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Electronic Supplementary Information (ESI) for Energy & Environmental Science.

# Sustaining vacancy catalysis via conformal graphene overlays boosts practical Li–S batteries

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## **Experimental Section**

#### Preparation of Al<sub>2</sub>O<sub>3</sub>@fG, Al<sub>2</sub>O<sub>3</sub>@mG, and Al<sub>2</sub>O<sub>3</sub>@tG:

The Al<sub>2</sub>O<sub>3</sub> powder materials were sourced from Shanghai St-nano Science and Technology Co., Ltd., China, with an average particle size of 50 nm and a purity of 99.9%. The graphene-coated Al<sub>2</sub>O<sub>3</sub> powder was synthesized using the high-temperature CVD method with an atmospheric pressure system supplied by Anhui BEQ Equipment Technology Co., Ltd., China. Overall, CH<sub>4</sub> (10 sccm) serves as the carbon precursor to enable controllable graphene growth under a mixed gas flow of 50 sccm H<sub>2</sub> and 100 sccm Ar. The thermal treatment was maintained for 30, 60 and 240 mins to derive few-layer, multi-layer and thick-layer graphene chainmail, respectively. Afterward, the furnace was cooled under an Ar flow to room temperature. The as-derived Al<sub>2</sub>O<sub>3</sub>@fG, Al<sub>2</sub>O<sub>3</sub>@mG and Al<sub>2</sub>O<sub>3</sub>@tG were sealed for storage. Likewise, TiO<sub>2</sub>@G, MgO@G and MoO<sub>3</sub>@G can also be readily synthesized by changing the types of powdery substrates.

## Preparation of Al<sub>2</sub>O<sub>3</sub>@fG/PP, Al<sub>2</sub>O<sub>3</sub>@mG/PP, Al<sub>2</sub>O<sub>3</sub>@tG/PP, and Al<sub>2</sub>O<sub>3</sub>/PP:

5 mg Al<sub>2</sub>O<sub>3</sub>@G or Al<sub>2</sub>O<sub>3</sub> was dispersed in 15 mL of ethanol, 9 mL of deionized water and 1 mL of 0.4 wt% LA133 with continuous ultrasonic treatment for 20 min. The suspension was then loaded on the PP separator by vacuum filtration. After vacuum drying at 50 °C, the modified separator was obtained with a mass loading of 0.24 mg cm<sup>-2</sup>.

#### Fabrication of sulfur cathode:

Sulfur impregnation was performed via a melt-diffusion method. A combination of sulfur with super P carbon was mixed at a ratio of 4:1 and grounded for 10 min. Then the mixture was sealed into a bottle and heated at 155 °C for 12 h. A slurry of as-obtained S/C (80 wt%), super P (10 wt%) and LA133 binder (10 wt%) casted onto a piece of Al foil was obtained by blade casting and dried in a vacuum oven at 55 °C overnight. The sulfur loading in the electrode was controlled to be 1.2 mg cm<sup>-2</sup> for typical sulfur electrodes.

#### Characterizations

X-ray diffraction (XRD) patterns were obtained by a Bruker D8 Advance Diffractometer with Cu-K $\alpha$  radiation. X-ray photoelectron spectroscopy (XPS) measurements were conducted on Escalab 250Xi Spectrophotometer using a monochromatic Al K $\alpha$  X-ray source. Morphologies and elemental mapping images were captured using Hitachi SU-8010 Scanning Electron Microscopy (SEM) and Talos F200X G2 Transmission Electron Microscopy (TEM) operated at 200 kV with an energy-dispersive X-ray spectroscopy (EDS) detector. Raman spectra were collected by a HORIBA LabRAM HR Evolution Confocal Raman instrument. The vacancy of the sample was detected by electron paramagnetic resonance (EPR) technique on a Bruker EMX spectrometer. Cryo-TEM characterizations were acquired using a Titan Krios G3i, equipped with a Falcon 3 Direct Electron Detector Camera. ToF-SIMS measurements were conducted using PHI nano ToF II by ULVAC-PHI. The sputter etching was performed using an Cs<sup>+</sup> beam (1 kV, 60 nA) to obtain a depth profile and the area of analysis was 50 × 50  $\mu$ m<sup>2</sup>.

## **PITT test**

Li<sub>2</sub>S<sub>8</sub> solution with a concentration of 0.2 mol L<sup>-1</sup> was prepared by dissolving Li<sub>2</sub>S and sulfur in tetraglyme

solution at a molar ratio of 1:7, followed by continuous stirring until complete dissolution. Al<sub>2</sub>O<sub>3</sub>@mG, Al<sub>2</sub>O<sub>3</sub>@tG, Al<sub>2</sub>O<sub>3</sub>@fG and Al<sub>2</sub>O<sub>3</sub> were dispersed into ethanol, and then dropped onto the carbon paper (CP) with a mass loading of 1.0 mg cm<sup>-2</sup>. As-prepared Al<sub>2</sub>O<sub>3</sub>@mG-CP, Al<sub>2</sub>O<sub>3</sub>@tG-CP, Al<sub>2</sub>O<sub>3</sub>@fG-CP, and Al<sub>2</sub>O<sub>3</sub>-CP were employed as cathode and lithium foil as anode. Then 25  $\mu$ L Li<sub>2</sub>S<sub>8</sub> electrolyte was dropped onto the cathode and 25  $\mu$ L typical electrolyte was dropped onto the anode. The assembled cells were potentiostatically discharged from 2.25 to 1.90 V with a per interval of 50 mV, followed by potentiostatically charged from 2.2 to 2.5 V with each interval of 100 mV.

#### Symmetric cell assembly and measurement

 $Li_2S_6$  solution with a concentration of 0.2 mol L<sup>-1</sup> was prepared by mixing Li<sub>2</sub>S and sulfur with a molar ratio of 1:5 in the DME/1,3-dioxolane (DOL) solution containing 0.5 mol L<sup>-1</sup> LiTFSI and 0.5 mol L<sup>-1</sup> LiNO<sub>3</sub>. Al<sub>2</sub>O<sub>3</sub>@mG-CP, Al<sub>2</sub>O<sub>3</sub>@tG-CP, Al<sub>2</sub>O<sub>3</sub>@tG-CP and Al<sub>2</sub>O<sub>3</sub>-CP were employed as two identical electrodes with a Celgard 2400 membrane. 50 µL as-prepared Li<sub>2</sub>S<sub>6</sub> solution was used as the electrolyte. CV tests of symmetric cells were performed at a scan rate of 0.5 and 50 mV s<sup>-1</sup> with the voltage ranging from -1 to 1 V.

### Li plating/stripping tests

The Li||Cu cells were assembled with Li foil as the counter electrode and bare copper foil (19 mm) as the working electrode. The cells were test at a current density of 0.5 mA cm<sup>-2</sup> and a capacity of 1.0 mAh cm<sup>-2</sup>. The Li||Li cells were assembled with two Li foils as the working electrodes. The electrolyte contains 0.5 M LiTFSI and 0.5 M LiNO<sub>3</sub> dissolved in DOL/DME (1:1 in volume), whose usage was 60  $\mu$ L.

#### **Electrochemical measurements**

The electrochemical measurements were carried out with CR2032 coin cells, which employs S/C as the cathode, lithium foil as anode, and Al<sub>2</sub>O<sub>3</sub>@mG/PP (Al<sub>2</sub>O<sub>3</sub>/PP) as the separator. The electrolyte contains 0.5 M LiTFSI and 0.5 M LiNO<sub>3</sub> dissolved in DOL/DME (1:1 in volume). The E/S ratio was controlled at 15  $\mu$ L mg<sup>-1</sup>. CV profiles at varied scan rates were recorded on the CHI660D electrochemical workstation. Galvanostatic charge/discharge profiles and rate/cycling performances were conducted on a LAND battery testing system with a voltage range of 1.7–2.8 V (vs. Li/Li<sup>+</sup>).

### **Theoretical calculations**

First-principles calculations were conducted using the Vienna Ab initio Simulation Package.<sup>1</sup> The generalized gradient approximation of Perdew-Burke-Ernzerhof functional was employed for the exchange correlation potential.<sup>2</sup> All slab models were built with 15 Å vacuum region to avoid the interaction between periodic layers. Oxygen vacancies were generated by the deletion of oxygen atoms. During the relaxation and adsorption calculations, the cutoff energy, energy convergence, and force convergence are set as 450 eV,  $10^{-5}$  eV, and 0.02 eV Å<sup>-1</sup>, respectively. The k-point grid with Monkhorst–Pack scheme was  $2 \times 1 \times 1$ . The correction of the Gibbs free energy was considered at 298.15 K. The adsorption energy was calculated from the Gibbs free energy difference of products and reactants. To analyze the chemical bond of intermediate species, the crystal orbital Hamilton population method was employed.<sup>3</sup> The climbing-image nudged elastic band calculations were implemented for the lithium-ion diffusion barrier and the dissociation of Li<sub>2</sub>S.

#### **Molecular dynamics simulations**

The large-scale atomic/molecular massively parallel simulator (LAMMPS) was employed for molecular dynamics simulations with  $3.4 \text{ nm} \times 3.1 \text{ nm} \times 8.8 \text{ nm}$  models.<sup>4</sup> There are 2061 atoms for Al<sub>2</sub>O<sub>3</sub>, and the graphene layer was set above the surface of Al<sub>2</sub>O<sub>3</sub>. Three different graphene layers namely, one, two, and three were places to reveal the effect of number of layers on surface oxygen vacancies and structures. The force field for C–C was the adaptive intermolecular reactive empirical bond order (AIREBO) potential,<sup>5</sup> and the force fields for Al–O, O–O, Al–Al, and C–O were Lennard-Jones (LJ) potentials parameters.<sup>6</sup> The canonical (NVT) ensemble was carried out at 300 K.<sup>7</sup>

#### **Finite element simulations**

The ion distribution profiles were obtained by performing finite element-based simulations for various geometry designs. The Nernst-Planck formulation describes the transport of Li ions in electrode materials, i.e., diffusion and electro-migration. The governing equations, considering ion flux, material balance, electro-neutrality, and electrode kinetics, are given as:

$$J_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \phi_l \tag{1}$$

$$\frac{\partial \mathbf{c}_{i}}{\partial t} + \nabla \cdot \boldsymbol{J}_{i} = \boldsymbol{R}_{i}$$
<sup>(2)</sup>

$$\sum_{i} z_i c_i = 0 \tag{3}$$

$$i_{loc} = i_0 (\exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(-\frac{\alpha_c F \eta}{RT}\right) )$$
(4)

where  $N_i$  is the transfer vector,  $J_i$  is the diffusion coefficient,  $c_i$  is the concentration,  $z_i$  is the charge number,  $u_i$  is the mobility (defined by the Nernst-Einstein equation),  $\phi_l$  is the electrolyte potential,  $R_i = \frac{\nu_i i_{loc}}{nF}$ .  $i_{loc}$  is local current density related to Li<sup>+</sup> concentration,  $i_0$  is exchange current density,  $\alpha_a$  is anode diffusion coefficient,  $\eta$  is overpotential,  $\alpha_c$  is cathode diffusion coefficient, R is ideal gas constant, T is temperature.

The initial concentration of Li<sup>+</sup> was set to be 1 M (1000 mol m<sup>-3</sup>). The boundary average current density of the anode is 50 A/m<sup>2</sup>, and the boundary voltage of the cathode is 0 V. As for the geometric parameters, the size of the membrane domain is  $15 \times 13.5 \ \mu\text{m}^2$  in the control group. In the experimental group, the size of the membrane domain is  $15 \times 13.5 \ \mu\text{m}^2$ , and the size of the coating domain is  $15 \times 13.5 \ \mu\text{m}^2$ .

# **Supplementary Figure and Table**



Fig. S1: XRD patterns of Al<sub>2</sub>O<sub>3</sub>@fG, Al<sub>2</sub>O<sub>3</sub>@mG, and Al<sub>2</sub>O<sub>3</sub>@tG.



Fig. S2: EPR spectrum of Al<sub>2</sub>O<sub>3</sub>.



 $\label{eq:Fig. S3: SEM images of (a) Al_2O_3, (b) Al_2O_3 @fG, (c) Al_2O_3 @mG and (d) Al_2O_3 @tG.$ 



Fig. S4: TEM images of (a) Al<sub>2</sub>O<sub>3</sub>, (b) Al<sub>2</sub>O<sub>3</sub>@fG and (c) Al<sub>2</sub>O<sub>3</sub>@tG.



**Fig. S5:** TEM images of Al<sub>2</sub>O<sub>3</sub>@mG.



Fig. S6: Corresponding elemental maps of Al<sub>2</sub>O<sub>3</sub>@mG.



Fig. S7: PITT curves of discharge process for Al<sub>2</sub>O<sub>3</sub>.



**Fig. S8:** (a) Current–time profiles and (b) corresponding calculated capacity along with response time in the PITT of charging process.



Fig. S9: Operando Raman spectra of the electrolyte with respect to Al<sub>2</sub>O<sub>3</sub>@mG/PP during the first cycle.



Fig. S10: CV curves of Al<sub>2</sub>O<sub>3</sub>-CP symmetric cell at a scan rate of 50 mV s<sup>-1</sup>.



**Fig. S11:** CV curves of (a)  $Al_2O_3@fG-CP$ , (b)  $Al_2O_3@tG-CP$  and (c)  $Al_2O_3-CP$  symmetric cells at a scan rate of 0.5 mV s<sup>-1</sup>.



**Fig. S12:** CV curves of (a) MgO@G-CP, (b) TiO<sub>2</sub>@G-CP and (c) MoO<sub>3</sub>@G-CP symmetric cells at a scan rate of 0.5 mV s<sup>-1</sup>.



Fig. S13: UV–Vis absorption spectra in Li<sub>2</sub>S<sub>6</sub> solution. Inset: Digital photo of visualized adsorption tests.



**Fig. S14:** (a) The optimized structures of  $Al_2O_3$ ,  $Al_2O_{3-x}$ , and  $Al_2O_{3-2x}$ . (b) Adsorption energies of  $Li_2S_2$  and the integrated crystal orbital Hamilton population (-ICOHP) of Al–S bonds.



Fig. S15: Strength of Al–S bond from the ICOHP calculations for  $Li_2S_4$  adsorption.



Fig. S16: The optimized structures of Al<sub>2</sub>O<sub>3</sub>@mG with various sulfur species.



Fig. S17: The optimized structures of Al<sub>2</sub>O<sub>3</sub> with various sulfur species.



**Fig. S18:** Projection density of states (PDOS) and crystal orbital Hamilton population (COHP) of Al–S bonding for (a) Al<sub>2</sub>O<sub>3</sub>, (b) Al<sub>2</sub>O<sub>3-x</sub>, and (c) Al<sub>2</sub>O<sub>3-2x</sub>.



Fig. S19: DFT simulation on the Li<sub>2</sub>S<sub>2</sub> dissociation barrier for (a) Al<sub>2</sub>O<sub>3</sub> and (b) Al<sub>2</sub>O<sub>3</sub>@mG.



Fig. S20: Optimized Li<sub>2</sub>S<sub>2</sub> dissociation state on Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>@mG.



Fig. S21: Ex situ EPR spectra of (a) Al<sub>2</sub>O<sub>3</sub>@fG and (b) Al<sub>2</sub>O<sub>3</sub>@tG.



**Fig. S22:** (a) CV curves of  $Al_2O_3$ @mG-CP symmetric cells with different cycles at a scan rate of 50 mV s<sup>-1</sup>. (b) Cycling performance of Li–S batteries with a resting time of 20 h after the 9<sup>th</sup> cycle at 0.5 C. (c) Comparison of major catalytic performance metrics among graphene overlays with varying layer numbers.



Fig. S23: Initial and final states of  $V_0$ -rich  $Al_2O_3$  with different graphene coatings by molecular dynamics simulations.



**Fig. S24:** Rate performances of  $Al_2O_3@fG/PP$  (up) and  $Al_2O_3@tG/PP$  (down) at a current density of 0.5–5 mA cm<sup>-2</sup> with a capacity of 1.0 mAh cm<sup>-2</sup>.



Fig. S25: Cycling performances of  $Al_2O_3$  (#G/PP and  $Al_2O_3$  (#mG/PP at 1.0 mA cm<sup>-2</sup> with a capacity of 1.0 mAh cm<sup>-2</sup>.



Fig. S26: Enlarged voltage profiles of Li||Li symmetric cells at 1.0 mA cm<sup>-2</sup> with a capacity of 1.0 mAh cm<sup>-2</sup>.



Fig. S27: SEM images of Li metal influenced by (a)  $Al_2O_3$ , (b)  $Al_2O_3@fG$ , (c)  $Al_2O_3@mG$  and (d)  $Al_2O_3@tG$  after cycling at 1.0 mA cm<sup>-2</sup> with a capacity of 1.0 mAh cm<sup>-2</sup>.



**Fig. S28:** (a) Voltage–capacity profiles of Li nucleation and (b) Coulombic efficiencies at 0.5 mA cm<sup>-2</sup> with a fixed capacity of 1 mA h cm<sup>-2</sup>.



Fig. S29: XPS depth profiling of F 1s spectra for (a) Al<sub>2</sub>O<sub>3</sub> and (b) Al<sub>2</sub>O<sub>3</sub>@mG.



Fig. S30: Atomic ratios of different elements at an etching time of 120 s.



Fig. S31: Atomic ratios in the SEI of (a) Al<sub>2</sub>O<sub>3</sub> and (b) Al<sub>2</sub>O<sub>3</sub>@mG.



Fig. S32: 3D reconstruction of the measured ToF-SIMS signal for  $LiN^-$  secondary ion of the SEI formed by (a)  $Al_2O_3$  and (b)  $Al_2O_3$ @mG.



Fig. S33: The proportion of different components in the SEI formed by (a) Al<sub>2</sub>O<sub>3</sub> and (b) Al<sub>2</sub>O<sub>3</sub>@mG.



**Fig. S34:** The adsorption structures of  $NO_3^-$  on the  $Al_2O_3$ .



Fig. S35: The adsorption sites and the corresponding adsorption energy of Li<sup>+</sup> on the Al<sub>2</sub>O<sub>3</sub>.



Fig. S36: The adsorption sites and the corresponding adsorption energy of  $Li^+$  on the  $Al_2O_3@mG$ .



Fig. S37: The structures of  $Li^+$  diffusion on the  $Al_2O_3$ ,  $Al_2O_{3-x}$ , and graphene.



Fig. S38: The kinetic energy barriers of  $Li^+$  diffusion on the (a)  $Al_2O_3$ , (b)  $Al_2O_{3-x}$ , and (c) graphene.



Fig. S39: Finite element method simulations of the spatial  $Li^+$  distributions on  $Al_2O_3$  after 1, 2, 3 and 4 s, respectively.



Fig. S40: Finite element method simulations of the spatial  $Li^+$  distributions on  $Al_2O_3$ @mG after 1, 2, 3 and 4 s, respectively.



Fig. S41: Tafel plots of the redox peaks corresponding to (a) peak i, (b) peak ii, and (c) peak iii.



Fig. S42: CV profiles of (a) Al<sub>2</sub>O<sub>3</sub>@mG, (b) Al<sub>2</sub>O<sub>3</sub>, and (c) PP at different scan rates.



Fig. S43: Fitted curves of Al<sub>2</sub>O<sub>3</sub>@mG, Al<sub>2</sub>O<sub>3</sub>, and PP.



Fig. S44: (a) Nyquist plots of Al<sub>2</sub>O<sub>3</sub>@mG, Al<sub>2</sub>O<sub>3</sub>, and PP. (b) Equivalent-circuit fitting.



Fig. S45: Galvanostatic charge/discharge profiles of (a) Al<sub>2</sub>O<sub>3</sub>@mG, (b)Al<sub>2</sub>O<sub>3</sub>, and (c) PP at different scan rates.



Fig. S46: Comparison of  $Q_{\rm H}$  and  $Q_{\rm L}$  capacities at 0.2 C.



Fig. S47: Cycling performances of Li–S batteries equipped with Al<sub>2</sub>O<sub>3</sub>@mG/PP under different sulfur loadings.



Fig. S48: Galvanostatic charge/discharge profiles of the pouch cell with  $Al_2O_3$ @mG modified separator at 0.2 C.

Mediators	Current density (mA cm <sup>-2</sup> )	Capacity (mAh cm⁻²)	Time (h)	Ref.	
Al₂O₃@mG	1.0	1.0	1860	This work	
Co/MoN	1.0	1.0	800	8	
MoSe <sub>2-x</sub> @GA	0.5	0.5	1800	9	
	1.0	1.0	800	Ū	
CoPNC	0.5	0.5	1000	10	
VC-1	1.0	1.0	500	11	
V <sub>8</sub> C <sub>7</sub> -VO <sub>2</sub>	3.0	1.0	400	12	
Ti <sub>0.87</sub> O <sub>2</sub>	2.0	1.0	300	13	
rGO/MoSSe	2.0	1.0	1200	14	
D-HVS	1.0	1.0	200	15	

Table S1: Comparison between our work and related Li anode mediators reported in Li–S batteries.

Mediators	Areal sulfur loading (mA cm <sup>-2</sup> )	Areal capacity (mAh cm⁻²)	Cycle number	Rate (C)	Ref.
Al₂O₃@mG	3.1	3.9	40	0.1	
	4.2	4.1	40	0.1	This work
	5.1	4.7	100	0.1	
MnO <sub>2</sub> @HCF	3.5	2.3	300	0.5	16
MoO <sub>2</sub> -CC	5.0	3.7	60	0.1	17
NiMoO <sub>4</sub> @NSCC	5.0	2.8	120	1.0	18
	4.0	2.3	120	1.0	
Al <sub>2</sub> O <sub>3</sub> /PAN	3.6	3.2	200	0.05	19
Mo-Ti/Mx-GN	8.4	7.2	40	0.2	20
CNTs/CNFs/Ni-Co	2.5	1.8	200	0.1	21

**Table S2:** Comparison of the electrochemical performances of high sulfur loading coin-type batteries between our work and related metal oxide mediators reported in Li–S batteries.

Materials	Areal capacity (mAh cm <sup>-2</sup> )	Capacity retention (%)	Cycle number	E/S ratio (µL mg⁻¹)	Ref.
Al <sub>2</sub> O <sub>3</sub> @mG	5.4 (0.2 C)	73.1	70	4.8	This work
VC	4.3 (0.2 C)	71.7	150	4.2	11
VS₄@RGO	3.9 (C/7)	82.0	50	7.2	22
FVO/CNT	5.79 (0.05 C)	81.0	12	3.0	23
EPSE	7.0 (0.05 C)	81.0	24	3.0	24
G-mSnO <sub>2</sub> /SnSe <sub>2</sub>	3.1 (0.25 C)	93.0	40	3.0	25
Co/MoN	2.9 (0.2 C)	61.2	20	10	8
TEMPO	2.4 (0.5 C)	78.0	44	7.0	26
12PEI_KB-PAA	2.7 (0.5 C)	57.3	80	N/A	27
B₄C@CNF	4.0 (0.1 C)	90.0	58	7.0	28

Table S3: Performance comparison of Li–S pouch cells between this work and recent reports.

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