Reducing shuttle effect with the interactions of polar TiN and

non-polar graphene for lithium-sulfur batteries

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Experimental section

Preparation of TiN/NG

The TiN/NG hybrid was prepared by a hydrothermal method combined with ammonia annealing, according to the previously reported procedure.^[1,2] Briefly, 200 mg graphene oxide powders were dispersed in 400 ml absolute ethanol with an ultrasonic treatment in ice-bath for 2 h. Afterwards, 10 mg hexadecylamine (HDA) as the reducer was dissolved in the above solution under continuous stirring to form the graphene. Specifically, 3.5 ml tetrabutyl titanate served as the titanium source, and 5ml deionized water were added dropwise into the mixed solution in turn. The above solution was maintained stirring for 6 h to make sure the titanium source was uniformly and sufficiently dispersed on graphene. Next, 200 ml deionized water was added to the solution. The mixture was then transferred to the Teflon-lined autoclave, and

hydrolyzed at 160 °C for 5 h. Afterwards, through a succession of processes including centrifuge, washing and freeze-drying, the TiO_2/G hybrid was obtained. It was further annealed at 800 °C for 3 h under an ammonia atmosphere in a tube furnace to obtain titanium nitride/nitrogen-doped graphene, which was noted as TiN/NG.

Preparation of NG and G

The suspension of graphene was prepared using the same procedure as the preparation of TiN/NG. After centrifuge, washing and freeze-drying, the graphene powder was obtained. Then it was annealed at 800 °C for 3 h under an ammonia atmosphere to obtain nitrogen-doped graphene, which was noted as NG. While, the graphene powder was annealed at 800 °C for 3 h under an argon atmosphere to obtain G.

Preparation of the sulfur cathodes

The TiN/NG/S, NG/S and G/S composites were prepared by a melt-diffusion method. The sulfur and TiN/NG powder were put into the mortar according to the mass ratio of 7:3. Then, grind constantly until sulfur was uniformly distributed into TiN/NG. Afterwards, the mixture was transferred to Teflon-lined autoclave, which was heated at 155 °C for 12 h. The TiN/NG/S hybrid was obtained after natural cooling to room temperature. To prepare the sulfur electrodes, 80 wt.% sulfur/carbon composite, 10 wt.% carbon black, and 10 wt.% polyvinylidene fluoride (PVDF) were mixed in an agate mortar using N-methyl-2-pyrrolidone (NMP) as solvent to form a slurry, and coated onto an aluminum foil with a material loading of 3 mg cm⁻², then dried in vacuum oven at 60 °C for 12 h. Afterwards the aluminum foil with active material was cut into eletrode tabs (14 mm in diameter), so we got TiN/NG/S cathodes. The NG/S and G/S composite cathodes were prepared by the same general procedure.

Preparation of the Li₂S₆ solution

Sulfur and Li_2S at a molar ratio of 5:1 were added to an appropriate amount of 1,2dimethoxyethane (DME, 99.5%, Alfa Aesar) and 1,3-dioxolane (DOL, 99.5%, Alfa Aesar) (1:1 ratio by volume) by vigorous magnetic stirring at 60 °C until the sulfur was fully dissolved.

Polysulfide adsorption test

A solution with a Li_2S_6 concentration of 50 mmol/l (calculated based on sulfur content) was used. 20 mg of TiN/NG and NG powder were separately added to 2 ml of Li_2S_6 solution and the mixtures were stood for 24 hours. A blank glass vial was also filled with the same Li_2S_6 solution as a comparison. Extracted the supernatant of the above solution (TiN/NG- Li_2S_6 , NG- Li_2S_6 , and Li_2S_6), and diluted 100 times by DOL and DME (1:1 ratio by volume) for absorbance analysis test.

Materials characterization

The morphology and structure of the materials were characterized by using a SEM (FEI Nova Nano SEM 430, 15 kV) and a TEM (FEI CM120). EDX elemental maps and HRTEM images were obtained on a FEI Tecnai F20 microscope equipped with an Oxford EDX analysis system with an acceleration voltage of 200 kV. Raman measurements were performed using a Jobin Yvon Lab RAM HR800 with a 632.8 nm He-Ne laser. XRD patterns were obtained on a Rigaku diffractometer (Cu K_a, λ =0.154056 nm). XPS measurements were carried out in an ultra-high vacuum ESCALAB 250 equipped with a monochromatic Al K_a X-ray source (1486.6 eV; anode operating at 15 kV and 20 mA). TGA was performed with a NETZSCH STA 449 C thermo balance in air with a heating rate of 10 °C min⁻¹ from room temperature to 1,000 °C. N₂ adsorption/desorption isotherms were determined using a UV-Vis spectrophotometer (VARIAN CARY 5000) at wavelength of 250-800 nm.

Electrochemical measurements

2025-type stainless steel coin cells were assembled inside an Ar-filled glove box. The electrolyte was lithium bis-trifluoromethaesulphonylimide (99%, Acros Organics, 1 M) dissolved in 1,3-dioxolane (DOL, 99.5%, Alfa Aesar) and 1,2-dimethoxyethane (DME,

99.5%, Alfa Aesar) (1:1 ratio by volume) with 0.2 M lithium nitrate (LiNO₃, 99.9%, Alfa Aesar) as the additive. Lithium metal foil (16 mm in diameter, 0.45 mm in thickness) was used as the anode and Celgard 2400 (19 mm in diameter, 25 μ m in thickness) as the separator. The assembly process was as follows: The sulfur cathode and separator were placed on the coin cell base in turn, after which 40 μ l electrolyte was added. Lithium metal foil and foamed nickel are sequentially placed, and then the coin cell lid was covered. The assembled coin cells were sealed by a battery sealing machine, and stood under an open circuit voltage for 12 hours, so that electrolyte and sulfur cathodes were fully immersed. Afterwards the electrochemical tests were performed.

A LAND galvanostatic charge-discharge instrument was used to perform electrochemical measurements. The C-rate used here was based on the theoretical specific capacity of sulfur (1C=1675mAhg⁻¹). The charge-discharge voltage range was 1.7-2.8 V. The CV and EIS measurements were performed using a VSP-300 multichannel workstation. The frequency range of the EIS measurements was 100 kHz to 10 mHz with an AC voltage amplitude of 5 mV at the open-circuit potential.



Fig. S1 (a) SEM images and (b-d) corresponding elemental mapping images of G/S materials.



Fig. S2 (a) SEM images and (b) corresponding elemental mapping images of NG/S materials.



Fig. S3 (a) SEM images and (b-f) corresponding elemental mapping images of TiN/NG/S materials.



Fig. S4 TG curve of TiN/NG. According to the surplus material TiO_2 was 40.4 wt.%, the ratio of TiN in original samples was about 31 wt.%.



Fig. S5 Nitrogen adsorption-desorption isotherm, BJH pore distribution and HK pore distribution of TiN/NG (a-c) and G (d-e).



Fig. S6 TG curve of TiN/NG/S, NG/S and G/S electrode materials. The ratio of S in all samples was about 70 wt.%.



Fig. S7 Nyquist plots of TiN/NG/S, NG/S and G/S electrodes. The inset is the corresponding equivalent circuit.



Fig. S8 (a) Optical photos of NG and TiN/NG materials soaked in Li_2S_6 solution after standing for 24 hours. (b) UV-vis absorption spectrum of supernatant of Li_2S_6 , NG- Li_2S_6 and TiN/NG- Li_2S_6 solution after diluting 100 times.

Reference

- [1] Y. Yue, P. Han, X. He, K. Zhang, Z. Liu, C. Zhang, S. Dong, L. Gu and G. Cui, J. Mater. Chem., 2012, 22, 4938.
- [2] F. Dabir, R. Sarraf-Mamoory, M. Loeblein, S. H. Tsang and E. H. T. Teo, *Materials and Design*, 2016, 90, 524.