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Fabrication of polyvinylidene fluoride tree-like nanofiber via one-step electrospinning

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ABSTRACT

A novel polyvinylidene fluoride (PVDF) tree-like nanofiber was controllably fabricated via one-step electrospinning by adding certain amount of salt into PVDF solution. A possible mechanism for the formation of the tree-like nanofibers was proposed by analyzing high speed camera photos of the spin jet and the result showed that the formation of tree-like nanofibers was due to the splitting of jets. The effects of salt type, salt content and processing parameter on the content of tree-like branches were investigated. The electrospun nanofibers were characterized by field emission scanning electron microscopy (FE-SEM), energy disperse spectroscopy (EDS), X-ray diffraction (XRD), pore size meter and mechanical properties measurement. It was found that the PVDF/TBAC tree-like nanofibers with improved crystallinity and mechanical strength. The decreased average pore size caused by the tree-like structure and the resistance to organic solvent, can make it as a potential candidate for membrane separation.

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1. Introduction

Nature has built a tremendous number of fascinating materials and structures with excellent properties, such as high strength, self-cleaning, structural colors and so on [1–3]. The emerging field of bionics allows human to mimic nature to exploit nanomaterials, nanodevices, and processes which provide desirable properties [4,5]. Along with a better understanding of materials in nature, it has been found that the most special properties of these substances come from their chemical elemental composition, as well as their multilevel micro-/nanostructures [6]. In the last few decades, considerable research has concentrated on hierarchically structured materials, especially on the micro-/nanometer scale, to explore the advantages of these unique structure-related properties [7–9].

As an increasingly popular nanofabrication technique, electrospinning has emerged as a versatile and effective method for manufacturing long continuous fibers with diameters ranging from several micrometers down to a few nanometers [10–14]. Therefore, electrospinning provides excellent prospects for construction of biomimetic structures [15,16]. Benefitting from the easily tunable compositions and structures of electrospun nanofibers, a variety of fascinating structures resembling natural objects have been successfully biomimicked via electrospinning, such as lotus leaf [17], butterfly wings [18], helical [19], necklace-like [20], rice-grain shape [21], water strider legs [22], and spider-web-like structure [23–25]. The aforementioned structures have unique surface or inner multilevel structure, either micro-, nano- or micro-/nano-combined structures, and result in some advantages or excellent performance in the applications of self-cleaning materials, tissue engineering, sensors, catalysts, etc. [26–29].

Inspired by a natural tree's hierarchical structures built up by many trunks and more branches, tree-like structured nanomaterials with multiscaled organizations has demonstrated more functionality and higher performance due to their significantly enhanced surface area [30–32]. M McCune et al. [33] reported the zinc oxide tree-like nanowire structures improved the overall power conversion efficiency of the solar cell due to its significantly enhanced surface area. Bai et al. [34] developed a tree-like structure TiO_2 nanofiber (NF)/ZnO nanorod (NR) materials by the combination of electrospinning of TiO_2 NFs and hydrothermal growth of ZnO NRs, and the tree-like structure improved the photocatalytic activity and antibacterial capability of nanomaterials through enlarging the specific surface area for mass transfer and providing more reaction sites. Although the tree-like materials mentioned above exhibited excellent performance, they were usually fabricated by a continuously multi-step method and the process was complicated.

In this paper, we first reported a facile process to prepare large-scale PVDF tree-like nanofibers by adding certain amount of tetrabutylammonium chloride (TBAC) into PVDF solution via one-step electrospinning. Tree-like nanofibers, as its name implies, are composed of trunk fibers and branch fibers, among them, the thick trunk fibers act as a skeleton support which can improve the mechanical strength, and

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the thin branch fibers act as connections props which can increase the surface area to volume ratio and decrease the pore size. To achieve this goal, the effects of salt type, salt content and processing parameter on the morphology of nanofibers were investigated. Based on the experimental results, the possible mechanism for the formation of tree-like nanofibers during electrospinning process was proposed. The PVDF tree-like nanofiber membrane (PVDF-TLNM) possessed the general properties and functions of conventional electrospinning nanofiber membrane, as well as the fascinating feature characters, such as extremely small pore size, excellent mechanical properties and strong chemical stability. More significantly, the PVDF-TLNMs could be used as promising materials for a variety of potential applications in separation field.

2. Experimental

2.1. Materials

PVDF ($M_w = 520{,}000$, Shanghai 3F New Materials Co., Ltd., China) was used as starting material. LiCl, $AlCl_3$, $CaCl_2$ (Tianjin Fengchuan Chemical Reagent Science And Technology Co., Ltd., China; analytical grade), tetrabutylammonium bromide (TBAB), tetraethylammonium chloride (TEAC) and TBAC (Aladdin Co., Ltd., China; analytical grade) were used as additives. *N*, *N*-dimethylformamide (DMF) and acetone (Tianjin Kermel Co., Ltd., China; analytical grade) were used as solvents. Ethylene carbonate (EC) and dimethyl carbonate (DMC) (analytical grade) were purchased from Tianjin Kermel Co., Ltd., China. All of the materials were used as received without further purification.

2.2. Fabrication of the tree-like nanofibers

PVDF solution at a concentration of 17 wt.% was prepared by dissolving PVDF powder in DMF/acetone mixture at a ratio of 3/1 (*v*/*v*) by vigorous stirring. PVDF/salt solutions were obtained by sequentially adding different kinds of salts in the PVDF solutions with stirring for 1 h. The concentration of used salts was selected to be 0.1 mol L^{-1}. Owing to the low solubility of inorganic salts in organic solvents, the concentrations of $AlCl_3$ and $CaCl_2$ were 0.05 mol L^{-1}. The TBAC concentrations were 0.02, 0.05, 0.10 and 0.15 mol L^{-1}, respectively. The setup for electrospinning is depicted in Fig. 1a. The polymer solution was in a horizontally placed graduated pipette with a metal needle and then attached to a micro syringe pump. The electrospinning process was carried out at applied voltage of 20–30 kV, tip to collector distance of 10–20 cm and spinning rate of 1.0–2.0 mL h^{-1}, respectively. The temperature was kept at 25 ± 2 °C and relative humidity (RH) was 25 ± 2%. The nanofiber membranes were collected on the surface of a grounded aluminum foil and the nonwoven polypropylene (PP).

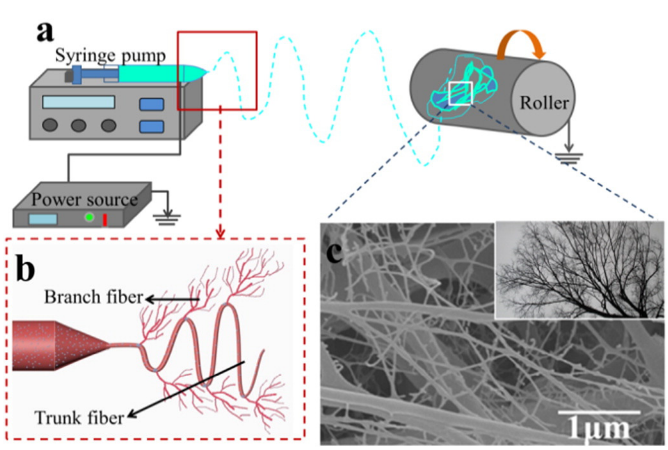

Fig. 1. Schematic diagrams illustrating the electrospinning process (a) and possible mechanism for the formation of tree-like nanofibers (b). (c) Typical FE-SEM image of PVDF/TBAC tree-like nanofibers and the inset is the optical image of tree branches.

2.3. Characterization

The conductivity of solutions was measured by using a conductivity meter (DJS-1C, Shanghai Rex Xinjing Instrument Co., Ltd., China). The conductivity electrode was inserted into the solution and completely submerged, and then read the readings after stabilization at room temperature. The morphology of nanofiber membranes was observed by field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi Ltd., Japan). The elements at the surface of the fibers were analyzed by energy disperse spectroscopy (EDS) connected to the FE-SEM. The photos of spinning jet were taken by a high-speed camera at a frame rate of 25,000 frames s^{-1} (VW-9000, KEYENCE, China). The content of tree-like structure was measured by Canny edge detection algorithm based on the software of MATLAB. The degree of crystallinity of nanofiber membrane was characterized by X-ray diffraction (XRD) (Rigaku D/MAX-2500, Japan). The pore size and distributions of nanofiber membranes were analyzed by pore size meter (PSM-165, Topas, GmbH, Germany). The mechanical properties were measured with a monofilament tensile testing machine (YG 005E, Wenzhou Fangyuan Instrument Co., Ltd., China), under a speed of 10 mm min^{-1} at room temperature.

3. Results and discussion

3.1. Effect of salt types on the morphology of nanofibers

The addition of salt can increase the electrical conductivity of the polymer solution, and has a great influence on the morphology of electrospun nanofibers [35,36]. In this study, PVDF nanofibers were fabricated by adding six kinds of salts and the effect of salt types on the morphology of PVDF nanofibers was studied. Fig. 2a shows that the PVDF nanofibers formed from the solution without salt exhibit a common circular structure and have a uniform diameter with an average diameter of 180 nm. Interestingly, the formation of tree-like nanofibers comprising of trunk fibers with 100 nm–500 nm diameter and branch fibers with 5 nm–100 nm diameter can be observed after adding organic branched salts (Fig. 2(b–d)) which corresponded to the sharply increased conductivity caused by the incorporation of organic salts (Table 1). Meanwhile, PVDF/TBAB nanofibers and PVDF/TBAC nanofibers showed more tree-like structures than PVDF/TEAC nanofibers and this was because the carbon chains of TBAB and TBAC were longer than that of TEAC, and the specific space steric structure reduced the forces between the PVDF molecules, which favors the slipping of the jets. In comparison with the fibers formed from PVDF/organic salts (Fig. 2(b–d)), PVDF/inorganic salts nanofibers (Fig. 2(e–g)) exhibited less tree-like structures. This was because the utilized inorganic salts have miniature effect on the electric conductivity of PVDF solution due to their low ion dissociation capacity in the PVDF solution as compared with the used organic branched salts (Table 1). Thus, it can be inferred that the increased conductivity of the solution is likely the primary factor to form these tree-like nanofibers and the organic branched salts with longer carbon chains have better effect on the tree-like structure than the inorganic salts. By comparison, the PVDF/TBAC nanofibers exhibit the best uniformity and the highest content of tree-like branches (over 55%), which make them optimal candidates for various future applications.

3.2. Effect of salt content on the morphology of nanofibers

The effect of TBAC content on the morphology of PVDF nanofibers was further investigated. As shown in Fig. 3, the conductivity of the polymer solution was largely improved with increase in the concentration of TBAC. The conductivity value was increased by 251 mS m^{-1}, when the concentration of TBAC was changed from 0.02 to

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