

Electronic Supporting Information for

**Synergistic design of core-shell $V_3S_4@C$ host and homogeneous catalysts
promoting polysulfides chemisorption and conversion for Li-S batteries**

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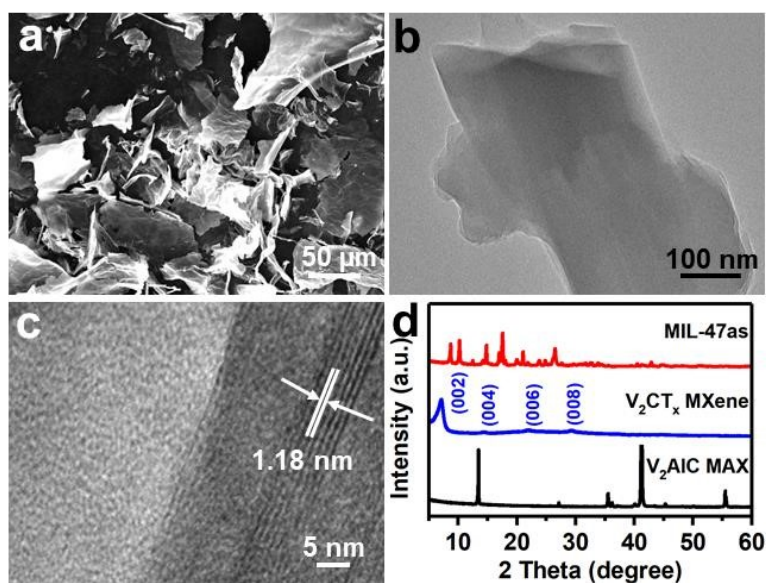


Fig. S1. (a) FESEM image, (b) TEM image and (c) HR-TEM image of the V₂CT_x; (d) XRD patterns of V₂AlC MAX, V₂CT_x and MIL-47as.

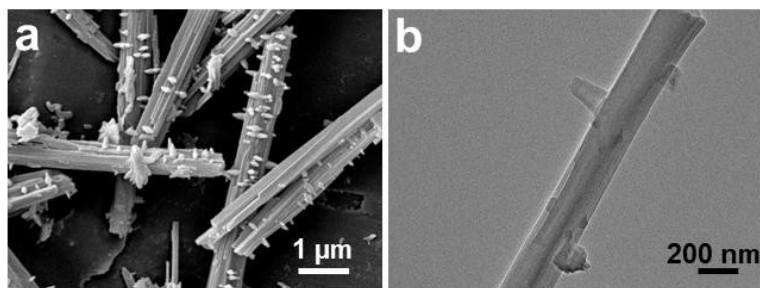


Fig. S2. (a) FESEM image and (b) TEM image of the MIL-47as.

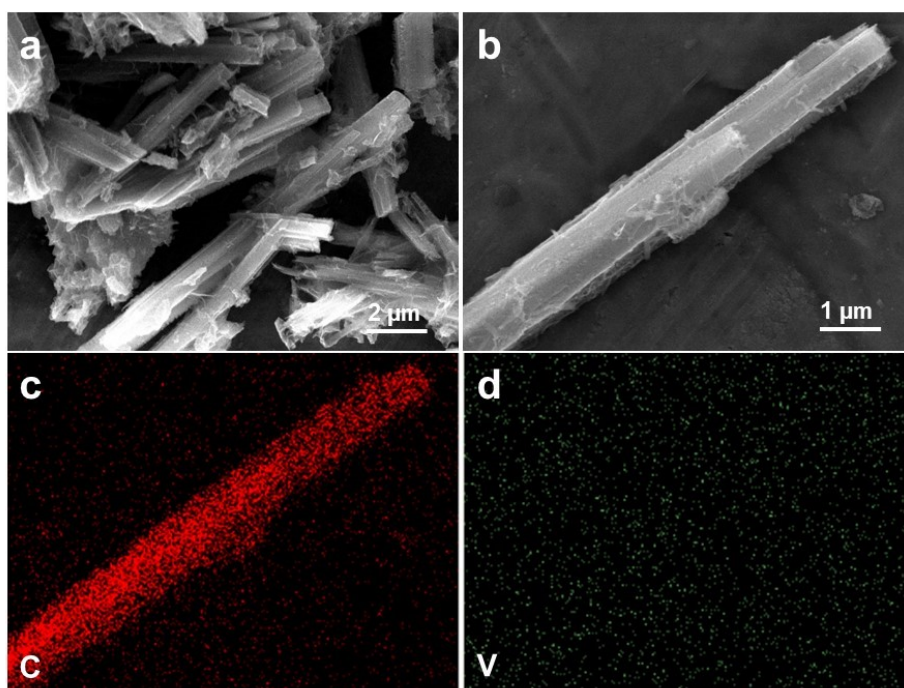


Fig. S3. (a, b) FESEM images and (c, d) corresponding elemental mapping images of the $V_3S_4@C$ after being etched by HCl solution.

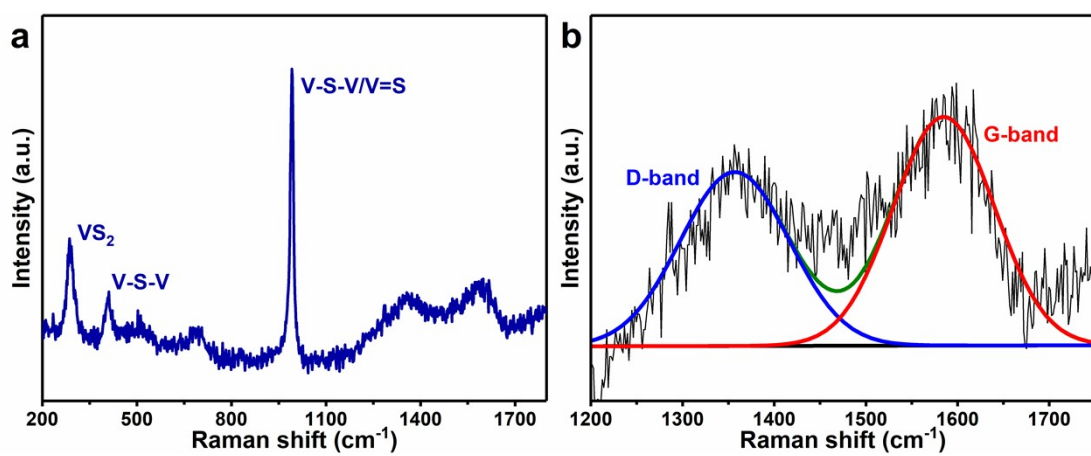


Fig. S4. (a) Raman spectrum of $V_3S_4@C$; (b) Enlarged region from 1200 to 1750 cm^{-1} and corresponding fitting curves of $V_3S_4@C$.

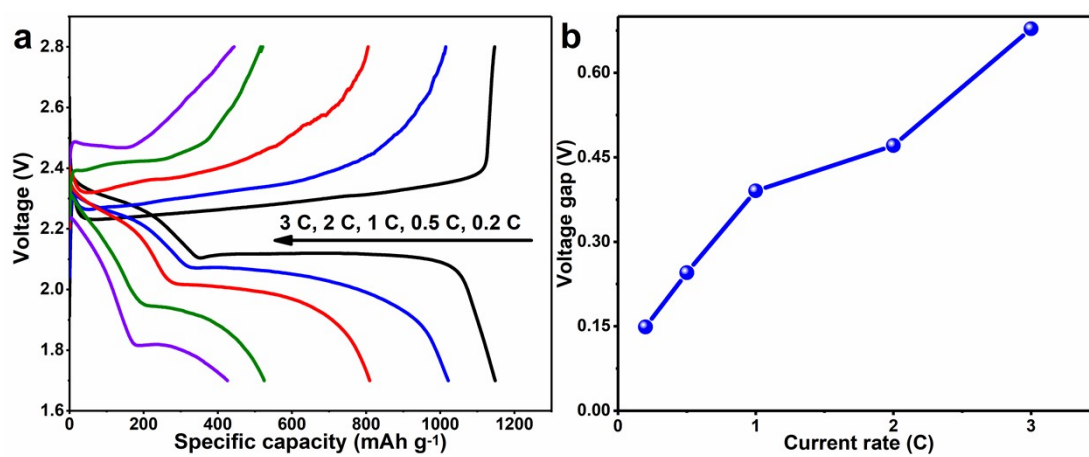


Fig. S5. (a) Galvanostatic charge-discharge plots and (b) voltage gaps of different rates for the S/V₃S₄@C cathode.

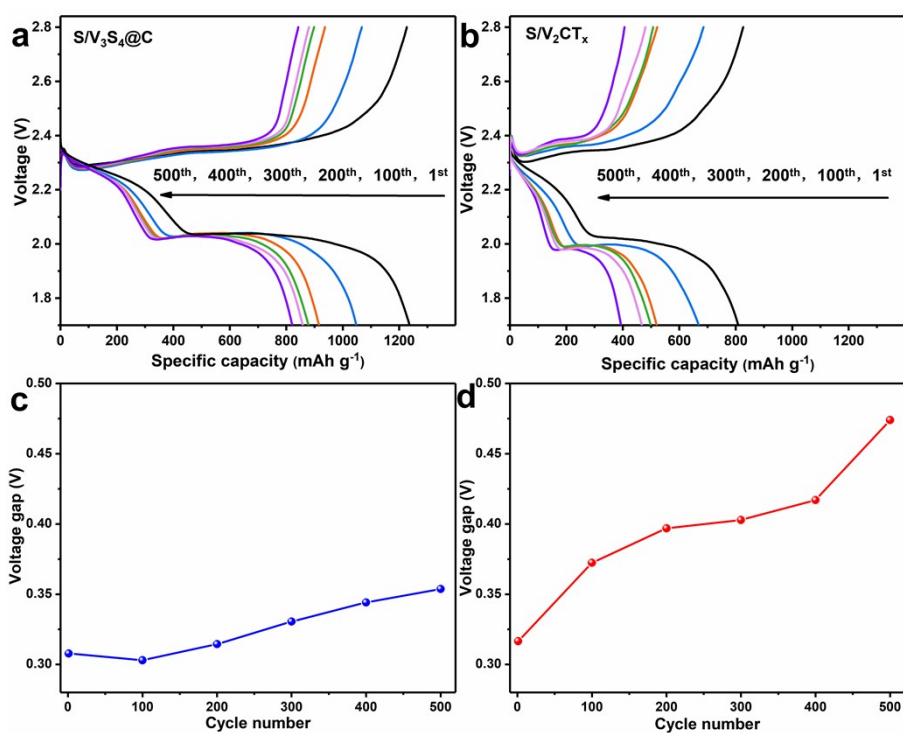


Fig. S6. The selected galvanostatic charge-discharge profiles of (a) S/V₃S₄@C and (b) S/V₂CT_x cathodes, and corresponding voltage gaps of (c) S/V₃S₄@C and (d) S/V₂CT_x cathodes.

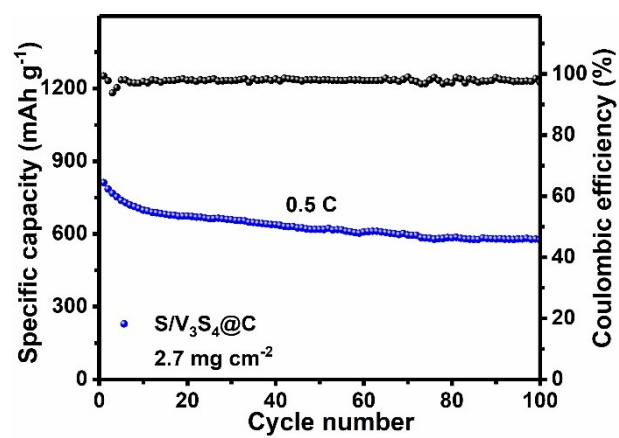


Fig. S7. Cycling performance of S/V₃S₄@C (S areal loading: 2.7 mg cm⁻²) at 0.5 C.

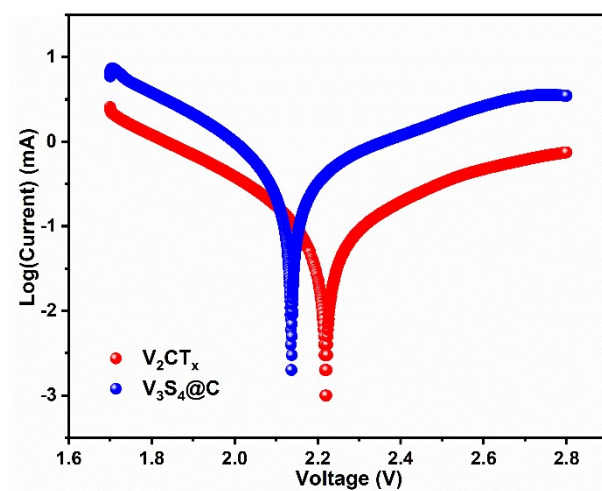


Fig. S8. Tafel plots of $V_3S_4@C$ and V_2CT_x as indicated.

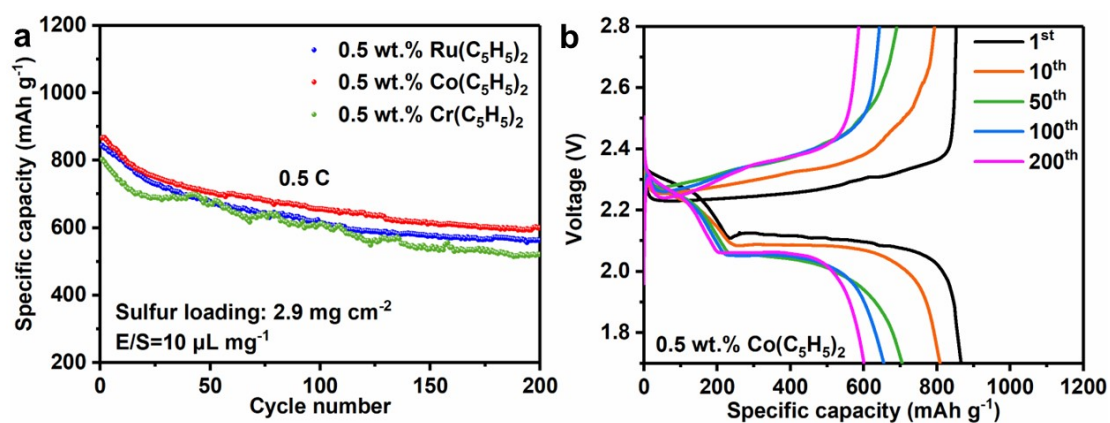


Fig. S9. (a) Cycling performance (0.5 C) of the S/V₃S₄@C cathode with high S loading (2.9 mg cm⁻²) and a E/S ratio (~10 μL mg⁻¹) in electrolytes with different HCs as indicated, and (b) selected charge-discharge profiles of the S/V₃S₄@C cathode with 0.5 wt.% Co-electrolyte.

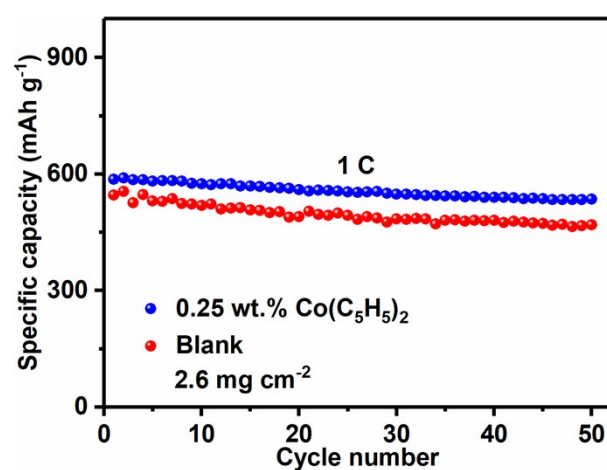


Fig. S10. Cycling performance (1 C) of the S/V₃S₄@C cathode with high S loading (2.6 mg cm⁻²) and low E/S ratio (~10 μL mg⁻¹) with/without 0.25 wt.% Co-electrolyte.

Table S1 Comparison in electrochemical performance of S/V₃S₄@C with/without 0.5 wt.% Co(C₅H₅)₂ in electrolytes and other similar cathodes.

Electrodes	Areal sulfur loading (mg cm ⁻¹)	E/S ratio (μL mg ⁻¹)	Performance (mAh g ⁻¹)	Cycle number	Reference
S/V ₃ S ₄ @C	2.1	10	~675.5 at 1 C	300	This work
S/V ₃ S ₄ @C, with 0.25 wt.% Co(C ₅ H ₅) ₂	4.6	8	~421.2 at 1 C	100	This work
VS ₂ @S	1.5	20	~413.0 at 1 C	200	1
S@VS ₄ @RGO	5	10	~853 at 0.2 C	100	2
SnS@C/S	1.5	10	~513 at 0.5 C	600	3
TiO ₂ -Ni ₃ S ₂	3.9	9	~504 at 0.3 C	500	4
MoSe ₂ @rGO/S	1.22 1.16	16	~823 at 1 C ~672 at 2 C	270 500	5
S/V ₃ S ₄ @C-7	2.3 4.2	16 – 25	~611.4 at 1 C ~389.3 at 1 C	500 500	6
MoS ₂ -MoN/S	1.2	/	~520 at 1 C	1000	7
Li ₂ S ₆ /ZnS _{1-x} -CC	1.7	15	~524 at 1 C	500	8
Co _{0.85} Se/NC-S	1	26	~799 at 1 C	400	9

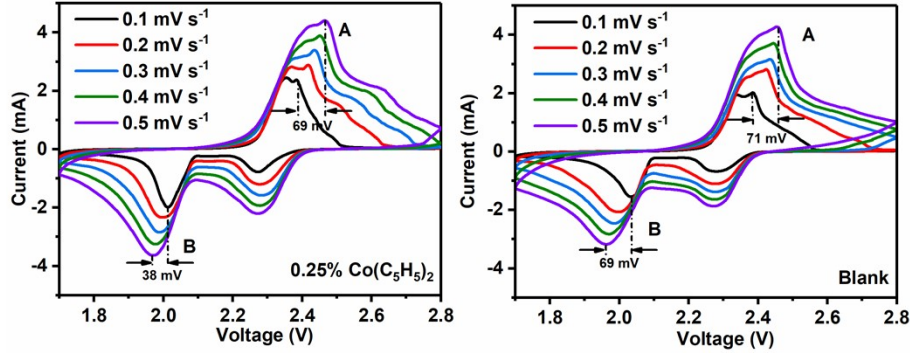


Fig. S11. CV curves of the S/V₃S₄@C cathode (a) with or (b) without 0.25 wt.% Co-electrolyte at different scanning rates.

According to the Randles-Sevcik formula:

$$I_p = (2.65 \times 10^5) n^{1.5} S D_{Li^+}^{0.5} \Delta C_{Li^+} v^{0.5}$$

therein, I_p is the peak current, n is the number of participating electrons in the reaction ($n=2$), S is the electrode area ($S=1.13 \text{ cm}^2$), ΔC_{Li^+} is the Li^+ ion concentration in the electrolyte and v is the scanning rate.¹⁰ The diffusion coefficient of the Li^+ ion (D_{Li^+}) is calculated by the linear fitting of I_p versus $v^{0.5}$, as shown in **Fig.911**. The D_{Li^+} value for peak A is 3.729×10^{-8} (Co-electrolyte) and $3.408 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ (blank), and for peak B is 2.521×10^{-8} (Co-electrolyte) and $1.948 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ (blank).

Reference

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