Waterproof, breathable and infrared invisible polyurethane/silica nanofiber membranes for wearable textiles

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Experimental Section

Preparation of nanofibers films

Prior to electrospinning, 16 wt% PU (Shanghai Jingjian Plastic Co., Ltd.) was dissolved in dimethylformamide and butyl acetate (DMF: BuAc=2:3) (Hangzhou Gaojing Fine Chemical Industry Co., Ltd.) by magnetic stirring for 8 hours. Subsequently, 0.25 wt% HDI (Shanghai Macklin Biochemical Co., Ltd.) was added to the PU emulsion, and the mixed emulsion was placed in an oil bath and stirred for 3 hours. Finally, 2 wt% APTES was added into the mixed emulsion. Heating and stirring were continued for 6 hours to obtain the spinning solution.

Electrospinning process was performed with a supplied voltage of 21 kV, working distance of 20 cm, and the spinning time was fixed at 4 hours. The mixed solutions were injected into a spinning syringe with 18 G steel needles, which were ejected out at a constant rate of 1 mL/h. The fibers were randomly stacked layer by layer on the tin foil of the receiver plate. The nanofibrous membranes were prepared at a constant temperature (27 ± 2°C) and relative humidity (28 ± 5%). The fiber membranes obtained at each stage were denominated as PU, PU/HDI, PU/HDI/APTES, respectively.

Hydrophobic treatment of nanofibers films

The above-mentioned PU/HDI/APTES nanofibers membranes were put into the preparation solution of SiO_2 to carry out the grafting reaction. Among them, tetraethyl orthosilicate (TEOS, Tianjin Kermeo Chemical Reagent Co., Ltd.) provides the silicon source; triethylamine (TEA, Shanghai Macklin Biochemical Co., Ltd.) adjusted the pH value of the solution; and hexadecyltrimethoxysilane (HDTMS, ≥85%, GC) was used as a hydrophobic modifier to prepare SiO_2. The nanofiber membrane after hydrophobic treatment at this stage was denominated as PU/SiO_2.

Characterizations and measurements

A scanning electron microscopy (SEM, ULTRA55, Carl Zeiss Smt Pte Ltd, Germany) was employed, with the purpose of observing the surface morphology and diameter state of the fibers. The diameter was obtained by testing 50 fibers with the image analysis software. The Fourier transform infrared (FTIR) spectra was recorded on a VERTEX70 infrared spectrometer (Bruker Spectrometer Co., Ltd), to test the molecular structure and functional groups of composite nanofiber membranes. The surface element composition of fibrous membranes was analyzed via an X-ray photoelectron spectrometer (XPS) (Thermo Fisher Scientific, USA).

The pore size measurements, such as mean pore size (Dmean), maximum pore size (Dmax), and porous size distribution of nanofibrous membranes were characterized with the capillary flow porometer (CFP, 1500AE, USA). The porosity was determined by an infiltration-discharging method [1,2]. It was based on the formula:

$$Porosity = 100\% \times \frac{V1}{V2}$$

where V1 is the volume of moisture released from fiber membrane, and V2 is the volume of alcohol released from fiber membrane after being soaked in alcohol. The air permeability and moisture permeability of nanofiber membranes were tested by YG461E-III automatic air permeability tester and YG601-I/II computer type fabric moisture permeability tester, respectively. The water vapor transmission rate (WVT) was calculated as follows [3-4]:

$$WVT = \frac{M_0 - M_1}{A} \times 24$$

where M_0-M_1 denotes the evaporated liquid mass and A is the testing area.

The water-resistant property was tested by a YG812 hydrostatic pressure tester. The wetting properties of the fiber membranes were analyzed using a JCY series static contact angle meter (Shanghai Fangrui Instrument Co., Ltd.). Under standard atmospheric pressure, the temperature was 28 ± 2 ℃, and the relative humidity was 40~60 %. The WCA was measured by the titration (3 μL) technique, and at least ten samples were tested to obtain an average value. Oil red and copper nitrate (Shanghai Macklin Biochemical Co., Ltd.) were used as dyes for oil absorption experiments. Mechanical properties were evaluated using a KES-G1 multifunctional mechanical tester at a crosshead speed of 10 mm/min. At least five samples were tested to obtain average values. A handheld infrared thermal imager (Filier E85, Hangzhou Xiaorui

Digital Technology Co., Ltd.) was used to judge the infrared invisibility of the PU/SiO_2 nanofiber membranes through thermal imaging technology.

References

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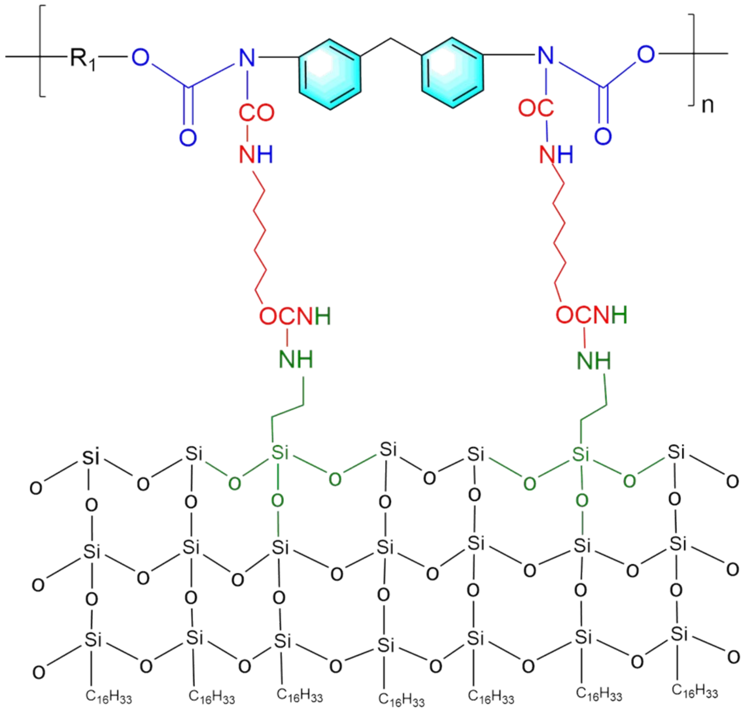

Figure S1. the chemical reaction mechanism during the preparation of PU/SiO_2 nanofiber membranes.

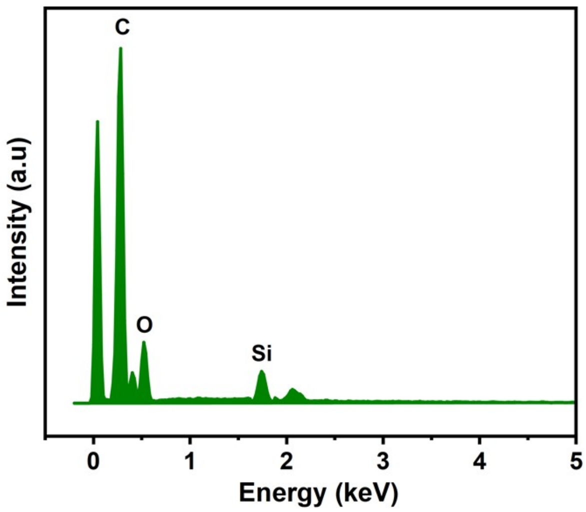

Figure S2. EDS showing the distribution of element.

Table S1. Surface atoms of PU membranes with different treatments.

Fibrous membranes	**C%**	**N%**	**O%**	**Si%**
PU	81.34	5.36	13.25	0.00
PU/HDI	78.94	7.48	13.57	0.00
PU/HDI/APTES	80.19	0.65	18.02	1.13
PU/SiO_2	54.16	0.05	36.86	8.9

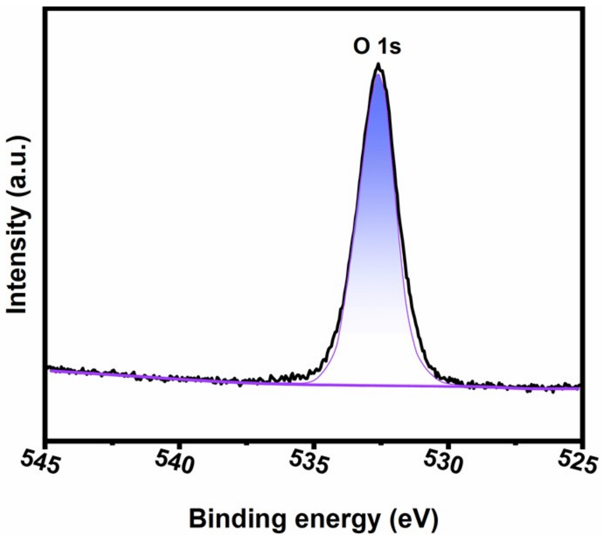

Figure S3. high resolution O 1 s spectrum of pure PU membranes.

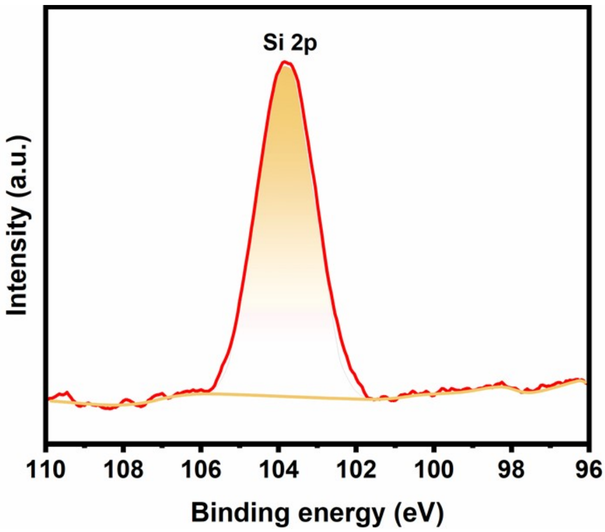

Figure S4. high resolution Si 2p spectrum of PU/SiO_2 membranes.

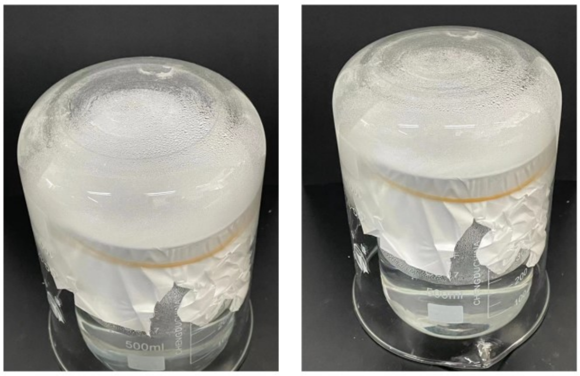

Figure S5. Demonstration of breathability of fiber membranes.

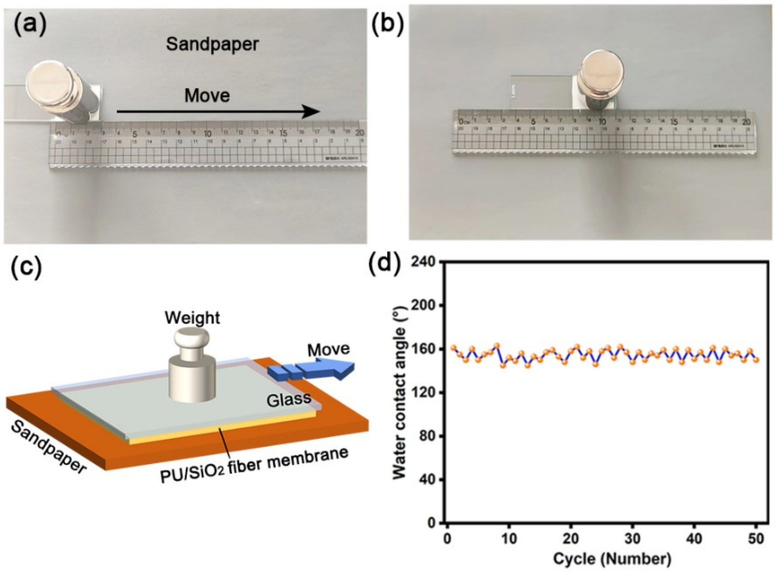

Figure S6. (a, b) Schematic diagrams of wear. (c) Schematic illustration of the sandpaper abrasion test. (d) WCA of the PU/SiO_2 fiber membrane after abrasion.

Video 1 Oil absorption process of Nanofibrous Membrane