

Supplementary Information

Three-dimensional crosslinked nano-structure via in-situ growth of carbon nanotubes/cobalt sulfide composites on porous carbon nanofibers for enhanced sodium storage

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CRedit author statement

Qian Shi: Investigation, Conceptualization, Writing-original draft. **Kaiyun Chen:** Formal analysis, Writing-review & editing. **Zhonghai Yu:** Methodology, Validation. **Zhiyong Dai:** Visualization, Formal analysis. **Jingxiao Wang:** Validation. **Yuanliang Chen:** Formal analysis. **Kun Cao:** Validation. **Lan Ma:** Writing-review & editing. **Rui Han:** Supervision. **Fanghua Tian:** Methodology. **Sen Yang:** Resources, Writing - Review & Editing, Supervision, Funding acquisition. **Yin Zhang:** Conceptualization, Writing-review & editing, Project administration, Funding acquisition.

Sample preparation

0.5g Zinc acetate dihydrate ($Zn(AC)_2 \cdot 2H_2O$) and 1g polyacrylonitrile (PAN) were dissolved in 10ml N, N-Dimethylformamide (DMF) with a stirring time of 2h and heating at 70 °C. The as-prepared solution was transferred into a syringe with a steel needle for electrospinning. The electrospinning voltage was 11kV and the distance between the needle and the collecting plate was 12cm. The as-prepared nanofibers were oxidized at 250°C for 1 h with a heating rate of 5°C/min. The oxidized nanofibers (named $Zn(AC)_2/PAN$ NF) were soaked in a $Co(AC)_2$ solution of 0.05 mol/L for 24h. After being dried at 50°C, 50mg $Zn(AC)_2/PAN$ NF with Co^{2+} on the surface was placed in a quartz boat with 100 mg melamine for carbonization in Ar. The carbonization temperature was 1000°C for 2h with a heating rate of 2°C /min, to obtain CFs@CNT/Co. The CFs@CNT/Co was sulfurized in Ar/ CS_2 atmosphere at 700°C for 2h, with

a heating rate of 5°C/min to synthesize CFs@CNT/CoS_x.

Material characterization

The X-ray diffraction (XRD, D8-ADVANCE, Cu K α radiation) was used to characterize the crystal structure of the samples, with measurements taken across a 2θ angle range of 10–80°. Raman spectroscopy (hr800) was used to analyze the molecular structure of the samples with a laser wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB Xi+, Al K α X-ray source) was conducted to investigate the surface elemental content and electronic states of the samples. Field emission scanning electron microscopy (SEM, JSM-7000F) was used to observe the morphology and elemental content of samples. The sample morphology and structure were observed through transmission electron microscopy (TEM, JEOF-2100F). The thermal behavior from room temperature to 800 °C under air is based on the thermogravimetric analysis (TGA, HITACHI STA7200). The nitrogen adsorption/desorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 analyzer.

Electrochemical testing

The active materials, Super P, and polyvinylidene fluoride (PVDF) were mixed in a mass ratio of 7:2:1, and then N-methyl-2-pyrrolidinone (NMP) was added and stirred to form a uniform slurry. The as-prepared slurry was evenly coated onto copper foil, which was then dried in a vacuum at 80 °C for 24 h. The dried copper foil was cut into 12 mm diameter electrodes and then packaged into coin cells in the glove box. The loading mass of active material is around 0.8-1 mg cm⁻². The sodium foil was used as the electrode in the coin cell. The water and oxygen concentrations in the glove box were lower than 0.1 ppm. 1.0 M NaCF₃SO₃ in diethylene glycol dimethyl ether (DIGLYME) was used as the sodium battery electrolyte. A LAND CT2001A system was used for galvanostatic current discharge/charge and GITT tests to determine the Na⁺ storage performance of the electrode across a voltage range of 0.01–3 V. Cyclic voltammetry (CV) curves were also obtained by using a CHI760 electrochemical test system.

Supplementary Figures

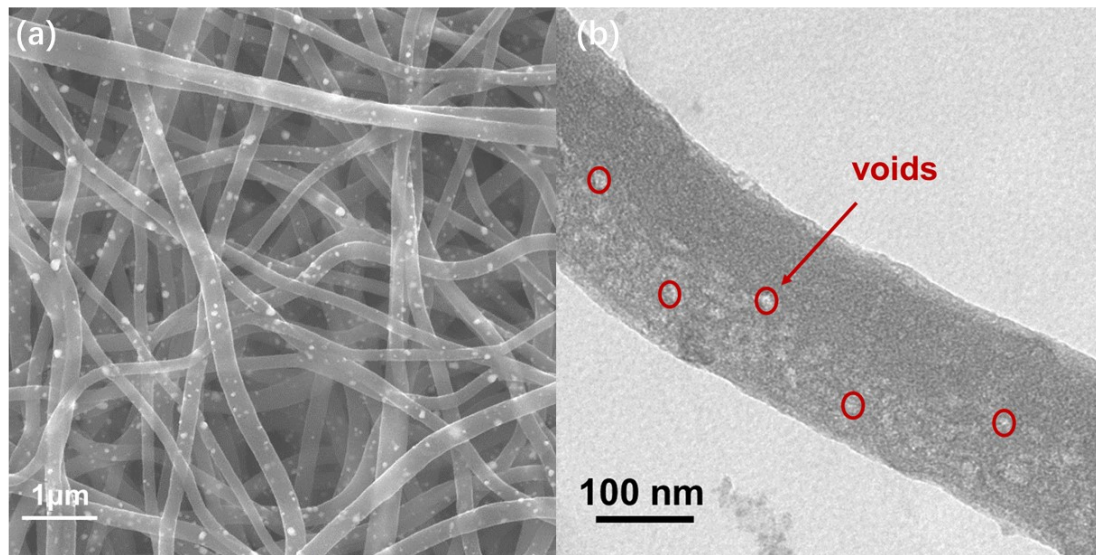


Fig. S1 (a) SEM image and (b) TEM image of CFs/Co.

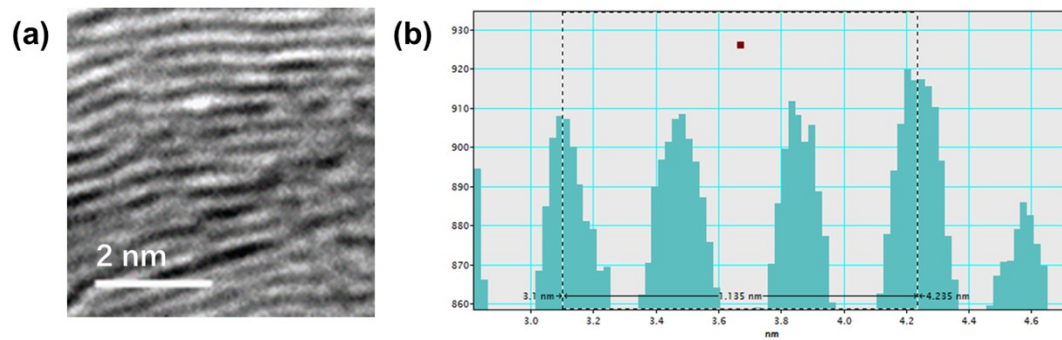


Fig. S2 (a) HRTEM image and (b) corresponding profile of carbon nanotubes.

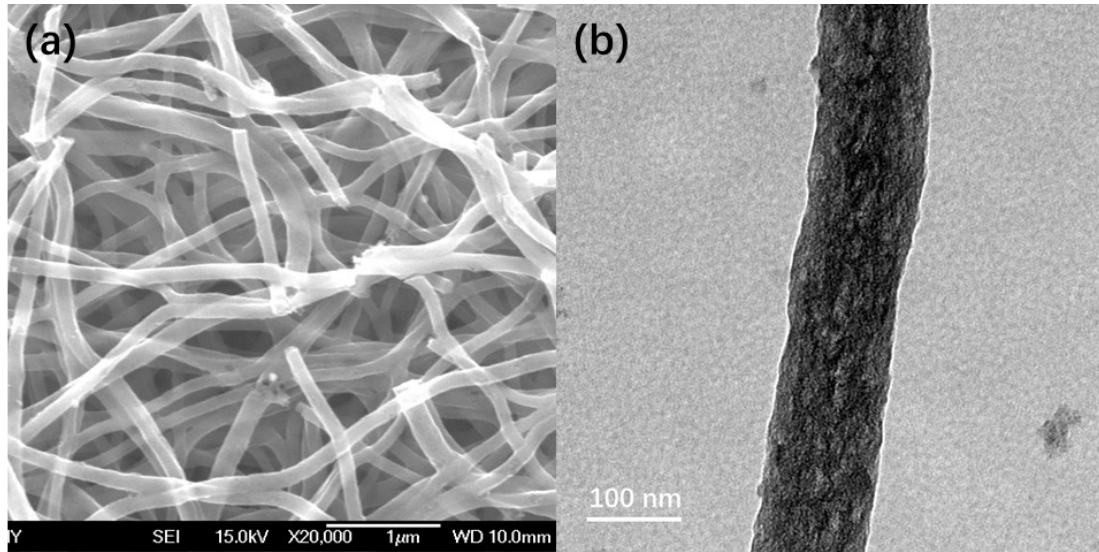


Fig. S3 (a) SEM image and (b) TEM image of CFs.

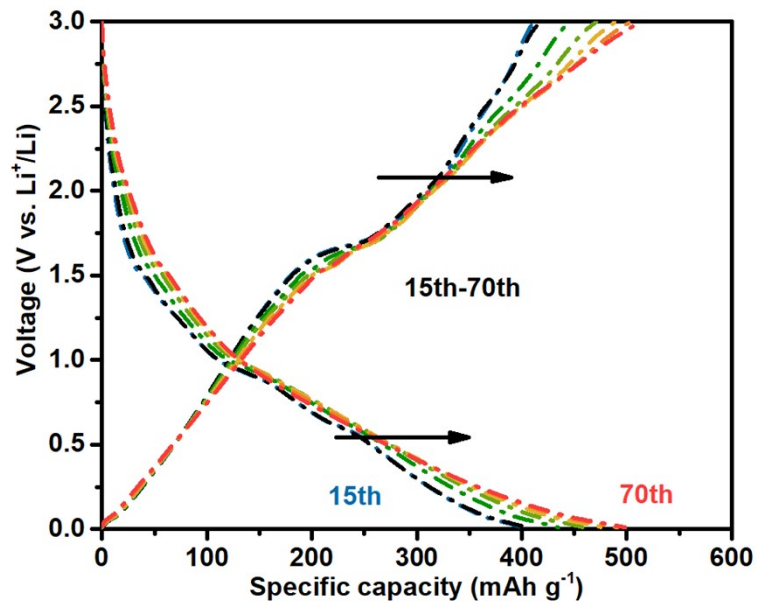


Fig. S4 Selected discharge-charge profiles of CFs@CNT/CoS_x for the 15th, 20th, 30th, 40th, 50th, 60th, and 70th cycles.

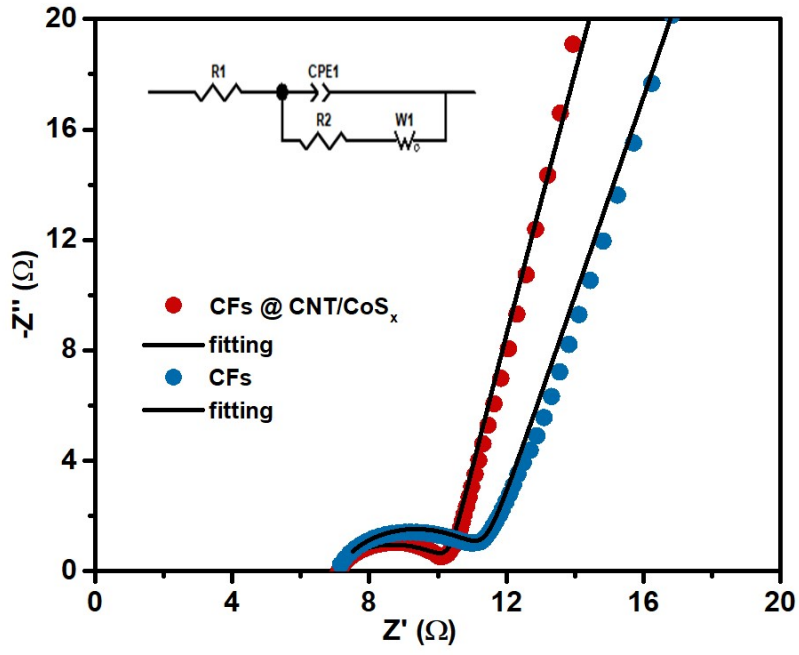


Fig. S5 Electrochemical impedance spectra of CFs@CNT/CoS_x and CFs.