Supplementary Information

Oxygen Doping in Antimony Sulfide Nanosheets to Facilitate Catalytic Conversion of Polysulfides for Lithium–Sulfur Batteries

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Methods

Theoretical Calculations

First-principle calculations were carried out using the all-electron code Fritz-Haber Institute *ab initio* molecular simulations package (FHI-aims).¹ The exchange-correlation potentials were treated by the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerholf (PBE).^{2,3} The default 'tight' element species (tier 2 level as described in Blum *et al.*) were used in our work. To account for the weak non-covalent intermolecular interaction, these functionals were augmented by the van der Waals scheme of Tkatchenko and Scheffler.⁴

According to previous studies,⁵ periodic slab model with three layers of Sb_2S_3 moieties was proposed to simulate the substrate. A vacuum layer of 20 Å was added to avoid image– image interaction in all calculations. Brillouin zone was sampled using a $3\times3\times1$ Gammacentered k-point mesh during geometry optimization and adsorption properties.

The diffusion barrier of Li on Sb₂S₃ surface was calculated based on the climb-image nudged elastic band (CI-NEB) method.⁶ A Monkhorst–Pack $3\times3\times1$ mesh was used to sample the reciprocal space and the calculation was considered to be converged when the residual force components on each ion were below 10^{-2} eV Å⁻¹.

The formation energy (E_f) of O impurities was calculated for comparing the relative stability of O-doped Sb₂S₃ surface by Equation (1).

$$E_f = E_{total}^{defect} - E_{total}^{perfect} + \sum_i n_i \mu_i$$
(1)

where, E_{total}^{defect} was the total energy of the supercell containing O impurities, $E_{total}^{perfect}$ was the total energy of the supercell without defects, n_i standed for the number of constituent element *i* being added/removed from the Sb₂S₃ surface, μ_i referred to the chemical potential, and the chemical potentials of O and S were obtained from oxygen gas and S₈ molecules, respectively.

The binding energies (E_b) between the polysulfides and Sb₂S₃ (010) surface were calculated using the same parameters as described above while van der Waals correction was added to capture those long-range correlations:

$$E_b = E_{slab + polysulfide} - E_{slab} - E_{polysulfide}$$
(2)

where, $E_{slab+polysulfide}$, E_{slab} and $E_{polysulfide}$ denoted the total energies of the binding system and their isolated phases, respectively. With this definition, a more negative value of E_b meant that the polysulfide was more favorable to be bonded with Sb₂S₃ slab.

And then we converted the ground state energy into Gibbs free energy at standard state (297.15 K, 0.1 Mpa), the ΔG was expressed as Equation (3).

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S \tag{3}$$

where, ΔG was the adsorption energy of each intermediate, ΔZPE and ΔS presented the differences of zero-point energy and entropy between the products and reactants, and T was the room temperature, 297.15 K. The change in free energy of a S₈ cluster when going from gas phase or solvent medium to adsorbing on the surface was treated as zero.

Preparation of SS-O NSs

The SS-O NSs were prepared by first dispersing 24 mg of Sb₂S₃ powder (> 99.99% purity, from Aladdin) in 8 mL of *N*,*N*-dimethylformamide (DMF, > 99.9% purity, from Aladdin) and then sonicating the dispersion for 6 h using a sonic tip (JY92-II DN, SCIENTZ, 60% of 900 W using 2 s on 3 s off pulsation). After sonication, the obtained dispersion was centrifuged (TG16-WS, Cence) for 30 min at 2000 rpm for the sedimentation of large particles. Then the supernatant, which contained the exfoliated Sb₂S₃, was washed by 1-methyl-2-pyrrolidone (NMP, > 99.5% purity, from Aladdin) for three times under centrifugation process. Afterwards, the suspension was centrifuged for another 30 min at 10000 rpm to collect the final products. The obvious color change of the Sb₂S₃ solution before and after sonication

implies successful exfoliation of Sb₂S₃ (Fig. S1a,b, ESI[†]). After centrifugation, a light brown dispersion with abundant single- or few-layer Sb₂S₃ nanosheets was obtained (Fig. S1c, ESI[†]). The Sb₂S₃ dispersion was illuminated by a red laser beam (650 nm), and a Faraday-Tyndall light-scattering effect was observed, revealing the uniform suspension of the nanosheets (Fig. S1d, ESI[†]).



Fig. S1 Optical photographs of the pristine Sb_2S_3 suspension (a) before sonication, (b) after sonication, (c) and (d) after centrifugation in NMP and corresponding Faraday-Tyndall effect.

Structural Characterization

The transmission electron microscopy (TEM), high-resolution transmission electron microscope (HRTEM), high-angle annular dark-filed scanning transmission electron microscopy (HAADF-STEM) images and the corresponding energy dispersive X-ray spectroscopy (EDX) elemental mapping of both pristine Sb₂S₃ and SS-O NSs were obtained with a FEI Themis Z TEM/STEM equipped with corrector-ready platform, a high-angle annular dark-field detector, and EDX detector operating at 200 kV. The thicknesses of prepared SS-O NSs were measured by an atomic force microscopy (AFM, Digital Instruments Nanoscope IIIa, Veeco, USA) under ambient condition in tapping mode. The concentration and species of LiPSs in the electrolyte were investigated by an UV–visible spectrophotometry (UV-1800, Shimadzu) in the wavelength between 200 and 850 nm. The

surface studies of materials were performed by an X-ray photoelectron spectroscopy (XPS, SES 2002, Gammadata-Scienta) equipped with a monochromatic Al K α X-ray source. Raman spectra were measured by a Raman microscopic system equipped with a 532 nm excitation laser (Renishaw inVia, Renishaw, UK).

Preparation of SS-O NSs/CNTs-S Cathodes

The SS-O NSs/CNTs-S cathode materials were prepared by a simple melt-diffusion approach as previous reported.^{7,8} Typically, the sulfur powder (> 99.99% purity, from Aladdin) was first mixed with multi-walled carbon nanotubes (CNTs, > 99.9% purity, inside diameter: 3-5 nm, from Aladdin) at a mass ratio of 7:3 by ground milling. The obtained mixture was stirred in carbon disulfide (CS_2 , > 99.9% purity, from Aladdin) for 12 h, followed by heating at 155 °C for 12 h in a vacuum oven, which allowed sulfur to immerse into the CNTs and form CNTs-S composites. The sulfur contents of the CNTs-S composites were controlled at ~ 70 wt%. Subsequently, the mixture of 80 wt% CNTs-S composites, 5 wt% polyvinylidene fluoride (PVDF), 14 wt% conductive agent and 1 wt% SS-O NSs was added into NMP solution to form slurry. After stirring for 4 h, the slurry was coated onto aluminum foil and dried at 55 °C overnight in vacuum oven. The foil was punched into 14 mm-diameter circles as the working cathodes. The areal sulfur loading of the cathode was ~ 0.8 mg cm⁻² for the normal electrochemical measurements. Considering the high sulfur mass loading in cathodes is a key factor for practical applications of Li–S batteries, the cathode with a high areal sulfur loading of $\sim 4.0 \text{ mg cm}^{-2}$ was also prepared. For comparison, the CNTs-S cathodes were prepared *via* the similar operations.

Electrochemical Measurements

The CR2025 coin cells were assembled using as-prepared cathode, lithium metal as an anode and a Celgard 2400 membrane as a separator in an Ar-filled glove box. The electrolyte was 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) with 1% LiNO₃ dissolved in a mixture of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1 by volume, Suzhou Dodo Chem. Ltd.). The ratio of the electrolyte/sulfur used in each cell was about 20 μ L mg⁻¹. Considering the accuracy of results, about six batteries were prepared and tested under the same operating conditions. Cyclic voltammetry (CV) measurements were performed on an electrochemical workstation (CHI 760E) between 1.6 and 2.8 V (*vs.* Li/Li⁺) with a sweep rate of 0.1 mV s⁻¹. Galvanostatic charge-discharge measurements were conducted by Neware battery Cycler (CT-4008T-5V20mA-164, Shenzhen, China) at various rates and the potential is between 1.6 and 2.8 V (*vs.* Li/Li⁺). Electrochemical impedance spectroscopy (EIS) analysis was performed with the same electrochemical workstation as CV. The frequency range was from 200 KHz to 0.01 Hz with an AC voltage amplitude of 5 mV. All electrochemical measurements aforementioned were performed at room temperature. The current and capacity were calculated based on the sulfur mass of the entire cathode.

Semi-in Situ XPS Measurements

Semi-in situ XPS measurements were carried out on an X-ray photoelectron spectroscopy (SES 2002, Gammadata-Scienta) equipped with a monochromatic Al K α X-ray source. After sixteen consecutive cycles, the coin cells were charged/discharged to different states at 1 C. Then the cathodes were extracted from the cells and dried within an Ar-filled glove box for XPS analysis. In order to retain the full information on surface electrochemically active species, the cathode surfaces were not washed with 1,3-dioxolane (DOL)/dimethoxyethane (DME) to remove the residual salt lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) before our XPS measurements. Consequently, the strong S 2p peaks due to LiTFSI (169.7 eV/170.8 eV) and sulfite arising from the decomposition of the LiTFSI with different degrees (167.3 eV/168.4 eV), are observed in all samples.^{9,10}

In Situ UV–Visible Measurements

The structure of the three-electrode system used for in situ UV-visible analysis has been

reported in our previous works.¹¹ The platinum wire was recognized as a counter electrode and the sealed Ag/AgCl was performed as a reference electrode. The glassy carbon electrode (diameter: 5 mm) with about 5 mg SS-O NSs/CNTs-S composites (mass ratio: 9:1) was used as a working electrode. The 0.5×10^{-3} M Li₂S₈ solution was used as electrolyte (volume: 600 µL), which was prepared by mixing sulfur and Li₂S at a molar ratio of 7:1 in dimethyl sulfoxide (DMSO, > 99.9% purity, from Aladdin) and stirring for 24 h in an Ar-filled glovebox. The three-electrode system was tested by CV between 1.6 and 2.8 V (*vs.* Li/Li⁺) at a scanning rate of 0.6 mV s⁻¹, and UV–visible absorption spectra were recorded simultaneously at each 0.1 V on a UV–visible spectrophotometry (UV-1800, Shimadzu). For comparison, the working electrode with pristine Sb₂S₃/CNTs was conducted in the same way.

In Situ Raman Spectroscopy

In situ Raman measurements were performed by a Renishaw inVia Raman microscopic system equipped with a 532 nm excitation laser (laser spot size: ~ 1 μ m). The simulated Li–S battery with a quartz window on positive shell and SS-O NSs/CNTs and pristine Sb₂S₃/CNTs electrodes were used here.¹¹ The electrode should be close enough to the quartz window to ensure the capture of related signals. The 0.5×10⁻³ M Li₂S₈ solution was used as electrolyte, which was prepared by the same method mentioned above. The cell was assembled and sealed in an Ar-filled glove-box. Then, it was run between 1.6 and 2.8 V (*vs.* Li/Li⁺) at a scan rate of 0.3 mV s⁻¹. Simultaneously, Raman spectra were recorded with a potential interval of 0.2 V. The typical acquisition time was 10 s per spectrum.



Fig. S2 Schematics of front and top views of undoped/O-doped Sb₂S₃ (010) surfaces: (a) the perfect Sb₂S₃ (010) structure, (b) an O atom adsorbed on a S₁ atom ($E_b = -0.62 \text{ eV}$), (c) an O atom bridged two or more surface atoms ($E_b = -0.79 \text{ eV}$), (d) an O atom substituted one S₁ atom ($E_b = -1.13 \text{ eV}$). The blue, yellow, and red balls are Sb, S, and O atoms, respectively. Based on the coordination number of surface atoms, two types of antimony cations (Sb₁ and Sb₂) and three types of sulfur anions (S₁, S₂ and S₃) can be identified.¹² S₁ is the most unsaturated one which shows the highest activity for O impurities.



Fig. S3 Top views of the bindings between Li_2S_n (n = 8, 6, 4, 2, 1) species and (a–e) O-doped/(f–j) undoped Sb₂S₃ (010) surface predicted *via* the first-principle calculations. The blue, yellow, red, and green balls are Sb, S, O, and Li atoms, respectively. The adsorption energies are in the range of $-1.01 \sim -2.72$ eV for all types of Li_2S_n (n = 8, 6, 4, 2, 1) on pristine Sb₂S₃ (010) surface *via* a Li–S bond.



Fig. S4 (a) TEM image of SS-O NSs and (b) the corresponding lateral size distributions.



Fig. S5 TEM image of pristine Sb_2S_3 .



Fig. S6 HRTEM of pristine Sb_2S_3 . Inset shows the corresponding SAED pattern.



Fig. S7 AFM image of SS-O NSs.



Fig. S8 Element content of (a) SS-O NSs and (b) pristine Sb_2S_3 . (c–e) HRTEM image of pristine Sb_2S_3 and its corresponding elemental mapping images.



Fig. S9 The initial four CV curves of the Li–S battery based on (a) pristine Sb₂S₃/CNTs-S cathode and (b) CNTs-S cathode at a scan rate of 0.1 mV s⁻¹. The reduction peak at 2.26 V (I) is ascribed to the reduction process of solid S₈ to soluble long-chain LiPSs (Li₂S_n, $4 \le n \le 8$), while the following reduction peak at 2.03 V (II) is due to the further reduction of the soluble long-chain LiPSs (Li₂S_n, $4 \le n \le 8$) to insoluble Li₂S₂/Li₂S. Correspondingly, the two adjacent oxidation peaks (III and IV) around 2.35 and 2.4 V are attributed to the reverse oxidization reactions of Li₂S₂/Li₂S to long-chain LiPSs (Li₂S_n, $4 \le n \le 8$) and eventually to S₈, respectively.^{7,13}



Fig. S10 The Nyquist plots of Li–S batteries with (a) CNTs-S, (b) pristine $Sb_2S_3/CNTs$ -S and (c) SS-O NSs/CNTs-S cathodes after 5th, 50th, 100th cycle at 1 C. The Nyquist plots of (d) CNTs-S, (e) pristine $Sb_2S_3/CNTs$ -S and (f) SS-O NSs/CNTs-S cathode and the corresponding equivalent electric circuits after 5th cycle. The Nyquist plots for the three cathodes after different cycles at 1 C can be fitted according to the equivalent circuits in Fig. S10

(ESI[†]).^{14,15} Fitted values of ohmic resistance (R_b), passivation layer impedance (R_{SEI}), and charge-transfer resistance (R_{ct}) regarding the spectra in Fig. S10 (ESI[†]), are listed in Table S1 (ESI[†]). Notably, the R_{ct} value of the SS-O NSs/CNTs-S cathode decreases gradually from 13.4 to 11.3 Ω after 100 cycles and is remarkably smaller than those of the pristine Sb₂S₃/CNTs-S and CNTs-S cathodes. Moreover, the slanted line at a low frequency range for SS-O NSs/CNTs-S cathode, which reflects a Li⁺ diffusion process in the cathodes, gradually turns to more parallel to the imaginary axis with cycles and their slopes are larger than those of pristine Sb₂S₃/CNTs-S and CNTs-S. The EIS results indicate that the SS-O NSs/CNTs-S cathode realizes a faster interfacial electron transfer and Li⁺ diffusion procedure due to the high electrical/ionic conductivity and catalytic ability of SS-O NSs.¹⁶

Table S1 The ohmic resistance (R_b), passivation layer impedance (R_{SEI}) and charge-transfer resistance (R_{ct}) of CNTs-S, pristine Sb₂S₃/CNTs-S, SS-O NSs/CNTs-S cathodes at different cycles.

Cathodes	Cycles	$R_b[\Omega]$	$R_{SEI} \left[\Omega \right]$	$R_{ct} [\Omega]$
CNTs-S	5	3.67	20.0	11.6
	50	3.93	41.3	18.3
	100	3.93	11.0	14.4
Pristine Sb ₂ S ₃ /CNTs-S	5	3.66	11.3	14.1
	50	3.71	6.11	15.6
	100	3.97	15.7	25.0
SS-O NSs/CNTs-S	5	3.83	22.3	13.4
	50	4.18	8.49	11.7
	100	4.1	8.43	11.3



Fig. S11 Cycling performance of SS-O NSs/CNTs-S cathode (sulfur loading = 4.0 mg cm⁻²) at 0.1 C.



Fig. S12 The *in situ* UV–visible spectra of (a) SS-O NSs/CNTs and (b) pristine Sb₂S₃/CNTs cathode in 0.5×10^{-3} M Li₂S₈ solution during discharge. The normalized absorbance of (c) S₈²⁻ (492 nm), (d) S₆²⁻ (475 nm), (e) S₄²⁻ (420 nm) and (f) S₃^{*-} (617 nm) on different cathodes during discharge.



Fig. S13 *In situ* Raman spectra of (a) SS-O NSs/CNTs-S, (b) bare glass carbon and (c) pristine Sb₂S₃/CNTs-S cathodes obtained during discharge from 2.8 to 1.6 V followed by a recharge process to 2.8 V. At the initial discharge stage, the characteristic Raman peaks of S_8^{2-} at 154 cm⁻¹ (Peak a), S_4^{2-} at 189 cm⁻¹ (Peak b), S_3^{*-} at 236 cm⁻¹ (Peak c),49 and Li–O at 495 cm⁻¹ (Peak d) can be observed in Fig. S13a (ESI[†]).¹⁷ The other peaks can be ascribed to the electrolyte and are shown in Fig. S13b (ESI[†]). In consideration of the interference of S–Sb bond in Sb₂S₃ material itself, the S–Sb bond (at 281.7 cm⁻¹) between surface Sb atom and S atom of LiPSs is not discussed here.

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