Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

A new configured lithiated silicon-sulfur battery built on 3D graphene with superior electrochemical performances

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Experimental section

Synthesis of 3D cpS-G cathode: Graphene oxide was prepared by modified hummers' method. 3D graphene networks were prepared by our previously reported sponge-assistant method, the details can be seen in literature.[s1] 100 mg sublimate sulfur was mixed with 10 mg 1, 3-diisopropenylbenzene (purchased from Tokyo Chemical Industry, Japan) and then placed onto a glass dish. The 3D graphene networks were then covered onto the mixture and heated to 180°C in an oven and kept at this temperature for 20 min. After cooling down to room temperature, 3D *cp*S-G networks were generated.

Material Characterization: Field emission scanning electron microscope (FE-SEM, S-4800) and high resolution transmission electron microscopy (JEOL, NEM-2100F) was employed to characterize the morphology and microstructure of the as-prepared samples. Raman spectra were obtained from a RENISHAW spectrometer (inVia Reflex) to investigate the characteristics of the S phase and graphene in the 3D G-*p*S networks. A He-Ne laser operating at λ=632.8 nm was used as the excitation source.

The sulfur content was determined by thermogravimetric analysis (TGA) by using NETZSCH TG 209 F1 Libra. Chemical bonding nature of C, O, and S was analyzed by X-ray photoelectron spectroscopy (Thermo escalab 250Xi). The cyclic voltammetry (CV) and galvanostatic charge-discharge measurements were tested via electrochemical workstation (PAR 2273) and battery cyclers (Arbin, BT2000).

Electrochemical measurements of half lithium-sulfur battery: CR2025-type coin cells were assembled for electrochemical measurements in Ar-filled glove box (the contents of oxygen and water are less than 0.1ppm) with the as-prepared 3D *cp*S-G networks directly using as electrode without any binder and conductive additive, Li metal as a counter electrode, a separator (Celgard 2300), and an electrolyte of 1 M LiTFSI in a mixture of 1,3-dioxolane (DOL), 1,2-dimethoxyethane(DMC) and tetraethylene glycol dimethyl ether (TEGDME) (volume ratio 5:4:1) (Yingze, China). Electrochemical properties were tested by battery cycler (Arbin, BT2000). Galvanostatic charge-discharge test was performed in a voltage ranges from 1.5 to 3.2 V. Cyclic voltammetry was carried out on PAR 2273 electrochemical workstation with the scan rate 5 mV S^{-1}.

Fabrication of 3D lithiated Si-G anode: 3D Si-G networks were firstly fabricated as our previously reported template-assistant method.[1] And then a pseudo battery was built from lithium foil and 3D Si-G network electrode without separator but with large amounts of electrolyte (1 M $LiPF_6$ in a 1:1 mixture of ethylene carbonate and dimethyl carbonate (Yingze, China). After keeping for 24h and removal of lithium, 3D lithiated Si-G network anode was obtained owing to the self-discharge of the pseudo battery.

Assemble of half lithium-silicon battery: CR2025-type coin cells were assembled for electrochemical measurements in Ar-filled glove box (the contents of oxygen and water are less than 0.1ppm) with the as-prepared 3D lithiated Si-G networks directly using as electrode without any binder and conductive additive, Li metal as a counter electrode, a separator (Celgard 2300), and an electrolyte of 1 M LiTFSI in a mixture of 1,3-dioxolane (DOL), 1,2-dimethoxyethane(DMC) and tetraethylene glycol dimethyl ether (TEGDME) (volume ratio 5:4:1) (Yingze, China). Galvanostatic charge-discharge test was performed in a voltage ranges from 0.005 to 2 V. Cyclic voltammetry was carried out on PAR 2273 electrochemical workstation with the scan rate 5 mV S^{-1}.

Assemble of lithiated silicon-sulfur full cells: CR2025-type coin cells were assembled for electrochemical measurements in Ar-filled glove box (the contents of oxygen and water are less than 0.1ppm) with the as-prepared 3D lithiated Si-G networks as anode electrode and 3D cpS-G networks as cathode electrode directly without any binder and conductive additive, a separator (Celgard 2300), and an electrolyte of 1 M LiTFSI in a mixture of 1,3-dioxolane (DOL), 1,2-dimethoxyethane(DMC) and tetraethylene glycol dimethyl ether (TEGDME) (volume ratio 5:4:1) (Yingze, China). The mass ratio of cathode and anode was 2:1 (3.2 mg/0.64 cm^2 3D cpS-G cathode, 1.6 mg/0.5 cm^2 3D Si-G anode). Galvanostatic charge-discharge test was performed in a voltage ranges from 1.4 to 3 V. Cyclic voltammetry was carried out on PAR 2273 electrochemical workstation with the scan rate 5 mV S^{-1}.

Energy density calculation: the energy density of full Si-S cells was calculated as the following formula:

$$E_{energy\ density} = C_{full\ cell\ based\ on\ total\ mass\ of\ cathode\ and\ anode} * V_{mid-value}$$

Where, $C_{\text{full cell based on total mass of cathode and anode}}$ was the stable capacity of ~620mAh/g calculated based on the mass of cathode materials, $V_{\text{mid-value}}$ is 1.85 V. So the energy density is 1147 Wh kg^{-1} based on the total mass of cathode and anode.

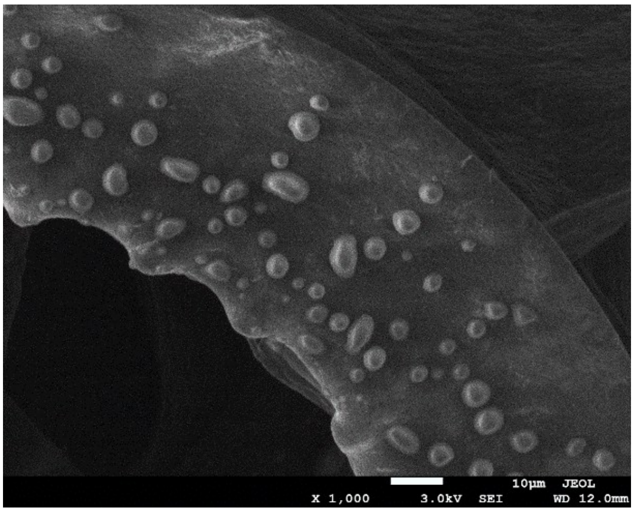


Fig. S1. SEM image of 3D S-G, showing the large quantities of particles with several micrometers on the nanowalls of 3D graphene. These particles are in the shape of hemispheres, which have small contact portion with graphene.

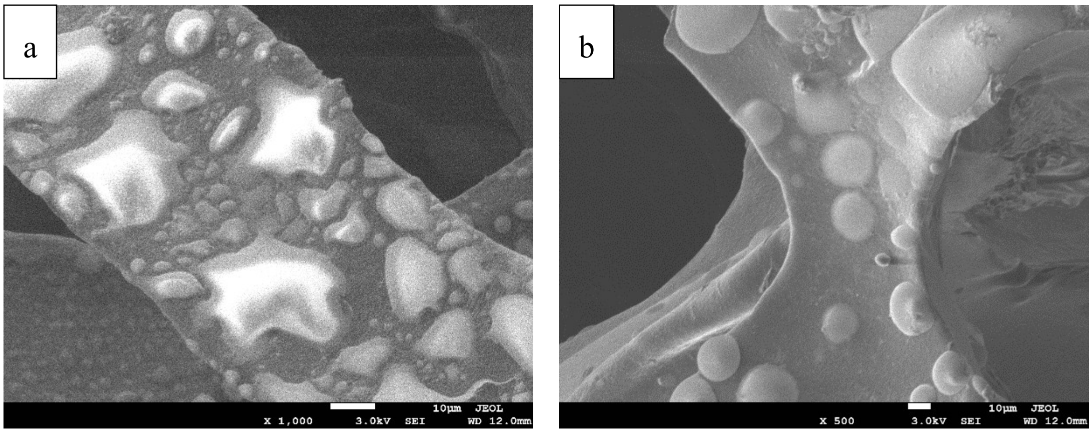


Fig. S2. SEM images of 3D *cp*S-G networks synthesized by adjusting the weight ratios of sulfur and DIB: a) 19:1, b) 4:1. It is shown that the higher ratio of sulfur and DIB leads to the formations of compact and big sulfur copolymer particles or films onto the nanowalls of 3D graphene, whereas the lower ratio of sulfur and DIB results in the formation of few sulfur copolymer particles without any pores.

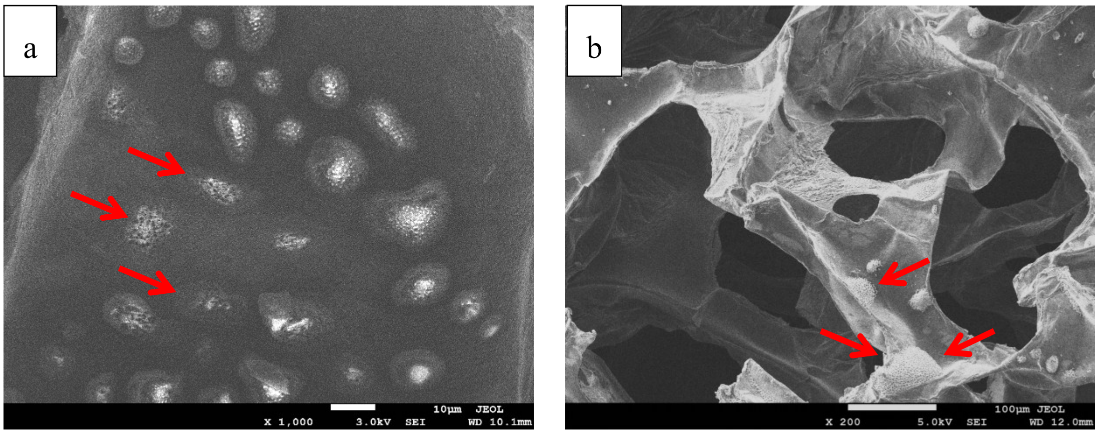


Fig. S3. SEM images of 3D *cp*S-G network synthesized by tuning the thermal treatment times: a) 10 and b) 30min. It is exhibited that the less thermal treatment time only leads to the partial formation of honeycombs. With increasing the treatment time to 30 min, most of the resultant honeycombs disappear, possibly ascribes to the large evaporation of polymetric sulfur.

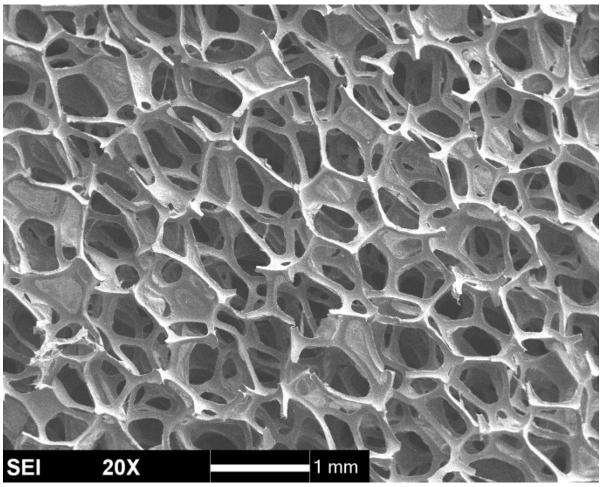


Fig. S4. SEM image of communical sponge, showing that the sponge has a three-dimensional structure with pore sizes of 50-500 micrometers.

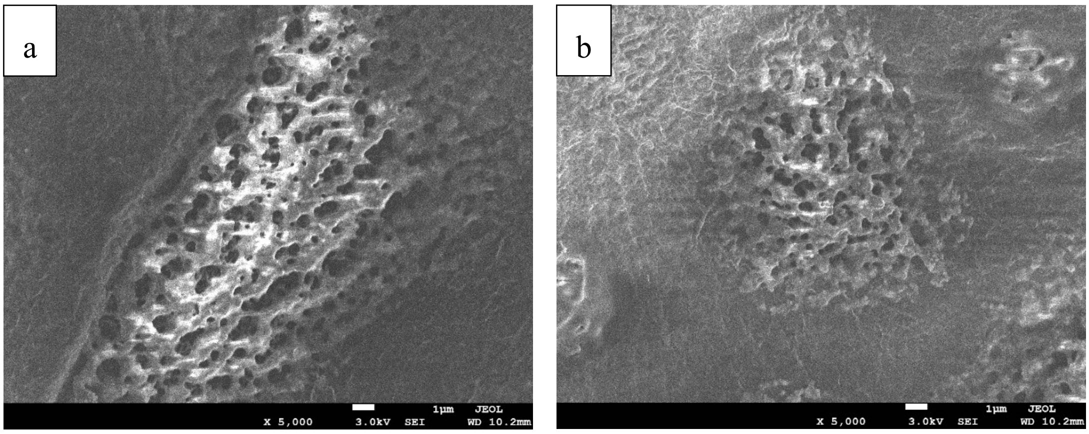


Fig.S5. Typical SEM images of the 3D *cp*S-G networks with honeycomb-like structure. It is clear that there are lots of pores into copolymer sulfur, which looks like honeycomb and denoted as "honeycomb-like" in our manuscript.

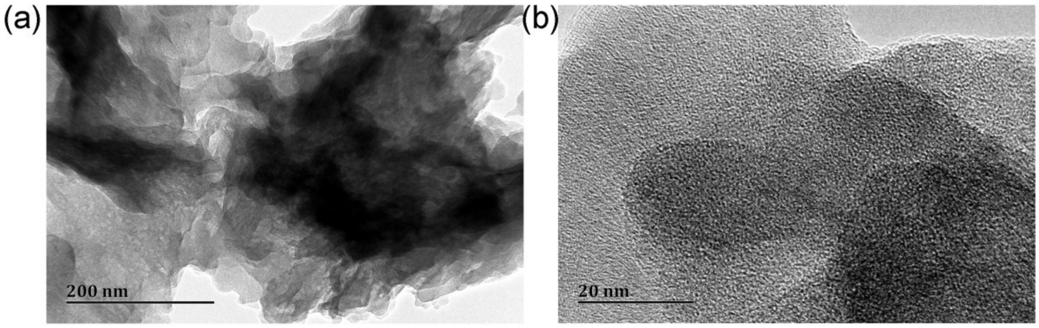


Fig. S6. TEM images of 3D *cp*S-G networks, indicating that sulfur should be in the state of polymeric sulfur rather than the crystalline sulfur.

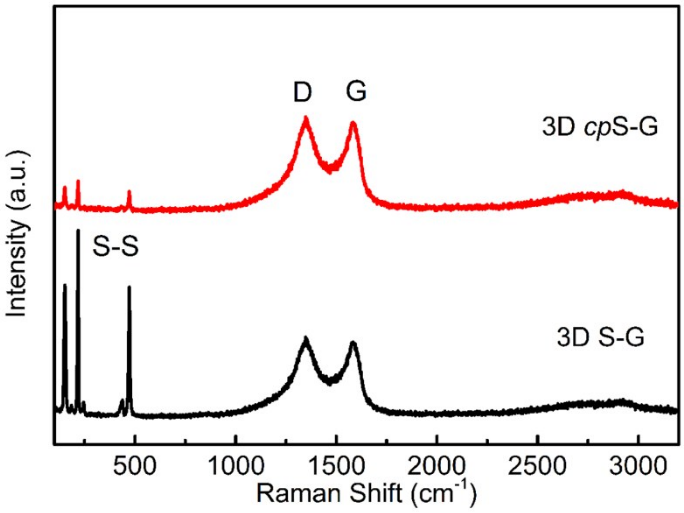


Fig. S7. Raman spectra of 3D *cp*S-G and 3D S-G networks. The peaks at 1350 and 1580 cm^{-1} represent the D and G bands of graphene, and the peaks appeared at 153, 217 and 472cm^{-1} correspond to S-S bonds.

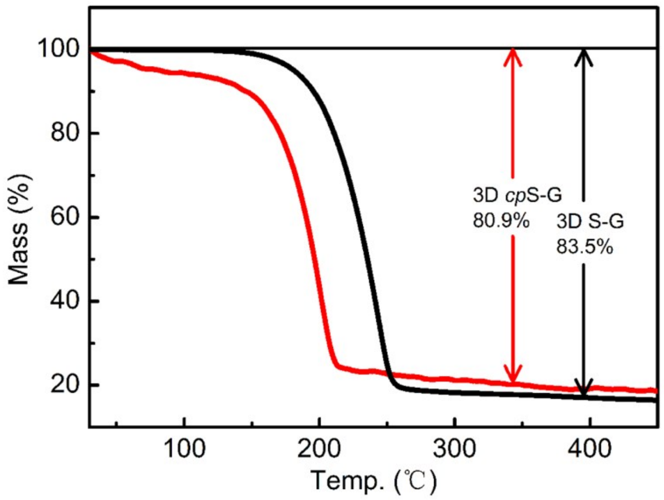


Fig. S8. TG curves of 3D *cp*S-G and 3D S-G networks, disclosing a high sulfur copolymer content of 80.9 wt.% in 3D *cp*S-G netwrok. Additionally, the fast weight loss temperature of 3D S-G network is at about 250℃, whereas that of 3D *cp*S-G network is at around 180℃, suggesting that sulfur should be in the state of sulfur copolymer in 3D *cp*S-G networks.

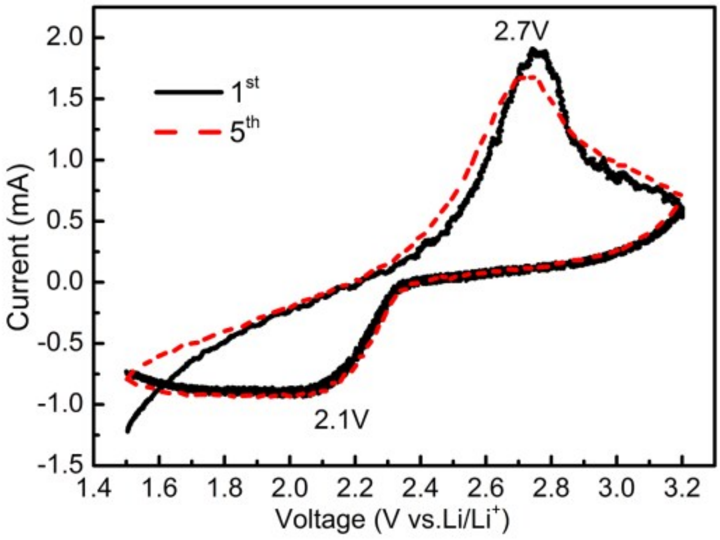


Fig. S9. Typical CV curves of 3D *cp*S-G networks in Li-S battery at a scanning rate of 5 mV s^{-1}.

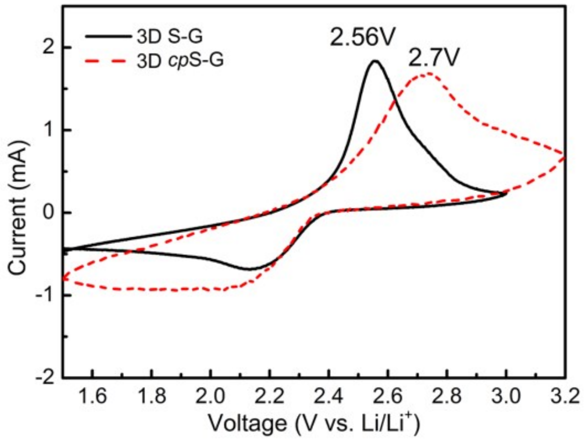


Fig. S10. Comparsion of CV curves of 3D *cp*S-G and S-G networks for Li-S battery. It is clear that the 3D *cp*S-G network has a higher cathodic peak at about 2.7V.

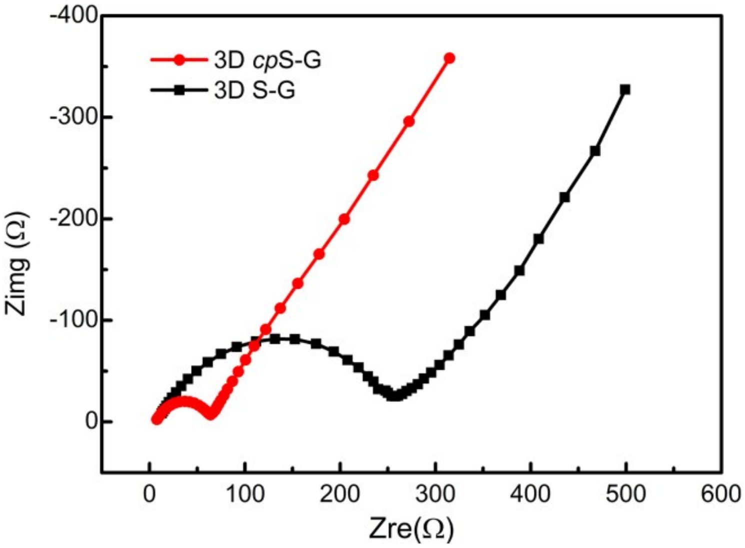


Fig. S11. AC impedance spectra of 3D *cp*S-G and 3D S-G networks, demonstrated that 3D *cp*S-G ntework possesses higher electrical conductivity than that of 3D S-G network.

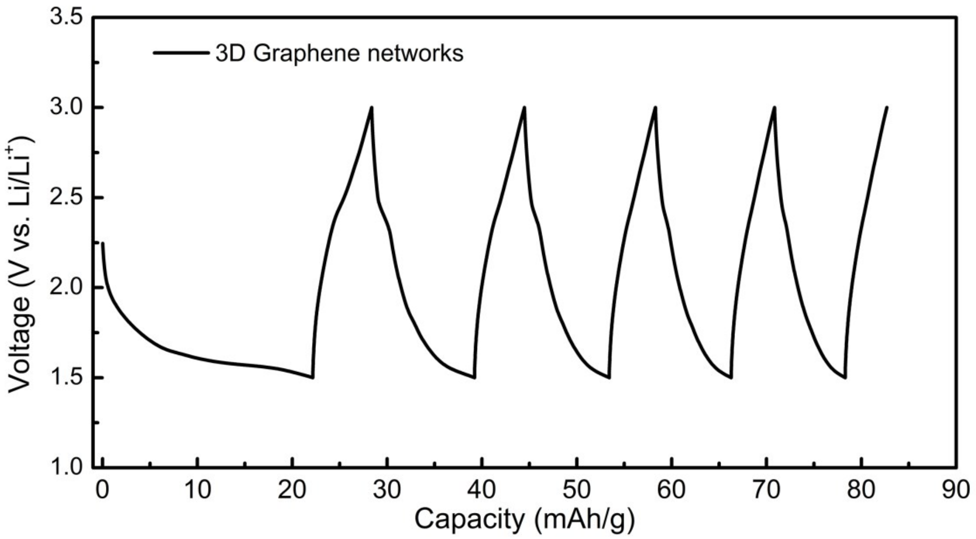


Fig. S12. The voltage profile of 3D graphene networks in voltage range from 1.5V-3.0V. The results showed the stable capacity of 3D graphene was only 7 mAh/g indicated the effect of graphene in 3D cpS-G is almost ignored.

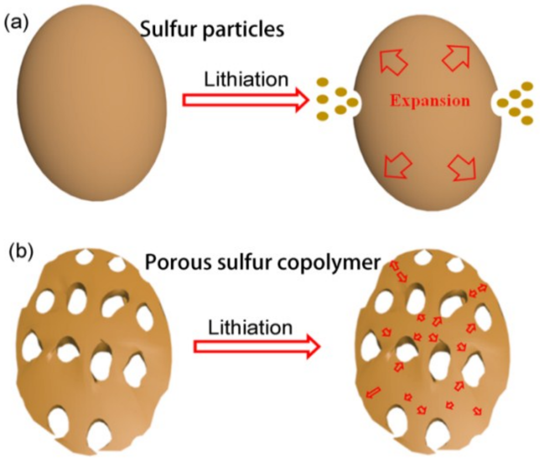


Fig. S13. The morphology change of a) sulfur particles and b) porous sulfur copolymer during the lithiation-delithiation cycles. Since there are multi-sizd pores in the sulfur copolymer, the volume change can be efficiently buffered during charge-discharge processes.

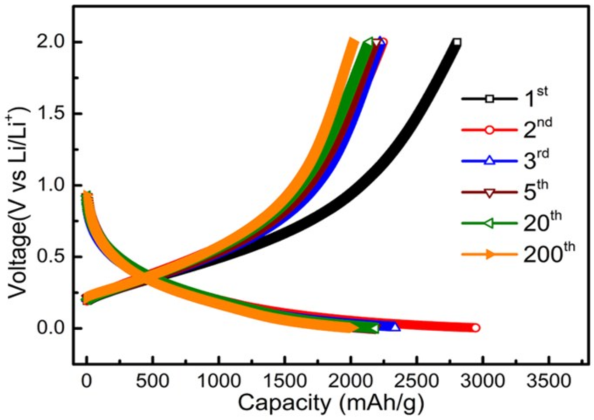


Fig. S14. Typical voltage profiles 3D of lithiated Si-G networks in an electrolyte of 1M LITFSI in a mixture of 1,3-dioxolane, 1,2-dimethoxyethane and tetraethylene glycol dimethyl ether (volume ratio 5:4:1). Since 3D Si-G was lithiated, the half battery was firstly operated from charge process. The specific capacity of 3D Si-G network is still stable at 2050 mAh g^{-1} even after 200 cycles.

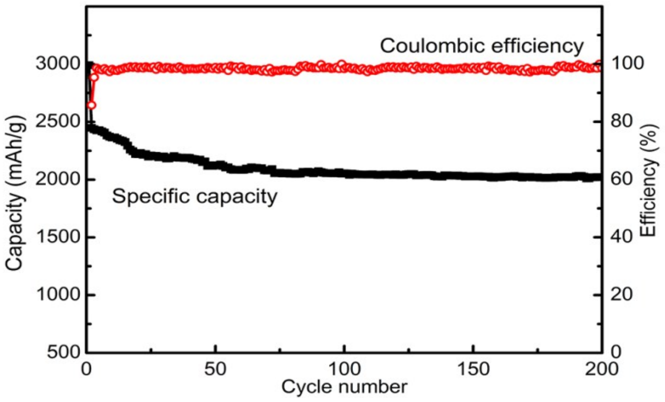


Fig. S15. The cycle performance of 3D lithiated Si-G network in TEGDME-based electrolyte. The good cycle performance of 3D lithiated Si-G networks in TEGDME-based electrolyte is clearly demonstrated. Even after 200 cycles, the reversible capacity is still stable at 2050 mAh g^{-1} in TEGDME-based electrolyte.

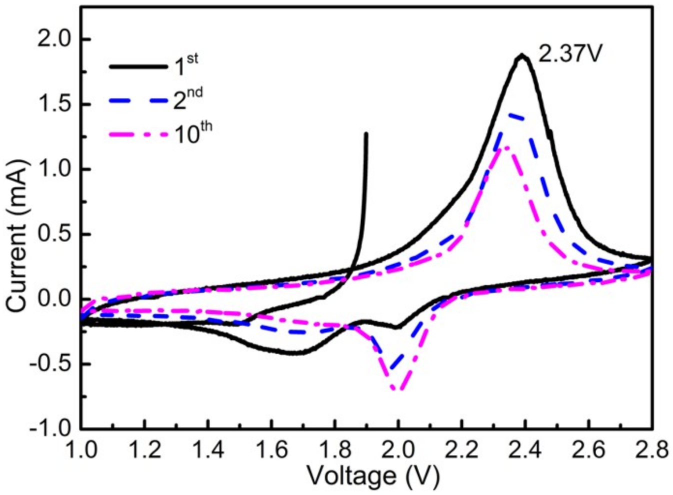


Fig. S16. Typical CV curves of full Si-S battery at a scanning rate of 5 mV s^{-1}. The cathodic peak is centered at 2.37V.

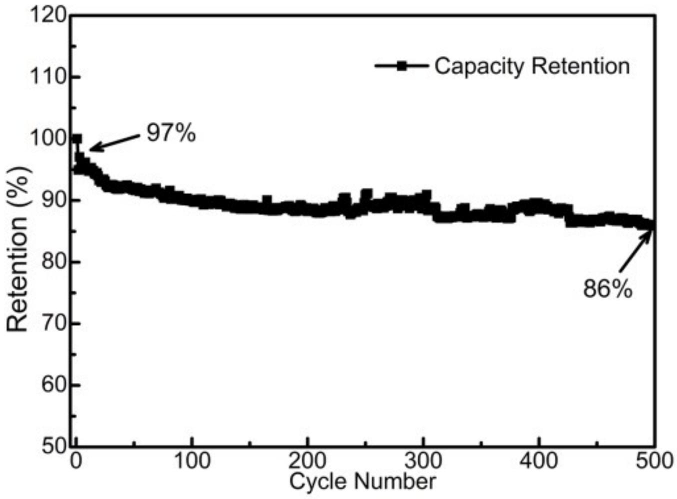


Fig. S17. Capacity retention of the full Si-S cell composed of 3D *cp*S-G cathode and Si-G anode. It exhibits a high capacity retention of 86% after 500 cycles, which means a slow capacity decay of only 0.028% per cycle.

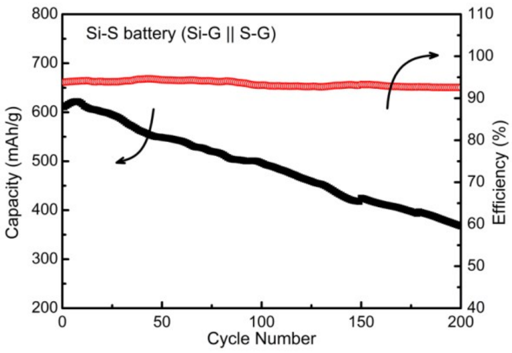


Fig. S18. Cycle performance of full Si-S battery which is assembled by 3D lithiated Si-G anode and 3D S-G cathode. Although the initial capacity of this Si-S battery is about 605 mAh g^{-1} (based on mass of electrode materials), the reversible capaciry rapidly decrease to 335 mAh g^{-1} after 200 cycles.

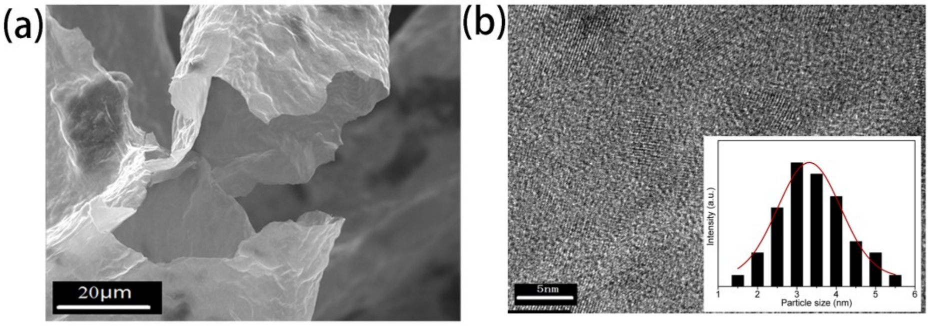
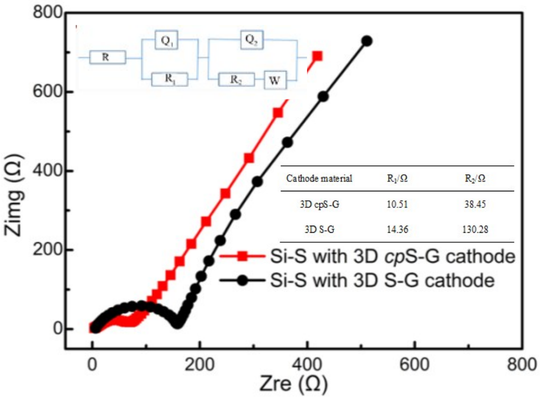


Fig. S19. Typicl SEM and TEM images of 3D Si-G networks, showing the ultrathin graphene nanowalls with nanosized silicon particles anochored onto the surface of graphene. The unique structure could accommodate efficiently the volume change of silicon, avoiding its pulverization during long charge-discharge process.



Cathode material	R_1/Ω	R_2/Ω
3D cpS-G	10.51	38.45
3D S-G	14.36	130.28

Fig. S20. AC impedance spectra of Si-S full cells after 200 charge-discharge cycles with 3D *cp*S-G and 3D S-G networks as cathodes, respectively, demonstrated that 3D *cp*S-G ntework possesses higher electrical conductivity than that of 3D S-G network. The kinetic difference of full Si-S cells with different cathodes was further investigated by modeling AC impendence spectra based on the equivalent circuit in upper-left corner, and the results was list in the right of this figure. Amonge these results, R_2 represent the charge-transfer resistance of the full cells. Thus, it is clear taht the charge-transfer resistance of full Si-S cell with 3D *cp*S-G cathode is far lower than that of full Si-S cell with 3D S-G cathode, indicating that the full Si-S cell with 3D *cp*S-G cathode has a faster electrochemical kinetics during lithium storage.

References:

S1: B. Li, S. Yang, S. Li, B. Wang, J. Liu, *Adv. Energy Mater.* **2015**, *5*, 1500289.