

## Electronic Supplementary Information

### **Dual-Function Sacrificing Template Directed Formation of MoS<sub>2</sub>/C Hybrid Nanotubes Enabling Highly Stable and Ultrafast Sodium Storage**

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## Experimental Section

**Synthesis of  $Sb_2S_3$  nanorods:**  $Sb_2S_3$  nanorods were prepared according to a previous report. Typically, 4 mmol  $SbCl_3$  and 8 mmol L-cysteine were dissolved in 80 mL distilled water (DIW) with the addition of 8mmol  $Na_2S \cdot 9H_2O$ . After stirring for 3h, the homogeneous solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. Finally, the dark-brown product was collected by centrifugation, washed three times with DIW and ethanol before drying at 60 °C overnight under vacuum to further use.

**Synthesis of  $MoS_2/C$ -HNT:** For the synthesis of  $MoS_2/C$  hybrid nanotubes, 50 mg of  $Sb_2S_3$  nanorods were dispersed into 20 ml of DI water under sonication, followed by adding 0.09 mmol of Phosphomolybdic acid and 72 $\mu$ L of pyrrole monomer. The above mixture was allowed to react for 30h at 50 °C under stirring. The product was then collected and washed with deionized water several times and dried at 60 °C in a vacuum oven for 12 h. The final product of  $MoS_2/C$ -HNTs can be obtained annealed at 700 °C for 4h in  $H_2/Ar$  (5 %) with a heating rate of 3 °C  $min^{-1}$ . The formation of  $WS_2/C$ -HNT and  $Mo_{0.5}W_{0.5}S/C$ -HNT can be easily achieved by replacing phosphomolybdic acid with phosphotungstic acid and using mixture of molybdphosphoric acid/ phosphotungstic acid with equal amount, respectively, while keeping other conditions constant. The synthesis of  $MoSSe/C$ -HNTs was carried out by slightly modified thermal annealing process. Instead of direct thermal annealing treatment, certain amount of Se power was loaded at the upstream of  $Sb_2S_3@PMo_{12}$  core/shell precursor nanowires.

**Materials Characterization:** X-ray diffraction (XRD, TTR-III, Japan) was used to test the crystal structure of synthesized materials with  $2\theta$  from 10 to 70° at a scanning rate of 2 °  $min^{-1}$ . The

morphology and structure of samples was investigated by field-emission scanning electron microscopy (FESEM, JSM-6700F, Japan) and transmission electron microscopy (TEM, H-7650, Japan; Talos F200X, USA) were utilized to analyze the morphology and structure of the synthesized materials. Surface Area and Porosity Analyzer (ASAP 2020) were utilized to characterize nitrogen sorption isotherms. The valence of several elements was researched by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, USA).

**Electrochemical Measurement:** The electrochemical performance were evaluated by assembling CR2016 coin-type cells. The electrode was fabricated by compressing a mixture of active materials, carbon black (Super-P) and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1 on the Copper foil with a loading mass of active materials about 1.2-1.5 mg cm<sup>-2</sup>. 1M NaClO<sub>4</sub> in propylene carbonate (PC) was used as electrolyte and Na foil was served as both reference and counter electrode with a glass fiber (Whatman) as separator. Cyclic voltammetry (CV) measurement was performed at voltage ranging from 0.01 to 3 V on a CHI660E electrochemical workstation. Galvanostatic discharge/charge tests were conducted on a NEWARE battery tester.

**Fabrication of Sodium-ion based Hybrid Capacitors:** For the sodium-based hybrid capacitors (NIHCs), after mixing the activated carbon (AC, 80 wt%), additive carbon black (10 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) binder in N-methyl-2-pyrrolidone (NMP), the prepared solution was coated on Cu foil with the loading mass of 1.2-1.5 mg cm<sup>-2</sup> and dried at 100 °C for 12 h in an oven. For the anode, the MoS<sub>2</sub>/C-HNT electrode in Na-half cells was pre-cycled for five times at 0.1 A g<sup>-1</sup> within the potential range of 0.01-3V followed by dismantling the cells in the glove box. The NIHCs were then built by assembling the preactivated MoS<sub>2</sub>/C-HNT anode and the AC cathode in CR2016 coin cells with the same separator and electrolyte as that in half cells with the mass ratio

of 1:3 (anode:cathode). The voltage range during the charge and discharge process of the NIHCs device was 0-4 V. The specific energy and power density of the NIHCs were calculated as follows:

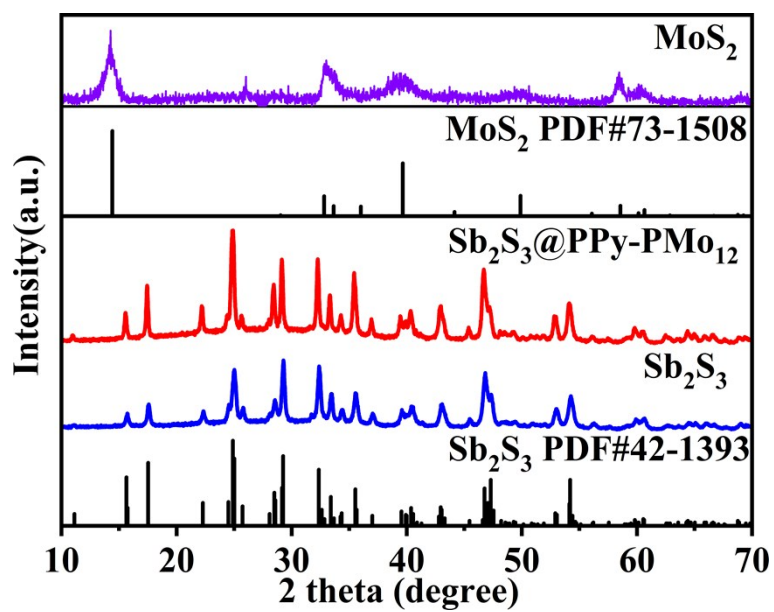
$$E = \int_{t_1}^{t_2} IV dt = \Delta V \frac{I}{m} t$$

$$P = \frac{E}{t} = \Delta V \frac{I}{m}$$

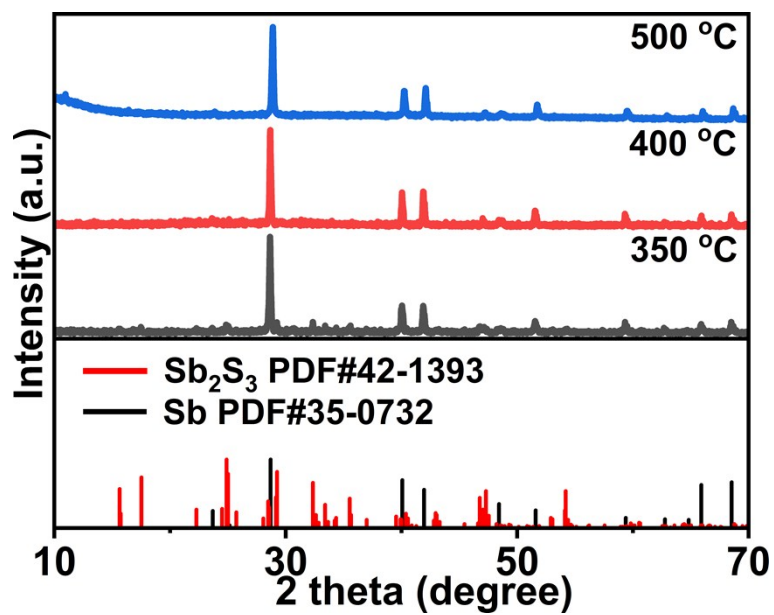
$$\Delta V = (V_{\max} + V_{\min}) / 2$$

Where E (Wh kg<sup>-1</sup>) is the energy density and P (W kg<sup>-1</sup>) is the power density. I is the constant discharge current (A), t<sub>1</sub> and t<sub>2</sub> are the start and end of discharge time (s), and t is the time period for a full discharge (s). V<sub>max</sub> is the potential at the beginning of discharge after the IR drop, V<sub>min</sub> is the terminal voltage in the discharge process. m is the total mass of the active material in both anode and cathode.

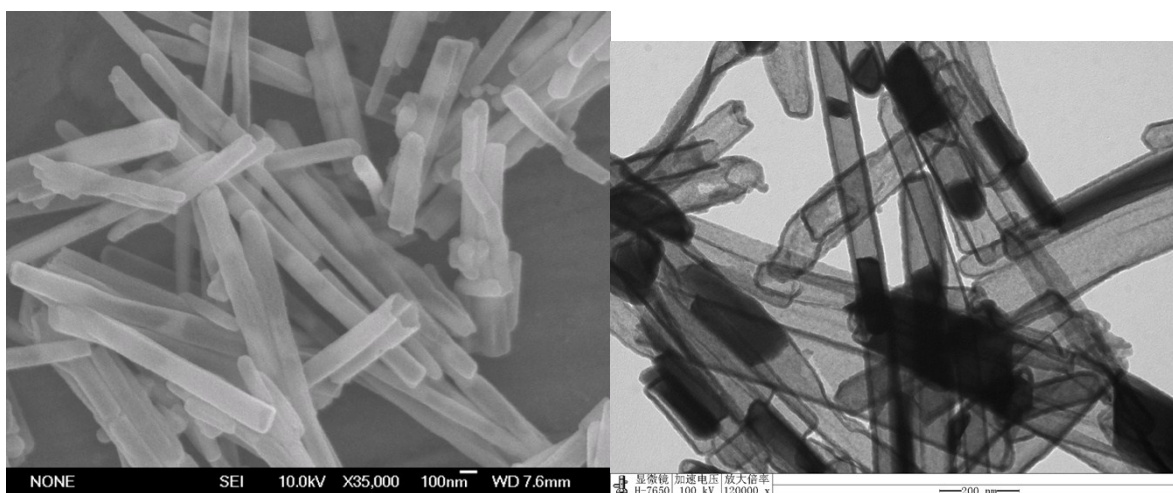
## 1. Characterization



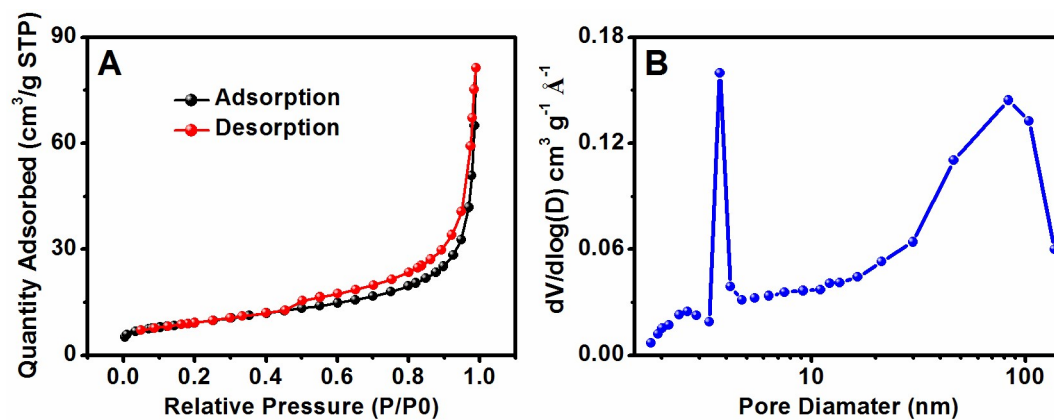
**Figure S1.** XRD patterns for Sb<sub>2</sub>S<sub>3</sub> nanowires, Sb<sub>2</sub>S<sub>3</sub>@PPy-PMo<sub>12</sub> core/shell nanowires and MoS<sub>2</sub>/C-HNTs.



**Figure S2.** XRD patterns of products after annealing the  $\text{Sb}_2\text{S}_3@PPy\text{-PMo}_{12}$  core/shell nanowires at 350, 400 and 500 °C for 4 h.

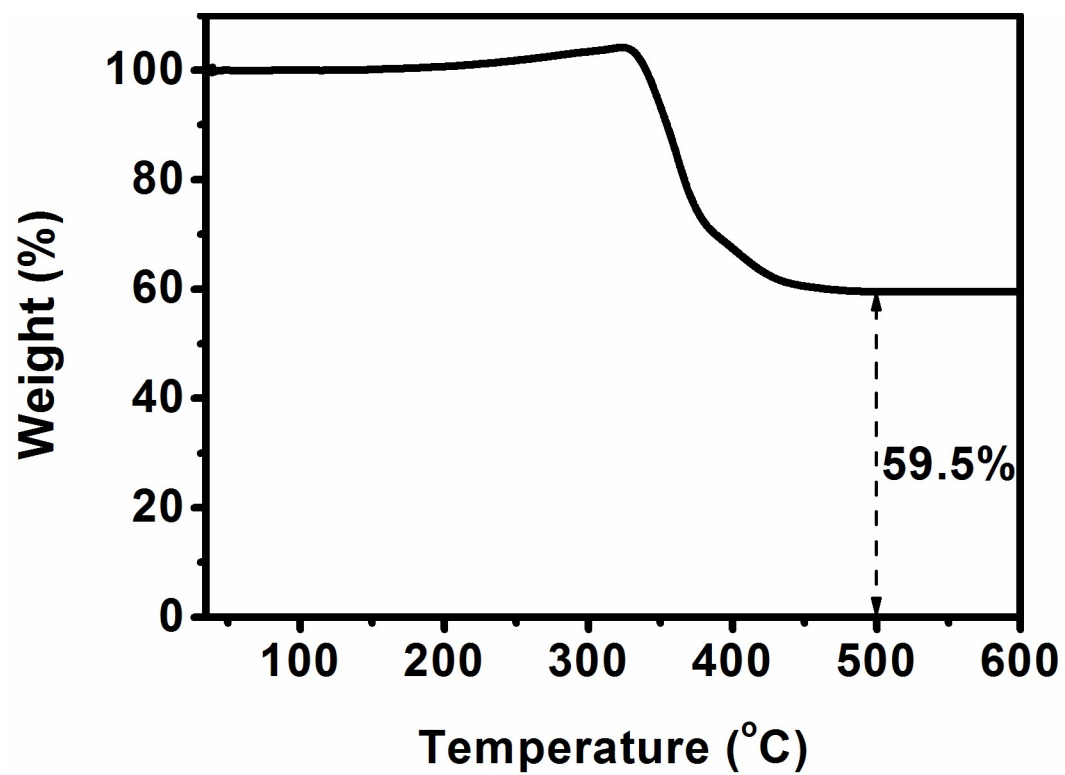


**Figure S3.** FESEM and TEM images of the product after annealing at 500 °C for 4 h.

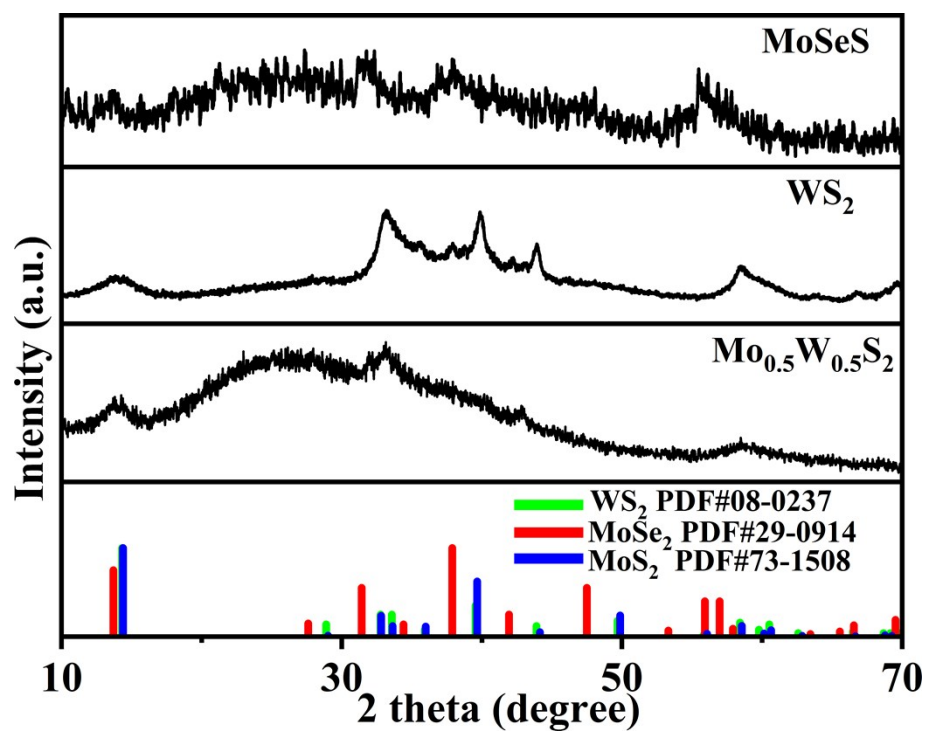


**Figure S4.** N<sub>2</sub> adsorption/desorption isotherms and corresponding pore size distribution of MoS<sub>2</sub>/C-HNTs.

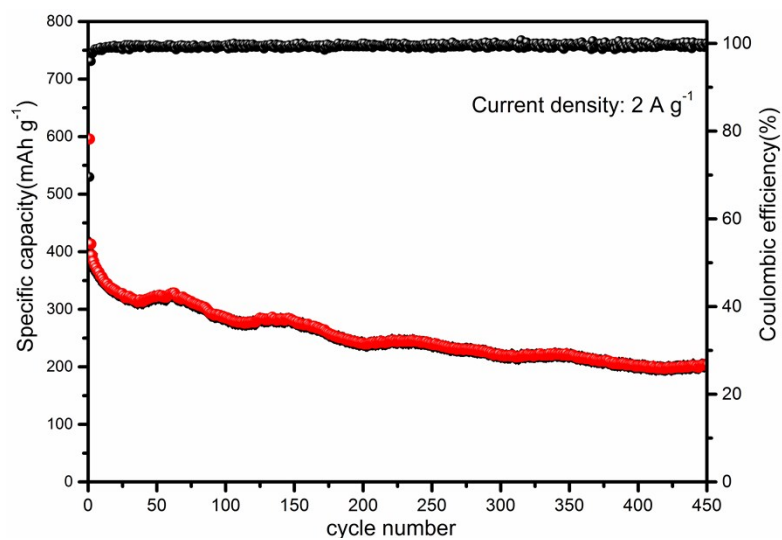




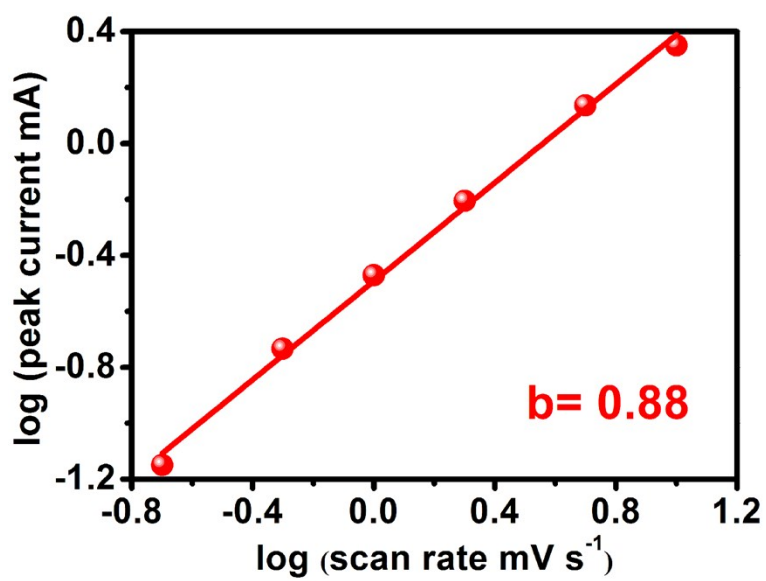
**Figure S5.** Thermogravimetric analysis of MoS<sub>2</sub>/C-HNTs under air.



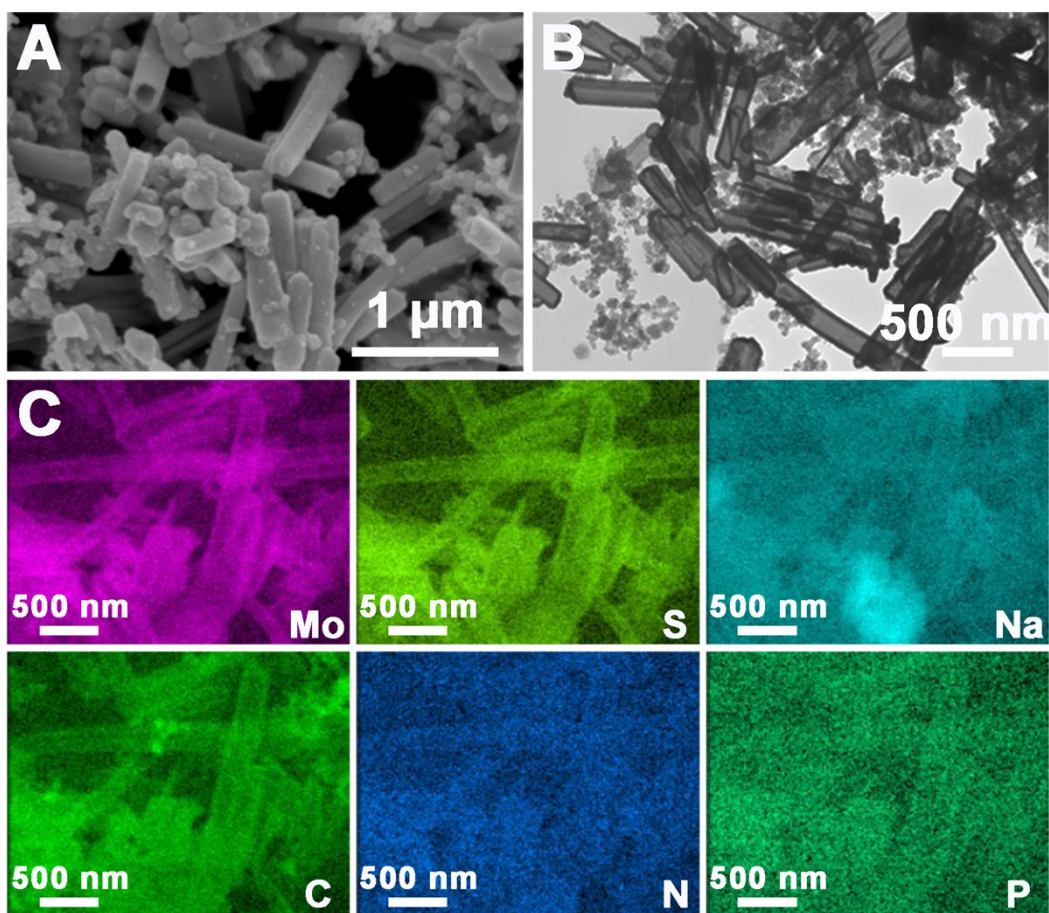
**Figure S6.** XRD patterns for WS<sub>2</sub>, MoWS<sub>2</sub> and MoSeS hybrid nanotubes.



**Figure S7.** Cycling performance of product annealing at 500 °C for 4 h with a half-cell configuration using Na metal as the counter electrode.



**Figure S8.** Plot of  $\ln$  (peak current) versus  $\ln$  (scan rate) at corresponding peak potential.



**Figure S9.** A) FESEM, B) TEM and C) Corresponding elemental mapping results for MoS<sub>2</sub>/C-HNT as anode after 5000 cycles at a current density of 10 A g<sup>-1</sup>.