Electronic Supplementary Information

High-Quality Janus Nanofibers Prepared Using Three-fluid Fluid Electrospinning

Deng-Guang Yu,[a,*] Jiao-Jiao Li,[a] Man Zhang,[a] and Gareth R. Williams[b,*]

[a] School of Materials Science & Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China.
[b] UCL School of Pharmacy, University College London, 29-39 Brunswick Square, London WC1N 1AX, UK.

* Corresponding authors. Email: ydg017@usst.edu.cn (DGY); g.williams@ucl.ac.uk (GRW). Tel: +86 215 527 0632 (DGY); +44 (0)207 753 5868 (GRW).

Materials and Experimental Methods

Materials

Polyvinylpyrrolidone K60 (PVP K60, M_w=360,000) was purchased from Sigma-Aldrich Ltd. (Shanghai, China). Shellac (batch number 20151214001; 97% purity, wax free) was supplied by the ShengHui Agricultural Science and Technology Co., Ltd. (Yunnan, China). Anhydrous ethanol was provided by the Shanghai Shiyi Chemical Co. Ltd. (Shanghai, China).

Experimental

All three spinnerets employed in this work (parallel, acentric and structured) were homemade using standard stainless steel (GB24511 in China) capillaries: 26G with an outer diameter (D_o) of 0.46 mm and an inner diameter (D_i) of 0.24 mm; 20G with D_o of 0.9 mm and D_i of 0.6 mm; and, 14G with D_o of 2.1 mm and D_i of 1.6 mm. Three syringe pumps (two KDS 100 and one KDS 200, Cole-Parmer, Vernon Hills, IL, USA) were used to drive the working fluids. A ZGF60kV/2mA power supply (Shanghai Sute Electrical Co. Ltd., Shanghai, China) was employed to provide an electrical field. Grounded collectors were prepared *in situ* and simply comprised a flat piece of cardboard wrapped with aluminum foil. All electrospinning processes were conducted under ambient conditions (24 ± 5 °C, and relative humidity of 52 ± 7 %). Other parameters are listed in Table S1. The electrospinning processes were recorded using a digital camera (PowerShot A640, Canon, Tokyo, Japan).

The morphologies of the products were assessed using a Quanta FEG450 scanning electron microscope (SEM; FEI Corporation, Eindhoven, Netherlands).

Prior to SEM experiments, samples were subjected to platinum sputter-coating in a nitrogen atmosphere to confer them with electrical conductivity. Detailed structural characteristics were investigated using a H-800 transmission electron microscope (TEM; Hitachi, Tokyo, Japan). TEM samples were prepared by placing a lacey carbon-coated copper grid on the collector during electrospinning.

Table S1. Experimental parameters

Spinneret	Working fluid [a]	Flow rate (mL/h)	Appl. Vol. (kV)	Collected Dis. (cm)
Parallel spinneret	Side I - PVP solution	1.0	12	15
	Side II - Shellac solution	1.0		
Acentric spinneret	Side I - PVP solution	1.0	12	15
	Side II - Shellac solution	1.0		
Structured spinneret	Shell - Pure ethanol	0.5	12	15
	Core side I - PVP solution	1.0		
	Core side II - Shellac solution	1.0		

[a] The PVP and shellac solutions consisted of 8.0 g PVP K60 and 80.0 g shellac in 100 mL anhydrous ethanol, respectively.

Additional Results

When the shellac concentration was reduced to an un-spinnable level of 30% (w/v), the separation of the PVP and shellac working fluids occurred much earlier than was observed with an 80% w/v shellac solution (see main manuscript). The two fluids can be seen to become detached at the stage of Taylor cone formation with the parallel spinneret I (Figure S1). The PVP and shellac products appear to be completely distinct (Figure S2).

Figure S1. Preparation of Janus nanofibers with 8% w/v PVP and 30% w/v shellac solutions, using the parallel spinneret I. The two fluids can be seen to separate at the point of exiting the spinneret, with each having its own Taylor cone.

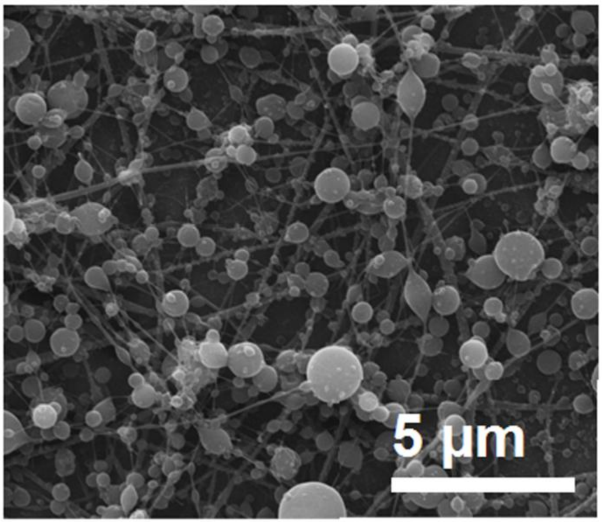

Figure S2. Preparation of nanofibers with 8% w/v PVP and 30% w/v shellac solutions using the parallel spinneret I. The products generated are observed to be a hybrid of PVP K60 nanofibers and shellac microparticles.

Using shellac concentrations of 30% (w/v), the separation of the PVP and shellac working fluids was not observed to occur at the Taylor cone stage with the acentric spinneret II (Figure S3). However, the products are still observed to have very irregular morphologies (Figure S4). Janus structures are seen for some fibers, but not for all (Figure S5).

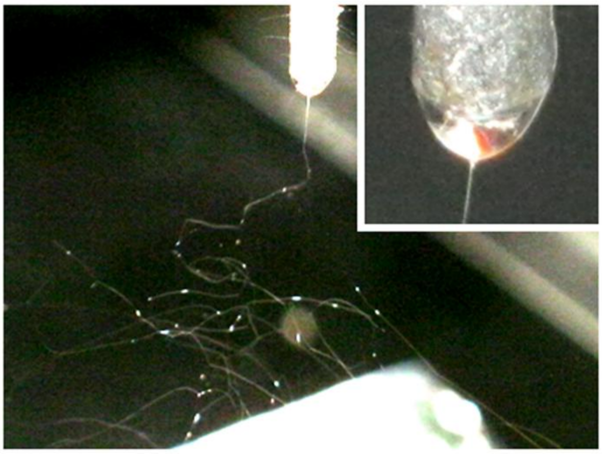

Figure S3. Preparation of nanofibers with 8% w/v PVP and 30% w/v shellac solutions using the acentric spinneret II. A stable Janus Taylor cone was observed, followed by bending and whipping.

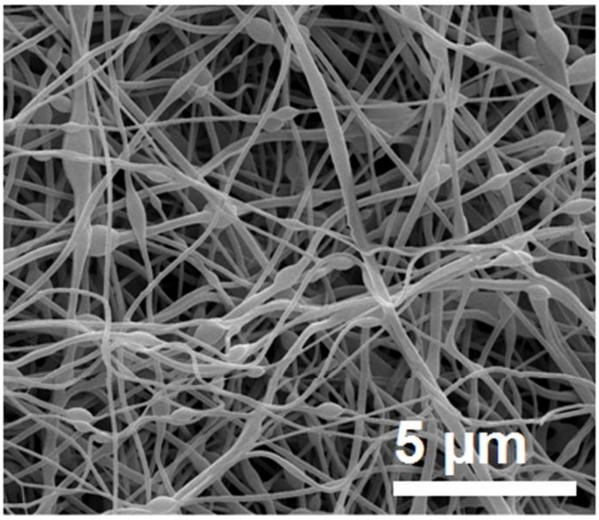

Figure S4. Nanofibers prepared with 8% w/v PVP and 30% w/v shellac solutions using the acentric spinneret II. The products are observed to be a combination of fibers and particle-fiber structures consisting of shellac and PVP K60, with some separation of the two sides.

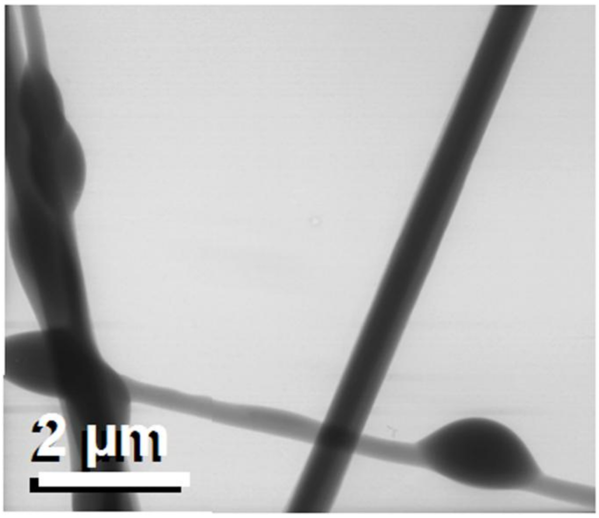

Figure S5. A TEM image of the products prepared from 8% w/v PVP and 30% w/v shellac solutions using the acentric spinneret II. The products generated are a combination of Janus fibers and particle-fiber structures consisting of shellac and PVP K60.

The structured spinneret (Figure S6) allows these problems to be overcome, as discussed in the main manuscript. This new spinneret can also be exploited to prepare other types of nanostructures (including core-shell, Janus, and core-shell with Janus core structures) through varying the fluids and their flow rates.

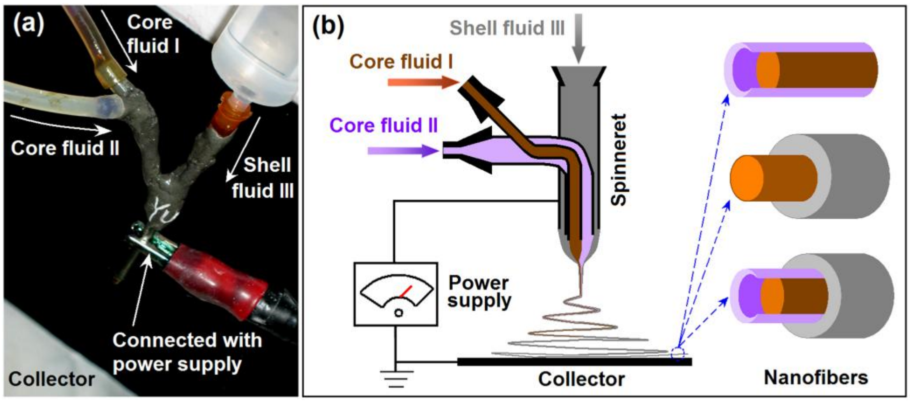

Figure S6. (a) A digital photo of the connection of the structured spinneret and its connections with the power supply and syringe pumps; (b) The exploitation of the structured spinneret for the fabrication of different kinds of nanostructures, including core-shell, Janus and core-shell with Janus core structures.