

## ELECTRONIC SUPPORTING INFORMATION

# Three-dimensional hierarchical NiCo<sub>2</sub>O<sub>4</sub> Nanowires@Ni<sub>3</sub>S<sub>2</sub> Nanosheets Core/Shell Arrays for Flexible Asymmetric Supercapacitor

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## **Experimental Section**

### **Preparation of pristine NiCo<sub>2</sub>O<sub>4</sub> NWAs**

Prior to synthesis, a piece of Ni foam (3×7 cm<sup>2</sup>) was degreased with 3 M HCl for half an hour to remove oxides and impurities, followed by washing thoroughly with deionized (DI) water and ethanol. Next, 1.5 mM of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 3 mM of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 2.5 mM NH<sub>4</sub>F, and 7.5 mM urea were dissolved in 80 ml DI water. The homogeneous pink solution was stirred with a magnetic stir bar at room temperature for 1 h. Subsequently, it was transferred into a Teflon-lined stainless steel autoclave (100 ml) with a piece of Ni foam. Afterwards, the autoclave was sealed and kept at 110 °C in an electric oven for 4 h. When the autoclave naturally cooled down to room temperature, the synthesized sample was collected, washed, vacuum dried and annealed at 320 °C for 2 h in air.

### **Synthesis of 3D hierarchical NiCo<sub>2</sub>O<sub>4</sub>@Ni<sub>3</sub>S<sub>2</sub> NWAs**

A piece (2.5×2.5 cm<sup>2</sup>) of as-prepared NiCo<sub>2</sub>O<sub>4</sub> NWAs was immersed into 20 ml DI water and ethanol mixture with 40 mg K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 200 mg NiSO<sub>4</sub> and 100 μl ammonium hydroxide solution (28%). After 20 min of chemical bath deposition, hierarchical NiCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub> NWAs were collected and thoroughly washed with DI water and dried in an electric oven at 60 °C overnight. Next, the intermediate NiCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub> samples were put into a 40 ml Teflon-lined stainless steel autoclave with 25 ml DI water and 20 mg Na<sub>2</sub>S·9H<sub>2</sub>O, and heated for 10 h at 90 °C. The collected samples were washed thoroughly, dried and annealed in argon at 450 °C for 3 h.

## Materials Characterization

The morphology and dimensions of the as-obtained  $\text{NiCo}_2\text{O}_4$ ,  $\text{NiCo}_2\text{O}_4@\text{Ni}(\text{OH})_2$ ,  $\text{NiCo}_2\text{O}_4@\text{Ni}_3\text{S}_2$  NWAs were characterized by scanning electron microscopy (SEM, JEOL JSM-7600F). Meanwhile, chemical composition and elemental distribution of the products was measured by Energy dispersive X-ray spectroscopy (EDX) on an Oxford INCA energy dispersive analyzer. The structure and crystallinity of the samples was measured by an X-ray diffractometer (Bruker, D8 Advance-Eco) equipped with a  $\text{Cu K}\alpha$  radiation ( $\lambda \approx 1.54 \text{ \AA}$ ) at 40 kV, 25 mA. Raman spectra was detected by a confocal Raman system with the 532 nm laser excitation (WITec Instruments Corp, Germany). Moreover, the morphology and structure was characterized by transmission electron microscopy (TEM) and High-resolution TEM (HRTEM) using the JEOL TEM-2010.

## Electrochemical Measurements

The electrochemical performance was measured in an aqueous electrolyte (3.0 M KOH) with a three-electrode configuration. In the typical setup, the as-prepared electrodes ( $2 \text{ cm}^2$ ), a platinum plate ( $1 \text{ cm}^2$ ), and an Ag/AgCl electrode was used as the working, counter, and reference electrode, respectively. Cyclic voltammetry (CV), galvanostatic charging-discharging, and electrochemical impedance spectroscopy (EIS) tests were carried out on an electrochemical workstation (VMP3, Biologic). The EIS was performed in the frequency range of  $10^{-2} \text{ Hz}$  to  $10^5 \text{ Hz}$ . In addition, the specific areal capacitance ( $C_s, F \text{ cm}^{-2}$ ) of the electrodes were calculated *via* the following equation:

$$Cs = \frac{It}{AV} \quad (1)$$

Where  $Cs$  is the specific areal capacitance,  $A$  ( $cm^2$ ),  $I$  (A),  $V$  (V), and  $t$  (s) represents the effective area of electrodes, current density, potential range, and discharge time, respectively. The specific capacitance of electrodes was obtained *via* substituting the area  $A$  ( $cm^2$ ) with the active mass  $m$  (mg), such as  $1.65 \text{ mg cm}^{-2}$ ,  $2.04 \text{ mg cm}^{-2}$ , and  $2.17 \text{ mg cm}^{-2}$  for  $NiCo_2O_4$  NWAs,  $NiCo_2O_4@Ni(OH)_2$  NWAs, and  $NiCo_2O_4@Ni_3S_2$  NWAs electrodes.

The as-fabricated ASC consists of the following:  $NiCo_2O_4@Ni_3S_2$  NWAs as cathode electrode, active carbon (AC) as anode electrode, and the PVA-KOH as solid-state electrolyte. The anode electrode was prepared using AC as the active material, combined with carbon black additive, and PVDF binder at a ratio of 8:1:1. The mixture was mixed with N-Methyl-2-pyrrolidone (NMP) to form a slurry and coated onto Ni foam ( $3 \times 7 \text{ cm}^2$ ) and left to dry in a vacuum oven at  $80^\circ\text{C}$  overnight. The PVA-KOH electrolyte was prepared *via* dissolving 3 g KOH and 6 g PVA in 70 ml DI water in oil bath. After naturally cooling down, the electrolyte was evenly coated on the surface of each electrode. Then the cathode and anode were assembled with the solid-state PVA-KOH as separator and electrolyte. The as-fabricated two-electrode ASC was characterized with CV and galvanostatic charging/discharging tests between 0 - 1.8 V. The energy density ( $E$ ,  $\text{mW h cm}^{-3}$ ), power density ( $P$ ,  $\text{W cm}^{-3}$ ), and volumetric capacitance ( $C_{VC}$ ,  $\text{F cm}^{-3}$ ) of the device was calculated based on the following equation:

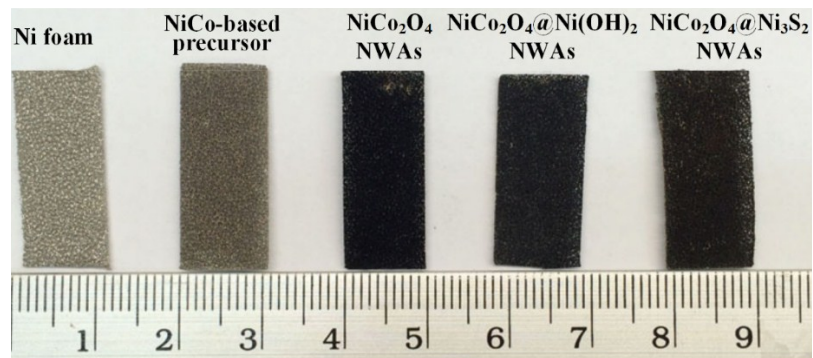
$$C_{VC} = 4 \frac{I dt}{A dV} \quad (2)$$

$$P = 3600 \frac{E}{\Delta t} \quad (3)$$

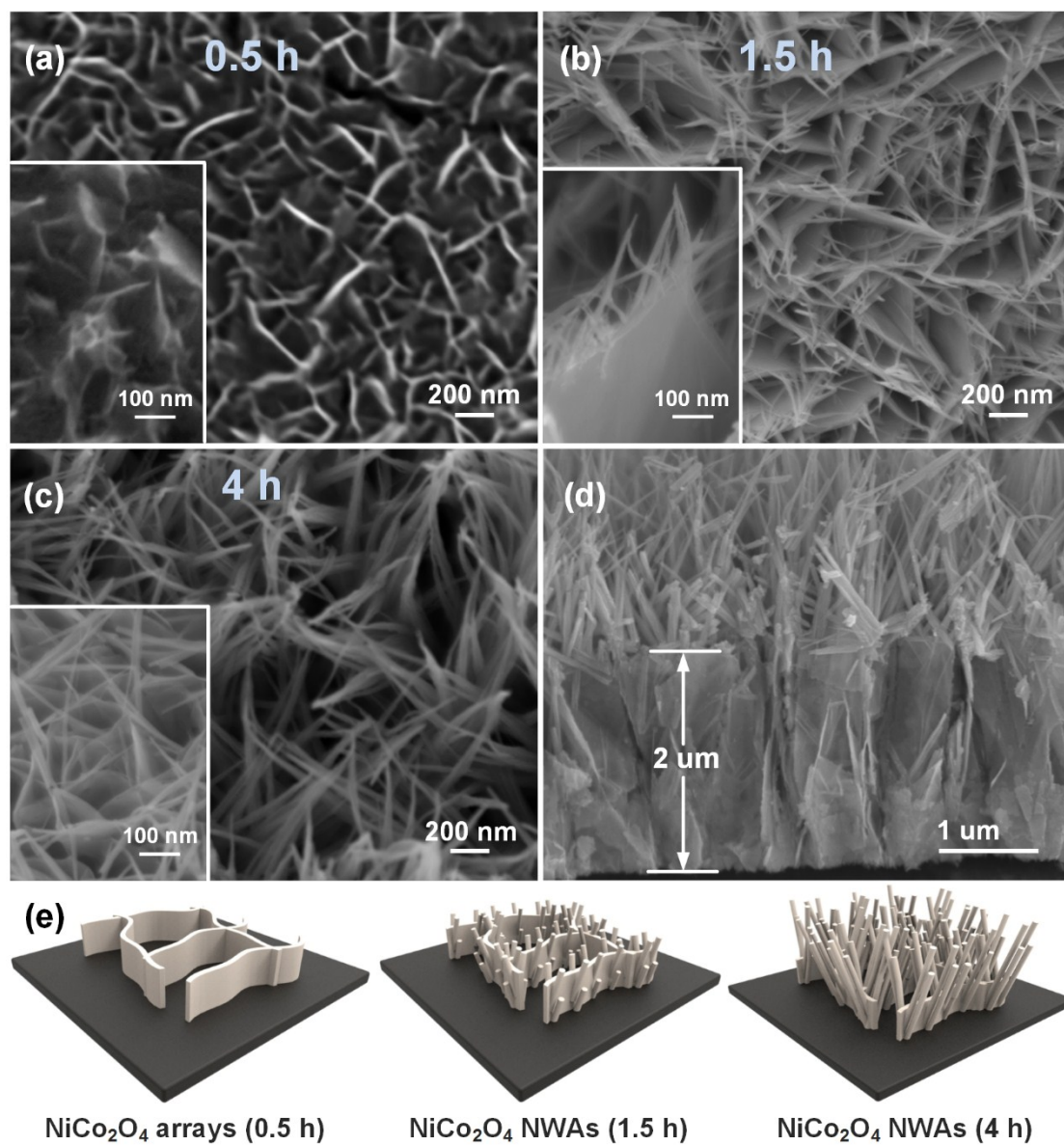
$$E = \frac{1}{2 \times 3.6} C(\Delta V)^2 \quad (4)$$

Where  $\Delta V$ ,  $I$ , and  $A$  represent the working potential window, discharge current ( $mA$ ), and the physical volume of the electrode ( $cm^3$ ), respectively. Meanwhile, the ASC was also tested at normal and bended condition.

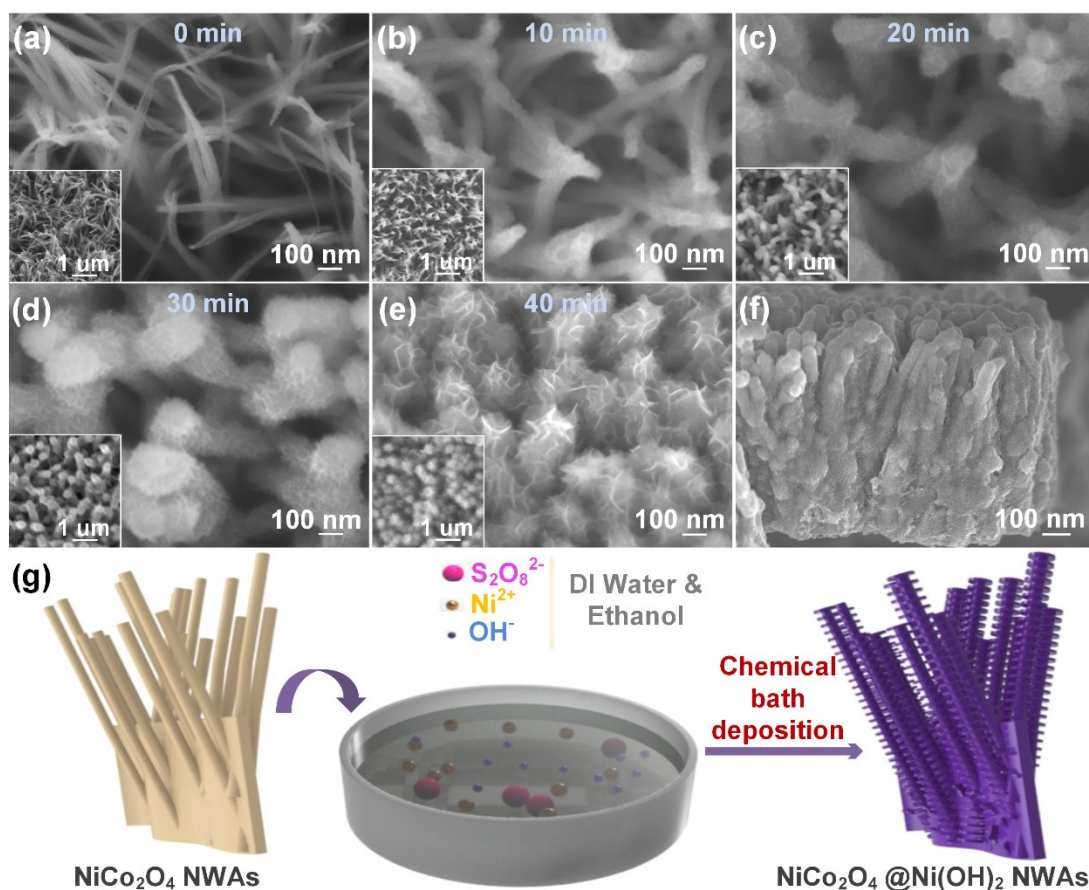
## FIGURES



**Figure S1.** Optical photographs of Ni foam after acid process, NiCo-based precursor, NiCo<sub>2</sub>O<sub>4</sub> NWAs, NiCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub> NWAs, and NiCo<sub>2</sub>O<sub>4</sub>@Ni<sub>3</sub>S<sub>2</sub> NWAs electrode.

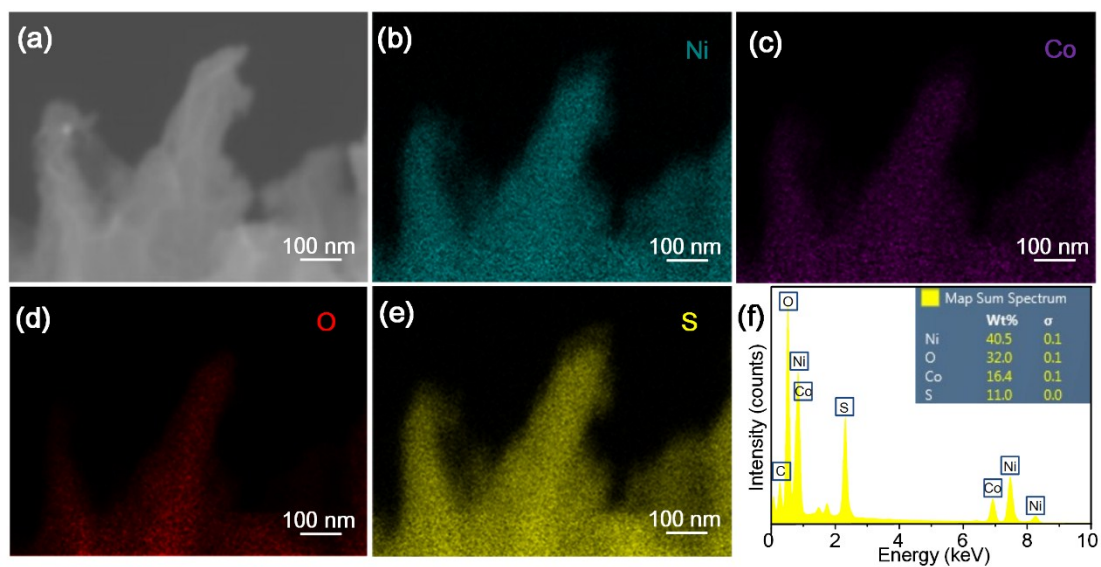


**Figure S2.** The SEM images showing the morphology evolution of vertical-grown  $\text{NiCo}_2\text{O}_4$  NWAs with different reaction time: (a)-(c); (d) cross-section image of **Fig. c**; (e) schematic diagram of growth process. The insets correspond to the specific high-magnified SEM.

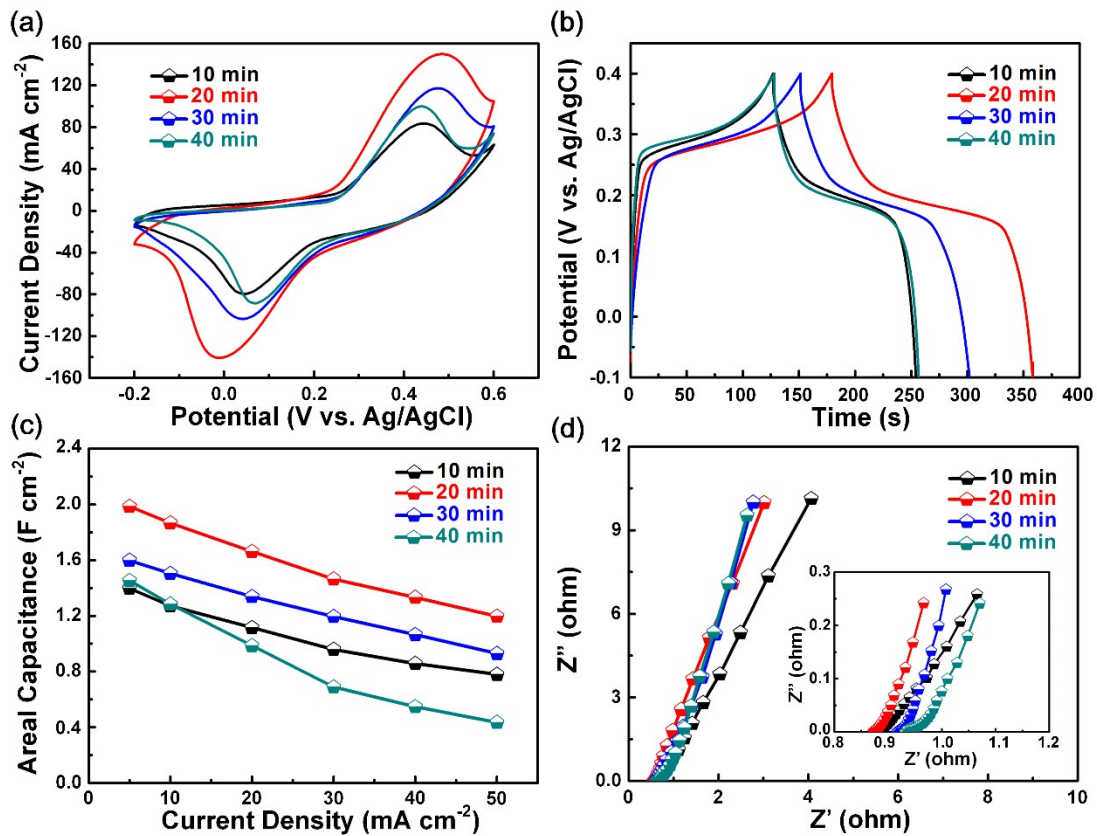


**Figure S3.** The SEM images of NiCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub> NWAs synthesized with various reaction time: (a) - (e); (f) cross-section image of **Fig. d**; (g) schematic illustration of the chemical bath deposition synthesis approach. The insets correspond to the specific low-magnified SEM.

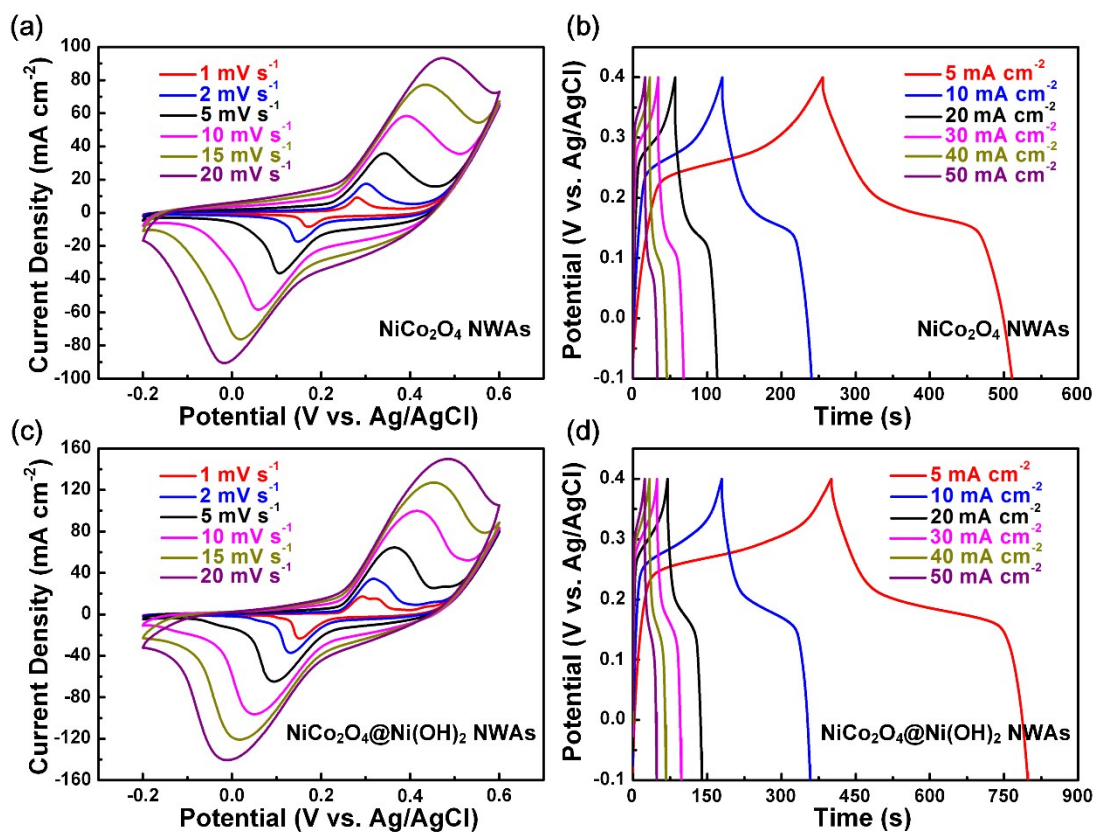




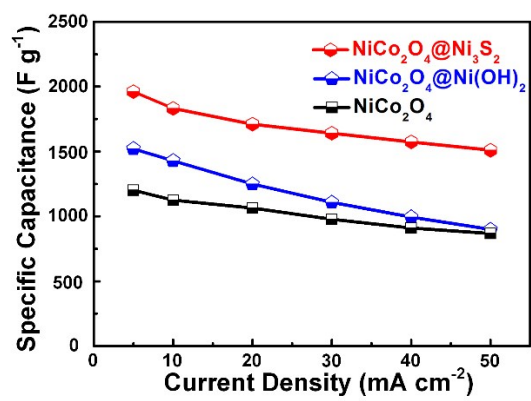
**Figure S4.** The SEM image of the hybrid  $\text{NiCo}_2\text{O}_4@\text{Ni}_3\text{S}_2$  nanostructure (a); elemental map of specific element (b) – (e); and EDX spectrum of Ni, Co, O, S.



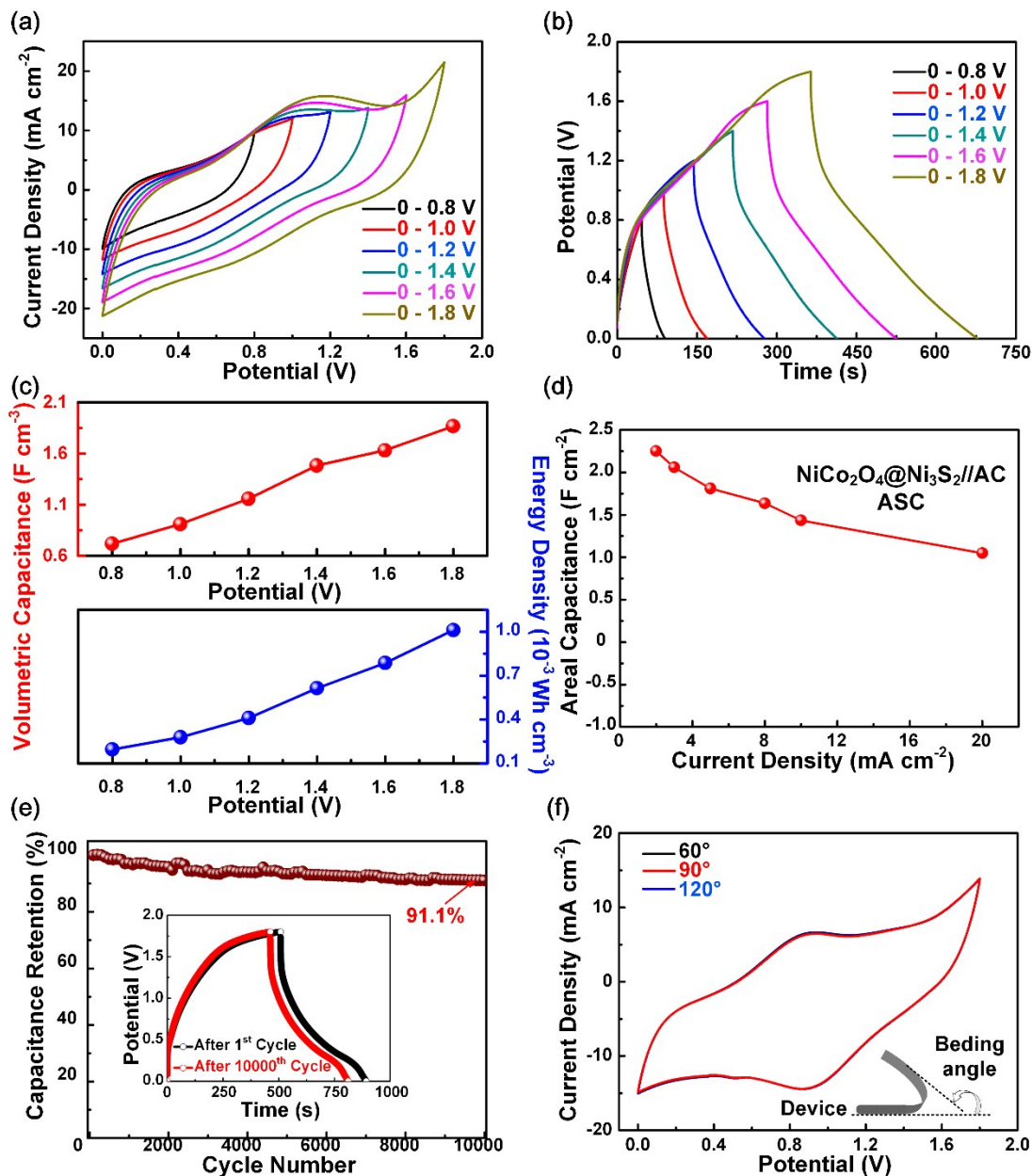
**Figure S5.** Comparison of (a) CV and (b) galvanostatic charge/discharge curves of NiCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub> NWAs electrodes fabricated at different deposition time; (c) specific area capacitance dependent on current densities; and (d) Nyquist plots of these electrodes. The inset of (d) is the enlarged EIS of these electrodes at high frequency region.



**Figure S6.** (a) CV and (b) galvanostatic charge/discharge curves of NiCo<sub>2</sub>O<sub>4</sub> NWAs electrodes at various scan rates and current densities; (c) CV and (d) galvanostatic charge/discharge curves of NiCo<sub>2</sub>O<sub>4</sub>@Ni<sub>3</sub>S<sub>2</sub> NWAs electrodes at various scan rates and current densities.



**Figure S7.** Specific capacitance dependent on current densities of NiCo<sub>2</sub>O<sub>4</sub> NWAs, NiCo<sub>2</sub>O<sub>4</sub>@Ni(OH)<sub>2</sub> NWAs, and NiCo<sub>2</sub>O<sub>4</sub>@Ni<sub>3</sub>S<sub>2</sub> NWAs electrode.



**Figure S8.** (a) CV curves of the ASC device at various operation voltages at a scan rate of  $20 \text{ mV s}^{-1}$ ; (b) galvanostatic charge/discharge curves collected at different potential windows at a current density of  $10 \text{ mA cm}^{-2}$ ; (c) specific areal capacitance and energy density calculated from discharge curves of (b); (d) specific areal capacitance dependent on current densities of the ASC; (e) cycling performance of the ASC (10000 cycles) and the inset is corresponding to the charge/discharge curve of the 1st and the 10000th cycles; (f) CV curves collected at a scan rate of  $20 \text{ mV s}^{-1}$  for the ASC at different bending angles.

**Table S1.** Summary of specific capacitance data of Ni-based electrode materials.

| Sample   | Technique                    | Capacitance             | Current density        | Ref       |
|--|------------------------------|-------------------------|------------------------|-----------|
| NiCo <sub>2</sub> O <sub>4</sub> @Ni <sub>3</sub> S <sub>2</sub>   | HT+ Chemical bath deposition | 3.0 F cm <sup>-2</sup>  | 5 mA cm <sup>-2</sup>  | This work |
| NiCo <sub>2</sub> O <sub>4</sub> @Ni-S                             | Electrodeposition            | 2.0 F cm <sup>-2</sup>  | 5 mA cm <sup>-2</sup>  | 1         |
| NiCo <sub>2</sub> O <sub>4</sub> @NiCo <sub>2</sub> O <sub>4</sub> | HT+ Chemical bath deposition | 1.55 F cm <sup>-2</sup> | 2 mA cm <sup>-2</sup>  | 2         |
| Ni(OH) <sub>2</sub> @NiCo <sub>2</sub> O <sub>4</sub>              | Electrodeposition            | 1.88 F cm <sup>-2</sup> | 10 mA cm <sup>-2</sup> | 3         |
| NiCo <sub>2</sub> S <sub>4</sub> @Metal Hydroxide                  | HT+ Electrodeposition        | 2.86 F cm <sup>-2</sup> | 4 mA cm <sup>-2</sup>  | 4         |
| Ni-Co Hydroxide /NiCo <sub>2</sub> O <sub>4</sub>                  | HT+ Electrodeposition        | 1.64 F cm <sup>-2</sup> | 2 mA cm <sup>-2</sup>  | 5         |
| NiCo <sub>2</sub> O <sub>4</sub> @Ni(OH) <sub>2</sub>              | HT+ Electrodeposition        | 3.88 F cm <sup>-2</sup> | 40 mA cm <sup>-2</sup> | 6         |
| NiCo <sub>2</sub> S <sub>4</sub>                                   | HT+ Annealing process        | 1.14 F cm <sup>-2</sup> | 4 mA cm <sup>-2</sup>  | 7         |
| NiCo <sub>2</sub> O <sub>4</sub> hollow microspheres               | HT+ Sintering                | 718.0 F g <sup>-1</sup> | 1 A g <sup>-1</sup>    | 8         |
| NiCo <sub>2</sub> S <sub>4</sub> @NiCo <sub>2</sub> O <sub>4</sub> | HT+ Annealing process        | 7.13 F cm <sup>-2</sup> | 5 mA cm <sup>-2</sup>  | 9         |
| NiCo <sub>2</sub> O <sub>4</sub> @NiO                              | HT+ Annealing process        | 2105 F g <sup>-1</sup>  | 1 A g <sup>-1</sup>    | 10        |
| NiCo <sub>2</sub> O <sub>4</sub> @MnO <sub>2</sub>                 | HT+ Annealing process        | 2.54 F cm <sup>-2</sup> | 5 mA cm <sup>-2</sup>  | 11        |
| NiCo <sub>2</sub> O <sub>4</sub> microspheres                      | HT+ Annealing process        | 2184 F g <sup>-1</sup>  | 1 A g <sup>-1</sup>    | 12        |
| NiCo <sub>2</sub> O <sub>4</sub> /MnO <sub>2</sub>                 | HT+ Annealing process        | 2687 F g <sup>-1</sup>  | 5 mA cm <sup>-2</sup>  | 13        |
| Ni <sub>3</sub> S <sub>2</sub>                                     | Electrodeposition            | 717 F g <sup>-1</sup>   | 2 A g <sup>-1</sup>    | 14        |
| Ni <sub>3</sub> S <sub>2</sub> /CNT                                | Sintering                    | 514 F g <sup>-1</sup>   | 4 A g <sup>-1</sup>    | 15        |
| CNT@NiCo <sub>2</sub> O <sub>4</sub>                               | Sintering                    | 1038 F g <sup>-1</sup>  | 0.5 A g <sup>-1</sup>  | 16        |

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