Supplementary Information

Structural tuning of copper sulfide material for sodium-ion batteries

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Experimental Section

Materials preparation

Synthesis of single-crystal CuS material: Copper(II) nitrate hydrate ($Cu(NO_3)_2 \cdot 3H_2O$, 1.5 mmol, 0.3624 g) and Polyvinylpyrrolidone (PVP, 5.4545×10^{-3} mmol, 0.1636g) were dissolved in 50 ml anhydrous ethanol. Then, sulfur powder (S, 4 mmol, 0.0961g) was added into the solution and adopted ultrasonic dispersion for 30 min. The mixing solution was then shifted to a 100 ml stainless steel autoclave lined with Teflon and heated at 180 ºC for 12 h and natural cooling. The samples were repeatedly washed with ethanol and deionized water and then dried in vacuum at 80 ºC for 12 hours to obtain the single-crystal CuS.

Synthesis of twin-crystal CuS material: Copper(II) nitrate hydrate ($Cu(NO_3)_2 \cdot 3H_2O$, 1.5 mmol, 0.3624 g), Polyvinylpyrrolidone (PVP, 5.4545×10^{-3} mmol, 0.2 g) and thiourea ($CS(NH_2)_2$, 6 mmol, 0.4567 g) were dissolved in 50 ml glycol. The mixing solution was then transferred to a 100 ml stainless steel autoclave lined with Teflon and heated at 150 ºC for 6 h and natural cooling. The samples were repeatedly washed with ethanol and deionized water and then dried in vacuum at 80 ºC for 12 hours to obtain the twin-crystal CuS.

Materials characterization

Scanning Electron Microscope (SEM, HITACHI S-4800) was employed to observe the morphology of the material. Powder X-ray diffraction with Cu Kα radiation in the 2θ range 10-80º was performed to detect the crystal structure of the material. Samples were prepared with the FEI HELIOS NanoLab 600i focused ion beam (FIB) at accelerating voltages of 0.5 to 30 kV and characterised by transmission electron microscopy (TEM), selected area electron diffraction and high resolution

TEM (HR-TEM) at an accelerating voltage of 300 kV using the spherical aberration corrected transmission electron microscope (AC-TEM: FEI Titan G2 60-300) measurements to investigate the surface and internal micro-structure of materials.

Electrochemical measurements

CR2025 type coin cell was used to evaluate the electrochemical properties of the material. Firstly, the electrodes were prepared by mixing the active material, the conductive material (acetylene black), sodium carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) in a weight ratio of 75:15:5:5 in deionised water to form a slurry. The slurry was then spread on the copper foil collector and the electrodes were dried in a vacuum at 80 ^{o}C for 12 hours. The electrodes were cut into electrode sheets of 1.5 cm diameter with an active material load of about 2 mg. Glass fibre and sodium metal were used as the separator and counter electrode respectively. 1.0 M $NaCF_3SO_3$ dissolved in diethylene glycol dimethylether (DIGLYME) was used as the electrolyte. The coin cell was then assembled in a glove box filled with argon gas. Constant current charge and discharge tests were carried out over a voltage range of 0.4-2.6V (*vs* Na/Na^+) using a Neware BTS-610 battery test system. An electrochemical workstation was used for cyclic voltammetry (CV) testing with a scan rate of 0.1-3.0 mV/s and a voltage range of 0.4-2.6 V.

Supplementary Figures

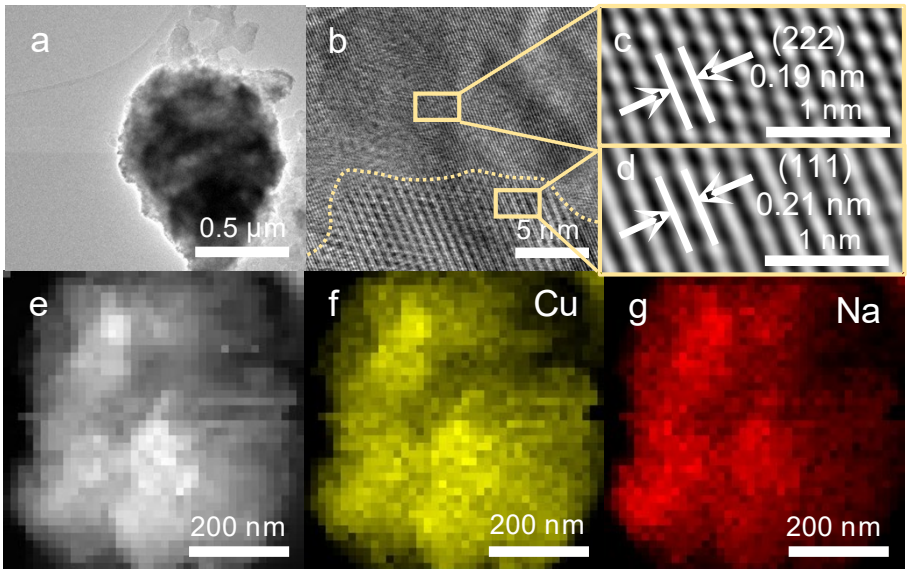

Figure S1. (a) TEM, (b-d) High resolution TEM with corresponding lattice spacing and (e-g) TEM mapping images of TC-CuS discharged to 0.4 V.

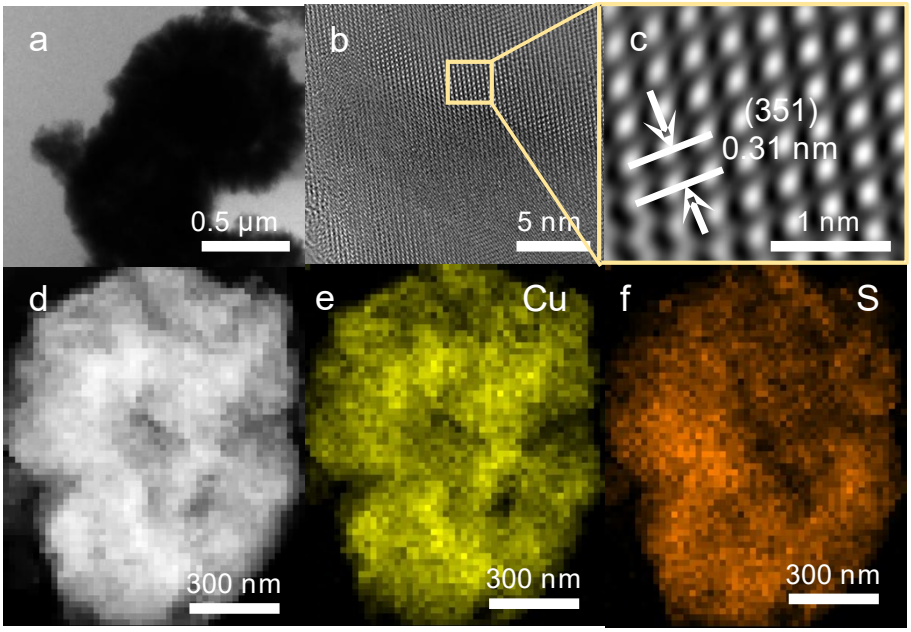

Figure S2. (a) TEM, (b, c) High resolution TEM with corresponding lattice spacing and (d-f) TEM mapping images of TC-CuS charged to 2.6 V.

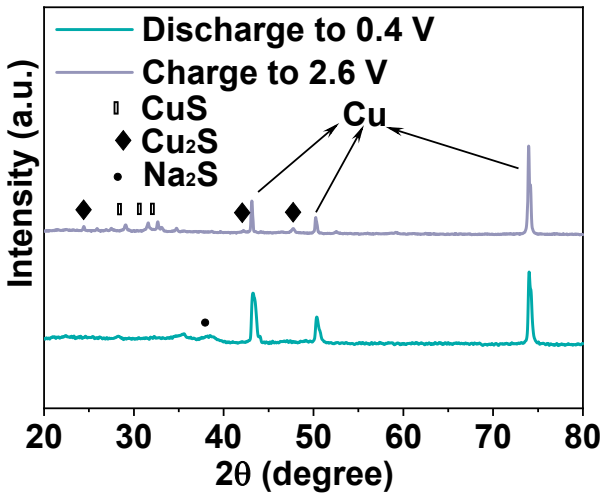

Figure S3. The XRD patterns of TC-CuS discharged to 0.4 V and charged to 2.6 V.

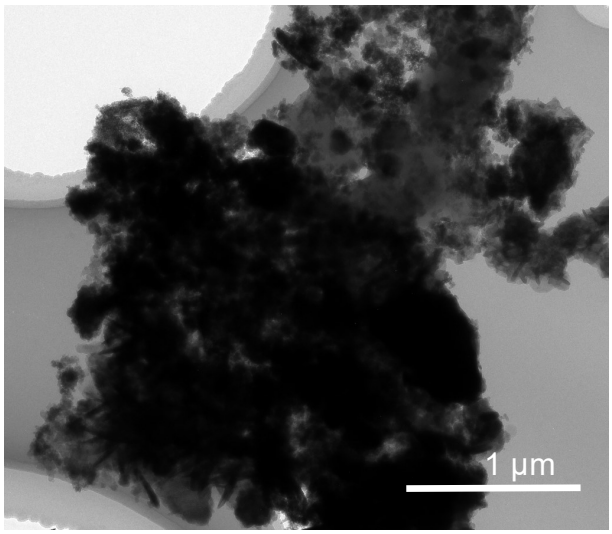

Figure S4. TEM images of SC-CuS after 150 cycles.

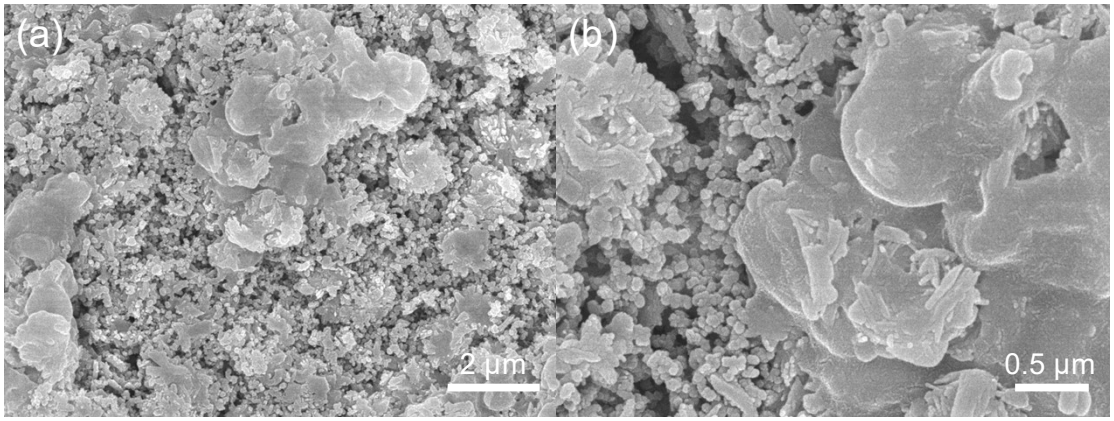

Figure S5. (a, b) SEM images of TC-CuS after 400 cycles.