

Electronic supplementary information

Bimetallic sulfide nanoparticles confined by dual-carbon nanostructures as anodes for lithium-/sodium-ion batteries

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Experimental section

1. Preparation of SDS/NiCoAl-LDH/GO precursor

The SDS/NiCoAl-LDH/GO precursor was prepared by using a co-precipitation method. In brief, a mixture was prepared by dissolving $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5 mmol), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (15 mmol), and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (5 mmol) in 100 mL of deionized water in a four-necked flask. 350 mg of graphene oxide (GO) aqueous suspension prepared by a modified Hummers method was ultrasonicated for 2 h in a 600 W ultrasonic cleaning machine, and then introduced into the above mixture solution with the continuous stirring for 30 min. A mixed solution of 0.5 mL of ammonia and 50 mL of 15 mM sodium dodecyl sulfate (SDS) was added dropwisely with vigorous stirring at 45 °C to keep the pH = 7, followed by sequential stirring for 30 min.

The obtained slurry was quickly transferred into a 100 mL Teflon vessel, and heated at 120 °C for 24 h. The obtained precipitates were centrifuged, washed with distilled water three times, and then subjected to the vacuum for drying.

2. Synthesis of $(\text{Ni}_{0.25}\text{Co}_{0.75})_9\text{S}_8/\text{N-CNTs/G}$ composite

The as-prepared precursor (80 mg) was dispersed in ethanol, and then 125 mg of thioacetamide was added. The mixture was sonicated for 10 min, and heated in a Teflon vessel at 120 °C for 24 h. The precipitate was collected, washed three times with distilled water, followed by drying. The as-prepared sulfide was grinded with melamine by a molar ratio of 1 : 3, then calcinated in a furnace under Ar atmosphere at 750 °C for 200 min at a ramping rate of 2 °C/min. The resulting $(\text{NiCo})_9\text{S}_8/\text{Al}_2\text{O}_3/\text{N-CNTs/G}$ was obtained after the selective removal of Al_2O_3 by using 10% hydrochloric acid for 20 h.

For comparison, $(\text{NiCo})_9\text{S}_8/\text{rGO}$ was prepared under the identical experimental conditions without melamine for calcination.

3. Characterization

X-ray diffraction (XRD) patterns was measured by using a Shimadzu XRD-6000 diffractometer filtered Cu K α radiation ($\lambda=1.5418 \text{ \AA}$). The scanning electron microscope (SEM, ZEISS Supra 55) with energy-dispersive X-ray spectroscopy was used to image the morphologies and dimensional sizes of the products. High-resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL JEM-3010 electron microscope with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) (Thermo VG Scientific) was recorded under high vacuum on samples dried onto silicon wafers using Al K α radiation of 1486.6 eV at 400 W (15 kV). Elemental analysis was employed for metal ions using a Shimadzu inductively coupled plasma optical emission spectrometer (ICP-OES).

4. Electrochemical measurements

The electrochemical properties were evaluated by using CR2032 coin-type cells, which were assembled in an Ar-filled glove box (H_2O and $\text{O}_2 < 0.1 \text{ ppm}$). Active material, Ketjen black, and poly (vinyl difluoride) (PVDF, Aldrich) were mixed into a uniform slurry, with a weight ratio of 7 : 2 : 1, and then cast on a Cu foil (99.6%, Goodfellow) to prepare the working electrodes. Then the working electrodes were dried at 80 °C under vacuum for 12 hours. The loading mass of the active material was ca. 10 mg cm⁻². Pure Li foil was used as the counter electrode, and Celgard 2400 film as a separator. The electrolyte was 1M LiPF₆ in ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC, 1:1:1 by volume), with 2% vinylene carbonate added. The cells were galvanostatically charged and discharged between 0.01 and 3.0 V (vs. Li⁺/Li or Na⁺/Na) on a Land CT2001A battery testing system (Land, P.R. China) at the constant temperature (25 °C).

The assembly and electrochemical measurement of the electrode for SIB is same to those for LIBs, except for the electrolyte. The electrolyte was a solution of 1 M NaClO₄ in ethylene carbonate/propylene carbonate (EC/PC, 5% fluoroethylene carbonate). A pure Na foil was used as the counter electrode and porous glass fiber (GF/D) was used as the separator. The discharge and charge measurements were carried out over a voltage range of 0.02–2.7 V.

Electrochemical impedance spectral (EIS) measurements and the cyclic voltammetry (CV) measurements were performed, with an electrochemical workstation (CHI 760E, ChenHua, Shanghai, China) at room temperature. The cyclic voltammetry experiments are firstly performed using coin-type cells with cut-off voltage of 0.01–3.0 V vs. Li⁺/Li or Na⁺/Na at a scan rate of 0.1 mV·s⁻¹.

Figure S1

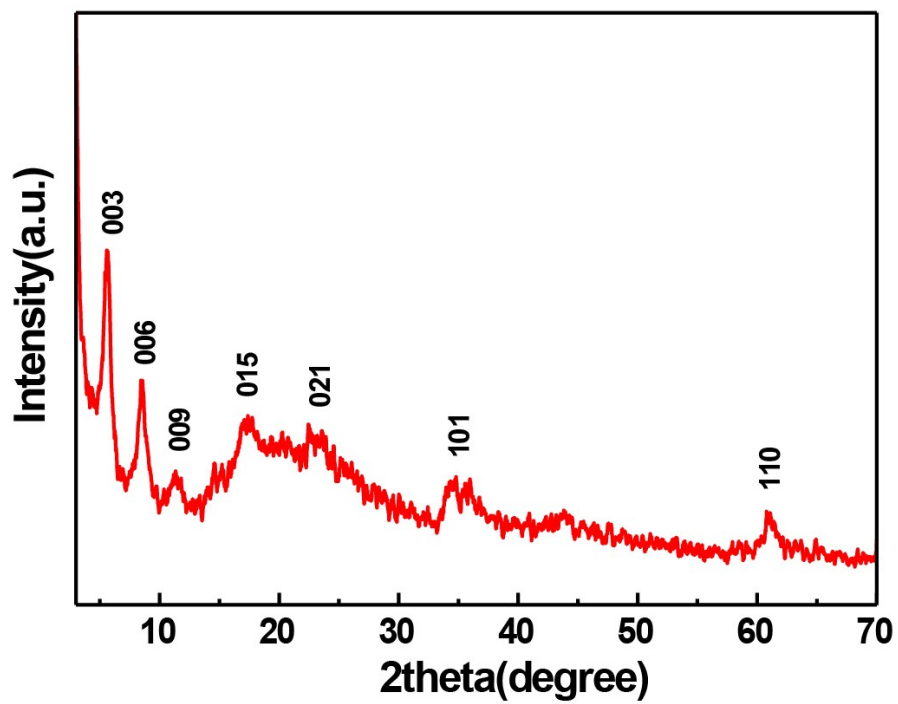


Fig. S1 The XRD patterns of SDS/NiCoAl-LDH/rGO precursor.

Table S1

Table S1 Atomic ratio of the product obtained by ICP-ES.

ICP-OES	Elemental content/ppm	Relative atomic ratio
$(\text{Ni}_x\text{Co}_y)_9\text{S}_8/\text{N-CNTs/rGO}$	Co	2.45
	Ni	1

Figure S2

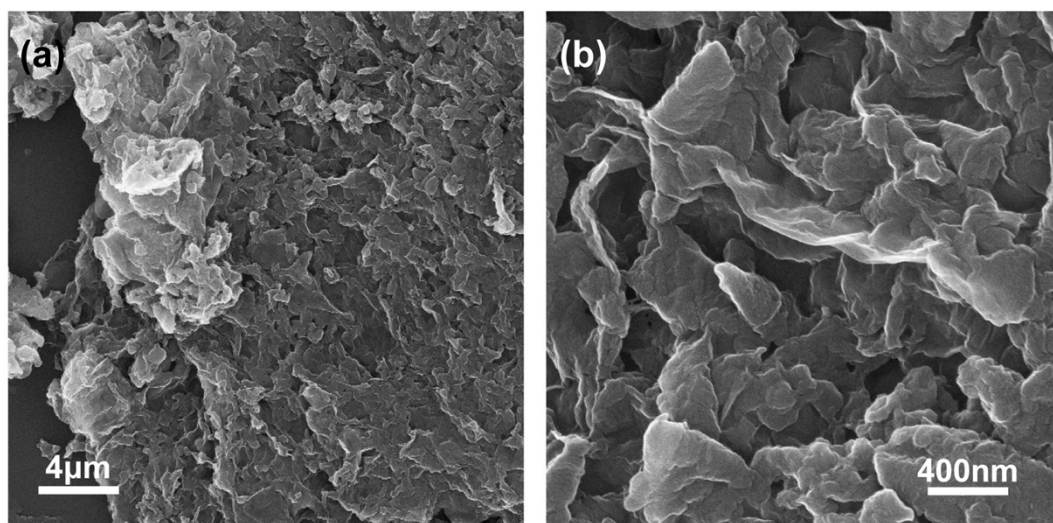


Fig. S2 SEM images of the SDS-intercalated NiCoAl-LDH/rGO precursor.

Figure S3

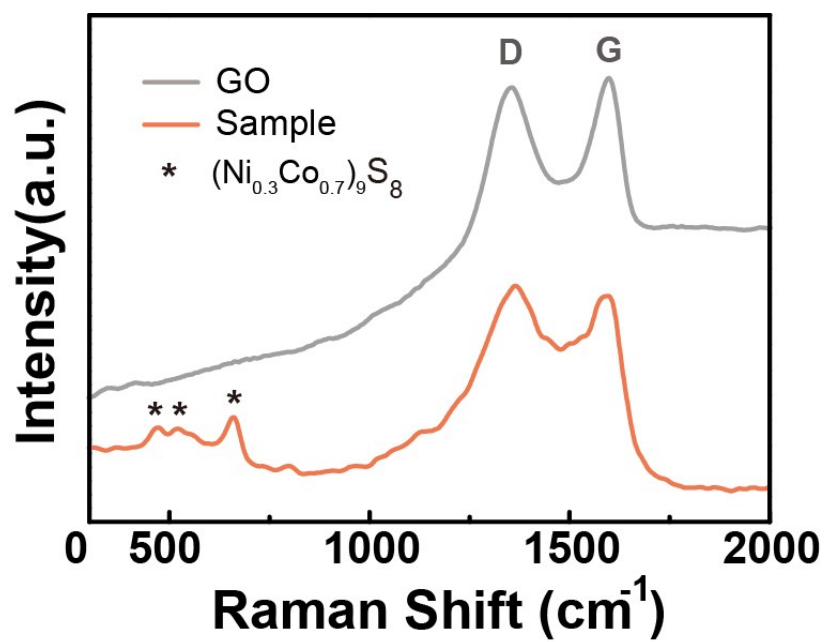


Fig. S3 Raman spectra of the (Ni_{0.3}Co_{0.7})₉S₈/N-CNTs/rGO composite.

Fig. S4

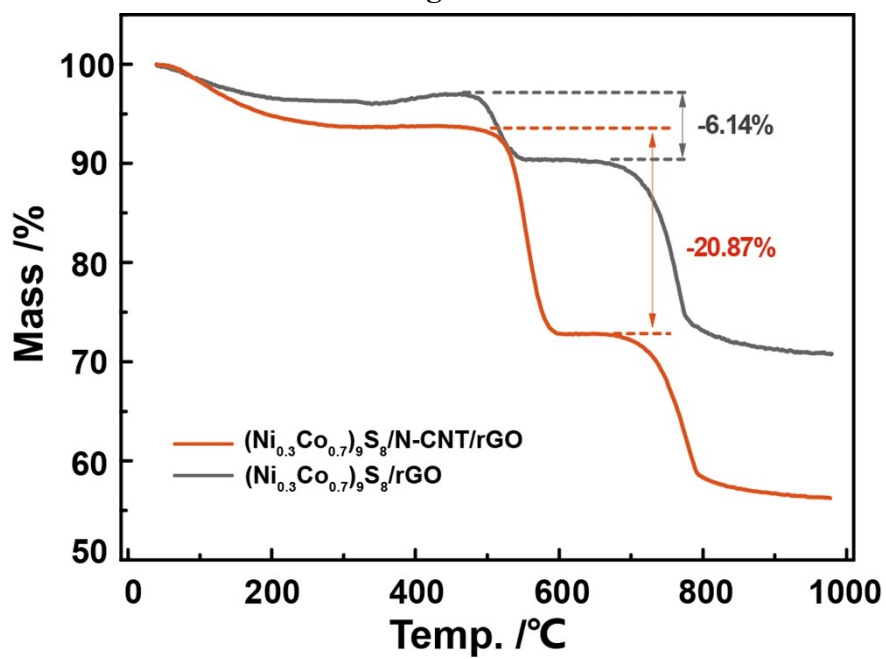


Fig. S4 The TG curves of $(\text{Ni}_{0.3}\text{Co}_{0.7})_9\text{S}_8/\text{N-CNTs}/\text{rGO}$ and $(\text{Ni}_{0.3}\text{Co}_{0.7})_9\text{S}_8/\text{rGO}$.

Figure S5

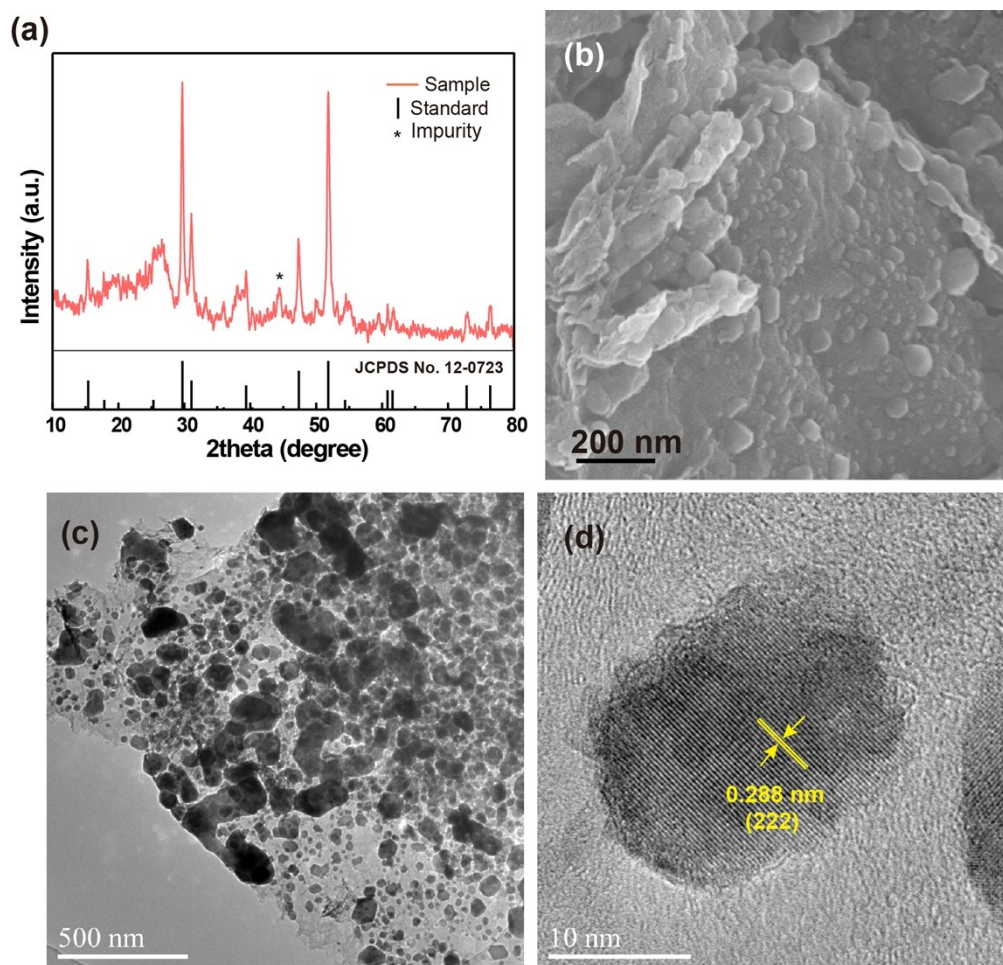


Fig. S5 The control sample $(\text{Ni}_{0.3}\text{Co}_{0.7})_9\text{S}_8/\text{rGO}$ (a) The XRD pattern; (b) SEM images (c) TEM images and (d) HRTEM images.

Figure S6

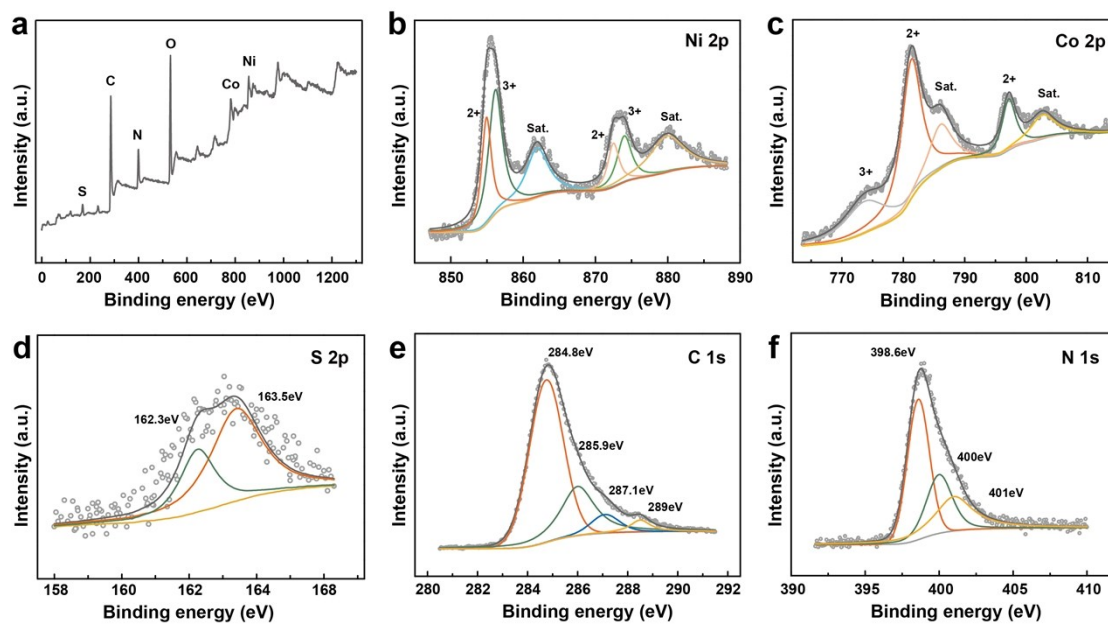


Fig. S6 XPS spectra: (a) a survey, (b) Co 2p, and (c) Ni 2p, (d) S 1s, (e) C 1s, and (f) N 1s spectra.

Figure S7

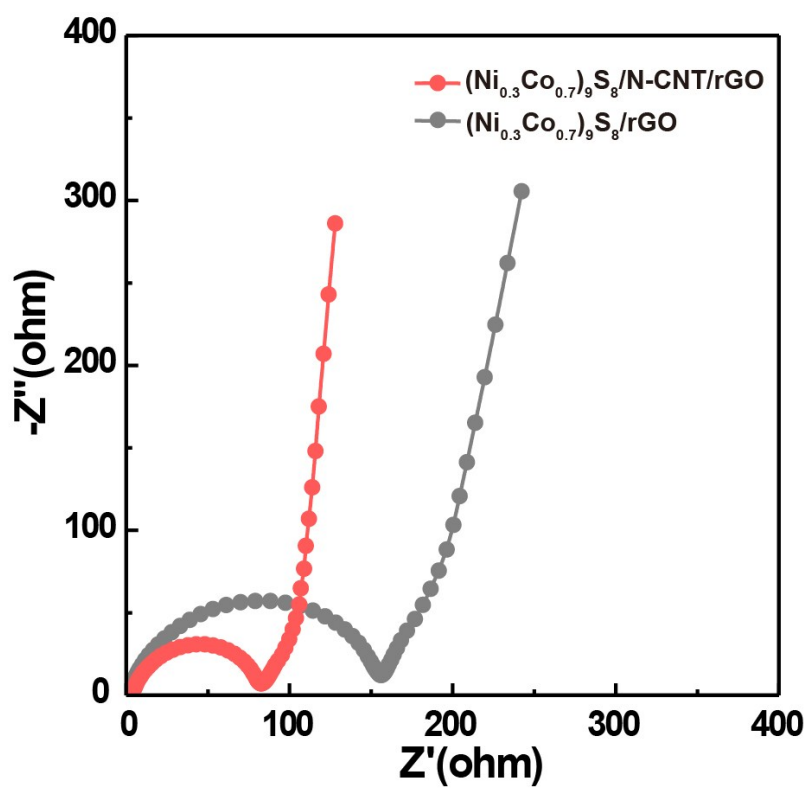


Fig. S7 The Nyquist plots of $(\text{Ni}_{0.3}\text{Co}_{0.7})_9\text{S}_8/\text{N-CNTs}/\text{rGO}$ and $(\text{Ni}_{0.3}\text{Co}_{0.7})_9\text{S}_8/\text{rGO}$ electrode.