Supplementary Information

Highly conductive $Ni(OH)_2$ nano-sheets wrapped $CuCo_2S_4$ nano-tube electrode with a core-shell structure toward high performance supercapacitor

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Experimental section

Chemical regents

All chemicals were of analytical grade without further purification and purchased from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd.

Synthesis of CuCo-precursors

Firstly, the carbon cloth was treated in nitric acid for 6 h at the temperature of 90 °C, then was washed with deionized water and ethanol to pH = 7. Secondly, a piece of carbon cloth was immersed into the 75 mL solution contained of 2 mmol of $Cu(NO_3)_2{\cdot}3H_2O$, 4 mmol of $Co(NO_3)_2{\cdot}6H_2O$, 12 mmol of $CO(NH_2)_2$, and 12 mmol of NH_4F in a 100 mL Teflon stainless-steel autoclave. The autoclave kept sealed and heated to 140 °C maintained for 6 h. After the autoclave cooled to room temperature, the product was removed and washed with deionized water and ethanol several times. Lastly, the CuCo-precursor was dried at 80 °C for 10 h in a vacuum environment.

Synthesis of $CuCo_2S_4$ nanotubes

The as prepared CuCo-precursor was immersed into the solution of Na_2S solution (75ml), with 20 mmol of Na_2S. Next, the mixture was transfer to the 100 mL Teflon stainless-steel autoclave. The autoclave kept sealed and heated to 120 °C maintained for 6 h and then cooled to room temperature. The as prepared product was washed with deionized water and ethanol several times. After dying the product heated at the temperature of 60 °C under vacuum for 12 h. Then the $CuCo_2S_4$ nanotubes were prepared.

Synthesis of $CuCo_2S_4$ nanotubes@$Ni(OH)_2$ nanosheets

$CuCo_2S_4$@$Ni(OH)_2$ was prepared by the electrochemical deposition method at constant potential of -1 V vs Hg/HgO. This electrochemical deposition process was carried out in a three-electrode system composed of carbon cloth covered by $CuCo_2S_4$ nanotubes as a working electrode, Hg/HgO as a reference electrode, and platinum as a counter electrode, respectively. The electrochemical deposition solution was 0.2 mol of $Ni(NO_3)_2 \cdot 6H_2O$ in 100 mL of deionized water. The electrochemical deposition time was 1, 5 and 10 min. The loading was calculated to be 3.3~5.3 mg/cm^2.

Material characterization

Scanning electron microscope (HELIOS NanoLab 600i) and transmission electron microscope (Tecnai G2 F30 and FEI Talos F200S) were taken to obverse the morphologies and microstructures of the samples; X-ray diffraction (XRD) measurements were carried out on a Philips X'pert diffract meter with Cu Kα irradiation (λ=1.54 Å). X-ray photoelectron spectroscopy (XPS) characterization of the products was executed on Thermo Fisher spectrometer with an Al Kα (hv=1486.69 eV) X-ray source. Nitrogen adsorption/desorption isotherms were measured on a Quantachrome

NOVA 4200 e system. Specific surface area and pore size distribution were determined by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) desorption analyses.

Electrochemical measurement

Electrochemical measurements of the electrodes were performed on CHI760D and PARSTAT 4000A electrochemical workstations at the room temperature. The three electrodes system was composed of a working electrode (1×1 cm^2) , Hg/HgO as a reference electrode and platinum as a counter electrode and all the measurements were carried out in the electrolyte of 1 M KOH solution.

The specific capacitance of the electrode according to the galvanostatic charge/discharge (GCD) measurements can be estimated by the following equation [1, 2]:

$$C = \frac{I\Delta t}{m\Delta V} \tag{1}$$

Where C (F g^{-1}) is the specific capacitance, I (A) is the discharge current, Δt (s) is the discharge time, ΔV (V) is the potential window, and m (g) is the mass of active materials.

An asymmetric super-capacitor ($CuCo_2S_4$@$Ni(OH)_2$-2 as positive electrode and active carbon as negative electrode) were measured in a two-electrode system in in the electrolyte of 1 M KOH solution. The mass ratio of two electrode material were calculated as:

$$\frac{m-}{m+} = \frac{C_+ \times V_+}{C_- \times V_-} \tag{2}$$

Where m (g) is the mass of the electrode materials (anode or cathode), C (F g^{-1}) is the specific capacitance, and V is the potential window. The energy density E (Wh kg^{-1}) and power density P (W kg^{-1}) can be calculated according to equations as follows:

$$\mathrm{E} = \frac{1}{2}CV^2$$

(3)

$$P = E / \Delta t \tag{4}$$

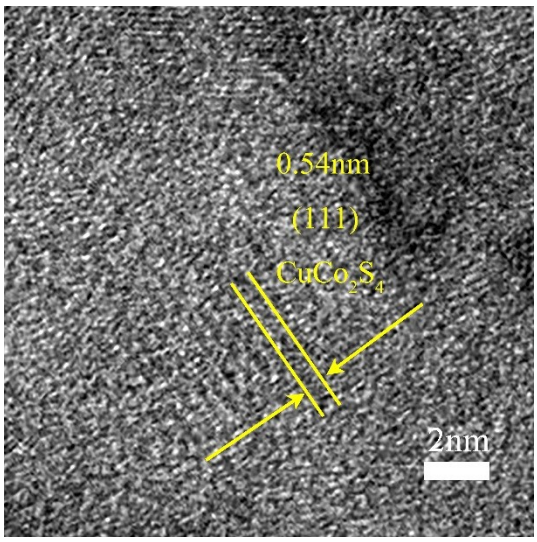

Figure S1 HRTEM image of $CuCo_2S_4$.

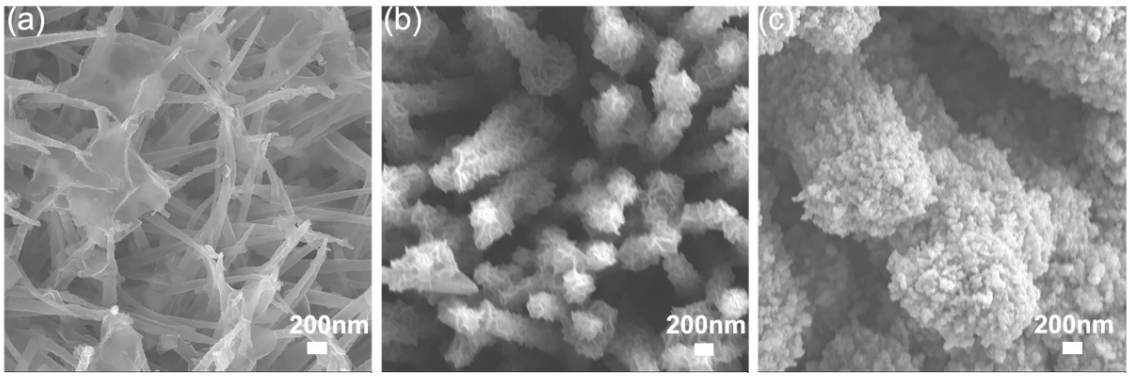

Figure S2 SEM images of $CuCo_2S_4$@$Ni(OH)_2$ with different electro-deposition time (a) 1 min, (b) 5 min, and (c) 10 min.

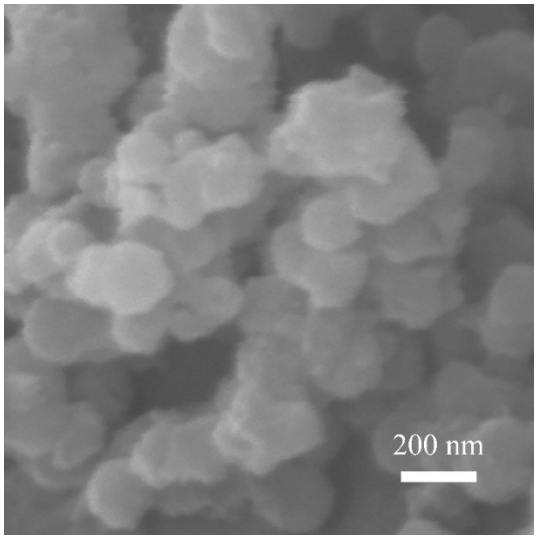

Figure S3 SEM patterns of $Ni(OH)_2$ deposited on carbon cloth with the electro-deposition time of 5 min.

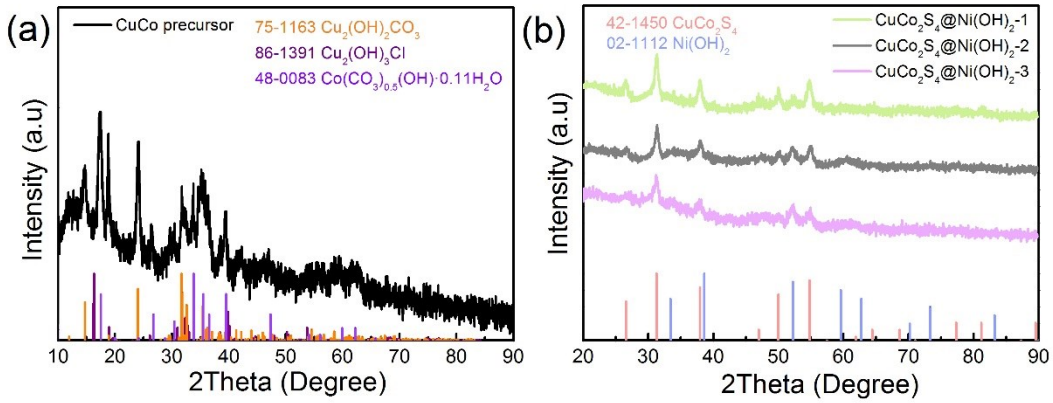

Figure S4 The XRD patterns of (a) CuCo precursors, (b) $CuCo_2S_4$@$Ni(OH)_2$ with different electro-deposition times.

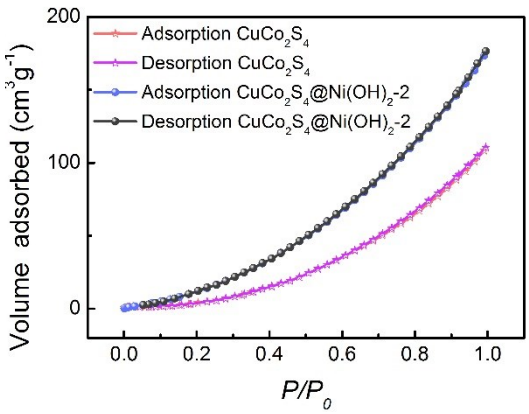

Figure S5 Nitrogen adsorption and desorption isotherms of $CuCo_2S_4$ and $CuCo_2S_4$@$Ni(OH)_2$.

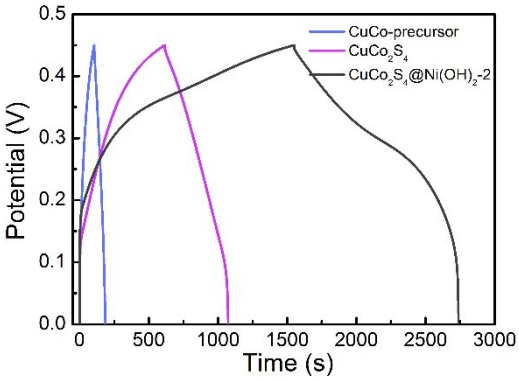

Figure S6 Comparison of GCD curves of CuCo precursors, $CuCo_2S_4$ and $CuCo_2S_4$@5$Ni(OH)_2$ electrodes at the current density of 1 A g^{-1}.

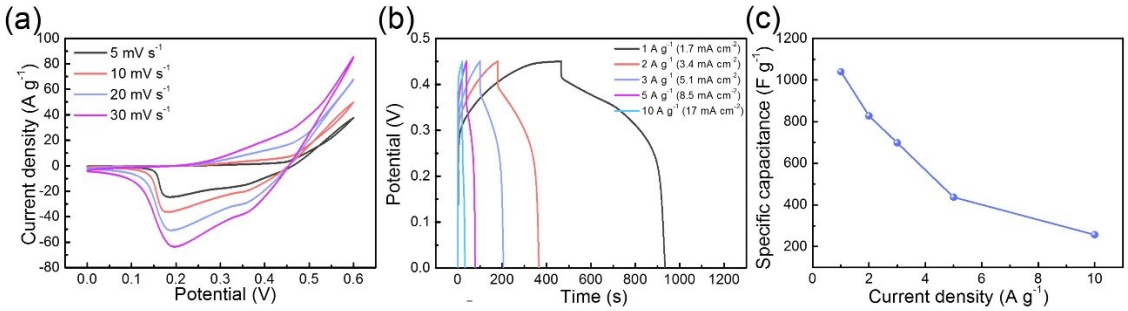

Figure S7 (a) CV curves of $Ni(OH)_2$ at different scan rates. (b) GCD curves of $Ni(OH)_2$ at different current densities. (c) Specific capacitances of $Ni(OH)_2$.

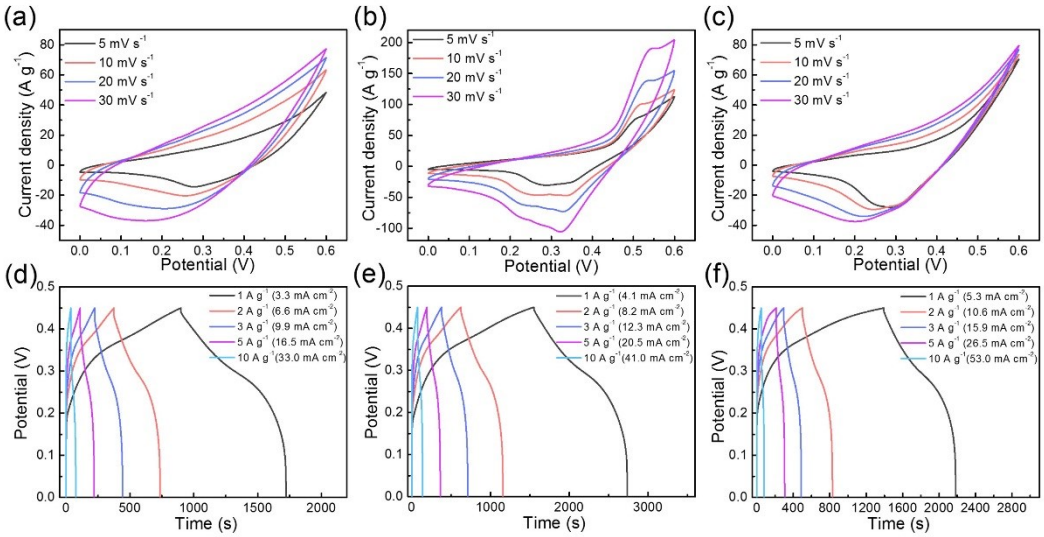

Figure S8 CV curves of $CuCo_2S_4$@$Ni(OH)_2$ with different deposition time, (a) 1 min, (b) 5 min and (c) 10 min. Galvanostatic charge/discharge curves of $CuCo_2S_4$@$Ni(OH)_2$ with different deposition time (d) 1 min, (e) 5 min and (f) 10 min.

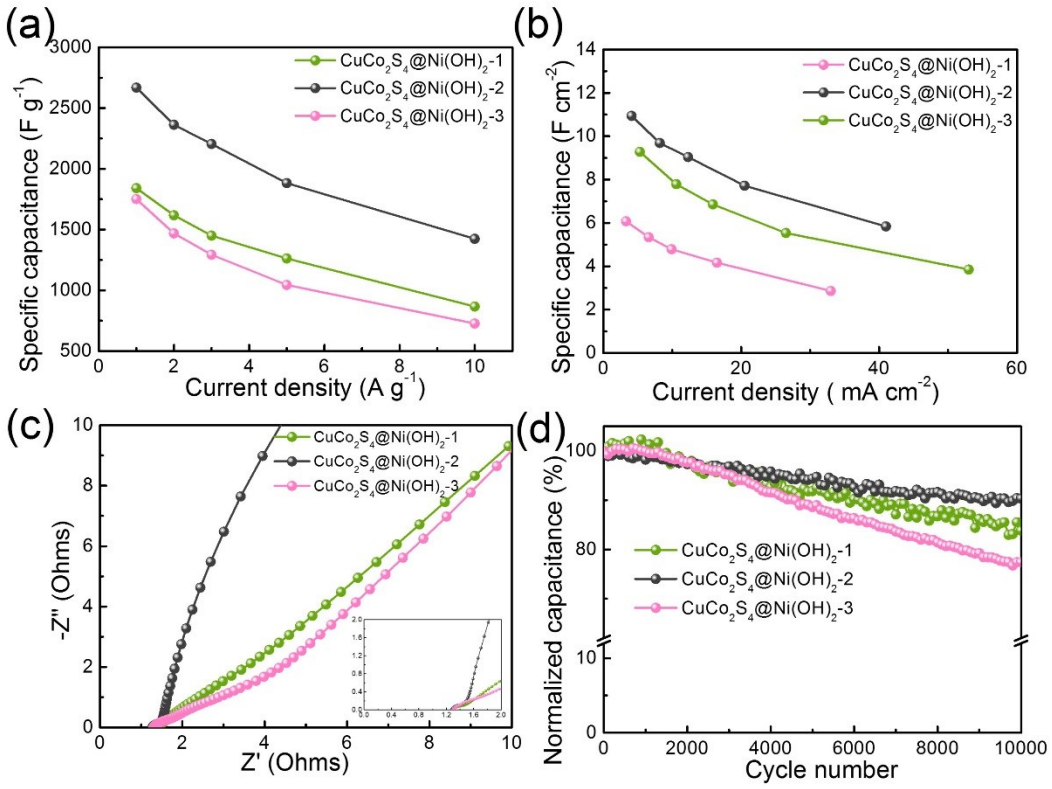

Figure S9 (a) Mass specific capacitance of $CuCo_2S_4$@$Ni(OH)_2$ with different deposition time. (b)

Areal specific capacitance of $CuCo_2S_4$@$Ni(OH)_2$ with different deposition time. (c) Nyquist plots in a frequency range from 0.1 Hz to 100 kHz of $CuCo_2S_4$@$Ni(OH)_2$ with different deposition time. (d) Cycling stability of $CuCo_2S_4$@$Ni(OH)_2$ with different deposition time.

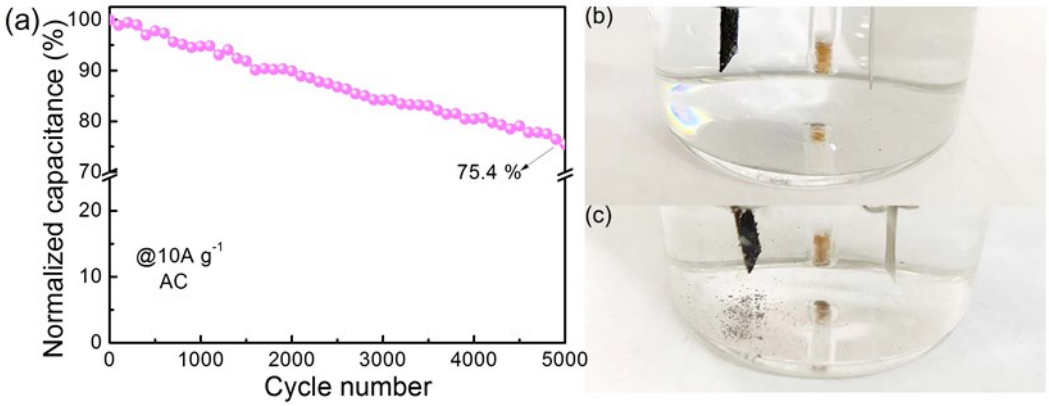

Figure S10 (a) Cycling performance of active carbon electrode, (b-c) Optical image of the electrolytic cell before and after the stability tests of active carbon.

References:

1 H. N. Jia, Y. F. Cai, S. Li, X. H. Zheng, L. F. Miao, Z. Y. Wang, J. L. Qi, J. Cao, J. C. Feng and W. D. Fei, *J. Colloid Interface Sci.*, 2020, **560**, 122-129.

2 H. N. Jia, H. Y. Liang, Z. Y. Wang, C. Li, X. H. Zheng, Y. F. Cai, J. L. Qi, J. Cao, J. C. Feng and W. D. Fei, *Dalton Trans.*, 2019, **48**, 8623-8632.