

Electronic Supplementary Information (ESI)

Hierarchical Ultrathin Rolled-up Co(OH)(CO₃)_{0.5} Films Assembled on Ni_{0.25}Co_{0.75}S_x Nanosheets for Enhanced Supercapacitive Performance

*Lu Bai, † Fang Fang, † Hongyu Sun, Xingxu Yan, Xiaoming Sun, * Jun Luo, * and Jing Zhu**

1. Experimental Section:

Step 1: Ni_{0.25}Co_{0.75}(OH)₂ nanosheet arrays on Ni foam were synthesized by a simple hydrothermal method (named H-NSAs). All of the chemicals were of analytical grade and used without further purification. In a typical procedure, Nickel foam (about 3 cm × 3.5 cm × 0.1 cm) was firstly cleaned with concentrated 3 M HCl solution in an ultrasound bath for several minutes in order to remove the surface NiO layer, and then deionized water and absolute ethanol were used for 5 min each to ensure the surface of the Ni foam was well cleaned. 2-mmol Co(NO₃)₂·6H₂O, 8-mmol NH₄F and 10-mmol CO(NH₂)₂ were dissolved in 36 mL of distilled water and stirred to form a clear solution. The aqueous solution and the Ni foam were transferred to a 40 mL Teflon-lined maintained at 90 °C for 6 h, and then allowed to cool to room temperature. The red thin film on the metal substrate was obtained and subsequently rinsed with distilled water, and dried at 80 °C for 6 h. The weight of Ni foam was accurately measured before and after hydrothermal process.

The curve a in Figure 2 shows the XRD pattern of H-NSAs, and the phase can be indexed to hexagonal Co(OH)₂ (JCPDF: 30-0443). (Marked “#” for Ni substrate, JCPDF: 04-0850) Energy disperse spectroscopy with the powder scraped from H-NSAs, is showed in Figure S2, indicating the atomic ratio of Ni to Co in the nanosheets is about 1 to 3, which is coincident with literature.¹ As the literature,¹ taking the high phase similarity of Ni(OH)₂ (JCPDF: 14-0117) and Co(OH)₂ into consideration, the nanosheets are denoted as Ni_{0.25}Co_{0.75}(OH)₂. Moreover, according to the previous literature,¹ the mass of Ni_{0.25}Co_{0.75}(OH)₂ (marked for m₁) can be calculated by the equation 1 for ~ 3.58 mg·cm⁻².

Step 2: S-NSAs was obtained by immersing the as-prepared Ni_{0.25}Co_{0.75}(OH)₂ nanosheet arrays in 2 mol·L⁻¹ NaS₂ solution for 24 hours at room temperature. Then, the black samples were rinsed several times by distilled water, dried at 80 °C for 6 h (named S-NSAs), and weighted.

Step 3: The S-NSAs are used as the scaffold for the growth of electroactive materials (ultrathin rolled-up Co(OH)(CO₃)_{0.5} nanofilms arrays) through a facial hydrothermal method. In the procedure, 2-mmol Co(NO₃)₂·6H₂O and 4-mmol CO(NH₂)₂ were dissolved in 36 mL of distilled water and stirred to form a clear solution. The aqueous solution and the scaffold (S-NSAs) were transferred to a 40 mL Teflon-lined maintained at 90 °C for 6 h. The black sample was collected, subsequently rinsed with distilled water, dried at 80 °C for 6 h (named UTNFSAs), and weighed. Surprisingly, the weight is smaller than that of S-NSAs, indicating the S-NSAs might be dissolved in the third step. The similar phenomenon also was discovered by Sun and his

coauthors,² so that could be understood.

Characterization: The samples were examined by employing field-emission scanning electron microscopy (FESEM & Element mapping; Hitachi, S5500, SEM&EDS; Merlin), transmission electron microscopy (TEM; FEI, Tecnai G²20 and JEOL 2011), X-ray photospectroscopy (XPS, Escalab 250, Al K α), and X-ray powder diffractometer (XRD) with Cu -K α irradiation ($\lambda= 1.5418$ Å). The electrochemical measurements were carried out at room temperature in a three-electrode glass cell connected to an electrochemical workstation (CHI 660D, chenghua, shanghai.). Fresh film on the metal substrate (1 cm \times 1 cm) was used as the working electrodes. A platinum electrode and a saturated calomel electrode were used as counter and reference electrodes, respectively. Freshly prepared 2 mol/L KOH aqueous solution was used as the electrolyte.

Mass of active material calculation:

The H-NSAs of specific mass-loading ' m_1 ' were calculated according to article reported by Sun and his coworker¹ from the Δ mass using Equation 1, where ' Δm ' was the mass difference between the Ni foam before and after hydrothermal process (step 1), ' $M_{Ni_{0.25}Co_{0.75}(OH)_2}$ ' was the molar mass of $Ni_{0.25}Co_{0.75}(OH)_2$, $M_{Ni_{0.25}Co_{0.75}(OH)_2} - M_{Ni_{0.25}}$ instead the molar mass of $Co_{0.75}(OH)_2$.

$$m^1 = \frac{\Delta m \times M_{Ni_{0.25}Co_{0.75}(OH)_2}}{M_{Ni_{0.25}Co_{0.75}(OH)_2} - M_{Ni_{0.25}}} \quad (\text{Equation 1})$$

The specific mass ' $m_{Ni_{0.25}}$ ' of Ni reacted from Ni substrate were calculated using Equation 2. Subtract the mass ' $m_{Ni_{0.25}}$ ' from the initial mass of Ni foam and the mass of inactive material Ni ' m ' can be obtained.

$$m^{Ni_{0.25}} = \frac{\Delta m \times M_{Ni_{0.25}}}{M_{Ni_{0.25}Co_{0.75}(OH)_2} - M_{Ni_{0.25}}} \quad (\text{Equation 2})$$

The mass of electroactive materials in S-NSAs (m_2) and in UTNFSA (m_3) were calculated according to the difference between the mass ' m ' and the mass of S-NSAs and UTNFSA after reaction.

The specific capacitances C were calculated from the galvanostatic discharge curves using Equation 3, where ' I ' was the current applied, ' $\Delta V/\Delta t$ ' was the slope of the discharge curve, and ' m ' was the mass of the sample on one electrode. If the ' m ' was replaced by the unit area, the derived equation could be used to calculate the areal capacitance.

$$C = \frac{I\Delta t}{m\Delta V} \quad (\text{Equation 3})$$

Capacitance calculation:

Theoretical capacitance calculation: Theoretical specific capacitance is calculated as equation 4:

$$C_{theor} = \frac{Q}{U} \quad (\text{Equation 4})$$

Where U is the voltage window, Q is electrical energy per gram of active material.

For $\text{Co(OH)(CO}_3\text{)}_{0.5}$, theoretical specific capacitance can be calculated as follow:

$$C_{\text{theor/Co(OH)(CO}_3\text{)}_{0.5}} = \frac{Q}{U} = \frac{2Na * e}{U * M} = \frac{2 * 96320}{0.5 * 105.93} = 3637 \text{ F/g}$$

Where Na is Avogadro constant which is 6.02×10^{23} , e is 1.6×10^{-19} . M (molar mass) is 105.93 g/mol. When U is 0.5 V, the theoretical pseudocapacitance is 3637 F/g.

For $\text{Ni}_{0.25}\text{Co}_{0.75}\text{S}_x$, the theoretical pseudocapacitance is calculated according to following equation.

$$C_{\text{theor/Ni}_{0.25}\text{Co}_{0.75}\text{S}_x} = \frac{Q}{U} = \frac{(0.25 + 2 * 0.75) * 96320}{0.5 * M}$$

When x is 1, the molar mass (M) of $\text{Ni}_{0.25}\text{Co}_{0.75}\text{S}_x$ is 90.92, thus its theoretical pseudocapacitance calculated is 3708 F/g. When x is more than 1, the theoretical pseudocapacitance is less than 3708 F/g.

In our work, the theoretical specific pseudocapacitance for the hierarchical nanoarray should be between $C_{\text{theor/Co(OH)(CO}_3\text{)}_{0.5}}$ and $C_{\text{theor/Ni}_{0.25}\text{Co}_{0.75}\text{S}_x}$.

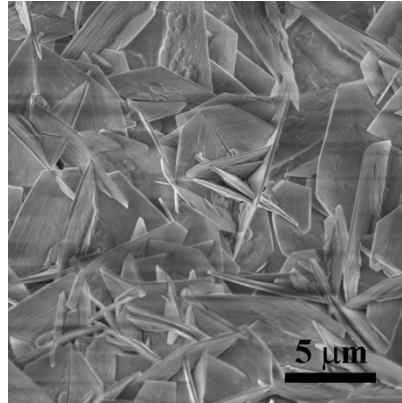


Figure S1. SEM image of H-NSAs.

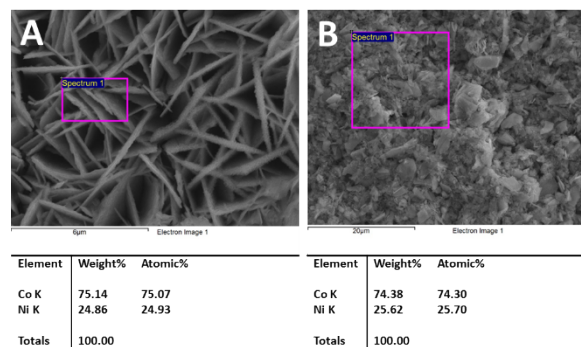


Figure S2. The ratio of the Nickel atoms and Cobalt atoms obtained by EDS in the corresponding boxed area of the SEM images, A) a small area and B) a big area. (The powder scratched from Ni foam substrate).

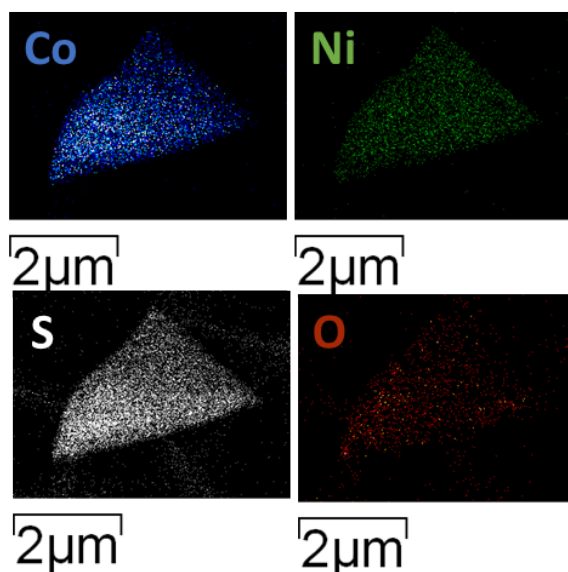


Figure S3. Elemental mappings of Co, Ni, S, and O acquired from a typical S-NSAs nanosheet by employing SEM (Hitachi S 5500).

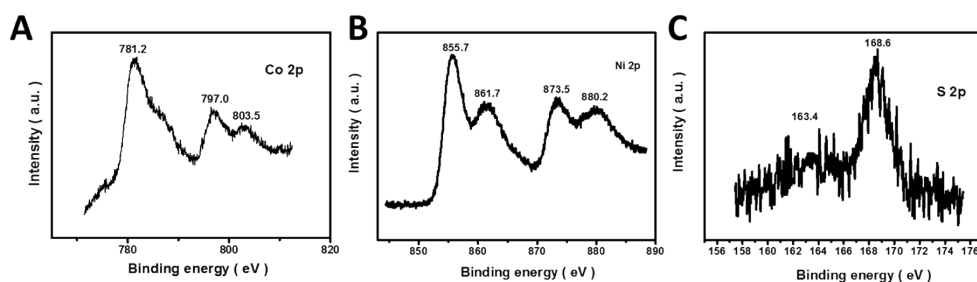


Figure S4. XPS spectra of A) Co 2p, B) Ni 2p, and C) S 2p with the UTNFSAs. The Co 2p XPS spectra of the composite exhibit two peaks at 781.2 and 797.0 eV, corresponding to the Co 2p_{1/2} and Co 2p_{3/2}, indicating the existence of Co²⁺ and the Ni 2p spectra show two obvious peaks at 855.7 and 873.5 eV which correspond to Ni 2p_{1/2} and Ni 2p_{3/2}. The main Ni 2p_{3/2} peaks is close to 854.9 eV for Ni²⁺ but much lower than 857.1 eV for Ni³⁺, suggesting that it was in the divalent state.³⁻⁵ In the S 2p spectrum, the appearance of the peak at 163.4 eV and 168.6 eV proves there is sulfur element in UTNFSAs.

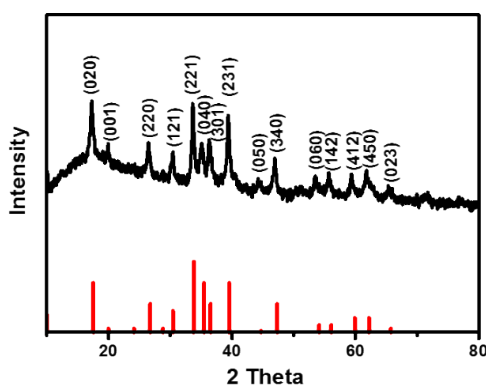


Figure S5. XRD patterns of the deposition in the procedure of step 3.

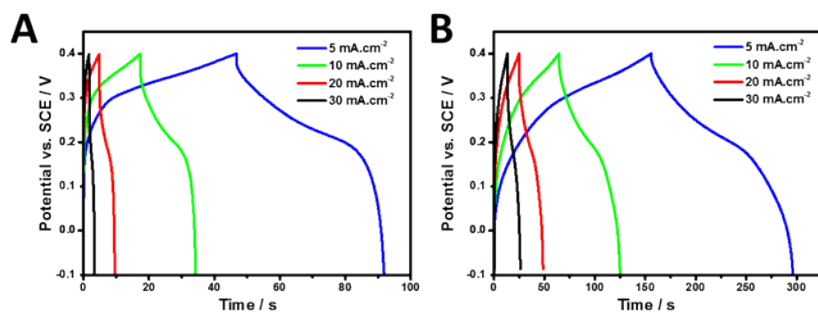


Figure S6. The galvanostatic charge/discharge curves of A) H-NSAs and B) S-NSAs at different current densities.

Table S1. Several calculated results of the H-NSAs, S-NSAs and UTNFSA.

Sample	Mass loading (mg cm^{-2})	Maximum areal capacitance (F cm^{-2})	Maximum specific capacitance (F g^{-1})
H-NSAs	3.58	0.45	125.59
S-NSAs	3.77	1.41	372.94
UTNFSA	3.45	5.9	1710.41

1. W. Zhu, Z. Lu, G. Zhang, X. Lei, Z. Chang, J. Liu and X. Sun, *Journal of Materials Chemistry A*, 2013, **1**, 8327-8331.
2. Q. Yang, Z. Lu, X. Sun and J. Liu, *Scientific Reports*, 2013, **3**.
3. M. Oku and K. Hirokawa, *Journal of Solid State Chemistry*, 1979, **30**, 45-53.
4. Y. Li, P. Hasin and Y. Wu, *Advanced Materials*, 2010, **22**, 1926-1929.
5. J. Xiao, L. Wan, S. Yang, F. Xiao and S. Wang, *Nano Letters*, 2014, **14**, 831-838.