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Superamphiphobic nanofibrous membranes for effective filtration of fine particles

Na Wang [a,1], Zhigao Zhu [a,1], Junlu Sheng [b], Salem S. Al-Deyab [c], Jianyong Yu [d], Bin Ding [a,d,*]

[a] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China
[b] College of Textiles, Donghua University, Shanghai 201620, China
[c] Petrochemical Research Chair, Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia
[d] Nanomaterials Research Center, Modern Textile Institute, Donghua University, Shanghai 200051, China

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ABSTRACT

The worldwide demands are rising for an energy-efficient and cost-effective approach that can provide advanced nanofibrous membranes with high filtration performance and superior antifouling properties. Here we report a novel synthesized fluorinated polyurethane (FPU) modified nanofibrous membrane optimized to achieve oil and non-oil aerosol particle filtration. By employing the FPU incorporation, the polyacrylonitrile/polyurethane (PAN/PU) composite membranes were endowed with superhydrophobicity with a water contact angle of 154° and superoleophobicity with an oil contact angle of 151°. Morphology, surface wettability, porous structure, and filtration performance could be manipulated by tuning the solution composition as well as the hierarchical structure. Furthermore, the as-prepared membranes can capture, for the first time, a range of different oil aerosol particles in a single-unit operation, with >99.9% filtration efficiency, by using the combined contribution of fiber diameter and surface roughness acting on the objective particles. Exemplified here by the construction of superamphiphobic nanofibrous membrane, numerous applications of this medium includes high efficiency particulate air filters, ultra-low penetration air filters, and respiratory protection equipment.

1. Introduction

Clean air is a vital resource for human life. However, population growth and enhanced human activities, together with the expansion of industrial and agricultural production, are creating unprecedented demands on clean air supplies all over the world [1,2]. The World Health Organization has reported that more than two million premature deaths each year can be attributed to the effects of urban outdoor air pollution and indoor air pollution, particularly in developing countries [3]. Fine particles, especially particulate matter with an aerodynamic diameter smaller than 2.5 μm (PM2.5), proved to be a major cause of adverse health effects ranging from the human respiratory tract to extrapulmonary organs [4,5]. Conventional filter materials based on nonwoven fibers (e.g. melt-blown fibers, glass fibers, and spun-bonded fibers) are incapable of capturing fine particles due to the micro-sized fiber diameter [6,7]. Nanofiber based filters are attractive for air filtration because of their enhanced filtration performance and improved service life in actual operating environments [8,9].

Nanofiber fabrication techniques include template synthesis, phase separation, sea-island spinning, etc. [10–12]. Although these methods can be used to construct nanofibrous membranes according to applications, they are usually difficult-to-control, time- or energy-intensive. Electrospinning, as an alternative to these methods, is increasingly becoming the subject of filter material investigation [13–15]. Owing to the tunable fiber diameter, high porosity, remarkable specific surface area, and interconnected porous structure, electrospun fibrous membrane is considered an effective medium for air filtration [16–19]. A series of electrospun filter materials have been fabricated by designing the filter structure or exceptional properties in combination with filtration modeling and mechanism [9,20–22]. However, the antifouling and mechanical properties of these membranes remain insufficient to allow them to compete with commercial polypropylene (PP) nonwoven membranes in practical working circumstance.

On the other hand, combining the advantages of electrospun nanofibers with surface modification to yield hybrid functional membranes has provided a facile way to construct filter media

* Corresponding author at: State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China. Fax: +86 21 62378202.
E-mail address: binding@dhu.edu.cn (B. Ding).
[1] These authors have contributed equally to this work.

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with controllable wettability [23–25]. In contrast to superhydrophobicity, the super-repellence to oil fluids seems more challenging, but shows great potential in antifouling filter media from hazardous chemical and biological contaminants [26,27]. Fluorinated polyurethane (FPU) containing perfluoroalkane segments (Fig. 1a), a class of low surface free energy materials with a wide range of interesting characters including low surface free energy, resistant to abrasion, and excellent hydrolytic stability, which make it a promising material for functional membranes with distinctive wettability [28,29]. To date, although it has been known for some time that nanofibers could be prepared from FPU [28], nearly no effort has been devoted to the development of FPU modified superamphiphobic air filter media.

In this contribution, we present the fabrication of superamphiphobic polyacrylonitrile (PAN)/PU nanofibrous filter media with robust fine particle filtration performance by the introduction of a novel synthesized FPU, as shown in Fig. 1a. With this aim in mind, PAN/PU composite membranes with interpenetrating bonding/non-bonding structures were constructed via regulated jet ratios of PAN and PU solutions. Key to our development design is that the use of FPU endowed the PAN/PU nanofibers with hierarchically roughened surface, which showed great influence on the wettability, porous structure, and filtration properties of resultant membranes. Furthermore, the FPU modified PAN/PU fibrous membranes were proven to be serviceable filter media with substantially high filtration performance to oil and non-oil aerosol particles, which is capable of providing robust operational stability, and effectively extending the service life.

2. Experimental

2.1. Materials

PAN (M_w = 90,000) was purchased from Kaneka Co., Ltd., Japan, PU (Elastollan1 2280A10) and 4,4-methylenebisphenylisocyanate (MDI) were purchased from BASF Co., Ltd., Perfluoro-1-decanol ($CF_3(CF_2)_7CH_2CH_2OH$) (TEOH-8) was purchased from Hengtong Fluorine Co., Ltd., China. Polytetrahydrofuran (PTMEG, M_n = 1000), triethylene glycol (TEG), *N*,*N*-dimethylformamide (DMF), dimethylacetamide (DMAc) and methanol were supplied by Shanghai Aladdin Chemical Co., China. All chemicals were of analytical grade and were used without further purification.

2.2. Synthesis of FPU

The synthesis of FPU was generally carried out via a three-step polymerization reaction (Scheme 1, ESI). Typically, an aqueous solution of MDI (12.5 g) dissolved in DMF (12 g) under nitrogen atmosphere was prepared, and another solution of TEOH-8 (9.28 g) in DMF (8 g) was added drop wise to the above solution. The feeding rate of one solution into another was set at so that it took 2 h to completely feed into the solution. Anhydrous PTMEG (7.5 g) as the soft segment was added to the mixture mentioned above and reactions were carried out at 60 °C for 1 h. Then, TEG (3 g) was added as the chain extender for reaction at 65 °C for 1 h, and the solution of TEOH-8 (2.32 g) in DMF (2 g) was added drop wise and polymerization reactions continued for 1 h at 70 °C. Finally, methanol was used as the blocking agent for reactions, and the amount of methanol was calculated from the concentration of isocyanate groups in the reaction system. The products were purified by precipitation using the excess water and dried in the vacuum oven at 50 °C, and then re-dissolved in DMAc and precipitated in an excess mixture of methanol and water to ensure sufficient removal of low molecular weight products. The purified products were washed with the mixture of methanol and water, and then dried at 60 °C to get the light yellow colored FPU. The structural confirmation by ^1H and ^{19}F nuclear magnetic resonance (NMR) spectroscopy and group affirmations by Fourier transform infrared (FT-IR) spectroscopy were presented in the ESI (Figs. S1–S3).

2.3. Preparation of polymer solutions

PAN solutions of concentrations 7, 9, 11, and 13 wt% were prepared by dissolving in DMF with stirring for 12 h, and the concentration of PU in precursor solution was 5 wt%. Additionally, PAN and PU solutions containing 0.25, 0.5, 0.75, and 1 wt% of the as-synthesized FPU were prepared using DMF, in which the concentration of PAN and PU was 11 and 5 wt%, respectively. The detailed compositions and properties of relevant solutions are listed in Table S1.

2.4. Fabrication of FPU modified PAN/PU composite nanofibers

The representative setup for fabrication of FPU modified PAN/PU nanofibers on the nonwoven substrate covered grounded

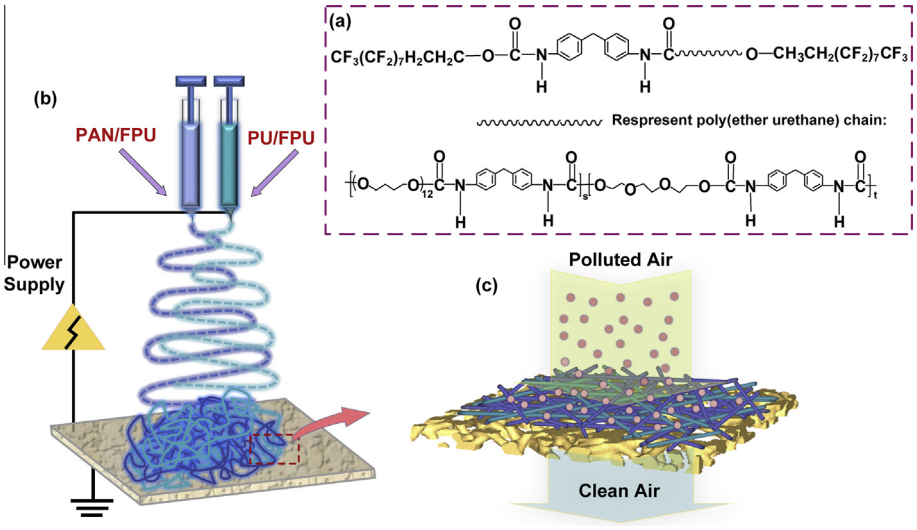

Fig. 1. (a) Illustration of the chemical structure of as-synthesized FPU. (b) Representation of the preparation of the NF-F filter membranes. (c) Filtration process of the NF-F membranes for aerosol particles.