Supporting Information

Controlled Sulfidation of Ternary Transition Metal towards high performance Electrode Materials for Supercapacitors

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Appendix S1

1 Experimental

1.1 Materials

The following chemicals were procured from commercial suppliers: nickel source ($Ni(NO_3)_2$ $6H_2O$), cobalt source ($Co(NO_3)_2$ $6H_2O$), ferric source ($Fe(NO_3)_3$ $9H_2O$), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), and thioacetamide (TAA) from Sinopharm Co., Ltd. KOH (electrolyte) was supplied by Shanghai McLean Biochemical Co., while carbon cloth (CC) was acquired from Changde Liyuan Material Co. All materials were of analytical purity. Experimental procedures utilized deionized water.

1.2 Synthesis of electrode material

1.2.1 Synthesis of NiCoFe-OH (NCF-OH)

All multi-component active substances were synthesized by the co-precipitation method. Taking NiCoFe-OH (NCF-OH) as an example, the synthesis process is as follows: Solution A: 0.4 mmol of each of the three metal nitrates was dissolved in 25 mL of deionized water. Solution B: 0.6 g of sodium hydroxide and 1.59 g Na_2CO_3 were dissolved in 25 mL of deionized water. Add solution B to solution A drop by drop, and stir well to keep the final pH of the mixed solution equal to 10. The mixed solution was centrifuged to obtain a precipitate and dried at 60 ℃ for 12 h.

1.2.2 Synthesis of NiCoFe-S (NCF-S)

Firstly, dissolve 240 mg of TAA in 10 mL of deionized water. Then add 120 mg of NCF-OH powder. Transfer the mixed solution into a reactor for sulfidation at 95 ℃

for 12 hours. After multiple cleanings, it was dried at 60 ℃ for 12 h. Finally, the electrode material NiCoFe-S_{95} (NCF-S_{95}) was obtained.

NiCoFe-S_{35} (NCF-S_{35}), NiCoFe-S_{55} (NCF-S_{55}), NiCoFe-S_{75} (NCF-S_{75}), and NiCoFe-S_{115} (NCF-S_{115}) were obtained by adjusting the hydrothermal temperature to 35, 55, 75, and 115 ℃, respectively.

In order to explore the reasons for the formation of the oxidation state, Ni-S_{75}, Co-S_{75}, and Fe-S_{75} were prepared by the same process.

1.2.3 Synthesis of the working electrode

The active material (8 mg), conductive agent (acetylene black), and PVDF were first ground together in an 8:1:1 weight ratio. The resulting powder was mixed with NMP to obtain a uniform slurry, which was coated on the current collector (1 cm × 1 cm carbon cloth) and dried overnight at 60 ℃.

1.3 Assembly of asymmetric supercapacitor (ASC)

ASCs were constructed with NCF-S_{95} (positive) and activated carbon (AC, negative) electrodes. A gel electrolyte comprising KOH and polyvinyl alcohol was uniformly applied.

1.4 Characterization:

The crystallographic characteristics were examined utilizing a D-max2500PC X-ray diffractometer (XRD) that employs Cu Kα radiation (λ = 1.5406 Å). The scan was conducted within the range of 20° to 70° at a steady speed of 3° per minute. Morphological traits were investigated using SU8010 scanning electron microscopy (SEM) and Spectra300 transmission electron microscopy (TEM). The chemical state

was analyzed using an X-ray photoelectron spectrometer (XPS, ESCALABX), applying charge correction where the binding energy of C 1s is set at 284.8 eV as the energy reference.

The NCF-OH and NCF-S served as the working electrodes, Pt as the counter electrode, and saturated calomel as the reference electrode. At room temperature, the electrochemical properties were evaluated using a CHI760E workstation with a three-electrode arrangement using a 6 M KOH electrolyte. Various techniques were employed, including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS).

Formula:

The specific capacitance of the electrode material can be calculated using equation (1).

$$Q = \frac{i_m \int Ydt}{1.8V|_{V_i}^{V_f}} \quad (1)$$

Where Q (mAh g^{-1}) designates the specific capacitance of the electrode, i_m (mA cm^{-2}), $\int Vdt$ is the integral value of the discharge process in the GCD curve, V is the voltage window, V_i and V_f are the initial and final values of the potential, respectively.

The charge storage mechanism was analyzed using equation (2):

$$i_p = a * b^v \quad (2)$$

Where i_p and v represent the peak current and scanning rate respectively, and a and b are constants. A b value close to 0.5 indicates that the diffusion-controlled process (battery-type behavior) dominates, while a value close to 1.0 indicates that the capacitive-controlled process (capacitor-type behavior) is dominant. Quantitative

analysis via equation (3):

$$i(v) = k_1 v + k_2 \quad (3)$$

Where i, v, k_1, and k_2 represent the output current, scan rate, and two constants, respectively.

Energy density (E, Wh kg^{-1}) and power density (P, W kg^{-1}) were calculated as:

$$E = \frac{C\Delta V}{7.2} \quad (4)$$

$$P = 3600\frac{E}{\Delta t} \quad (5)$$

where C is specific capacitance (F g^{-1}), ΔV is the operating potential window (V) and Δt is discharge time (s).

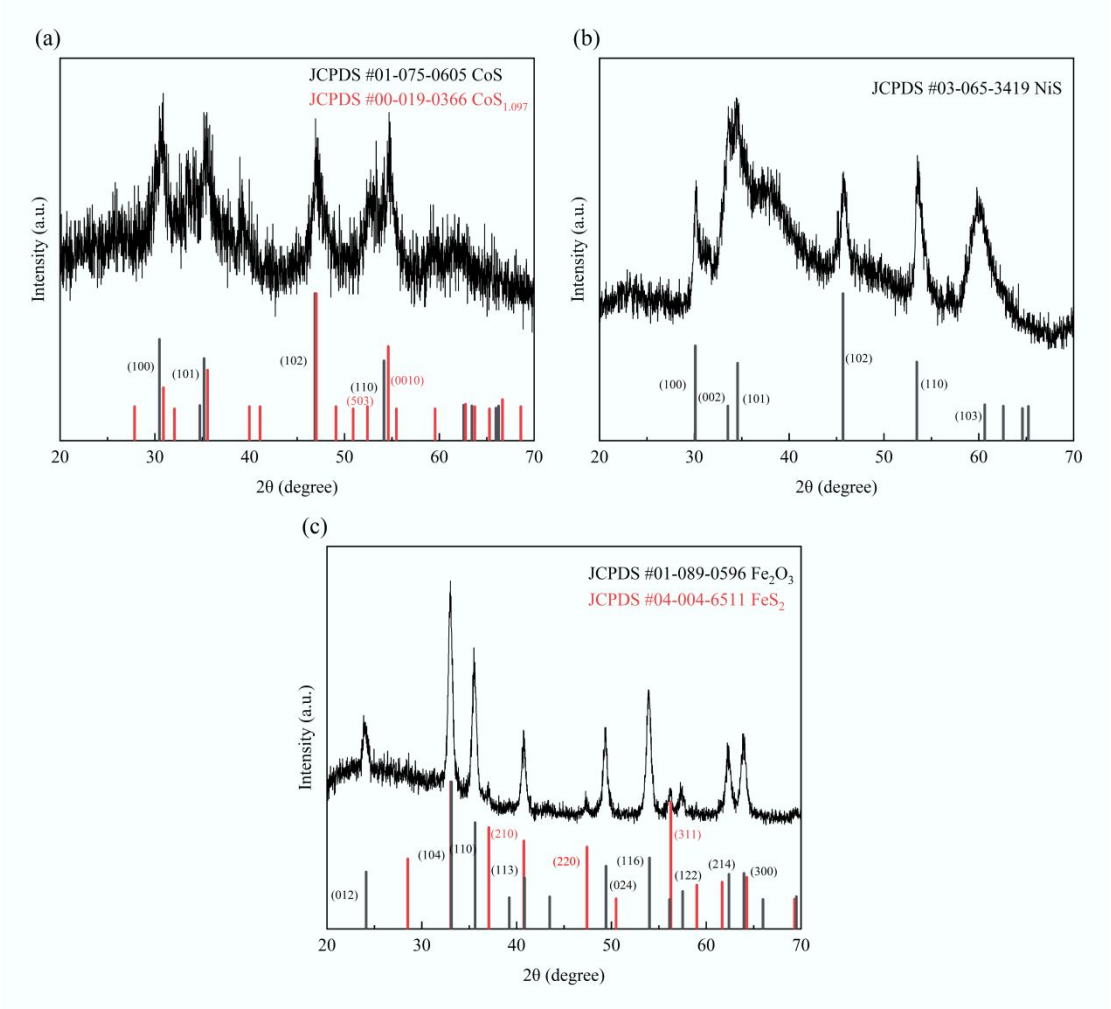

Fig. S1 XRD pattern of (a) Co-S_{75}, (b) Ni-S_{75}, and (c) Fe-S_{75}.

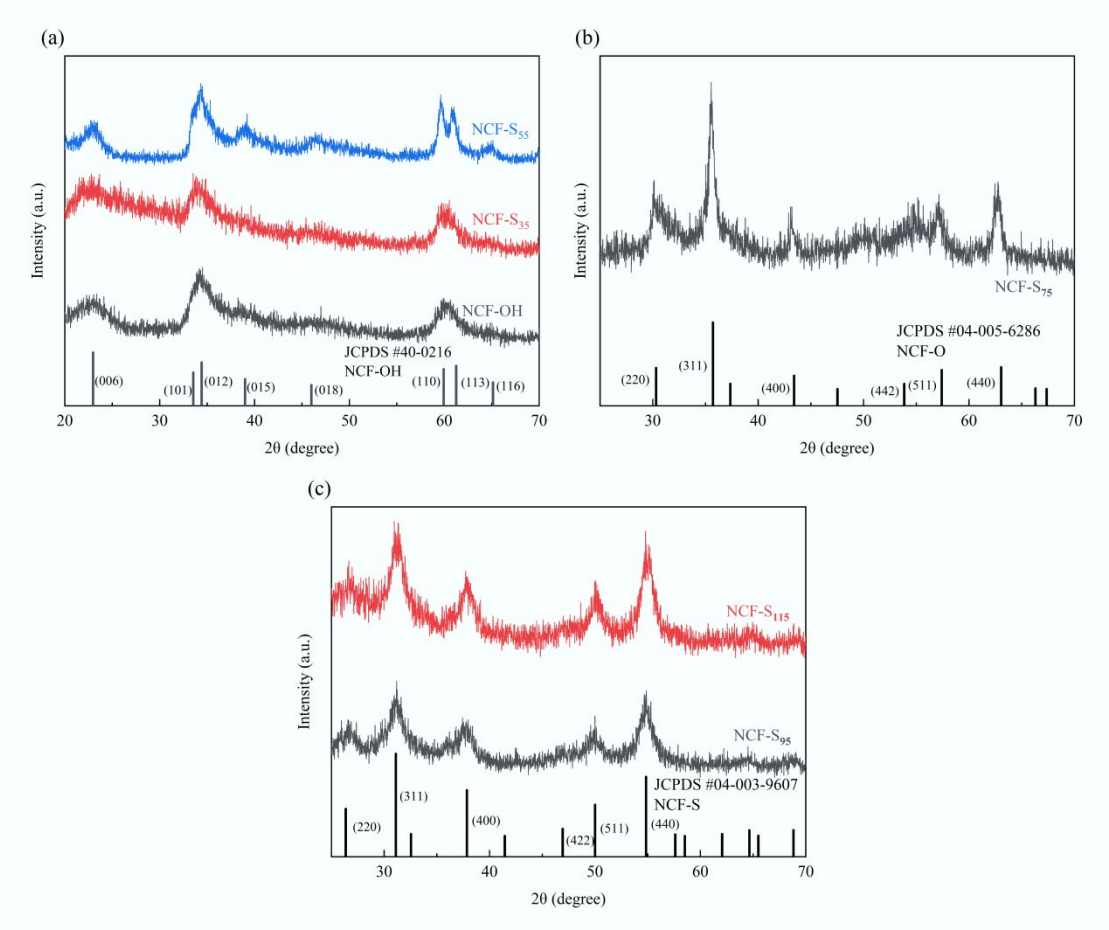

Fig. S2 XRD pattern of (a) NCF-OH, NCF-S_{35}, and NCF-S_{55}, (b) NCF-S_{75}, and (c) NCF-S_{95}, and NCF-S_{115}.

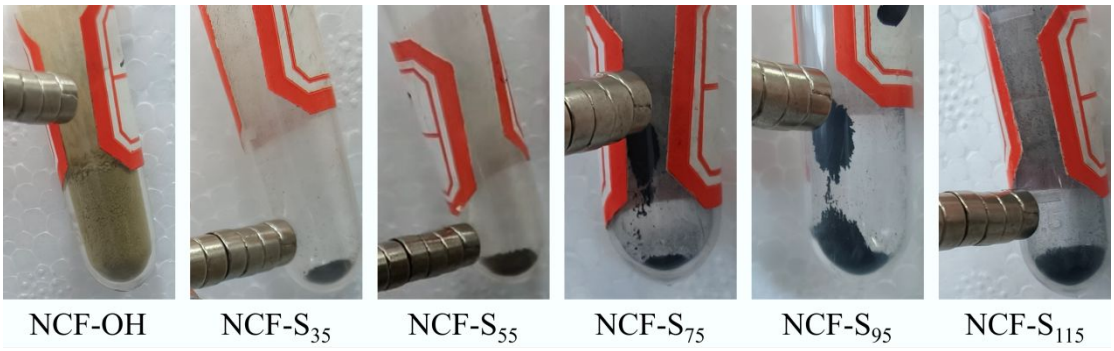

Fig. S3 Magnetism of NCF-OH, NCF-S_{35}, NCF-S_{55}, NCF-S_{75}, NCF-S_{95}, and NCF-S_{115}.

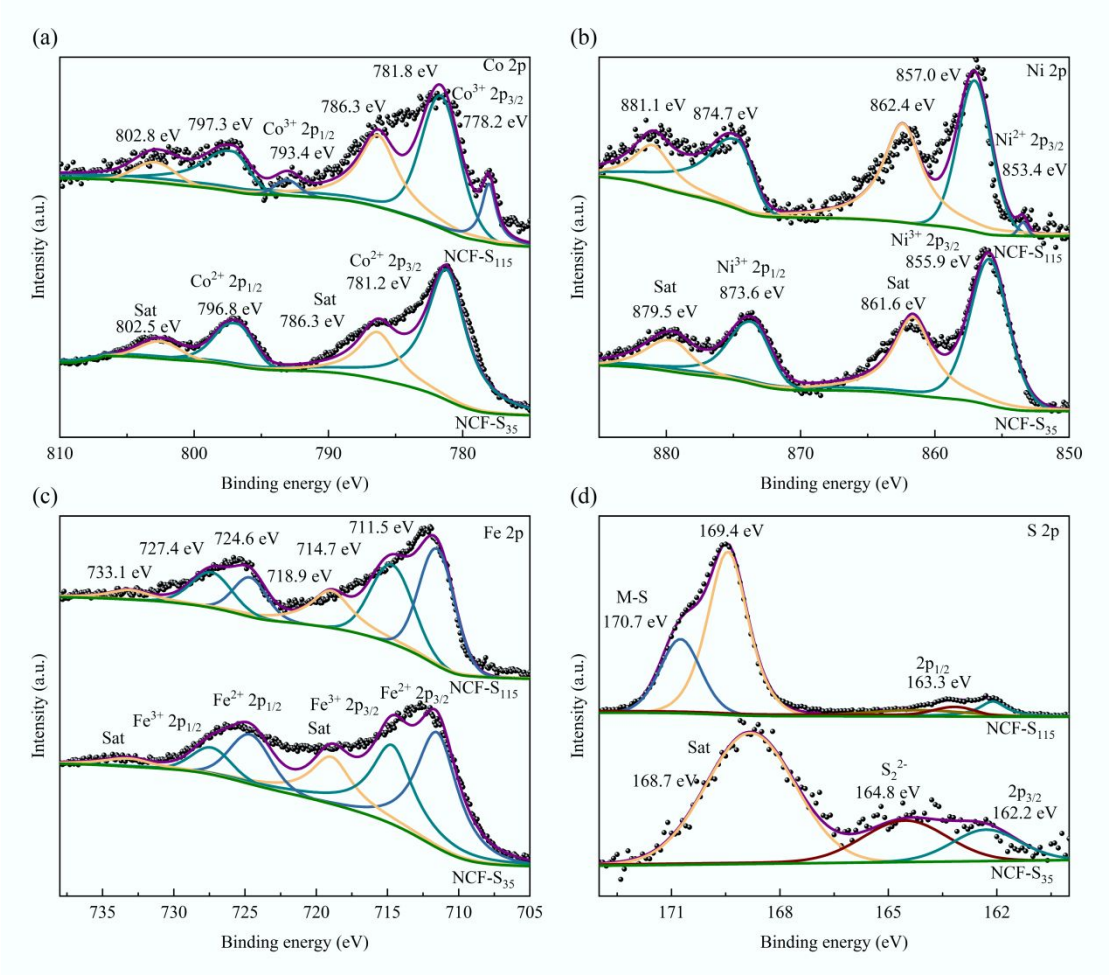

Fig. S4 High-resolution spectra of (a)Co 2p, (b Ni 2p, (c) Fe 2p, and (d) S 2p of NCF-S_{35} and NCF-S_{115}.

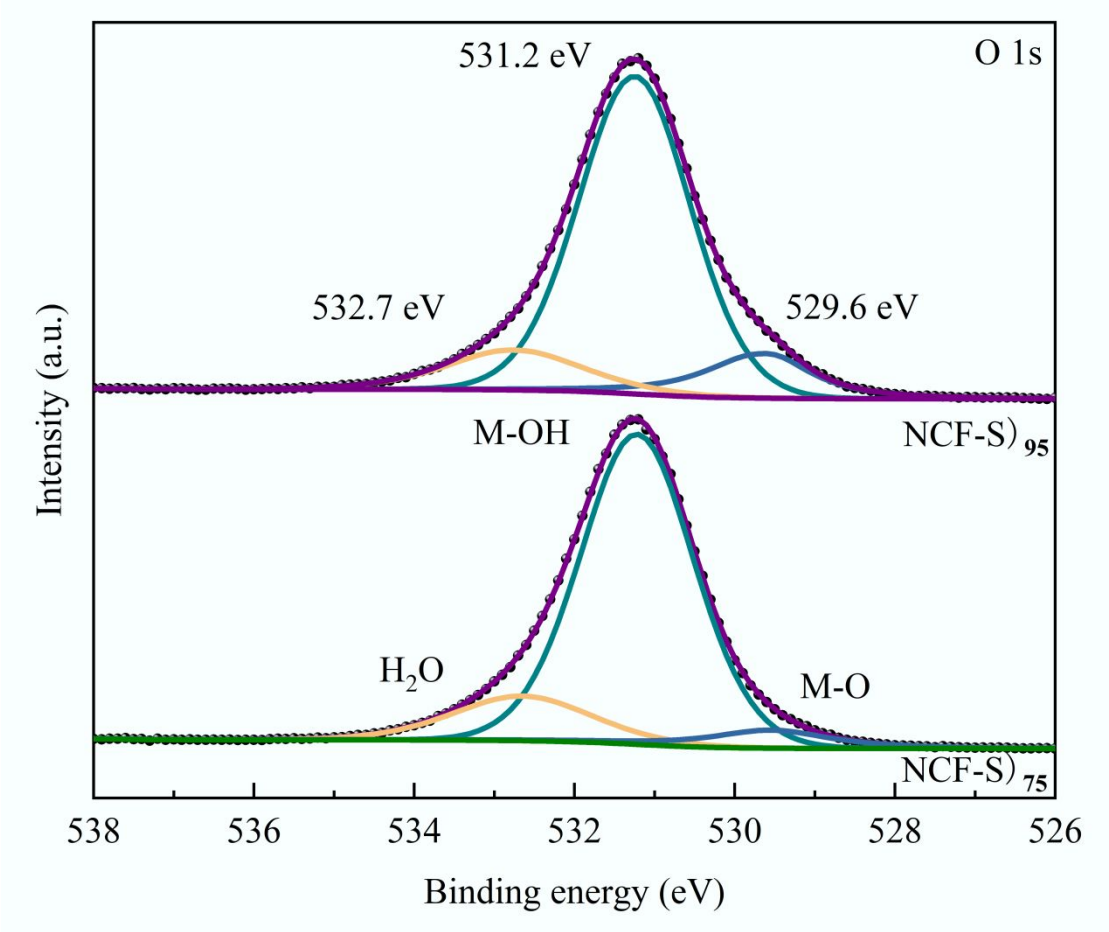

Fig. S5 High-resolution spectra of O 1s of NCF-S_{75} and NCF-S_{95}.