# Electronic Supplementary Information

# 3D Hierarchical porous $Co_{1-x}S$@C derived from ZIF-67 single crystalsself-assembling superstructurewith superior pseudocapacitance

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## 1. EXPERIMENTAL SECTION

### 1.1. Materials Synthesis

**Synthesis of urchin-like $2CoCO_3·3Co(OH)_2·H_2O$ (CCH):**

Typically, 0.291 g $Co(NO_3)_2·6H_2O$, 0.111 g $NH_4F$, and 0.18 g urea were dissolved in 40 ml deionized water, using ultrasonication for 10 minutes and stirred for 30 minutes, to form a homogeneous solution. The reaction solution was transferred into a 50ml Teflon-lined stainless-steel autoclave and kept in an oven at 120°C for 12h. At room temperature, the pink-colored precipitate was collected by centrifugation, washed with deionized water several times, and dried in a freezing dryer.

**Synthesis of hollow-urchin-like ZIF-67 superstructures (HU-ZIF-67S):**

10 mg CCHs were dissolved in 40 ml deionized water. Then, 15 mg 2-methylimidazole and 1 ml triethylamine were orderly added to the above solution, using sonication and vigorous stirring for 30minutes. The solution was then transferred to a 50 ml Teflon-lined stainless-steel autoclave and kept in an oven at 100 °C for varying durations. The resulting products were collected by centrifugation, washed with methanol several times to eliminate the residual organic matter, and dried overnight in a vacuum at 70 °C.

**Synthesis of hierarchical porous hollow urchin-like (HPHU) $Co_{1-x}S$@C composites:**

First, 100 mg HU-ZIF-67S were dispersed into 40 ml ethanol. Then, 100 mg of thioacetamide (TAA) was added into the above solution and continuously stirred for 30 minutes. The mixture was put into a 50 ml Teflon-lined autoclave and maintained at 150 °C for 3 hours. After it naturally cooled to room temperature, the product was collected by vacuum filtration and washed with water and ethanol. Finally, the products were pyrolyzed at 550 °C in Ar atmosphere, and HPHU-$Co_{1-x}S$@C composites were successfully obtained.

**Synthesis of activated carbon (AC):**

Similar to our previous report, AC was prepared from gelatin. Typically, the purchased gelatin was carbonized under Ar flow at 800 °C for 2 hours. Then, the as-prepared product was immersed in 5 wt% HCl solution for 12 hours, stirred constantly, and collected by filtration. After that, the product was mixed with KOH in the mass ratio of 1:4 and further activated at 700 ºC for 1 hour under an $N_2$ atmosphere to obtain the porous activated carbon.

### 1.2. Material Characterization

FSEM (JEOL, Japan) equipped with EDX was employed to characterize the surface morphologies of as-prepared samples. JEM-2100 electron microscope (TEM) was employed to investigate the microstructures of as-prepared samples. Panalytical X' pert PRO MRD with Cu Kα radiation was used to characterize the crystalline structures. KRATOS AXIS DLD spectrometer was used to examine the X-ray photoelectron spectroscopy (XPS) of the as-prepared samples. Micrometritics ASAP 2020 volumetric adsorption analyzer was used to record the $N_2$ adsorption isotherm of samples at the temperature at 77 K.

### 1.3. Electrochemical Measurements

We prepared working electrodes by mixing active material with poly-tetrafluoroethylene, conductive graphite, and acetylene black in the weight ratio of 8:0.5:0.75:0.75. By using isopropanol as wetting agent, the slurry was spread onto a piece of nickel foam with the mass loading of 5 mg $cm^{-2}$. The foams were dried overnight at 60 ºC and pressed at 10 M Pa before testing.

The electrochemical measurements of electrode material were carried out in CHI760E, via a three-electrode system in a 6.0 M KOH aqueous electrolyte. A saturated calomel electrode (SCE) served as the reference electrode and a Pt foil as the counter electrode.

The specific capacity of electrode material was calculated by the following equation:

$$C = \frac{I \cdot t}{m \cdot V} \qquad (1)$$

In where, $I$ is the discharging current, $t$ is the discharging time, $m$ is the masss loading of active-material, and $V$ is the operating potential window.

HSC electrochemical performance was measured in a CHI760E, but via a two-electrode system. In order to balance the charge between the positive electrode and the negative electrode of HSC, the optimized mass ratio is 0.45. In this work, the active masses of the positive electrode were 3 mg, and the active masses of the negative electrode were 6.7 mg.

The specific capacity of HSC ($C_{HSC}$) was calculated by the following equation:

$$C_{HSC} = \frac{I \cdot t}{m_{total} \cdot V} \qquad (2)$$

In where, $I$ is the discharging current, $t$ is the discharging time, $m_{total}$ is the total active-material mass loading of both electrodes, and $V$ is the operating voltage window.

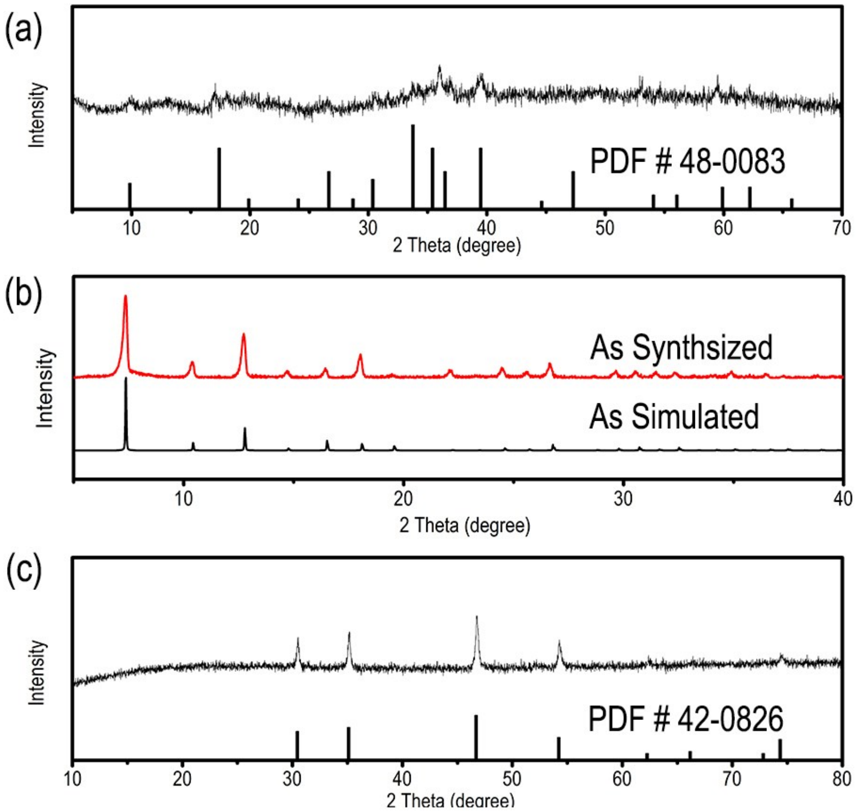
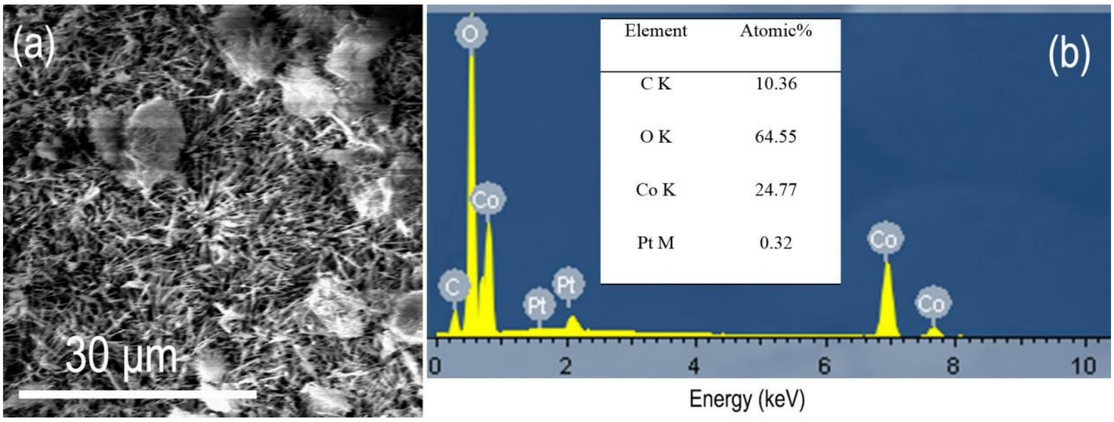
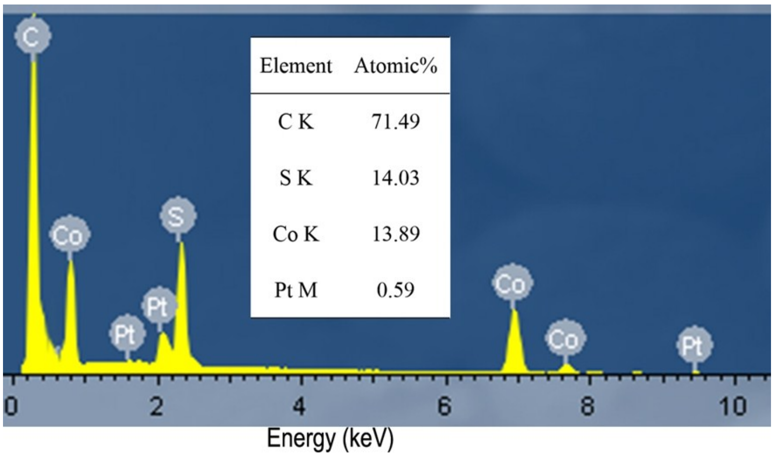


**Fig. S1.** (a) XRD pattern for urchin-like CCH, (b) XRD pattern for HU-ZIF-67S, (c) XRD pattern for HPHU-$Co_{1-x}S$@C.



| Element | Atomic% |
|---|---|
| C K | 10.36 |
| O K | 64.55 |
| Co K | 24.77 |
| Pt M | 0.32 |

Fig. S2. SEM and EDX characterization of urchin-like CCH. (a) SEM image, (b) EDX spectrum.



| Element | Atomic% |
|---|---|
| C K | 71.49 |
| S K | 14.03 |
| Co K | 13.89 |
| Pt M | 0.59 |

Fig. S3. EDX spectrum of HUPU-$Co_{1-x}S$@C.

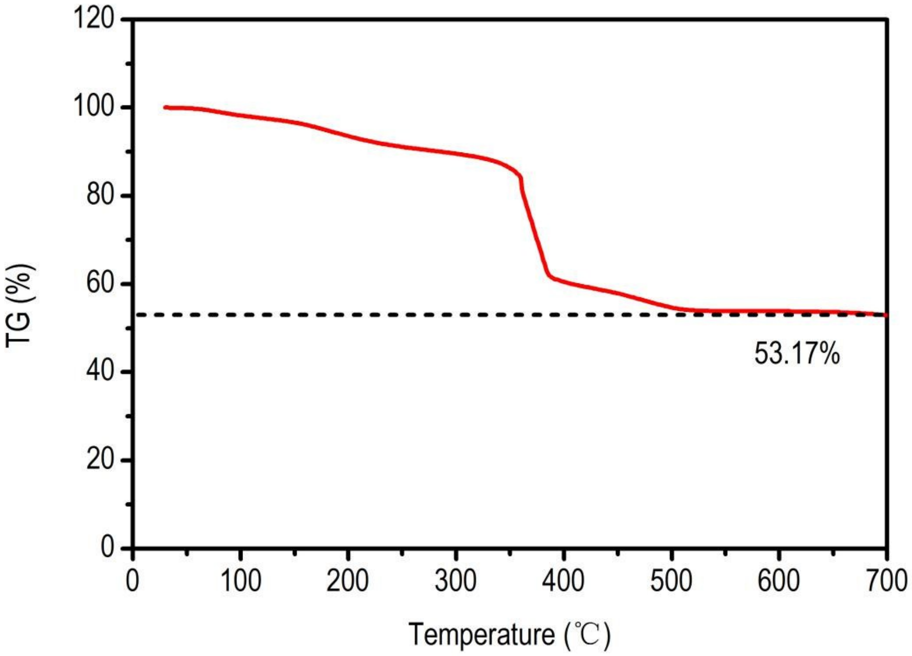


Fig. S4. TGA characterization of HUPU-$Co_{1-x}S$@C.

According to the following equation (3), the $Co_{1-x}S$ contents are about 60.2 %, the content of the carbon substrate is 39.8%.

$$wt_{Co_{1-x}S} = wt_{Co_3O_4} \times \frac{3M_{Co_{1-x}S}}{M_{Co_3O_4}} \tag{3}$$

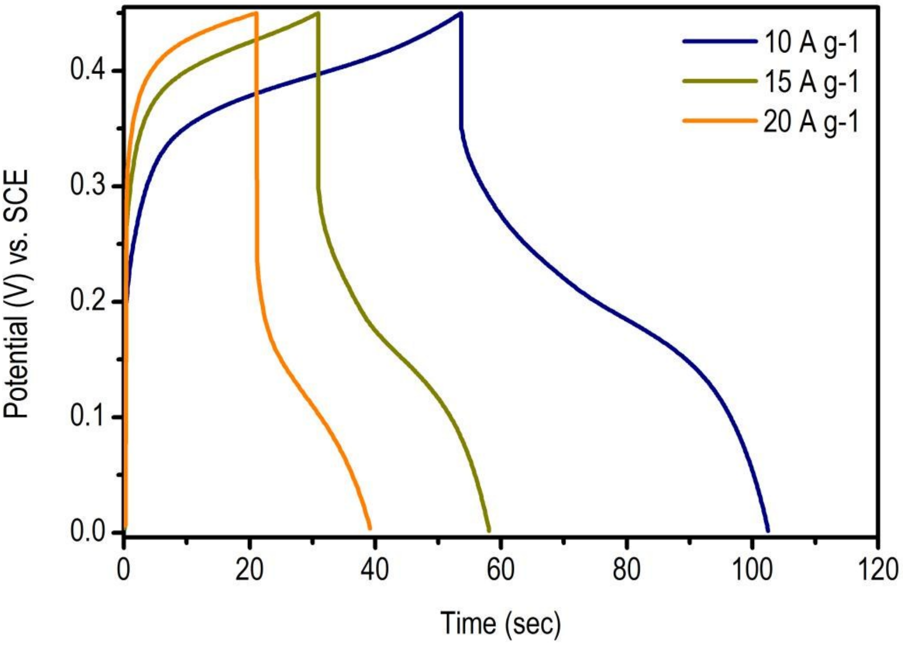


**Fig. S5.** Charge/discharge curves of HPHU-$Co_{1-x}S$@Cat the current density from 10 to 20 A $g^{-1}$.

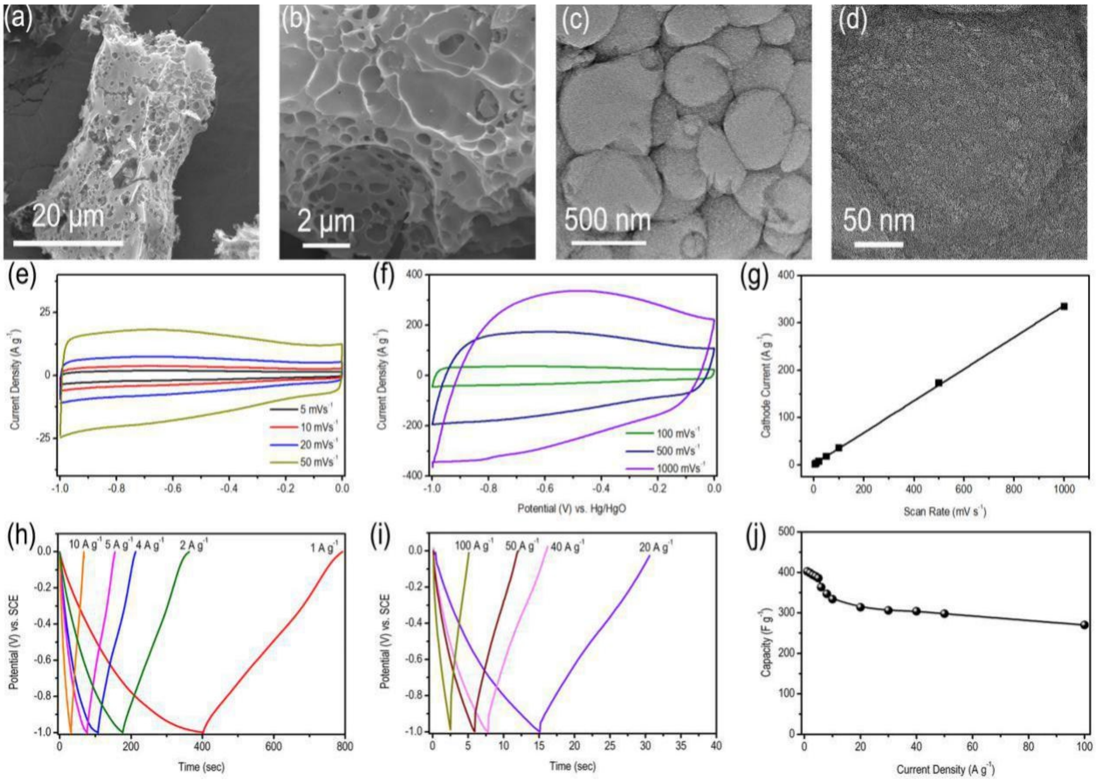


**Fig. S6.** Structural and electrochemical characterization of AC: (a, b) FESEM. (b, c) TEM. (e, f) CV curves at scan rates range from 5 to 1000 mV s$^{-1}$,(g) Peak current of CV curves at different scan rate, (h, i) Galvanostatic charge/discharge curves at the current densitiesfrom 0.5 to 100A g$^{-1}$, (j) The specific capacitance of HPHU-Co$_{1-x}$S@C at different current densities.

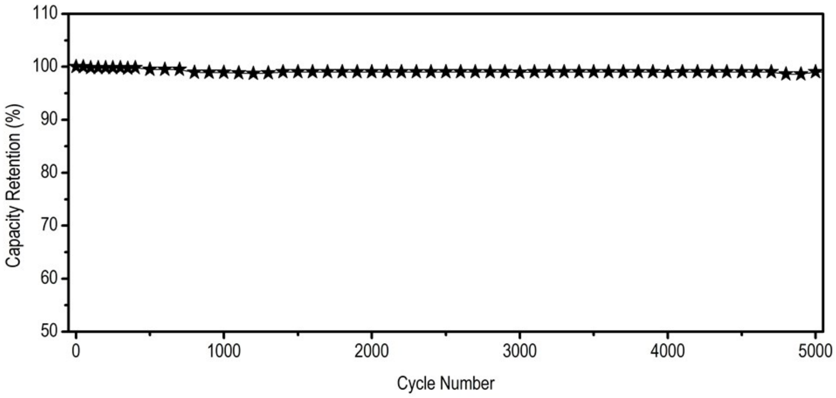


**Fig. S7.** Cycling performance of AC at the constant current density of 5 A $g^{-1}$.

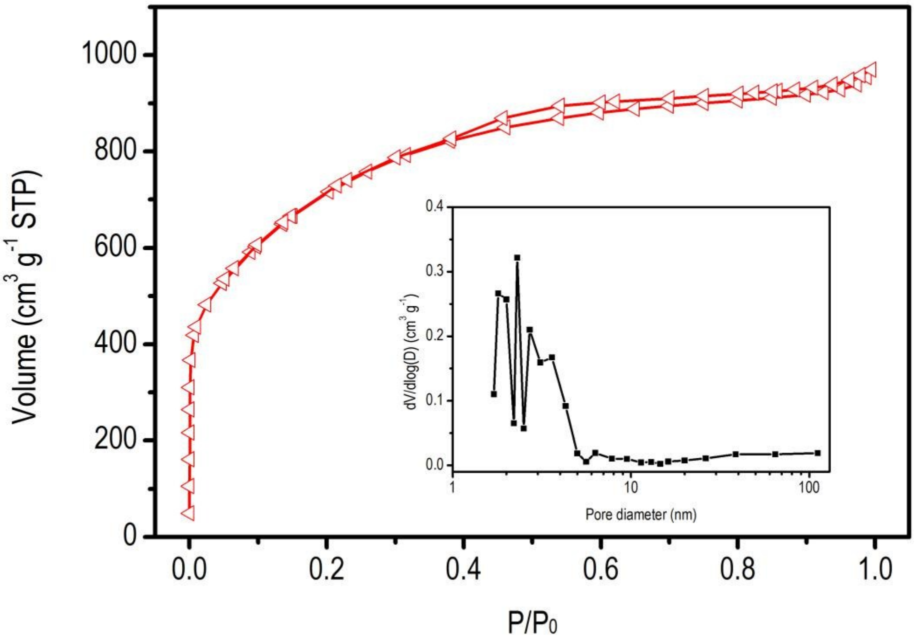


**Fig. S8.** $N_2$-sorption isotherms and pore-size distribution of activated carbon

**Table S1** The surface area, pore size, and pore volume of activated carbon.

| **Sample** | **SurfaceArea($m^2g^{-1}$)** | **Average pore diameter (nm)** | **PoreVolume($cm^3g^{-1}$)** |
|---|---|---|---|
| **AC** | **2468.41** | **2.52** | **1.86** |

**Table S2** Comparison of the specific capacity of metals sulfides in the present work and the reported work

| Materials | Loading Mass (mg cm$^{-2}$) | Current density | Specific Capacity | Reference |
|---|---|---|---|---|
| $Co_{1-x}S$ | Not report | 1 A g$^{-1}$ | 998 F g$^{-1}$ | **Ref.1** |
| CoS | Not report | 1 A g$^{-1}$ | 224 F g$^{-1}$ | **Ref.2** |
| $NiCo_2S_4$ | Not report | 1 A g$^{-1}$ | 1231 F g$^{-1}$ | **Ref.3** |
| $Ni_xCo_{9-x}S_8$@C | Not report | 2 A g$^{-1}$ | 1404 F g$^{-1}$ | **Ref.4** |
| $NixCo_{3-x}S_4$ | 5 | 2 A g$^{-1}$ | 1203 F g$^{-1}$ | **Ref.5** |
| NiS | 1 | 1 A g$^{-1}$ | 668 F g$^{-1}$ | **Ref.6** |
| $NiCo_2S_4$ | Not report | 4 A g$^{-1}$ | 738 F g$^{-1}$ | **Ref.7** |
| $NiCo_2S_4$ | Not report | 1 A g$^{-1}$ | 1498 Fg$^{-1}$ | **Ref.8** |
| rGO/$CoNiS_x$/N–C | 3 | 1 A g$^{-1}$ | 1028.2 Fg$^{-1}$ | **Ref.9** |
| $Co_9S_8$-NSA/NF | Not report | 0.5 A g$^{-1}$ | 1098.8 F g$^{-1}$ | **Ref.10** |
| $NiCo_2S_4$ nanotube | Not report | 50 mV s$^{-1}$ | 603 F g$^{-1}$ | **Ref.11** |
| $NiCo_2S_4$@G | Not report | 1A g$^{-1}$ | 1432 F g$^{-1}$ | **Ref.12** |
| $NiCo_2S_4$ | Not report | 1A g$^{-1}$ | 1296 F g$^{-1}$ | **Ref.13** |
| $NiCo_2S_4$ | 3 | 1A g$^{-1}$ | 1722 F g$^{-1}$ | **Ref.14** |
| H-3DRG@$NiCo_2S_4$ | Not report | 1A g$^{-1}$ | 783 F g$^{-1}$ | **Ref.15** |
| **HPHU-$Co_{1-x}S$@C** | **5** | **1 A g$^{-1}$** | **1871 F g$^{-1}$** | **This Work** |

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