Electronic Supplementary Information

Directly growing pristine Cu-CAT metal-organic framework as an anode material for high-energy sodium-ion capacitor

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Experimental section

Pretreatment of nickel foam

The nickel foam was pressed flat under 5 MPa and carefully cleaned with 3 M hydrochloric acid solution in an ultrasonic bath for 20 min, and then washed in sequence with deionized water and absolute ethanol. Afterwards, the compressed nickel foam was dried at 60 °C under a vacuum oven.

Preparation of Cu-CAT nanowire anode

Cu-CAT nanowire anode was synthesized through a one-step solution process. In a typical process, copper acetate monohydrate (8 mg, 0.04 mmol) and HHTP (6.5 mg, 0.02 mmol) were added in 1 mL solvent mixture of water/DMF (v: v = 1:1) under sonication for 10 min in a 20 mL glass vial. The treated nickel foam was then immersed into the reaction solution and heated in an oven at 85 °C for 15 h. After cooling down to room temperature, the nickel foam was taken out and washed with a small amount of deionized water, and dried in a vacuum oven at 60°C. Cu-CAT nanowire anode on nickel foam was finally obtained. The mass loading of Cu-CAT nanowire is ~0.4 mg cm^{-2}. Cu-CAT crystallite powder can also be collected at the bottom of the glass vial.

Characterizations

The morphology and crystalline structure of Cu-CAT nanowire anode were characterized by SEM (Hitachi S-4800, Japan), XRD with Cu Kα (Rigaku RU-200B/D/MAX-RB, China), TEM (Tecnai-G2-F30) with EDX spectroscopy and FTIR (Nicolet Is5, ThermoFishe, USA). Nitrogen sorption isotherms were measured at 77 K on BELSORP-max analyzer after pretreated under vacuum at 100°C for 12 h. The specific surface area was calculated from the N_2 adsorption isotherm using the BET equation. The pore size distribution was determined by NLDFT modeling. The valence states and the surface chemical composition were analyzed by XPS (Thermo Scientifc Escalab 250X, USA).

Electrochemical measurements

For half-cell testing, CR2032-type coin cells were assembled in an Ar-filled glove box with a moisture level below 1 ppm. Na foil was used as the counter electrode, Cu-CAT nanowires or AC as the working electrode, and polypropylene film as separator. Stainless steel spacers and shrapnel were also inserted in the cell to ensure good electrical contact between the layers. Electrolytes of 1.0 M $NaClO_4$ in EC/PC/FEC (1:1:0.05) was used. The AC electrode was prepared by mixing the AC (KYP-50, Kuraray, 80%) with PVDF (10 wt%) and acetylene black (10 wt%) in NMP solvent. The resulting slurry was uniformly pasted onto aluminum foil (16 μm) and dried at 120 °C for 2 h. Electrochemical profiles of Cu-CAT and AC were examined using LAND CT2001 tester. Cyclic voltammetry (CV) tests were performed on a CHI660E electrochemical workstation (Shanghai, Chenhua).

SIHC device was assembled by using pre-sodiated Cu-CAT as anode and AC as cathode with optimized weight ratio of 1:4.6. The electrolyte was 1.0 M $NaClO_4$ in EC/PC/FEC (1:1:0.05) with the polypropylene film as the separator. The full cell was also cycled on a LAND CT2001 tester at different rates.

The gravimetric/volumetric energy and power densities of the device were calculated based on $E = \int IV(t)\mathrm{d}t$ and $P = E/\Delta t$, where I is the discharging current (A g^{-1} or A cm^{-3}), $V(t)$ is discharging voltage at t, dt is time differential, and Δt is the total discharging time. The mass was estimated based on all active materials and the volume was based on all components of the device including anode, cathode and separator.

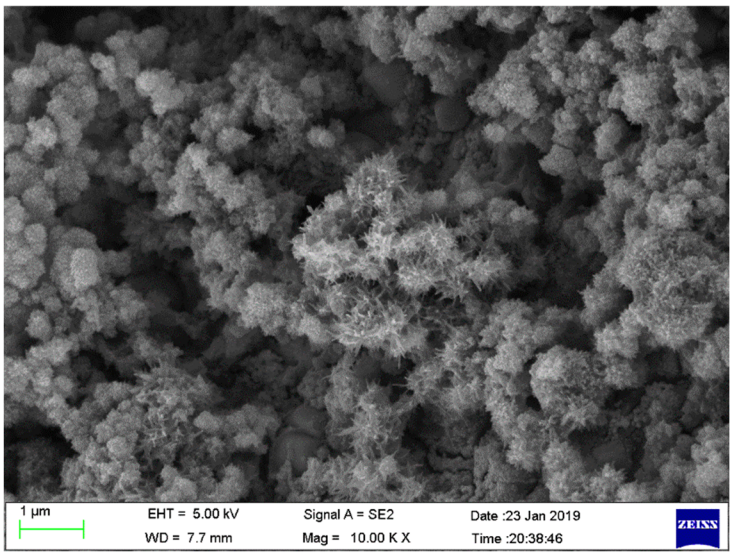

Figure S1. Low-magnification SEM image of the Cu-CAT anode, showing the nanowire cluster-assembled electrode architecture.

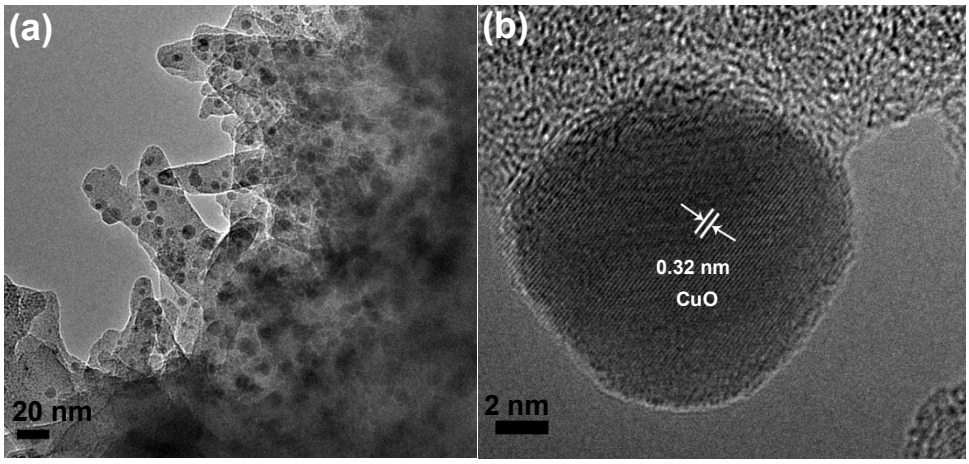

Figure S2. (a) TEM image of Cu-CAT after prolonged electron beam irradiation. (b) HRTEM image of the precipitated copper oxide particles.

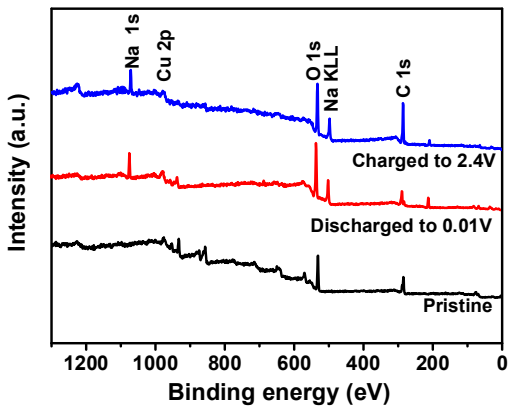

Figure S3. XPS spectra of the Cu-CAT anode at different states: the pristine, discharged to 0.01 V and charged to 2.4 V.

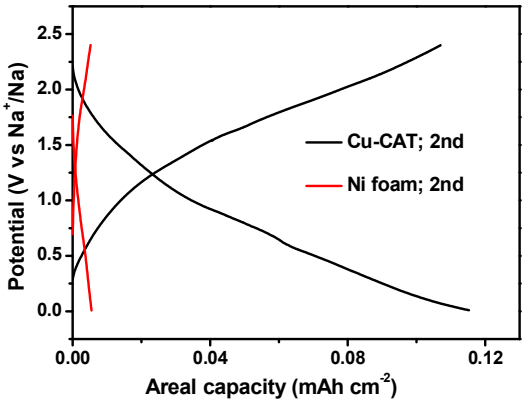

Figure S4. Galvanostatic charge/discharge profiles of Cu-CAT anode and pure Ni foam. Apparently, the reversible capacity contribution from Ni foam is negligible.

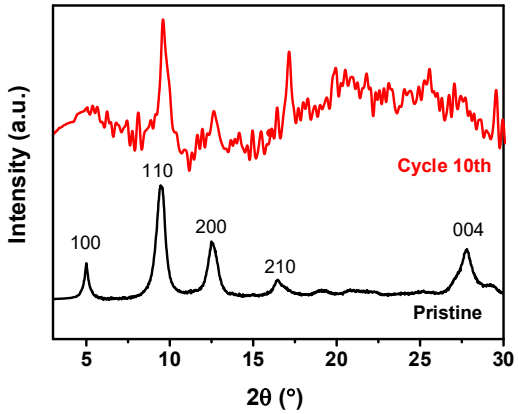

Figure S5. XRD patterns of the Cu-CAT anode before and after cycling.

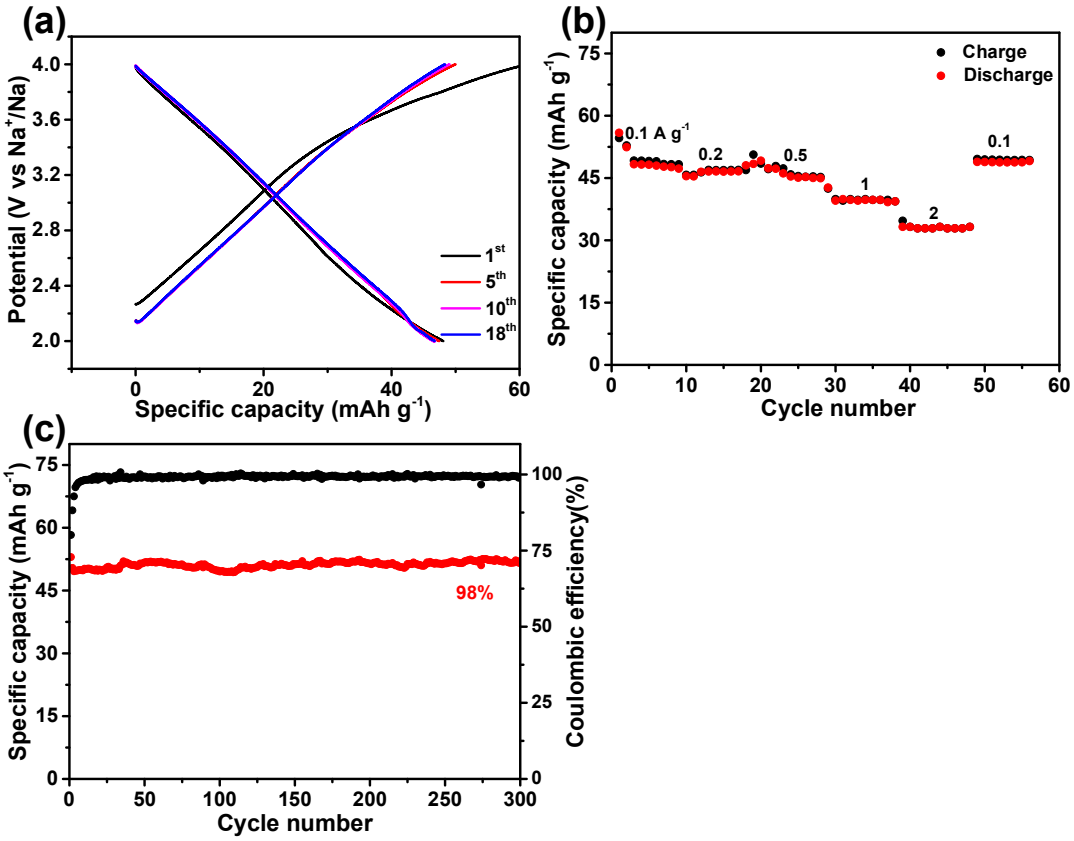

Figure S6. Electrochemical performance of the AC cathode: (a) The charge and discharge profiles. (b) Rate performance. (c) Cycling performance.