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Preparation and characterization of antibacterial electrospun chitosan/poly (vinyl alcohol)/graphene oxide composite nanofibrous membrane

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ABSTRACT

In this paper, chitosan (CS)/poly (vinyl alcohol) (PVA)/graphene oxide (GO) composite nanofibrous membranes were prepared via electrospinning. Such nanofibrous membranes have been characterized and investigated for their morphological, structural, thermal stability, hydrophilic and antibacterial properties. SEM images showed that the uniform and defect-free nanofibers were obtained and GO sheets, shaping spindle and spherical, were partially embedded into nanofibers. FTIR, XRD, DSC and TGA indicated the good compatibility between CS and PVA. There were strong intermolecular hydrogen bonds between the chitosan and PVA molecules. Contact angle measurement indicated that while increasing the content of GO, the distance between fibers increased and water drop showed wetting state on the surface of nanofibrous membranes. As a result, the contact angle decreased significantly. Meanwhile, good antibacterial activity of the prepared nanofibrous membranes were exhibited against Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus*.

1. Introduction

Electrospinning, a broadly employed technology for non-woven fiber preparation via the electrostatic force between polymer solution and collection plate using natural and synthetic polymers as raw materials, has attracted widely attention [1]. The range of the radius of nanofibers prepared by electrospinning technique is stable relatively, usually from several nanometers to several microns. Electrospun nanofiber has many advantages such as extremely high specific surface area and porosity, wide ductility of size and shape, the controllability of the nanofiber components and the design of the nanofiber formation [2]. Electrospinning is regarded as a well-known and versatile technique to fabricate fiber materials including composite fiber, porous structure fiber, polymer fiber and so on. Electrospun polymer nanofibers have potential array of wide ranging applications such as filtration, material enhancement, insulation isolation and energy storage, etc [3,4]. The electrospun nonwoven fibrous membranes prepared with biocompatible materials are widely used in biomedical fields, such as wound dressing, artificial tissue scaffold and so on [5].

Chitosan, also named as poly *N*-acetyl-2-amino-2-deoxy-D-glucopyranose, is a linear and semi-crystalline macromolecular polysaccharide [6]. Chitosan is one of the rare alkaline polysaccharides in nature that does not dissolve in neutral water but solubilizes in acidic aqueous solutions [7]. Chitosan has excellent biological properties, such as biocompatibility, biodegradability, non-toxicity, low immunogenicity and antibacterial activity [8]. Its antibacterial activity comes from the positively charged -NH_2 in the chain, which could engender electrostatic interaction with anionic groups on the microorganism cell membrane, change the permeability of cell membrane and result in the decline of microbial cells [9–12]. Because of the excellent biological properties of chitosan, it has potential array of wide ranging biomedical applications such as wound healing, wound dressing, antibacterial encapsulation, tissue engineering scaffolds, separation membranes, biosensors, drug delivery, etc. [13–15].

However, chitosan due to the existence of amino groups on the chains is not electrospinnable [16]. A common approach to improve the electrospinnability of CS is to blend it with other easily-electrospinnable polymers such as Poly(vinyl alcohol) (PVA) [17], Polyethylene oxide (PEO) [18] and Polylactic acid (PLA) [19]. PVA is usually selected as an electrospun material, because of its great

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water solubility, high tensile strength and flexibility. Due to the low toxicity and biocompatibility, PVA has been investigated in the medical field such as implantable medical devices, artificial pancreas, hemodialysis and drug delivery applications [20].

The graphene oxide (GO) prepared via modified Hummer's method has low production cost and sufficient supply [21]. GO contains abundant oxygen containing functional groups, such as hydroxyl, carbonyl, carboxyl and epoxy groups, on its nanosheet basal plane and edge. These functional groups interact strongly with polar solvents and polymer matrices to disperse GO better in the polymer matrix [22]. Thus, GO possesses great hydrophilicity [23]. Since GO nanosheets act as an implantable and biocompatible platform for accelerated cell growth and tissue regeneration, it could serve in widely range of biomedical applications which demand great implantable performance and biocompatibility. Thus, it is excellent to enhance the properties of chitosan without compromising its biocompatibility [24]. Besides, polymer composite materials with GO have been used widely in biomedical field due to the excellent antibacterial performance of GO towards gram positive bacteria and negative bacteria [25–27].

Electrospun fibers due to nano-scale structure are conducive to absorption of drug and permeation of water, which act as the decisive factor for wound healing effect [28]. So electrospinning is widely used in ranging biomedical applications such as wound healing, wound dressing and so on. Chitosan/PVA nanofibers have been obtained by electrospinning mixed polymeric solutions with different ratios of chitosan and PVA. Electrospun nanofibrous membrane due to its excellent biocompatibility, biodegradability, low immunogenicity, antibacterial activity and cell binding capacity which could promote the healing of wound efficiently, has been used in the range of wound healing and wound dressing [29].

In this work, we proposed a strategy of fabricating CS/PVA/GO composite nanofibrous membranes with enhanced antibacterial performance. Through the proposed preparation procedure, electrospinning solution of CS/PVA/GO can be obtained and then used for the fabrication of CS/PVA/GO composite nanofibrous membranes. The morphology of the electrospun composite nanofibers was examined by scanning electron microscopy (SEM). The structure, crystallinity, thermal stability and hydrophilic property of the nanofibrous membranes were measured using attenuated total refraction Fourier transform infrared spectroscopy (ATR-FTIR), X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and contact angle measurement. Additionally, the antibacterial activity of composite nanofibers against Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* was investigated.

2. Experimental

2.1. Materials

CS was supplied by Zhejiang Golden-Shell Pharmaceutical Co., Ltd., with a 90%–91% deacetylation degree. PVA (degree of polymerization is 1700, deacetylation degree 87%–89%) was obtained from Aladdin Industrial, Inc. Acetic acid was commercially available from Tianjin Zhiyuan Reagent Co., Ltd. Graphite powder was purchased from Qingdao Tianyuan graphite Co., Ltd. Concentrated H_2SO_4 was purchased from Beijing Chemical Works. Sodium nitrate was supplied by Tianjin Kermel Co., Ltd. Potassium permanganate was obtained from Tianjin Chemical Reagent Factory and H_2O_2 (30%) were obtained from Xilong Chemical Co., Ltd. The Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* were obtained from Guangdong culture collection center. Distilled water was used in this study. All of the materials unless otherwise stated, were of analytical grade and all of the materials were used as received without further treatment.

2.2. Preparation of GO dispersion

Graphene oxide was obtained by the modified Hummer's method [30]. Dried graphite powder was stirred slowly in cold concentrated H_2SO_4 and then sodium nitrate was added to the suspension. Potassium permanganate was added gradually and the temperature of the mixture was controlled in the range of 12 °C–14 °C. The mixture was stirred for 4 h. Then, the temperature of mixture was reached up to 35 °C for 30 min. After that, distilled water was slowly added to the mixture with the temperature maintained in the range of 45 °C–50 °C. Afterwards, the dilute suspension was stirred at 90 °C for an additional 30 min. The reaction was terminated by the addition of a certain amount of distilled water and 30% H_2O_2 solution. Gradually, the colour of the dispersion turned from dark brown to yellow. Several repeated filtration were carried out to wash the mixture using distilled water until the pH value of solution reached 6–7. Then it was centrifuged at 5000 rpm for 5 min and solid content of the sediment was determined. The GO mixed solution of 0.01 g/mL, formed by adding appropriate amount of distilled water, was treated with ultrasonic to obtain the uniform GO dispersion.

2.3. Preparation of electrospun CS/PVA/GO composite nanofibrous membranes

CS solution was prepared by dissolving 5 wt% of CS powder in distilled water with 5% w/w acetic acid. PVA powder was dissolved into distilled water at 70 °C, stirring to obtain PVA solution (5 wt%). The CS/PVA/GO electrospun precursor solutions were prepared as follows: GO dispersion (1 wt%, aqueous solution), CS solution (5 wt%) and PVA solution (5 wt%) were mixed with a certain volume. Chitosan solution was mixed with aqueous PVA solution in a weight ratio of 3:7, 2:8 and 1:9. The content of GO was 0 wt%, 1 wt%, 3 wt% and 5 wt% of CS, respectively. The electrospun precursor solution was adequately stirred but the stirring speed was not too fast, avoiding influencing the spinning process and the nanofibrous membranes forming, because of the formation of bubble in the solution.

Afterwards, electrospinning process was conducted by an apparatus comprised of the following parts: a syringe, a high voltage power and a metal plate for collecting nanofibers. A 10 mL syringe with electrospun precursor solution was linked to a flat-end metal needle with inner diameter of 0.7 mm. Set up the electrospinning parameters as follows: DC voltage was 23 kV, collecting distance between needle tip and collector was 15 cm. The needle was displayed with a horizontal plane of 15° and perpendicular to the collecting plate. The electrospinning process was carried out by pushing the polymer solutions into the needle, which depended on the gravity of the electrospun precursor solutions. The whole process was undertaken at the ambient temperature of 25 °C with a relative humidity of less than 45%. After 12 h of electrospinning process, the collector with electrospun nanofibers was dried overnight at room temperature. The schematic illustration is portrayed in Fig. 1.

2.4. Characterization

The morphology of CS/PVA/GO composite nanofibrous membranes was observed by scanning electron spectroscopy (JSM-7500F, JEOL). Prior to the analysis, the samples were coated with gold using a sputter coater. FTIR spectroscopy was used to determine the chemical functional groups of CS/PVA/GO composite nanofibrous membrane. This method was performed using