

Supplementary Information for

A Layered porous ZrO₂/RGO composite as sulfur host for Lithium-Sulfur Batteries

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Experimental Part

Materials synthesis

Preparation of GO

Graphene oxide (GO) was synthesized by the modified Hummers method. Typically, 0.5 g Graphite power was added to 15 ml concentrated sulfuric acid, and ultrasonic for 10 min. Then, 1.5 g potassium permanganate was gradually added to the graphite solution under vigorous stirring. The reaction was allowed to proceed at 50 °C for 3h before the solution was cooled in an ice bath and diluted with 150 ml deionized water. After stirring for 15min, 15ml hydrogen peroxide was added to the reaction solution. The mixture was then centrifugated and washed several times with 10% hydrochloric acid and water. The resultant GO gel was attained by centrifugation at 1 4000 rpm.

Preparation of ZrO₂/RGO

A simple synthetic process was used to prepare ZrO₂ particles with a few nanometers thick on the RGO. First, 3 ml GO gel with a concentration of 30 mg/ml was dispersed into 50 ml isopropanol, and was sonicated for 30 min before the adding of 0.62 mmol ZrOCl₂ • 8H₂O. Subsequently, 5 ml NaOH solution was added into the above mixture and stirred at 40 °C for 2 h. After that, the mixture was transferred into a

100ml Teflon-lined autoclave and maintained at 180 °C for 15 h. The sample was obtained and washed with water and ethanol repeatedly. Finally, the product was dried at 60 °C for 12 h for further synthesis.

Preparation of S@ZrO₂/RGO

The S@ZrO₂/RGO nanocomposite was prepared using a melt-diffusion strategy. Typically, sublimed sulfur was mixed homogeneously with ZrO₂/RGO power with a mass ratio of 4:1. Then, the mixture was heated at 155 °C for 12 h in a quartz tube with argon gas flow. For comparison, S@RGO with a sulfur content of 66 % was also prepared under the same conditions. Sulfur contents were determined by thermogravimetric analysis respectively (**Fig. S3**).

Materials Characterization

The morphologies and microstructures of the composites were characterized by X-ray diffraction (XRD, RIGAKU SCXmini), X-ray photoelectron spectroscopy (XPS, ESCALAB 250), scanning electron microscope (SEM, JSM-6700F), and transmission electron microscope (TEM, Tecnai G2 F20). To evaluate the mass content of sulfur in the composites, thermogravimetric analyses (TGA, NETZSCH STA449C) were carried out under N₂ flow with a heating rate of 10K min⁻¹.

Electrochemical measurements

To fabricate the working electrodes, 80 wt% S@ZrO₂/RGO composite, 10 wt% conductivity agent (Ketjen black, KB), and 10 wt% PVDF were mixed with N-methyl-2-pyrrolidone (NMP) and then pasted on Ni foam. The areal loading of sulfur is 1mg/cm² on average. The electrodes were dried at 60 °C for 12 h in a vacuum. Cells were assembled in an Ar-filled glove box with the concentration of moisture and oxygen below 1 ppm. Pure lithium foil was used as both counter and reference electrode. The electrolyte was 1.0 M lithium bis(trifluoromethane)sulfonamide lithium salt (LiTFSI, Sigma-Aldrich) dissolved in a mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 by volume), with 0.25 M LiNO₃ as an additive to help passivate the surface of the lithium anode and reduce the shuttle effect, the amount of electrolyte for each cell is about 0.12 ml. A Celgard 2300 membrane was used as the separator. Galvanostatic discharge/charge cycles were performed on a LAND 2001A system over a voltage range of 1.8 to 2.8 V (vs. Li). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy measurements were conducted by CHI660C Electrochemical Workstation. The CV tests were carried out by with the voltage range from 1.5 V to 3.0 V, at a scan rate of 0.2 mV s⁻¹. Electrochemical impedance spectrums (EIS) were carried out on 3-electrode cells by

applying an AC voltage of 5 mV over the frequency range from 1 mHz to 100 kHz. The specific capacities in this article were calculated based on the mass of sulfur.

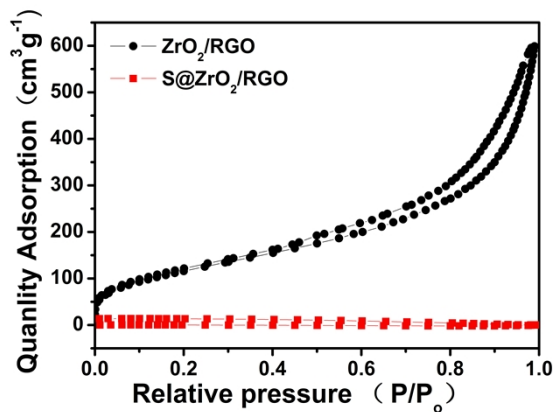


Fig. S1. Nitrogen adsorption-desorption isotherms of ZrO₂/RGO and S@ZrO₂/RGO composites.

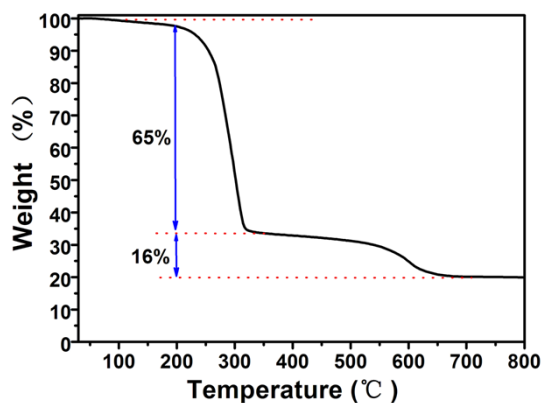


Fig. S2. TGA cure of the S@ZrO₂/RGO composite, under oxygen condition.

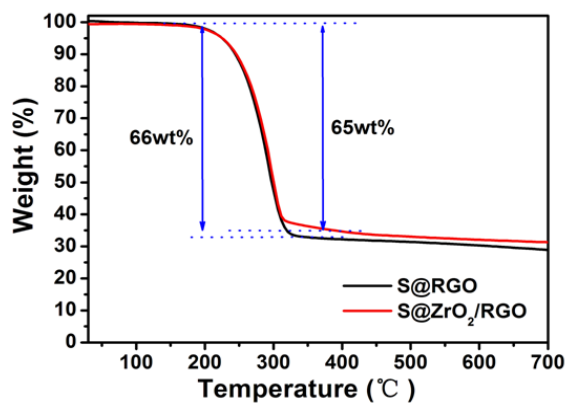


Fig. S3. Thermogravimetric analysis of sulfur loading in the S@RGO composite and the S@ZrO₂/RGO composite, under N₂ condition.

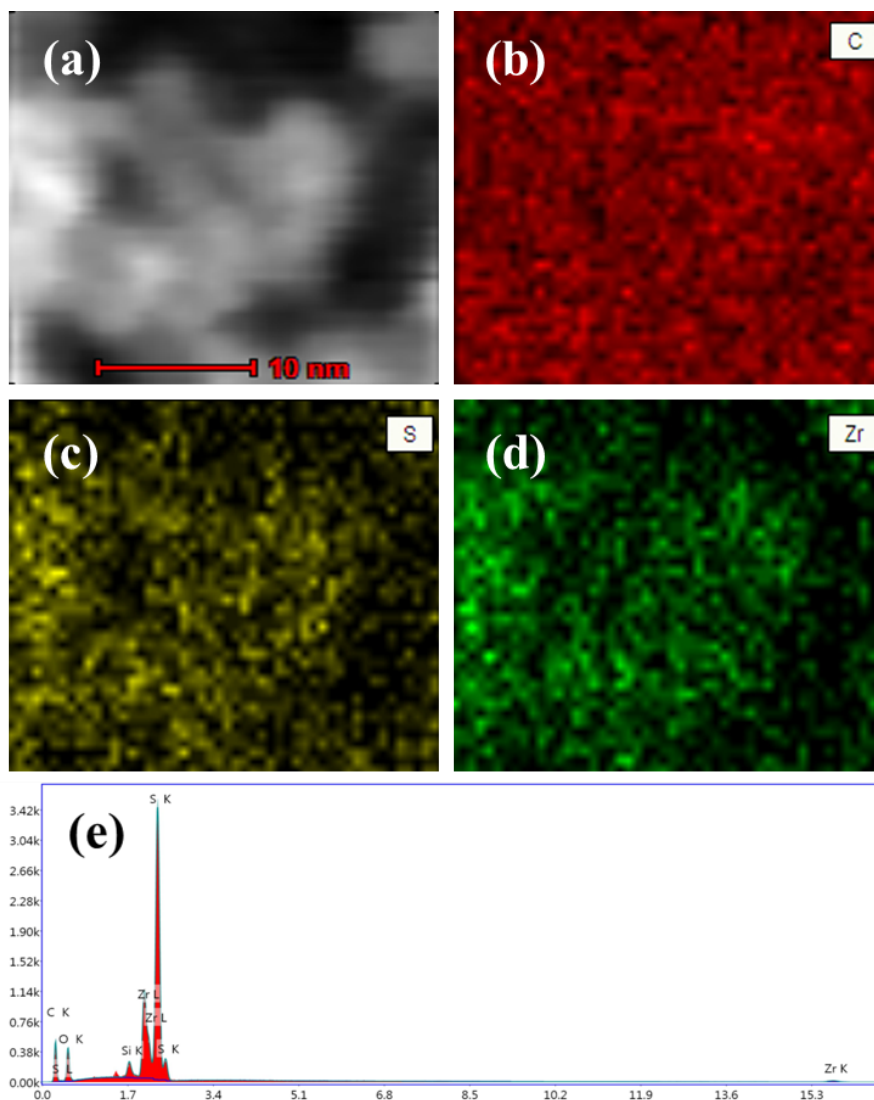


Fig. S4. (a-d) Elemental mapping images of S@ZrO₂/RGO composite, and (e) The corresponding EDX spectrum of S@ZrO₂/RGO composite.

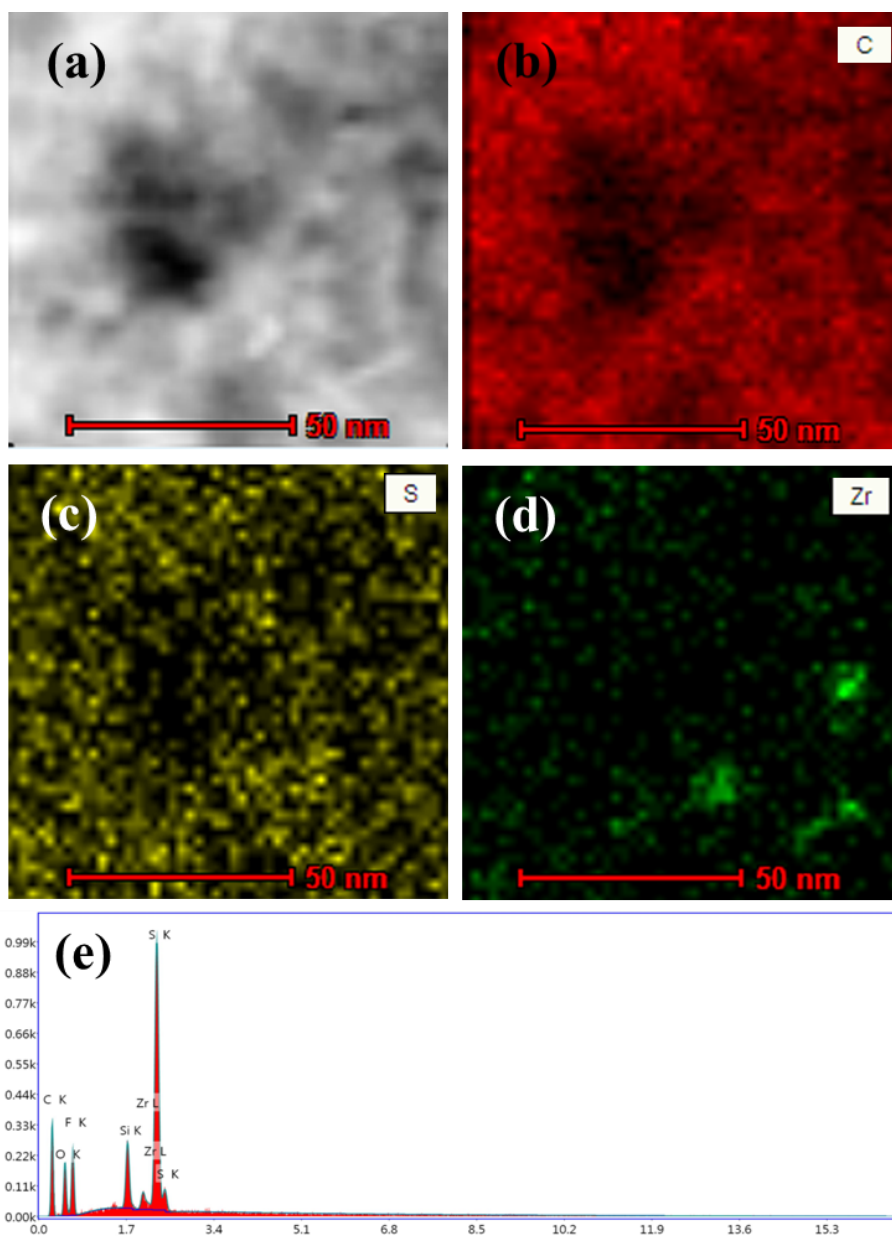


Fig. S5. (a-d) Elemental mapping images of S@ZrO₂/RGO composite after 20 cycles, and (e) The corresponding EDX spectrum of S@ZrO₂/RGO composite after 20 cycles.

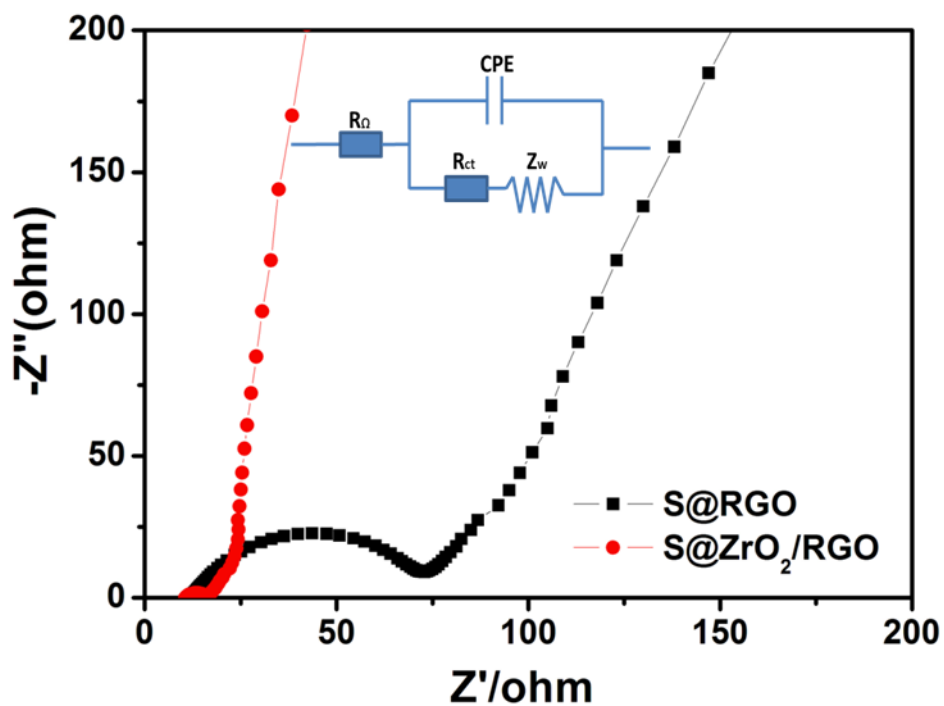


Fig. S5. (a) EIS patterns and equivalent circuit of the S@ZrO₂/RGO and S@RGO cathode after cycling at the rate of 0.2 mV s⁻¹ for 5 times. (R_Ω : Ohm resistance; R_{ct} : charge-transfer resistance; Z_w : Warburg diffusion impedance; CEP: constant phase element) .