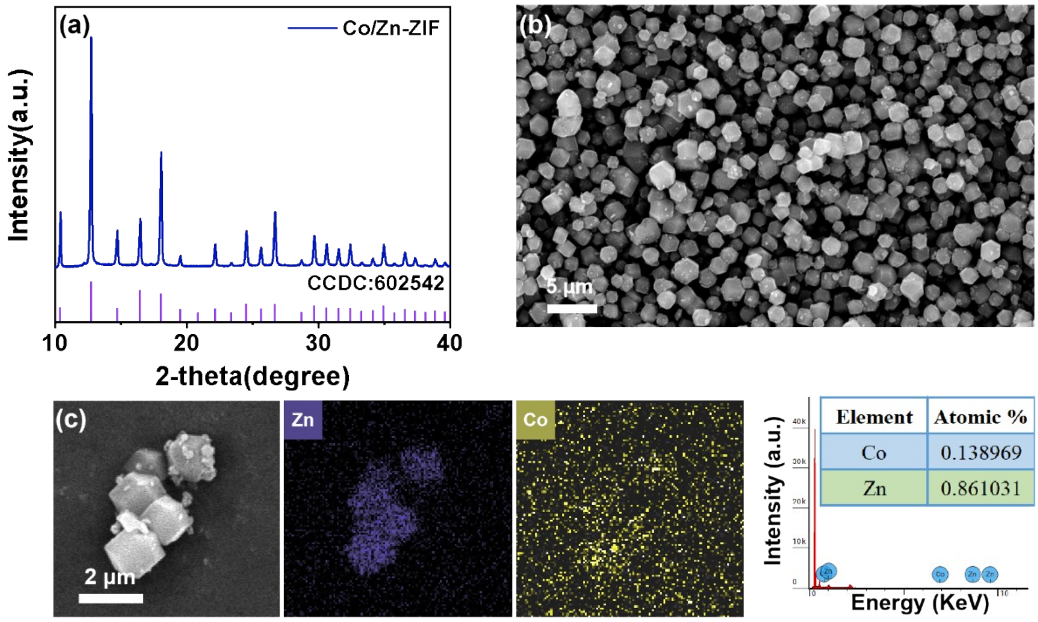

Fig. S1 (a) XRD pattern, (b) SEM, and (c) Elemental mappings of Co/Zn-ZIF.

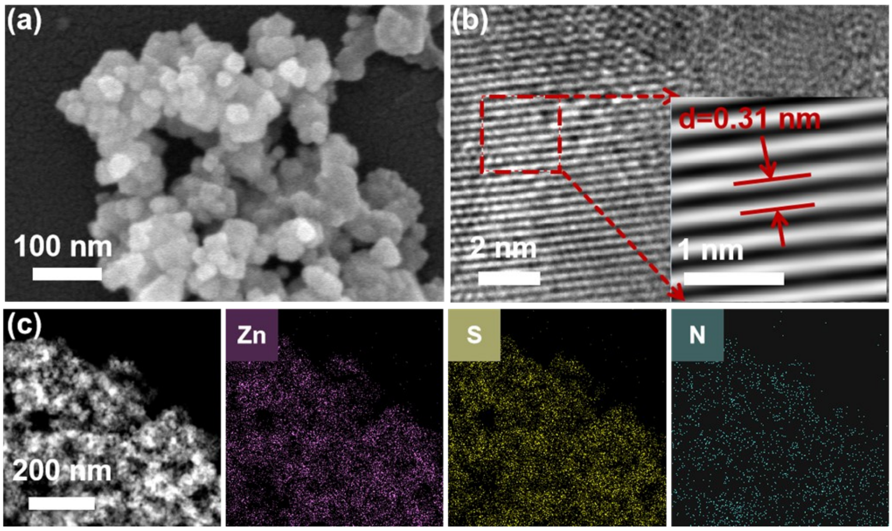

Fig. S2 (a) SEM image, (b) HRTEM image, and (c) Elemental mappings of ZnS.

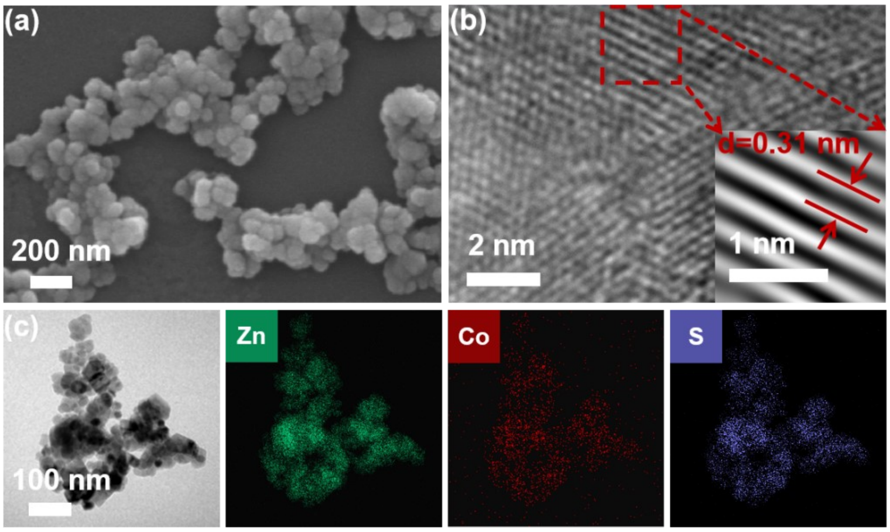

Fig. S3 (a) SEM image, (b) HRTEM image, and (c) Elemental mappings of Co-ZnS.

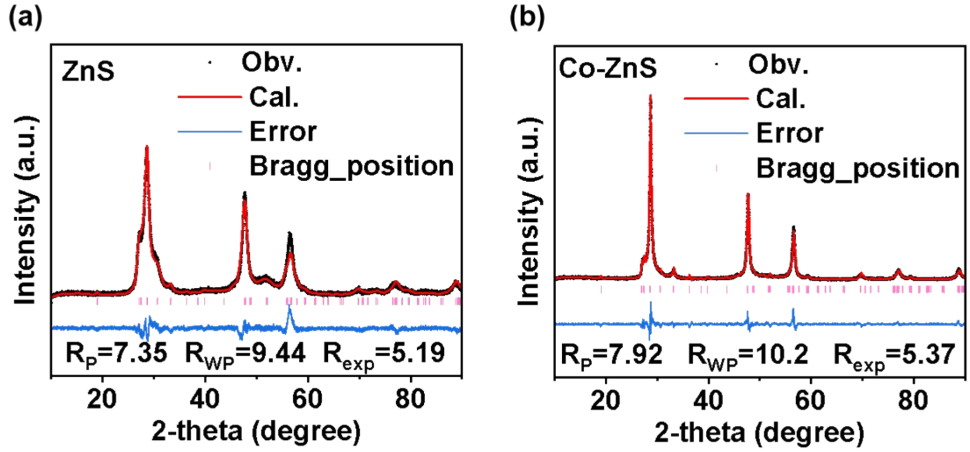

Fig. S4 Rietveld refined XRD patterns of (a) ZnS and (b) Co-ZnS.

Details calculation of TGA.

Since ZnS is fully converted to ZnO, the amount of ZnS is calculated according to the following formula：

$$ZnS/(wt\%) = \frac{M_{ZnS}}{M_{ZnO}} \times \frac{W_{ZnO}}{W_{Composite}(at\ 500^{o}C)} \times 100$$

Specifically, W_{ZnO} is the final weight of zinc oxide, $W_{composite}$ is the total weight of the composite material (at 500^{o}C), and M_{ZnS} and M_{ZnO} are the molecular weight of zinc sulfide and zinc oxide, respectively.

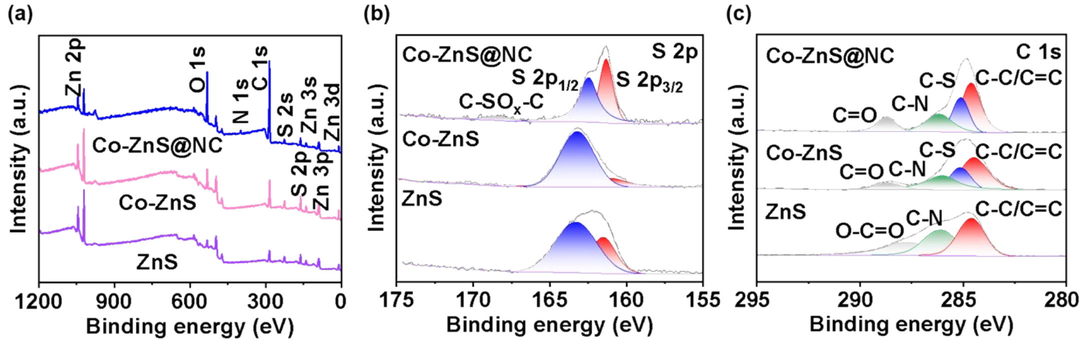

Fig. S5 XPS tests of (a) survey spectra, (b) S 2p, and (c) C 1s of three samples.

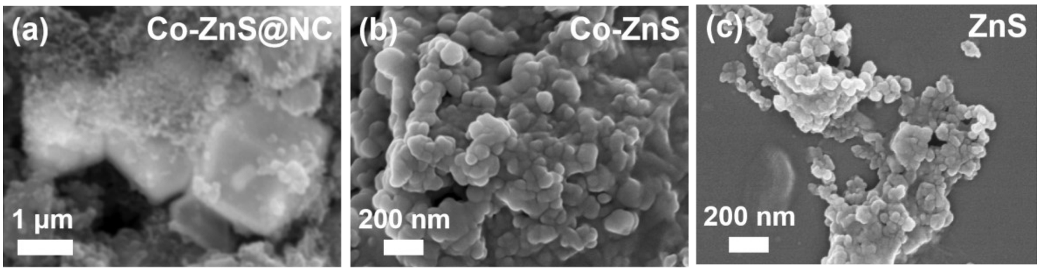

Fig. S6 SEM images of (a) Co-ZnS@NC, (b) Co-ZnS, and (c) ZnS after 100 cycles at a current density of 0.5 A g^{-1}.

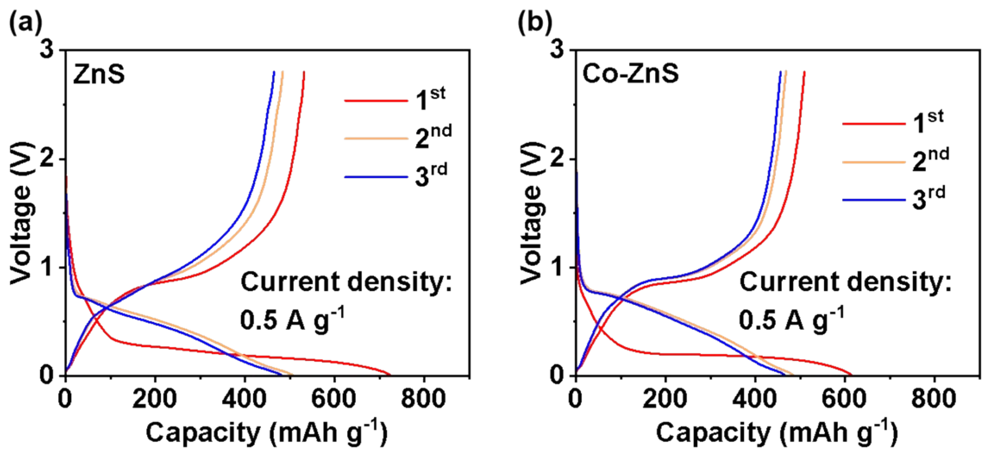

Fig. S7 Charge-discharge curves of (a) ZnS and (b) Co-ZnS at 0.5 A g^{-1}.

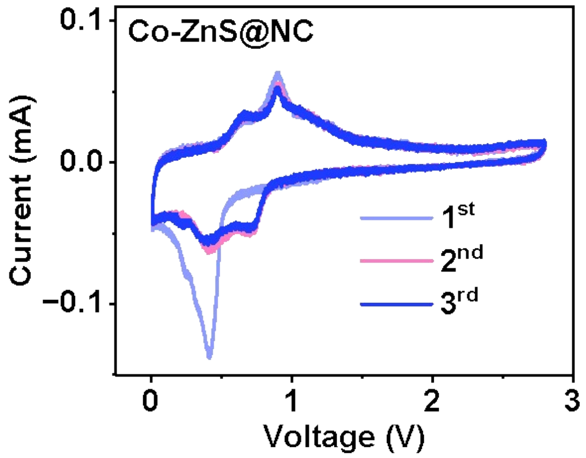

Fig. S8 Cyclic voltammograms of Co-ZnS@NC at a scan rate of 0.1 mV s^{-1}.

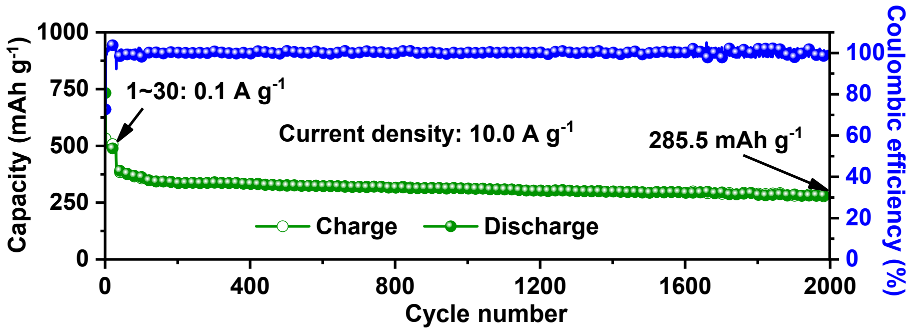

Fig. S9 Cycling performance of Co-ZnS@NC at 10.0 A g^{-1}.

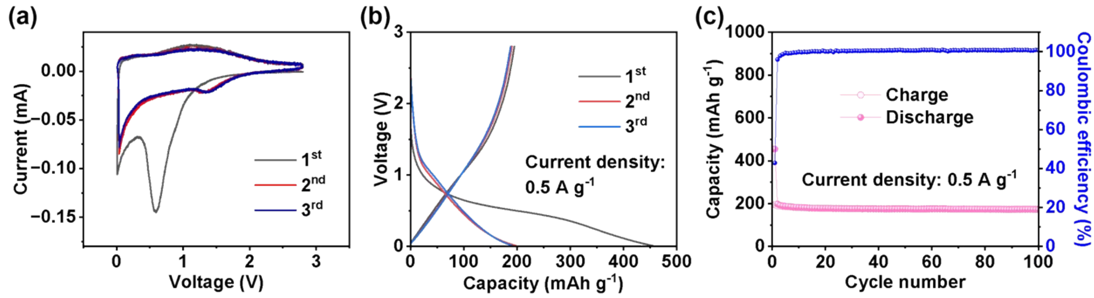

Fig. S10 Electrochemical properties of NC anode (a) First three CV curves at 0.1 mV s^{-1}, (b) Charge/discharge curves, (c) Cycling performance.

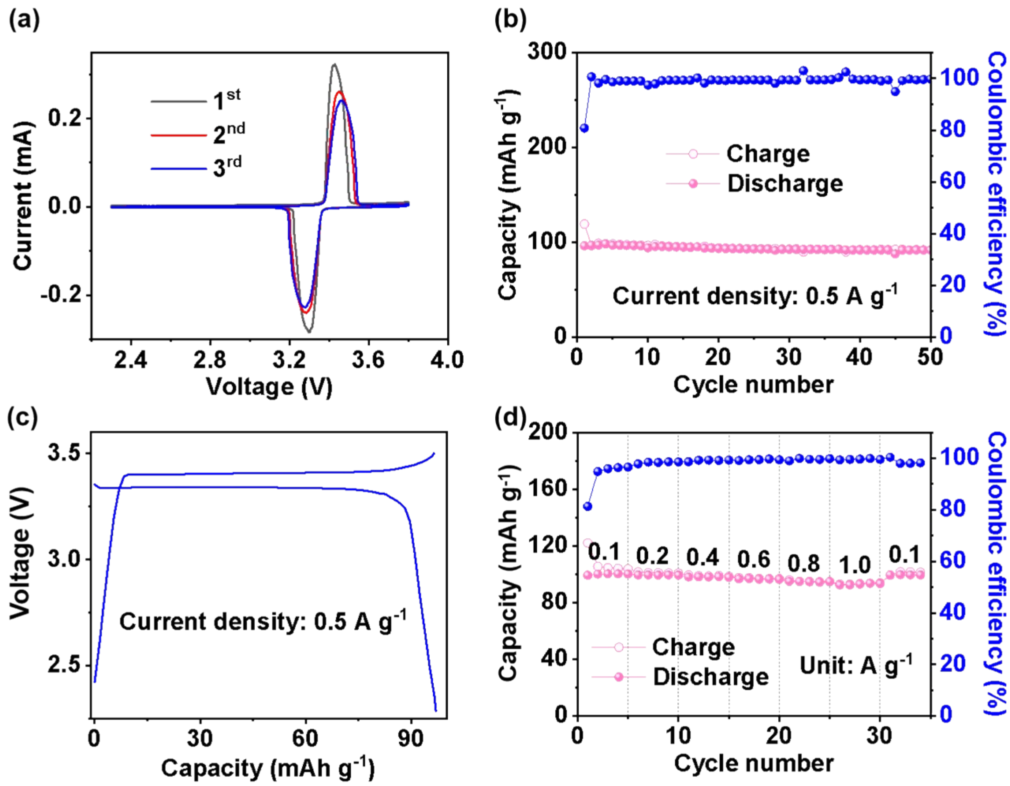

Fig. S11 Electrochemical properties of NVP (a) First three CV curves at 0.1 mV s^{-1}, (b) Cycling performance, (c) Charge/discharge curves, (d) Rate capability.

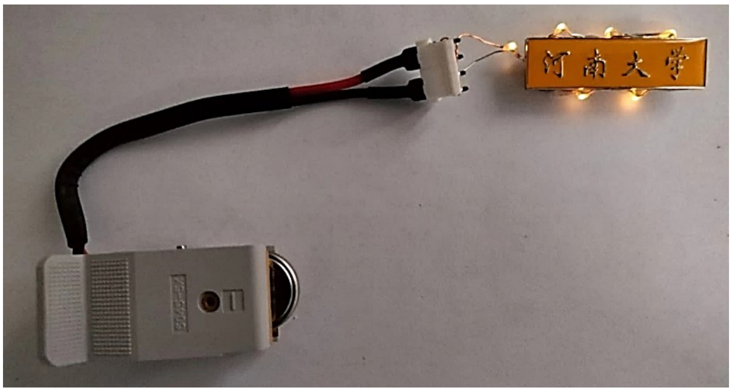

Fig. S12 Light bulbs powered by full cell.

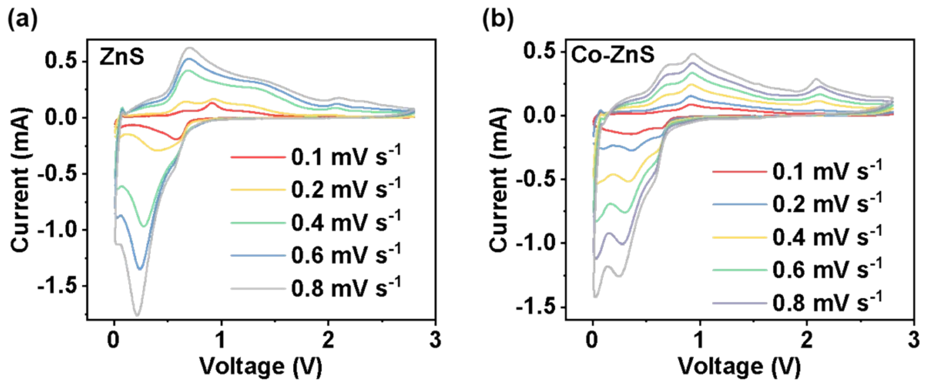

Fig. S13 CV curves of (a) ZnS and (b) Co-ZnS.

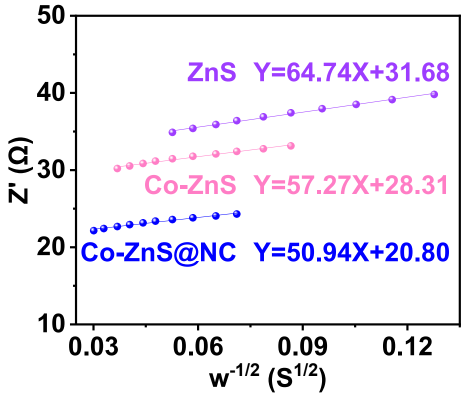

Fig. S14 The relationship between $Z^{'}$ and $\omega^{-1/2}$ in low-frequency regions of different anodes.

The sodium ion diffusion coefficients (D_{Na+}) of anode are calculated according to the following formula:

$$D = \frac{R^2T^2}{2A^2n^4C^2F^4\sigma^4}$$

$$Z^{'} = R_e + R_{ct} + \sigma\omega^{-1/2}$$

where D represents the Na^+ diffusion coefficient, A and n stand for the surface area and charge transfer number per molecule in the electrochemical reaction, F and C correspond to the Faraday constant and Na^+ concentration, σ and ω are the Warburg factor and angular frequency ($\omega = 2\pi f$), R and T represent the gas constant and absolute temperature.

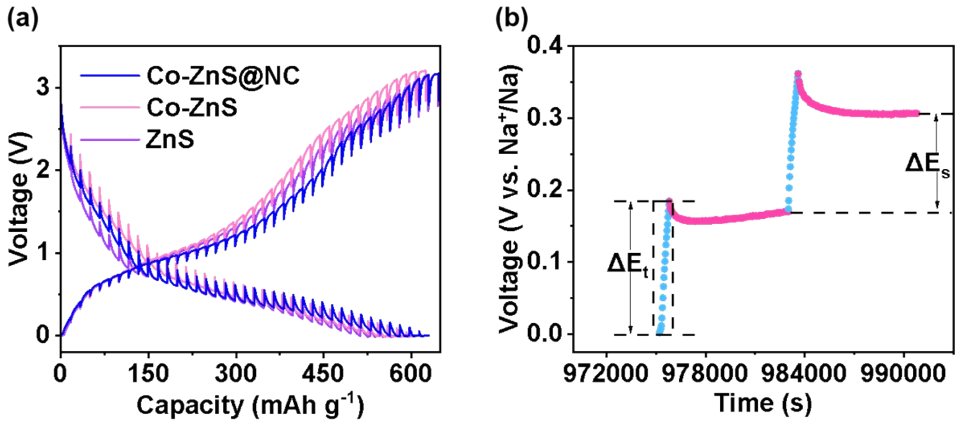

Fig. S15 (a) GITT results of the three samples, and (b) the corresponding detailed diagram with a single current pulse for 10 min followed by an open-circuit for 120 min.

The diffusion coefficients of Na^+ in the Co-ZnS@NC anode are further calculated *via* GITT measurements, which can be calculated using the following equation:

$$D = \frac{4}{\pi\tau}\left(\frac{m_a V_m}{M_a S}\right)^2\left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2$$

in which τ is the relaxation time, m_a, M_a, and V_m are the mass, molar weight, and molar volume of the active materials, respectively. S is the contact area between electrode and electrolyte, ΔE_s is the voltage change caused by the pulse current, and ΔE_τ is the voltage change during a constant current pulse, excluding the *iR* drop.

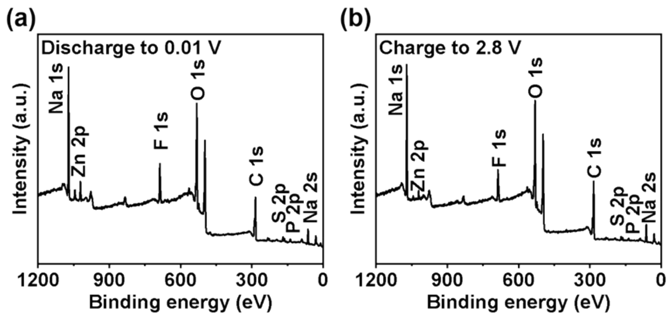

Fig. S16 XPS survey spectra of Co-ZnS@NC at (a) discharge to 0.01 V and (b) charge to 2.8 V.

Table S1 ICP analysis results for sample Co-ZnS@NC.

Sample mass m_0 (g)	Test element	Sample elemental content W (%)
0.0446	Co	0.58
0.0446	Zn	45.11

Table S2 Measured parameters derived from Rietveld refined XRD for three samples.

Parameter	ZnS	Co-ZnS	Co-ZnS@NC
a (Å)	3.810	3.808	3.806
b (Å)	3.810	3.808	3.806
c (Å)	18.690	18.690	18.690
V ($Å^3$)	234.980	234.711	234.483

Table S3 Peak area ratio of S 2p for XPS spectra of three samples.

S 2p	ZnS	Co-ZnS	Co-ZnS@NC
S $2p_{1/2}$	69.4%	82.8%	52.6%
S $2p_{3/2}$	30.6%	17.2%	47.4%

Table S4 ZnS-based anode reported for SIBs.

Materials	Voltage (V)	Rate capability		Ref.
		Capacity (mAh g^{-1})	Current density (mA g^{-1})	
CC-ZnS/CNT	0.01-3.0	346.0	5.0	7
$ZnIn_2S_4$	0.01-2.5	394.3	5.0	14
Sb/ZnS@C	0.01-1.8	214.3	1.6	20
ClO^{4-} doped ZnS	0.01-3.0	203.0	4.0	24
$ZnSnS_3$	0.01-3.0	256.6	2.0	25
ZnS/CuS@C	0.4-3.0	298.9	10.0	26
ZnS/NPC	0.01-3.0	182.4	4.0	27
ZnS/MWCNTs	0.01-3.0	315.0	5.0	28
Fe_7S_8@ZnS/N-C	0.01-3.0	337.6	5.0	29
Co-ZnS@NC	0.01-2.8	368.8	20.0	This work