

## Electronic Supplementary Information

# Facile and Effective Synthesis of Reduced Graphene Oxide Encapsulated Sulfur via Oil/Water System for High Performance Lithium Sulfur Cells

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## Experimental Section

### Chemicals and Materials

Sulfur (S, Aladdin reagent, AR), carbon disulfur (CS<sub>2</sub>, Aladdin reagent, AR), hydrazine monohydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, Tokyo Chemical Industry Co., Ltd, 98%), graphite powders (325 mesh, Alfa Aesar, 99.8%, AR), potassium permanganate (KMnO<sub>4</sub>, Aldrich Reagent, AR), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, ≥98%, Beijing Chemical Work, AR), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, ≥85%, Beijing Chemical Work, AR), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%, Aladdin Reagent, AR), hydrochloric acid (HCl, 36%-38%, Beijing Chemical Work, AR), deionized water, absolute alcohol (Hong-xin Chemical Works), ketjen black-EC600JD (KB, Akzo Nobel Corp, AR), N-methyl-2-pyrrolidinone (NMP, Aladdin Reagent, AR), polyvinylidene fluoride (PVDF, DuPont Company, 99.9%), separator (polypropylene film, Celgard), electrolyte [1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) with the volume ratio of 1:1, Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd] were used as received.

### The synthesis of the graphene oxides

Graphite oxide (GO) was synthesized by a modified Hummers method.<sup>1</sup> Briefly, a 9:1 mixture of concentrated H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> (45:5 mL) was added to a mixture of graphite flakes (0.375 g) and KMnO<sub>4</sub> (2.25 g). The reaction was then heated to 50 °C and stirred for 24 h. The reaction was cooled to room temperature and poured onto ice (200 mL) with 30% H<sub>2</sub>O<sub>2</sub> (3 mL). After that, the mixture was centrifuged (8000 rpm for 5 min). The remaining solid material was then washed in succession with 200 mL

of 30% HCl for two times, and 200 mL of water for three times. For each wash, the mixture was centrifuged (13000 rpm for 20 min) and obtains the remaining material. The final resulting material was freeze-dried for 24 hours to obtain graphene oxide. Graphite oxide was further diluted in deionized water, ultrasonication for 60 min to obtain graphene oxide.

### **Synthesis of the S@rGO composite**

100 mg Sulfur was dissolved in 2 ml CS<sub>2</sub> to form a homogeneous solution, and then dropped it in 50 ml GO (2 mg/ml) solution with ultrasonic radiation. Subsequently, CS<sub>2</sub> was allowed to completely evaporate from the solution under ultrasonic condition to obtain the S@GO composite. Then 400 µl N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O was added with stirring for 12 hours at room temperature in order to reduced GO to reduced graphene oxide (rGO). The composite S@rGO was collected by consecutive centrifugation and water-washing cycles as well as lyophilization.

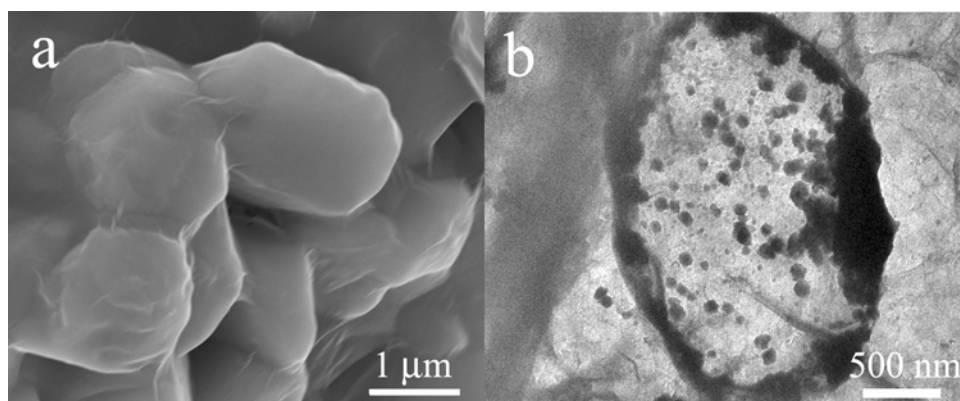
### **Characterization**

X-ray diffraction (XRD) patterns were recorded by a Bruker D8 Focus power X-ray diffractometer with Cu K $\alpha$  radiation. Scanning electron microscope (SEM) was performed by a Hitachi S-4800 field emission scanning electron microscope, whereas energy dispersive spectroscopic (EDS) was done using a Bruker AXS microanalysis at an accelerating voltage of 20 kV. Samples for SEM were prepared by dispersing the as-prepared product in ethanol by sonicating for about 5 min, and then depositing it onto a silicon wafer, attached to SEM brass stub. Transmission electron microscope (TEM) was performed on a FEI Tecnai G2 S-Twin instrument with a field emission

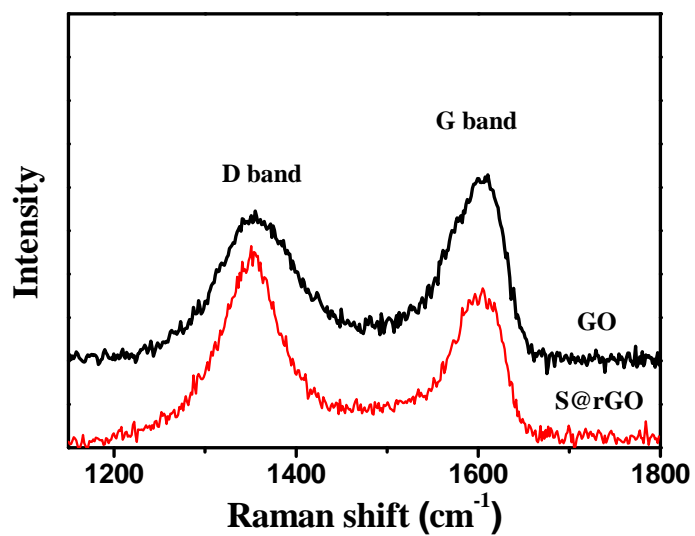
gun operating at 200 kV. Samples dispersed in ethanol were applied onto the Cu grid with carbon film and dried in air before TEM imaging. Raman spectra were collected with a Renishaw 2000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter at ambient conditions. The componential analysis was determined by FlashEA1112 elemental analyzer.

### **Electrochemical tests**

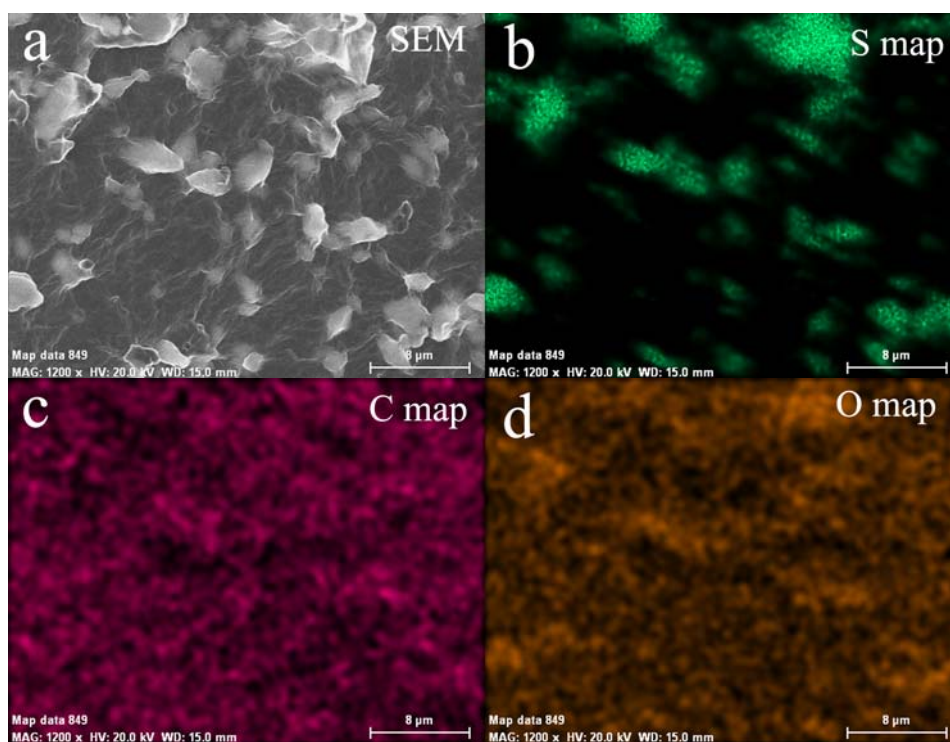
The working electrode was prepared by casting slurry containing 80% active material, 10% KB and 10% PVDF onto an aluminum foil. The S-rGO electrode slurry containing 52% element S, 28% rGO, 10% KB, and 10% PVDF binder was also prepared in the same way to compare with the working electrode. After vacuum drying at 60 °C for about 24 hours, the electrode disks ( $d = 12$  mm) were punched, tabletted and weighed. Coin-type cells of 2025 were assembled in an Ar-filled glove box with H<sub>2</sub>O and O<sub>2</sub> content below 1 ppm, with Li foil as anode. The electrolyte is 1 M of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane and 1,2-dimethoxyethane (volume ratio 1:1). The charge/discharge performances were tested between 1.2 V and 3 V, using LAND CT2001A multi-channel battery testing system at room temperature. The cyclic voltammetry (CV) measurements and impedance plots were carried out with a BioLogic VMP3 station.



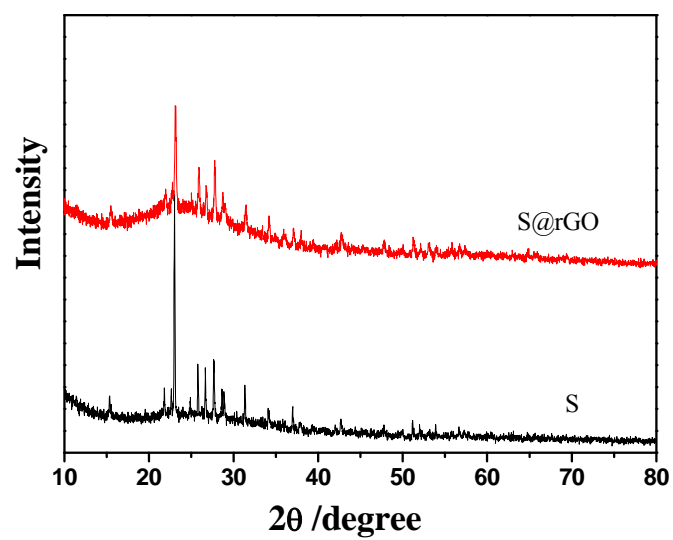
**Fig. S1** (a) SEM and (b) TEM images of S@GO composite.



**Fig. S2** Raman spectra of the GO solution and S@rGO composite.

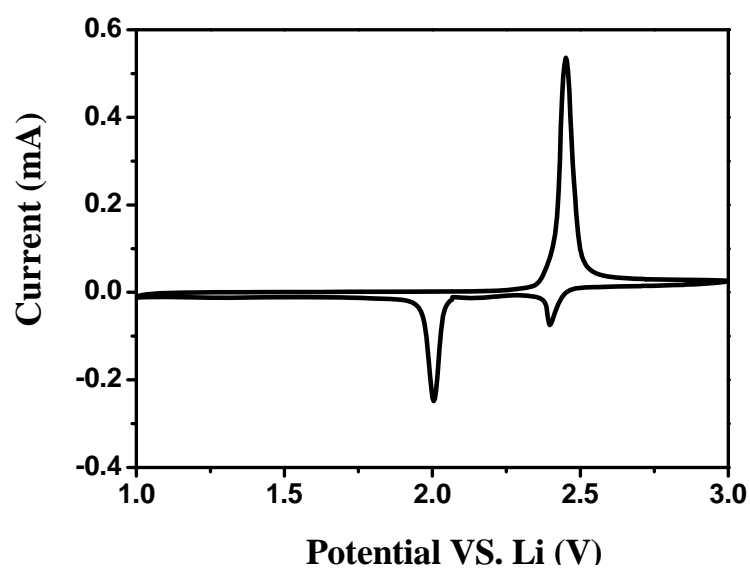


**Fig. S3.** EDS characterization of S@rGO composite. (a) SEM image of rGO coated sulfur particles. (b) EDS sulfur mapping of the region shown in (a). (c) EDS carbon mapping of the region shown in (a). (d) EDS oxygen mapping of the region shown in (a).

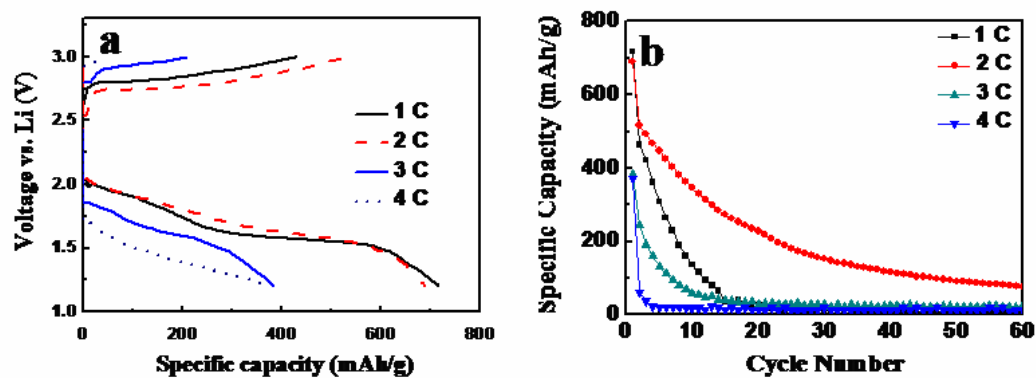


**Fig. S4** XRD patterns of the element S and S@rGO composite.

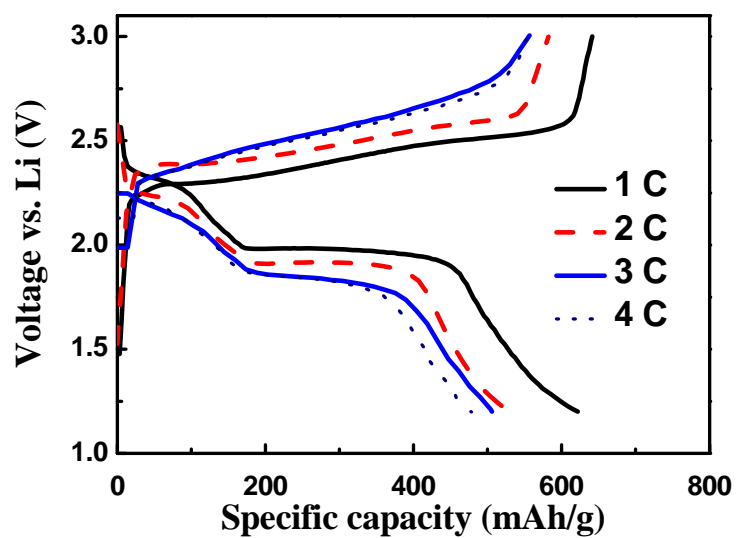




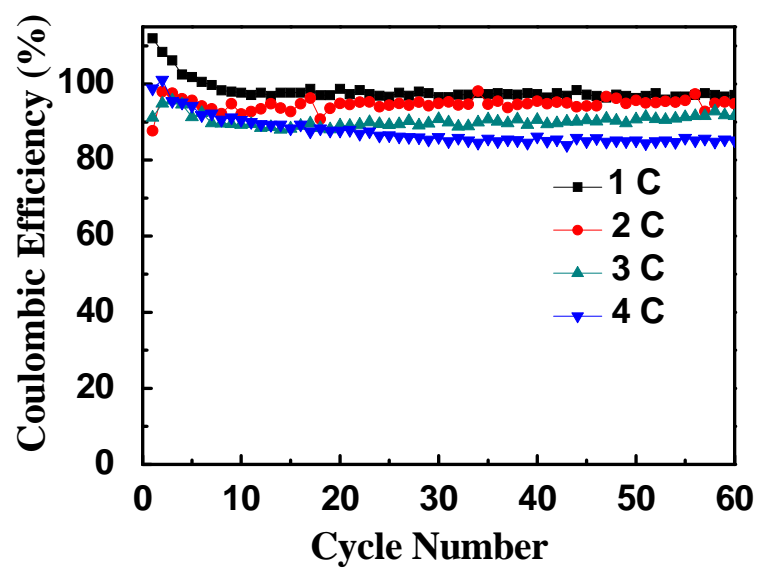
**Fig. S5** Cycling voltammetry curve of the S@rGO cathode in the first cycle at scan rate of 0.1 mV s<sup>-1</sup>.



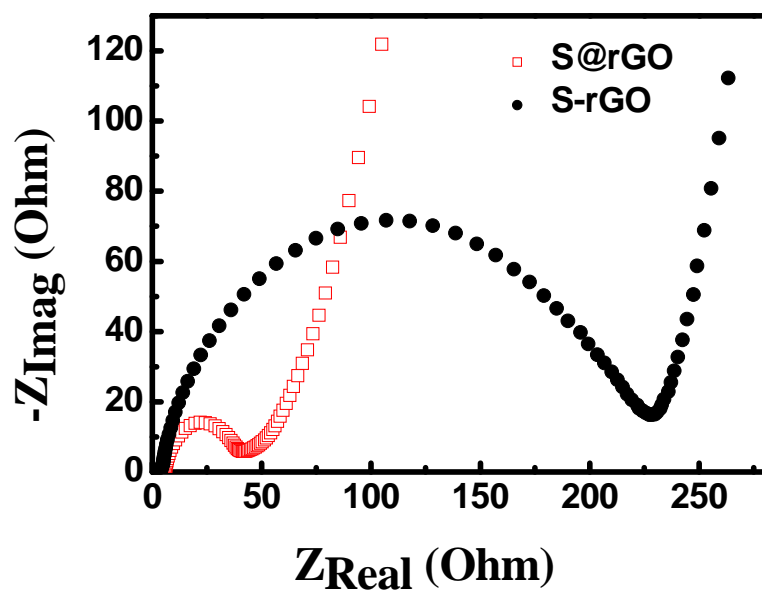
**Fig. S6** (a) First cycle charge/discharge voltage profiles of the S-rGO cathodes at various C rates. (b) Cycle performance of the S-rGO cathodes at various C rates.



**Fig. S7** The 60<sup>th</sup> cycle charge/discharge voltage profiles of the S@rGO cathodes at various C rates.



**Fig. S8** Coulombic efficiencies of S@rGO cathodes.



**Fig. S9** Impedance plots of S- rGO and S@rGO cathodes.

## Reference

- [1] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, *ACS Nano*, 2010, **4**, 4806.