Supporting Information

Ultralong-term Cycling Stability of an Integrated Carbon-Sulfur Membrane with Dual Shuttle-Inhibiting Layers of Graphene "Nets" and a Porous Carbon Skin

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Experimental Section

Preparation of CSG film: Graphene oxide (GO) was synthesised according to a modified Hummers' method. Porous carbon spheres (Sigma Aldrich) were mixed with active sulfur (Sigma Aldrich) with the mass ratio of 1 : 3, and the mixtures were heated at 190 ºC in a sealed stainless steel autoclave in Ar for 12 h. The obtained carbon-sulfur (CS) nanoparticles were hybridized with graphene oxide sheets with a mass ratio of 25 : 1 under high speed stirring and strong sonication. Hybrid CS / GO solution (60 mL, 0.1 mg/mL according to GO) was filtrated under vacuum, resulting in the formation of CS/GO membrane. The obtained CS/GO film was reduced with hydrazine vapour at 90 ºC for 48 h, thus forming CSG hybrid film. Also, pure carbon nanoparticle / graphene film was prepared with the same approach without the introduction of active sulfur.

Preparation of CSG/PC membrane: A small amount (5 mL, 1 mg/mL) of GO / carbon nanoparticle hybrid solution was firstly filtrated to form a GO - carbon nanoparticle layer, following by the addition of a large amount of CS / GO solution (60 mL), resulting in the formation of carbon-sulfur nanoparticles / graphene oxide / porous carbon layer (CSGO/PC) membrane. The obtained CSGO/PC membrane was reduced by hydrazine vapour according to the same method mentioned above, resulting the formation of CSG/PC membrane. CSG/PC membrane was cut into circular slices with a diameter of 0.8 cm. Each circular CSG/PC cathode achieves a weight of 4 mg, realizing a high areal sulfur loading of 7.2 mg/cm^2. In addition, the PC skin side was close to the separator.

Characterization: Morphology characterizations of the membranes were carried out using a field-emission scanning electron microscope (FESEM, Hitachi, SU8010). An energy dispersive spectroscometer (EDS) equipped to the FESEM was used to examine the elemental mappings. Crystal structures of samples were carried out by an X-ray diffraction instrument (XRD, Bruker D8). Thermogravimetric analysis (TGA) was performed at a heating rate of 10 ºC /min up to 800 ºC under an argon atmosphere. X-ray photoelectron spectroscopy (XPS, Thermo escalab 250Xi) was conducted with monochromatic Al Kα X-ray at 14 kV. Here, the electrical conductivity of films was tested based on a four-probe resistivity testing system (RTS-8).

Electrochemical measurement: The obtained CSG/PC membranes and CSG films were cut into discs of 12 mm in diameter, which were directly used as sulfur cathode without any binder and conductive additions. 1.0 M lithium bis-trifluoromethane sulfonylimide (LiTFSI) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) at a volume ratio of 1:1 with 0.5 wt% $LiNO_3$ additive was used as the electrolyte. CR2032 coin cells were assembled with lithium foil as the anode and Celgard 2400 as the separator in an argon-filled glove. 0.15 mL of electrolyte was used for each Li-S battery. CV curves of the Li-S cells were recorded on an ARBIN electrochemical working station (MSTAT-5V/5mA/32Ch) at a scan rate of 0.1 mV/s. Discharge-charge measurements, coupling with rate capability and long-term cycling stability were tested on LAND 2001A systems. Electrochemical impedance measurements were carried out based on a CHI 660D electrochemical working station from 100 kHz to 0.01 Hz with an AC voltage of 10 mV.

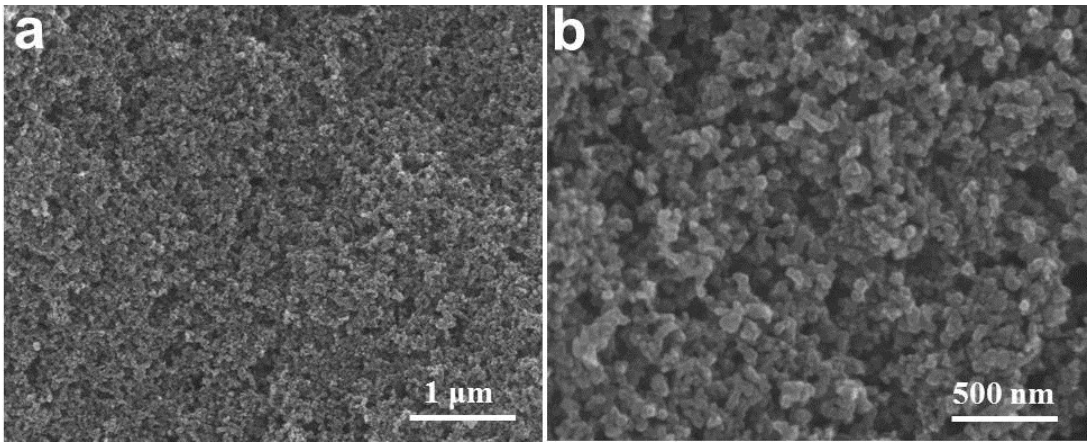

Fig. S1 SEM images of porous carbon nanoparticles at low and high magnifications.

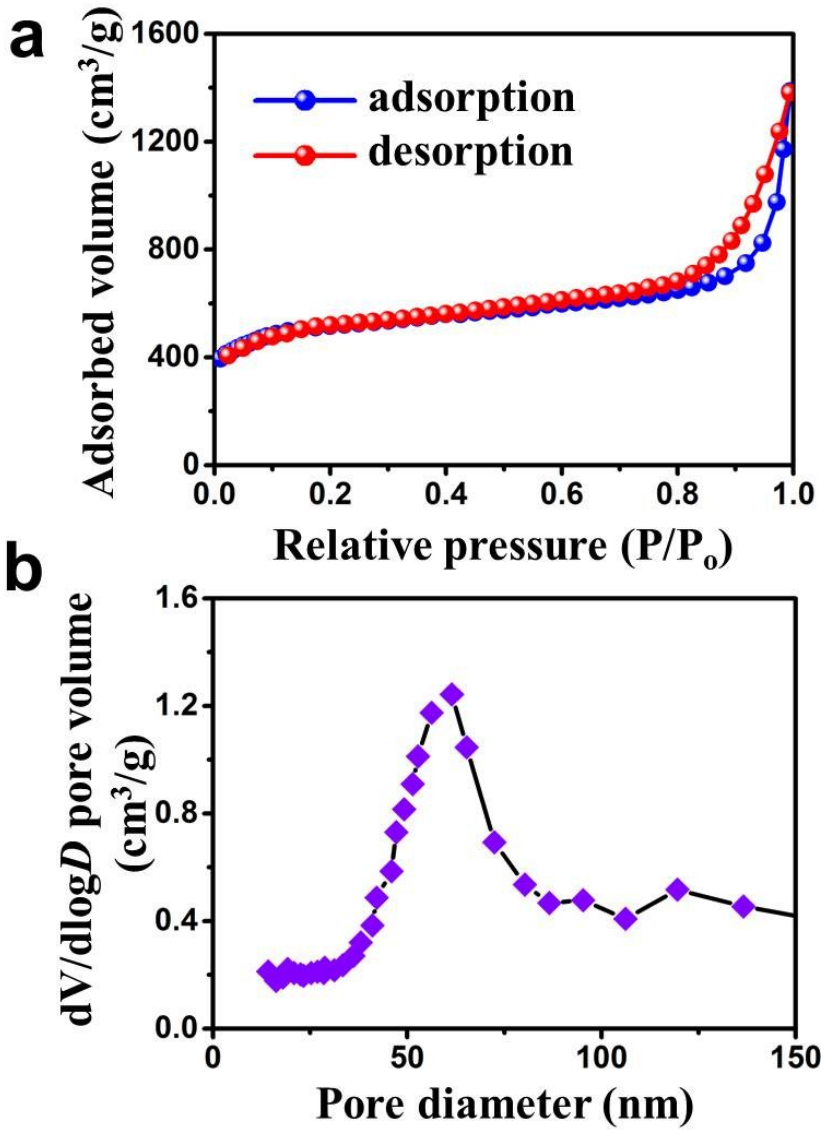

Fig. S2 (a) Nitrogen physisorption isotherm and (b) corresponding pore size distribution of carbon nanoparticles.

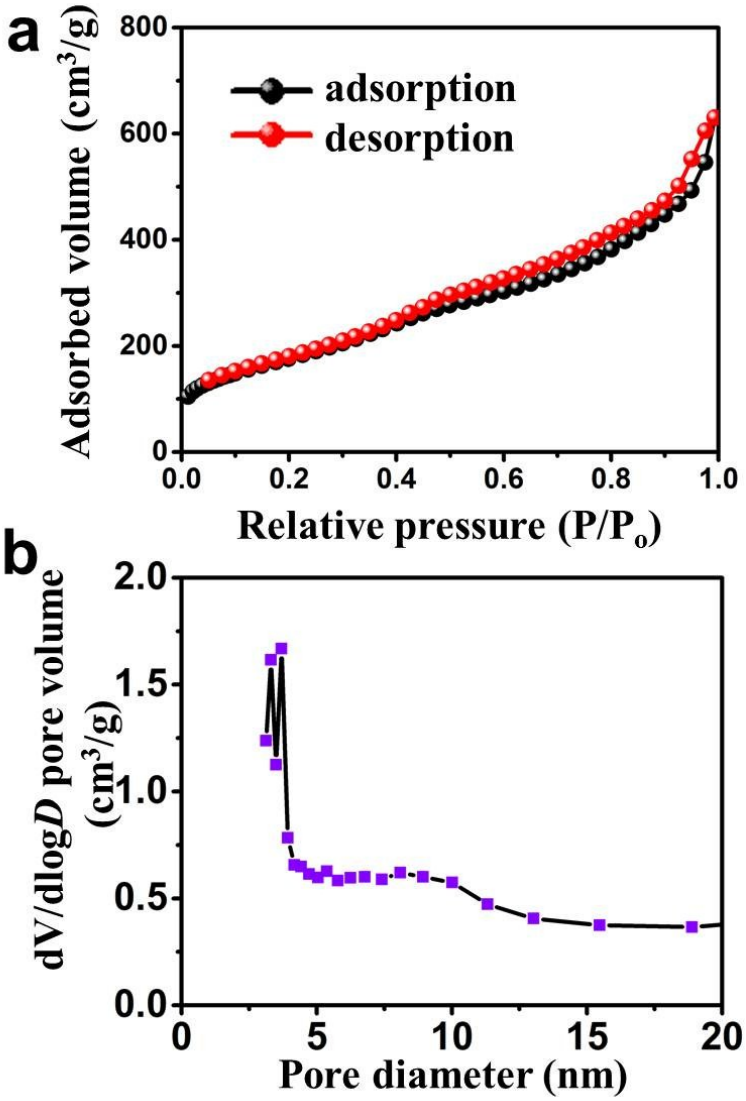

Fig. S3 (a) Nitrogen physisorption isotherm and (b) corresponding pore size distribution of PC skin.

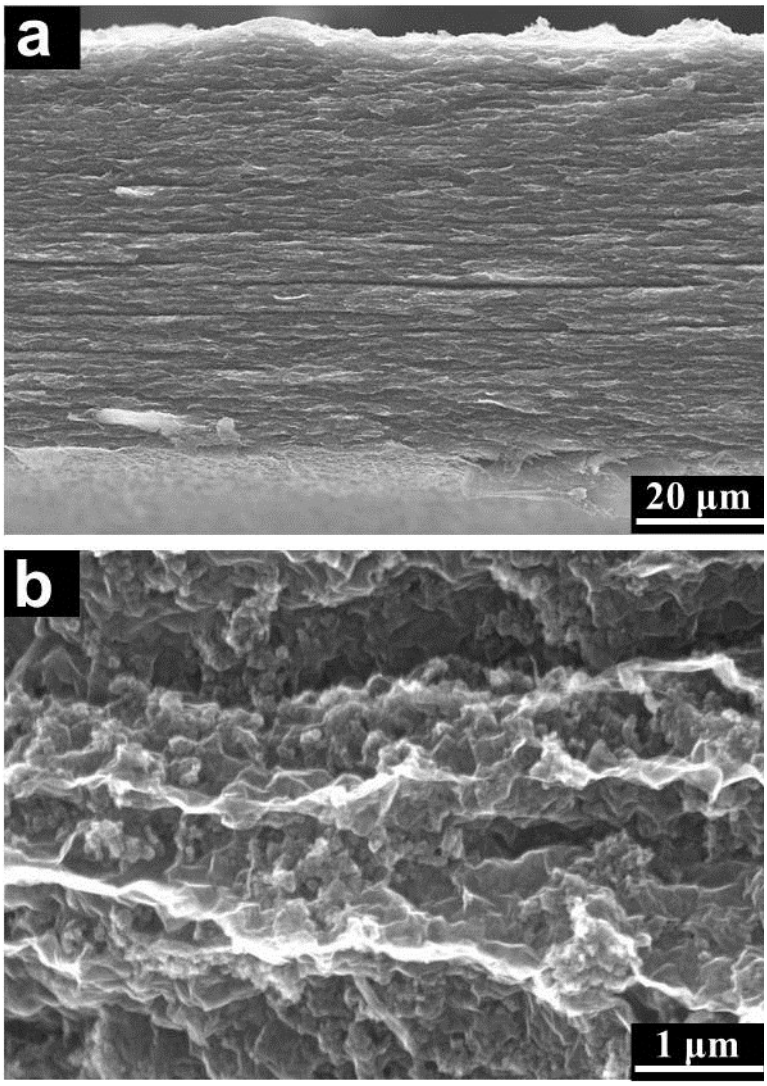

Fig. S4 SEM images of CSG film at (a) low and (b) high magnifications.

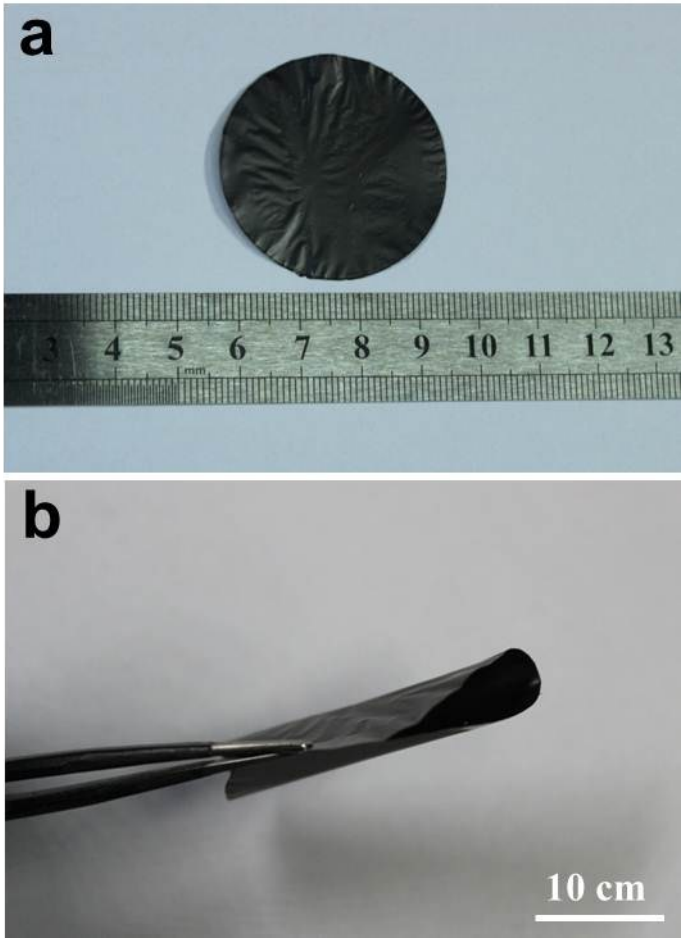

Fig. S5 Digital images of (a) CSG/PC membrane and (b) its flexibility.

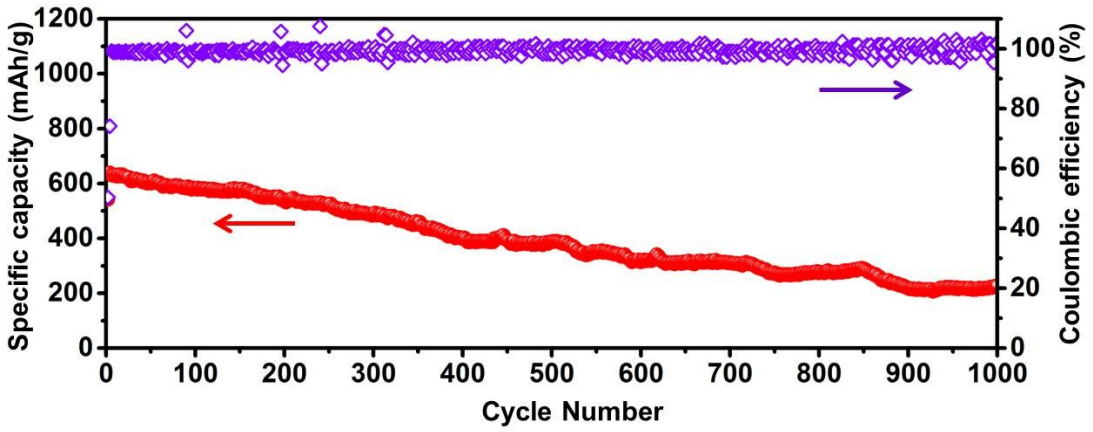

Fig. S6 Long-term cycling stability of CSG film at 0.5 C as well as its corresponding Coulombic efficiencies.

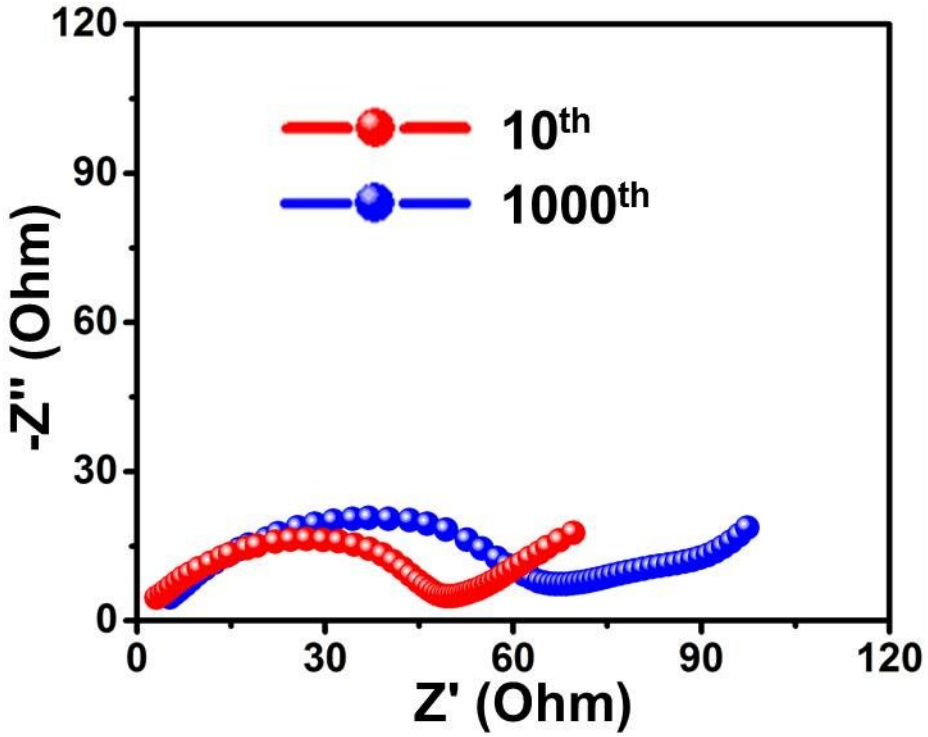

Fig. S7 Nyquist plots of Li-S batteries with CSG/PC membrane after being cycled for 10 and 1000 times, respectively.

Table S1. Impedance parameters calculated from the EIS curves of CSG film and CSG/PC membrane according to the equivalent circuit.

Cathodes	R_e **(Ω)**	R_s **(Ω)**	R_{ct} **(Ω)**
CSG film	5.8	1.3	85.5
CSG/PC membrane	3.9	1.1	47.7

Table S2. Impedance parameters calculated from the EIS curves of CSG/PC membrane according to the equivalent circuit.

CSG/PC	R_e **(Ω)**	R_s **(Ω)**	R_{ct} **(Ω)**
10^{th}	4.1	2.5	48.2
1000^{th}	6.5	2.7	68.3