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Sandwich structured polyamide-6/polyacrylonitrile nanonets/bead-on-string composite membrane for effective air filtration

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ABSTRACT

Air filtration proposed for nanofibers require their adequately thin fiber diameters and porous packing structure. The ability to construct stable and large cavity structures by extremely thin fibers would have broad technological implications for areas ranging from individual protection and industrial security to environmental governance; however, it has proved extremely challenging. Here we report a strategy to design and create sandwich structured polyamide-6/polyacrylonitrile/polyamide-6 (PA-6/PAN/PA-6) composite membrane for effective air filtration via sequential electrospinning. Our approach allows the PAN bead-on-string fibers and two-dimensional (2D) PA-6 nanonets to assemble into stable filtration medium with tunable porous structure and mechanical properties on a large scale, by facilely regulating the solution concentration, applied voltage, combined with weight ratio of PA-6/PAN. With integrated features of ultrathin (~20 nm) nanonets and bead-on-string fibers supported cavity, the resulting PA-6/PAN/PA-6 composite membrane exhibits robust mechanical properties, high filtration efficiency of 99.9998%, and low pressure drop of 117.5 Pa for filtrating ultrafine airborne particles in multiple capture manners; and it successfully gets rid of the potential safety hazards caused by unexpected electret failure. The successful synthesis of PA-6/PAN/PA-6 medium would not only make it a promising candidate for air filtration, but also provide new insights into the design and development of composite membranes for various applications.

1. Introduction

The particulate matter (PM) pollution in air, especially the notorious $PM_{2.5}$ and its attached biological matter involving bacteria and viruses, causes growing impact on people's living quality, and it poses serious health threats to the public, fatally interferes with equipment operation, as well as influencing climate and ecosystems [1–3]. Moreover, increasingly stringent regulations for fine particle emissions have also contributed to the urgent need for high performance filters [4,5]. By virtue of the integrated features of cost-effective, ease of scalable synthesis, universality across various filtration fields, etc., the fibrous filter gains its absolute mainstream status for airborne particle filtration [6,7]. However, the conventional fibrous media (melt-blown fibers, glass fibers, and spun-bonded fibers) still suffer from many performance disadvantages due to their micro-sized fiber diameter, including relatively low filtration efficiency, high air resistance, and deep bed filtration manner, especially unavailability for capturing the fine particles [8–10]. Although several strategies consisting of the electret treatment and recklessly increasing material (packing density and basis weight) have partly improved the filtration efficiency; the followed fatal flaws are brought to the conventional fibrous media, such as bulkiness, high energy and material consumption, and safety hazards from unexpected failures [11].

The nanofiber based filtration media, as a porous material with small pore size and high porosity which both benefit from the relatively small diameter, evoke more and more attentions due to their enhanced filtration performance (especially the filtration efficiency) for the airborne particle filtration [12–14]. Various routes have been proposed to fabricate the nanofibers, including drawing [15], template synthesis [16], phase-separation [17], sea-island spinning [18], plasma treatment [19], etc. Among them the electrospinning has emerged as the most versatile and effective technology for large-scale fabricating nanofibers with controlled morphologies and functional components from various materials [20–22]. And, many electrospun filter media (usually with

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diameter of 100 nm ~1 μm), such as poly(vinyl alcohol) [23], PAN/poly(acrylic acid) [24], PAN/polyurethane (PU) [25], polyvinyl chloride/PU [6], polyetherimide [26], polyamide-66 (PA-66) [27], and so on, have been successfully fabricated so far. However, some drawbacks still remain: (i) the limited refinement of diameter, resulting in the inadequate filtration efficiency; (ii) the circular cross-sections, smooth surfaces, and high packing density, causing the low air flow penetration and high energy consumption.

Electrospinning/netting [28,29], which overcomes the bottleneck problem of conventional electrospinning technique, provides a versatile method for generating 2D spider-web-like ultrathin (~20 nm) nanonets with large quantities and uniform size. Previously, the novel PA-66 nanofiber/nets (NFN) membranes were fabricated and successfully applied for air filtration in our group for the first time [27]. Although the membranes show robust filtration efficiency due to their extremely small diameter and 2D pore structures, they still undergo high pressure drop (~200 Pa) due to the inadequate cavity structures. Meanwhile, several efforts have been devoted to enhancing the cavity structures for filters, such as polysulfone/titania [30], PAN/silica [31], porous beaded poly(lactic acid) [32], and so on. These filtration media exhibit better air permeability, however, the potential safety hazard from the employed nanoparticle detachment and weak mechanical properties remains uncertain in actual operating environments [33]. Considering the previously acquired success in nanonets and the original theory of that larger void in the medium can substantially reduce friction induced air resistance [34,35], the combination of 2D ultrathin nanonets and bead-on-string fiber supported cavity structure can be an effective strategy to enhance the filtration performance for the filtration materials. Both the PA-6 and PAN are mostly chosen as the starting polymer for producing nanofibers owing to their respective desirable properties ranging from robust mechanical properties and chemical stability to ease of processing; and considerable efforts have been devoted to the variables in these two electrospun fibrous membranes [36,37]. However, nearly no effort has been given to the development of sandwich structured PA-6/PAN/PA-6 composite membrane, let alone this membrane with novel 2D nanonets and stable cavity structures for airborne particle filtration.

In this study, we have designed and fabricated the sandwich structured PA-6/PAN/PA-6 composite membrane, involving stable cavity structures supported by PAN bead-on-string fibers and 2D PA-6 nanonets comprising of interlinked ultrathin nanowires (~20 nm), for airborne particle filtration via sequential electrospinning. The number and size of the beads in PAN membrane are finely controlled by tuning the solution concentration and applied voltage, and their effect on the filtration performance of the membranes is systematically studied. Moreover, sandwich-like PA-6/PAN/PA-6 composite membranes with nanonets and bead-on-string structures are thoroughly designed and optimized based on varying the weight ratio of PA-6/PAN/PA-6. Additionally, the pore structures, mechanical properties, and filtration performance of the composite membranes are carefully investigated; and, a filtration simulation based on pore structures is proposed. Benefiting from the ultrathin nanonets and stable cavity structures, the composite membrane proves to be serviceable filter medium with effective filtration performance for ultrafine airborne particles, which is capable of providing robust operational stability and effectively extending the service life.

2. Experimental section

2.1. Materials

PAN (M_w = 90,000) was supplied by Spectrum Chemicals & Laboratory Products Co., Ltd., USA. PA-6 (M_n = 18,000) was obtained from UBE Industries Ltd., Japan. *N, N*-dimethylformamide (DMF), formic acid (>88%) (HCOOH), and isopropyl alcohol (> 99.7%) were purchased from Shanghai Chemical Reagents Co., Ltd., China. The Hollingsworth & Vose (H&V) PE13070NAH (72 g/m^2) and PE13090NAH (90 g/m^2) nonwoven filters, as two kinds of meltblown media both used as disposable respirators, were supplied by Hollingsworth & Vose (Asia Pacific) Co., Ltd., China. The nonwoven polypropylene substrate with negligible filtration performance (filtration efficiency of 3% and pressure drop of 1 Pa under the face velocity of 32 L/min) was kindly provided by Shandong Huaye Nonwoven Fabric Co., Ltd., China. All chemicals were of analytical grade and were used as received without further purification.

2.2. Preparation of fibrous membranes

4, 6, 8, 10, and 12 wt% PAN solutions were prepared by using DMF with a vigorous stirring process for 12 h at room temperature. Similarly, 15 wt% PA-6 solution was obtained by dissolving PA-6 chips in HCOOH with stirring for 24 h. The detailed compositions and properties of the relevant solutions were presented in Table S1.

The fabrication of nanofibrous membranes was performed by using the DXES-3 spinning equipment (Shanghai Oriental Flying Nanotechnology Co., Ltd., China). Typically, the homogeneous solutions were loaded into 10 mL plastic syringes and injected through 6-G metal needles with the controllable feed rate for electrospinning. The grounded stainless roller covered with nonwoven polypropylene substrate was rotating at a speed of 50 rpm keeping a tip-to-collector distance of 20 cm. In order to guarantee the uniformity of nanofiber membranes including their thickness and basis weight, we uniformly placed four plastic syringes on the injection pump which horizontally moved backwards and forwards at a speed of 200 cm/min within a fixed distance by using the mechanical slide unit. And, simple electric shield device on every needle was also employed to ensure that the jets were flying forward, thus the nanofibers could be uniformly deposited during the quadrature motion process caused by the synchronous movement of the stainless roller and mechanical slide unit. For the PAN solo membranes, the fibers formed with various PAN concentrations were deposited on the nonwoven substrate with a solution feed rate of 1 mL/h under various voltages ranging from 20 to 35 kV with interval of 5 kV. While for the PA-6/PAN/PA-6 composite membranes, the PA-6, PAN (6 wt%), and PA-6 solutions were sequentially electrospun onto the same substrate with respective controlled solution feed rates (0.3 mL/h for PA-6, 1 mL/h for PAN) under a voltage of 30 kV. And, the basis weights of PAN solo membranes and PA-6/PAN/PA-6 composite membranes, together with the weight ratio of PA-6/PAN/PA-6 in composite membranes were adjusted by carefully regulating the depositing time. All samples were vacuum-dried at 60 °C for 1 h to remove the residual solvent and charges.

2.3. Characterization

The viscosity, surface tension, and conductivity of the PAN and PA-6 solutions were measured using a viscometer (SNB-1A, Shanghai Fangrui Instrument Co., Ltd., China), a surface tension meter (QBZY-1, Shanghai Fangrui Instrument Co., Ltd., China), and a conductivity meter (FE30, Mettler-Toledo Group, Switzerland), respectively. To measure the charge density carried by the moving jets during electrospinning, the typical method of mesh target was introduced and a special experimental system was set up as follow: the high precision multimeter (Fluke F15B+, Fluke electronic instrument Co., Ltd., China) which was used for measuring the current induced by residual charges on the moving liquids, connected the