

## Supporting Information

### Self-templated formation of hierarchically yolk-shell-structured ZnS/NC dodecahedra with superior lithium storage properties

Ping Wang <sup>a,b</sup>, Aihua Yuan <sup>\*a,c</sup>, Zhitao Wang <sup>c</sup>, Xiaoping Shen <sup>d</sup>, Hantao Chen <sup>c</sup>, Hu Zhou <sup>\*a</sup>

<sup>a</sup> School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, PR China.

<sup>b</sup> School of Chemical & Materials Engineering, Zhenjiang College, Zhenjiang 212000, PR China.

<sup>c</sup> School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, PR China.

<sup>d</sup> School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, PR China.

\*Corresponding author E-mail: *aihua.yuan@just.edu.cn* (A. H. Yuan), *zhmiao119@sina.com* (H. Zhou).



Fig. S1 EDS results of ZnS(x h)/NC.

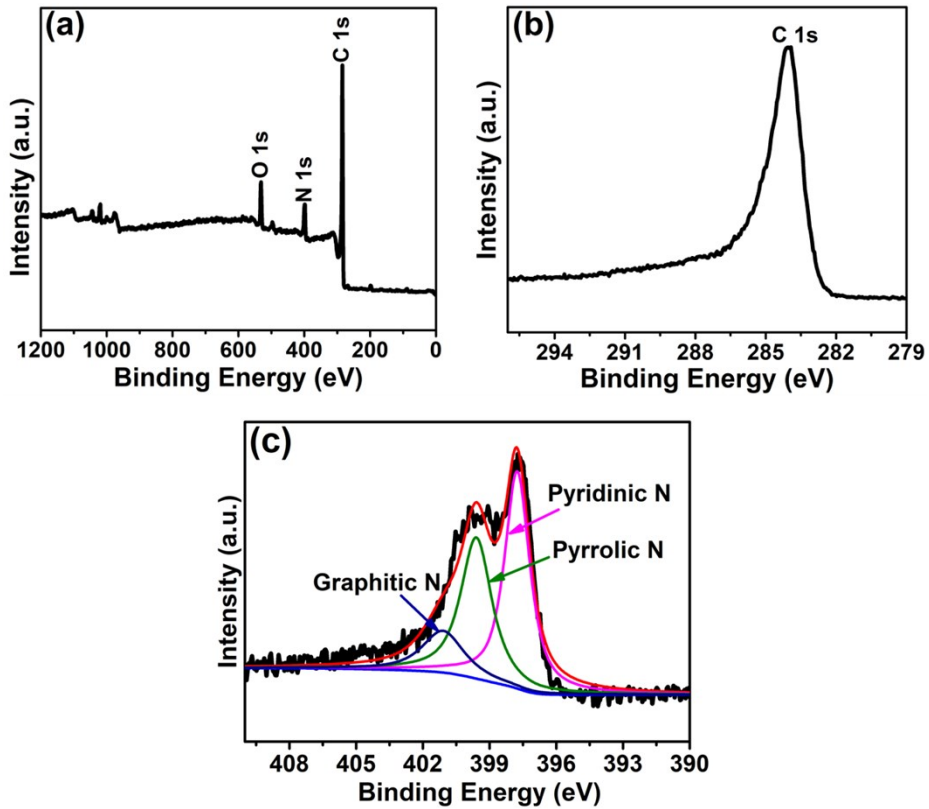
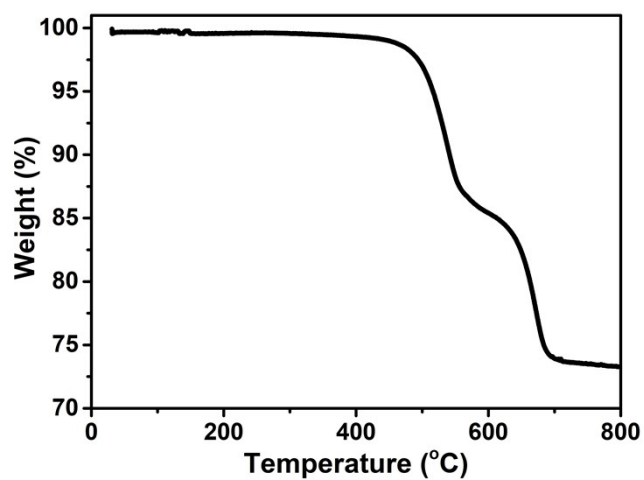
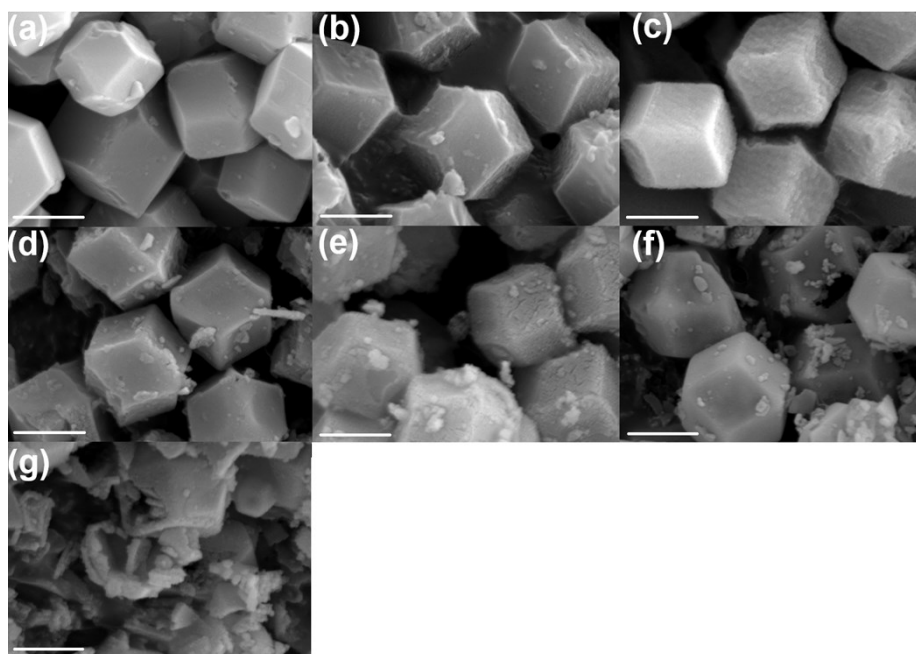


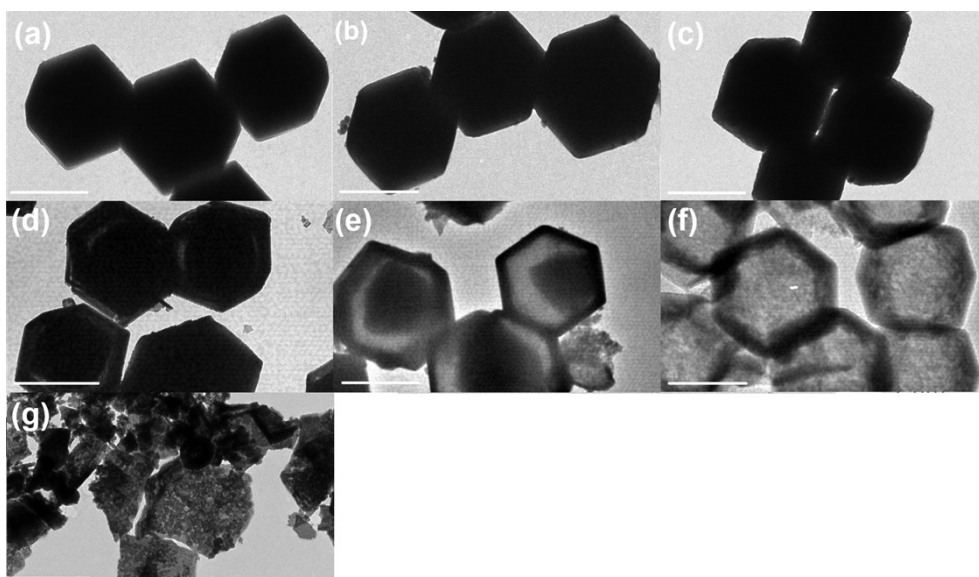
Fig. S2 XPS spectra of NC: (a) survey, (b) C1s, and (c) N1s.



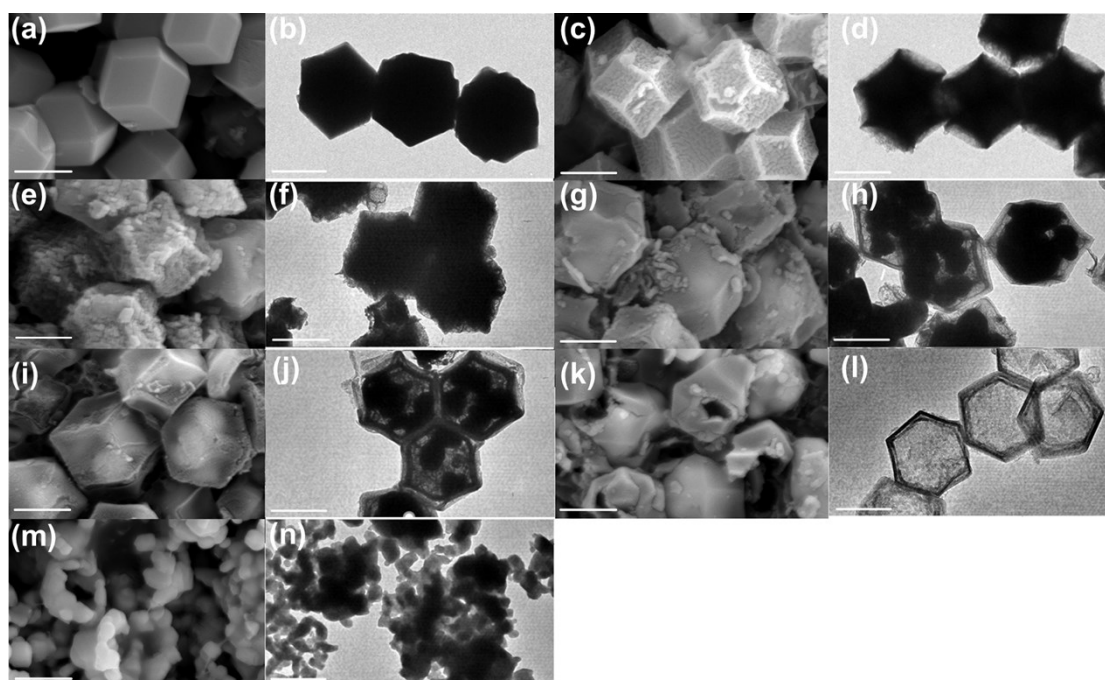
**Fig. S3** TG curve of ZnS(72 h)/NC.



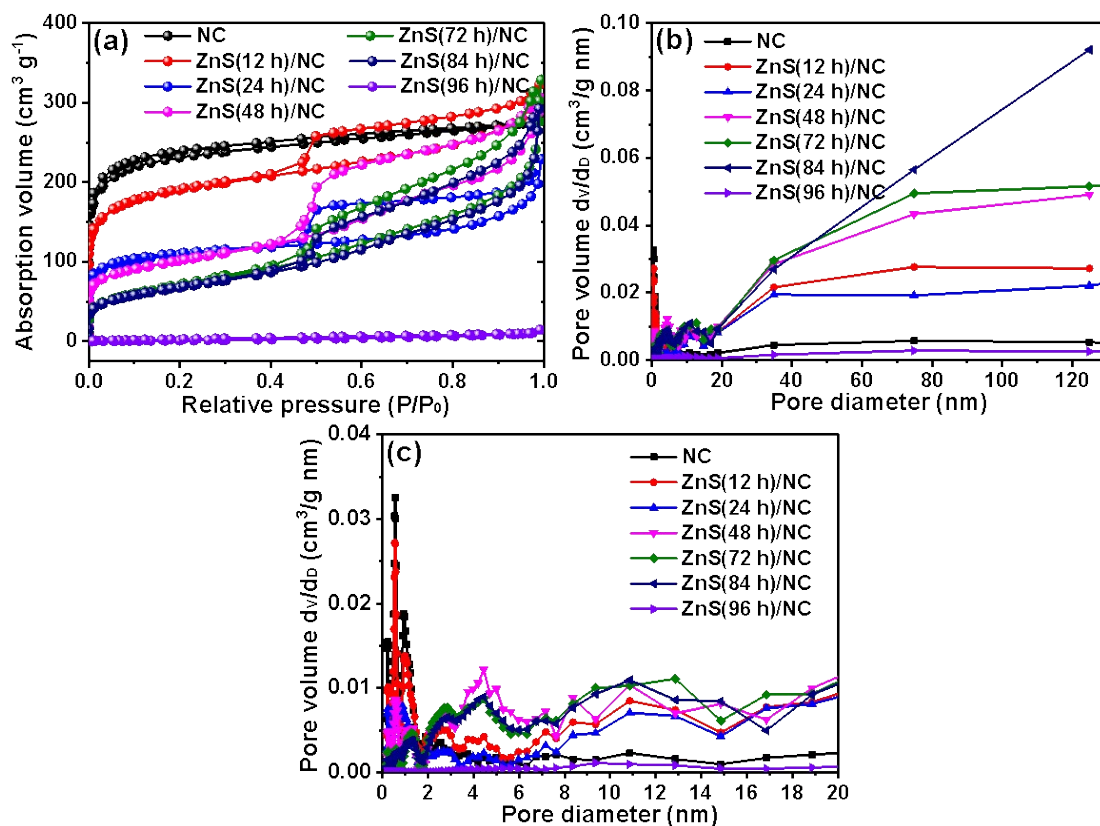
**Fig. S4** SEM images of (a) ZIF-8, (b) ZnS(12 h)@ZIF-8, (c) ZnS(24 h)@ZIF-8, (d) ZnS(48 h)@ZIF-8, (e) ZnS(72 h)@ZIF-8, (f) ZnS(84 h)@ZIF-8, and (g) ZnS(96 h)@ZIF-8. The scale bar represents 1 μm.



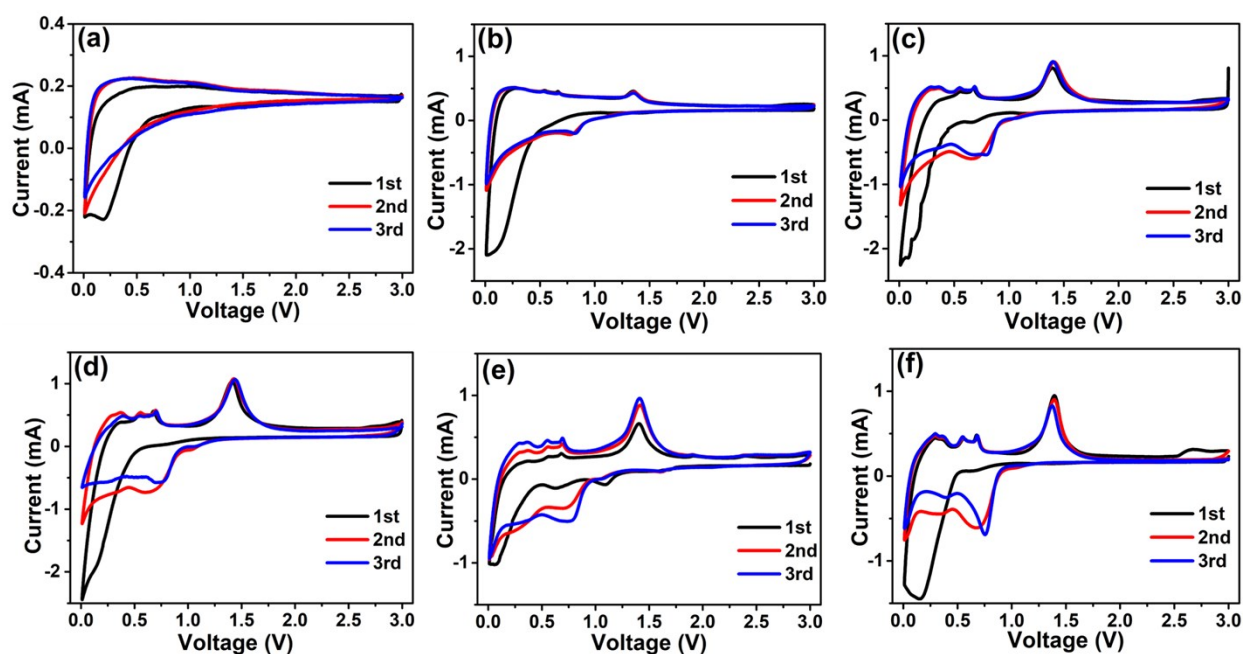
**Fig. S5** TEM images of (a) ZIF-8, (b) ZnS(12 h)@ZIF-8, (c) ZnS(24 h)@ZIF-8, (d) ZnS(48 h)@ZIF-8, (e) ZnS(72 h)@ZIF-8, (f) ZnS(84 h)@ZIF-8, and (g) ZnS(96 h)@ZIF-8. The scale bar represents 1  $\mu\text{m}$ .



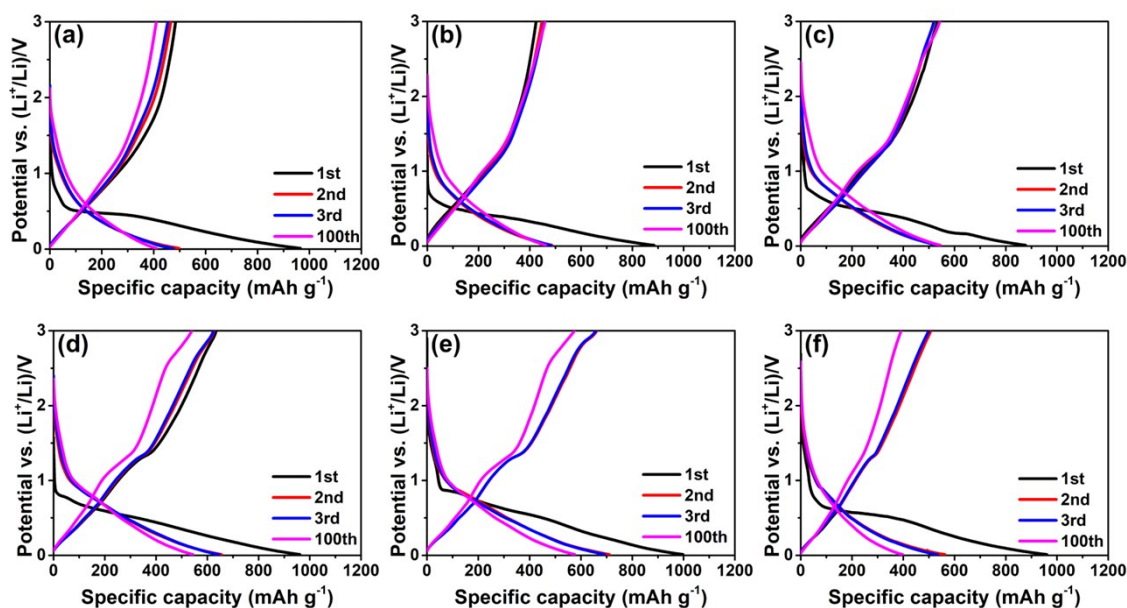
**Fig. S6** SEM and TEM images of (a, b) NC, (c, d) ZnS(12 h)/NC, (e, f) ZnS(24 h)/NC, (g, h) ZnS(48 h)/NC, (i, j) ZnS(72 h)/NC, (k, l) ZnS(84 h)/NC, and (m, n) ZnS(96 h)/NC. The scale bar represents 1  $\mu\text{m}$ .



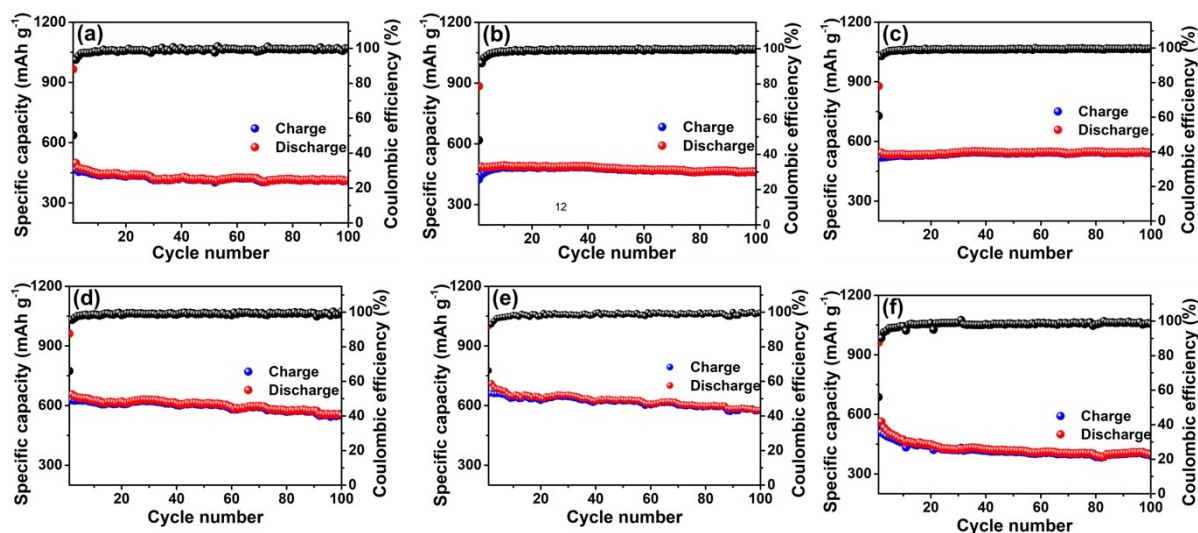
**Fig. S7** (a)  $N_2$  adsorption-desorption isotherms (77 K) and (b, c) pore size distributions of NC and  $ZnS(x\text{ h})/NC$  ( $x = 12\sim 96$ ).



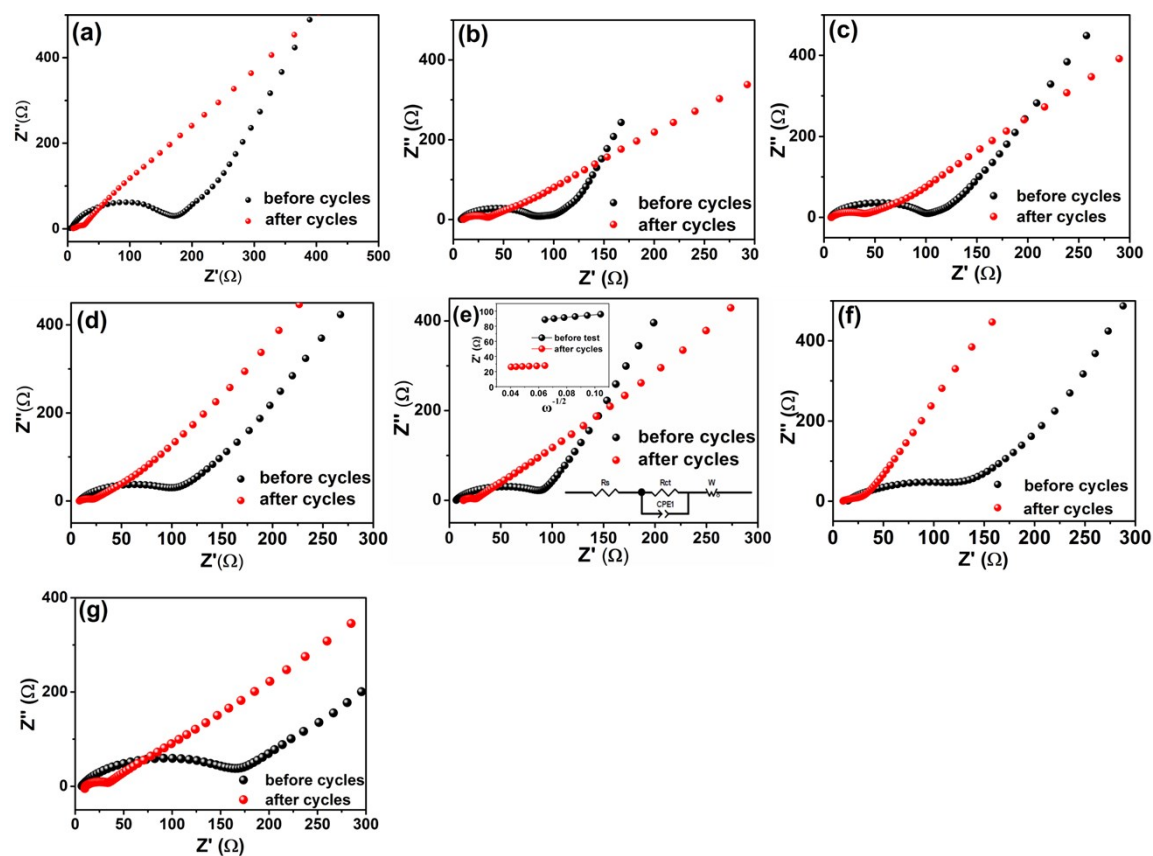
**Fig. S8** Cyclic voltammetry curves of (a) NC, (b)  $ZnS(12\text{ h})/NC$ , (c)  $ZnS(24\text{ h})/NC$ , (d)  $ZnS(48\text{ h})/NC$ , (e)  $ZnS(84\text{ h})/NC$ , and (f)  $ZnS(96\text{ h})/NC$ .



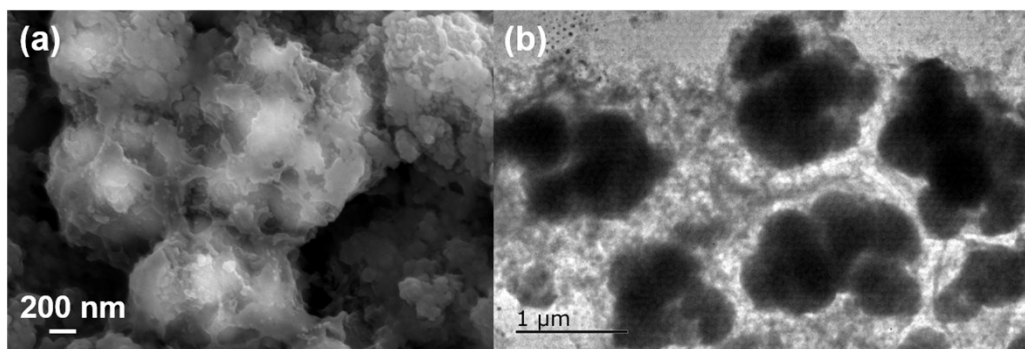
**Fig. S9** Galvanostatic discharge-charge voltage profiles at  $100 \text{ mA g}^{-1}$  of (a) NC, (b) ZnS(12 h)/NC, (c) ZnS(24 h)/NC, (d) ZnS(48 h)/NC, (e) ZnS(84 h)/NC, and (f) ZnS(96 h)/NC.



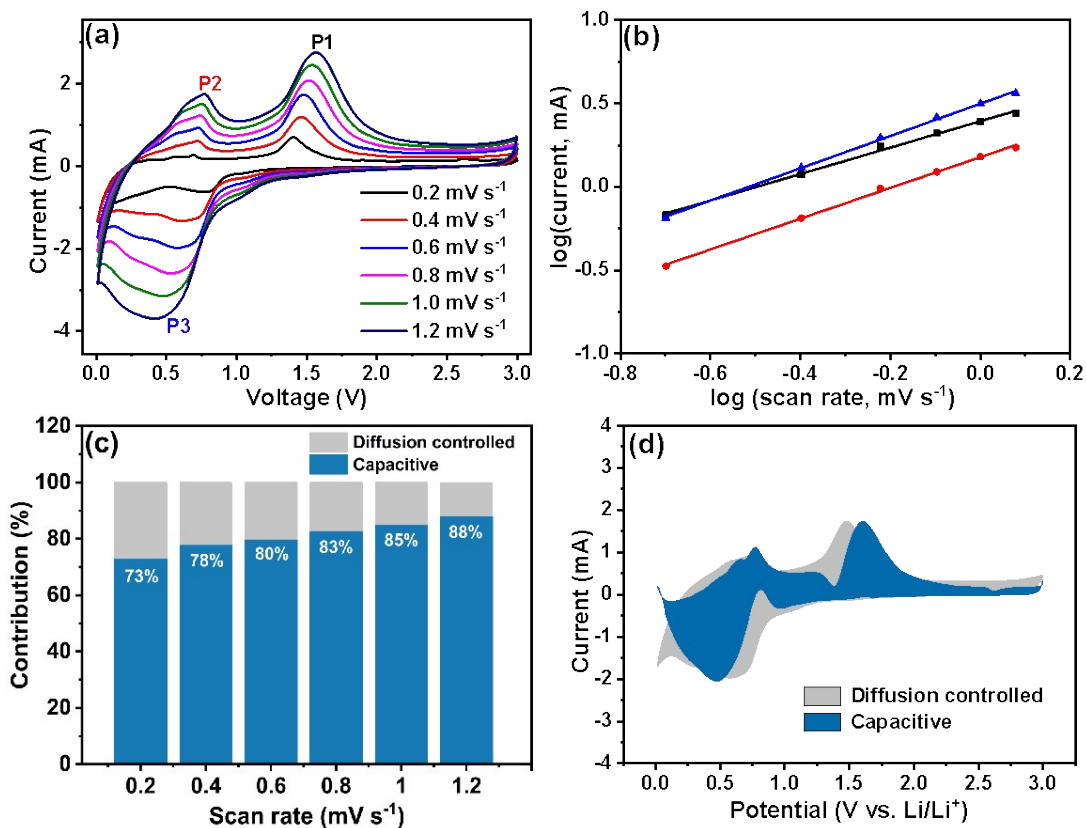
**Fig. S10** Cycling performance and coulombic efficiency in the voltage window of  $0.01 \sim 3.0 \text{ V}$  vs.  $\text{Li}/\text{Li}^+$  at  $200 \text{ mA g}^{-1}$  of (a) NC, (b) ZnS(12 h)/NC, (c) ZnS(24 h)/NC, (d) ZnS(48 h)/NC, (e) ZnS(84 h)/NC, and (f) ZnS(96 h)/NC.



**Fig. S11** Impedance spectrum as-prepared sample. (a) NC, (b) ZnS(12 h)/NC, (c) ZnS(24 h)/NC, (d) ZnS(48 h)/NC, (e) ZnS(72 h)/NC (inset: the plot of  $Z_{re}$  vs. the reciprocal root square of the low angular frequencies ( $\omega^{-1/2}$ )), (f) ZnS(84 h)/NC, (g) ZnS(96 h)/NC.



**Fig. S12** (a) SEM and (b) TEM images of the ZnS(72 h)/NC electrode after the cycles.



**Fig. S13** (a) CV curves of ZnS(72 h)/NC at different scan rates; (b) Determination of the  $b$ -value by plotting the linear relationship between  $\log(i)$  and  $\log(v)$ ; (c) Charge contribution ratios from capacitive and diffusion-controlled process at various scan rates; (d) Separation of the capacitive and diffusion-controlled currents at a scan rate of 0.6  $\text{mV s}^{-1}$ .



**Table S1** Electrochemical performances of ZnS-based anode materials for LIBs.

Materials	Specific capacity (mAh g <sup>-1</sup> )	Cycle number	Current density (mA g <sup>-1</sup> )	Reference
<b>ZnS(72 h)/NC</b>	<b>757</b>	<b>200</b>	<b>200</b>	<b>this work</b>
	<b>~500</b>	<b>1000</b>	<b>2000</b>	
ZnS-C/graphene	571	120	1000	S1
ZnS/graphene	570	200	200	S2
ZnS-rGO	776	100	100	S3
ZnS@NC	690	100	100	S4
ZnS/NPC	1067	200	100	S5
ZnS NR@HCP	840	300	600	S6
ZnS/C NPs	506	600	500	S7
ZnS-QDS@NC	506	300	840	S8
ZnS-C	530	600	100	S9
ZnS/C	570	150	100	S10
ZnS/C	741	300	100	S11
ZnS-C	868	300	1000	S12
ZnS/C	482	300	400	S13
ZnS/nano-cell	1134	100	500	S14
Zn-Co-S@N-C	668	300	1000	S15

**Table S2** Electrochemical impedance fitting parameters of ZnS(72 h)/NC.

Cycles	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$\sigma$ ( $\Omega$ S <sup>-1/2</sup> )	$D_{Li^+}$ (cm <sup>2</sup> s <sup>-1</sup> )
before test	7	93	179	$9.86 \times 10^{-13}$
after cycles	13	15	73	$5.9 \times 10^{-12}$

The diffusion coefficients ( $D$ ) of Li<sup>+</sup> ions can be calculated from the following formula of  $D = R^2 T^2 / (2A^2 n^4 F^4 C^2 \sigma^2)$  where  $A$  is the surface area of electrode,  $n$  is the number of electrons per molecule attending electronic transfer reaction,  $F$  is the Faraday constant,  $C$  is the concentration of Li<sup>+</sup> in the electrode,  $\sigma$  is the slope of the line  $Z' \sim \omega^{-1/2}$ ,  $R$  is the gas constant, and  $T$  is ambient temperature. The  $F$  and  $R$  values are 96500 C mol<sup>-1</sup> and 8.314 J K<sup>-1</sup> mol<sup>-1</sup>, respectively.

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