

Preparation of sp^2 carbon-bonded π -conjugated COF aerogels by ultrasound-assisted mild solvothermal for multi-functional applications

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General Information

Materials

O-dichlorobenzene (o-DCB, AR), n-butyl alcohol (n-BuOH, AR) and ethanol (EtOH, AR) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Tetrahydrofuran (THF, AR), potassium hydroxide (KOH, AR) were purchased from Shanghai Macklin biochemical technology Co., Ltd. 2,4,6-Trimethyl-1,3,5-triazine (TMTA) and 1,4-Diformylbenzene (DFB) were brought from Shanghai Tensus Biotech Co., Ltd. Cu foil Ketjen Black and Super p was purchased from Shenzhen Kejingzhida Technology Co., Ltd. Unless otherwise noted, all reagents were used as received.

Characterization

Thermogravimetric testing (TGA, NETZSCH TG-DSC_STA449C) was performed in a nitrogen atmosphere and analyzed at temperatures ranging from 28-600°C (10°C/min). Powder X-ray Diffraction (PXRD, D8 ADVANCE) test employed a Cu K α source ($\lambda = 1.54056 \text{ \AA}$). Attenuated total reflectance Fourier transform-infrared (ATR FT-IR) spectroscopy were recorded with a Bruker Tensor II Spectrometer (4000-400 cm^{-1}). Solid-state ^{13}C cross-polarized magic-angle spinning nuclear magnetic resonance (CP-MAS NMR) were performed on a Bruker AVANCE III 400MHz. Nitrogen adsorption isotherms were measured at 77k using an ASAP2000-M+C instrument. The samples were pre-degassed at 120 °C for 6 h under vacuum. Surface area and pore size distributions were calculated by the Brunner-Emmett-Taylor (BET) adsorption model and the NLDFT model, respectively. Scanning electron microscope (SEM, Hitachi S-4800, 5Kv) and high resolution transmission electron microscopy (HRTEM, JEOL JEM-2100, 200kV) was used for morphological characterization. Elemental analysis was conducted on a vario EL III elemental analyzer.

Experimental instrumentation

Freeze-drying was performed by a T-frame general type counter top vacuum freezer (SJIA-10N) and the minimum freeze-drying temperature is -50°C.

Piezoresistive sensing tests were performed using an electrochemical workstation (CH1660E).

Experimental section

Preparation of DT-COF aerogel

DT-COF aerogels were prepared using ultrasound-assisted mild solvothermal technique. Briefly, 12.3 mg of 2,4,6-trimethyl-1,3,5-triazine (TMTA) (0.1 mmol), 20.1 mg of 1,4-diformylbenzene (DFB) (0.15 mmol), and 17 mg of KOH (0.3 mmol) were dissolved in a solvent mixture containing 0.6 ml of *o*-DCB, 1.4 ml of *n*-BuOH. The mixture was sonicated for 10 min to homogeneously disperse and then forming a translucent sol. The sol was reacted at a low temperature of 90 °C for 2 days to form a yellow gel with a three-dimensional network, followed by washing with THF to remove impurities, EtOH to replace THF, and ionized water to replace EtOH to avoid pore collapse due to solvent evaporation during drying. DT-COFs aerogels with great mechanical properties were obtained by freeze-drying. DT-COF aerogels weighed 28.7 mg, had a diameter of 1.15 cm, a height of 1.50 cm, and a density of 18.43 mgcm⁻³.

Adsorption experiment

Tweezers were used to clip the DT-COF aerogel for adsorption experiments as well as aerogel transfer during the experiments.

When using DT-COF aerogel for adsorption of various solvents, the weight of DT-COF aerogel is firstly measured, and then the DT-COF aerogel is placed in the solvent for 10 min, followed by taking it out and weighing its mass. The adsorption amount is obtained by dividing the weight of absorbed solvent by that of DT-COF aerogel.

Preparation of sulfur positive electrode

The lithium-sulfur (Li-S) battery sulfur cathode was prepared as follows: (1) sulfur powder and Ketjen Black were mixed and ball-milled for 2 h in accordance with the mass ratio of 4:1; (2) the ball-milled sulfur/carbon (S/C) mixture was added to a tetrafluoroethylene reactor, sealed after 12 h of static standing in an argon atmosphere, and then heated for 24 h in a blast oven at 155 °C, and then cooled down to room temperature to obtain the S/C complex with a mass fraction of 80 wt.% sulfur monomers; (3) the S/C complex, Super P and PVDF were prepared by mixing fully in accordance with the mass ratio of 7:2:1, and then prepared into the S/C complex.

fraction of 80 wt.% sulfur monomers of the S/C complex; (3) the S/C complex, Super P and PVDF were prepared into a sulfur cathode slurry by sufficiently mixing the S/C complex, Super P and PVDF according to the mass ratio of 7:2:1, in which the solvent used was NMP; (4) the sulfur cathode slurry was uniformly coated on the aluminum foil, and then dried in a vacuum oven at 60 °C, and the final sulfur cathode (sulfur loading. 1.2 mg cm⁻²).

Electrochemical performance test

The CR2025 coin battery was assembled with DT-COF aerogel, PP as the diaphragm, and lithium foil as the anode in a glove box under high-purity argon atmosphere, and then left to stand for 24 h. The amount of electrolyte used in the lithium-sulfur batteries depended on the sulfur loading of the cathode pole piece, and it was generally 25 μLmg⁻¹.

The cyclic voltammetry (CV) curves of the assembled coin batteries were measured by an electrochemical workstation CHI660C, with the scanning speed set at 0.1 - 0.5 mV s⁻¹ and the scanning voltage interval set at 1.7 - 2.8 V (vs. Li/Li⁺).

The interfacial impedance of the assembled coin cell was tested using the AC impedance module of the electrochemical workstation, and the frequency range was set to 1 - 100 kHz.

The electrochemical cycling performance of the assembled coin cell was tested by a battery tester Neware. Long-term cycling performance tests were performed at a charge/discharge rate of 0.5 C (1 C = 1675 mA g⁻¹) and a voltage range of 1.7 - 2.8 V (vs. Li/Li⁺). The rate performance tests were set up to perform charge/discharge tests at different current densities (0.1 C - 2.5 C).

Preparation of DT-COF aerogel piezoresistive sensors

Simple piezoresistive sensors were prepared to tests with different compression ratios by placing DT-COF aerogel between two layers of Cu foil. In the motion test experiments on different parts of the human body, in order to ease the test, the DT-COF aerogel was cut into pillars with a thickness of 4 mm, connected to an electrochemical workstation (CHI660E) and placed between insulating tapes and adhered to the test site. The corresponding current changes were recorded according to the loading-unloading

compression and the action. Volunteers participated in experiments based on the DT-COF aerogel piezoresistive sensor, which is used to detect a variety of simple human motions, and informed consent was obtained from the volunteers.

Calculation of aerogel sensing sensitivity

The sensitivity (S) of the DT-COF aerogels is calculated by the following equation to test the performance of sensing.

$$S = \frac{\frac{\Delta I}{I_0}}{\frac{P - P_0}{P_0}} = \frac{I - I_0}{P - P_0} \quad (1)$$

where I and P are the current and pressure of the DT-COF aerogel at the force loading state, respectively, and I_0 and P_0 are the current and pressure of the aerogel in the initial state.

Regeneration of DT-COF aerogel after adsorption cycle

Solvent exchange of the used aerogel was performed using ethanol and water, and regenerated DT-COF aerogel was dried by using freeze-drying, which can keep the original state. Regenerated DT-COF aerogel can continue to test the recoverability and reusability.

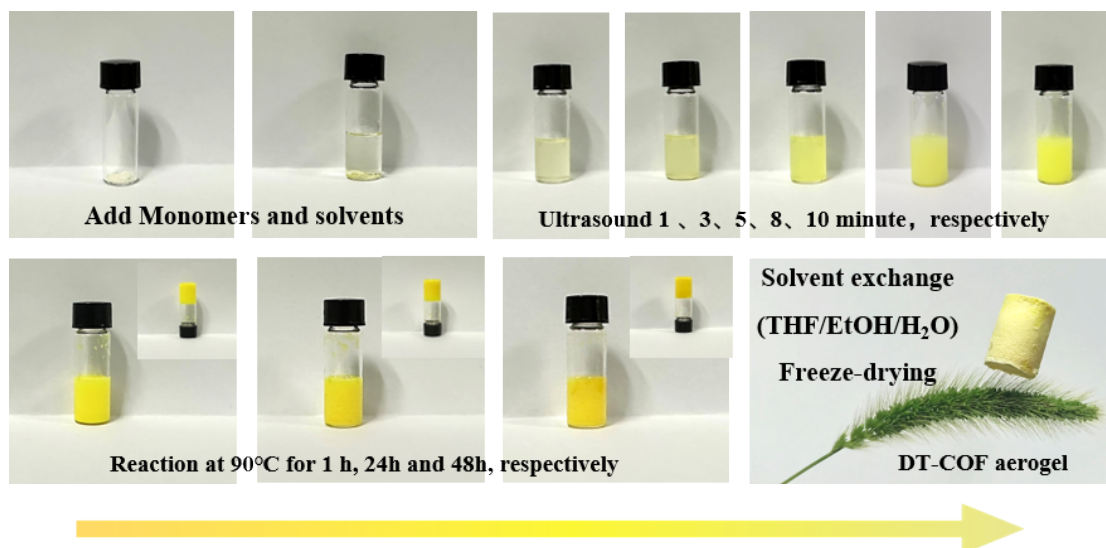


Fig. S1 Digital image of the process of preparing DT-COF aerogel.

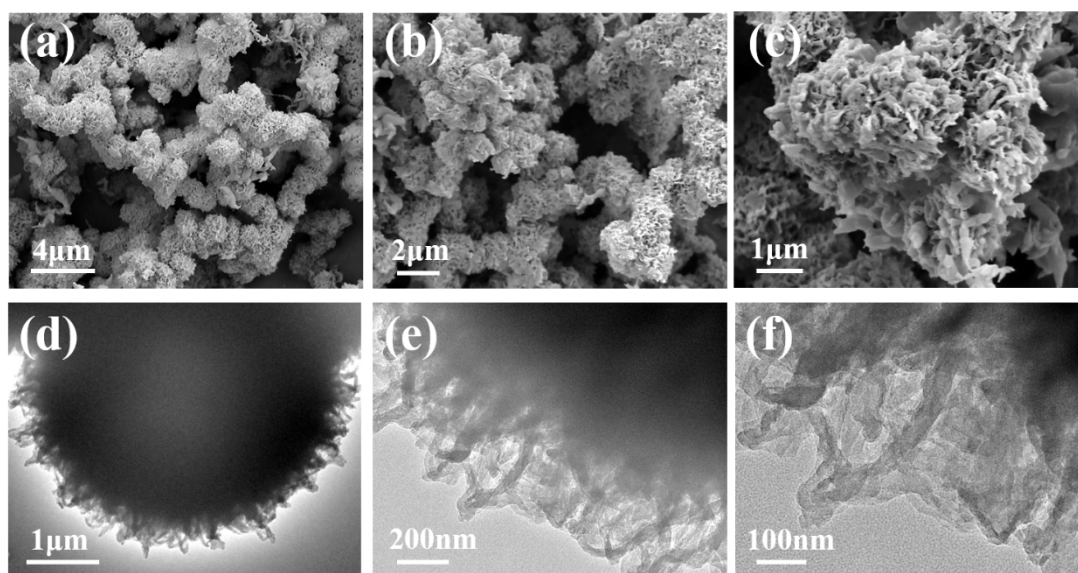


Fig. S2 SEM (a-c) and TEM (d-f) images of DT-COF aerogel.

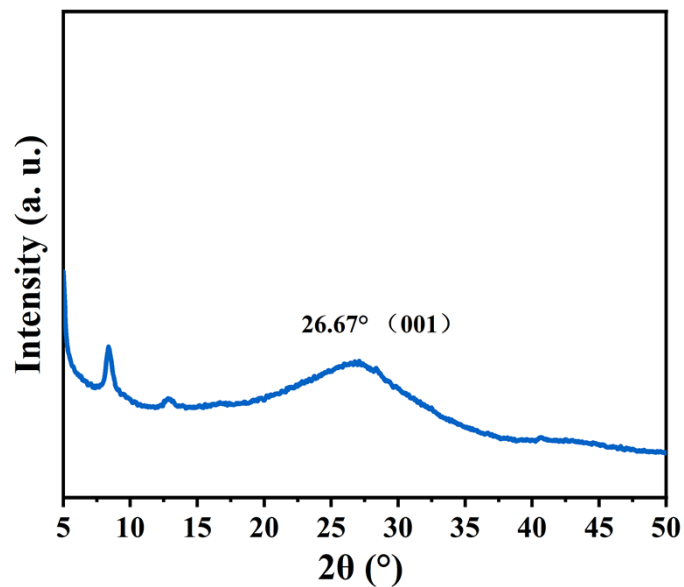


Fig. S3 Experimental PXR D patterns wide-angle test of DT-COF aerogel.

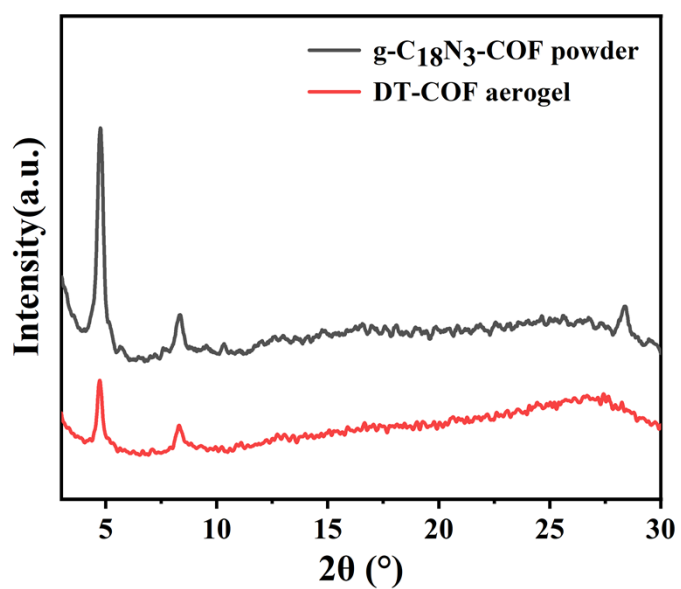


Fig. S4 The PXR D patterns of powder g-C₁₈N₃-COF and DT-COF aerogel.

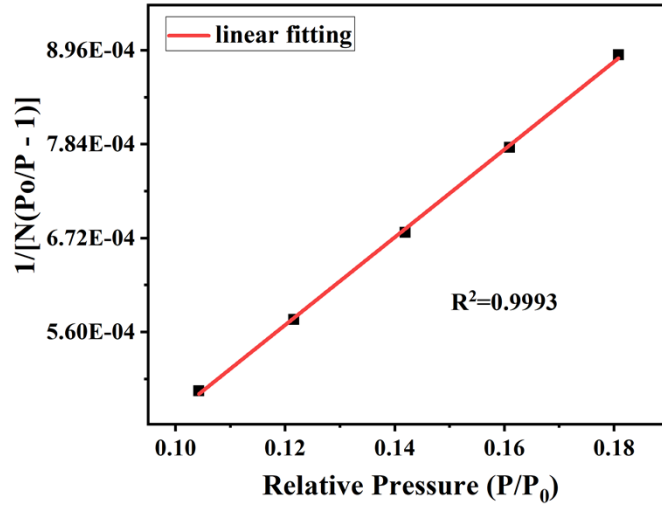


Fig. S5 BET plot of DT-COF aerogel calculated from the adsorption curve under low-pressure.

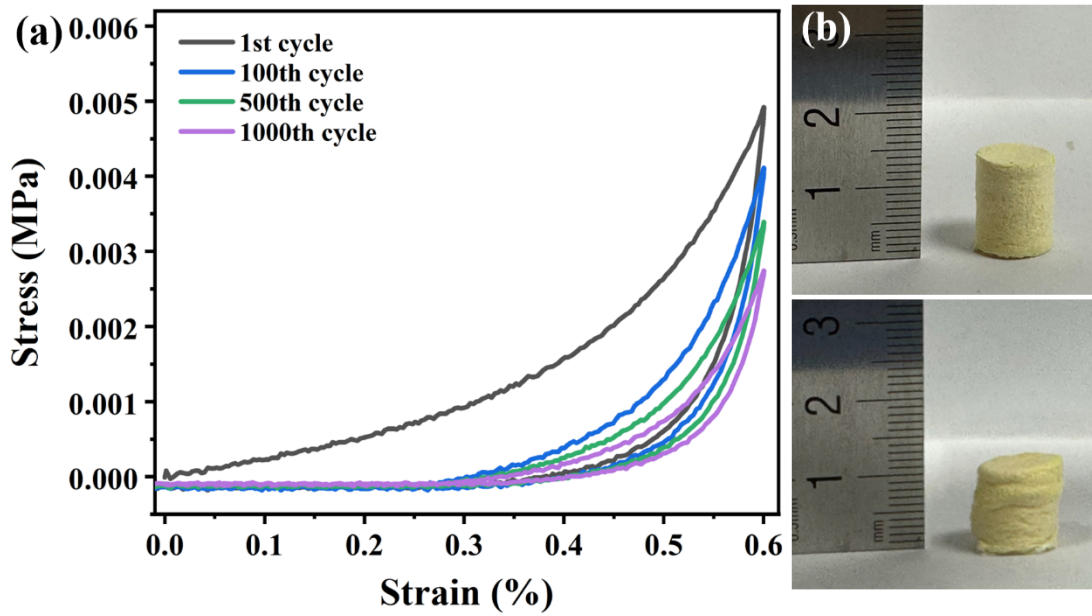


Fig. S6 (a) Stress-strain curves of DT-COF aerogel after 1000 compression recovery cycles at a compression ratio of 60%; (b) Digital photographs of DT-COF aerogel before and after compression (1000 cycles).

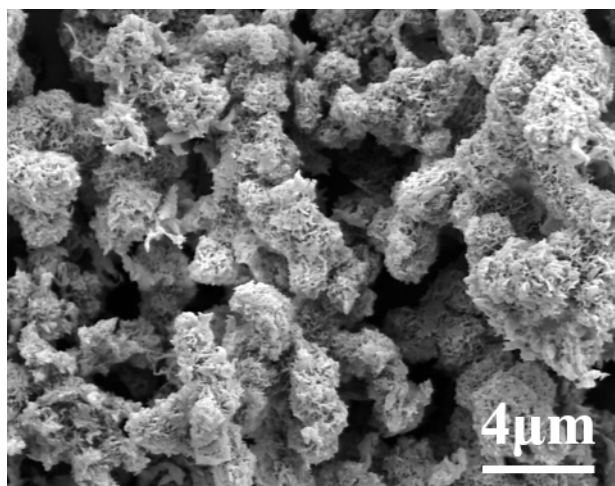


Fig. S7 SEM images of DT-COF aerogel after repeat 1000 cycles.

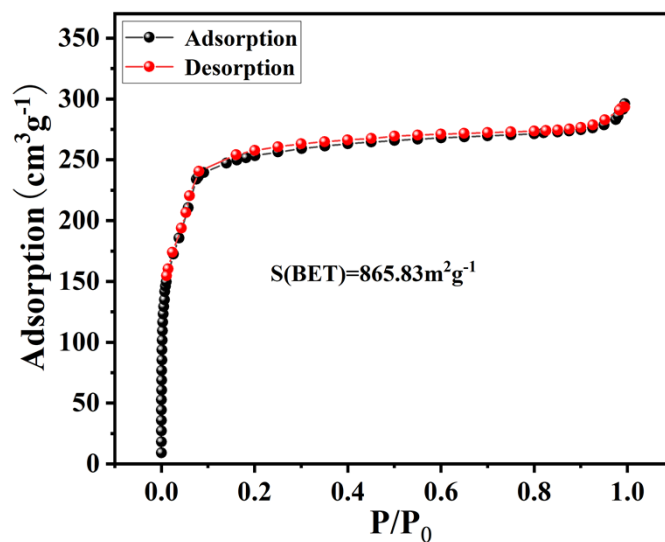


Fig. S8 Nitrogen adsorption and desorption isotherms for DT-COF aerogel after 1000 cycles.

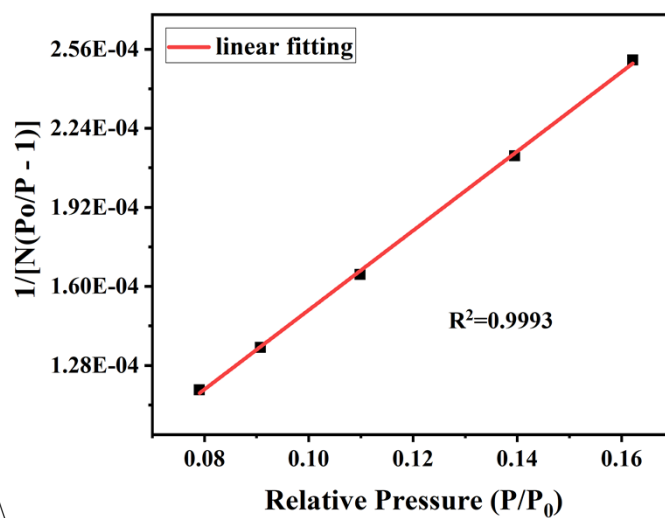


Fig. S9 BET plot of DT-COF aerogel after 1000 cycles calculated from the adsorption curve under low-pressure.

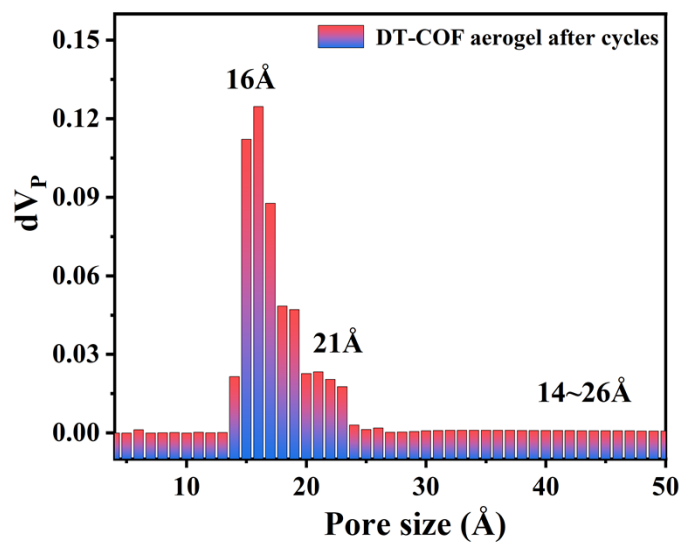


Fig. S10 Pore size distribution (PSD) profile calculated from NLDFT of DT-COF aerogel after 1000 cycles.

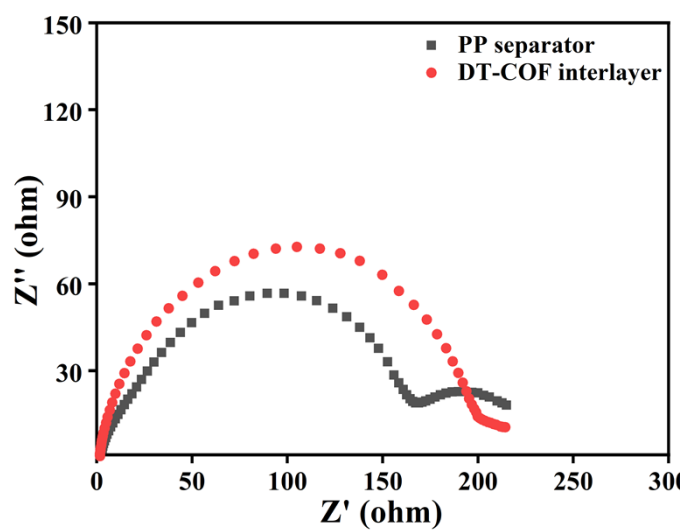


Fig. S11 EIS spectra of Li symmetric batteries with PP and DT-COF aerogel interlayer.

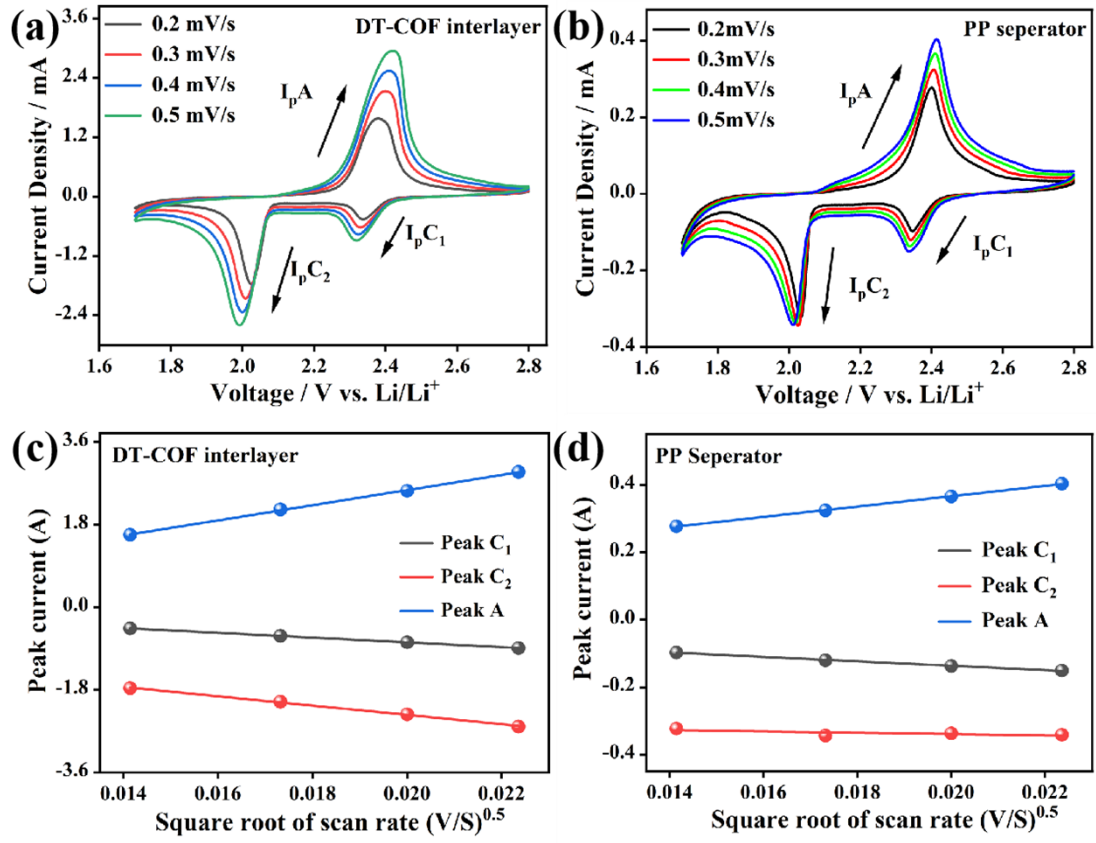


Fig. S12 CV curves of different separator at different scan rates (a) PP separator and (b) DT-COF aerogel interlayer. CV peak current (c) PP separator and (d) aerogel interlayer versus square root of scan rates.

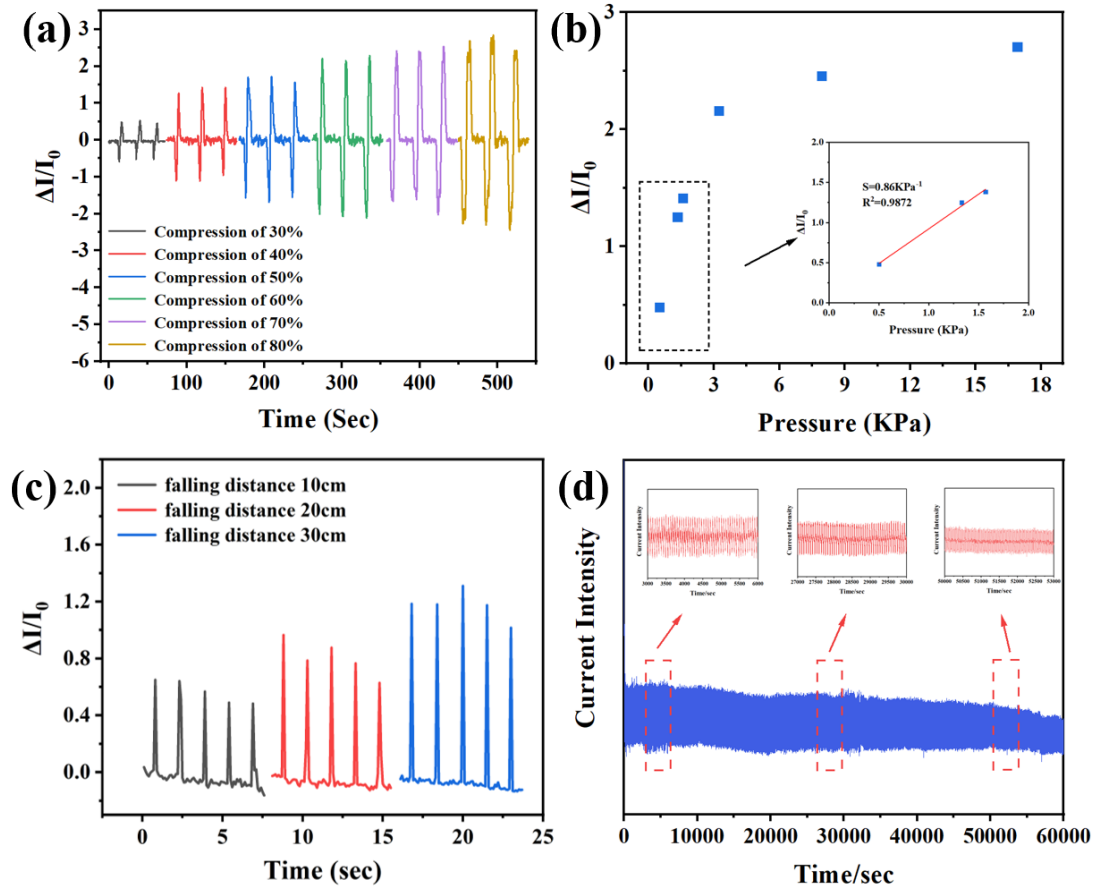


Fig. S13 (a) Current change versus time curves of DT-COF aerogel for loading-unloading at different pressures. (b) The sensitivity of DT-COF aerogel under different pressures. (c) Current change of DT-COF aerogel when water drops fall from different heights (10-30cm). (d) Current change versus time curve of DT-COF aerogel for 2600 cycles repeated loading-unloading tests at 60% compressive strain.

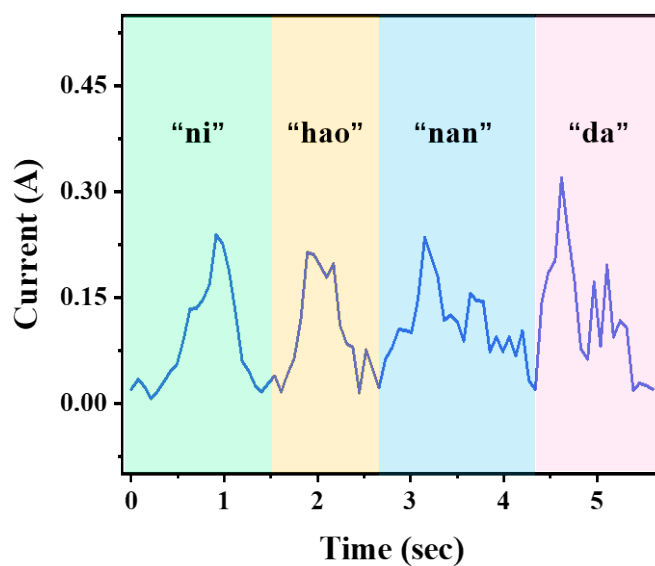


Fig. S14 Signals for pronunciations of “ni hao nan da” (Chinese abbreviation for ‘Hello, Nanjing University’) of DT-COF aerogel.

Table S1 Elemental analysis of DT-COF aerogels.

	C wt.%	N wt.%	H wt.%
Theoretical value	80	15.56	4.44
Experimental value	75.38	15.21	6.74

Table S2 Fractional atomic coordinates of DT-COF aerogels.

Atom	X	Y	Z
C1	1.18326	-0.41573	0.31133
N2	1.22162	-0.44994	0.2504
C3	1.29258	-0.41277	0.14877
N4	1.32641	-0.3389	0.11004
C5	1.28842	-0.30349	0.16565
N6	1.21757	-0.34269	0.26639
C7	1.32471	-0.45533	0.07987
C8	1.39806	-0.42976	-0.00825
C9	1.42445	-0.47684	-0.10585
C10	1.37805	-0.54822	-0.23513
C11	1.40392	-0.59662	-0.29432
C12	1.47719	-0.57623	-0.22242
C13	1.52519	-0.50295	-0.12208
C14	1.49937	-0.45386	-0.06939
C15	1.1094	-0.45267	0.40358

C16	1.31525	-0.22881	0.11538
C17	1.38717	-0.1748	0.0277
C18	1.06674	-0.52879	0.44711
C19	1.49626	-0.63126	-0.24167
C20	1.5618	-0.62614	-0.12686
C21	1.57086	-0.68728	-0.10039
N22	1.51817	-0.75492	-0.19633
C23	1.52498	-0.81492	-0.15546
N24	1.58851	-0.80583	-0.01951
C25	1.64287	-0.73863	0.08016
N26	1.63262	-0.68055	0.03809
C27	1.46277	-0.88184	-0.24141
C28	1.70902	-0.72793	0.21855
C29	1.76052	-0.66085	0.36878
C30	1.8349	-0.6354	0.43685
C31	1.87185	-0.6729	0.33888
C32	1.94839	-0.63849	0.36141
C33	1.99014	-0.56583	0.48282
C34	1.95235	-0.53192	0.61896
C35	1.87625	-0.56582	0.59316
H36	1.29091	-0.51046	0.10239
H37	1.43418	-0.37504	0.01482
H38	1.32441	-0.56653	-0.28995
H39	1.36758	-0.64788	-0.38335
H40	1.57936	-0.48427	-0.08147
H41	1.53567	-0.40168	0.00762
H42	1.08527	-0.42142	0.42706
H43	1.2776	-0.2124	0.14864
H44	1.42616	-0.19007	0.03729
H45	1.09194	-0.55927	0.43024
H46	1.45707	-0.68115	-0.33352
H47	1.60383	-0.57716	-0.04477
H48	1.42085	-0.87558	-0.34091
H49	1.71952	-0.76999	0.20517
H50	1.74226	-0.62543	0.42673
H51	1.84423	-0.72451	0.23876
H52	1.97348	-0.66636	0.27638
H53	1.97953	-0.4816	0.73357
H54	1.85159	-0.53798	0.68471
C55	0.40811	0.89853	-0.05823
C56	0.48395	0.95383	-0.04185
C57	0.50455	1.02818	-0.10519
C58	0.3536	0.91687	-0.15606

C59	0.37396	0.99021	-0.22451
C60	0.44908	1.04598	-0.192