Electronic Supplementary Information (ESI)

Gallate-MOF derived CoS_2/C composites as an accelerated catalyst for room-temperature sodium−sulfur batteries

Qiuyang Ma,[a,b] Jing Ai, [a,b] Haoda Zou, [a,b] Hengli He, [a,b] Zhongyuan Li, [a,b] Jawayria Mujtaba, [*a,b] and Zhen Fang[*a,b,c]

[a] College of Chemistry and Materials Science, Key Laboratory of Electrochemical Clean Energy of Anhui Higher Education Institutes, Anhui Normal University, Wuhu 241000, PR China

[b] Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Normal University, Wuhu 241000, PR China

[c] Anhui Provincial Engineering Laboratory for New-Energy Vehicle Battery Energy-Storage Materials, Wuhu 241000, PR China

[*] Corresponding authors: fzfscn@mail.ahnu.edu.cn; jawayria.m@icloud.com

Synthesis of Co-gallate precursor: 1.36 g gallic acid ($C_7H_6O_5$) was dissolved in solvents consist of 10 mL anhydrous ethanol solution under with vigorous stirring at room temperature. After 10 mins, 10 mL 0.05 M KOH was added and stirred vigorously. Then, 0.0364 g hexadecyl trimethyl ammonium bromide (CTAB) and 0.952 g $CoCl_2.6H_2O$ was separately dissolved into the above uniform solution to form a clear pink solution under stirring. Subsequently, 10 mL ethylene glycol solution was injected into the suspension under stirring for 10 min. Finally, the mixture solution was sealed in a 50 mL Teflon-lined stainless-steel and heated at 160℃ for 12 h. After that, the obtained Co-gallate sample was washed with alcohol/distilled water, dried under 60°C overnight.

Synthesis of the microprisms CoS_2/C Materials: Typically, for the CoS_2/C composite fabrication, 100 mg Co-gallate and 1 g sulfur powder were put at each end of a quartz boat, and then heated at 600°C for 2 h under N_2 atmosphere flow. The black product is denoted as CoS_2/C.

Synthesis of the C Materials: The contrast sample was synthesized by carbonizing gallic acid directly and named as C.

Synthesis of the microprisms Co_3O_4/C Materials: Typically, for the Co_3O_4/C composite fabrication, 100 mg Co-gallate powder were putted at a quartz boat, and then heated at 400°C for 2 h under N_2 atmosphere flow. The black products were denoted as Co_3O_4/C.

Synthesis of the microprisms $CoSe_2$/C Materials: Typically, for the $CoSe_2$/C composite fabrication, 100 mg Co-gallate and 300 mg selenium powder were putted at each end of a quartz boat, and then heated at 500°C for 2 h under H_2/Ar atmosphere flow. The black products were denoted as $CoSe_2$/C.

Synthesis of S@CoS_2/C, S@Co_3O_4/C, S@$CoSe_2$/C and S@C Composites. The as-prepared composites (CoS_2/C, Co_3O_4/C, $CoSe_2$/C and C) and sulfur were mixed in a certain weight ratio and transferred to a tube furnace. The mixture was heated at 155°C for 12 h, then heated at 200°C for 30 min to eliminate the surface sulfur. The products were denoted as S@CoS_2/C, S@Co_3O_4/C, S@$CoSe_2$/C and S@C.

Materials Characterization. The phases of the as-prepared composites were

investigated by X-ray diffraction (XRD, Bruker D8). The morphologies and structure of products were characterized by Scanning electron microscopy (SEM, Hitachi 8100), transmission electron microscopy (TEM, Hitachi HT7700) and high-resolution (HR)-TEM imaging (HRTEM, Hitachi H-9500). Raman spectroscopy were collected on a Renishaw InVia (532 nm laser) and X-ray photoelectron spectroscopy (XPS) spectra data were tested on a Thermo ESCALAB250Xi spectrometer. Thermogravimetric analysis (TGA, Mettler Toledo TGA-2) can test the sulfur contents. The BET surface areas and textural properties were achieved using a Quantachrome Instruments (USA).

Electrochemical Measurements. The 70 wt% active materials (S@CoS_2/C, S@Co_3O_4/C, S@$CoSe_2$/C and S@C), 20 wt% acetylene black and 10 wt% carboxymethyl Cellulose (CMC) were homogenized mixed in water to form a slurry, and casted on the carbon coated Cu foil, then dried at 60 °C for 12 h under vacuum. In the following step, the electrodes were catted into circular disks with a diameter of 12 mm, and the average mass loading was up to 2 mg cm^{-2}. The coin cells were assembled in an Ar-filled glovebox by using active sulfur as the cathode, Na metal as the counter electrode and glass fiber (GF/D, Whatman) as separator. The electrolyte for RT Na-S batteries was 1 M $NaSO_3CF_3$ dissolved in diethylene glycol dimethyl ether (DEGDME). The galvanostatically charged-discharge experiments were tested on Neware Battery system. Cyclic voltammetry (CV, 0.1 mV s^{-1} sweep rate over the range 0.8–2.8 V) and electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (CHI 660E).

Preparation of Na_2S_6 Solution and Adsorption Test. Sulfur and Na_2S (molar ratio 5:1) were mixed in DEGDME and stirred continuously for 12 h at 80 ℃ until all solids were completely dissolved to obtain a dark yellowish black Na_2S_6 solution. For the polysulfide adsorption test, 20 mg of CoS_2/C or C powder was added into Na_2S_6 solution and kept for 6 h. All the steps were completed in the glovebox. The supernatant was analyzed by UV-vis absorption spectrum.

Symmetric-cell assembly. The electrode was prepared by mixing active materials (CoS_2/C or C) and CMC with a weight ratio of 9:1 in water, and casted on the carbon

coated Cu foil. Two identical electrodes were used as working and counter electrodes, and 25 μL 0.2 M Na_2S_6 was the electrolyte. The cyclic voltammetry measurements of the symmetric cells were performed within a voltage window between -1.0 and 1.0 V with a scan rate of 50 mV s^{-1}.

Catalytic Effect Evaluation. Sulfur and Na_2S (molar ratio 7:1) were mixed in DEGDME and stirred continuously for 12 h at 80 ℃ until all solids were completely dissolved to obtain Na_2S_8 solution. Nucleation and dissolution measurements of Na_2S were performed with 0.2 M Na_2S_8 2032 coin-type cells, which were assembled with the electrode containing 90 wt % of the active material (CoS_2/C or C) and 10 wt% of CMC. 25 μL of 0.2 M Na_2S_8 was dropped on the cathode, and 25 μL of DEGDME electrolyte was added to the anode side (Na metal).

The Tafel plots were conducted for the cells with the electrodes (CoS_2/C or C) as working electrodes, Na foils as counter electrodes, 25 μL Na_2S_6 electrolyte, scanning rate of 2 mV s^{-1}, and the voltage range from 0.8−2.8 V. The exchange current density was obtained by the manually fitted for the linear region of the semi-logarithmic Tafel plot according to the Bulter-Volmer equation.

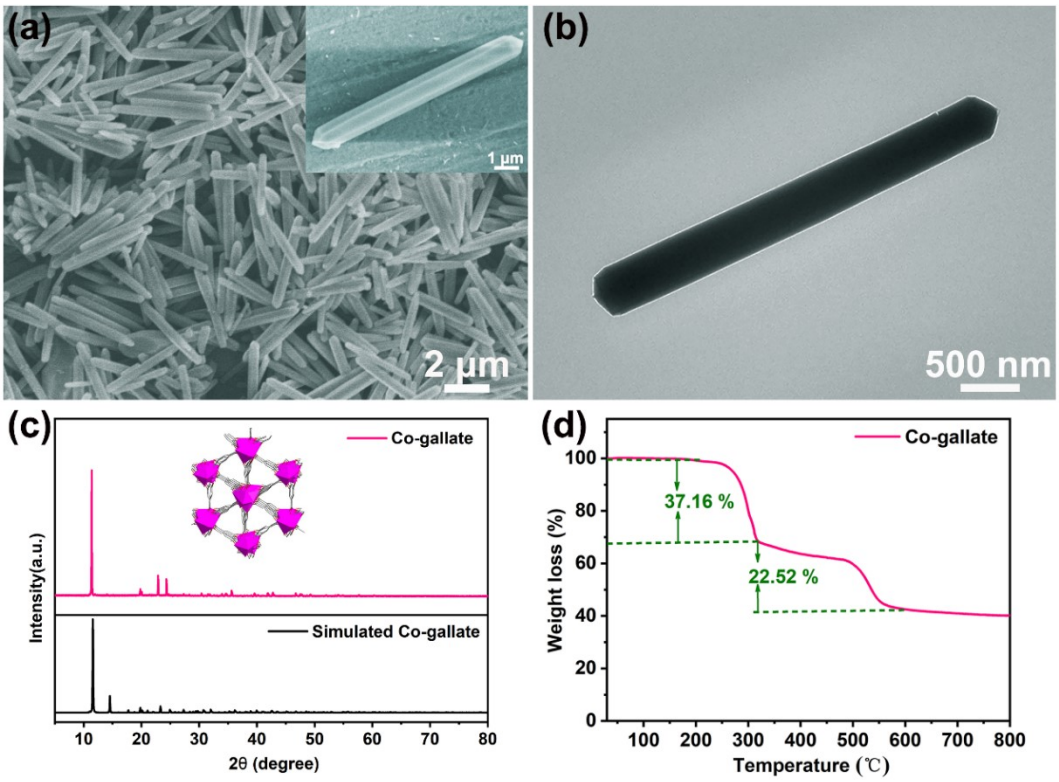

Fig. S1. SEM (a) and TEM (b) images of Co-gallate. (c) XRD patterns of Co-gallate.

(d) TGA curve of Co-gallate treated in N_2 with a heating rate of 10 ℃ min^{-1}.

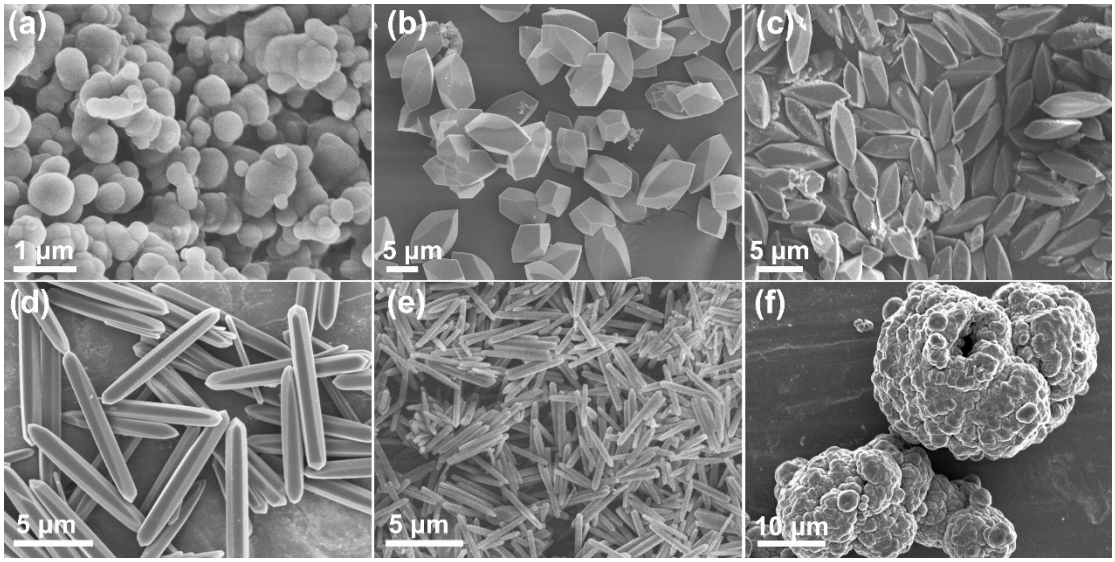

Fig. S2. SEM images of Co-gallate after the hydrothermal reaction in different solutions (a) KOH, (b) KOH + anhydrous ethanol and (c) KOH + anhydrous ethanol +ethylene glycol and at different reaction temperatures (d) 120 ºC (e) 160 ºC and (f) 200 ºC for 12 h.

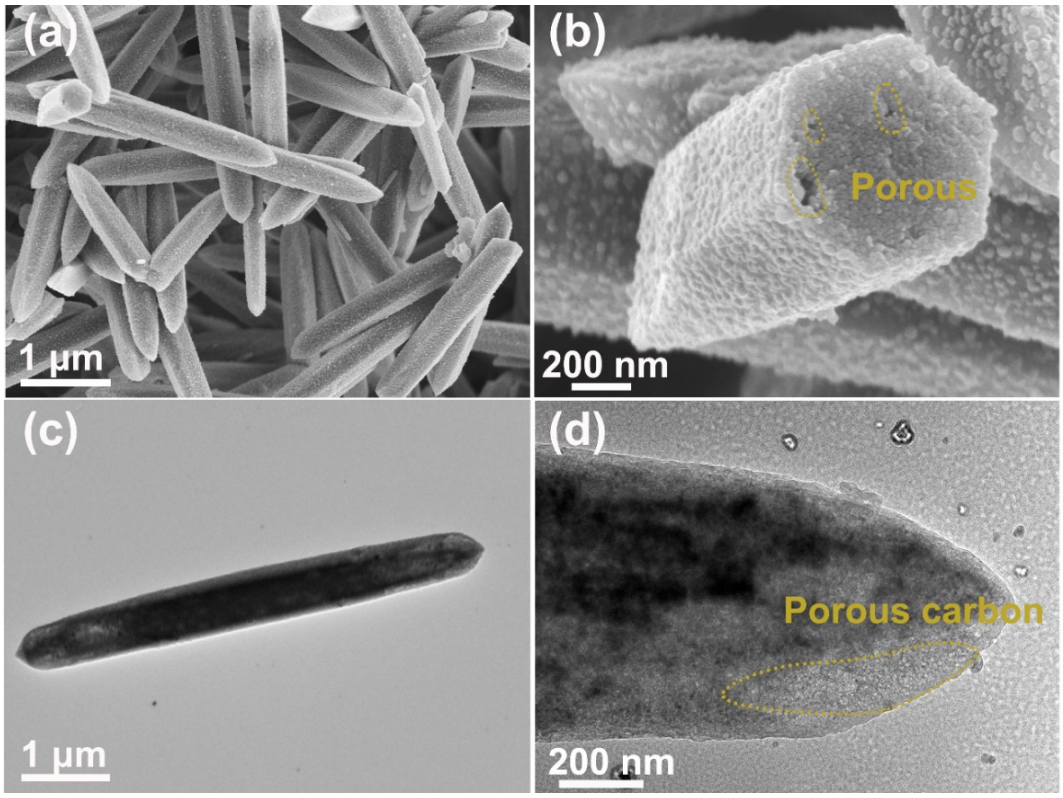

Fig. S3. SEM (a, b) and TEM (c, d) images of CoS_2/C.

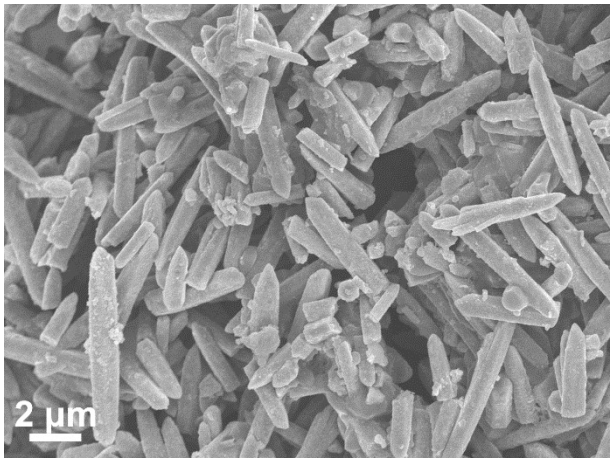

Fig. S4. SEM image of S@CoS_2/C.

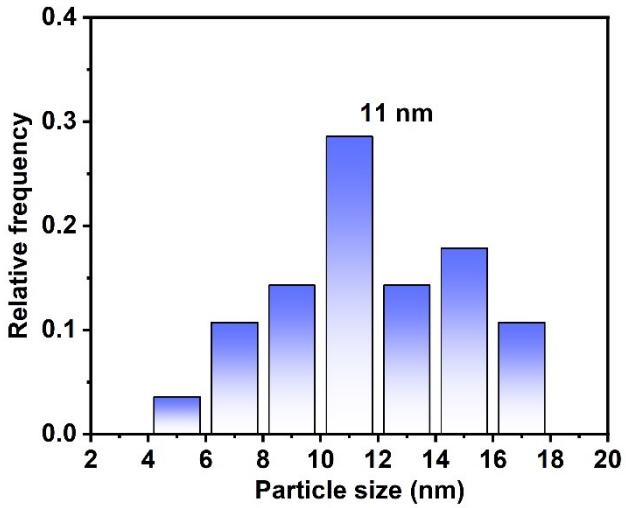

Fig. S5. The normal distribution of particle size of CoS_2 nanoparticles in S@CoS_2/C.

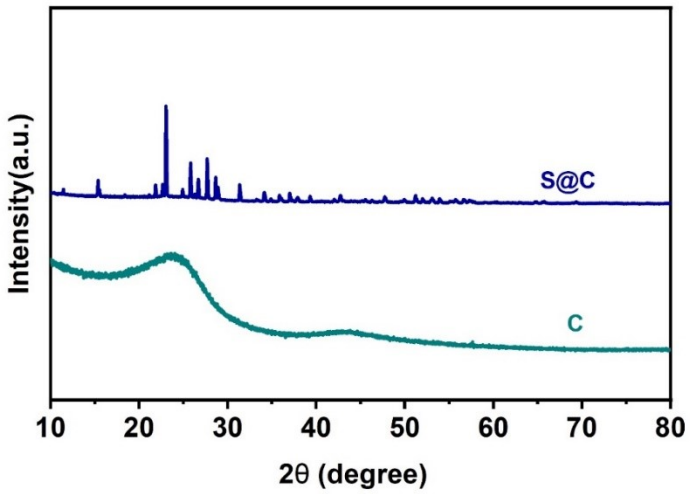

Fig. S6. X-ray diffraction (XRD) patterns of C and S@C.

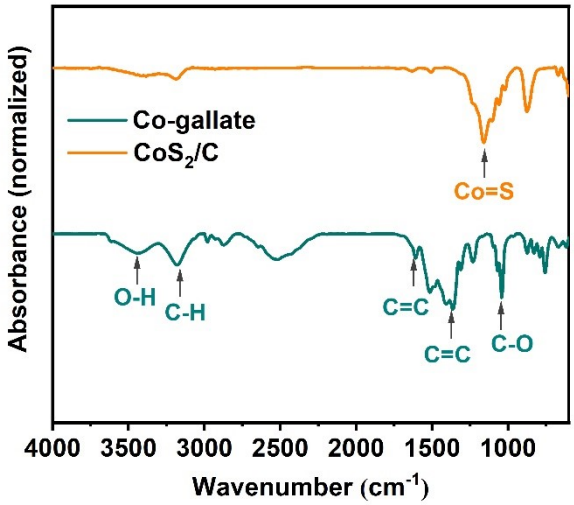

Fig. R7. FTIR spectra of the Co-gallate and CoS_2/C.

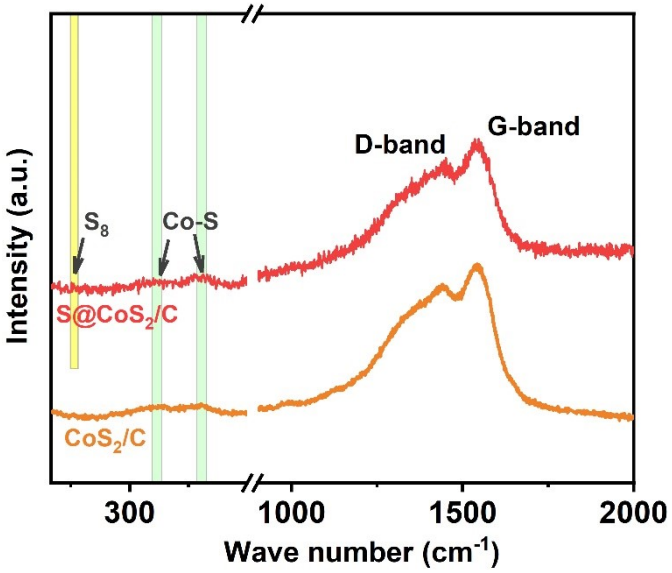

Fig. S8. Raman spectrums of CoS_2/C and S@CoS_2/C.

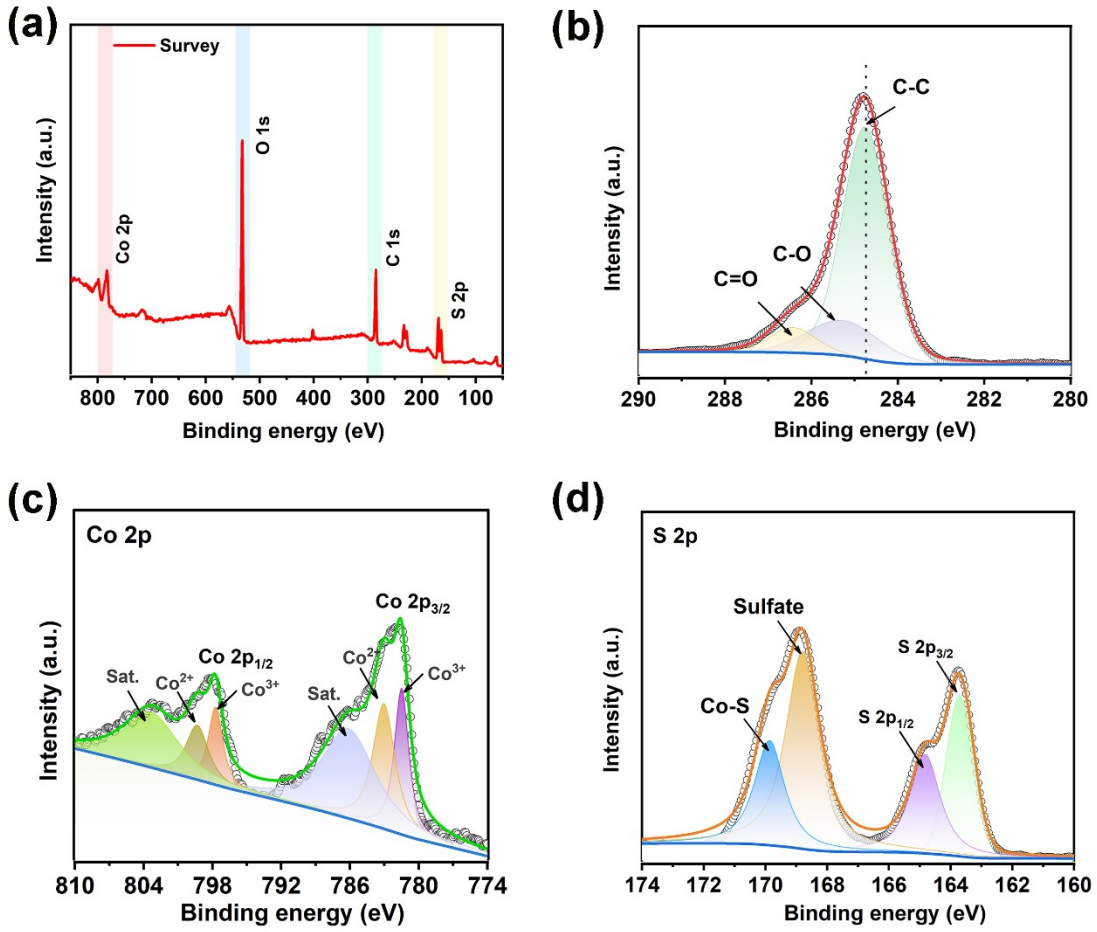

Fig. S9. XPS survey spectrum (a) and (b) C of S@CoS_2/C. High-resolution XPS spectra of (c) Co 2p and (d) S 2p of S@CoS_2/C.

Note for Fig. S9. The high-resolution C 1s spectrum was fitted with different peaks, with main peaks at binding energy of ≈284.8 eV related to C-C bonding, which was used as a reference.

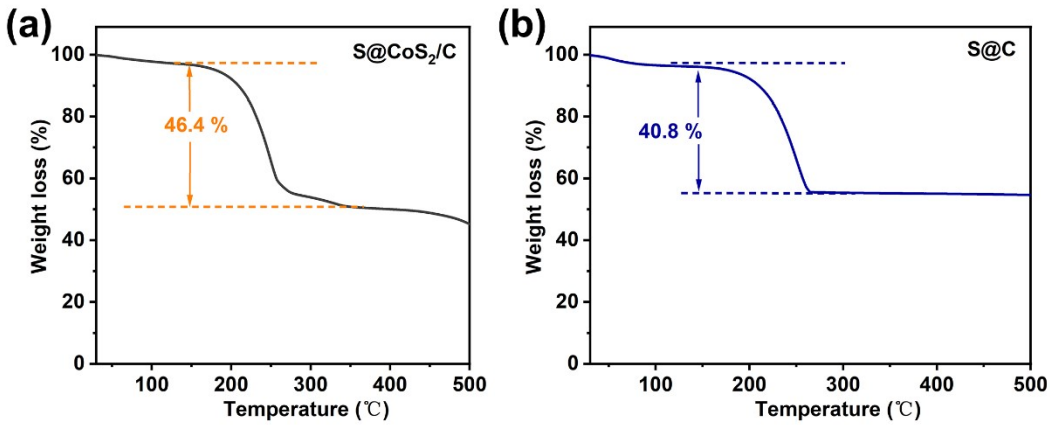

Fig. S10. TGA curve of the S@CoS_2/C and S@C composites.

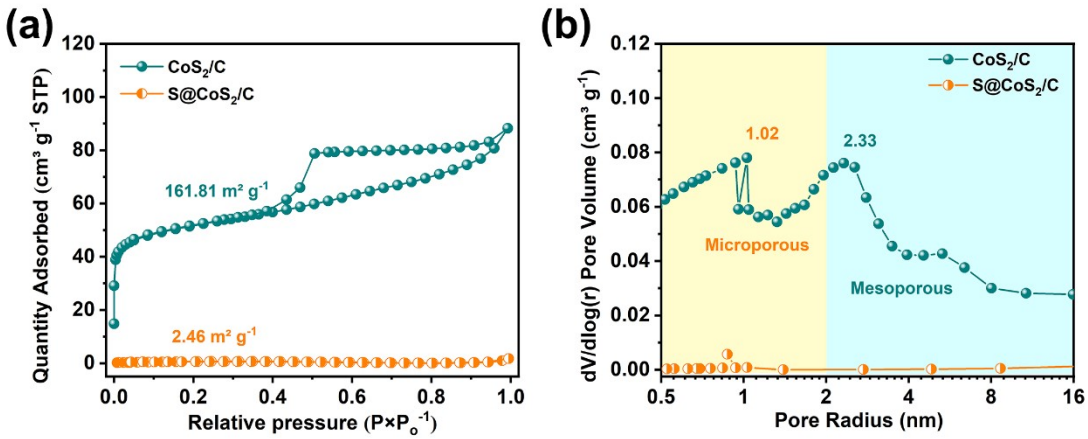

Fig. S11. (a) Nitrogen adsorption-desorption isotherms and (b) the corresponding pore size distributions of CoS_2/C and S@CoS_2/C.

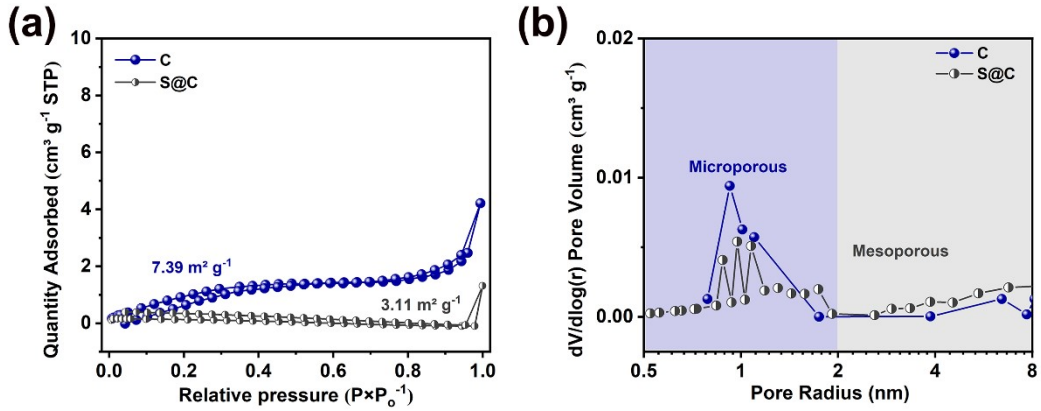

Fig. S12. (a) Nitrogen adsorption-desorption isotherms and (b) the corresponding pore size distributions of C and S@C.

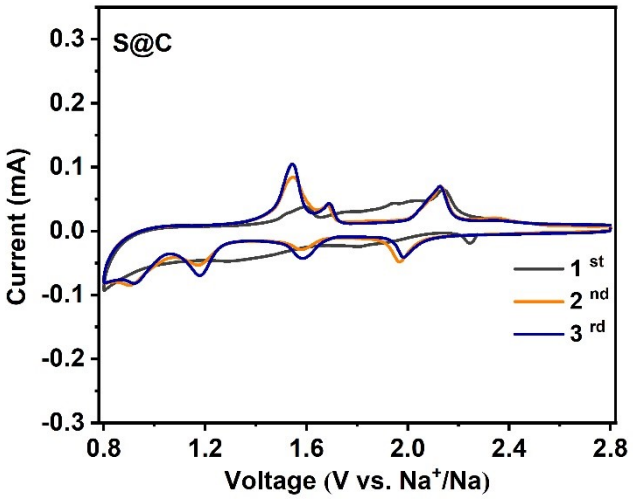

Fig. S13. Cyclic voltammetry curves of the S@C at a scan rate of 0.1 mV s^{-1}.

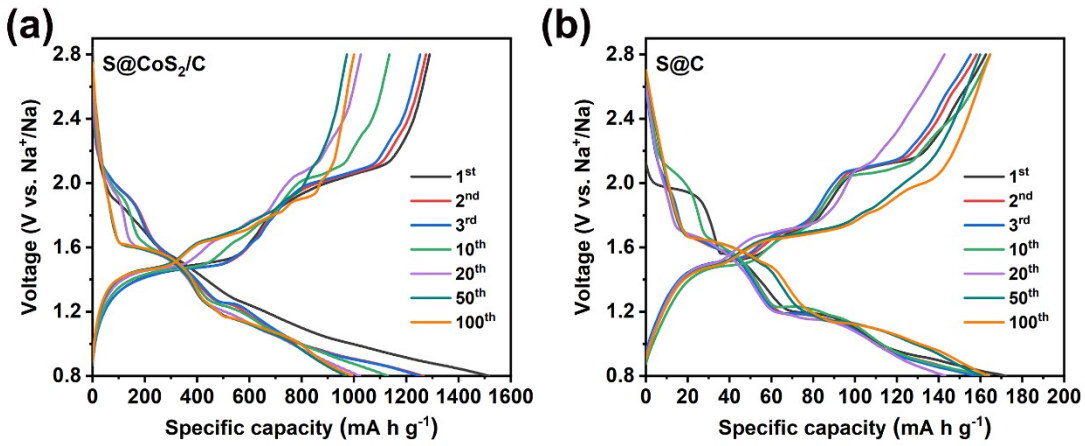

Fig. S14. Galvanostatic charging/discharging curves of different electrodes at 0.1 A g^{-1}.

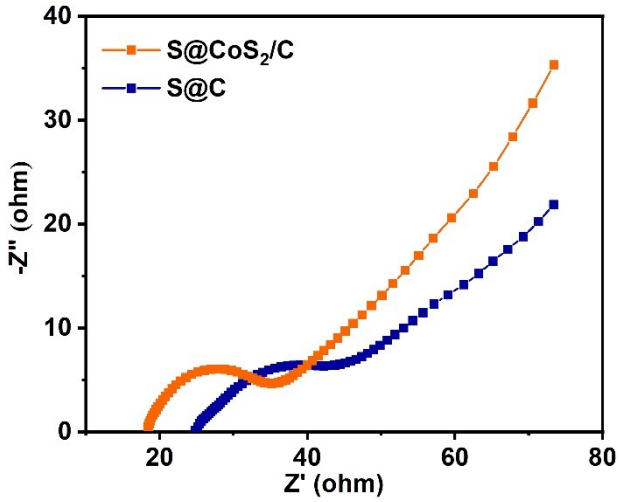

Fig. S15. Nyquist plots of the fresh cells of S@CoS_2/C and S@C electrodes.

Note to Fig. S15: The semicircle represents the high-frequency region ascribed to the charge-transfer resistance (R_{ct}) and the sloping line represents the low-requency region associated with diffusion of Na^+ in the cathode.[1]

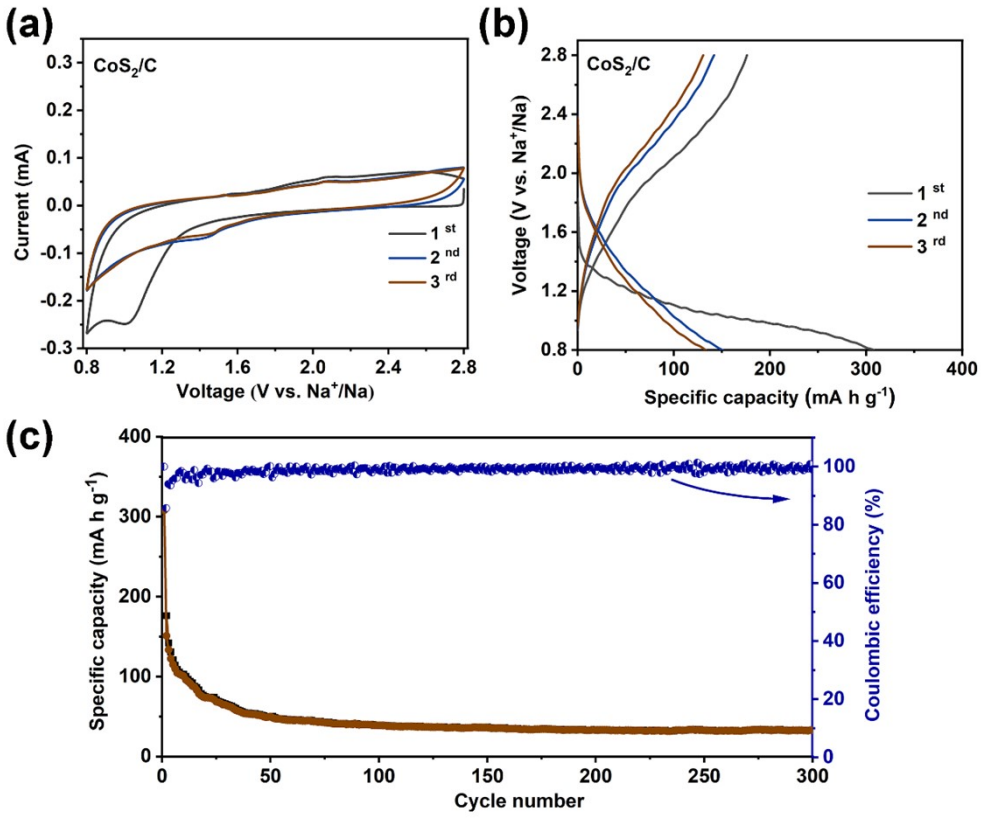

Fig. S16. (a) CV curves (b) Charging and discharging curves and (c) cycling performance of pure CoS_2/C (without sulfur) electrode.

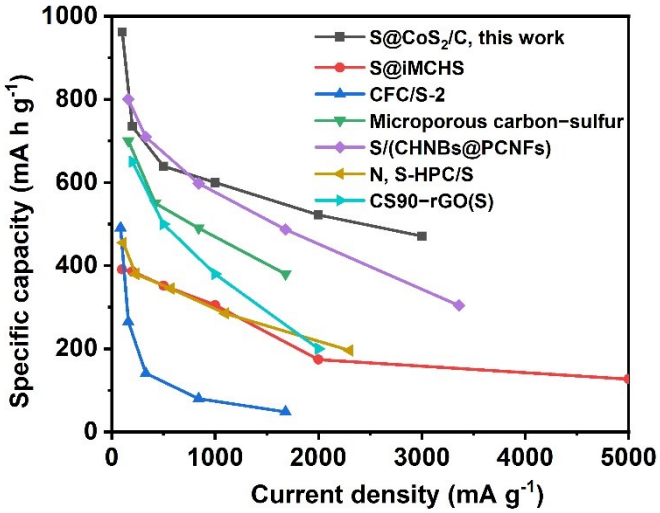

Fig. S17. Rate performance of S@CoS_2/C cell compared to reported counterparts in the literature.

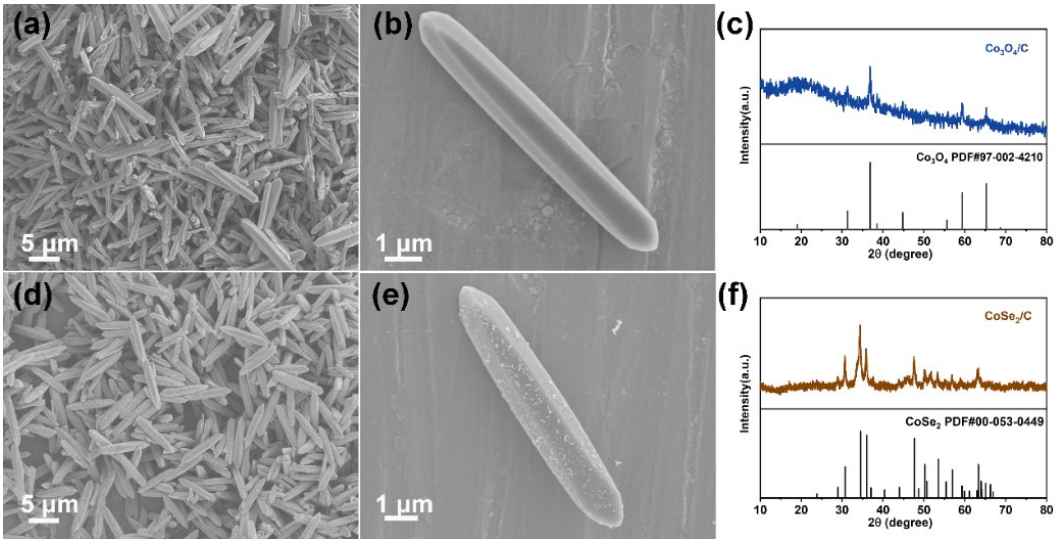

Fig. S18. (a, b) SEM images and (c)XRD pattern of Co_3O_4/C. (d, e) SEM images and (f) XRD pattern of $CoSe_2$/C.

Note for Fig. S18. The SEM of Co_3O_4/C and $CoSe_2$/C with the same morphology to the Co-gallate precursor were obtained after calcination in the different atmospheres Fig. R2a, b (Co_3O_4/C) and Fig. R2d, e ($CoSe_2$/C). The XRD pattern shown in Fig. R2c, f additionally confirmed that the phase structure of Co_3O_4 (PDF # 97-002-4210) and $CoSe_2$ (PDF # 00-053-0449).

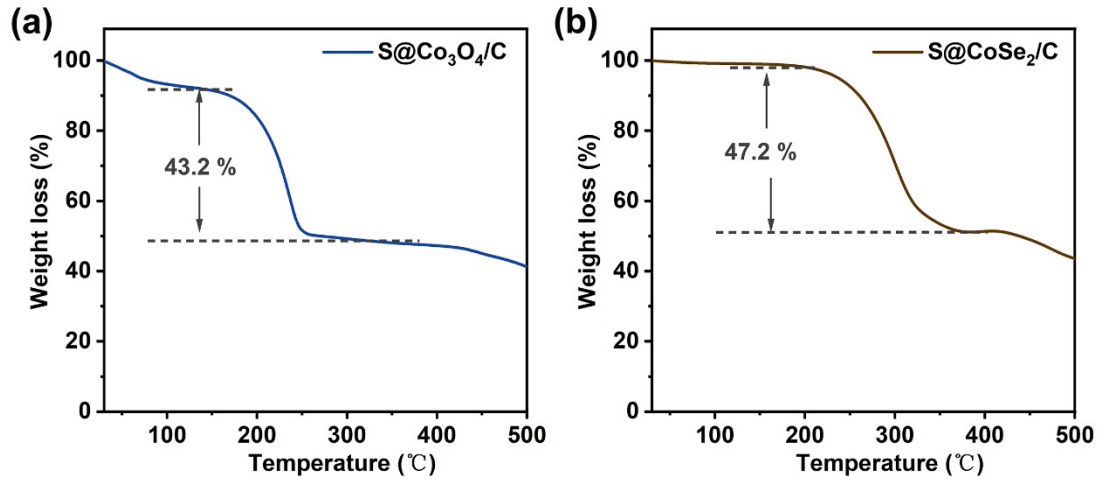

Fig. S19. (a, b) Thermogravimetry curves of $S@Co_3O_4/C$ and $S@CoSe_2/C$, respectively.

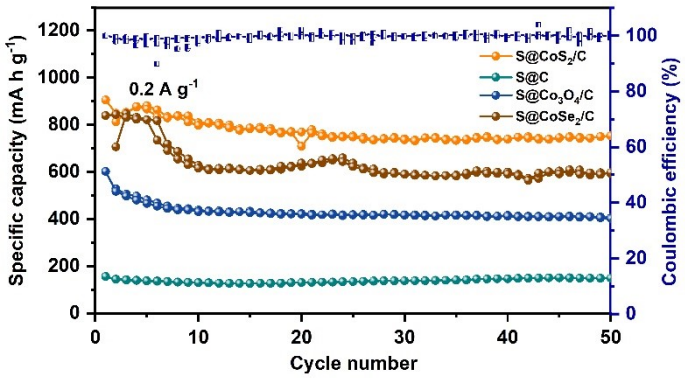

Fig. S20. The cycle performance of $S@CoS_2/C$, S@C, $S@Co_3O_4/C$ and $S@CoSe_2/C$ cathodes at a current density of 0.2 A g^{-1}.

Note for Fig. S20. The $S@CoS_2/C$ electrode delivers an initial reversible capacity of 905 mA h g^{-1}, retaining excellent reversible capacity of 753 mA h g^{-1} after 50 cycles. Additionally, the first cycle reversible capacity of $S@Co_3O_4/C$ is 602 mA h g^{-1}, the capacity is retained 405 mA h g^{-1} after 50 cycles. The first cycle reversible capacity of $S@CoSe_2/C$ is 839 mA h g^{-1}, and drops down to 598 mA h g^{-1} after 50 cycles. The S@C displays the lowest capacity, which shows the initial reversible capacity of 149 mA h g^{-1} after 50 cycles. These results demonstrate that the $S@CoS_2/C$ electrode demonstrates a greatly improved capacity and long-term cycling performance.

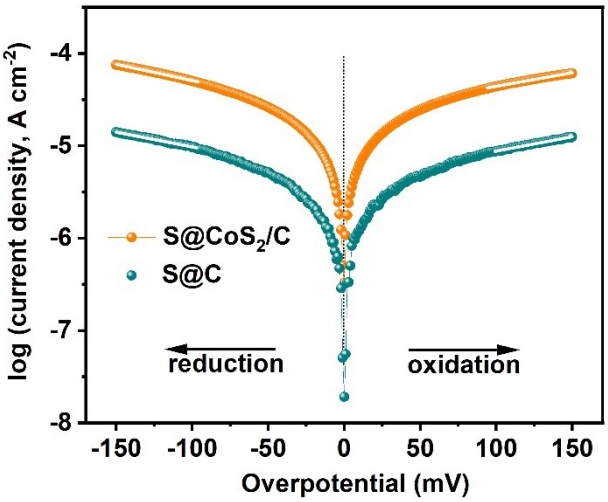

Fig. S21. The Tafel curves for CoS_2/C and C.

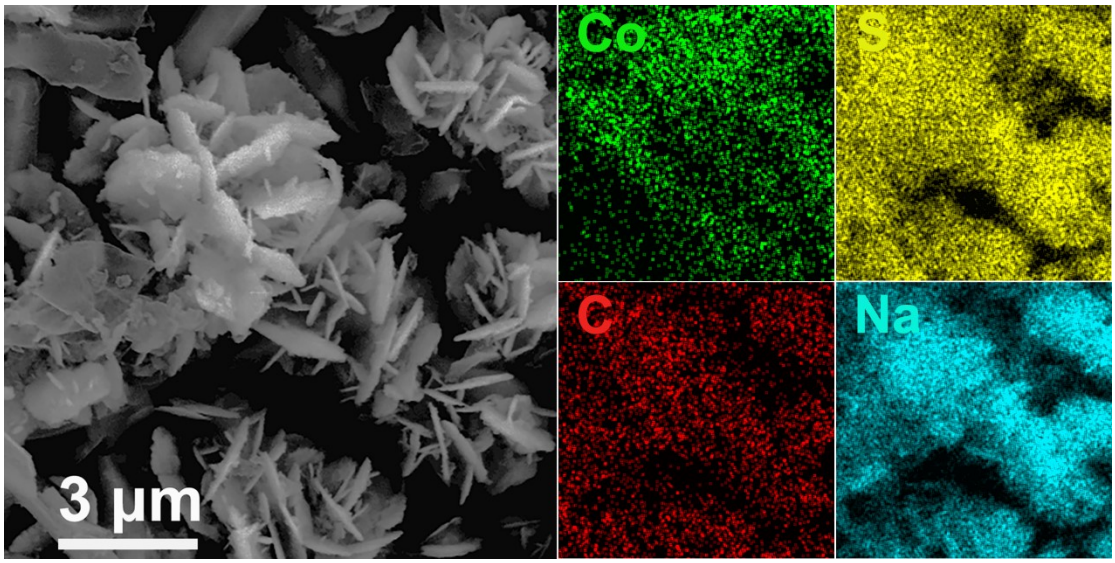

Fig. S22. SEM image and corresponding EDS elemental mappings of electrodeposition test for the CoS_2/C electrode.

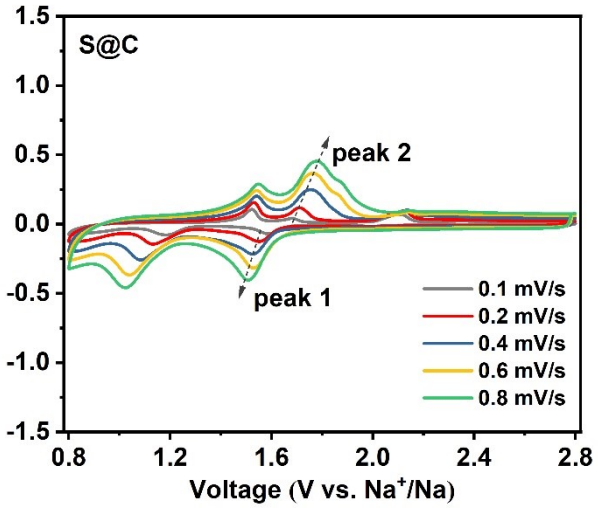

Fig. S23. CV curves of S@C at different scan rates from 0.1 to 0.8 mV s^{-1}.

Table S1: Comparison of this work with previously reported RT Na-S batteries.

Electrode materials	**Rate performance**	**Cycling performance**	**Ref.**
S@CoS_2/C	471 mA h g^{-1} at 3 A g^{-1}	623 mA h g^{-1} at 1.0 A g^{-1} after 870 cycles	This work
S@iMCHS	127 mA h g^{-1} at 5 A g^{-1}	292 mA h g^{-1} at 0.1 A g^{-1} after 200 cycles	2
CFC/S-2	48 mA h g^{-1} at 1.68 A g^{-1}	120 mA h g^{-1} at 0.16 A g^{-1} after 300 cycles	3
Microporous carbon−sulfur	380 mA h g^{-1} at 1.68 A g^{-1}	500 mA h g^{-1} at 0.16 A g^{-1} after 250 cycles	4
S/(CHNBs@PCNFs)	304mA h g^{-1} at 3.36 A g^{-1}	786 mA h g^{-1} at 0.16 A g^{-1} after 50 cycles	5
N, S-HPC/S	196 mA h g^{-1} at 2.3 A g^{-1}	378 mA h g^{-1} at 0.23 A g^{-1} after 250 cycles	6
CS90−rGO(S)	200 mA h g^{-1} at 2 A g^{-1}	285 mA h g^{-1} at 1.0 A g^{-1} after 100 cycles	7

References

1. J. Zhang, C.-P. Yang, Y.-X. Yin, L.-J. Wan and Y.-G. Guo, *Adv. Mater.*, 2016, **28**, 9539–9544.
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