

Supporting Information

Long-term cycling stability of NiCo₂S₄ hollow nanowires supported on biomass-derived ultrathin N-doped carbon 3D networks as anode for lithium-ion batteries

Xiaoyu Wu, Songmei Li,* Bo Wang, Jianhua Liu, Mei Yu

Key Laboratory of Aerospace Advanced Materials and Performance of Ministry of Education, School of Materials Science and Engineering, Beihang University, Beijing, 100191, P. R. China

* Corresponding author. Tel: +86 10 82317103; fax: +86 10 82317103.
E-mail address: songmei_li@buaa.edu.cn.

Experimental Section

Synthesis of the Chitin-NC substrates

The synthesis of Chitin-NC substrate was based on a modified repeated freezing-thawing process as we reported before.^{1, 2} In a typical synthesis, the chitin powder (purchased from Golden-Shell Biochemical Co. Ltd. (Zhejiang, China)) was washed by NaOH (5 wt. %) and HCl (7 v/v% HCl) aqueous solutions repeatedly to remove the residual protein and mineral. Then 5 g of the purified chitin powders, 11g of NaOH, and 4g of urea were dispersed into 100 mL of DI water with rigorous stirring. The obtained suspension was frozen at -30 °C for 4 h and thawed at room temperature repeatedly, until the chitin powders were dissolved completely to form a pale yellow solution. After centrifuged to remove air bubbles, the chitin-based solution was spread on a glass plate to form a film of ~0.2 mm in thickness. Subsequently, the film loaded on glass plate was immersed into ethanol as coagulants and kept for 2 h to obtain chitin hydrogels, and washed by running water until the NaOH and urea were removed. It should be noted that the chitin hydrogel films were punched into wafers of 12 mm in diameter here after washing for the subsequent applications. After being frozen rapidly by liquid nitrogen and dried in a freezer dryer, the dried chitin-based wafers were carbonized in argon atmosphere at 800 °C for 2 h to obtain the products of chitin-derived N-doped carbon (Chitin-NC).

Synthesis of the NiCo₂S₄/Chitin-NC composites

In order to obtain well-mixed NiCo₂S₄/Chitin-NC composites with integrated structures, the Ni²⁺ and Co²⁺ ions were firstly introduced during the preparation of the Chitin-NC substrates. Typically, after the removal of NaOH and urea by running water-washing as mentioned above, the chitin hydrogel films were punched into wafers of 16 mm in diameter for the subsequent use as battery electrode. Then the chitin wafers were immersed into a Ni²⁺/Co²⁺-based aqueous solution containing 0.2 M Co(NO₃)₂·6H₂O and 0.1 M NiCl₂·6H₂O, and kept under vacuum at 60 °C for 12 h with continuous stirring to promote the infiltration of Ni²⁺ and Co²⁺ ions into the chitin-based wafers. When immersing into NaOH solution, these nearly transparent wafers turned into dark in color, which can be described to the formation of Ni(OH)₂ and Co(OH)₂ precipitates,

thus confirming the existence of Ni^{2+} and Co^{2+} ions in the wafers. Then the as-prepared $\text{Ni}^{2+}/\text{Co}^{2+}$ -involved chitin wafers were dried and carbonized as before to obtain the $\text{Ni}^{2+}/\text{Co}^{2+}$ -involved Chitin-NC substrates. The growth of NiCo_2S_4 nanoarchitectures on the substrates was based on a modified hydrothermal reaction and the following sulfurization. Before the hydrothermal reaction, 0.24 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.58 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.22 g of urea and 0.29 g of hexadecyl trimethyl ammonium bromide were dissolved in 20 mL of DI water with stirring to form a transparent pink solution. After putting a piece of $\text{Ni}^{2+}/\text{Co}^{2+}$ -involved Chitin-NC wafer, the reaction solution was then kept under vacuum at 60 °C for 12 h with continuous stirring to further facilitate the efficient infiltration of $\text{Ni}^{2+}/\text{Co}^{2+}$ -based solution with the substrate. After that, the solution with chitin-based wafer was transferred to a Teflon-lined stainless steel autoclave and heated at 120 °C for 2 h, and then cooled down naturally to room temperature. The obtained NiCo-precursors/Chitin-NC composites were rinsed by DI water and ethanol carefully, then immersed into a 0.1 M Na_2S solution and heated at 160 °C for 12 h. After cooling, the as-prepared $\text{NiCo}_2\text{S}_4/\text{Chitin-NC}$ composites were taken out carefully from the solution and washed by hot DI water (preheated at 80 °C) and ethanol several times to remove the leftover reactants as well as the sulfur deposition that may existed, and then dried at 60 °C overnight. The NiCo-precursor residues at the bottom of the autoclave were also washed and sulfurized into NiCo_2S_4 powders with the same manners, and collected as a comparison sample for the subsequent characterization and performance measurement. And for comparison, $\text{NiCo}_2\text{S}_4/\text{Chitin-NC}$ composites with different mass loading of NiCo_2S_4 have been synthesized by adjusting the ratio of raw materials.

Microscopic Characterization

Powder X-ray diffraction system (XRD, Rigaku D/max 2200PC) equipped with Cu $K\alpha$ radiation was used to determine the crystallographic structures of the as-prepared products. Their morphology and structures were characterized by a JEOL JSM-7500F scanning electron microscope (SEM) and a JEOL JEM-2100F transmission electron microscope (TEM). Energy-dispersive X-ray spectroscopy (EDS) equipped on the SEM was used to determine the elemental compositions. And the chemical compositions and

valence states of the products were further characterized by the AXIS UTLTRADLD X-ray photoelectron spectroscope (XPS), which was equipped with a dual Mg K α -Al K α anode for photoexcitation. N₂ adsorption/desorption measurements were performed on an ASAP-2010 surface area analyzer. Thermal gravimetric analysis (TGA) was carried out on a Pyris Diamond TG/DTA under a static air atmosphere in the temperature range of 25-700 °C to analyze the content of NiCo₂S₄ in the composites.

Electrochemical measurements

For the battery test, the electrochemical lithium storage performance of these products was measured based on CR2025 coin-type cells assembled in an argon-filled glove box. The as-synthesized Chitin-NC and NiCo₂S₄/Chitin-NC composites wafers with ~12 mm in diameters and ~0.2 mm in thickness were used directly as working electrodes without any conductive additives and polymer binders. The specific mass loading of the active material (NiCo₂S₄) for the testing electrodes were calculated by the average weight of 10 pieces of the wafers, which are consistent with the TGA results. However, considering the electrochemical activity of Chitin-NC, the specific capacities of the composites were calculated on the weight of the whole anode, not only just the NiCo₂S₄. A piece of Li foil was used as both the counter electrode and the reference electrode, the Celgard 2400 polypropylene microporous film was used as separator, and a solution of 1 M LiPF₆ in ethylene carbonate and dimethyl carbonate (1:1, v/v) was used as electrolyte. And the collected NiCo₂S₄ powders were also assembled into working electrodes for comparison by pasting a N-methylpyrrolidinone (NMP) slurry on Cu foils. The NMP slurry was composed of the NiCo₂S₄ powders, conductive carbon black and polyvinylidene fluoride binder (8:1:1, w/w/w). Cyclic voltammetry (CV) curves were measured by a multichannel Arbin BT2000 battery-testing system at a scan rate of 0.1 mV s⁻¹. And the galvanostatic charge-discharge measurements, as well as the galvanostatic intermittent titration technique (GITT) measurements were performed on a LAND CT2001A battery-testing instrument. All these electrochemical tests were conducted in the potential range of 0.005-3V (vs. Li⁺/Li). Electrochemical impedance spectroscopy (EIS) measurements were performed using a Princeton PARSTAT 2273 electrochemistry system in the frequency range from 100 kHz to 0.01 Hz.

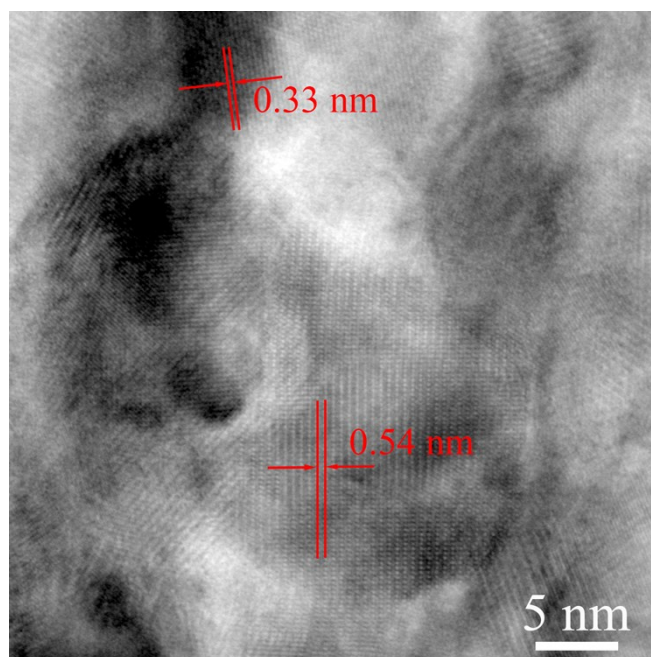


Fig. S1 HRTEM image of the NiCo₂S₄ hollow nanowires dispersed from the composites.

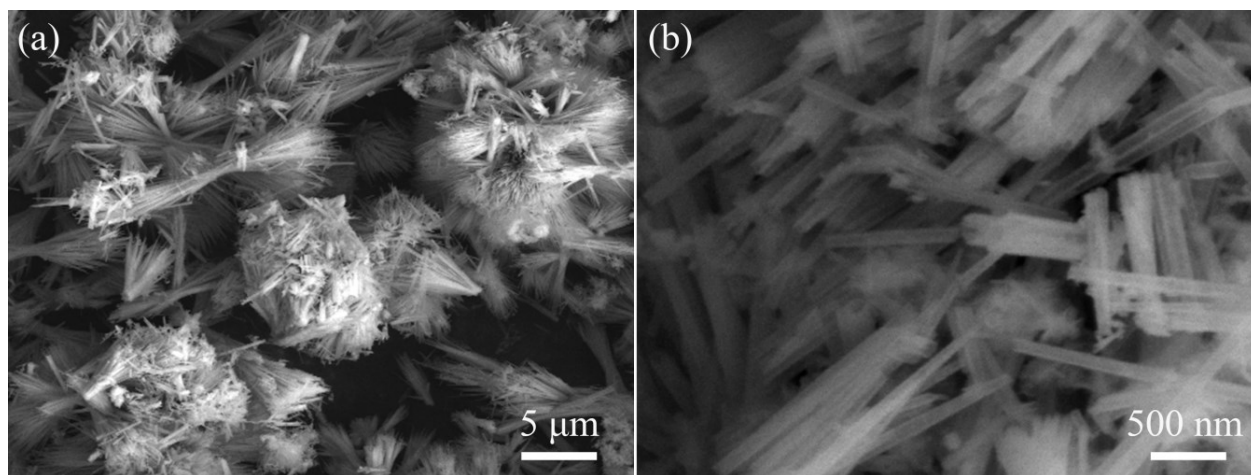


Fig. S2 Typical SEM images of the collected NiCo₂S₄ powders.

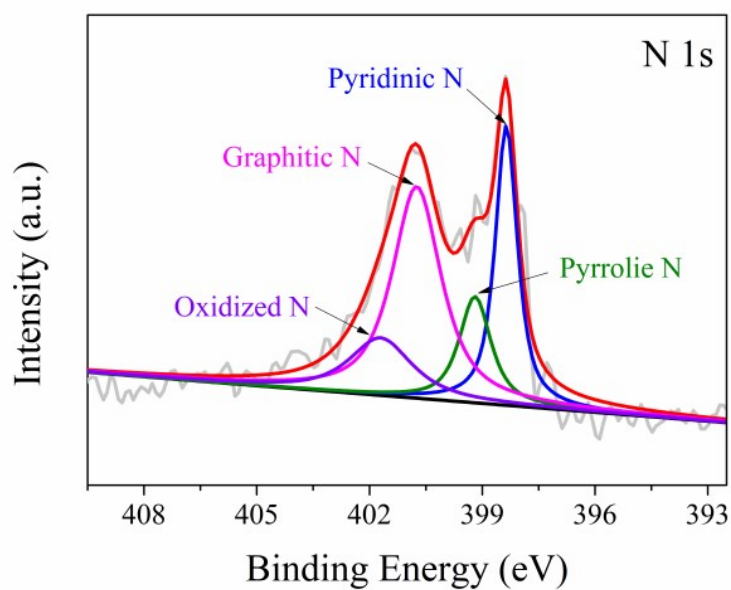


Fig. S3 High-resolution N 1s XPS spectrum of the NiCo₂S₄/Chitin-NC composites and its deconvolution spectra.

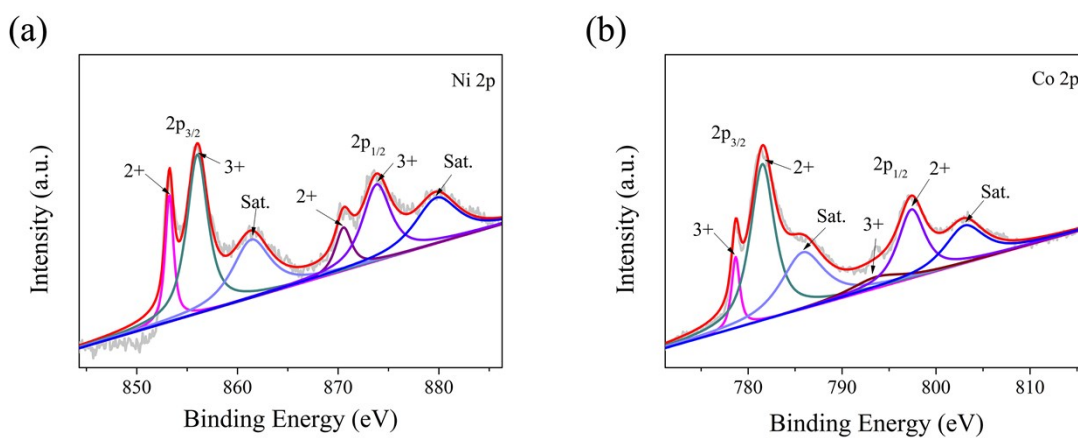


Fig. S4 High-resolution XPS spectra of (a) Ni 2p and (b) Co 2p in the NiCo₂S₄/Chitin-NC composites and their deconvolution spectra.

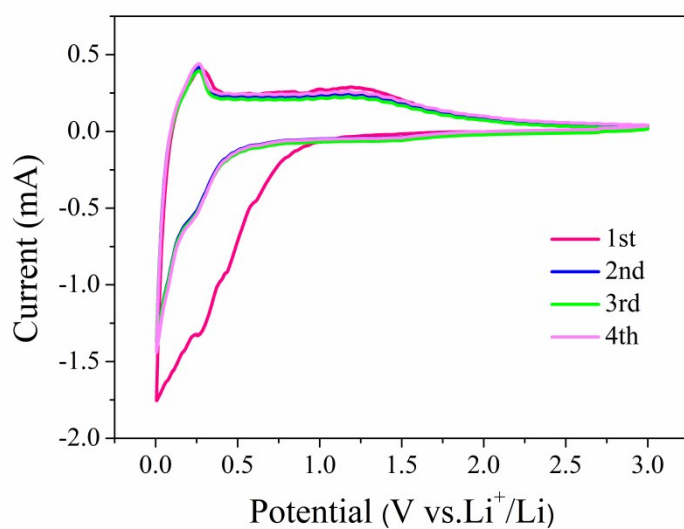


Fig. S5 CV curves of the Chitin-NC electrode at 0.1 mV s^{-1} from 0.005 to 3.0 V.

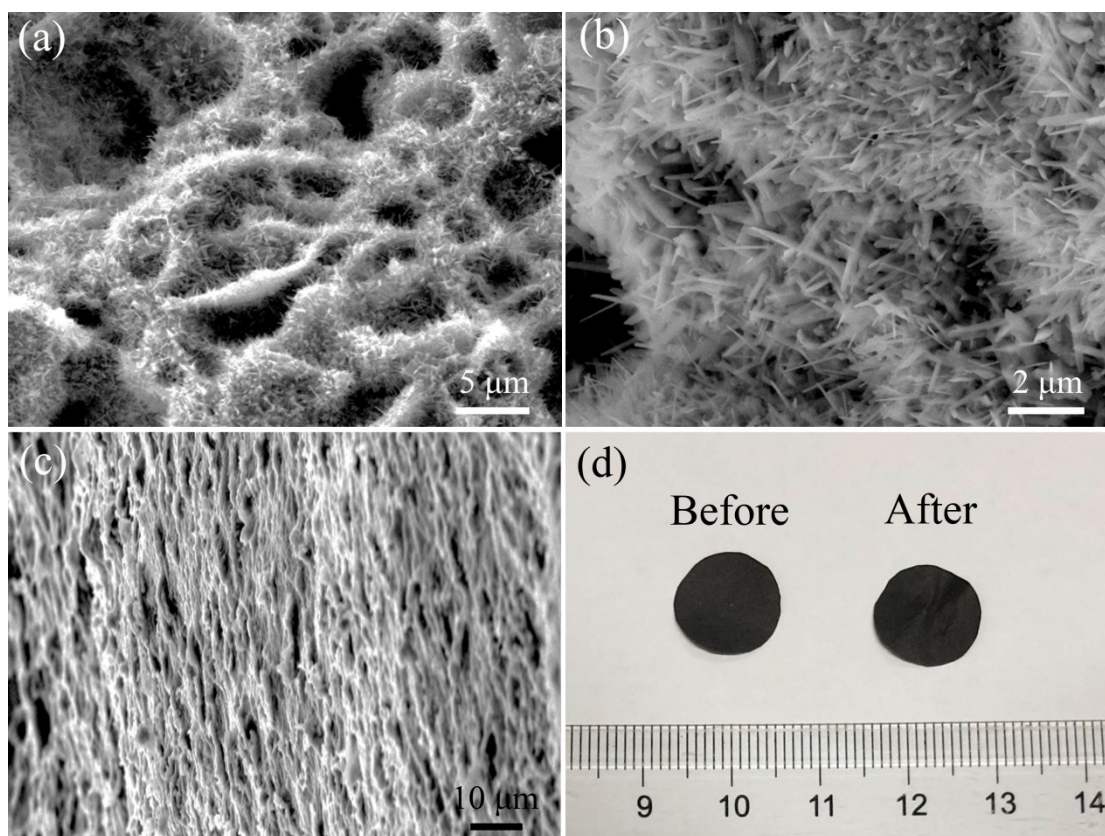


Fig. S6 (a-c) SEM images of the $\text{NiCo}_2\text{S}_4/\text{Chitin-NC}$ composites after 500 cycles, (d) optical image of the $\text{NiCo}_2\text{S}_4/\text{Chitin-NC}$ electrode wafer before and after 500 cycles.

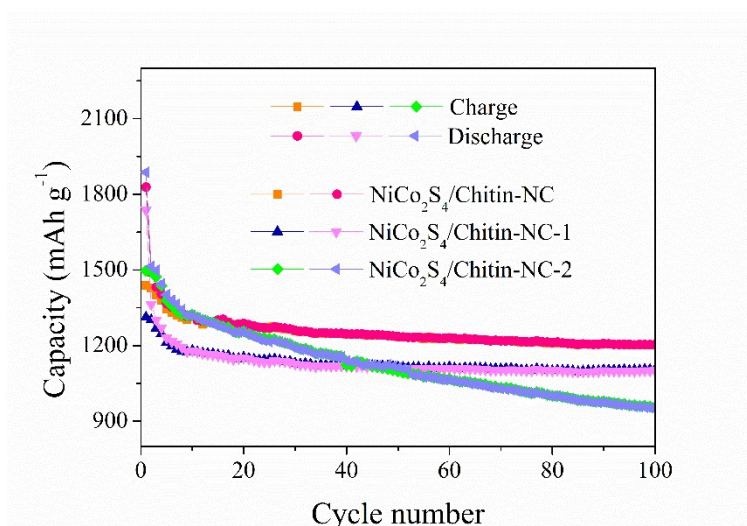


Fig. S7 Comparison of cycling performance of the NiCo₂S₄/Chitin-NC composites electrodes with different mass loading of NiCo₂S₄ at 500 mA g⁻¹ (NiCo₂S₄/Chitin-NC 0.31 g; NiCo₂S₄/Chitin-NC-1 0.19 g; NiCo₂S₄/Chitin-NC-2 0.40 g).

Table S1 Comparison of the lithium-storage performance

Anode materials	Capacity (mAh g ⁻¹)	Current rate (mA g ⁻¹)	Cycles	Ref.
NiCo ₂ S ₄ /Chitin-NC	1198	500	500	This work
NiCo ₂ S ₄ @C	427	500	500	3
NiCo ₂ S ₄ /Ni _{0.96} S	965	200	100	4
CoS-NP/ACF	576.7	100	200	5
CoS NFs-rGO	939	100	100	6
NiS NFs-rGO	521	100	100	6
NiS-graphene	887	59	60	7
NiS ₂ /CNHs	490	3000	5000	8
CoS/CNT	521	100	100	9
NiS/CNT	546	100	100	9

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