Supporting information

Unidirectional Water-Penetration Composite Fibrous Film via Electrospinning

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Experimental section

Fabrication of PU/c-PVA composite fibrous film: A steel wire gauze (washed by alcohol, acetone, and distilled water) was used as collector and membrane support. PVA (M_w = 20,000 ~ 30,000, Acros Organics) was dissolved in distilled water under magnetic stirring, at temperature of 80 ± 5°C for 6 h to obtain PVA aqueous solution. PVA/glutaraldehyde (GA) electrospinning precursor was prepared by mixing PVA aqueous solution with GA (PVA: H_2O: GA = 1: 2.3: 1.67 (wt)). PVA/GA precursor was electrospun with a metal needle of 19 G and collected above on the steel wire gauze. The distance between the needle tip and collector was 20 cm, and the voltage was set at 20 kV. Then the PU (Sigma-Aldrich) was dissolved in tetrahydrofuran (THF) and N,N-dimethyl formamide (DMF) (PU: THF: DMF = 1: 2.14: 5 (wt)) to obtain uniform precursor solution by stirring for 4 h. About 2 mL of the precursor solution was placed in a 5 mL syringe with a metal needle of 17 G. The precursor was electrospun and collected above on the former c-PVA film. The distance between the needle tip and collector was 20 cm, and the voltage was set at 15 kV. The thickness of both c-PVA and PU layer membrane depends on the electrospinning time. After electrospinning, the composite fibrous membrane was placed in HCl gas atmosphere to crosslink PVA with GA.

Materials Characterization: SEM images were taken by field-emission scanning electron microscope (JSM-6700F, Japan). The diameter of the fibers was measured on
the basis of SEM images. Contact angles were measured on an OCA20 contact-angle system (Dataphysics, Germany) at 25°C. 2 μL deionized water droplets were dropped onto the surface. The average contact angle value was obtained by measuring at five different positions of a same sample. Fourier transform infrared (FT-IR) spectra were obtained with a Bruker-EQuiNOX55 spectrometer in multiple internal reflection mode.

**S1: Experimental setup of electrospinning**

**Fig. S1** Schematic illustration of electrospinning experimental setup. The setup is composed of a syringe with metal nozzle. Under suitable electric field, the viscous fluid jet is stretched and solidified to fibers, which are collected on the grounded wire nets.

**S2: The FT-IR spectrum of PVA and crosslinked PVA is presented in Fig. S2.** The large bands observed between 3500 - 3200 cm\(^{-1}\) are linked to the stretching O-H from the intermolecular and intramolecular hydrogen bonds (region I). The vibration band between 3000 - 2800 cm\(^{-1}\) refers to the stretching C-H from alkyl groups (region II), and the peaks between 1750 - 1690 cm\(^{-1}\) (region III) are due to the stretching C=O and C-O from acetate group remaining from PVA. Compared with crosslinked PVA spectrum (curve (a)) and PVA spectrum (curve (b)), the O-H stretching vibration peak \(\nu = 3300 - 3350\) cm\(^{-1}\) was relatively decreased, and the considerable reduction of the intensity of O-H (region I) indicate a possible formation of acetal bridge. The GA crosslinked PVA sample reveals two important bands at \(\nu = 2926.6\) cm\(^{-1}\) and 2857.2
cm\(^{-1}\) of C-H stretching corresponded to aldehydes, a duplet absorption with peaks attributed to the alkyl chain. The bands at 895.3 cm\(^{-1}\) and 856.5 cm\(^{-1}\) exhibit the characteristics of skeletal vibrations of syndiotactic and isotactic PVA stereosequences, respectively.

**Fig. S2** FT-IR spectra from crosslinked PVA (c-PVA) and PVA. Region I, region II and region III are linked to the stretching O-H from the intermolecular as well as intramolecular hydrogen bonds, the stretching C-H from alkyl groups, and the stretching C=O and C-O from acetate group remaining from PVA, respectively. Compared with c-PVA spectrum (curve (a)) and PVA spectrum (curve (b)), the O-H stretching vibration peak \(\nu = 3300 - 3350\) cm\(^{-1}\) was relatively decreased, and the considerable reduction of the intensity of O-H (region I) indicate a possible formation of acetal bridge. The GA crosslinked PVA sample reveals two important bands at \(\nu = 2926.6\) cm\(^{-1}\) and 2857.2 cm\(^{-1}\) of C-H stretching corresponded to aldehydes, a duplet absorption with peaks attributed to the alkyl chain. The bands at 895.3 cm\(^{-1}\) and 856.5 cm\(^{-1}\) exhibit the characteristics of skeletal vibrations of syndiotactic and isotactic PVA stereosequences, respectively.

**S3:** Hydrostatic pressures measurement. The hydrostatic pressure is measured though fix the area of composite film, dip water slowing to the tubular container, then record the height of water column when water begin to penetrate from the film (Fig. S3). In order to know whether the unique PU or c-PVA film with same thickness of the
composite film owns the novel unidirectional water penetration phenomenon or not, we prepared unique PU and c-PVA fibrous film. The comparison details are shown in Table S1 below.

**Fig. S3** Illustration of hydrostatic pressure measurement.

**S4:** Wenzel-Cassie state and Wenzel state of water droplet

**Fig. S4** (a) Wenzel-Cassie state of smaller water droplet; (b) Wenzel state of larger water droplet.

**S5:** Water contact angle of spin-coating film and electrospun fibrous PU film

**Fig. S5** Water droplet on (a) spin-coating PU film, CA=79.1±0.9°; (b) electrospun fibrous PU film, CA=142.2±1.5°.
Table S1. Comparison between unique PU, c-PVA film and PU/c-PVA composite film

<table>
<thead>
<tr>
<th></th>
<th>Thickness/µm</th>
<th>Electrospinning Time/ mins</th>
<th>▼ penetration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU film</td>
<td>36.0 ± 1.3</td>
<td>21</td>
<td>● no penetration</td>
</tr>
<tr>
<td>c-PVA film</td>
<td>35.9 ± 1.7</td>
<td>24.5</td>
<td>● (water absorbed)</td>
</tr>
<tr>
<td>PU/c-PVA composite</td>
<td>PU = 7 ± 1.5</td>
<td>5</td>
<td>▼</td>
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S6: The relationship between the c-PVA thickness and unidirectional water penetration. When fixed the PU film thickness at about 7.0 µm and water volume about 0.1 mL, water can penetrate from hydrophobic PU side to hydrophilic c-PVA side when the thicknesses of c-PVA are 27.4 ± 2.2 µm, 29.1 ± 1.0 µm, and 32.3 ± 3.1 µm, respectively (green dotted square inset in Fig. S6). However, if the thicknesses of c-PVA below 27.4 ± 2.2 µm or above 32.3 ± 3.1 µm, the unidirectional water penetration can not be realized. That is, when the c-PVA thickness is less then 27.4 ± 2.2 µm, no enough CF provided by hydrophilic c-PVA can overcome the resistance provided by the channel length of porous media (red dotted square inset in Fig. S6). However, if c-PVA is too thick, the resistance is much larger than the CF, and water droplet can be fully absorbed by c-PVA film instead of penetrating across it (blue dotted square inset in Fig. S6).
The relationship between the c-PVA thickness and unidirectional water penetration. Fix the PU film thickness at about 7.0 μm and water volume about 0.1 mL. In this work, water can penetrate from hydrophobic PU side to hydrophilic c-PVA side when the thicknesses of c-PVA are 27.4 ± 2.19 μm, 29.1 ± 1.0 μm, and 32.3 ± 3.12 μm, respectively. However, if the thicknesses of c-PVA below 27.4 ± 2.19 μm or above 32.3 ± 3.12 μm, the unidirectional water penetration cannot be realized.