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Supporting Information

Superelastic and Ultralight Polyimide Aerogels as Thermal Insulators and Particulate Air Filters

Zhenchao Qian, Zhen Wang, Yi Chen, Shengrui Tong, Maofa Ge, Ning Zhao and Jian Xu**

Experimental section

Materials:

Pyromellitic dianhydride (PMDA, 99%), paraformaldehyde (96%) and Bisphenol-A (97%) were purchased from Acros. PMDA was dried at 150 ^{o}C under vacuum for 3 h prior to use. Aniline (99.5%) was supplied from J&K and 4,4'-oxydianiline (ODA, 98%) was obtained from Alfa Aesar. Trichloromethane, 1,4-dioxane, sodium hydroxide, anhydrous magnesium sulfate of analytical grade were purchased from Beijing Chemical Works. *N*,*N*-Dimethylacetamide (DMAC, 99.8%, water $\leq$ 50 ppm) was product from Innochem. Unless otherwise specified, all commercial reagents were used as received.

Preparation of PI nanofibers:

ODA (4.0 g, 20 mmol) was dissolved in DMAC (60.0 g) at 0 ^{o}C under N_2 atmosphere. PMDA with a 2 mol % excess was portion-wise added into the solution in 2 hours under vigorous stirring. After stirring for 12 hours, a light yellow viscous solution containing 12 wt % PAA was obtained and stored at -4 ^{o}C.

Electrospinning was carried out using a TL-01 spinning machine (Shenzhen Tongli Weina Technology Co. LTD, China). The PAA solution was spun from a syringe equipped with a 21 gauge needle at a feeding rate of 0.2 mL h^{-1}. A drum covered by aluminum foil rotated at 500 rpm for collecting nanofibers. The distance between the spinneret and the collector was 20 cm and the applied voltage was set at 14 kV. A constant temperature of 30 ^{o}C was maintained during the electrospinning. Then, the electrospun nanofiber membranes were thermally imidized by heating up to 100, 150, 200, 250 and 300 ^{o}C at a rate of 5 ^{o}C min^{-1}, and staying at each temperature stage for 0.5, 0.5, 0.5, 1 and 1 h, respectively.

Fabrication of PINFAs:

A typical procedure for the fabrication of PINFAs is as follows: 0.12 g polyimide nanofiber membranes were cut into pieces and added to 1,4-dioxane (30 g). The mixture was homogenized by a homogenizer at 5,000 rpm for 2 h to form a uniform dispersion. Then, the mixture was poured into a mold, frozen at -4 ^{o}C for 2 h, subjected to freeze-drying for 24 h and then heated at 500 ^{o}C for 15 min in air.

Synthesis of benzoxazine:

Benzoxazine was synthesized according to the literature.[1] Bisphenol-A (22.8 g, 0.1 mol), paraformaldehyde (12.1 g, 0.4 mol), and aniline (18.6 g, 0.2 mol) were added in a round-bottomed flask and stirred at room temperature for 20 min. The mixture was then refluxed for 4 h in the flask equipped with a condenser, followed by the addition of 200 mL of trichloromethane. The solution was washed three times with 1 wt% NaOH aqueous solution, and several times with distilled water until a neutral pH value was showed. The organic phase was dried with anhydrous magnesium sulfate and filtered. The solvent was removed under reduced pressure to obtain benzoxazine as yellowish powder.

Fabrication of un-PINFAs and pbo-PINFAs:

The fabrication of un-PINFAs was same as that of PINFAs except the heat treatment. A typical procedure for the fabrication of pbo-PINFAs is as follows: 0.024 g benzoxazine monomer was added into the PI nanofiber dispersion mentioned above. The mixture was frozen at -4 ^{o}C for 2 h, and followed by freeze-drying for 24 h. The obtained monolith was heated at 200 ^{o}C for 2 h to cross-link the benzoxazine.

Fabrication of carbonized un-PINFAs:

Carbonization was carried out in a furnace at 1000 ^{o}C for 1 h with a heating rate of 10 ^{o}C min^{-1} in a flow of N_2.

Characterization:

Scanning electron microcopy (SEM) was performed on a JEOL JSM-7500F at an accelerating voltage of 5 kV. The specific surface area was determined by Quantachrome NOVA 1200e. The aerogels were degassed at 150 ^{o}C for 12 h prior to N_2 adsorption/desorption measurements at 77 K. The surface area was obtained from the adsorption curve by the Brunauer-Emmet-Teller (BET) method. Thermal conductivity was measured on a Hot Disk 2500s thermal constants analyzer, which was based on transient plane sources. The skeletal density was measured by UltraPYC 1200e automatic density analyzer (Quantachrome). The porosity of PINFAs was determined by the following formula:

$$\text{Porosity}(\%) = (1 - \rho / \rho_s) \times 100\%$$

where ρ was the density of the aerogel, and ρ_s was the skeletal density.

The compression and tensile tests were performed on Instron (model 3365) equipped with 100-N and 10-kN load cells. For compression tests, cylindrical samples with diameters of ~18 mm and lengths of ~22 mm were employed, and the strain rate was 10 mm min^{-1}. A 1000-cycle loading-unloading fatigue test was conducted at a strain of 80% and a strain rate of 50 mm min^{-1}. Tensile tests were measured at a loading speed of 5 mm min^{-1} using dumbbell-shaped samples about 10 mm in width and 10 mm in thickness. The Young's modulus was taken as the slope of the initial linear portion of the stress-strain curve. Thermogravimetric analysis was operated on Pyris 1 TGA (PerkinElmer, America) at a heating rate of 10 °C min^{-1} from 50 to 800 °C in air or nitrogen stream with a flow rate of 20 mL min^{-1}. Normal incidence sound absorption was measured on PINFAs with thickness of 10 mm by type SW 466 Impedance Tubes, a production of BSWA Technology Co., Ltd. (China), according to the ISO10534-2 standard (ISO, 1998). ATR-FTIR spectra were collected with a BRUKER TENSOR 27 FTIR spectrometer. Raman spectra were obtained on a DXR Raman microscope (Thermo Fisher Scientific Inc.). XPS measurements were carried out with a Thermo Scientific ESCALAB 250Xi using 200 W monochromated Al Kα radiation.

Evaluation of filtration performance: Heavily polluted air in hazy days in Beijing (21±3 ^{o}C, 20±10% relative humidity, February 2017) with concentration of $PM_{2.5}$ above 200 μg m^{-3} was fed at a velocity of 0.25 m s^{-1} through a piece of sample immobilized by a flange. The concentration of $PM_{2.5}$ was tested by TSI Dusttrak^{TM} II Aerosol Monitor 8532 handheld. The filtration efficiency was calculated using the following equation:

$$Filtration\ efficiency\left(\%\right) = (C_0 - C) / C_0 \times 100\%$$

where C_0 and C represent the mass concentration of $PM_{2.5}$ before and after filtration, respectively. Pressure drop was tested by TSI 8130 (TSI Inc., MN, USA) with a velocity of 0.18 m s^{-1}. The number concentration of $PM_{2.5}$ in the range of 15 - 685 nm before and after filtration was evaluated by Scanning Mobility Particle Sizers (SMPS, including a differential mobility analyzer (DMA, TSI 3081), a condensation particle counter (CPC, TSI 3776), and an electrostatic classifier (EC, TSI 3080)).

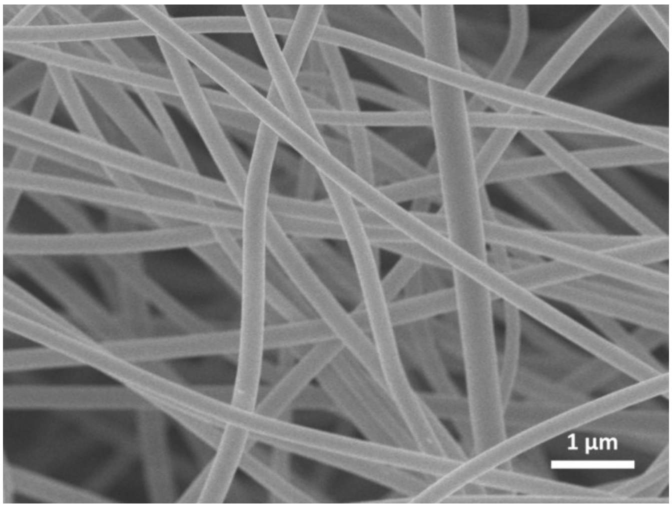

Figure S1. SEM image of PI nanofibers with an average diameter of 235±50 nm.

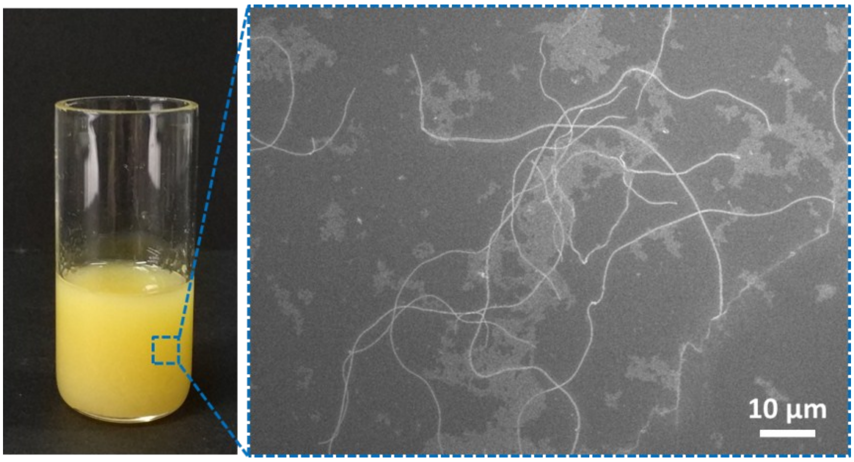

Figure S2. Photograph of the dispersion of PI nanofibers in dioxane and SEM image of the PI nanofibers cast on the glass from the dispersion.

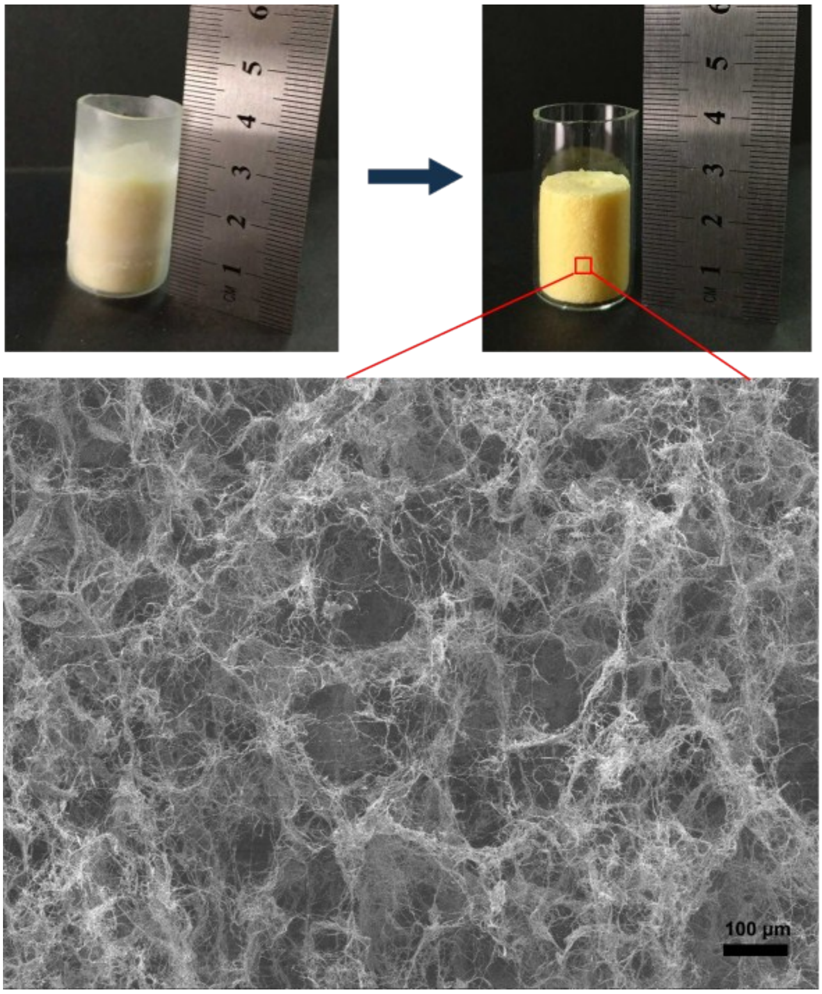

Figure S3. Photos showing the little volume change between the frozen dispersion and the freeze-dried monolith. SEM image of the resultant fibrous cellular architecture.

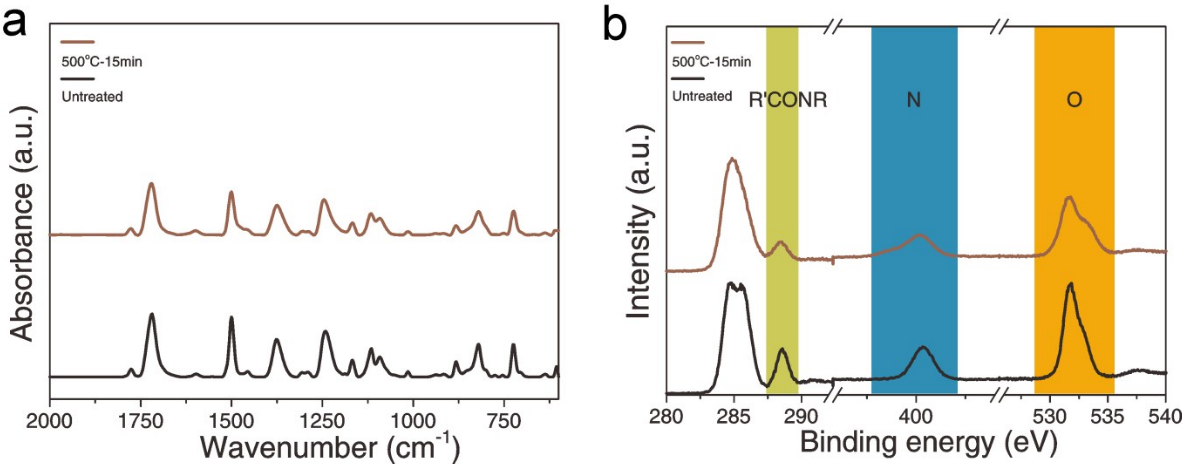

Figure S4. (a) ATR-FTIR and (b) XPS spectrum of PINFAs and un-PINFAs.

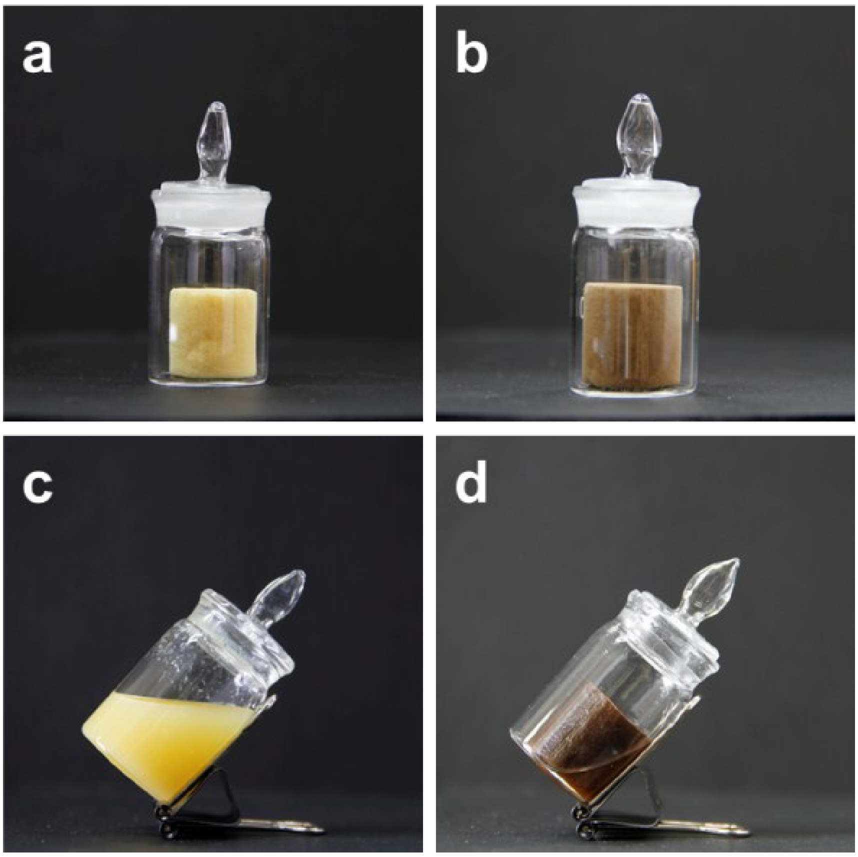

Figure S5. Photographs of (a) un-PINFAs, (b) PINFAs, and (c) un-PINFAs and (d)

PINFAs after sonification in dioxane.

Table S1. The porosity of PINFAs with different densities. [a]

ρ (mg cm^{-3})	4.6	9.4	13.1
Porosity (%)	99.6	99.3	99.0

[a] The skeletal density of PINFA is 1.31 g cm^{-3}.

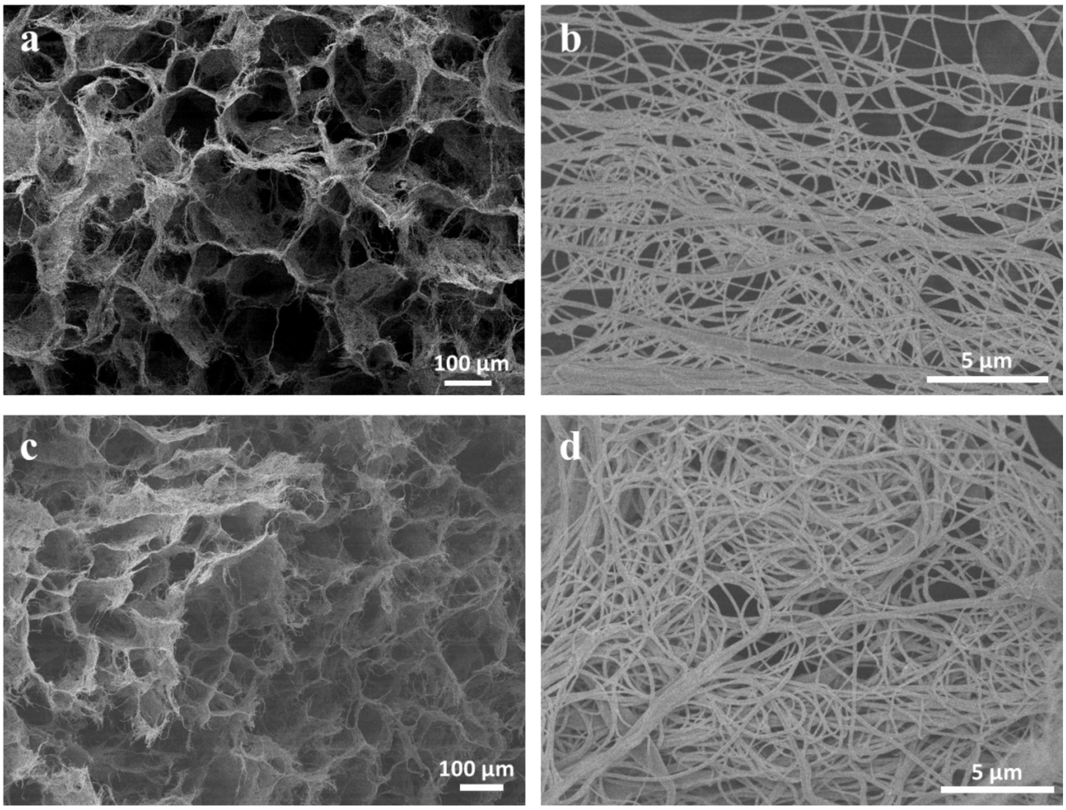

Figure S6. SEM images of PINFAs with a density of 9.4 (a, b) and 13.1 mg cm^{-3} (c, d), respectively.

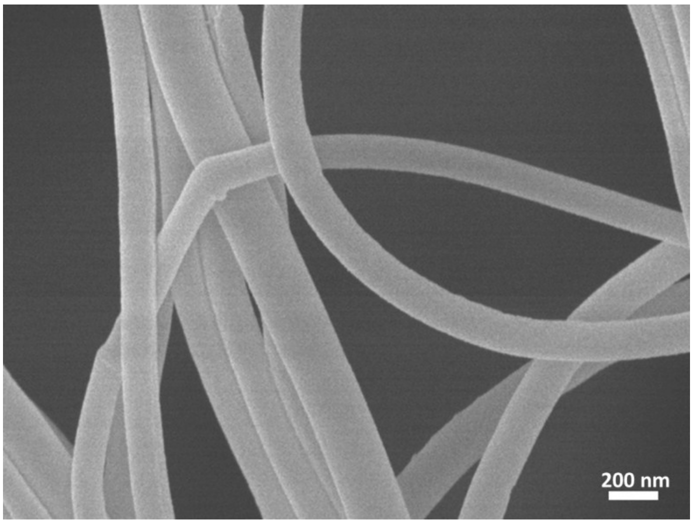

Figure S7. SEM image of un-PINFAs without bonding between nanofibers.

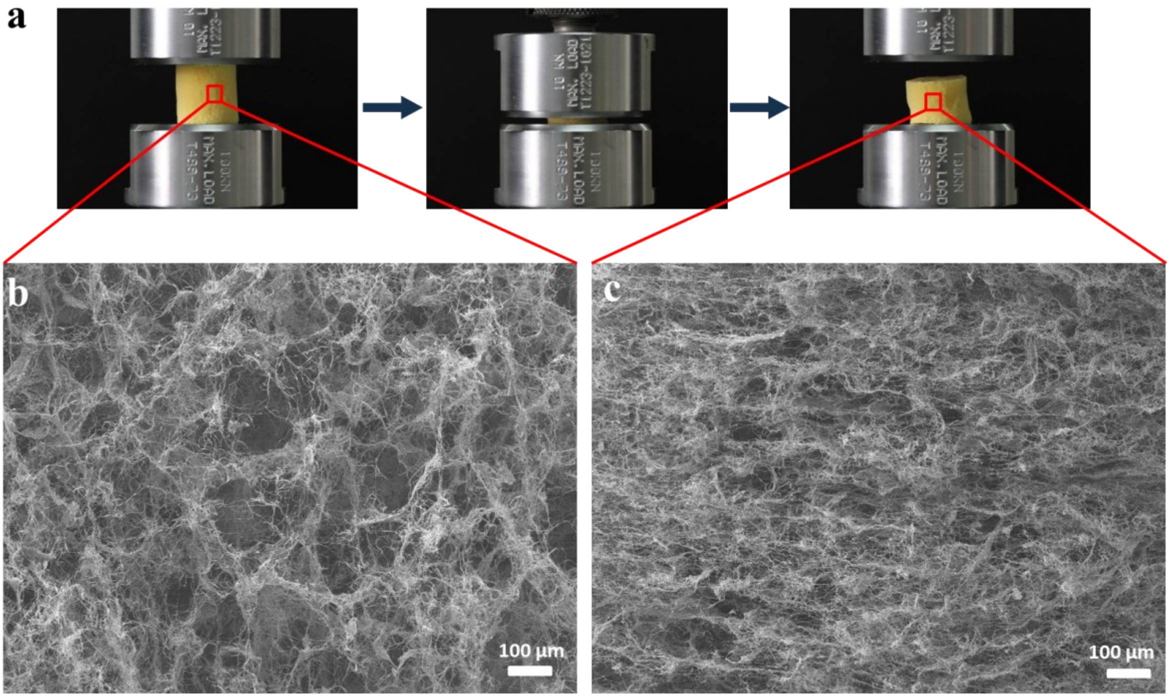

Figure S8. (a) Photographs of un-PINFAs partially recovered from a 90% compressive strain. SEM images of the sample before (b) and after compression (c).

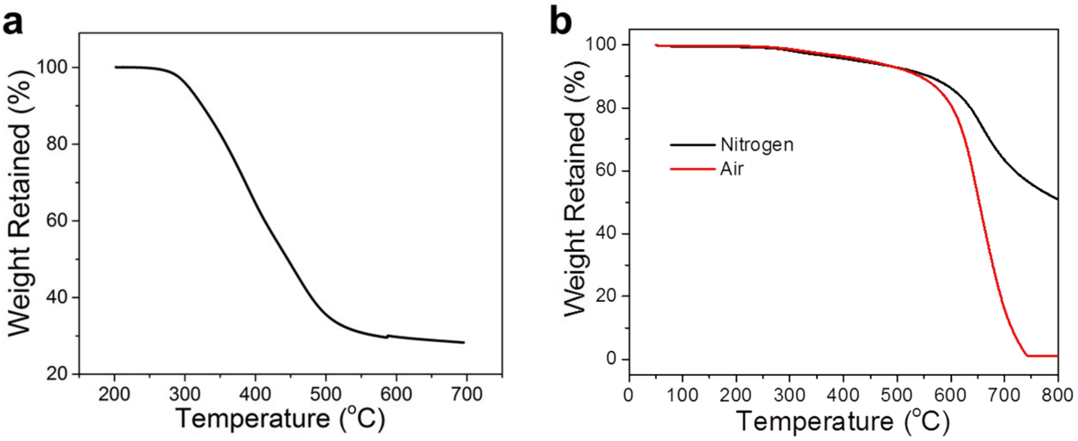

Figure S9. TGA curves of (a) the crosslinker polybenzoxazine under nitrogen atmosphere and (b) pbo-PINFAs under nitrogen and air atmosphere.

Table S2. Mechanical performances of different PINFAs.

Samples	Density ($mg\ cm^{-3}$)	Young's modulus (kPa)	Stress at 90% strain (kPa)	Plastic deformation (%)
un-PINFAs	5.6	2.6±0.9	11.1±1.3	30±3
pbo-PINFAs	5.4	2.9±0.7	17.2±2.8	7±1
PINFAs	4.6	6.1±1.5	19.6±3.0	0

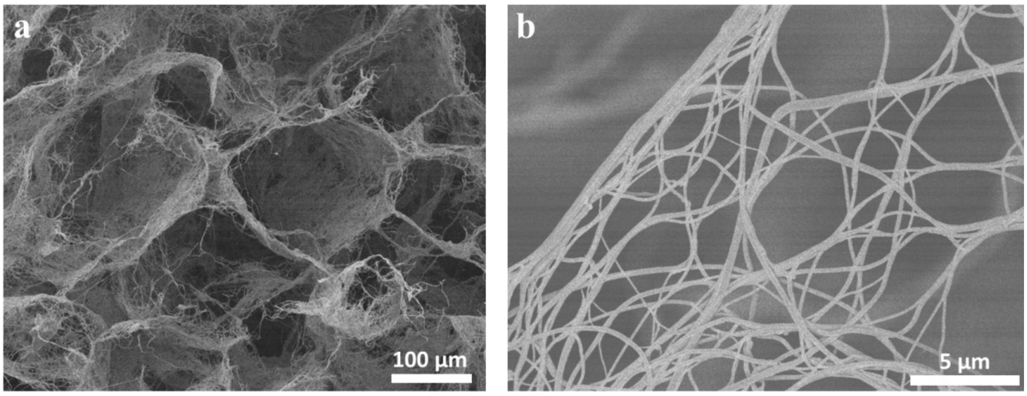

Figure S10. SEM images of PINFAs after 1000 loading-unloading fatigue compressive cycles at ε of 80%.

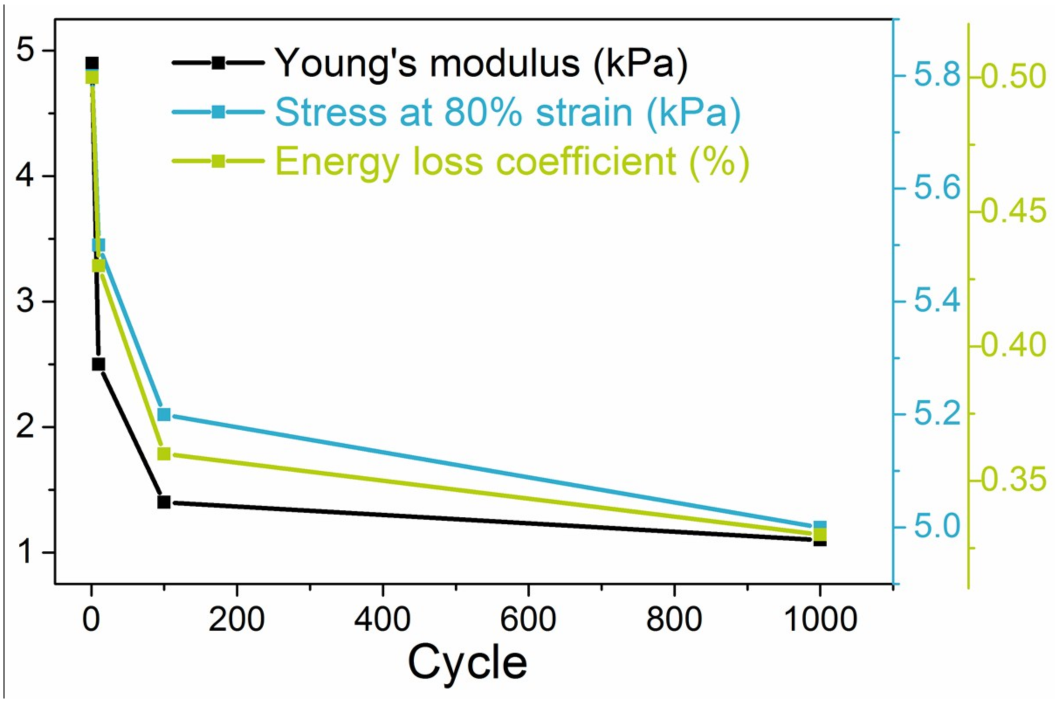

Figure S11. Variation of energy loss coefficient, Young's modulus and stress at ε of 80% of PINFAs during 1000 cycles.

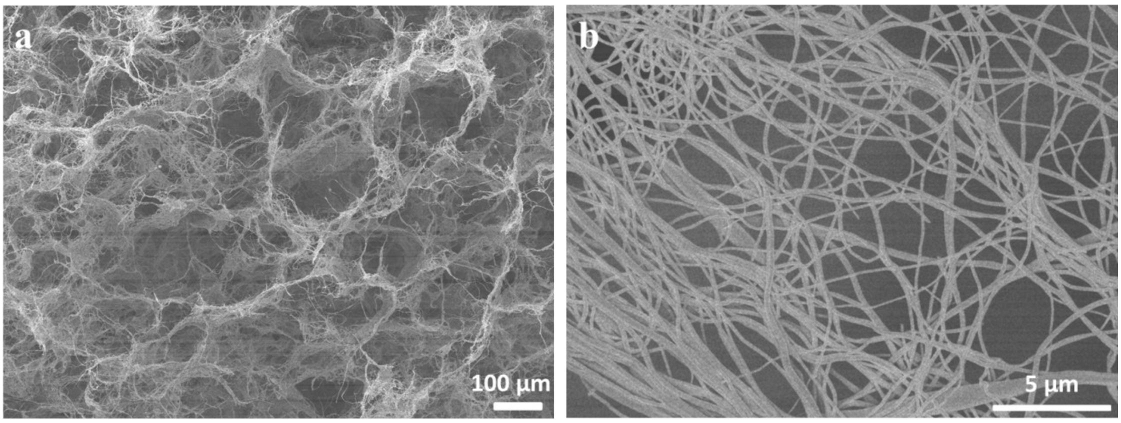

Figure S12. SEM images of PINFAs after 500 loading-unloading fatigue tensile cycles at ε of 5%.

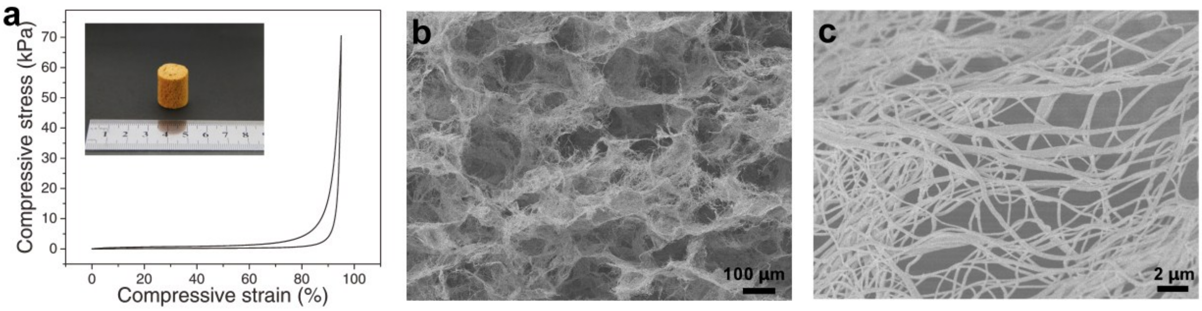

Figure S13. (a) Compressive stress-strain curves of PINFAs after being heated at 300 ^{o}C for 240 h. The Young's modulus is 5.5 kPa and the stress at ε of 95% is 70.0 kPa. The inset shows the macroscopic shape of the sample after the thermal treatment. (b, c) SEM images of the sample after the thermal treatment.

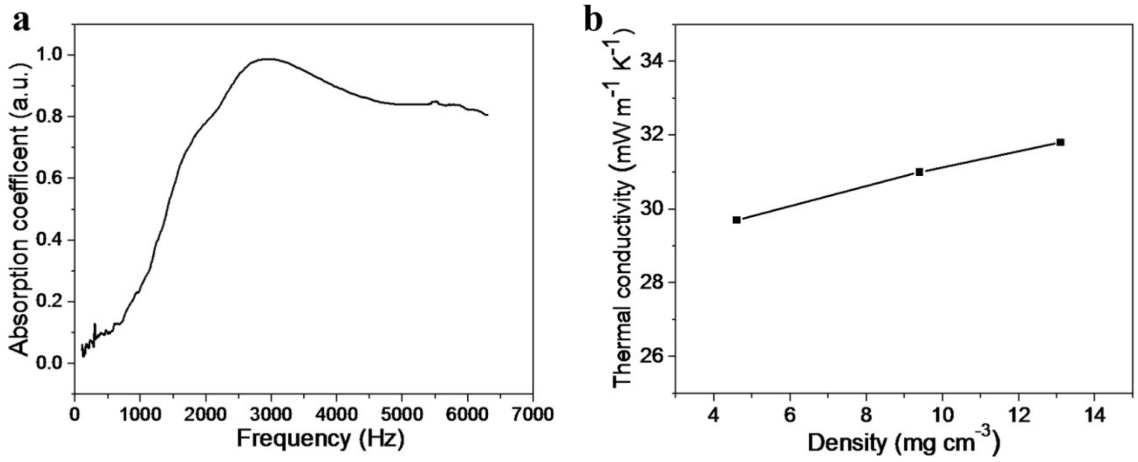

Figure S14. (a) Acoustic absorption coefficient for PINFAs. (b) Thermal conductivity of PINFAs with different densities at ambient condition.

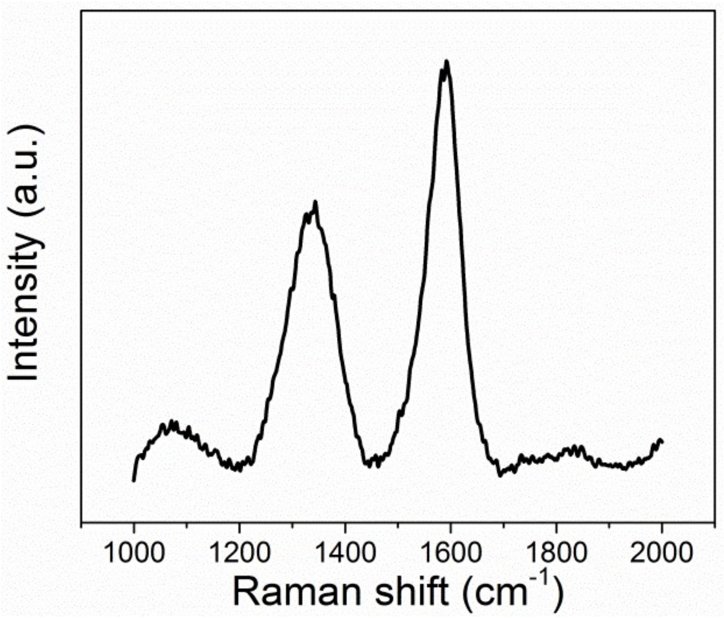

Figure S15. Raman spectrum of carbonized PINFAs. I_D/I_G is 0.65, implying an abundant sp^2-carbon content and good electric conductivity.

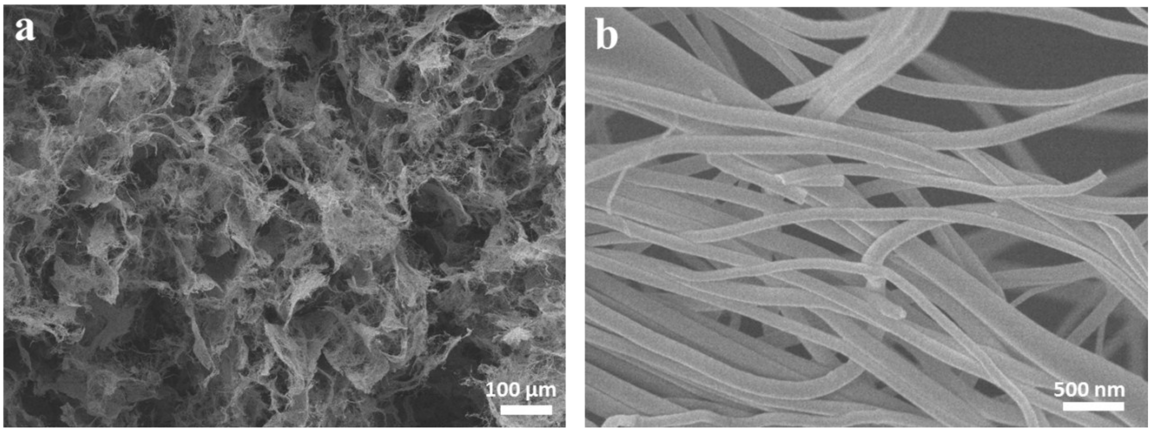

Figure S16. SEM images of carbonized PINFAs. A weight loss of 51.3±1.8 wt % and a volume shrinkage of 40.5±1.9% occurred after carbonization, giving the resultant carbonized aerogel with a density as low as 4.6 mg cm^{-3}, and the cellular architecture was retained.

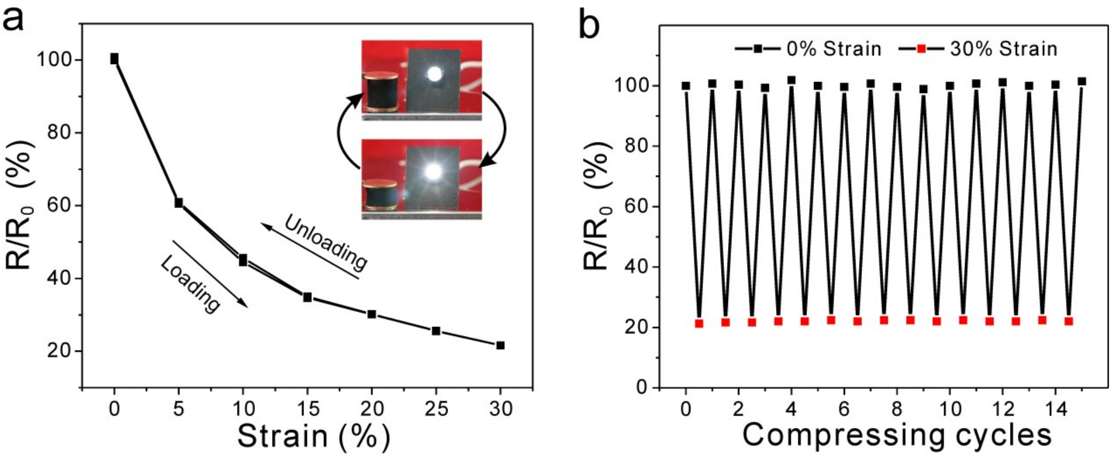

Figure S17. (a) Normalized resistance of the carbonized aerogels varies under loading-unloading cycle with strain of 30%. Inset: photographs showing the LED was brightened on compression and recovered on release of the carbonized aerogels. (b) Variation of R/R$_0$ during 15 cycles of compression.

Reference:

(1) X. Ning and H. Ishida, *J. Polym. Sci., Part A: Polym. Chem.*, 1994, **32**, 1121-1129.