Supporting information for
Stable jet electrospinning for easy fabrication of aligned ultrafine fibers
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EXPERIMENTAL SECTION

Materials. Poly(L-lactic acid) (PLLA, MW 100,000 Da), UHMWPEO (MW > 5,000,000 Da), polycaprolactone (PCL, MW 70,000–90,000 Da) and chitosan (DD > 85%) were purchased from Polysciences, Avocado, Sigma-Aldrich and Zhejiang Golden-Shell Biochemicals, respectively. A higher molecular weight PLLA (MW 500,000 Da) was provided by Jinan Daigang Biomaterials. Unless otherwise noted, PLLA from the Polysciences was the primary material used for SJES. 2,2,2-trifluoroethanol (TFE) and fluorescein isothiocyanate (FITC) were obtained from Sigma-Aldrich and Aladdin Chemicals, respectively. Dichloromethane (DCM), acetic acid (HAc), dimethyl sulfoxide (DMSO), methanol, sodium hydroxide (NaOH), ethanol and acetone were all supplied by the Sinopharm Chemicals. All of the above materials were used as received without further purification.

Preparation of Spinning Solutions. Solutions of UHMWPEO doped PLLA (5 wt%) were prepared by dissolving the PLLA and UHMWPEO in TFE. Whereas the solvents used for making UHMWPEO doped PCL (3 wt%) and chitosan (3 wt%) solutions were TFE and a mixed solvent system of 3 wt% HAc and DMSO (10:1, w/w), respectively. All the polymer solutions were stirred with a Multi-Stirrer H05-1 (Meiyingpu Co. Ltd., China) at room temperature for 24 h until transparent solutions were obtained.

FITC Labeling of Chitosan. FITC-conjugation of chitosan was performed as described previously. Briefly, 10 mL of dehydrated methanol and 5 mL of FITC in methanol (2.0 mg/mL) were added in turn to 10 mL of chitosan (1% in 0.1 M HAc) in the dark at ambient temperature. After 3 h, the conjugated polymer was precipitated in 0.2 M NaOH. The precipitate was pelleted by centrifugation at 10,000 g for 15 min and washed with a solvent mixture of methanol:water (70:30, v/v). The washing and pelletization were repeated until no fluorescence was detected in the supernatant (Perkin-Elmer LS-5B luminescence spectrometer, λex 490 nm, λem 520 nm). The conjugated chitosan was re-dissolved in 10 mL of 0.1 M HAc and dialyzed in the dark against 5 L of water for 3 days. The water was replaced with fresh one every 6 h. Finally, the conjugated chitosan was freeze-dried.

Stable Jet Electrospinning. The setup for SJES is essentially the same as the conventional electrospinning configuration except for the formation of a stable jet during the process (Fig. 1a). A polymer solution was loaded into a 10 mL plastic syringe equipped with a 22-Gauge stainless-steel needle. The needle was connected to a high voltage power supply (TXR1020N30-30, TESLAMAN Co. Ltd) that is capable of generating direct current voltage up to 30 kV. The distance between the tip of the needle and the collector was more than 15 cm. Specific polymer solution was extruded via using a syringe pump (KDS100, KD Scientific) at a constant flow rate between 0.01 and 3 mL h^-1. At a critical voltage, a stable jet was ejected from the apex of the Taylor cone. For solutions involving volatile solvents such as TFE and DCM, the dried filament can be directly wound up to the rotating collector. When electrospinning chitosan, its stable jet was first introduced into a coagulation bath containing a mixture of ethanol and acetone at 5:5 to coagulate and solidify the filament before being wound up to the rotating collector. For coaxial electrospinning, a custom-made compound spinneret was used to allow PLLA solution (template) flow out from the inner capillary and shell layer chitosan solution from outer capillary was coated onto PLLA. All SJES was performed at ambient conditions of room temperature (~25 °C) and humidity 30-50%.

Characterization. Viscosity of the polymer solutions was measured using a LVDV-II Pro viscometer (Brookfield Viscometer). Rheological properties were examined on a stress-controlled ARES-RFS rheometer (TA Instruments) with a shear deformation of 10% over a frequency range of 0.1-100 rad/s. In SJES, jet emitted as a single stable jet was monitored by a high-speed microscope (VW-9000, Keyence) at 2000 frames/s. The photograph of a single filament from SJES, winded onto a rotating drum, was taken by a digital camera (Nikon D5000, Japan). Morphology of the SJES fibers was examined by scanning electron microscopy (SEM, TM-1000 Hitachi) at an accelerating voltage of 15 kV, and the average diameters of SJES fibers in the experiment was measured from the SEM images by using an ImageJ software. Core-shell structure of the as-electrospun PLLA-chitosan fiber from SJES was verified by TEM observation at 80 kV (JEM-2100F, JEOL). FTIR spectra were obtained with an Avatar 380 FTIR spectroscopy (Nicolet-Thermo, USA). The infrared spectra of the samples were measured over a wavelength range of 4000–500 cm^-1 with a resolution of 4 cm^-1.

Reference
**Fig. S1** (a) SEM image of electrospun PLLA prepared from a 5 wt% solution of PLLA/TFE, showing ‘bead-on-string’ morphology. (b) Viscosity of UHMWPEO doped PLLA/TFE solutions as a function of mass ratios of PLLA to UHMWPEO. Formulations of PLLA/UHMWPEO at mass ratios of below 90:10 enable formation of stable jet during electrospinning.

**Fig. S2** TEM image of the chitosan-coated PLLA fiber showing the formed core-shell structure.
**Fig. S3** SEM images of core-shell structured PLLA-Chitosan fibers before (A) and after (C) washing with aqueous acetic acid (3 w%) at 37 °C for 36 h, showing finer sizes after washing. Plots B and D provide the size distributions before and after washing treatment, respectively.

**Fig. S4** FTIR spectra of (a) chitosan coated PLLA fibers, (b) chitosan, (c) PLLA-chitosan fibers after washing, and (d) PLLA fibers. In (c), disappearance of characteristic bands of chitosan, at 1592 cm⁻¹ corresponding to amino groups, suggests that the chitosan sheath layer of the PLLA-chitosan composite fibers was washed away by the used aqueous acetic acid solution. The peak at 1752 cm⁻¹ corresponds to the typical C=O stretching mode of PLLA.