Supplementary Information for

Mildly reduced less defective graphene oxide/ sulfur/carbon nanotubes composite films for high-performance lithiumsulfur batteries

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1. Synthesis of LGO and CGO, and their films

LGO: LGO was prepared from graphite *via* a low-temperature reaction process.^{S1,S2} Briefly, graphite powder (325 mesh, 3.0 g) was dispersed in concentrated sulfuric acid (72 mL) which was pre-cooled at 0°C in a flask. After stirring for 3 h, potassium permanganate (9.0 g) was added slowly in small portions for at least 2 h to keep the temperature of the suspension to be lower than 5°C. Then, the mixture was further stirred for 16 h at 0°C. Successively, pre-cooled diluted sulfuric acid (60 mL, 10 wt %) was slowly dropped into the reaction mixture within 6 h by a peristaltic pump. In the same manner, cooled water (60 mL) was also added slowly within another 6 h. Finally, 1,500 mL ice-water mixture was added to terminate the reaction and 50 mL hydrogen peroxide (30 % aqueous solution) was introduced to remove residual potassium permanganate. It should be noted that all the reaction processes in this system were controlled below 5°C. The mixture was washed with 250 mL HCl aqueous solution (1:10, v/v) and water to remove metal impurities and acid, respectively. The obtained paste was dispersed in distilled water and purified by dialysis for 2 weeks, followed by centrifugation at 2,000 rpm to remove non-exfoliated aggregates and at 10,000 rpm for 1 h to concentrate LGO dispersion.

CGO: CGO was prepared from graphite using a modified Hummers' method developed by our group.^{S3,S4} Briefly, graphite powder (325 mesh, 3.0 g) was slowly dispersed in concentrated sulfuric acid (70 mL) in a beaker at room temperature. After stirring for 3 h, the beaker was transferred to an ice-bath under vigorous agitation, and potassium permanganate (9.0 g) was added slowly in a small portion to keep the temperature of the suspension lower than 10°C. Subsequently, the reaction mixture was transferred to a 35°C water bath for about 0.5 h under stirring. Then 140 mL of cooled water was added into the mixture, and then stirred for another 15 min at 95°C. Additional 500 mL cooled water was poured and 15 mL H₂O₂ (30% aqueous solution) was added until gas evolution was completed, and then the colour of the solution was turned from brown to yellow. The mixture was filtered and washed with 250 mL HCl aqueous solution (1:10, v/v) to remove metal ions followed by washing with deionized water under mild bath sonication. The obtained dispersion was purified by dialysis for two weeks and then repeated centrifugation at 3,000 rpm to remove the non-exfoliated graphite particles and other impurity. The final pure GO aqueous was concentrated by centrifugation at 10,000 rpm for 1 h. The concentrated GO solution was diluted to desired concentration for the subsequent application.

LGO and CGO films: The LGO or CGO film was fabricated by cast drying LGO or CGO dispersion (8 mg mL⁻¹) onto a polystyrene petri dish at room temperature.

2. Electrochemical performances of the Li-S batteries assembled with mrCGO/S/CNTs and HI-rCGO/S/CNTs cathodes

In order to further investigate the positive effect of mrLGO in Li-S batteries, CGO was employed to take place of LGO to prepare composite cathode. The mrCGO/S/CNTs cathode has the same morphology with that of mrLGO/S/CNTs (**Fig. S10**). To demonstrate its electrochemical performance, CV tests were conducted. The cell assembled with mrCGO/S/CNTs cathode showed an initial specific capacity of 378 mAh g^{-1} at 0.2 C, and a stable specific capacity of 305 mAh g^{-1} with a good reversibility. These results indicate an ultralow utilization of sulfur because of the low conductivity of this cathode, and an efficient suppression of shuttle effect ascribed to the oxygen containing groups of mrCGO. In order to improve its discharge capacity, chemical reduction of CGO with HI was performed. The initial specific capacity of HI-rCGO/S/CNTs was increased up to 812 mAh g^{-1} at 0.2 C. However, most of the oxygen containing groups of CGO were removed during the process of HI reduction. Thus, the HI-rCGO/S/CNTs cathode suffered from severe capacity fading, and its specific capacity decreased to 401 mAh g^{-1} after 200 cycles at 0.2 C. This phenomenon is similar to that of HI-rLGO/S/CNTs.

3. The synergistic effect between mrLGO and CNTs in Li-S batteries

To investigate the superior electrochemical performances of our ternary composite cathodes, two-component composite cathodes of mrLGO/S and HI-rLGO/S were also prepared by using the same method described in main text. The sulfur contents of mrLGO/S and HI-rLGO/S composites electrodes were measured to be 50.0 % and 49.8 % respectively (**Fig. S12**). The CV curves of the cell assembled with mrLGO/S cathode shows weak redox waves because of the poor conductivity of this electrode (**Fig. S13a**). After reduction with HI, lithium reaction kinetic of HI-rLGO/S cathode was improved (**Fig. S13b**). The cycling curve exhibits an unsatisfactory reversibility with an initial specific capacity of 890 mAh g⁻¹ at 0.2 C with only a retention of 28.1% after 100 cycles (**Fig. S13c**). These results indicate that the introduction of CNTs enhanced the lithium reaction kinetics and discharge capacity caused by the synergistic effect between mrLGO and CNTs.^{S5,S6}

4. Supplementary table

Film	Conductivity (S m ⁻¹)
LGO	N/A ^a
CGO	N/A ^a
mrLGO	2,890
mrCGO	585
HI-rLGO	85,600
HI-rCGO	36500

 Table S1 Electrical conductivities of different composite films

^anot detectable

5. Supplementary figures



Fig. S1 TEM image of a LGO/S composite.



Fig. S2 TEM image of the commercial CNTs.



Fig. S3 SEM image of the fractured cross section of LGO (a) and CGO (d), mrLGO (b) and mrCGO (e), HI-rLGO (c) and HI-rCGO (f); Scale bars in the images are 10 μ m.



Fig. S4 XPS spectra of (a) mrLGO and mrCGO, and (b) HI-rLGO and HI-rCGO.



Fig. S5 Raman spectra of (a) mrLGO and mrCGO, and (b) HI-rLGO and HI-rCGO.



Fig. S6 TGA curves of mrLGO/S/CNTs, HI-rLGO/S/CNTs, mrCGO/S/CNTs, and HI-rCGO/S/CNTs composite films.



Fig. S7 Coulombic efficiencies of mrLGO/S/CNTs and HI-rLGO/S/CNTs cathodes during cycling tests at 0.2 C.



Fig. S8 SEM images and corresponding EDX elemental mappings of mrLGO/S/CNTs (a, b, c) and HI-rLGO/S/CNTs (d, e, f) cathodes after 200 cycles at 0.2 C; Scale bar = $10 \mu m$.



Fig. S9 SEM image of a HI-rLGO/S/CNTs composite film.



Fig. S10 SEM image of a mrCGO/S/CNTs composite film.



Fig. S11 Cycling performances of mrCGO/S/CNTs and HI-rCGO/S/CNTs cathodes at 0.2 C.



Fig. S12 TGA curves of mrLGO/S and HI-rLGO/S composites films.



Fig. S13 CVs of (a) mrLGO/S and (b) HI-rLGO/S cathodes at a scan rate of 0.1 mV s^{-1} , and (c) cycling performance of HI-rLGO/S cathode at 0.2 C.

Supplementary references

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