
Biomimetic spinning of soft functional fibres via spontaneous phase separation

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Supplementary Methods

An optical microscope (OM), Nikon Eclipse LV1000 equipped with Digital Sight DS-U1, was used to record the phase transition of the precursor PANSion fiber under ambient conditions (75% RH at 24 °C). An image stitching process was conducted so that a long-range view of PANSion fiber with solvent droplets on it could be observed. Universal tensile tests were carried out to assess the mechanical properties of fibers. Note that the sandpaper tabs were attached to both ends of the fiber samples to ensure a good grip force during testing. The sample gauge length was set to 20 mm. The sample diameter was calculated based on the OM images. The testing speed was set at 50 mm/min. Testing speeds from 10, 100, to 1000 mm/min were used to assess the strain-rate-dependent effect. Cyclic tensile tests were conducted at 50 mm/min on the same sample, from 10 to 300% strain, consecutively. For the low-temperature durability test, PANSion fiber was first stretched at room temperature and then immersed into a liquid nitrogen bath (−196 °C) for 30 s. Subsequently, the fiber was lifted out of the liquid nitrogen bath. Immediately, the frozen fiber recovered its mechanical property and could be stretched again at room temperature. Differential scanning calorimetry (DSC 25, TA Instruments) was conducted in the temperature range from −50 to 25 °C at a ramping rate of 5 °C/min under a nitrogen environment, from which the glass transition temperature (T_g) was derived. Thermogravimetric analysis (TGA, Q50, TA Instruments) was carried out in the temperature range from 50 to 600 °C at a ramp rate of 10 °C/min.

Field-emission scanning electron microscopy (FE-SEM, Zeiss Supra 300 equipped with Oxford Ultim Max silicon drift detector) was used for observing the surface and cross-section morphologies. 3 kV of accelerating voltage was used to avoid any possible sample degradations or damage. While 10 kV was used for energy dispersive X-ray (EDX) analysis because of the relatively high absorption energy of silver at the L-edge. Transmission electron microscopy (TEM, JEOL JEM 2010F at 200 kV) was used to verify the existence of silver nanoparticles (AgNPs). TEM samples were prepared via a microtome cutting approach, where fibers were embedded in a resin (epoxy embedding medium kit from Sigma-Aldrich). Ultraviolet-visible (UV-Vis) spectra were recorded from 800 to 200 nm using the model Agilent Cary 5000. Fourier-transform infrared (FTIR) spectra were recorded using Agilent Cary 600 from 400-4000/cm.

Nanowizard 4 atomic force microscopy (AFM, JPK Germany) was used to conduct the single-molecule force spectroscopy (SMFS) experiments at room temperature. AFM cantilever (MLCT-Bio-DC, Bruker, United States) with a spring constant (k) of ~40 pN/nm was used. The equipartition theorem was used to calibrate the k of each cantilever in a solution with an accurate value before the experiment. Typically, an 800 μ L solution was added to a clean glass coverslip for AFM-SMFS measurement. First, the cantilever contacted the surface with an indentation force of ~1 nN for 1 s and randomly picked up a molecule. Then, the cantilever moved up vertically, in which the captured PAN or PANSion molecular chain was stretched. Finally, the chain broke upon further stretching, leading to a rupture force peak in the force-extension curve. Igor Pro 6.12 (WaveMetrics 486 Inc.) was used for AFM-SMFS data analysis, and the worm-like-chain (WLC) model was used to fit the data as an interpretation of polymer elasticity.

Rheological properties of spinning dopes were characterized using a Rheometer (Anton Paar, MCR 302) with a parallel plate of Ø25 mm in the shear rate range. First, the viscosity characterization was conducted in the shear rate range from 0.1 to 1000 1/s, from which data were fitted using a Carreau-Yasuda model¹⁻³:

$$\eta = \eta_0 \times [1 + (\dot{\gamma}\tau)^a]^{\frac{n-1}{a}} \quad (1)$$

where τ is the relaxation time of viscoelastic fluids ($\tau = 1/\dot{\gamma}_c$, $\dot{\gamma}_c$ is the critical shear rate of the onset of shear-thinning). n is the characteristic power-law exponent at high shear rates, and the coefficient a describes the transformation between the zero-shear-rate region and the power-law region. An oscillatory amplitude sweep was done at a constant angular frequency of 0.628 rad/s in the strain range of 0.1–2000%. An oscillatory frequency sweep was done at a controlled shear strain of 1% over the frequency range of 0.1–200 rad/s. Step-strain characterization was done on a sample after 96 hours of curing by alternating strains between 5% and 1000%. The electrical conductivity (ρ) of PANSion fiber was calculated based on the following equation:

$$\rho = \frac{\pi d^2 R}{4L} \quad (2)$$

where L is the length, R is the electrical resistance, and d is the diameter of fibers. All resistance and capacitance data were collected using a Keithley multimeter (Model 2450).

The energy saving from polymer melting via a thermal drawing or extrusion process was calculated using the following equation:

$$W_{melting} = \rho_{polymer} \cdot C_{p(polymer)} \cdot T_{melting (polymer)} \quad (3)$$

Typical elastomers were selected as examples and the corresponding results were listed in **Supplementary Table 2**.

Supplementary Text 1

Comparison between PANSion and other typical polymer elastomers

The results were plotted in **Supplementary Figure 2**. Note that polyacrylonitrile (PAN) fiber or the film itself is not stretchable (failure strain < 1% via wet spinning approach in our study) nor conductive. To obtain a highly stretchable fiber, we started with PAN polymer and silver ions to synthesize the PANSion. As demonstrated in the main text, PANSion fiber is highly stretchable. At the same time, conductivity was also achieved which did not require any additional processing from the synthesis. In contrast, the typical elastic polymer as shown in the figure (including styrene-ethylene-butylene-styrene (SEBS), polydimethylsiloxane (PDMS), polyurethane (PU), etc) is usually a pure polymer system. But the synthesis of these elastomers is even more complicated than that of our PANSion. More importantly, only mechanical softness and stretchability can be achieved with a very low electrical conductivity for those elastomer. For instance, while synthesizing the PDMS from monomers of dimethyldichlorosilane, only mechanical stretchability can be obtained but no conductivity. Therefore, we assigned the stretchability and the conductivity as intrinsic properties to PANSion (to put it in another way, PANSion is similar to conducting polymer in terms of conductivity but with a high stretchability, see b and c in the figure).

For energy cost, since no melting process is involved with our approach, there is nearly no energy consumption (theoretically) during the spinning process via the manual stretching (human labor is not considered for simplification). Note that energy input is needed when preparing the PANSion spinning solution from the magnetic stirring for our case. Heating is not needed as PAN and silver nitrate (AgNO_3) are quite soluble in DMF. For most other fiber spinning methods, a large quantity of energy is still required during the spinning process. For instance, for the thermal drawing method, melting is usually required to draw a fiber which is an energy-intensive process (see details in Method and Supplementary Table 2). For wet spinning, sometimes a specific temperature must be maintained for the coagulation bath to sufficiently solidify the precursor fibers. Another disadvantage of wet spinning is the need for a coagulation bath which usually consumes a large quantity of water, salt solutions, or a mixture of water and organic solvents. Note that a small volume of DMF is needed when preparing the PANSion spinning solution. The stretchability of PANSion fibers is comparable to most elastic polymer fibers. Another advantage of PANSion fibers is the intrinsic conductivity which is usually obtained via multi-step post-treatments for previously published results.

When comparing our spinning method to other published results of directly drawing fibers in air, the significant difference is that we achieved unified heterogeneous functions of high stretchability and conductivity simultaneously. To the best of my knowledge, our work is the first study on the ambient-conditions spinning technique for functional soft fiber preparation via a single-step spinning process. For instance, Wu et al.⁴ reported a spinning dope consisting of supramolecular polymer–colloidal hydrogels that can be drawn into fibers at room temperature. However, it required the addition of silica nanoparticles and the obtained fibers displayed limited stretchability or conductivity, which impeded

their applications in wearable electronics. Zhao et al.⁵ found that a sodium polyacrylate hydrogel fiber can be prepared by drawing in air but it was not stable when in contact with water, which brought about complications on additional post-treatments. Overall, our ambient-condition spinning approach, to produce functional soft fibers under ambient conditions with unified mechanical and electrical properties, is of great interest and will advance other scientific fields more broadly, such as green fabrication, sustainable fiber electronics, smart textiles electronics, artificial spinning techniques, percolated conductive polymer, and coordination complex chemistry, etc.

Supplementary Text 2

Preparation of PANSion gel dope

To achieve good ambient-conditions spinnability, the viscosity of the dope is critical and purposely adjusted. We found that the concentration of PAN solutions and the addition of AgNO_3 are two important factors. First, for the base solution of PAN, a too-thin (<5 wt%) or too-thick (>15 wt%) solutions is not capable of forming a stable thread during the mechanical stretching because of capillary instability or cohesive failure. Although 10 wt% PAN solution is unstable to support the continuous fiber drawing under ambient conditions, this concentration can be easily achieved at room temperature, which also possesses an appropriate viscosity. On the one hand, the medium concentration was high enough to achieve a viscous solution. On the other hand, it was also in an appropriate range of the weight ratio between PAN and DMF. Thus, the powder of PAN can be easily dissolved into DMF at room temperature by mechanically stirring. Thus, we selected the 10 wt% PAN solution as the base solution for our following studies. Second, we noticed that the weight ratio with a value of 2:1 between AgNO_3 and PAN (namely, 1.177 M Ag^+ in 10 wt% PAN solution) is appropriate to establish a strong and dynamic supramolecular network after a specific time of room-temperature curing as reported elsewhere⁶. In fact, for the ratio of 2:1, the density of crosslinking via $[\text{Ag}(\text{N}\equiv\text{C}-)_x]^+$ complexes is sufficient to produce a favorable entangled network structure. Third, when extending the curing time at room temperature, we observed a continuous increase of viscosity, storage, and loss modulus via rheological measurements, which confirmed that the formation of $[\text{Ag}(\text{N}\equiv\text{C}-)_x]^+$ complex is done at a slow reaction rate. In another word, during the room-temperature curing, the silver-coordinated supramolecular structure gradually grew, forming a strong and dynamic structure. Consequently, after an appropriate time of curing at room temperature, the PANSion gel dope became viscoelastic and highly drawable, achieving a good spinnability.

Therefore, by varying the room-temperature curing time, the properties of PANSion solutions can be adjusted, such as the entanglement density of the supramolecular chain network via $[\text{Ag}(\text{N}\equiv\text{C}-)_x]^+$ complexes. Once an appropriate viscosity is reached for the spinning dope, the continuous drawing of a precursor PANSion gel fiber can be realized under ambient conditions (75% RH, ~ 24 °C). This approach is referred to as phase separation-enabled ambient (PSEA) spinning. Note that a too-high or too-low crosslinking density of the supramolecular network may lead to poor spinnability.

It is important to point out here that the spinnability of PANSion spinning solution is dictated by a combination of a few factors, e.g., the concentration of silver ions (Ag^+), the curing time, the curing temperature, the PAN polymer concentration, storage conditions, and shelf life, etc. In our current work, we explored the influence of curing time on the spinnability while the curing temperature, Ag^+ concentration (1.177 M), and PAN polymer concentration (10wt%) were fixed. Generally, the influence of the curing temperature, Ag^+ concentration, and PAN polymer concentration on the spinnability was obvious. For instance, in our current study, we noticed that a PAN solution of 2 wt% is too thin to obtain a spinnable gel dope because of the insufficient inter- or intrachain interactions. The curing temperature

can be raised so that a high crosslinking rate via $[\text{Ag}(\text{N}\equiv\text{C}-)_x]^+$ complexes is expected. That is to say, the high viscosity of the spinning dope can be achieved in a short time. Meanwhile, the Ag^+ concentration may also show an impact on the viscosity as a higher concentration of Ag^+ indicates a possible higher density of the crosslinker, $[\text{Ag}(\text{N}\equiv\text{C}-)_x]^+$ complexes. Furthermore, the interaction among these factors on the spinnability is also very interesting but is challenging to investigate. For instance, the viscosity of spinning solutions was continuously increased when extending the curing time regardless of the curing temperature or Ag^+ concentration. But insufficient curing or over-curing on the spinning solution would result in no spinnability either because the solution is too thin, or gelation occurs. That is to say, one can obtain a suitable spinnability by controlling the combination of the factors mentioned above. Another thing worth mentioning here is that the time window for spinning is also important for potential industrial production. For instance, the room temperature curing for ~ 72 h could generate a spinnable dope, which maintains good spinnability even after ~ 24 hours of room temperature storage. Although high-temperature curing (*i.e.*, $50\text{--}60$ °C) may shorten the preparation time of the spinning solution, it may also limit the time window for smooth spinning under ambient conditions. These results confirm that room-temperature curing would allow a wider time window to work with the dope but require a longer time to reach the optimal spinnability. Nevertheless, more work is still needed to elaborate on the interactions among these factors for the spinning solution.

Supplementary Text 3

CG-MD simulation

To assess large temporal and spatial scales, we performed molecular dynamics (MD) simulations with coarse-grained (CG) models, which took a group of atoms as a bead (**Supplementary Figure 25a**). Specifically, PAN was represented by a bead-spring model with one monomeric unit as one bead (type A). A Ag^+ was modeled along with a NO_3^- as one bead (type B). A bead of type C represented a DMF molecule. A water cluster consisting of four molecules was taken as a bead of type D. In CG-MD simulations, the reduced unit of length was $\sigma_0 = 0.52$ nm, corresponding to the diameter of the PAN monomeric unit. The reduced units of energy, mass, and time were $\epsilon_0 = k_B T$ with $T = 550$ K, $m_0 = 53$ amu, and $\tau_0 = 1.63$ ps, respectively. The non-bonded interactions between CG beads were described by Lennard-Jones (9-6) potential⁷:

$$V_{\text{LJ}}(r) = 6.75\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^9 - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (4)$$

where r_{ij} is the distance between beads i and j , and the interaction parameters ϵ_{ij} and σ_{ij} are listed in **Supplementary Table 5**. Note this potential was truncated at $r_{\text{cut}} = 3.0 \sigma_0$.

The harmonic potential was employed to describe bond stretching interactions in the bead-spring model of PANSion:

$$V_{\text{bond}}(r) = \frac{1}{2} K_{\text{bond}} (r - r_0)^2 \quad (5)$$

where $r_0 = 0.5 \sigma_0$ and $K_{\text{bond}} = 2704 \epsilon_0 / \sigma_0^2$. The angle bending interactions for PAN molecules were described by a numerical potential reported previously⁸, which was obtained by bottom-up coarse-graining from all-atom simulations.

The simulation system of the PANSion solution was composed of 50 PAN chains with a length of 2,000 monomeric units, 33,333 AgNO_3 molecules, and 170,000 DMF molecules. The equilibrium structure of the PANSion solution was derived from the MD simulation under an isothermal-isobaric ensemble. Then the PANSion solution with a size of $32.2 \text{ nm} \times 32.2 \text{ nm} \times 36.1 \text{ nm}$ was placed in a larger box with a dimension of $104.0 \text{ nm} \times 104.0 \text{ nm} \times 36.1 \text{ nm}$. The cylinder of PANSion solution is periodic in an axial direction to represent a fiber surrounded by water vapor molecules. Initially, there were 180,000 water molecules in the gaseous state and 620,000 in a liquid state in a reservoir. The number of molecules is scaled for the fiber precursors with a diameter of 23, 29, 37, and 46 nm. Brownian dynamics under canonical ensemble was employed as a thermostat to control the reduced temperature at $T^* = 0.545$, corresponding to $T = 300.0$ K. The fiber formation through nonsolvent vapor-induced phase separation was then simulated by CG-MD simulations. The 100% humidity in our simulations was defined as the

saturated vapor in a gas-liquid equilibrium simulation. It is noteworthy that to accelerate the simulations, the density of water vapor was higher than that of the real one in real experiments. In force-extension simulations, two PAN chains with a length of 70 monomeric units (CG particles) and one AgNO₃ molecule were initially placed in a box. After the equilibrium for 0.8 ns, the two chain ends on the two sides of the box were moved oppositely in a manner of the stretching-releasing and stretching-to-break at a constant speed of 2.84 nm/ns. The coordination interactions are explicitly expressed by the dynamic bond model with $E_{\text{bind}} = 3.0$ and $E_{\text{bar}} = 4.0$ k_BT with $T = 300.0$ K and the other model parameters are the same as the reference⁹.

The humidity was sustained because the consumed vapor water molecules (absorbed by the PANSion gel fiber) were supplied from the reservoir using a constant chemical potential method with¹⁰:

$$F^\mu(z) = k(n^{CR} - n_0)G_\omega(z, Z_F) \quad (6)$$

and

$$G_\omega(z, Z_F) = \frac{1}{4\omega} \left[1 + \cosh \left(\frac{z - Z_F}{\omega} \right) \right]^{-1} \quad (7)$$

where n_0 is the target constant concentration; k is the spring constant; $G_\omega(z, Z_F)$ is non-zero only for $z \sim Z_F$, with an intensity peak proportional to ω^{-1} and width proportional to ω . The method was illustrated in **Supplementary Figure 24b**. We employed the parameters $n_0 = 0.0176$, $k = 1000.0$, $\sigma_F = 1.0$, $\omega = 0.1$, and $\text{Len_CR} = 10.0$ in reduced units in the simulation for the case of 75% RH. All CG-MD simulations were performed on GPU by the GALAMOST^{11,12}.

Supplementary Text 4

Bioinspired spinning of PANSion fibers under ambient conditions

To reproduce the silk fabrication process by spiders – as closely as possible – we eliminated the inclusions of external sources in our PSEA spinning approach, such as high temperature, high pressure, coagulation bath, the thermal drying, etc. To achieve this goal of spinning fibers under ambient conditions (75% RH at ~24 °C), two requirements are essential: (1) the ability to form a stable continuous precursor thread in air; (2) spontaneous phase transition from the liquid/gel phase to a solid phase under benign conditions. In this work, by introducing the $[\text{Ag}(\text{N}\equiv\text{C}-)_x]^+$ complexes, the modified supramolecular network of spinning dope was strong and dynamic, which guaranteed the stability of precursor gel fibers when being continuously drawn under ambient conditions. Meanwhile, our PSEA spinning approach utilized water molecules from the ambient humidity as nonsolvent to induce the spontaneous phase transition. Consequently, by combining the spinnable gel dope and the nonsolvent-vapor-induced phase separation (NVIPS) effect, a biomimetic spinning process can be achieved under room temperature and atmospheric pressure.

We noticed that both PAN and PANSion solutions could undergo phase separation once the solvent composition changed (*i.e.*, in contact with sufficient water molecules). Compared to PAN solution, PANSion dope presented a higher tendency of liquid to solid phase transition under ambient conditions (**Supplementary Figure 22**). This confirms that spinnable PANSion dope is key to the success of our PSEA spinning approach. Specifically, the origin of phase transition can be interpreted in terms of thermodynamics and polymer chemistry, which have significant influences on the PANSion fiber formation under ambient conditions. From the point of view of thermodynamics, Gibb's free energy of mixing, G_m , indicates the compatibility of dissimilar constituents during mixing. The simplified free energy change of the mixture can be written as^{13,14}:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (8)$$

where ΔH_m is the enthalpy of mixing (heat of mixing), and $T\Delta S_m$ is the entropy of mixing. A homogeneous solution (namely, miscible) at the molecular level is only realized at the condition $\Delta G_m < 0$. When the sign of ΔG_m becomes positive, the thermodynamic driving force for phase separation is generated. For our case of PANSion dope, the gain in the free energy of mixing due to the entropy S_m could be negligible as the polymer chain is sufficiently long. The increased interactions among neighboring PANSion chains after forming $[\text{Ag}(\text{N}\equiv\text{C}-)_x]^+$ complexes (*i.e.*, crosslinking) can be viewed as a type of polymerization (note that it can also be regarded as a chemical cooling process), which usually reduces the ΔS_m term by decreasing the freedom in chemical configurations of molecules¹⁴, whereas the physical cooling of the system is expressed by the reduction in T . Thus, the $T\Delta S_m$ term decreases, and the phase separation is equivalently induced.

Under the conditions of 75% RH at ~24 °C, water molecules from the environmental humidity triggered the phase separation of PANSion dope when directly spinning fibers in air. When holding the precursor fiber in air, the solvent precipitated out of the fiber and formed a solvent shell on the fiber's surface. Next, with the gradual accumulation of the solvent, it is eventually broken into separate droplets due to surface tension of tendency for minimizing the interfacial energy¹⁵. As a result, a solid fiber was obtained by removing the solvent droplets. While phase separation was still ongoing, the elastic stress within the fiber also continuously grew due to the molecular chains' extension, contraction, orientation, and repacking (to balance the capillary pressure¹⁶), thus becoming sufficiently strong to form a self-supporting fiber (instead of breaking up from the ultimate necking or pinching-off effect). The volume change of the precursor fiber [*i.e.*, diameter, $D(t)$] can be described with the following equation, which decays exponentially with time:

$$D(t) = \left(\frac{\eta_p D_f^4}{\tau' \sigma} \right)^{\frac{1}{3}} \exp \left(-\frac{t}{3\tau'} \right) \quad (9)$$

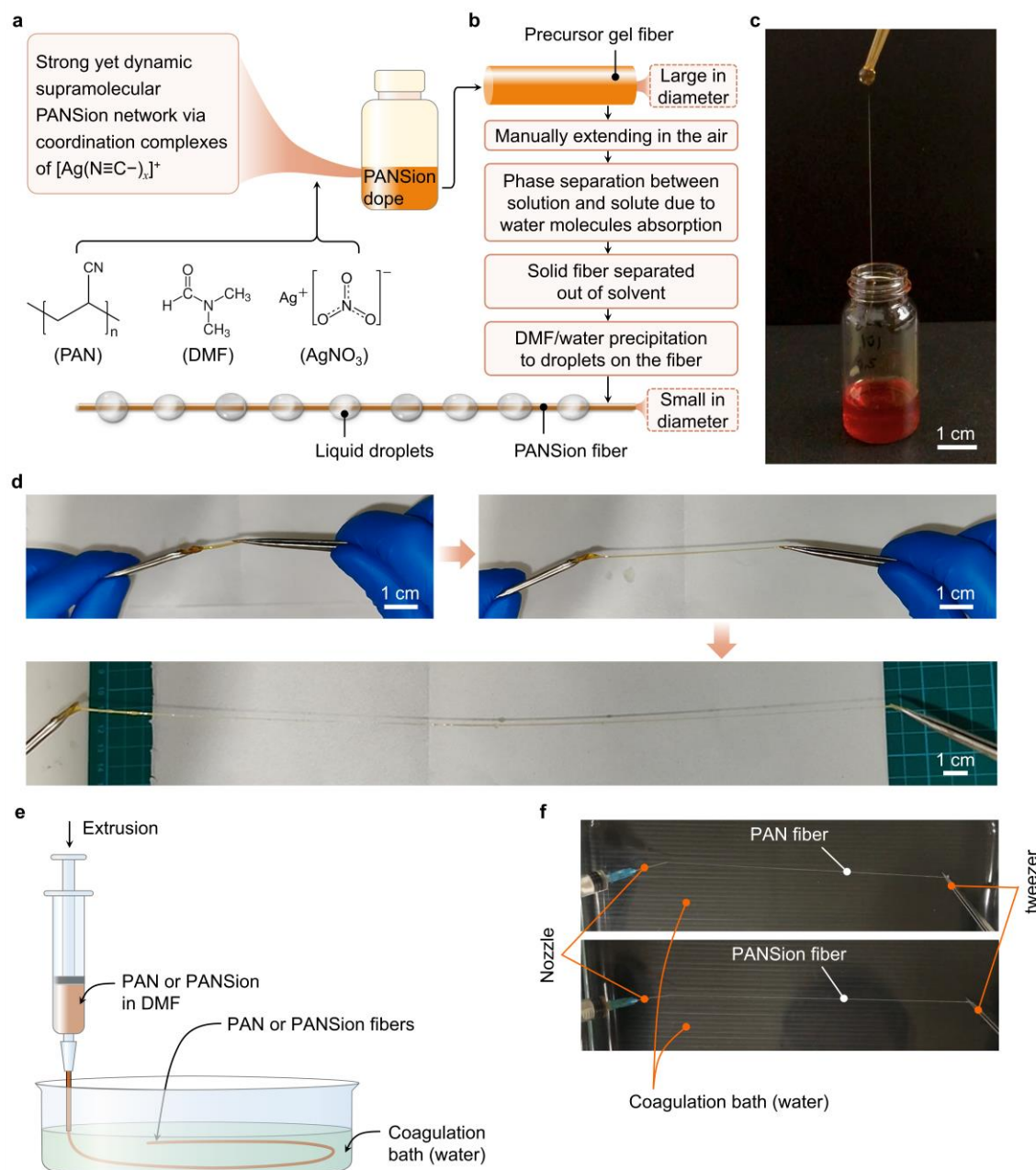
where D_f is the final diameter upon phase separation, η_p is the polymer viscosity, and σ is the polymer surface tension. Here we use diameter change in percentage [$D(\%)$] instead of absolute values so that the above equation is modified as follows:

$$D(\%) = A \exp \left(-\frac{t}{3\tau'} \right) + D_f \quad (10)$$

This relationship precisely described the experimental data extracted from the OM images. However, the dynamic process of PANSion fiber formation is complicated because of the spatially and temporally nonhomogeneous growth of extensional stress, the action of visco-elastic-capillary forces, and the evaporation and diffusion of DMF and water. More work is needed to investigate and reveal the detailed fiber formation mechanism.

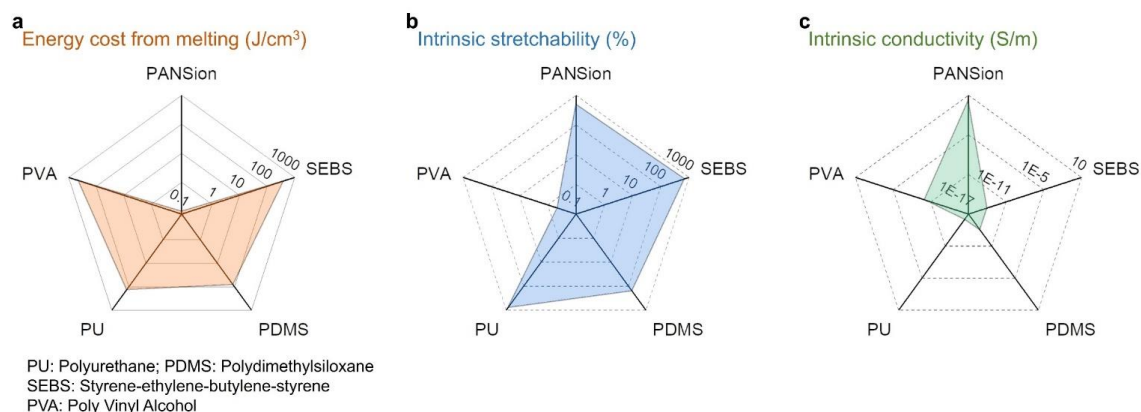
For the wet spinning approach, fibers can be readily fabricated for both PAN and PANSion solutions. Once the extruded PAN or PANSion solutions came into contact with the water bath, water molecules (in the liquid phase) were excessive as nonsolvent, resulting in unstable spinodal decomposition. Additionally, the phase separation via wet spinning occurred at a super-fast rate compared to our proposed PSEA spinning approach. Consequently, the as-prepared PAN and PANSion fibers via wet spinning (fibers@WS) showed different morphologies and properties compared to PANSion fibers via the PSEA spinning method (fibers@PSEA). For instance, PAN fibers@WS were with porous structure compared to the solid internal structure of PANSion fibers@PSEA. Noticeably PANSion fibers@WS were less stretchable than that of PANSion fibers@PSEA. Such property differences could also be observed among silk fibers prepared by different approaches: excellent performance when naturally spun by spiders, whereas inferior performance when manually regenerated via a wet-spinning approach. Note that we only used the two cases of PANSion fibers@WS and PAN fibers@WS as demonstrations to

showcase our PANSion fibers@PSEA. Details on optimizing the process for PAN or PANSion fiber@WS preparation were beyond the current topic and not included in the present study. Furthermore, the mechanisms of the different morphologies and properties of fibers via either the wet spinning or our PSEA spinning approach are not the focus of the current study, which may be discussed in future studies. Therefore, we used fibers@WS as control experiments to manifest the importance of introducing $[\text{Ag}(\text{N}\equiv\text{C}-)_x]^+$ complexes to obtain the spinnable PANSion dope, that was suitable for fiber preparation under ambient conditions via our PSEA spinning method – just like the spider spinning.



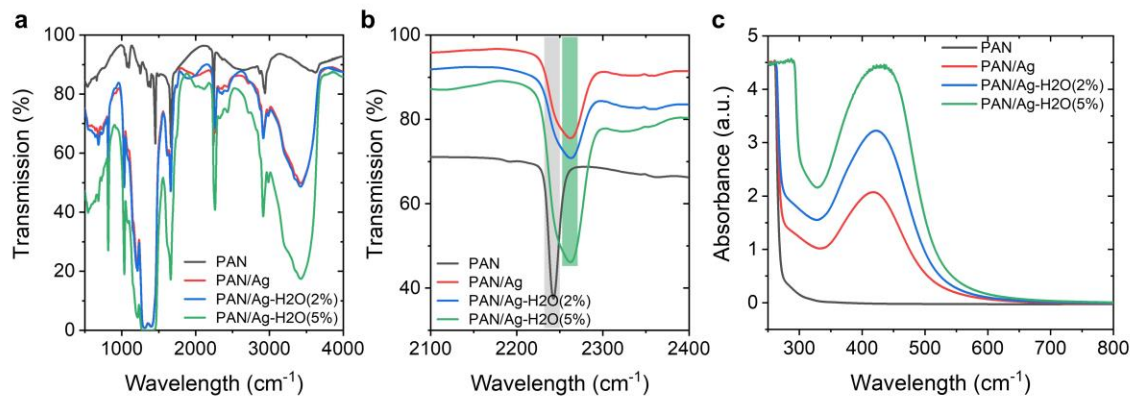
Supplementary Figure 1

Schematics of the PSEA spinning approach and wet spinning approach for PANSion fiber preparation. **a** and **b**, Preparation of PANSion gel dope (**a**) and the spinning process of a PANSion fiber via PSEA spinning approach by taking advantage of the NVIPS effect (**b**). **c**, Direct spinning of a PANSion fiber under ambient conditions (75% RH, ~24 °C). **d**, Manually spinning a PANSion fiber via the PSEA spinning method using two tweezers in air. **e** and **f**, Schematic of wet-spinning process (**e**), and the corresponding digital photos when spinning PAN (top) or PANSion (bottom) fibers (**f**).



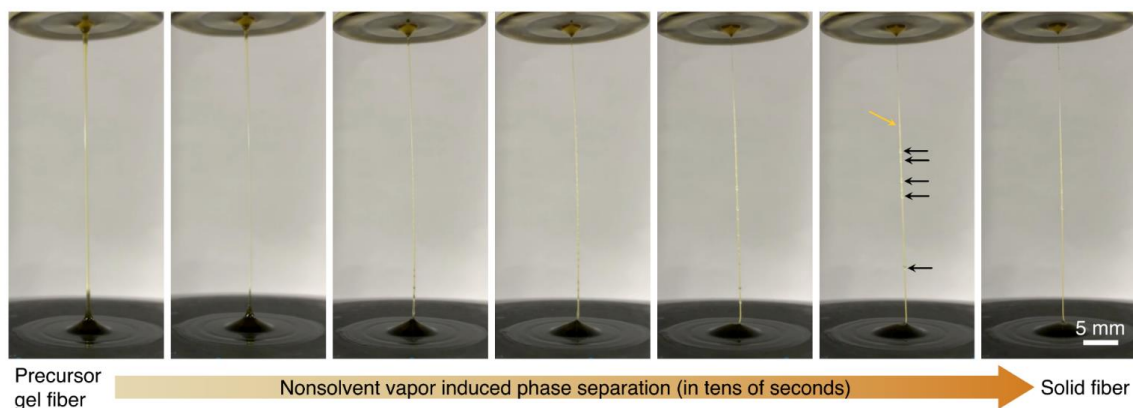
Supplementary Figure 2

Comparison between PANSion and other typical polymer elastomers in terms of energy cost from the melting process, intrinsic stretchability, and intrinsic conductivity. a, Energy cost from polymer melting via the thermal drawing process. **b,** Intrinsic stretchability. **c,** Intrinsic conductivity.



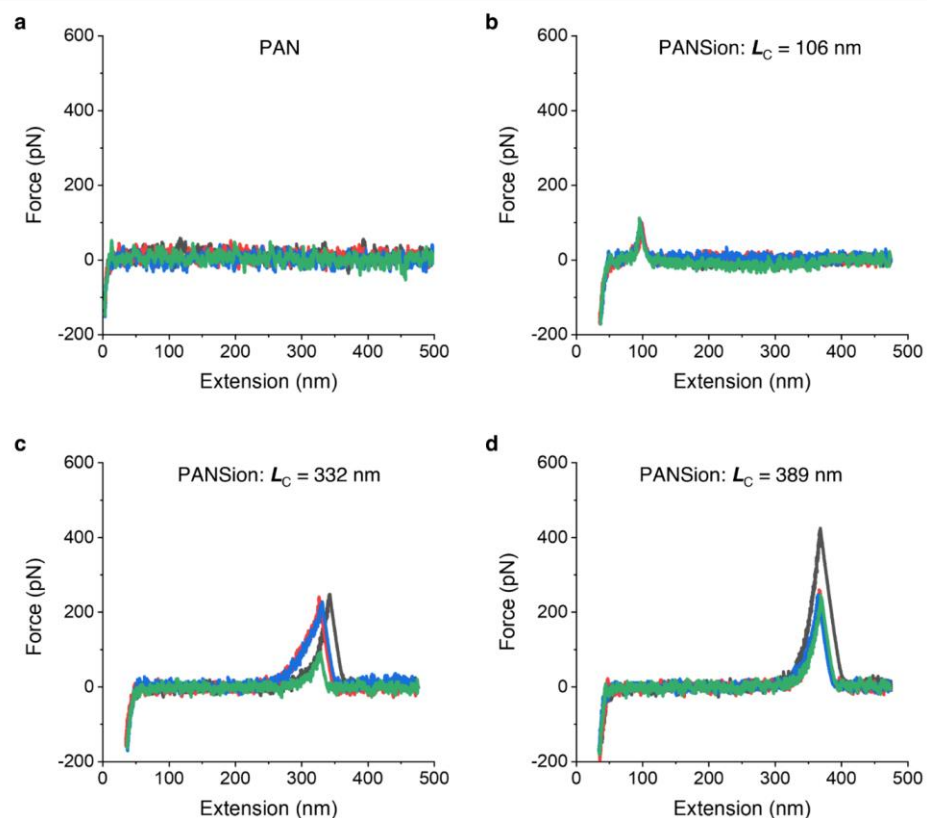
Supplementary Figure 3

Fourier-transform infrared spectroscopy (FTIR) and ultraviolet-visible spectroscopy (UV-Vis) results. **a–b**, FTIR results of dried films from four different solutions, including PAN (i.e., PAN in DMF), PAN/Ag (i.e., PAN and silver ions in DMF), PAN/Ag-H₂O(2%) (i.e., PAN and silver ions in a mixture of DMF and H₂O where H₂O is 2 wt.%) and PAN/Ag-H₂O(5%) (i.e., PAN and silver ions in a mixture of DMF and H₂O where H₂O is 5 wt.%). The enlarged area as shown in (b) indicated the chemical environment change of nitrile groups (C≡N). For instance, the shoulder peak next to the nitrile groups was assigned to the formation of [Ag(N≡C–)_x]⁺ complexes for samples of PAN/Ag, PAN/Ag-H₂O(2%), and PAN/Ag-H₂O(5%), demonstrating the transition from a PAN network to a PANsion network. **c**, UV-Vis results of the four samples above, indicating the formation of *in situ* AgNPs due to the presence of a characteristic peak at ~422 nm.



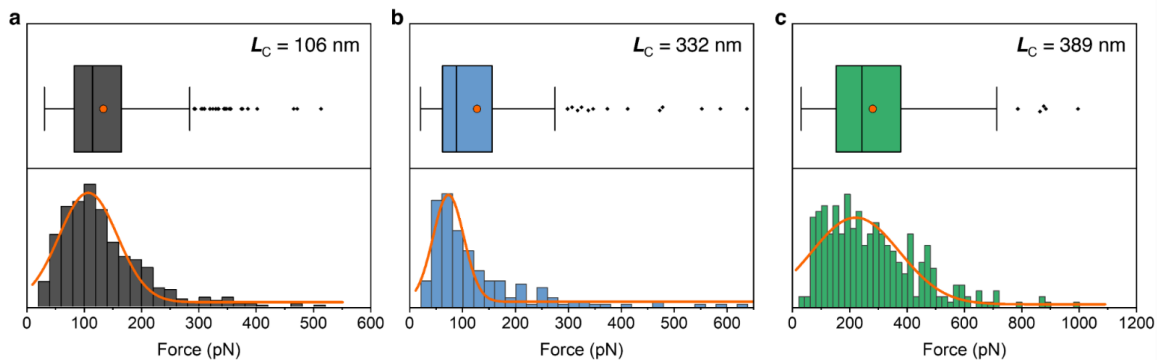
Supplementary Figure 4

Time-sequence images of holding a PANSion gel fiber between two metal plates under ambient conditions (75% RH, ~24 °C). Phase separation occurred spontaneously once a gel fiber was drawn into air. Liquid droplets (*i.e.*, the mixture of DMF/H₂O) precipitated and then fell off the fiber. Black arrows marked the liquid droplets, and yellow arrows marked the solid fiber.



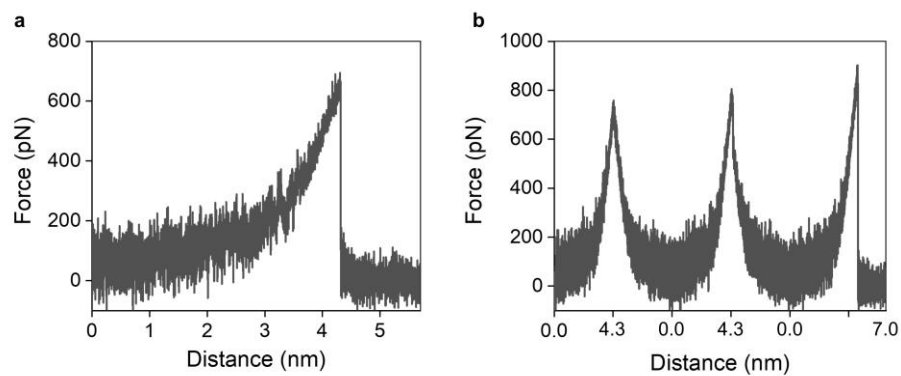
Supplementary Figure 5

Force-extension curves of AFM-SMFS results. **a**, Results for PAN solutions with no detectable force rupture peaks. **b–d**, Results for PANSion solutions with force rupture peaks at different contour lengths (L_C) averaged at 106 nm (b), 332 nm (c), and 389 nm (d).



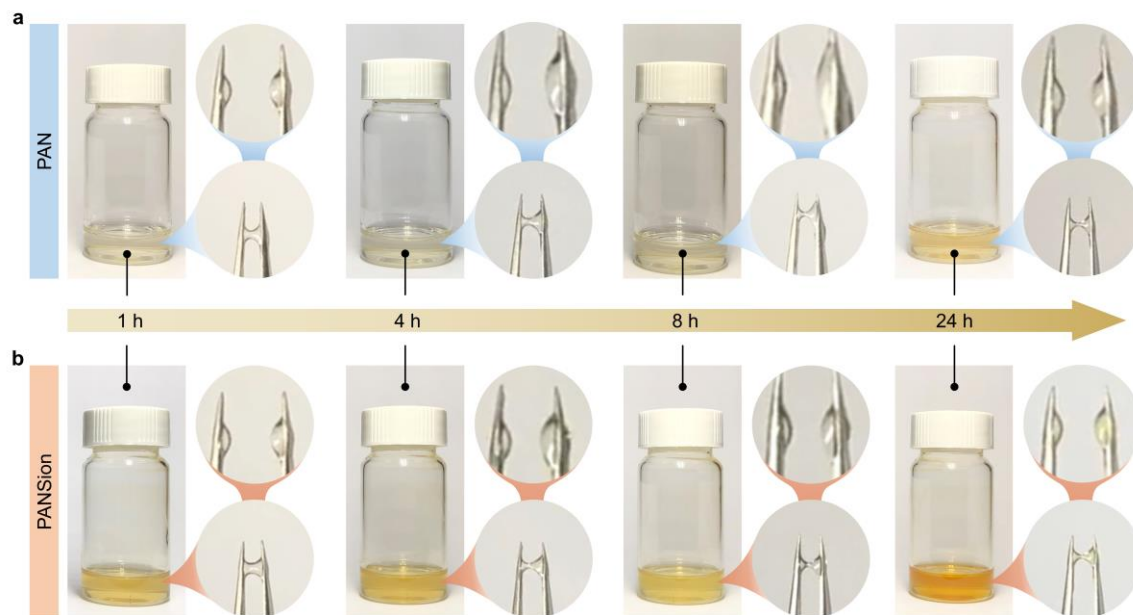
Supplementary Figure 6

Box and histogram plots of the rupture forces from AFM-SMFS tests for PANSion solutions at each representative contour length. a–c, Results corresponding to the three contour lengths of 106 nm (a), 332 nm (b), and 389 nm (c), respectively. Data is represented as mean $\pm$ s.d., $n = 500$ independent tests for $L_C = 106$ nm, 170 for $L_C = 332$ nm, and 389 for $L_C = 106$ nm. Box plot with centre line at the median, upper bound (right) at 75th percentile, lower bound (left) at 25th percentile, whiskers at minimum and maximum values with black dots as the outliers. The filled orange dots represented the mean values, and the orange curves were the Gaussian fitting results.



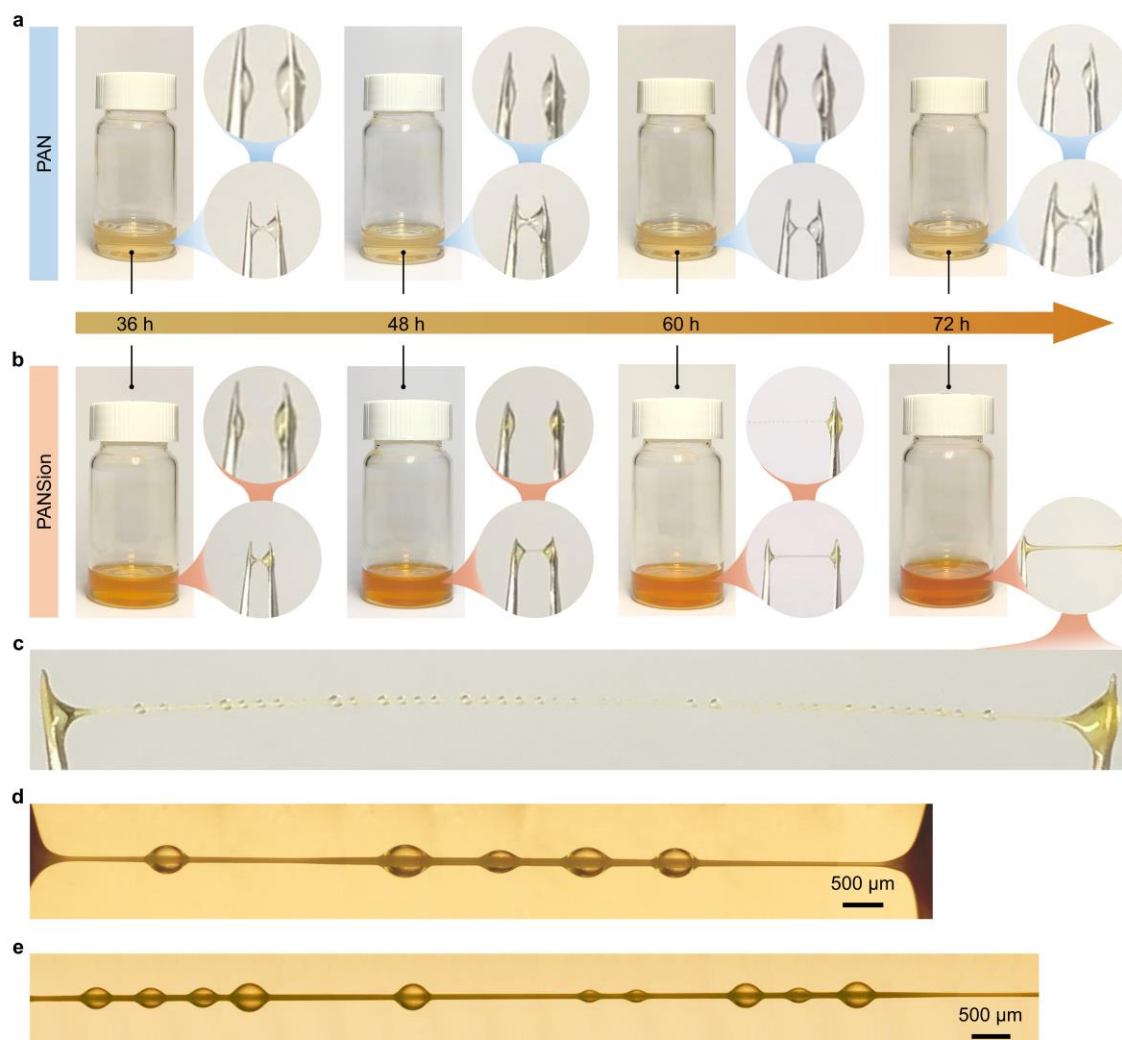
Supplementary Figure 7

CG-MD simulation results of a PANSion network at a molecular level. a, Single stretching to break. **b**, Cyclic stretching-releasing with a final stretching to break. These results demonstrated the elasticity of PANSion networks.



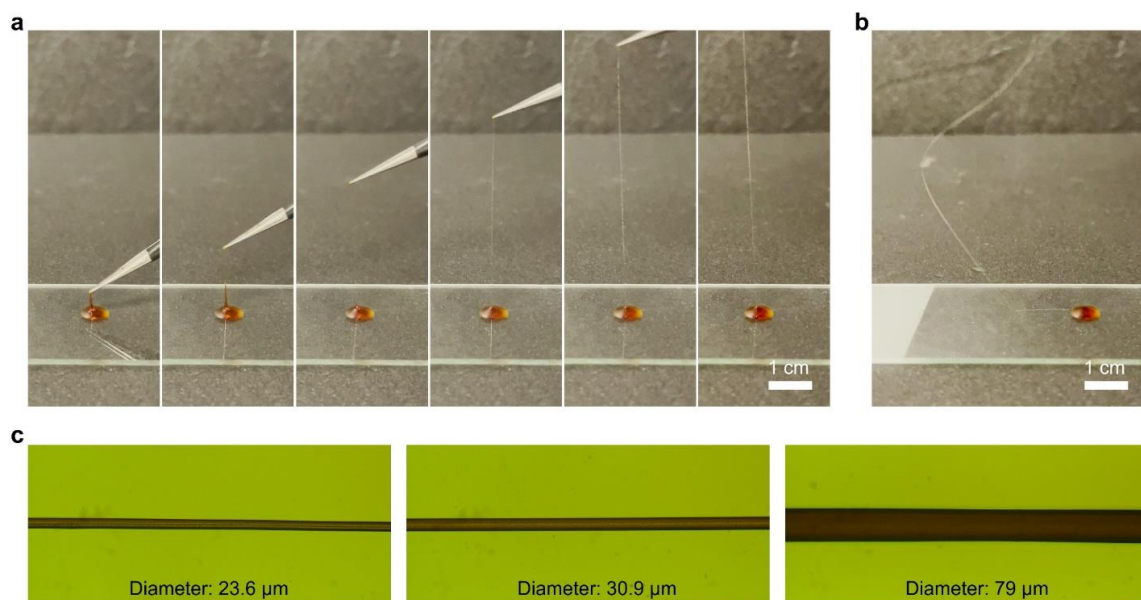
Supplementary Figure 8

Spinnability comparison between the PAN and PANSion dopes after 0–24 hours of curing. a, PAN dope. b, PANSion dope. Both dopes cannot generate self-supporting fibers under ambient conditions.



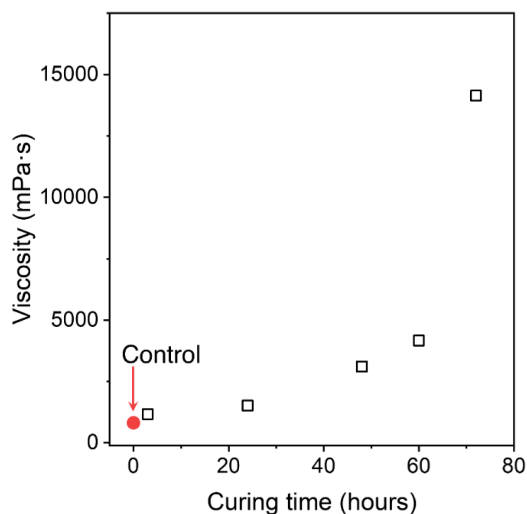
Supplementary Figure 9

Spinnability comparison between the PAN and PANSion dopes after 36–72 hours of curing. a, PAN dope. **b,** PANSion dope. **c,** A fiber formed between two legs of a tweezer using PANSion dope after 72 h of curing. **d** and **e,** OM images showing the liquid droplets hanging on the fibres.



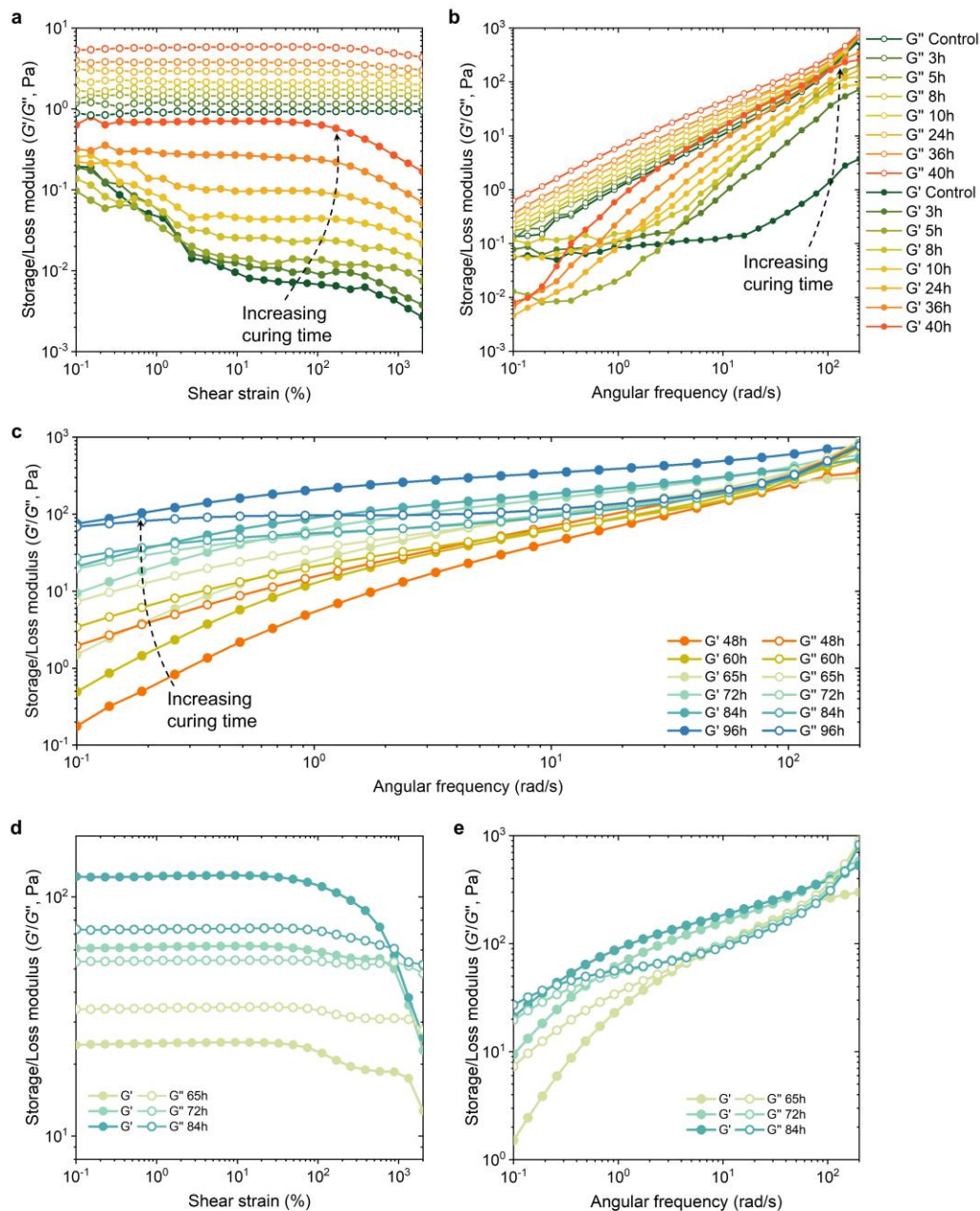
Supplementary Figure 10

Demonstration of spinning fiber using a non-reducing solvent of NMP. **a-b**, Spinning fibers using a spinning dope with NMP as the solvent via our PSEA spinning method. **c**, Fibers with different diameters can be obtained. Note that NMP is a non-reducing solvent.



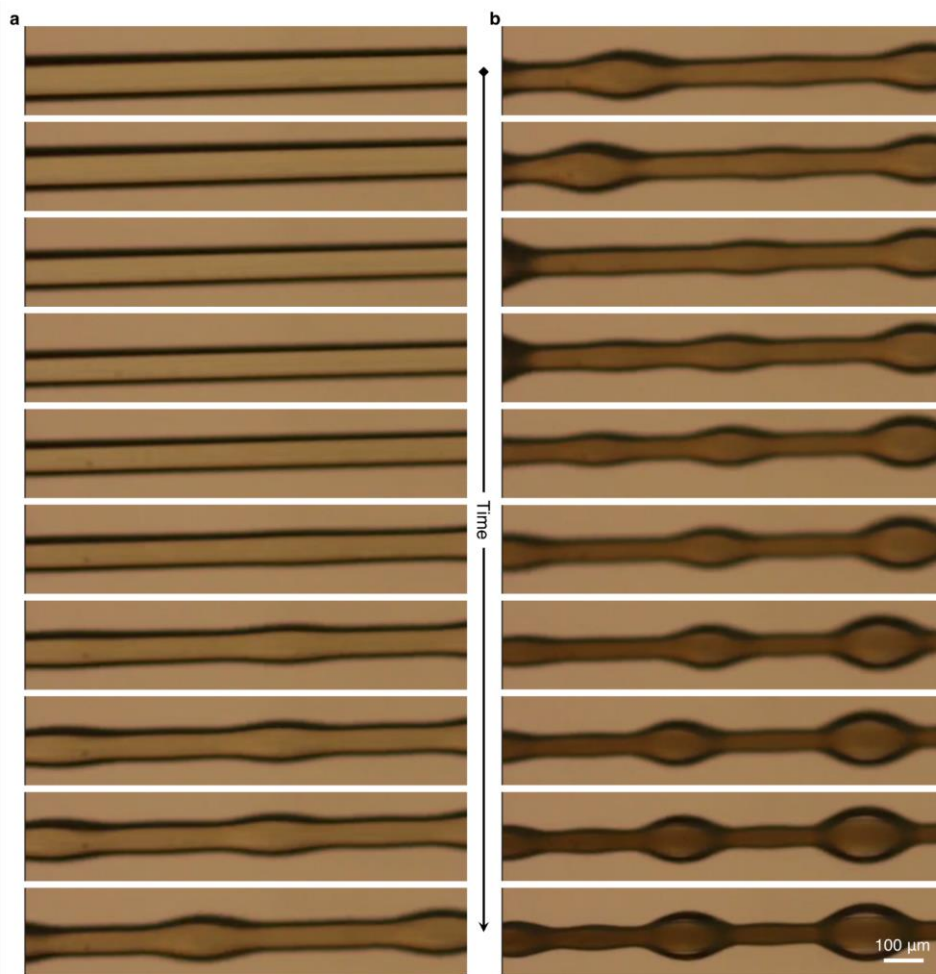
Supplementary Figure 11

Viscosity changes of PANSion dope after curing for various times. A significant viscosity increase was recorded after 60 hours of curing for PANSion dope, indicating strong inter- or intra-chain interactions via $[\text{Ag}(\text{N}\equiv\text{C}-)_x]^+$ complexes. Viscosity data were obtained by extrapolating the fitting curves when shear rate $\dot{\gamma} \rightarrow 0$. The filled red dot was the result for the control sample of PAN.



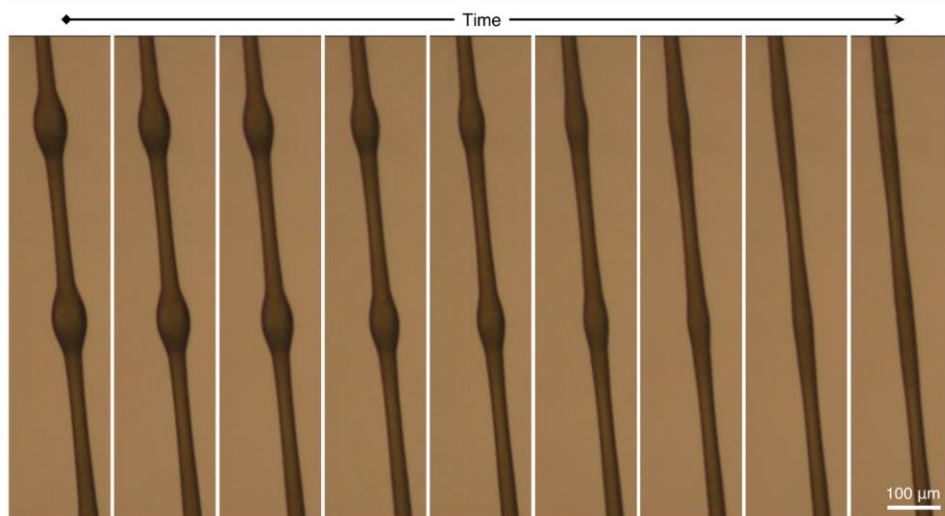
Supplementary Figure 12

Rheological measurements of PANSion dope after curing for various times. **a**, Oscillatory amplitude sweep results in the range of 0.1 to 2000% strains at 24 °C (frequency $\omega = 1$ rad/s). **b** and **c**, Oscillatory frequency sweep results in the range of 0.1 to 200 rad/s at 24 °C (amplitude strain = 1%) for samples after 0–40 hours of curing (**b**) and 48–96 hours of curing (**c**). **d** and **e**, Plots of both amplitude (**d**) and frequency (**e**) sweep results for samples after 65, 72, and 84 hours of curing.



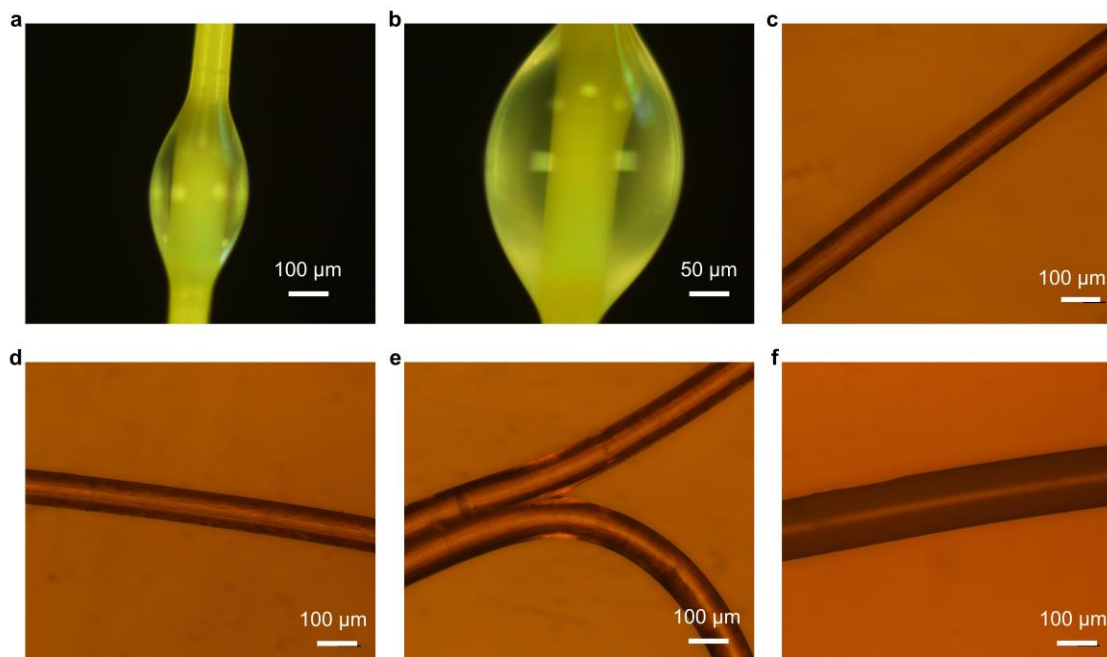
Supplementary Figure 13

Phase separation of a PANSion gel fiber under ambient conditions. **a**, Fiber diameter shrinkage with spontaneous solvent droplet formation induced by the phase separation. **b**, Continuous diameter shrinkage with solvent droplets flowing along with the fiber due to gravitational effects.



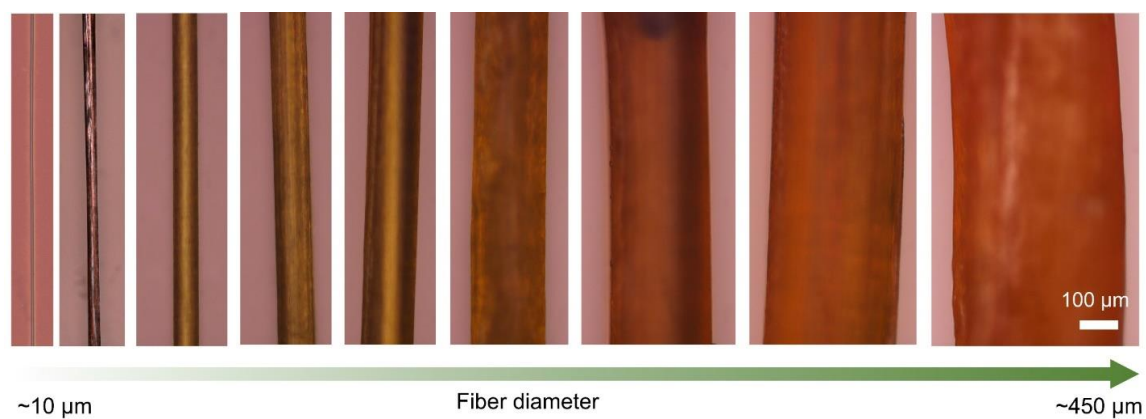
Supplementary Figure 14

Solvent droplets removal from the PANSion fiber. Due to gravitational effects, the solvent droplets can be easily removed by holding the fiber inclinedly or vertically to obtain a clean, freestanding, and solid PANSion fiber.



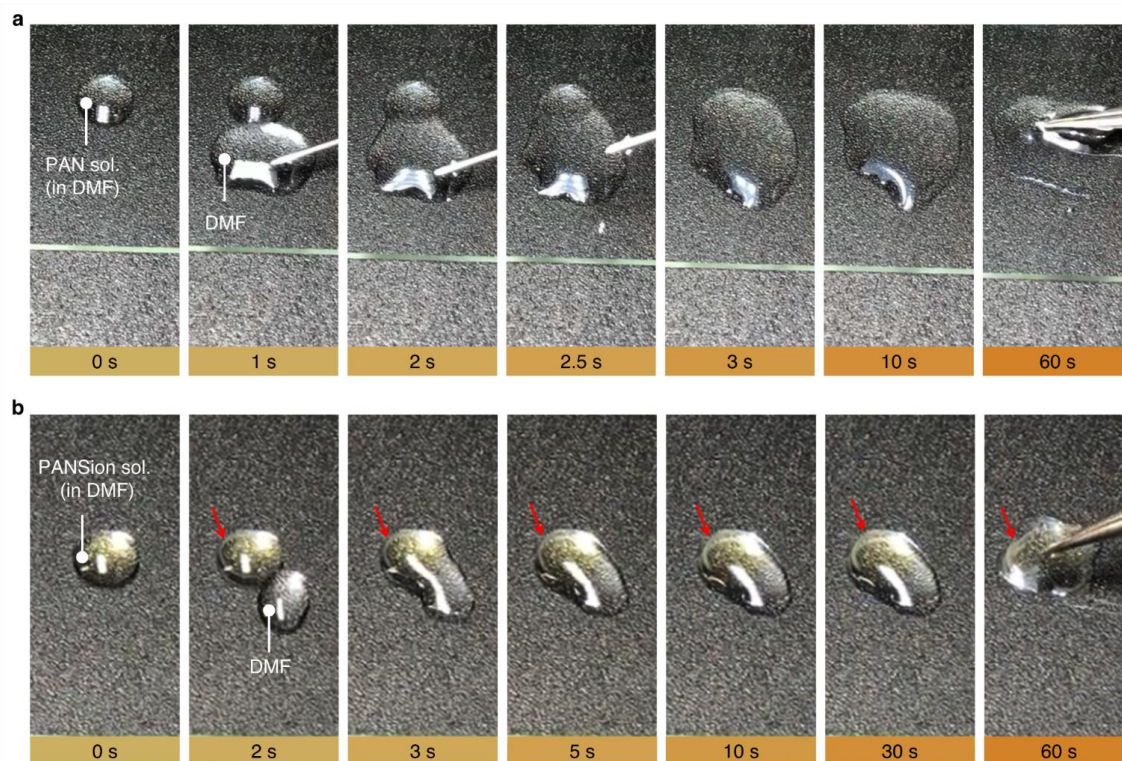
Supplementary Figure 15

OM images of PANSion fiber. **a** and **b**, Fibers with solvent droplets. **c–f**, As-prepared PANSion fibers with uniform diameter and good flexibility.



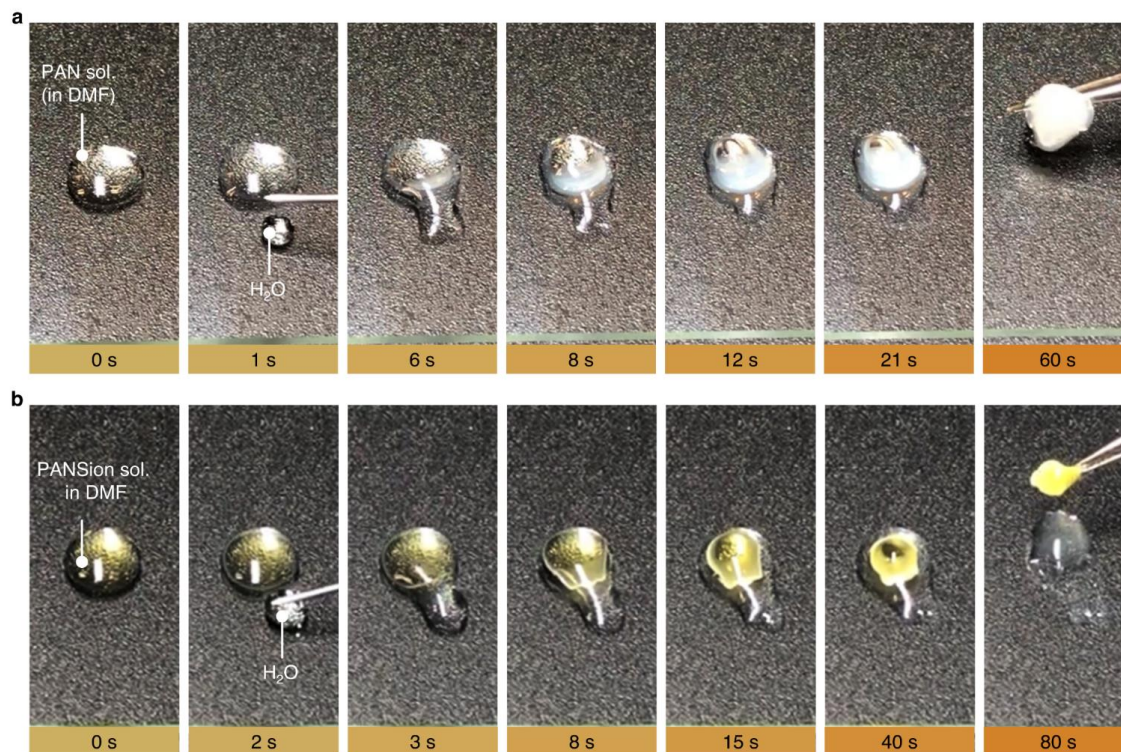
Supplementary Figure 16

PANSion fibers with various diameters from ~10 μm to ~450 μm. Note that the fiber diameter can be readily adjusted by controlling the stretching ratio when manually spinning fiber via our PSEA spinning approach.



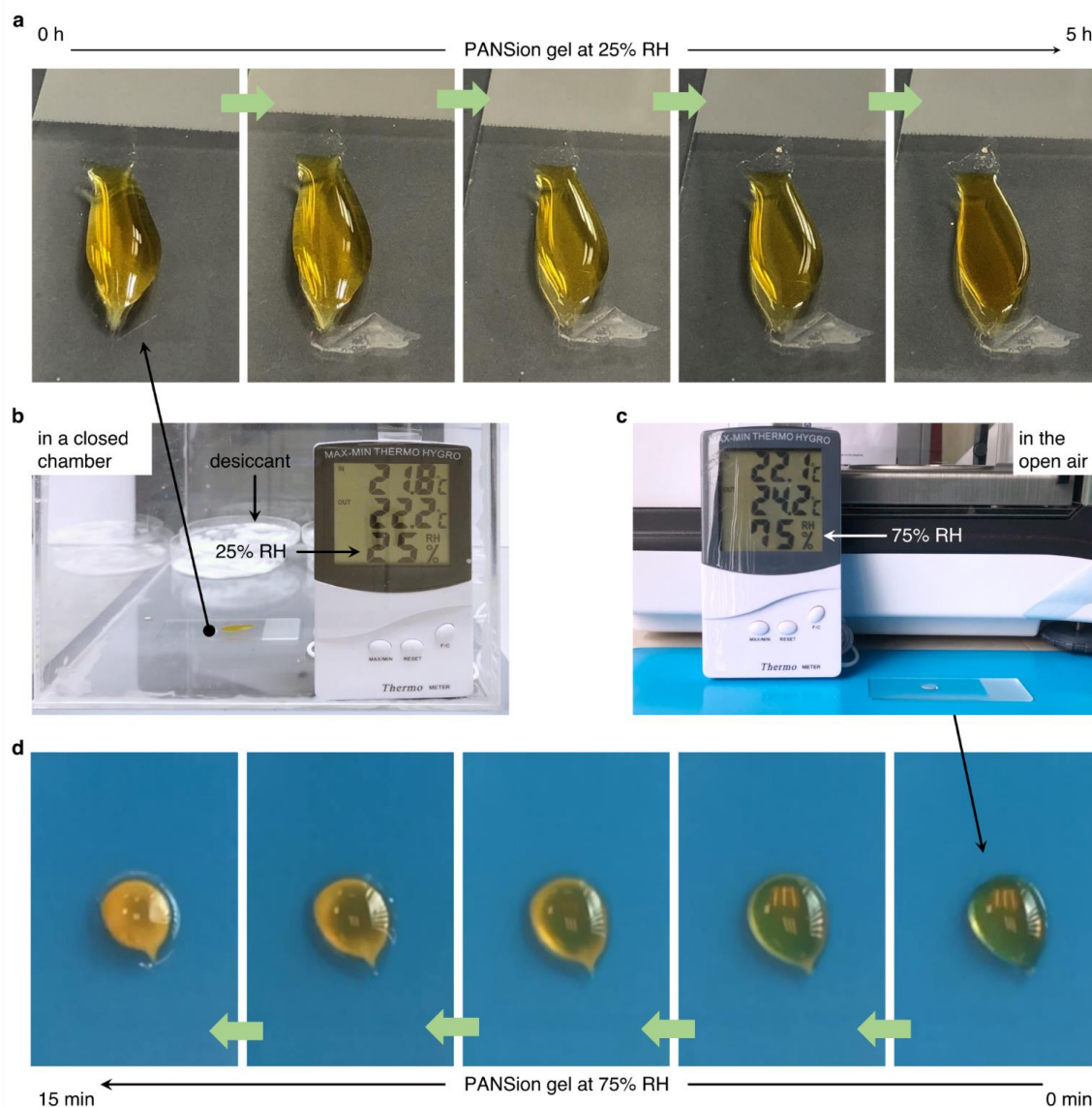
Supplementary Figure 17

Observations of the PAN and PANSion solution droplets when coalescing with DMF solvent. a, Time-sequence images of PAN solution droplet when coalescing with DMF solvent. **b,** Time-sequence images of PANSion solution droplet when coalescing with DMF solvent. The red arrows in (b) showed the onset of phase separation for the PANSion solution droplet under the high relative humidity (75% RH), which was not observed for the PAN solution droplet (within 60s).



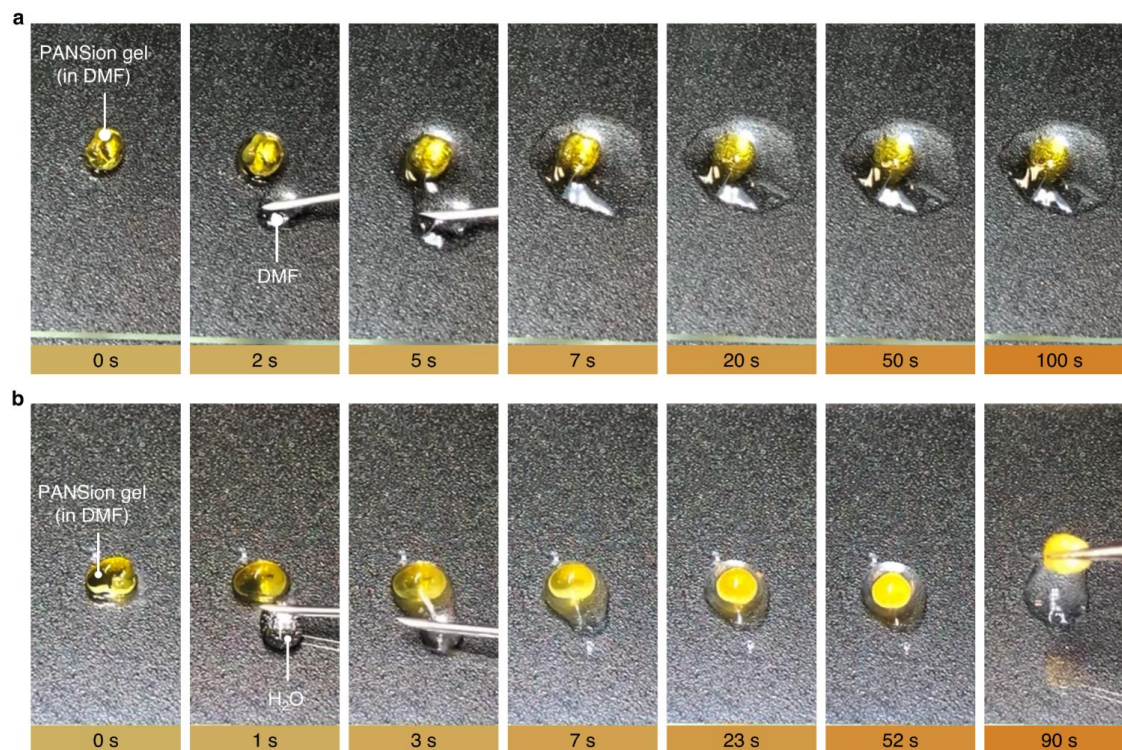
Supplementary Figure 18

Observations of PAN and PANSion solution droplets when coalescing with water. **a**, Time-sequence images of PAN solution droplet when coalescing with water. **b**, Time-sequence images of PANSion solution droplet when coalescing with water. For both solution droplets, water successfully induced the phase separation.



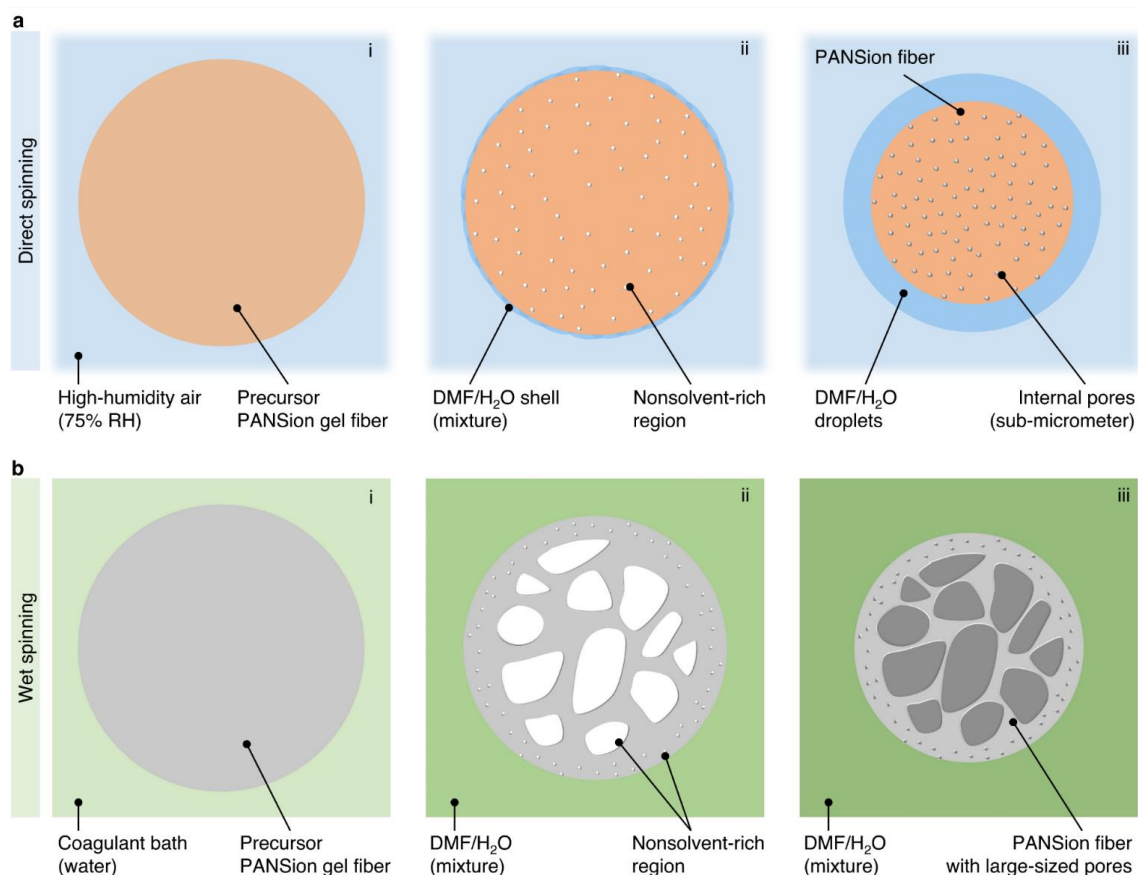
Supplementary Figure 19

Observations of the phase separation of PANSion gel at 25% and 75% RH. **a** and **b**, The setup with controlled humidity at ~ 25% RH (**b**) and the time-sequence images of PANSion gel (**a**). No volume change or phase separation was recorded. **c** and **d**, Our lab environment with humidity at 75% RH (**c**) and the time-sequence images of PANSion dope showing phase separation (**d**).



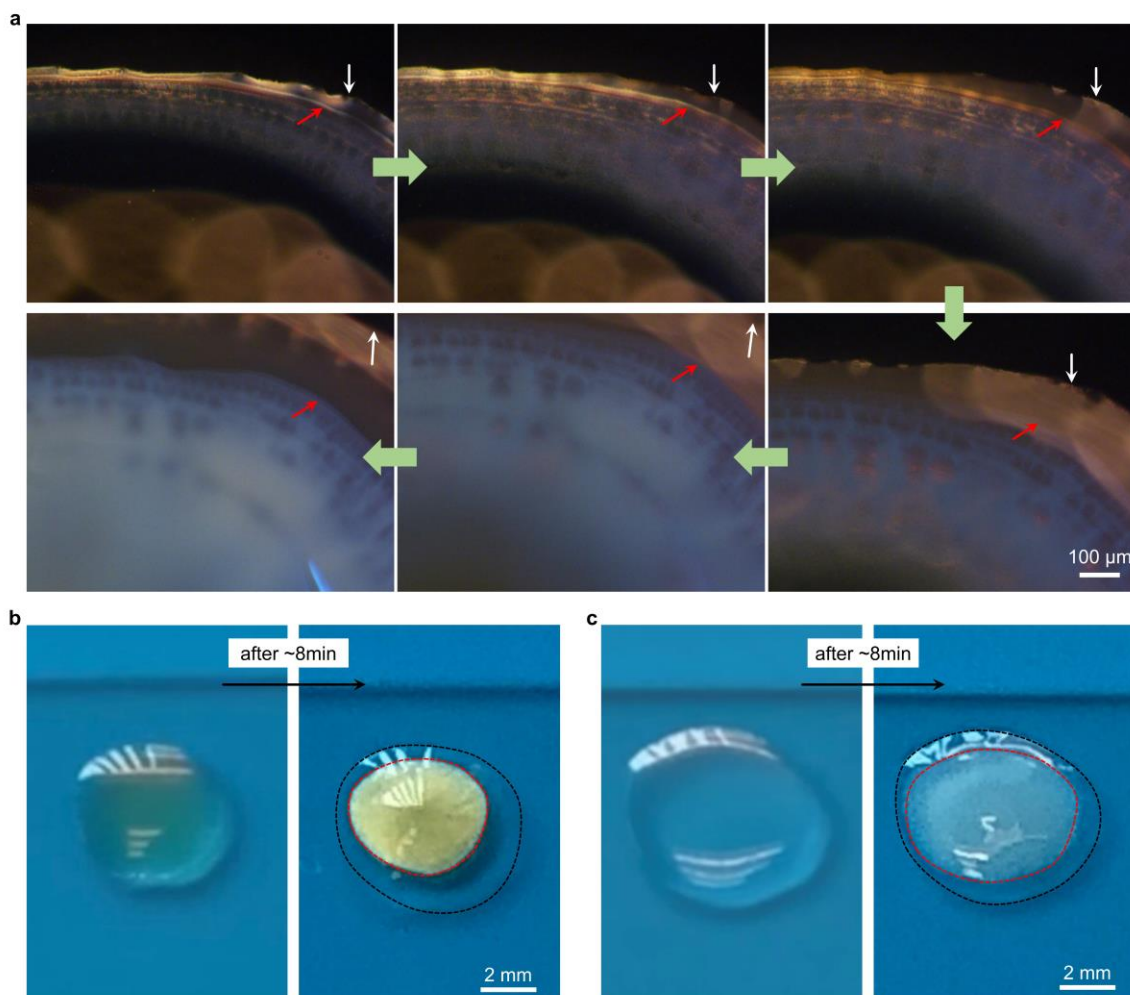
Supplementary Figure 20

Observations of the phase separation for PANSion gel when in contact with DMF and water (75% RH). **a**, Time-sequence images of PANSion gel when in contact with DMF. **b**, Time-sequence images of PANSion gel when in contact with water. Redispersion of PANSion gel occurred when in contact with DMF, while phase separation occurred when in contact with water.



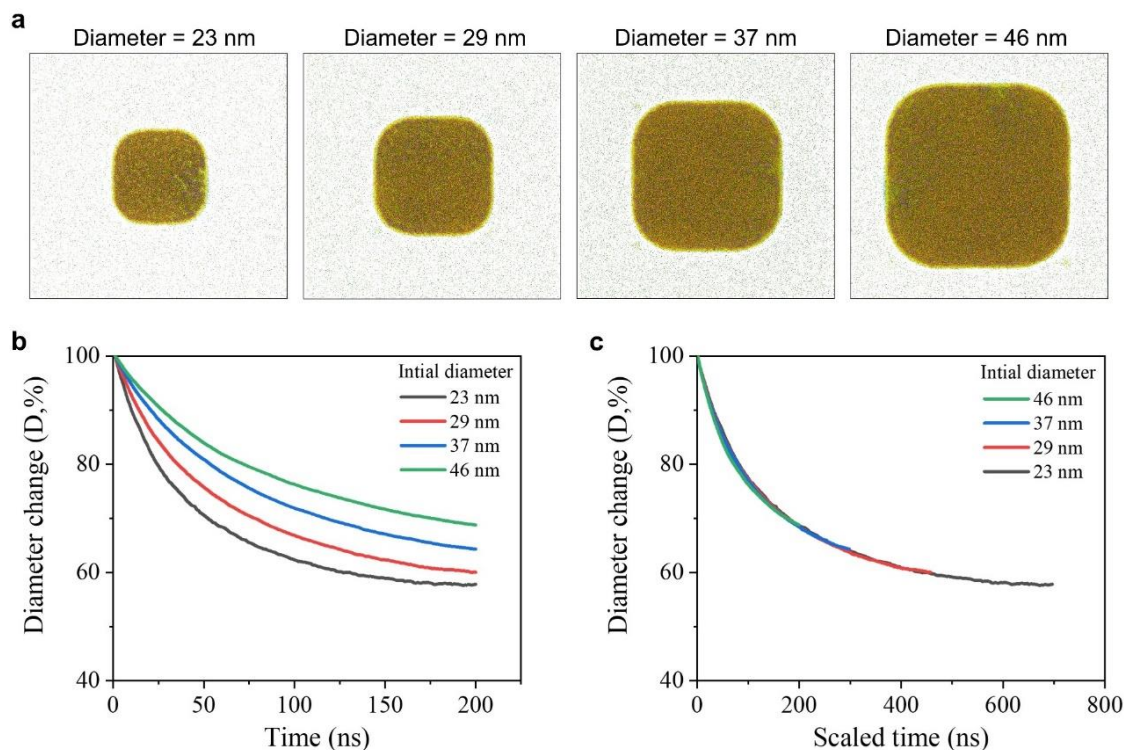
Supplementary Figure 21

Schematics of fiber formation via PSEA spinning and wet spinning approaches. **a**, PSEA spinning approach. **b**, Wet spinning. For the PSEA spinning method, the metastable phase separation occurred, resulting in a near-homogenous structure. In contrast, unstable decomposition occurred during wet spinning, leading to the polymer-rich and nonsolvent-rich regions (*i.e.*, big internal pores).



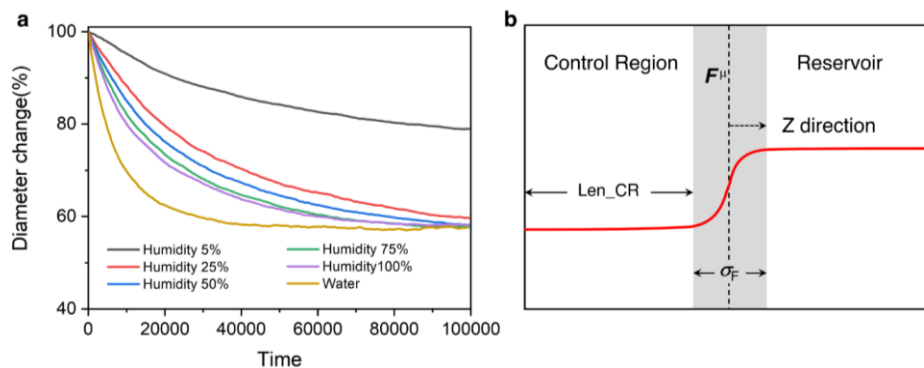
Supplementary Figure 22

Observations of the phase separation for PANSion and PAN solution droplets under ambient conditions (75% RH). **a**, Time-sequence OM images of a PANSion solution droplet when exposure to 75% RH. White and red arrows marked the edges of liquid and solid phases, respectively. **b** and **c**, The initial and final states of a PANSion (b) and PAN (c) droplet after exposure to 75% RH. The dashed circles in red and black marked the edges of the solid and liquid phases, respectively.



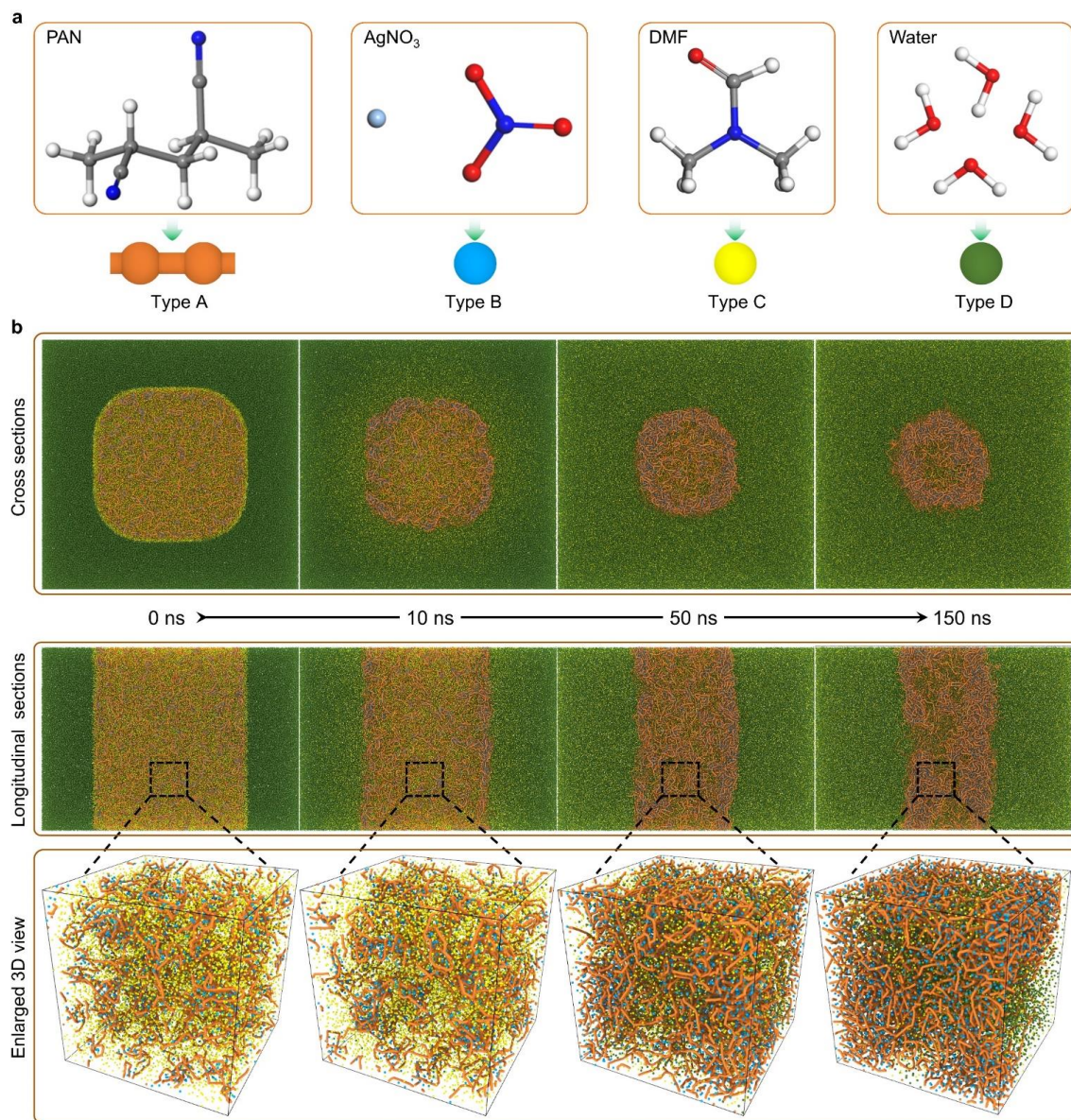
Supplementary Figure 23

CG-MD simulation results of the phase separation for fibers with different initial diameters. **a**, Snapshots of fibers with a diameter of 23, 29, 37, and 46 nm. **b**, The raw data of the diameter change profiles for all four fibers. **c**, The diameter changes profiles with a scaled time of $\sim 1/(d^2)$, where d is the initial diameter. Note that the relationship between fiber diameter changes and time (described by equations (2) and (3) in the main text) is adaptable to any as-fabricated PANSion fibers with different initial diameters. When the time is scaled with $\sim 1/(d^2)$, the diameter change profiles of different-sized fibers almost overlapped with each other (see b and c).



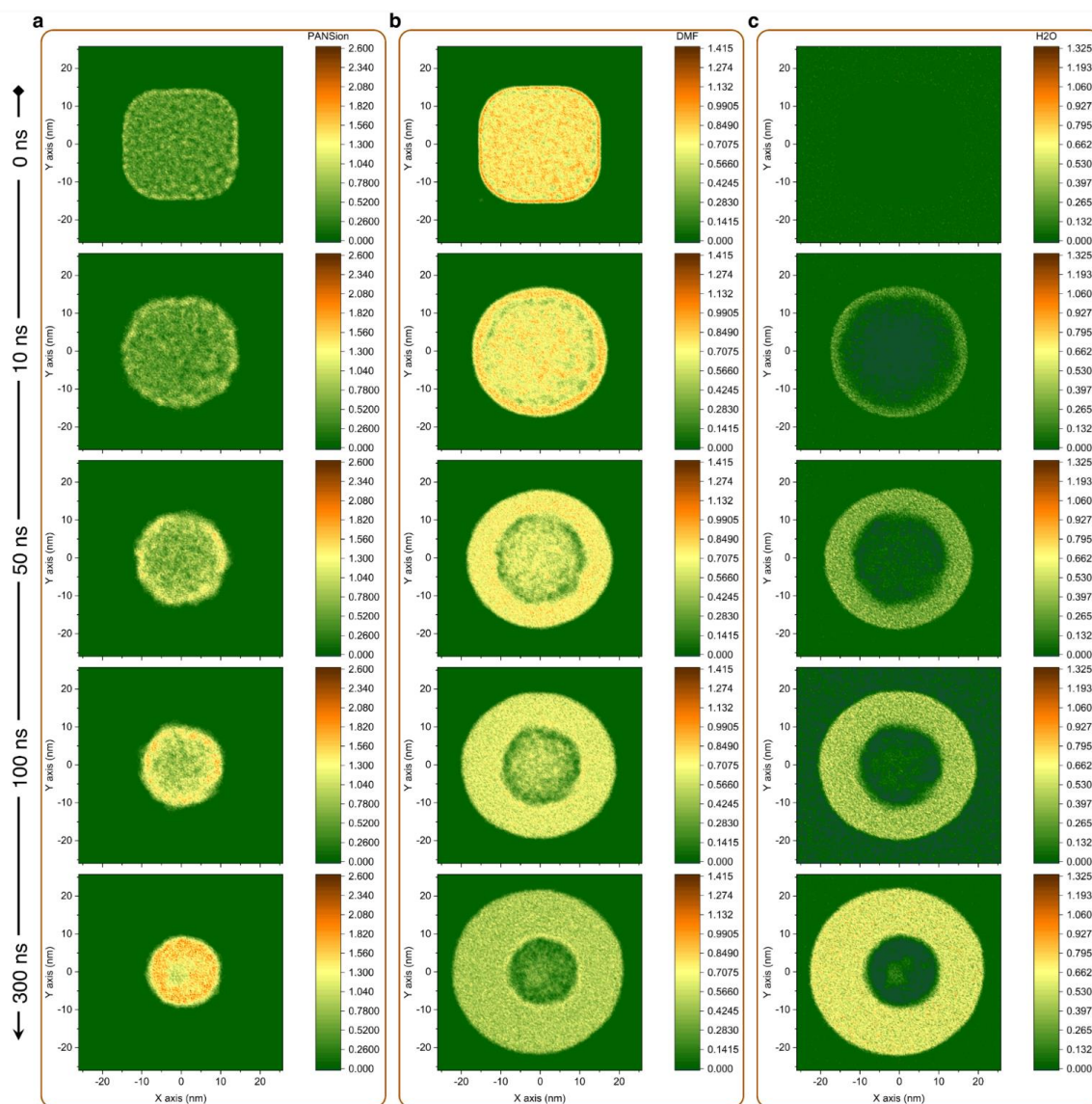
Supplementary Figure 24

The profiles of diameter changes of PANSion fibers from CG-MD simulations under different humidity conditions. a, Diameter changes under different humidity. The wet spinning process (labeled as “water”) was also included for comparison. **b**, The illustration of the controlled humidity environment in CG-MD simulations and the corresponding water reservoir.



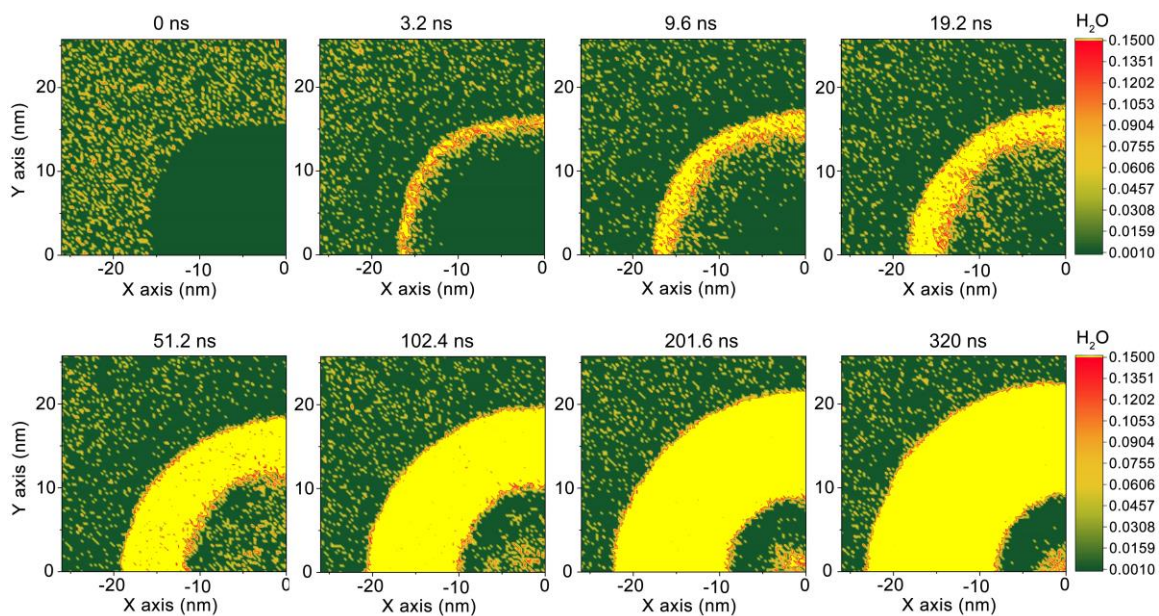
Supplementary Figure 25

CG-MD models and the simulated results. **a**, Schematic of the molecules represented by specific beads. **b**, Simulated CG-MD results of PANSion fiber via wet spinning, showing a structural evolution of big internal pores formation during the phase separation because of the unstable spinodal decomposition.



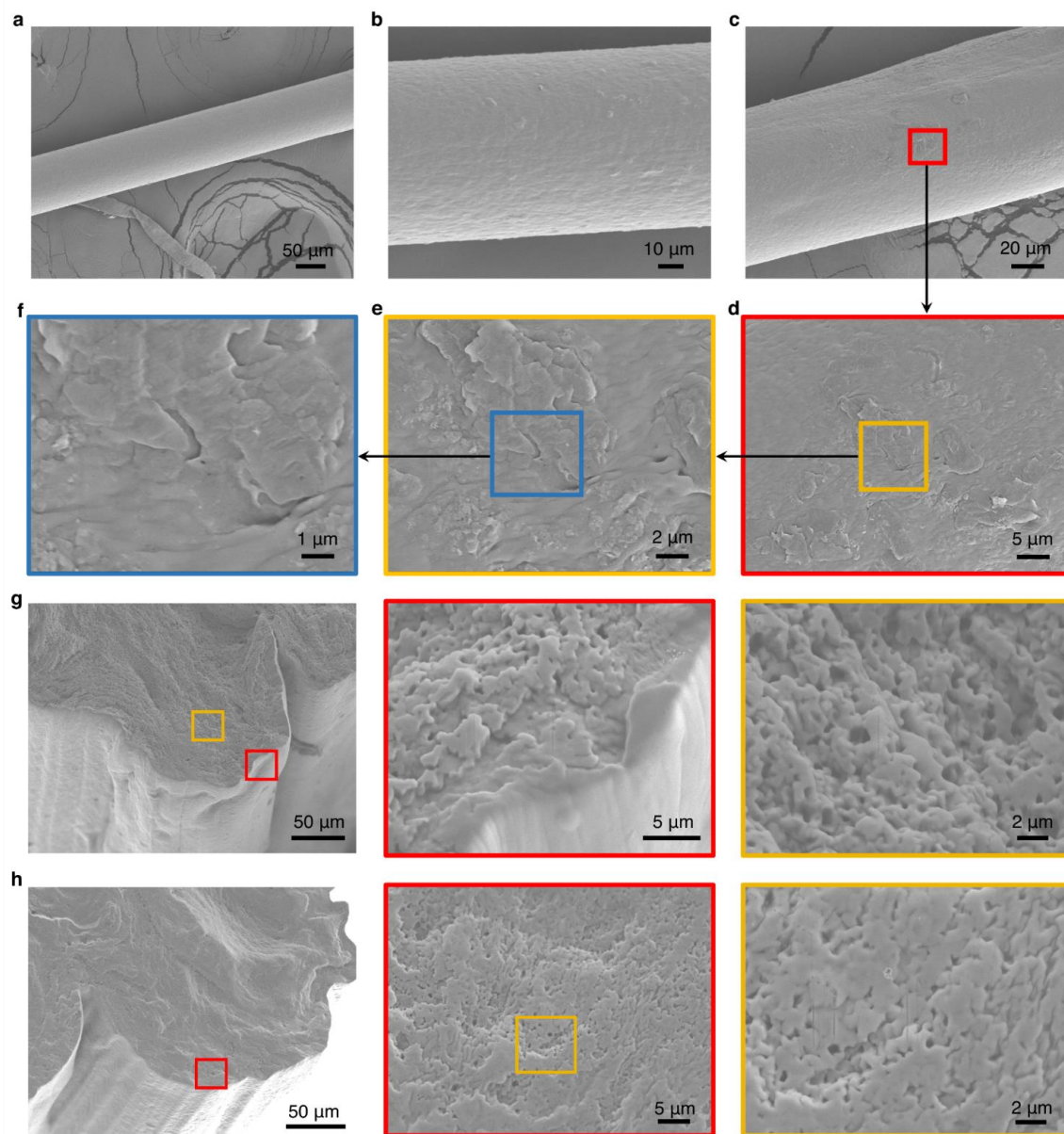
Supplementary Figure 26

Composition density evolutions of the precursor fiber during the phase separation. **a**, Composition of PANSion (solute). **b**, Composition of DMF (solvent). **c**, Composition of water (nonsolvent).



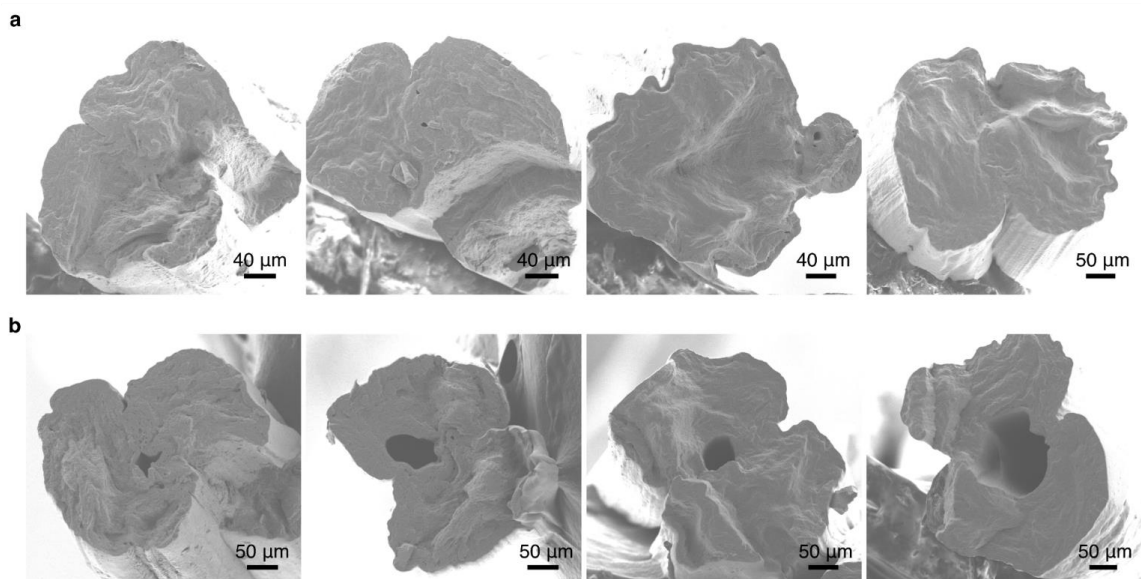
Supplementary Figure 27

Close-up observation of the water molecule density during the phase separation. Some water molecules went inside the precursor gel fiber. Water is miscible with DMF but is a poor solvent for PAN. Therefore, the absorbed water molecules drove the phase separation between DMF and PAN. Note that most adsorbed water molecules stayed out of the fiber and draw the DMF out from the precursor fiber, forming a mixed solution on the fiber surface.



Supplementary Figure 28

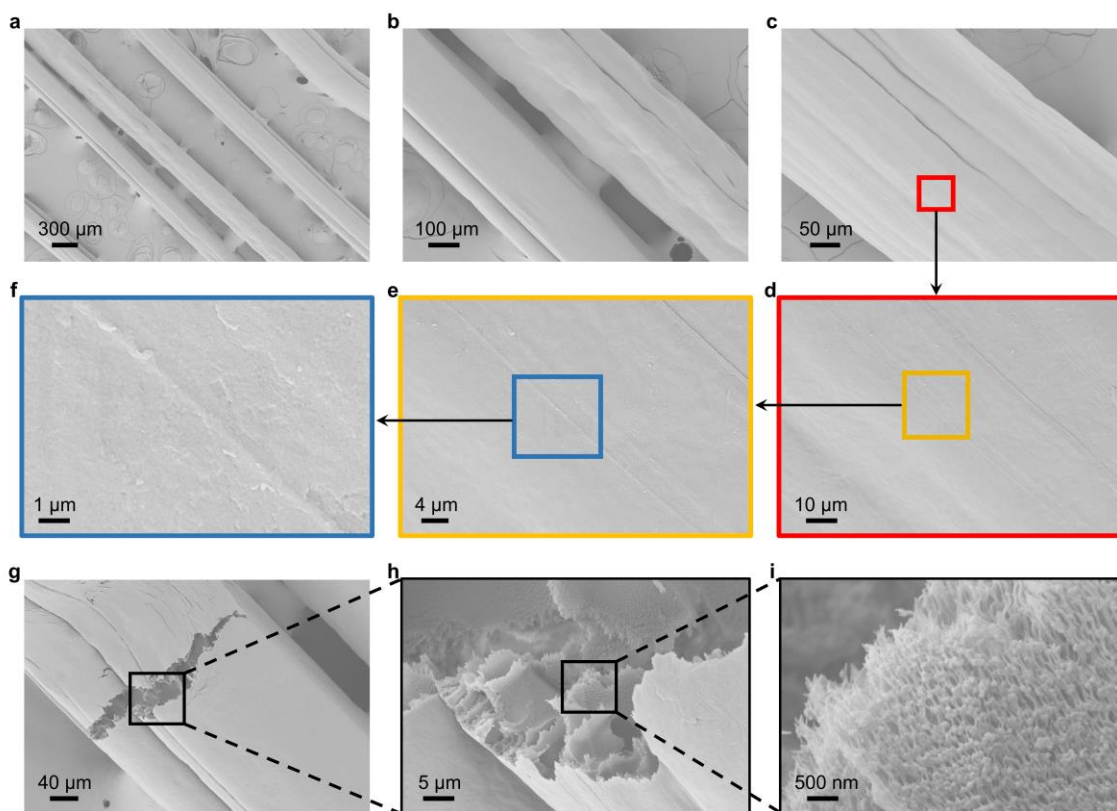
SEM images of PANSion fibers via PSEA spinning approach. **a–c**, SEM images at low (a) and high (b and c) magnifications, displaying a uniform fiber diameter and smooth surface. **d–f**, Enlarged area in (c) showing the corresponding fine surface features with sub-micrometer scale roughness. **g** and **h**, Cross sections showing the presence of nanoscale pores which were possibly resulted from the sub-microscale phase separation during spinning¹⁴.



Supplementary Figure 29

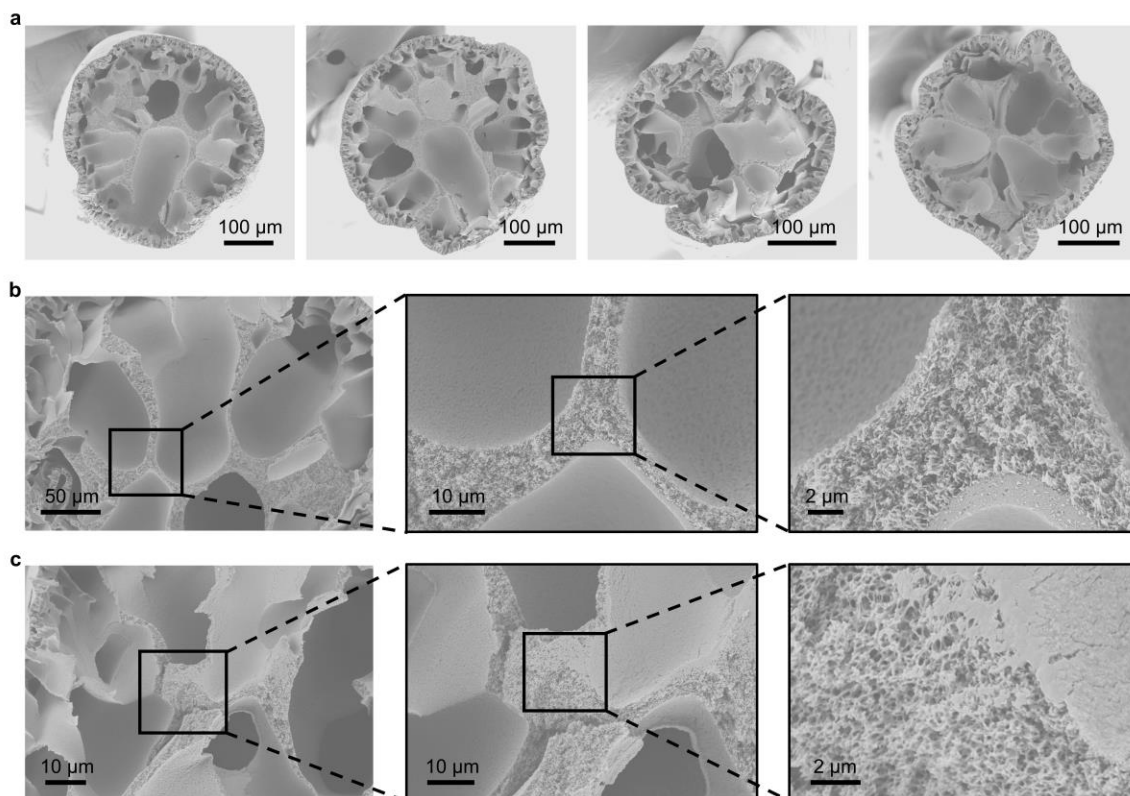
SEM images of cross-sectional morphologies of PANSion fibers via the PSEA spinning approach.

a, Fibers with a solid core. **b**, Fibers with a hollow core. Our proposed PSEA spinning approach needs further parameter optimization to enable fine structure control in future studies.



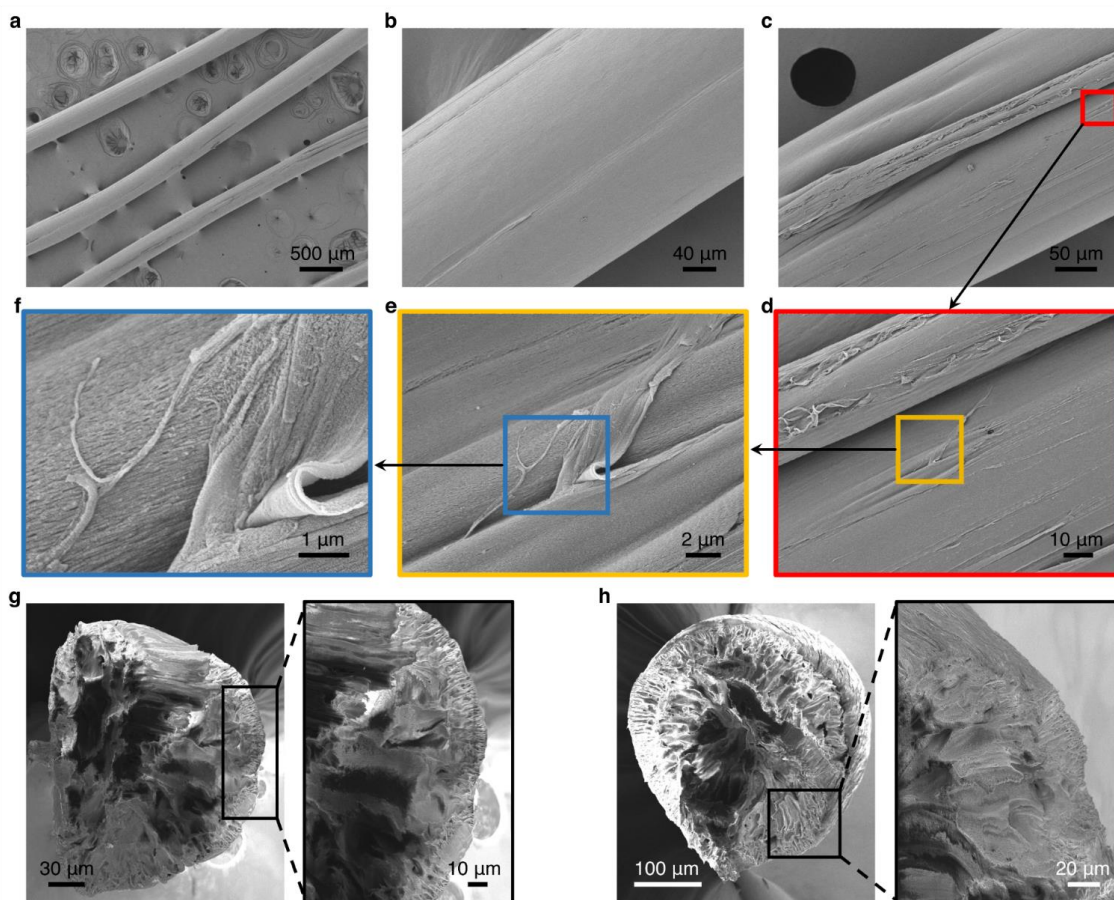
Supplementary Figure 30

SEM images of PAN fibers via wet spinning approach. **a–c**, Representative SEM images showing a uniform fiber diameter but with grooves on the fiber surface. **d–f**, Enlarged area in (c) showing the fiber's surface features. **g–i**, Morphologies of the cracked area of a fiber at different magnifications.



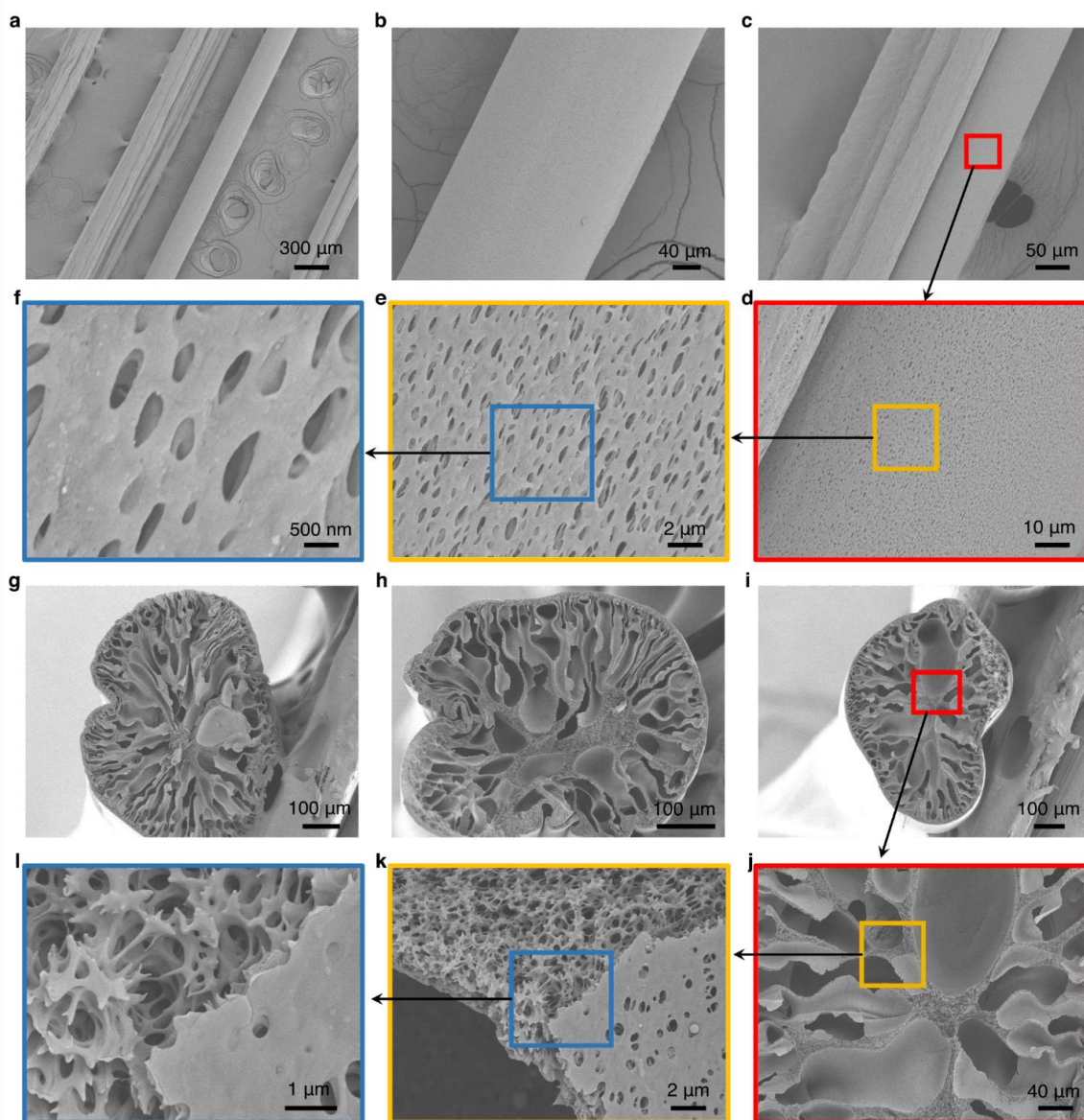
Supplementary Figure 31

SEM images of cross-sectional morphologies of PAN fibers via wet spinning approach. **a**, Four representative SEM images showing the cross-sectional porous structures. **b** and **c**, Two sets of the fine structures of the pore walls with self-assembled PAN molecular chains.



Supplementary Figure 32

SEM images of PANSion fibers via wet spinning approach using the as-prepared PANSion solution. **a–c**, Representative SEM images showing the fiber diameter and folding/groove structures. **d–f**, Enlarged area in (c) showing the fine structure of the folding and grooves. **g** and **h**, Two representative cross-sectional morphologies showing both large (in the core) and small (in the shell) pores.



Supplementary Figure 33

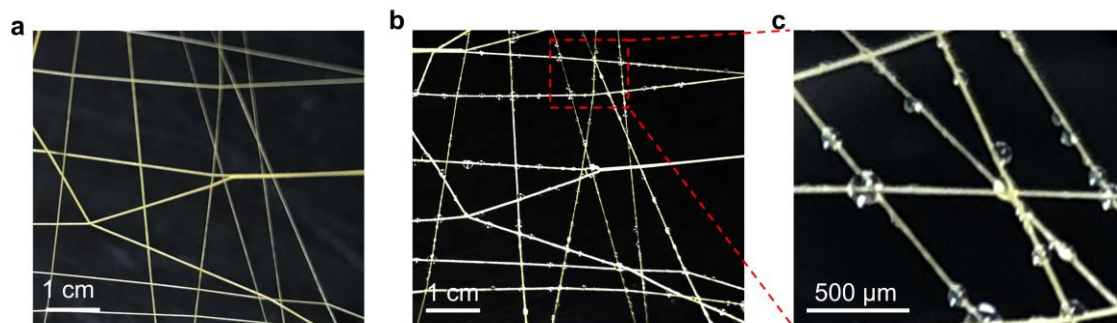
SEM images of PANSion fibers via wet spinning approach using the spinnable PANSion gel dope.

Fibers were obtained by immersing the precursor gel fibers in the water coagulation bath once a thread was drawn in air. **a–c** Representative SEM images showing the fiber diameter and folding/groove structures. **d–f**, Enlarged area in (c) showing the fine structure of the fiber surface with lots of sub-micrometer scale pores. **g–i** Representative SEM images showing the fiber's cross-sections with lots of big pores. **j–l**, Enlarged area in (i) showing the fine structure of the pore walls.



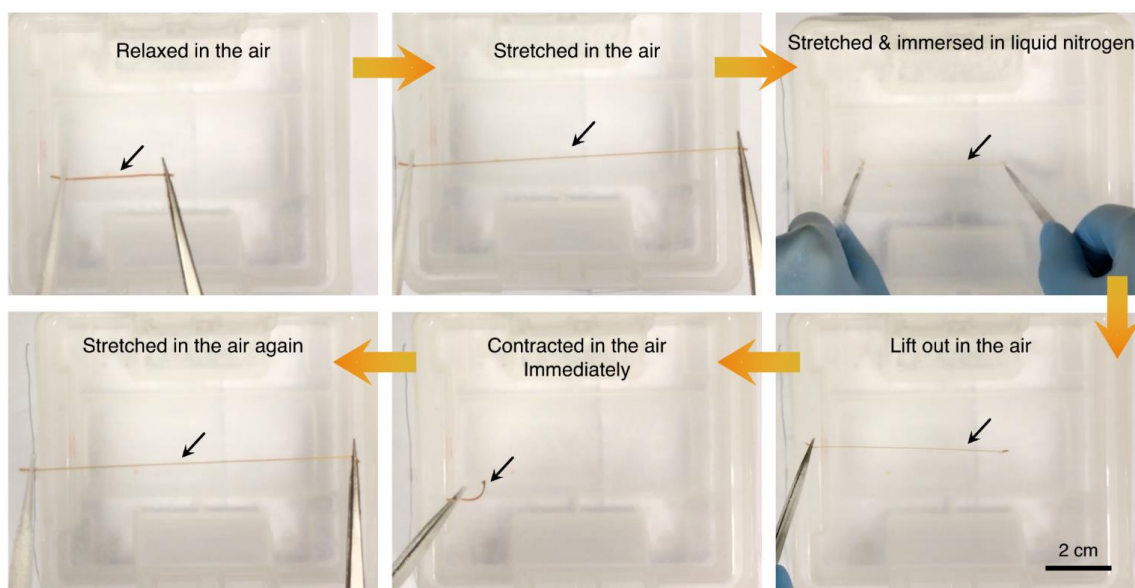
Supplementary Figure 34

Stability of PANSion fibers in DMF solvent and water. PANSion fibers were re-dissolved in DMF solvent. In contrast, the water did not exert any obvious decomposing effect.



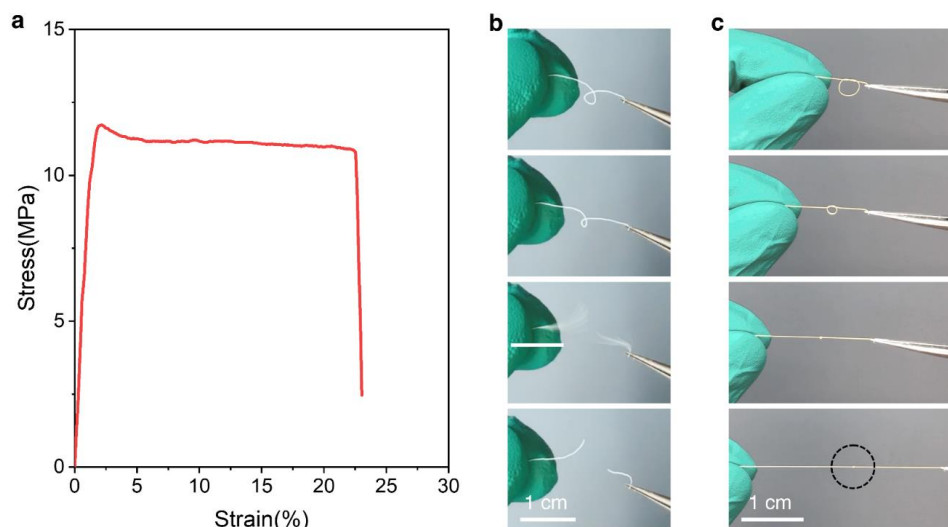
Supplementary Figure 35

A web made from PANSion fibers. a and b, A web made of PANSion fibers in a dry state (a) and wet state with water droplets (b). **c,** The enlarged view of the dashed area in (b).



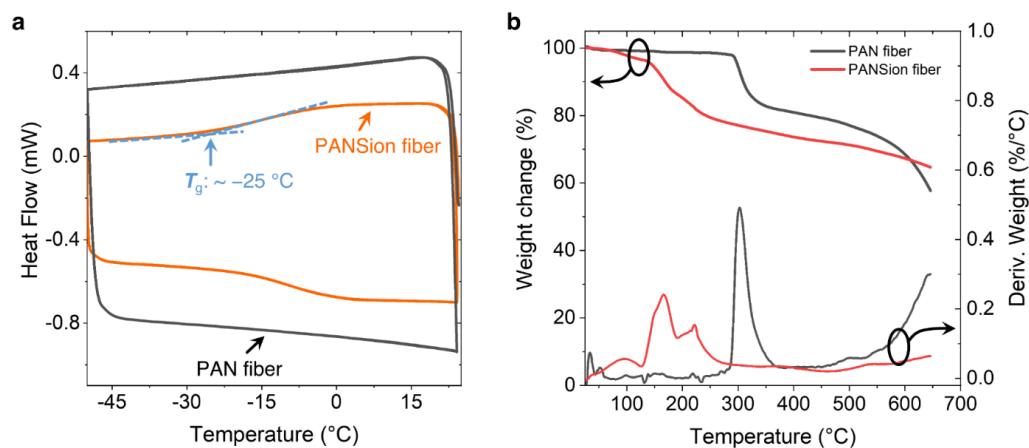
Supplementary Figure 36

Stretchability of PANSion fiber after low-temperature quenching. PANSion fiber was first stretched in air and then immersed in liquid nitrogen ($-196\text{ }^{\circ}\text{C}$) for 30 seconds, resulting in a frozen fiber. Once lifting it out, the fiber contracted and recovered its stretchability immediately.



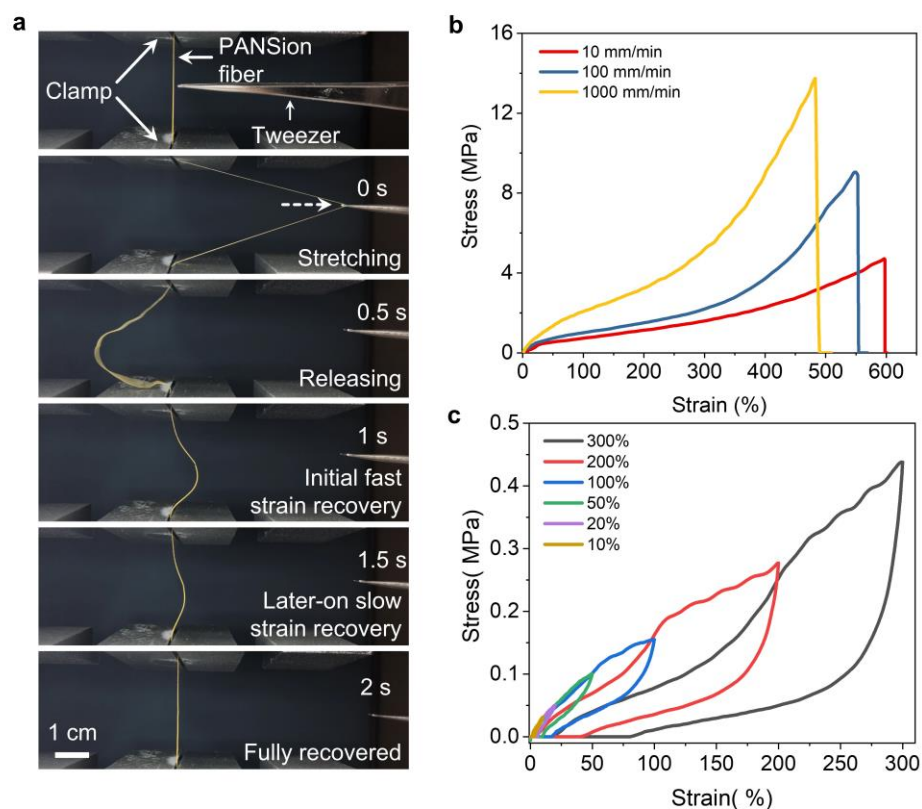
Supplementary Figure 37

Mechanical properties of different fibers. **a**, Stress-strain curve of PANSion fiber via wet spinning approach using PANSion gel dope. **b** and **c**, The comparison of knittability between PAN fiber@WS and PANSion fibers@PSEA.



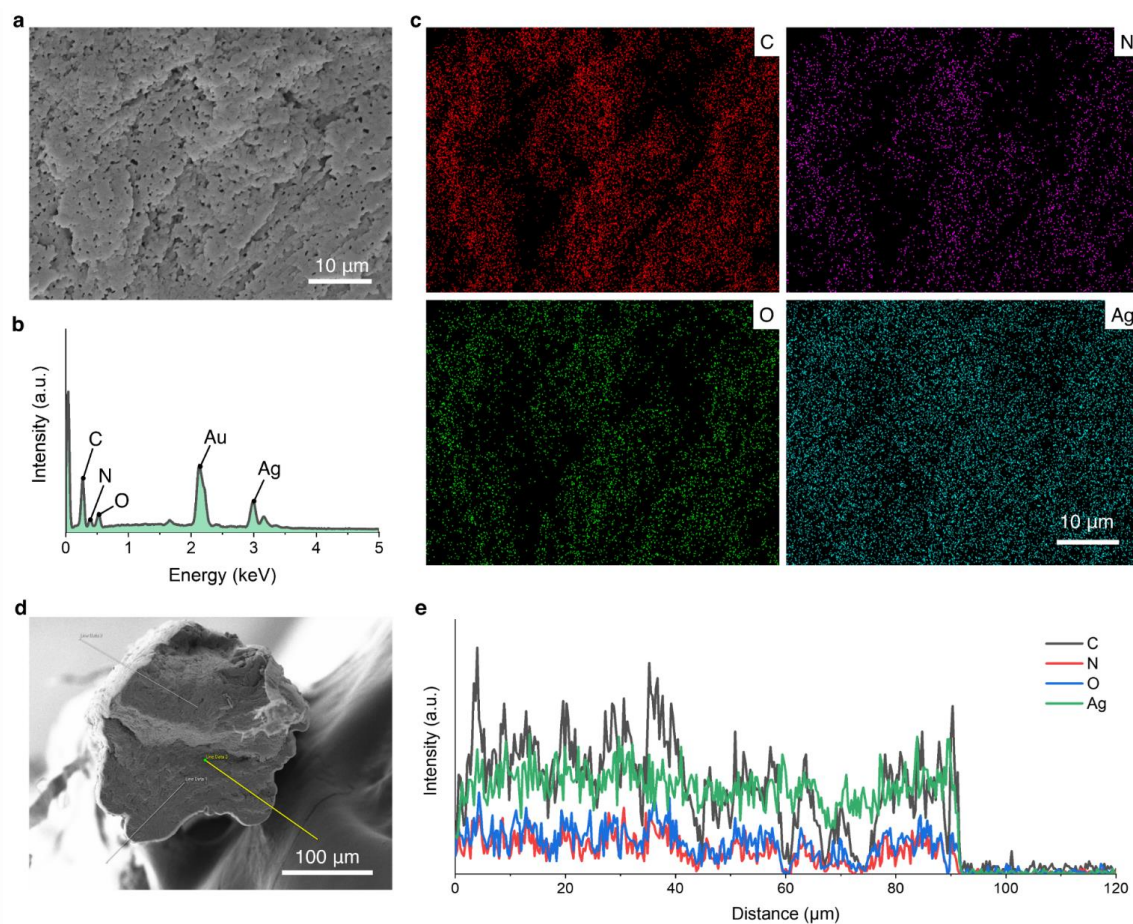
Supplementary Figure 38

DSC and TGA results of PAN and PANSion fibers. **a**, DSC results showing a glass transition temperature at $\sim -25\text{ °C}$ for PANSion fibers. In contrast, no glass transition temperature was detected for PAN fiber in the tested temperature range. **b**, TGA results indicating that more remaining DMF content in PANSion fibers compared to that of PAN fibers.



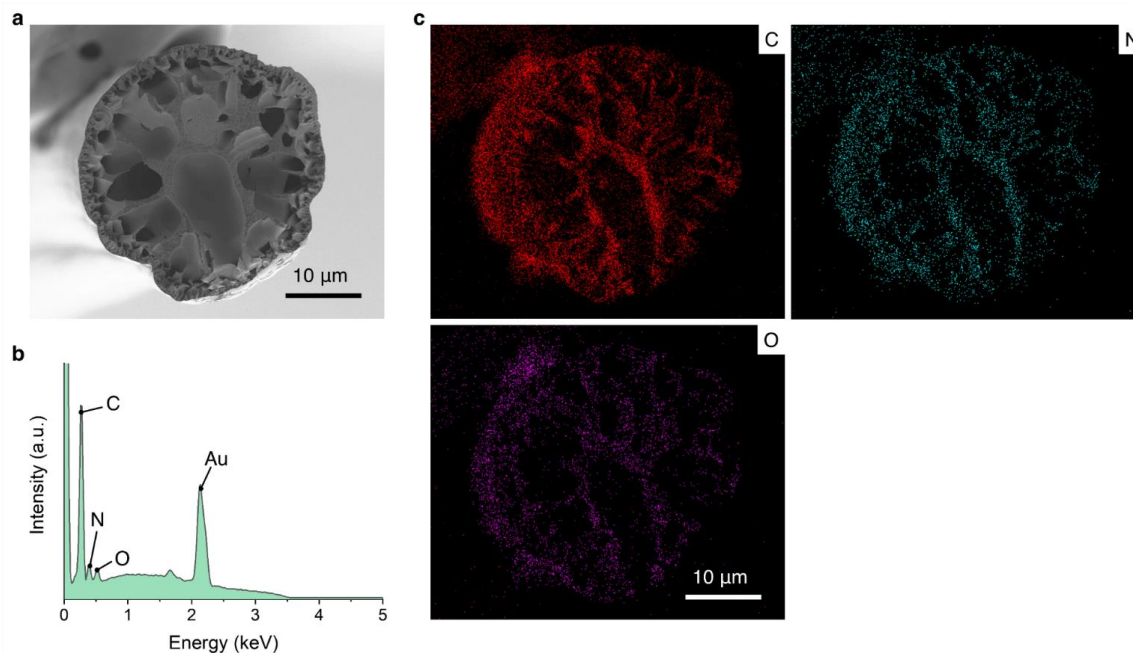
Supplementary Figure 39

Mechanical properties of PANSion fibers. **a**, Time-sequence images showing the fast strain recovery of PANSion fiber with a moderate strain hysteresis effect. **b**, The strain-rate effect (10 to 1000 mm/min) on PANSion fiber, showing a higher Young's modulus and tensile strength at a higher strain ramp rate. **c**, Consecutive stretching-releasing cycles while increasing the maximum strain from 10 to 300%.



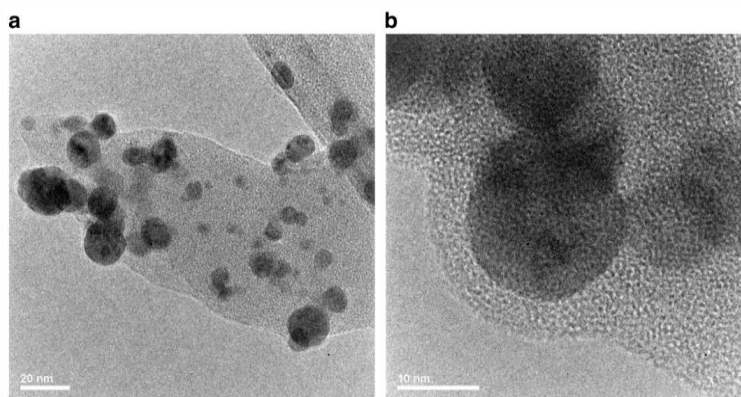
Supplementary Figure 40

Elemental composition analysis of PANSion fiber by EDX. **a** and **b**, SEM image of the fiber's cross-section (a) and its corresponding EDX spectrum (b). **c**, EDX mapping of the area shown in (a), including elements of C, N, O, and Ag. **d** and **e**, The radial element distribution analysis via EDX line scanning (d, marked by a yellow line) and the corresponding linescan profiles of C, N, O, and Ag elements (e).



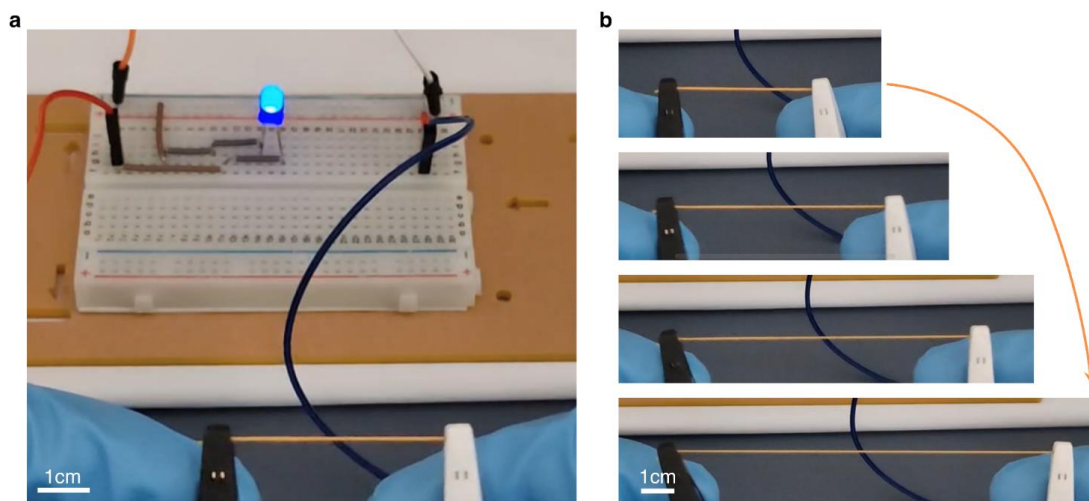
Supplementary Figure 41

Elemental composition analysis of PAN fiber by EDX. **a** and **b**, SEM image of the fiber's cross-section (a) and its corresponding EDX spectrum (b). **c**, EDX mapping of the area shown in (a), including elements of C, N, and O. No silver trace was detected.



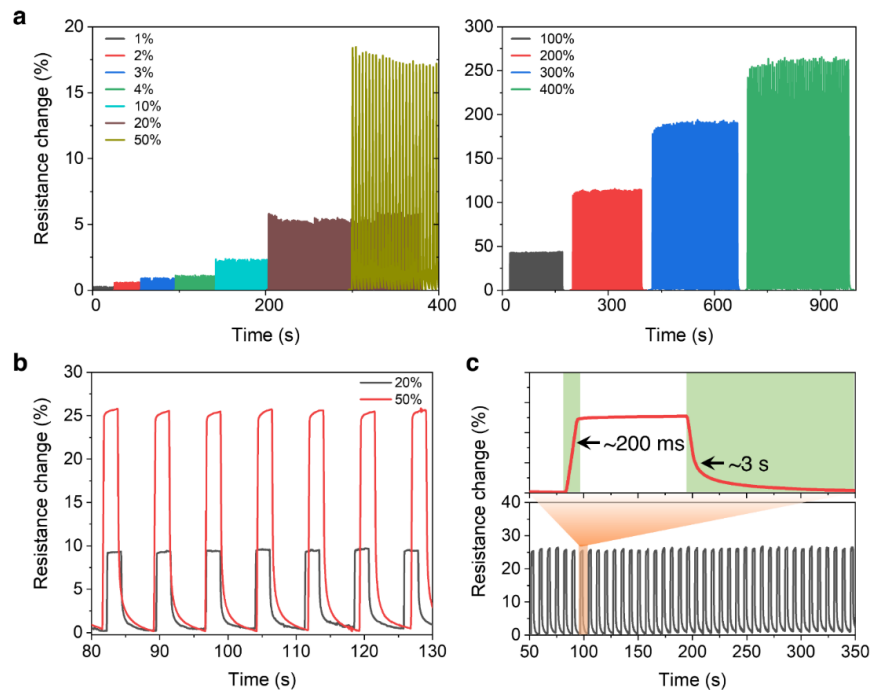
Supplementary Figure 42

TEM images of PANSion fiber. **a**, Silver nanoparticles (AgNPs) with different sizes. **b**, Silver nanoparticles at high magnification.



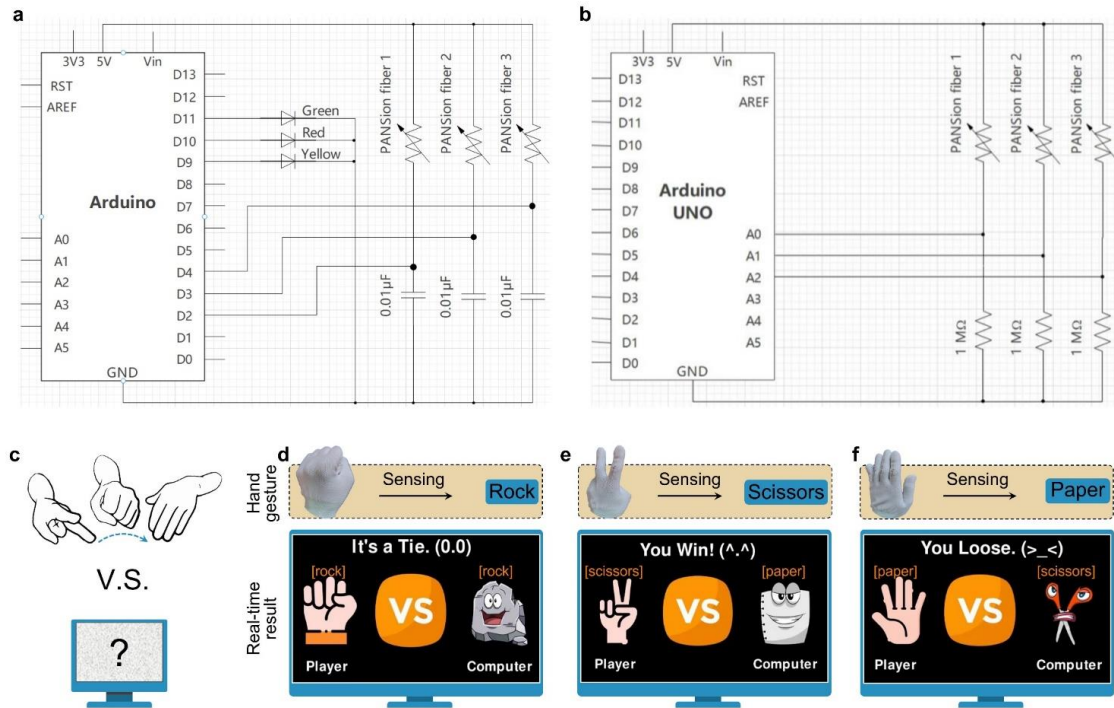
Supplementary Figure 43

PANSion fiber as a stretchable conductor. a, The setup of the circuit. **b,** Different stretching stages.



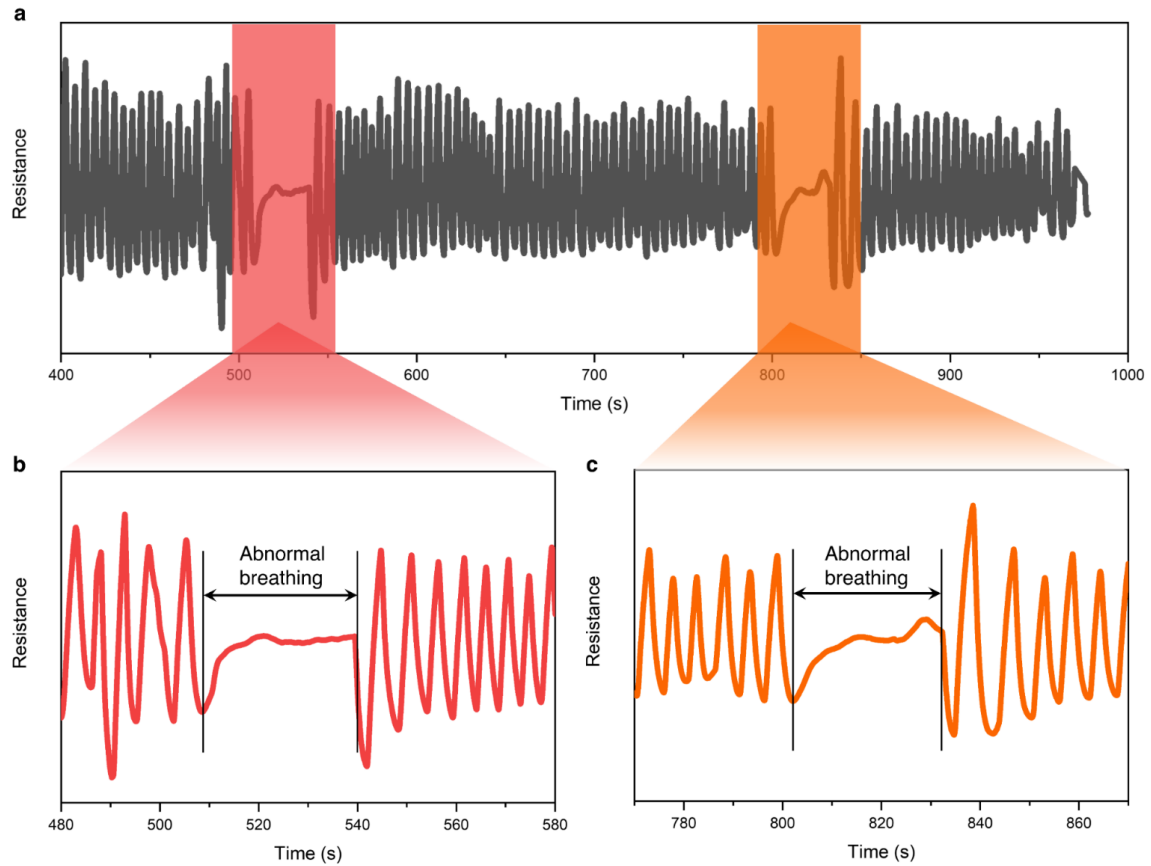
Supplementary Figure 44

PANSion fiber as strain sensors. **a**, The sensing performance as a piezoresistive sensor at both small (left) and large strains (right). **b**, Cyclic stretching-releasing at 20% and 50% strains. **c**, Response time and recovery time.



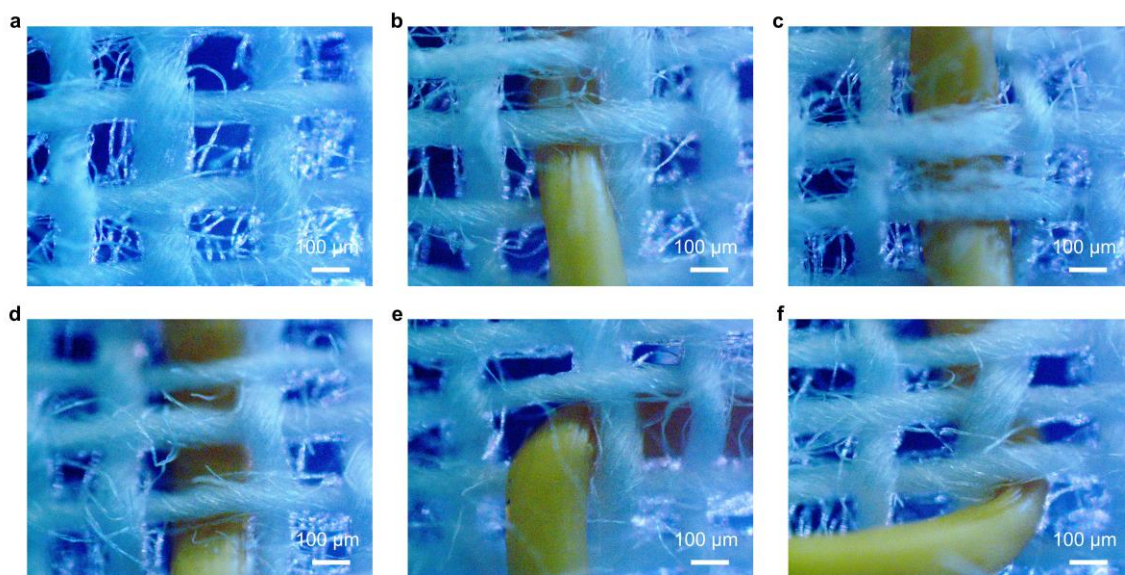
Supplementary Figure 45

Circuit diagrams for the sensing glove and its application for a hand gesture game. **a**, The circuit diagram to command the on-and-off switch of LEDs. **b**, The circuit diagram to monitor finger bending status. **(c–f)** Playing the rock–paper–scissors hand game against a computer player while wearing the sensing glove. Hand gestures can be detected by monitoring the bending status of the fingers, enabling the representation of “rock” (d), “scissors” (e), and “paper” (f), respectively.



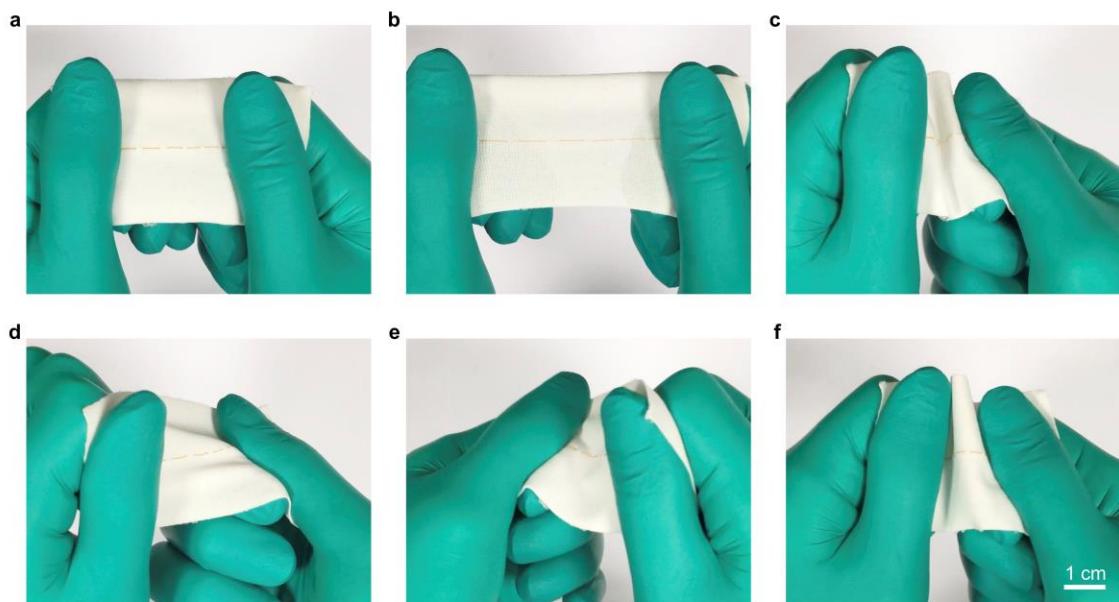
Supplementary Figure 46

Breath monitoring data collected from the simulated situations of obstructive sleep apnea-hypopnea syndrome (OSAHS). a, Data of the breathing rate when sleeping. **b** and **c**, The abnormal breathing rate detected based on the signal perturbations.



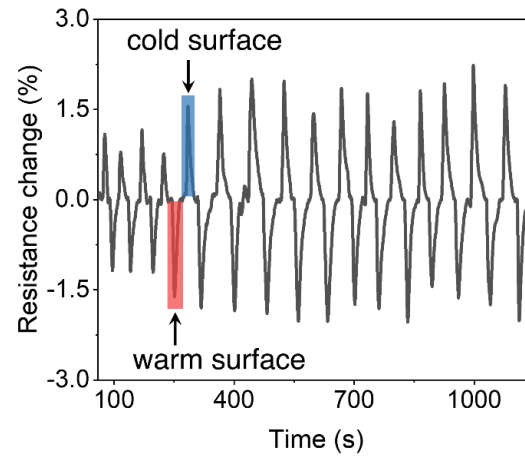
Supplementary Figure 47

Textiles with sewn PANSion fibers. **a**, A bare cotton textile. **b–f**, PANSion fibers as yarns in weft or warp direction (b–d), or the transition from weft to warp direction (e and f).



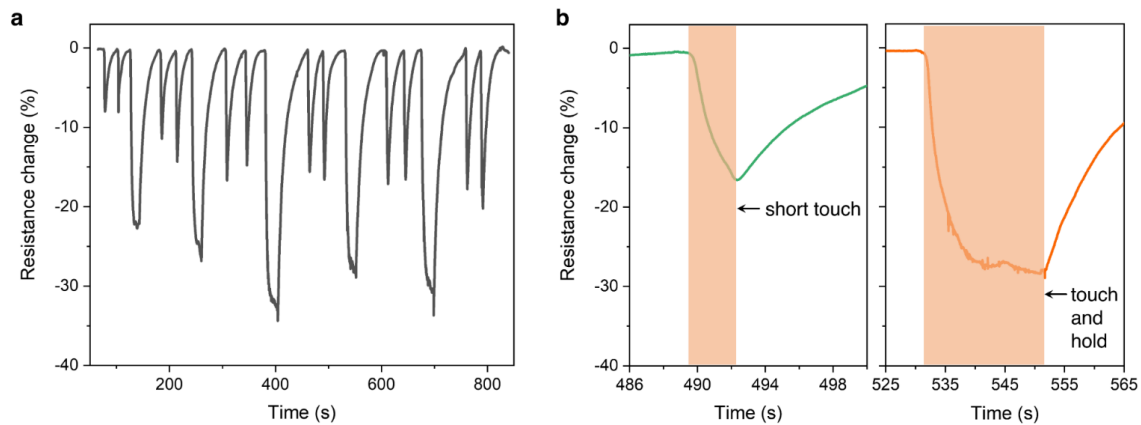
Supplementary Figure 48

Cotton textile with a sewn PANSion fiber showing no compromised mechanical properties, still stretchable, twistable, and bendable.



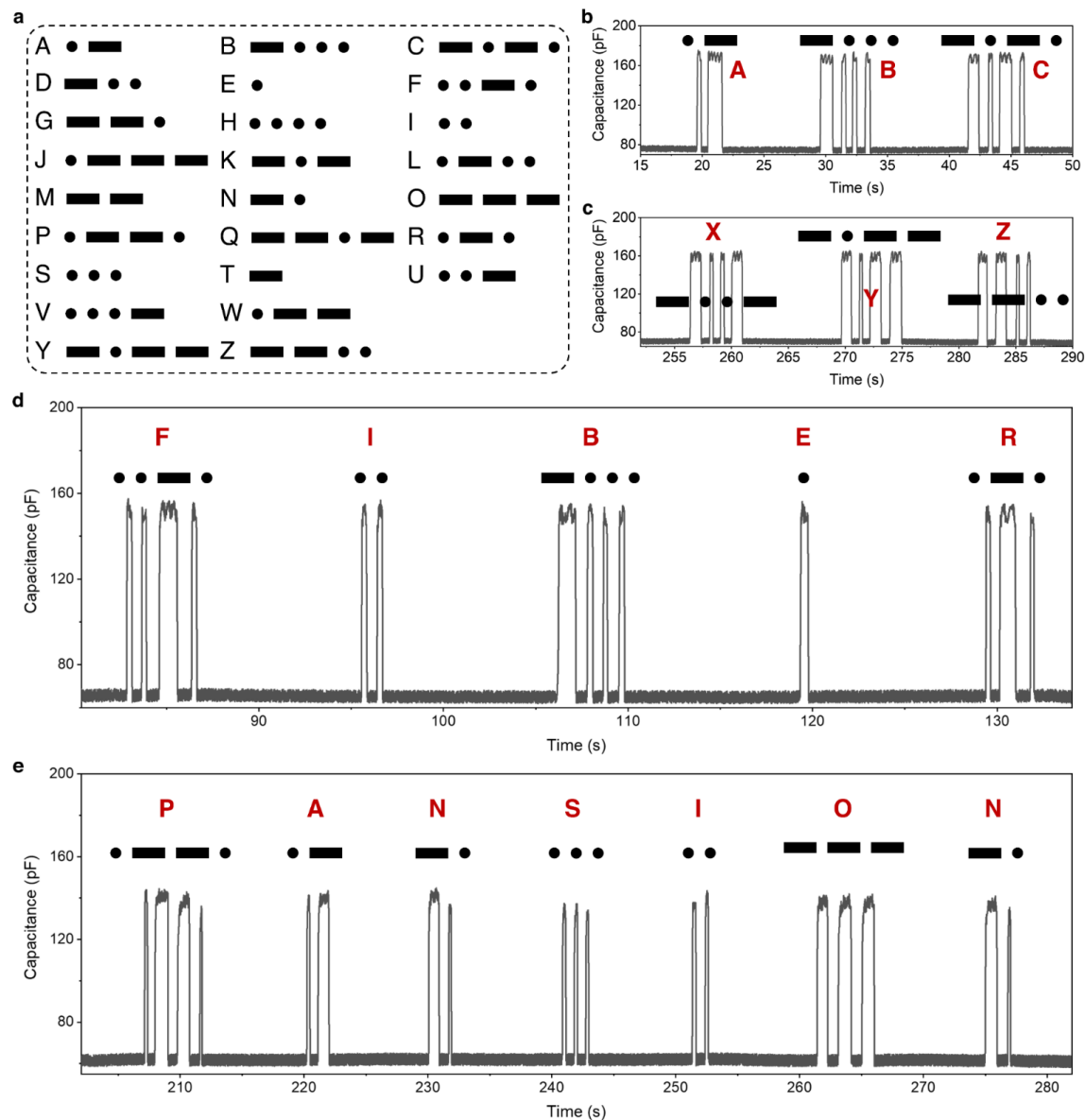
Supplementary Figure 49

Resistance changes of the sensing glove when approaching cold and warm surfaces, alternatively.



Supplementary Figure 50

Resistance changes of the sensing glove when being touched by a human finger. a, Resistance changes from the short and long (dynamic) finger touches. **b,** Comparison of electrical signals between short touch and long touch (touch-and-hold).



Supplementary Figure 51

Application demonstration using the sensing glove as a human-machine interface for encrypt communications. **a**, Table of Morse Code. **b** and **c**, Examples of letters "A", "B", "C", "X", "Y", and "Z", which were decoded from the patterns of capacitance change signals in a specific time range. **d** and **e**, the words "FIBER" and "PANSION" expressed in Morse Code by touching the sensing glove.

Supplementary Table 1

Different methods of preparing conductive fibers for soft and stretchable electronics.

Preparation method	Fillers	Spinning conditions					Post-treatment	Application	Refs
		Light	Heating /Cooling (°C)	Coagulation bath	High voltage (kV)	High pressure (MPa)			
Self-lubricated spinning	X ^a	UV ^b	X	water	X	X	Solvent exchange	Actuator	17
Commercial PU ^c fiber	X	X	X	X	X	X	AgNP ^d coating	Sensor	18
Multifiber coaxial twisting	X	X	X	X	X	X	Sheath coating	Sensor; energy generator	19
Electrospun SBS ^e fiber	X	X	X	X	18.0	X	AgNP coating	Sensor	20
Air-blow spinning	X	X	450	X	X	0.15	Embedding on elastomers; annealing	Sensor	21
Air-blow spinning	GO ^f	X	X	ethanol	X	X	Solvent exchange; annealing	Conductor	22
Thermal drawing	Liquid metal	X	150–350	X	X	X	Fiber core dissolving	Energy generator	23
Gelation extrusion	CNT ^f	X	–20	X	X	X	X	Sensor; energy generator	24
Hydrothermal annealing	GO/CNT	X	220	X	X	X	X	Conductor	25
Wet spinning	X	X	X	NH ₄ OH NH ₄ Cl	X	X	X	Conductor	26
Wet spinning	X	X	X	Buffer (pH5.0)	X	X	Surface coating	High strength	27
Wet spinning	X	UV	X	Ca ²⁺ solution	X	X	Solvent exchange	Sensor	28
Coaxial printing	CNT	X	X	X	X	X	X	Energy generator	29
Extruding in air	HFIP ^g	X	60	X	X	X	CNT coating	Sensor	30
Spider spinning	X	X	X	X	X	X	PEDOT:PSS/CNT coating	Sensor	31
Spinning in air	Silica NPs ^h	X	X	X	X	X	Twist insertion	Impact absorption	32
Spinning in air	Silica NPs	X	X	X	X	X	X	Damping capacity	4
Spinning in air	X	X	80	X	X	X	Sheath coating	Conductor	5
Our PSEA spinning approach	X	X	X	X	X	X	X	Sensors	This work

^a“X” indicates “not required”; ^bUV: ultraviolet; ^cPU: polyurethane; ^dAgNP: silver nanoparticle; ^eSBS: styrene-block-butadiene-block-styrene; ^fGO: graphene oxide, CNT: carbon nanotube; ^gHFIP: hexafluoro-iso-propanol; ^hNPs: nanoparticles.

Supplementary Table 2

Comparison between PANSion fiber and other elastic fibers in terms of intrinsic stretchability, conductivity, and energy efficiency.

	Melting Temp. (°C)	Stretchability (%)	Conductivity (S/m)	Density (g/cm ³)	Heat capacity (J/g/°C)	W _{melting} (J/cm ³)
SEBS	350	700 ³³	10 ⁻¹⁴³⁴	0.91	1.25 ²³	398.125
PDMS	53	160 ³⁵	10 ⁻¹⁴³⁶	0.97	1.625 ²³	83.54125
PU	171	800 ³⁷	10 ⁻¹⁶³⁸	1.2	0.665 ²³	136.458
PVA	233	0.46 ³⁹	10 ⁻¹⁰⁴⁰	1.3	1.5 ²³	454.35
PAN	322	1	10 ⁻¹⁰⁴¹	1.184	64	24399.87
PANSion	-	>500	1.82	-	-	≈ 0

Note that we assigned the stretchability and conductivity as intrinsic properties to PANSion as they were obtained from the single-step synthesis process with no additional treatments. PAN is not stretchable (<1% failure strain) nor conductive. PAN with post-added conductive fillers was not stretchable, either⁴².

Supplementary Table 3

Fitting parameters of an empirical model to describe the profile of fiber diameter change during phase separation.

Equation	$D(\%) = A \exp\left(-\frac{t}{3\tau'}\right) + D_f$
A	46.73039 ± 0.97034
D_f	59.50032 ± 0.46156
$3\tau'$	10.4002 ± 0.42883
Reduced Chi-Square	1.19503
R-Square	0.99043
Adj. R-Square	0.98974

Supplementary Table 4

Mechanical properties of PAN and PANSion fibers via wet spinning and PSEA spinning approaches.

	Strength (MPa)	Failure strain (%)	Modulus (MPa)
PAN@WS	12.000 ± 0.928	0.822 ± 0.104	1525.1 ± 290.1
PANSion@WS	12.727 ± 1.853	24.456 ± 7.552	1034.5 ± 125.9
PANSion@DS	6.277 ± 0.506	563.028 ± 34.666	2.05 ± 0.15

Supplementary Table 5

The parameters of non-bonded interactions in CG-MD simulations.

$\epsilon_{ij}/\sigma_{ij}$	A	B	C	D
A	$0.0895\epsilon_0/0.89\sigma_0$	$0.895\epsilon_0/0.678\sigma_0$	$0.358\epsilon_0/0.89\sigma_0$	$0.112\epsilon_0/0.89\sigma_0$
B		$0.0895\epsilon_0/0.89\sigma_0$	$0.313\epsilon_0/0.89\sigma_0$	$0.112\epsilon_0/0.89\sigma_0$
C			$0.448\epsilon_0/0.089\sigma_0$	$0.560\epsilon_0/0.89\sigma_0$
D				$0.560\epsilon_0/0.89\sigma_0$
Note: A represents PAN, B represents AgNO ₃ , C represents DMF, D represent H ₂ O				

Supplementary References

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