Supporting Information

A Highly Conductive Carbon-Sulfur Film with Interconnected Mesopores as Advanced Cathode for Lithium-Sulfur Batteries

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1. Experimental section

1.1 Materials Synthesis

Graphite powder was purchased from Qingdao Henglide Graphite Co., Ltd. Graphene oxide (GO) was synthesized according to a modified Hummers' method [12]. MC materials were prepared by phenolic resol and triblock copolymer Pluronic F127 [13]. Typically, 0.8 g of phenol and 2.5 mL of formalin aqueous solution (37%) were added into NaOH aqueous solution (0.1 M, 20 mL), which was stirred at 70 ºC for 30 min, and then 1.28 g triblock copolymer Pluronic F127 in 20 mL pure water was added. Then the mixture was further stirred for 30 min at 66 ºC for 2 h before 67 mL water was added to dilute the solution. After 16 h, the mixture was cooled naturally. 17.7 mL of the obtained solution prepared above was transferred into an autoclave and diluted with 40 mL water. Then the autoclave was heated to 130 ºC and kept there for 24 h, resulting in the formation of the yolk yellow floccules. The carbonization of floccules was carried out at 700 ºC in Ar atmosphere for 3 h, achieving the preparation of MC materials with sphere morphology. MC-S hybrid was synthesized with a melt-diffusion approach. Typically, MC materials with powder morphology were firstly treated in mixed acid solution (70%, H_2SO_4:HNO_3 = 3:1), resulting in the formation of MC with good dispersibility. The dried MC powder was mixed with native sulfur (Sigma Aldrich) with mass ratio of 1:3, which were sealed in a Teflon pot saturated with argon and heated at 190 °C for 24 h. The obtained MC-S materials were further ball-milled for 4 h to relieve the interfacial contact between different MC-S spheres. Then the MC-S hybrids (0.2 g) were dispersed into GO solution (50 mL, 1 mg/mL) under strong sonication. Hybrid solution (6 mL) of GO and MC-S was treated under vacuum filtration to prepare the free-standing GO/MC-S film, which was further reduced by hydrazine vapor without direct contact, achieving the preparation of GMC-S film. The GMC-S film was further treated at 210 °C under Ar atmosphere for 10 min in order to remove the sulfur outside the MC materials into the porous structures created by crumpled graphene sheets, and also remove the residual oxygen-containing groups of graphene sheets. Here, the sulfur content in GMC-S film can be facilely adjusted by changing the mass ratio of MC-S and GO material.

Different sulfur contents of about 45%, 55%, 67% and 74% are achieved in different GMC-S films, which are donated as GMC-S4, GMC-S5, GMC-S6 and GMC-S7. Here, the areal sulfur loadings are about 3.24, 3.65, 4.07 and 4.38 mg/cm^2 for GMC-S4, GMC-S5, GMC-S6 and GMC-S7 film.

1.2. Characterization

The morphologies and microstructures of the prepared materials were characterized by emission scanning electron microscopy (FESEM, SU-8010, Hitachi) and transmission electron microscopy (TEM, F20, FEI). Energy dispersive spectroscopy (EDS) mappings were conducted with an EDAX analysis system (TEAM Octane Super). X-ray diffraction analysis was performed on an X-ray powder diffractometer (Bruker, D8 ADVANCE) with filtered Cu Kα radiation. X-ray photoelectron spectroscopy was carried out on a Thermo ESCALAB 250Xi system with Al Kα radiation of 1486.6 eV. Sulfur content was measured on a thermogravimetric analysis (TA 50) at a heating rate of 10 °C/min in N_2 up to 800 °C. The electrical conductivity of GMC-S film was tested based on a four-probe system.

1.3. Electrochemical Measurements

Electrochemical performance was evaluated using a two-electrode system with lithium metal as counter electrode. GMC-S film was punched out into circular disks with diameter of 1 cm, and was used as working electrode without any further treatment. Pure S, MC-S hybrids and MC materials were mixed with super P carbon black and poly(vinylidene fluoride) (PVDF) binder at weight ratio of 80:10:10 in N-methyl pyrrolidone (NMP) solvent. The obtained slurry was cast on Al foil and dried at 80 °C for 24 h. 1 M lithium bis(trifluoromethanesulfonyl) imide (LITFSI) dissolved in dimethoxyethane:1,3 dioxolane (DME:DOL, 1:1 by volume) was used as the electrolyte with 0.5 M $LiNO_3$ added. The amount of electrolyte used in each cell is about 0.35 mL. The batteries were assembled in an Ar-filled glove box (H_2O, O_2 < 0.1 ppm) with a polypropylene film (Celgard-2300) as the separator. Cyclic voltammetry (CV) curves were carried out on an ARBIN BT2000 system in the voltage range of

1.8 - 3.0 V at a sweep rate of 0.1 mV/s. The galvanostatic charge and discharge were tested on a LAND 2001A battery testing system. Electrochemical impedance spectroscopy (EIS) was performed on a Solartron analysis system (SI 1260, SI 1287) with an amplitude of 10 mV in the frequency range from 100 kHz to 0.01 Hz at room temperature. The current rate and specific capacity of the batteries were calculated based on the weight of sulfur.

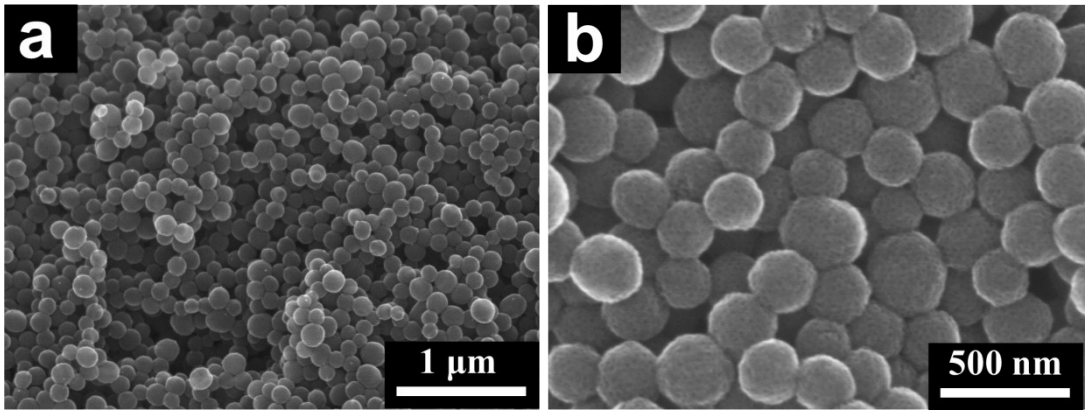


Fig. S1 Morphology and microstructure of MC materials at (a) low and (b) high magnifications.

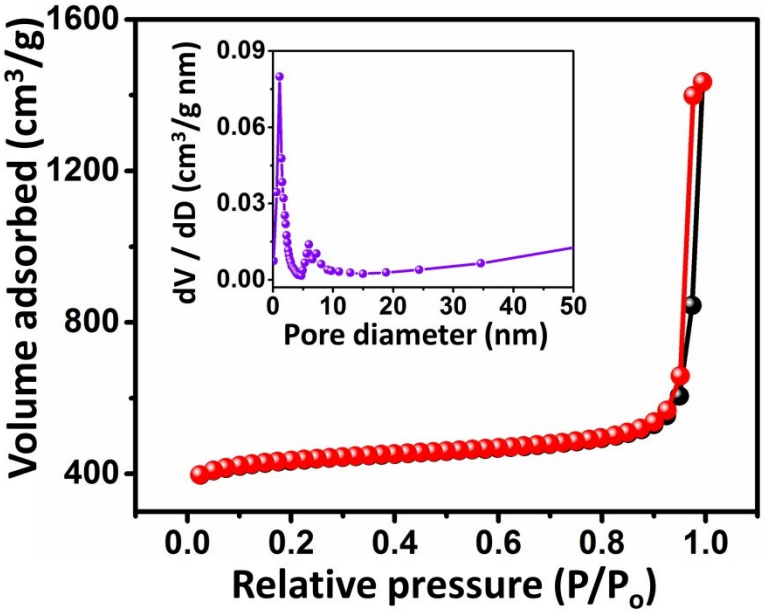


Fig. S2 N_2 adsorption/desorption isotherm of MC material coupling with the corresponding pore size distribution curve (inset). A narrow pore size distribution around 3 nm can be observed, as indicated by the inset curve.

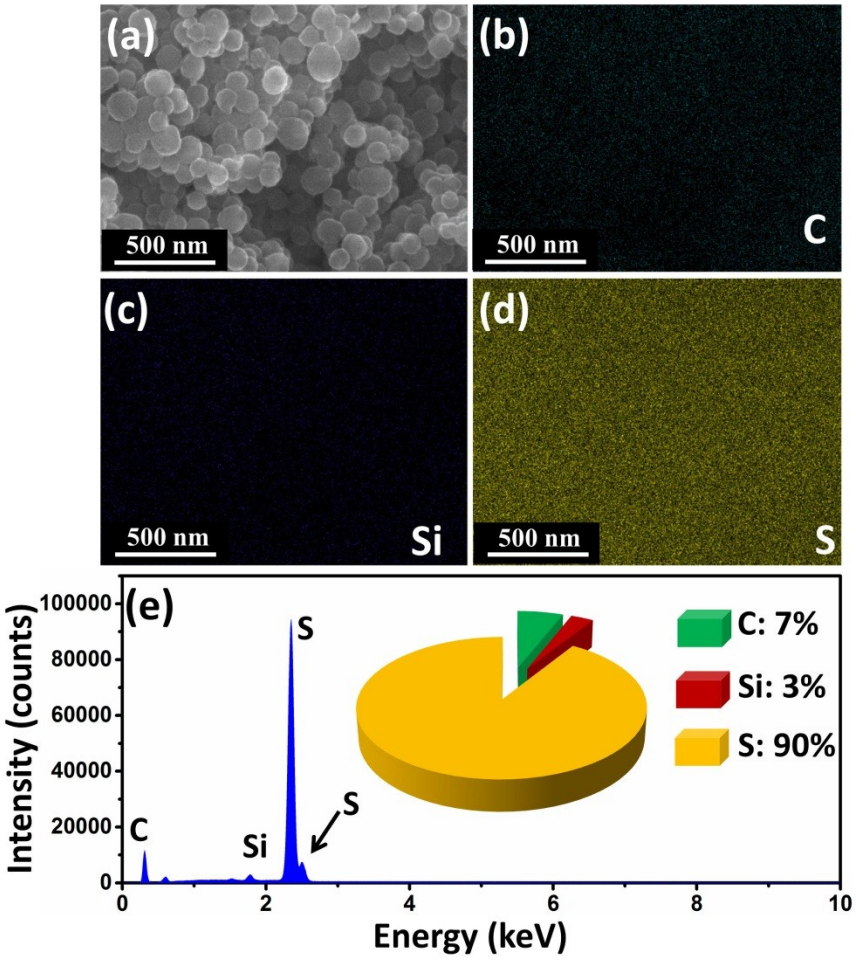


Fig. S3 (a) SEM image of MC-S hybrid, and the corresponding elemental mappings of (b) carbon, (c) silicon and (d) sulfur, as well as the EDS spectrum taken from the whole area.

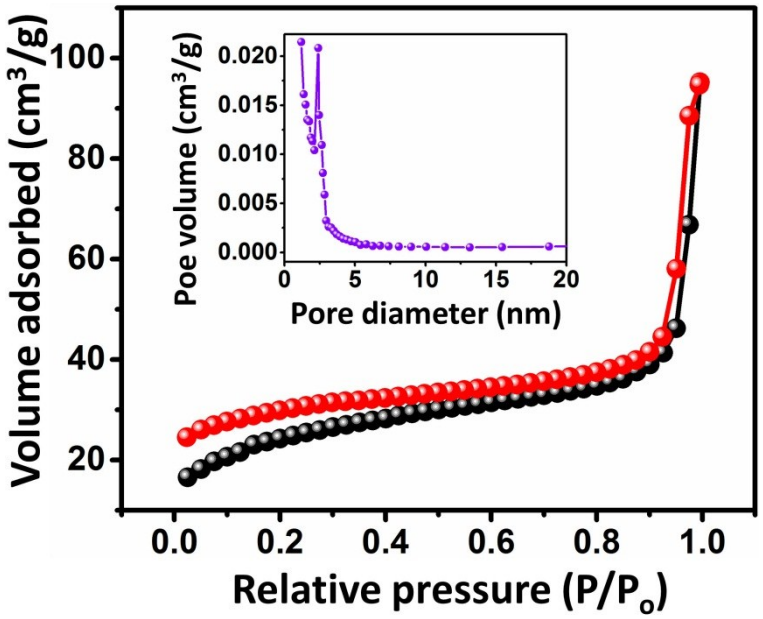


Fig. S4 N_2 adsorption/desorption isotherm of MC-S hybrid. Inset: pore size distribution curve.

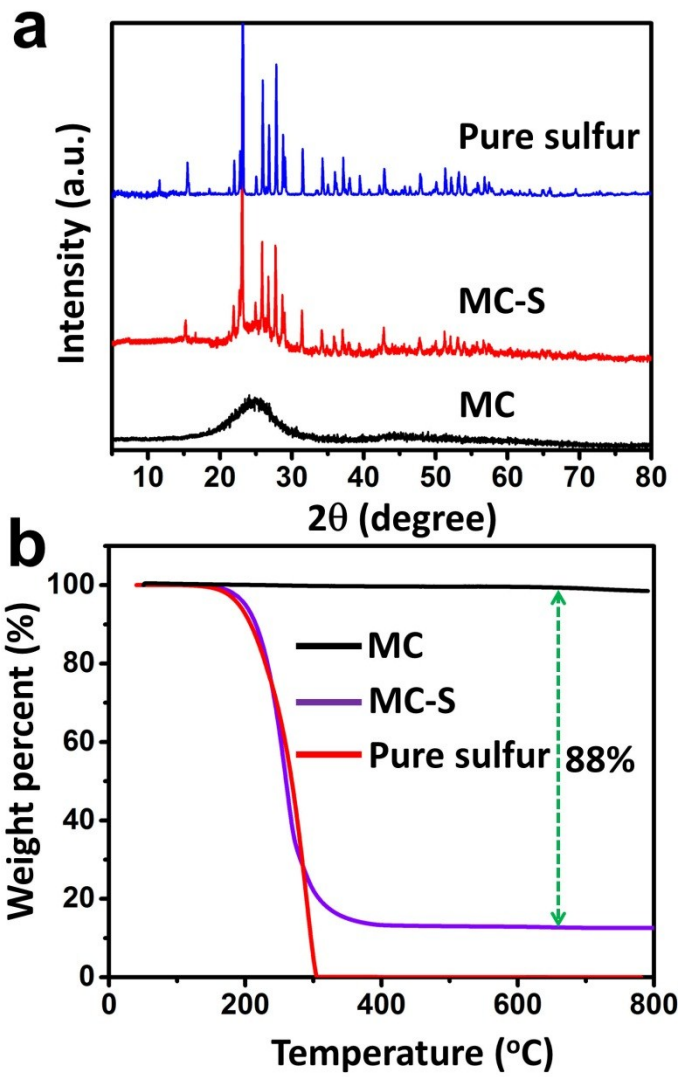


Fig. S5 (a) XRD patterns and (b) TGA curves of prepared MC, MC-S hybrid and pure sulfur.

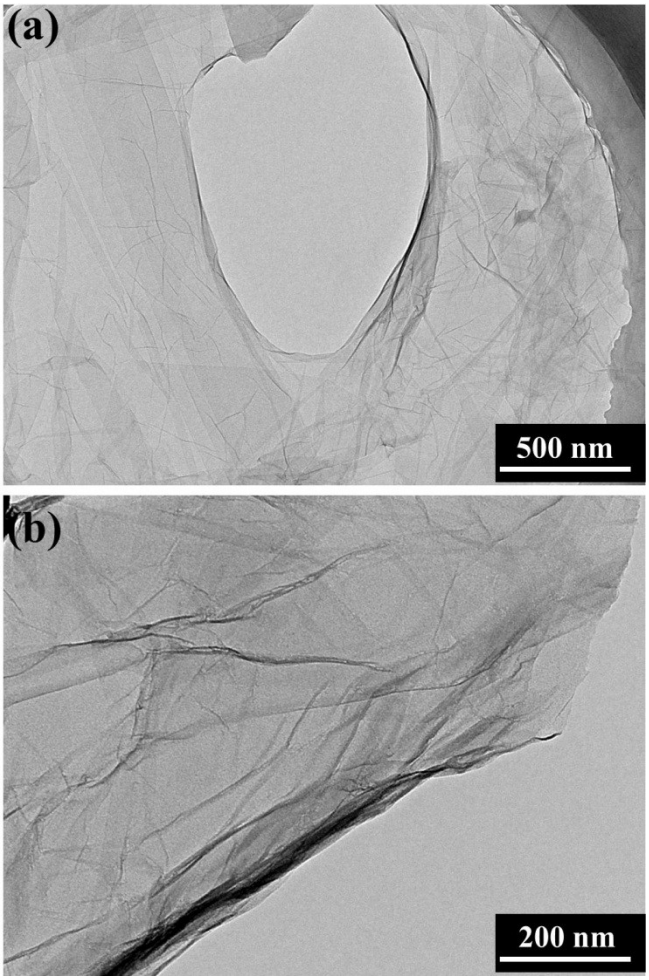


Fig. S6 TEM images of graphene sheets at low and high magnifications.

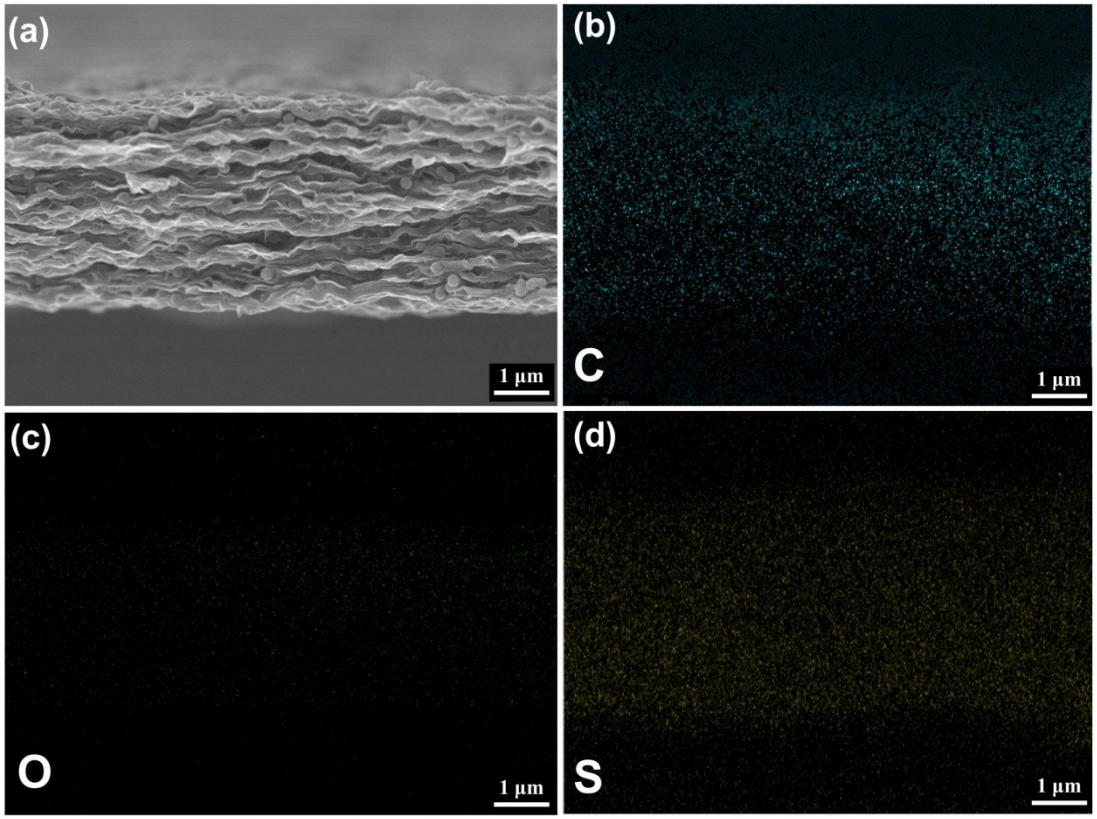


Fig. S7 (a) SEM image of GMC-S film and the corresponding element mapping images of (b) carbon, (c) oxide and (d) sulfur.

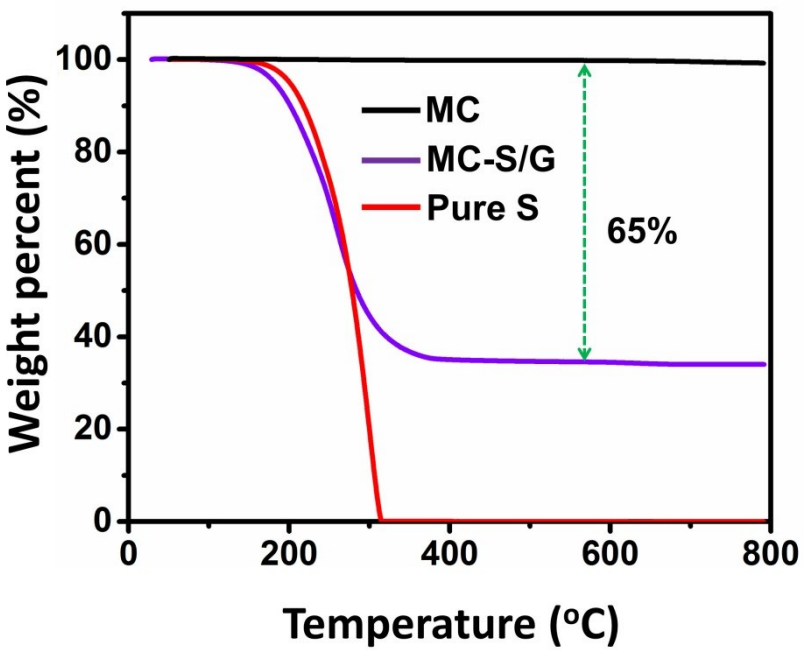


Fig. S8 TGA curves of MC material, pure sulfur and GMC-S film.

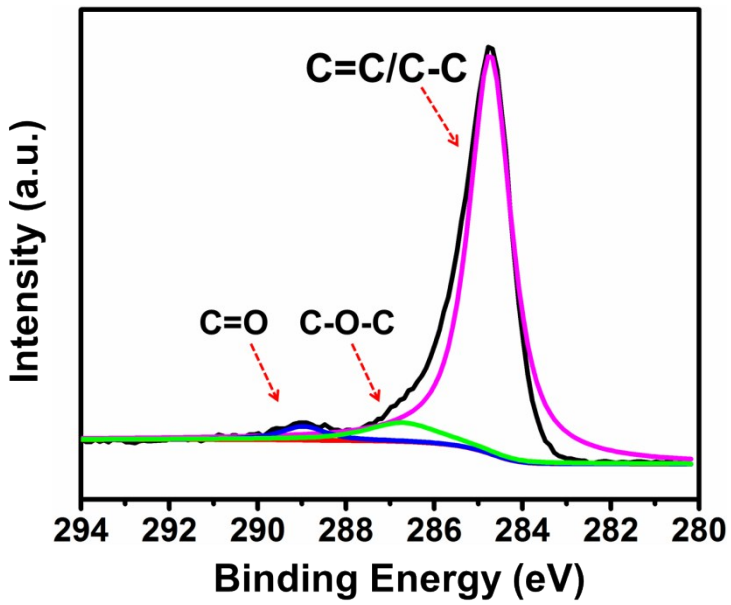


Fig. S9 High-resolution XPS spectra of C 1s region for GMC-S film.

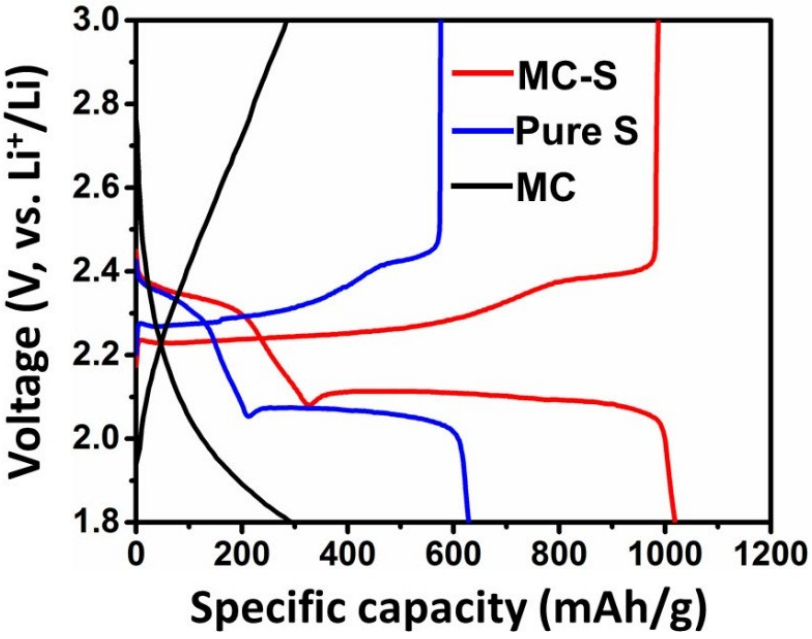


Fig. S10 Charge/discharge curves of MC material, MC-S hybrid and pure S at 0.1 C on the 2nd cycle.

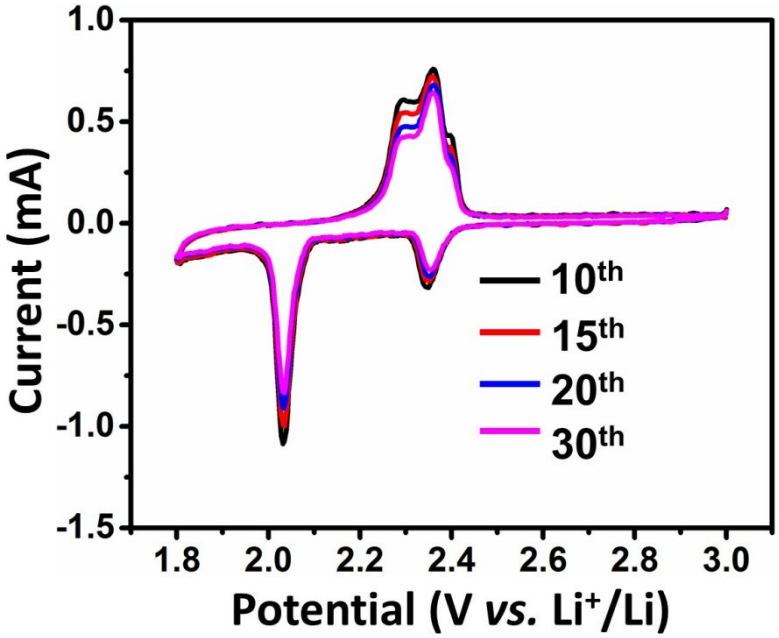


Fig. S11 CV curves of Li-S battery with GMC-S electrode on different cycles from the 10^{th} to the 30^{th}.

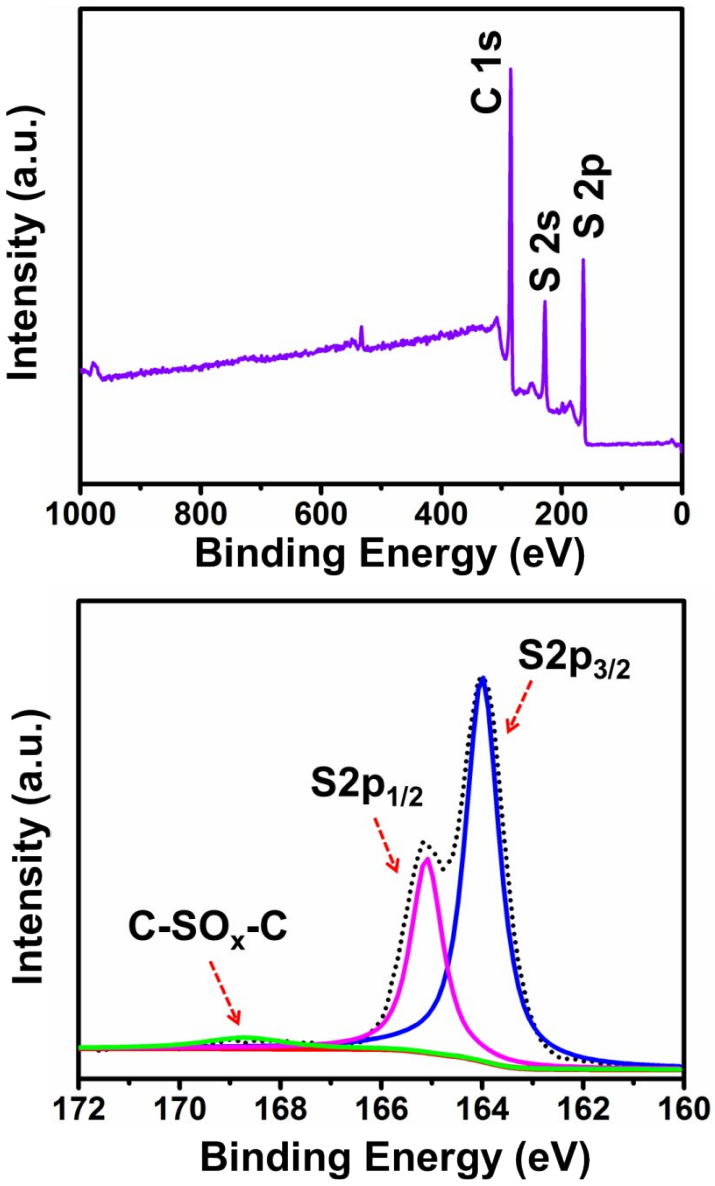


Fig. S12 (a) XPS survey spectrum and (b) high-resolution S 2p spectra of GMC-S film.

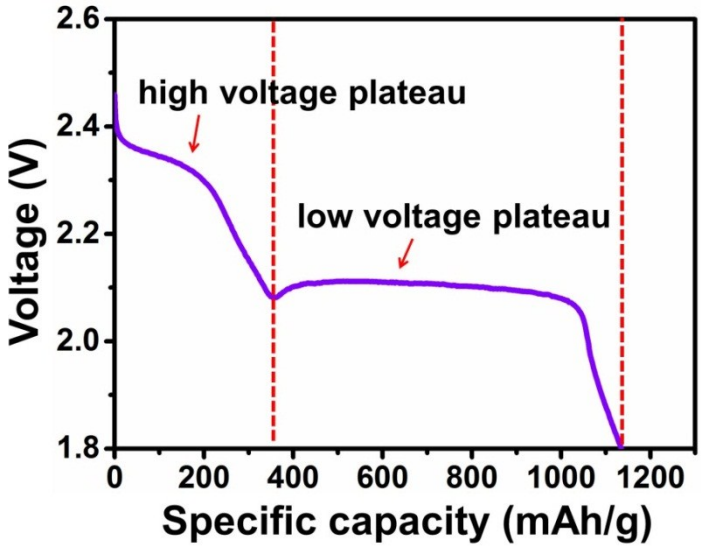


Fig. S13 Discharge curve divided by high and low voltage plateaus.

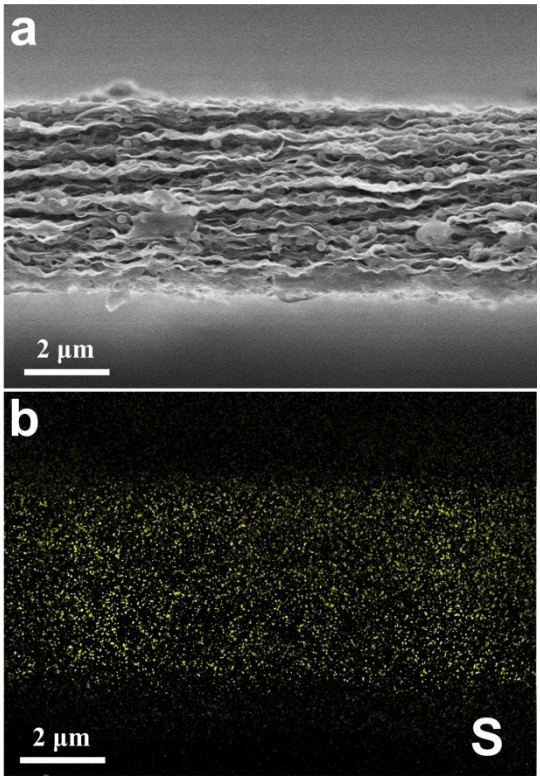
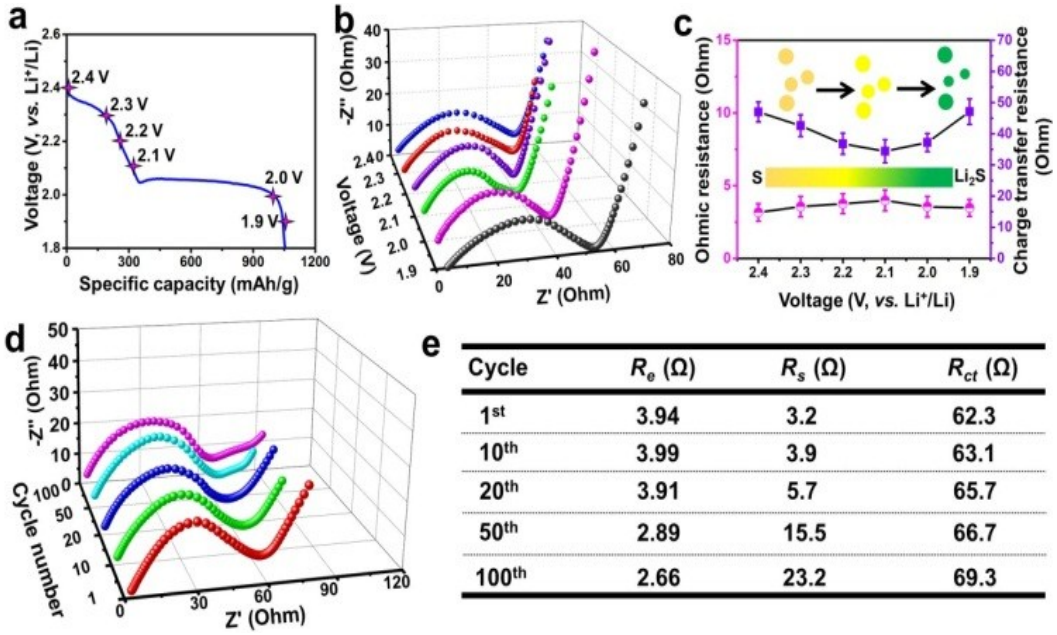


Fig. S14 (a) SEM image of GMC-S film after being cycled for 500 cycles and (b) EDS mapping of sulfur element in the selected cross section of GMC-S film.



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Cycle	R_e (Ω)	R_s (Ω)	R_{ct} (Ω)
1st	3.94	3.2	62.3
10th	3.99	3.9	63.1
20th	3.91	5.7	65.7
50th	2.89	15.5	66.7
100th	2.66	23.2	69.3

Fig. S15 Electrochemical impedance of Li-S battery with GMC-S electrode. (a) Discharge curve of Li-S battery with GMC-S electrode at 1 C. (b) EIS curves at various voltage pots remarked in (a). (c) Re and Rct values derived from the EIS curves. (d) Nyquist plots of Li-S battery with GMC-S film after being cycled at different times from 1 to 100. (e) Impedance parameters calculated from the EIS curves based on the equivalent circuit.

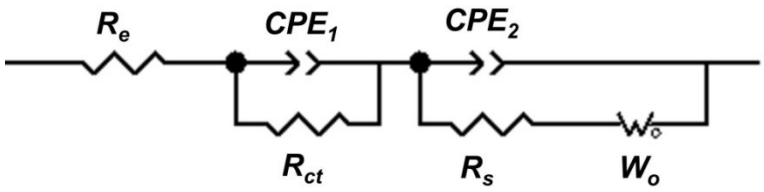

Fig. S16 Equivalent circuit established to match for the Nyquist file of Li-S battery with GMC-S electrode.

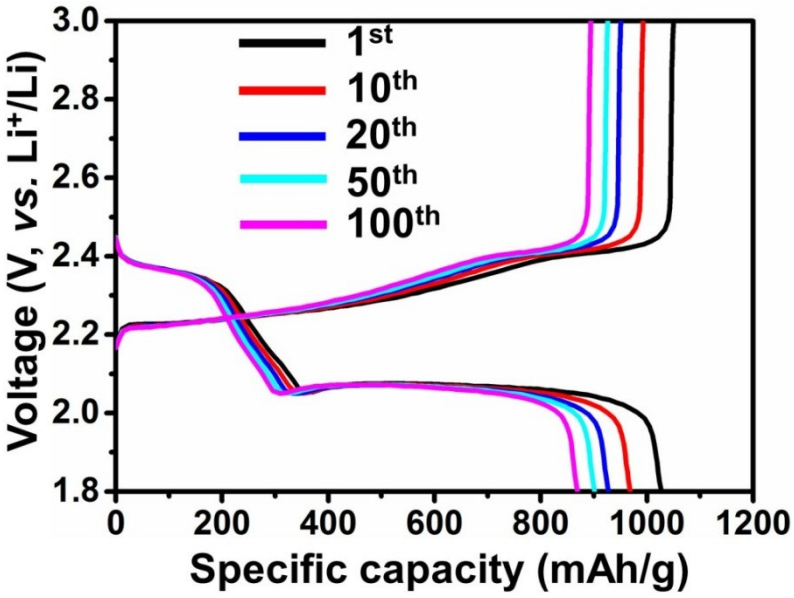

Fig. S17 Discharge curves of Li-S battery with GMC-S electrode at different cycles from the 1st to the 100th.

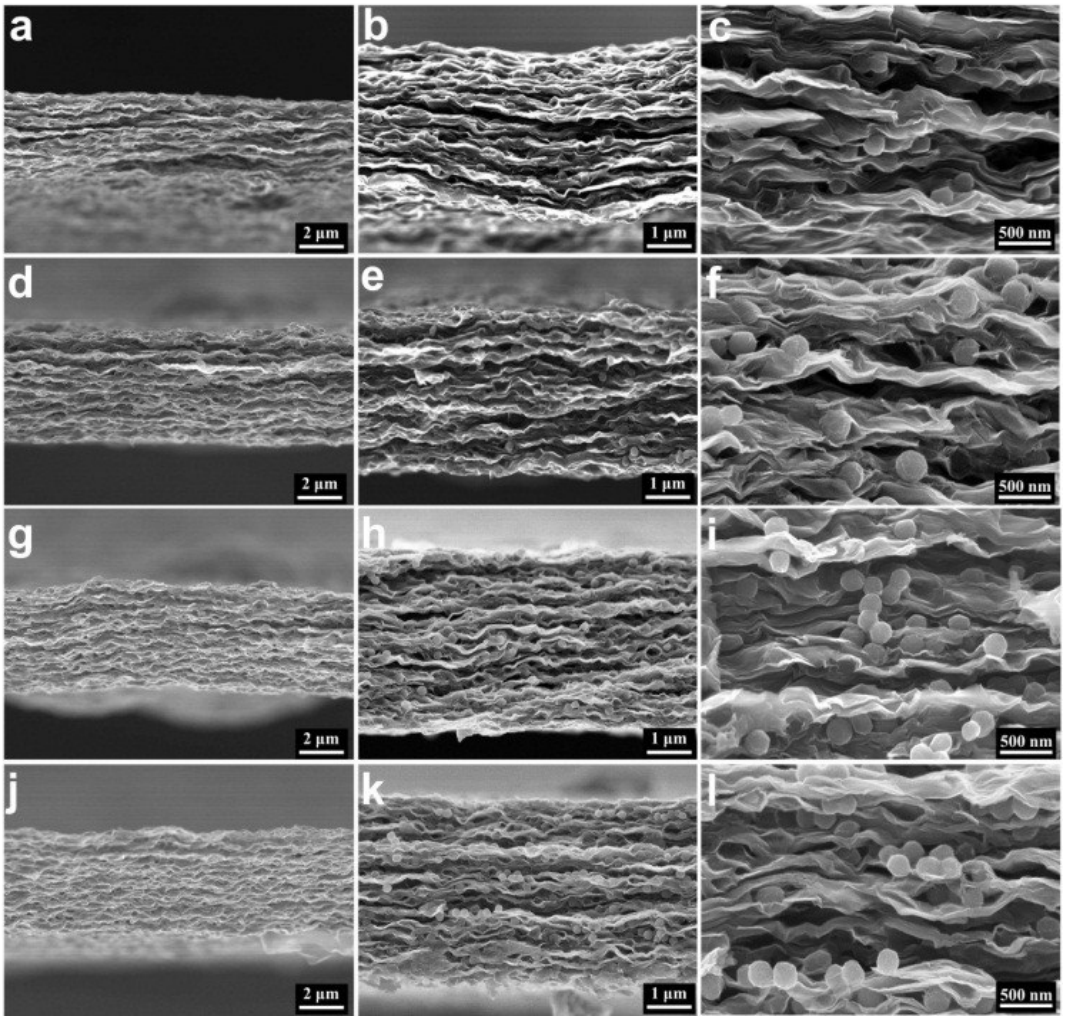

Fig. S18 SEM images of (a - c) GMC-S4, (d - f) GMC-S5, (g - i) GMC-S6, (j - l) GMC-S7 with different magnifications.

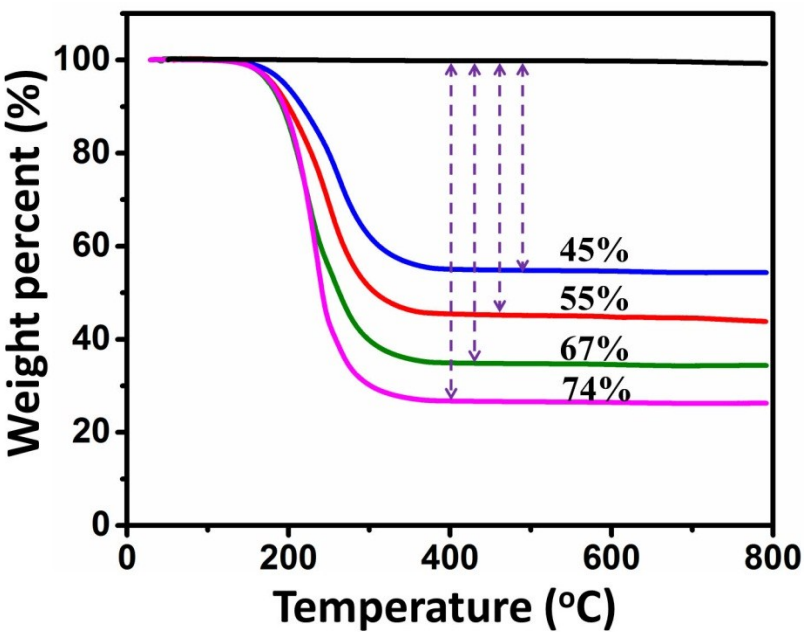

Fig. S19 Typical TGA curves of GMC-S films with different sulfur contents of 45%, 55%, 67% and 74%, which were denoted as GMC-S4, GMC-S5, GMC-S6 and GMC-S7, respectively.

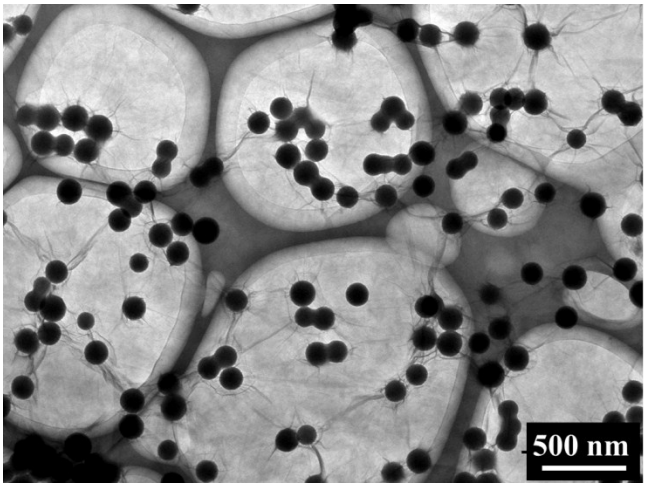

Fig. S20 TEM images of GMC-S7 material.

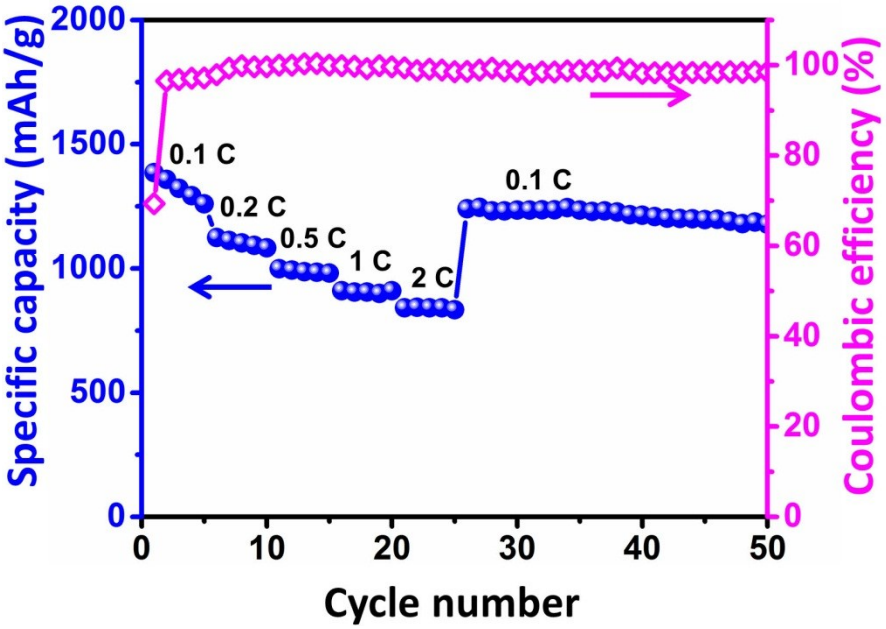

Fig. S21 Rate capability of Li-S battery with GMC-S7 electrode at different rates from 0.1 to 2 C.

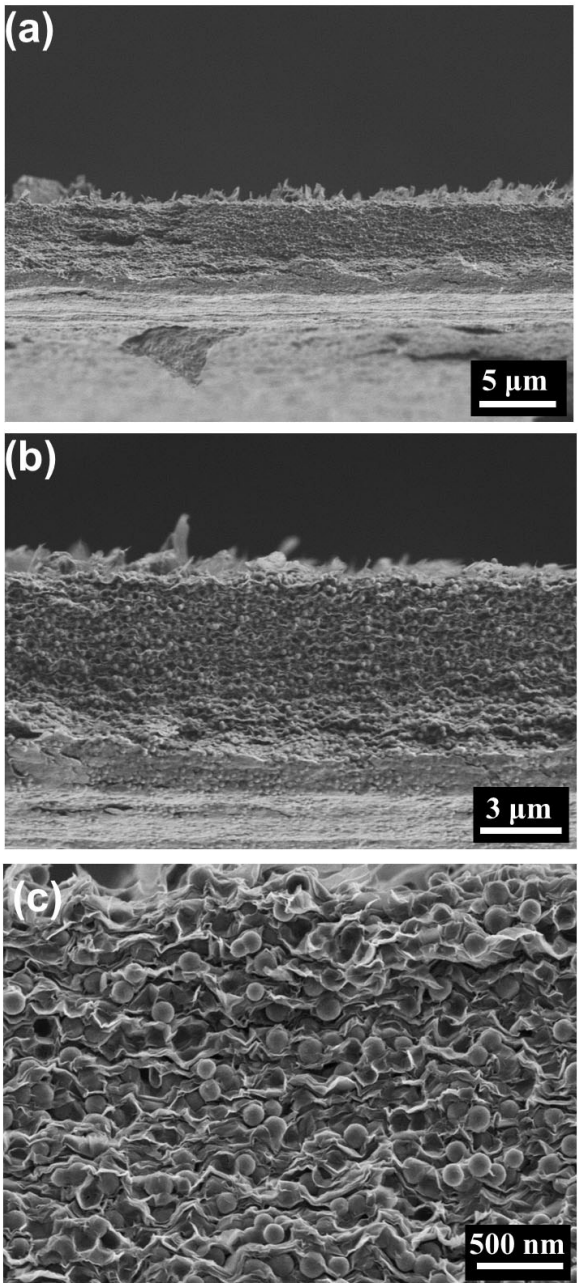

Fig. S22 SEM images of the cross section of GMC-S materials with a sulfur content up to 80%.

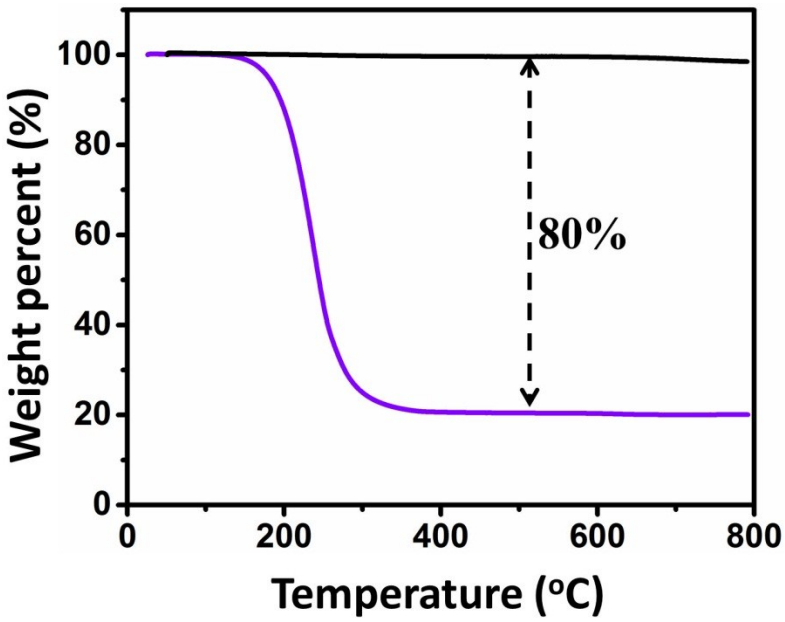

Fig. S23 TGA curve of GMC-S material with a higher sulfur content up to 80%.

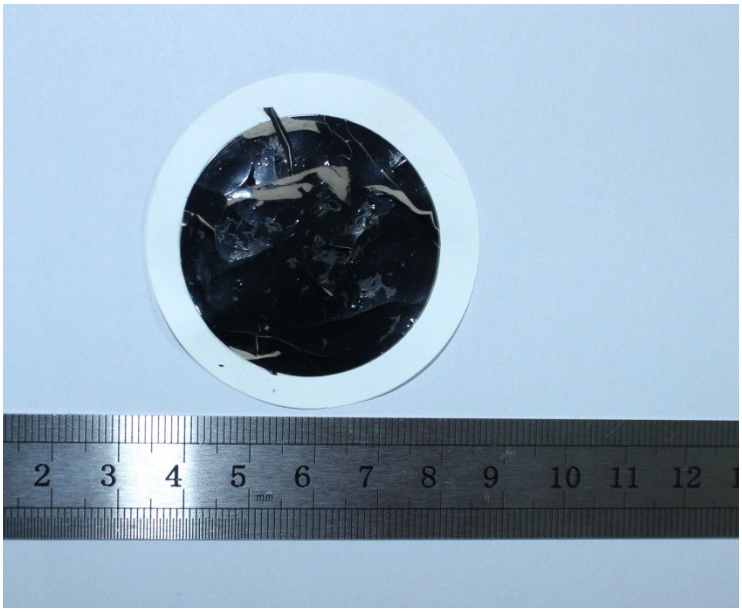

Fig. S24 Optical image of GMC-S material with a higher sulfur content up to 80%.