Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Materials

Construction of high-performance flexible hybrid capacitor at extreme work temperature (-20 °C)

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1 Experimental detail

1.1 Materials

All reagents are analytically pure without further purification. In a typical procedure, 9 cm^2 nickel foam (NF) were immersed into 1 M HCl solution and sonicated for 30 min. Next, the NF was repeatedly washed with ethanol and deionized water, respectively, and then dried overnight.

1.1.1 Preparation of $ZnCo_2S_4$ nanowire arrays

The synthetic route of $ZnCo_2S_4$ sample is divided into two steps: the preparation of $ZnCo_2O_4$ precursor and subsequent vulcanization treatment. Firstly, in a typical procedure, 0.29 g of $Zn(NO_3)_2{\cdot}6\ H_2O$, 0.58 g of $Co(NO_3)_2{\cdot}6\ H_2O$, 0.037 g of NH_4F and 0.03 g of urea were added in turn to 50 mL of deionized water. Then a piece of pretreated nickel foam was put into the above mixed solution. After that, the reaction was carried out at 150 ℃ for 6 h. The NF covered by the precursor was taken out and rinsed with deionized water and ethanol several times and calcined at 350 °C for 2 h. Then, the prepared $ZnCo_2O_4$ precursor was immersed into 50 mL solution containing 0.4g $Na_2S{\cdot}9H_2O$ powder and kept at 120 ℃ for 4 h to obtain like-wires $ZnCo_2S_4$.

1.1.2 Preparation of $ZnCo_2S_4$@$Ni(OH)_2$

First, 1 mmol $Ni(NO_3)_2{\cdot}6H_2O$ and 2 mmol urea were dissolved in 60 mL deionized water and stirred for 15 min to form a pink solution. $ZnCo_2S_4$ product was immersed into the above solution and then transferred into a 100 mL Teflon-lined stainless steel autoclave and kept at 120 ◦C for 2 h. Several experiments were

conducted with different reaction times (0, 1, 2, 4 h).After cooling to room temperature, the as-obtained products were cleaned with deionized water and ethanol several times and then dried at 60 ◦C for 12 h. Finally, the obtained products were denoted as ZCS, ZCSN-1, ZCSN-2 and ZCSN-4, respectively. The average mass loading of them is 1.5, 2.1, 2.2 and 2.4 mg cm^{-2}.

1.1.3 Synthesis of negative electrode

Polyvinylidene fluoride (PVDF) powders were blended with acetylene black and Activated carbon (AC) in a mass ratio of 1:2:7. NMP organic solvent was dropped into the mixture to form uniform slurry and spread evenly on the clean NF (1 cm^2).

1.2 Physical and chemical characterization

The sample is stripped of the NF using ultrasound and then collected for analysis to remove the effect. (The morphology and structure of the samples were observed using scanning electron microscopy (Gemini SEM 300, GER) and transmission electron microscope (GZF20, TEM, USA). The pore size distribution is measured via Brunauer-Emmett-Teller (BET, Micromeritics ASAP). XPS instrument (XPS, Thermo Scientific Kα) is important to characterize the surface element distribution and the valence state of the as-prepared samples.

1.3 Electrochemical measurements

The electrochemical performances of the samples were evaluated in a CHI660H electrochemical workstation using a conventional three electrode configuration in 3 M KOH. The as-obtained electrode materials, Hg/HgO electrode and platinum plate are served as working electrode, reference electrode and counter one, respectively. Cyclic

voltammetry (CV) curves were measured in the potential window from 0 to 0.6 V at different scan rates. Galvanostatic charge-discharge (GCD) curves at different current densities were obtained from 0 to 0.5 V. Electrochemical impedance spectroscopy (EIS) were performed between 0.01 Hz and 100 kHz at 5 mV. The specific capacity (C, C g^{-1}) and Coulombic efficiency (η) can be calculated by the following Eqs. (1) and (2):

$$C=I\Delta t/m \quad (1)$$

$$\eta(\%)=\Delta t_d/\Delta t_c 100 \quad (2)$$

where C, I and m represent specific capacitance (C g^{-1}), discharge current (A) and the mass loading of active substance (g), respectively. Δt is discharge time(s). Δtc and Δtd are charge time and discharge time at the same current.

For ASC device, $ZnCo_2S_4$@$Ni(OH)_2$ sample and AC were served as positive and negative electrode. A piece of cellulose paper in the gel electrolyte serves as a separator. The energy density (E, Wh kg^{-1}) and power density (P, W kg^{-1}) can be calculated through the following equations:

$$E=1/2C_s(\Delta V)^2 \quad (3)$$

$$P=3600E/\Delta t \quad (4)$$

where C_s refers specific capacitance, m is total mass loading of two electrodes, ΔV is defined as voltage window and Δt represents discharge time.)

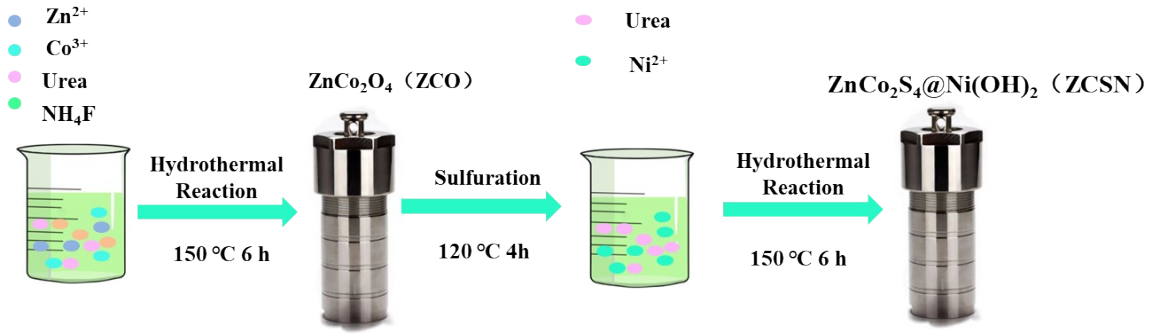

Figure S1 The fabrication schematic of materials

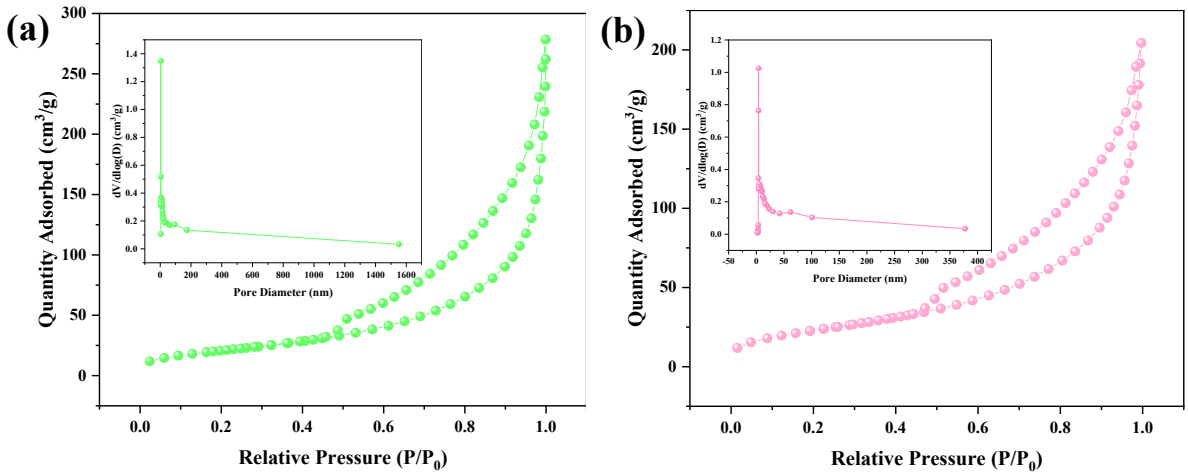

Figure S2 N_2 adsorption-desorption isotherms and corresponding pore size distribution curves of ZCSN-1 (a) and ZCSN-4 (b)

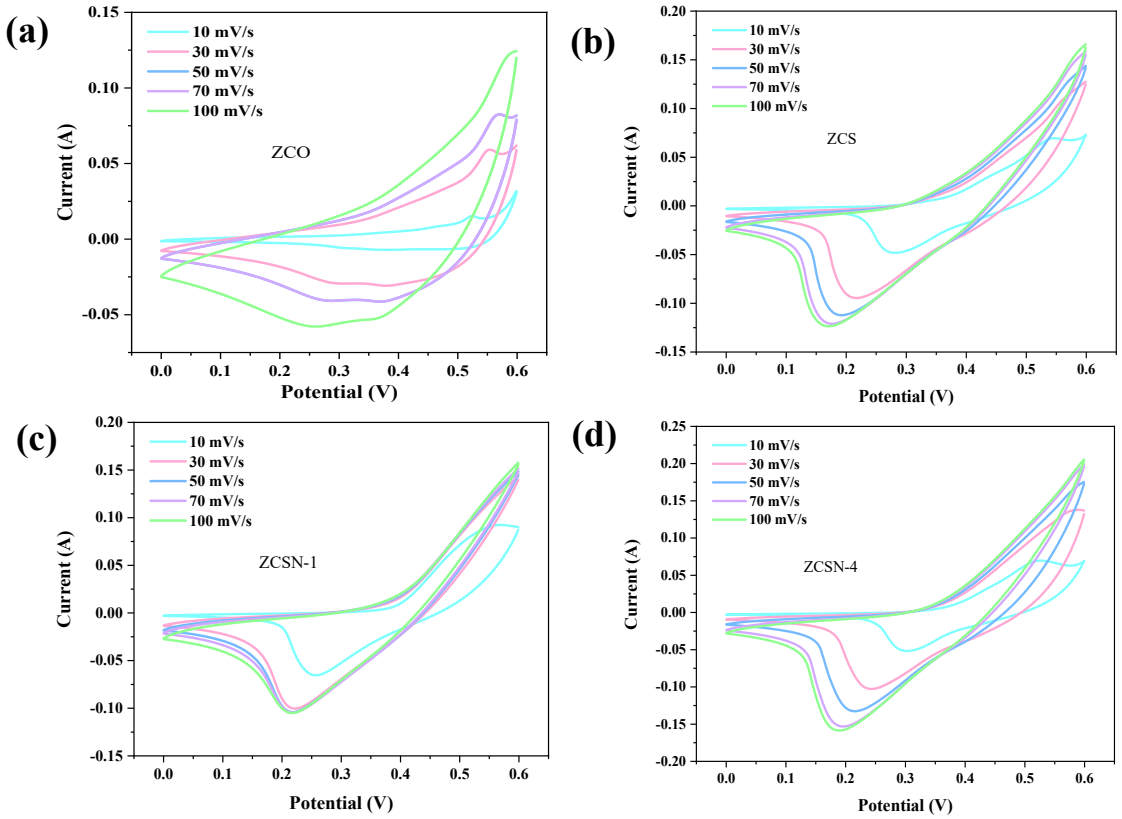

Figure S3 CV curves of ZCO (a) ZCS (b) ZCSN-1 (c) and ZCSN-4 (d) samples

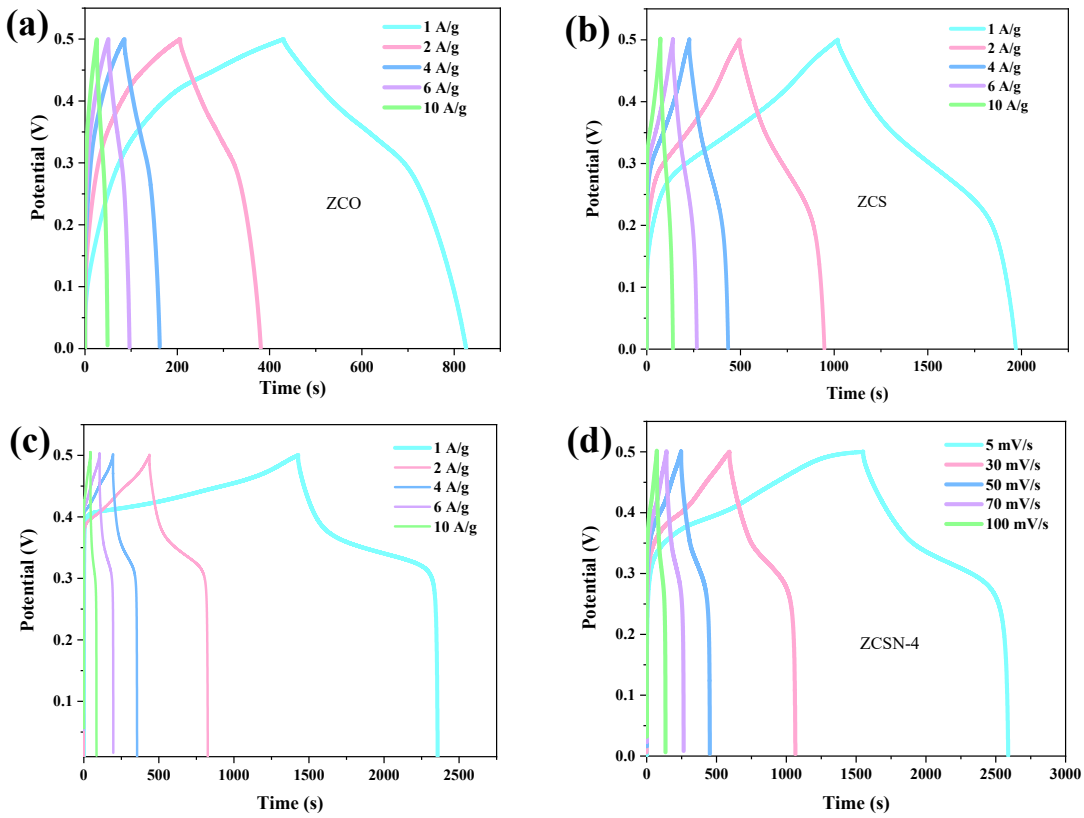

Figure S4 GCD curves of ZCO (a) ZCS (b) ZCSN-1 (c) and ZCSN-4 (d) samples