Electronic Supplementary Information for

Self-assembled sulfur/reduced graphene oxide nanoribbon paper as free-standing electrode for high performance lithium-sulfur batteries

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Experimental section:

Synthesis of GONRs. The GONRs were synthesized through unzipping of our home-made CNTs with H₂SO₄ and KMnO₄ as oxidant. In brief, CNTs (1.0 g) were added into concentrated H₂SO₄ (130 mL) and sonicated for 0.5 h to evenly distribute them. The formed mixture was stirred for 1h at room temperature with a mechanical agitator. Subsequently, KMnO₄ (5.0 g) was slowly added and the mixture was left to react for 1 h at room temperature then heat treated at 70 °C for 2 h. After the reaction, the obtained brown solution was slowly poured into ice water (500 mL) containing H₂O₂ (10 mL, 30 wt%). The GONRs was centrifuged and washed with deionized water for at least five times and re-dispersed in water to form a homogeneous dispersion. **Preparation of S/RGONRP.** Thioacetamide (TAA, 200mg) was added into GONRs dispersion (4 mgmL⁻¹, 10mL) and sonicated for 30 min to uniformly mixed with each other. Soon afterwards, the mixture was sealed in a glass vial (inner diameter 5 cm) and heated at 95 °C for 6 h to form hydrogel. Afterwards, the obtained hydrogel was directly dried at 40 °C in an oven then paper-like structure was obtained after 12 h. The paper could be easily floated and detached from the bottom of glass vial after adding DI water. And after another drying process at 40 °C, the final flexible S/RGONRP was obtained.

Preparation of S/RGO, S/RGONRA and S/GNRs. For comparison, three contrastive samples were prepared. S attached on reduced graphene oxide (S/RGO) was synthesized using the similar method for preparing of S/RGONRP. The only difference was that graphene oxide (GO, 4mg mL⁻¹) was used as raw material instead of GONRs. S attached on reduced graphene oxide nanoribbon aerogel (S/RGONRA) was prepared through freeze-drying of obtained RGONRs hydrogel instead of evaporation (as shown in Fig. S5). Graphene nanoribbons (GNRs) were prepared by thermal treatment of GONRs at 800 °C for 1h in the protection of N₂. Then, 60 mg GNRs and 75 mg S (calculated to be with a sulfur content of 55.5 wt%, similar to S/RGONRP) was ground together to form a homogeneous mixture. The obtained mixture was heated at 155 °C for 6 h to melt and diffuse S on the surface of GNRs. The obtained black powder was denoted as S/GNRs.

Characterization. The morphology of products was characterized by scanning electron microscopy (SEM, QUANTA 450), field-emission scanning electron microscopy (FESEM, SUPARR 55) and transmission electron microscopy (TEM, JEM-2000 EX). The crystalline phases of the products were examined using Rigaku D/MAX-2400 diffractometer (XRD) equipped with a rotating anode and a CuK α radiation source (λ =0.15418 nm). X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo ESCALAB 250 spectrometer employing an Al-K α X-ray source. Thermal stability of the samples were assessed by thermal gravimetric analysis (TGA, DTG-60AH) in nitrogen with temperature ranging from 30 °C to 600

°C at a heating rate of 10 °C min⁻¹. Elemental analysis (Vario EL III) was performed to determine the elemental composition of the samples.

Electrochemical measurements. The S/RGONP and S/RGONRA were cut into small discs with diameter of 14 mm and directly used as electrodes for Li-S batteries. The sulfur content of the whole electrodes were found to be 54.5 wt% (determined by elemental analysis), with a typical sulfur mass loading of 1 mg cm⁻². For the powder samples, slurry was prepared by mixing 70% active electrode material (S/GNRs or S), 20% acetylene black, 10% polyvinylidene fluoride (PVDF) binder. Then working electrodes were fabricated by slurry casting on Al foil. The electrodes were dried at 60 °C overnight. Coin type cells were assembled in a glove box under argon atmosphere (water and oxygen concentration less than 0.1 ppm). For Li-S batteries, it consisted of a prepared electrode, polypropylene separator, and lithium foil as the counter electrode. The electrolyte used in this experiment was 1.0 M Libistrifluoromethanesulphonylimide in 1, 3-dioxolane and 1, 2-dimethoxyethane (1:1 by volume) with 1.0 wt% LiNO₃ additive. And the amount of electrolyte in a single cell is 30 µl. The galvanostatic charge/discharge tests were carried out on a Land CT2001A battery test system between 1.5-3.0 V using 2016 coin-type cells. The cyclic voltammograms (CV) was conducted using a multichannel electrochemical workstation (VMP-300) between 1.5 and 3.0 V at a scan rate of 0.1 mV s⁻¹.



Figure S1. FE-SEM a) and TEM b) images of pristine carbon nanotubes (CNTs) synthesized by a floating catalyst chemical vapor deposition method as reported.¹ The diameters of CNTs range in 25-71 nm with average value of 43 nm. c) TEM images of GONRs. The GONRs have flat structure and high aspect without tube cavities, indicating that the CNTs have been fully unzipped. And the diameter of GONRs increase to ~121 nm which is about three times the diameter of CNTs. (d) the digital image shows GONRs can be well dispersed in water and form uniform colloidal dispersion confirmed by evident Tyndall effect when a beam of light passing through it.

Figure S2 a) Side-view SEM image of S/RGONRP. b) Enlarged image of selected part in image a), exhibiting numerous of nanoribbon structures. c) Thickness distribution of S/RGONRP based on image a). The thicknesses of S/RGONRP range in 28-33 μ m with an average value of 30.8 μ m.

Figure S3 a) Digital photograph reflects the difference between the RGONRs hydrogel and RGO hydrogel after the S²⁻ induced self-assembly. The inset images exhibit the obtained samples after drying process. The diameter of S/RGONRP is about ~5 cm which is similar to the S/RGONR hydrogel. Although the RGO hydrogel is also formed after the S²⁻ reduction process, large volume shrinkage can be seen from the picture. And only hard and small (diameter: ~1 cm) plate is obtained after the drying process, which cannot be used as free-standing electrode for Li-S batteries. b-d) SEM images of S/RGO feature the dense stacking of graphene sheets. e-g) Elemental mapping images of C, O, S components based on image d) confirm sulfur to be formed also through the reaction between S²⁻ and oxygen functional groups attached on GO.

Figure S4 Comparative thermal gravimetric analysis (TGA) of S/RGONRP, pure S and GONRs. The test was taken at N₂ atmosphere with a heating rate of 10 °C min⁻¹. For GONRs, the weight loss below 100 °C ascribes to the evaporation of chemically or physically absorbed water while the interval distributes in 100-600 °C is due to the pyrolysis of functional groups.² A big weight loss of 49.1 wt% is obtained between 100-600 °C, confirming there are large amount of functional groups attached to the surface of GONRs. As shown in the curve of S/RGONRP, there is no evident weight loss until the temperature reaches 160 °C which is similar to the curve of pure S, indicating the GONRs are partially reduced by S²⁻ and S is formed simultaneously. The weight loss of S/RGONRP at 600 °C is 65.0 wt% corresponds to the sublimation of formed sulfur and the pyrolysis of residual oxygen containing functional groups.

Samples	C (wt%)	O (wt%)	S (wt%)	H (wt%)	N (wt%)
GONRs	46.1	51.3	0	2.4	0.2
S/RGONRP	38.3	6.2	54.5	0.3	0.7

Table S1 Elemental analysis of GONRs and S/RGONRP.

The contents of C, O, S, H, N in GONRs and S/RGONP were confirmed by elemental analysis (EA). The oxygen content decreased from 51.3 wt% to 6.2 wt% and sulfur content increased from zero to 54.5 wt% after the S²⁻ induced reduction process.

Figure S5 a) Digital images show the formation process of S/RGONRA. b-d) SEM images of S/RGONRA. e-g) Elemental mapping images of C, O, S components based on picture b). The resultant aerogel has a black and foam-like appearance. Different from the densly stack of RGONRs in S/RGONRP synthesized by direct drying, the 3D S/RGONRA is constructed by large amount of interconnected 2D sheet-like structures with macropores ranging from tens to hundreds of micrometers as shown in the SEM image (Fig. S5b-d). The sulfur is homogeneously coated on the surface of RGONRs as confirmed by elemental mapping (Fig. S5e-g).

Figure S6 Charge and discharge voltage profiles of a) S/RGONRP; b) S/GNRs; c) S/RGONRA; d) pure S. The initial discharge capacity of S/RGONRP is 1544 mAh g⁻¹ much higher than the 1237 mAh g⁻¹ of S/GNRs, 1435 mAh g⁻¹ of S/RGONRA and 650 mAh g⁻¹ of pure S. And a discharge capacity of 851 mAh g⁻¹can still be kept after 100 cycles at a current density of 0.5 C. This value is also much higher than the capacity of S/GNRs (586 mAh g⁻¹), S/RGONRA (500 mAh g⁻¹) and pure S (115 mAh g⁻¹). The S/RGONRP shows longer voltage plateau and lower polarization compared with S/GNRs and S/RGONRA. While, there is no evident voltage plateau in the profile of pure S when the current density increase to 0.5 C, which can be ascribed to their bulk structures and poor electrical conductivity. Through the comparison, it can be inferred that the GNRs can not only act substrate to disperse S nanoparticles but also improves their electrical conductivity. And compare with the melt-diffusion sulfur, the in-situ formed sulfur exhibits better utilization and more stable cycling performance, which can be ascribed to their uniform dispersion and covalently bonded with the surface of RGONRs. In addition, the 2D S/RGONRP electrode shows higher capacity and more stable cycling performance than the 3D S/RGONRA, which confirms the compact assembly of RGONRs provides sufficient physical confinement for sulfur and polysulfides during cycling

Figure S7 Comparisons of specific capacities of S/RGONRP with graphene, CNT and GNR based cathodes for Li-S batteries at different current densities from some previous literature (L1: S/RGO,³ L2: S/RGO,⁴ L3: S/RGO,⁵ L4: S/mesoporous graphene paper,⁶ L5: S/RGO paper,⁷ L6: S/hydroxylated CNTs,⁸ L7: S/polyaniline-GNRs,⁹ L8: S/partially unzipped CNTs,¹⁰ This work: S/RGONRP).

Figure S8 a) Digital image of S/RGONRP electrode after cycling at 0.5 C for 100 times. b,c) SEM images feature the nanostructures of electrode. d-f) Elemental mapping images of C, O, S components based on image c). As shown in image a), the S/RGONRP electrode keeps intact after deep cycling. And the fishnet-like structure constructed by numerous of RGONRs can still be kept (image b,c). The elemental mapping results (image d-f) reveal sulfur element evenly distributed on the surface of electrode, which directly confirm the interconnected network of RGONRP provides effective confinement to sulfur/polysulfides.

Figure S9 Electrochemical impedance spectra of S/RGONRP and S/RGONRA. The impedance of S/RGONRP is less than half value of S/RGONRA, indicating the evaporation induced compact assembly of RGONRs which is more favorable for charge transfer than the loose aerogel structures obtained by freeze-drying.

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