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Electrospinning chitosan nanopowders into biocompatible polymeric mats

Xueqiong Yin, Jiazhi Ma, Junhua Chen, Wenyuan Dong, Qinhuan Zeng, and Li Zhu

Chitosan nanopowders can be electrospun into nanofibers together with a poly(vinyl alcohol) solution to create chitosan-based mats with good blood compatibility.

In recent years, nanofibrous mats have been widely researched in the field of biomaterials because of their unique structures.[1] Chitosan (poly-β-1,4-D-glucosamine), the N-deacetylated derivative of chitin, has good biocompatibility, biodegradability, and bioactivities. These properties make the preparation of nanofibrous chitosan mats for application in biomaterials an appealing prospect.

One popular method for preparing nanofibrous mats is electrospinning.[2] It is, however, challenging to prepare nanofibrous chitosan mats using this technique because of the high viscosity of chitosan solution, and the strong molecular interaction between chitosan molecules. For these reasons, chitosan can only be electrospun in certain unique solvents, or in a mixture solution with other polymers such as poly(vinyl alcohol), PVA.[3] Because chitosan is a positively charged polymer, however, electrospinning the material in a high-voltage electrostatic field would theoretically stretch the small chitosan particles, thus creating fibers.[4,5]

Based on this theory, we have proposed and demonstrated a new electrospinning method for chitosan nanopowders. Furthermore, we have investigated the morphology, wettability, and blood compatibility of the resulting nanofibrous mats to determine their suitability for biomedical applications. We first prepared chitosan nanopowders (NCTS) from chitosan through ball-milling (at 20Hz in an MM400 ball mill, for 4h). After this process, we found that the molecular weight of the chitosan was decreased—from 3.4×10^5 to 0.8×10^5 g/mol—and that the particle size of the chitosan was reduced (from 2.9μm to 385nm). We were able to confirm, though, that the material exhibited no obvious structural change after ball-milling (by carrying out Fourier transform IR spectroscopy on the NCTS).

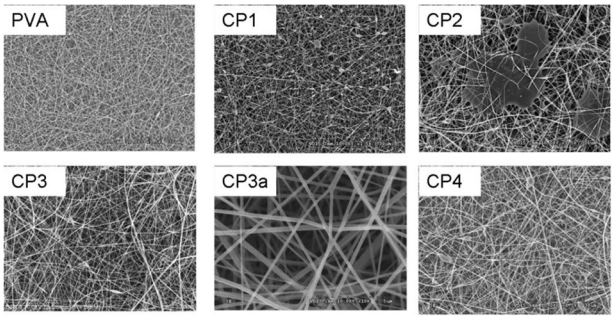

Figure 1. *Scanning electron microscope (SEM) images of chitosan nanopowders/poly(vinyl alcohol) (NCTS/PVA) samples—with 8wt% PVA—prepared under different conditions (i.e., by varying the voltage and the distance between the injector and collector, respectively, during electrospinning) at a magnification of 1500×. PVA: 30kV, 22cm. CP1: 30kV, 10cm. CP2: 35kV, 10cm. CP3: 35kV, 16cm. CP3a: Magnification of CP3 (10,000×). CP4: 40kV, 16cm.*

To prepare the nanofibrous mats, we electrospun the obtained NCTS (200mg) together with a PVA solution of 16g (i.e., 8wt%). First, we stirred the electrospinning solution magnetically, and then delivered the solution to the electrostatic spinning instrument (DT-200 from Dalian Dingtong Science and Technology Development Co., Ltd.) using a syringe under a constant feed rate (0.7mL/h). We thus fabricated NCTS/PVA mat samples with different morphologies by varying the voltage and the distance between the injector and the collector. Under these conditions, we found that the fabrication of a mat with only nanofibers (i.e., without any 'beads') required a voltage of 35kV and a distance of 16cm. Scanning electron microscope images show that the fiber diameters—in the range of 200–700nm—were distributed evenly within the NCTS/PVA samples (see Figure 1). Furthermore, in each case, all of the chitosan nanopowders were stretched into nanofibers.

To investigate the applicability of the NCTS/PVA mats in biological systems, we measured the stability of the samples in water. We

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found that, in samples that did not include a crosslinking agent, the fiber structure of the mat became indistinct after contact with water (at 37°C for 30min). We attribute this result to surface fibers becoming swollen, or dissolving. After we introduced a crosslinking agent (glutaraldehyde), on the other hand, the morphology of the mats exhibited no obvious change after processing with water. The water contact angle of NCTS/PVA mats was between 48.8 and 66.2°, whereas that of the crosslinked mats ranged from 133.1 to 135.1°. These results show that crosslinking led to a significant enhancement of the hydrophobicity of the samples. Indeed, the scanning electron microscope images and water contact angles shown in Figure 2 demonstrate that the glutaraldehyde-crosslinked NCTS/PVA mats were stable in water, indicating that they may be suitable for application in biosystems.

In the next part of our study, we investigated the blood compatibility of our NCTS/PVA samples by measuring coagulation times and carrying out platelet adhesion experiments. We found that the addition of NCTS extended the activated partial thromboplastin time (i.e., which characterizes the blood coagulation) of PVA. Furthermore, the NCTS/PVA samples with nanofibers showed no adsorption of platelets, indicating a good anticoagulation property (see Figure 3). These results show that NCTS/PVA samples achieve good blood compatibility.

In summary, we have successfully prepared chitosan nanofibers from chitosan nanopowders to create NCTS/PVA mats. This methodology represents a novel route toward the preparation of chitosan nanofibers through electrospinning. We found that NCTS/PVA samples crosslinked with glutaraldehyde were stable in water and expressed good blood compatibility, indicating the potential of the mats for use as blood-contacting biomaterials. Furthermore, the method of directly electrospinning charged nanopowders into nanofibers may be relevant

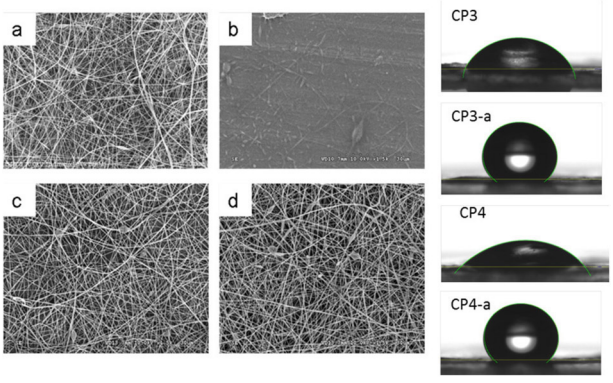

Figure 2. *SEM images of samples before and after they were processed with water. CP3 (a) before and (b) after processing with water. Crosslinked CP3 (CP3-a) (c) before and (d) after processing with water. The water contact angles of the mats are also shown (right panel). CP4-a: Crosslinked CP4.*

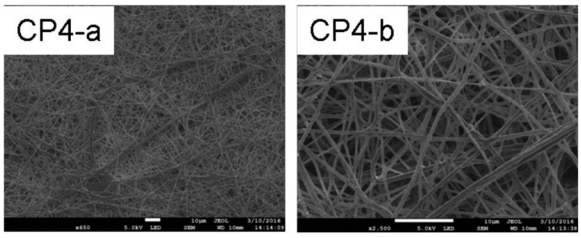

Figure 3. *SEM images of NCTS/PVA after contact with platelet-rich plasma at different magnifications: (a) 650× and (b) 2500×.*

for use in other polymer systems to prepare nanocomposite fibers. In our future work, we intend to electrospin chitosan derivatives (containing –COOH, $–NH_2$, and $–SO_3H$) onto a biocompatible polymer to obtain heparin-like anticoagulant biomaterials.

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Author Information

Xueqiong Yin, Jiazhi Ma, Junhua Chen, Wenyuan Dong, Qinhuan Zeng, and Li Zhu
Hainan Provincial Fine Chemical Engineering Research Center
Hainan University
Haikou, China

Xueqiong Yin received her PhD in mineral processing in 2002, and is currently working as a professor at Hainan University. Her research interests include nanomaterials, polysaccharides, environmental materials, and natural resources.

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