Supporting Information

Stabilization of polysulfides via lithium bonds for Li–S batteries

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Methods

Synthesis of g-C₃N₄, g-C₃N₄@CFM, Graphene@CFM, VC@CFM. The g-C₃N₄ powder was synthesized according to procedures described in previous papers.^{1, 2, 3} In detail, melamine (99%, Wako) was heated at 550 °C for 4h in static air with a ramp rate of 2.3 °C min⁻¹: the cooling rate was kept at around 1°C/min. The resultant yellow agglomerates were ball-milled into powder. Then, the powder was placed in an open ceramic container and was heated at 500 °C for 2 h with a ramp rate of 5°C min⁻¹. Finally, a light yellow powder of g-C₃N₄ was obtained with a yield of about 8 wt%. To obtain the g-C₃N₄ coated carbon fiber mesh (CFM, specific surface area: ~5 m^2/g , Figure S1) composites, the slurry of the guanidine hydrochloride and polyvinylidene fluoride (PVDF) with a 9 : 1 mass ratio in an N-methyl pyrrolidone (NMP) was pasted on a CFM (diameter is 9 mm), then the sample was heated at 550 °C for 3.5 h in an Ar atmosphere with a flow of 100 sccm and a ramp rate of 2.3 °C min⁻¹; the cooling rate was kept at around 1°C min⁻¹. The Graphene or VC (VULCAN XC72) coated CFM electrodes were prepared using the same method, i.e., the slurry of the Graphene or VC and polyvinylidene fluoride (PVDF) with a 9 : 1 mass ratio in an N-methyl pyrrolidone (NMP) was pasted on a CFM (diameter is 9 mm). Then, a heat treatment was performed as described in preparing $g-C_3N_4$ coated CFM. The mass loading of the g-C₃N₄, VC, Graphene on CFM is ~10 wt%.

Synthesis of Li₂S₆ in TEGDME. The preparation of Li₂S₆ solutions was adopted from a method reported by Manthiram et al.⁴ In detail, the Li₂S (99.9% purity, Alfa Aesar) and elemental sulfur (S₈) powders were mixed with a molar ratio of 4 : 3 ($4Li_2S + 3S_8 \rightarrow 4Li_2S_6$) in a solvent of tetra (ethylene) glycol dimethyl ether (TEGDME) in an Ar-filled glove box. The resultant mixture was maintained at 50 °C for 12 h under stirring and then was centrifuged at 5000 rpm for 10 min to remove the precipitations, giving rise to a red-brown solution, which corresponds to the average composition of Li₂S₆. To determine the solution concentration, the as-obtained Li₂S₆ solution was dried in vacuum to evaporate the TEGDME until the weight indeclinable and then the concentration was calculated to be 0.3 mol L⁻¹.

Battery assembly. All devices were assembled in an Ar gas filled glovebox. Tetra (ethylene) glycol dimethyl ether (TEGDME, >99.9%, Sigma) was dried over 4 Å molecular sieve. The electrolyte was prepared by dissolving 1 mol L⁻¹ Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, >99.95%, Sigma) and 0.2 mol L⁻¹ LiNO₃ (>99.9%, Wako) in TEGDME. The Li/dissolved polysulfide coin cell (CR2032) was assembled with the cathode (CFM, VC@CFM, Graphene@CFM, or g-C₃N₄@CFM), Celgard 2400 separator, lithium foil anode and electrolyte. In detail, the same amount of the polysulfide catholyte (7uL 0.3 mol L⁻¹ Li₂S₆) was added into each electrode, corresponding to 0.4 mg (0.6 mg cm⁻²) of sulfur. The blank electrolyte (45 uL) was added on a Celgard 2400 separator and the lithium metal anode was placed on the separator. In

addition, the Li/dissolved polysulfide cells with additive-free electrolyte (1 mol L^{-1} LiTFSI without LiNO₃ in TEGDME) were also fabricated and tested for a comparison.

Measurements and characterization. X-ray diffraction was performed on a Bruker D8 Advanced diffractometer with Cu K α (λ =1.5406Å) radiation. Chemical state and composition were characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi). Galvanostatic discharge/charge was conducted on a Hokuto discharging/charging system. The Li-S cells were rest for 10h before electrochemical tests and all electrochemical measurements were conducted at 25 °C. Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDS, LEO Gemini Supra 35) were obtained with an accelerating voltage of 5kV and 15kV, respectively.

DFT calculations. First-principles calculations were performed using the Vienna Ab initio Simulation Package (VASP)^{5, 6} within the projector augmented-wave approach.⁷ Generalized gradient approximation (GGA) in the parameterization of Perdew, Burke, and Ernzerhof (PBE)⁸ pseudopotential was used to describe the exchange-correlation potential. Besides the standard DFT calculations, the vdW-DF2 functional was used to account for the van der Waals (vdW) interaction.⁹⁻¹¹ The Li(1s,2s,2p), S(3s,3p), C(2s,2p), and N(2s,2p) orbitals are treated as valence states. The plane-wave cutoff was set to 520 eV. Geometry optimizations were performed by using a conjugate gradient minimization until all the forces acting on ions were less than 0.01 eV/Å per atom. The k-point mesh is $3 \times 3 \times 2$ in the structural relaxation. In the calculations of electronic structure, a denser $5 \times 5 \times 3$ mesh is adopted for the k-point sampling. The surface model is based on a $6a \times 6b$ Graphene and a $2a \times 2b$ g-C₃N₄ monolayer (Figure S2), both separated by a vacuum layer of 20Å. The optimized structures for lithium polysulfides are also shown in Figure S2. To find the ground-state of S_8/Li_2S_n adsorbed on the Graphene/g- C_3N_4 , various initial configurations are calculated and the most energetically favorable geometries (Figure S3, S4) are used for further analysis. The adsorption energy between the surface and adsorbed molecule is determined by $E_a =$ $E_{\text{surf.}} + E_{\text{ads.}} - E_{\text{ads.}@\text{surf.}}$, where $E_{\text{surf.}}$, $E_{\text{ads.}}$, and $E_{\text{ads.}@\text{surf.}}$ denote the total energies of the pristine surface, the adsorbed molecule, and the adsorbed surface, respectively.



Figure S1. Nitrogen-adsorption-desorption isotherms of the CFM, VC, $g-C_3N_4$, VC@CFM, $g-C_3N_4$ @CFM, and Graphene@CFM samples, respectively.



Figure S2. Sealed vials of a Li_2S_6 -DME solution (1), and after contact with pristine CFM (2) and g-C₃N₄@CFM (3), immediately upon contact and after 2 h interaction.

3



Figure S3. Illustration of structural models adopted in this work. Upper: Graphene (left) and $g-C_3N_4$ (right) monolayer. Lower: optimized conformations of S_8 and Li_2S_n (n = 1, 2, 4, 6, 8) molecules. Color scheme: green, yellow, brown, and blue spheres refer to Li, S, C, and N atoms, respectively.



Figure S4. Relaxed geometries of lithium polysulfides adsorbed on Graphene. The flat Graphene layer is almost unchanged in the presence of the adsorbates. Color scheme: green, yellow, and brown spheres refer to Li, S, and C atoms, respectively.



Figure S5. Relaxed geometries of lithium polysulfides adsorbed on a monolayer of $g-C_3N_4$. Significant structural distortions are induced by the surface adsorption. Color scheme: green, yellow, brown, and blue spheres refer to Li, S, C, and N atoms, respectively.



Figure S6. Rate performance of the $g-C_3N_4@CFM$ and pristine CFM cathode at different current densities from 0.1 to 0.5 C (voltage range: $1.8 \sim 2.8$ V).



Figure S7. Comparison of $g-C_3N_4@CFM$ and pristine CFM without LiNO₃ additive in the electrolyte at a 0.1C rate (167.2 mA g⁻¹) showing (a) the first discharge and subsequent charge profiles, and (b) the Coulombic efficiency upon cycling (CE = charge capacity / discharge capacity).



Figure S8. Galvanostatic discharge/charge profiles of the Graphene@CFM (**a**) and VC@CFM (**b**) electrodes at 0.1C (1C=1672 mA g^{-1}).

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