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Electronic Supplementary Information (ESI)

Micro-Engineering the Grain Boundary of $NiCo_2O_4/NiCo_2S_4$ Nanowire Arrays to Achieve the Enhanced Charge Storage

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Physical characterization

Crystal structure of as-prepared samples was studied on a Shimadzu XD-3A diffractometer where XRD patterns were recorded at 10 ° min^{-1} using Cu- Kα radiation with λ=0.15418 nm. Their microstructure was investigated on a Carl Zeiss scanning electron microscope and a JEOL (JEM-2000 FX) transmission electron microscope.

High angle annular dark field scanning transmission electron microscopy (STEM) images of the catalysts were taken using the same JEOL instrument operating at 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI-5702 spectrometer and C1 s peak at 285.0 eV was used as a reference for binding energies calibration.

Electrochemical measurements

Electrochemical performance of as-prepared $NiCo_2O_4/NiCo_2S_4$ was studied using a CHI 660E electrochemical workstation. The experiments were carried out in a three-electrode configuration with a 1×1 cm^2 sample, activated carbon (AC) and Hg/HgO (1.0 M KOH) serving as a working electrode, a counter electrode and a reference electrode respectively. Cyclic voltammetry (CV) graphs were recorded in a three- and a two-electrode systems in 1 M KOH aqueous electrolytes. Galvanostatic charge/discharge (GCD) and cycling tests were conducted using a LAND CT2001A battery measurement system. Areal specific capacity (C_a), energy density (E) and power density (P) were calculated according to the following equations:

$$C_a = 2I \times \int V\, dt / (A \times V) \quad (1)$$

$$E = C_m \times (\Delta V)^2 / 2 \quad (2)$$

$$P = E / \Delta t \quad (3)$$

where I, t, m, ΔV, and A represent discharge current (mA), discharge time (s), total mass of active materials (g), electrode potential window (V), and electrode surface area (cm^2) respectively.

Prior to assembly of the asymmetric supercapacitor, mass loadings of both cathode

and anode were balanced according to the following equation:

$$m^{+}/m^{-} = C^{-} \times \Delta E^{-} / (C^{+} \times \Delta E^{+}) \qquad (4)$$

where mass ratio of cathode to anode particles was set at 0.3.

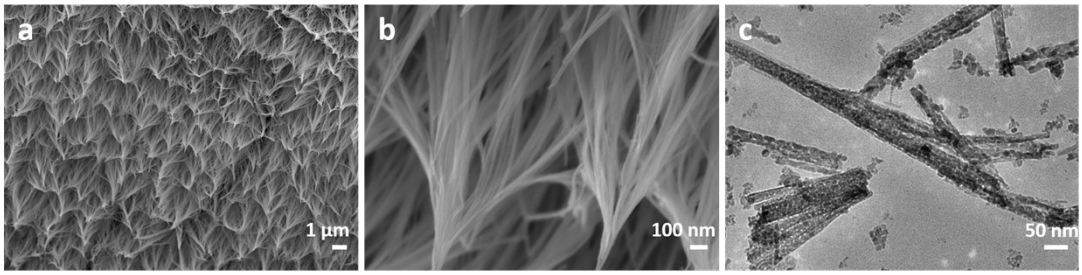

Fig. S1 (a, b) SEM and (c) TEM of $NiCo_2O_4$ rods.

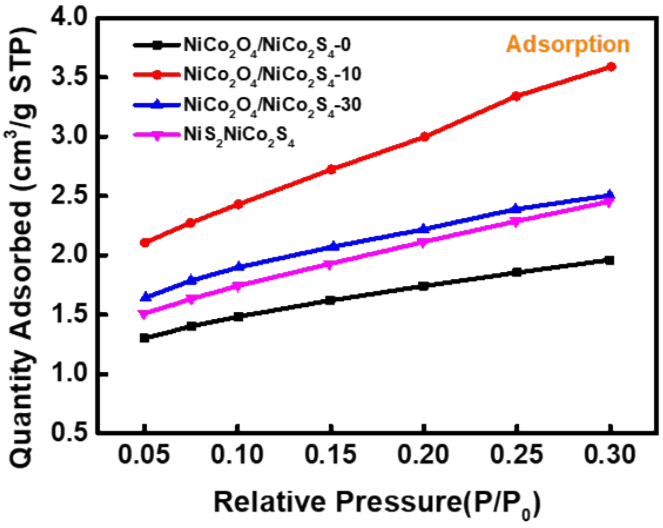

Fig. S2 N_2 isotherms of all samples.

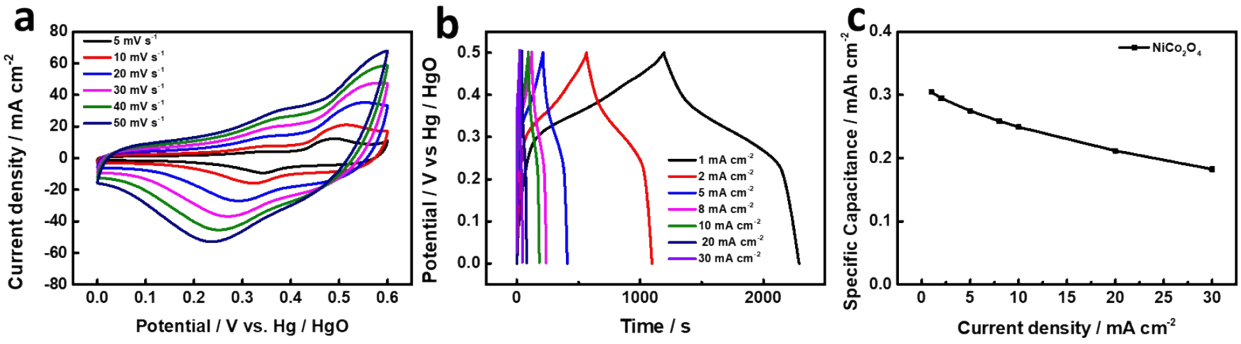

Fig. S3 CV(a), GCD(b) and area specific capacitance vs. current density curves(c) of $NiCo_2O_4$.

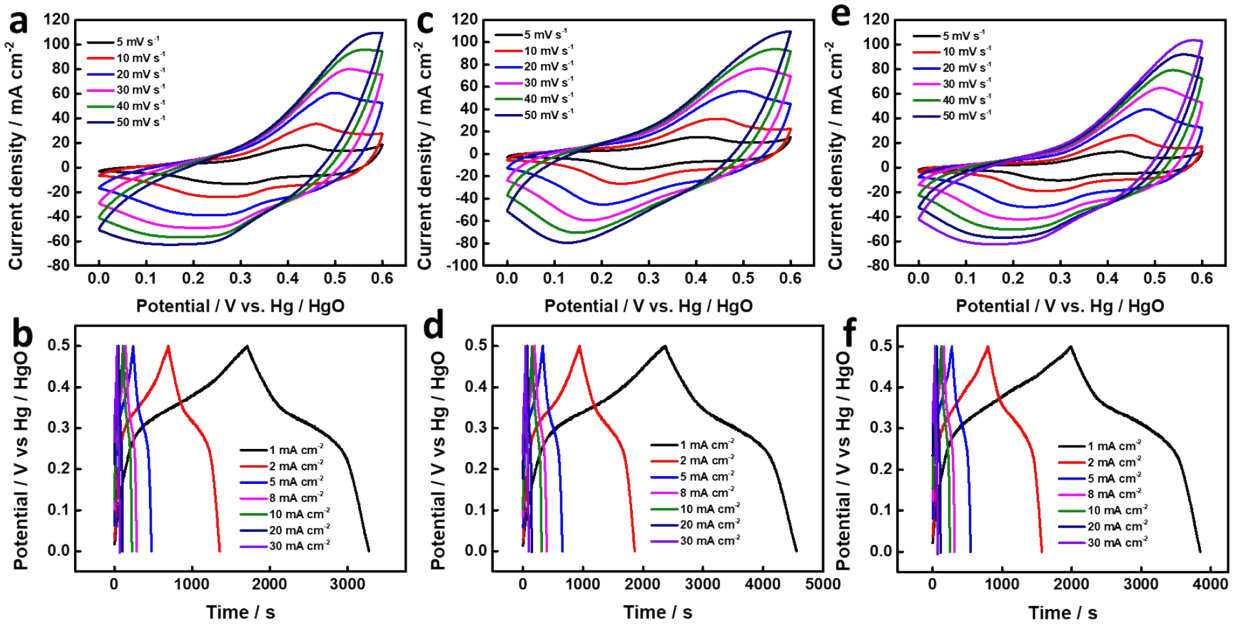

Fig. S4 (a) CV curves of $NiCo_2O_4/NiCo_2S_4$-0 at various scan rates; (b) GCD curves of $NiCo_2O_4/NiCo_2S_4$-0 at different current densities; (c) CV curves of $NiCo_2O_4/NiCo_2S_4$-30 at various scan rates; (d) GCD curves of $NiCo_2O_4/NiCo_2S_4$-30 at different current densities. (e) CV curves of $NiS_2/NiCo_2S_4$ at various scan rates; (d) GCD curves of $NiS_2/NiCo_2S_4$ at different current densities.

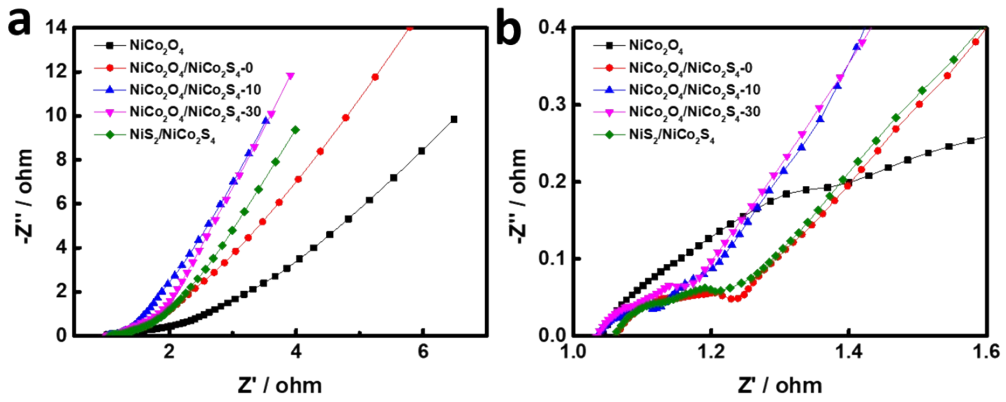

Fig. S5 EIS of all the samples.

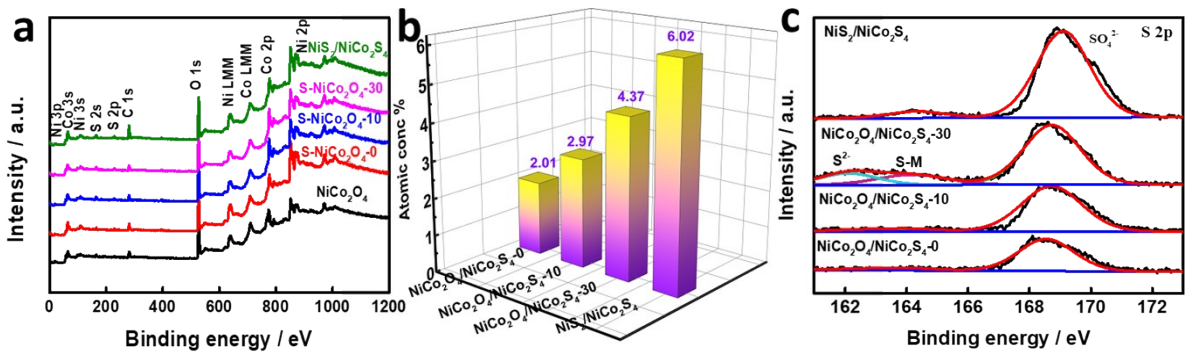

Fig. S6 (a) XPS survey spectrum, (b) S atomic content based on the integral area from a, and (c) the fitted S 2p XPS of the all samples.

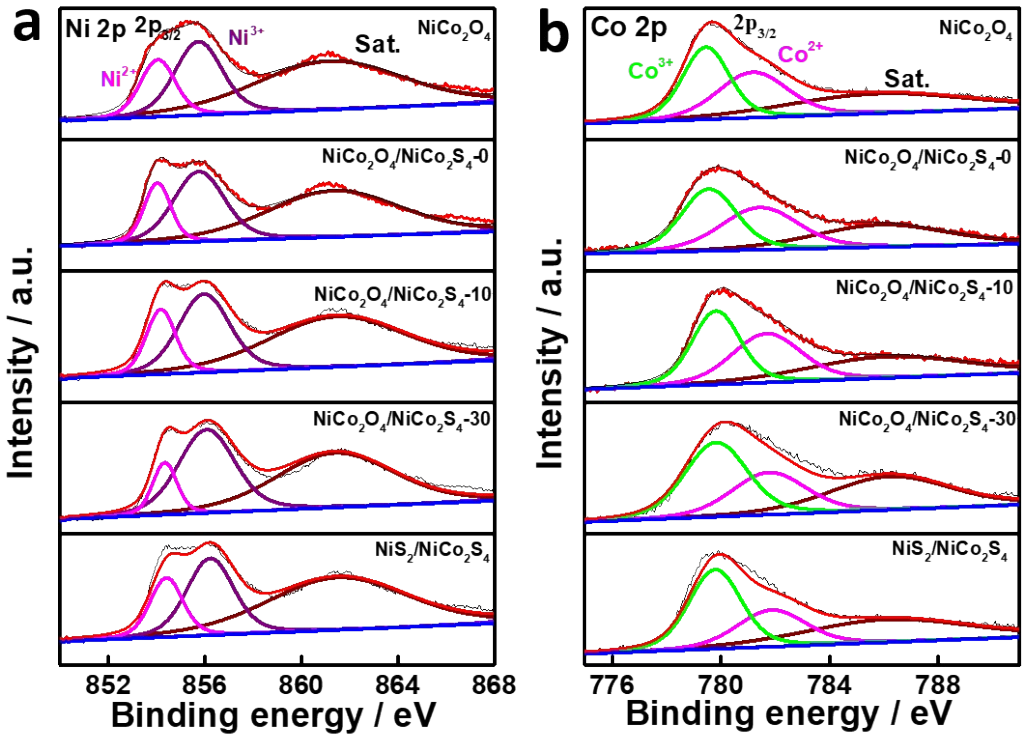

Fig. S7 The fitted Ni 2p XPS and Co 2p XPS spectra of the samples.

Table S1. The fitted impedance from EIS of all the samples.

Samples	Rct(ohm)	Zw(ohm)
$NiCo_2O_4$	1.051	2.087
$NiCo_2O_4/NiCo_2S_4$ -0	1.072	3.393
$NiCo_2O_4/NiCo_2S_4$ -10	1.046	5.269
$NiCo_2O_4/NiCo_2S_4$ -30	1.045	4.79
NiS_2/ $NiCo_2S_4$	1.067	4.69

Table S2. The conductivity of the samples.

Samples	Square resistance/mΩ	Conductivity/KS/mm
$NiCo_2O_4$	6.05495	0.10898
$NiCo_2O_4/NiCo_2S_4$-0	6.53595	0.10338
$NiCo_2O_4/NiCo_2S_4$-10	5.23399	0.12680
$NiCo_2O_4/NiCo_2S_4$-30	5.54320	0.12196
NiS_2/ $NiCo_2S_4$	5.86631	0.11463

Table S3. The binding energy of the fitted Ni species of the samples.

Sample	Binding energy and atomic percentage of Ni species (eV/%)	
	Ni(+2)	Ni(+3)
$NiCo_2O_4$	854.03/31.16%	855.72/68.84%
$NiCo_2O_4/NiCo_2S_4$-0	854.03/30.68%	855.78/69.32%
$NiCo_2O_4/NiCo_2S_4$-10	854.18/28.87%	855.95/71.13%
$NiCo_2O_4/NiCo_2S_4$-30	854.32/21.53%	856.06/78.47%
NiS_2/ $NiCo_2S_4$	854.45/24.71%	856.23/75.29%

Table S4. The binding energy of the fitted Co species of the samples.

Sample	Binding energy and atomic percentage of Co species (eV/%)	
	Co(+2)	Co(+3)
$NiCo_2O_4$	781.23/50.29%	779.47/49.71%
$NiCo_2O_4/NiCo_2S_4$-0	781.50/52.58%	779.57/47.42%
$NiCo_2O_4/NiCo_2S_4$-10	781.69/53.67%	779.83/46.33%
$NiCo_2O_4/NiCo_2S_4$-30	781.87/50.48%	779.83/49.52%
NiS_2/ $NiCo_2S_4$	781.97/47.51%	779.83/52.49%

Table S5. Comparison of cycle stability of the different samples.

Samples	Stability	Ref
$NiCo_2O_4/NiCo_2S_4$	88.1%(9000 cycles)	This work
P-$NiCo_2S_4$	87.5%(5000 cycles)	1
$NiCo_2S_4$@$NiCo_2O_4$	82% (1000 cycles)	2
$NiCo_2S_4$/rGO//AC	90.2% (10000 cycles)	3
$NiCo_xO_y$	77% (1500 cycles)	4
$NiCo_2S_4$	87% (5000 cycles)	5
NiMn-G-LDH@$NiCo_2S_4$	86.4% (10000 cycles)	6

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