

Super-resilient and highly sensitive graphene oxide/cellulose-derived carbon aerogel

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S1. Details on experimental methods

Materials. Hydroxypropyl methyl cellulose (HPMC) was purchased from Macklin, China. Graphite powders were purchased from Nanjing XFNANO MaterialsTech Co., Ltd. 98 wt% H₂SO₄ and KMnO₄ were purchased from Aladdin, China.

Preparation of HPMC/GO suspension. GO was prepared through oxidizing graphite powders via a modified Hummers method¹, and then the obtained GO suspension was ultrasonicated (KQ-100B) for 10 min. To obtain HPMC/GO suspension, 1.08 g HPMC was dissolved in 33.92 mL deionized water, and then added 10.00 g GO suspension (1.8 wt%, 0.18 g GO). The above mixture was stirred for 12 h (500-600 rpm) and then ultrasonicated for another 1 h to make sure the remove of air bubbles and the homogeneous mixing of HPMC and GO.

Fabrication of aerogels. HPMC/GO suspension (15 mL) was poured into a plastic box (38 mm × 29 mm × 22 mm), and then the box was placed on a steel box filled with liquid nitrogen. After directional freeze-casting and freeze-drying (in a lyophilizer for 48 h), an aerogel (A-HPMC/GO-6, A and 6 represent aerogel and the mass ratio of HPMC to GO, respectively) was obtained. A-HPMC/GO-x with same solid content but different mass ratios of HPMC to GO (x= 1, 2, 4, 6, 8, 10 and 20, representing 1:1, 2:1, 4:1, 6:1, 8:1, 10:1 and 20:1, respectively) were prepared by the same method. In addition, pure HPMC aerogel (A-HPMC) and pure GO aerogel (A-GO) were fabricated from pure HPMC solution and GO suspension. To investigate the effect of directional freezing-casting on the structure and mechanical performance of carbon aerogel, control sample A-R-HPMC/GO-6 was prepared via a random freeze-drying method by immersing a plastic box containing HPMC/GO suspension in liquid nitrogen and then freeze-drying.

Pre-oxidation of aerogels. The aerogel was heated to 240 °C^{2, 3} (0.5 °C min⁻¹) in air using a muffle furnace and held for 4 h to obtain pre-oxidized aerogels before carbonization.

Fabrication of carbon aerogels. The pre-oxidized aerogel was carbonized in a tube furnace under N₂ atmosphere. There are three stages during carbonization. The first stage was carried out from room temperature to 300 °C (5 °C min⁻¹). In the second stage, the sample was pyrolyzed from 300 °C to 400 °C at a heating rate of v °C min⁻¹ ($v = 0.5, 1, 3$, respectively) and held at 400 °C for 1 h. In the last stage, aerogel was heated to 750 °C (5 °C min⁻¹) and kept at 750 °C for 2 h to obtain a carbon aerogel. Aerogels (A-HPMC/GO-x, A-HPMC, A-GO and A-R-HPMC/rGO-6) treated by both pre-oxidation and carbonization were named as C-HPMC/rGO-x, C-HPMC, C-rGO and C-R-HPMC/rGO-6, respectively. For comparison, C-N-HPMC/rGO-6 was prepared by directly carbonizing A-HPMC/GO-6 (without pre-oxidation).

Characterizations. The morphologies of all aerogels were observed on scanning electron microscopy (SEM, Merlin, Zeiss) and transmission electron microscopy (TEM, JEM-2100F). Thermal gravity analysis (TGA) was performed on a Pyris Diamond TG/DSC-200 with a heating rate of 10 °C min⁻¹ at the temperature range of 25 to 700 °C in a N₂ atmosphere. The surface area of carbon aerogel was determined from N₂ (77.4 K) adsorption-desorption isotherms using an ASAP-2046 surface area analyzer. The surface area was calculated using a Brunauer-Emmett-Teller (BET) method in the linear range of P/P₀=0.01-0.1. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer using Cu K α radiation as the X-ray source. Infrared (IR) data were recorded on a Fourier transform IR spectrometer (VERTEX 70, Bruker Corp., Germany). Raman spectra were carried out on Raman spectrometer (LabRAM ARAMIS-Horiba Jobin Yvon) operating under 532 nm excitation. Compression, elasticity, and fatigue

resistance were performed on a compressive instrument (Instron 5565). The electrical current was measured on an electrochemical workstation (CHI 660E).

Assembly and testing of sensor. The C-HPMC/rGO-6-based sensor was assembled by placing C-HPMC/rGO-6 into two pieces of PET substrates adhered with Al sheets. The strain and loading pressure were conducted by using Instron 5565. The real-time current was recorded on CHI 660E (applying a voltage of 1 V).

S2. Figures for characterization, experimental results

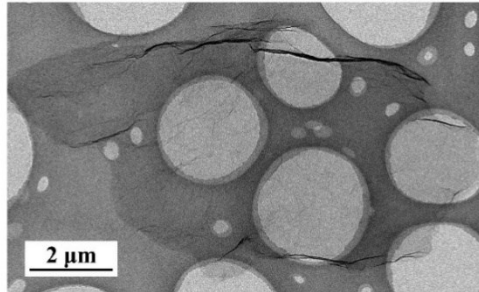


Figure S1. Transmission electron microscopy (TEM) image of GO.

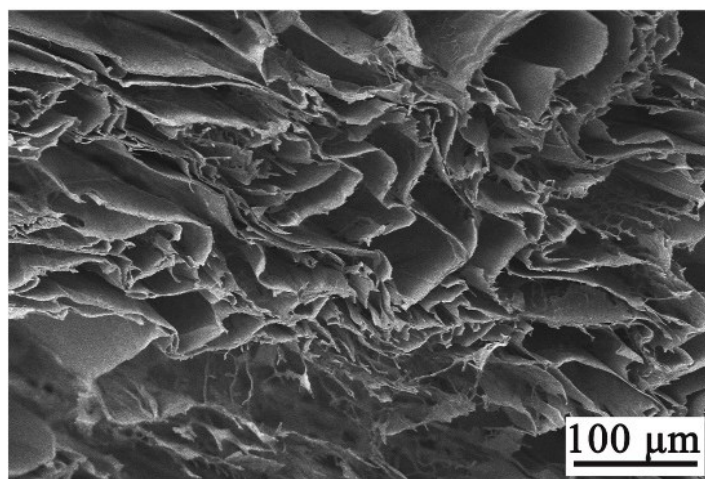


Figure S2. Scanning electron microscopy(SEM) images of A-HPMC.

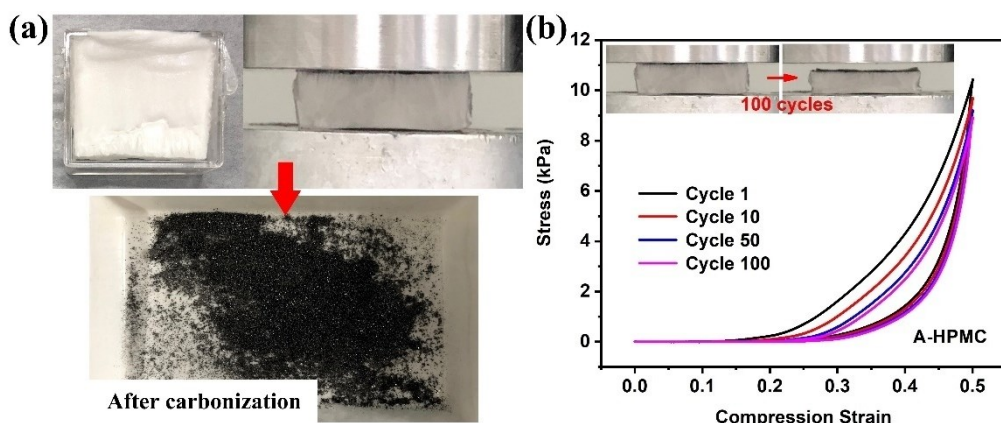


Figure S3. Digital photographs of (a) A-HPMC and C-HPMC. (b) Stress-strain curves of A-HPMC.

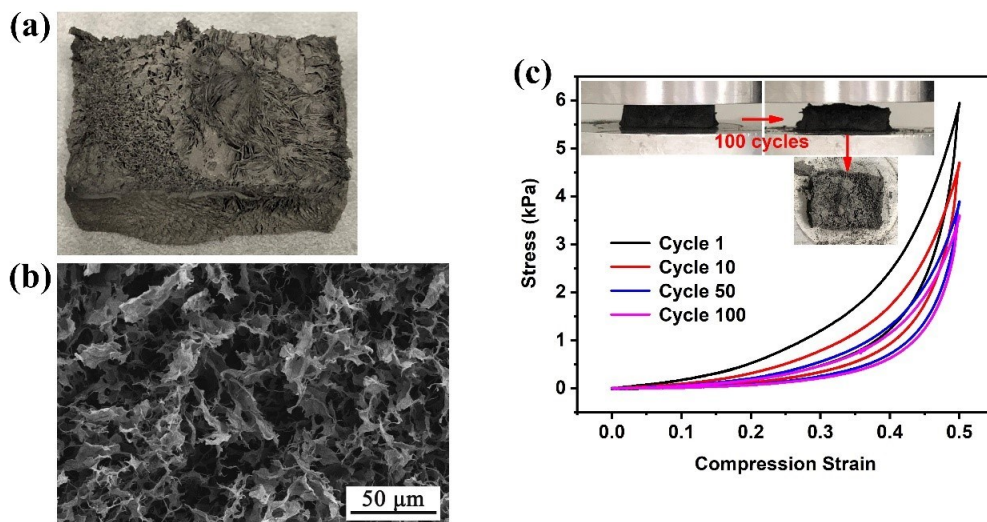


Figure S4. (a) Digital photograph, (b) SEM image, and (c) stress-strain curves of C-R-HPMC/rGO-6 (fabricated by random freeze-casting).

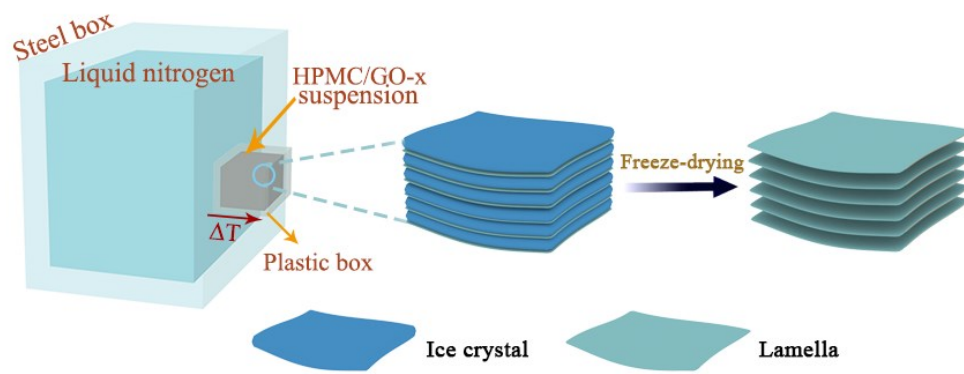


Figure S5. The schematic diagram of directional freezing.

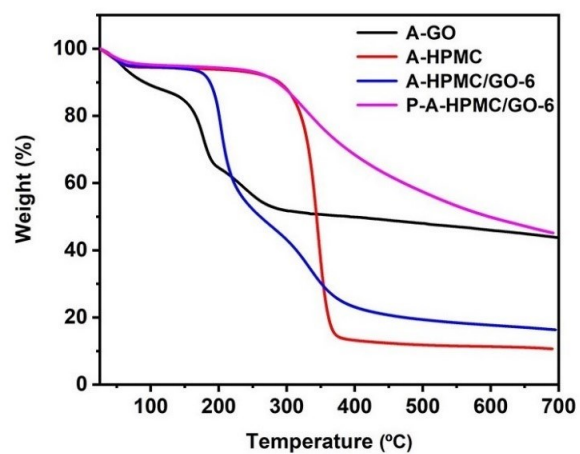


Figure S6. Thermogravimetric analysis (TGA) curves of the as-prepared aerogels.

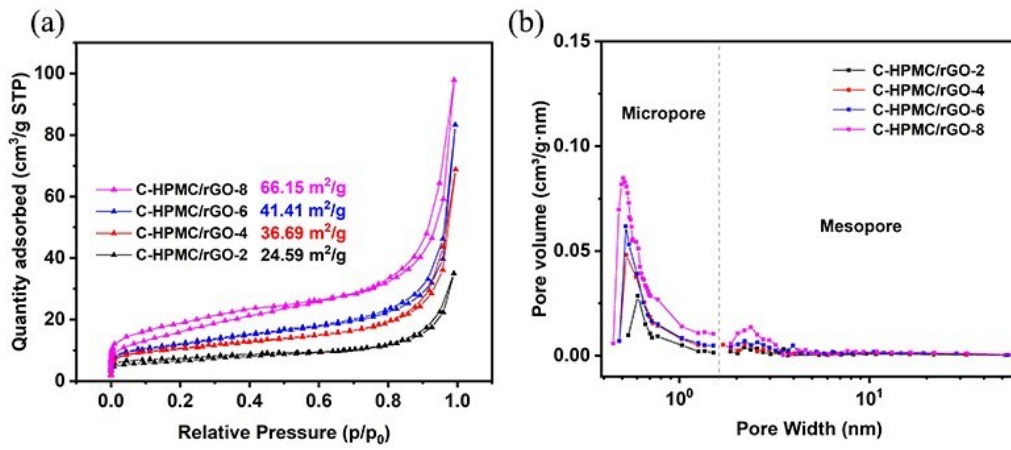


Figure S7. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distributions of C-HPMC/rGO-x.

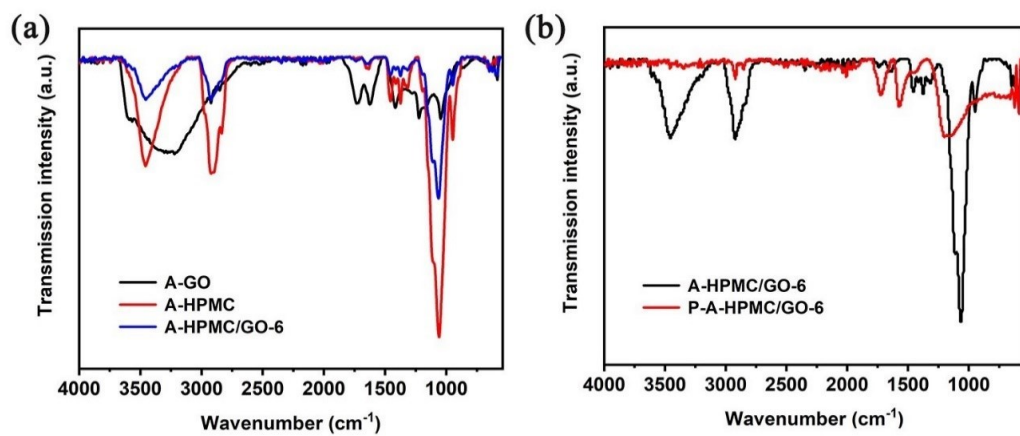


Figure S8. FT-IR spectra of the as-prepared aerogels.

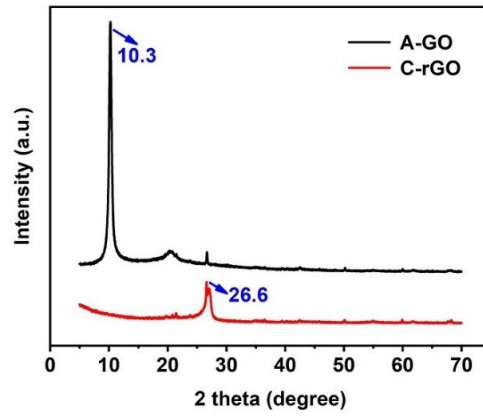


Figure S9. XRD patterns of A-GO and C-rGO.

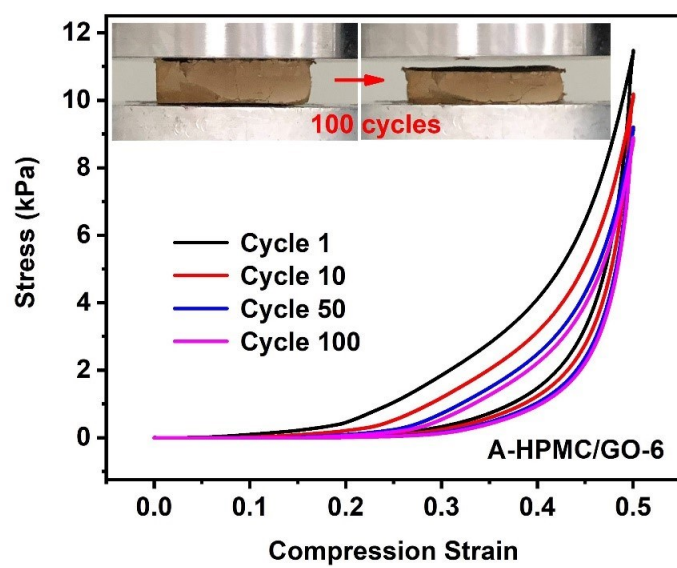


Figure S10. Stress-strain curves of A-HPMC/GO-6.

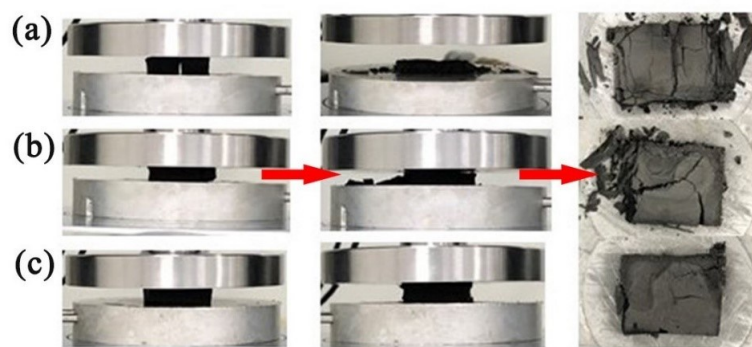


Figure S11. Digital photographs of C-HPMC/rGO-6 with different solid contents after 10 cycles: (a) 5 wt%, (b) 7 wt%, and (c) 9 wt%, respectively.



Figure S12. Digital photographs of C-HPMC/rGO-x.

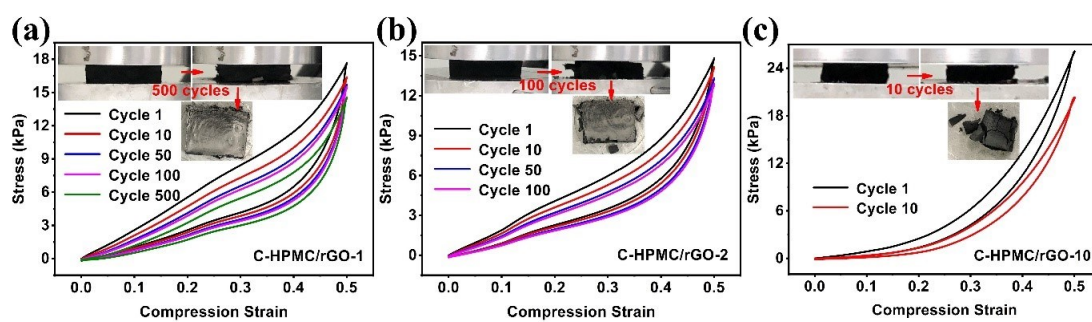


Figure S13. Stress-strain curves of (a) C-HPMC/rGO-1, (b) C-HPMC/rGO-2, (c) C-HPMC/rGO-10.

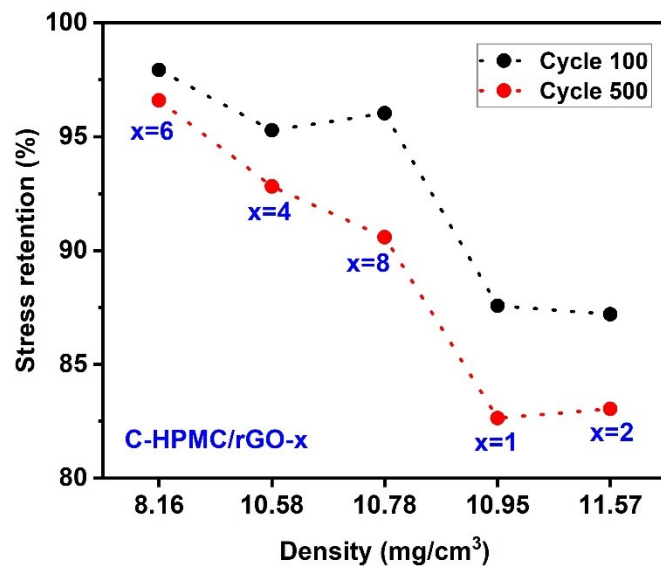


Figure S14. Mechanical properties of C-HPMC/rGO-x vs density.

S3. Tabulated results

Table S1. Stress retentions (30% strain) of C-HPMC/rGO-6 with different heating rates (300-400 °C).

Heating rate (°C min ⁻¹)	500 th (%)	1000 th (%)
0.5	90.54	88.58
1.0	88.70	86.93
3.0	83.87	81.14

Table S2. Stress retentions of C-HPMC/rGO-6 with different treatment before carbonization at 30% strain.

Process	500 th (%)	1000 th (%)
With pre-Oxidation	94.73	94.10
Without pre-Oxidation	90.54	88.58

Table S3. Stress retentions of C-HPMC/rGO-x with different mass rates of HPMC to GO at 50% strain.

Cycles	100 th	500 th	1000 th
1:1	87.58%	82.64%	-
2:1	87.20%	83.05%	-
10:1	Collapsed after 10 cycles		
20:1	Collapsed after 1 cycles		

S4. References

1W. S. H. Jr and R. E. Offeman, 1958, **80**, 1339.

2A. C. Pastor, F. Rodriguez-Reinoso, H. Marsh and M. A. Martinez, *Carbon*, 1999, **37**, 1275-1283.

3H. Wu, S.-w. Fan, X.-w. Yuan, L.-f. Chen and J.-l. Deng, *New Carbon Materials*, 2013, **28**, 448-453.