Supporting information

Topochemical and phase transformation induced Co_9S_8/NC nanosheets for high-performance sodium-ion battery

Yining Li, Shimei Wu, Chilin Liu, Zhiting Liu, Wei Yang, Yufei Zhang* and Haosen Fan*

Experimental section

Chemicals and materials

Cobaltous nitrate hexahydrate (99%), 2-methylimidazole(99.5%), thiourea and methyl alcohol were purchased from Macklin (Shanghai, China). Polyvinylidene fluoride (99%) was purchased from Yuanye (Shanghai, China). Acetylene black (99.5%) was purchased from Yilongsheng (Suzhou, China). All chemicals were directly used without further treatments.

Synthetic methods

Slightly improved on the traditional method, 0.582g $CO(NO_3)_2 \cdot 6H_2O$ (1mmol) was dissolved in 20ml methanol solution, and 0.328g 2-methylimidazole (2mmol) was dissolved in 20ml methanol solution. After being completely dissolved by ultrasound for 5 minutes, the methanol solution of $CO(NO_3)_2 \cdot 6H_2O$ was quickly added into the methanol solution of 2-methylimidazole while stirring. After the solution was aged for 24 hours, a methanol solution containing ZIF-67 was obtained. The ZIF-67 was rinsed with methanol, and the precipitation collected by centrifugation was dried overnight under a vacuum at 60℃. The prepared ZIF-67 (2mmol) was added to 20 ml of completely dissolved deionized water containing thiourea (4mmol). After ultrasonic dissolution, the solution was transferred to a polytetrafluoroethylene-lined autoclave and heat treated at 160℃ for 12h. It was cleaned with deionized water, collected by centrifugation and dried overnight under vacuum at 60℃ to obtain ZIF-67S. ZIF-67S was annealed in a tube furnace under nitrogen atmosphere, heated to 400℃, held for 2 hours at a heating rate of 5℃/min, and the final product Co_9S_8/NC was obtained. For comparison, ZIF-67 was directly annealed and vulcanized to obtain the final product CoS_2/NC.

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. Thereafter, added N-Methyl-2-pyrrolidinone (NMP) 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 60℃. 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 $NaPF_6$ as anode, separator, and electrolyte, respectively. Galvanostatic charge-discharge tests were measured on the NEWARE battery tester at 0.01-2.8V. Cyclic voltammetry (CV) test window voltage ranged from 0.01-2.8V at the scan rate of 0.1mV s^{-1}. The electrochemical impedance spectroscopy (EIS) was tested with frequency range from 0.01Hz to 100KHz.

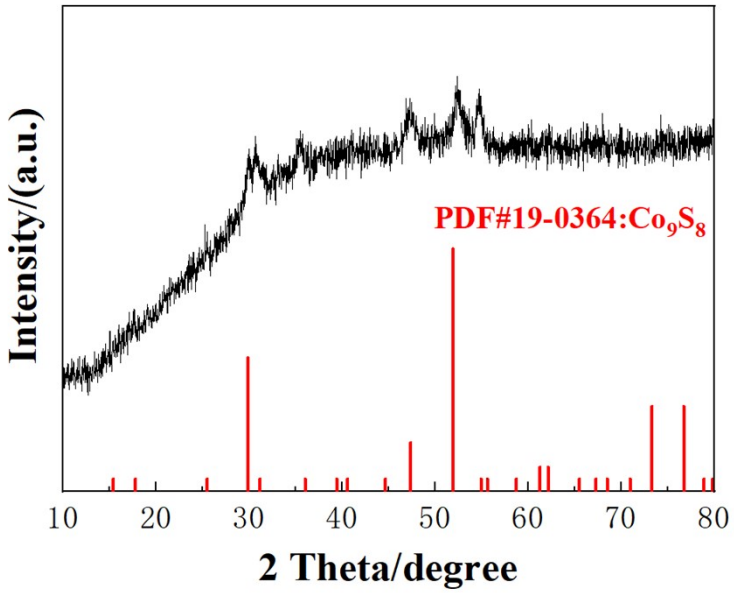

Fig.S1. XRD of ZIF-67s.

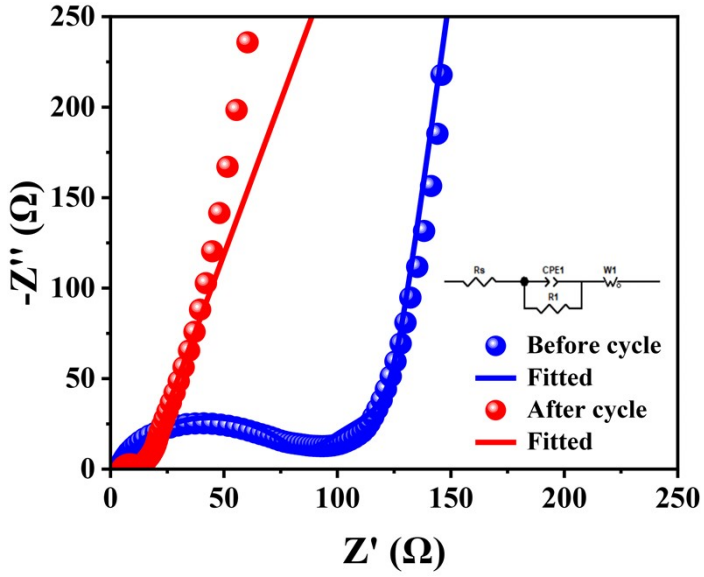

Fig.S2. Nyquist plots and related equivalent circuits of Co_9S_8/NC in SIBs.

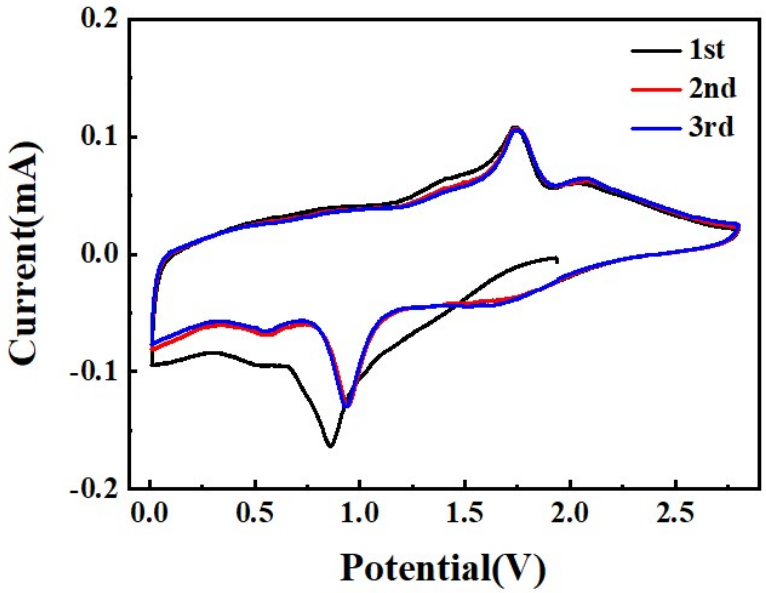

Fig.S3. CV of CoS_2/NC at 0.1mV s^{-1}.