

Supporting Information

## Structure-tunable Janus Fibers Fabricated Using Spinnerets with Varying Port Angles

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### Experimental

Two different electrospinnable solutions were prepared for this investigation. One solution consisted of 10% (w/v) polyvinylpyrrolidone K60 (PVP K60,  $M_w=360,000$ , Sigma Aldrich, London, UK) and 1% (w/v) rhodamine b (99%, Fisher Scientific, London, UK) in a mixed solvent of ethanol and *N,N*-dimethylacetamide (DMAc) with a volume ratio of 8:2, and the other solution was composed of 13% (w/v) Eudragit<sup>®</sup> L100 (EL100,  $M_w=150,000$ , supplied by Röhm GmbH & Co. KG, Darmstadt, Germany) and 2% (w/v) ANS-NH4 (Fisher Scientific, London, UK) in a mixture of ethanol and DMAc with a volume ratio of 9:1.

Two syringe pumps (KDS100 and KDS200, Cole-Parmer, UK) were used to drive the working fluids. A high voltage power supply (FuG Elektronik GmbH, Germany) provided voltages between 0-60 kV. Aluminium foil was used to collect the electrospun fibers, at a vertical distance of 15 cm from the nozzle tip of the spinneret. Four side-by-side spinnerets were manufactured in stainless steel (Speedform, Birmingham, UK). The two ports had an internal diameter of 0.3mm, were spaced 0.2mm apart at the outlet, and were arranged at angles of 40°, 50°, 60° and 70°. All electrospinning processes were carried out under ambient conditions (temperature  $22 \pm 2$  °C and relative humidity  $20 \pm 3\%$ ). Electrospun fibers were stored in a vacuum desiccator for further investigation. A camera (PowerShot A640, Canon, Tokyo, Japan) was used to observe the side-by-side electrospinning process.

The surface morphologies of electrospun fibers were assessed using a Quanta FEG450 field-emission scanning electron microscope (FESEM, FEI Corporation, Netherlands). Prior to FESEM experiments, samples were subjected to gold sputter-coating in a nitrogen atmosphere to confer them with electrical conductivity. Over 100 points were collected from FESEM images using Image J software (National Institutes of Health, USA) to determine the

average fiber width/diameter. The elemental composition of the samples was analyzed by an Energy Dispersive Spectrometer (EDS, IE300X, Oxford, U.K.) attached to the FESEM. Detailed structural characteristics were observed using a JEM2100F transmission electron microscope (TEM, JEOL, Tokyo, Japan). TEM samples were collected by directly placing a lacey carbon-coated copper grid on the collector during the side-by-side electrospinning process.

The arrangement of the apparatus is shown in Fig. s1. Two syringe pumps delivered the working fluids to the spinneret through elastic silicone tubing. An alligator chip was used to connect the spinneret with the power supply. Aluminum foil used as fiber collector was placed vertically under the spinneret.

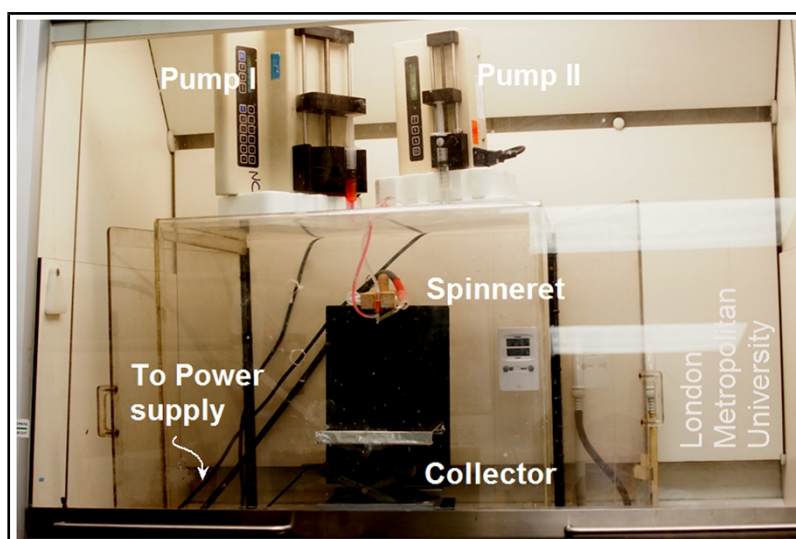
Before the side-by-side electrospinning, single fluid electrospinning was conducted to prepare monolithic nanofibers from each of the two fluids used in the side-by-side spinneret, to establish conditions under which each fluid was independently capable of producing good quality nanofibers. Under optimized electrospinning conditions (needle capillary of internal diameter 0.3mm, applied voltage of 12 kV, a fixed collection distance of 15 cm and a flow rate of 1.0 mL/h), the resultant nanofibers of PVP and EL 100 have an average diameter of  $0.72 \pm 0.17 \mu\text{m}$  (Fig. s2a) and  $0.83 \pm 0.12 \mu\text{m}$  (Fig. s2b), respectively.

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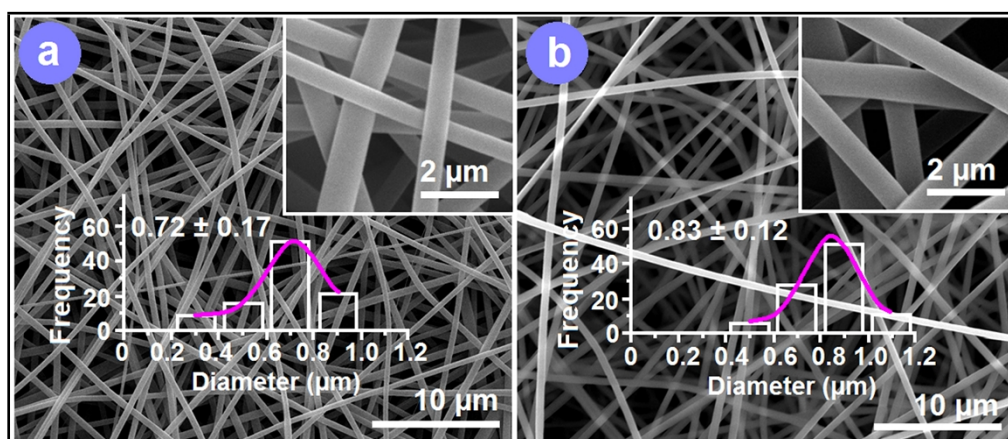
X-ray diffraction (XRD) analyses were performed using a D/Max-BR instrument (RigaKu, Tokyo, Japan). The diffractometer was supplied with Cu  $K\alpha$  radiation, and patterns were collected over the  $2\theta$  range  $5^\circ$ - $60^\circ$  at 40 mV and 30 mA. The XRD patterns of the raw materials and the composite fibers are shown in Fig. s4. From Fig. s4a, it is clear that the raw polymer matrices of PVP and EL100 are amorphous, since their diffraction patterns are diffuse with one or two diffraction halos. In contrast, the raw dyes of ANS-NH<sub>4</sub> and

rhodamine b are crystalline materials, as verified by the many distinct reflections in their patterns. However, in the patterns of the monolithic nanofibers and their Janus products ( $\theta=60^\circ$ , Fig. s4b), no sharp peaks of ANS-NH<sub>4</sub> or rhodamine b appeared, suggesting that they were completely transformed into an amorphous physical form in the fibers. Thus the side-by-side electrospinning developed here can be a useful tool for generating structural nanocomposites, with suitable selection of polymer matrix.

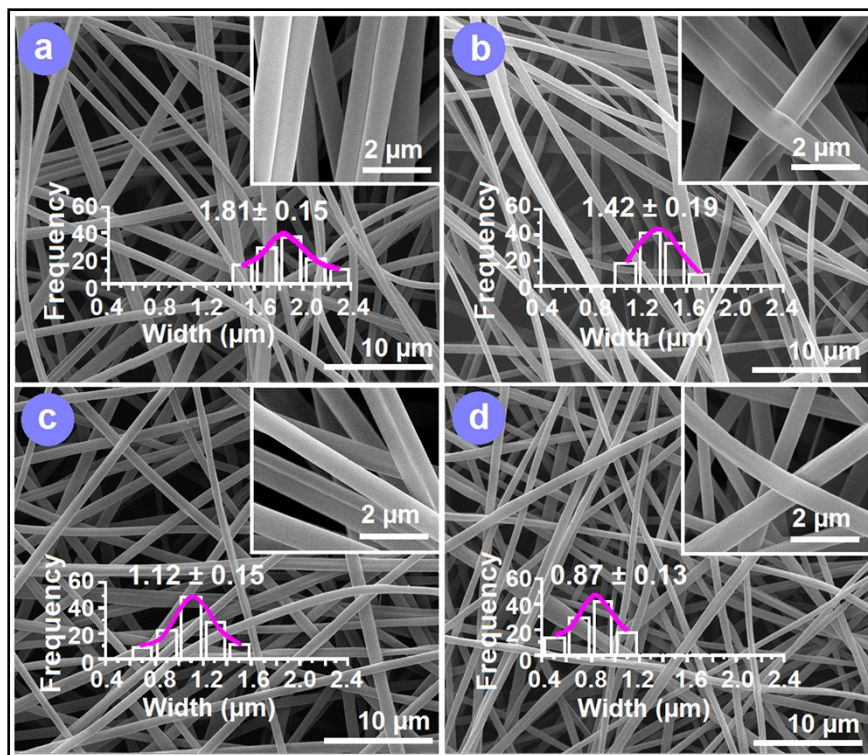
## Figures



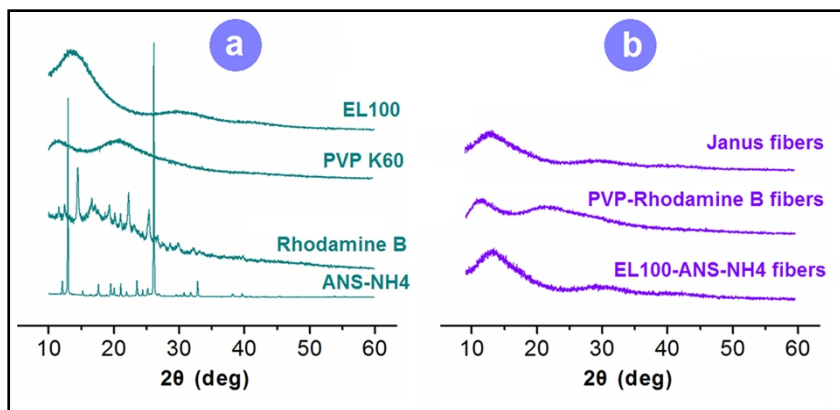
**Fig. s1** The arrangement of the apparatus for side-by-side electrospinning



**Fig. s2** FESEM images of monolithic nanofibers fabricated by single fluid electrospinning of each of the two fluids used to produce Janus nanofibers: (a) nanofibers consisting of PVP and rhodamine b; (b) nanofibers consisting of EL100 and ANS-NH<sub>4</sub>.



**Fig. s3** FESEM images of Janus nanofibers prepared using spinnerets with different port angles: (a) 40°; (b) 50°; (c) 60°; (d) 70°.



**Fig. s4** XRD patterns of the raw materials (a) and the composite nanofibers (b).