Electronic Supplementary Material

Carbon-doped surface unsaturated sulfur enriched CoS_2@rGO aerogel pseudocapacitive anode and biomass-derived porous carbon cathode for advanced lithium-ion capacitors

Yunpeng Shang[1], Xiaohong Sun (✉)[1], Zhe Chen[1], Kunzhou Xiong[1], Yunmei Zhou[1], Shu Cai[1], Chunming Zheng (✉)[2]

1 School of Materials Science and Engineering, Key Laboratory of Advanced Ceramics and Machining Technology of Ministry of Education, Tianjin University, Tianjin 300072, China

2 School of Chemistry and Chemical Engineering, State Key Laboratory of Hollow Fiber Membrane Materials and Membrane Processes, Tiangong University, Tianjin 300387, China

E-mails: sunxh@tju.edu.cn (Sun X); zhengchunming@tiangong.edu.cn (Zheng C)

The calculation process of the lithium-ion diffusion coefficient by GITT test:

The specific operation of the GITT test is to relax for 20 min every 10 min of discharge at 0.2 A/g in the first cycle. The following equation calculates the ionic diffusion coefficient (D_{Li+}):

$$D_{Li+} = \frac{4}{\pi}\left(\frac{m_B V_M}{M_B A}\right)^2 \left(\frac{\Delta E_s}{\tau(dE_\tau / d\sqrt{\tau})}\right)^2 \quad \left(\tau \ll \frac{L^2}{D_{Li+}}\right) \tag{1}$$

where the m_B, V_M, and M_B represent the mass, molar volume, and molar mass of active material; A and L represent the contact surface area with electrolyte and the average thickness of the electrode, respectively. If the functional relationship between voltage (V) and the square root of the relaxation time ($\tau^{0.5}$) after fitting can show a good linear relationship, then Equation 1 can be simplified to the following equation:

$$D_{Li+} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B A}\right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2 \quad (2)$$

where ΔE_τ and ΔE_s represent the voltage change caused by pulse and voltage change caused by the discharge.

Also, it can be seen from FigureS1 that the average thickness of the CS-CoS_2@rGO and CoS_2@rGO electrodes is approximately 100 μm. After calculation, the values of τ, L, and D_{Li+} meet the additional condition of Equation 1. Therefore, it is proved that the calculation process of the lithium-ion diffusion coefficient (D_{Li+}) is appropriate and practical.

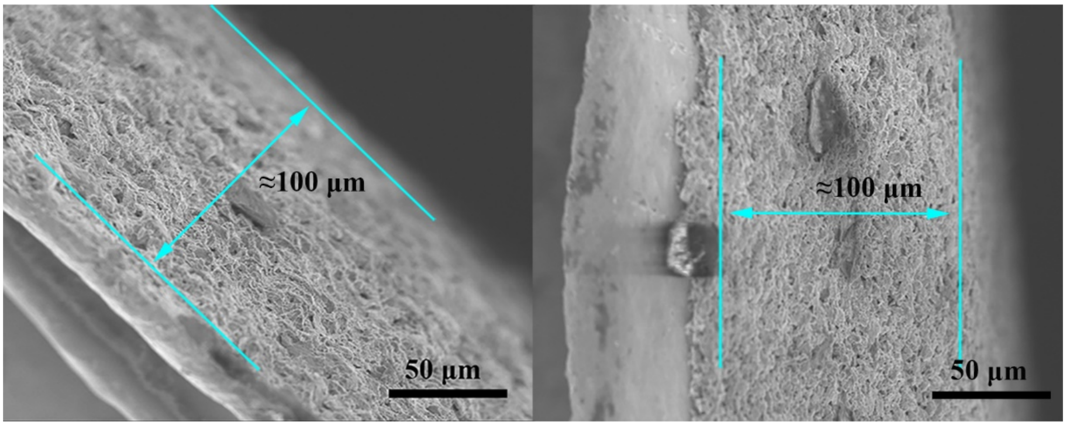

Figure S1 SEM images of electrode average thickness: (a) CS-CoS_2@rGO; (b) CoS_2@rGO.

Quantitative kinetic analysis:

Current response with varying scan rate in cyclic voltammetry can distinguish the charge storage mechanism by the following equation:

$$i = av^b \quad (3)$$

$$log\ (i) = b\ log\ (v) + log\ (a) \quad (4)$$

where *i* is the response current (mA), *v* is the scan rate (mV/s), and fitting parameter *b* can be obtained from the slope of the log (*i*) versus log (*v*) plot. While the value of *b* is 1, the current response trend to be proportional to the scan rate, representing the charges were stored by a capacitor process. The value of *b* is 0.5; namely, the current is of the square root of the scan rate, indicating a diffusion dominated process occurred.

Furthermore, to quantificate the contribution of diffusion dominated process and pseudocapacitive type process, current response with varying scan rates in cyclic voltammetry can also be analyzed by the following equation:

$$i = k_1 v + k_2 v^{1/2} \quad (5)$$

$k_1 v$ and $k_2 v^{1/2}$ stand for the current contribution of capacitor type and battery type under a fixed scan rate, respectively. Fit every point in the CV plot and plotting separate curves using $k_1 v$ and $k_2 v^{1/2}$ can visually observe the current contribution of different mechanisms, and capacity also can be quantified after integration of the plots.

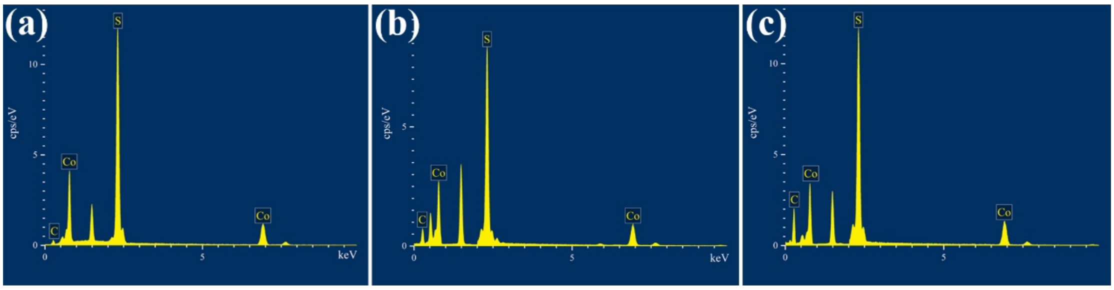

Figure S2 EDS spectrum of (a) CS-CoS_2, (b) CS-CoS_2@rGO and (c) CoS_2@rGO.

Table S1 Elements atomic ratio measured by calibrated EDS (Error ±2-3 %).

Elements Atomic %	CS-CoS_2	CS-CoS_2@rGO	CoS_2@rGO
C	8.58	59.01	74.05
Co	28.57	11.62	8.06
S	62.85	29.37	17.89

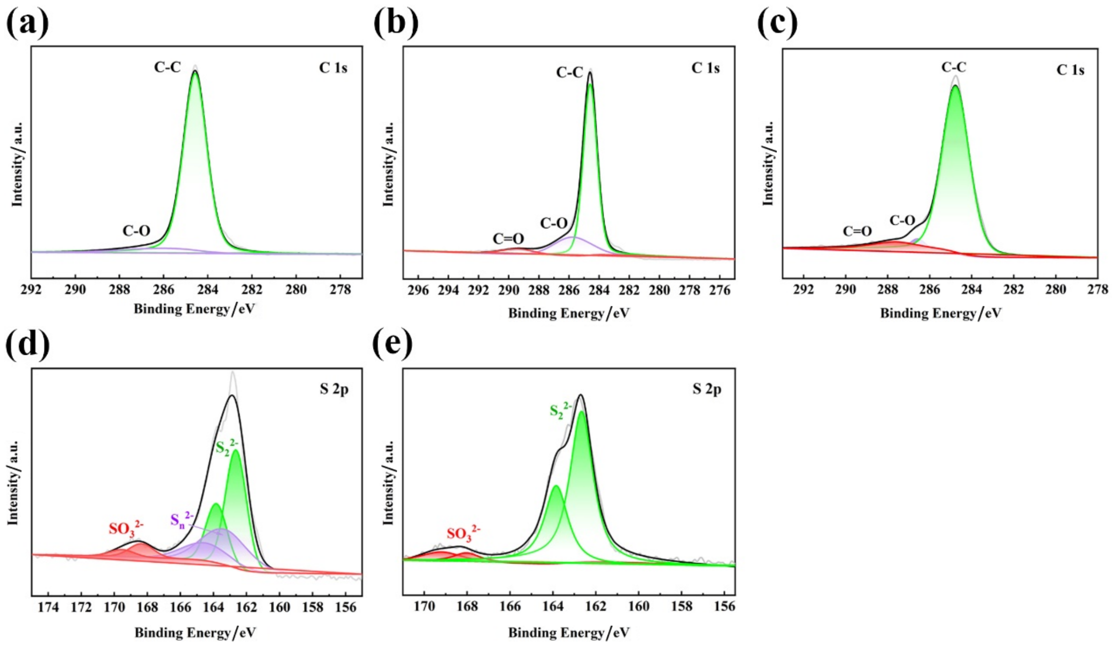

Figure S3 C 1s XPS peak deconvolution of (a) CS-CoS_2, (b) CS-CoS_2@rGO and (c) CoS_2@rGO; S 2p XPS peak deconvolution of (d) CS-CoS_2, (e) CoS_2@rGO.

Table S2 Elements atomic ratio obtained by sensitivity-corrected XPS test.

Elements Atomic %	CS-CoS_2	CS-CoS_2@rGO	CoS_2@rGO
C	78.41	94.87	85.57
Co	2.04	0.33	1.81
S	12.08	1.98	3.92
O	7.47	2.82	8.72

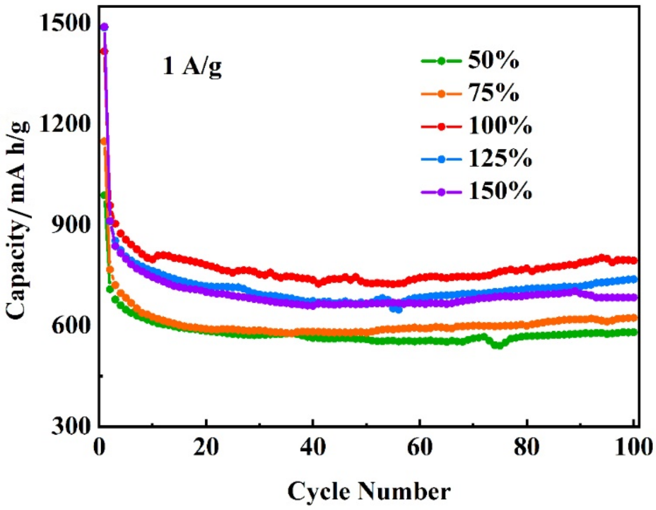

Figure S4 Performance comparison of CS-CoS_2@rGO samples with different CoS_2 loading mass on graphene sheets.

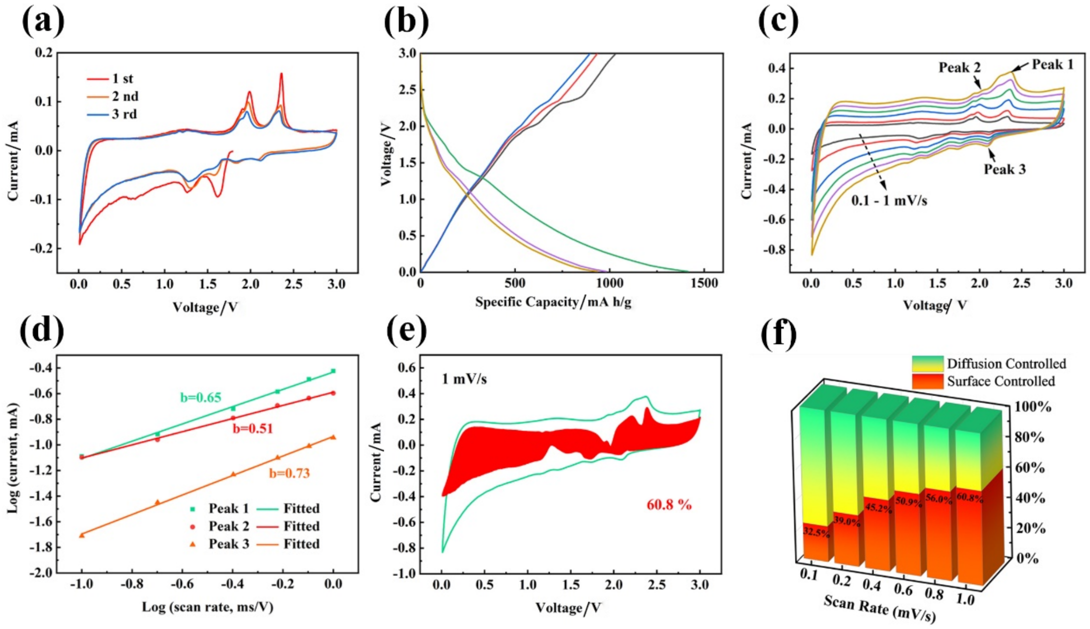

Figure S5 (a) CV curves at 0.1 mV/s, (b) GCD curves at 0.1 A/g, (c) CV curves at different scan rates, (d) b values, (e) capacitance contribution at 1 mV/s and (f) capacitance contribution at different scan rates of CoS_2@rGO.

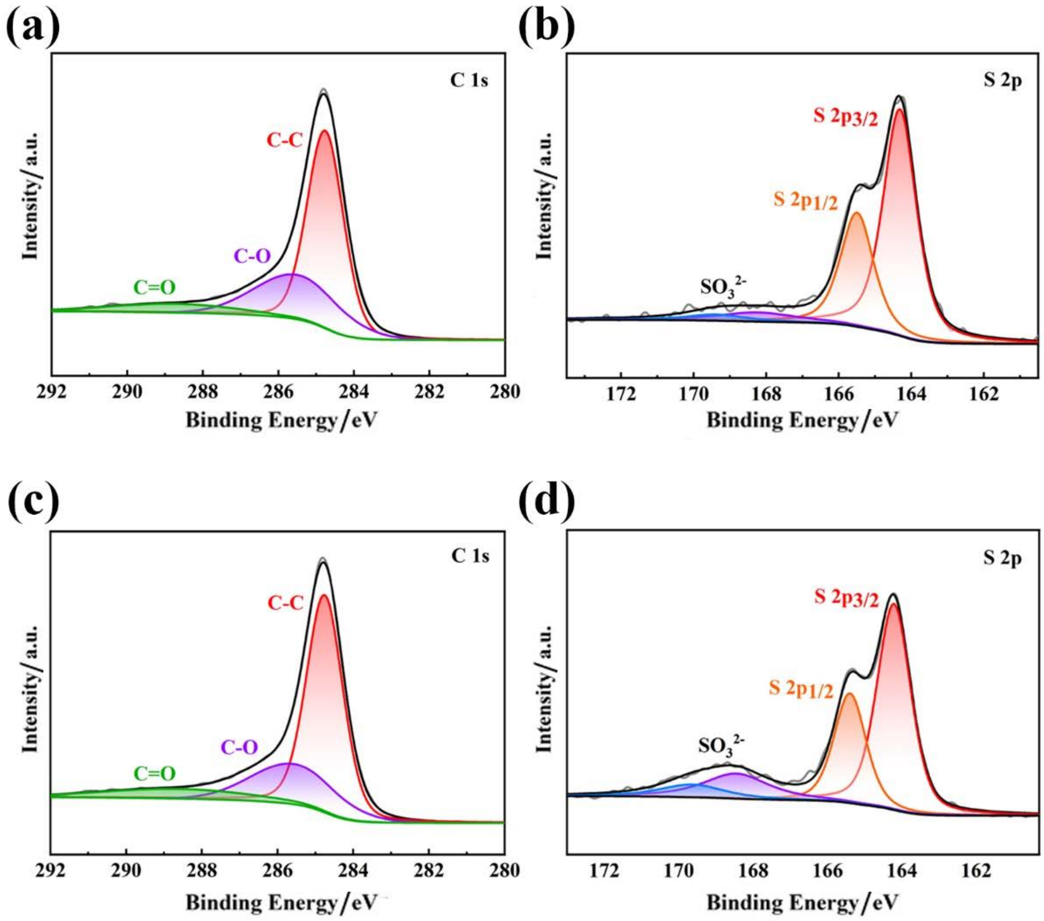

Figure S6 (a) C 1s and (b) S 2p XPS peak deconvolution of C-G; (c) C 1s and (d) S 2p XPS peak deconvolution of C-H.

Table S3 Biochar elements atomic ratio obtained by sensitivity-corrected XPS test.

Elements Atomic %	C-D	C-G	C-H
C	91.05	93.29	91.27
S	1.17	1.13	2.17
O	7.78	5.58	6.56

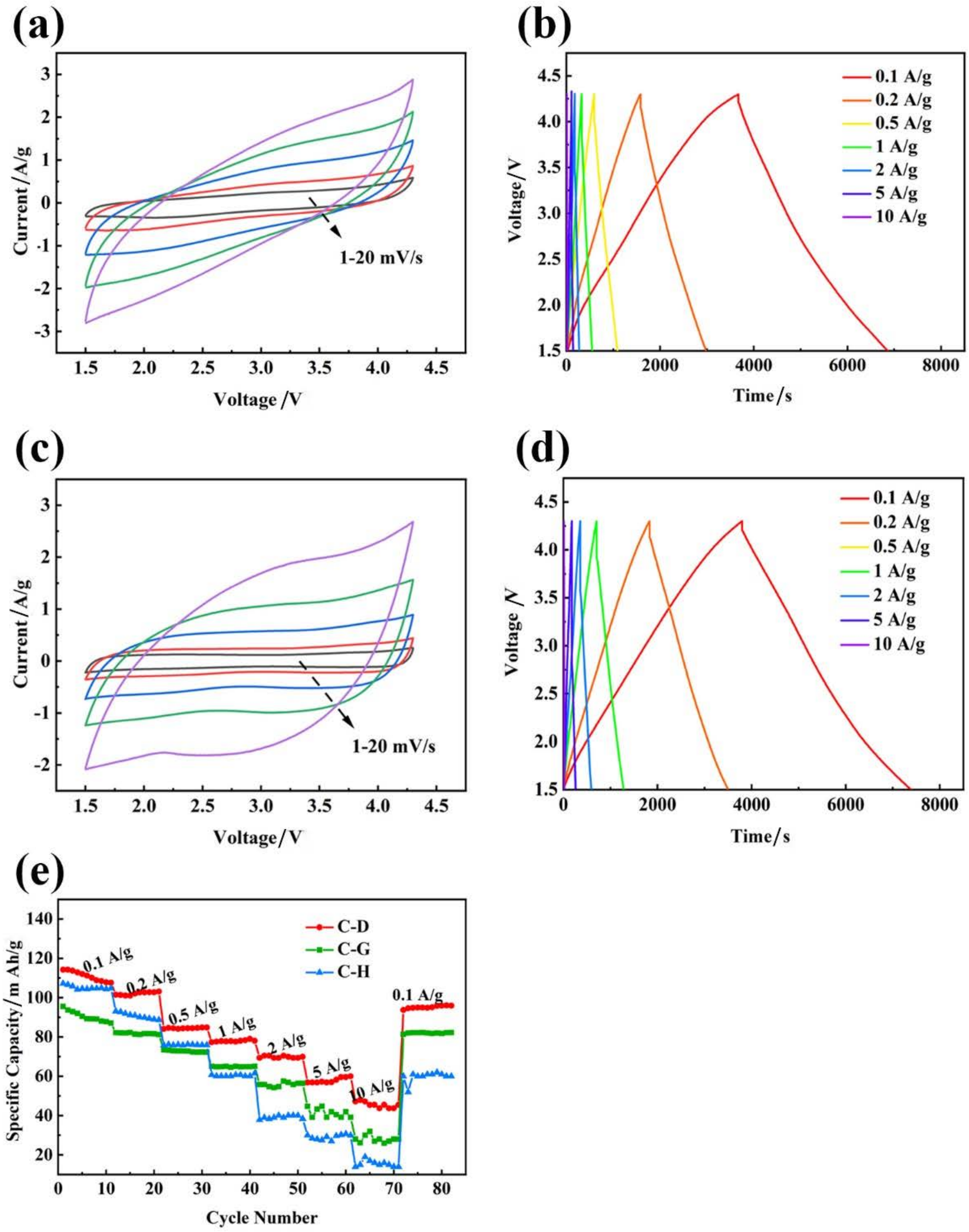

Figure S7 (a) CV curves and (b) GCD curves of C-G; (c) CV curves and (d) GCD curves of C-H; (e) Capacity rate performance of C-D, C-G, and C-H.