Supporting Information

TiO_2/SiO_2 spiral crimped Janus fibers engineered for stretchable ceramic membranes with high-temperature resistance

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S4: Experimental section - Materials

Titanium isopropoxide (TIP; 95%, CAS546-68-9, Macklin) was used as the precursor and polyethylene oxide (PEO; Mw = 600,000, CAS68441-17-8, Rhawn) as the polymer template to prepare the TiO_2 component of composite nanofibers. While tetraethyl orthosilicate (TEOS; 98%, CAS562-90-3, Macklin) was used as the precursor and polyvinyl alcohol (PVA, 1788, CAS9002-89-5, Macklin) as the polymer template to prepare SiO_2 component of composite nanofibers. Other chemicals, ethanol absolute (EtOH; 99.7%, CAS64-17-5, Sinopharm) and glacial acetic acid (Hac; 99.5%, CAS64-19-7, Aladdin), were used to regulate the hydrolysis process of TIP. Phosphoric acid (H_3PO_4; 85%, CAS7664-38-2, Collins) was used to promote the hydrolysis of TEOS to form a stable sol. Dopamine hydrochloride (DA; 98%, CAS62-31-7, Macklin) was used as a dopant for TiO_2. All chemicals were used directly without further purification.

S5: Experimental section - Preparation of the TiO_2/SiO_2 NFMs

An ultra-light, stretchable and elastic ceramic nanofibrous membranes composed of spiral crimped nanofibers were prepared by conjugate electrospinning united with calcination treatment. Firstly, the spinning solution was prepared by the following procedures. Dissolve the PEO powder in HAc, then stir the solution until clear. Then, 0.1wt% DA was added to EtOH by ultrasonic treatment for 20 minutes, after which it was added to the above solution and then stirred for 2h. The mass ratio of PEO: HAc: EtOH was 0.1: 2: 3. Subsequently, TIP was added to the above mixed solution and stirred for 1h. The weight ratio of TIP to PEO powder was 14: 1, and TiO_2 precursor solution could be obtained. Equivalent mass TEOS was mixed with deionized water, followed by the addition of 0.5% H_3PO_4 to promote hydrolysis, stirring for 8h, and a stable silica sol was configured. The PVA aqueous solution with 10% concentration was stirred in a water bath at 80℃ for 2h until the solid was entirely dissolved. The SiO_2 precursor solution was obtained by mixing the silica sol with the PVA solution at a mass ratio of 1:1 and stirring for 8h. The precursor of SiO_2/TiO_2 NFMs were fabricated via conjugate electrospinning. The TiO_2 precursor and SiO_2 precursor solutions were divided into two 10ml syringes, with one syringe connected to the

positive electrode at high voltage and the other connected to the negative one, and the receiving device was grounded. The spinning solution was injected at a certain speed during the electrospinning. The TiO_2 precursor solution was applied a voltage of 6kV for stretch, and the SiO_2 precursor solution was applied a voltage of 9kV. The relevant humidity and temperature were maintained at (45±3%) and (25±3℃) throughout the entire electrospinning process. The distance between receiving device (a rotating disk) and spinneret was 15 cm, and the disk rotated at a speed of 45 rpm, obtaining the precursor of TiO_2/SiO_2 NFMs.

Furthermore, the spun samples were dried completely in an oven at 40℃ to eliminate any residual solvents. Then, these samples were annealed in a muffle furnace, and the temperature was heated at 5℃/min to 200℃ for 1h, then heated at 800℃ for 20 min, and the stretchable TiO_2/SiO_2 nanofibrous membrane was prepared. In order to study the influence of calcination temperature relating to the crystal structure of hybrid nanofibrous membranes, they were also annealed at different temperatures (300 ~ 700℃).

S6: Experimental section - Material characterization

The morphology and microstructure of TiO_2/SiO_2 NFMs were observed through digital camera, scanning electron microscope (SEM; VEGA 3lum, Czech), as well as a field emission scanning electron microscope (FE-SEM; SU8010, China). The element distribution of a single spiral crimped nanofiber was performed with energy dispersive spectrometer (EDS; SU8010, China). The crystallization properties were examined using transmission electron microscopy (TEM; JEM-2100, Japan). X-ray photoelectron spectroscopy (XPS; Escalab 250Xi, China) was used to analyze the chemical composition and bonding states of TiO_2/SiO_2 NFMs. The crystal structure of specimens was tested by X-ray diffraction (XRD; D8 ADVANCE, Germany). The thermal analysis of specimens in air was studied with thermogravimetric analyzer (TGA; TGA8000, China). The changes in chemical bonds were characterized by Fourier

Transform Infrared spectrometer (FTIR; Nicolet6700, USA). The tensile recovery properties and tensile strength of TiO_2/SiO_2 NFMs were measured by dynamic mechanical analyzer (DMA; DMA850, USA). The dynamic tensile properties of the material were characterized by *in situ* cyclic uniaxial tensile tests inside an SEM. The thermal insulation properties of TiO_2/SiO_2 NFMs were recorded by infrared thermal camera (Fluke TiS75+, USA). The thermal conductivity of specimens was assessed with hot disk instrument (TPS2500S, Switzerland).

S7: Supporting Figures S1-S17, Table S1 and Formula S1

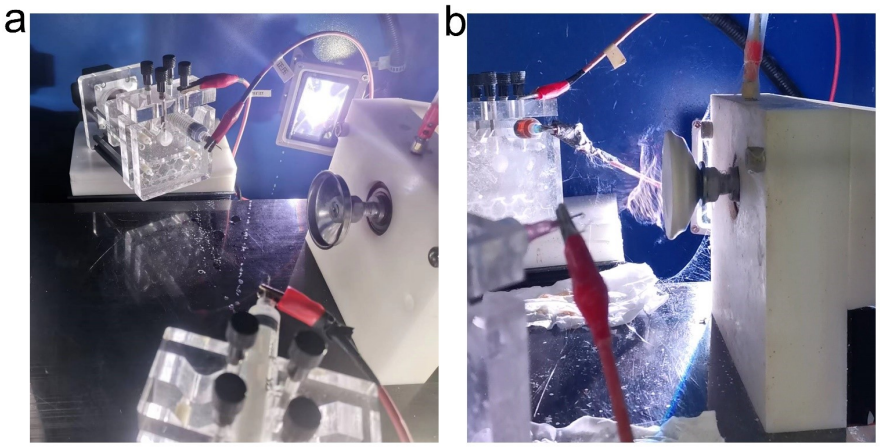

Figure S1. Conjugate electrospinning. (a) Two spinning solutions subjected to positive and negative voltages respectively. (b) Fibers intertwined and piled onto the rotating disk.

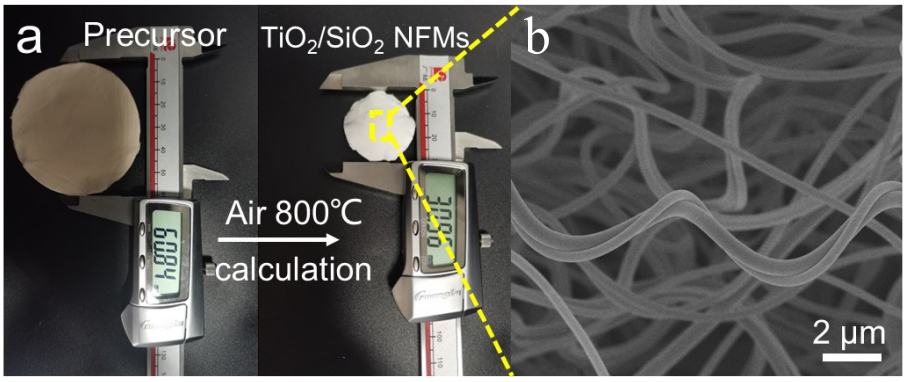

Figure S2. (a) The size changes of TiO_2/SiO_2 NFMs before and after calcination at 800℃, (b) SEM image of TiO_2/SiO_2 spiral crimped Janus fibers.

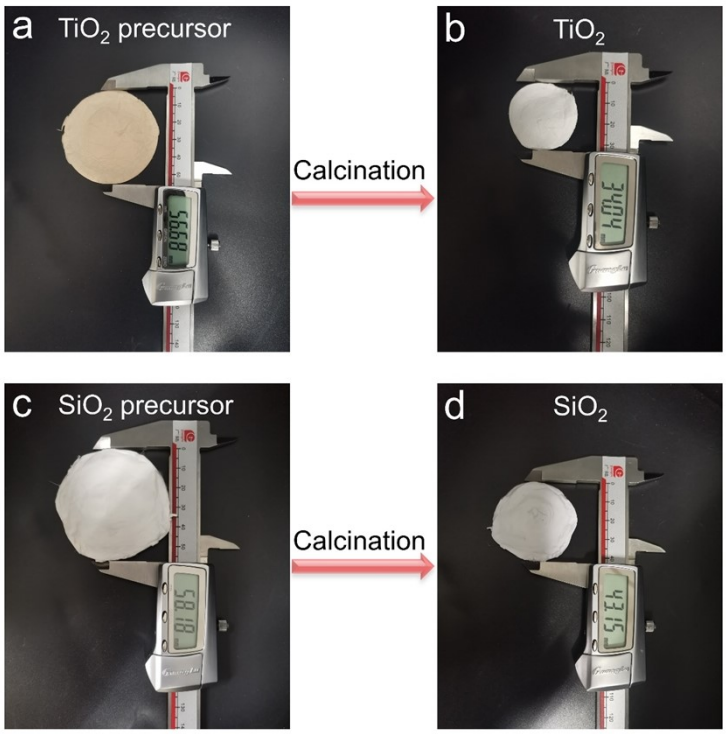

Figure S3. The size changes of TiO_2 and SiO_2 nanofibrous membrane before and after calcination at 800℃, (a) TiO_2 NFM precursor, (b) TiO_2 NFM, (c) SiO_2 NFM precursor and (d) SiO_2 NFM.

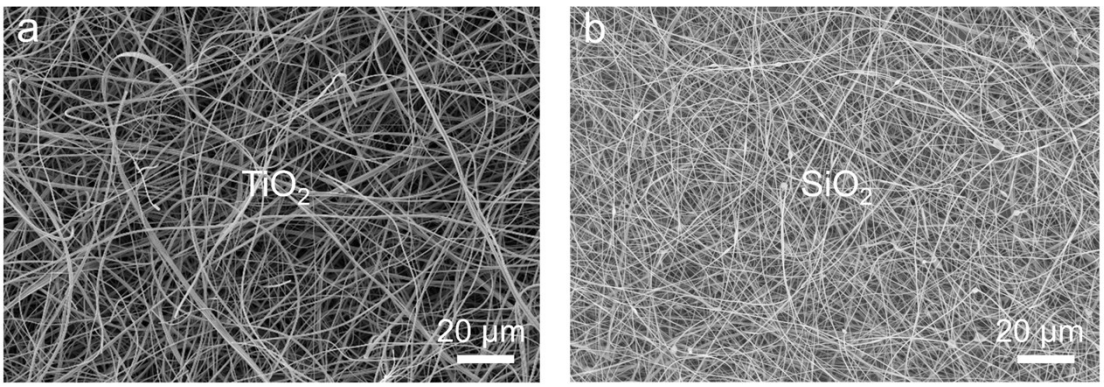

Figure S4. The SEM images of (a) pure TiO_2 and (b) pure SiO_2 nanofibrous membranes.

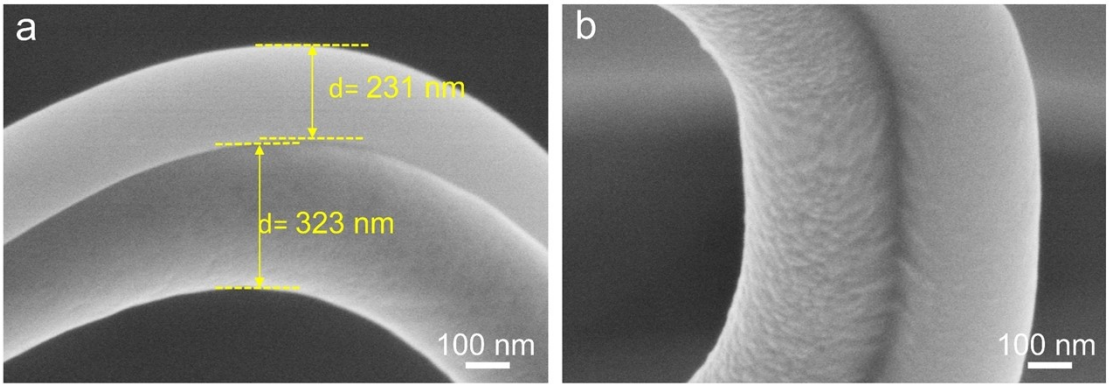

Figure S5. (a-b) SEM images at high magnification to observe the surface morphology and diameter of a single spiral crimped composite fiber.

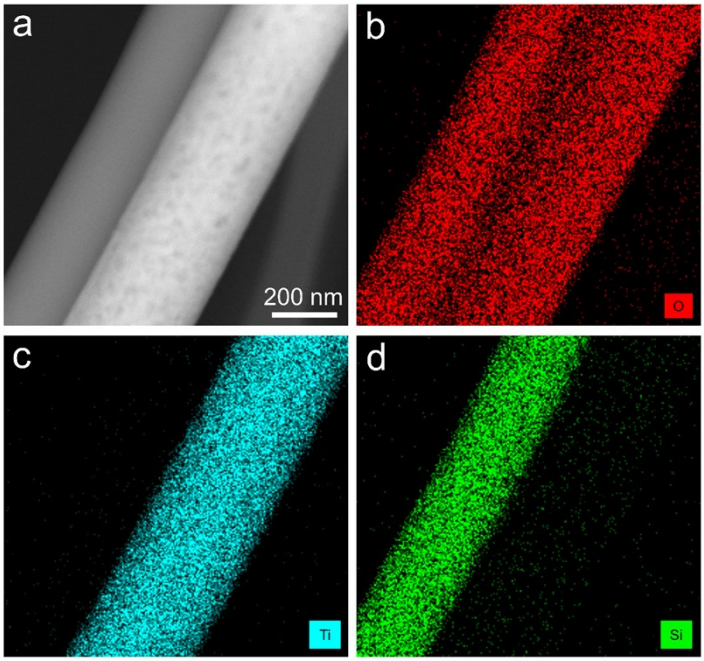

Figure S6. TEM elemental mappings of a single spiral crimped composite fiber, (a) TEM, (b) O element, (c) Ti element, (d) Si element.

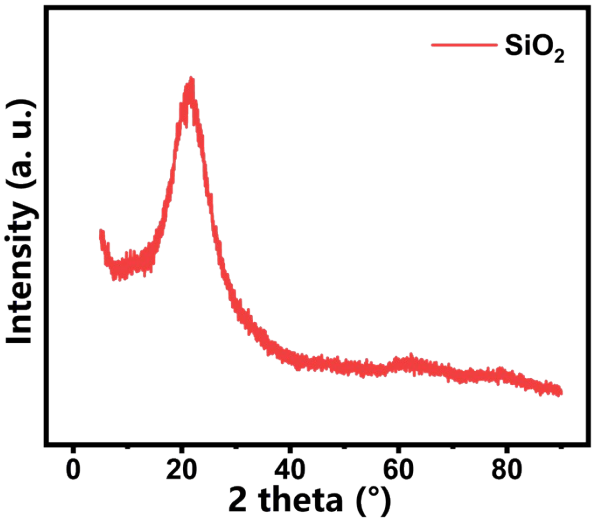

Figure S7. The XRD spectrogram of SiO_2 nanofibrous membrane.

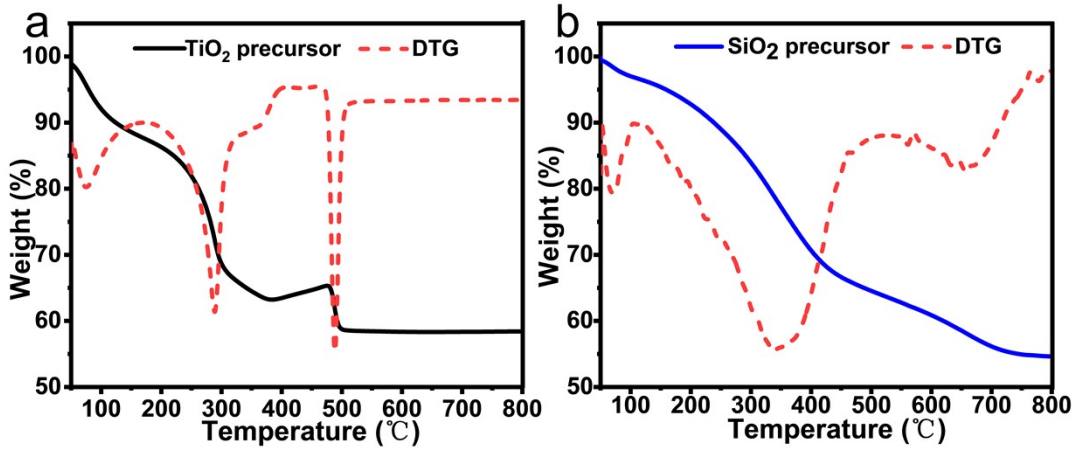

Figure S8. TG and DTG diagrams of (a) TiO_2 and (b) SiO_2 gel nanofibrous membranes.

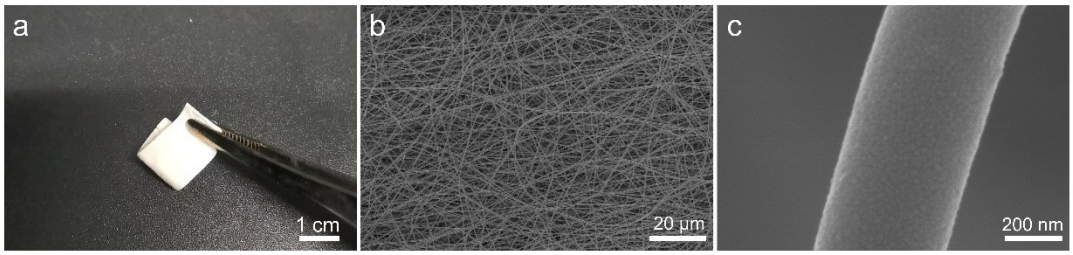

Figure S9. Pure TiO_2 nanofiber membrane calcined at 800℃. (a) Bending and folding photographs. (b) SEM image of TiO_2 membrane. (c) An enlarged view of a single TiO_2 nanofiber in (b).

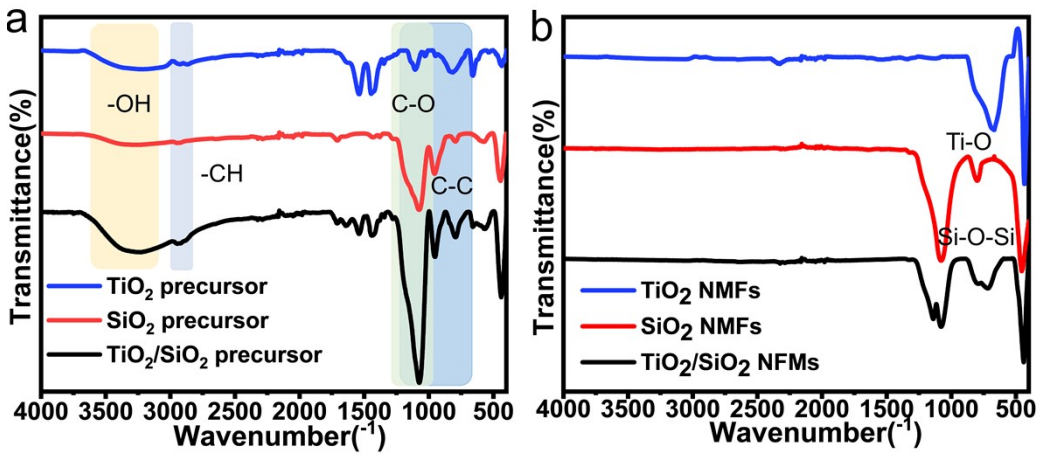

Figure S10. FTIR spectra of (a) TiO_2 precursor, SiO_2 precursor and TiO_2/SiO_2 precursor, and (b) TiO_2, SiO_2 and TiO_2/SiO_2 NFMs.

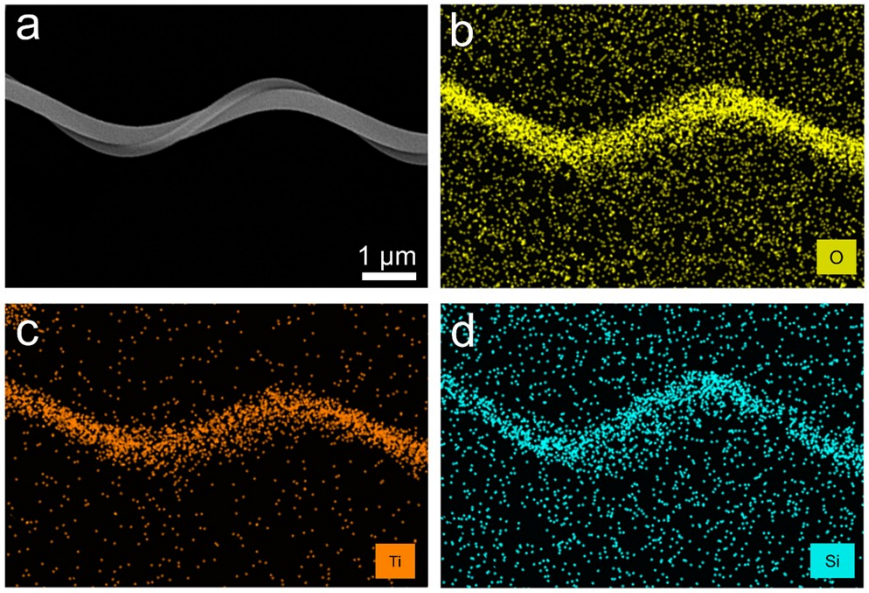

Figure S11. SEM elemental mapping of a single composite gel fiber, (a) SEM, (b) O element, (c) Ti element, (d) Si element.

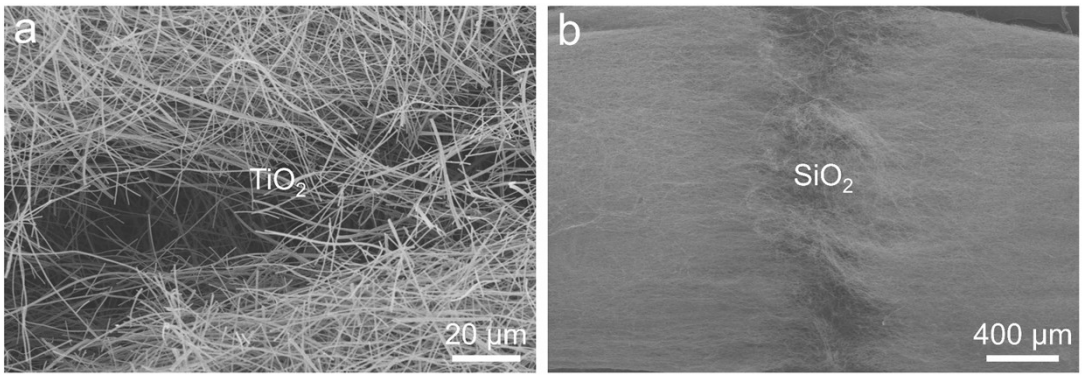

Figure S12. SEM images for the brittle breakage of TiO_2 NFM (a) and the slip of SiO_2 NFM (b).

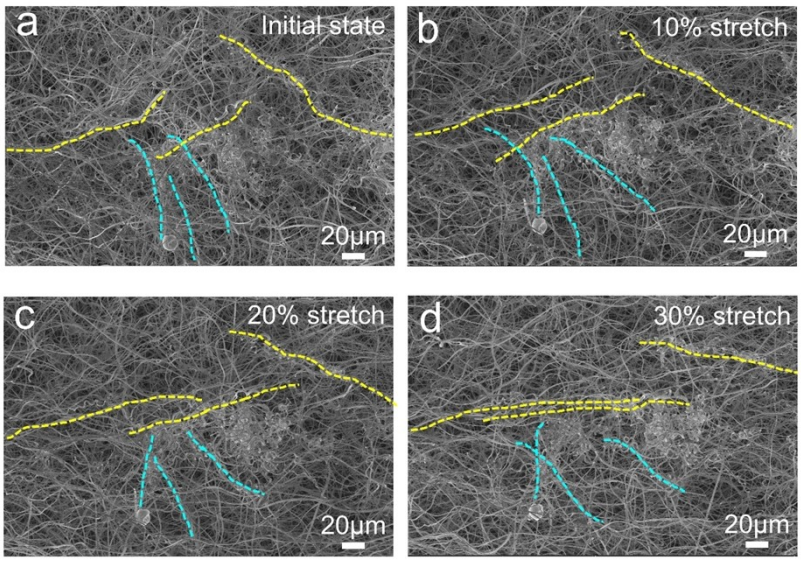

Figure S13. *In situ* tensile observation of TiO_2/SiO_2 NFMs, showing the tensile evolution process. (a) Initial state, (b) 10% stretch, (c) 20% stretch and (d) 30% stretch.

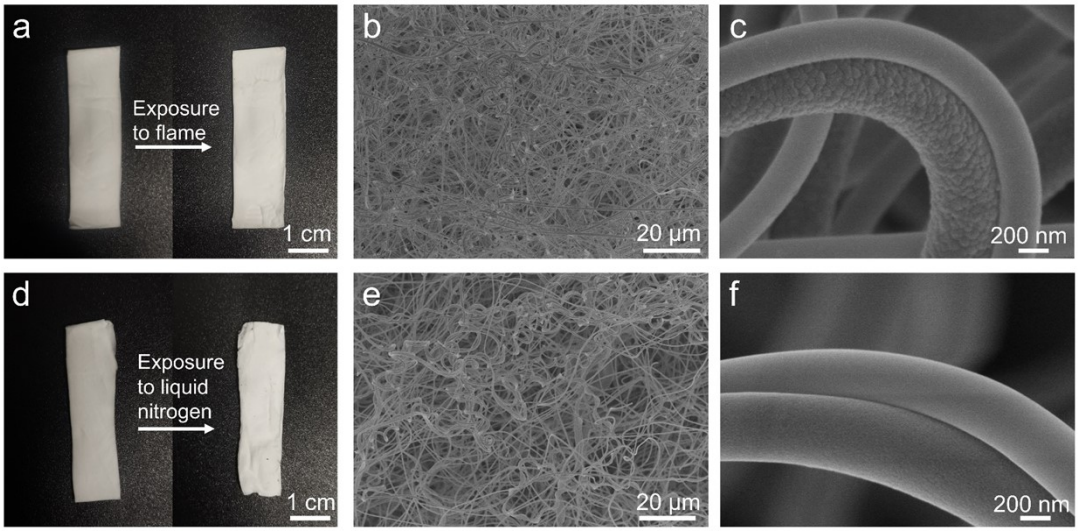

Figure S14. The appearance of TiO_2/SiO_2 NFMs after repeated exposure to flame and liquid nitrogen. (a) Pictures of TiO_2/SiO_2 NFMs before and after exposure to flame. (b) SEM image of (a). (c) The single fiber in (b). (d) Pictures of TiO_2/SiO_2 NFMs before and after exposure to liquid nitrogen. (e) SEM image of (d). (f) The single fiber in (e).

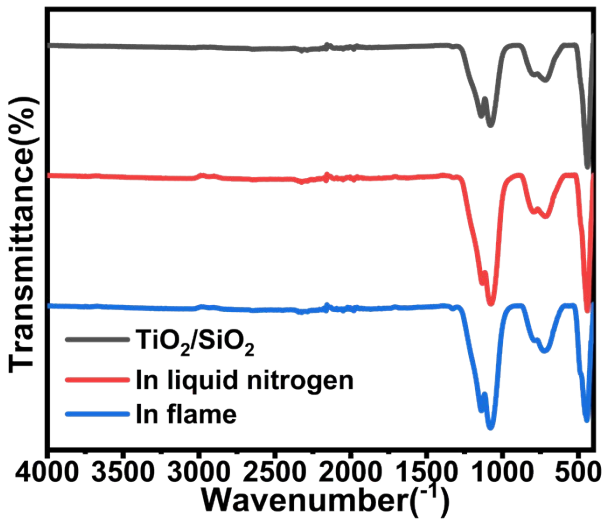

Figure S15. The FTIR spectra of TiO_2/SiO_2 NFMs after repeated exposure to flame and liquid nitrogen, compared to the raw sample.

Figure S16. Photographs and the corresponding infrared images of TiO_2/SiO_2 NFMs heated at different times. (a, e) 0 min. (b, f) 10 min. (c, g) 20 min. (d, h) 30 min.

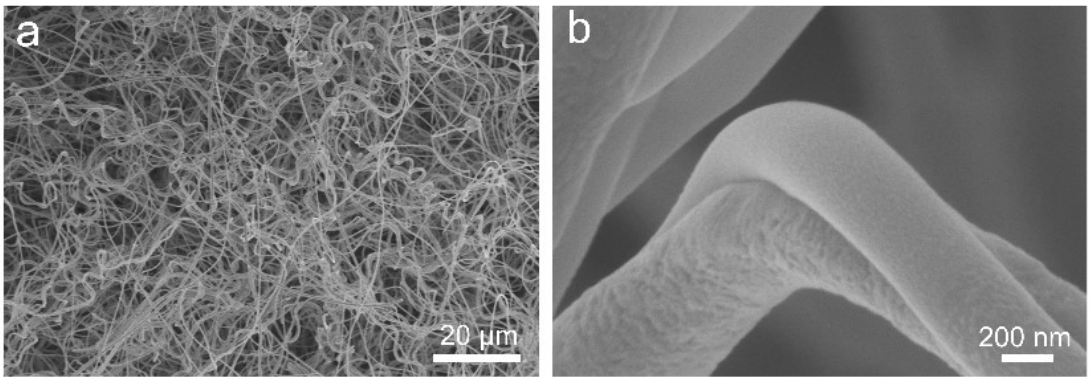

Figure S17. (a) SEM image of TiO_2/SiO_2 NFMs after placing on a self-made alcohol lamp heating table for 30 min. (b) An enlarged view of a single spiral crimped composite fiber in (a).

Table S1. The changes in diameter of circular NFMs over drying time and the corresponding crimp index of complex nanofibers.

Drying time (h)	Diameter of circular NFMs (mm)	Crimp index (%)
0	54.00	6.96
24	39.16	9.40
48	37.85	17.11
72	33.69	30.86
96	33.70	33.01
Calcinated	28.38	45.78

Formula S1. The crimp index of the spiral crimp fibers was calculated by the following formula:

$$\text{Crimp index (\%)} = \frac{L - L_0}{L} \times 100\%$$

where L is the straight length of the crimped fiber, and L_0 is the length of the crimped fiber in its natural state.