

Supplemental Information

Atom-Economical Constructing Carbon Nanotube Architecture for Flexible Supercapacitors with Ultrahigh Areal and Volumetric Capacities

Zhenhua Li, Qihui Yang, Kui Fan, Wenfu Xie, Wang Qiao, Mingfei Shao* and Min Wei

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

**Corresponding authors. E-mail address: shaomf@mail.buct.edu.cn*

1. Experimental Procedures

1.1 Production of Co@CNTs nanoarray and Co@CNTs nanosheet

1.1.1 Preparation of Co₃O₄ nanowire arrays

The Co₃O₄-NWAs was synthesized using a *in-situ* growth process on the Ni foam substrate.¹ Typically, 5 mmol of Co(NO₃)₂·6H₂O, 10 mmol of NH₄F and 25 mmol of urea were dissolved in 50 mL of deionized H₂O, which was then poured into a Teflon-lined stainless steel autoclave. A piece of Ni foam (30×20×0.5 mm; pretreated with absolute ethanol, acetone and deionized water, each for 15 min) was immersed into the above solution, sealed, heated at 120 °C for 4 h. After the reaction, the obtained sample was washed thoroughly with deionized water and then calcinated at 350 °C in air for 2 h.

1.1.2 Preparation of CoAl-LDH@ZIF-67

CoAl-LDH was prepared in a three-neck flask equipped with a reflux condenser.² Typically, 10 mM of CoCl₂·6H₂O, 5 mM of AlCl₃·6H₂O and 35 mM of urea were dissolved in 400 mL of deionized water. The solution was then heated at 97 °C under refluxing and continuous stirring for 48 h. The resulting product was filtered, washed with deionized water and ethanol for several times, and finally dried at ambient temperature in air.

CoAl-LDH@ZIF-67 was synthesized as follows:² 50 mL, 0.1 M of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ methanol solution was added into a 50 mL methanol solution containing 0.2 g CoAl-LDH, and then a 2-methylimidazole (MeIM) methanol solution (50 mL, 0.8 M) was rapidly poured into the above solution under magnetic stirring at room temperature for 15 min. The product was collected by centrifugation and washed several times by methanol.

Pure ZIF-67 was synthesized in methanol at room temperature. Typically, 50 mL, 0.8 M of 2-methylimidazole (MeIM) methanol solution was rapidly poured into 50 mL, 0.1 M of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ methanol solution with magnetic stirring at room temperature for 12 h. The product was collected by centrifugation and washed several times by methanol.

1.1.3 Production of Co@CNTs-NAs and Co@CNTs-NSs via SSCVD method

Co@CNTs-NAs and Co@CNTs-NSs were co-produced through the one-step SSCVD process. Typically, the powdered sample of CoAl-LDH@ZIF-67 (0.1 g) was placed in a porcelain boat ($\text{Al}_2\text{O}_3 \geq 99\%$), and a piece of Ni foam ($30 \times 20 \times 0.5$ mm) supported Co_3O_4 -NWAs is installed horizontally over the porcelain boat. A temperature-programmed furnace was used to perform the CNTs growth process under H_2 atmosphere at $800\text{ }^\circ\text{C}$ for 2 h, and the heating rate was $2\text{ }^\circ\text{C min}^{-1}$. The CoAl-LDH@ZIF-67 can be replaced by pure ZIF-67.

1.2 Preparation of positive and negative electrode for SCs and the FSSCs

1.2.1 Preparation of Co@CNTs@LDH-NAs as positive electrode for SCs

The Co@CNTs@LDH-NAs was prepared using a facile electrosynthesis method.³ The Ni foam supported Co@CNTs-NAs was used as the working electrode in an electrochemical cell with a three-electrode configuration, by using Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The electrolyte for electrodeposition of CoNi-LDH was obtained by dissolving 0.15 M of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.15 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 50 mL of distilled water. The potentiostatic deposition was carried out at a potential of -1.0 V vs. SCE at room temperature. The resulting Ni foam supported Co@CNTs@LDH-NAs was withdrawn and rinsed with distilled water. The mass-loading of

the active material was controlled by adjusting the electrosynthesizing time, which was obtained by the mass difference between the Ni foam supported Co@CNTs@LDH-NAs and pure Ni foam substrate. Co₃O₄@LDH and Ni foam/LDH were synthesized with the same procedure by changing the Co@CNTs-NAs with to Co₃O₄-NWAs or Ni foam.

1.2.2 Preparation of negative electrode for SSCs

The Co@CNTs-NSs was first processed to hollow and porous structure via acid etching. Typically, the Co@CNTs-NSs was dispersed and stirred in a 10 wt% HF solution for 24 h, and the resulting material was washed extensively with deionized water. This process was repeated 4 times, and the final product (CNT(NSs)) was dried at 60°. Then, the CNTs-NSs was supported on Ni foam electrode via dip-coating method. In this process, CNTs-NSs, acetylene black and polyvinylidene fluoride (PVDF) were mixed and dispersed in ethanol with mass ratio of 8:1:1. The mixture was treated by ultrasonic for 10 min. Subsequently, Ni foam was immersed into the above solution, and then was withdrawn and dried. The mass-loading of the electrode material was controlled by repeating the above deposition process for several cycles. The obtained Ni foam supported CNTs-NSs electrode was used as the negative electrode for the FSSC.

1.2.3 Preparation of PVA–KOH solid electrolyte

The PVA–KOH solid electrolyte was prepared as follows: PVA (5.0 g) and KOH (5.0 g) were dissolved in 50 mL of water with vigorous and continuous stirring for 5 h at 90 °C, to obtain a complete dissolution and formation of a jell-like solution. The resulting gel was heated at 60 °C in a vacuum oven to evaporate excess water. The resulting PVA–KOH polymer membrane was stored in a polyethylene bag before use.

1.2.3 Preparation of FSSCs

The Co@CNTs@LDH-NAs//CNTs-NSs FSSC device was fabricated by assembly of a PVA–KOH solid electrolyte membrane between the Co@CNTs@LDH-NAs/Ni foam and the CNTs-NSs/Ni foam electrode face-to-face. After hot pressing at 60 °C for 5 min, the

electrolyte was solidified to produce a sandwich structure. The area of all the fabricated FSSC is 0.5 cm² and the thickness is 0.8 mm; the total mass load of the active materials in this FSSC is 16 mg cm⁻² (4 mg cm⁻² for Co@CNTs@LDH-NAs and 12 mg cm⁻² for CNTs-NSs).

1.3 Characterizations

Shimadzu XRD-6000 diffractometer with a Cu K α source was used to measure the X-ray diffraction patterns of the samples (scan range:3 $^{\circ}$ –70 $^{\circ}$, scan step: 5 $^{\circ}$ min⁻¹). Thermo VG ESCALAB 250 X-ray photoelectron spectrometer was used to perform the X-ray photoelectron spectra (XPS) of the samples with a pressure of about 2 \times 10⁻⁹ Pa and using Al K α X-rays as the excitation source. Raman microspectrometer (Renishaw, inVia-Reflex, 532 nm) was used to carry out the raman measurements with 532 nm of excitation by using a confocal. The pore size analysis was performed by Barrett-Joyner-Halenda (BJH) method, using a Quantachrome Autosorb-1CVP analyzer. The morphology investigation was using a Zeiss SUPRA 55 scanning electron microscope (SEM, with an accelerating voltage of 20 kV), which combine with energy dispersive X-ray spectroscopy (EDX). Transmission electron microscope (TEM) images were recorded using a Philips Tecnai 20 and JEOL JEM-2010 high-resolution transmission electron microscope with an accelerating voltage of 200 kV.

1.4 SCs performance measurements

Electrodes were tested on a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co., China) in a three-electrode electrochemical cell using a 1 M KOH aqueous solution as electrolyte at room temperature. A Pt wire and a SCE electrode were used as the counter and reference electrode, respectively. The distance between the working electrode and the counter electrode was 2 cm.

The specific capacity of the samples was calculated from the charge/discharge curves based on the following equation:

$$C = \frac{I \times \Delta t}{m} \quad (1)$$

where C is the specific capacity; I (A) refers to the discharge current; Δt (s) represents the discharge time; and m corresponds to the total weight of the active materials or the area (&volume) of the electrodes.

The energy density and power density of the FSSC device were calculated using the following equations:

$$C = \frac{I \times \Delta t}{m} \quad (2)$$

$$E = \frac{C \times \Delta V^2}{2} \quad (3)$$

$$P = \frac{E}{\Delta t} \quad (4)$$

where C is the capacity of the FSSC; I (A) represents the discharge current; Δt (s) represents the discharge time; m is the total weight of the active materials or the total volume of the FSSC; E and P correspond to the energy density and power density, respectively.

2. Supplemental Figures and Table

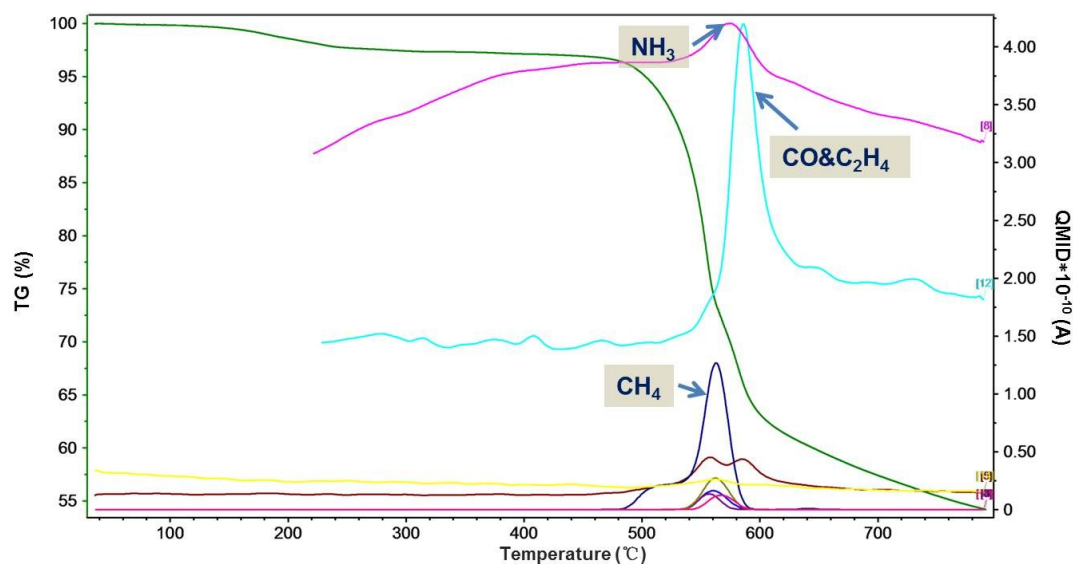


Fig. S1 TG-MS spectra of different volatiles escaped from ZIF-67 during the pyrolysis process (cyan line: CO&C₂H₄; navy line: CH₄; magenta line: NH₃).

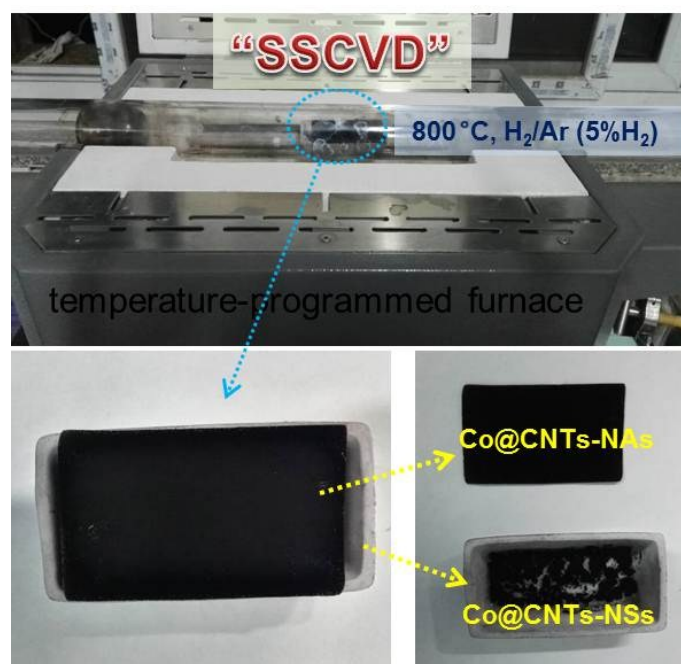


Fig. S2 Photograph demonstration for the production of Co@CNTs-NA and Co@CNTs-NS based on the SSCVD method.

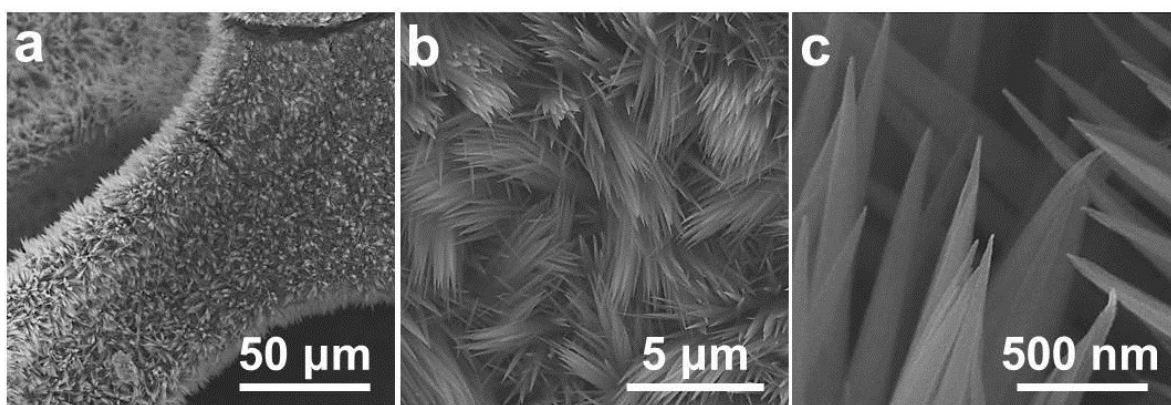


Fig. S3 SEM images of the Co₃O₄-NWAs with different magnification.

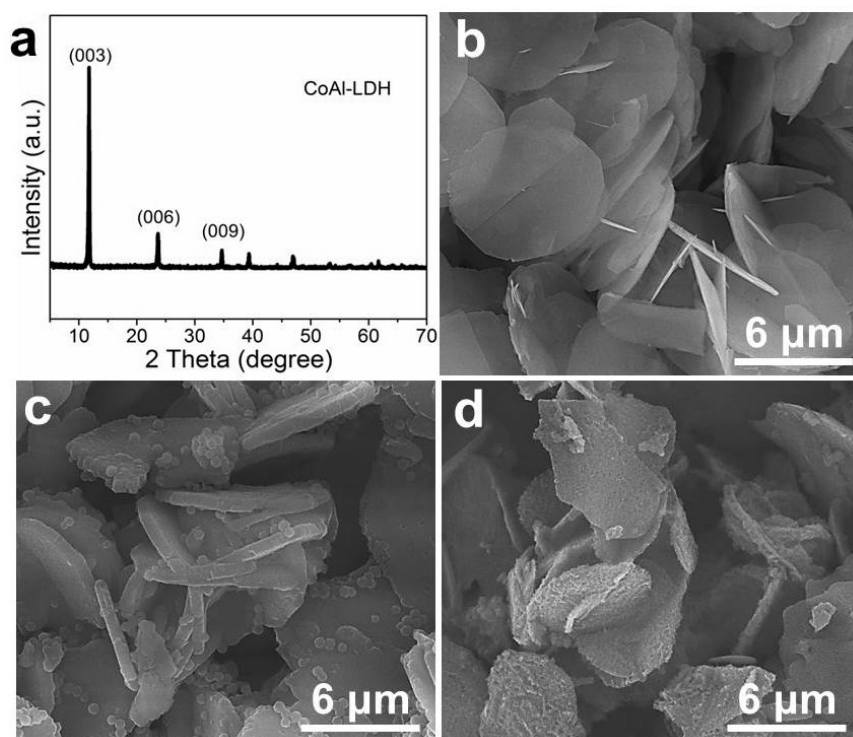


Fig. S4 (a) XRD pattern of CoAl-LDH. (b-d) SEM images of (b) CoAl-LDH, (c) CoAl-LDH@ZIF-67 and (d) Co@CNTs-NSs.

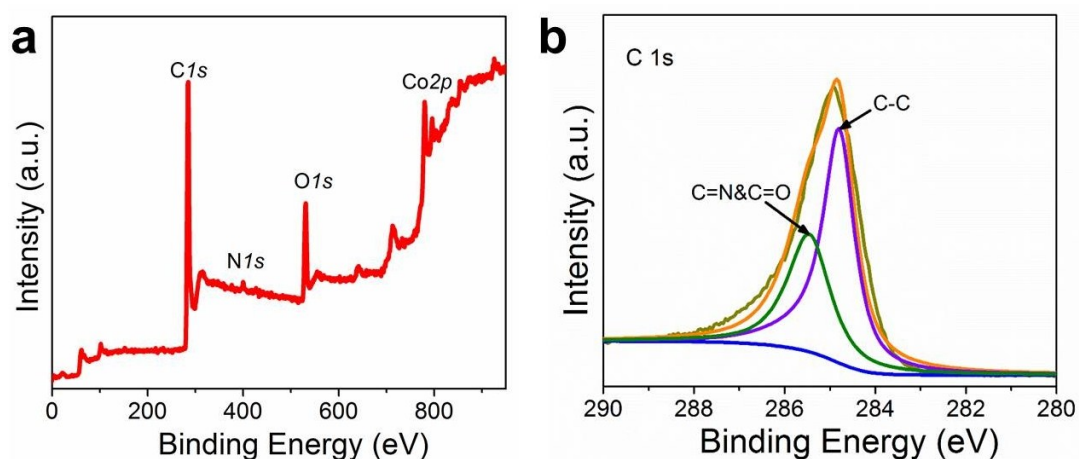


Fig. S5 (a) Full XPS spectrum of Co@CNTs-NAs. (b) High-resolution XPS spectra of C 1s for Co@CNTs-NAs.

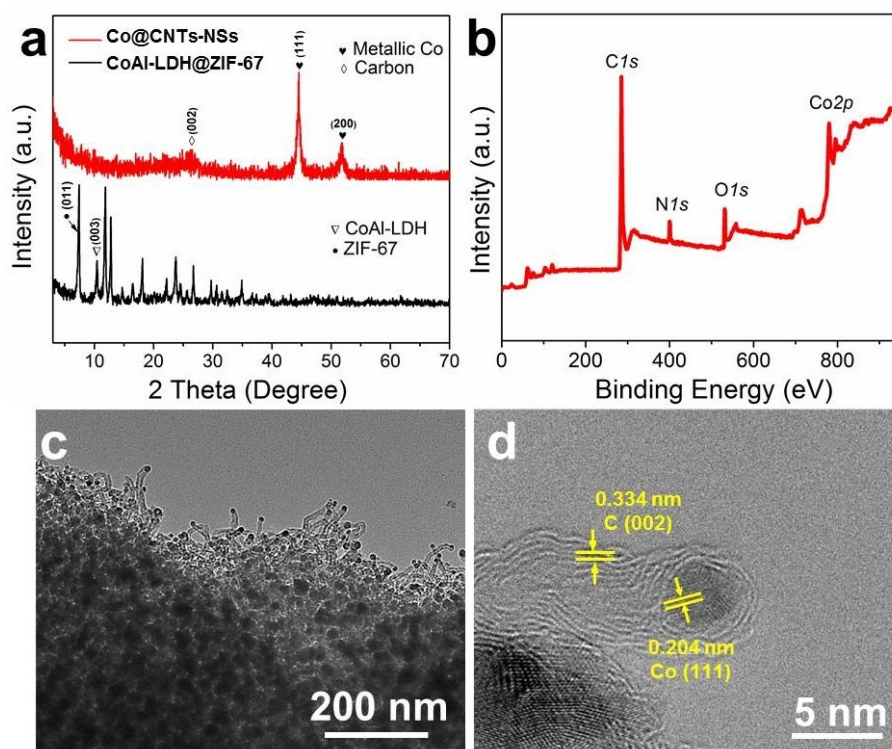


Fig. S6 (a) XRD patterns of CoAl-LDH@ZIF-67 and Co@CNTs-NSs. (b) Full XPS spectrum of Co@CNTs-NSs. (c) TEM image and (d) HRTEM image of Co@CNTs-NSs.

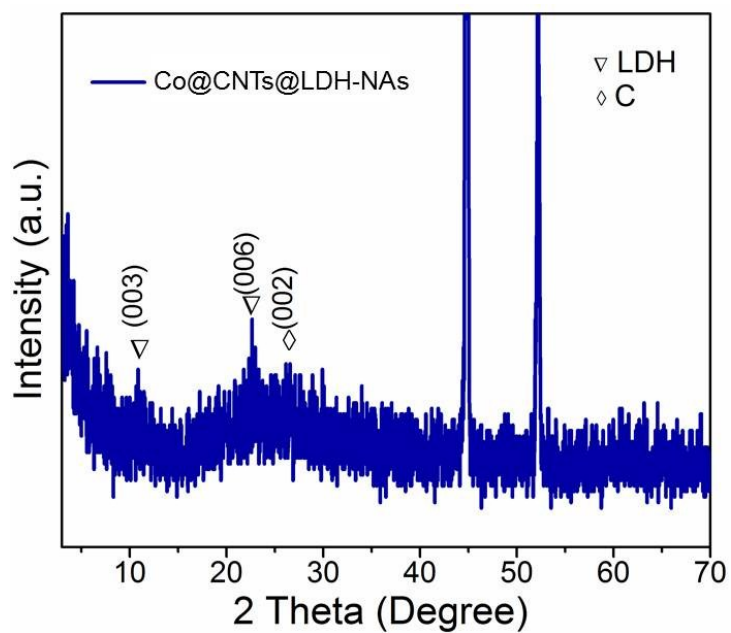


Fig. S7 XRD pattern of Co@CNTs@LDH-NAs.

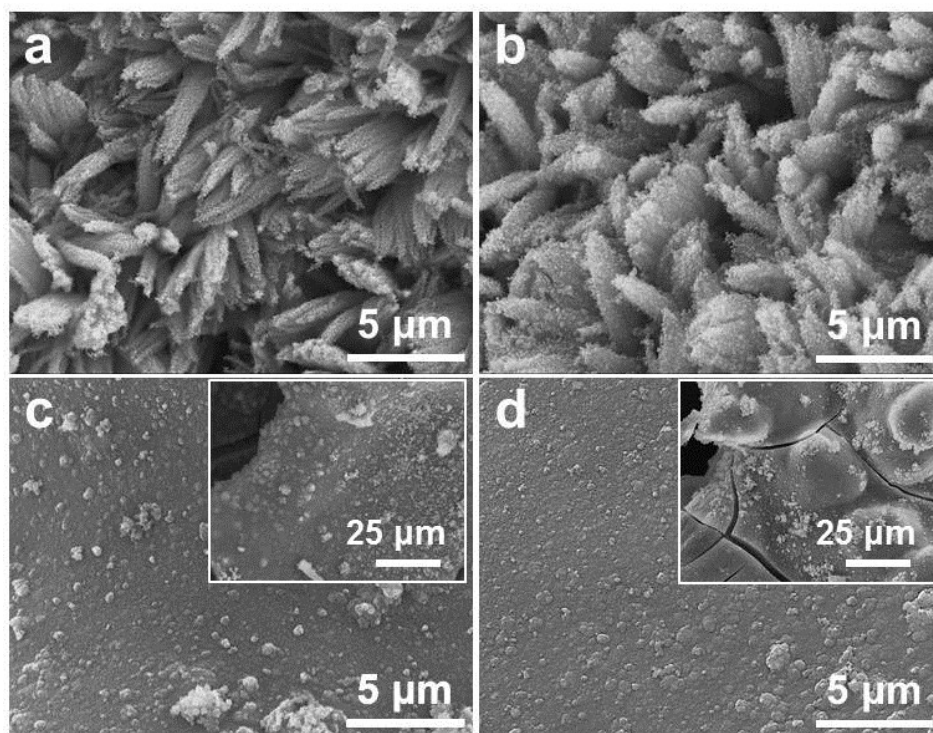


Fig. S8 SEM images of Co@CNTs@LDH-NAs with different mass-loading of CoNi-LDH: (a) 0.5 mg cm^{-2} , (b) 2 mg cm^{-2} , (c) 10 mg cm^{-2} , and (d) 15 mg cm^{-2} .

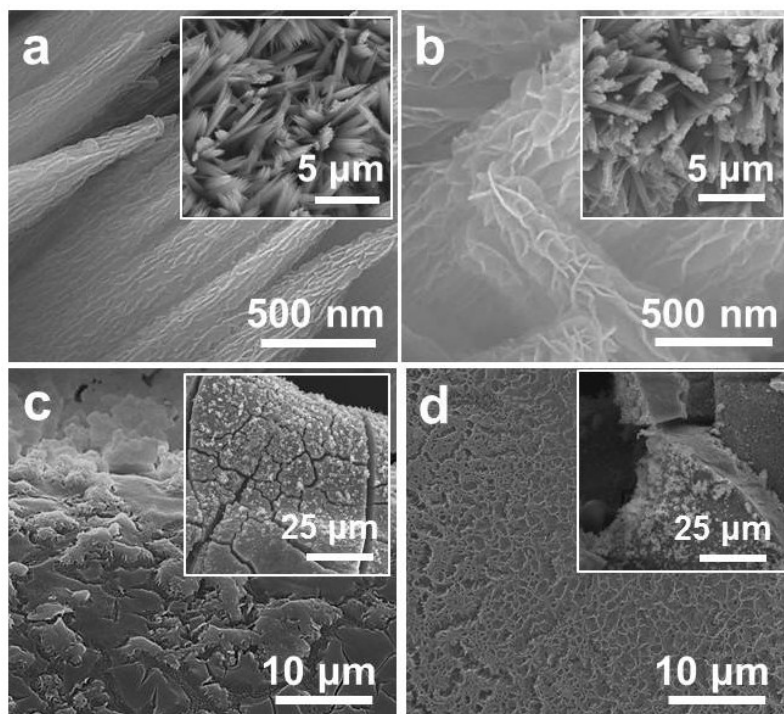


Fig. S9 SEM images of $\text{Co}_3\text{O}_4@\text{LDH}$ with different mass-loading of CoNi-LDH: (a) 0.5 mg cm^{-2} , (b) 2 mg cm^{-2} , (c) 10 mg cm^{-2} , and (d) 15 mg cm^{-2} .

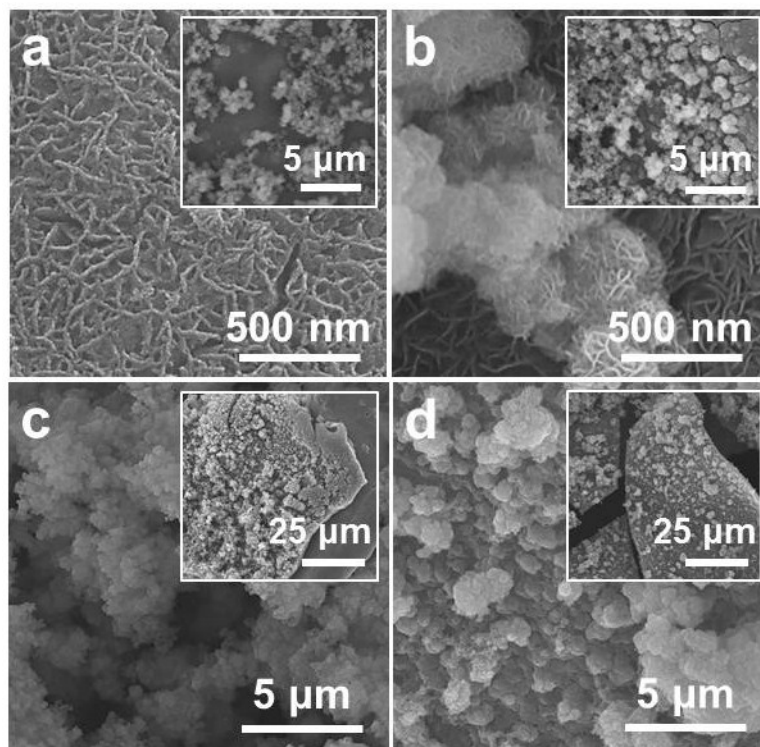


Fig. S10 SEM images of Ni foam/LDH with different mass-loading of CoNi-LDH: (a) 0.5 mg cm^{-2} , (b) 2 mg cm^{-2} , (c) 10 mg cm^{-2} , and (d) 15 mg cm^{-2} .

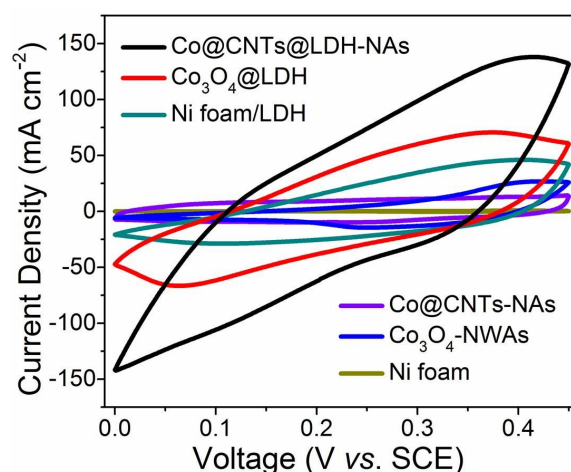


Fig. S11 CV curves of Co@CNTs@LDH-NAs, Co₃O₄@LDH, Ni foam/LDH and Co@CNTs-NAs, Co₃O₄-NWAs, Ni foam at scan rate of 10 mV s⁻¹ in 1 M KOH.

Table S1. Comparison of the areal&volumetric capacity for Co@CNTs@LDH-NAs with reported flexible and supported electrodes in previous literatures.

Electrodes	Areal mass loading (mg cm ⁻²)	Areal&Volumetric capacity		Ref.
		(mAh cm ⁻² /mAh cm ⁻³)		
Co@CNTs@LDH-NAs	15	3.18/63.6		This work
Co ₃ O ₄ @LDH	15	1.4/28		
Ni foam/LDH	15	0.65/12.9		
Co ₃ O ₄ @NiCo ₂ O ₄	1.5	0.26/-		1
ZnO@C@LDH	2.8	0.78/-		3
Ni(OH) ₂ @NiCo ₂ O ₄	/	0.65/-		4
NiCo ₂ O ₄ @Co _{0.33} Ni _{0.67} (OH) ₂	5.5	0.71/-		5
Co _x Ni _{1-x} (OH) ₂ /NiCo ₂ O ₄	1	0.21/12.1		6
NiCo ₂ O ₄ @MnO ₂	/	0.41/-		7
NiCo ₂ O ₄ @CoMoO ₄	12.3	1.83/-		8
CuCo ₂ O ₄ nanobelts	/	0.3/-		9
Ni ₃ S ₂ -CP-60	23.1	1.94/-		10
Co ₃ O ₄ nanosheet	1.4	0.48/4.75		11
CNTs-PPy	3.3	0.28/-		12

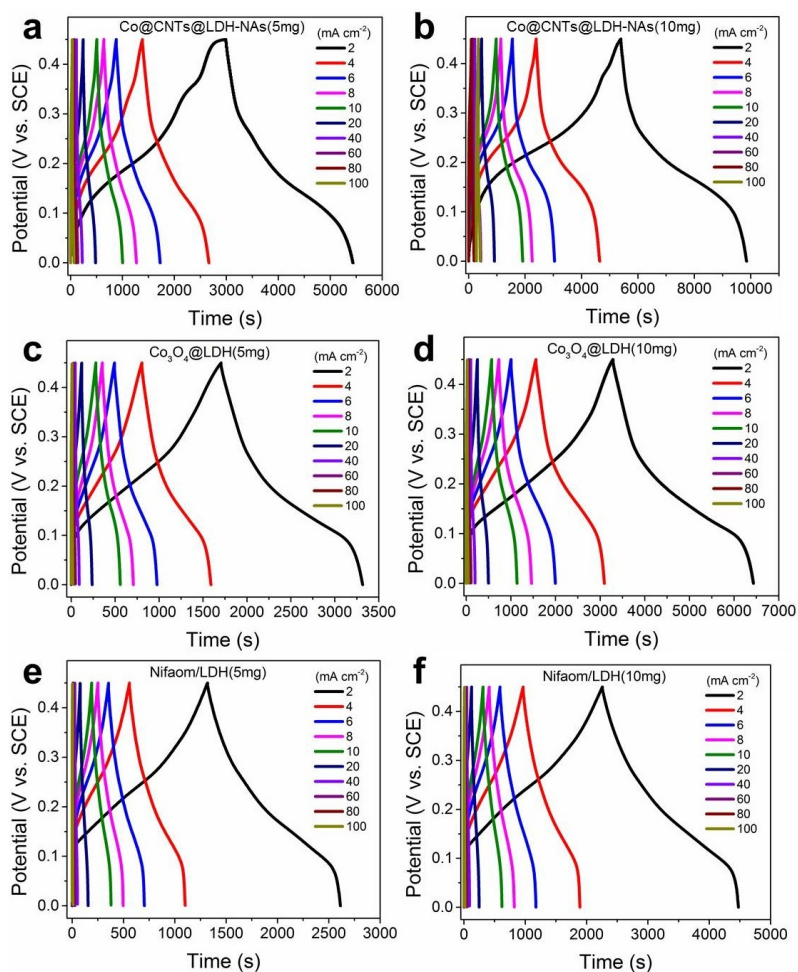


Fig. S12 GV charge/discharge curves of Co@CNTs@LDH-NAs, Co₃O₄@LDH and Ni foam/LDH with different mass-loading at various current densities.

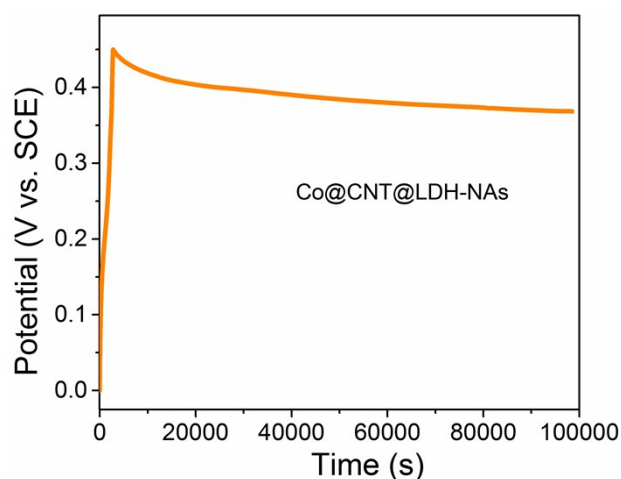


Fig. S13 Open circuit voltage curve of Co@CNTs@LDH-NAs after charge to 0.45 V vs. SCE in 1M KOH solution.

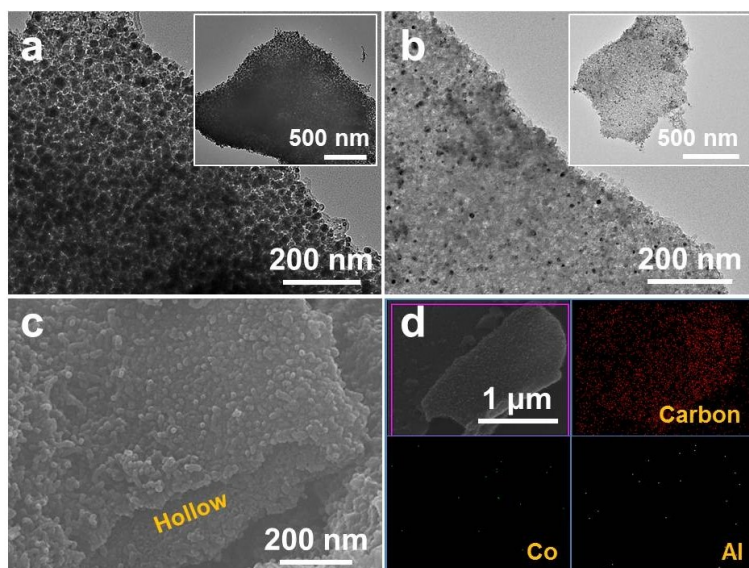


Fig. S14 TEM images of (a) Co@CNTs-NSs and (b) CNTs-NSs. (c) SEM image of CNTs-NSs. (d) EDS-mapping of the CNTs-NSs.

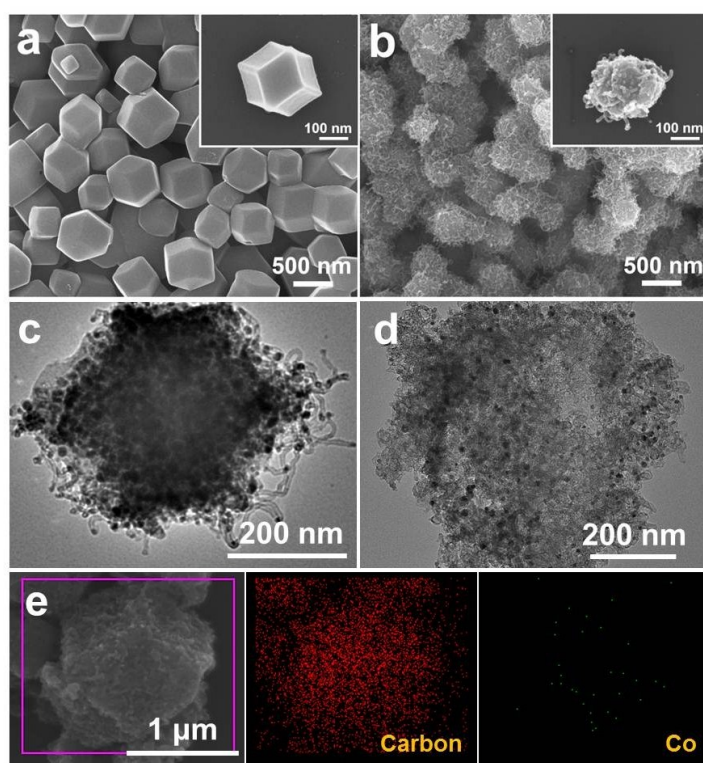


Fig. S15 SEM images of (a) ZIF-67 and (b) CNTs-NPs. TEM images of CNTs-NPs (c) before and (d) after acid etching. (e) EDS-mapping of the CNTs-NPs.

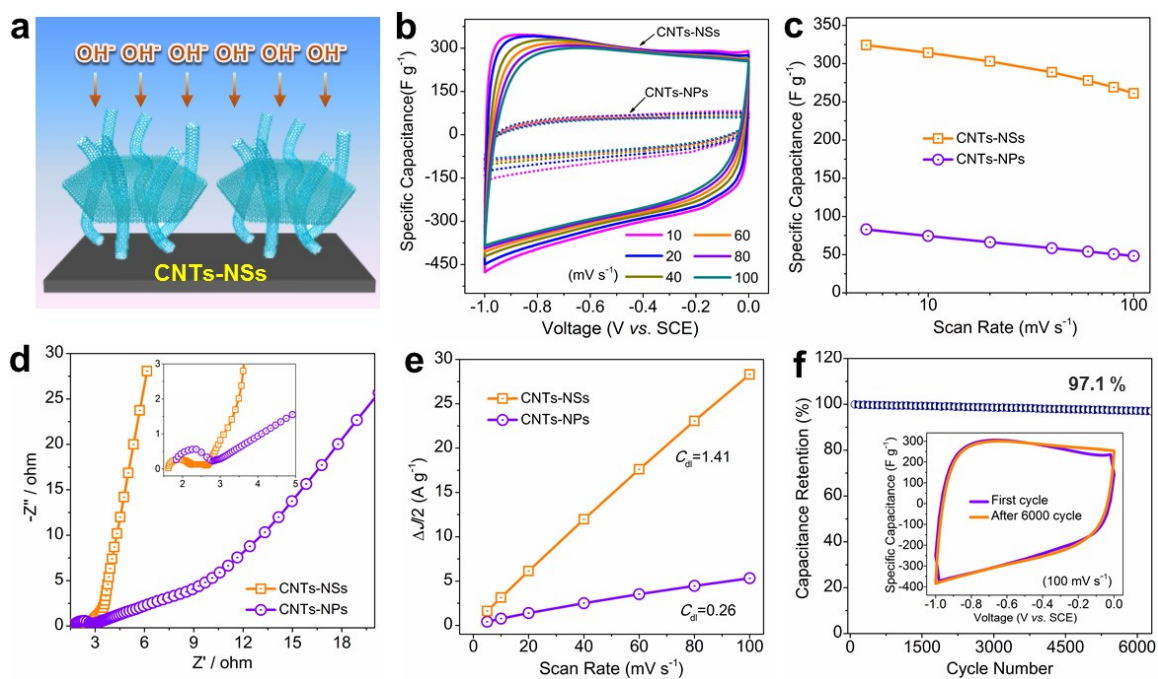


Fig. S16 (a) A schematic illustration of the CNTs-NSs assemble electrode. (b) CV curves of CNTs-NSs and CNTs-NPs at various scan rates. (c) Comparison of rate performances, (d) Nyquist plots and (e) double layer capacitance (C_{dl}) of the two samples. (f) Cycling performance of the CNTs-NSs electrode.

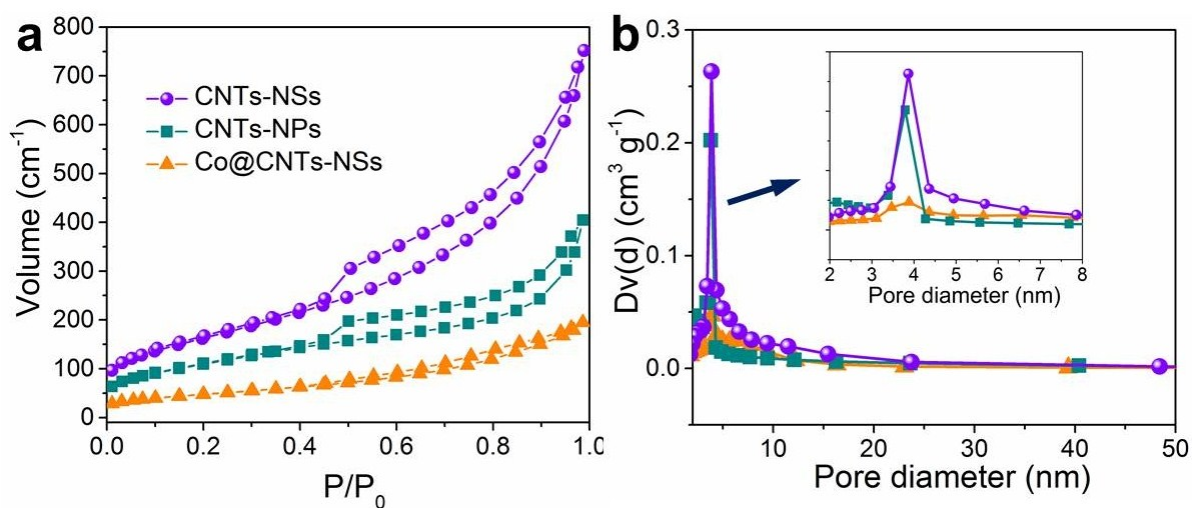


Fig. S17 (a) N_2 sorption isotherms of Co@CNTs-NSs, CNTs-NPs and CNTs-NSs. (b) The corresponding pore size distribution of the three samples.

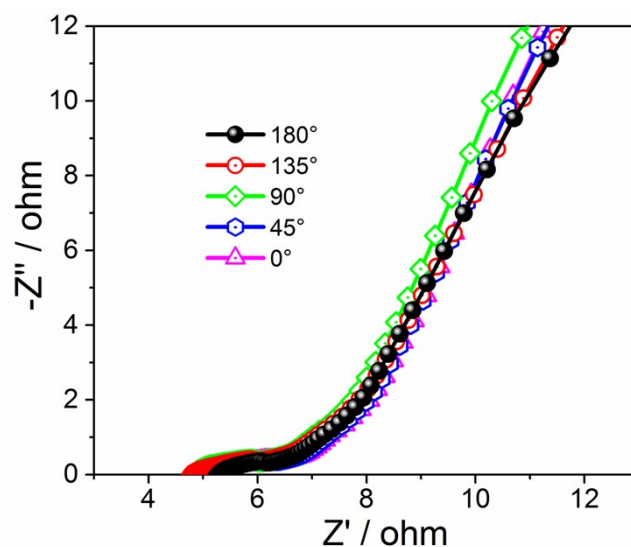


Fig. S18 EIS spectra of FSSC device bending at different angles.

3. Supplemental References

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