## **Supporting Information for**

## **Bifunctional Hierarchical Porous Carbon Network Integrated with In-Situ Formed Ultrathin Graphene Shell for Stable Lithium-Sulfur Battery**

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Figure S1. SEM image of porous GO film (containing nickel acetate).



Figure S2. Nitrogen adsorption-desorption isotherms of G-PG film and G-HPC film.



Figure S3. XRD patterns of pure sulfur, G-PG, G-HPC and G-HPC/S films.



Figure S4. TEM images of G-PG sample (a), G-HPC sample (b) and G-HPC/S sample (c). STEM image (d) of G-HPC/S sample and the corresponding elemental mapping of carbon (e) and sulfur (f).



Figure S5. TG curves of G-HPC film tested under air atmosphere and G-HPC/S tested under nitrogen atmosphere.



Figure S6. SEM image (a) and corresponding elemental carbon mapping (b) and sulfur mapping (c) of G-HPC/S electrode.



Figure S7. Nitrogen adsorption-desorption isotherms curves of G-HPC/S sample and G-PG/S sample.



Figure S8. CV curves of G-HPC/S cathode at a scan rate of 0.1 mV s<sup>-1</sup>.



Figure S9. (a) Low magnification and (b) high magnification SEM images of PG/S electrode.



Figure S10. TGA profile of G-PG/S electrode.



Figure S11. SEM images of the original (a) and artificially shaved (b) surface of porous GO films.



Figure S12. (a) The cross-section morphology of HPC electrode without graphene nano shell after shaving by a blade coater. Top-view SEM image (b) and slope-sectional SEM image (c) of HPC.



Figure S13. Nyquist plots of the HPC/S cathode after different cycles at the rate of 0.5 C.



Figure S14. Galvanostatic discharge/charge profiles of G-HPC/S cathode (a) and HPC/S cathode (b) at different cycles at 0.5 C.



Figure S15. SEM images of the surface (a) and along  $45^{\circ}$  cross-section (b) of G-HPC/S electrode cycled for 50 times at 0.5 C.



Figure S16. (a) SEM image of CNTs/graphene/S layer of G-HPC/S cathodes after 50 cycles at 0.5 C. (b) Top-view SEM image of multi CNTs/graphene/S layers of G-HPC/S cathodes after 50 cycles at 0.5 C and its corresponding carbon (c) and sulfur (d) mapping.



Figure S17. SEM images of the surface of Li counter electrode in the G-HPC/S cell (a) and HPC/S cell (b) after cycling for 50 times at 0.5 C.



Figure S18. Initial galvanostatic discharge profiles and 2<sup>nd</sup> discharge profiles after resting for 120 h of the HPC/S cell (a) and the G-HPC/S cell (b).

Table S1. Comparisons of sulfur loading, cyclic performances and rate performances
in previously reported works and this work.

	Sulfur	Cyclic performances			Rate performances			
Sample name	loading (mg/cm <sup>2</sup> )	Current (mA/cm <sup>2</sup> )	Capacity (mAh/g) /Number	Rate (C)	Capacity (mAh/g)	Current (mA/cm <sup>2</sup> )	Notes	Reference
This work	3.6	3.015	~750 /200	0.5	764.7	6.03		
N-doped carbon foam	1.2	1.005	~800 /200	0.5	696	4.02	Severed as interlayer	49
hollow carbon foam	-	-	653.5 /100	0.1	~180	-	75% sulfur loading	50
Fibrous Hybrid of Graphene	2.0	1.50	~700 /50	~0.5	670	6.0		52
graphene- sulfur	1.0-1.2	0.402	~750 /100	0.2	581	4.02		51
N-doped carbon	5.0	0.42	550 /100	0.05	-	-		53
Free-Standing Carbon- Nanotube Paper	6.3	0.38	700 /150	0.05	-	-		31