

Electronic Supporting Information:

Promoting Overall Sulfur Redox Kinetics for Li-S Batteries via Interfacial Synergy in a NiS-NiTe₂ Heterostructure-Modified Separator

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Electronic Supplementary Information contains Experimental Section and Fig. S1-S9.

Experimental Section:

Chemicals: All chemicals were analytical grade and used without further purification. Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) was purchased from Xiya Reagent Co., Ltd. Urea was obtained from Sinopharm Chemical Reagent Co., Ltd. Lithium sulfide (Li₂S), sulfur powder (S) and tellurium powder (Te) were procured from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Multi-walled carbon nanotubes (CNTs, >99.9 %) were acquired from Nanjing Xianfeng Nano Co., Ltd.

Synthesis of Ni(OH)₂ nanoflowers: Ni(OH)₂ nanoflowers (Ni(OH)₂ NF) was synthesized using a hydrothermal method as per established literature procedures.^{S1} Specifically, 0.7 g of Ni(NO₃)₂·6H₂O and 0.3 g of urea were dissolved in 35 mL of distilled water. Following thorough stirring to ensure homogeneity, the resulting mixture was transferred to a 50 mL Teflon-lined autoclave and maintained at 120 °C for 12 h. The resulting sample was collected

through centrifugation, subjected to multiple water rinses, and subsequently dried under vacuum conditions at 60 °C for 12 h.

Synthesis of NiS, NiTe₂, NiS-NiTe₂: A total of 50 mg of Ni(OH)₂ NF was positioned in a porcelain boat downstream, while mixed powders of S/Te, each weighing 100 mg, were placed in another porcelain boat upstream. The annealing process was conducted up to 600 °C for 2 h at a heating rate of 1 °C min⁻¹ under a N₂ atmosphere, resulting in the formation of NiS-NiTe₂. For comparison, NiS and NiTe₂ samples were obtained by incorporating only 100 mg of S or 100 mg of Te through the same aforementioned procedure, respectively.

Synthesis of modified separators and sulfur cathodes: The NiS-NiTe₂ modified separator was fabricated using a straightforward surface coating method. Specifically, 70 wt% of NiS-NiTe₂, 20 wt% of carbon nanotubes (CNTs), and 10 wt% of polyvinylidene fluoride (PVDF) were meticulously blended in 1-methyl-2-pyrrolidinone (NMP) solvent through vigorous stirring to form a homogeneous slurry. Subsequently, this slurry was coated onto a pristine Celgard 2500 polypropylene (PP) separator. The functionalized separator underwent overnight drying at 45 °C under vacuum conditions, followed by cutting into 19 mm diameter discs. The areal mass loading of the interlayer materials was approximately 0.3 mg cm⁻².

As for the sulfur-carbon nanotube (CNT-S) composite, it was prepared using a melt diffusion approach. Specifically, CNTs and sulfur powder were ground in a 1:4 weight ratio and subjected to heating at 155 °C for 10 h.

Synthesis of lithium polysulfide (Li₂S₆) solution and visual adsorption test: A Li₂S₆ solution was meticulously prepared by dissolving elemental sulfur and Li₂S (in a 5:1 molar ratio) in a mixed solvent comprising 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (v/v = 1:1). The solution underwent vigorous stirring at 65 °C for 12 hours. Subsequently, 10 mg samples were introduced into 3 mL of a 5 mM Li₂S₆ solution. UV-Vis absorption spectra were acquired ex-situ after immersing the samples in the Li₂S₆ solution for 12 h. All these procedures were executed within an argon-filled glove box to maintain an inert atmosphere.

Symmetric-cell assembly and evaluation of polysulfide conversion kinetics: The electrode was meticulously fabricated by blending active materials and polyvinylidene fluoride (PVDF) in a weight ratio of 9:1 within N-methyl-2-pyrrolidone (NMP) solvent. The resulting slurry was then coated onto an aluminum foil substrate. A 0.5 M Li_2S_6 electrolyte was prepared by stirring sulfur and lithium sulfide in a 1 M solution of bis(trifluoromethanesulfonyl)imide lithium salt (LiTFSI) in a solvent mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (v/v = 1:1) at 65 °C within an argon-filled glove box overnight. For the electrochemical testing, two identical electrodes were employed as working and counter electrodes, both exhibiting a mass loading of 1.0 mg cm^{-2} . The electrolyte consisted of 25 μL of 0.5 M Li_2S_6 . Cyclic voltammetry measurements of the symmetric cells were conducted over a voltage window spanning from -1.0 to 1.0 V at various scan rates. Electrochemical impedance spectra were acquired across a frequency range of 0.01-10⁵ Hz.

Li_2S nucleation measurements: For the liquid–solid conversion kinetics, a 0.2 M Li_2S_8 solution was prepared by blending elemental sulfur and Li_2S (in a 7:1 molar ratio) and dissolving the mixture in a tetraglyme solution with vigorous stirring. Investigations into the precipitation of Li_2S on various reactive surfaces were carried out using 2025 coin-type cells, employing a Celgard 2500 polypropylene (PP) membrane separator. In these experiments, 25 μL of 0.5 M Li_2S_8 was applied to the cathode, and 25 μL of LiTFSI electrolyte was added to the anode side. The cells underwent galvanostatic discharge at 0.1 mA down to 2.06 V, followed by maintaining the voltage at 2.05 V to allow Li_2S nucleation until the current dropped below 10⁻⁵ A. The Li_2S nucleation capacity was determined by calculating the integral area of the curve using Faraday's Law.

Li-S cell assembly and electrochemical performance measurements: The sulfur cathode materials (CNT/S) were mixed with Super P and PVDF in a weight ratio of 8:1:1 in NMP and stirred to obtain a uniform slurry, which was then coated on aluminum foil, vacuum-dried at 45 °C overnight, and cut into 12 mm-diameter disks to form the sulfur electrodes. The sulfur mass loading was 1 mg cm^{-2} . Li metal and Celgard 2500 PP were used as the anode and

separator, respectively. 1.0 M LiTFSI in DOL and DME (v/v =1:1) with 1 wt% LiNO₃ additive was used as the electrolyte. Electrochemical tests were conducted by assembling 2025 coin-type half-cells in an argon-filled glove box where the oxygen and water contents were below 0.1 ppm. The galvanostatic discharge/ charge measurements were conducted with a LAND CT2001A system (China) within a voltage window of 1.7-2.8 V under various C-rates (1 C=1675 mA g⁻¹). Cyclic voltammetry was performed with Chenhua electrochemical workstation (CHI 660E). Electrochemical impedance spectroscopy was conducted with Chenhua electrochemical workstation (CHI 660E) over the frequency range 0.01-10⁵ Hz. All electrochemical experiments were performed at 28 °C. The specific capacity of the Li-S battery was calculated according to the sulfur mass.

Materials characterization: Powder X-ray diffraction (PXRD) was executed using a X'Pert3Powder instrument (PANalytical, Netherlands) employing Cu K α radiation at room temperature. Scanning electron microscopy (SEM) was carried out on a Nova NanoSEM 450 field-emission scanning electron microscope with acceleration voltages set at 15 kV. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) were performed utilizing a JEM-1400-plus instrument (Japan). Raman spectroscopy was conducted on an InVia-Reflex system by Renishaw, utilizing a laser source with a wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) data were acquired using an ESCALAB 250Xi instrument from Thermo Fisher Scientific. Thermo-gravimetric analysis (TGA) was conducted on an STA499f5 analyzer, applying a heating rate of 10 °C min⁻¹. Ultraviolet-visible (UV-Vis) spectra were obtained using a Hitachi U-3900H UV/Vis spectrophotometer.

Theoretical calculations: Theoretical calculations based on Density Functional Theory (DFT) were conducted in this study using the Vienna ab initio simulation package (VASP). Projector-augmented-wave (PAW) potentials were employed, and the generalized gradient approximations (GGA) of Perdew–Burke–Ernzerhof (PBE) pseudopotentials were applied for the exchange–correlation functional. The adhesion bonding energy (E_b) of Li₂S_n (n = 2, 4, 6, 8) was computed using the formula $E_b = E_{M/Li_2S_n} - E_M - E_{Li_2S_n}$, where E_{M/Li_2S_n} represents the total

energy of the adsorbed system, E_M is the total energy of the surface, and $E_{\text{Li}_2\text{S}_n}$ is the total energy of the isolated Li_2S_n polysulfide. In this context, more negative values indicate a greater likelihood of adsorbate-surface interactions due to the energy advantage.

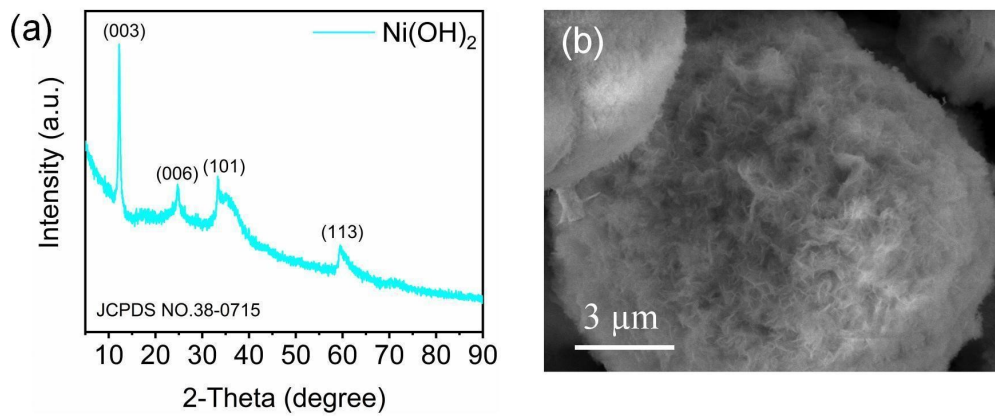


Fig. S1 (a) XRD pattern of Ni(OH)₂; (b) SEM of Ni(OH)₂.

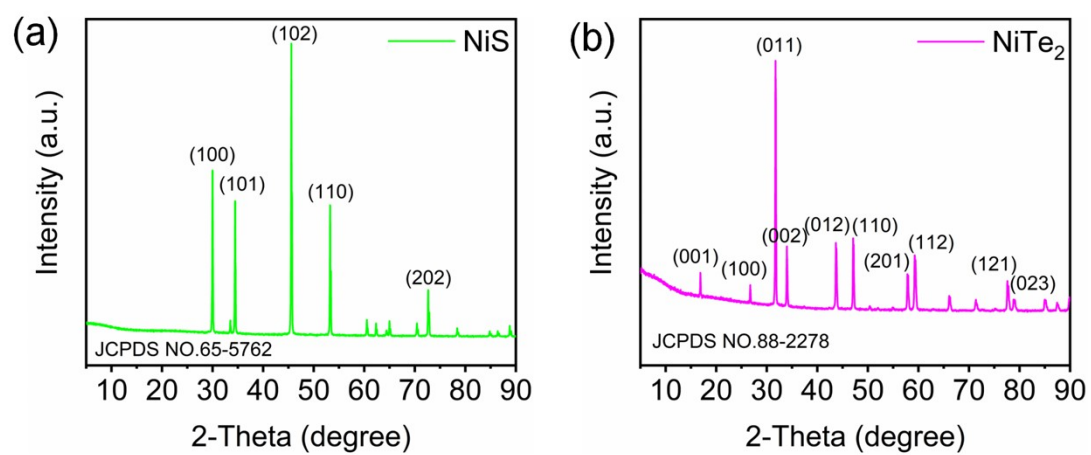


Fig. S2 XRD patterns of (a) NiS and (b) NiTe₂.

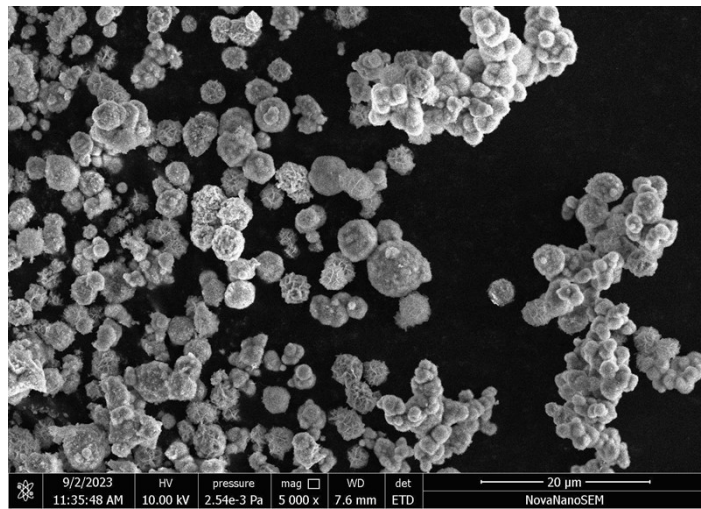


Fig. S3 SEM image of NiS-NiTe₂ at low magnification.

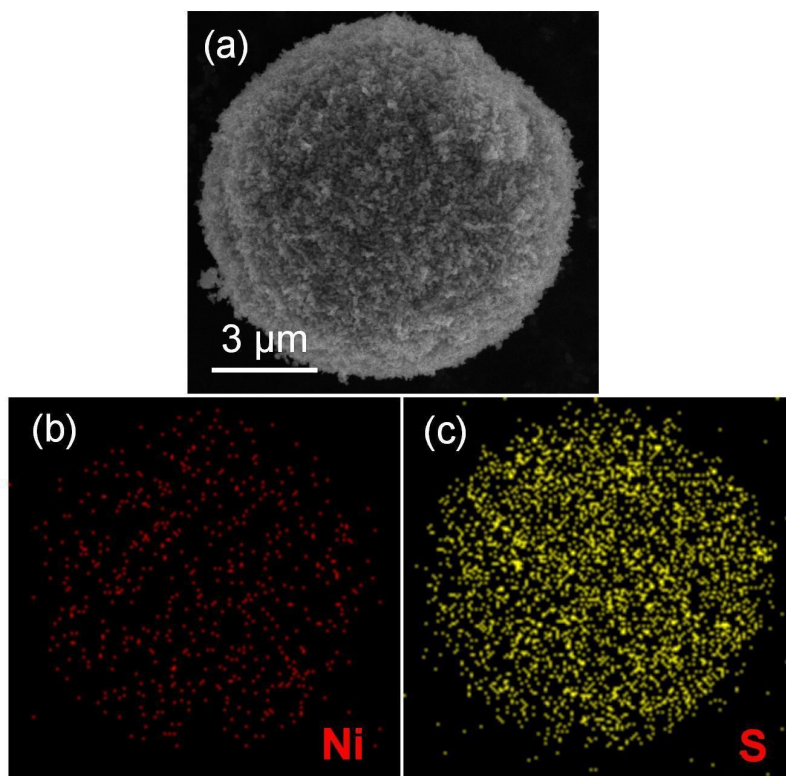


Fig. S4 (a) SEM of NiS, (b, c) corresponding elemental mapping of NiS.

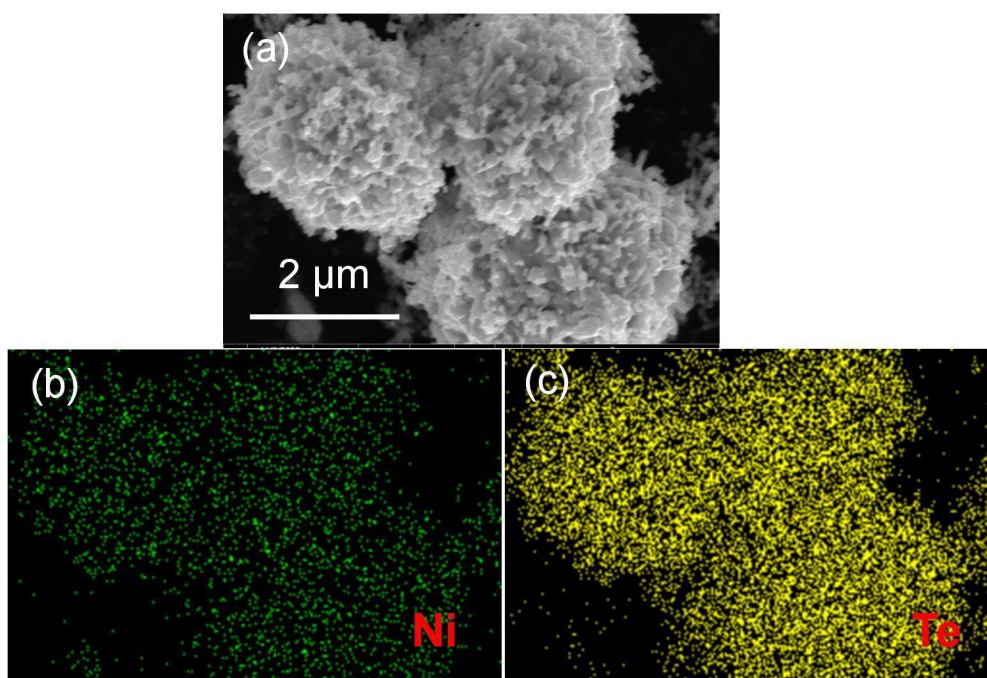


Fig. S5 (a) SEM of NiTe₂, (b and c) corresponding elemental mapping of NiTe₂.

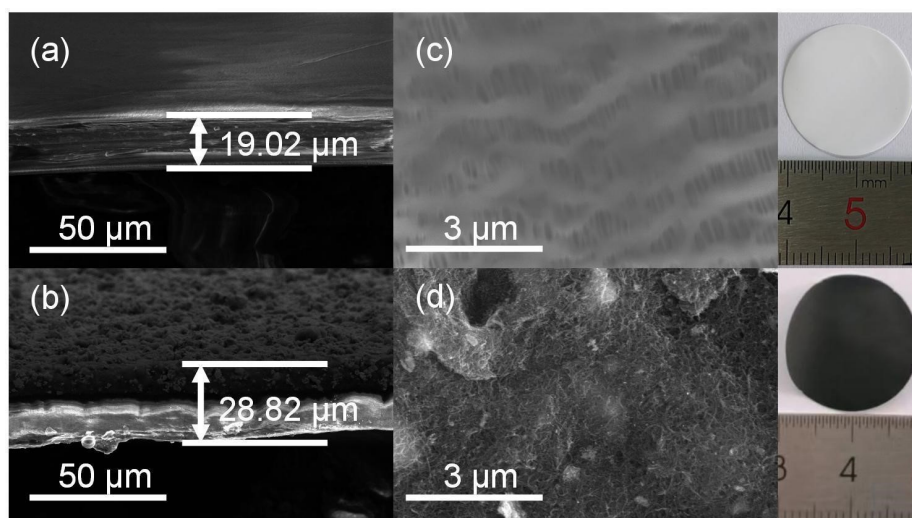


Fig. S6 SEM and cross-sectional SEM images of (a, b) PP separator and (c, d) NiS-NiTe₂ modified separator.

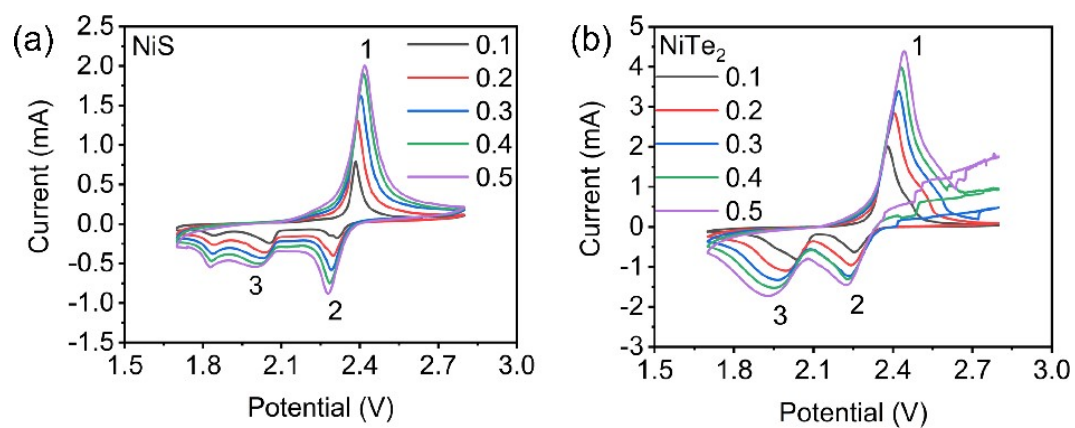


Fig. S7 Cyclic voltammetry curves of Li-S cells paired with (a) NiS and (b) NiTe₂.

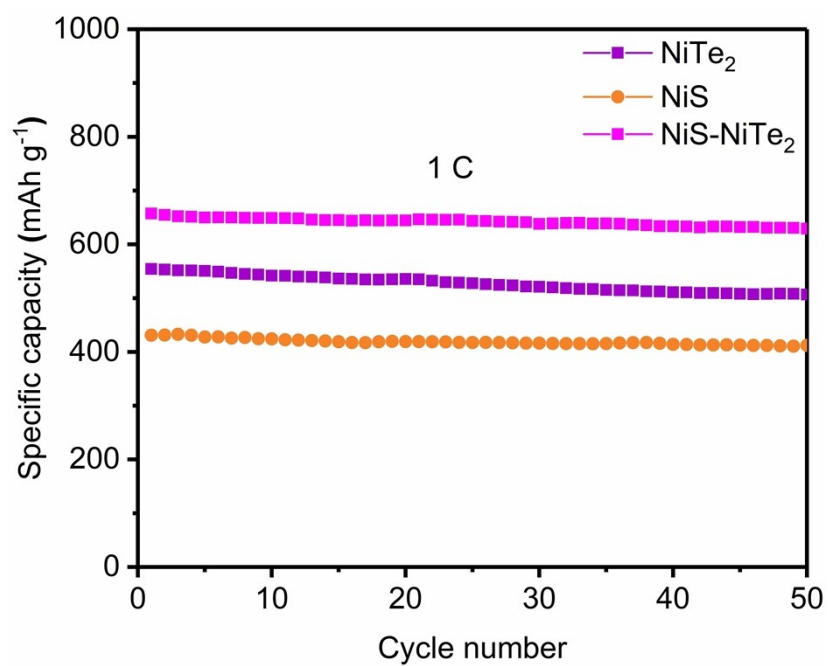


Fig. S8 Cycling performances of the NiS-NiTe₂, NiS and NiTe₂-based Li-S batteries at the current density of 1 C.

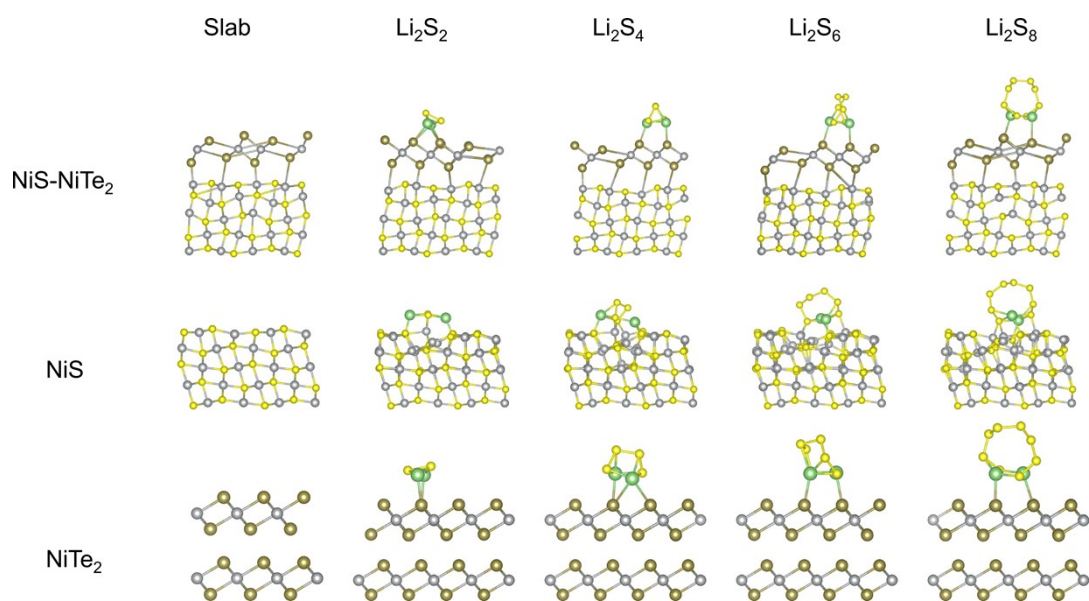


Fig. S9 Geometrically stable configurations of LiPS_n adsorption of NiS-NiTe_2 , NiS and NiTe_2 .

References:

- S1. C. Gao, G. Wei, C. Wang, X. Zhou, X. Zhao, Q. Zhao, S. Wang and F. Kong, *J. Alloys Compd.*, 2023, **959**, 170545.