Supporting information for

In situ formation of carbon fiber@Ni_3S_2 non-woven electrode with ultrahigh areal and volumetric capacitance

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Experimental details

Preparation of Ni-CP: In this work, electroplating was employed to prepare Ni / carbon paper (Ni-CP) composite. The detailed process is: CP with a size of 1cm × 2.5 cm × 0.017 cm (thickness) was connected to the negative electrode of a DC power supply, and two pieces of Ni plate were connected to the positive electrode, as shown in Figure 1a in the main text. The electrolyte was an aqueous $NiSO_4$ solution with a concentration of 240 g L^{-1}. In the process of electroplating, a current density of 20 mA cm^{-2} was used for different time to prepare the samples denoted as Ni-CP-x (where x is the time in minutes).

Preparation of Ni_3S_2-CP: The as-prepared Ni-CP-x was immersed in an S-alcohol solution, in which different masses of S were used in a mole ratio of n_S:n_{Ni} =2:1. The hydrothermal method was used to prepare Ni_3S_2-CP**.** The autoclave was kept at 180 °C for 10 h in an oven and then cooled down to room temperature, yielding the Ni_3S_2-CP.

Characterization of materials. The morphology of the samples was studied by field emission scanning electron microscopy (FESEM, JSM-6700F), and X-ray diffraction (XRD) analysis was performed using an X′pert PRO X-ray diffractometer with Cu Kα radiation (λ = 0.154 nm). The specific surface area (SSA) and pore volume were calculated by N_2 adsorption-desorption measurements, which were carried out on an ASAP 2460 surface area and porosity analyzer device.

Electrochemical measurements.

The cyclic voltammetry (CV) measurements were performed on an electrochemistry workstation (CHI 660 C) using a three-electrode system in 2 M KOH solution at room

temperature. The three-electrode assembly was constructed using Ni_3S_2-CP-x as the working electrode, platinum foil as the counter electrode, and Hg/HgO electrode as the reference electrode. Galvanostatic charge–discharge (GCD) measurements were also performed on the three-electrode system. The specific capacitance was calculated from the discharge process of the GCD according to Equations (1-3):

$$C\frac{2 \times i \times \int Udt}{U^2|_{U_i}^{U_f}} \quad (1)$$

$$C_a = \frac{C}{S} \quad (2)$$

$$C_v = \frac{C}{V} \quad (3)$$

where *C*is the specific capacitance of the electrode (F); *i* is the current density (A); $\int Udt$ is the integral current area; *U* is the potential (V) with initial and final values of U_i and U_f, respectively; C_a is the specific areal capacitance (F cm^{-2}); C_v is the specific volumetric capacitance (F cm^{-2}); *S* and *V* are the surface area and volume of the electrode, respectively.

For all materials, after activation for 50 cycles of CV (discharge to 0 V for the last cycle), the open circuit potential gradually became stable, and then electrochemical impedance spectroscopy (EIS) was conducted in the frequency range of 10^{-2} to 10^5 Hz at the stable open circuit potential with an alternating current amplitude of 5 mV.

Table S1. Areal loading of different electrodes and corresponding specific capacitance based on mass, area, and volume.

Electrodes	loading/ mg cm^{-2}	Cs/ Fg^{-1}	Areal Cs/ F cm^{-2}	Volumetric Cs/ F·cm^{-3}
Co_3O_4 nanosheet/ NF [1]	1.4	2735 (2 Ag^{-1})	3.8	38
Co_3O_4 nanowire/NF [2]	1.48	1019 (3.38 Ag^{-1})	1.5	15
$Ni(OH)_2$/NF [3]	0.5	3152 (4 Ag^{-1})	1.6	16
$NiMoO_4$/NF [4]	0.8	3205 (6 Ag^{-1})	2.56	25.6
$NiCo_2O_4$/NF [5]	0.8	2010 (2 Ag^{-1})	1.68	16.8
$NiCo_2O_4$@MnO_2/NF [6]	1.4	2364 (1.4 Ag^{-1})	3.31	33.1
$Ni(OH)_2$/3D graphene [7]	1	1440 (10 Ag^{-1})	1.4	14
$Ni(OH)_2$/3D graphene [8]	0.2	1560 (0.5 Ag^{-1})	0.78	7.8
$CoMoO_4$/3D graphene [9]	0.51	2741 (1.4 Ag^{-1})	1.4	14
$Co_xNi_{1-x}(OH)_2$/3Dgraphene [10]	0.09	1847 (5 Ag^{-1})	0.17	1.7
$NiMoO_4$/CP [11]	0.8	1587 (6.25 Ag^{-1})	1.27	74.7
$Co_xNi_{1-x}(OH)_2$/$NiCo_2O_4$/CP [12]	1	1640 (2 Ag^{-1})	1.64	96.5
Co_3O_4/CP [13]	0.4	1190 (0.25 Ag^{-1})	0.48	28.2
Co_3O_4/CP [13]	1.4	948 (0.25 Ag^{-1})	1.33	78

Note: NF is Ni foam; CP is carbon fiber paper.

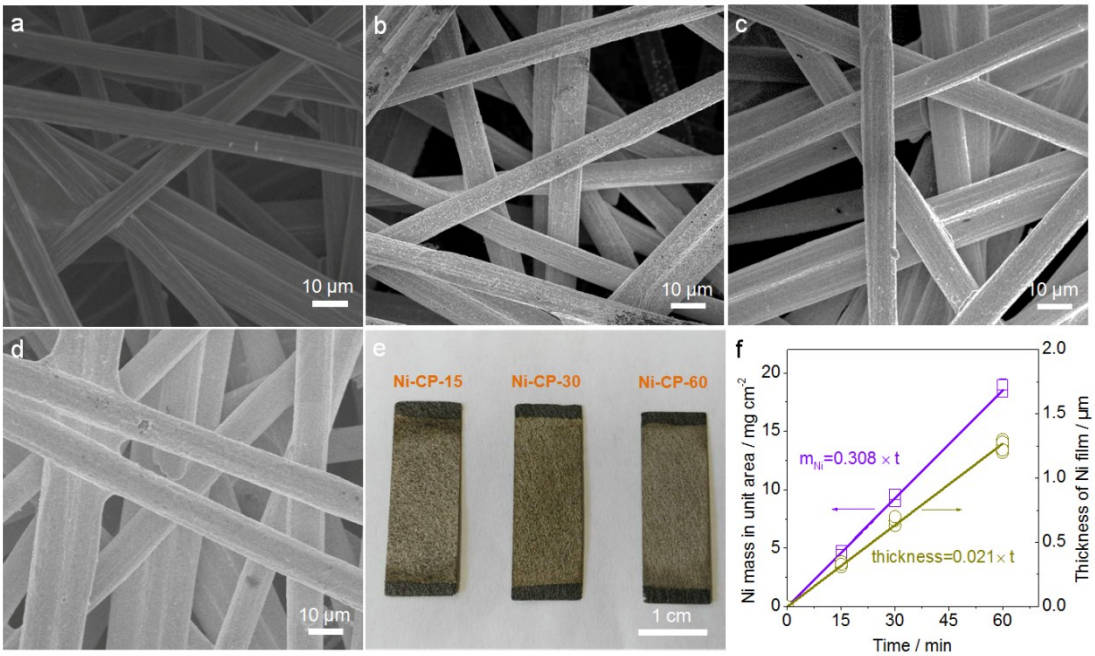

Figure S1. SEM images of (a) carbon paper, (b) Ni-CP-15, (c) Ni-CP-30, (d) Ni-CP-60. (e) Photograph of prepared Ni-CP-x samples. (f) The dependence of the mass and the thickness of the Ni film on the electroplating time.

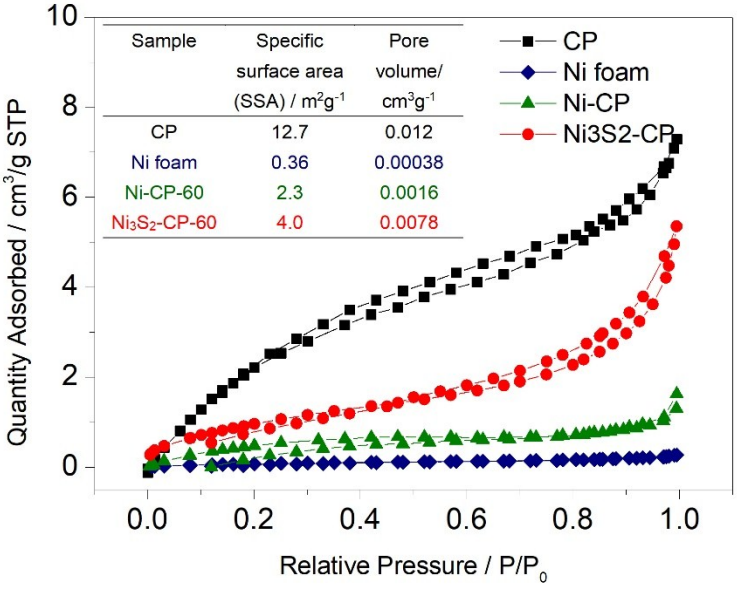

Figure S2. N_2 adsorption-desorption isotherms of CP, Ni foam, Ni-CP-60 and Ni_3S_2-CP-60 and the calculated specific surface area (SSA) and pore volume values.

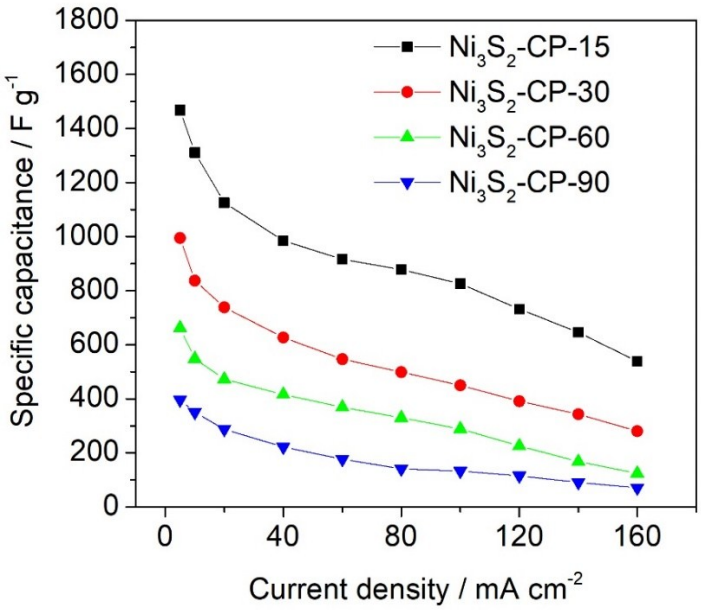

Figure S3. The gravimetric capacitances of samples.

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