Construction of Ni/Ni_3N Heterojunction as Lithium Polysulfides Reversible Micro-Reaction Centers

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Experimental section

Preparation of Materials

Hollow carbon nanotubes (CNT) were firstly synthesized using the method which has been reported in the previous work[1]. Next, 15 mL of ethanol, 0.2 g of CNT and 0.4 g of $NiCl_2 \cdot 6H_2O$ mixed uniformly by ultrasonication, and then the mixture was dried at 50°C. The obtained powder was calcined at 600 °C for 3 h in a pure ammonia atmosphere to obtain the Ni/Ni_3N-CNT, and calcined at 500°C for 3 h to obtain the Ni_3N-CNT.

The Ni/Ni_3N-CNT/S electrode materials were obtained through a typical melt-diffusion approach. Sulfur powder was well-mixed with Ni/Ni_3N-CNT with a weight ratio of 6:4. Then the mixture was heated at 155°C for 12 h in an argon atmosphere. The Ni_3N-CNT/S was also prepared through the same procedure.

Adsorption test

The first step in this section is to prepare the Li_2S_6 solution (5 mM). Li_2S and S were firstly dissolved in a solution of DME/DOL (v/v = 1:1) with a molar ratio of 1:5, followed by continuous stirring at 60°C for 18 h. Next, Ni/Ni_3N-CNT and Ni_3N-CNT with the same weight (20 mg) were added to the Li_2S_6 solution (2 mL), respectively. Finally, the mixed solutions were vigorously shaken for 2 min and then rested at room temperature for 3 h.[2, 3]

Electrochemical measurements of LSBs

The active materials (Ni/Ni_3N-CNT/S and Ni_3N-CNT/S), polyvinylidene fluoride (PVDF), and acetylene black with the weight ratio of 7:1:2 was dispersed in NMP to form a uniform slurry. Then the slurry was coated onto an Al foil and dried at 50 °C for 12 h under vacuum. The diameter of the electrode was 1.2 cm, and the sulfur loading was 1.2 mg cm^{-2} in long cycle performance at 1 C and 5 C, the sulfur loading was 5 mg cm^{-2} in Figure 7b.

Electrochemical performances were tested in a standard CR2032 simulated battery with Li foil and PP as the anode and separator, respectively. Under normal conditions, the electrolyte is a solution of 1.0 M LiTFSI and 1.0 % $LiNO_3$ dissolved in DME/DOL (v/v = 1:1). The electrolyte dosage was accurately controlled with an electrolyte/sulfur ratio≈50 μL mg^{-1}. Galvanostatic charge/discharge measurements were performed on a Neware battery testing system in a potential window of 1.7-2.8 V. CV were conducted on a CHI760E electrochemical workstation at different scan rates in the potential range of 1.7-2.8 V. EIS spectra were obtained on a CHI760E electrochemical workstation, the frequency ranged from 100 kHz to 0.01 Hz and the amplitude was 5 mV.

Material Characterization

Morphological characterization of the prepared samples was measured using scanning electron microscope (SEM, Hitachi S-4800), Transmission electron microscope (TEM), and high-resolution TEM (Tecnai G2F30S-Twin). X-ray diffractometer (XRD) tests of the samples were conducted by using Cu Kα radiation (Shimadzu XRD-6100AS). Nitrogen adsorption/desorption isotherms and Brunauer-Emmett-Teller surface area were gained with a MicromeritcsGeminiV2380 analyzer operating at 77 K. X-ray photoelectron spectroscopy (XPS) analysis was obtained using an ESCALAB250 spectrometer with Mg Kα radiation as the excitation source. TGA (METTLER) was conducted in air at a heating rate of 10 °C min^{-1}.

Theoretical Calculation

Here the density functional theory (DFT) calculations were performed based on plane-wave technique as implemented in Vienna ab initio simulation package (VASP).[4] The projector augmented wave (PAW) approach was adopted to describe the ion-electron interaction.[5] The generalized gradient approximation (GGA) in the form of functional of Perdew, Burke, and Ernzerhof (PBE) was used to describe the exchange-correlation energy.[6] An energy cutoff of 450 eV was used for the plane wave-basis set. The revised Perdew-Burke-Ernzerhof (RPBE) functional was employed to describe the adsorption of sulfides on metal surfaces.[7] To avoid the artificial interactions, a vacuum space with at least 20 Å was inserted along *z* direction. Considering the crystal lattice match between Ni and Ni_3N, the model of (001) surface was built in this work. A Monkhorst-Pack k-point mesh of 3×3×1 was used.[8] For the surface model, the lower

two atomic layers of the slabs were fixed during optimization while other atoms were fully relaxed.

When the polysulfides including (especially S_8 and Li_2S_8) adsorbed on the metal surface, these molecules would be decomposed and therefore the reaction energy of the discharge process from Li_2S_6 to Li_2S on the metal surfaces was computed based on the reaction sequence of $*Li_2S_6 \rightarrow *Li_2S_4 \rightarrow *Li_2S_2 \rightarrow *Li_2S$. The corresponding reaction energy was calculated by:

$$E_{*Li_2S_4} + \frac{1}{4}E_{S_8} - E_{*Li_2S_6}$$

$$E_{*Li_2S_2} + \frac{1}{4}E_{S_8} - E_{*Li_2S_4}$$

$$E_{*Li_2S} + \frac{1}{4}E_{S_8} - E_{*Li_2S_2}$$

in which $E_{*Li_2S_x}$ is the energy of the Li_2S_x molecule adsorbed on catalysts, E_{Li} is the energy of Li atom in lithium metal and E_{S_8} is the energy of isolated S_8. The adsorption energy (E_{ads}) was computed by the equation:

$$E_{ads} = E_{tot} - E_{Li_xS_y} - E_{cat}$$

where E_{tot}, $E_{Li_xS_y}$ and E_{cat} represent the total energy of the complex of the adsorbates (Li_xS_y molecules) and the catalysts, the isolated Li_xS_y molecules and the catalysts, respectively.

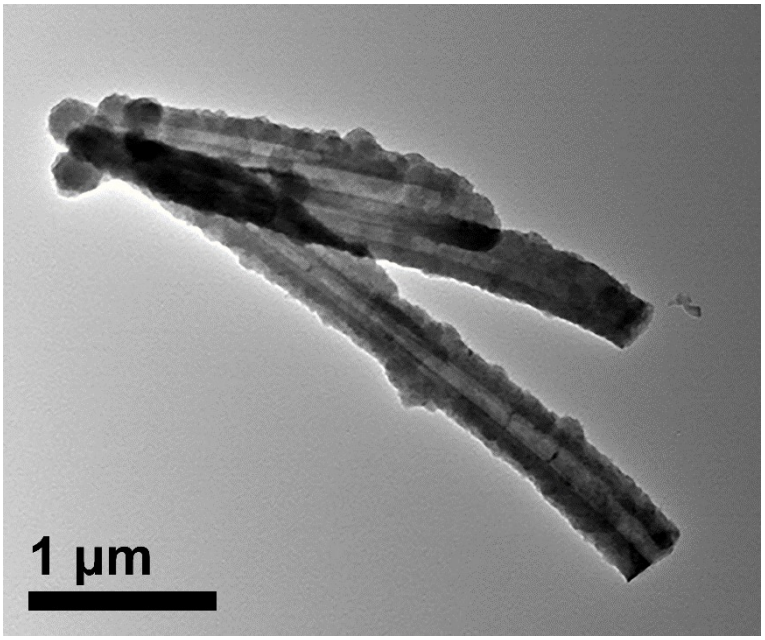

Figure S1. TEM images of the CNT.

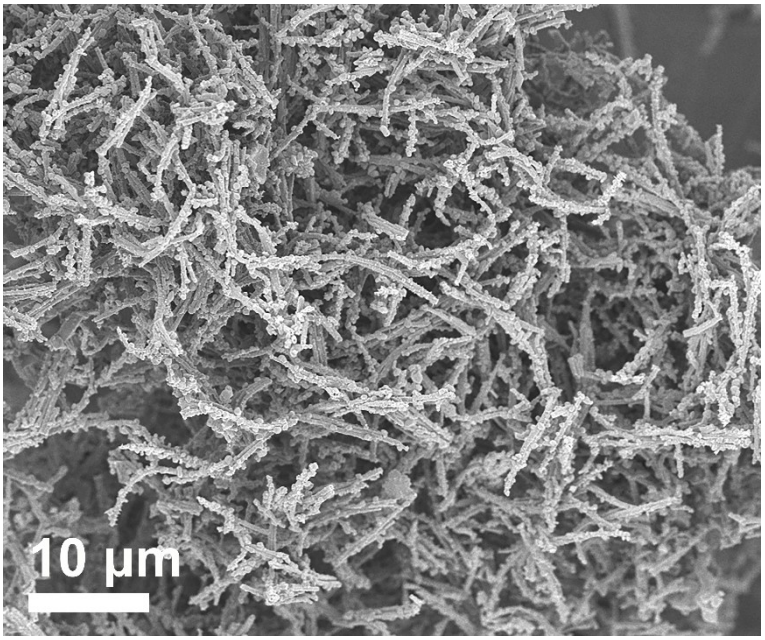

Figure S2. SEM images of the Ni/Ni_3N-CNT.

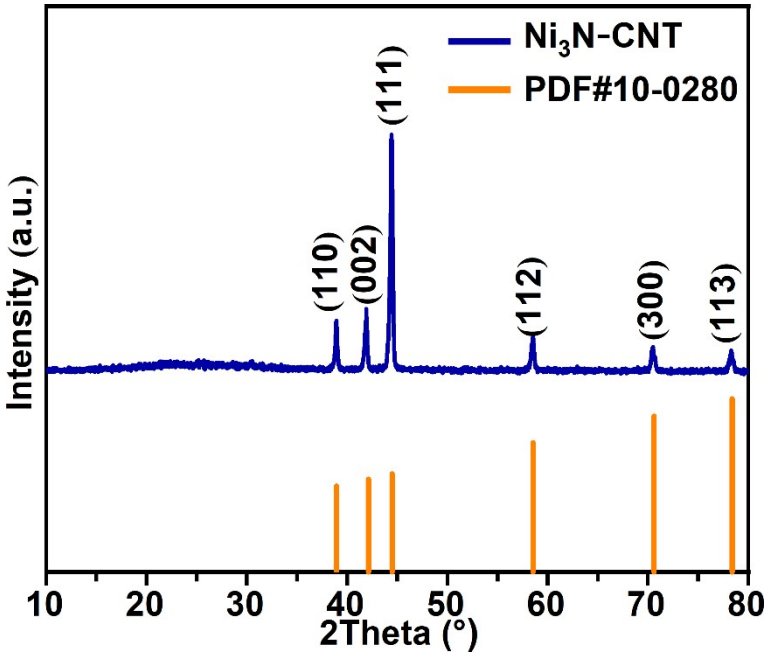

Figure S3. XRD patterns of the Ni_3N-CNT.

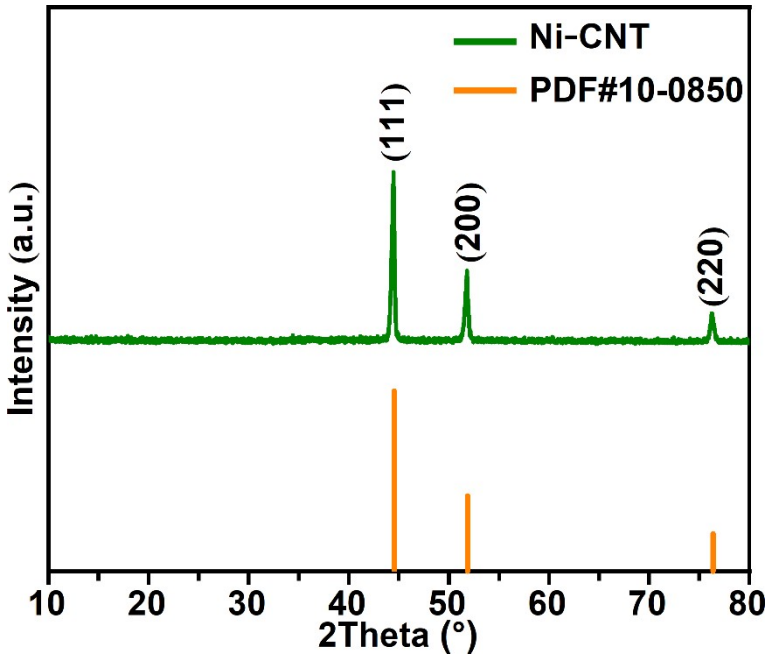

Figure S4. XRD patterns of the Ni-CNT.

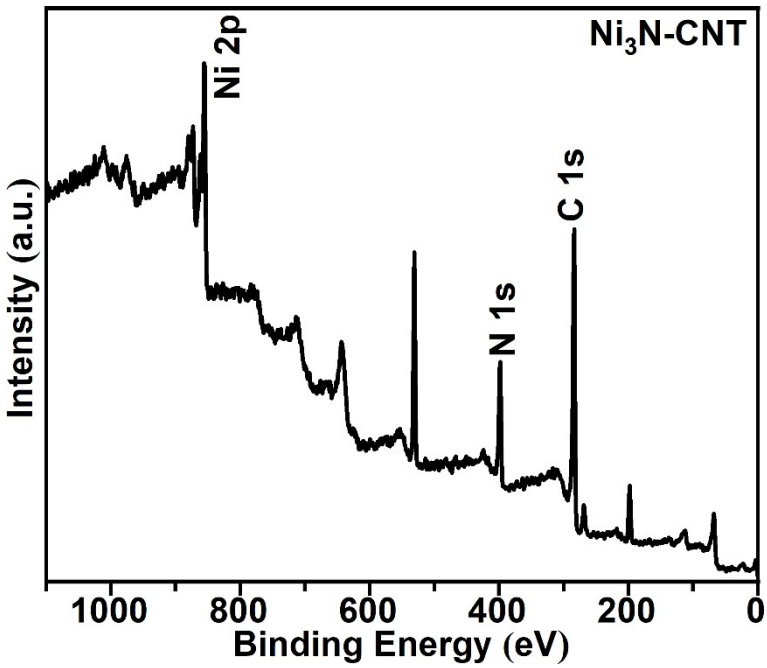

Figure S5. XPS survey spectrum of the Ni_3N-CNT

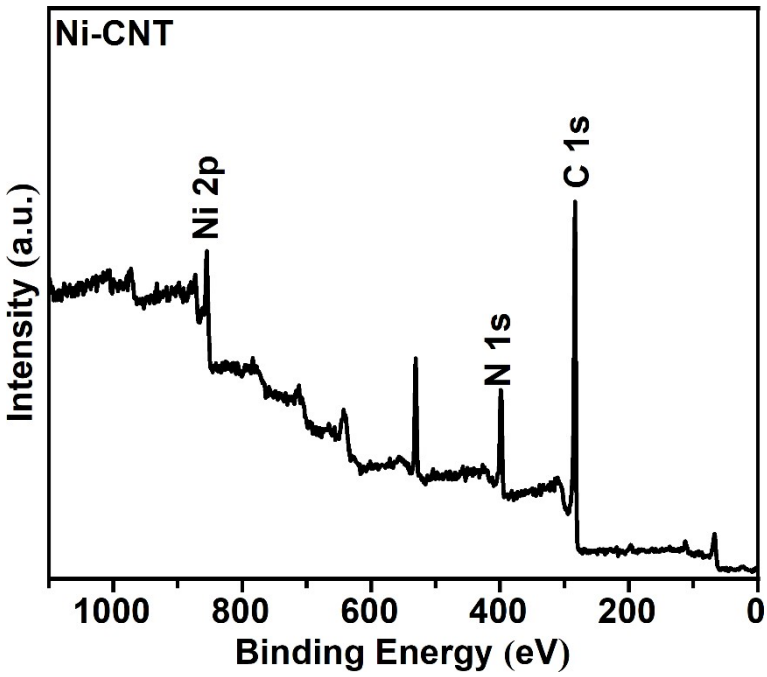

Figure S6. XPS survey spectrum of the Ni-CNT.

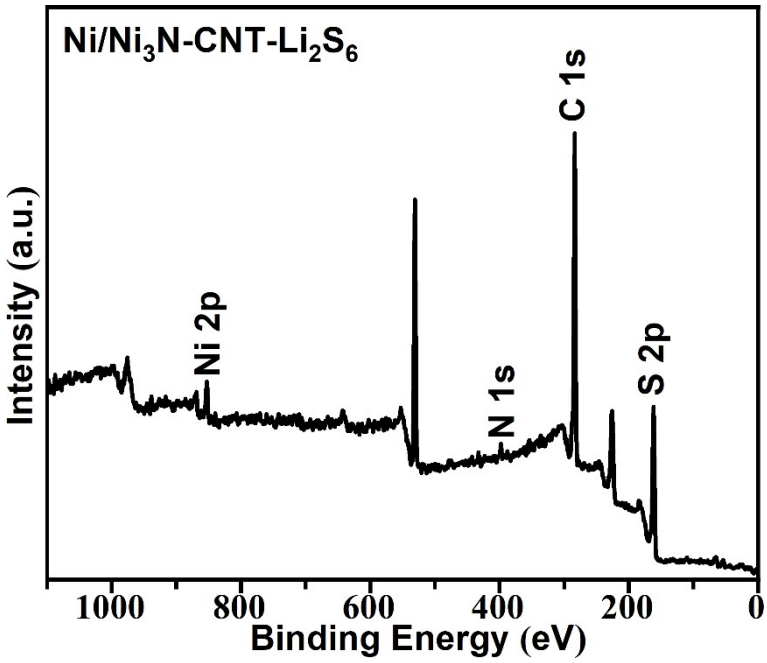

Figure S7. XPS survey spectrum of the Ni/Ni_3N-CNT-Li_2S_6.

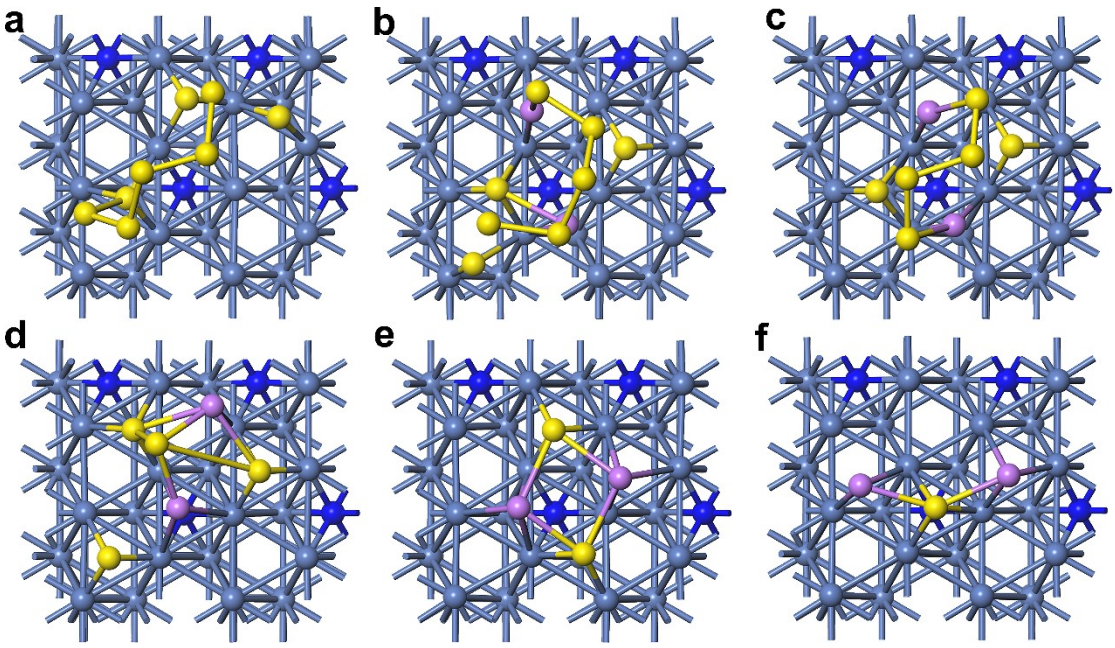

Figure S8. Optimized structures of S_8 (a), Li_2S_8 (b), Li_2S_6 (c), Li_2S_4 (d), Li_2S_2 (e) and Li_2S (f) on the Ni/Ni_3N surface. Yellow, purple balls represent S, Li atoms, respectively.

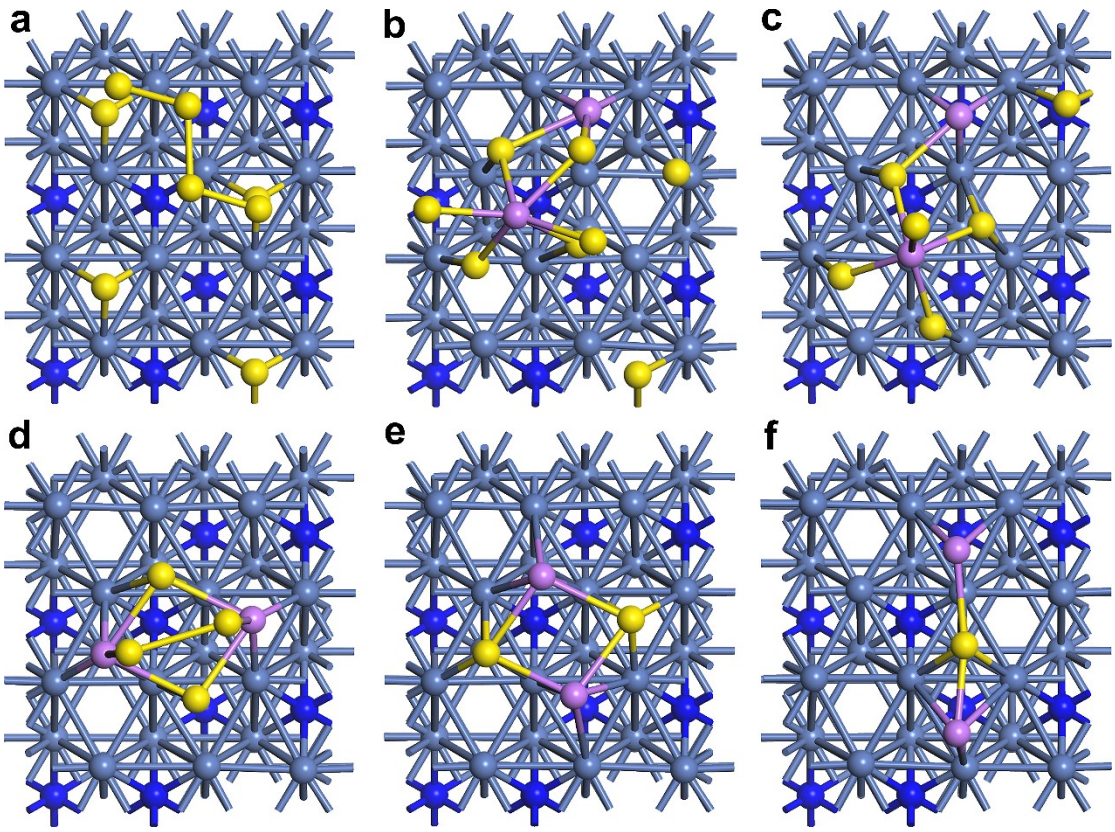

Figure S9. Optimized structures of S_8 (a), Li_2S_8 (b), Li_2S_6 (c), Li_2S_4 (d), Li_2S_2 (e) and Li_2S (f) on the Ni_3N surface. Yellow, purple balls represent S, Li atoms, respectively.

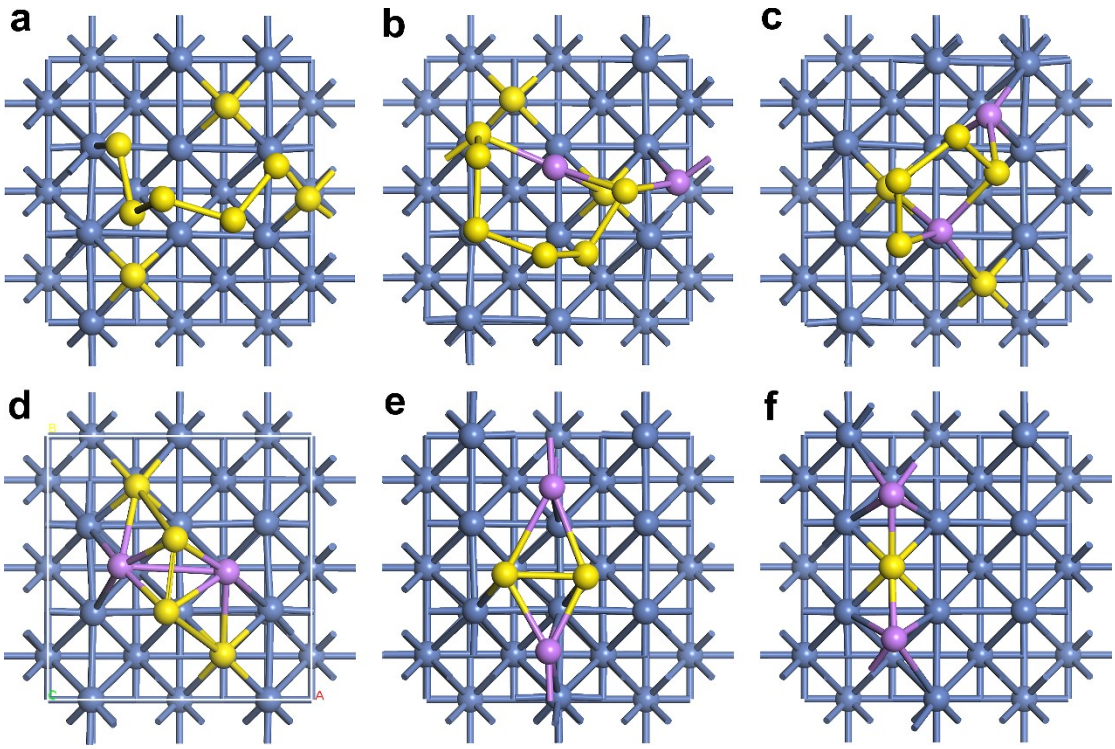

Figure S10. Optimized structures of S_8 (a), Li_2S_8 (b), Li_2S_6 (c), Li_2S_4 (d), Li_2S_2 (e) and Li_2S (f) on Ni the surface. Yellow, purple balls represent S, Li atoms, respectively.

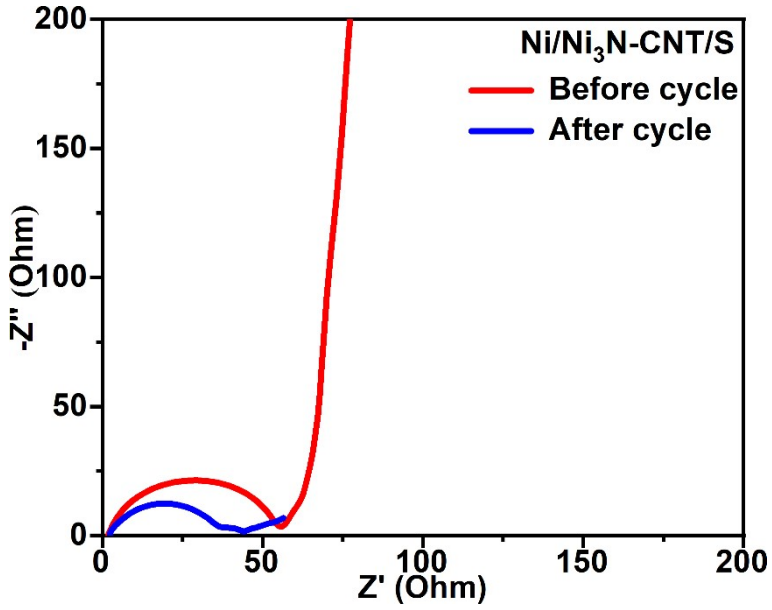

Figure S11. Nyquist plots of the Ni/Ni_3N-CNT/S electrode before and after cycling.

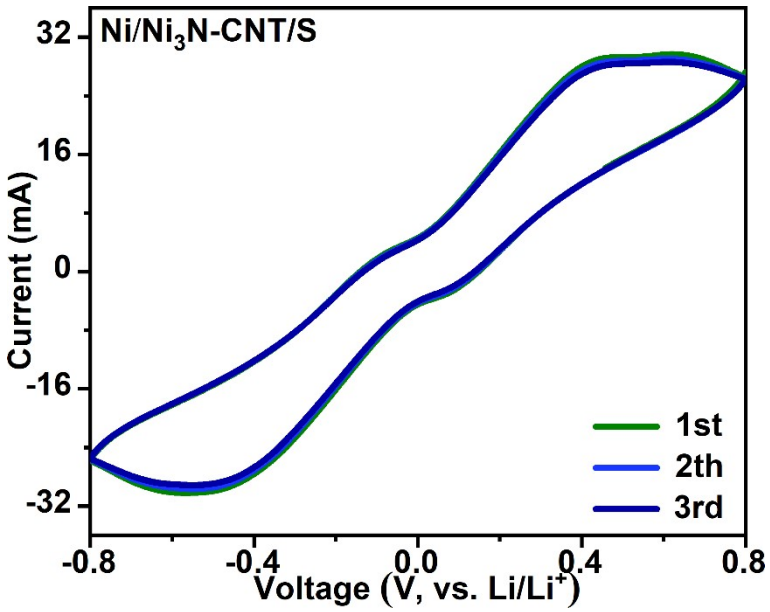

Figure S12. CV curves of Ni/Ni_3N-CNT and CNT symmetric cells in the first three cycle.

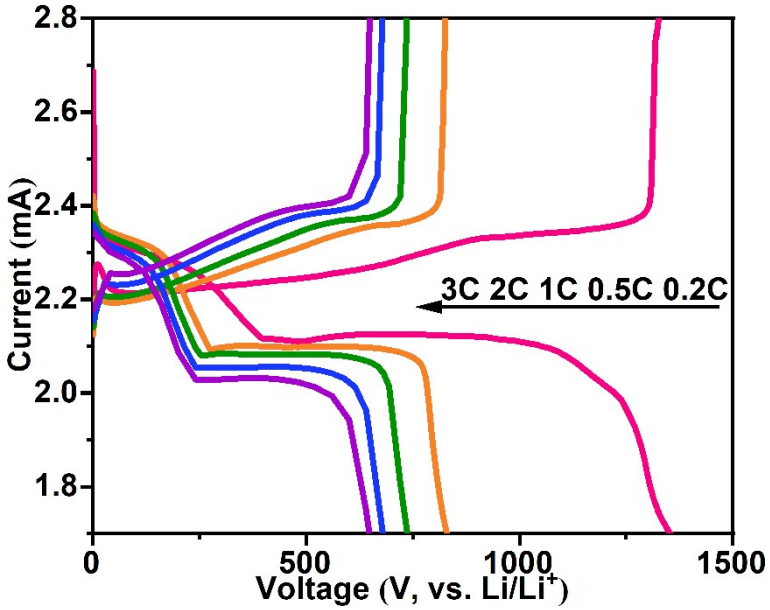

Figure S13. Galvanostatic charge-discharge curves of the Ni/Ni_3N-CNT/S electrode at 0.2-3 C.

References

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