## **Supporting Information:**

## Engineering Metal Sulfide with Hierarchical Interfaces towards Advanced Sodium-ions Storage

Wenqing Zhao,<sup>a</sup> Limin Zhang,<sup>a</sup> Feng Jiang,<sup>a</sup> Xinghua Chang,<sup>a</sup> Yue Yang,<sup>a</sup> Peng Ge,<sup>\*a</sup> Wei

Sun,\*a and Xiaobo Ji<sup>b,c</sup>

<sup>a</sup>School of Minerals Processing and Bioengineering, Central South University,

Changsha 410083, Hunan, China

<sup>b</sup>College of Chemistry and Chemical Engineering, Central South University,

Changsha 410083, Hunan, China

°State Key Laboratory of Powder Metallurgy, Central South University,

Changsha 410083, Hunan, China.

\*Corresponding authors: Prof. Dr Peng Ge, Prof. Dr Wei Sun.

Tel: +86-731-88879616; Fax: +86-731-88879616

E-mail: gp-gepeng@csu.edu.cn, sunmenghu@csu.edu.cn





Fig. S1. Peak deconvolution of D-band and G-band for carbon (a) and SS/Sb@C-1 (b), XRD of combustion product at 800°C in air atmosphere (c), FTIR spectra from 400-

2000cm<sup>-1</sup>.



Fig. S2. High-resolution XPS spectra for SS/Sb@C-1 of C1s (a), Sb3d (b), S2p (c).



Fig. S3. SEM images of Sb<sub>2</sub>S<sub>3</sub> (A), SS/Sb@C-1 (B), SS/Sb@C-2 (C).



Fig. S4. TEM images of  $Sb_2S_3$  (A,D), SS/Sb@C-1 (B,E), SS/Sb@C-2 (C,F).



Fig. S5. Charge/discharge platforms at various cycles for Sb<sub>2</sub>S<sub>3</sub> (a), SS/Sb@C-1 (b), SS/Sb@C-2 (c).



Fig. S6. Linear relation of log(i) and log(v) at peak 1 (D) (a), the capacitive contribution (in pink) and the diffusion contribution (in cyan) at  $0.3 \text{mV} \text{ s}^{-1}$  of Sb<sub>2</sub>S<sub>3</sub> (b), SS/Sb@C-1 (c).

Process		Chemical equation	Mechanism
	D1	$Sb_2S_3 + xNa^+ + xe^- \rightarrow Na_xSb_2S_3$	Intercalation
Discharging	D2	$Na_xSb_2S_3 + (6-x) Na^+ + (6-x) e^- \rightarrow 2Sb + 3Na_2S$	Conversion
	D3	$2Sb + 6Na^+ + 6e^- \rightarrow 2Na_3Sb$	Alloying
Charging	C4	$2Na_3Sb \rightarrow 2Sb + 6Na^+ + 6e^-$	Dealloying
	C5	$2Sb + 3Na_2S \rightarrow Na_xSb_2S_3 + (6-x) Na^+ + (6-x) e^-$	Inverse conversion
	C6	$Na_xSb_2S_3 \rightarrow Sb_2S_3 + xNa^+ + xe^-$	Extraction

Table S1.	Electrocher	nical read	ction m	echanism	of SS/Sb@C-2.

Scan rate/ mV s <sup>-1</sup>	0.1	0.3	0.5	0.7	0.9	
$Sb_2S_3$	13.2	20.0	27.5	29.5	31.3	
SS/Sb@C-1	41.4	48.7	59.8	63.6	65.5	
SS/Sb@C-2	80.1	81.5	86.6	89.2	93.0	

Table S2. Capacitive contribution of the as-prepared samples at various scan rates.

(Capacitive contribution, %)

Voltage	-1.0	-0.4	-0.01	0.6	1.5	2.5
Sb <sub>2</sub> S <sub>3</sub>	109.2	223.7	348.5	216.7	149.5	77.3
SS/Sb@C-1	53.0	129.2	195.6	98.52	60.7	51.3
SS/Sb@C-2	47.7	53.73	88.1	58.4	47.0	42.4

Table S3. Value of  $R_{ct}$  for the target samples at di  $\square$  erent charge/discharge voltages.

 $(\mathbf{R}_{\mathrm{ct}}, \Omega)$