

## Electronic Supplementary Material

### **2D holey cobalt sulfide nanosheets derived from metal organic frameworks for high-rate sodium ion batteries with superior cyclability**

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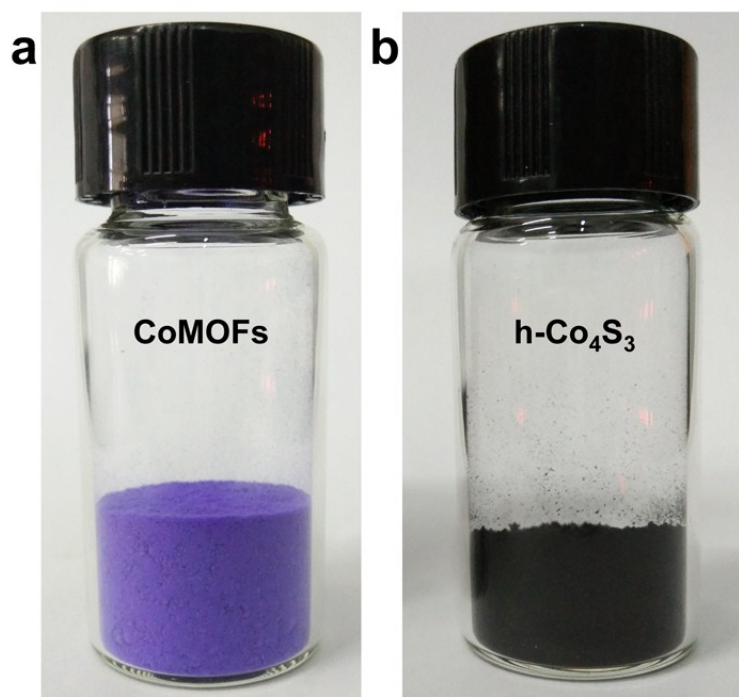
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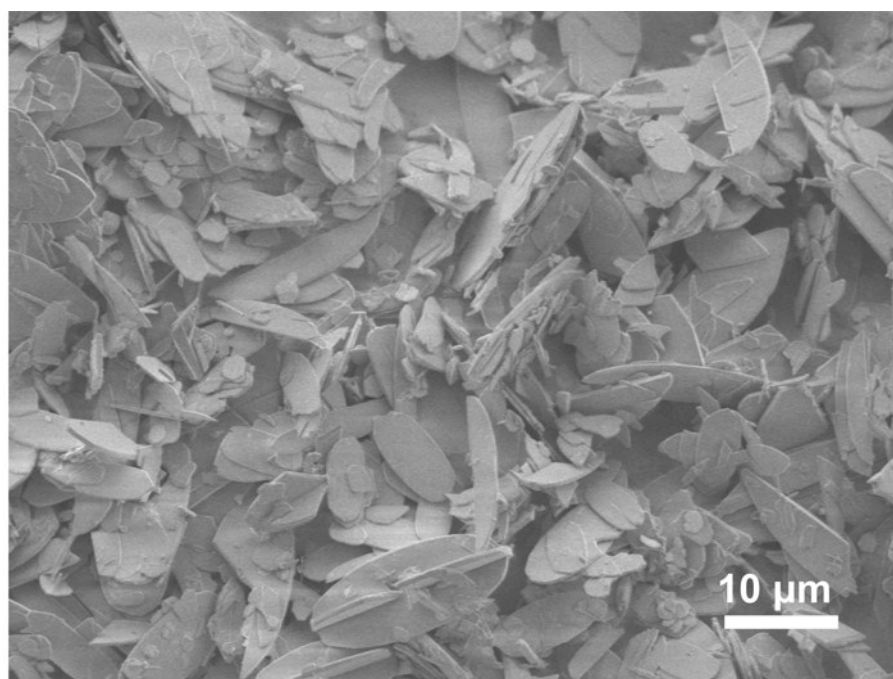
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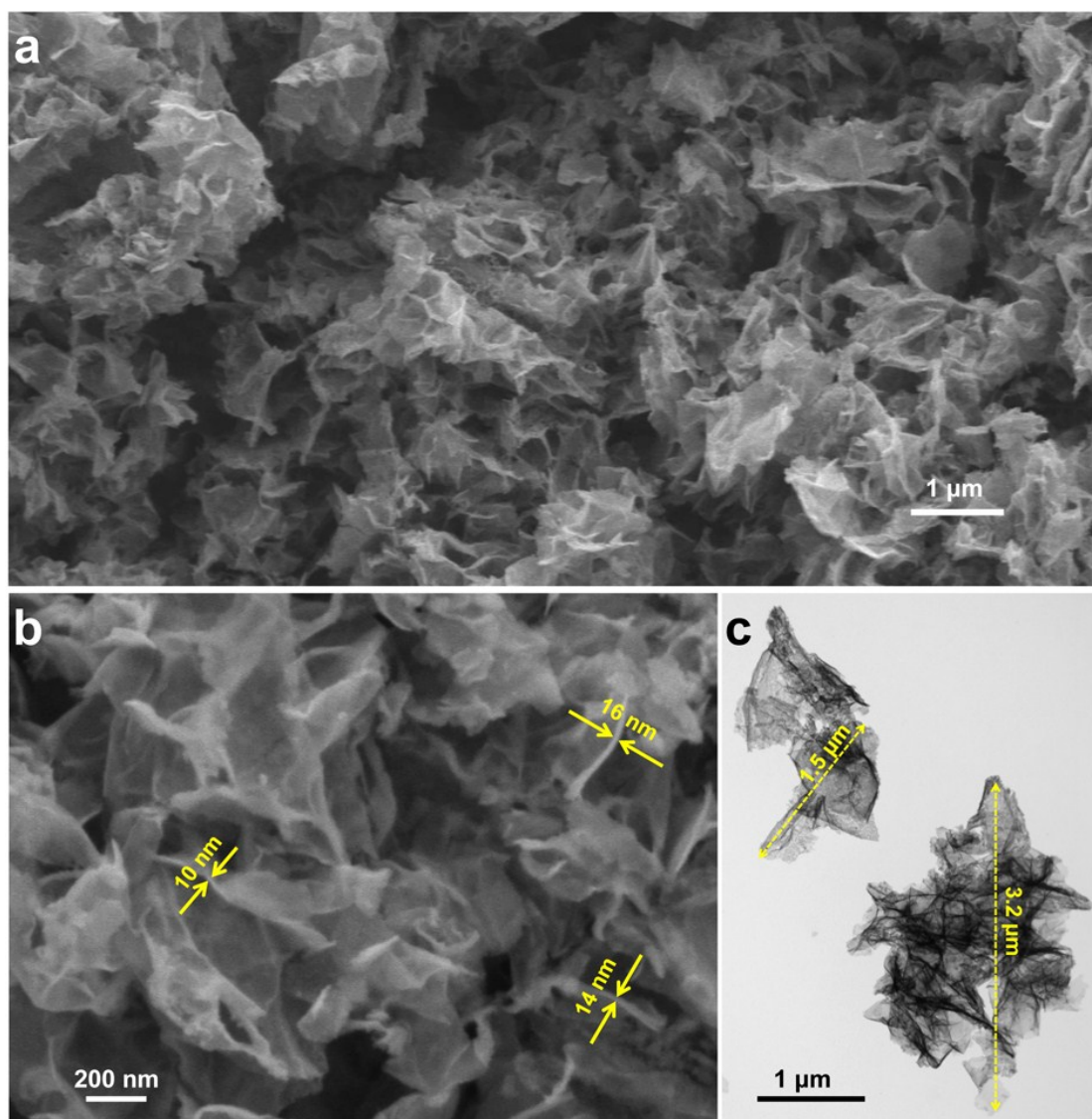
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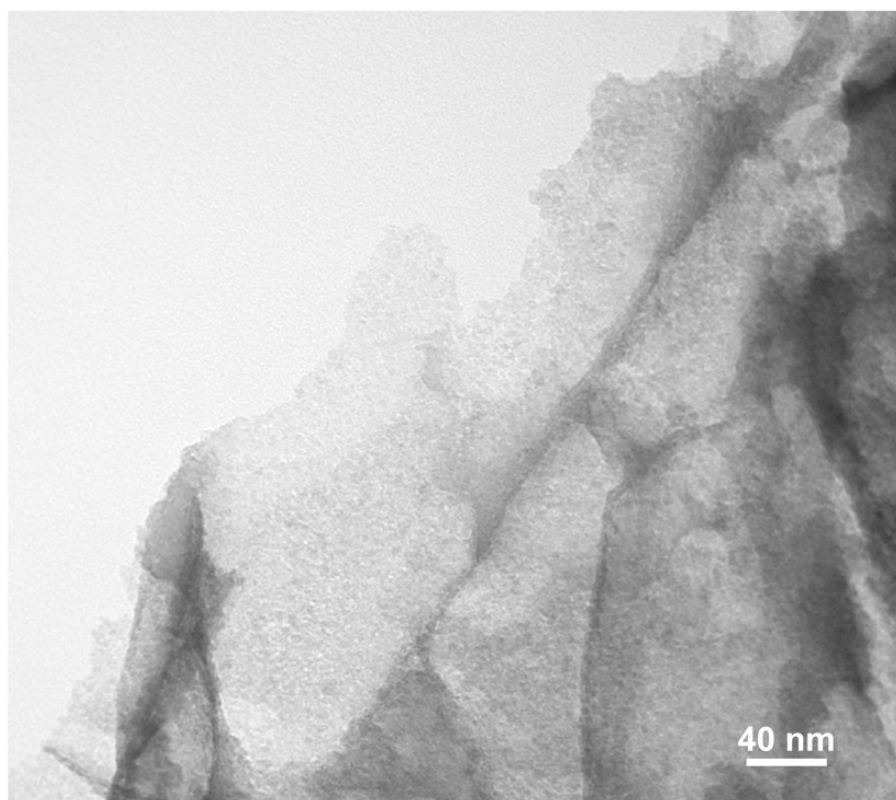
**Figure S1.** Photos of (a) CoMOFs and (b) h-Co<sub>4</sub>S<sub>3</sub> samples.



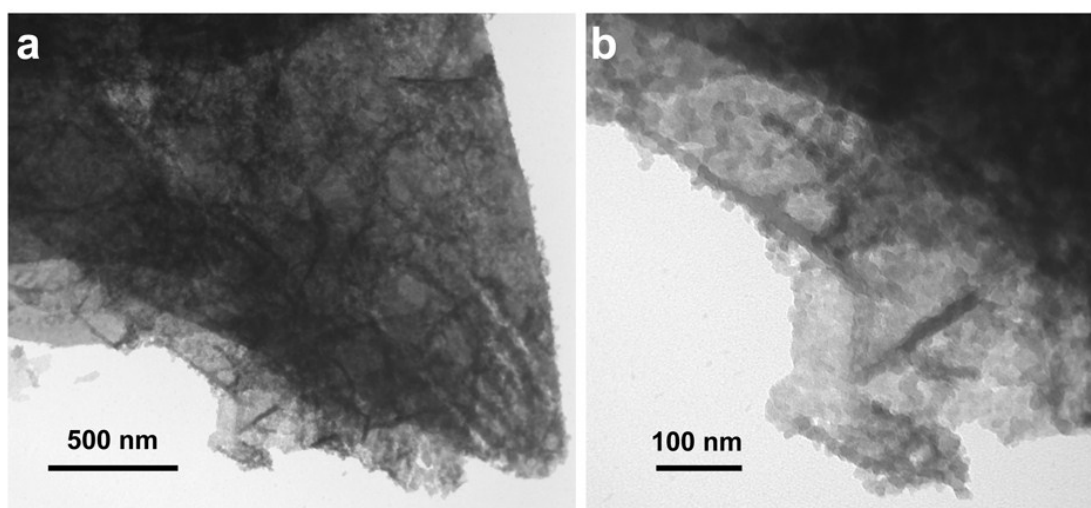
**Figure S2.** SEM image of CoMOFs.



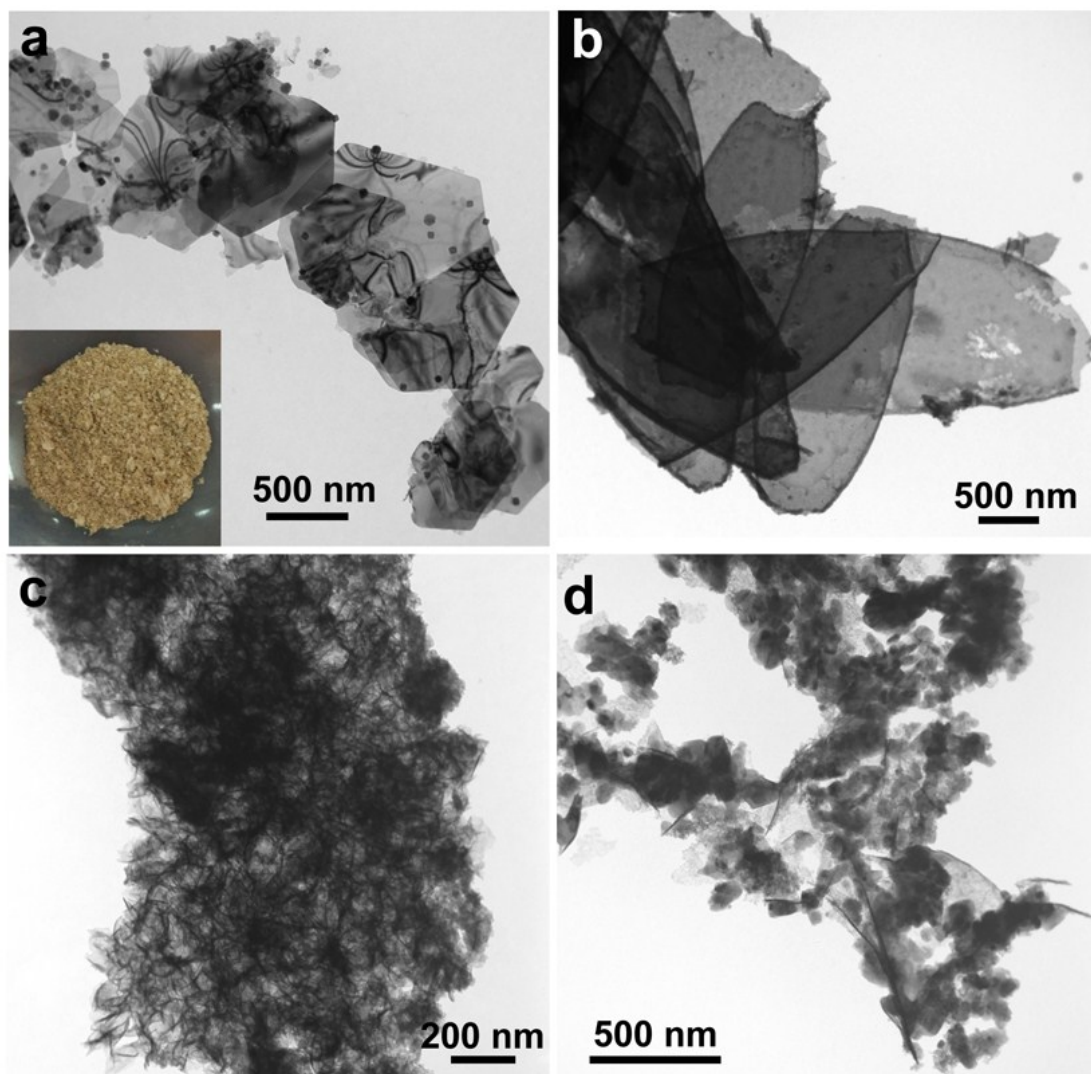
**Figure S3.** (a) Low-magnification and (b) high-magnification SEM images, and (c) TEM image of  $\text{CoS}_x$  nanosheets.



**Figure S4.** TEM image of  $\text{CoS}_x$  nanosheets.

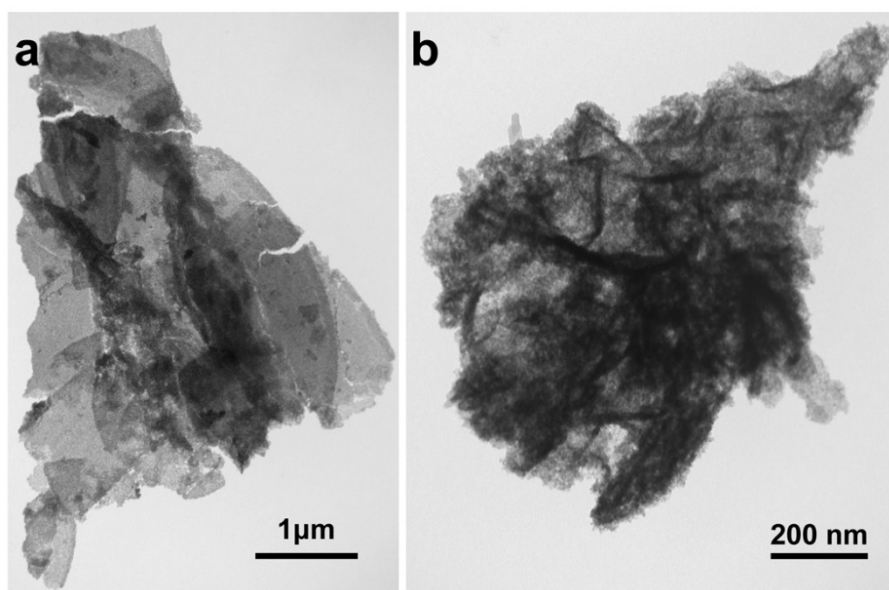


**Figure S5.** (a) TEM and (b) HRTEM images of the  $\text{CoS}_x$  products obtained after a sulfuration reaction time of 10 min.



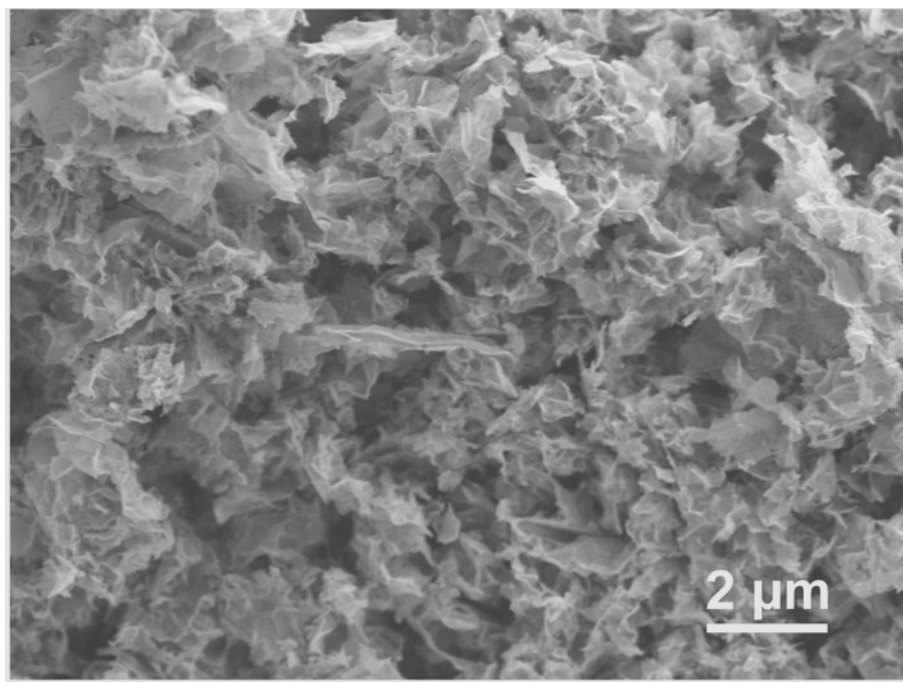
**Figure S6.** (a) TEM image of  $\text{Co(OH)}_2$  nanosheets synthesized at 85 °C in  $\text{H}_2\text{O}$  without TAA. Inset: the photograph of  $\text{Co(OH)}_2$  nanosheets. (b,c) TEM images of  $\text{CoS}_x$  products prepared in alcohol (b) and mixed reaction solution of  $\text{H}_2\text{O}$  (40 mL) and alcohol (140 mL) (c). (d) TEM image of  $\text{CoS}_x$  product prepared with the sulfuration reagent of  $\text{Na}_2\text{S}$ . The CoMOFs were unstable at 85 °C in  $\text{H}_2\text{O}$  without TAA, and would release the  $\text{Co}^{2+}$  ions, resulting in the generation of  $\text{Co(OH)}_2$  nanoplates (Figure S6a). While in alcohol, the growth of  $\text{CoS}_x$  would surpass the dissolution of the CoMOFs, therefore, the sulfuration reaction between  $\text{S}^{2-}$  ions from TAA and  $\text{Co}^{2+}$  ions from CoMOFs occurred at the surface of CoMOFs. With the

processing of the sulfuration reaction, the hollow leaf-like nanostructures were obtained (Figure S6b). It is noted that the kinetics between the dissolution of the CoMOFs and the growth of the  $\text{CoS}_x$  could be well controlled by employing mixed reaction solution of  $\text{H}_2\text{O}$  and alcohol, and ultra-thin wrinkle  $\text{CoS}_x$  nanosheets were prepared (Figure S6c). While  $\text{Na}_2\text{S}$  was used as sulfuration agent instead of TAA, the rate of the  $\text{CoS}_x$  growth would be too fast due to the excessed release of  $\text{S}^{2-}$  ions, thereby the product displayed the existence of particles on nanosheets (Figure S6d).

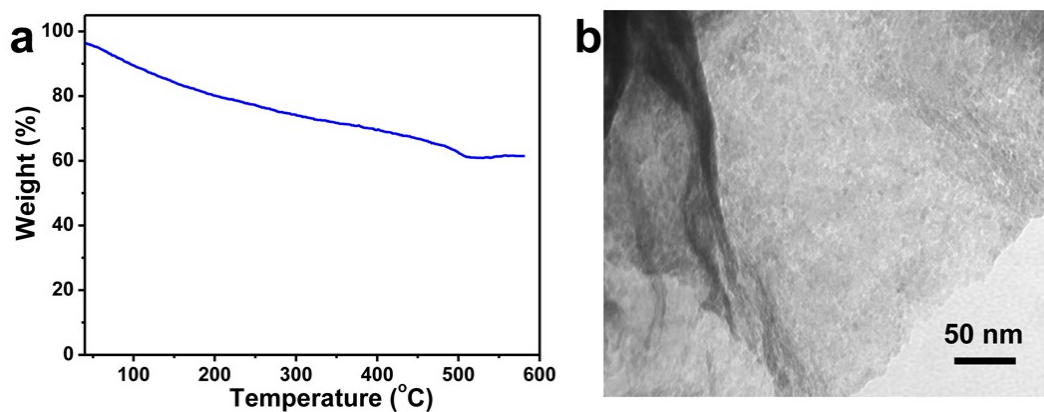


**Figure S7.** TEM images of (a) Zn MOFs derived product and (b) ZnCo MOFs derived product synthesized under the same procedures with  $\text{CoS}_x$  nanosheets except for the use of ZnMOFs and ZnCoMOFs precursors, indicating the unique roles of CoMOFs precursor in forming large-area  $\text{CoS}_x$  nanosheets

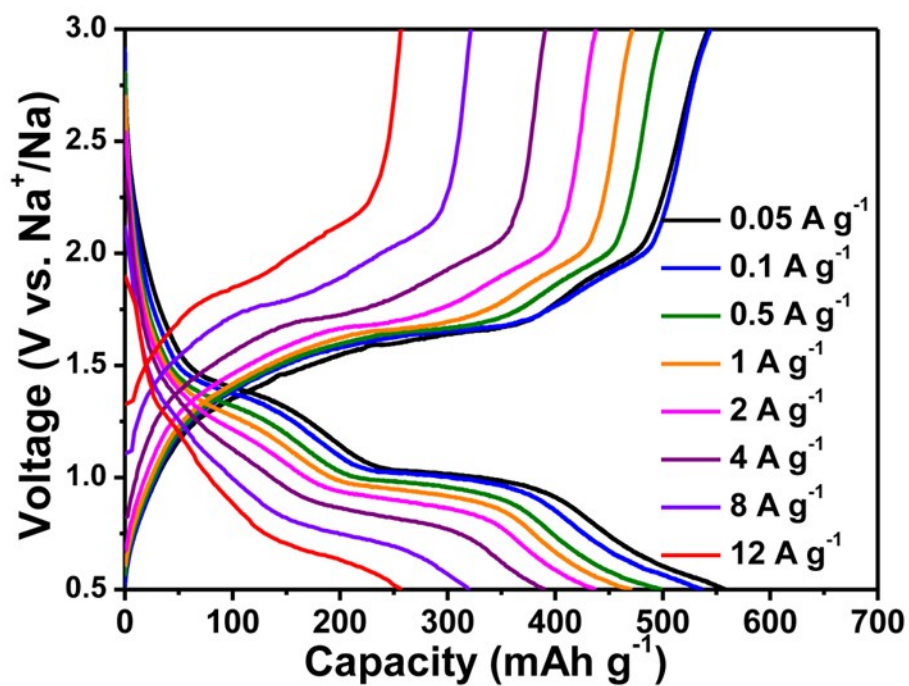




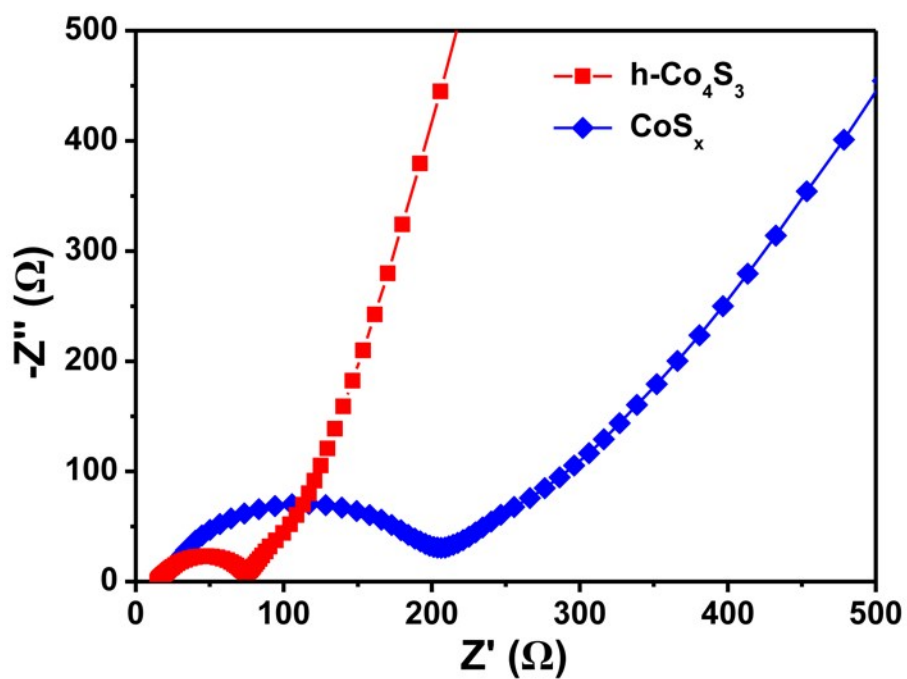
**Figure S8.** Low-magnification SEM image of h-Co<sub>4</sub>S<sub>3</sub> nanosheets.



**Figure S9.** (a) Thermogravimetric analysis of CoS<sub>x</sub> nanosheets conducted in nitrogen atmosphere. (b) TEM image of the sample (detonated as CoS<sub>x</sub>-350 °C) synthesized by annealing treatment of CoS<sub>x</sub> nanosheets at lower temperature of 350 °C in nitrogen atmosphere.

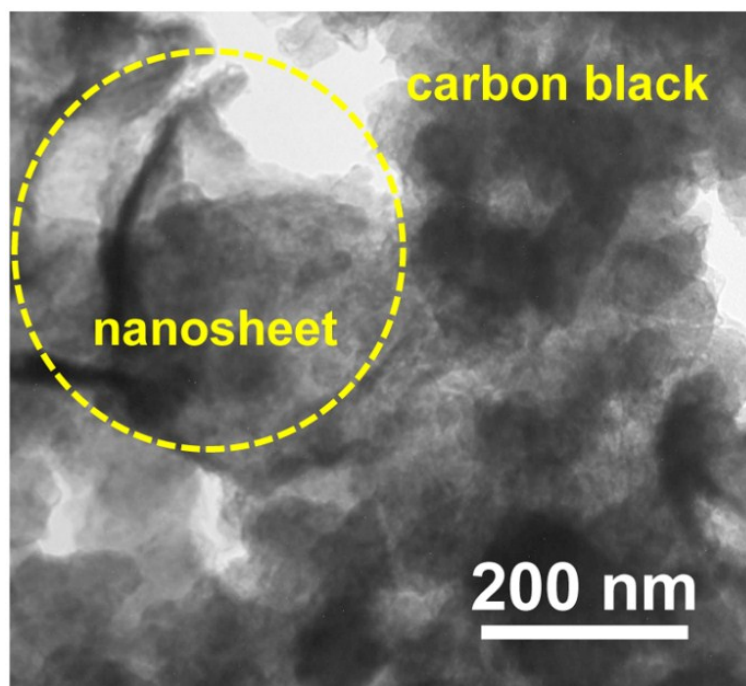


**Figure S10.** Galvanostatic charge and discharge profiles of h-Co<sub>4</sub>S<sub>3</sub> anode cycled at different current densities from 0.05 to 12 A g<sup>-1</sup>.

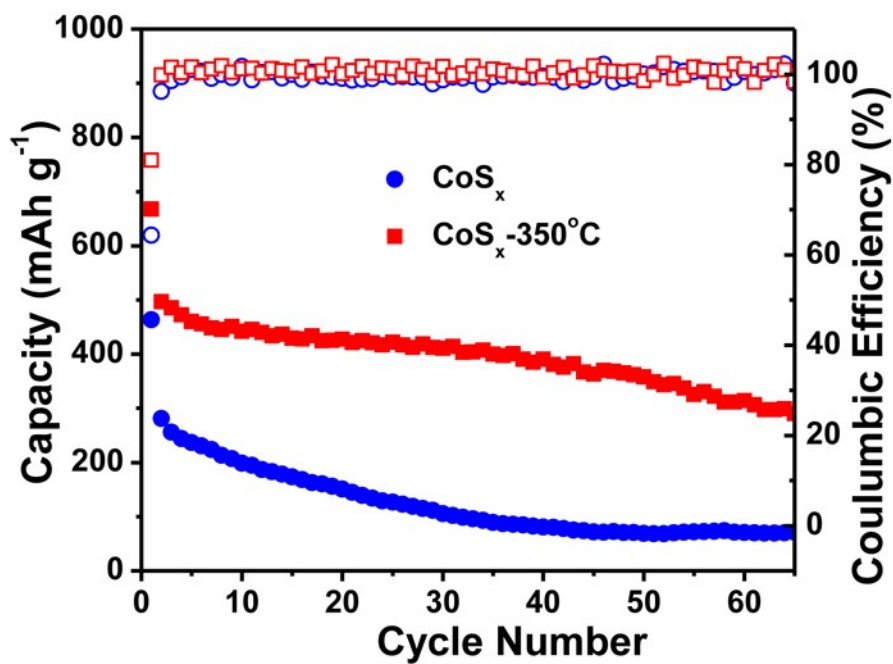


**Figure S11.** Electrochemical impedance spectroscopies of h-Co<sub>4</sub>S<sub>3</sub> and CoS<sub>x</sub> electrodes.





**Figure S12.** TEM image of cycled h-Co<sub>4</sub>S<sub>3</sub>, showing the nanosheets marked in the yellow circle were well kept without pulverization.



**Figure S13.** Cycling performance of CoS<sub>x</sub> and CoS<sub>x</sub>-350 °C electrodes in DGM-based electrolyte tested at 0.1 A g<sup>-1</sup>.

**Table S1** Comparison of the lateral size and thickness of MOFs derived nanosheets in this work and other reported Co based nanosheets

Materials	Preparation method	Lateral size (nm)	Thickness (nm)	Reference
<b>CoS<sub>x</sub> nanosheet</b>	sulfuration of CoMOFs with TAA	micrometer scale(~1000-3000)	<16	<b>This work</b>
<b>h-Co<sub>4</sub>S<sub>3</sub> nanosheet</b>	annealing treatment	micrometer scale(~1000-3000)	<30	<b>This work</b>
CoS nanosheet	sulfuration of Co(OH) <sub>2</sub> with Na <sub>2</sub> S	<200	<25	Ref.[1]
CoS <sub>x</sub> nanosheet	electrodeposition	<50	<20	Ref.[2]
nickel cobalt sulfide nanosheet	electrodeposition	<200	<25	Ref.[3]
NiCo <sub>2</sub> S <sub>4</sub> nanosheets	sulfuration of NiCo-precursor with Na <sub>2</sub> S	<500	<50	Ref.[4]
NiCo-layered double hydroxides	etching of ZIF67 with Ni(NO <sub>3</sub> ) <sub>2</sub>	<300	<50	Ref.[5]
Co(OH) <sub>2</sub> flower-like nanosheets	hydrothermal treatment of MOF	~1000	<30	Ref.[6]
CoNi hydroxide nanosheets	in situ decomposition of Co-based acetate hydroxide MOFs	<100	<3	Ref.[7]
porous Co <sub>3</sub> O <sub>4</sub> nanosheets	pyrolysis process of Co-based MOF nanoplates in air	micrometer scale	~30	Ref.[8]
holey Co <sub>3</sub> O <sub>4</sub> nanosheets	GO templated synthesis	micrometer scale	~30	Ref.[9]

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