

Superhydrophilic and mechanical robust PVDF nanofibrous membrane through facile interfacial Span 80 welding for excellent oil/water separation

Yajie Ding^{1,2}, Jindan Wu², Jianqiang Wang^{1,3*}, Haibo Lin¹, Jiping Wang², Ge Liu⁴,
Xiaoqiang Pei⁴, Fu Liu^{1,3*}, Chuyang Y. Tang⁵

1. Key Laboratory of Marine Materials and Related Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, 315201, P. R. China;

2. MOE Key Laboratory of Advanced Textile Materials & Manufacturing Technology, Zhejiang Sci-Tech University, Hangzhou, 310018, P. R. China;

3. University of Chinese Academy of Sciences, Beijing, 100049, P. R. China;

4. Key Laboratory of Healthy & Intelligent Kitchen System Integration of Zhejiang Province, Ningbo Fatile Kitchen Ware Company, Ningbo, 315201, P. R. China.

5. Department of Civil Engineering, The University of Hong Kong, Hong Kong, 999077, P. R. China

*Correspondences to

Dr. Jianqiang Wang, E-mail: wangjianqiang@nimte.ac.cn; Prof. Fu Liu, E-mail:

fu.liu@nimte.ac.cn; Fax: +86-574-86325963; Tel: +86-574-86325963;

ABSTRACT:

We report a novel and facile welding strategy using Span 80 to simultaneously enhance the mechanical robustness and superhydrophilicity of an electrospun poly(vinylidene fluoride) (PVDF) nanofibrous membrane. By taking advantage of its amphiphilic property, span 80 micelle is able to attach PVDF nanofibers due to the strong affinity between the hydrophobic segments of Span 80 and PVDF. The as-prepared PVDF nanofibrous membrane exhibited simultaneously improved stress (from 1.7 ± 0.3 MPa to 8.8 ± 0.6 MPa). Meanwhile, superhydrophilic property was endowed through the self-assembly of Span 80 on the hierarchical surface of PVDF membrane. Water contact angle (WCA) and under-water oil contact angle (UOCA) of the modified membrane was nearly 0 and $154.9 \pm 2^\circ$, respectively. This membrane had a water permeability of $18482.7 \pm 287.3 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ for 1, 2-dichloroethane-in-water emulsion with a separation efficiency of 96.3%. The welded PVDF nanofibrous membrane exhibited extraordinary robustness, resisting to long-term washing of water and oil-in-water emulsion.

Keywords: Superhydrophilic; PVDF nanofibrous membrane; Nanofiber welding; Span 80.

1. Introduction

Nanofibrous membranes obtained from electrospun method have received increasing attention due to their unique properties of high porosity, large surface area and controllable structure [1-4]. Especially, nanofibrous membranes have been considered as exceptional candidates for oil/water treatment because of their intrinsic microstructure obtained by the random assembling of nanofibers and super-low mass transfer resistance [5-9]. Many efforts have been devoted to the fabrication of superwetting nanofibrous membrane through the combination of roughness construction and surface energy manipulation [10-14]. However, the poor mechanical property and relatively complicated modification processes significantly limited their practical applications in environmental remediation [15]. Secondary pollution might be caused due to the leaching of nanofibers into to the solutions even in the low applied pressure applications, such as oil/water separation, adsorption and catalysis. Therefore, development of facile method is of primary importance for the fabrication of mechanically robust and superwetting nanofibrous membranes.

To improve the mechanical properties of nanofibrous membranes, welding strategies have been developed to bond the random stacking nanofibers. Some notable examples include UV/visible light induced crosslinking [16-19], heating induced crosslinking [20, 21], chemical induced crosslinking [22-25], solvent vapor induced crosslinking [24, 26] and sintering induced crosslinking [27]. Despite the successful enhanced of mechanical properties, these welding methods are often limited to specific polymers or reactions. In addition, the crosslinking processes are relatively complicated. More universal and facile welding strategies are thus highly desirable. Besides the mechanical property improvement, the interface construction is another critical issue for fabricating of superwetting membranes. To date, many types of superwetting nanofibrous membranes have been fabricated obeying the rule of combination of hierarchical structure and enhanced surface energy [28]. Significant progresses have been made through structure manipulation [13, 29-36] and surface covalent grafting/*in situ* polymerization [37-40] for the fabrication of superwetting nanofibrous membranes. Nonetheless, these

membranes usually suffer from low mechanical properties, relatively complicated modification process and significant reduction of porosity and pore size. Therefore, the facile and effective strategy for simultaneous enhancement of mechanical and interface chemical properties was still a challenge for fabrication of superwetting nanofibrous membrane.

In this study, we present a facile Span 80 interface welding method for fabricating a mechanically robust and superhydrophilic PVDF nanofibrous membrane. The robust bond as a cross-over point between nanofibers can be considered as a non-covalent grafting of Span 80 [41]. Specifically, three-dimensional welding structure was obtained due to the strong affinity of the hydrophobic segment of Span 80 and PVDF, resulting in a mechanically robust PVDF nanofibrous membrane. Meanwhile, the hydrophobic PVDF nanofibrous membrane was transformed to superhydrophilic membrane due to a self-assembly of Span 80 with the hydrophilic segments exposing to the external environment at the interface of PVDF nanofibers. The obtained mechanically robust and superhydrophilic PVDF nanofibrous membrane showed potential applications for separating oil-in-water emulsions. The Span-80 welding strategy proposed in this study provides new ideas for facilely fabricating superwetting nanofibrous membranes with enhanced mechanical properties.

2. Experimental section

2.1. Materials. Poly (vinylidene fluoride) (PVDF, $M_w=180,000$, pellets, France) was obtained from Sigma-Aldrich. Sodium laurylsulfonate (SDS, AR, 98%, China) was purchased from Aladdin Industrial Corporation. N, N-dimethylformamide (DMF), n-butyl alcohol, chloroform, n-hexadecane, n-hexane, and 1,2-dichloroethane were all analytically pure reagent and got from Sinopharm Chemical Reagent Co., Ltd, China. Span 80 (Nonionic surfactant, $M_w=428.61$, China) was bought from Aladdin Industrial Corporation. All reagents were used as received.

2.2. Fabrication and modification of PVDF nanofibrous membrane. PVDF nanofibrous membrane (NM) was fabricated according to method reported in our previous study [33]. Typically, a PVDF/DMF homogeneous solution was prepared by dissolving 25.0 g PVDF pellets in 75.0 g DMF at 70 °C with continuous stirring for 6 h. This PVDF/DMF solution was used for the fabrication of PVDF nanofibrous membrane through electrospinning (SS-2535H, Ucalery, China). Detailed electrospun conditions were as follows: collection distance (distance between the needle and the collection roller) was 15 cm; applied voltage was kept at 16.5 kV (+13.5 kV, -3.0 kV); flow rate was remained at 1.0 mL h⁻¹, humidity was below 40%. The temperature was kept at 30 °C during the whole electrospinning process. A rotating drum with a constant rolling speed of 80 rpm was used for the collection of PVDF nanofibers.

The modification processes for the fabricated membranes were as follows. Firstly, PVDF nanofibrous membranes were soaked in n-hexane, n-hexadecane and Span 80 for 30 min, respectively. The corresponding membranes were denoted as NMH, NMD and NMS, respectively. Then, different concentrations (1, 3, 5 and 10 g L⁻¹) of Span 80/hexane solutions were used to treat the PVDF nanofibrous membranes to obtain a welded membrane. To get a symmetry melting structure, Span 80/hexane solution was filtrated through the PVDF nanofibrous membrane under gravity for different time (0.5-3 h). The membranes treated with different time were denoted as NMS-x (x=0.5, 1, 1.5, 2, 2.5, 3, respectively). Finally, the obtained nanofibrous membrane was dried naturally (hexane was evaporated quickly) and then was stored in deionized water for further use. A schematic illustration was presented for the fabrication and modification process of PVDF nanofibrous membrane (Fig.1).

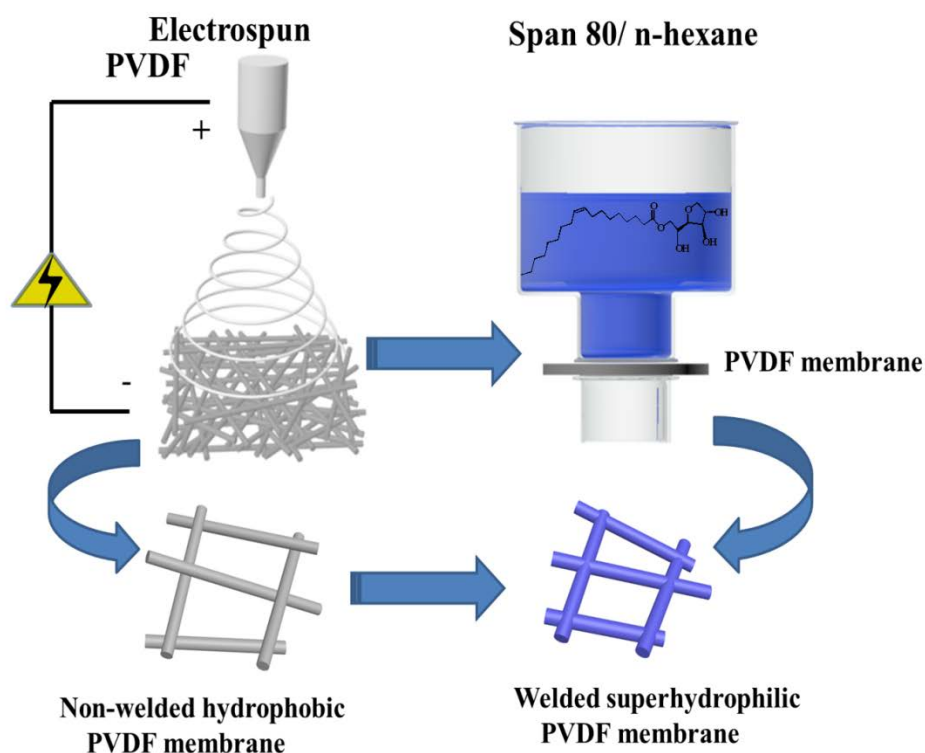


Figure 1. Schematic illustration of preparation and modification process of PVDF nanofibrous membrane.

2.3. Separation experiments of oil-in-water emulsions. The surfactant-stabilized oil-in-water emulsions were prepared as follows: firstly 40 mg of SDS was dissolved in 396 mL of water. After that, 4.0 mL of oils (1, 2-dichloroethane, n-hexane, n-hexadecane or chloroform) were mixed with the above solution with the aid of powerfully stirred for at least 6 h to produce the off-white emulsion. The prepared emulsions can be stable for at least 24 h without obvious stratification. [13].

The oil-in-water separation performance of the PVDF nanofibrous membrane was evaluated using a custom-made dead-end filtration device using gravity as the driving force. The PVDF nanofibrous membrane was sandwiched between two silica glass tubes with inside diameter of 1.6 cm. The membrane was wetted with deionized water before the emulsion separation experiments. A freshly prepared oil-in-water emulsion was then poured into the glass tube (water head was kept at 15 cm) and the real-time

permeation performance of membranes was recorded every five minutes.

2.4. Characterizations. The surface topographies of membranes were characterized using scanning electron microscopy (FE-SEM, Hitachi-S4800, Japan) with an applied voltage of 4 kV. Before sample testing, a thin layer of platinum was sputter-coated on the nanofibrous membrane. Chemical compositions of the membranes were analyzed through ATR-FTIR using Microscopic infrared spectrometer device (Micro-FTIR, Agilent- Cary660+620, China). The carbon, oxygen and fluorine element distribution of NMS-2 membrane was characterized by a transmission electron microscopy (EDAX-TEM, Tecnai F20, USA). The stress–strain curves of nanofibrous membranes were obtained by universal material testing machine (Instron-5567, China). The reported value was the average value of five samples. The tested rectangular strips were 10 mm in width and 100-140 mm in length. The distance between two fixtures is 50 mm and the load speed was 10 mm/min. The thickness of the nanofibrous membranes were measured using a Thickness Tester (CHY-CA, China). Water contact angle (WCA) and under-water oil contact angle (UOCA) were measured by a DCAT21 surface tension/dynamic contact angle goniometer (China). The obtained value was averaged five repetitions at different place with water or oil drops (2 μ L). The sizes of off-white emulsions and filtrates were observed by a polarized thermal microscope (OLYMPUS-BX51, Japan). Oil concentrations in the feed and the corresponding filtrates were analyzed by total organic carbon analyzer (TOC, multi N/C-2100, Germany). Porosity (ϵ %) of nanofibrous membranes were calculated by the weight of the nanofibrous membrane before and after butanol wetting [42],

$$\text{porosity } (\epsilon \%) = \frac{M_{BuOH}/\rho_{BuOH}}{(M_{BuOH}/\rho_{BuOH})+(M_{PVDF}/\rho_{PVDF})} \times 100\%$$

(2)

where M_{BuOH} and M_{PVDF} are the weight of butanol and dry membrane, ρ_{BuOH} and ρ_{PVDF} are the density of n-butanol and PVDF, respectively.

3. Results and discussion

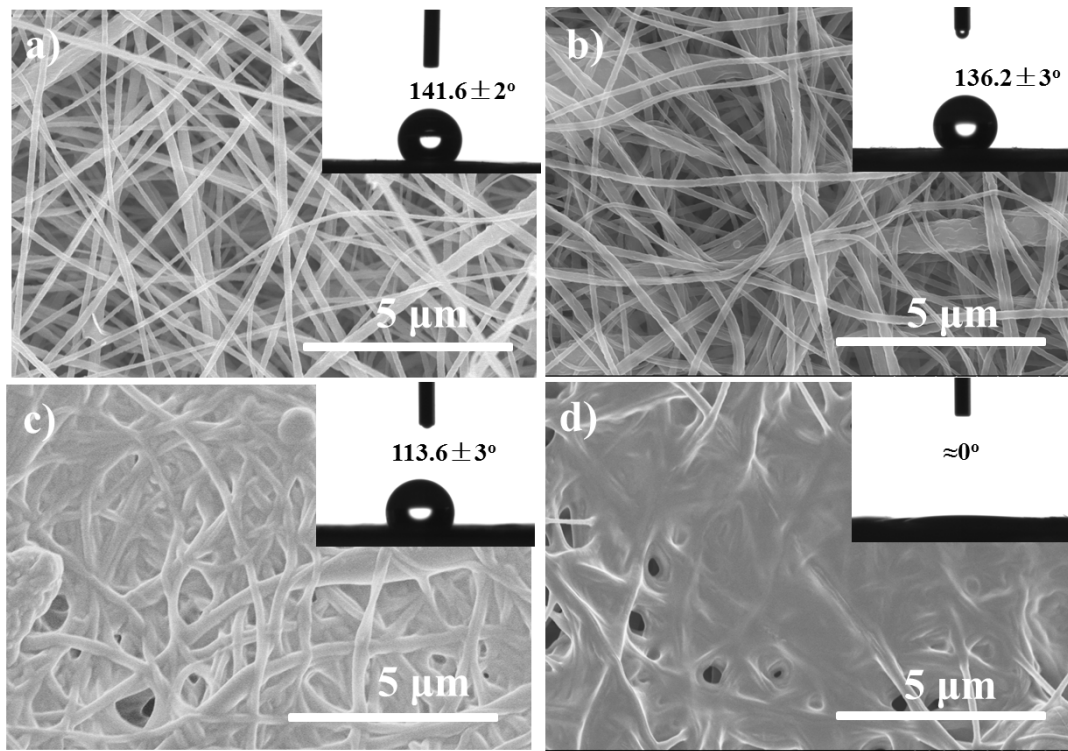


Figure 2. SEM images of a) pristine, b) n-hexane treated, c) n-hexadecane treated and d) Span 80 treated PVDF nanofibrous membranes. An immersion time was 30 min was applied. The insert images show the contact angle results of the corresponding membranes.

3.1. Morphologies modulation of the nanofibrous membranes. Figure 2 presents the SEM micrographs of PVDF nanofibrous membrane before and after soaking by different solvents. As Figure 2a shows that the pristine PVDF nanofibers were randomly stacked with relatively loose structure. This loose structure results in relatively low mechanical property of nanofibrous membrane. In order to address this problem, a “welded structure” for the nanofibrous membrane was designed. Therefore, different solvents that might be used for the welding of nanofibers through swelling were selected for this process according to the following criterions: 1) non-polar solvents because of the strong polar property of PVDF (polar term of PVDF solubility parameter $\delta_p=12.5 \text{ MPa}^{1/2}$, Table 1), and 2) similar dispersive terms of solubility parameter with PVDF ($\delta_d=17.2 \text{ MPa}^{1/2}$, Table 1) [43]. In this study, hexane and hexadecane were used for this target due to their appropriate solubility parameters ($\delta_{d\text{-hexane}}=14.9 \text{ MPa}^{1/2}$, δ_p -

hexane=0 MPa^{1/2}, $\delta_{d\text{-hexadecane}}=16.4$ MPa^{1/2}, $\delta_{p\text{-hexadecane}}=0$ MPa^{1/2}, Table 1). As shown in Figure 2b, PVDF nanofibrous membrane kept its random stacking after being immersed in n-hexane for 30 min, indicating its configuration stability in non-polar solvent. However, the PVDF nanofibers were seriously merged together when n-hexadecane was used (Figure 2c). This phenomenon might be mainly ascribed to the following two reasons: 1) smaller solubility parameter difference between PVDF and hexadecane ($\Delta\delta_d=0.8$ MPa^{1/2}) compared to PVDF and n-hexane ($\Delta\delta_d=2.3$ MPa^{1/2}) and 2) higher viscosity of n-hexadecane compared to n-hexane. Therefore, slight swelling of nanofibers and surface coating of n-hexadecane occurred on the surface of PVDF membranes.

Table 1. Hansen solubility parameters of PVDF, hexane and hexadecane [43].

Materials	Solubility parameters (Mpa ^{1/2})			
	δ_d	δ_p	δ_h^*	δ
PVDF	17.2	12.5	9.2	23.2
Hexane	14.9	0	0	14.9
Hexadecane	16.4	0	0	16.4

* δ_h stands for the hydrogen term of the solubility parameters.

Inspired by these results, Span 80, a common surfactant composed of a hydrophobic segment and a hydrophilic segment was explored for the welding of PVDF nanofibers. Span 80 possesses an aliphatic hydrocarbon chain containing seventeen carbons (Figure 1), similar to that of n-hexadecane containing sixteen carbons. In addition, Span 80 can reduce the liquid/polymer interfacial tension, which will reduce the energy barrier for surface coating and swelling [44]. Therefore, the hydrophobic segment of Span 80 can attack the PVDF nanofiber due to their high affinity, and produced an interconnected welding structure. The hypothesis was confirmed by SEM results (Figure 2d) as obvious surface wrapping can be found after treated by Span 80. The loosely packed nanofibers were tightened together by the bond. More importantly, the PVDF

nanofibrous membrane exhibited superhydrophilic property after Span 80 embedment, as the water drop (2.0 μL) can permeate into the membrane within 5 s. In contrast, the water contact angles of the pristine, n-hexane treated and n-hexadecane treated PVDF nanofibrous membranes were $141.6 \pm 2^\circ$, $136.2 \pm 3^\circ$, and $113.6 \pm 3^\circ$, respectively. These results indicated that molecular self-assembly of Span 80 occurred during the inter-welding process with the hydrophilic segments of Span 80 exposing to the external environment. This self-assembly process was similar with the surface enrichment phenomenon during the electrospinning when amphiphilic materials were used [45, 46], that is the hydrophobic segments of Span 80 was partially embed in PVDF nanofibers. The Span 80 induced welding strategy is quite easier than the surface grafting of surfactant method [47]. The amphiphilic Span 80 (HLB=4.3) forms a micelle in hexane and will go through a configuration transformation and rearrangement with hydrophobic segments towards hydrophobic PVDF nanofiber, while hydrophilic segments stretch outwards. It is noted that the surface welding strategy in our study is intrinsically different from the common blending method, and the assembled Span 80 just occurred at the interface of the PVDF nanofibers [48-50]. Therefore, a simultaneous nanofiber welding and hydrophilic modification was realized through this one-step Span 80 interface self-assembly method.

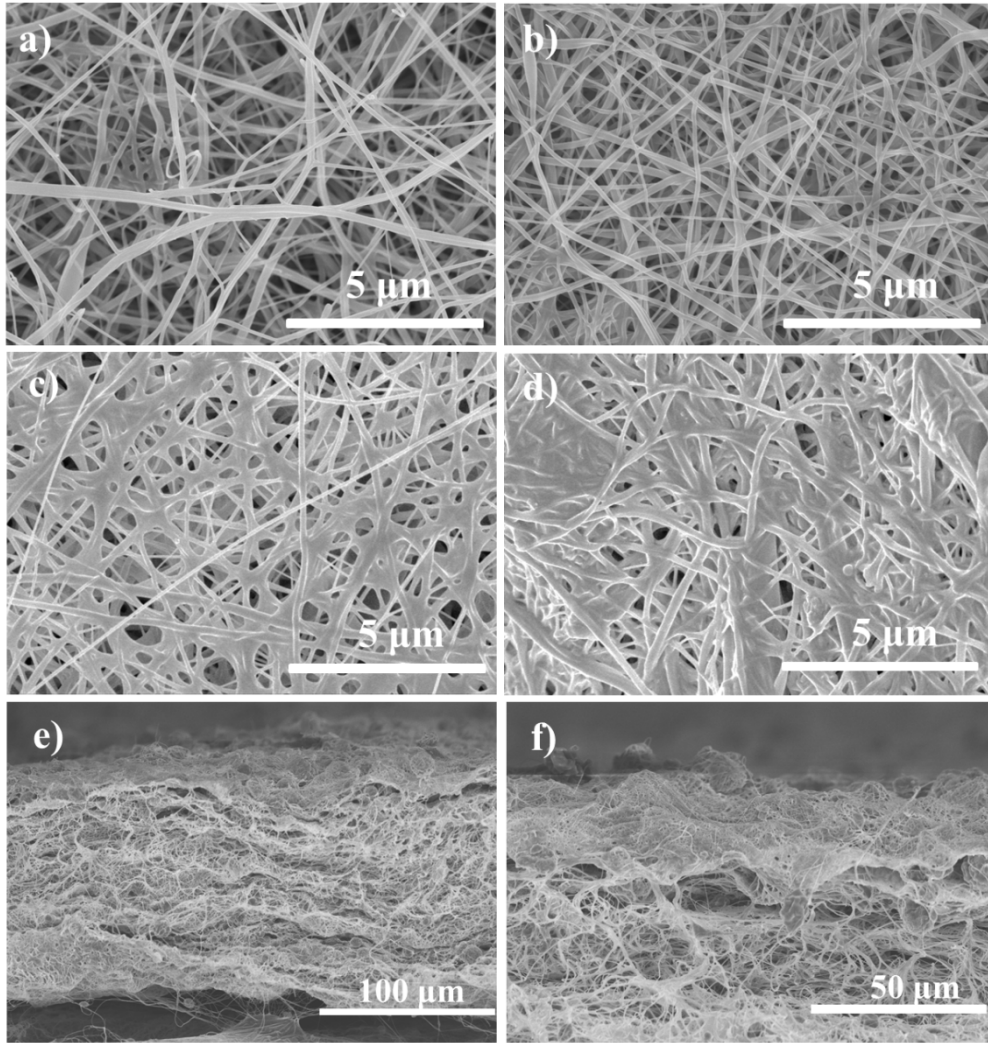


Figure 3. SEM micrographs of PVDF nanofibrous membrane statically immersed by Span 80/n-hexane solution for 30 min with different concentrations: a) 1 g L^{-1} , b) 3 g L^{-1} , c) 5 g L^{-1} and d) 10 g L^{-1} . Cross-section image of the PVDF membrane after immersed in 5 g L^{-1} Span 80/n-hexane solution for 30 min with different magnification (e and f).

Since the simple Span 80 treatment has a substantial effect on both morphology and surface chemistry of PVDF nanofibrous membrane, appropriate manipulation of this process is of great interests. Due to the great different effects of n-hexane and Span 80 for welding PVDF nanofibers, Span 80 was diluted by n-hexane to finely manipulate the properties of PVDF nanofibrous membrane. The results (Figure 3) indicated that more PVDF nanofibers were merged together as the Span 80 concentration increased

from 1 g L^{-1} to 10 g L^{-1} . It is mainly due to the kinetic enhancement when the Span 80 concentration increased [44]. Specifically, when the concentration of Span 80 was lower than 5 g L^{-1} , slight nanofiber welding structure without much crosslinking point between nanofibers can be found (Figure 3a and 3b). Most of the nanofibers were merged together when the concentration of Span 80 was higher than 5 g L^{-1} (Figure 3c and 3d), the welding knots between individual nanofibers contribute to the mechanical property enhancement of nanofibrous membrane. However, the surface porosity was seriously reduced with increasing the Span 80 concentration. Therefore, in consideration of both mechanical property and surface porosity of the nanofibrous membrane, 5 g L^{-1} of Span 80/hexane was used in the following experiments for the modifications.

As discussed above, Span 80 treatment has an appreciable effect on the welding of PVDF nanofibers. However, asymmetric structures were obtained using the Span 80 static immersion modification method. Welding structures only appeared on the top surface, while the inner bulk kept less influenced. Figure 3e-3f shows the relative dense top layer covering a loose nanofibrous sublayer. This is because that Span 80 can only diffuse onto the membrane surface and fail to further diffuse into the bulk due to the hindrance of the denser surface layer. However, symmetric welding of the nanofibers should be favorable for enhancing the mechanical property of the nanofibrous membrane [51]. Therefore, a gravity-driven flow-through filtration of Span 80/n-hexane solution was used instead. Figure 4a-4f shows the morphologies of PVDF nanofibrous membranes with different filtration time (0.5-3.0 h). As the results indicated that the amount of welding point between nanofibers was increased as the filtration time increased. In addition, symmetric structure was obtained through this filtration method, as it was can be confirmed by the cross-section (inserts of Figure 4a and 4d) and bottom version (Figure S1 and S2) of the nanofibrous membrane.

The modified PVDF nanofibrous membrane displayed superior mechanical robustness. As shown in Figure 4g, the mechanical stress of PVDF nanofibrous

membrane was significantly improved from 1.7 ± 0.3 MPa to 8.8 ± 0.6 MPa when Span 80 solution filtration reached up to 3 h (more than fivefold increase), while the strain was simultaneously enhanced from ~48% to ~80% and the tensile modulus was also increased from 5.5 to 8.9 MPa. The independent nanofibers in pristine nanofibrous PVDF membrane could be easily slipped, detached and broken under external stretch. In this case, the strength actually more depends on the pristine membranes. In comparison, the welding nanofibrous membrane exhibits enhanced mechanical behavior in terms of stress, strain and modulus. The inter-welding cross-over points bond the adjacent nanofibers together to form robust mats. The enhancement of Young's modulus reflects the high resistance to elastic deformation. A comparison of the mechanical property of PVDF nanofibrous membrane modified using different method was presented in Table 2. As Table 2 shows that thermal treatment was a common strategy to enhance the mechanical property. However, a relatively high temperature (150-160 °C) was required which will significantly increase the energy consumption for fabricating nanofibrous membrane. Blending was another strategy used for this target; however, the stress enhancement was mainly attributed to the enhancement of each single nanofibers. The welding points between fibers were missing which will weaken the integration of the nanofibrous membrane. In comparison, the Span 80 welding strategy proposed in this study presented a facile and effective method for enhancing the mechanical property of nanofibrous membrane. Moreover, the reduced porosity (Figure 4h) provided the evidence that the nanofibrous membrane was filled by welding structure. Therefore, the Span 80 welding strategy on PVDF nanofibrous membrane exhibits its superior properties to common grafting or blending methods. In addition, the water contact angle decreased from $141.6^\circ \pm 2^\circ$ to nearly 0° after Span 80/hexane filtration and the underwater oil contact angle maintains as $154.9^\circ \pm 2.4^\circ$ (Figure 4i), suggesting its simultaneous transformation from hydrophobicity to superhydrophilicity.

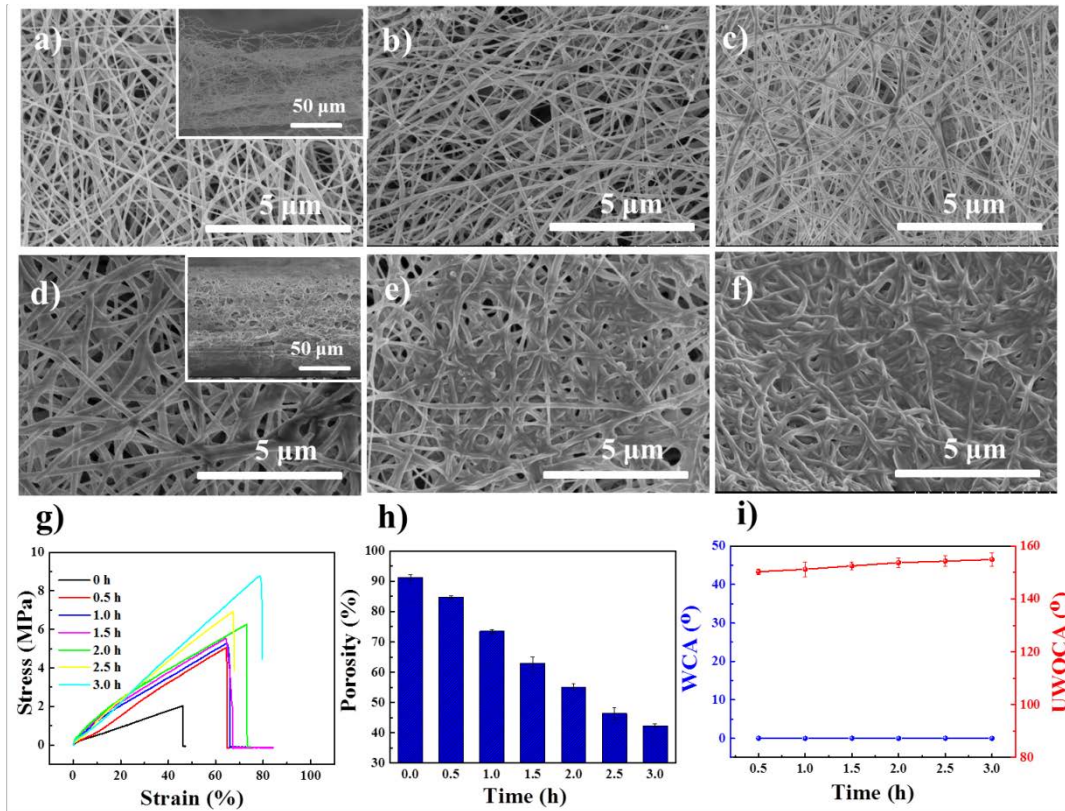


Figure 4. SEM micrographs of the PVDF nanofibrous membrane after filtrated by 5 g L⁻¹ Span 80/n-hexane with different time: a) 0.5 h, b) 1.0 h, c) 1.5 h, d) 2.0 h, e) 2.5 h and f) 3.0 h. g) Stress-strain, h) porosity and i) contact angle results of the PVDF nanofibrous membranes after filtration of 5 g L⁻¹ Span 80/n-hexane with different time. Inserts are the corresponding cross-section SEM images.

Table 2. Comparison of mechanical property of PVDF nanofibrous membranes before and after modification through different methods.

Material	Modification		Stress (MPa)		Strain (%)		Reference
	Type	Method	Before	After	Before	After	
PVDF		160 °C for 2 h	1.9	6.5	30	35	[52]
	Thermal treatment	150 °C for 3 h	0.4	8.5	--	--	[53]
		150 °C for 1 h	1.2	3.1	76.9	73.9	[54]
		160 °C for 2 h	3.3	9.5	16.9	26.7	[55]
	Blending	PU blended	4.0	7.4	76.5	156.1	[56]
SiO ₂ blended		3.8	5.5	375	375	[57]	

	Carbon nanotube	0.6	4.2	81	48	[58]
	blended					
	PVB blended	2.1	14.8	4.8	30	[59]
Span 80						
welding	Span 80 welded	1.7	8.8	48	80	This study

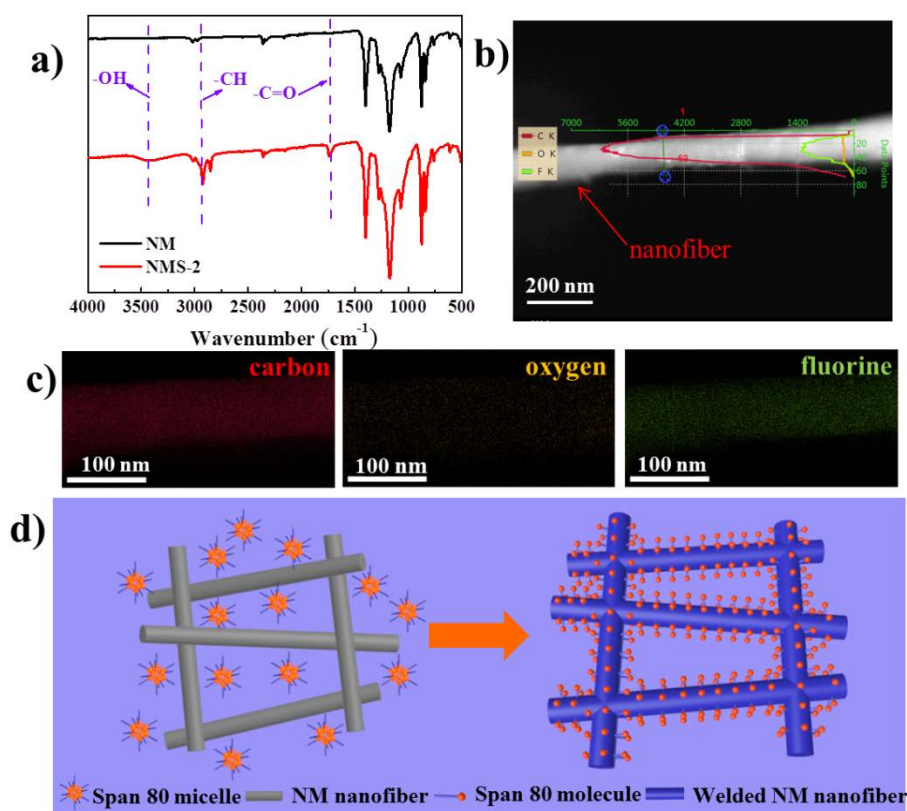


Figure 5. a) ATR-FTIR spectra of PVDF and NMS-2 nanofibrous membrane; b) Energy dispersive spectroscopy results of NMS-2 membrane obtained from TEM characterization process; c) Element mapping results of NMS-2 nanofiber; d) Schematic illustrating the mechanism of Span 80 induced nanofiber welding.

3.2. Mechanism of Span 80 modification and its stability property. As indicated in Figure 5a, new peaks at 3417 cm^{-1} , 2924 cm^{-1} and 1740 cm^{-1} corresponding to the stretching vibration of $-\text{OH}$, C-H and C=O bonding appeared in NMS-2 membrane. The ATR-FTIR results confirmed the presence of Span 80 on the surface of PVDF

nanofibers. The chemical composition of individual PVDF nanofiber was acquired by energy spectrum analysis using TEM. The energy dispersive X-ray spectroscopy (EDAX) results revealed that the content of oxygen element was up to 6.92 wt%, manifesting the existence of Span 80 on the surface of PVDF nanofiber (Figure 5b). Element mapping results suggested uniform dispersing of Span 80 on the surface of PVDF nanofiber (Figure 5c). As discussed in section 3.1, a self-assembly of Span 80 occurred and wrapped PVDF nanofibers, resulting in the hydrophilic segments exposing to the external environment. This self-assembly process played a critical role for welding and knitting PVDF nanofibers. Firstly, the Span 80 micelles diffused and contacted with the surface of PVDF nanofiber, and the micelles disintegrated at the surface due to the strong affinity between PVDF and the hydrophobic segment of Span 80. The similar solubility parameters of PVDF and hexadecane might be responsible for breaking the micelle by the intrusion of heterogeneous interface (as discussed in section 3.1). Finally, the dissociative Span 80 was rearranged and bonded firmly onto PVDF nanofibers with the hydrophilic segment exposing to the external environment (partially embedded in PVDF nanofibers). A schematic diagram was shown in Figure 5d to illustrate the Span 80 induced welding of PVDF nanofibers.

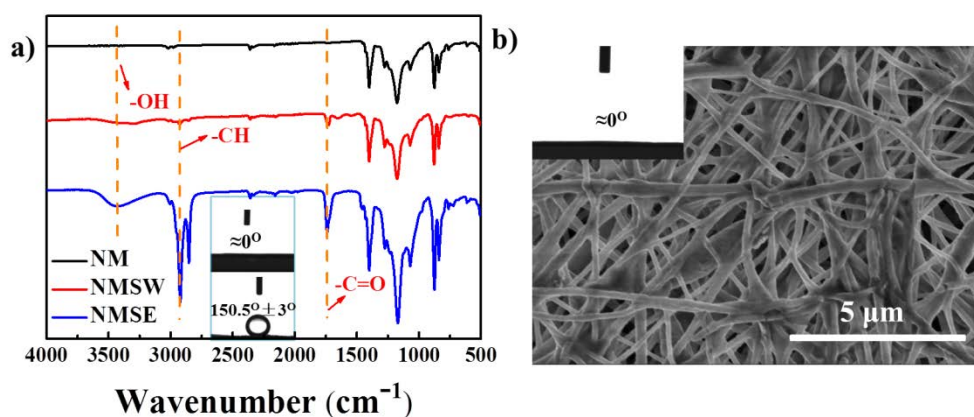


Figure 6. a) ATR-FTIR spectra of the NMS-2 membrane after being soaked in water (NMSW) and oil-in-water emulsion (NMSE) for 10 days (The inserts are the corresponding results of contact angle). b) SEM micrograph of NMS-2 membrane after being immersed in deionized water for 10 days.

The long-term stability of the inter-welding nanofibrous membrane in water and oil/water emulsions was evaluated. As illustrated in Figure 6a, the anchored Span 80 was quite stable even after immersion in water or 1, 2-dichloroethane-in-water for 10 days since clear characteristic absorption peaks of Span 80 can be found. Meanwhile, the water contact angle and underwater oil contact angle maintained as nearly 0° and $150.5^\circ \pm 3^\circ$ respectively (insets of Figure 6a). As Figure 6b shows that NMS-2 membrane maintains inter-welding structure and nanofibers are firmly bonded together without splitting after 10 days washing in deionized water, displaying the robustness of the inter-waving structure.

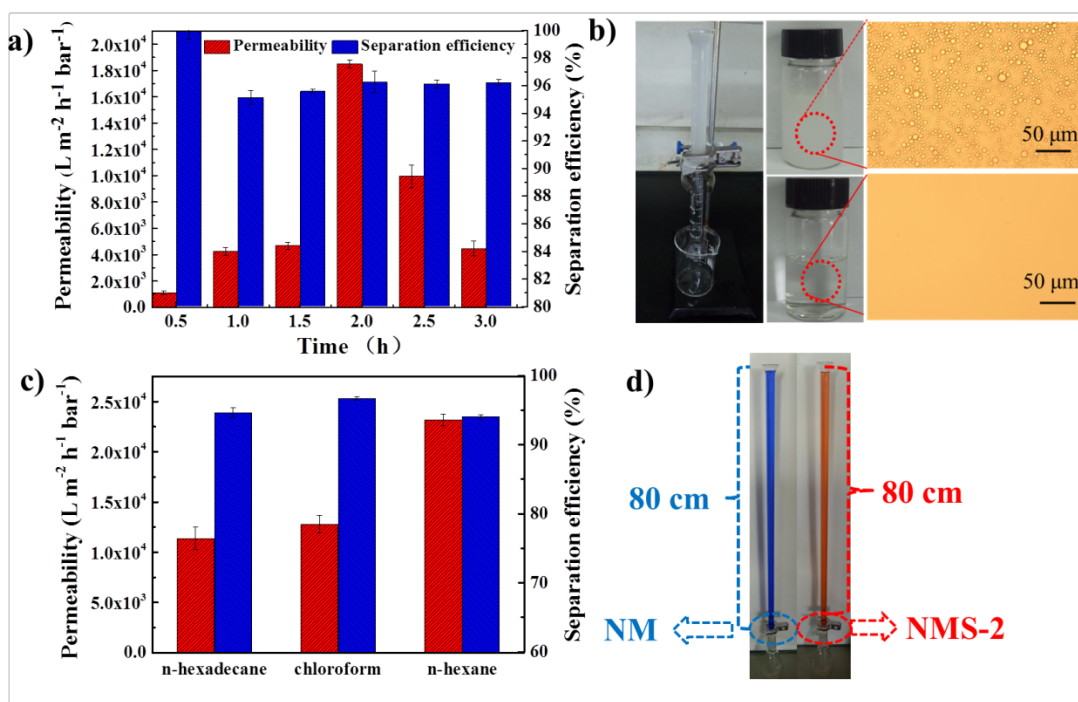


Figure 7. a) Permeate flux and separation efficiency for permeating the 1, 2-dichloroethane-in-water emulsion through the NMS-x membrane ; b) custom-made gravity driven dead-end filtration device and the microscopy images of off-white emulsions and filtrates; c) Permeability and separation efficiency of the NMS-2 membrane for SDS stabilized oil-in-water emulsion using different oil (n-hexadecane, chloroform and n-hexane). d) NM and NMS-2 membrane stands an 80-cm height of water and oil column, respectively.

3.3. Oil-in-water emulsion separation performance. Figure 7a shows the separation performances of different PVDF nanofibrous membranes for 1, 2-dichloroethane-in-water emulsion. As illustrated, the permeability increased from 1117.1 ± 143.6 to $18482.7 \pm 287.3 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ when the filtration time of Span 80 extended from 0.5 to 2 h due to the enhanced hydrophilicity of the inter-connected pores inside the membrane. However, when the Span 80 filtration time was longer than 2 h, the permeability gradually decreased to $4468.3 \pm 574.5 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$. The decreased porosity minimized the water channel and impeded the flow through the membrane as shown in Figure 4h, and therefore decreased the permeability of the nanofibrous membrane according to the Kozeny-Carman model [60]. By manipulating the balance between channel hydrophilicity and porosity, the optimal modification time was about 2 h, and the NMS-2 nanofibrous membrane presented a high permeability of $18482.7 \pm 287.3 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ with a separation efficiency of 96.3%. Polarized thermal microscope was applied to present the intuitive results for the oil-in-water separation (Figure 7b). The image shows that numerous oil droplets (2-10 μm) present in original off-white emulsion, while no oil droplet is found in the collected filtrate, suggesting effectiveness of the NMS-x membrane for separating off-white oil-in-water emulsion. Besides, the NMS-2 membrane also showed favorable separation performances for n-hexadecane-in-water, chloroform-in-water and n-hexane-in-water emulsion with the corresponding permeability of 11373.9 ± 1148.9 , 12795.7 ± 861.7 and $23154.2 \pm 574.5 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, severally (Figure 7c). Meanwhile, the NMS-2 membrane showed highly intercept performance for various emulsions ($> 94\%$). The intrusion pressure of PVDF membrane before and after modification was marked as 8.30 kPa, corresponding to water and oil column with a height of 80 cm (Figure 7d). The NMS-2 membrane (2.0 cm^2) can prop up oil that is about 70 k times heavier than their own weight for up to 24 h without oil intrusion. The uniformly inter-welding structure is responsible for the integrity of the nanofibrous membrane.

4. Conclusions

A mechanically robust and superhydrophilic PVDF nanofibrous membrane was

successfully fabricated through electrospinning followed by a facile Span 80/n-hexane filtration method. The amphiphilic Span 80 played a critical role of simultaneously enhancing both mechanical strength and hydrophilicity. The hydrophobic segments of Span 80 micelle tend to rearrange, assemble and wrap on PVDF nanofiber due to their similar solubility parameter. While the hydrophilic segments of Span 80 expose to the external environment, endowing the PVDF membrane with inter-welding structure and superhydrophilic property. The obtained PVDF nanofibrous membrane (NMS-2) showed enhanced mechanical strength, elongation and modulus compared to the pristine PVDF membrane. The under-water oil contact angle of NMS-2 membrane was $154.9^\circ \pm 2^\circ$, showing its superoleophobicity. Permeability of NMS-2 membrane was as high as $18482.7 \pm 287.3 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ for oil-in-water emulsions with a separation efficiency of 96.3%. The welding structure of PVDF nanofibrous membrane was robust enough to stand the long term washing of water and oil-in-water emulsion. Distinctly from complicated covalent grafting or blending methods, Span 80 mediated welding can facilely endow the membrane with superior performances.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at XXX.

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