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Electronic Supplementary Information for

Hierarchical Co-doped $Ni(OH)_2$@SnS_2 double-shell crystalline structure on carbon cloth with gradient pore distribution for superior capacitance

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The crystalline formation mechanism of the composites is followed the equation as follows:

First solvothermal reaction:

$CH_3NH_2C{=}S + 2CH_3CH_2OH \rightarrow CH_3(NH_2)C(OC_2H_5)_2 + H_2S$

$Sn^{4+} + 2H_2S \rightarrow SnS_2 + 4H^+$

Second hydrothermal reaction:

$C_6H_{12}N_4 + 6H_2O \rightarrow 4NH_3 + 6CH_2O$

$NH_3 + H_2O \rightarrow NH^{4+} + OH^-$

$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2$

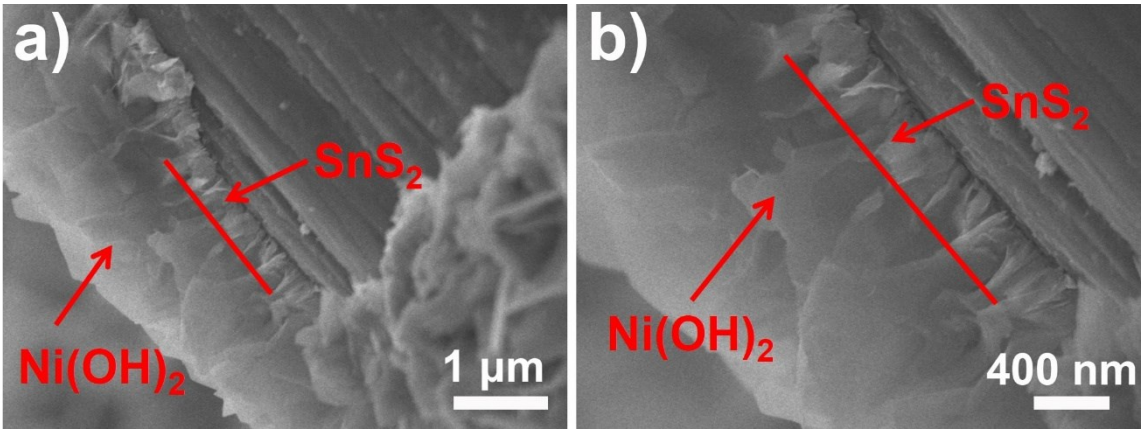

Fig. S1 a, b) SEM of the cross-sectional view of the SnS_2@Co-$Ni(OH)_2$-3/CC composite.

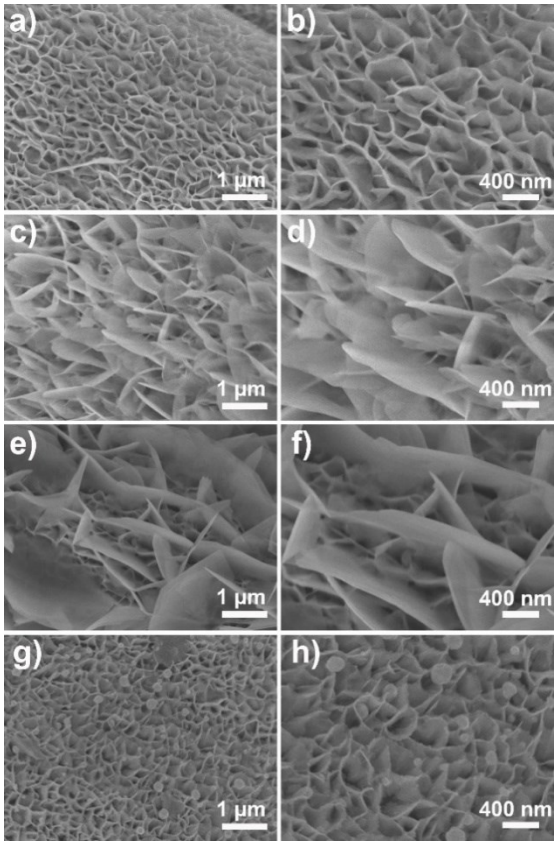

Fig. S2 SEM images of SnS_2@Co-Ni$(OH)_2$-3 composites grown with different amount of NH_4F. a, b) without NH_4F (0 mmol), c, d) with half dosage of NH_4F (3.4 mmol), e, f) with a dosage of NH_4F (6.75 mmol), g, h) with double dosage of NH_4F (13.5 mmol).

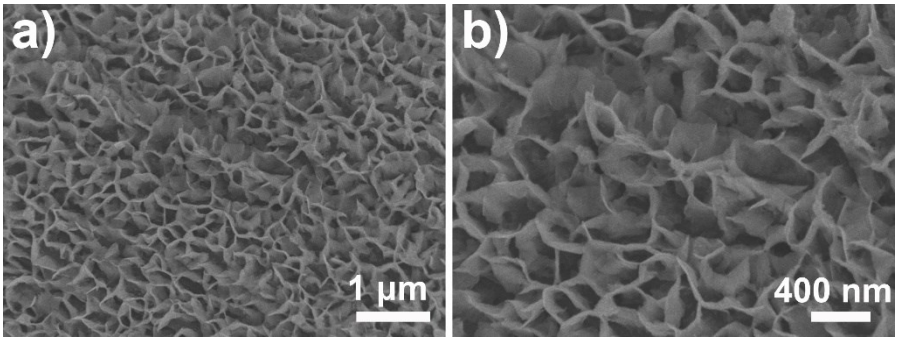

Fig. S3 a, b) SEM images of SnS_2@Co-Ni$(OH)_2$-3 composites grown without HMT additive.

The NH_4F is mainly act as the crystalline growth guiding agent and the HMT is the alkali source to offer the hydroxide ions, thus the dosage can greatly influence the

growth of the Co-Ni$(OH)_2$ outer layer. The SEM images show the composites grown without NH_4F (**Fig. S2a, b**) and with a double dosage of NH_4F (**Fig. S2g, h**) cannot effectively grow Co-Ni$(OH)_2$ outer layer. Moreover, the size of the Co-Ni$(OH)_2$ nanosheets grown with half dosage of the NH_4F (**Fig. S2c, d**) is obvious smaller than that of the SnS_2@Co-Ni$(OH)_2$-3 composites with a dosage of NH_4F (**Fig. S2e, f**), further demonstrate the importance of the NH_4F dosage. Furthermore, the composite grown without HMT (**Fig. S3**) cannot effectively anchor the Co-Ni$(OH)_2$ outer layer as well. Meanwhile, the mass ratio of different elements of those composites (**Table S1**) detected by the EDS mapping further demonstrate the important of the NH_4F as guiding agent and HMT as alkali source.

Table S1. The mass ratio of different elements in the SnS_2@Co-Ni$(OH)_2$-3 (0, 3.4, 6.75, 13.5 mmol NH_4F or 0 mmol HMT) calculated from the EDS results.

Elements (wt.%) / Samples	Ni	Co	O	Sn	S	C
SnS_2@Co-Ni$(OH)_2$-3 (0 mmol NH_4F)	2.8	0	0	24.8	10.8	61.6
SnS_2@Co-Ni$(OH)_2$-3 (3.4 mmol NH_4F)	16.0	2.4	17.4	22.2	8.1	30.3
SnS_2@Co-Ni$(OH)_2$-3 (6.75 mmol NH_4F)	24.2	6.4	15.9	16.3	6.2	26.7
SnS_2@Co-Ni$(OH)_2$-3 (13.5 mmol NH_4F)	3.7	0	8.2	18.0	8.6	61.5
SnS_2@Co-Ni$(OH)_2$-3 (0 mmol HMT)	4.1	0	0	15.7	6.0	74.3

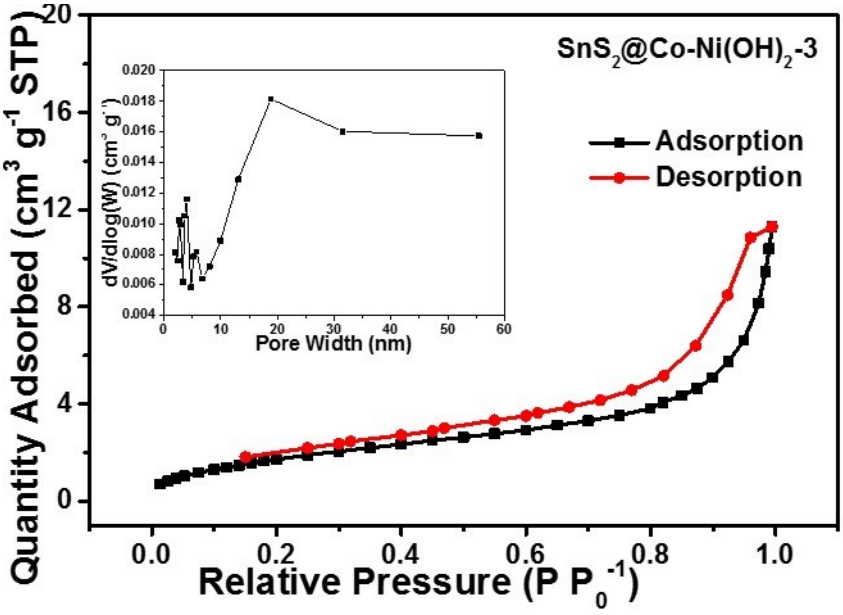

Fig. S4 N_2 absorption/desorption isotherm and pore-size distribution of SnS_2@Co-$Ni(OH)_2$-3.

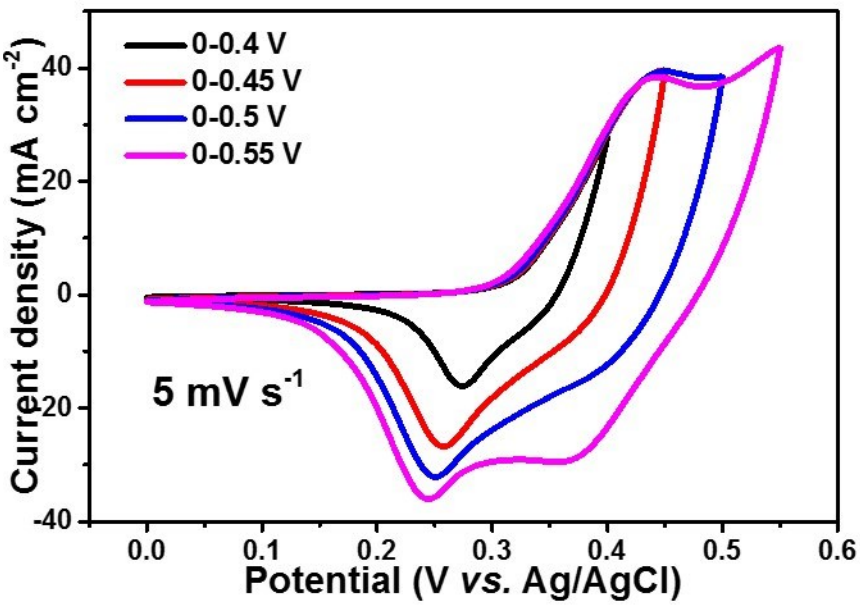

Fig. S5 CV curves of the SnS_2@Co-Ni$(OH)_2$-3 electrode at different operation potential.

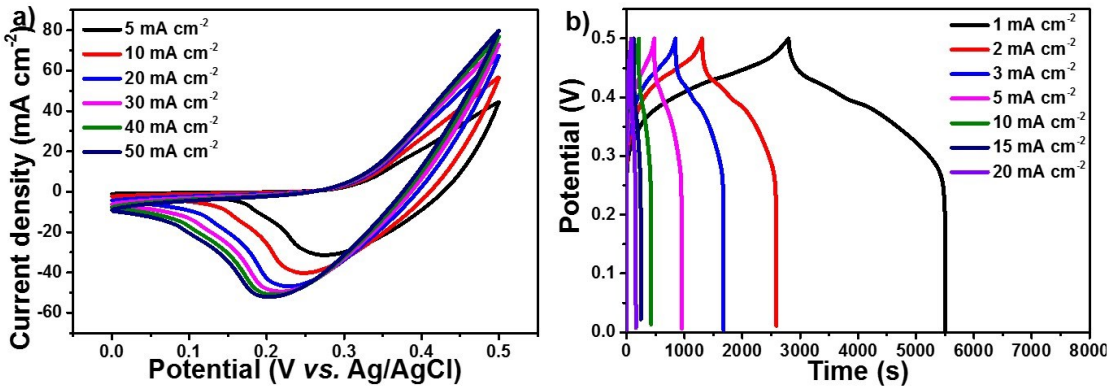

Fig. S6. a) CV curves from 5 to 50 mA cm^{-2} and b) GCD curves from 1 to 20 mA cm^{-2} of SnS_2@Co-$Ni(OH)_2$ /CC-3.

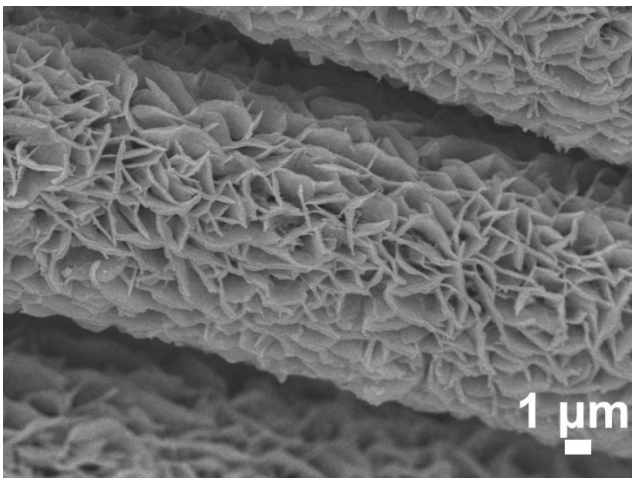

Fig. S7. SEM images of the SnS_2@Co-Ni$(OH)_2$ /CC-3 composites after cycling.

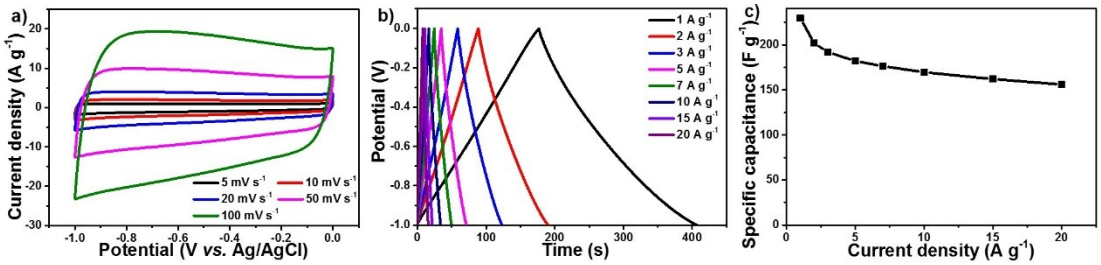

Fig. S8. Three electrode performance of the a-MEGO electrode in2 M KOH, a) CV, b) GCD curves and c) rate performance.