

## Supporting Information

### An Integrated Na<sub>2</sub>S–Electrocatalyst Nanostructured Cathode for Sodium–Sulfur Batteries at Room Temperature

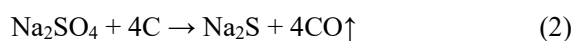
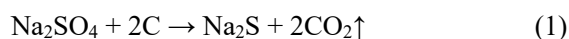
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#### Determination of Na<sub>2</sub>S-loading in the composite:

The Na<sub>2</sub>S loading in the composite was calculated on the basis of the work of M. Kohl [1]. At the chosen temperatures for carbothermal reduction, the reaction of sodium sulfate results in sodium sulfide, carbon dioxide and carbon monoxide.



The Na<sub>2</sub>S loading in the composite after carbothermal reduction therefore was calculated with 60.5 wt. % (1) and 75.8 wt. % (2) via the molar masses and used mass of Na<sub>2</sub>SO<sub>4</sub> and carbon. So the Na<sub>2</sub>S loading in the composite was between 60.5 wt. % and 75.8 wt. % according to the reaction stated above.

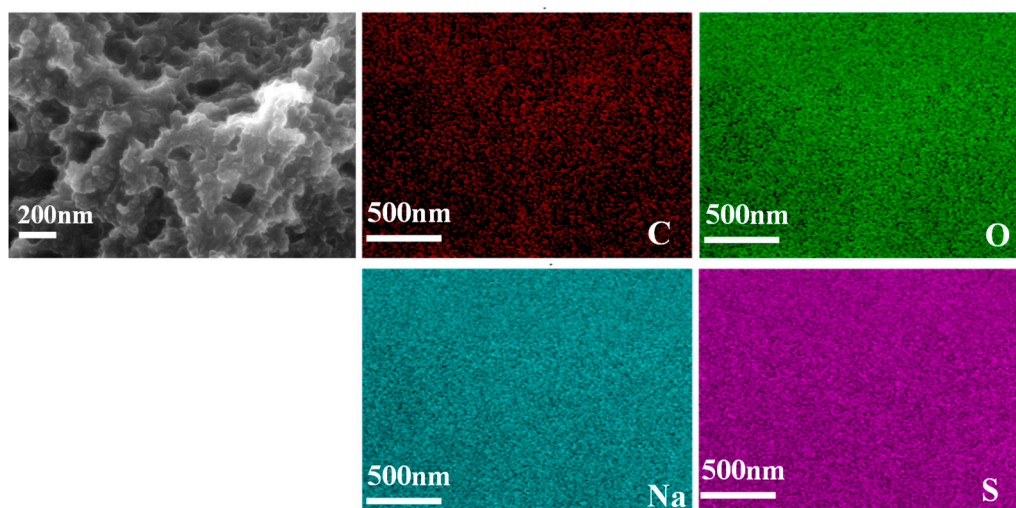


Figure S1. SEM images and corresponding elemental mapping of Na<sub>2</sub>S@C.

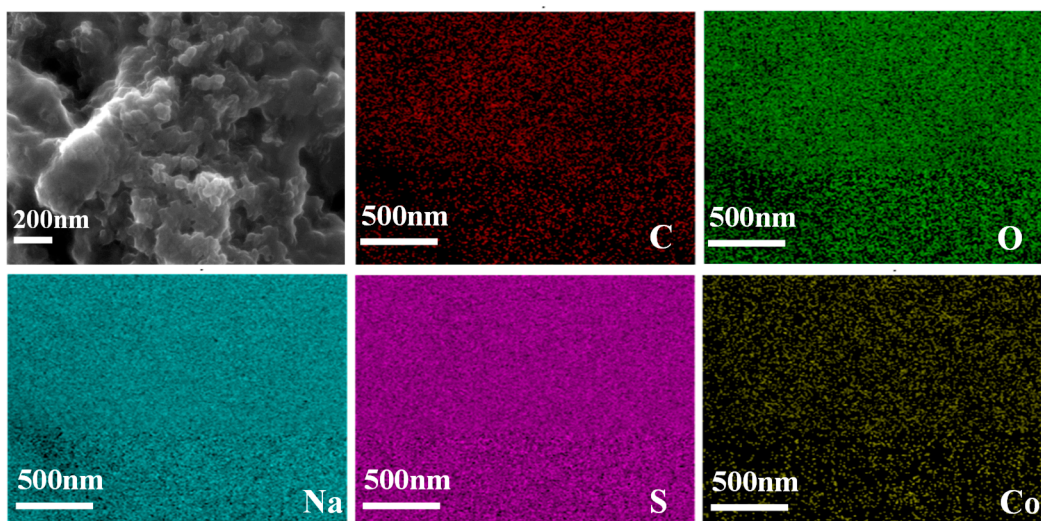


Figure S2. SEM images and corresponding elemental mapping of  $\text{Na}_2\text{S-Na}_6\text{CoS}_4/\text{Co}@\text{C}$ .

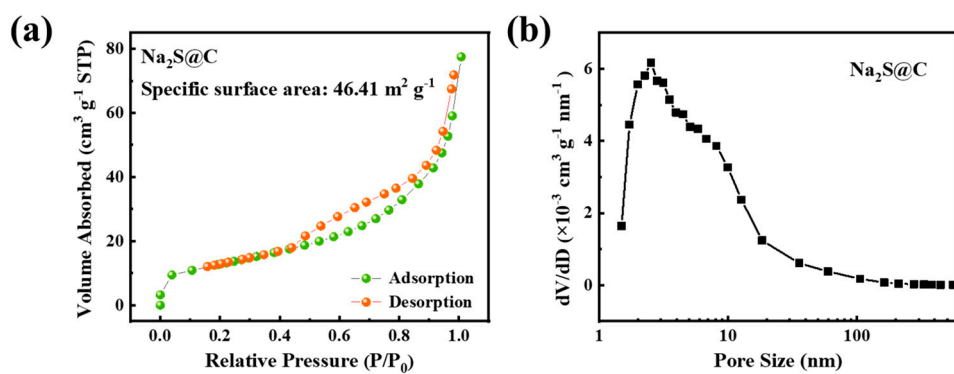


Figure S3. (a)  $\text{N}_2$  adsorption-desorption isotherm of  $\text{Na}_2\text{S}@\text{C}$ . (f) Pore size distribution of  $\text{Na}_2\text{S}@\text{C}$ .

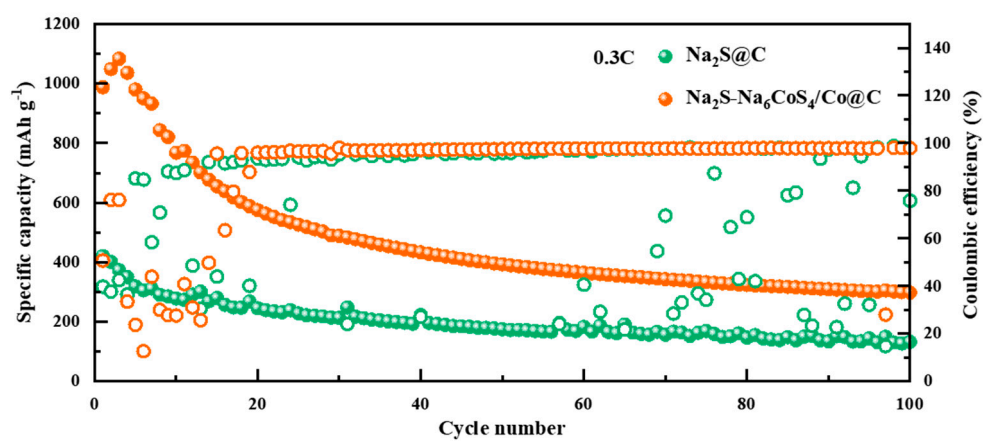


Figure S4. Cycling stability of  $\text{Na}_2\text{S}@\text{C}$  and  $\text{Na}_2\text{S-Na}_6\text{CoS}_4/\text{Co}@\text{C}$  at 0.3 C rate.

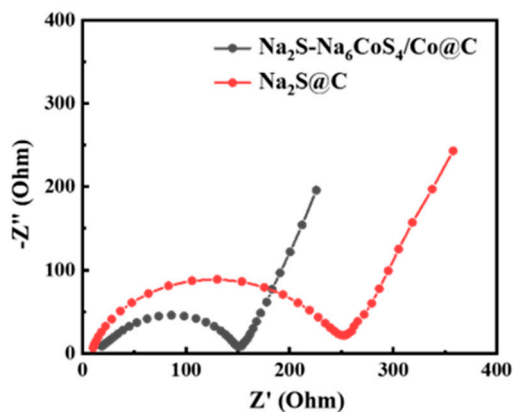


Figure S5. EIS analysis of Na<sub>2</sub>S@C and Na<sub>2</sub>S-Na<sub>6</sub>CoS<sub>4</sub>/Co@C after 100 cycles.

Table S1. Impedance parameters for Na<sub>2</sub>S-Na<sub>6</sub>CoS<sub>4</sub>/Co@C and Na<sub>2</sub>S@C cathodes after 100 cycles state simulated from the equivalent circuits.

| Cathode  | R <sub>s</sub> (Ω) | R <sub>ct</sub> (Ω) |
|--|--------------------|---------------------|
| Na <sub>2</sub> S-Na <sub>6</sub> CoS <sub>4</sub> /Co@C | 22.35              | 101.1               |
| Na <sub>2</sub> S@C                                      | 11.46              | 183.1               |

Table S2. A comparison of Na<sub>2</sub>S-Na<sub>6</sub>CoS<sub>4</sub>/Co@C cathode with reported Na<sub>2</sub>S-based cathodes in electrochemical performance

| Cathode                                | Anode                   | Electrolyte  | Rate (C)/Retention capacity (mAh·g <sup>-1</sup> )/Cycles | Energy density (Wh kg <sup>-1</sup> ) | Ref |
|--|-------------------------|--|---|---------------------------------------|-----|
| Na <sub>2</sub> S@MWCNT                | Na foil                 | 1.5M NaClO <sub>4</sub> and 0.3M NaNO <sub>3</sub> in TEGDME                         | 0.1/50/560<br>0.3/50/380                                  | ~ 250                                 | S2  |
| Hollow nano-Na <sub>2</sub> S          | Prepassivation Na metal | 1M NaPF <sub>6</sub> in DME/DOL with Na <sub>2</sub> S/P <sub>2</sub> S <sub>5</sub> | 0.84/100/600<br>1.26/100/400                              | /                                     | S3  |
| Na <sub>2</sub> S@C                    | Hard Carbon             | 1M NaClO <sub>4</sub> in TEGDME with 1vol % FEC                                      | 0.2/—/350   | /                                     | S4  |
| Na <sub>2</sub> S@C                    | Carbon paper            | 1M NaCF <sub>3</sub> SO <sub>3</sub> in DIGLYME with 5 % FEC                         | 0.5/500/174   | 230                                   | S5  |
| Na <sub>2</sub> S/Na <sub>2</sub> Te@C | Na foil                 | 1 M NaFSI in 1.2 M DME and 1 M TTE   | 0.1/150/590<br>1/700/526                                  | /                                     | S6  |

|  |         |  |                            |   |           |
|--|---------|--|----------------------------|---|-----------|
| Na <sub>2</sub> S–Na <sub>6</sub> CoS <sub>4</sub> /Co@C | Na foil | 1M NaCF <sub>3</sub> SO <sub>3</sub> in DIGLYME with 5wt % FEC | 0.1/100/346<br>0.3/100/298 | / | This work |
|--|---------|--|----------------------------|---|-----------|

## References

- [1] Kohl, M.; Brückner, J.; Bauer, I.; Althues, H.; Kaskel, S. Synthesis of highly electrochemically active Li<sub>2</sub>S nanoparticles for lithium–sulfur-batteries. *J. Mater. Chem. A* **2015**, 3, 16307–16312.
- [2] Yu, X.; Manthiram, A. Na<sub>2</sub>S–Carbon Nanotube Fabric Electrodes for Room-Temperature Sodium–Sulfur Batteries. *Chem. Eur. J.* **2015**, 21, 4233 – 4237.
- [3] Wang, C.; Wang, H.; Hu, X.; Matios, E.; Luo, J.; Zhang, Y.; Lu, X.; Li, W. Frogspawn-Coral-Like Hollow Sodium Sulfide Nanostructured Cathode for High-Rate Performance Sodium-Sulfur Batteries. *Adv. Energy Mater.* **2019**, 9, 1803251.
- [4] Bloi, L.; Pampel, J.; Dörfler, S.; Althues, H.; Kaskel, S. Sodium Sulfide Cathodes Superseding Hard Carbon Pre-sodiation for the Production and Operation of Sodium–Sulfur Batteries at Room Temperature. *Adv. Energy Mater.* **2020**, 10, 1903245.
- [5] Geng, M.; Han, D.; Huang, Z.; Wang, S.; Xiao, M.; Zhang, S.; Sun, L.; Huang, S.; Meng, Y. A stable anode-free Na-S full cell at room temperature. *Energy Storage Mater.* **2022**, 52, 230–237.
- [6] Gao, W.; Su, L.; Yu, Y.; Lu, Y.; Liu, X.; Peng, Y.; Xiong, X.; He, J.; Chen, Y.; Wu, Y. Stable Dendrite-Free Room Temperature Sodium-Sulfur Batteries Enabled by a Novel Sodium Thiotellurate Interface. *Angew Chem. Int. Ed.* **2024**, e202412287.