

1 Supporting Information for
2 **Alleviating polarization by designing ultrasmall Li₂S nanocrystals**
3 **encapsulated in N-rich carbon as a cathode material for high-capacity,**
4 **long-life Li-S batteries**

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18 **1. Experimental Section:**

19 **1.1 Materials preparation**

20 **The Nano Li₂S@NRC composites:**

21 Li₂S(Alfa Aesar, China), anhydrous ethanol(Sigma-Aldrich, China),PAN (Mw=150,000,
22 Sigma-Aldrich, China) were used as pristine materials. 200mg Li₂S were added into
23 10ml anhydrous ethanol to prepare the light yellow solution under stirring. Then
24 above-mentioned solution was slowly dropped into the PAN/DMF solution(20 mgml⁻¹
25 ¹).The mass ratio between Li₂S and PAN was 1:1.The mixed solution was heated at
26 150° C to evaporate the solvent in the argon atmosphere under stirring. The
27 resultant solid materials were stabilized at 280° C with a heating rate of 2° Cmin⁻¹,and
28 subsequently carbonized at 700° C for 1 hour with a heating rate of 5° Cmin⁻¹ in
29 argon atmosphere to finally obtain the Nano Li₂S@NRC cathode materials.

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31 **The Micro Li₂S@NRC composites:**

32 200mg commercial Li₂S were added into the PAN/DMF solution(20 mg ml⁻¹).The

1 mass ratio between Li_2S and PAN was 1:1. The solution was heated at 150°C to
2 evaporate the DMF solvent in the argon atmosphere under stirring. The resultant
3 solid materials were stabilized at 280°C with a heating rate of 2°Cmin^{-1} , and
4 subsequently carbonized at 700°C for 1 hour with a heating rate of 5°Cmin^{-1} in
5 argon atmosphere to finally obtain the micro- $\text{Li}_2\text{S}@$ NRC cathode materials.

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7 **The Micro- Li_2S :**

8 The commercial Li_2S power was purchased from Alfa Aesar, China.

9

10 **1.2 Characterization**

11 The as-prepared samples were characterized using a Scanning Electron Microscope
12 (SEM) (FEI Quanta 400 FEG). Transmission electron microscope (TEM) images were
13 recorded using a Tecnai G2 F20 S-TWIN equipped with energy dispersive X-ray
14 microanalysis (EDX) at 200 kV. XRD was recorded using a Bruker D8 diffractometer,
15 using $\text{Cu K}\alpha$ radiation. Sulfur content of the samples was analyzed using an elemental
16 analyzer (CHNS, Vario EL Cube, Elementar), and the vendor specified uncertainty of
17 the elemental analysis measurements is within $\pm 0.01\%$.

18

19 **1.3 Electrochemical measurement**

20 Due to the sensitivity of Li_2S to moisture, all the electrode preparation and cell
21 assembly procedures were carried out in an argon-filled glove box (H_2O and O_2
22 concentrations < 0.1 p.p.m). The nano- $\text{Li}_2\text{S}@$ NRC composites were grounded with
23 acetylene black (AB, Alfa Aesar, China) and polyvinylidene fluoride (PVDF) binder in a
24 weight ratio of 7: 2: 1 using a mortar and pestle, followed by dispersion in N-methyl-
25 2-pyrrolidinone (NMP, Alfa Aesar, China) to form a slurry. After 12 hours stirring, the
26 slurry was then coated onto aluminum foil using doctor blade and dried at 60°C in
27 vacuum to form the working electrode, and the mass loading of Li_2S was about 1.53
28 mg cm^{-2} . 2025-type coin cells were assembled using lithium foil as the counter
29 electrode. The cathode was separated from a lithium anode by a separator (Celgard

1 2400). The electrolyte used was 1M LiTFSI in a mixed solvent of DOL and DME at a
2 volume ratio of 1:1, containing 1wt% LiNO₃. Galvanostatic cycling tests of the coin
3 cells was conducted using Neware battery test system (Shenzhen Neware technology
4 Co., Ltd) at different rates between 1.5 and 2.8V after the first charge to 3.8V at 0.05
5 C in order to activate the Li₂S. Cyclic voltammograms (CV) were recorded with a coin
6 cell using an AutoLab electrochemical workstation (PGSTAT302N) at a scan rate of
7 0.1 mVs⁻¹. The AC impedance of freshly prepared cells was measured at the open
8 circuit potential (OCP), using an AutoLab electrochemical workstation (PGSTAT302N).
9 The AC testing voltage amplitude was ±5 mV, and the frequency ranged from 100
10 kHz to 0.1 Hz.

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12 2. Supplemental figures and tables

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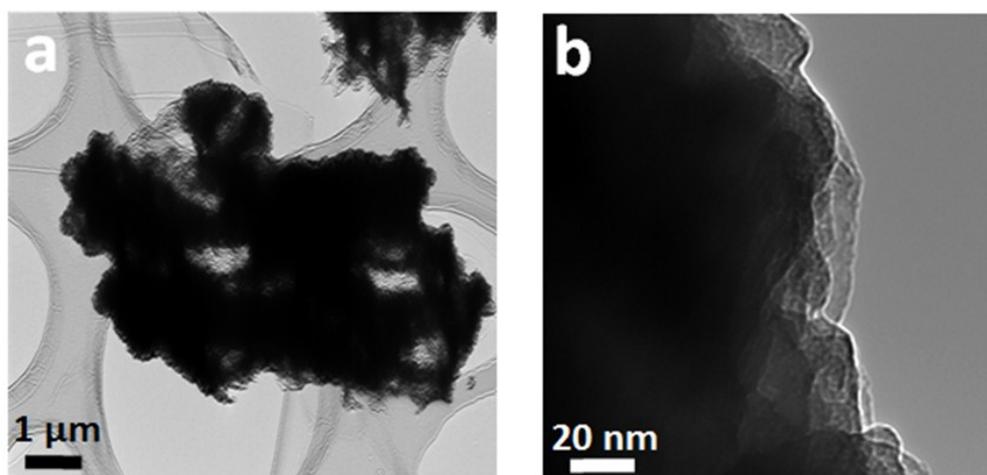
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Table S1. Elemental analysis of Nano-Li₂S@NRC materials

Element	Li	S	C	H	N
Wt%/element	--	44.38	28.37	0.71	7.93
Wt%/composition	62.99(Li ₂ S)		37.01 (NRC)		

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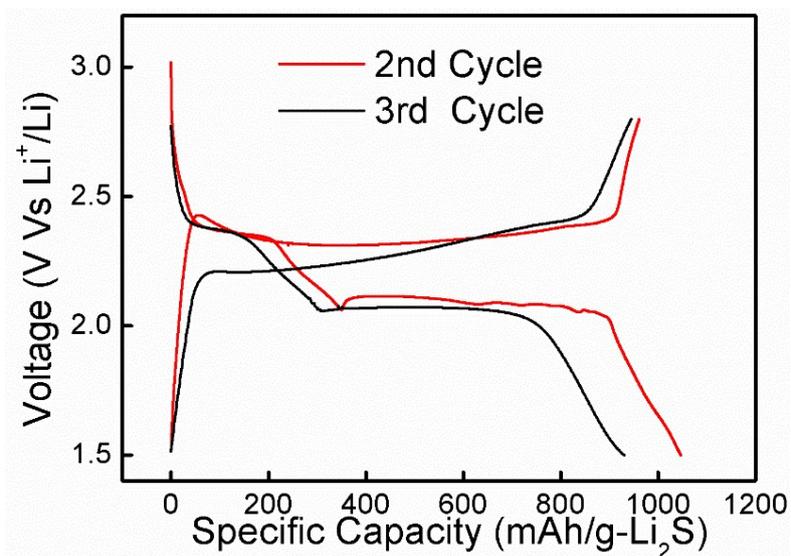
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18 Figure S1.(a-b). The TEM photograph of micro-Li₂S@NRC material with
19 different resolution

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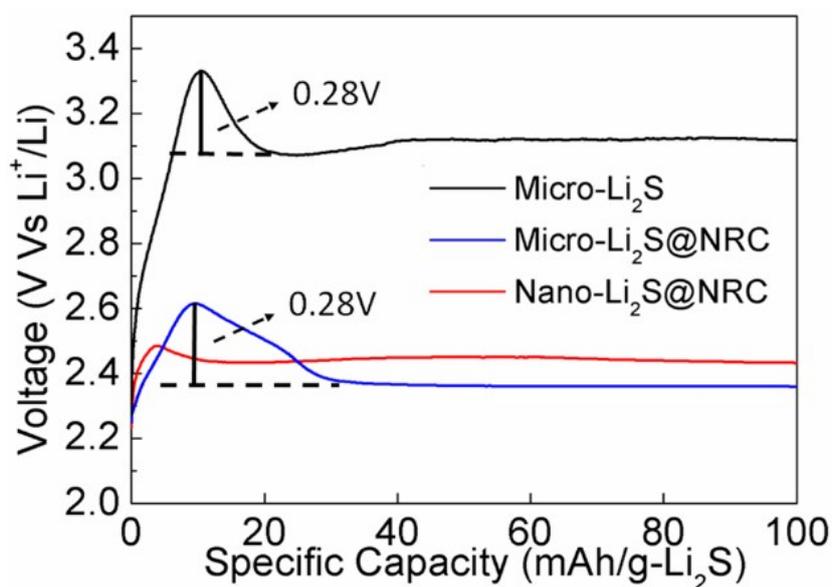
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4 Figure S2. The charge/discharge profile of nano-Li₂S@NRC cathode at 0.25C.

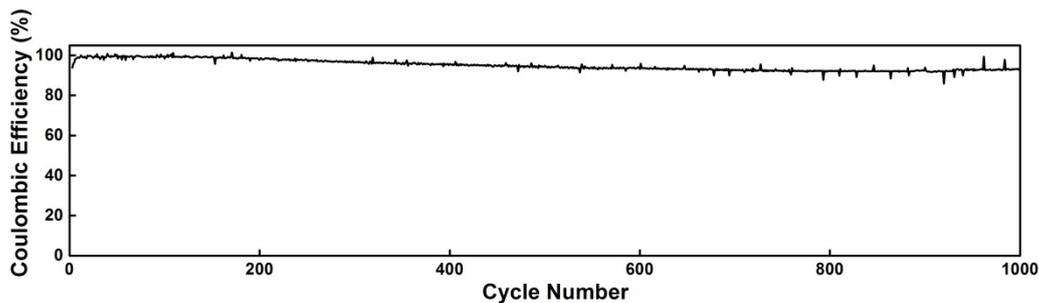
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7 Figure S3. The first charge curves of micro-Li₂S, micro-Li₂S@NRC and nano-
8 Li₂S@NRC cathodes at 0.05C in the narrow region.

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Figure. S4 The Coulombic efficiency of the nano-Li₂S@NRC cathode at 0.5 C.

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Table S2. Comparison of electrochemical performance of previous works

Cathodes	Initial capacity (mAh/g)	Current density	Cycle number	Stable capacity after cycle	Decay rate per cycle	ref
Li ₂ S/HNG	1190	1C	500	689	0.084%	1
Nano-cluster Li ₂ S	1186	0.1C	50	919	0.43%	2
Nano Li ₂ S/rGO	1288	0.5C	145	994	0.15%	3
Meso-Li ₂ S/C	1149	0.5C	100	732	0.365%	4
Porous Li ₂ S@C	971	0.08C	200	622	0.179%	5
Li ₂ S/ pyrrole	1478	0.2C	100	936	0.36%	6
Nano Li ₂ S@NRC	1503	0.25C	100	1107	0.26%	This work
pPAN-S/GN	1376	0.5C	500	811	0.041%	
	1500	0.1C	50	1000	0.66%	7

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Note: the capacity of Li₂S-based cathode is calculated base on sulfur.

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