## Supporting Information

## Engineering Chitosan to a Recyclable and Flame-Resistant Gel Electrolyte via a Dual Cross-linked Strategy for Flexible Supercapacitors

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## **Experiments:**

*Calculation:* The ionic conductivity  $\sigma$  (S cm<sup>-1</sup>) was calculated from electrochemical

impedance spectroscopy of the GPEs using Equation (1):

$$\delta = \frac{L}{R \times A}_{\dots} \tag{1}$$

where L (cm) is the distance between the two electrodes, i.e., the thickness of the electrolyte, R ( $\Omega$ ) represents the resistance of the electrolyte, obtained from the intercept on the real axis in the Nyquist plot at high frequencies, and A (cm<sup>-2</sup>) is the geometric area of the electrode/electrolyte interface.

The specific capacity C (F g<sup>-1</sup>) was calculated from GCD curves of the devices using Equation (2):

$$C = \frac{I \times \Delta t}{\Delta V \times m}$$
(2)

where I(A) refer to the applied current,  $\Delta t$  (s) represents the discharging time, m (g) is the single electrode mass of active materials, and  $\Delta V$  (V) is the operating voltage window of the supercapacitor, respectively. The energy density E (W h kg<sup>-1</sup>) and power density P (W kg<sup>-1</sup>) were calculated by the following equations (Equation (3), (4)):

$$E = \frac{C(\Delta V)^2}{2 \times 3.6}$$

$$P = \frac{3600 \times E}{\Delta t}$$
(3)

where C (F g<sup>-1</sup>) represents the specific capacitance,  $\Delta V$  (V) denotes the operating voltage window of the supercapacitor, and  $\Delta t$  (s) is the discharging time.

*Methods:* The sodium boric solution was synthesized by adding an appropriate amount of water and an equal amount of boric acid and sodium hydroxide solution into the volumetric flask. For the preparation of 2 M B(OH)<sub>4</sub>Na solution, the general procedure is to dissolve 8 g of NaOH (0.2 mol) in an appropriate amount of deionized water, then add the NaOH solution to the 12.36 g of B(OH)<sub>3</sub> (0.2 mol) in small amounts several times under the stirring of a glass rod until the clear and transparent solution was achieved, finally the solution was transfered to a 100 mL volumetric flask to prepare a 2 mol/L solution. Similarly, different concentration of sodium borate solution could be prepared. The electrode sheet was prepared by mixing and grinding activated carbon, acetylene black, and polytetrafluoroethylene (PTFE) in a mass ratio of 8:1:1, and a small amount of ethanol was dispersed and coated on the surface of nickel foam (2 cm × 3 cm), which was dried under vacuum at 80 °C for 12 h to remove the ethanol, after which the active substance was brought into close

contact with nickel foam under a pressure of 1 MPa. A flexible supercapacitor with electrode sheet/ gel electrolyte/ electrode sheet was assembled with aluminum plastic film as the outer package. The thickness of the gel electrolyte is 300  $\mu$ m, the mass of activated carbon at the single-sided electrode is 0.22 mg, and the collector fluid is nickel foam (the porosity was 97.2%).



Figure S1. Dissolution mechanism of chitosan in different acid solutions.



**Figure S2.** Digital images of the CS-LA, CS-HOAc and CS-VA membranes before and after immersion in water.



Figure S3. <sup>11</sup>B-NMR spectra in  $D_2O$  of the boric acid before and after addition of sodium hydroxide.



**Figure S4.** The XPS spectra at B 1s regions of the boric acid, sodium borate aqueous solution and CS-LA-B(OH)4Na GPEs.



Figure S5. SEM images of the surface of (a) CS-HOAc-B(OH)<sub>4</sub>Na and (b) CS-VA- $B(OH)_4Na$  GPEs.



Figure S6. SEM images of the cross-section of (a) CS-LA-B(OH)<sub>4</sub>Na, (b) CS-HOAc-B(OH)<sub>4</sub>Na, and (c) CS-VA-B(OH)<sub>4</sub>Na GPEs.



Figure S7. Flame retardant tests of (a) CS-LA-B(OH)<sub>4</sub>Na GPEs and (b) CS-LA.



Figure S8. Flame retardant tests of unpackaged CS-LA-B(OH)<sub>4</sub>Na GPEs-based SC.



**Figure S9.** SEM images of cross section of the CS-LA-B(OH)<sub>4</sub>Na GPEs after combustion: (a) 500 times, (b) 1000 times, (c) 2000 times, (d) 5000 times.



**Figure S10.** EIS of CS-LA-B(OH)<sub>4</sub>Na, CS-HOAc-B(OH)<sub>4</sub>Na and CS-VA-B(OH)<sub>4</sub>Na GPEs.



**Figure S11.** EDS of (a) the surface and (b) the cross-sectional of the GPEs and comparison of the distribution of boron and sodium elements.



Figure S12. ESW of CS-LA-B(OH)<sub>4</sub>Na GPEs.



Figure S13. (a) CV curves at 10 mV s<sup>-1</sup> of the CS-LA-B(OH)<sub>4</sub>Na GPEs-based SC under different voltage, (b) GCD curves at 1 A g<sup>-1</sup> of the CS-LA-B(OH)<sub>4</sub>Na GPEs-based SC under different voltages.



Figure S14. CV curves at 10 mV s<sup>-1</sup> of the CS-LA-B(OH)<sub>4</sub>Na GPEs-based SC under different temperatures.



**Figure S15.** (a) CV curves at 10 mV s<sup>-1</sup> and (b) GCD curves at 1 A g<sup>-1</sup> of the CS-LA-B(OH)<sub>4</sub>Na GPEs-based SC under the pressure of heavy objects of different masses.



Figure S16. Digital images of the recycled GPEs.



**Figure S17.** Comparison of the ESW of the recycled GPEs with that of the original GPEs.



Figure S18. Comparison of the EIS of the recycled GPEs and the original GPEs.



**Figure S19.** The basic electrochemical properties of the recycled GPEs with the same charge/discharge voltage (0-1.4 V).



**Figure S20.** The GCD curves at 0.5 A  $g^{-1}$  of the recycled GPEs-based SC compared with the original GPEs-based SC.



**Figure S21.** Comparison of specific capacitance of recycled GPEs and original GPEs based SCs at different charge/discharge rates.

рН	Structure					
4	B(OH) <sub>3</sub>					
5	$B(OH)_3 \cdot B_5O_6(OH)_4 \cdot B_3O_3(OH)_4$					
6	$B(OH)_3 \cdot B_5O_6(OH)_4 \cdot B_3O_3(OH)_4$					
7	$B(OH)_3 \cdot B_5O_6(OH)_4^- \cdot B_3O_3(OH)_4^- \cdot B_4O_5(OH)_4^- \cdot B(OH)_4^-$					
8	$B(OH)_3 \cdot B_3O_3(OH)_4 \cdot B_4O_5(OH)_4 \cdot B(OH)_4$					
9	$B(OH)_3 \\ \\ \circ B_3O_3(OH)_4 \\ \\ \circ B4O_5(OH)_4 \\ \\ \circ B(OH)_4 \\ \\ \circ B_3O_3(OH)_5 \\ \\ \\ \circ B_3O_3(OH)_5 \\ \\ \circ B_3O_3(OH)_4 \\ \\ OH)_4 \\ \\ \circ B_3O_3(OH)_4 \\ \\ OH)_4 \\ OH)_4 \\ \\ OH)_4 \\ \\ OH)_4 \\ OH)_4 \\ OH)_4 \\ \\ OH)_4 \\ OH)_4 \\ OH)_4$					
10	$B(OH)_3 \cdot B_3O_3(OH)_4 \cdot B_4O_5(OH)_4 \cdot B(OH)_4 \cdot B_3O_3(OH)_5$					
11	$B(OH)_4$ $\sim B_3O_3(OH)_5$					
12	B(OH) <sub>4</sub> -					

Table S1. Structure of boric acid in aqueous solution with different pH values<sup>[1]</sup>

	Maximum voltage (V)	Specific capacitance (F/g)	Ionic conductivity (mS/cm)	Energy density (Wh/kg)	Power density (W/kg)	Capacity retention (%)		
This work	1.4	51.36	24.02	13.98	700	92		
CS/PAM <sup>[2]</sup>	1.4	31.89	17.4	8.7	350.3	32		
CS/KOH <sup>[3]</sup>	1.3	70*	4.5	5.1	32.5	89		
CS/LiClO <sub>4</sub> <sup>[4]</sup>	1.5	29.6	8.67	7.87	95.97	93*		
CS/PNMA <sup>[5]</sup>	1.4	32	35.2	8.74	69.99	70*		
CS/MC <sup>[6]</sup>	0.9	9.97	0.66	0.77	578.55	71*		
CS/MgCl <sub>2</sub> <sup>[7]</sup>	0.9	33.2	1.03	13.1	550	46.9		
*For the specific value not given in the report, it is estimated based on the existing data and charts								

Table S2. Comparison of the electrochemical performance of chitosan-based SCs

[1] M. Mutailipu, K. R. Poeppelmeier, S. Pan, Chem. Rev. 2021, 121, 1130.

[2] H. Yang, X. Ji, Y. Tan, Y. Liu, F. Ran, J. Power Sources 2019, 441, 227174.

[3] S. Zallouz, J.-M. Le Meins, C. Matei Ghimbeu, Energy Adv. 2022, 1, 1051.

[4] R. Na, G. Huo, S. Zhang, P. Huo, Y. Du, J. Luan, K. Zhu, G. Wang, *J. Mater. Chem. A* **2016**, *4*, 18116.

[5] Q. Zhang, L. Zhao, F. Ran, Renew. Energ. 2022, 194, 80.

[6] S. B. Aziz, M. H. Hamsan, M. A. Brza, M. F. Z. Kadir, S. K. Muzakir, R. T. Abdulwahid, *J. Mater. Res. Technol.* **2020**, *9*, 8355.

[7] M. H. Hamsan, S. B. Aziz, M. M. Nofal, M. A. Brza, R. T. Abdulwahid, J. M. Hadi, W. O. Karim, M. F. Z. Kadir, *J. Mater. Res. Technol.* **2020**, *9*, 10635.