Carbon aerogel with super mechanical and sensing performances for wearable piezoresistive sensor

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S1. Details on experimental methods

Preparation of CNC. 15 g cellulose (average grain diameter, 90 μ m, purchased from Aladdin, China) was added into 150 mL 64 wt% H₂SO₄ (98%, purchased from Guangzhou Chemical Reagent Factory) solution, and the mixture was stirred at 55 °C for 60 min. Then the reaction was stopped by adding 1 L cold deionized water, and the suspension was centrifuged for 10 min (5000 rpm) for 2 times to separate the CNC. The obtained CNC was dialyzed against deionized water for 2 days to obtain CNC suspension with 2 wt% concentration.

Preparation of Mxene nanosheets. Ti₃C₂ MXene was prepared by selectively etching the Al layer in the precursor Ti₃AlC₂ (Nanjing Mission new Materials Co. Ltd. , http://www.njmission.com/) with HCI (AR, purchased from Guangzhou Chemical Reagent Factory) and LiF (purchased from Aladdin).¹ 1.5 g Ti₃AlC₂ was added to 30 mL HCI solution (6 M) containing 1.5 g LiF (purchased from Aladdin) in a Teflon beaker, and the mixture was stirred at 35 °C for 30 h (Caution: used with adequate ventilation, wearing chemical splash goggles (not safety glasses) together with a face shield, as well as prot clothing). The resulting product was washed with deionized water and centrifugated at 5000 rpm for several times until the pH of the supernatant >6, and a clay-like sediment was obtained. The sediment was then dispersed in deionized water and ultrasonicated for 2 h to exfoliate the MXene flakes. The unexfoliated MXene was removed after centrifugation at 4000 rpm for 10 min. The concentration of the obtained MXene suspension was ~4 mg mL⁻¹.

Fabrication of carbon aerogels. Firstly, 10 g MXene suspension (0.4 wt%, 40 mg MXene) and 8 g CNC suspension (2 wt%, 160 mg CNC) were dispersed in 22 g deionized water, stirred for 10 min, and then ultrasonicated for 30 min to make sure that CNC and MXene were sufficiently dispersed. After that, 13 mL of above mixture was placed in a plastic box (38 mm × 29 mm ×18 mm) and tied to an open lidless steel box. Then, liquid nitrogen was added into the steel box to create a temperature gradient, whereas parallel ice columns with long-range alignment formed because of the growth of ice nucleus along horizontal direction. The samples were freeze-dried to obtain MX/CNC, MXene and CNC aerogels (the volume was about 13 cm³). The aerogels were carbonized in a tube furnace via a two-stage process under N₂ atmosphere. The first stage was carried out from 30 °C to 200 °C with a heating rate of 5 °C min⁻¹ and held for 2 h. In the second stage, sample was pyrolyzed from 200 to 700 °C with a heating rate of 3 °C min⁻¹ and then held for another 2 h to obtain C-MX/CNC and C-CNC aerogels. For comparison, pure MXene (5 mg/mL) aerogels were also prepared with the same process.

Compression, elasticity, fatigue resistance and compression-responding conductivity. Compression, elasticity and cycling tests were performed on an Instron 5565 equipped with a 50 N load cell. Cuboidal sample (about 25 mm × 20 mm × 11 mm) was placed between two compression stages with the top stage applying uniaxial compression and release on carbon aerogel along the vertical direction. The resistance of carbon aerogel was recorded using a multimeter (VC 890D), and the electrical current was recorded on an electrochemical workstation (CHI660E).

Assembly and sensing test of compressible and wearable sensor. The sensor was fabricated by placing the Mxene-derived aerogel (the thickness of aerogel was controlled at 1 mm by cutting) between two Ni electrodes adhered to 10-µm-thick poly (ethylene terephthalate) (PET) substrates. The tiny strain was conducted by a micrometer (NSCING, 0.001 mm), while a micro load was provided by 50 µL water droplet. The compression-induced resistance change was recorded on a multimeter (VC 890D). the real-time current signals were recorded on a 2400 digital source-Meter and CHI660E electrochemical workstation (Shanghai Chenhua Instruments Corp., Shanghai, China Co).

Real-time current signal of bendable sensor. A plain and arc-shaped PET (150-µm-thick) sheet with Ni electrode were used to sandwich the as-prepared aerogel, and the distances between PET sheets were about 1 mm for bending test. The real-time current signals were recorded on a 2400 digital source-Meter.

Characterizations.

The atomic force miscroscopy (AFM) images were conducted by a Bruker Multi Mode 8 scanning probemicroscope (SPM, VEECO) in tapping mode. XRD patterns were measured on a Bruker D8 diffractometer. Micromorphology was characterized with TEM (JEM-2100F) and SEM (Merlin, Zeiss). X-ray photoelectron spectra (XPS) were recorded on Thermo Scientific Thermo

SCIENTIFIC K-ALPHA with an exciting source of Al•K α (1286.6 eV). TGA of aerogels was performed on a simultaneous thermal analyzer (Pyris Diamond TG/DSC-200, US). A total of 5.0–10.0 mg of sample was placed in an aluminum pan, and heated from ambient temperature to 200 °C at a rate of 15 °C min⁻¹, then heated from 200 °C to 700 °C at a rate of 3 °C min⁻¹ in a nitrogen atmosphere with a flush rate of 25 mL min⁻¹.

S2. Figures for characterization, experimental results



Fig. S1. The Tyndall effect of MXene (left) and CNC suspensions (right).



Fig. S2. SEM image of MAX phase (Ti_3AIC_2) (a) and MXene (Ti_3C_2) (b), AFM image of MXene sheet (c), and SEM image

of MXene (d) and C-MXene (e).



Fig. S3. Schematic illustration of the freeze casting.



Fig. S4 Surface SEM images of MXene (before annealing) (a), C-MXene (after annealing) (b), CNC (before annealing) (c), C-CNC (after annealing) (d), MX/CNC (before annealing) (e), S C-MX/CNC (after annealing) (f).



Fig. S5. Digital photographs of (a) MXene aerogel, (b) CNC aerogel, and (c) MX/CNC aerogel



Fig. S6. SEM morphologies and element mappings of C-MX/CNC sheets. (a) C-MX/CNC sheets on AAO template. SEM image (b) and EDX layered imaging (c) of C-MX/CNC sheets. Uniform distributions of C (d), O (e), and Ti (f) on the surface of C-MX/CNC sheets.



Fig. S7. Digital photographs of the compressibility, elasticity, and bendability of MXene, C-MXene, MX/CNC and C-MX/CNC aerogels. The compression and collapse of (a) MXene, (b) C-MXene and (c) MX/CNC aerogels before annealing. (d) The super compressibility and elasticity of C-MX/CNC. (e) The excellent bendability of C-MX/CNC.



Fig. S8. Heights of C-MX/CNC before and after cycling test at a strain of 50%. (a) The original height. (b) The height after 1000 cycles. (c) The height after 10000 cycles.



Fig. S9. (a) Schematic of sensing mechanism of the aerogel. (b)The resistance of C-MX/CNC during compression..



Fig. S10. Assembling equipment for detecting tiny strain and gauge factor.

S3. Tabulated results

 Table S1. Comparison of stress and height retention of various carbon materials.

Materials	Stress retention	Height retention	Compression strain and cycle numbers	Reference
GO/CNT	88%	100%	50%, 1000	2
RF-GO	90%	88.6%	50%, 100	3
Graphene oxide	~92%	92%	50%, 15	4
aerogel				
C-CNC/rGO-X	71.2%	91.8%	50%, 10000s	5
	55.1%	85%	99%, 100	
C–G monolith	86%	98%	50%, 250000	6
	60%	93%	80%, 10000	
UCM aerogel	72%	84.7%	60%, 1000	7
Carbonaceous nanofibrous	75%	95.7%	50%, 1000	8
aerogels				
Elastin hybrid cryogels	91.2%	100%	80%, 100	9
	73.2%	87.8%	97.5%, 100	
Graphene aerogel	89.8%		50%, 20	10
Biomimetic graphene aerogel	85%		50%, 1000	11
	77%		90%, 100	
C-MX/CNC	93.2%	100%	50%, 1000	This work
	87.9%	95.4%	50%, 10000	
	0.868	100%	95%, 10	
	72.3%	76.2%	95%, 100	

Table S2. Comparison of sensitivity of various pressure sensors.				
Materials	Sensitivity (initial pressure)	Reference		
Carbonaceous nanofibrous aerogels	1.02 kPa⁻¹ (> 3 kPa)	8		
Carbon nanotubes/graphene	19.8 kPa⁻¹ (>300 Pa)	12		
Graphene/PDMS	8.5 kPa ⁻¹ (> 1 Pa)	13		
SWNTs/PDMS films	1.80 kPa⁻¹ (>0.6 Pa)	14		
MXene/reduced graphene oxide aerogel	22.56 kPa⁻¹ (> 1.25 kPa)	15		
CB@PU	0.068 kPa ⁻¹ (>91Pa)	16		
CuNWs	0.7 kPa ⁻¹ (>30 Pa)	17		
EMCP	~175 kPa⁻¹ (>10 Pa)	18		
Graphene oxide foam	15.2 kPa ⁻¹ (>200 Pa)	19		
MFSOTE	28.9 kPa ⁻¹ (>5000 Pa)	20		
Gold film/ PDMS microstructure	50.17 kPa ⁻¹ (>10.4 Pa)	21		
Carbon foam	100.29 kPa ⁻¹ (>14.4 Pa)	22		
rGO/PI	0.18 kPa ⁻¹	23		
Graphene aerogels	0.18 kPa ⁻¹	24		
Graphene–Polyurethane Sponge	0.26 kPa⁻¹	25		
C-MX/CNC	114.6 kPa⁻¹ (>1Pa)	This work		

Movie S1. The comparison of C-MX/CNC at a strain of 95%.

movie S2. The comparison of C-MX/CNC at a strain of 50%.

S4. Reference

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S5. Author Contributions

Hao Zhuo and Yijie Hu contributed equally to this work. H.Z.and Y.H. designed the research with supervision by L.Z. and R.S.. Z. C., K. W., J. Y. and Q. L. contributed to characterize the performances with supervision by X.P.. Q.L. and C.L involved in the analysis of mechanical mechanism.