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Supporting Information

Hierarchical $NiCo_2O_4$ Nanosheets/Nitrogen Doped Graphene/Carbon Nanotube Film with Ultrahigh Capacitance and Long Cycle Stability as Flexible Binder-free Electrode for Supercapacitor

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Experimental Section

Synthesis of GO and modified Multiwalled carbon nanotube

The GO was prepared by a previous modified Hummers' method[1, 2] but with a slight modification from flake graphite. The products of GO was further dispersed to form homogeneous GO aqueous solution (2 mg mL^{-1}), after a vigorous ultrasonication，then 50 mL GO solution was stirring with a slowly adding of potassium permanganate (1.2 g) at room temperature in order to activate GO and continuous stirred 48 h. Subsequently the hydrochloric acid (30 mL, 36%) was added to the mixture and keeping the reaction for 24 h，then added hydrogen peroxide (30 mL, 30%) with agitation for a another 24 h. Finally it was purified by a further step of dialysis to remove the excess acid and the remaining salt, the activated GO (1mg mL^{-1}) was obtaind for the following experiments. Multiwalled carbon nanotube (95 % purity, 10-20 nm average diameter size, 100-160 g m^{-2}, ShenZhen Nanoport, LTD) was modified to ensure water solubility through a 70 °C hot hydrothermal bath in 3M Nitric acid treating for 2 hours, the MWCNTs solution was got after purification and dispersion (1 mg mL^{-1}).

Synthesis of NGN/CNTs flexible film:

The sodium dodecyl sulfate (SDS, 5 mg) was added into MWCNTs aqueous (1.5 mL) with ultrasonication for 15 minutes, then GO solution (20 mL) was mixed with MWCNTs solution for another 15 minutes ultrasonication. The mass ratio of GO:CNTs was 13.3:1. To prepare the NGN/CNTs film, the homogeneous mixture solution was filtered using a mixed cellulose ester filter membrane (0.22 um pore size) by vacuum suction. Once the filtration was completed, the filter membrane was transferred into a petridish, the thick film was peeled off carefully from the filter membrane after freeze drying, then the film was transferred into 80 mL Teflon-lined autoclave with ammonium hydroxide and kept in 180 °C for 24 hours. The NGN/CNTs film was obtained. Moreover，the NGN film was obtained by the same way without MWCNTs.

Synthesis of mesoporous $NiCo_2O_4$ nanosheets supported on NGN/CNTs flexible film

In a typical process, 0.4 mmol $NiCl_2·6H_2O$, 0.8 mmol $CoCl_2·6H_2O$ and 30 mmol urea were successively added into a mixture of 5 mL deionized water and 30 mL methanol with vigorous stirring forming homogeneous solution. Then the solution was transferred into a 40 mL Teflon-lined autoclave, a piece of the film was immersed, following kept at 120 °C for 6h. After cooled down , the product was taken out and washed with deionized water and absolute ethanol several times, then dried at 60 °C overnight, the obtained sample was marked as NiCo-precursor/NGN/CNT. In order to get the $NiCo_2O_4$/NGN/CNTs flexible film, the NiCo-precursor/NGN/CNTs flexible film was annealed at 300 °C for 2 h with a heating rate of 1 °C min^{-1} .For comparison, the flower-like $NiCo_2O_4$ powders was synthesized in the same method without the adding of NGN/CNTs film.

The carbon fibers was successively cleaned by ultrasonication in 5 M HCl aqueous solution, deionized water and absolute ethanol in sequence for 15 min, respectively. The Ni foam was washed with 2 M HCl to remove the possible surface oxide layer, and subsequently cleaned with ethanol and deionized water. The samples of $NiCo_2O_4$ NGN film, $NiCo_2O_4$\carbon fiber and $NiCo_2O_4$\Ni foam were synthesized under the same conditions.

Material Characterization

The crystal structures were measured through X-ray diffraction (XRD) by a Bruker D8 Advanced X-ray diffractometer with Cu Kα radiation (0.15406 nm). Raman spectra were measured on a HORIBA Scientific LabRAM HR Raman spectrometer system using a 532.4 nm laser. X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI 550 spectrometer with Al-K_α (1486.6 eV) as the X-ray source. Scanning electron microscopy (FE-SEM, Hitachi S4800) and transmission electron microscopy (TEM, JEOL JEM-2100) were used to investigate the micro/nanoscale structure of the samples.

Electrochemical measurement

All electrochemical measurements were carried out using a two electrode or three electrode system in 6 M KOH electrolyte at room temperature. The as-prepared $NiCo_2O_4$/NGO/CNTs (1 cm ×1 cm) was served as the working electrode, a platinum foil and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode respectively in a three electrode system. The $NiCo_2O_4$/NGO/CNTs and NGO/CNTs were directly served respectively as the flexible cathode and anode electrodes for asymmetric supercapacitors. The cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were carried out with a CHI 660B electrochemical working station.

In the three-electrode system, the specific gravimetric capacitance(C_g, F g^{-1}) of the electrodes can be calculated by the following equation:

$$C_g = \frac{I\Delta t}{m\Delta V} \qquad (1)$$

Where C_g (F g^{-1}) is the gravimetric capacitance, I (A) is the discharge current, Δt (s) refers to the time for a full discharge, m (g) represents the mass of active material (or the total electrode), and ΔV (V)is the potential change after a full discharge.

The specific volumetric capacitance (C_{vc}, F cm^{-3}) of the electrodes can be calculated *via* the following equation:

$$C_v = \frac{I\Delta t}{Vol\,\Delta V} \qquad (2)$$

Where C_v (F cm^{-3}) is the volumetric capacitance, I (A) is the discharge current, Δt (s) refers to the time for a full discharge, *Vol* represents the volume of the whole electrode materials, and ΔV (V) is the whole potential window during the discharge process.

The asymmetric supercapacitor (ASC) was fabricated and measured in a two-electrode system. The specific gravimetric capacitance (C_{gc}, F g^{-1}) and volumetric capacitance (C_{vc}, F cm^{-3}) of the ASC was calculated based on the following equation:

$$C_{gc} = \frac{I\Delta t}{M\Delta V} \qquad (3)$$

$$C_{vc} = \frac{I\Delta t}{VOL\,\Delta V} \qquad (4)$$

Where C_{gc} (F g^{-1}) is the gravimetric capacitance, C_{gv} (F cm^{-3}) is the volumetric capacitance, I (A) is the discharge current, Δt (s) refers to the time for a full discharge, M (g) represents the total mass of active material (or the whole mass) in two electrode, *VOL* (cm^{-3}) represents the total volume of two electrodes, and ΔV (V) is the potential window of the ASC.

The energy density E (E_g, E_v; W h kg^{-1}, W h L^{-1}) and power density P (W kg^{-1}, W L^{-1}) of the device could be calculated as follow equation:

$$E_g(Wh\,kg^{-1}) = \frac{1000\,C_{gc}V^2}{2 \times 3.6} \qquad (5)$$

$$E_V(Wh\,L^{-1}) = \frac{1000\,C_{vc}V^2}{2 \times 3.6} \qquad (6)$$

$$P(W\,kg^{-1}\,or\,W\,L^{-1}) = \frac{3600E}{\Delta t} \qquad (7)$$

Where V (V) is the potential of the ASC, Δt (s) is the corresponding discharging time.

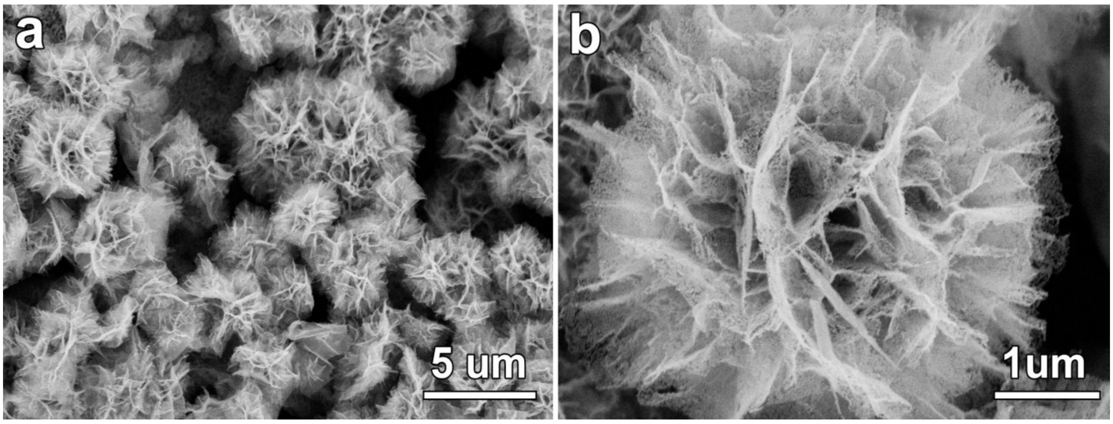

Fig. S1 SEM images of $NiCo_2O_4$ powder.

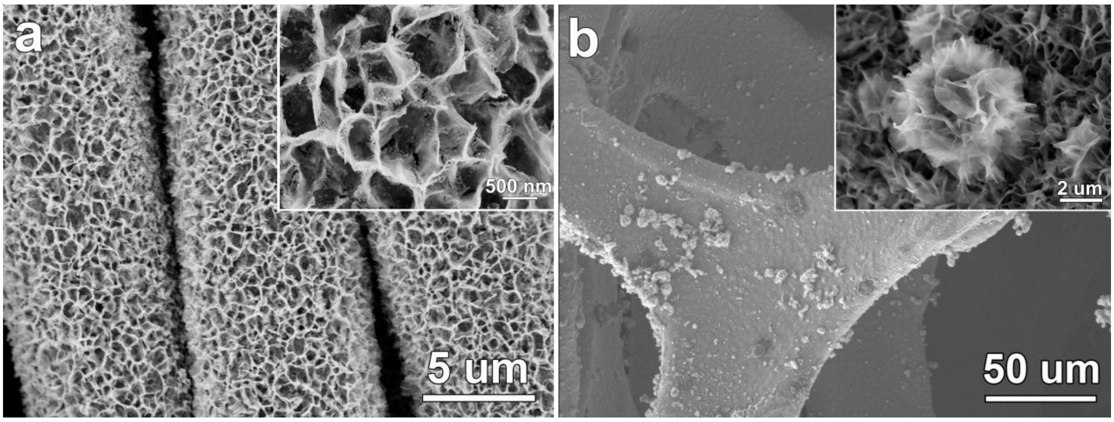

Fig. S2 SEM images of (a) $NiCo_2O_4$/carbon fiber, (b) $NiCo_2O_4$/Ni foam.

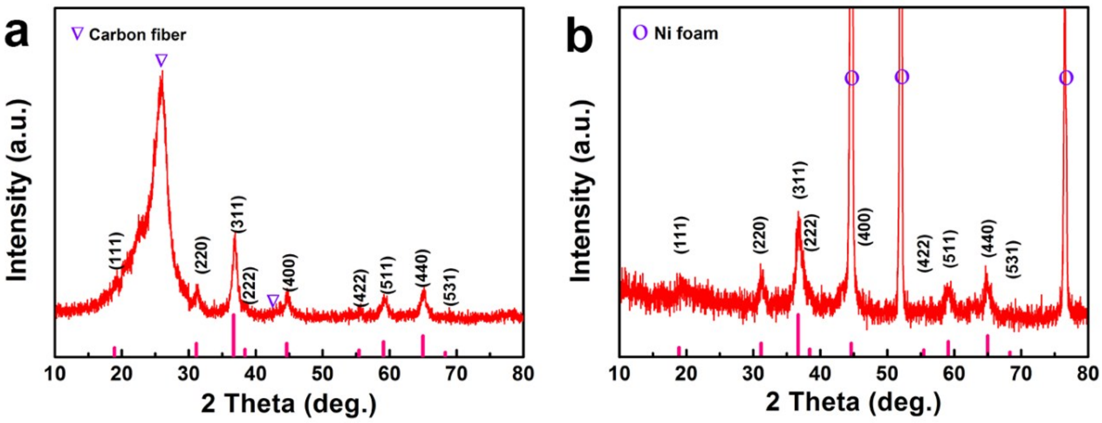

Fig. S3 XRD patterns of (a) $NiCo_2O_4$/carbon fiber and (b) $NiCo_2O_4$/Ni foam.

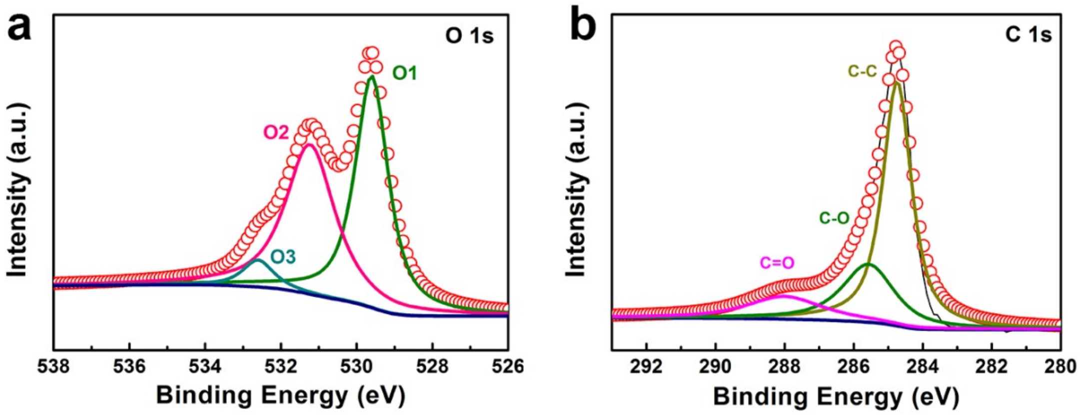

Fig. S4 XPS results of (a) O 1s, (b) C 1s for $NiCo_2O_4$/NGN/CNTs:

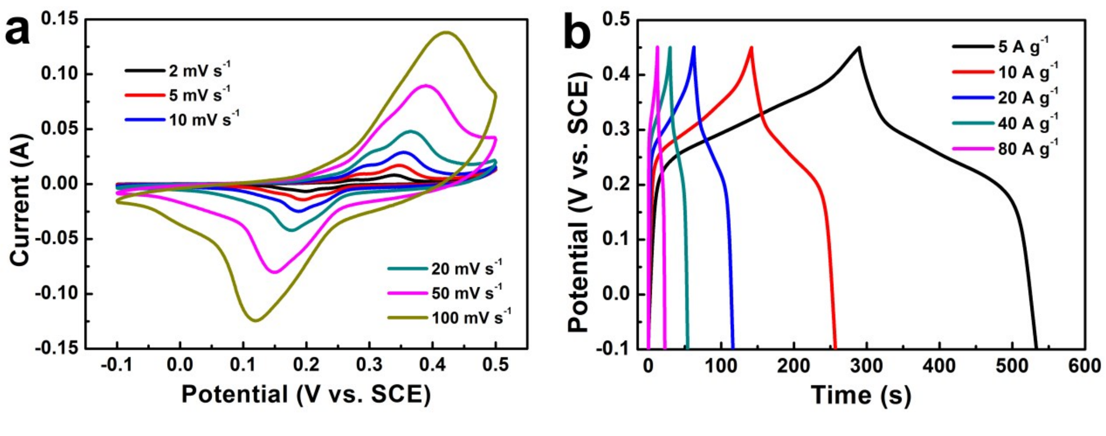

Fig. S5 (a) CV and (b) GCD curves of $NiCo_2O_4$ /NGN.

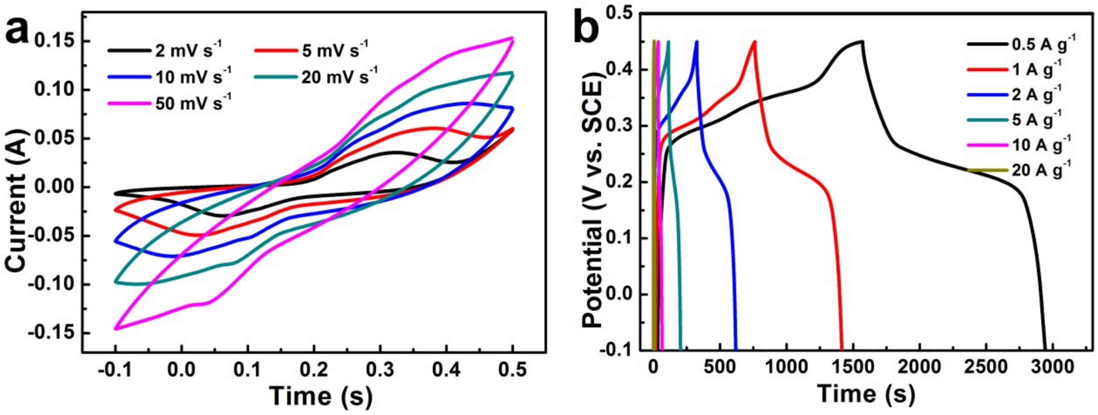

Fig. S6 (a) CV and (b) GCD curves of of $NiCo_2O_4$ powder.

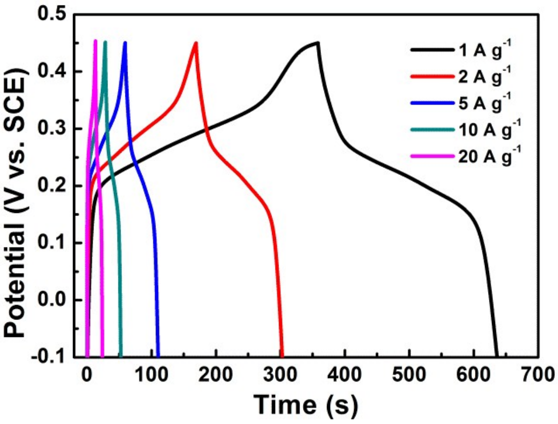

Fig. S7 GCD of $NiCo_2O_4$ /NGN/CNTs based on the total mass of electrode.

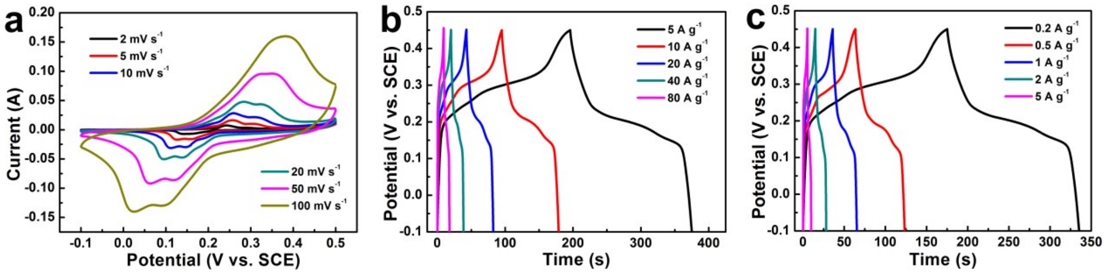

Fig. S8 $NiCo_2O_4$/carbon fiber: (a) CV, (b) GCD based on the active materials of electrode and (c) GCD based on the total mass of electrode.

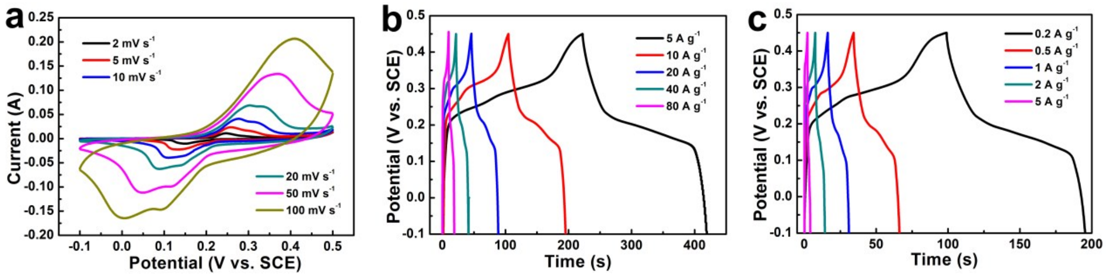

Fig. S9 $NiCo_2O_4$/Ni foam: (a) CV, (b) GCD based on the active materials of electrode and (c) GCD based on the total mass of electrode.

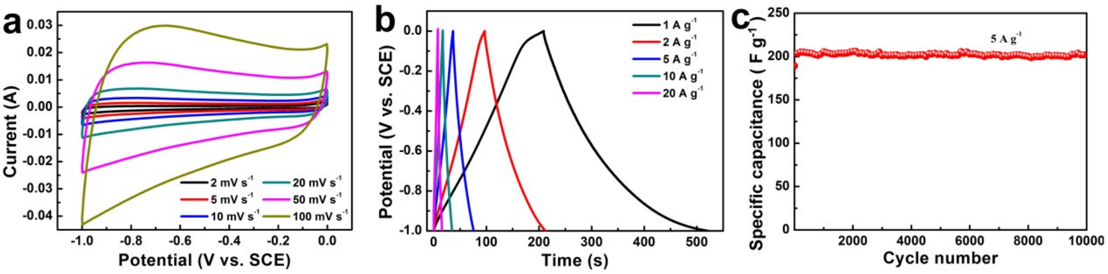

Fig. S10 (a) CV, (b) GCD and (c) Cycle stability of NGN/CNTs film

Table S1. Comparision of electrochemical performance of our work with recently representative works of Ni-based materials and some other available pseudocapacitive materials.

Reference	Type of materials	Gravimetric capacitance	Volumetric capacitance	Rate capability	Cycling stability
This work	$NiCo_2O_4$/NGN/CNTs	2292.7 F g^{-1} (5 A g^{-1})	482.7 F cm^{-3} (2 mA)	73.5% (5 to 80 A g^{-1})	120% (10000 cycles)
This work	$NiCo_2O_4$/carbon fiber	1629.1 F g^{-1} (5 A g^{-1})	24.0 F cm^{-3} (2.5 mA)	76.7% (5 to 80 A g^{-1})	--
This work	$NiCo_2O_4$/Ni foam	1804.6 F g^{-1} (5 A g^{-1})	100.3 F cm^{-3} (3 mA)	73.4% (5 to 80 A g^{-1})	--
3	$NiCo_2O_4$/Ni Fiber	336 F g^{-1} (2.5 mA)	29.7 F cm^{-3} (2.5 mA)	95.5% (2.5 to 20 mA)	80% (5000 cycles)
4	$NiCo_2O_4$ nanosheets/Ni wires	--	10.3 F cm^{-3} (0.08 mA)	--	78% (5000 cycles)
5	Network-like mesoporous $NiCo_2O_4$/carbon cloth	1843.3 F g^{-1} (1 A g^{-1})	33.75 F cm^{-3} (0.33 mA)	80% (1 to 32 A g^{-1})	10% (4000 cycles)
6	$NiCo_2O_4$–rGO composite	1222 F g^{-1} (0.5 A g^{-1})	--	62.8% (0.5-40 A g^{-1})	91.6% (3000 cycles)
7	CNT@$NiCo_2O_4$	1038 F g^{-1} (0.5 A g^{-1})	--	64% (0.5-10 A g^{-1})	100% (1000 cycles)
8	$NiCo_2O_4$ NS/3DGN	2173 F g^{-1} (6 A g^{-1})	--	58.2% (6 to 80 A g^{-1})	94% (14000 cycles)
9	HP-CF@$NiCo_2S_4$	599.2 F g^{-1} (2 mV s^{-1})	--	71.2% (2-20 mV s^{-1})	--
10	$NiCo_2O_4$ nanograss/Ni foam	807.7 F g^{-1} (1mA cm^{-2})	--	74% (1 to 30 mA cm^{-2})	--
11	$NiCo_2O_4$@MnO_2	913.6 F g^{-1} (0.5 A g^{-1})	--	55.2% (0.5 to 20 A g^{-1})	81.1% (3000 cycles)
12	$NiCo_2O_4$ nanosheets/ Ni foam	2330 F g^{-1} (4.5 A g^{-1})	--	39% (1.8-48.6 mA cm^{-2})	82% (3000 cycles)
13	$NiCo_2O_4$ nanoneedle	1118 F g^{-1} (6 A g^{-1})	--	18.9% (3.12-22.24 mA cm^{-2})	89% (2000 cycles)
14	$NiCo_2O_4$ Nanowire Arrays/Carbon Textiles	1102 F g^{-1} (8 A g^{-1})	--	79% (1-20 A g^{-1})	100% (5000 cycles)
15	m-WO_{3-x}/Carbon Nanocomposites	103 F g^{-1} (1 mV s^{-1})	340 F cm^{-3} (1 mV s^{-1})	--	92.3% (2000 cycles)
16	MoO_{3-x} nanobelt/CNTs	337 F g^{-1} (0.5 A g^{-1})	291 F cm^{-3} (0.5A g^{-1})	63.6% (0.5-10 A g^{-1})	--
17	Graphene foam/MnO_2	395 F g^{-1} (1 A g^{-1})	230 F cm^{-3}	--	80.4% (5000 cycles)

Table S2. Comparison of electrochemical performance of reported ASC device.

Reference	Type of SCs	C_{gv}, C_{vc}	E_{gmax}	E_{vmax}	Cycling stability
This work	$NiCo_2O_4$/NGN/CNTs // NGN/CNTs	77.6 F cm^{-3} (2.8 mA)	42.71 W h kg^{-1} (775 W kg^{-1})	25.90 W h L^{-1} (469.9 W L^{-1})	86% (10000 cycles)
5	NWM $NiCo_2O_4$ carbon cloth based SCs	5 F cm^{-3}	38.3 W h kg^{-1}	--	89% (4000 cycles)
18	$NiCo_2O_4$/graphene//HF AC	113 F g^{-1} (0.5 A g^{-1})	48 W h kg^{-1} (250 W kg^{-1})	76.3 W h L^{-1}	98% (5000 cycles)
6	NiCo2O4–rGO/AC	99.4 F g^{-1} (0.5 A g^{-1})	23.3 W h kg^{-1} (324.9 W kg^{-1})		83% (2500 cycles)
19	GNiF//GTF	44.8 F g^{-1} 58.5 F cm^{-3} (1 A g^{-1})	18 W h kg^{-1} (850 W kg^{-1})	23.5 W h L^{-1}	--
20	$NiCo_2S_4$ NS/NCF// OMC/NCF	128 F g^{-1} (5 mV s^{-1})	45.5 W h kg^{-1} (512 W kg^{-1})	--	70.4% (10000 cycles)
11	$NiCo_2O_4$@MnO_2//AC	120.9 F g^{-1} (0.25 A g^{-1})	37.8 W h kg^{-1} 187.5 W kg^{-1}	--	1.62% (3000 cycles)
21	$NiCo_2O_4$@NiO//AC	73.1 F g^{-1} (1 A g^{-1})	31.5 W h kg^{-1} 215.2 W kg^{-1}	--	89% (3000 cycles)
22	Ni-Co oxide//AC	288 F g^{-1} (0.5 A g^{-1})	19.5 W h kg^{-1} 150 W kg^{-1}	--	102% (1000 cycles)

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