**Electronic Supplementary Information** 

## Polymer Cage as an Efficient Polysulfide Reservoir for Lithium-Sulfur Batteries

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## **1. Experimental section**

1.1. *Synthesis of rGO*: A graphene oxide (GO) was prepared and purified by using a modified Hummer's method according to previous literature.<sup>1</sup> In a typical process, 0.5 g of sodium borohydride was added into aqueous dispersion of GO (100 mL, 1 mg mL<sup>-1</sup>) under magnetic stirring. After the mixture turned black, it was washed with ethanol and deionized water to remove the impurities. Finally, the reduced graphene oxide (rGO) was synthesized by using vacuum freezing and drying technology at -40 °C for 12 h.

1.2. Synthesis of S@PVP@rGO: In a typical process, 0.632g of sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>; Aladdin) was dissolved into 50 mL of deionized water under magnetic stirring. Then, 0.5 g of rGO was added in the above solution under vigorous stirring to obtain a homogeneous mixer. On the other hand, 1.20 g of polyvinylpyrrolidone (PVP) (molecular weight of ~58,000; Aldrich) was dissolved into 50 mL of deionized water under magnetic stirring. Then, the PVP solution was added into Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>@rGO as an aqueous solution. After the stirring process about 2 hours, 0.5 mL of concentrated hydrochloric acid (HCl) was added into  $Na_2S_2O_3@rGO@PVP$  solution. Under the reaction process, the color of solution became darken gradually. The mixed solution was washed alternately with PVP solution and deionized water for 3 times. Then, the obtained solid materials were dried in the oven at 50 °C for 12 hours.

1.3. Preparation of S@PVP@rGO Electrode and Electrochemical Measurement: Briefly, 0.2 g of polyvinylidene fluoride (PVDF) binder was completely dissolved into N-methyl-2pyrrolidene (NMP) under magnetic stirring. Then, 0.8 g of S@PVP@rGO was added into above solution to form ropy and homogenous slurry. Subsequently, the slurry was coated on aluminum foil (Al foil) by using the doctor blade method with thickness of 300 µm. Then, the electrode was dried at 50 °C for 18 h in the vacuum oven. Finally, the electrode was cut into wafer with diameter of 12 mm. According to the characterization results, a typical mass loading of active sulfur was found as  $\sim 2.3$  mg cm<sup>-2</sup>. The CR2016-type coin cells were assembled in the argon-filled glove box. The prepared electrode was acted as a positive electrode with separator of diaphragm Celgard 2400, reference/counter electrode of lithium foil, and the mixed solution of 1, 3-dioxolane and 1, 2-dimethoxyethane (volume ratio of 1:1) containing 1 M of lithium bis (trifluromethanesulfonyl) imide (LiTFSI) added 0.1 M of LiNO<sub>3</sub> was acted as an electrolyte. The galvanostatic discharge-charge of above cells was tested at a voltage in the ranging between 1.5 and 3.0 V (vs. Li/Li<sup>+</sup>) with different current rates by using a LANHE cell test system (CT2001A 5 V 20 mA and 50 mA). The cyclic voltammetry (CV) measurements were performed between the potential range of 1.5 and 3.0 V with various scan rates. The Electrochemical impedance spectroscopy (EIS) studies were analyzed at the charged state with frequency in the ranging between 100 KHz and 10 mHz and AC amplitude of 5 mV.

2.4. Characterization of Materials: The scanning electron microscopy (SEM) images were obtained from Hitachi S-4800 field emission scanning electron microscopy (FESEM) which equipped with EDS. The thermogravimetric analysis (TGA) was conducted by using a METTLER instrument at heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere. The N<sub>2</sub> adsorption-desorption isotherms and pore-size distribution were obtained at 87.3 K by using a quadrasorb SIMP apparatus. The Raman spectra were recorded on a by using a HORIBA instrument with Ar laser source of 633 nm in a macroscopic configuration. The X-ray photoelectron spectroscopy (XPS) measurements were carried out with Phi X-tool XPS instrument. The transmission electron microscopy (TEM) analysis was conducted by using JEOL JEM-2100 transmission electron microscopy with an accelerating voltage of 200 kV.



Figure S1. High- resolution SEM images of S@PVP spheres with longer time heat

treatment.



Figure S2. (a) SEM image of S@PVP@rGO and corresponding element mapping of (b) Over view, (c) C element, (d) N element, (e) O element and (f) S element.



Figure S3. TG curve of PVP and rGO.



Figure S4. Raman spectra for pure sulfur, rGO, PVP and S@PVP@rGO (inset depicts a partial enlargement of S@PVP@rGO raman spectra).



Figure S5. (a) XPS survey spectrum of S@PVP@rGO, (b) High-resolution S  $_{2p}$  spectra of S@PVP@rGO.



Figure S6. EIS curve of Li-S batteries with S/C and S@PVP cathodes.



**Figure S7**. Cycling performance and coulombic efficiency of S@PVP cathode and S/C cathode at a rate current of 0.2 C for 300 cycles.



**Figure S8**. Rate capability of coin-type Li-S batteries with S@PVP and S/C cathodes with various current rates (0.1 C, 0.2 C, 0.5 C, 1 C and 2 C) at the potential in the ranging between 1.5 and 3.0



Figure S9. Cycling performance and coulombic efficiency of S@PVP cathode and S/C cathode at a rate current of 1 C for 100 cycles.



Figure S10. Pure electrolyte and  $Li_2S$ /electrolyte solutions in the presence of pure sulfur and S@PVP@rGO.

Method	First Discharge Capacity (mAh g <sup>-1</sup> )	C-Rate Capacity (mAh g <sup>-1</sup> )	Total Cycle Number	Degradation Rate Per Cycle	Coulombic Efficiency	Sulfur contens in electrode	Reference
S@PVP@rGO	1,350 (0.1C)	1,086 (0.2) 976 (0.5C) 864 (1C) 735 (2C)	495 (1C)	0.071%	~100%	2.3 mg•cm <sup>-2</sup>	This work
Si/SiO <sub>2</sub> @porous carbon deposited polysulfide	1230 (0.1C)	1002 (0.5C) 907(1C) 730 (2C)	500 (2C)	0.063%	~100%	3.1~3.5 mg•cm <sup>-2</sup>	Adv. Mater. 2016, 28, 3167-3172
layer-by-layer strategy	1201 (0.2C)	910 (1C) 785 (2C)	200 (0.5C)	0.13%	>97.5%	1.9 mg•cm <sup>-2</sup>	Adv. Mater. 2015, 27, 1694-1700
Pomegranate-like microclusters organized by ultrafine Co nanoparticles@nitrogen- doped carbon subunits as sulfur hosts for long-life lithium-sulfur batteries	1350 (0.1C)	905 (1 C) 823 (2 C)	400 (2C)	0.08%	100%	1.9 mg•cm <sup>-2</sup>	J. Mater. Chem. A, 2018, 6, 14178-14187
Sulfphilic Few-Layered MoSe <sub>2</sub> Nanoflakes Decorated rGO as a Highly Effcient Sulfur Host for Lithium-Sulfur Batteries	1608 (0.1C)	1270 (0.25 C) 1123 (0.5 C), 988 (1 C) 863 (2 C)	500 (2C)	0.051%	~100%	~1.6 mg•cm <sup>-2</sup>	Adv. Energy Mater. 2019 1901896
Nitrogen-doped double- shelled hollow carbon spheres and wrapped with graphene to Encapsulate sulfur	1360 (0.2C)	600 (2C) 430 (3C)	200 (0.5C)	0.19%	~100%	3.9 mg•cm <sup>-2</sup>	Adv. Energy Mater. 2015 5. 1901896

 Table S1. Comparison of electrochemical performances of Li-S battery systems with same electrode of physical enveloping strategy.

## Reference

1. B. Li, S. Yang, S. Li, B. Wang, J. Liu, Adv. Energy Mater., 2015, 5, 1500289.