Supporting information

Sacrificial Mo-S modification and P doping co-assisted activation strategy to enhance electrochemical performance of cobalt carbonate hydroxide hydrate

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1. Experimental

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1.1 Raw material

$Co(NO_3)_2 \cdot 6H_2O$ (≥98.5%) and urea (CH_4N_2O, ≥99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Ammonium molybdate ($(NH_4)_6Mo_7O_{24} \bullet 4H_2O$, ≥99.0%) was purchased from Sinopharm Chemical Reagent Co, Ltd. Ammonium fluoride (NH_4F, ≥98%) was purchased from Tianjin Zonghengxing Chemical Reagents Ltd. Thioacetamide (TAA) (C_2H_5NS, ≥99%) was supplied by Tianjin Tianli Chemical Reagents Ltd. Sodium hypophosphite (NaH_2PO_2, 99.0%) and potassium hydroxide (KOH, 95%) come from Sinopharm Chemical Reagent Co, Ltd. Deionized (DI) water were used throughout all experiments.

Nickel foam (Purity: ~99.99%, Porosity: ≥96.0%, Average hole diameters: ~0.25 mm, Surface density: 350 ± 25 g/m^2) was obtained from Hefei Kejing Materials Technology Co. Ltd. CC (Surface density: ~170 g m^{-2}) was supplied by Shanghai Lishuo Composite Materials Technology Co, Ltd.

1.2 Characterizations

Phase structure of the as-prepared products was characterized on Rigaku Ultima IV X-ray diffractometer with Cu Ka radiation (λ=1.5406 Å). The morphology, lattice structure and element content of products was analyzed by scanning electron microscopy (SEM, Zeiss Gemini SEM 300), transmission electron microscope (TEM, Tecnai, G220 UTWIN) and HR-TEM (JEOL 2100F) with energy dispersive X-ray spectroscopy (EDX). X-ray photoelectron spectroscopy (XPS) analysis was realized on a PHI Quantera II X-ray photoelectron spectrometer. Brunauer-Emmett-Teller (BET, ASAP2460) was used to characterize the specific surface area of the materials.

Electrochemical analyses were carried out with a three-electrode on a CHI760E electrochemical workstation (Shanghai Chenhua Instrument Corp.) in 1 M KOH aqueous solution at room temperature. The as-prepared electrode (1 cm×1 cm), platinum plate electrode (1 cm×1 cm) and Hg/HgO (1M KOH) electrode were used as the working electrode, the counter electrode and the reference electrode, respectively. Electrochemical impedance spectroscopy (EIS) measurements were recorded at open-circuit potential in the frequency range of 100 kHz to 100 mHz. For the ASCs, two-electrode system was used with CCHH/Mo-S/P/A (1.0×1.0 cm^2) as the cathode, commercial conductive carbon cloth (CC) (1.0×1.0 cm^2) as the anode and 1 M KOH as electrolyte.

2. Electrochemical performance calculation:

Based on GCD curves, the areal capacities and specific capacities of the as-synthesized electrodes were calculated according to the equation S1 and S2, respectively:

$$Q_s = \frac{I\int_0^{\Delta t} V dt}{S \times \Delta V_{mean}} = \frac{I\int_0^{\Delta t} V dt}{S \times \frac{\Delta V}{2}} = 2\frac{I\int_0^{\Delta t} V dt}{S \times \Delta V} \quad (S1)$$

$$Q_m = \frac{I\int_0^{\Delta t} V dt}{m \times \Delta V_{mean}} = \frac{I\int_0^{\Delta t} V dt}{m \times \frac{\Delta V}{2}} = 2\frac{I\int_0^{\Delta t} V dt}{m \times \Delta V} \quad (S2)$$

where Q_s, Q_m, I, Δt, V, ΔV_{mean}, S, m, and ΔV are the areal capacity (C cm^{-2}), specific capacity (C g^{-1}), discharge current (A), discharge time (s), operating potential (V), mean value of operating potential (V), area of the device (cm^2), mass (g), and potential window (V) of electroactive materials, respectively.

For the fabrication of ASC device, areal capacity (Q, C cm^{-2}), energy density (E, W h cm^{-2}) and power density (P, W cm^{-2}) of device were calculated from current charging/discharging curves using the following equations, respectively.

$$Q = 2\frac{I\int_{0}^{\Delta t_s} V_s dt}{S \times \Delta V_s}$$

$$E = \frac{I\int_{0}^{\Delta t_s} V_s dt}{3.6 \times S}$$

$$P = \frac{3600 \times E}{\Delta t_s}$$

where I, S, Δts, Vs and ΔVs are the discharge current (A), area of the device (cm^2), discharge time (s), operating voltage (V), and voltage window (V) of the discharge process, respectively.

3. Supplementary figures and tables:

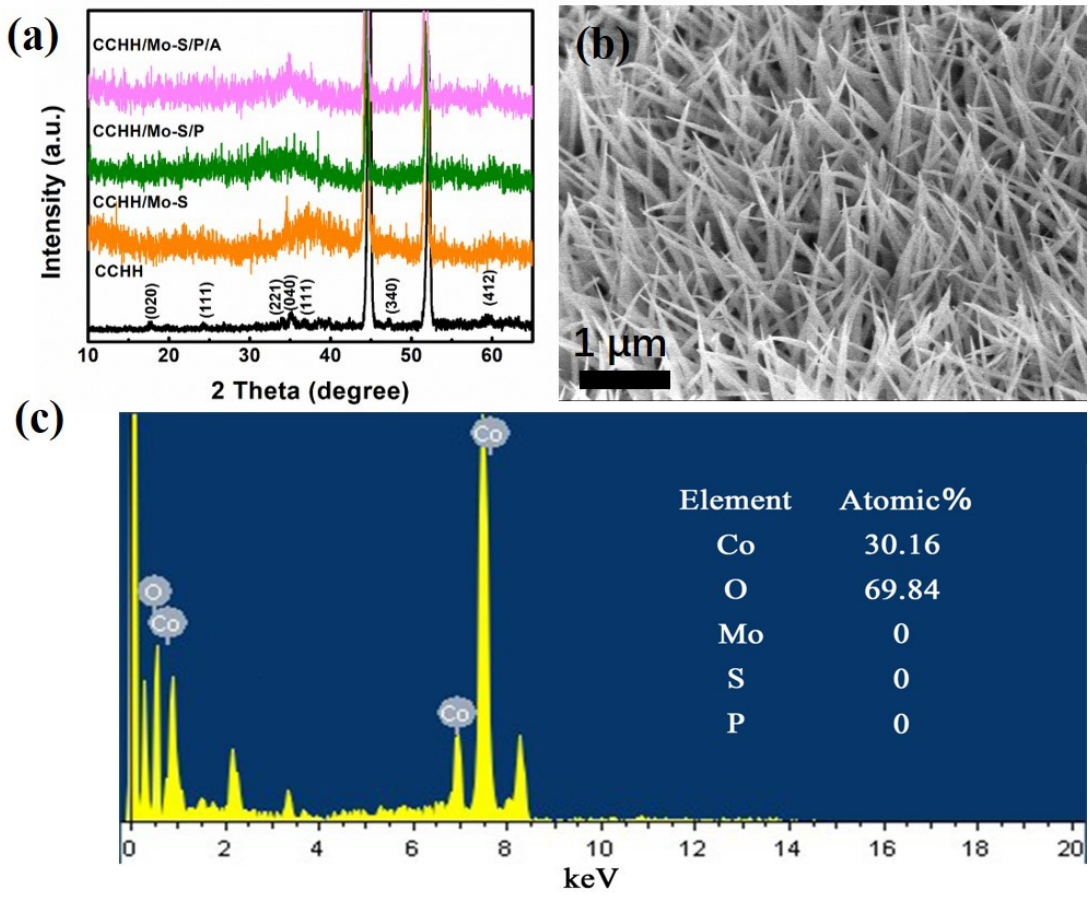

Fig. S1 (a) XRD patterns of the CCHH, CCHH/Mo-S, CCHH/Mo-S/P and CCHH/Mo-S/P/A. (b) SEM image of CCHH. (c) EDS data of the CCHH/Mo-S/P/A.

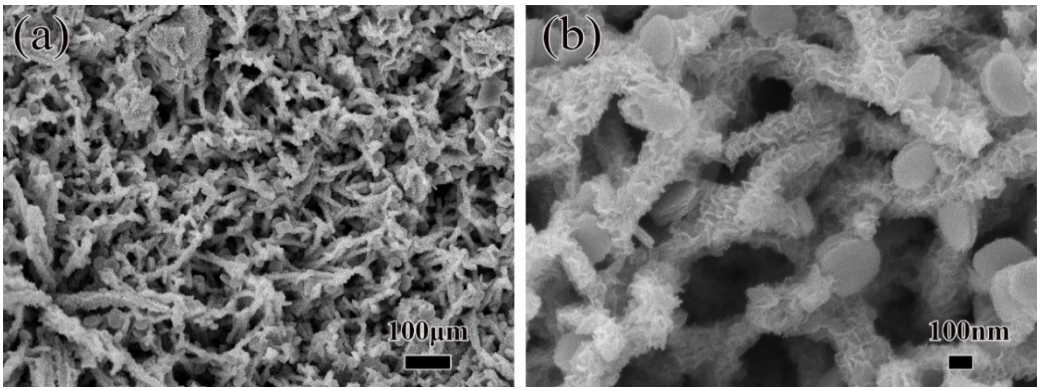

Fig. S2 SEM images of the CCHH/A at different magnifications.

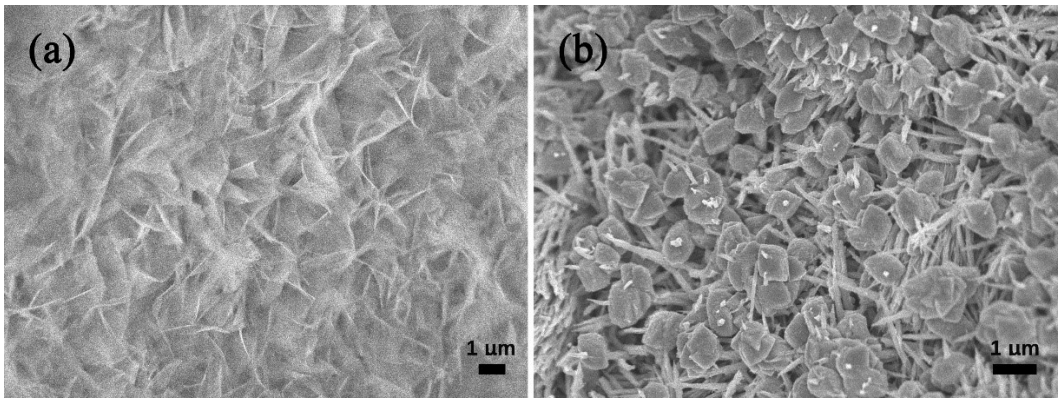

Fig. S3 (a) SEM image of CCHH/Mo-S/A. (b) SEM image of CCHH/P/A

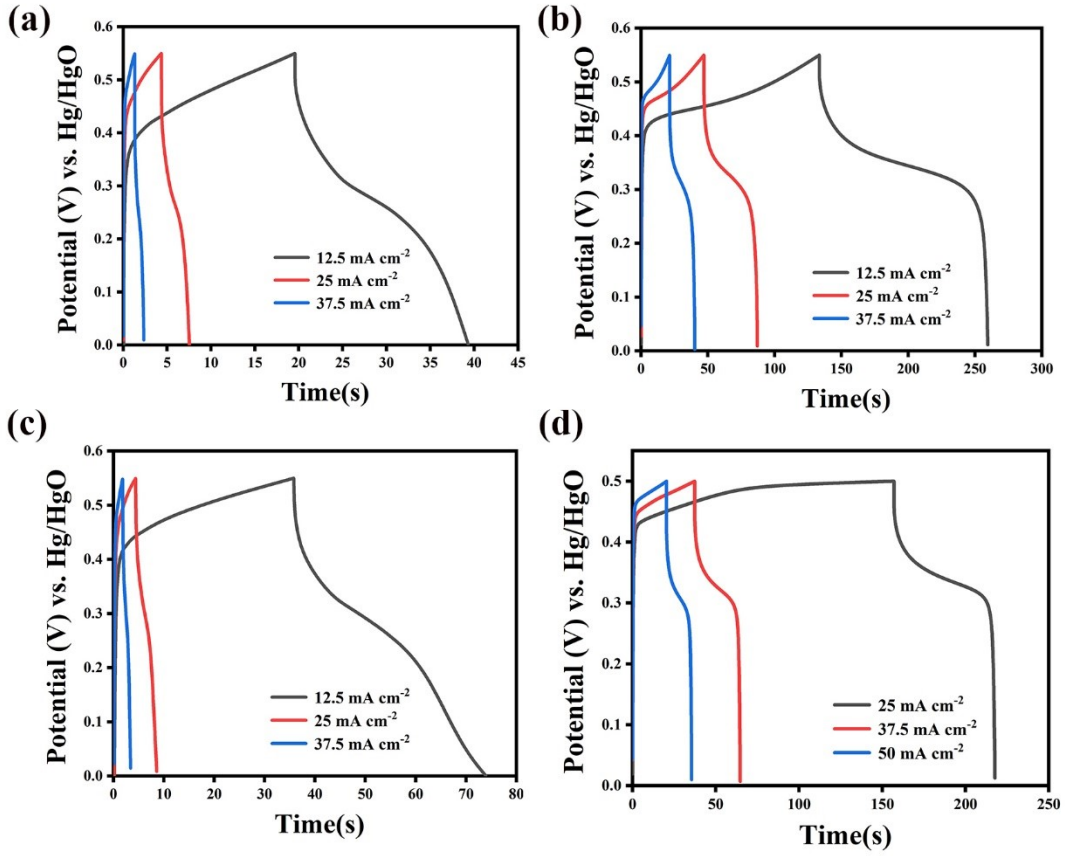

Fig. S4 GCD curves at different densities of the (a) CCHH/A, (b) CCHH/Mo-S/A, (c) CCHH/P/A and (d) CCHH/Mo-S/P.

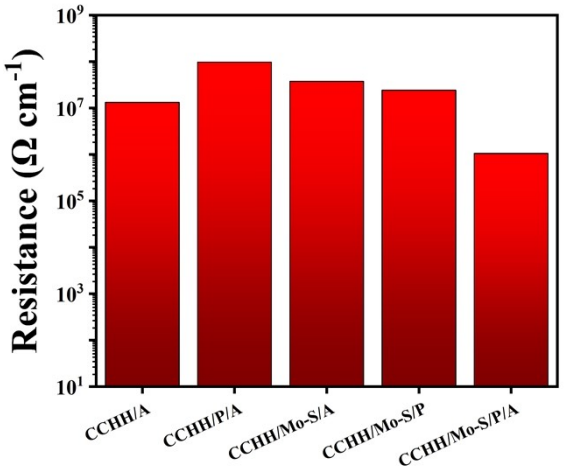

Fig. S5 Comparison of resistance for CCHH/A, CCHH/P/A, CCHH/Mo-S/A, CCHH/Mo-S/P and CCHH/Mo-S/P/A.

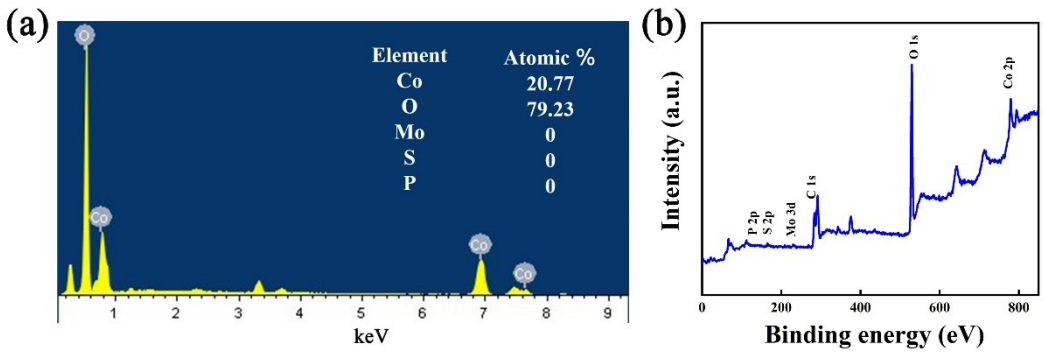

Fig. S6 (a) EDS data and (b) XPS survey spectra of the CCHH/Mo-S/P/A after 10000 cycles.

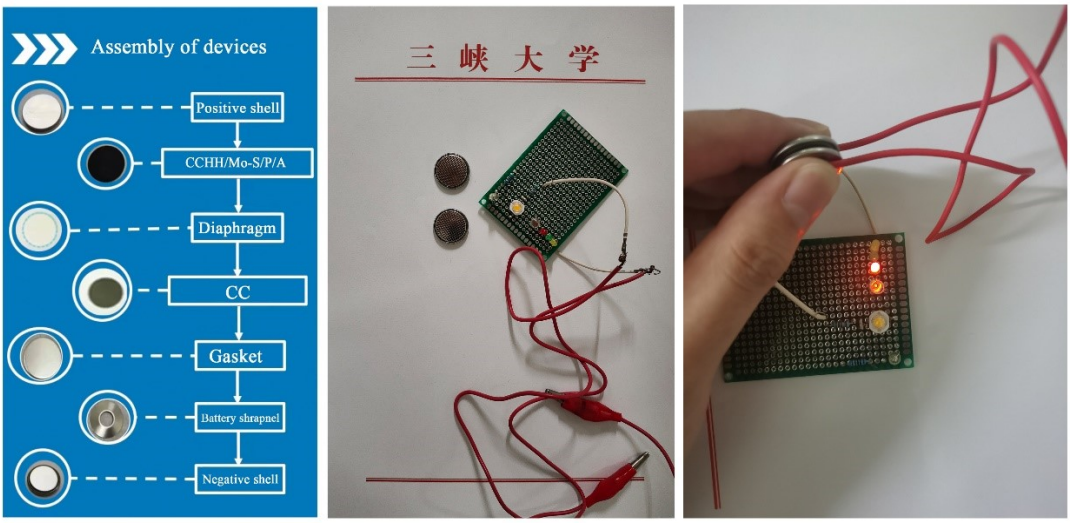

Fig. S7 CCHH/Mo-S/P/A//CC device assembly process and lighting LED indicator.

Table S1. Comparison of the specific capacitance between this work and several reports on Co-based binary metal electrode materials.

Materials	Electrolyte	Operation Voltage (V)	Specific capacitance	Current density	Ref.
$FeCo_2S_4$	6 M KOH	0~0.4	1.644 F cm^{-2} (0.66 C cm^{-2})	50 mA cm^{-2}	[20]
$FeCo_2S_4$	1 M KOH	0~0.4	7.66 F cm^{-2} (3.06 C cm^{-2})	5 mA cm^{-2}	[21]
Co-Mo-S	1 M KOH	0~0.45	1,080 F g^{-1} (468 C g^{-1})	1 A g^{-1}	[22]
$CoNi_2S_4$	6 M KOH	0~0.4	1,576.8 F g^{-1} (630.72 C g^{-1})	0.5 A g^{-1}	[23]
$NiCo_2S_4$	2 M KOH	0~0.45	1,777 F g^{-1} (799.65 C g^{-1})	8 A g^{-1}	[24]
$CuCo_2S_4$	4 M KOH	0~0.5	908.9 F g^{-1} (454.45 C g^{-1})	5 mA cm^{-2}	[25]
$CuCo_2S_4$	2 M KOH	0~0.4	1,852 F g^{-1} (740.8 C g^{-1})	2 A g^{-1}	[26]
$CoMoS_4$	6 M KOH	0~0.45	415 F g^{-1} (186.75 C g^{-1})	0.5 A g^{-1}	[27]
$Co_3S_4/CoMo_2S_4$	3 M KOH	0~0.45	1,457.8 F g^{-1} (656 C g^{-1})	1 A g^{-1}	[28]
Co-Mo-S	1 M KOH	0~0.5	1,805.28 F g^{-1} (902.64 C g^{-1})	0.5 A g^{-1}	[29]
$Co_9S_8@MoS_2$	1 M KOH	0~0.5	213 mAh g^{-1}	1 A g^{-1}	[30]
$Mo_{0.7}Co_{0.3}S_2$-C_3N_4	2 M KOH	0~0.4	1,225 F g^{-1} (490 C g^{-1})	0.5 A g^{-1}	[31]
$NiCo_2S_4$@N, S	6 M KOH	0~0.4	1,145 F g^{-1} (458 C g^{-1})	1 A g^{-1}	[32]
Ni-Co-S	1 M KOH	0~0.5	1,454 F g^{-1} (727 C g^{-1})	1 A g^{-1}	[33]
Ni-Co-S/$Co(OH)_2$	3 M KOH	0~0.5	1,440 C g^{-1} (720 C g^{-1})	1 A g^{-1}	[34]
Mn-Co-S	1 M KOH	0~0.45	1,158 F g^{-1} (521.1 C g^{-1})	1 A g^{-1}	[35]
Co-Mo-O-S	6 M KOH	0~0.35	1,134 F g^{-1} (396.9 C g^{-1})	1 A g^{-1}	[36]
Co-Mo-O	3 M KOH	0~0.6	1,437.5 F g^{-1} (862.5 C g^{-1})	1.5 A g^{-1}	[37]
$NiCo_2O_4$	2 M KOH	0~0.35	879 F g^{-1} (307.65 C g^{-1})	0.5 A g^{-1}	[38]

CCHH/Mo-S/P/A	1 M KOH	0~0.55	1429 C g^{-1} (4.29 C cm^{-2})	12.5 mA cm^{-2} (4.2 A g^{-1})	This work