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Supporting Information

Phase Boundary Enhanced Ni_3N-Co_3N@CNTs Composite Materials for Lithium Ion Batteries

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1. Materials and methods

1.1 Synthesis of metal nitrides and CNTs composite materials

1.1.1 Synthesis of Ni_3N-Co_3N@CNTs

The Ni_3N-Co_3N@CNTs was produced according our previous work[1]. 15 mg sulfonated polystyrene coated CNTs were ultrasonic dispersion in 40 mL deionized water. For synthesis of Ni_3N-Co_3N@CNTs, 225 mg $Ni(NO_3)_2 \cdot 6H_2O$, 225 mg $Co(NO_3)_2 \cdot 6H_2O$, 35.5 mg hexamethylenetetramine and 7.25 mg citric trisodium salt dehydrate were added to above solution. Then the mixed solution was heated to 90 °C for 6 h with stirring. The black products Ni-percursor@CNTs were collected by centrifugation. After washed with deionized water and ethyl alcohol for several times, the products were transferred to vacuum oven dried at 60 °C for 12 h. The Ni_3N@CNTs finally were obtained by annealing Ni-precursor@CNTs at 375 °C for 2 h with heating ramp rate of 1 °C min^{-1} under ammonia flows velocity of 140 sccm.

1.1.2 Synthesis of Ni_3N@CNTs

The method is same as synthesis of Ni_3N-Co_3N@CNTs without the addition of $Co(NO_3)_2 \cdot 6H_2O$ in the reaction solution.

1.1.3 Synthesis of Co_3N@CNTs

The method is same as synthesis of Ni_3N-Co_3N@CNTs without the addition of $Ni(NO_3)_2 \cdot 6H_2O$ in the reaction solution.

1.2 Characterization

SEM images were collected using a JSM-7000F field-emission scanning electron microscopy (FESEM; HITACHI, su-8010) and TEM images were collected by using a JEM-2100 transmission electron microscope (JEOL, JEM-2100). Crystallographic information of the sample was collected using powder X-ray diffraction (XRD; Rigaku Smartlab X-ray diffractometer). Element analysis was tested using X-ray photoelectron spectroscopy (Kratos, AXIS ULtrabld). Thermogravimetric analysis (METTLER-TOLEDO TGA 1) was carried out under a flow of air with a temperature ramp of 10 ^{o}C/min from room temperature to 800 ^{o}C.

1.3 Electrochemical Measurements

The lithium storage performances were tested in 2025-type coin cell. The electrodes were prepared by mixing active materials (70%), conductive carbon black (super P, 20%) for conductive agent and Polyvinylidene Fluoride (10%) as binding materials. The electrode mass loading is circa 1.5 mg cm^{-2}. Pure lithium metal foil is used for counter electrode and the separator is microporous polypropylene film. The electrolyte is 1.0 M $LiPF_6$ in 1:1 w/w ethylene carbonate/diethyl carbonate. The CV tests are received from electrochemical workstation Chenhua CHI660e (Shanghai , China). The cycling performances were evaluated by Neware battery testing system (CT-4008). To characterize the resistance change during the cycling process, the electrochemical impedance spectra (EIS) were also collected on CHI 660e for with an amplitude of 5 mV over a frequency range from 100 kHz to 0.01 Hz.

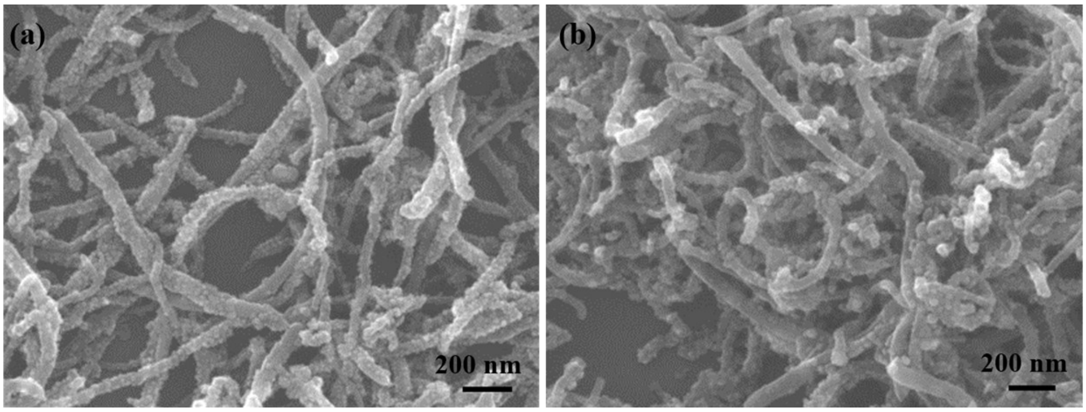

Figure S1. SEM images of a) Ni_3N@CNTs and b) Co_3N@CNTs.

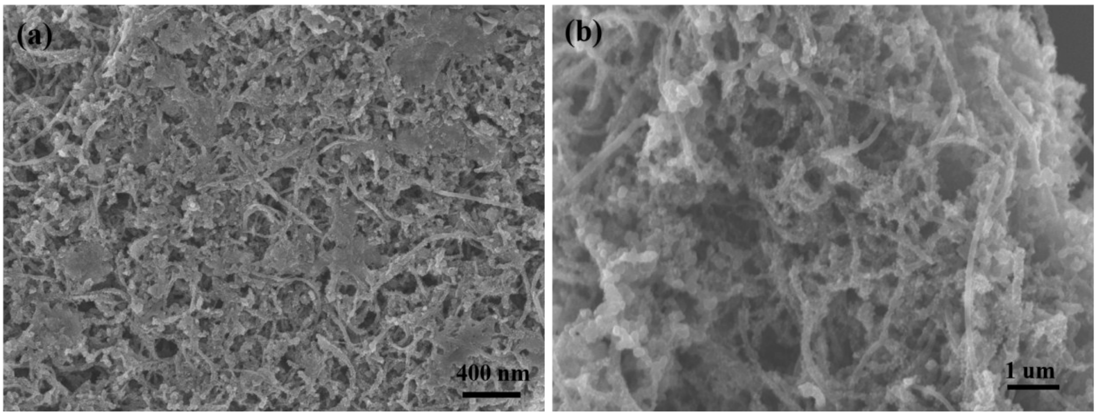

Figure S2. FESEM images of Ni_3N-Co_3N@CNTs after 30 cycles.

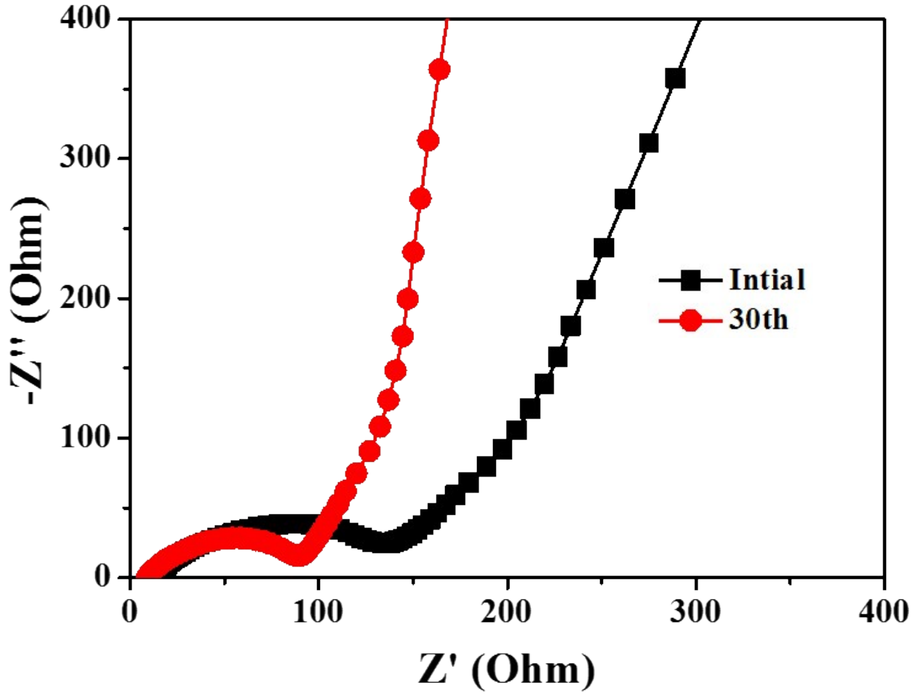

Figure S3. Nyquist plots of the Ni_3M-Co_3N@CNTs electrode measured with an amplitude of 5 mV over a frequency range from 100 kHz to 0.01 Hz.

Table S1. Comparison in lithium storages of our work with previous literatures.

Materials	Current density	Capacity	Cycle number	Reference
Co_3N thin film	7 μA cm^{-2}	420 mAh g^{-1}	40	2
Fe_3N thin film	7 μA cm^{-2}	440 mAh g^{-1}	40	2
Ni_3N thin film	7 μA cm^{-2}	320 mAh g^{-1}	40	3
Fe_3N@Carbon cages	100 mA g^{-1}	370 mAh g^{-1}	500	4
$Ni_{0.33}Co_{0.67}N$	250 mA g^{-1}	400 mAh g^{-1}	50	5
Ni_3N@carbon cloth	1 C	498 mAh g^{-1}	120	6
Cu_3N nanoparticles	1 A g^{-1}	290 mAh g^{-1}	150	7
Ni_3N nanoparticles	100 mA g^{-1}	350 mAh g^{-1}	50	8
TiN@MWCNTs	300 mA g^{-1}	447 mAh g^{-1}	100	9
Ni_2N thin film	120 mA g^{-1}	461.9 mAh g^{-1}	100	10
Ni_3N@CNTs	400 mA g^{-1}	249.8 mAh g^{-1}	600	This work
Co_3N@CNTs		327.4 mAh g^{-1}		
Ni_3N-Co_3N@CNTs		553.26 mAh g^{-1}		

Table S2. Comparison in capacitive contributions for lithium storage of our designed Ni_3N-Co_3N@CNTs composites with previously reported literatures.

Material	Scan rate (mV s^{-1})	Capacitive effects	Reference
TiO_2 nanoparticles	0.5	55%	11
TiO_2@C	1	63.86	12
Co_3O_4@N-carbon sphere	1	68.2	13
rGO/Fe_3O_4/AC	1	67.3%	14
Ni_3N-Ni_3S_2 nanoparticles	1	35.2%	15
MoO_{3-x}@glucose	1.1	32.1%	16
pristine Nb_2O_5	1	77%	17
Sn@carbon sphere	0.4	43.3%	18
Ni_3N-Co_3N@CNTs	1	80.42%	This work

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