Electronic Supplementary Information

Novel Fibers Fabricated Directly from Chitin Solution and Their Application as Wound Dressing

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Experimental Section

Materials

Raw chitin powder was purchased from Zhejiang Golden Shell Biochemical Co. Ltd. (China) and purified by established method before use. Specifically, raw chitin was treated with 5 wt% NaOH solution for 10 h with stirring to remove residual protein. The resultant suspension was filtered and washed with distilled water. Subsequently, the chitin powder was treated with 7% (v/v) commercial hydrochloric acid aqueous solution for 1 day to remove residual minerals. After filtration and rinsing, the treated sample was dispersed in a 5 wt% NaOH solution for 24 h. Finally, the samples were bleached by 1.7 wt% sodium chlorite solution at 80^{o}C for 6h in a 0.3M sodium acetate buffer, and then washed with distilled water and oven dried to obtain purified chitin powder. The degree of acetylation (DA) of the original and purified chitin powder was calculated to be 90% and 94%, respectively, according to

$$A_{1560} / A_{2875} = 0.0125 \times DA + 0.2 \quad (1)$$

where A_{1560}/A_{2875} is the absorbance ratio of the absorption bands at 1560cm^{-1} and 2875 cm^{-1} in Fourier transform infrared (FT-IR) spectra [1]. The molecular weight (M_w) was determined to be 3.2×10^5 in 5% (w/v) LiCl/DMAc by dynamic light scattering (DLS, ALV/GGS-8F, ALV, Germany). All the other chemical reagents were purchased from commercial sources in China, and were of analytical-grade.

Characterization

FT-IR spectra of chitin fibers were recorded on a Fourier transform infrared spectrometer (model 1600, Perkin-Elmer Co., USA) at room temperature. X-ray diffraction (XRD) measurements were carried out on a WXRD diffractometer (D8-Advance, Bruker, USA) with Cu Kα radiation (λ= 0.15406 nm) at 40 kV and 30mA. The XRD pattern was recorded in the range 2θ = 5–30° at a scanning speed of 2°/min. Cross-polarization/magic angle spinning (CP/MAS) solid-state ^{13}C NMR spectra were recorded on a Bruker AVANCE-600 Spectrometer (^{13}C frequency = 150.96 MHz) with a standard 4 mm rotor at ambient temperature. The spinning rate and the relaxation time were 5.0 kHz and 4.0 s, respectively. The cross polarization time was 1.0 ms. The lyophilized fibers and nonwoven fabrics were trimmed into small particles and dried in vacuum oven at 6^{o}C for 48 h before use.

Scanning electron microscopy (SEM) of fibers was carried out on a Hitachi S-570 (Japan) microscope. The wet fibers were frozen in liquid nitrogen, snapped immediately, and then freeze-dried. The air-dried fibers were cut into short staples with medical scissors. The surfaces and fracture sections were sputtered with gold for observation. Cross section of a bunch of dried fibers obtained by a Y172 fiber slicer was observed on an ordinary optical microscope. The fineness (linear density) of chitin fibers were measured on a precision electronic balance by weighing 200 single fibrils each with a length of 5cm, and for every sample, three parallel measurements were conducted. If a fibril with a total length of 1000m weighs 1g, then its titer value was 1 tex or 10 dtex. The mechanical properties of the films at the dry state were

measured on an electronic single fiber strength tester (LLY-06, Wuhan Textile University, China) according to ASTM method D2256-80[2]. For each sample, 50 single fibrils were tested and an average value was recorded to calculate the tensile strength and elongation at break.

To test the water uptake, the chitin nonwoven and commercial gauze were preconditioned at 40 °C for 48 h and weighed (W0). After immersing in distilled water until an equilibrium was reached, the extra water were removed with filter paper and the samples were weighed again (W_t). The water uptake ratio was measured according to the following equation[3]

$$\text{water uptake}(\%) = \frac{W_t - W_0}{W_0} \times 100 \quad (2)$$

For each sample, three parallels were tested to obtain an average value. As a result, The air permeability for both chitin nonwoven fabrics and gauze were measured on a YG 461E/II numerical air permeability tester (Ningbo Textile Instrument Factory, Zhejiang, China) under a pressure of 100Pa, according to a national standard of GB/T 5453-1997. The testing area was 20 cm^2 and a nozzle of 8.0 mm was selected. For each sample, five parallels were tested to obtain an average value. The tensile strength of chitin nonwoven fabrics was measured on a a universal testing machine (CMT 6503, Shenzhen SANS Test machine Co., Ltd., China) according to ISO527-3-1995 (E) at a speed of 1mm/min. Ten parallels were measured and the average value was reported.

Results

Structure of pure chitin fibers and nonwoven fabrics

Figure S1 shows the FT-IR spectra of the purified chitin powder, the regenerated chitin fibers and the chitin nonwoven. The characteristic absorption peaks of α-chitin at 1660, 1620 (amide I), and 1560cm^{-1} (amide II) [4] appeared in FT-IR spectra for all samples. The N-H stretching vibration peak around 3200 cm^{-1}, amide I and amide II hardly changed after dissolution and regeneration from the alkali/urea solution. This indicated that no obvious deacetylation occurred during dissolution and regeneration, which were mainly physical processes. Furthermore, according to calculation based on Eq. (1), the DA values of chitin fiber and chitin nonwoven were 93%, showing no clear variation when compared to that of the chitin powder (94%). XRD patterns of the chitin powder, chitin fibers and chitin nonwoven are shown in Figure S2. The chitin fibers and nonwoven fabrics retained the intrinsic crystal form of α-chitin as well as raw and purified chitin powder. The crystal plane was labeled above the curves. The crystallinity (χ_c) and the crystallite size of the chitin could be calculated by multi-peak fitting and the Scherrer equation

$$L_{hkl}=K\lambda/\beta_0\cos\theta \quad (3)$$

where K= 0.9; L_{hkl} was the crystallite size in the vertical direction to the *hkl* plane; λ was the wavelength (0.154nm) and β_0 was the full width at half maximum for 2θ.[1] The χ_c and L_{hkl} values for the chitin powder, chitin fibers and chitin nonwoven are listed in Table S1. For fibers and nonwoven after a process of dissolution and

regeneration, there was a clear decrease in the crystallinity as well as in the crystallite size. This could be explained by the intervention of solvents which generally involves disruption of the original crystal form. Compared to fibers, the crystallinity and crystallite size for nonwoven fabrics slightly improved, probably due to the hot pressing induced orientation, which increased the tendency of ordered arrangement.

Solid state ^{13}C NMR spectra of the purified chitin powder, chitin fibers and chitin nonwoven are presented in Figure S3. The spectrum of the chitin powder exhibited eight main signals, including sharp peaks at 172.2 and 22.2 ppm assigned to the carbonyl and methyl carbons, respectively. And peaks at 103.2, 82.1, 74.9, 72.4, 59.7 and 54.1 ppm were ascribed to C1, C4, C5, C3, C6, and C2 on the glucosamine unit of chitin, respectively, as labeled above the curves. Notably, the signals assigned to C3 and C5 for both the regenerated chitin fibers and chitin nonwoven appeared as two separate peaks, indicating the same α-chitin structure as the ingredient, which was in accordance with FTIR and XRD.

References

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Table S1 structural properties of purified chitin powder, chitin fibers and chitin nonwoven.

Sample	DA (%)	χ_c (%)	L_{020} (nm)	L_{110} (nm)
Chitin powder	94	77	8.76	5.92
Chitin fibers	93	45	7.09	3.22
Chitin nonwoven	93	56	8.13	4.43

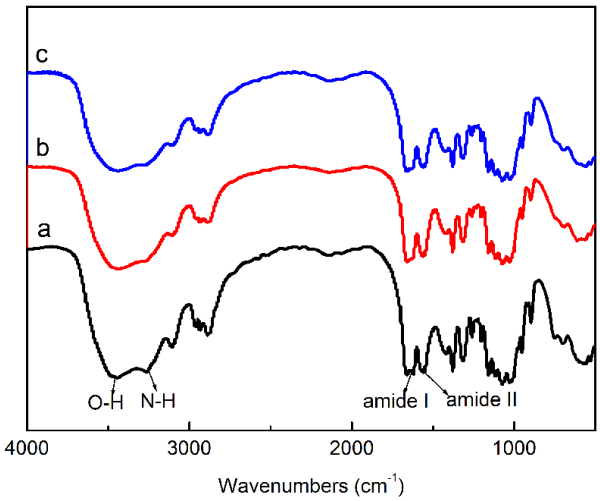


Figure S1. FTIR spectra of the purified chitin powder (a), regenerated pure chitin fibers (b) and chitin nonwoven fabrics (c).

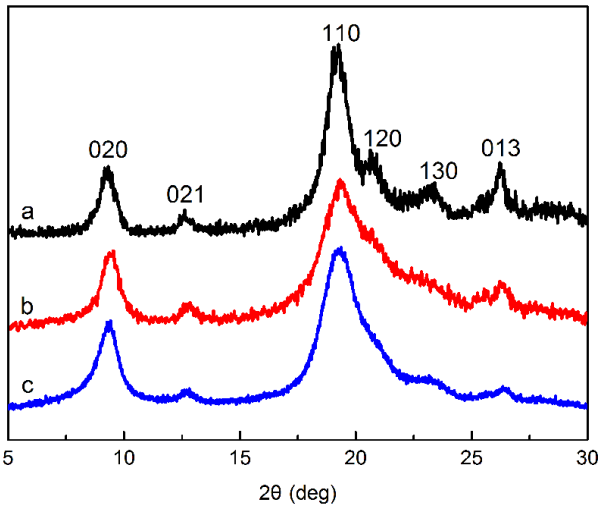


Figure S2. XRD patterns of the purified chitin powder (a), regenerated chitin fibers (b) and chitin nonwoven fabrics (c).

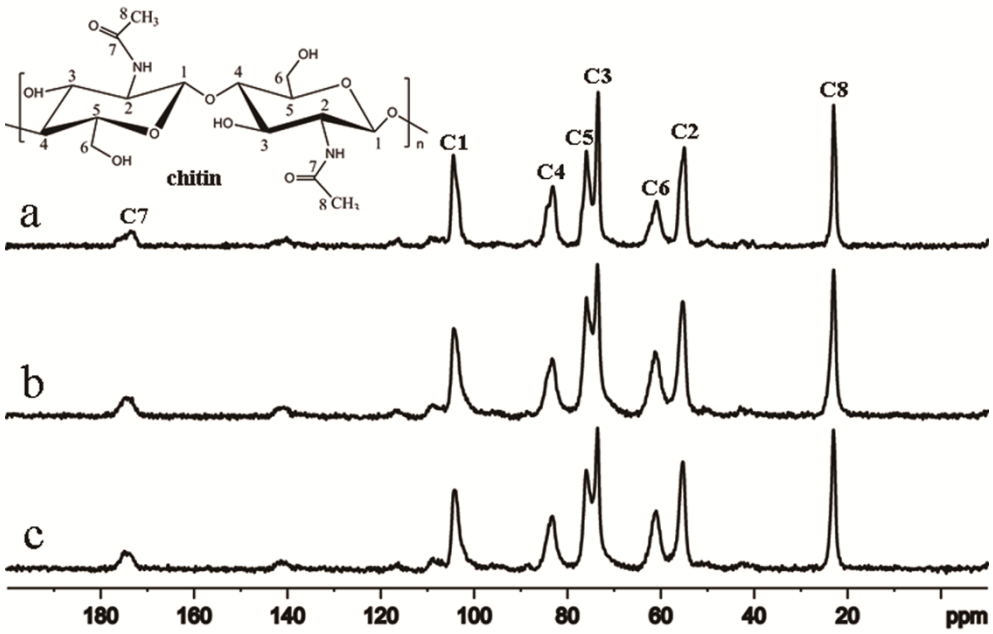


Figure S3. Solid state ^{13}C NMR spectra of the purified chitin powder (a), regenerated chitin fibers (b) and chitin nonwoven fabrics (c).

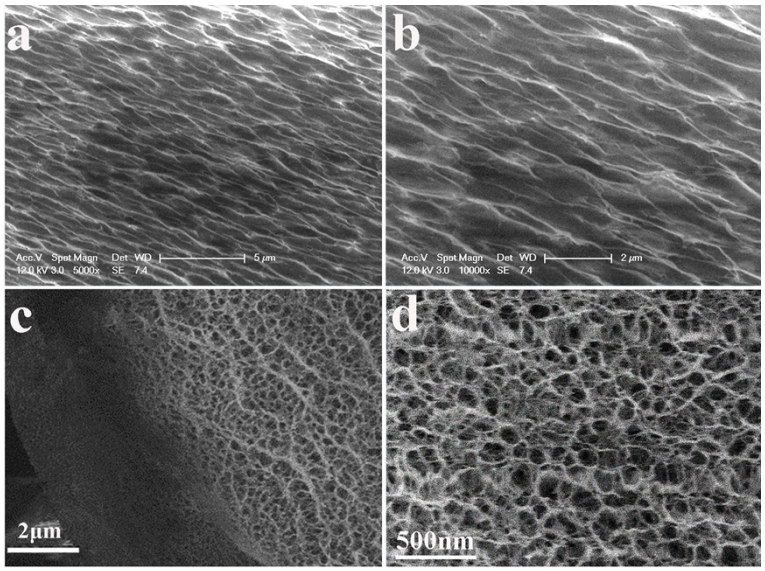
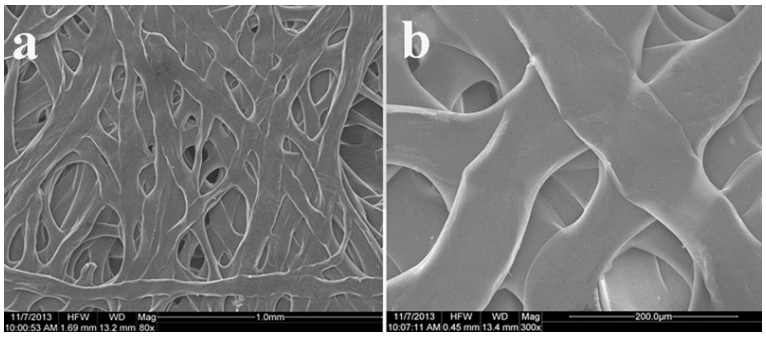


Figure S4. SEM images for wet chitin fibers lyophilized and fractured in liquid nitrogen: (a-b) surface at different magnification; near the sheath (c) and around the core (d) in the cross section. Scale: 5μm for (a), 2μm for (b-c) and 500nm for (d).

1 

2 **Figure S5.** SEM images of surface of chitin nonwoven fabrics made of chitin fibers

3 without solvent exchange to acetone. Scales: 1mm in (a) and 200 μm in (b).

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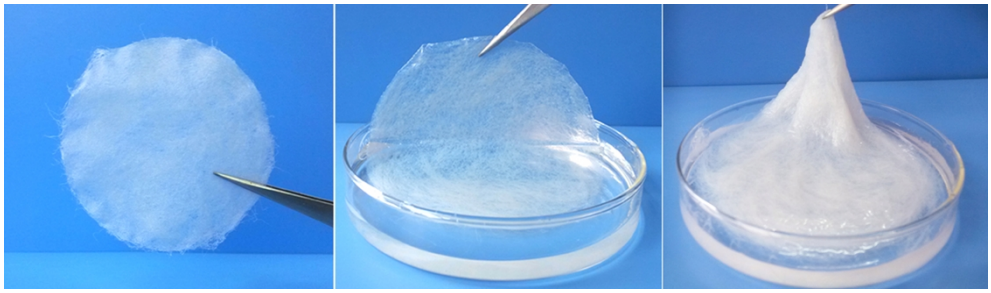

Figure S6. Photographs of chitin nonwoven fabrics without solvent exchange at dry state (a), just being soaked in water (b) and kept in water over several hours (c).

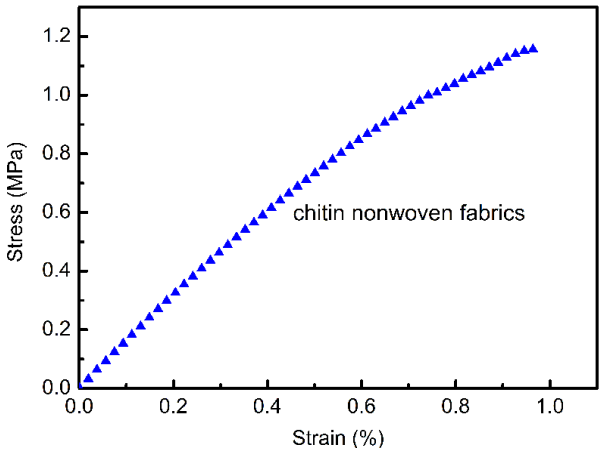

Figure S7. Stress-strain curve of chitin nonwoven fabrics.