Supplementary information

A freestanding hierarchically structured cathode enables high sulfur loading and energy density of flexible Li-S batteries

Jianpeng Liu,[a,†] Zhong Li,[a,†] Beibei Jia,[a,†] Juncheng Zhu,[b,*] Wenliang Zhu,[c,*] Jianping Li,[d] Hao Pan,[d] Bowen Zheng,[a] Liangyin Chen,[e] Giuseppe Pezzotti,[c] and Jiliang Zhu[a*]

[a]College of Materials Science and Engineering, Sichuan University, Chengdu 610064, China.
[b]School of Chemistry and Materials, University of Science & Technology of China, Hefei, Anhui 230026, China.
[c]Ceramic Physics Laboratory, Kyoto Institute of Technology, Sakyo-ku, Matsugasaki, Kyoto 606-8585, Japan.
[d]Automotive & Transportation Engineering, Shenzhen Polytechnic, Shenzhen 518055, Guangdong, China.
[e]Institute for Industrial Internet Research (I3R), Sichuan University, Chengdu 610064, China
[†]These authors contributed equally to this work.
[*]Email address: jc1998@mail.ustc.edu.cn (JC Z), wlzhu@kit.ac.jp (WL Z), jlzhu167@scu.edu.cn (JL Z)

Supplementary Methods

Method S1. Synthesis of graphene oxide (GO)

GO nanosheets were synthesized using pre-oxidized graphite powder via an improved Hummer's method. Typically, 7.5 g P_2O_5, 7.5 g $K_2S_2O_8$ and 9 g graphite powder were mixed in 55 mL concentrated sulfuric acid and stirred at 80℃ for 5 h. The mixture was filtrated, washed with deionized water and dried overnight to obtain pre-oxidized graphite powder.

The as-prepared pre-oxidized graphite powder, together with 4.5 g $NaNO_3$ were dispersed in 245 mL concentrated sulfuric acid in an ice bath. Then, 27.8 g $KMnO_4$ was slowly added into the solution at a system temperature of below 5 ℃. After 4 hours of ice bath, the mixture was transferred into a water bath of 35 ℃ and vigorously stirred for 4 hours. Finally, the mixture was filtrated, washed with diluted HCl and deionized water, respectively, and dried overnight to obtain GO films.

The investigated 3D graphene (3D-G) was obtained by adding ammonia and hydrazine hydrate into a mixture of anhydrous ethanol and water with dispersed GO, keeping the system at 100 ℃ for 2 h, and then drying up the filtrated cream in a freezer.

Method S2. Schematic illustration of soft-packaged cell assembly

Soft-packaged cells with different capacities were assembled in an Ar-filled glove box. The anode was fabricated by rolling lithium foil (250 μm) onto Cu foil (9 μm). Typically, the cathode and membrane were overlapped and folded into a U shape. Then the anode was inserted into the "U". The whole material was folded again and put into an Al-laminated-film bag. Electrolyte was injected and the battery was vacuumpackaged after 30 min. The same electrolyte as used in coin cell was utilized in the soft-packaged cell. The ratio of electrolyte volume (μL) to the electrode material (S) mass (mg) was 2.9:1 in all test cells. All the cells were packaged at minus ninety kilopascals.

Supplementary Figures

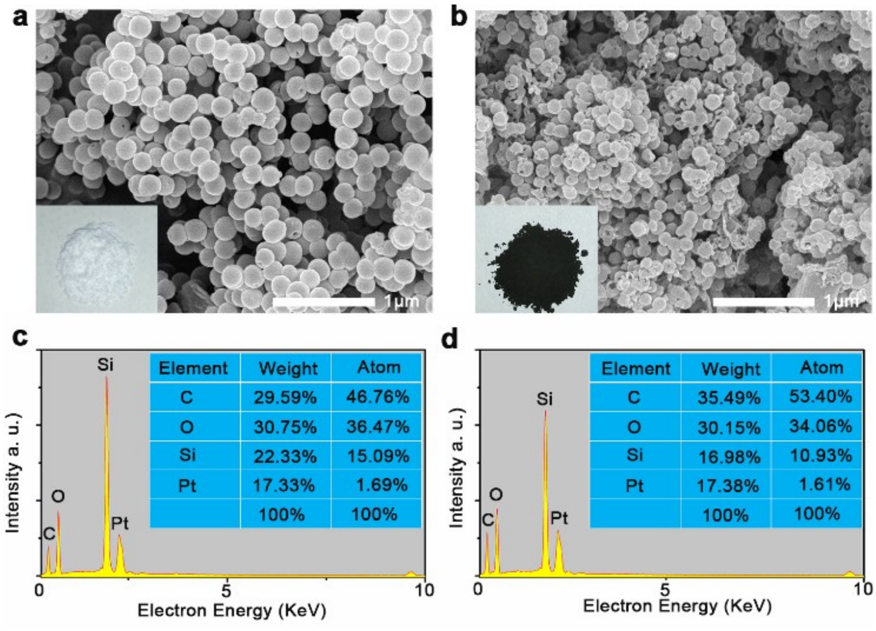


Fig. S1 | SEM images and EDS spectra of HM-SiO_2 (a,c) and CHM-SiO_2 (b,d). (Pt was detected due to the sputtered Pt coating on the samples for SEM measurements)

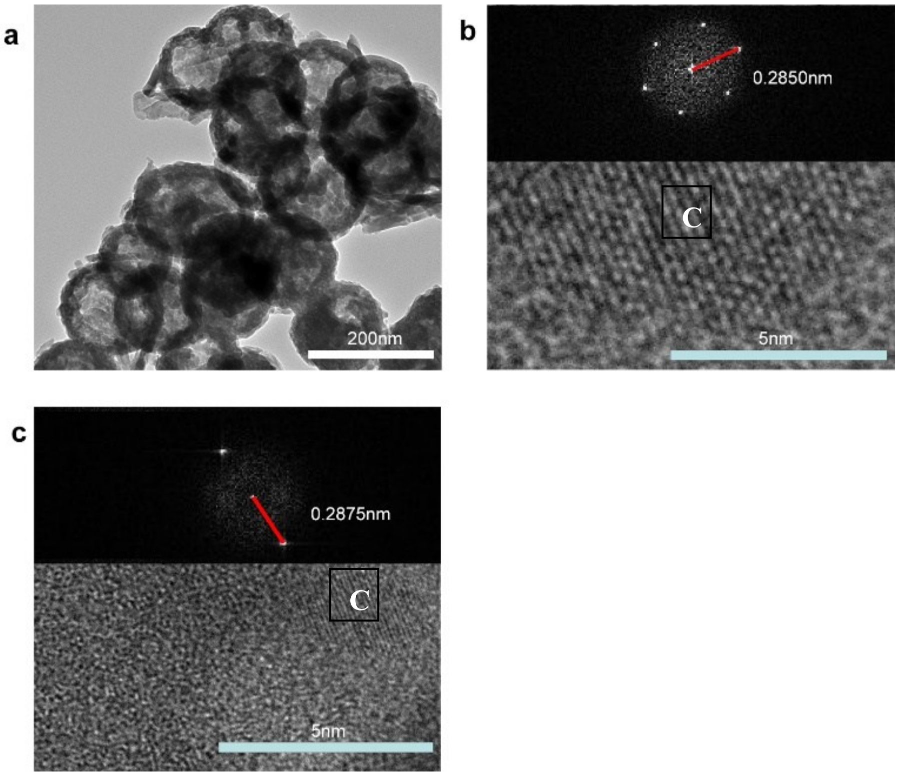


Fig. S2 | (a) TEM image of CHM-SiO_2. (b, c) HRTEM images of CHM-SiO_2.

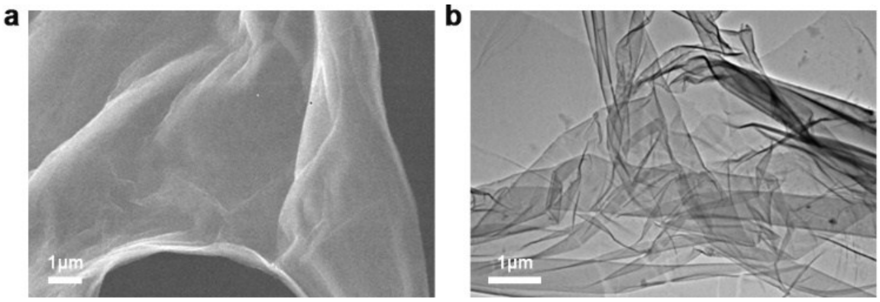


Fig. S3 | Microscopic characterization of 3D-G. (a) SEM image of 3D-G. (b) TEM image of 3D-G.

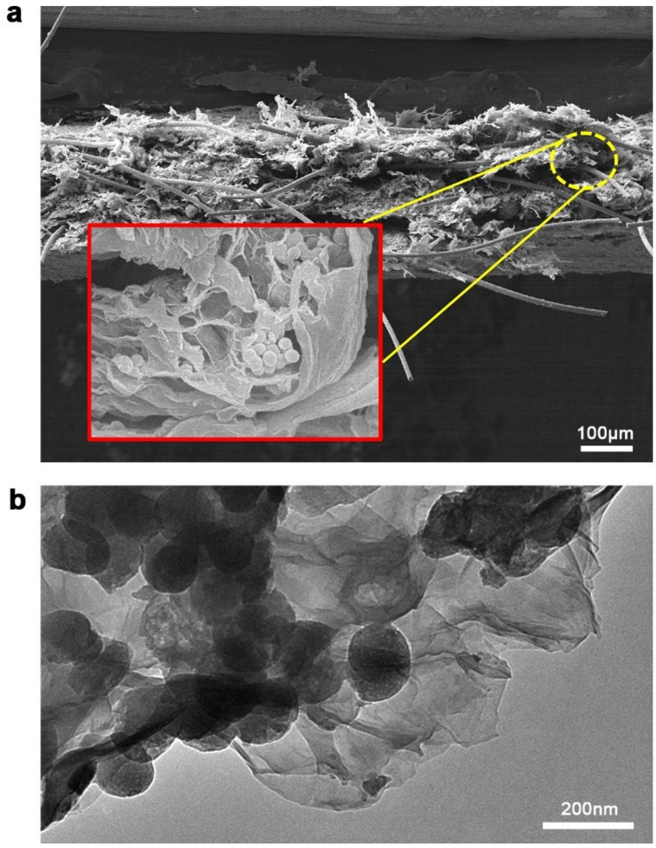


Fig. S4 | (a) Cross-sectional SEM image of 3D-GCSS. (b) TEM image of CHM-SiO_2/S on 3D-G.

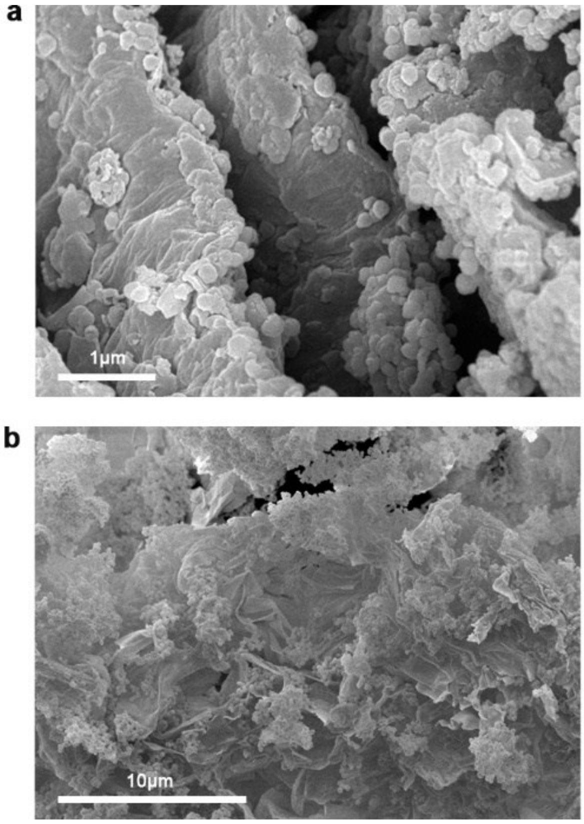


Fig. S5 | SEM images of CHM-SiO_2 composited with (a) super P and (b) graphite.

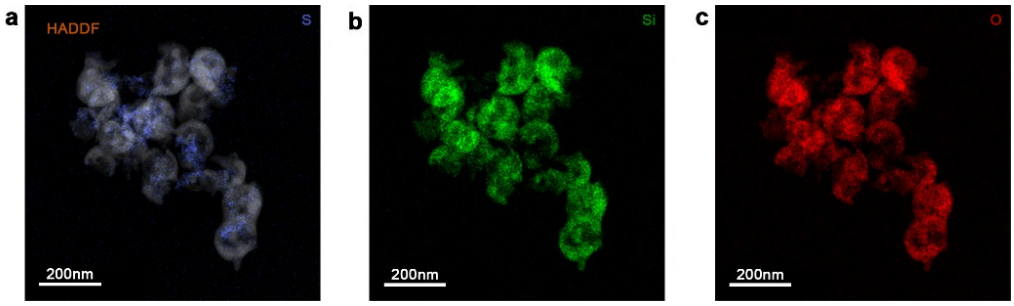


Fig. S6 | Elemental mapping of (a) S, (b) Si and (c) O in the CHM-SiO_2/S composite.

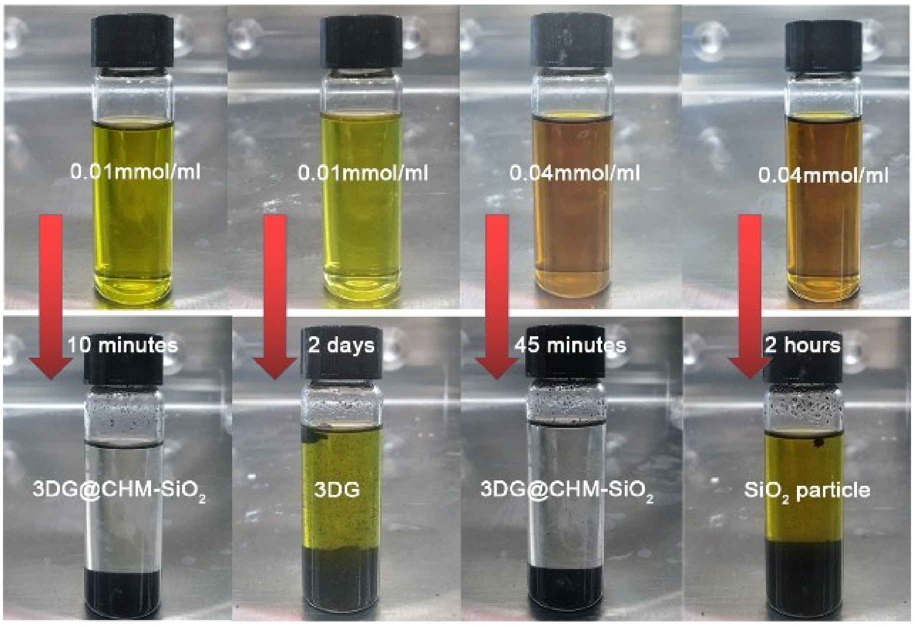


Fig. S7 | Variations of solution color with the addition of 3D-GCS, 3D-G and commercial SiO_2 in an electrolyte solution of Li_2S_6. The yellow/brown Li_2S_6 solution quickly became transparent and colorless upon adding 3D-GCS demonstrating good affinity and strong capability for LiPS-adsorption of 3D-GCS.

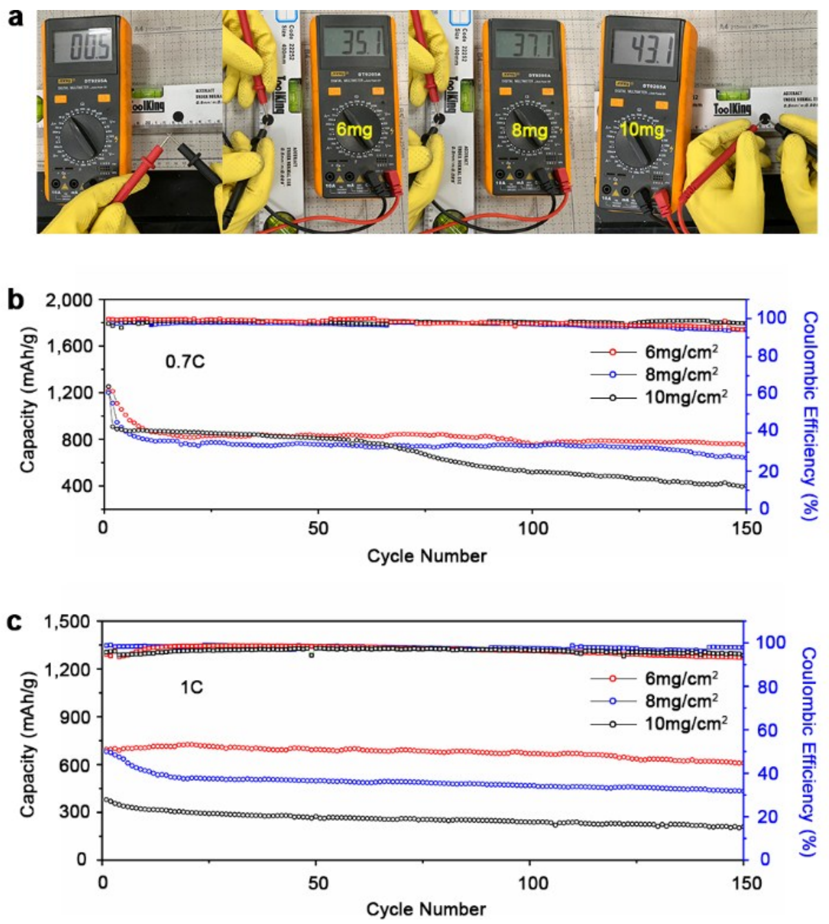


Fig. S8 | (a) Electrical resistance of 3D-GCSS with different sulfur loading. (b,c) Cycling performance at (b) 0.7C and (c) 1C current rates.

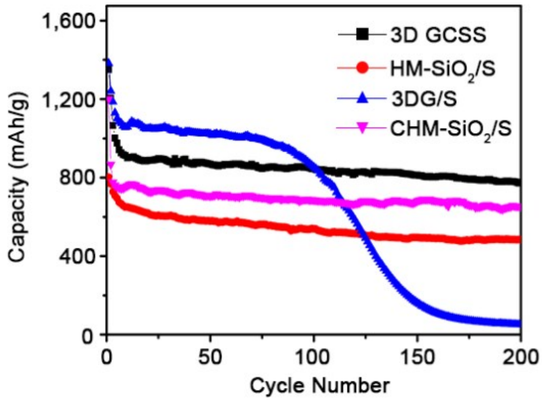


Fig. S9 | Cycling performances of hollow-mesoporous SiO_2/S (HM-SiO_2/S), carbon-encapsulated hollow-mesoporous SiO_2/S(CHM-SiO_2/S), 3D-graphene/S (3D-G/S) and 3D-GCSS/Al.

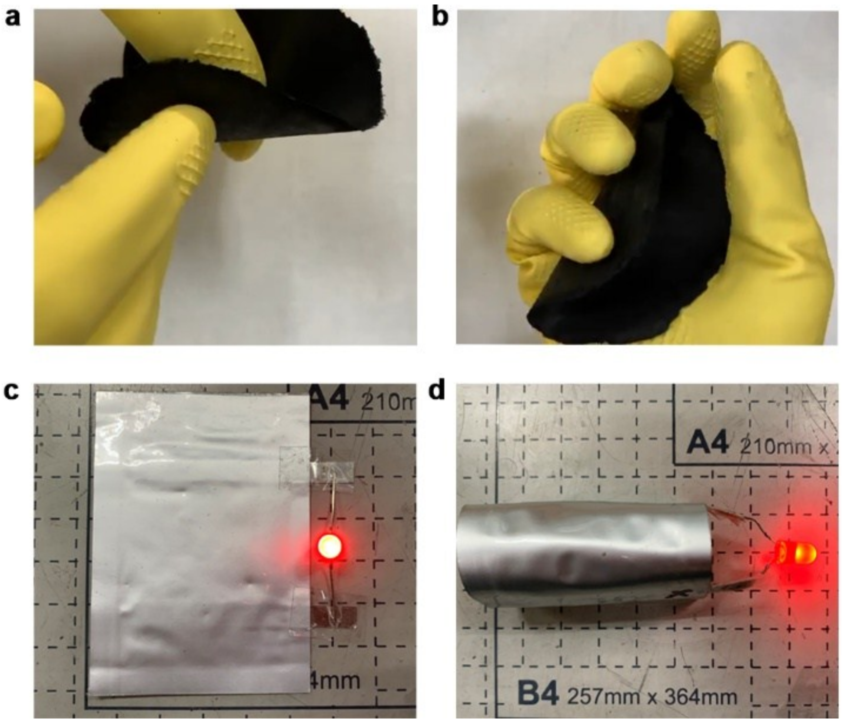
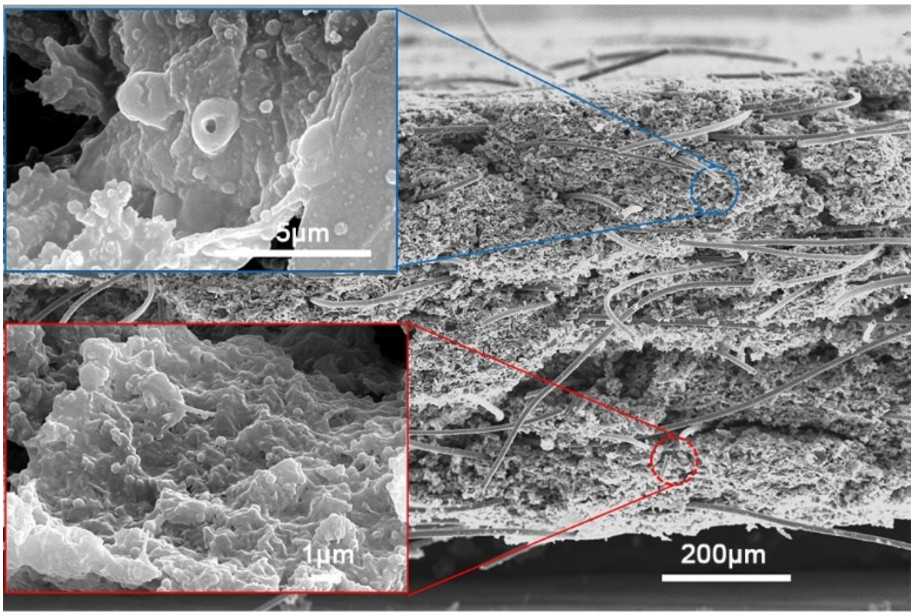
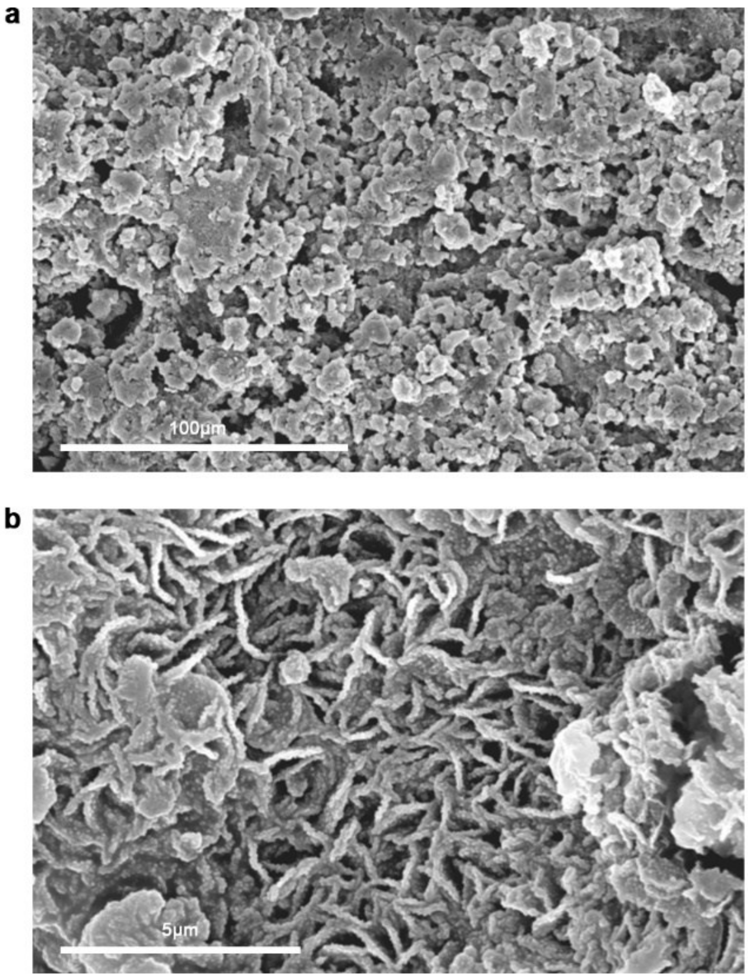


Fig. S10 | (a,b) The 3D-GCSS electrode under force shows structural integrity and stability. (c,d) The optical images show a red LED lighted by a (c) flat and (d) bent Li–S soft-packaged cell.



Supplementary Figure 11 | The cross-sessional SEM image of the 3D-GCSS after cycling.



Supplementary Figure 12 | SEM images of the cross section of the Li anode after cycling obtained at different magnifications. (a) Scale bar, 100 μm. (b) Scale bar, 5 μm.

Supplementary Tables

Table S1 | EIS fitting results of 3D-GCSS and 3D-GCSS/Al.

Cathode	Rs	Rct	W-R	W-T	W-P	CPE1-T	CPE1-P	Rct2	CPE2-T	CPE2-P
3D-GCSS/Al	4	79.38	19.19	10.4	0.27566	1.5567E^{-5}	0.7768	25.14	9.2774E^{-4}	0.7343
3D-GCSS	2	5	2.601	2.632	0.29552	1.8E^{-4}	0.706	0.25	1.454	3.288E^{-10}

Table S2 | Cycling performance of HM-SiO_2/S, CHM-SiO_2/S and 3D-G/S.

Cathode	**5th Cycling**		**200th Cycling**		**Capacity Retention (%)**
	Discharge Capacity (mAh/g)	**Coulombic Efficiency (%)**	**Discharge Capacity (mAh/g)**	**Coulombic Efficiency (%)**	
3D-GCSS/Al	1250.0	99.2	772.4	96.1	61.8
HM-SiO_2/S	650.3	99.8	484.5	97.3	74.5
3D-G/S	1241.0	96.5	51.2	82	4.1
CHM-SiO_2/S	974.3	100.0	650.6	98.6	66.8

Table S3 | Comparisons of the references.

Coin Cell				
Ref.	**Sulfur Loading**	**Cycles (Cycling Rate)**	**Initial Capacity**	**Capacity Retention**
5	6.2 mg/cm^2	100（0.5mA and 1 mA/cm^2 before and after 5th）	7.8 mAh/cm^2	83%
6	5.4 mg/cm^2	200（0.5C）	1105 mAh/g	799 mAh/g
8	56wt%	500（1C）	1036 mAh/g	681 mAh/g
11	9.6 mg/cm^2	100	12.3 mAh/cm^2	78%
12	1 mg/cm^2	200（0.1C）	1670 mAh/g	1142 mAh/g
14	2.5 mg/cm^2	100（0.2C）	983 mAh/g	858 mAh/g
15	70wt%	20（0.1C）	1400 mAh/g	More than 1000 mAh/g
16	1.1 mg/cm^2	100（0.1C）	1264 mAh/g	866 mAh/g
17	2.9 mg/cm^2	100（0.2C）	1396 mAh/g	844 mAh/g
18	14.36 mg/cm^2	350（0.2C）	1000 mAh/g	645 mAh/g
19	2.0~3.0 mg/cm^2	1500（1C）	745 mAh/g	273 mAh/g
20	1.5~2.1 mg/cm^2	50（0.3A/g）	1278 mAh/g	1150 mAh/g
21	3.9 mg/cm^2	100（0.2C）	1360 mAh/g	940 mAh/g
22	1.5 mg/cm^2	800（2C）	780 mAh/g	480 mAh/g
23	1.0~2.0 mg/cm^2	200（0.2C）	1420 mAh/g	985 mAh/g
24	1~3 mg/cm^2	100（0.1C）	1044 mAh/g	99%
25	0.4~0.6 mg/cm^2	1000（0.5C）	1030 mAh/g	700 mAh/g
26	4.8 mg/cm^2	100（0.5C）	1510 mAh/g	1267 mAh/g
27	9.3 mg/cm^2	100（0.2C）	More than 1000 mAh/g	665 mAh/g

28	4 mg/cm^2	100（0.2C）	600 mAh/g	570 mAh/g
29	4.7 mg/cm^2	90（0.2C）	900 mAh/g	700 mAh/g
35	5 mg/cm^2	400（0.34 A/g）	1500 mAh/g	841 mAh/g
37	1.3 mg/cm^2	100（0.75 A/g）	1052 mAh/g	950 mAh/g

Soft-packaged Cell

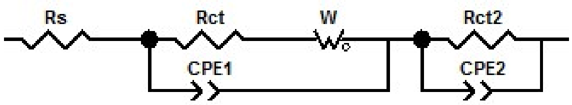
Ref.	**Sulfur Loading**	**Cycles**	**Capacity**	**Energy Density**
5	6.9 mg/cm^2	11	1Ah level	366 Wh/kg 581 Wh/L
8	—	50	1187 mAh/g	1416 Wh/kg (For Cathode)
16	—	30	985 mAh/g (under bending condition)	N/A
25	0.4~0.6 mg/cm^2	Discharge for over 20 h	1110 mAh/g	N/A

Cell performance of this work

Cell type	Cell parameters	Calculation item	Surfer load（mg/cm^2）	Current density (1 C=1672 mA/g)	Energy density (Wh/kg)
Coin	Cathode surface area: 1.1 cm^2 2302 TYPE	Cathode	6	0.50 C	2050
				0.70 C	1701
				1.00 C	973
			8	0.50 C	1880
				0.70 C	1566
				1.00 C	960
			10	0.50 C	1549
				0.70 C	1277
				1.00 C	534
Soft-packaged Cell	Cathode: 160 cm^2 Capacitance: 2.15 Ah Size: 4 cm×5 cm×3 mm	Entire cell	20	0.75 mA/cm^2	371
		Cathode	20	0.75 mA/cm^2	1055

		Cathode + Anode	20	0.75 mA/cm^2	782
Pouch Cell shown in the movies	Cathode: 27 cm^2 Capacitance: 0.6 Ah Size: 3 cm×9 cm×300 μm	Cathode	20（Fixed bending） 20（Continuous bending for 1000 cycles）	0.1 C	1616

Table S4 | The EIS fitting results of soft-packaged cell.



Cycling Condition	Rs	Rct	W-R	W-T	W-P	CPE1-T	CPE1-P	Rct2	CPE2-T	CPE2-P
Before discharging	1.28	0.38	1.22	1	0.105	E^{-4}	0.85	0.15	0.01	0.8
After 1st	1.4	1.09	0.7	8.6	0.25	$1.9\ E^{-4}$	0.78	0.15	0.01	0.9
After 5th	1.35	1.12	1.155	22	0.29	$8E^{-5}$	0.87	0.15	0.01	0.9
After 15th	1.1	1.15	0.5	5	0.325	$7E^{-5}$	0.879	0.54	0.2	0.32

Table S5 | The EIS fitting results of bending soft-packaged cell.

Mechanical bending (1200 times)										
Condition	**Rs**	**Rct**	**W-R**	**W-T**	**W-P**	**CPE1-T**	**CPE1-P**	**Rct2**	**CPE2-T**	**CPE2-P**
Before bending	1.37	1.0	0.6	9	0.25	$7.5E^{-5}$	0.85	0.3	0.19	0.4
After bending	1.15	1.2	0.7	4	0.295	$7E^{-5}$	0.89	0.33	0.3	0.39

Supplementary Movies

Movie S1 | Exhibition of the flexibility of the freestanding 3D GCSS.

Movie S2 | Exhibition of the constant bending and folding of the Li-S soft-packaged battery.

Movie S3 | Exhibition of the dynamic bending experiment of the Li-S soft-packaged battery.

Movie S4 | Exhibition of 180 degrees folded 1 Ah Li-S soft-packaged battery attached on the small electric toy vehicle.

Movie S5 | Exhibition of the small electric toy vehicle driven by 1 Ah battery in a circle with a diameter of 20 cm.