

# Interlaced Amphiphobic Nanofibers for Smart Waterproof and Breathable Membranes with Instant Waterproofness Monitoring Ability

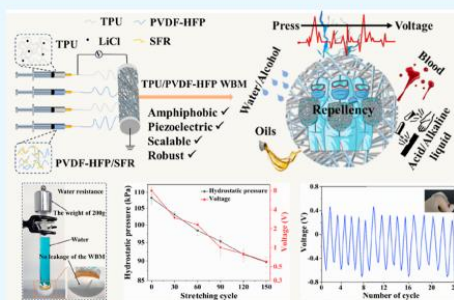
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**ABSTRACT:** Electrospun nanofiber-based waterproof and breathable membranes (WBM) that can provide a high level of protection and excellent air permeability and functionality are becoming promising core materials in numerous fields. However, large challenges still remain in the facile preparation of high-performance and smart WBMs capable of forecasting the failure of waterproof protection. Herein, amphiphobic TPU/PVDF-HFP nanofiber membranes with an interlaced fibrous structure are prepared by a one-step multineedle electrospinning technology. The obtained membranes demonstrate outstanding waterproofness with a hydrostatic pressure of over 108 kPa, a high air permeability of over  $10 \text{ mm s}^{-1}$ , and a water vapor transmission rate (WVTR) of  $8.40 \text{ kg m}^{-2} \text{ d}^{-1}$ , as well as excellent mechanical properties with a tensile strength of 6.07 MPa and a tensile strain of 117.11%. These make them extremely suitable for WBM applications. More importantly, due to the robust interlaced fibrous structure and the piezoelectric property of PVDF-HFP, the hydrostatic pressure of the TPU/PVDF-HFP membranes can be easily monitored and predicted by measuring the voltage output, indicating excellent hydrostatic pressure monitoring capability. The addition of low-surface-energy chemical materials endows the membranes with durable amphiphobicity against various harsh conditions, which further enhances the waterproof property. Such versatile nanofiber membranes would be desirable for potential applications in protective clothing and wearable electronic products and would provide a source of inspiration for the fabrication of smart WBMs.

**KEYWORDS:** TPU nanofibers, piezoelectric PVDF-HFP nanofibers, interlaced fibrous structure, waterproof and breathable, monitor



## 1. INTRODUCTION

Most of the waterproof and breathable membranes [waterproof and breathable membranes (WBMs)] are composed of either nonporous hydrophilic membranes or microporous hydrophobic membranes.<sup>1,2</sup> The latter is more attractive owing to the porous structure (i.e., the pore size ranging from 0.2 to  $3 \mu\text{m}$ ) that can make them repellent to liquid water ( $>50 \mu\text{m}$ ) but facilitate transmission of water vapor (around  $2.64 \times 10^{-4} \mu\text{m}$  in diameter) and air.<sup>3–5</sup> Several methods have been explored for the preparation of microporous hydrophobic membranes, such as biaxial stretching,<sup>6</sup> phase separation,<sup>7</sup> electrospinning,<sup>2,8–11</sup> etc. Among them, the most representative one is the polytetrafluoroethylene (PTFE) microporous hydrophobic membrane prepared by the biaxial stretching method, which has good waterproofing and breathable ability. However, PTFE membranes face problems of the complex preparation process, limited elasticity (approximately 30%), and slow decomposition, which cause harm to the human body and environment.<sup>12–15</sup> Therefore, it is necessary to search for a facile and versatile method to fabricate high-performance hydrophobic microporous WBMs.

Electrospinning technology has become an emerging and popular technique for manufacturing fibrous materials for diversified applications, such as environmental protection, energy harvesting and storage, protective membranes, etc.<sup>16–19</sup> Generally, the preparation of nanofiber WBMs can be divided into two categories: one-step electrospinning method and the post-treatment method.<sup>5,20–22</sup> In consideration of its simplicity and high effectiveness, the one-step electrospinning method has drawn much attention, which can be subdivided into two categories: direct spinning of hydrophobic polymers and hydrophobic dopant-modified nanofibers. Jiang et al.<sup>23</sup> reported microsphere-fiber interpenetrated superhydrophobic polyvinylidene fluoride (PVDF) nanofiber membranes by exploring a high humidity-induced electrospinning approach.

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kPa after 25 washing cycles, and the corresponding output voltage diminished from 8 to 0.4 V with a similar trend (Figure 5e). Therefore, the piezoelectric voltage can be applied to predict the hydrostatic pressure change resulting from mechanical deformation and washing.

The underlying mechanism of the nanofiber membranes' high waterproofness, outstanding breathability, and hydrostatic pressure monitoring ability was explored and is illustrated in Figures 5f and S15, which was attributed to the robust interlaced fibrous structure of PVDF-HFP nanofibers and TPU nanofibers. The elastic TPU nanofibers provide sufficient entanglement among nanofibers, allowing the membrane to withstand large tensile deformation without structure failure. In the meantime, the hydrophilic feature of TPU facilitates water vapor transport. The thin PVDF-HFP nanofibers distributed in the TPU/PVDF-HFP nanofiber membrane can not only greatly improve its hydrophobicity but also effectively reduce the pore size. As a result, it shows greatly enhanced waterproofness. The high hydrostatic pressure of TPU/PVDF-HFP nanofiber membranes can be explained by the Young–Laplace equation, as shown in Figure S15. The excellent structural stability of the membrane guarantees it to have a constant piezoelectric response under deformation. Any destruction (e.g., long time washing and continuous stretching) to the fibrous structure may cause fiber dislocation or breakage, which affect the voltage output and hydrostatic pressure synchronously; as a result, they exhibit nearly the

same change trend. Therefore, the piezoelectric voltage can intuitively reflect the hydrostatic pressure variation.

The hydrophobicity of the TPU/PVDF-HFP membrane also showed high durability against a variety of mechanical or chemical damages. As can be seen from Figure 5g, the WCA of the membrane only had a slight drop from 147.2 to 140.5° after 3 h of boiling water treatment. When the membrane was irradiated by UV light, there was no obvious change to its WCA after 24 h of UV irradiation (Figure 5h). The abrasion resistance of the membranes was measured according to the sandpaper abrasion method (see Figure S16). It experienced only a minor decrease in the WCA from 147.2 to 140.1° after 35 abrasion cycles, still demonstrating hydrophobicity, as shown in Figure 5i. These results indicated that the TPU/PVDF-HFP nanofiber membrane obtained could suffice for everyday wear and use. Moreover, the membranes exhibited excellent resistance to numerous chemicals, such as acidic solution, alkaline solution, salt solution, cyclohexane, and medical alcohol disinfectant. This characteristic may provide them with potential applications in harsh conditions, as seen in Figure S17, being immersed in these liquids for 24 h, washed with water, and then dried at 50 °C, their WCAs did not change significantly and still maintained good hydrophobicity. Besides, the thermal stability of the TPU/PVDF-HFP nanofiber membrane was studied by thermogravimetric analysis, as shown in Figure S18. It did not show any obvious weight loss until 260 °C, indicating good thermal stability, and it can meet the requirements of WBMs.

#### 4. CONCLUSIONS

Amphiphobic nanofiber membranes composed of interlaced TPU nanofibers and PVDF-HFP nanofibers were fabricated by a one-step multineedle electrospinning technique. When the weight ratio of TPU/PVDF-HFP was 1:1, the resulting TPU/PVDF-HFP nanofiber membranes achieved excellent comprehensive properties, including a waterproofness ability of 108.2

kPa, a WVT rate of 8.40 kg m<sup>-2</sup> d<sup>-1</sup>, an air permeability of 10.1 mm s<sup>-1</sup>, a tensile stress of 6.07 MPa, and a tensile strain of 117.11%. In particular, the membrane showed a structure-related piezoelectric response. The output voltage depreciated with continuous destructive action such as washing and stretching, proving to be an accurate and simple method for indicating the waterproof condition of the membranes. Moreover, the membranes exhibited high durability in terms of liquid repellency to various aqueous liquids and oils and possessed outstanding self-cleaning and antifouling properties. We hope the fabrication strategy reported in this work could provide valuable insight for the development of the next generation of smart WBMs.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.4c01305>.

Chemical structure of SFR; SEM images of TPU/PVDF-HFP nanofibers with different TPU, PVDF-HFP, LiCl, and SFR concentrations; pore size distribution, porosity, and WCA of the membranes; effect of membrane thickness on hydrostatic pressure; and self-cleaning property (PDF)

Good flexibility of the TPU/PVDF-HFP nanofiber membrane (MP4)

Experiment demonstrating both the waterproofness and air breathability of the TPU/PVDF-HFP nanofiber membrane (MP4)

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# Optimization of electrochromic Mo doping WO<sub>3</sub> films: A study on dual-phase stacked structures for energy-efficient smart windows

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## ARTICLE INFO

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## ABSTRACT

Amorphous tungsten trioxide (a-WO<sub>3</sub>) films were prepared on ITO conductive glass via electrodeposition and subsequently crystallized to obtain crystalline WO<sub>3</sub> (c-WO<sub>3</sub>) films by heating a-WO<sub>3</sub>. A dual-phase stacked WO<sub>3</sub> film was fabricated by covering Mo-a-WO<sub>3</sub> film onto c-WO<sub>3</sub>/ITO substrate using electrodeposition and thermal-assisted electrodeposition methods, respectively. Optimization of electrochromic performance was achieved by varying Mo doping levels (0–5 atom%). Results demonstrate that appropriate Mo doping (3 atom%) enhances the electrochromic properties of a-WO<sub>3</sub> films. Mo doping introduced structural distortions that reduced energy barriers and enhanced ion mobility, leading to improved electrochemical and electrochromic properties. The intermediate c-WO<sub>3</sub> layer improves adhesion between a-WO<sub>3</sub> top film and ITO glass substrate, while the porous structure of a-WO<sub>3</sub> layer increases the number of active sites for electrochromic reactions. Mo3-a-WO<sub>3</sub>/c-WO<sub>3</sub> dual-phase stacked film with doping 3 atom% Mo shows an optical modulation range of 83.4 % at 633 nm, a coloration efficiency of 74.3 cm<sup>2</sup>/C, rapid response time (bleaching/coloration: 3.4 s/6.1 s), and 86.6 % retention of its maximum current density after 2000 cycles, respectively. The high oxidation ion diffusion coefficient ( $3.53 \times 10^{-10}$  cm<sup>2</sup>/s) and reduction diffusion coefficient ( $1.55 \times 10^{-10}$  cm<sup>2</sup>/s) were also observed. This dual-phase stacked film shows significant improvements in electrochromic performance due to the synergistic effects between the dual phases and Mo-doping. Electrochromic device (ECD) assembled with Mo3-a-WO<sub>3</sub>/c-WO<sub>3</sub> dual-phase films as the working electrode, ITO glass as the counter electrode, and 1 mol/L LiClO<sub>4</sub>/PC solution as the electrolyte exhibited an optical modulation range of 74.2 % and response time (bleaching/coloring) of 6.8 s/3.7 s. These findings confirm that ECD with Mo-a-WO<sub>3</sub>/c-WO<sub>3</sub> dual-phase films offer excellent electrochromic performance.

## 1. Introduction

Electrochromism represents an advanced energy-saving technology that facilitates reversible and sustained changes in the optical properties of materials when a small voltage is applied [1,2]. These controlled optical transitions enable the regulation of thermal conditions in various environments, contributing significantly to energy efficiency. This versatile technology has been widely adopted in applications such as smart windows, automotive anti-glare mirrors, flexible wearable electronics, and supercapacitors [3–9].

Among the various electrochromic materials, tungsten trioxide (WO<sub>3</sub>) stands out due to low cost, rapid response time, and superior

electrochemical properties, which made WO<sub>3</sub> electrochromic film become a focal point of research [10–12]. To achieve high efficiency and scalability of WO<sub>3</sub> film, many modification methods have been investigated, including optimizing structure [13], enhancing crystallinity [14], doping beneficial impurities [15], and developing hybrid [16] or multilayer composite films [17].

Various processes, such as template-directed synthesis, chemical vapor deposition, electrodeposition, sol-gel methods [18–20], are used for the preparation of modified WO<sub>3</sub> thin films, in which electrodeposition has garnered significant attention due to its ability to finely control film porosity and thickness by adjusting parameters such as electric field, pH, and deposition time. PATIL et al. [21] demonstrated that WO<sub>3</sub>

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