



# Chitosan nanofibers fabricated by combined ultrasonic atomization and freeze casting



Yihan Wang<sup>a,b,1</sup>, Minato Wakisaka<sup>a,\*</sup>

<sup>a</sup> Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, 2–4, Hibikino Wakamatsu-ku Kitakyushu-shi, Fukuoka 8080196, Japan

<sup>b</sup> School of Food Science and Engineering, Yangzhou University, Yangzhou 225127, China

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## ABSTRACT

Aligned chitosan nanofibers exhibiting diameters smaller than 100 nm were easily prepared by combining ultrasonic atomization with freeze casting. A major advantage of this approach is the use of distilled water as main solvent. Scanning electron microscopy demonstrated that fiber diameter and morphology mainly depended on the atomizing tools, freezing temperature, and chitosan solution viscosity. Minimum diameter and uniform orientation were achieved using an electric flosser as an atomizing tool, liquid nitrogen as a coolant, 0.4 wt% aqueous chitosan solution (molecular weight = 22 kDa), and a small amount of lactic acid as solvent at 0 °C. The resulting chitosan nanofibers may find application in biomedical and food engineering. Moreover, this new technology may be applicable to other natural and synthetic water-soluble polymers.

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## 1. Introduction

Nanofiber production from polysaccharides has attracted tremendous research attention because of their biological importance, such as biodegradability and biocompatibility. Chitosan, a natural cationic polysaccharide polymer produced by chitin deacetylation, provides nanofibers exhibiting many unique characteristics, such as metallic ion adsorption (Wang, Du, Fan, Liu, & Hu, 2005) and antimicrobial activity (Kurita, 2006; Muzzarelli, 2012; Muzzarelli et al., 2012; Wang, Du, & Liu, 2004). These properties make them useful as wound dressing materials (Ma, Xie, Jiang, Shuler, & Bartlett, 2013), food preservatives (Roller & Covill, 1999; Liu, Du, Wang, & Sun, 2004), food packaging materials (Barikani,

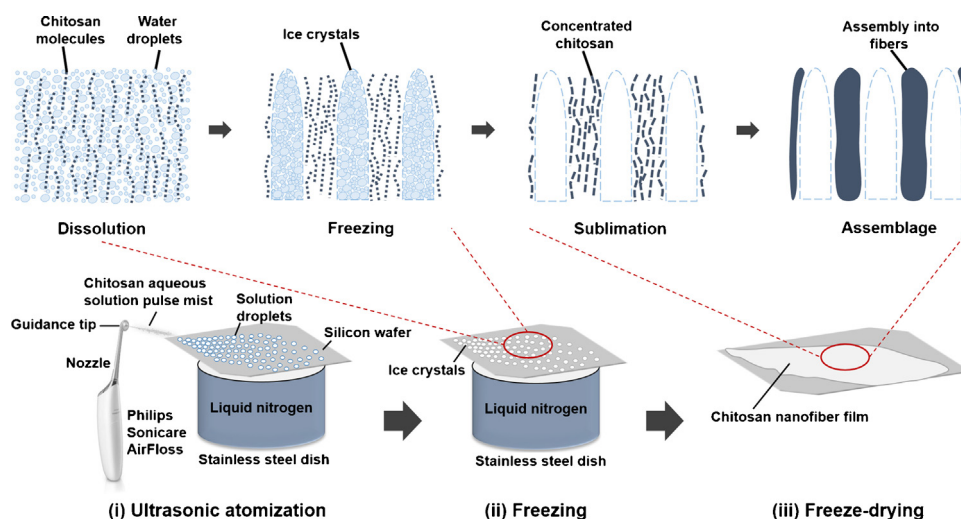
Oliaei, Seddiqi, & Honarkar, 2014), and immobilization scaffolds for microalgae (Eroglu et al., 2012).

Existing methods deployed for manufacturing chitosan-based nano- to submicron-scale fibers and composite nanofibers generally involve wet spinning and electrospinning, which have reached their full development (George & Qin, 1993; Li & Hsieh, 2006; Liao et al., 2011; Liu & Bai, 2005; Manisara, Ratana, & Pitt, 2006; Ignatova, Starbova, Markova, Manolova, & Rashkov, 2006; Muzzarelli, El Mehtedi, & Mattioli-Belmonte, 2014; Ohkawa, Cha, Kim, & Nishida, 2004; Ohkawa & Yamamoto, 2002; Park, Jeong, Yoo, & Hudson, 2004; Seo et al., 2005; Shin et al., 2006; Zhou, Yang, & Nie, 2006). However, these methods present several challenges. Wet spinning requires complex processes and costly investment. In addition to electric shock risks, electrospinning using high-voltage electrical fields faces issues in controlling fiber orientation and displays sensitivity to the conductivity of the spinning dope solution. Also, the polycationic nature of chitosan results in the excessive surface tension of this solution, enhancing the electrical force requirements and, thus, hindering this technique (Dutta et al., 2013; Min et al., 2004). Various nanofiber fabrication methods, such as rotary jet-spinning (Badrossamay, McIlwee,

\* Corresponding author. Tel.: +81 93 695 6066; fax: +81 93 695 6066.

E-mail addresses: [wang-yihan@edu.life.kyutech.ac.jp](mailto:wang-yihan@edu.life.kyutech.ac.jp), [yvanwong@126.com](mailto:yvanwong@126.com) (Y. Wang), [wakisaka@life.kyutech.ac.jp](mailto:wakisaka@life.kyutech.ac.jp) (M. Wakisaka).

<sup>1</sup> Permanent address: 8–5, Huatian Residence Community, Tianyi Town, Ningcheng County, Chifeng City, Inner Mongolia Autonomous Region, China. Tel.: +81 80 3900 9956.



**Fig. 1.** Schematic illustration of the ultrasonic atomization–freeze casting of chitosan nanofibers. (i) The PSAF nozzle was kept parallel to the silicon wafer surface cooled using liquid nitrogen, and the aqueous chitosan solution was atomized along the edge. The solution droplets froze rapidly into ice crystals, which grew perpendicular to the cold surface, displaced, and phase separated the polymer in an orderly manner, essentially templating the chitosan molecules; (ii) subsequently, these crystals were removed by lyophilization; and (iii) the concentrated chitosan assembled into a nanofiber film.

Goss, & Parker, 2010), handspinning (Watanabe, Kim, Enomoto, & Kim, 2011), and solution blowing (Behrens et al., 2014; Liu, Xu, Zhuang, & Cheng, 2014), have emerged as prospective techniques for chitosan-based materials. However, these methods invariably require environmentally harmful volatile organic solvents to maintain or enhance fiber performance without guaranteeing that these solvents completely evaporate, which is potentially dangerous for biomedical and food engineering applications.

Freeze casting (ice templating), which is inspired by the nature of sea ice, uses only water as the main solvent (Wu & Yan, 2013). Freeze casting is extensively investigated for simple freeze-drying (Lee, Zhang, & Gao, 2014) and jet-rapid freezing (Spender et al., 2012) and has also been used in fiber fabrication. In a typical ice-templating process involving an aqueous polymer solution or suspension frozen using a refrigerator, dry ice, or liquid nitrogen, the freezing rate strongly impacts the structures obtained upon ice mold removal (Gutierrez, Ferrer, & Monte, 2008). When the freezing rate sufficiently exceeds the polymer's Brownian diffusion, the polymer solutes segregate between ice clusters, and upon ice sublimation under vacuum, the polymer solutes form an aligned fiber structure, which is the reverse replica of the ice template. In contrast, when the freezing rate is lower than the polymer's Brownian diffusion, the growing ice crystals steadily drive out the polymer solutes into a macroscopically separated phase and forms random polymer structure (Lee, Zhang, & Gao, 2014). Therefore, uniformly oriented polymer fibers are generated by rapid freezing. Conventional freeze casting has produced fibers showing larger diameters and mixtures with film-like or lamellar structures, which require further improvement (Wang & Wakisaka, 2014).

In this study, we create a new approach based on solution blowing and ice templating and propose an ultrasonic atomization combined with freeze casting to prepare chitosan nanofiber.

## 2. Experimental

### 2.1. Materials

Purified chitosan powder (deacetylation degree: 85%,  $M_W < 15$  kDa) was purchased from Polysciences Inc. (Warrington, PA). Chitosan (deacetylation degree: 80%,  $M_W =$  ca. 420 kDa) was purchased from Tokyo Chemical Industry co., Ltd. (Tokyo, Japan). Chitosan 10 powder (deacetylation degree: 80%,  $M_W =$  ca.

22 kDa), formic acid (assay: 98.0%), acetic acid (assay: 99.7%), and L-lactic acid (assay: 85.0–92.0%) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All chemicals were of analytical grade, for laboratory research and investigational use only and used as received. The circular silicon wafer presented a diameter of 10 cm.

### 2.2. Preparation of atomizing solutions

Two chitosan solutions were obtained by the following compositions: (1) dissolving chitosan powder (4.0 g) and formic or acetic acid (1.0 ml) in distilled water (95.0 ml) and (2) dissolving chitosan powder (4.0 g) and L-lactic acid (2.0 ml) in distilled water (94.0 ml), respectively. The added acid amount ensured that chitosan was completely dissolved into a clear solution without an excess residue. Chitosan samples of different molecular weights were dissolved in L-lactic acid. All samples stirred at low speed overnight. (AS ONE HSD-4, Japan). The resulting 4 wt% chitosan hydrogels were diluted to the desired low concentrations with distilled water and their viscosity were measured. The whole process was achieved in a low-temperature laboratory to limit chitosan degradation.

### 2.3. Ultrasonic atomization–freeze casting of chitosan nanofiber

A chitosan solution was poured into the reservoir of the Philips Sonicare AirFloss (PSAF) device (PHILIPS HX8111/32, Mexico) and atomized several times until the nozzle produced a full solution mist. A stainless steel dish was filled with liquid nitrogen, ice/NaCl, or dry-ice/ethanol and covered with a silicon wafer until the wafer surface just began to freeze. The PSAF nozzle tip was 5 cm from the wafer center and flush with its edge. It was kept parallel to the wafer surface while one single layer was atomized along this edge. Next, the wafer was immediately placed into a freeze dryer (EYELA FDU-1200, Japan) and lyophilized under vacuum for about 5 h at  $-52^\circ\text{C}$  (Fig. 1). To achieve atomization at different temperatures, the solution was split through three small beakers. The first beaker was placed in the freezer compartment of a refrigerator at approximately  $0^\circ\text{C}$  until just frozen into an ice–water mixture. The second beaker was kept at room temperature; ca.  $25^\circ\text{C}$ , the third beaker was heated to  $37^\circ\text{C}$ . Common household sprayer and air brush equipped with a 0.2 mm nozzle and a 2.5 ml cup (RICH RB-2,

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