Anchoring Ni$_3$FeN on a carbon nanofibers as an efficient polysulfide adsorption and catalyst center for improved Li-S battery

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Experimental section

Synthesis of NiFe-LDH and Ni₃FeN. 170 mg $Fe(NO_3)_3 \cdot 9H_2O$, 367.5 mg $Ni(NO_3)_2 \cdot 6H_2O$, and 9 g urea were dissolved in 50 mL water and stirred in oil bath (synchronous reflux device) at 100 °C for 6 h. After the reaction, the NiFe-layered double hydroxides (NiFe-LDH) were washed (vacuum filtered) three times with deionized water, and then freeze-dried for 12 h. Then, the as-prepared NiFe-LDH was treated at 400 °C in ammonia atmosphere for 2 h to prepare Ni_3FeN.

Synthesis of CNFs@Ni₃FeN and CNFs. 1.2 g Polyacrylonitrile (PAN) (Mw=150000), 0.012 g Polystyrene (PS) (Mw=280000) and 0.1 g F127 were dissolved in 10 mL N, N-dimethylformamide (DMF) under intense stirring at 50 °C, then the synthesized Ni_3FeN was added and stirred together to obtain the precursor. The precursor was injected into the syringe to prepare carbon nanofibers, which were spun at the voltage of 18 kV and the speed of 0.5 mL/h. The distance between the tip and the rotating cylinder was maintained at 16 cm, and the nanofibers were collected at the speed of 30 rpm through a rotating drum coated with aluminum foil. After electrospinning, the fibers were stabilized in air at a speed of 1 °C/min for 2 h at 260 °C. Subsequently, the fibers were carbonized in argon atmosphere (800 °C, 2 h) to obtain the composite of porous carbon nanofiber and Ni_3FeN, which is recorded as CNFs@Ni₃FeN. The CNFs was synthesized by the same method as CNFs@Ni₃FeN without introducing Ni_3FeN.

Synthesis of CNFs@Ni₃FeN@S and CNFs@S. A certain amount of sulfur powder was dissolved in CS_2. After the sulfur powder was completely dissolved, the CNFs@Ni₃FeN sheet was added to the S solution, in which the mass ratio of sulfur powder to CNFs@Ni₃FeN was 4:1. Then, the sample was transferred to the ventilator. After the CS_2 was volatilized completely, the mixture of CNFs and S was placed in the ampoule bottle and sealed with a spray gun. Afterwards, the mixture was heated to 155 °C at a rate of 5 °C/min and heat treated for 12 h to fully mix CNFs@Ni₃FeN and sulfur powder to get CNFs@Ni₃FeN@S. The synthesis method of CNFs@S was the same as the above method CNFs@Ni₃FeN@S.

Materials Characterization

X-ray diffraction (XRD) was used for qualitative phase analysis of materials (Cu Kα, λ=1.5418 Å, 10°~90°, 20°/min, 40 KV, 30 mA, Bruker D8, Japan). The scanning electron microscopy (SEM) (AMRAY 1000B) and transmission electron microscopy (TEM) (JEM-2010) was used to observe the morphology of the material. The Fourier transform infrared (FT-IR) spectra of the materials were evaluated on Nicolet IS10

(Thermo Fisher Scientific). The content and valence of elements and the bond cooperation between elements were evaluated by X-ray photoelectron spectroscopy (XPS) recorded by k-alpha (Thermo Fisher Scientific Company), in which the radiation source was mono Al Kα. The Raman spectrum was carried out on RM-1000 (Renishaw) and the excitation laser was 632.8 nm. The loading amount of S in the material was determined by thermogravimetric analysis (TGA) in N_2 atmosphere (heating rate 10 °C/min) (TG50 analyzer, Mettler-Toledo).

The preparations of Li_2S_4 and Li_2S_6 catholyte

(1) Preparation of Li_2S_4 electrolyte (0.02 mol/L)： The mixture of lithium sulfide (Li_2S) and sulfur powder with a molar ratio of 1:3 was added to 1,2-dimethoxyethane (DME), and then the Li_2S_4 solution was obtained by magnetic stirring for 24 h, so that the polysulfide adsorption experiment could be carried out in the later stage.

(2) Preparation of Li_2S_6/Tetraethylene glycol dimethyl ether electrolyte (2.5 mol/L): The mixture of lithium sulfide (Li_2S) and sulfur (S_8) with a molar ratio of 1:5 was added to the LiTFSI (lithium bis[(trifluoromethyl)sulfonyl]imide) of 0.5 mol/L, which also contained lithium nitrate ($LiNO_3$) (0.15 mol/L), followed by magnetic stirring to obtain Li_2S_6/Tetraethylene glycol dimethyl ether electrolyte for 24 h under the condition of heating in the glove box.

Static adsorption and the interaction between $CNFs@Ni_3FeN$ and Polysulfide

The CNFs and $CNFs@Ni_3FeN$ with the same surface area were added to the configured 1.5 mL Li_2S_4 electrolyte solution. The exact addition of CNFs and $CNFs@Ni_3FeN$ was determined by their respective specific surface areas. Subsequently, the material placed in the glove box filled with high purity argon for 3 h and observe the color change after adsorption.

Battery assembly and electrochemical tests

(1) Half battery assembly and test: First, $CNFs@Ni_3FeN@S$ or $CNFs@S$, polyvinylidene fluoride (PVDF) and Ketjen black with a weight ratio of 8:1:1 was mixed in an NMP solvent to form a stable slurry, which was then coated on aluminum foil to prepare the working electrode. Then, they were dried in a vacuum drying oven at 80 °C for 12 h. The electrode was rolled after drying, and the rolling range was controlled at 15-60 um. After that, the rolled electrode sheet was cut into a round sheet with a diameter of 14 mm and the sulfur loading was about 3.5 mg cm^{-2}. The 2025 button batteries were assembled in a glove box filled with high purity argon. The

cathode material was CNFs@Ni$_3$FeN@S or CNFs@S, lithium plate was the anode, and Celgard polypropylene (PP) membrane was the separator. The electrolyte was 1 M LiTFSI dissolved in DME/DOL (V$_{DME}$: V$_{DOL}$=1:1) solution, in addition, 2% LiNO$_3$ was used as additive.

The cycle performance and rate performance of the battery was tested at 1.7-2.8 V under a certain current density, and the equipment was LAND Battery Test system (CT2011). The redox performance of the materials and the catalytic performance of Ni$_3$FeN was characterized by cyclic voltammetry (CV). The tested voltage range was from 1.7 to 2.8 V and the scanning rate was 0.1 mV s^{-1}. CV measurements were performed on Princeton Electrochemistry Workstation. Electrochemical impedance spectroscopy (EIS) was tested on CHI604E. The frequency range of the test was 0.01 Hz to 100 kHz.

(2) Symmetrical battery assembly and test:

The CNFs@Ni$_3$FeN@S or CNFs@S, PVDF and Ketjen black with a weight ratio of 8:1:1 was mixed in an NMP solvent to form a stable slurry, which was then coated on aluminum foil to prepare the working electrode. Then, the mixed slurry was coated on the aluminum foil and dried at 80 °C for 12 h. After that, the electrode was rolled and cut into a disc with a diameter of 14 mm and the sulfur loading was about 1.24 mg cm^{-1}. The prepared electrode was used as the positive and negative electrode of the symmetrical battery, the separator was made of PP membrane, and the electrolyte was prepared with Li$_2$S$_6$/tetraethylene glycol dimethyl ether solution. The symmetrical cells were tested by CV (-0.8-0.8 V, 50 mV s^{-1}) and potentiostatic mode EIS (0.1-10 kHz) on the electrochemical workstation.

(3) In-situ FT-IR experiments： The CNFs@Ni$_3$FeN@S, polyvinylidene fluoride (PVDF) and Ketjen black with a weight ratio of 8:1:1 was mixed in an NMP solvent to form a stable slurry, which was then coated on carbon paper to prepare the working electrode. Then, they were dried in a vacuum drying oven at 80 °C for 12 h. Afterwards, the dried electrode sheet was cut into round pieces with a diameter of 16 mm. The assembly process of the battery used for In-situ FT-IR test was similar to that of the half battery. Subsequently, the assembled simulated battery was placed on the in-situ infrared equipment and connected to the LAND system for in-situ infrared testing. LAND system was selected for battery charge and discharge system, and the charge-discharge current is 0.5 C.
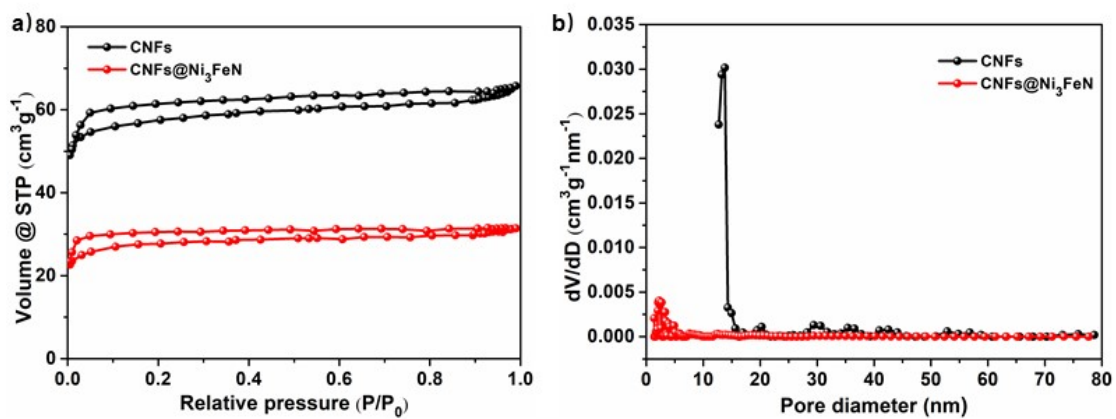
Fig. S1 a) N_2 adsorption-desorption isotherms. b) Pore size distribution of CNFs and CNFs@Ni_3FeN.