

## Supporting Information

### **The improvement of pitch activation by graphene for long-cycle Li-S batteries**

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## **Experimental**

### *Materials and chemicals*

Graphene was synthesized by a modified electrochemical exfoliation of graphite.<sup>1</sup> A coal tar pitch with a softening point of 75 °C was gifted by Taiyuan Coal Coking Co., Ltd. Potassium hydroxide (KOH, 85% Tianjin Kermel Chemical Reagent Co., Ltd.), sodium dodecyl sulfate (SDS, Aladdin), sublimed sulfur powder, (99.5%, -100 mesh, Alfa Aesar), 1-Methyl-2-Pyrrolidone (NMP, 99%), polyvinylidene Fluoride (PVDF, Aladdin), ketjenblack (ECP-200L). The porous membranes were Celgard 2400 membranes. The electrolyte is a combination of 1 M lithium bis(trifluoromethane sulfonyl)imide and 1 wt% LiNO<sub>3</sub> dissolved in a 1:1 (v/v) mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME). All the chemicals were used without further purification.

### *Synthesis of pC/G composites*

4.0 g of CTP and 0.4 g of SDS was mixed with graphene in aqueous dispersion (33 mL, 4.8 mg/mL) with stir for 12 h at room temperature. Then, 12 g of KOH was added into the above mixture and stirred for another 12 h. After drying at 100 °C, the mixture was transferred to a nickel crucible, and the crucible was placed in the center of a tube furnace. Under a flow of argon, the furnace temperature was ramped to 380 °C and kept for 2 h, then increased to 700 °C at the rate of 5 °C/min and further held for 2 h. Next, we rinsed annealed sample into deionized water and filtered for >6 times until pH = 7 to recycle the basic activator. The aqueous solution was concentrated through heating for next-turn activation. White crystal was obtained after heating at 100 °C for 6 h. The black solid was completely washed with deionized water and dried at 105 °C, denoted as pC/G. For comparison, chemical activation of the mixture of pitch and SDS without graphene, was carried out, named as pC. An optimized alkali-carbon ratio of 3/1 was employed for all the activated samples.

#### *Electrode fabrication*

Briefly, 0.11g, 0.3 g and 0.61 g of sublimed sulfur were respectively mixed with 0.1 g of pC/G powder in a mortar and grinded 30 min. Then, all the S-pC/G composites were heat-treated in a tube furnace at 155 °C for 12 h and 300 °C for 0.5 h at a ramping rate of 5 °C/min in a sealed glass bottle under Ar flow, named as S-pC/G-X (X=51.3%, 71.2% and 85.8%). S-pC and S-Graphene were prepared by the same procedure outlined above.<sup>2</sup>

Coin cells (CR2016) were assembled in an Ar-filled glovebox with 1 M LiTFSI and 1 wt% LiNO<sub>3</sub> in DOL-DME solution (1:1 by volume) as the electrolyte. And the separator membrane was Celgard 2400 and the counter electrode was lithium metal foil. The working electrode consisted of 80 wt % active materials, 10 wt % ketjenblack, and 10 wt % poly(vinylidene fluoride) (PVDF) binder in N-Methyl-2-pyrrolidone (NMP), with a typical sulfur loading of around 3.0 mg/cm<sup>2</sup>.

#### *Electrochemical Tests*

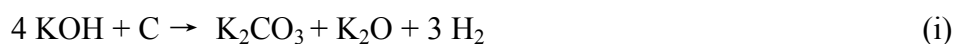
The galvanostatic charge-discharge tests data were conducted on a battery test system (LAND CT2001A instrument) at room temperature within under the voltage range of 1.7 – 2.8 V (vs. Li<sup>+</sup>/Li) with the charging and discharging rate ranging from 0.05 to 2 C (1 C = 1675 mA/g). Cyclic voltammetry (CV) were tested using CHI660E at room temperature with a scan rate of 0.5 mV/s in the range of 1.5 – 3.0 V (vs. Li<sup>+</sup>/Li). The electrochemical impedance (EIS) measurements were tested over the frequency range of 100 kHz to 0.01 Hz. All electrochemical measurements were performed under normal condition.

### **Material Characterizations**

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu K $\alpha$  ( $\lambda = 1.54059 \text{ \AA}$ ) radiation line. Morphologies of the samples were examined by SEM (JSM-7001F), TEM and HRTEM (JEM-2100F) at an acceleration voltage of 200 kV. Raman spectra were taken on a laser Raman microscope (Jobin-Yvon HR-800) with an excitation line at 488 nm. HAADF-STEM was measured by a JEM ARM200F equipped with double aberration correctors in Institute of physics, Chinese Academy of Sciences, and a cold field 3 emission gun operated at 200 kV. Synchrotron x-ray absorption spectroscopy was acquired at beam line U19, National Synchrotron Radiation Laboratory, Hefei, China. The surface area and porosity of different samples were measured by nitrogen adsorption/desorption at 77 K using ASAP-2010 instrument (Micromeritics, USA). X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB 250 spectrometer (Thermo Scientific) with an Al K $\alpha$  X-ray source that has a 500 mm electron beam spot. Thermogravimetric analysis (TGA, STA409PC, Netzsch, Germany) was performed under oxygen flow at a temperature ramp rate of 5 °C/min. Fourier transform infrared (FTIR) spectroscopy was carried out using the KBr-pellet method in transmission mode on a Nicolet 380 FT-IR spectrometer.

### **Extended figures and discussion**

It is well-known to use KOH activation to form the pores of activated carbon. During KOH activation, there are three main activation processes, as shown by Equations (i) (ii) and (iii) as follows.<sup>3</sup> Potassium in various compounds reacts with carbon to form gas to consume carbon to form pores.



To reveal the composition of the recycled activator, XRD pattern was recorded as shown in Figure S2. The three potassium compounds ( $\text{KOH}$ ,  $\text{K}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ ) are all found. At high temperature,  $\text{KOH}$  can be converted to  $\text{K}_2\text{O}$  and  $\text{K}_2\text{CO}_3$  and  $\text{K}_2\text{O}$  can be return to  $\text{KOH}$  after water washing.<sup>4,5</sup>  $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$  crystal was the product of drying at  $100^\circ\text{C}$  and can be dissolved in water to form next-turn chemical activator. Wholly, the recovery of the  $\text{KOH}$  activator is beyond 61%.

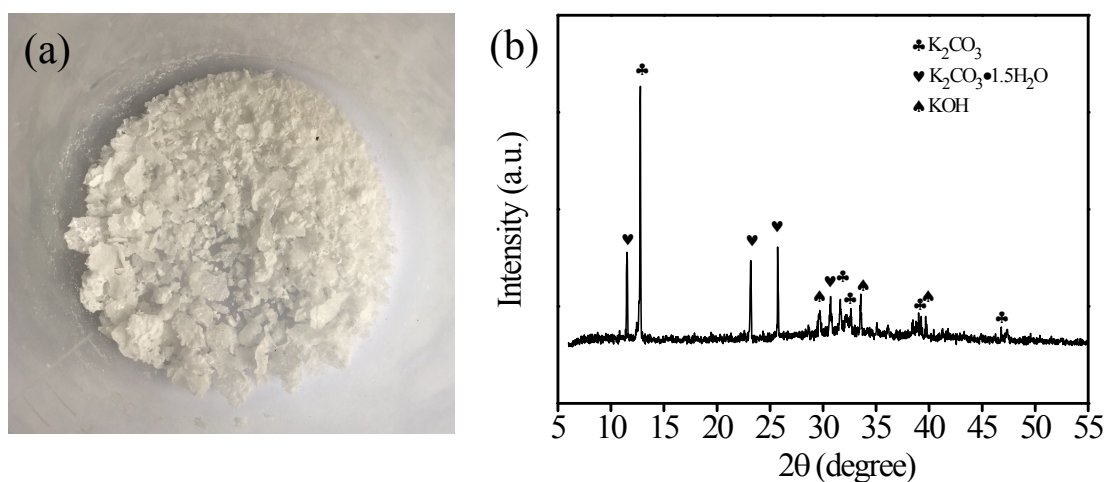


Figure S1. (a) The photograph of white crystals obtained from the filtrate of activated product. (b) XRD patterns of the sample (a).

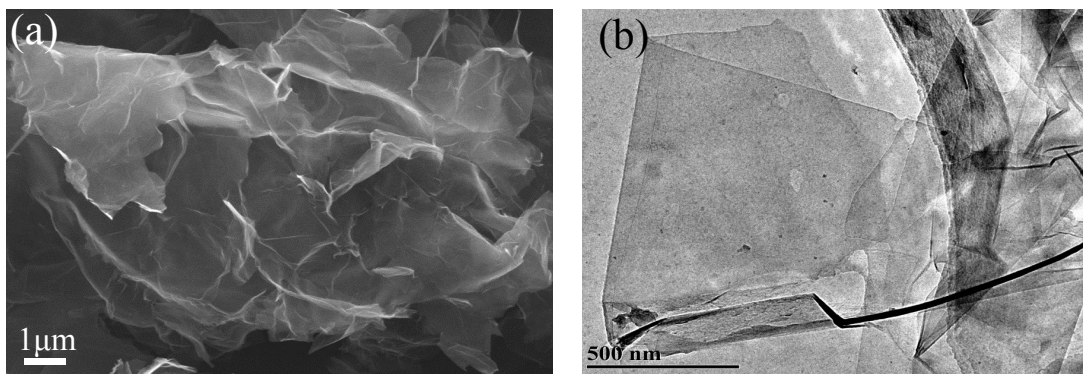


Figure S2. (a) SEM and (b) TEM image of electrochemically-exfoliated graphene.

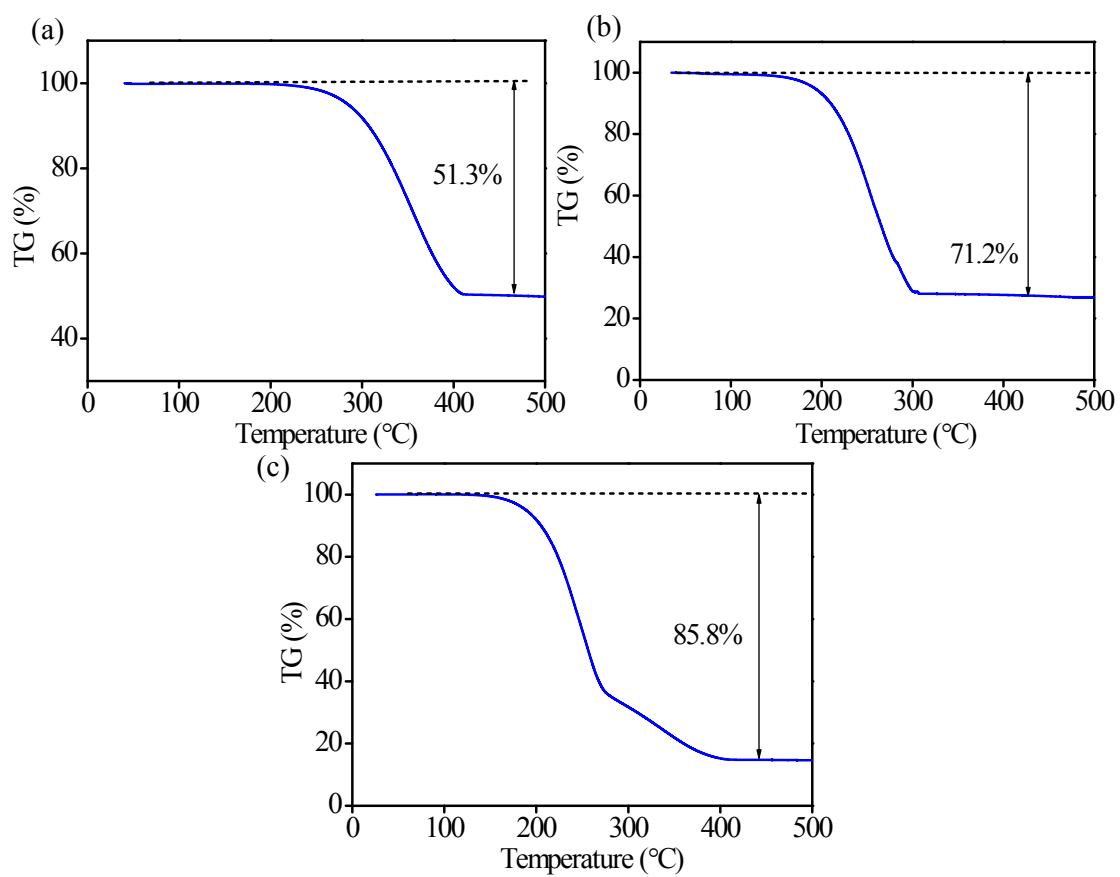


Figure S3. TGA data of the samples of pC/G loaded with different amounts of sulphur. The sulphur content was estimated as (a)  $W_s=51.3\%$ , (b)  $W_s=71.2\%$  and (c)  $W_s=85.8\%$ .

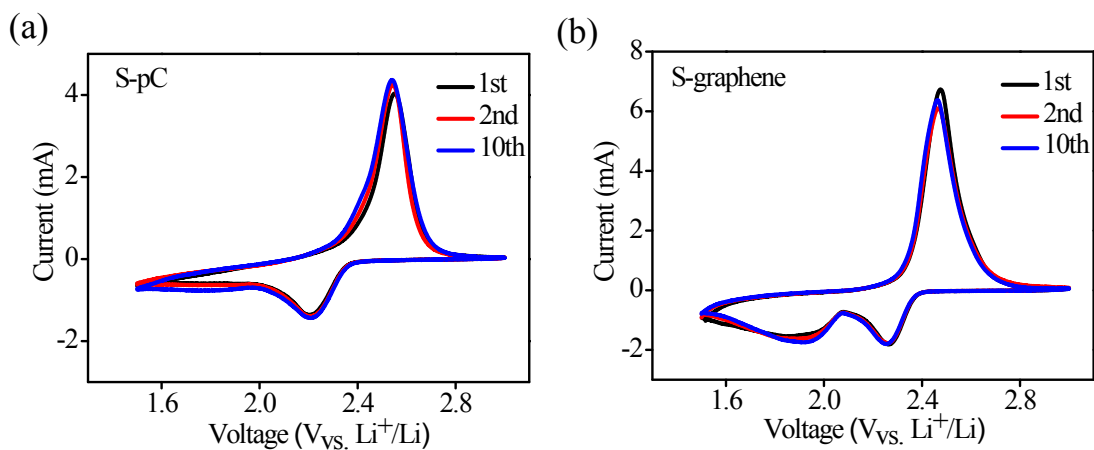


Figure S4. Cyclic voltammetry of the cathode material from 1.5V to 3.0 V at a scanning rate of 0.5 mV/s. (a) S-pC, and (b) S-graphene.

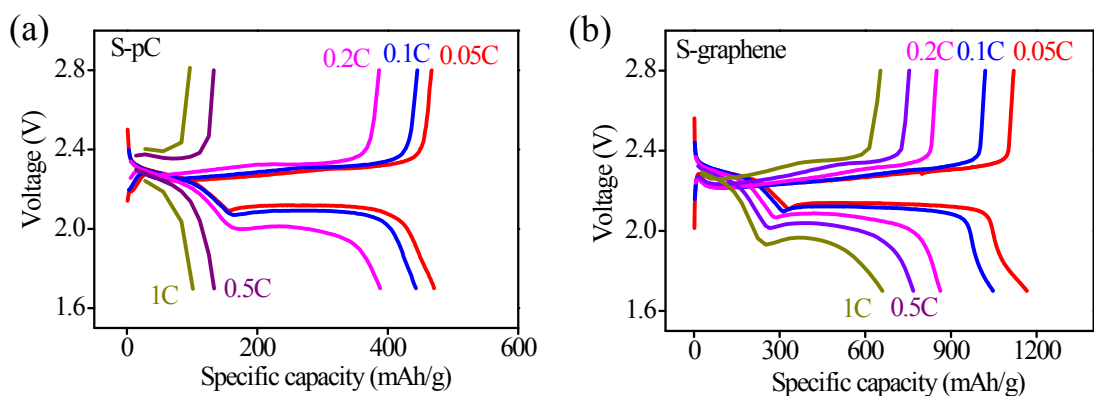


Figure S5. Discharge/charge voltage profiles of (a) S-pC and (b) S-graphene composite at 0.05 C, 0.1 C, 0.2 C, 0.5 C and 1 C.

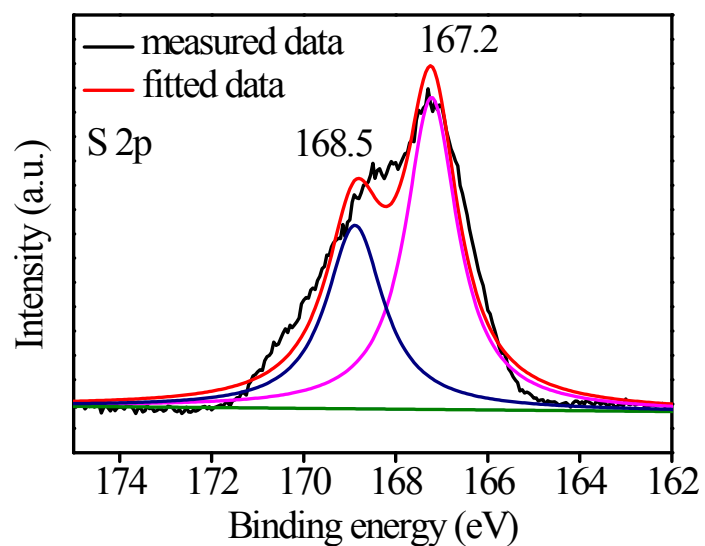


Figure S6. S 2p XPS spectrum of the S-pC/G cathode after 1500 cycles at 1 C.

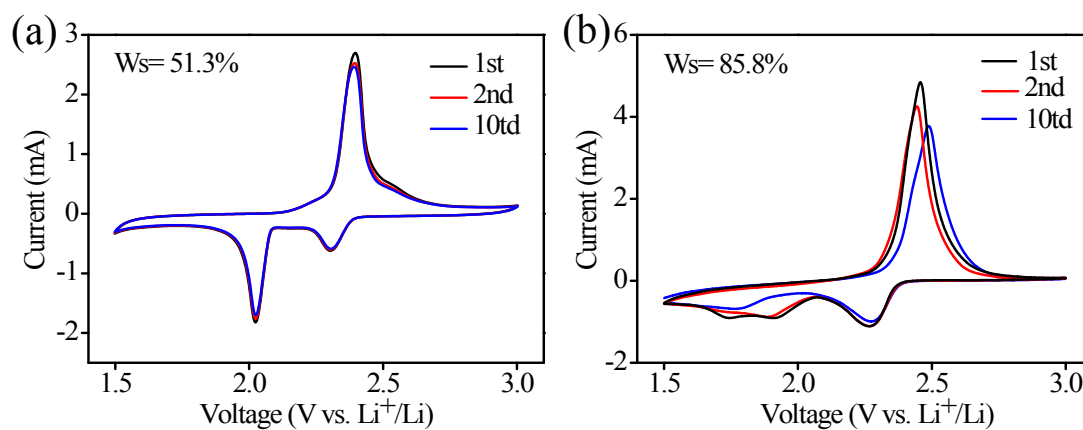


Figure S7. CV curves of the cathode materials ranging from 1.5 V to 3.0 V at a scan rate of 0.2 mV/s. (a)  $W_s=51.3\%$  and (b)  $W_s=85.8\%$ .

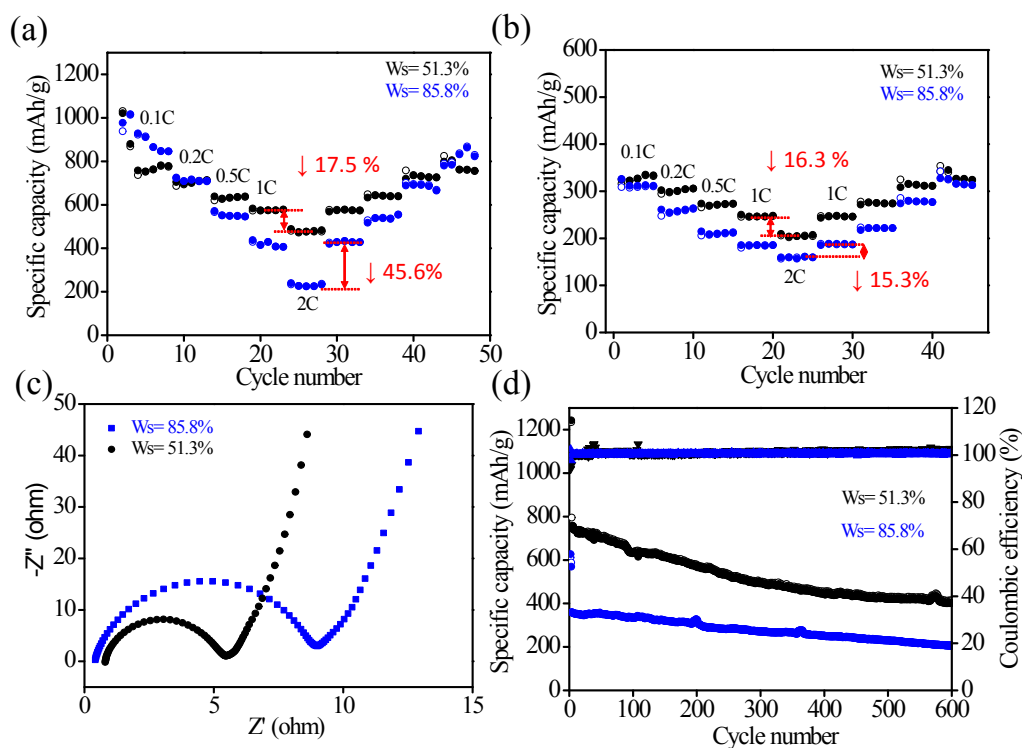


Figure S8. The electrochemical performances of S-pC/G loaded with different contents of sulphur ( $W_s=51.3\%$  (black) and  $W_s=85.8\%$  (blue)). (a) Rate capabilities at 0.1 C, 0.2 C, 0.5 C, 1 C and 2 C. (b) Rate capabilities of the S-pC/G-85.8% with the initial and after 1000 cycles. (c) EIS curves from  $10^{-2}$  Hz to  $10^5$  Hz and (d) Long cycling performances at 1 C.

## References

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