Supplementary Information

Morphology-controlled synthesis of the NiCo-carbonate layered double hydroxide as an electrode material for solid-state asymmetric supercapacitor

Sudhir Kumar, Biraj Kanta Satpathy and Debabrata Pradhan*

Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302, W. B., India

*E-mail: deb@matsc.iitkgp.ac.in

Table S1. Synthesis conditions of the NiCo-CH electrode materials.

Materials	Solvent (mL)	$Ni(NO_3)_2 \cdot 6H_2O$ (mmol)	$Co(NO_3)_2 \cdot 6H_2O$ (mmol)	CTAB (g)	Urea (mmol)	Temperature (°C)	Time (h)	Atomic % Ni:Co
NiCo-CH-120	20 (H_2O) + 15 (EG)	2	1	0.5	15	120	12	51:49
NiCo-CH-140	20 (H_2O) + 15 (EG)	2	1	0.5	15	140	12	53:47
NiCo-CH-160	20 (H_2O) + 15 (EG)	2	1	0.5	15	160	12	63:37
NiCo-CH-180	20 (H_2O) + 15 (EG)	2	1	0.5	15	180	12	65:35
NiCo-CH-200	20 (H_2O) + 15 (EG)	2	1	0.5	15	200	12	66:34
NiCo-CH-180 (1:2)	20 (H_2O) + 15 (EG)	1	2	0.5	15	180	12	33:67
NiCo-CH-180 (1:1)	20 (H_2O) + 15 (EG)	1	1	0.5	15	180	12	53:47
NiCo-CH-180 (Without CTAB)	20 (H_2O) + 15 (EG)	2	1	NA	15	180	12	64:36
NiCo-CH-180 (Cal. at 500 °C)	20 (H_2O) + 15 (EG)	2	1	0.5	15	180	12	64:36
NiCo-CH-180 (6 h)	20 (H_2O) + 15 (EG)	2	1	0.5	15	180	6	59:41
NiCo-CH-180 (18 h)	20 (H_2O) + 15 (EG)	2	1	0.5	15	180	18	65:35
NiCo-CH-180 (24 h)	20 (H_2O) + 15 (EG)	2	1	0.5	15	180	24	63:37
NiCo-CH-180 (48 h)	20 (H_2O) + 15 (EG)	2	1	0.5	15	180	48	63:37
NiCo-CH-180 (72 h)	20 (H_2O) + 15 (EG)	2	1	0.5	15	180	72	63:37
NiCo-CH-180 (in H_2O)	35 (H_2O)	2	1	0.5	15	180	12	56:44
NiCo-CH-180 (in EG)	35 (EG)	2	1	0.5	15	180	12	58:42

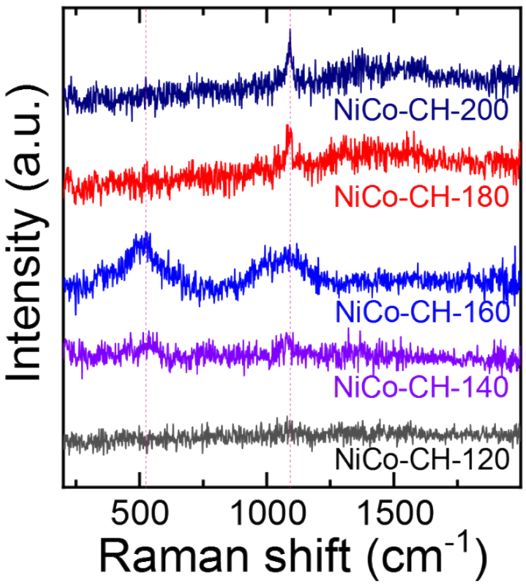

Fig. S1 Raman Spectra of the sample which are prepared at different growth temperature.

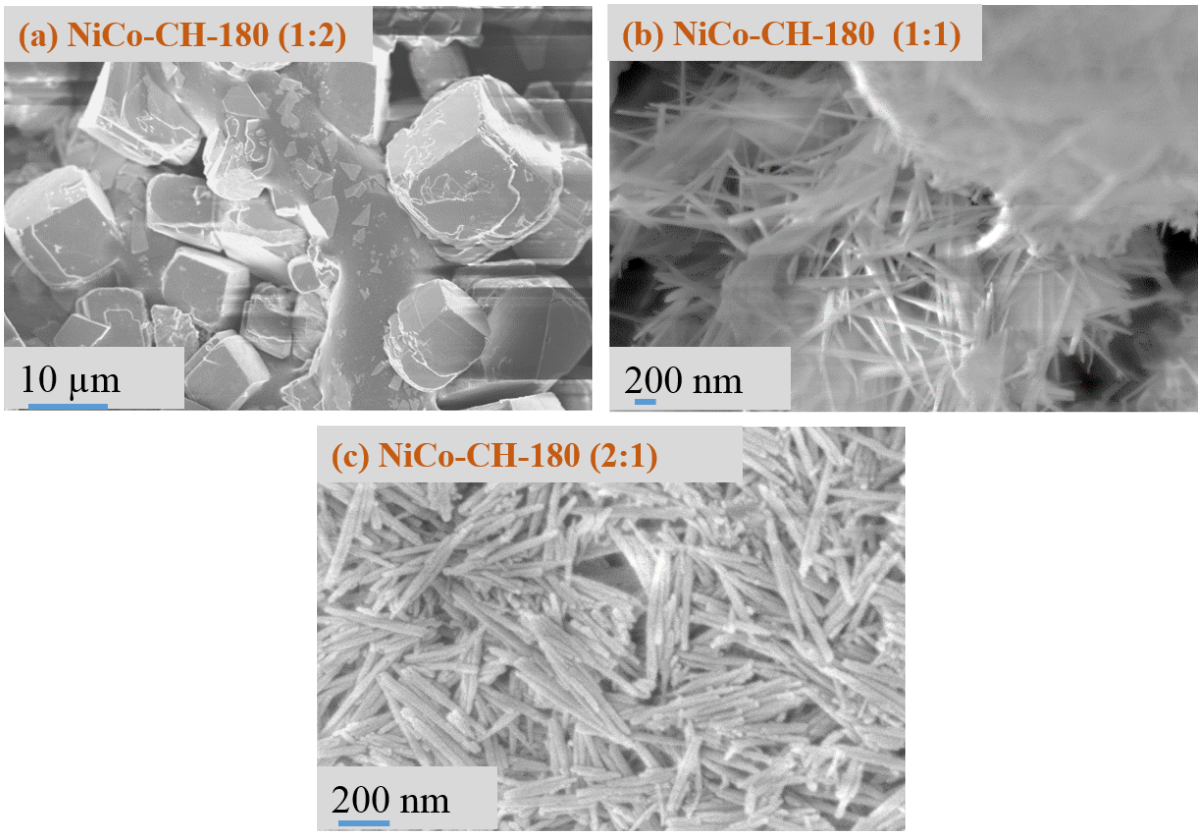

Fig. S2 FESEM images of NiCo-CHs synthesized using different Ni:Co precursor ratios, (a) NiCo-CH-180 (1:2), (b) NiCo-CH-180 (1:1), and (c) NiCo-CH-180 (2:1) with other parameters fixed (180 °C, mixed solvent of 15 mL EG + 20 mL water, and 12 h).

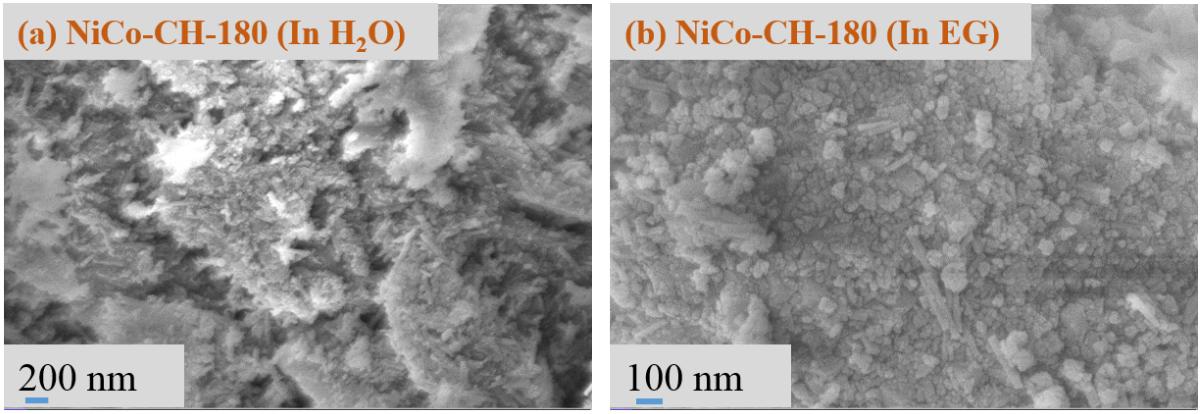

Fig. S3 FESEM image of NiCo-CH obtained using only (a) water and (b) EG as solvent with other synthesis parameters fixed (180 °C, 2:1 Ni:Co precursor, and 12 h).

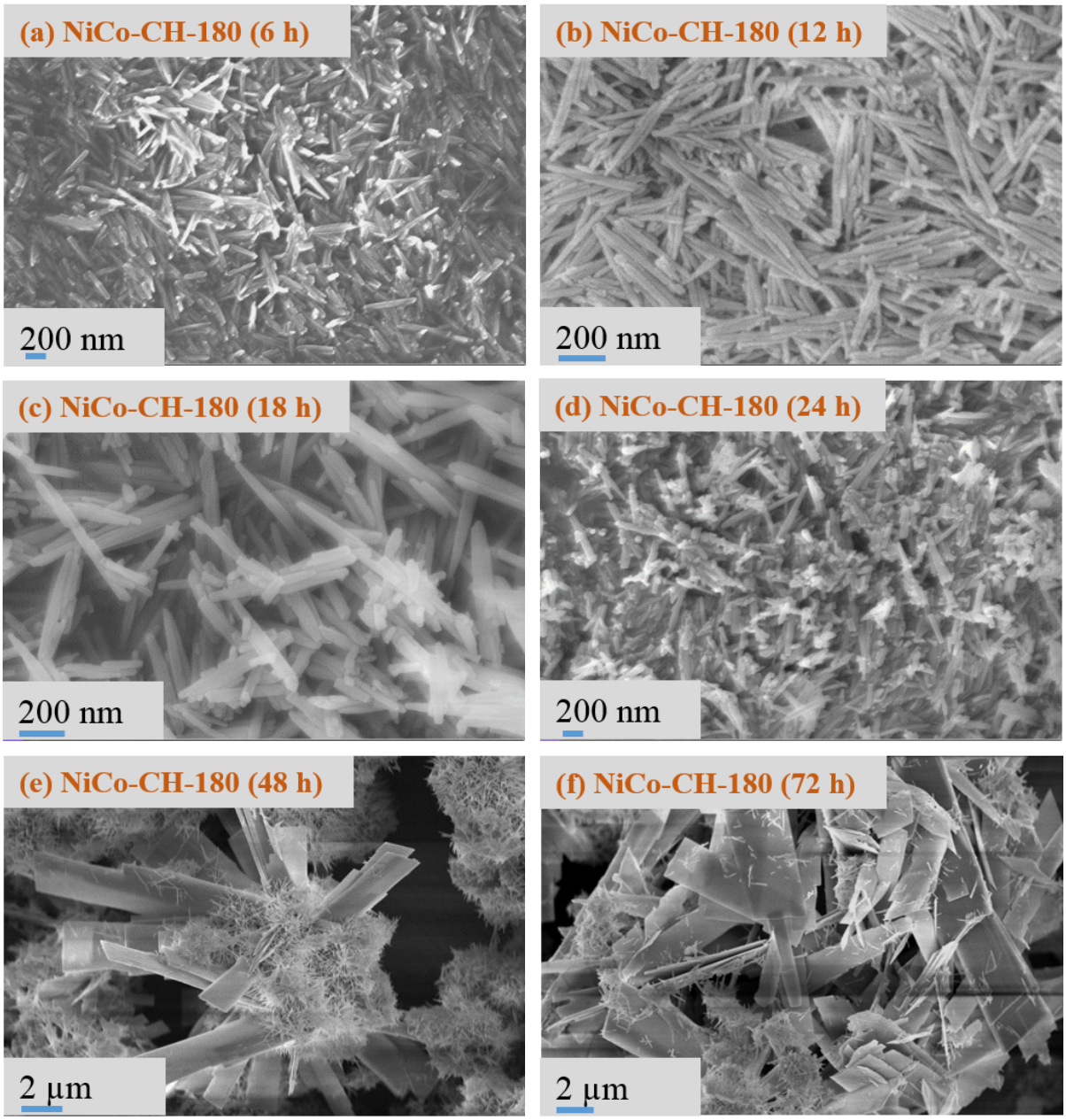

Fig. S4 FESEM images of NiCo-CH obtained by varying the solvothermal reaction durations (a) 6 h, (b) 12 h, (c) 18 h, (d) 24 h, (e) 48 h and (f) 72 h with other synthesis parameters fixed, i.e., 180 °C, 2:1 Ni:Co precursor, and mixed solvent of 15 mL EG + 20 mL water).

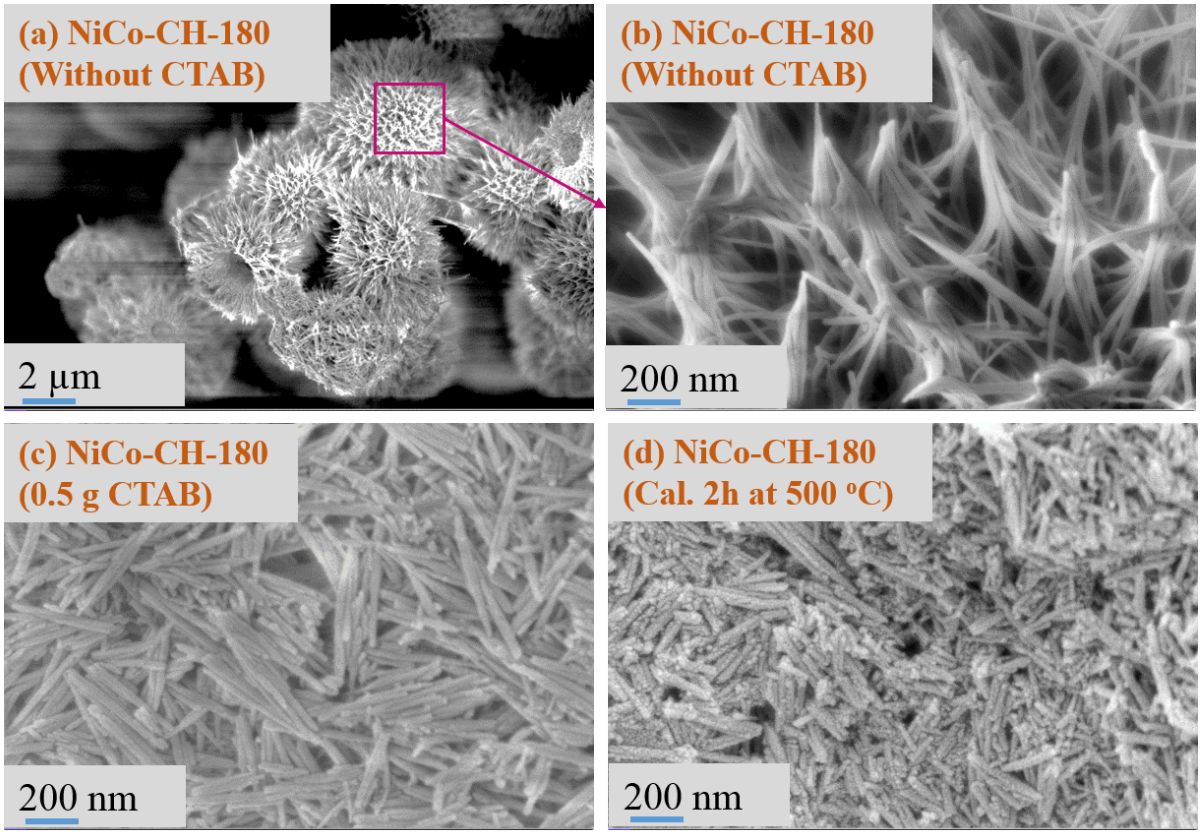

Fig. S5 FESEM images of NiCo-CH (a,b) without CTAB, (c) with 0.5 g CTAB, and oter reaction parameters fixed (i.e., 180 °C, 2:1 Ni:Co precursor, and mixed solvent of 15 mL EG + 20 mL water) and (d) NiCo-CH-180 calcined for 2 h at 500 °C.

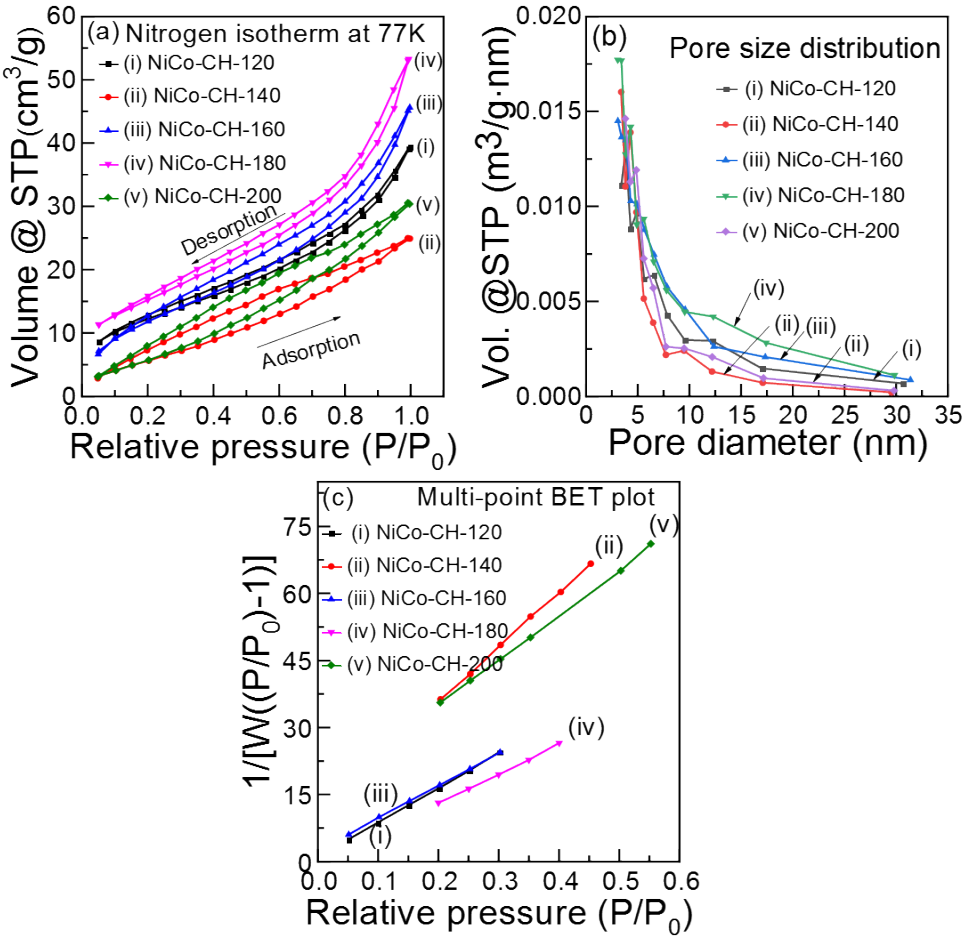

Fig. S6 (a) BET N_2 adsorption-desorption loops, (b) pore size distribution, and (c) multi-point plot of NiCo-CH-120, NiCo-CH-140, NiCo-CH-160, NiCo-CH-180, and NiCo-CH-200.

Table S2. Textural properties of NiCo-CH-120, NiCo-CH-140, NiCo-CH-160, NiCo-CH-180, and NiCo-CH-200.

Sample	*Specific surface area (m^2/g)*	*Pore volume (cc/g)*	*Pore radius (Å)*
NiCo-CH-120	43.7	0.05	16
NiCo-CH-140	26.0	0.04	15
NiCo-CH-160	46.3	0.06	15
NiCo-CH-180	52.6	0.07	17
NiCo-CH-200	30.0	0.05	15

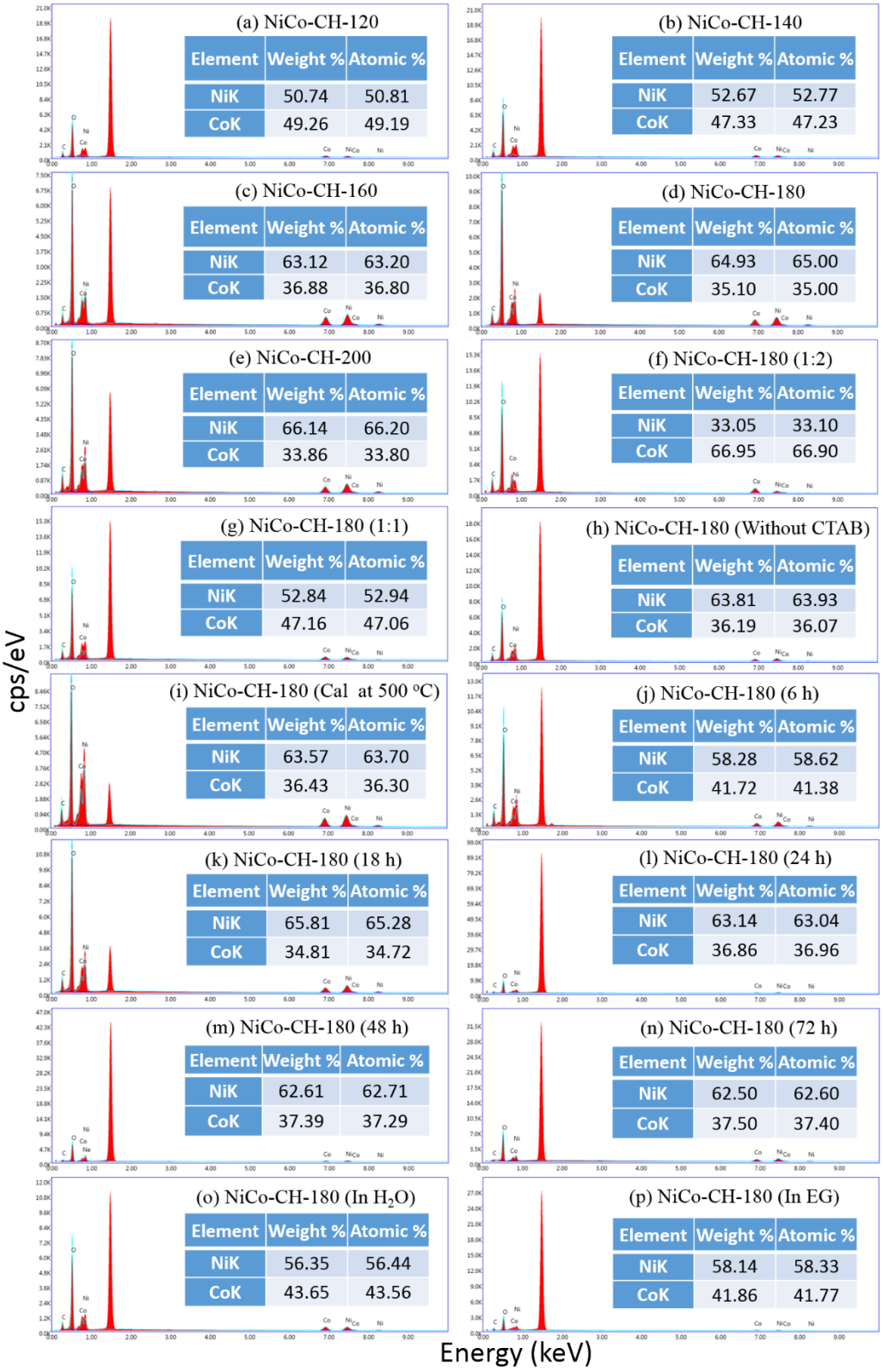

Fig. S7 EDX spectra of the synthesized NiCo-CHs samples. The inset shows the Ni and Co composition of the respective sample.

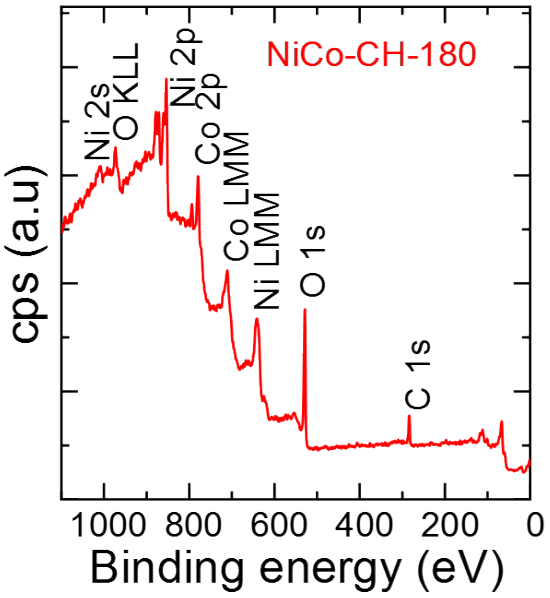

Fig. S8 XPS survey spectrum of NiCo-CH-180.

Table S3. The positions and areas of deconvoluted XPS peaks obtained from Fig. 3a and 3b for NiCo-CH-180 sample.

Species	Peak values	Peak area
Ni^{2+} $2p_{3/2}$	854.5	21037
Ni^{3+} $2p_{3/2}$	856.1	15498
Ni $2p_{3/2}$ (Sat.)	860.5	37795
Ni^{2+} $2p_{1/2}$	872.2	11099
Ni^{3+} $2p_{1/2}$	874.4	7500
Ni $2p_{1/2}$ (Sat.)	879.1	20237
Co^{3+} $2p_{3/2}$	779.7	9421
Co^{2+} $2p_{3/2}$	781.4	5332
Co $2p_{3/2}$ (Sat.)	783.9	15200
Co^{3+} $2p_{1/2}$	796	4718
Co^{2+} $2p_{1/2}$	797.7	2585
Co $2p_{1/2}$ (Sat.)	802.2	7065

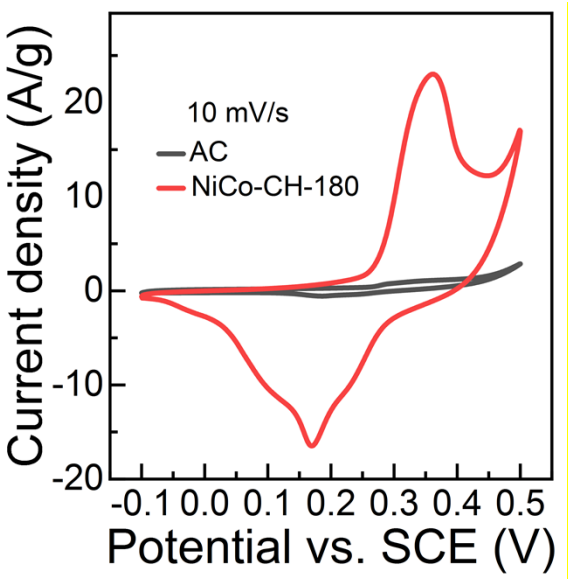

Fig. S9 CV profiles of NiCo-CH-180 and AC at 10 mV/s scan rate in the 2 M KOH electrolyte.

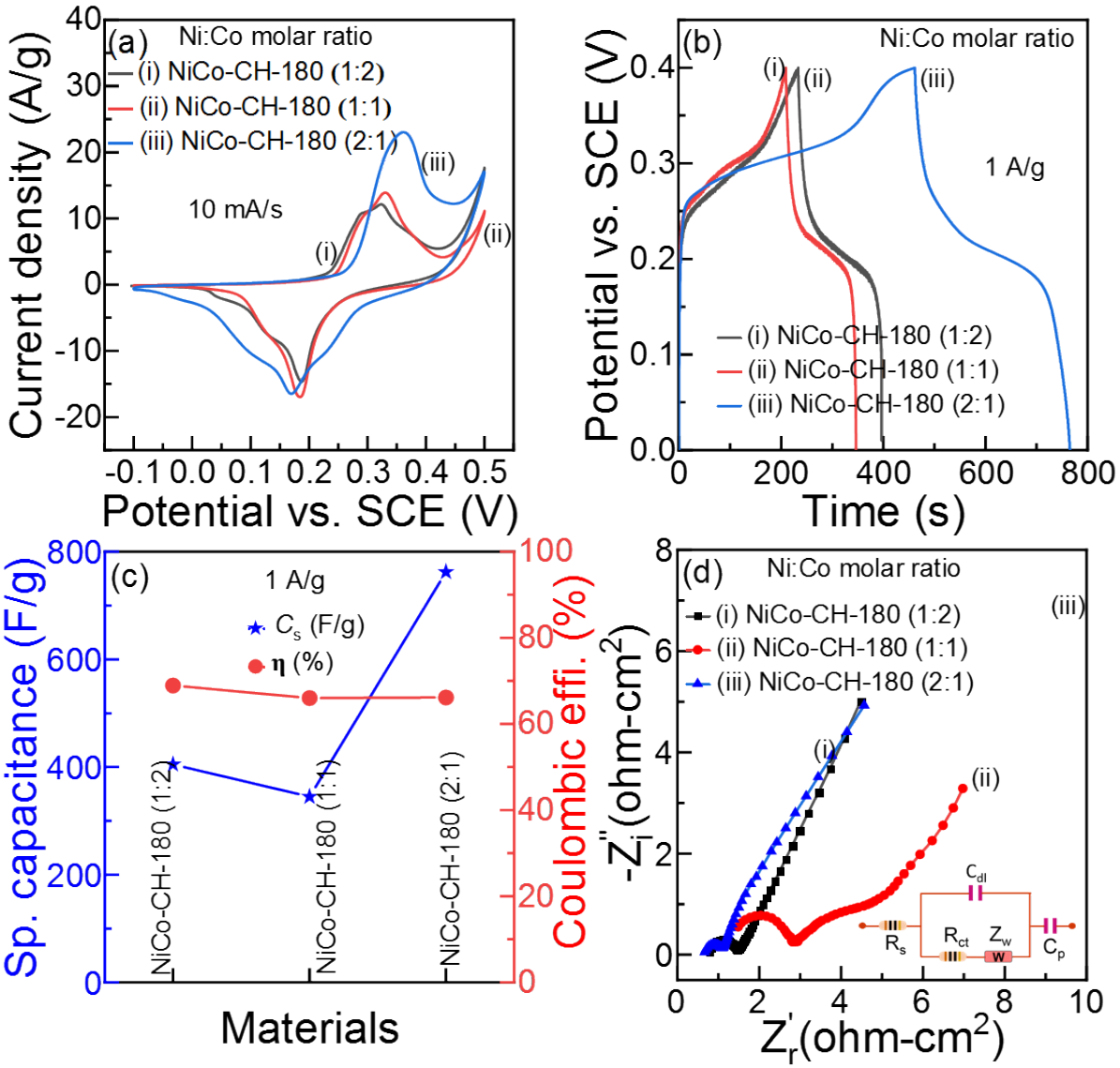

Fig. S10 Electrochemical performance characterization. (a) CV curves at 10 mV/s scan rate, (b) GCD curves at 1 A/g current density, (d) specific capacitance and coulombic efficiency at 1 A/g current density, and (c) Nyquist plots of NiCo-CH-180(1:2), NiCo-CH-180(1:1), and NiCo-CH-180(2:1). The inset in (c) shows an equivalent circuit diagram.

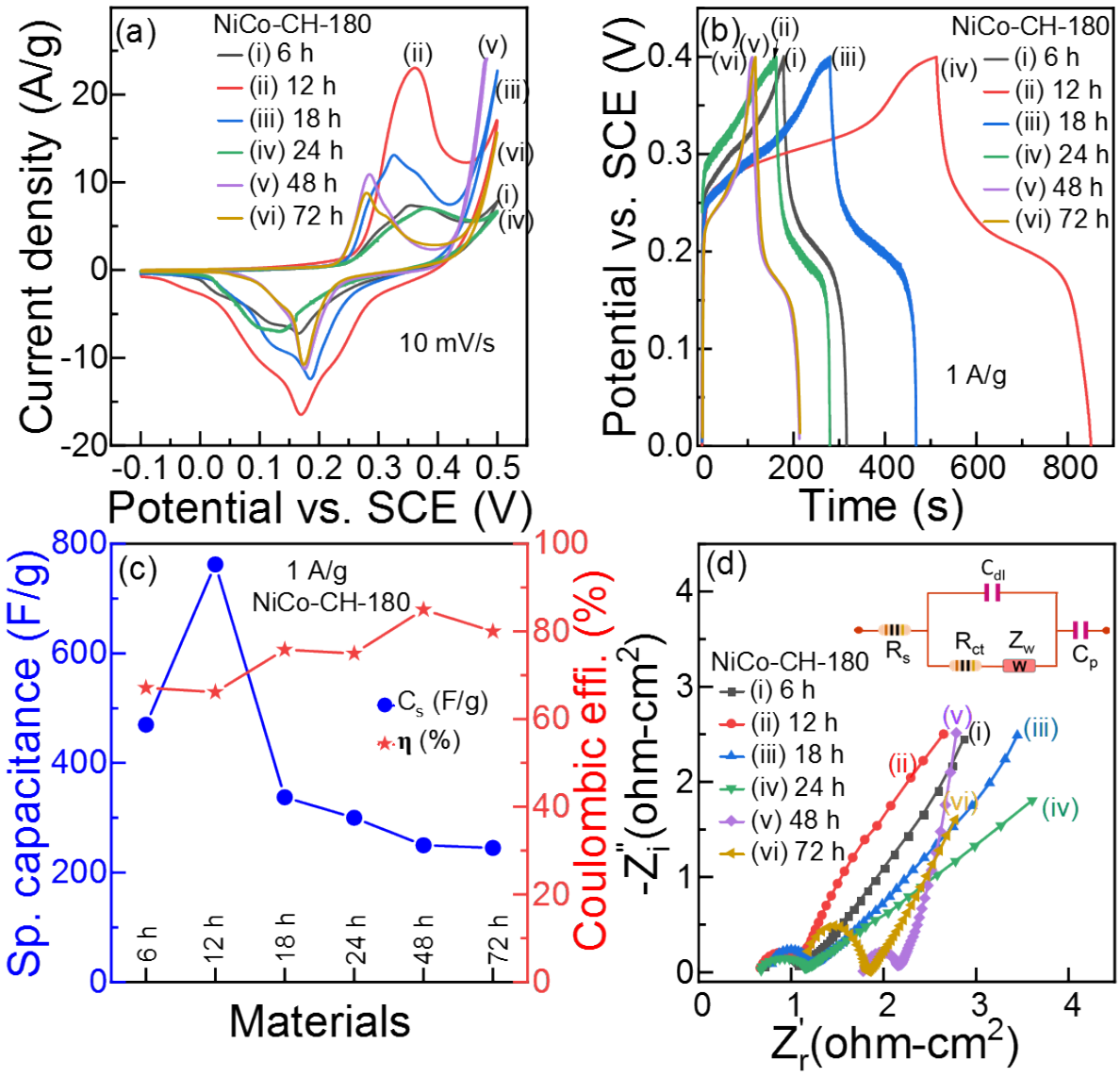

Fig. S11 Electrochemical performance characterizations. (a) CV curves at 10 mV/s scan rate, (b) GCD curves at 1 A/g current density, (c) specific capacitance and coulombic efficiency at 1 A/g current density, and (d) Nyquist plots of NiCo-CH-180 (6 h), NiCo-CH-180 (12 h), NiCo-CH-180 (18 h), NiCo-CH-180 (24 h), NiCo-CH-180 (48 h), and NiCo-CH-180 (72 h).

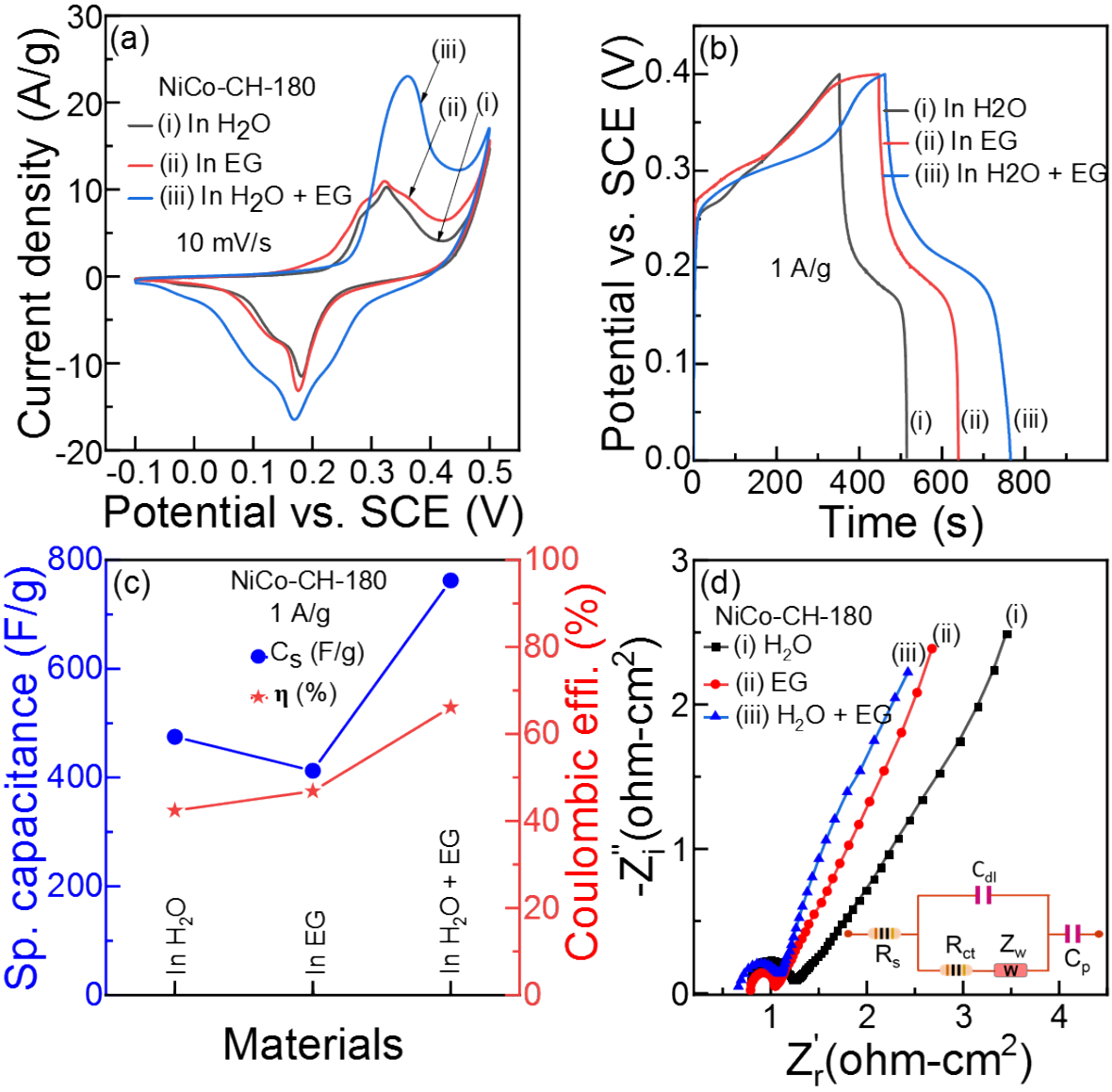

Fig. S12 Electrochemical performance characterizations (a) CV curves at 10 mV/s scan rate, (b) GCD curves at 1 A/g current density, (c) specific capacitance and coulombic efficiency at 1 A/g current density, and (d) Nyquist plots of NiCo-CH-180 (in H_2O), NiCo-CH-180 (in EG), and NiCo-CH-180 (in H_2O + EG).

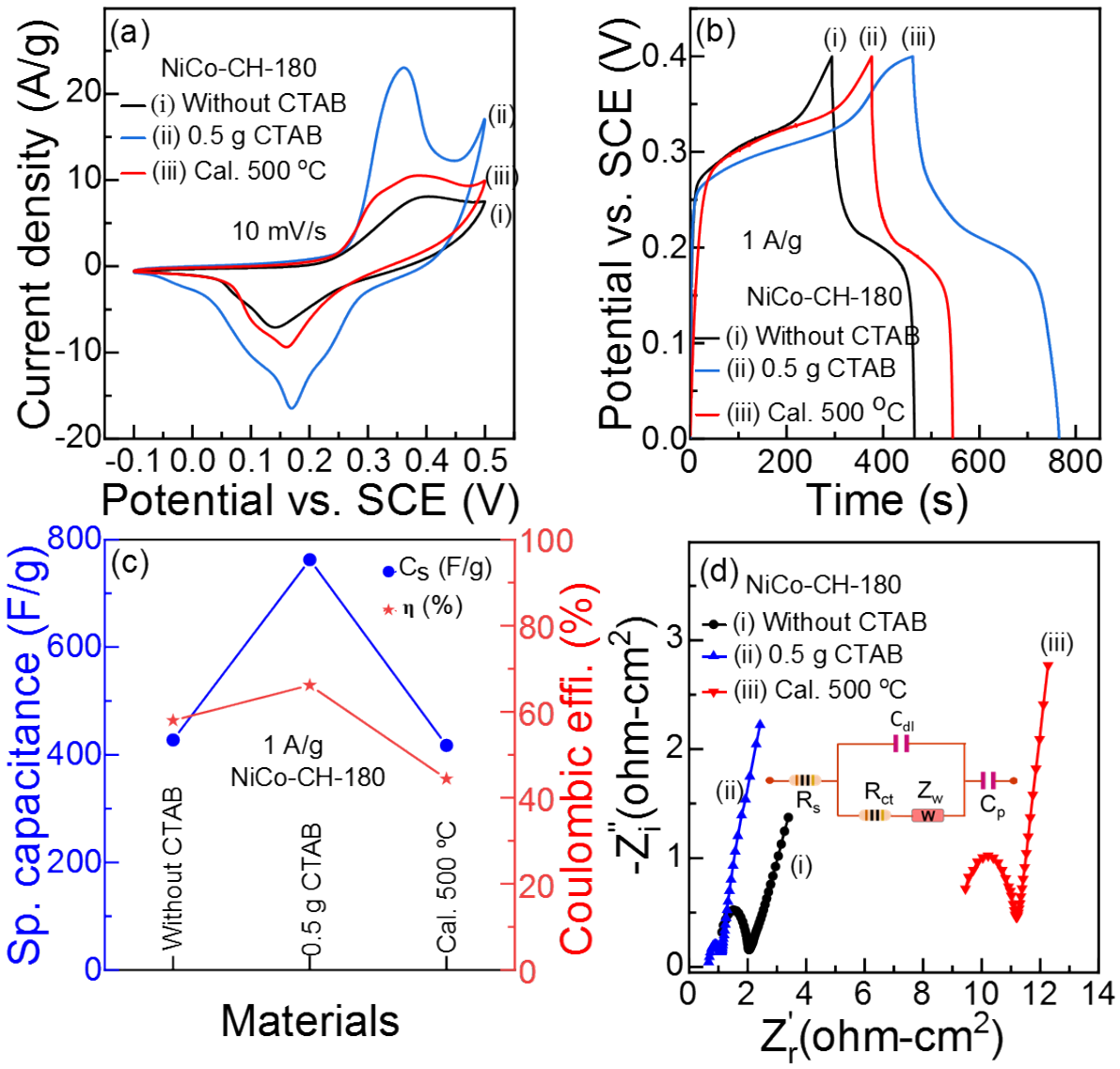

Fig. S13 Electrochemical performance characterizations (a) CV curves at 10 mV/s scan rate, (b) GCD curves at 1 A/g current density, (c) specific capacitance and coulombic efficiency at 1 A/g current density, and (d) Nyquist plots of NiCo-CH-180 (without CTAB), NiCo-CH-180 (with 0.5 g CTAB), and NiCo-CH-180 (calcined for 2 h at 500 °C).

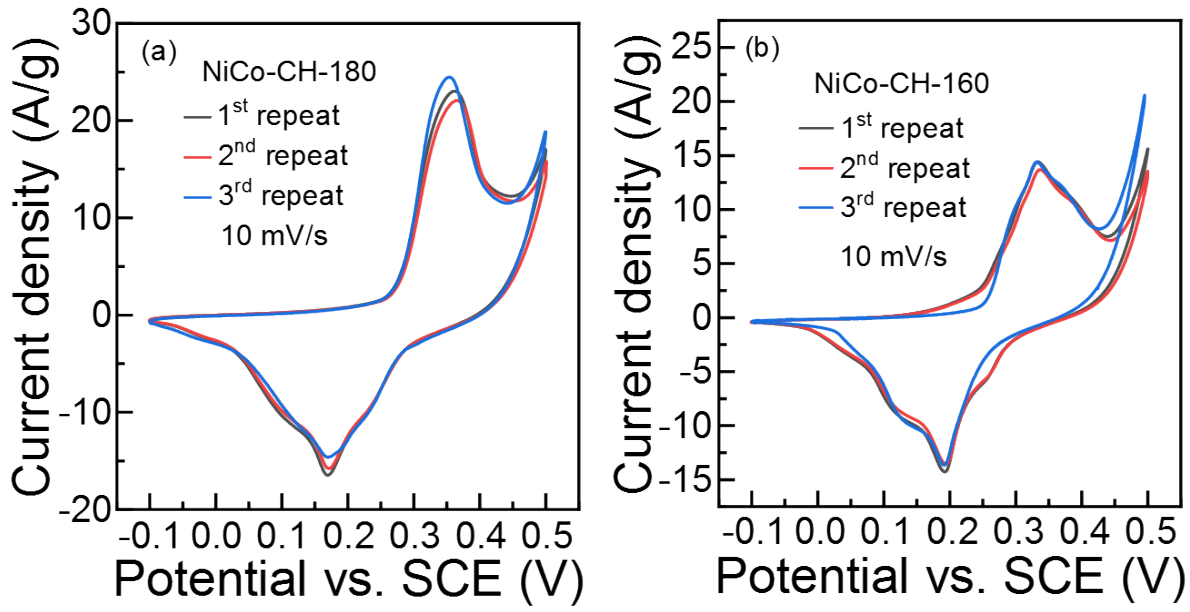

Fig. S14 CV profiles of (a) NiCo-CH-180 and (b) NiCo-CH-160 samples prepared by three sets of experiments.

Table S4. Electrochemical storage performance of the as-synthesized electrode materials.

Electrode materials	Sp. capacitance (C_s, F/g) @1 A/g	Columbic efficiency (η, %)	Solution resistance (R_s, Ω)	Charge transfer resistance (R_{ct}, Ω)	Warburg resistance (Z_w, Ω)	Morphology
NiCo-CH-120	300	70.2	0.82	0.63	0.2	Bundles of nanowires
NiCo-CH-140	302.5	72.8	0.76	0.41	0.19	Nanorods
NiCo-CH-160	545	61.5	0.68	0.4	0.08	Nanorods
NiCo-CH-180	**762.5**	**66.2**	**0.66**	**0.36**	**0.02**	**Nanorods**
NiCo-CH-200	312.5	62.5	0.93	0.65	0.053	Microplates
NiCo-CH-180 (1:2)	405	68.94	0.805	0.55	0.342	Microcubes
NiCo-CH-180 (1:1)	345	66	1.36	1.64	0.07	Nanowires
NiCo-CH-180 (Without CTAB)	427.5	57.96	0.71	0.45	0.018	Microflowers or urchins
NiCo-CH-180 (Cal. at 500 °C)	417.5	44.4	9.4	1.8	0.012	Nanorods
NiCo-CH-180 (6 h)	470	67.2	0.7	0.42	0.173	Nanorods
NiCo-CH-180 (18 h)	337.5	75.8	0.78	0.52	0.13	Nanorods
NiCo-CH-180 (24 h)	300	75	0.71	0.5	0.2	Agglomerated nanorods
NiCo-CH-180 (48 h)	250	80	1.76	0.54	0.4	Nanorods and microplates
NiCo-CH-180 (72 h)	245	82	1.25	0.65	0.42	Nanorods and microplates
NiCo-CH-180 (In H_2O)	475	42.4	0.76	0.48	0.25	Nanoparticles with nanorods
NiCo-CH-180 (In EG)	412.5	46.9	0.84	0.37	0.51	Nanoparticles

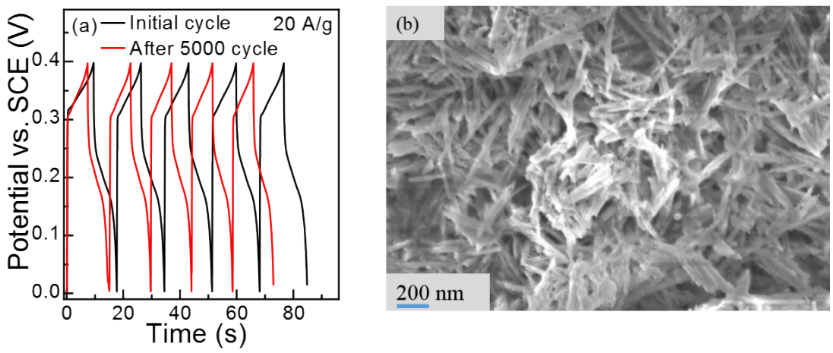

Fig. S15 (a) Initial and after 5000 GCD cycles at 20 A/g current density for NiCo-CH-180 and (b) FESEM image of NiCo-CH-180 electrode material after 5000 GCD cycles of electrochemical stability test.

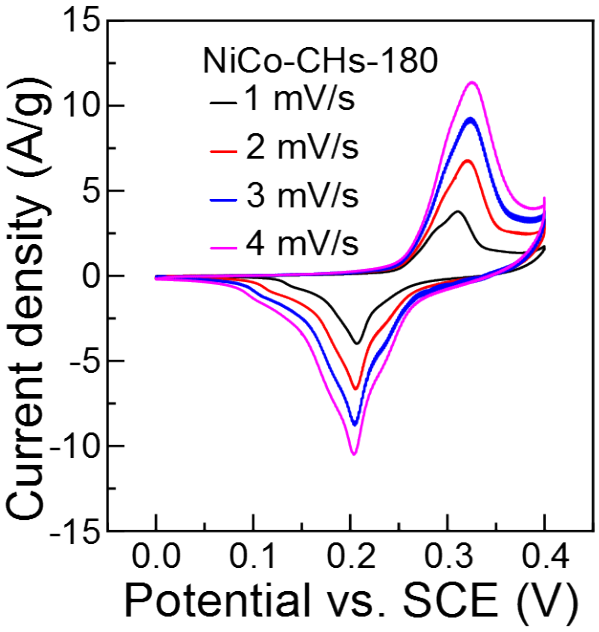

Fig. S16 Cyclic voltammograms (CV) of NiCo-CH-180 at 1 to 4 mV/s scan rate.

Table S5. Electrochemical performances of the NiCo-CH-180//AC ASC device.

Current density (i, A/g)	Specific capacitance (C_s, F/g)	Coulombic efficiency (η, %)	Energy density (ED, Wh/kg)	Power density (PD, kW/kg)
2	166	80	52	1.5
3	142	91	44.4	2.25
4	120	90	37.5	3
5	106	91	33.3	3.75
10	60	90	18.7	7.5