Supporting Information

Porous 3D graphene-based biochar materials with high areal sulfur loading for lithium-sulfur batteries

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Experimental Methods

1. Preparation of graphite oxide (GO)

Graphite oxide was prepared from natural graphite (Jinglong Co., Beijing, China) according to a modified Hummers method [1]: 120 mL 98 wt% H_2SO_4 was poured into a beaker containing a mixture of 5 g natural graphite and 2.5 g $NaNO_3$, and then the mixture was stirred in an ice bath for 30 min. 15 g $KMnO_4$ was added slowly into the mixture, which was allowed to react for 2 h at a temperature no more than 20°C. Then, the temperature was risen to 35°C, and the reaction was performed for another 2 h. After that, the reactant mixture was poured slowly into 360 mL distilled water under violent stirring condition so as to control the temperature no more than 90°C, followed by further reaction at 75°C for 1 h. After the mixture was diluted to 1.5 L, 50 mL 30 wt% H_2O_2 was added to consume the remaining $KMnO_4$ and the produced MnO_2. The as-obtained mixture was a bright yellow suspension. After filtered and washed with 5 wt% HCl and distilled water, the filter cake was freeze-dried for 24 h to obtain the graphite oxide.

2. Measurement of the electrical conductivity of the carbon products.

The measurement of the electrical conductivity of the carbon products is carried out according to previous reported [2]. The electrical conductivity of the products was tested by the following method. Typically, the products were mixed with 2 wt% polytetrafluoroethylene (PTFE) as a binder, and homogenized in an agate mortar. Then it was rolled into 150-200 μm thickness sheet and cut into 2 cm × 1 cm sheet to get the resistance (R). The conductivity of the film was calculated using the formula $\lambda = L / (R \times W \times d)$, where λ is the electrical conductivity of sample, L, W, d is the length, width and thickness of the sheet, respectively.

Supplementary Figures and Tables

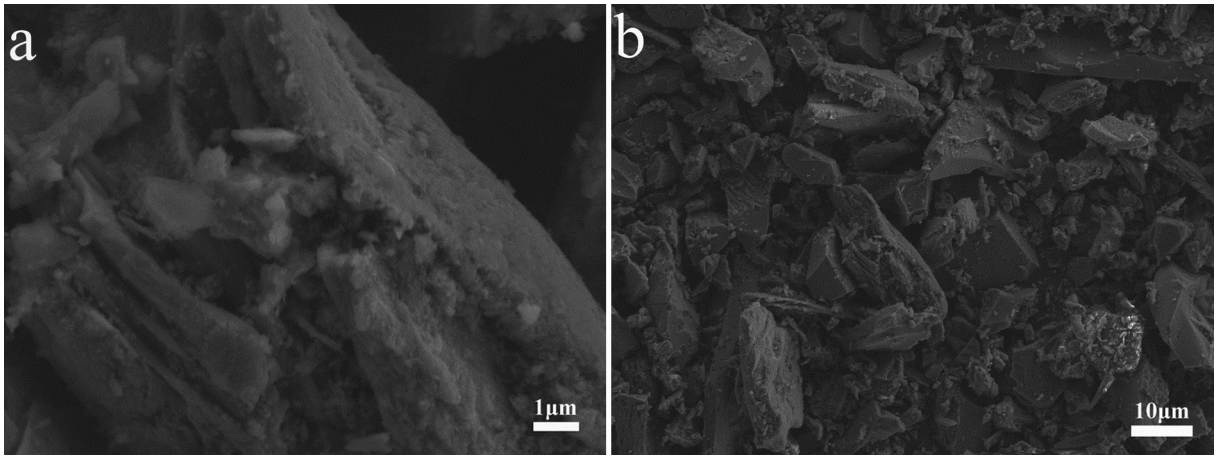

Fig. S1 (a) High and (b) low-magnification SEM images of AC-S composite.

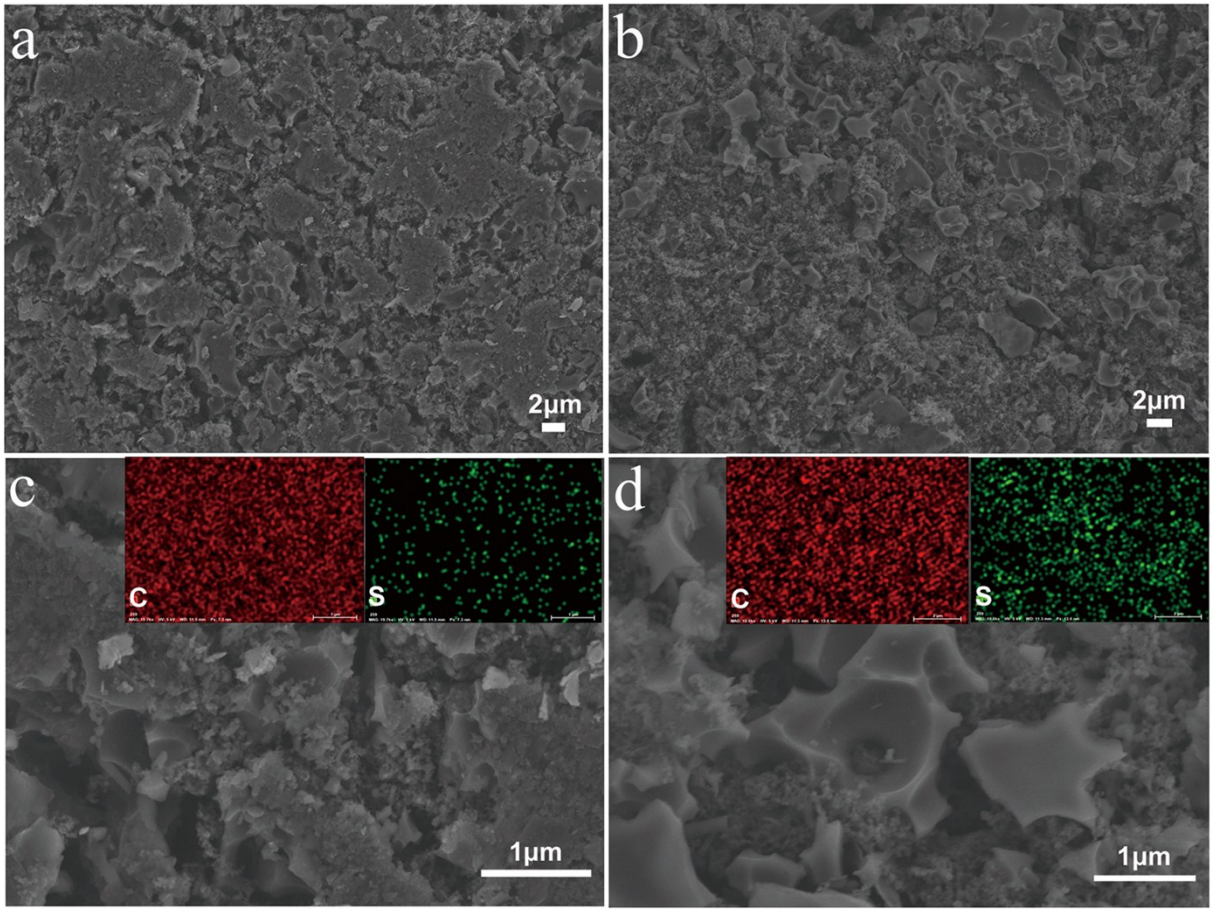

Fig. S2 SEM images of the PBG-S cathode electrode (a, c) before cycling and (b, d) after 50 cycles in 1C. Elemental mapping of sulphur and carbon is inside (c) and (d).

Fig. S2 was provided to compare the morphology of PBG-S cathode electrode before and after cycling. Fresh PBG-S cathode electrode in Fig. S2a, c exhibits a smooth morphology with active material and binder. The PBG-S cathode electrode after 50 cycles in 1C (Fig. S2b, d) still shows a relatively smooth morphology with more exposed PBG-S particles. Fig. S2c,d display the elemental mapping results of the fresh and cycled PBG-S cathode electrode, and sulphur signal is distributed homogenously in fresh PBG-S cathode electrode, and it is noteworthy to mention that the signal became stronger in the cycled electrode, indicating that a seriously shuttle effect occurred in PBG-S (63.2 wt%) cathode electrode.

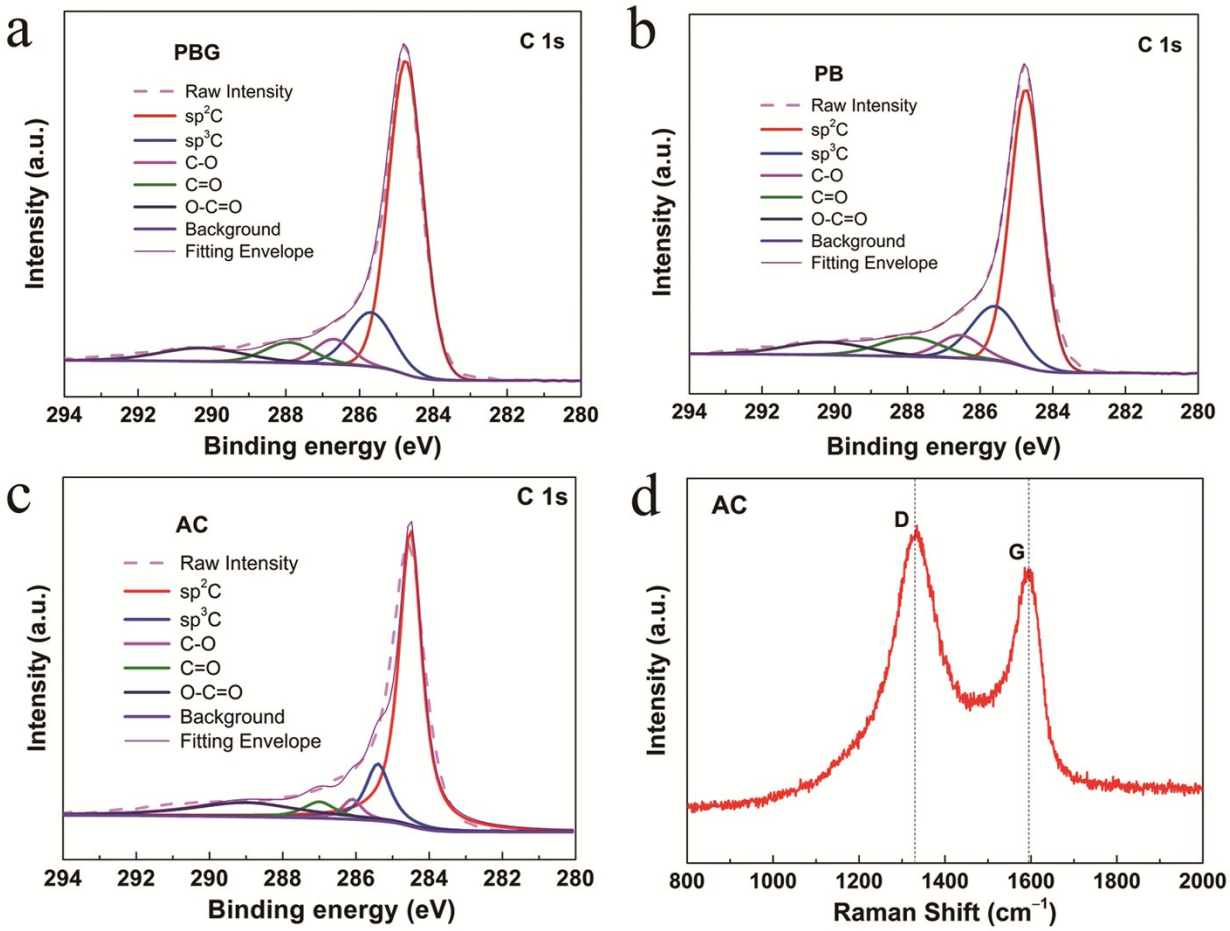

Fig. S3 High-resolution spectrum of C 1s for (a) PBG, (b) PB and (c) AC. (d) Raman spectra of AC

Table S1. Surface elemental concentrations and relative contents of functional groups derived from C 1s XPS spectra of PB and PBG

Samples	C1s fitting binding energy (eV; relative percentage,%)				
	C=C(sp^2)	C-C(sp^3)	C-O	C=O	O-C=O
PBG	284.75 (66.41)	285.69 (14.67)	286.70 (5.72)	287.91 (6.15)	290.27 (7.05)
PB	284.74 (59.90)	285.59 (17.88)	286.55 (6.62)	287.91 (8.29)	290.25 (7.32)
AC	284.73 (63.26)	285.45 (13.72)	286.21 (3.94)	287.2 (4.86)	289.57 (14.22)

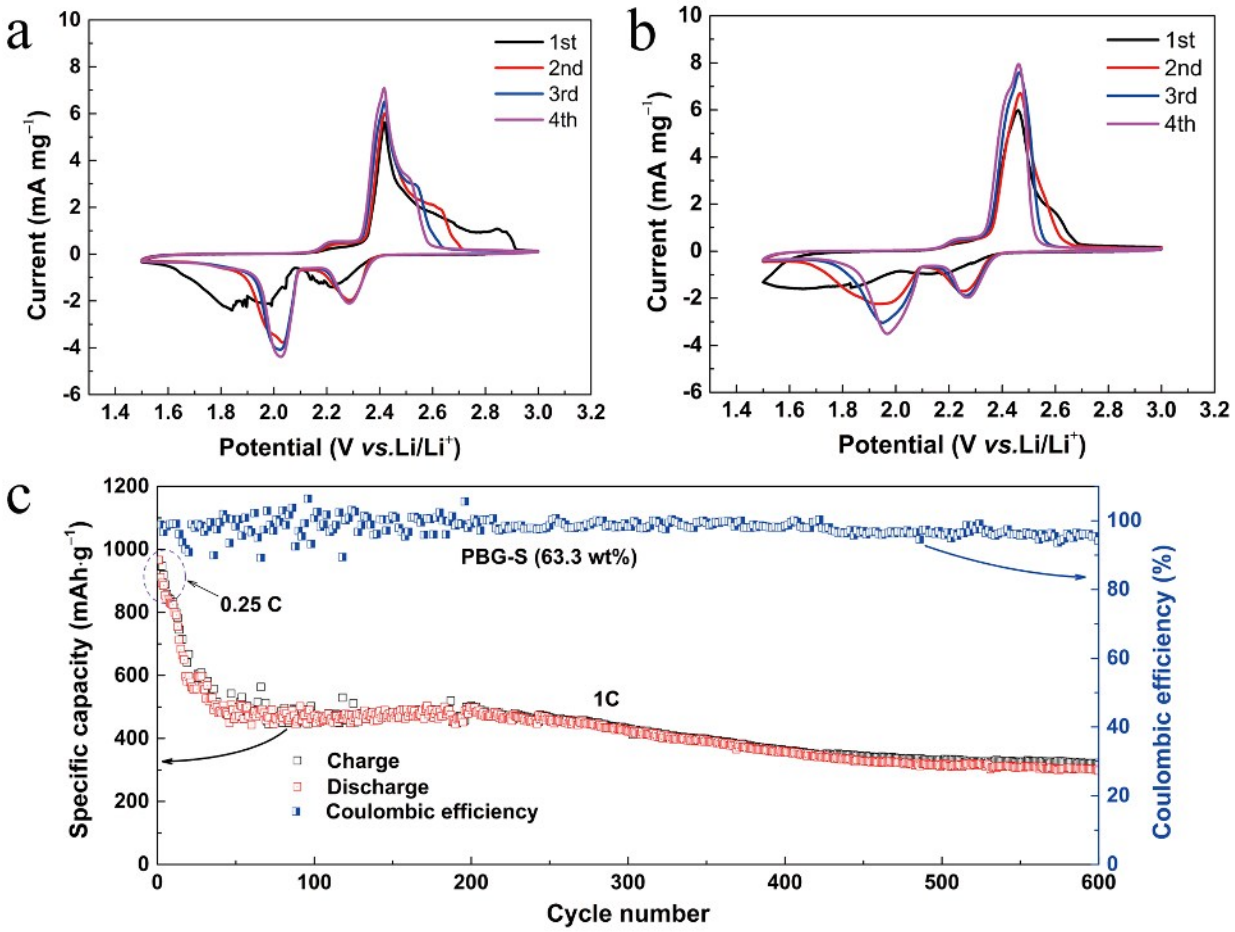

Figure. S4 Initial four cycles of CV curves of (a) PB-S and (b)AC-S at a scan rate of 0.2 mV s^{-1}. (c) Cycling performances of PBG-S composite cathodes at 1C for 600 cycles.

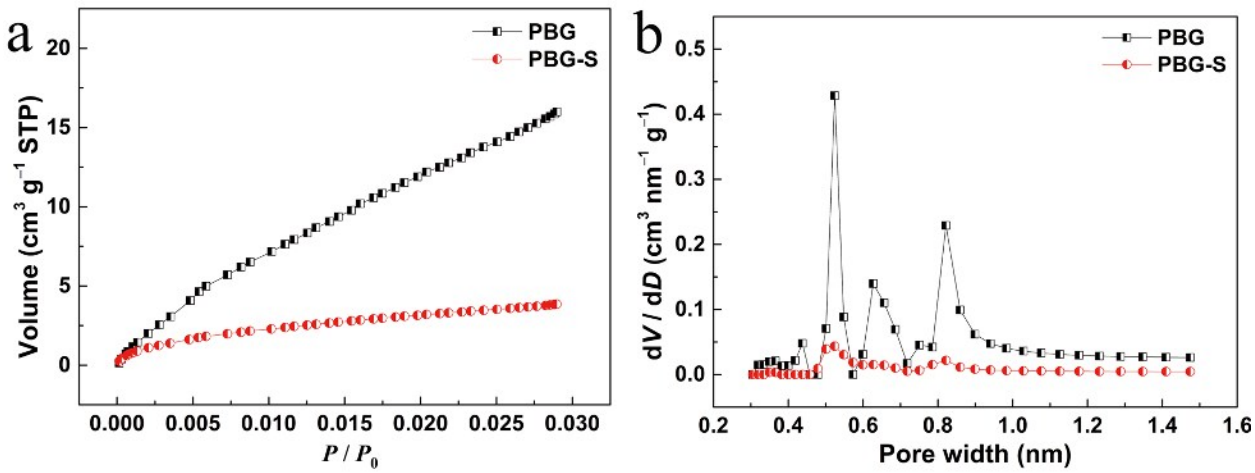

Figure S5. (a) CO_2 adsorption isotherms and (d) the corresponding pore size distribution of PBG, PBG-S with DFT method.

Table S2. Porosity parameters derived from the CO_2 adsorption isotherms and densities of PBG and PBG-S

Sample	S_{CO2} [a] [m^2 g^{-1}]	V_{CO2} [b] [cm^3 g^{-1}]	Pore size [c] [nm]
PBG	172.95	0.062	0.524
PBG-S	19.67	0.007	0.516

[a] SSA calculated with DFT method from the CO_2 adsorption isotherm;

[b] Pore volume calculated with DFT method from the CO_2 adsorption isotherm;

[c] Adsorption average pore width Calculated with DFT CO_2 adsorption isotherm.

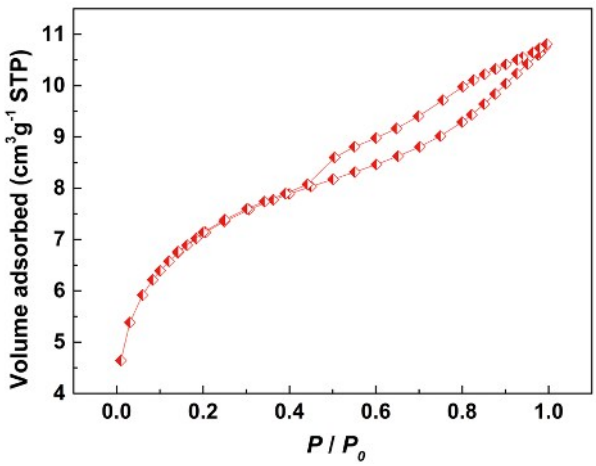

Fig. S6 N_2 adsorption–desorption isotherms of the PBG-S (63.2 wt%) composites.

Supplementary References

1. D. Liu, Q. Li and H. Zhao, *J. Mater. Chem. A*, 2018, **6**, 11471-11478.
2. L. Zhang, F. Zhang, X. Yang, G. K. Long, Y. P. Wu, T. F. Zhang, K. Leng, Y. Huang, Y. F. Ma, A. Yu and Y. S. Chen, *Sci. Rep.*, 2013, **3**, 1408.