Supporting Information

The combination of Zn-$NiCo_2S_4$ and Zn-air batteries at cell level: a hybrid battery makes the best of both worlds

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Materials and characterization

All chemicals were of analytical grade, commercially available from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China) and used as received without further purification. PXRD patterns were recorded on X-ray diffractometer with Cu KR (λ=1.5418 Å) radiation (Philips X'Pert Pro Super, Philips). Raman spectroscopy was conducted with an excitation wavelength of 633 nm (LabRAMHR-800, HORIBA). N_2 sorption analysis was conducted using an ASAP 2020 accelerated surface area and a porosimetry instrument (Micromeritics, Norcross, GA), equipped with an automated surface area, at 77 K using Barrett-Emmett-Teller (BET) calculations for the surface area. The pore size distribution plot was based on the original density functional theory model. The morphology was observed on an ultra plus field emission scanning electron microscope (SEM, ultra plus, ZEISS) and a transmission electron microscopy (TEM, JEOL, JEM-2100F). XPS was performed with Mg Kα radiation (1253.6 eV) as an excitation source (ESCALab MKII, Thermo Scientific, Waltham, MA). Electrochemical experiments were conducted on CHI-660E electrochemical workstation. The LAND-CT2001A testing devices were used to analyze the battery charge-discharge performance.

Preparation of 3DNCC and $NiCo_2S_4$/3DNCC

After washed with deionized water and ethanol for three times respectively, the filter paper was cut into rectangular slices (4.0 × 2.5 cm^2) with a sharp blade. Five filter paper slices was placed in urea 2 M solution for 10 h, and then pyrolyzed under protection of flowing Ar at 400 °C for 2 h to generate black **3DNCC**.

3DNCC with appropriate size was put in a 100 mL Teflon lined stainless steel autoclave which contains $NiCl_2 \cdot 6H_2O$ (0.71 g), $CoCl_2 \cdot 6H_2O$ (1.43 g), $Na_2S \cdot 9H_2O$ (2.4 g) and H_2O (100 mL). The Teflon lined stainless steel autoclave was heated at

200 °C for 18 h and **$NiCo_2S_4$/3DNCC** was obtained.

Charge-discharge property

$NiCo_2S_4$/3DNCC or **3DNCC** (working area 1 × 1 cm^2) was used as the working electrode. Carbon rod and Ag/AgCl electrode were used as counter and reference electrodes, respectively. Freshly prepared aqueous KOH solution (1 M) was used as the electrolyte.

ORR and OER activities study

ORR was performed in 0.1 M KOH. In ORR, linear sweep voltammetry (LSV) curves were recorded at 5 $mV \cdot s^{-1}$. Different rotating speeds of the rotating disk electrode (RDE) (including 400, 800, 1200, 1600 and 2000 rpm) were employed for the ORR measurements. Cyclic voltammetry (CV) cycling was carried out from -0.1 to 1.5 V versus RHE a scanning rate of 10 $mV \cdot s^{-1}$. In OER, LSV curves were also measured at 5 $mV \cdot s^{-1}$. In ORR, the electron transfer number was determined by using the Koutechy-Levich (K-L) equation (Eq. S1). In this equation j is the measured current density, j_k is the kinetic current density, and ω is the electrode rotating rate. The parameter B could be calculated from the slope of the K-L plots based on the following Levich equation (Eq. S2), in which n is the electron transfer number per oxygen molecule, F is the Faraday constant (F = 96485 $C \cdot mol^{-1}$), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH ($D_0 = 1.9 \times 10^{-5}$ $cm^2 \cdot s^{-1}$), v is the kinetic viscosity (v = 0.01 $cm^2 \cdot s^{-1}$), and C_0 is the bulk concentration of O_2 ($C_0 = 1.2 \times 10^{-6}$ $mol \cdot cm^{-3}$). The value 0.2 is applied when the rotation speed is expressed in rpm.

$$1/j = 1/j_k + 1/B\omega^{1/2} \quad (S1)$$

$$B = 0.62nF(D_0)^{2/3}(V)^{-1/6}C_0 \quad (S2)$$

Zn-$NiCo_2S_4$HB hybrid battery assemble

The Zn-air battery was assembled with a home-made cell in the size 4.2 × 4 × 4

cm^3. In this battery, the Zn plate acts as anode with working area 3.2 cm^2. One side of **$NiCo_2S_4$/3DNCC** was covered by PTFE layer and this side was used as air diffusion layer. After covered by PTFE, the **$NiCo_2S_4$/3DNCC** was employed as cathode directly. The working area of air cathode is also 3.2 cm^2. The cell was filled with 10 mL mixture solution of KOH (4.0 M) and $Zn(OAc)_2 \cdot 2H_2O$ (0.2 M). In measurement, no additional oxygen was inlet into this battery.

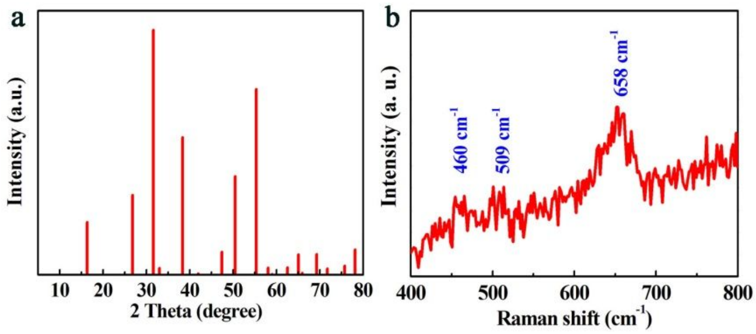

Figure S1 (a) Standard PXRD pattern of $NiCo_2S_4$; (b) Enlarged Raman of **$NiCo_2S_4$/3DNCC**

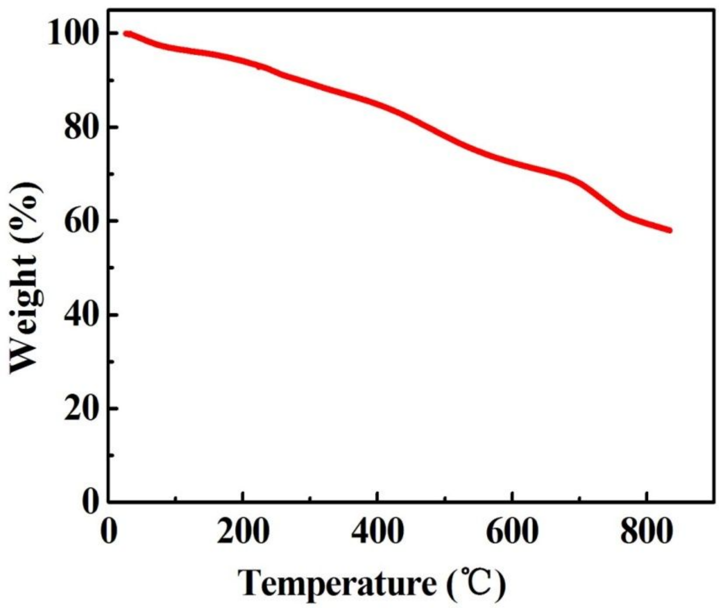

Figure S2 TGA of $\mathbf{NiCo_2S_4}$**/3DNCC**

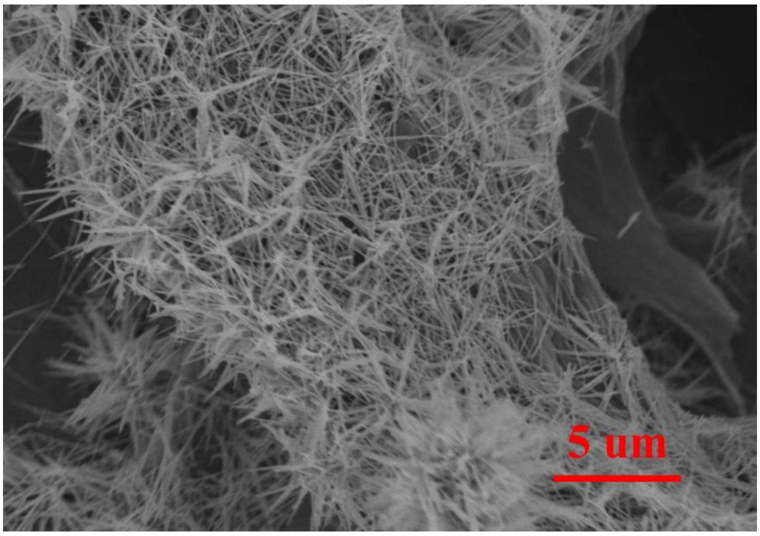

Figure S3 SEM of **$NiCo_2S_4$/3DNCC**

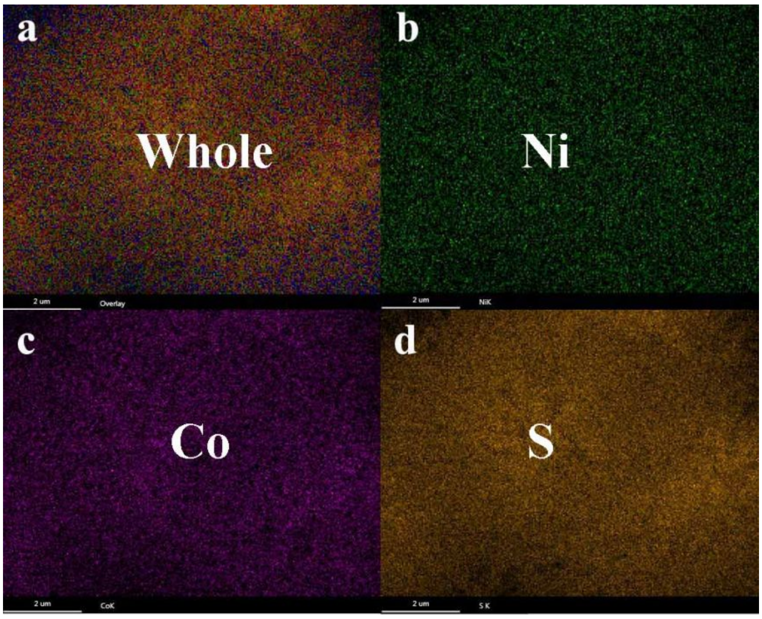

Figure S4. EDS mapping of **$NiCo_2S_4$/3DNCC**

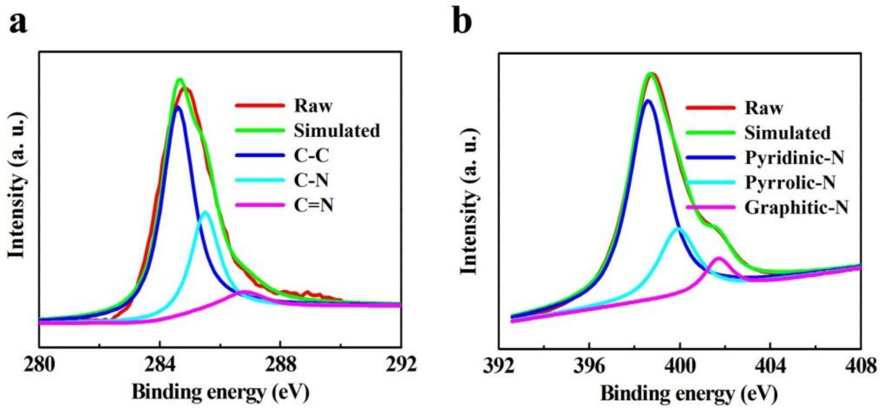

Figure S5. (a) High resolution C 1s spectrum of **$NiCo_2S_4$/3DNCC**; (b) High resolution N 1s spectrum of **$NiCo_2S_4$/3DNCC**

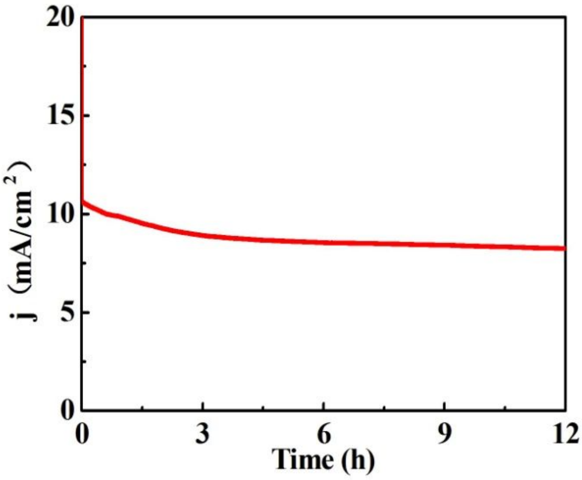

Figure S6 I-T curve of **$NiCo_2S_4$/3DNCC** for 12 h

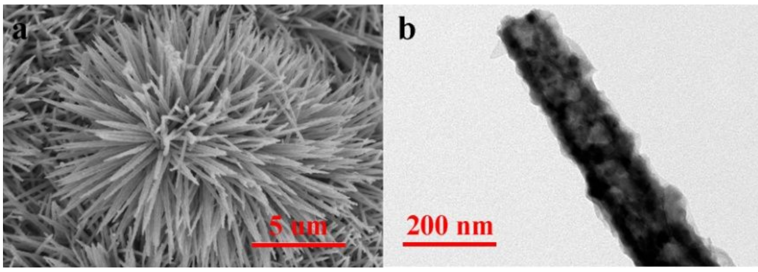

Figure S7 (a) SEM of recycled **$NiCo_2S_4$/3DNCC**; TEM of recycled **$NiCo_2S_4$/3DNCC**

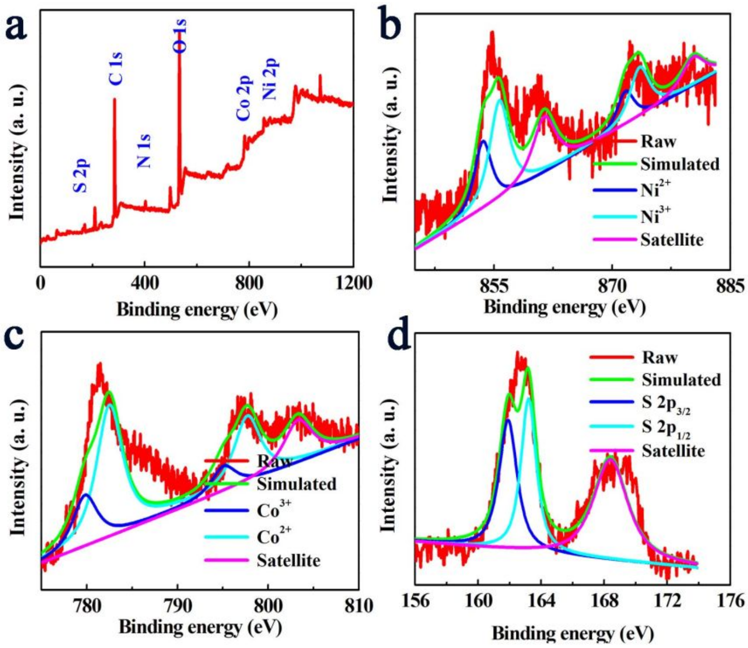

Figure S8 (a) XPS survey of recycled **$NiCo_2S_4$/3DNCC**; (b) High resolution Ni 2p spectrum of recycled **$NiCo_2S_4$/3DNCC**; (b) High resolution Co 2p spectrum of recycled **$NiCo_2S_4$/3DNCC**; (b) High resolution S 2p spectrum of recycled **$NiCo_2S_4$/3DNCC**