

Supporting information

Evolution of the effect of sulfur confinement in graphene-based porous carbons for use in Li-S batteries

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1. Experimental Section

Preparation of the 3D graphene hydrogel: Graphite oxide was prepared from natural flake graphite (800 mesh) using a modified Hummers method as reported. A GO colloidal suspension with a concentration of 2 mg mL⁻¹ was prepared by ultrasonication of the GO (170 mg) in de-ionized water (85 mL) for 2 h. The suspension was placed in a 100 mL Teflon-lined autoclave and then treated with a hydrothermal method in a muffle furnace at 150 °C for 6 h to obtain the black hydrogel.

Preparation of the PGA-x: In order to research the structure changes depended on the evaporation-induced drying period, a series of hydrogels were dried at 70 °C for 0 h, 2 h, 5 h, 7 h, and 12 h, and then treated with freeze-drying for 24 h, which are denoted PGA-0, PGA-2, PGA-5, PGA-7 and PGA-12 respectively.

Preparation of the PGA-x/S hybrids: PGA-x/S hybrids were prepared by a melt impregnation method. PGA-x and sulfur powders with a mass ratio of 4:6 were ground together to form a homogeneous mixture and heated at 155 °C for 12 h in an argon atmosphere. After the

process, the molten sulfur was impregnated on the layers of PGA-x, the as-prepared mixed powder was denoted PGA-x/S.

2. Sample characterization

Structure characterization: SEM and TEM observations were performed using Hitachi S-4800 (Hitachi, Japan) and JEM 2100F (JEOL, Japan) instruments, respectively. Raman spectra were recorded by a micro-Raman spectroscope (JY HR800) with 532.05 nm incident radiation and a 50× objective. Thermogravimetric analysis (TG, Rigaku, Japan) was conducted in air with a heating rate of 5 °C min⁻¹ up to 500 °C. Nitrogen adsorption was measured by a BEL mini-instrument and the sample was outgassed under vacuum at 200 °C for 12 h before measurement. The specific surface areas were obtained by BET analyses of the adsorption isotherms. Total pore volume was calculated by the nitrogen adsorption amount at P/P₀=0.99. The pore size distribution was calculated using density functional theory (DFT). XRD measurements were conducted at room temperature using a specular reflection mode (Bruker D-8, Cu K α radiation, $\lambda=0.154056$ nm). XPS analyses were recorded by a Physical Electronics PHI5802 instrument using a magnesium anode (mono-chromatic K α X-rays at 1253.6 eV) as the source.

Electrochemical performance measurement: The PGA-x/S cathode consisting of PGA-x/S (80 wt%), super P (10 wt%) as a conducting agent and PVDF (10 wt%) dissolved in NMP as a binder was prepared. The as-prepared sample was coated on the Al foil and dried under vacuum at 50 °C for 24 h. The foil was then pressed to obtain a circular pellet with a diameter of 10 mm and used as the cathode. The areal loading density of PGA-x/S (x=0, 2, 5, 7, 12) is in the range of 1.7~1.9 mg cm⁻², which is about 1.0 mg cm⁻² calculated based on the mass of sulfur. A 2032-type coin cell was used to assemble the test cell in an Ar-filled glove box (MBraun) and Li foil was used as the counter and reference electrode. The electrolyte was 1.0 M LTFSE dissolved in DOL: DME (1:1 volume) with LiNO₃ (0.5 wt%) additive. The volume of the electrolyte added in each coin cell was 0.2 mL.

CV curves were obtained using an Autolab workstation at a scan rate of 0.2 mVs⁻¹ within a potential range of 1.5-3.0 V (vs. Li⁺/Li). A LAND galvanostatic charge-discharge instrument was used to test the cycle and the rate performance. The current density set for the cell testing here is based on the mass of sulfur in PGA-x/S hybrid and varied from 0.5 A g⁻¹ to 5.0 A g⁻¹.

The shuttle factor proposed by Mikhaylik and Akridge was defined to reflect the extent of shuttle effect as follows:

$$f = k_s \cdot Q_H / I \quad (1)$$

k_s is the heterogeneous reaction constant related with polysulfide diffusion and reaction, Q_H is the theoretical charge/discharge capacities of the high plateau, and I is the charge/discharge current. Based on the assumptions reported in the previous literature,¹ the Coulombic efficiency (C_{eff}) was a function of the shuttle effect:

$$C_{eff} = \frac{2 + (\ln(1 + f)) / f}{2 - (\ln(1 - f)) / f} \quad (2)$$

The shuttle factor can be calculated based on the Coulombic efficiency of cells at different sulfur loading concentrations while larger shuttle factor implied severer shuttle effect.²

References:

1. J.-Q. Huang, Q. Zhang, S.-M. Zhang, X.-F. Liu, W. Zhu, W.-Z. Qian and F. Wei, *Carbon*, 2013, **58**, 99-106.
2. X. B. Cheng, J. Q. Huang, H. J. Peng, J. Q. Nie, X. Y. Liu, Q. Zhang and F. Wei, *J. Power Sources*, 2014, **253**, 263-268.

3. Supplementary Figures

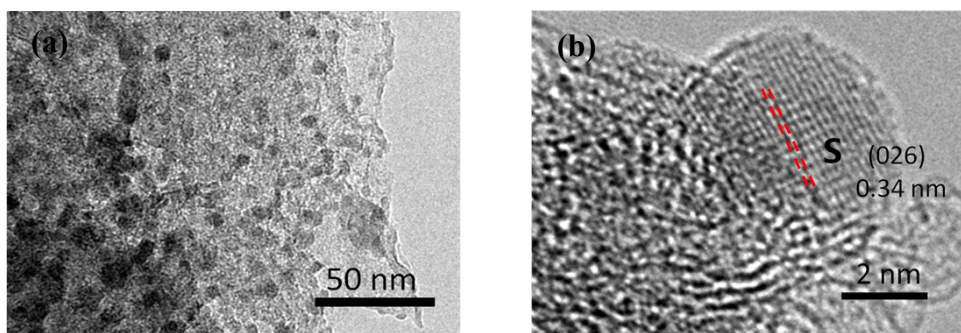


Figure S1. TEM and HRTEM images of PGA-5/S.

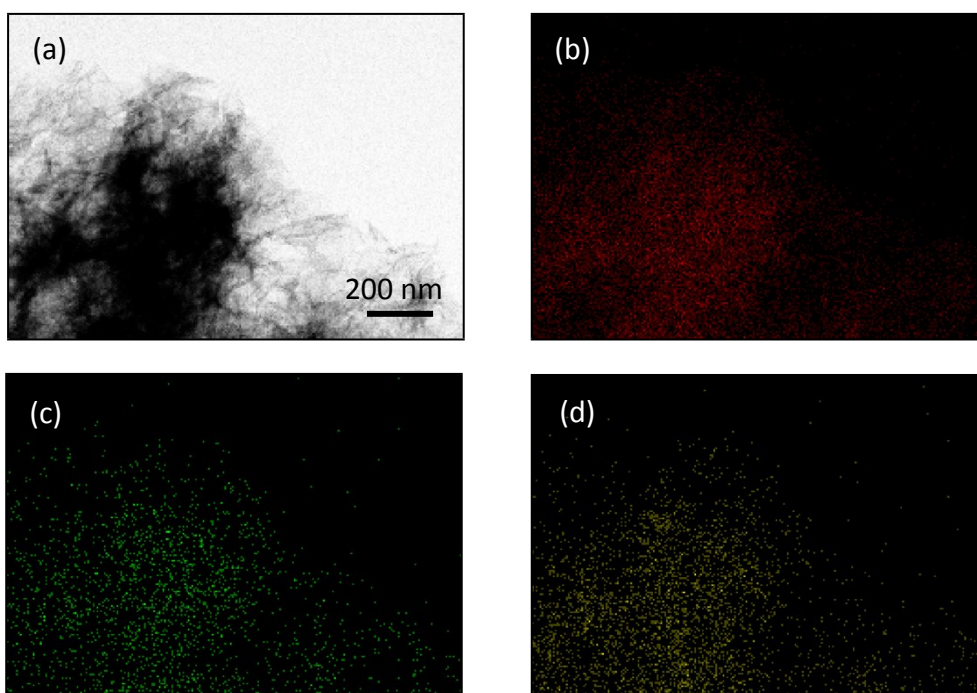


Figure S2. (a) TEM image of PGA-5/S. (b) element C, (c) element O and (d) element S mappings by the EDS equipped on the TEM.

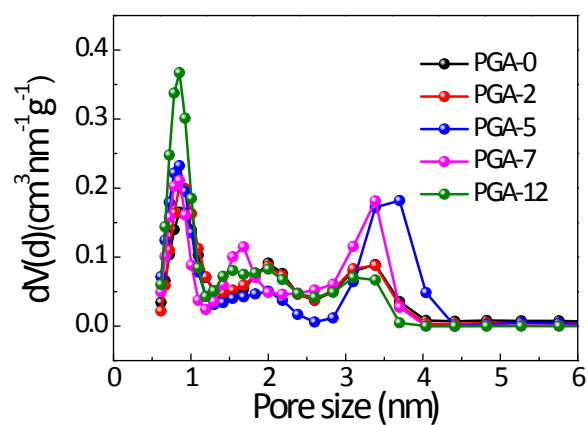


Figure S3. Pore size distributions of PGA-x.

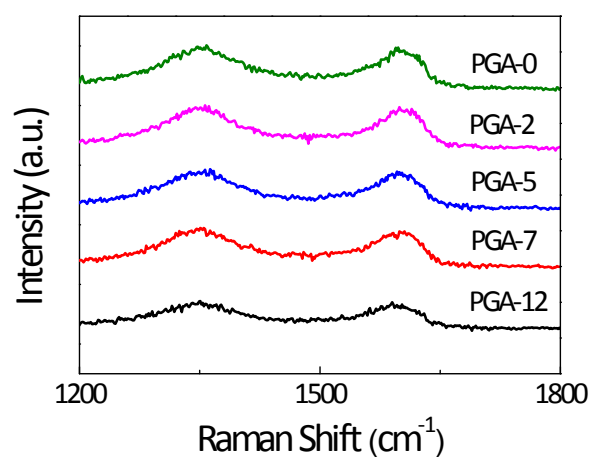


Figure S4. Raman spectra of PGA-x.

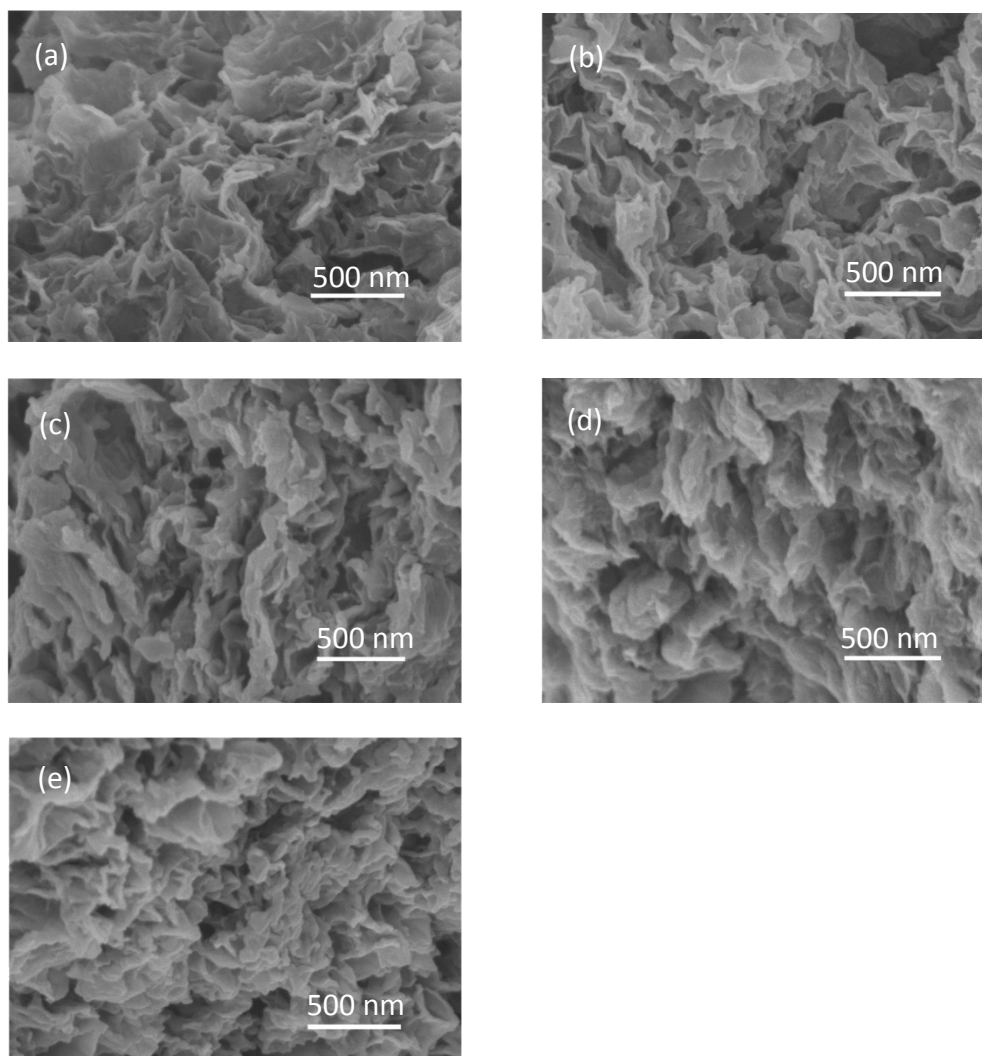


Figure S5. SEM images of PGA-x/S (from (a) to (e), x=0, 2, 5, 7 and 12, respectively).

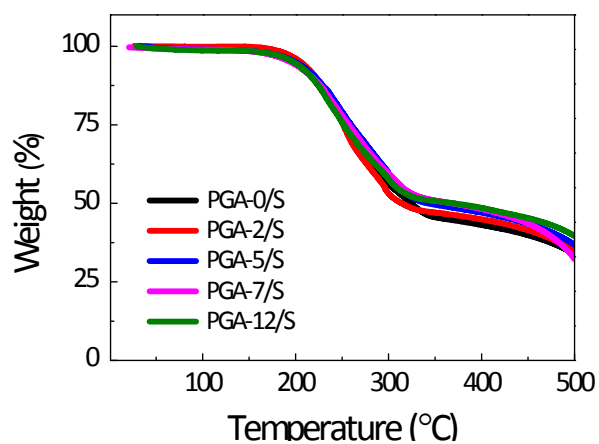


Figure S6. TG curves of PGA-x/S. All the samples were heated at a rate of 5 °C min⁻¹.

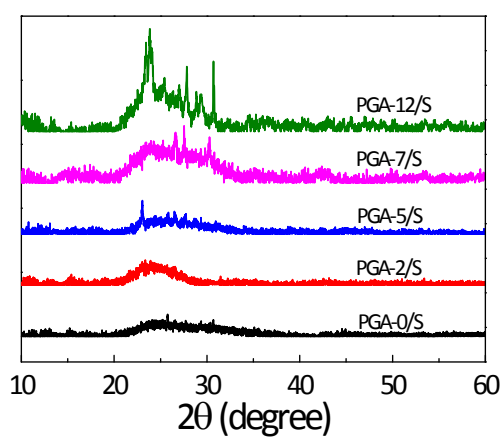


Figure S7. The XRD patterns of PGA-x/S.

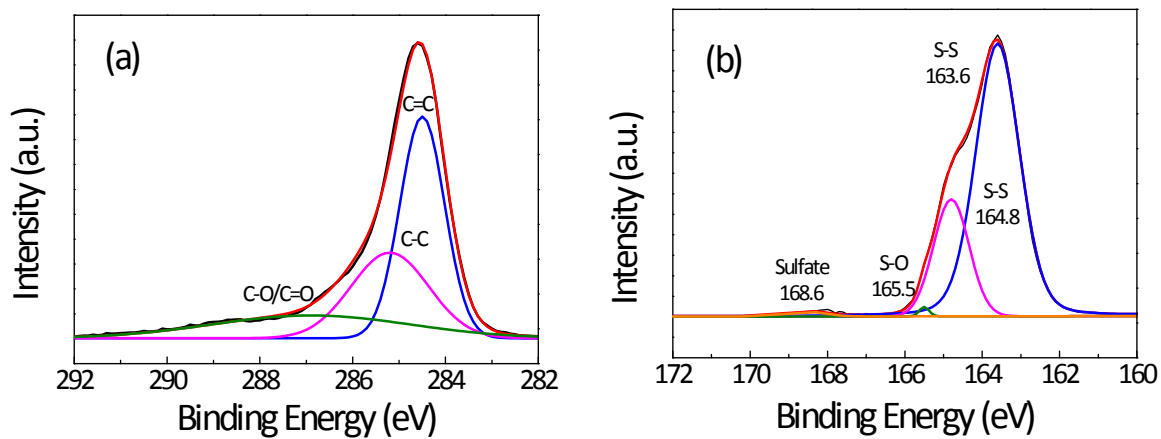


Figure S8.(a) C1s and (b) S2p XPS spectra of PGA-5/S

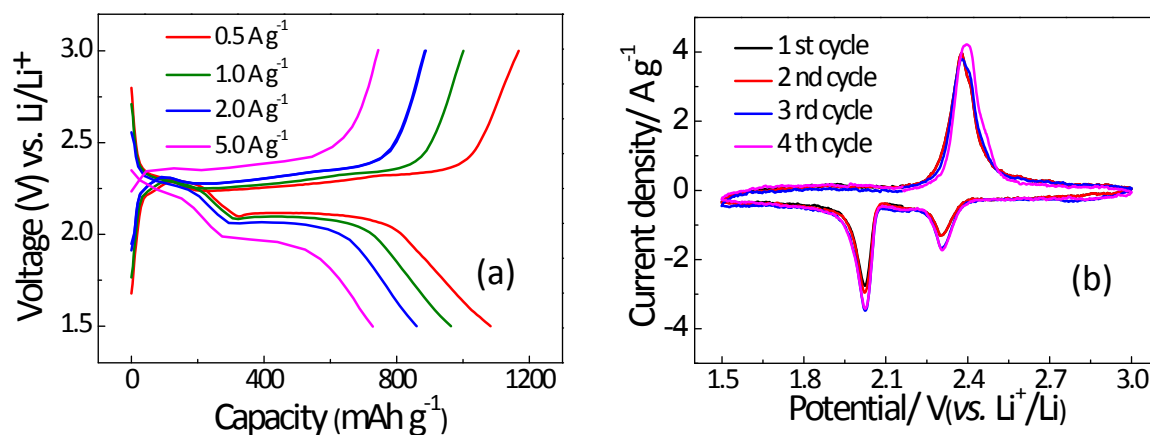


Figure S9. The electrochemical performance of PGA-5/S cathode: (a) CV profiles; (b) Galvanostatic charge-discharge profiles.

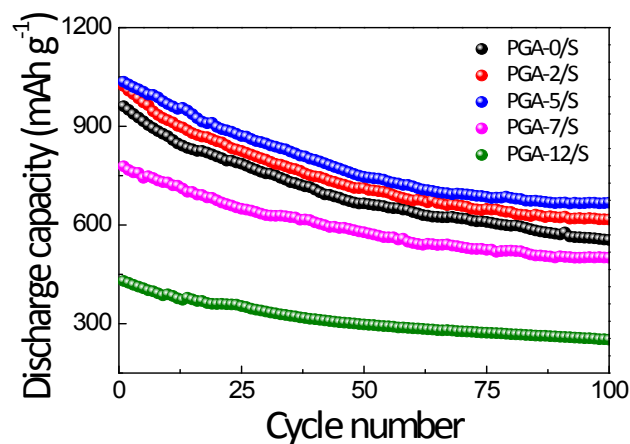


Figure S10. Cyclic performance measured in a voltage range of 1.5-3.0 V vs. Li/Li⁺ with current density of 0.5 A g⁻¹ during 100 cycles;

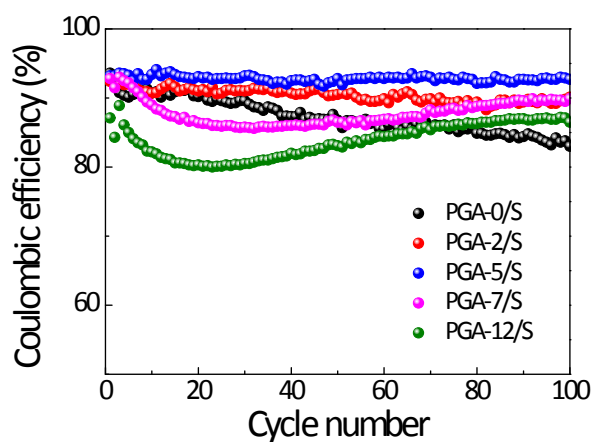


Figure S11. The Coulombic efficiency of PGA-x/S cathodes.