1D hybrid metal coordination polymers derived hierarchical $Co_{1-x}S$/NC/MnS/NC nanowires for advanced sodium-ion battery

Haibin Wang, Lantao Chen, Feng Xu, Yufei Zhang* and Haosen Fan*

Experimental section

Synthesis of $Co_{1-x}S$/MnS/NC

CoMn-NTA precursor was prepared by a simple hydrothermal method, and all materials were used as received without purification. Above all, 2.14 g $CoCl_2 \cdot 6H_2O$, 1.07 g $MnCl_2 \cdot 4H_2O$, and 0.9 g nitrogen triacetic acid were added with 45 mL deionized water and 15 mL isopropyl alcohol. Then, after stirring for 20 min, the mixed solutions were transferred to a 100 mL Teflon-lined autoclave. The Teflon-lined autoclave was placed in an oven, and the temperature was raised from room temperature to 180 ℃. After 24 h for 180 ℃, the pink product was collected by filtration and washed several times with water and ethanol. The final product was obtained by drying the obtained powder at 60 ℃ for 12 h and put into the porcelain boat by annealing at 600 ℃ under the protection of N2 with a heating rate of 3 ℃ min^{-1}. Then, the sulfur powder and the annealed powder were placed in the upper and middle part with a mass ratio of 2:1 and sulphuration at 600 °C in nitrogen with a heating rate of 3 °C min^{-1}. After sulfidation for 2 h, the final $Co_{1-x}S$/MnS/NC was synthesized.

Synthesis of $Co_{1-x}S$/MnS

$Co_{1-x}S$ was synthesized using the same method as the $Co_{1-x}S$/MnS/NC, except with the addition of no $MnCl_2$. The same is true of MnS, only without the addition of $CoCl_2$.

Material characterization

The crystal structure of materials was analyzed by X-ray diffraction (XRD, PANalytical PW3040/60 X-ray powder diffractometer equipped with Cu-Kα radiation). The scanning electron microscopy (SEM, JSM-7001F high-resolution microscope) and transmission electron microscopy (TEM, JEOL JEM2100F microscope) were recorded to characterize the micro-morphology of the synthesized products. The elemental composition and molecular structure were determined by X-ray photoelectron spectroscopy (XPS, Al-Kα).

Electrochemical measurements

All the electrochemical performances were evaluated in 2032-type coin cells assembled from the materials as the anode. The working electrodes were made of 70 wt% active material, 20 wt% acetylene black, and 10 wt% polyvinylidene fluoride, respectively. The loading of active material is 0.8 mg cm^{-2}. Then, N-Methyl-2-pyrrolidinone (NMP) was added to the above mixture and ground thoroughly to the slurry. Then the slurries were coating on copper foil and dry overnight in vacuum oven at 80℃. Then the coin cells were assembled under the argon-filled ultra-pure glove box with using sodium coil, Whatman glass fiber GF/D, and 1.0M $NaClO_4$ as anode, separator, and electrolyte, respectively. Galvanostatic charge-discharge tests were measured on the NEWARE battery tester at 0.01-3.0V. Cyclic voltammetry (CV) test window voltage ranged from 0.01-3.0V at the scan rate of 0.1mV s^{-1}. The electrochemical impedance spectroscopy (EIS) was tested with frequency range from 0.01Hz to 100KHz.

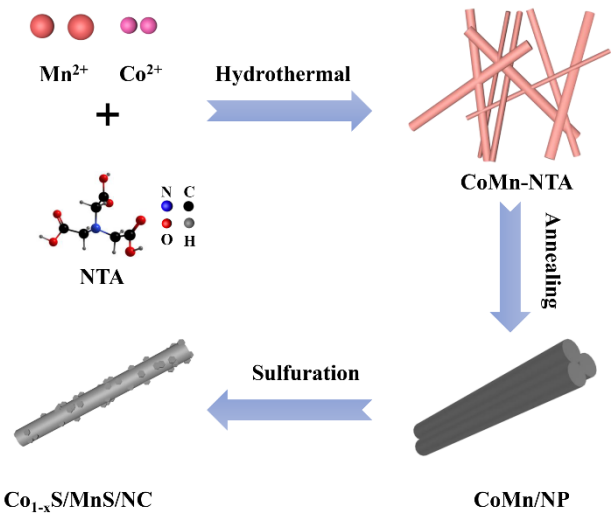

Fig. S1 The scheme of synthetic process of $Co_{1-x}S$/MnS/NC heterostructure.

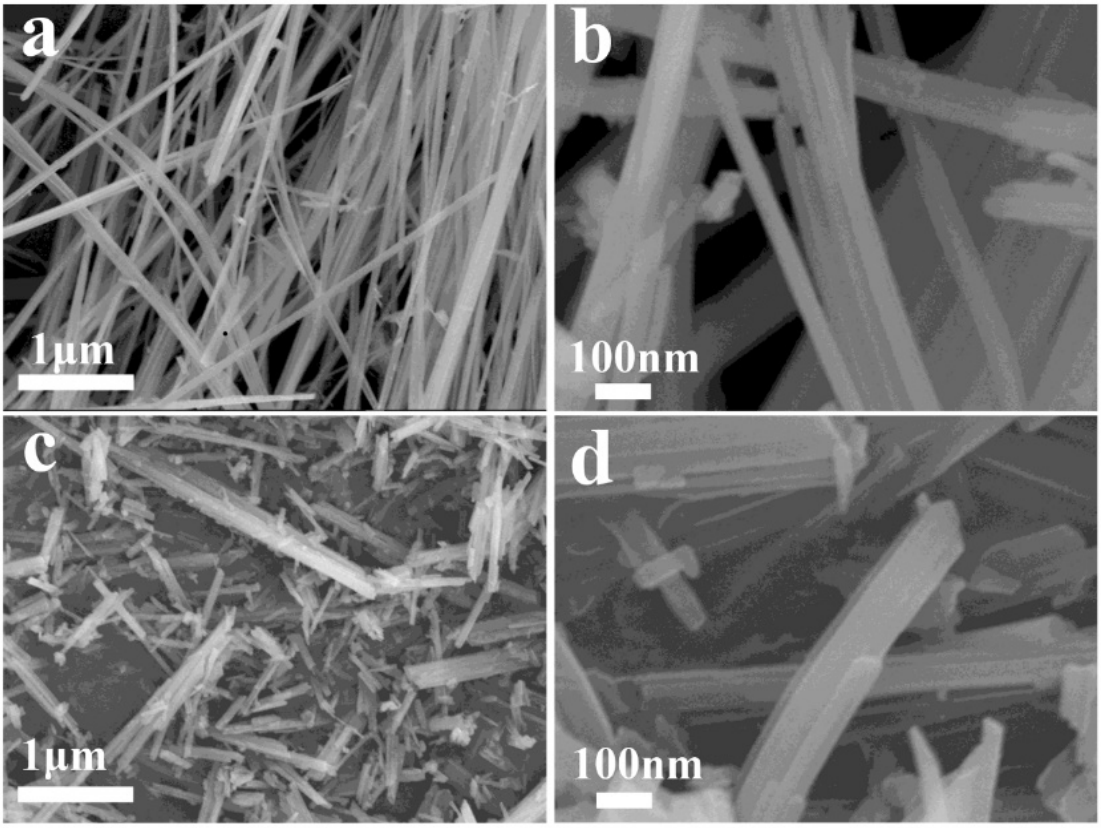

Fig. S2 SEM images of (a, b) Co-NTA precursors. (c, d) Mn-NTA precursors.

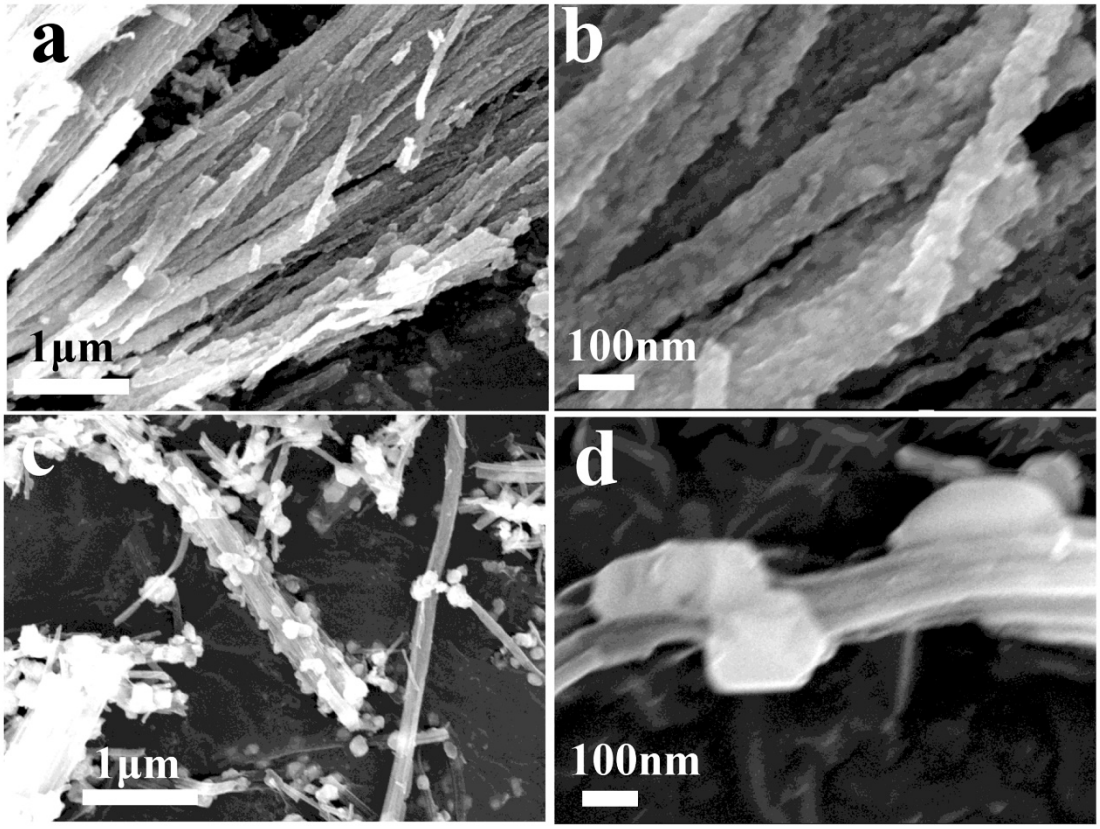

Fig. S3 SEM images of (a, b) Annealing Co-NTA. (c, d) Annealing Mn-NTA.

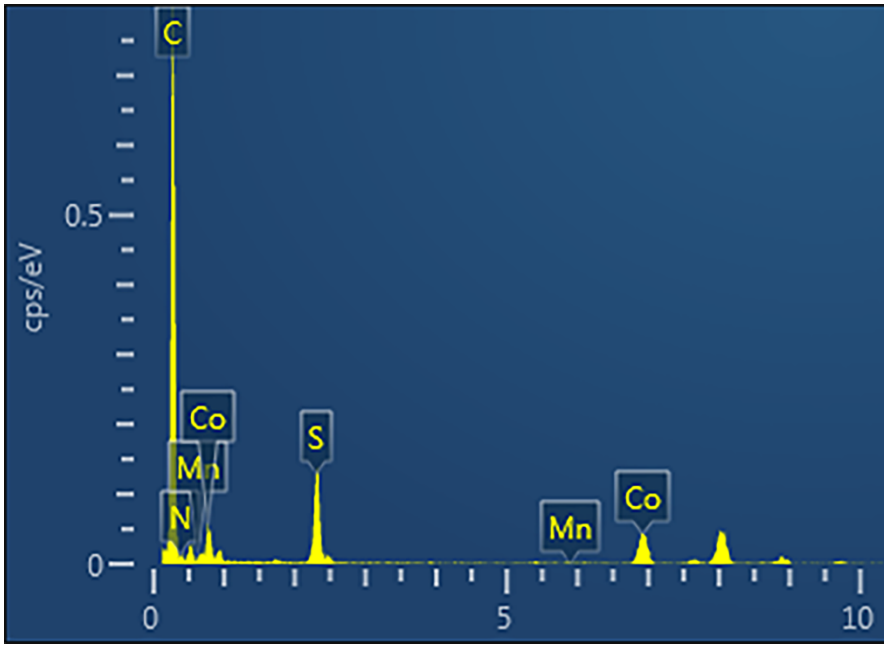

Fig. S4 Energy-dispersive X-ray spectroscopy (EDS) spectrum of $Co_{1-x}S$/MnS/NC

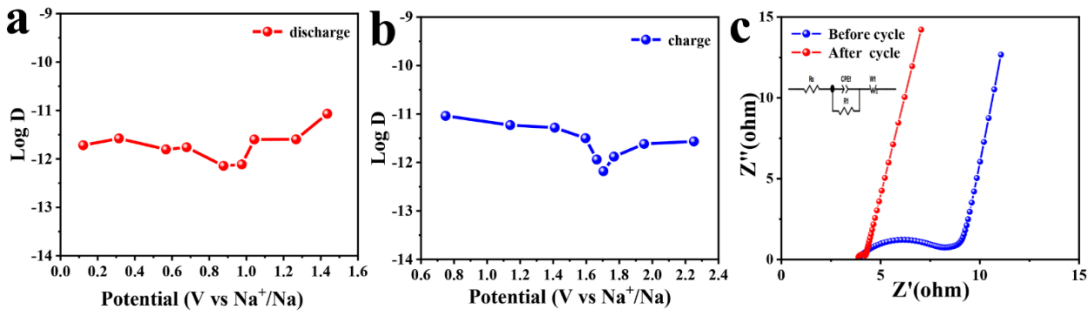

Fig. S5 (a) The diffusion coefficient of Na^+ in discharge processes. (b) The diffusion coefficient of Na^+ in charge processes. (c) Nyquist plots of $Co_{1-x}S$/MnS/NC in SIBS (inset: equivalent circuit).