Electronic Supplementary Information

Carbon-coated ReS_2 hierarchical nanospheres to inhibit polysulfide dissolution in ether-based electrolytes for high-performance Na-ion batteries

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Experimental section

Preparation of ReS_2 nanospheres: The ReS_2 nanospheres were prepared using a hydrothermal method. In a typical procedure, 0.5 mmol of ammonium perrhenate (NH_4ReO_4, AR 99.99%) and 2.0 mmol of thioacetamide (TAA, CH_3CSNH_2, AR 99%) were dissolved in 35 mL deionized water in a 50 mL Teflon-lined stainless steel autoclave. The autoclave was then sealed and maintained at 180 °C for 24 h. After cooled down to room temperature naturally, the black precipitates were collected by centrifugation, washed with deionized water and ethanol several times, and dried in vacuum at 50 °C.

Preparation of ReS_2/C nanospheres: The as-prepared ReS_2 nanospheres (80 mg) and glucose ($C_6H_{12}O_6 \cdot H_2O$) (80 mg) powders were added in absolute ethanol (5 mL). The mixture was ultrasonicated and magnetically stirred. The mixed ReS_2 and glucose were then collected by centrifugation and dried in vacuum at 50 °C. Finally, the ReS_2/C composite nanospheres were obtained by heating the dried ReS_2 and glucose mixture at 600 °C for 2 h in a chemical vapor deposition furnace at a heating rate of 5 °C/min.

Materials Characterization: Morphologies, structures and elemental analysis of the various samples were performed on field emission scanning electron microscope (SEM, ZEISS Gemini 500), transmission electron microscope (TEM, JEOL JEM-2100F, 200 kV) equipped with energy dispersive X-ray spectroscopy (EDS) capability. Crystal phases were characterized by X-ray diffraction (XRD, X-Pert PRO

MPD diffractometer, Cu Kα radiation). Carbon content was measured on an elemental analyzer (Elementar vario EL cube). Chemical bonding states were investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi). Raman spectroscopy was recorded on a confocal micro-Raman system (LabRAM HR Evolution) at 532 nm excitation.

Coin-cell Fabrication and Electrochemical Measurements: To prepare the working electrodes, the as-prepared ReS_2/C (or ReS_2 nanospheres) were mixed with acetylene black (AB) and sodium carboxymethyl cellulose (CMC) with a weight ratio of 6: 2: 2. The mixture with addition of deionized water was then ground into a slurry, which was coated on the copper foil and dried at 80 °C for 12 h in the vacuum oven. The electrode discs with a diameter of 12 mm were punched. The electrochemical performance was investigated by assembling CR2032 coin cells in an argon-filled glove box. The electrolyte was selected by dissolving $NaPF_6$ in diethylene glycol dimethyl ether (DEGDME) with a concentration of 1.0 mol/L. For comparison, 1.0 mol/L $NaClO_4$ or $NaPF_6$ solutions in the ethylene carbonate (EC) and propylene carbonate (PC) (1:1 in volume) were also used as the electrolyte. For half-cell fabrication, sodium metal foil served as the counter electrode, and glass microfiber (Whatman) worked as the separator. The discharge/charge behaviors were measured using the Neware system (5 V 10 mA or 5 V 50 mA). A CHI660E electrochemical workstation was employed to measure the cyclic voltammetry (CV) curves (0.01-3.0 V) and electrochemical impedance spectroscopy in frequency range of 0.1 Hz to 100 kHz.

Full-cell fabrication and electrochemical measurements: For full-cell fabrication, the ReS_2/C anode was firstly discharged and charged for 5 cycles in a half-cell at 0.1 A/g during the pre-sodiation process. The commercial $Na_3V_2(PO_4)_3$ was chosen as the cathode material. $Na_3V_2(PO_4)_3$, AB, and polyvinylidene difluoride (PVDF) were mixed at a weight ratio of 7:2:1 to make a slurry and then coated on an Al foil current collector to fabricate the $Na_3V_2(PO_4)_3$ cathode. The electrode discs with a diameter of 12 mm were punched. The electrolyte of 1.0 mol/L $NaPF_6$ in DEGDME was employed. The active material loading of the $Na_3V_2(PO_4)_3$ cathode was 0.93 mg cm^{-2}, and the active material loading of the ReS_2/C anode was 1.13 mg cm^{-2}. The weight ratio of $Na_3V_2(PO_4)_3$:ReS_2/C was approximately 0.82:1. The voltage window was set in the range of 1.0–3.8 V for testing electrochemical performance of the full cells.

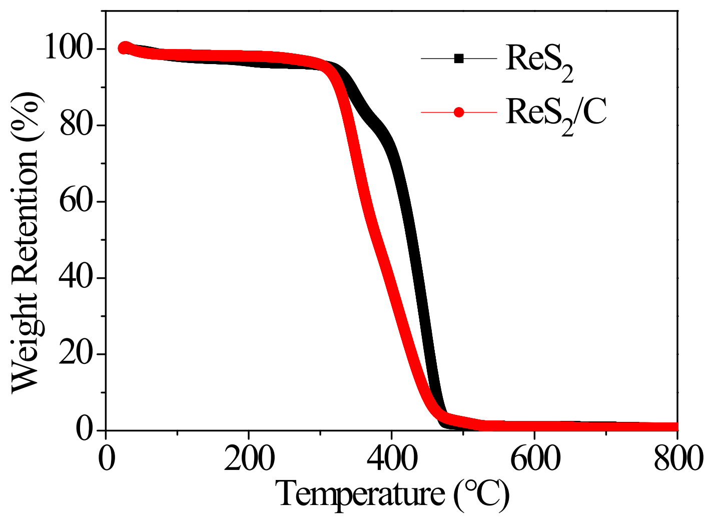

Fig. S1 TG curves of the ReS_2/C and ReS_2 samples tested in air atmosphere.

TG analysis was applied to evaluate the C content of ReS_2/C and ReS_2 samples. The two samples were tested in the temperature ranging from 30 to 800 °C with a heating rate of 10 °C min^{-1} in air atmosphere as shown in **Fig. S1**. However, it fails to calculate C content using the TG analysis. Upon heating, ReS_2 can be oxidized to form Re_2O_7 that has a low boiling point of 360 °C. Therefore, the resulting Re_2O_7 converted from ReS_2 will be completely evaporated during the heating process.

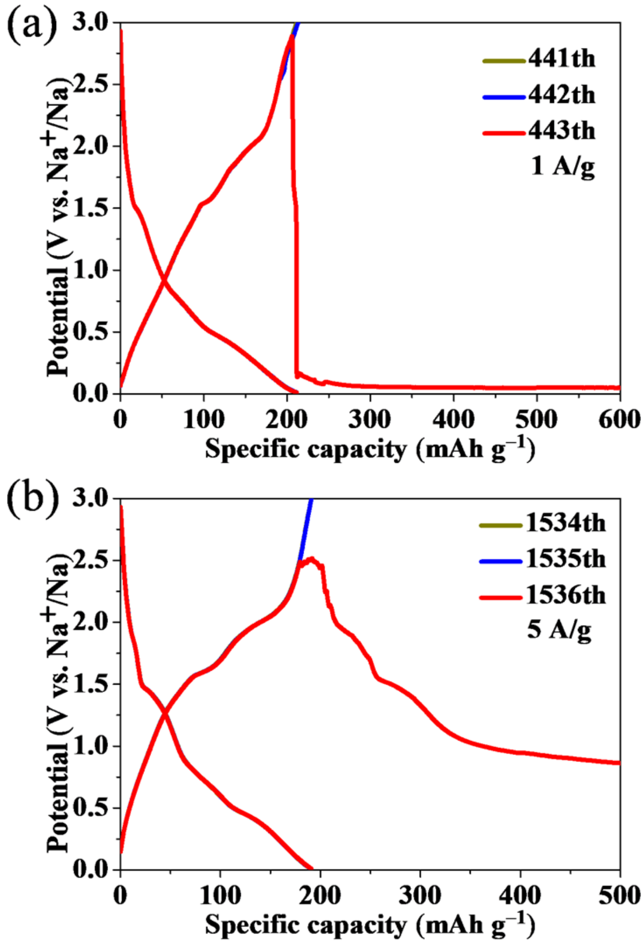

Fig. S2 The last three discharge/charge curves of the ReS_2 nanospheres for long-term cycling at different current densities.

Table S1 Recent advances of ReS_2-based anodes for sodium storage performance.

Anodes	Cycling performance	Rate performances	Potential windows	Electrolyte	Ref.
ReS_2@C	0.2 A/g 400 cycles	388 mAh/g (0.1 A/g) 225 mAh/g (2 A/g)	0.01-3 V	N/A	[1]
ReS_2/N-CNFs	245 mAh/g at 0.1 A/g after 800 cycles	N/A	0.01-3 V	$NaSO_3CF_3$ in diglyme	[2]
ReS_2/C Nanocomposite	~100 mAh/g at 2 A/g after 600 cycles	365 mAh/g (0.1 A/g) 145 mAh/g (2 A/g)	0.01-2.5 V	$NaPF_6$ in EC/DEC	[3]
v-ReS_2/rGO	375 mAh/g at 0.1 A/g after 100 cycles	376 mAh/g (0.2 A/g) 255 mAh/g (5 A/g)	0.01-3 V	$NaClO_4$ in EC/DEC	[4]
1D TiO_2@ReS_2	118 mAh/g at 1A/g after 1000 cycles	304 mAh/g (0.1 A/g) 195 mAh/g (5 A/g)	0.01-3 V	$NaClO_4$ in EC/DEC	[5]
rGO@ReS_2@N-C	192 mAh/g at 2 A/g after 4000 cycles	392 mAh/g (0.2 A/g) 231 mAh/g (10 A/g)	0.01-3 V	$NaClO_4$ in EC/DEC	[6]
$NiCoS_4$@ReS_2	396 mAh/g at 1 A/g after 500 cycles	297 mAh/g (3 A/g)	0.01-3 V	$NaPF_6$ in EC/DEC	[7]
MXene@ReS_2@C	202 mAh/g at 2 A/g after 200 cycles	323 mAh/g (0.1 A/g) 233 mAh/g (1 A/g) 138 mAh/g (5 A/g)	0.01-3 V	$NaClO_4$ in EC/DEC	[8]
ReS_2/C Nanospheres	210 mAh/g at 10 A/g after 3000 cycles	426 mAh/g (0.2 A/g) 386 mAh/g (1 A/g) 281 mAh/g (5 A/g) 241 mAh/g (10 A/g) 185 mAh/g (20 A/g)	0.01-3 V	$NaPF_6$ in DEGDME	This work

References:

[1] X. Zhang, C. Shen, H. Wu, Y. Han, X. Wu. W. Ding, L. Ni, G. Diao and M. Chen, Filling few-layer ReS_2 in hollow mesoporous carbon spheres for boosted lithium/sodium storage properties. *Energy Storage Mater.*, 2020, **26**, 457-464.

[2] M. Mao, C. Cui, M. Wu, M. Zhang, T. Gao, X. Fan, J. Chen, T. Wang, J. Ma and C. Wang, Flexible ReS_2 nanosheets/N-doped carbon nanofibers-based paper as a

universal anode for alkali (Li, Na, K) ion battery. *Nano Energy*, 2018, **45**, 346-352.

[3] Y. Von Lim, S. Huang, Q. Wu, Y. Zhang, D. Kong, Y. Wang, T. Xu, Y. Shi, Q. Ge, L. K. Ang and H. Y. Yang, Rhenium disulfide nanosheets/carbon composite as novel anodes for high-rate and long lifespan sodium-ion batteries. *Nano Energy*, 2019, **61**, 626-636.

[4] S. Liu, Y. Liu, W. Lei, X. Zhou, K. Xu, Q. Qiao and W.-H. Zhang, Few-layered ReS_2 nanosheets vertically aligned on reduced graphene oxide for superior lithium and sodium storage. *J. Mater. Chem. A*, 2018, **6**, 20267-20276.

[5] X. Wang, B. Chen, J. Mao, J. Sha, L. Ma, N. Zhao and F. He, Boosting the stable sodium-ion storage performance by tailoring the 1D TiO_2@ReS_2 core-shell heterostructures. Electrochim. Acta., 2020, **338**, 135695.

[6] B. Chen, H. Li, H. Liu, X. Wang, F. Xie, Y. Deng, W. Hu, K. Davey, N. Zhao and S. Z. Qiao, 1T′-ReS_2 Confined in 2D-Honeycombed Carbon Nanosheets as New Anode Materials for High-Performance Sodium-Ion Batteries. *Adv. Energy Mater.*, 2019, **9**, 1901146.

[7] Z. Li, R. Sun, Z. Qin, X. Liu, C. Wang, S. Lu, Y. Zhang and H. Fan, Coupling of ReS_2 nanosheet arrays with hollow $NiCoS_4$ nanocubes enables ultrafast Na^+ diffusion kinetics and super Na^+ storage of a $NiCoS_4$@ReS_2 heterostructure. *Mater. Chem. Front.*, 2021, **5**, 7540-7547.

[8] X. Liu, M. Wang, B. Qin, Y. Zhang, Z. Liu and H. Fan, 2D-2D MXene/ReS_2 hybrid from $Ti_3C_2T_x$ MXene conductive layers supporting ultrathin ReS_2 nanosheets for superior sodium storage. *Chem. Eng. J.*, 2022, **431**, 133796.