



# Manufacture of electrospun all-aqueous poly(vinyl alcohol)/cellulose nanocrystal composite nanofibrous mats with enhanced properties through controlling fibers arrangement and microstructure



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## ABSTRACT

Uniform fibers composed of two concentrations of poly(vinyl alcohol) (PVA) separately reinforced with up to 20 wt% cellulose nanocrystals (CNCs) were successfully produced by electrospinning. The CNCs were well dispersed in both 5 wt% PVA (5PVA) and 7 wt% (7PVA) aqueous solution prior to nanofiber manufacture. Composite nanofibers with controllable ultra-thin diameters of around 200 nm were generated reproducibly at all CNC contents investigated, and the nanofiber diameter turned out to be much smaller at higher CNC content. Interestingly, with the same CNC loading, nanofibrous mats produced from 7PVA reinforced with CNC nanoparticles had higher degree of crystallinity than nanocomposite with 5PVA as the matrix due to the more orderly stack of 7PVA nanofibers as well as the stronger interactions between PVA molecular chains and CNC nanoparticles. High mechanical performance nanocomposite fibrous mats were successfully fabricated by electrospinning an all-aqueous system for their potential application in biological field.

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## 1. Introduction

Polymer nanocomposites have been a subject of increasing interests as part of the development of novel structural and functional heterogeneous materials that occur at nanoscale [1,2]. Incorporation of mechanically robust nanoscale fillers, e.g. graphene, carbon nanotubes and inorganic nanoparticles, into polymer matrices has been widely investigated to fabricate high-performance nanocomposites [3]. Recently, one strong trend is the utilization of renewable or naturally derived nanoscale fillers to develop green nanocomposite materials with diverse advanced functionalities in response to environmental and economical demands [4–6]. Cellulose nanocrystals (CNCs), one of the strongest and stiffest natural polymers, are promising green nanofillers to improve the properties and versatility of polymer nanocomposites since they offer a unique combination of desirable properties and environmental benefits [7–10]. CNCs are rod-like, highly crystalline particles that are readily isolated through the controlled acid hydrolysis of cellulosic materials [11]. The main motivation to develop

CNCs as reinforcing agents are their low density, large specific surface area, as well as the ability to act as a significant enhancement at low loading levels [12]. Particularly, CNCs are usually used to reinforce the mechanical properties of polymer materials due to their high elastic modulus and mechanical strength obtained from the densely and orderly crystallized structure after acid hydrolysis [13,14]. Furthermore, along with the good biocompatibility, bioactivity and non-toxicity of cellulose derivatives [15,16], CNC-reinforced biocomposites can also be widely utilized in the biological fields, e.g., tissue engineering [17]. However, although CNCs have been successfully incorporated into many polymers as effective nanofillers, including poly (lactic acid) [18], poly (ethylene oxide) [19], and poly (vinyl acetate) [20], full exploitation of the intrinsic properties of CNCs to controllably tune and predict the performances of nanocomposites remains to be solved.

One-dimension (1D) polymer nanomaterials, especially polymeric nanofibers, have received growing attentions as a result of their distinct properties and applications superior to their bulk counterparts [21,22]. Electrospinning of polymer solutions or melts is a highly versatile technique that can be used to generate continuous 1D polymeric nanofibers [23], a process of whipping of polymer solutions under electrostatic forces [24]. Owing to their small fiber diameter, high surface-to-volume ratio and controllable porous structures, electrospun nanofibrous mats have been studied for a

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variety of applications such as filtration materials, membranes, drug delivery, and protective clothing [25–28]. One obvious shortcoming of the electrospinning technique, however, is that organic solvents harmful to the environment and human health were commonly used as electrospinning carrier [29], because organic solvents usually have better dissolving capacity and quicker evaporation rate than those of the aqueous phase. Therefore, there are both theoretical and practical motivations for developing a non-solvent electrospinning system, namely one with all-aqueous components.

Polyvinyl alcohol (PVA), a kind of highly water-soluble, nontoxic, and biocompatible polymer, is an ideal candidate to produce nanofibers by electrospinning under an all-aqueous condition. Over the past few years, numerous studies have been done on electrospun PVA fibers produced from PVA/water solutions to explore the effects of production conditions [30], molecular weights [31], and solution compositions [32]. Electrospun PVA nanofibers, however, were not sufficiently strong for many applications due to poor molecular chain orientation along the fiber long-axis resulting from low stretching forces during fiber formation [33,34]. Furthermore, the semi-crystalline structure of PVA led to a loose packing of PVA particles even under ordered orientation [35]. In order to improve the properties (e.g., low mechanical strength) and develop the functionalities (e.g., biomedical application), a large number of approaches, including crosslinking [36], post-treatment [37], and blending [38,39], have been conducted to fabricate electrospun PVA nanofibers. Among them, incorporating nanoparticles into PVA matrix was considered to be one of the most effective methods for reinforcing electrospun PVA nanofibers. Considering the excellent dispersion of CNCs in water and the large amount of surface hydroxyl [40,41], CNCs are the most suitable green nanofillers to reinforce the properties of PVA nanofibers because of the super enhancement effect of bulk CNCs [42], and the strong physical crosslinking from the hydrogen bond interaction between CNCs and PVA chains [43]. Furthermore, utilizing CNCs as nanofillers can also provide better electrospinnability owing to their high surface charge originated from the residues of acid hydrolysis. However, the majority of researches on CNCs as nanofillers has focused on either bulk or thin film materials [44], whereas only a few studies have recently reported on using CNCs as nanofillers for manufacturing 1D polymer nanocomposites, especially on fabricating CNC-reinforced PVA nanofiber by electrospinning technique [43,45]. More importantly, the structure–property relationship of electrospun PVA/CNC nanocomposites, particularly the special effects of CNCs and nanofibrous microstructure on the thermal and mechanical properties of the nanocomposites, have not been fully investigated and understood.

In this study, a series of PVA/CNC composite nanofibers with different CNC contents was fabricated via an electrospinning process using two PVA solutions with different CNC loading levels (Fig. 1). The main objective of this study was to investigate the influence of CNC loading levels and solution concentrations on the morphology and properties of electrospun PVA nanofibers reinforced by wood-based CNCs. Evaluations of PVA/CNC nanocomposite performances, especially mechanical properties, were undertaken to elucidate the structure–property relationship. The long-term perspective in this research is to develop an all-aqueous electrospinning system to manufacture fully biocompatible, environmental-friendly, and low-cost 1D high-performance fibrous nanocomposites for their potential applications in biological fields.

## 2. Experimental section

### 2.1. Materials

Poly(vinyl alcohol) (PVA) powders ( $M_w = 220,000$ ) were

purchased from Aladdin (Shanghai, China), and its degree of hydrolysis was 98% as received. 98% sulfuric acid were purchased from Aladdin (Shanghai, China). Commercial microcrystalline cellulose (KY100S MCC, moisture content = 75%, Daicel, Japan) was used as the raw material for producing cellulose nanocrystals (CNCs). Deionized water was used throughout the study.

### 2.2. Preparation of cellulose nanocrystals

The CNC suspensions were isolated by acid hydrolysis of MCCs as reported in our previous research [46]. Briefly, 40 g of MCC were mixed with 170 mL of 64 wt% sulfuric acid aqueous solutions at 45 °C for 1 h under vigorous magnetic stirring. The resulting suspensions were then cooled down to ambient temperature and washed with deionized water by successive centrifugations (10,000 rpm, ambient temperature, and 15 min) until neutral pH. Dialysis against deionized water was performed for 7 days to remove free acid molecules from the suspensions. After dialysis, the yield was calculated by withdrawing a known, small amount of the sample and obtaining its oven-dried weight. The CNC suspensions were kept refrigerated until use.

### 2.3. Preparation of spinning solutions

A certain amount of PVA was dissolved in deionized water under magnetic stirring at 90 °C for 2 h to obtain 12 wt% PVA solution in stock. Certain amounts of CNC suspensions and deionized water were added into 12 wt% PVA solution to keep the concentrations of PVA/CNC mixture in the spinning solutions at 5 and 7 wt%, respectively. The mixtures were vigorously stirred overnight at ambient temperature to obtain homogeneous PVA/CNC suspensions, which were stored in the refrigerator for no longer than 3 days prior to use. The CNC loading levels in respect to the PVA weight were chosen at 0, 5, 10, 15, and 20 wt%. The samples were designated as  $x$ -PVA or  $x$ -PVA/CNC- $y$ , where  $x$  (wt %) was the total concentration of PVA in water and  $y$  (wt %) was the concentration of CNCs in the polymer matrix.

### 2.4. Electrospinning set-up

The electrospinning apparatus (Yong Kang Le Ye, Beijing, China) used was the same as in our previous paper [29,46]. The spinning solutions were loaded into a 10 mL plastic, disposable syringe (Zhi Yu Co., Shanghai, China) with a stainless steel needle (i.d.: 0.6 mm). The needle was connected to the positive terminal of a voltage generator set of the electrospinning apparatus. A rectangular piece of aluminum foil (240 mm length and 150 mm width) was covered on the rotative cylinder collector connected to the negative electrode of the power supply (ground) to collect the electrospun nanofibrous mats. The flow rate of the polymer solutions was automatically controlled by a syringe pump. The obtained nanofibrous mats were carefully detached from the aluminum foil and stored at ambient temperature for 24 h prior to characterization.

### 2.5. Characterization of spinning solution

Conductivity, viscosity, and surface tension of PVA/CNC spinning solutions were characterized at ambient temperature using a conductivity meter (DDSJ-318, Lei Ci Co., Shanghai, China), a digital rotational viscometer (SNB-1, Heng Ping Co., Shanghai, China), and a surface tension meter (JK99B, Zhong Chen Co., Shanghai, China), respectively.

The morphologies of isolated CNCs and spinning solutions were observed using a transmission electron microscopy (TEM, Hitachi-7650, Japan). For analysis, aqueous CNC suspensions and prepared

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