Supporting Information

Rational Design of Unique ZnO/ZnS@N-C

Heterostructures for High-Performance Lithium-Ion Batteries

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EXPERIMENTAL SECTION

Synthesis of ZnO/ZnS@N-C/CNTs composites.

ZnO/ZnS@N-C/CNTs composite was synthesized by a MOFs-assisted method. Firstly, ZnS/ZIF-8/CNTs precursor, where ZIF-8 is zeolitic imidazolate framework-8, was obtained via a one-pot solvothermal method. Typically, 0.20 g of activated CNTs was dispersed in 35 mL of methanol by ultrasonication. Then 1.10 g of $Zn(NO_3)_2$ · $6H_2O$ was dissolved under vigorous stirring. After that 15 mL of methanol containing 2.04 g of 2-methylimidazole (2MI) was added into the above solution. Then 30 mL of ethylene glycol/deionized water (v/v = 2:1) solution containing 0.6 g of thioacetamide (TAA) was added into the above solution. The as-obtained solution was transferred to a 100 mL Teflon-lined autoclave and heated at 180 °C for 18 h. After cooling down naturally, the ZIF-8/ZnS/CNTs precursor was obtained by centrifugation, washing, and drying. Secondly, the ZIF-8/ZnS/CNTs precursor was annealed at 500 °C for 3 h in Ar atmosphere to prepare ZnO/ZnS@N-C/CNTs composite (denoted as ZnO/ZnS@N-C/CNTs-0.6).

To optimize the components and morphology of the composites, the concentration of TAA was resized to obtain different ZnO/ZnS@N-C/CNTs samples. When the mass of TAA was 0.1, 0.3, and 0.9 g, the corresponding products were denoted as ZnO/ZnS@N-C/CNTs-0.1, ZnO/ZnS@N-C/CNTs-0.3, and ZnO/ZnS@N-C/CNTs-0.9, respectively. For comparison, ZnO@N-C/CNTs composite was synthesized via the above process without the addition of TAA. ZnS/CNTs was also obtained via the same process without the addition of 2MI.

Materials characterization

The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAXrB X-ray diffractometer (Cu Kα radiation). Scanning electron microscopy (SEM, Hitachi Instruments Co.,

Ltd., SU-8010, operating at 200 kV) and transmission electron microscopy (TEM, Philips Tecnai 20, 200 kV, linked to an energy-dispersive spectral (EDS) analysis instrument) were used to observe the morphology of the as-prepared samples in detail. X-ray photoelectron spectroscopy (XPS) was conducted on a VG Multilab 2000 (VG Inc.) photoelectron spectrometer using monochromatic Al K α radiation under vacuum at 2 × 10⁻⁶ Pa. The elemental compositions of the materials were confirmed by inductively coupled plasma – atomic emission spectroscopy (ICP-AES, USA Agilent 725) and elemental analysis (EA, Perkin-Elmer 2400 Series II CHNS/O). The N₂ adsorption/desorption curves were determined by Brunauer-Emmett-Teller (BET) measurements using a Quantachrome Autosorb-IQ2 surface area analyzer. Specific surface areas were measured by Brunauer-Emmett-Teller analysis, and mesopore and size distributions were calculated using the Barrett-Joyner-Halenda (BJH) model.

Electrochemical measurements

The electrochemical measurements of the samples as anode materials for LIBs were evaluated using CR2032 coin type cells. The electrodes were prepared by mixing the active materials, acetylene black, and poly(vinyl difluoride) in 1-methyl-2-pyrrolidinone in a weight ratio of 7:2:1 to form a slurry. The mixed slurry was then pasted on copper foil and dried in vacuum at 100 °C for 12 h. Li foil was used as counter electrode, and 1 M LiPF₆ dissolved in a mixture of ethylene carbonate, dimethyl carbonate, and ethylmethyl carbonate solution (EC:DMC:EMC = 1:1:1 v/v/v) was used as electrolyte. All the cells were assembled in an Ar-filled glove box. The galvanostatic charge-discharge curves, cycling performances, and rate performances were acquired on a Land Battery-Testing System. Cyclic voltammetry (CV, 0.1 mV s⁻¹, 0.01-3.0 V, vs. Li⁺/Li) and electrochemical impedance spectroscopy (EIS, 100 kHz and 0.01 Hz) measurements were

conducted on a CHI604E electrochemical workstation.

Theoretical Calculations

The calculations were performed based on the density functional theory (DFT) approach using the DMol3 package.^{1,2} The effects of exchange correlation interaction were treated according to the Perdew-Burke-Ernzerhof generalized-gradient approximation (GGA-PBE). All-electron Kohn-Sham wave functions were expanded in a double numerical basis with polarized orbital (DNP).³ Sampling of the irreducible wedge of the Brillouin zone was performed with a regular Monkhorst-Pack $6 \times 6 \times 6$ grid of special k-points.⁴ The convergence criteria for relaxation were 1.0×10^{-5} Ha, 0.002 Ha/Å, and 0.005 Å for the energy, gradient, and atomic displacement, respectively.



Figure S1. XRD patterns of the ZIF-8/ZnS/CNTs-0.1, ZIF-8/ZnS/CNTs-0.3, ZIF-8/ZnS/CNTs-0.6, and ZIF-8/ZnS/CNTs-0.9 composites.



Figure S2. SEM images of the as-prepared precursors: (a) ZIF-8/ZnS/CNTs, (b) ZIF-8/CNTs, and

(c) ZnS@CNTs composites.



Figure S3. Nyquist plots of the as-prepared ZnO@N-C/CNTs, pure ZnS/CNTs, and ZnO/ZnS@N-C/CNTs electrodes measured at open-circuit potential (inset is the equivalent circuit, *Rs* means electrolyte resistance, *Rct* means charge transfer resistance, W_0 means Warburg impedance, *CPE1* means constant phase element.).



Figure S4. (a) Typical XPS survey spectrum and (b) deconvoluted C 1s spectrum for the ZnO/ZnS@N-C/CNTs-0.6 composite.



Figure S5. (a) XRD patterns and (b) SEM images of the ZnO@N-C/CNTs. (c) XRD patterns and (d) SEM images of the pure ZnS@CNTs composites.



Figure S6. SEM images of the as-prepared samples of (a-b) ZnO/ZnS@C/CNTs-0.1, (c-d) ZnO/ZnS@C/CNTs-0.3, and (e-f) ZnO/ZnS@C/CNTs-0.9 composites.



Figure S7. (a) N_2 adsorption-desorption isotherms and (b) pore size distributions of the as-prepared ZnO@N-C/CNTs, pure ZnS/CNTs, and ZnO/ZnS@N-C/CNTs composites.



Figure S8. (a, b) SEM images of the ZnO/ZnS@C/CNTs-0.6 fresh electrode, (c, d) SEM images and (e, f) TEM images of the ZnO/ZnS@C/CNTs-0.6 electrode after 200 cycles at 100 mA g⁻¹.

Materials	ZnS (wt. %)	ZnO (wt. %)	C (wt. %)
ZnO/ZnS@N-C/CNTs-0.1	25.899	29.589	47.40
ZnO/ZnS@N-C/CNTs-0.3	53.30	8.91	37.79
ZnO/ZnS@N-C/CNTs-0.6	57.424	1.458	41.12
ZnO/ZnS@N-C/CNTs-0.9	58.976	0.243	40.781
ZnO@N-C/CNTs		38.23	61.77
Pure ZnS/CNTs	53.35		46.65

 Table S1. Compositions of the ZnO@N-C/CNTs, pure ZnS/CNTs, and ZnO/ZnS@C/CNTs

 composites according to the ICP and element analysis results.

 Table S2. Comparison of BET specific surface areas, pore distributions, and pore volumes of ZnO@N-C/CNTs, pure ZnS/CNTs and ZnO/ZnS@C/CNTs composites.

Materials	Specific Surface Area (m ² g ⁻¹)	Pore Diameter (nm)	Pore Volume (cc g ⁻¹)
ZnO/ZnS@N-C/CNTs-0.1	110.623	3.704	0.735
ZnO/ZnS@N-C/CNTs-0.3	103.685	8.999	0.402
ZnO/ZnS@N-C/CNTs-0.6	98.123	13.145	0.399
ZnO/ZnS@N-C/CNTs-0.9	49.903	34.472	0.455
ZnO@N-C/CNTs	365.263	3.945	0.643
Pure ZnS/CNTs	57.487	3.712	0.39

Table S3. Comparison of the electrochemical properties of the as-prepared ZnO@N-C/CNTs,
pure ZnS/CNTs, and ZnO/ZnS@N-C/CNTs composites with previously reported zinc oxides and
sulfides.

Materials	Cycling stability		Rate capability		Ref.	
	Current density (mA g ⁻¹)	Initial discharge capacity (mAh g ⁻¹)	Capacity Retention (mAh g ⁻¹ /cycles)	Current density (mA g ⁻¹)	Capacity Retention (mAh g ⁻¹ /cycles)	
ZnS/C	100	~1300	570/150	n/a	n/a	[5]
ZnO/ZnO@C	100	878	839/50	5000	307/500	[6]
ZnS NR@HCP-600 ^{a)}	600	945	840/300	n/a	n/a	[7]
nano-ZnS-C	100	694	530/600	500	530/600	[8]
ZnS-QDs@mNC ^{b)}	840	1243/140	506/300	0.3 mA cm ⁻²	1.82 mAh cm ^{-2/30}	[9]
Core-shell-like ZnS/C nanocomposite	100	1256	741/300	200	750/500	[10]
ZnO@NC@CNTs ^{c)}	100	~1300	~850/200	1000	300/100	[11]
ZnS/NPC ^{d)}	100	~1450	1067/200	1000	856.8/1000	[12]
ZnS/graphene	100	1464	633/200	2000	370/200	[13]
Hollow ZnS@C	100	1489	760/240	n/a	n/a	[14]
GLC@ZnS030 ^{e)}	500	~1150	1134/100	1000	890/200	[15]
ZnO@ZnS nanorod	200	~972.5	513.4/100	n/a	n/a	[16]
ZnO/ZnS@N-C/CNTs -0.6	100	1663.6	1042.4/210	1000	386.6/400	Our work

^{a)}HCP means hollow carbon polyhedra, ^{b)}ZnS-QDs@mNC means ZnS quantum dots@multilayered N-doped carbon matrix, ^{c)}NC and N-C both mean N-doped carbon, ^{d)}NPC means nitrogen-doped porous carbon polyhedra, and ^{e)}GLC@ZnS means graphene-like nano-cell.

Materials	$R_{ct}\left(\Omega ight)$	$R_{s}\left(\Omega ight)$
ZnO/ZnS@N-C/CNTs-0.1	58.29	7.06
ZnO/ZnS@N-C/CNTs-0.3	64.98	3.32
ZnO/ZnS@N-C/CNTs-0.6	70.57	3.80
ZnO/ZnS@N-C/CNTs-0.9	78.12	3.45
ZnO@N-C/CNTs	72.47	4.12
Pure ZnS/CNTs	82.10	3.61

Table S4. Electrical parameters of the as-prepared electrodes, determined from the fitting results

 of the impedance spectra presented in Figure S3.

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