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Electronic Supporting Information

Graphene Nanoscroll-based Integrated and Self-standing electrode with a Sandwich Structure for Lithium Sulfur Battery

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Contents

Experimental section

Materials:

In this work, graphene oxides (GO) are purchased from Tanfeng Tech. Inc (Suzhou, China). Other reagents are analytical grade without further purification and purchased from Chengdu Kelong Chemical Reagents Corporation.

Synthesis of integrated cathodes

GNS and MnO_2 nanowires are synthesized in the same way to our previous work.[1] And then, the composite of sulfur and GNS (S@GNS) is prepared according to the approach reported eleswhere.[2] Typically, 10 mg GNS are uniformly dispersed in 140 mL deionized (DI) water, followed ultrasonically treatment. Meanwhile, 80 mg sublimed sulphur are uniformly dispersed in 5 mL ethylene diamine (EDA). After mixing the above two solution together, 0.1 M hydrochloric acid solution is added into the mixture, companying with stirring for 5 min. Finally, a grey residue is harvested after centrifugal washing, and denoted as S@GNS. Through changing the mass of the sublimed sulfur, a series of S@GNS composites with different sulfur content can be easily obtained.

9 mg GNS and 3mg MnO_2 nanowires are dispersed into ethanol solution, respectively. And then, MnO_2 dispersion is added into the GNS solution slowly under ultrasonic process and continuous stirring to form GNS/MnO_2 dispersion. Meanwhile, the S@GNS dispersion is obtained by adding the as-prepared S@GNS into the mixture solution of ethanol and deionized water (v/v, 1:4). Finally, the GNS/MnO_2 dispersion, S@GNS dispersion and GNS/MnO_2 dispersion are filtrated layer by layer to form a sandwich-like membrane (Sand-GM/S-m). The as-obtained Sand-GM/S-m has a diameter of 40 mm, and the mass loading of GNS/MnO_2 (per layer) is about 0.96 mg cm^{-2}. By punching the as-prepared Sand-GM/S-m to small wafers with the diameters of 12 mm, the electrode denoted as Sand-GM/S can be obtained. A kind of all GNS supported sandwich-like electrode is also prepared by removing the MnO_2 nanowires in the Sand-GM/S electrode, which is marked as Sand-G/S.

Adsorption test:

Stoichiometric amounts of sulfur and Li_2S are dissolved into 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) mixed solution (v/v, 1:1) to prepare Li_2S_n ($4 \leq n \leq 8$) solution. To prepare a typical 5 mM Li_2S_n ($4 \leq n \leq 8$) solution, sulfur (16.8 mg) and Li_2S (3.4 mg) are dissolved in DME/DOL mixed solution (15 mL; v/v, 1:1). Then the mixed solution is magnetically stirred and heated at 55 °C overnight in an Ar-filled glove box to yield the red-brown Li_2S_n ($4 \leq n \leq 8$) solution.

GNS and GNS/MnO_2 films (GNS-m and GNSM-m) have been prepared through the same vacuum filtrating method. To evaluate the adsorption ability of GNS and GNS/MnO_2 hybrid toward soluble polysulfides visually, GNS-m and GNSM-m with same mass (5mg) are immersed in the as-obtained Li_2S_n ($4 \leq n \leq 8$) solution (3mL) overnight.

Materials characterization:

The content of sulfur in composite materials are measured by thermogravimetric analysis (TGA) using a simultaneous TGA/DSC-2 instrument (METTLERTOLEDO, USA) under nitrogen atmosphere with a heating rate of 10 °C min^{-1} from room temperature to 600 °C. The crystalline structure of material is detected by an X-ray diffraction (XRD) using a Bruker DX-1000 diffractometer (Cu Kα radiation) in the range of 10° to 80° at a scan rate of 0.06° s^{-1}. Morphologies of as-prepared materials are characterized by field-emission scanning electron microscopy (FESEM, Hitachi S-4800) equipped with an energy-dispersive X-ray spectroscopy (EDS; Oxford XMax) system. X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Kratos) analysis is performed to identify the chemical element composition on the surface of materials. Li_2S_n ($4 \leq n \leq 8$) solution recollected from adsorption test are examined by UV-visible absorption spectrophotometry (UV-vis, Shimadzu UV3600).

Electrochemical performance measurements:

For the electrochemical performance tests, CR2032 coin-type cells are assembled in an Ar-filled glove box directly using the Sand-G/S and Sand-GM/S as cathode, lithium foil as anode, and Celgard 2400 as separator. The electrolyte is 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.95%, Aldrich) dissolved in

1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, v/v) with 0.1 M $LiNO_3$ electrolyte additive. The amount of electrolyte added in one cell follows these rules: If the mass of sulfur below 0.001 g, the amount of electrolyte in one cell is about 0.040 mL g^{-1} S. When the mass of sulfur is more than 0.001 g, for every 1.000 g of sulfur, the amount of electrolyte is increased by 0.020 mL. Galvanostatic charge/discharge measurements are performed on a cell test instrument (Neware BTS-610 battery tester, China). During electrochemical performance testing, both the current rate set and the specific capacity are referred to the mass of sulfur in the cathode (1 C = 1675 mAh g^{-1}). Cyclic voltammetry (CV) measurements and electrochemical impedance spectroscopy (EIS) testing are performed using a PARSTAT multichannel electrochemical workstation (Princeton Applied Research, USA). The scan rate and voltage range of CV are 0.1 mV s^{-1} and 1.5-2.8 V, respectively. For the EIS testing, the frequency range is 100 kHz to 10 mHz, and the AC voltage amplitude is 5 mV. All the electrochemical tests are performed at ambient temperature

Supporting figures

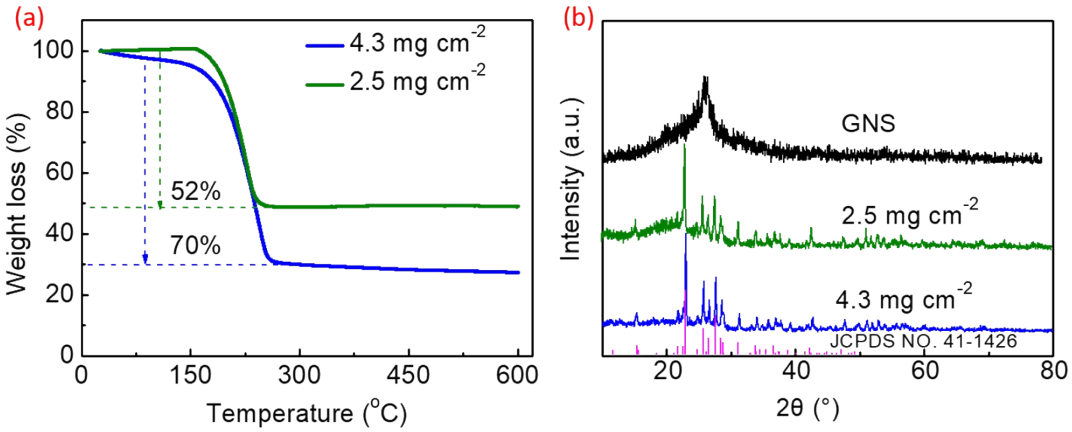

Figure S1 (a) TGA curves of Sand-GM/S electrodes, (b) XRD patterns of Sand-GM/S electrodes and pure GNS

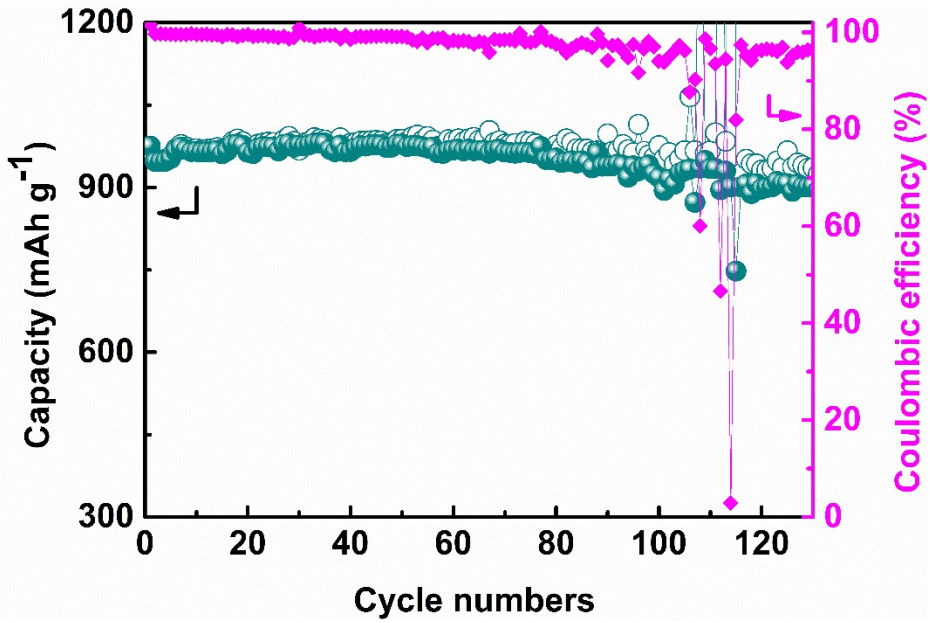

Figure S2 Cycling performance of Sand-G/S electrode at 0.5C

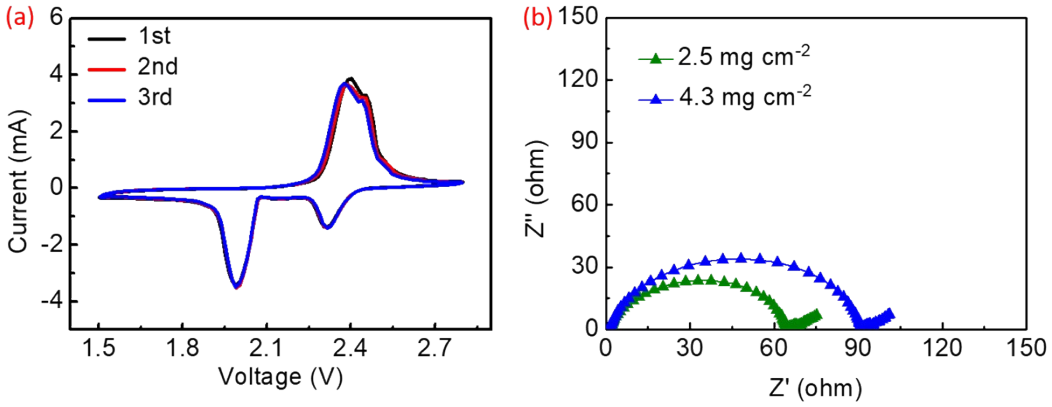

Figure S3 (a-b) CV and EIS cruves of Sand-GM/S electrodes

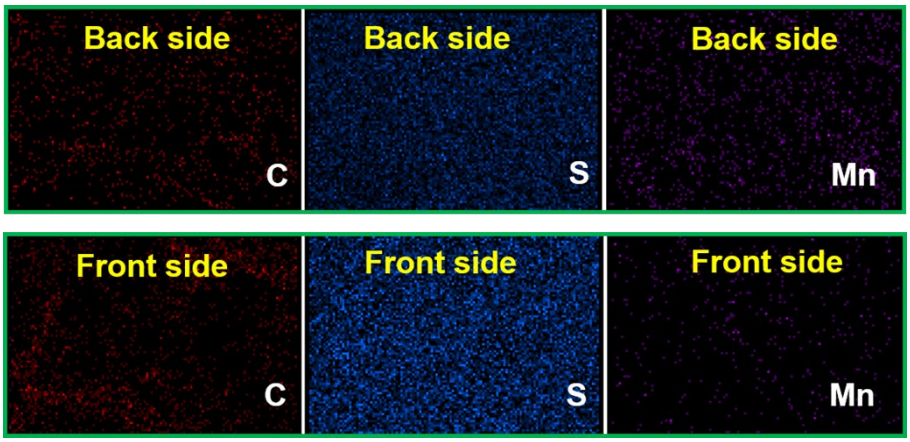

Figure S4 S mapping images of two sides of cycled Sand-GM/S electrode

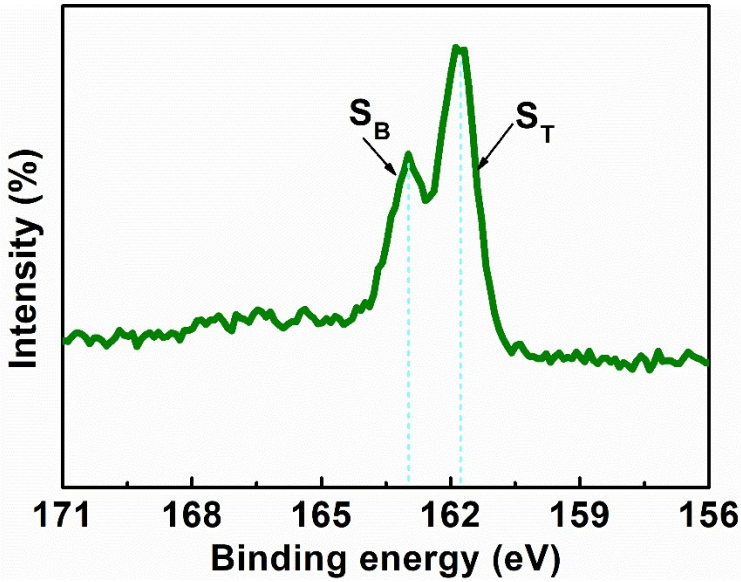

Figure S5 S2p spectra of Li_2S_n ($4 \leq n \leq 8$)

References

1. Y. Guo, Y. Zhang, Y. Zhang, M. Xiang, H. Wu, H. Liu and S. Dou, *J. Mater. Chem. A*, 2018, **6**, 19358-19370.
2. C. Wang, H. Chen, W. Dong, J. Ge, W. Lu, X. Wu, L. Guo and L. Chen, *Chem. Commun.*, 2014, **50**, 1202—1204.