Electronic Supplementary Information (ESI)

Facile control of intra-fiber porosity and inter-fiber voids in electrospun fibers for selective adsorption†

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Experimental details

Materials and electrospinning solution

The starting materials include two kinds of polystyrene (PS) with molecular weights of M_w=350 000 g mol^{-1} (Aldrich) and M_w=208 000 g mol^{-1} (Wako), tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) (Shanghai Chemical Reagents Co., Ltd, China). Two kinds of oils such as motor oil (Shanghai RuiBei SINOPEC Co., Ltd., China) and sunflower seed oil (Standard foods China Co., Ltd., China) are used for adsorption in this study. The iron acetylacetonate used as a traceable element was purchased from Aladdin Chemistry Co. Ltd., China. 20 wt% PS (M_w=350 000 g mol^{-1}) and 30 wt% PS (M_w=208 000 g mol^{-1}) dissolved in the mixtures of THF and DMF with a weight ratio of 1/4 were prepared. The polyurethane (PU) resign was kindly obtained from Suzhou Baoze Polymer Co., Ltd., China, which was also diluted to be a concentration of 50 wt% by adding a 20 g DMF to the 20 g initial solution.

Preparation of fibrous mats

The electrospinning setup used in this work was produced by Shanghai Oriental Flying Nanotechnology Co., Ltd., China. By this equipment, multi-nozzles electrospinning with different polymer solutions can be achieved as shown in Fig. S3, which was placed in a chamber connected with a dehumidifier used for the controlling of relative humidity (RH). In electrospinning, the multi-nozzles connected with a syringe pump were fixed on a support that could be moved with a speed of 10 m/min along the slipway paralleled to the rotating roller with a linear velocity of 30 m/min. All the fibrous mats were prepared at a solution feed rate of 4 mL/h and with a

constant work distance of 15 cm under the applied voltage of 20 kV. All the experiments were carried out at a temperature of 24±1 ^{o}C.

Characterization

The morphology of as-prepared fibrous mats was examined by a field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi Ltd., Japan). The diameters of fibers were measured using an image analyzer (Adobe Photoshop CS2 9.0). The specific surface area, pore size distribution of the fibrous mats were characterized by nitrogen adsorption using a surface area and porosity analyzer (Micromeritics, ASAP 2020). The specific surface area (SSA) of fibers was obtained from the nitrogen adsorption data in the relative pressure range from 0.03 to 0.35 by using the Brunauer-Emmett-Teller (BET) method. The fine structures of as-spun fibers were also characterized by synchrotron radiation small-angle X-ray scattering (SAXS) at beamline BL16B1 of Shanghai Synchrotron Radiation Facility (SSRF).

The water contact angles (WCAs) of the fibrous mats were measured and recorded immediately after placing a 5 mg water droplet on the sample using a contact angle analyzer (SL200, USA Kino Industry Ltd.). Average WCAs were obtained by measuring the same sample at least five different positions.

Oil sorption evaluation of the as-prepared fibers was conducted according to our previous study,[1] following the equation:

$$Q = \frac{m_0 - m_s}{m_s} \quad (1)$$

where Q is the oil sorption capacity (g/g), m_0 is the total mass of wet sorbent after drained, and m_s is the initial mass of sorbent (g). The wet sorbent was taken out using

a nipper, drained for 1 min and then weighed. For each sample, the measurement was repeated three times independently, and the average value was calculated.

The single fiber with different porous structures after an oil (with an addition of 0.5 wt% iron acetylacetonate) sorption was characterized by the scanning transmission X-ray microscopy (STXM) BL08U1A at SSRF. The absorption contrast images of the single fiber taken from different samples at the iron absorption and pre-absorption edges energy (708.7 eV and 704 eV) was obtained. The distribution of iron element within as-prepared single fiber was calculated by using the software of Dual Energy Element Distribution.[2]

The tensile properties of as-prepared fibrous mats were tested on a tensile test (LLY-06E, Laizhou Electron Instrument Co., China) with a cross-head speed of 10 mm/min at constant temperature of 24 ^{o}C and humidity of 40%. All samples (10 mm×5 mm) were prepared from the large fibrous mats. The thickness of samples was evaluated by an YG-141N fabric thickness gauge (Nantong Hongda Experiment Instruments Co., Ltd., China) for five times independently, and the average value was obtained. The tensile stress and strain of these fibrous mats were calculated:[3]

$$tensile \quad stress = \frac{load}{area \quad of \quad cross-section} \tag{2}$$

$$strain = \frac{elongation}{initial \quad length} \times 100\% \tag{3}$$

Five specimens of each sample were tested for tensile behavior.

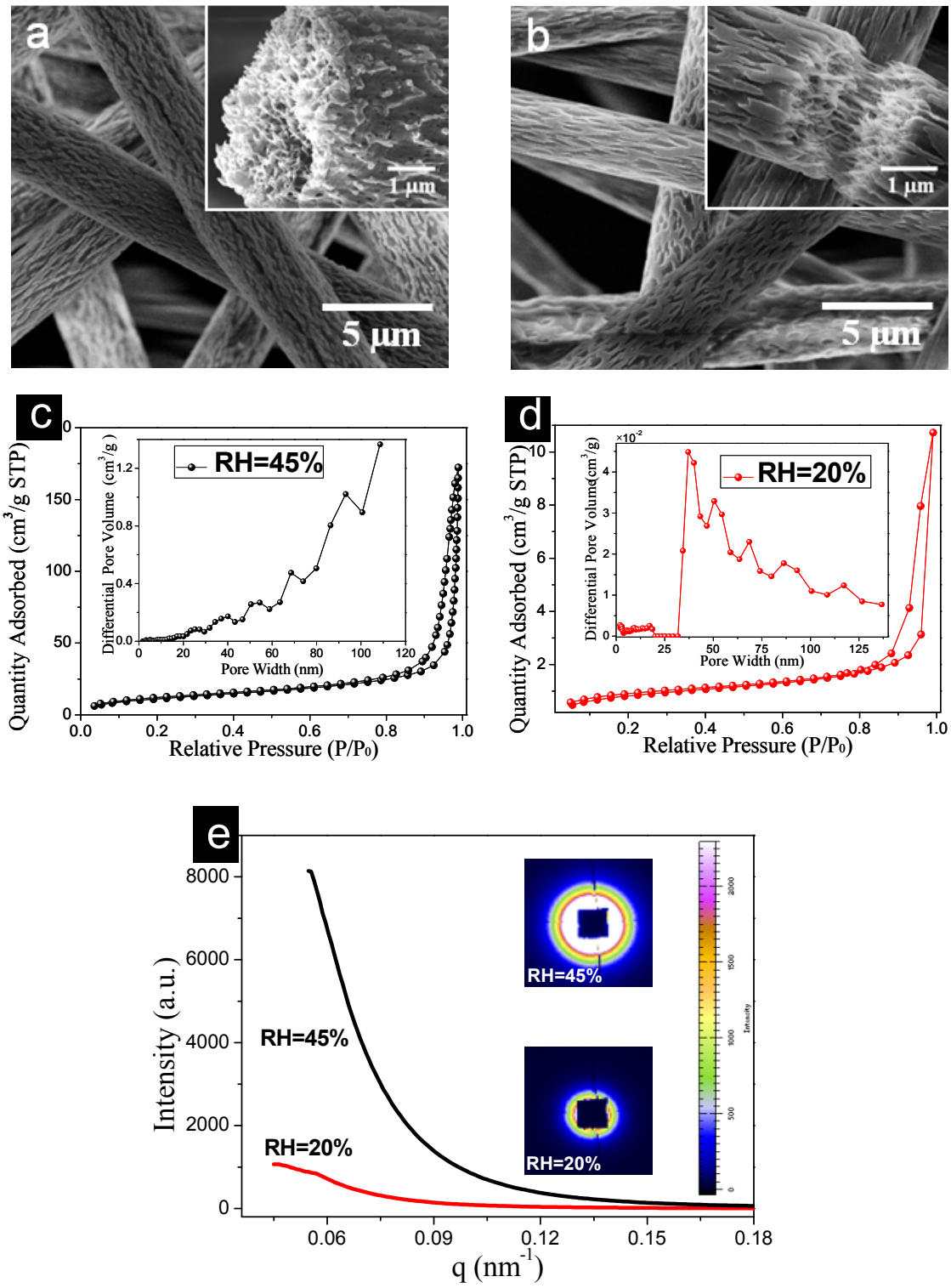


Figure S1. FE-SEM images of PS (M_w=208 000 g mol^{-1}) fibrous mats formed at a RH of (a) 45% and (b) 20%. Nitrogen adsorption-desorption isotherms and differential pore volume vs. pore width of as-prepared fibers formed at a RH of (c) 45% and (d) 20%. (e) SAXS 2D scattering patterns and SAXS curves of as-prepared fibers formed at different RH. (Fit2D software was used to analyze the 2D SAXS data.)

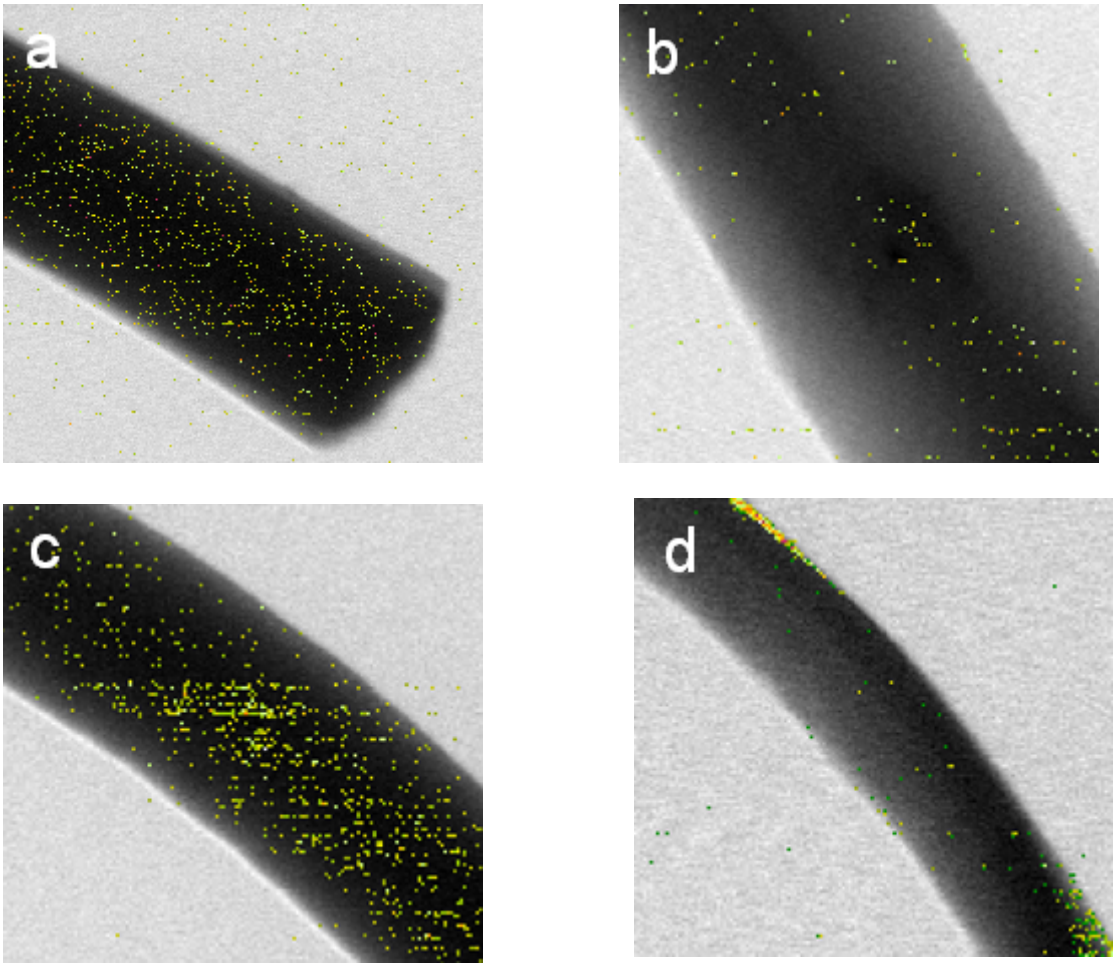


Figure S2. Iron element distribution of a single fiber formed at the RH of (a) 45% and (b) 20%. Iron element distribution of the single fiber formed at the RH of (c) 45% and (d) 20% after a washing using deionized water containing detergent to remove the sorbed oil.

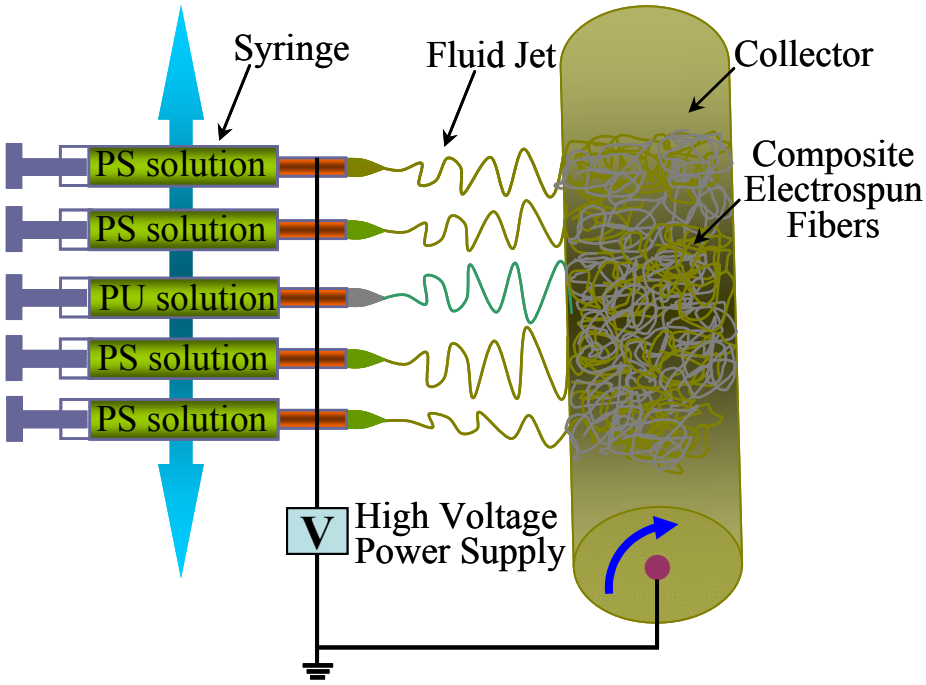
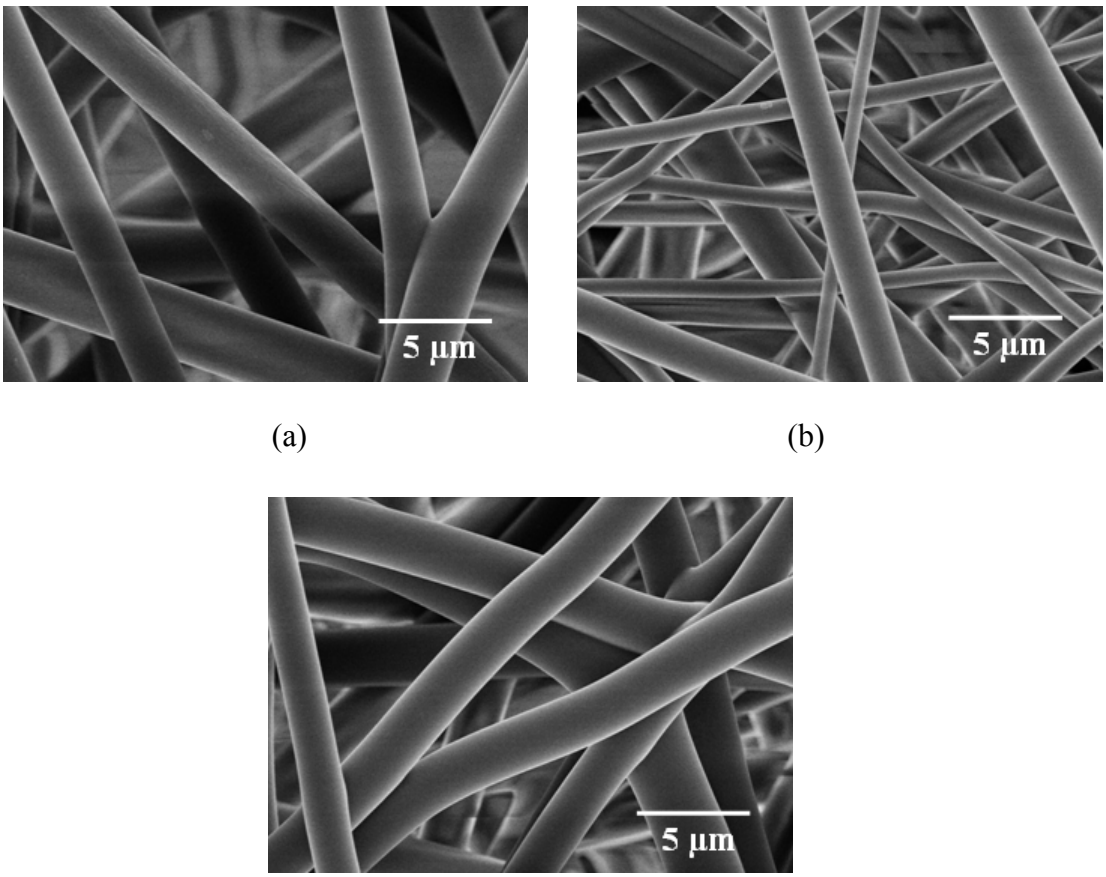


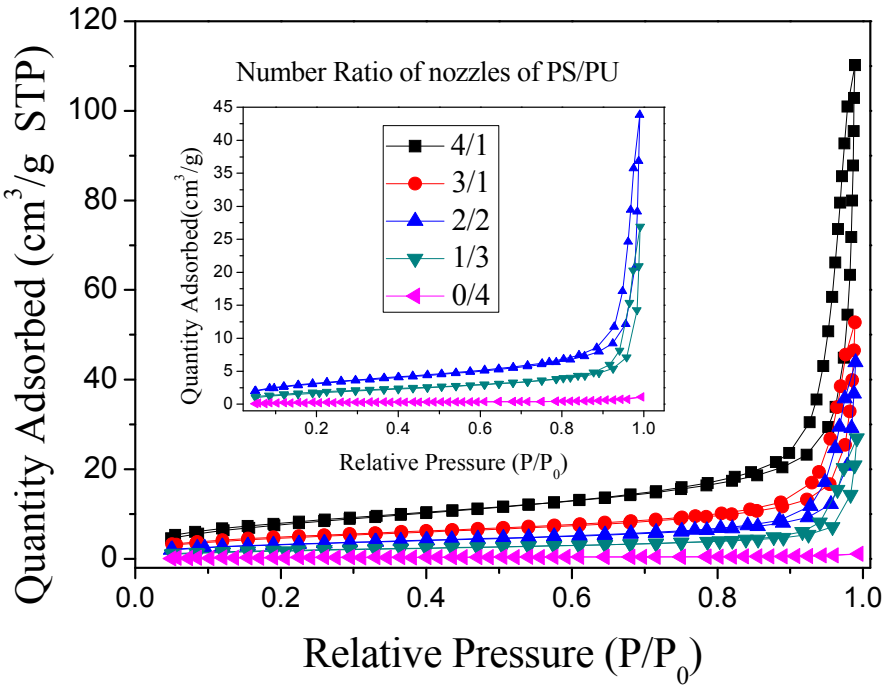
Figure S3. A schematic diagram to show the multi-nozzles electrospinning used in this study.



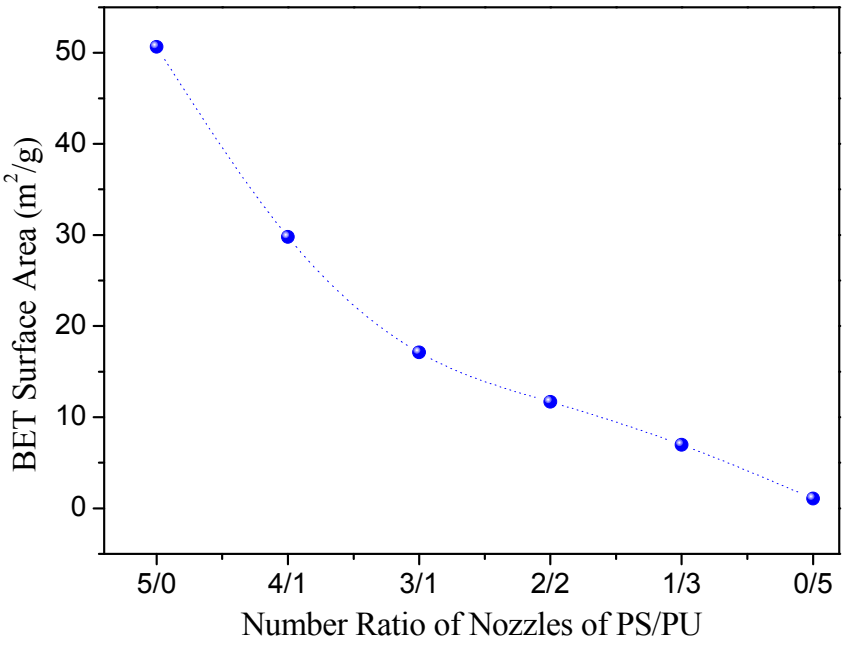
(a) (b)

(c)

Figure S4. FE-SEM images of as-prepared fibrous mats formed with various PS/PU nozzle ratios: (a) 2/2; (b) 1/3; (c) 0/4.



(a)



(b)

Figure S5. (a) Nitrogen adsorption-desorption isotherms and (b) SSA of as-prepared fibrous mats formed with various PS/PU nozzle ratios.

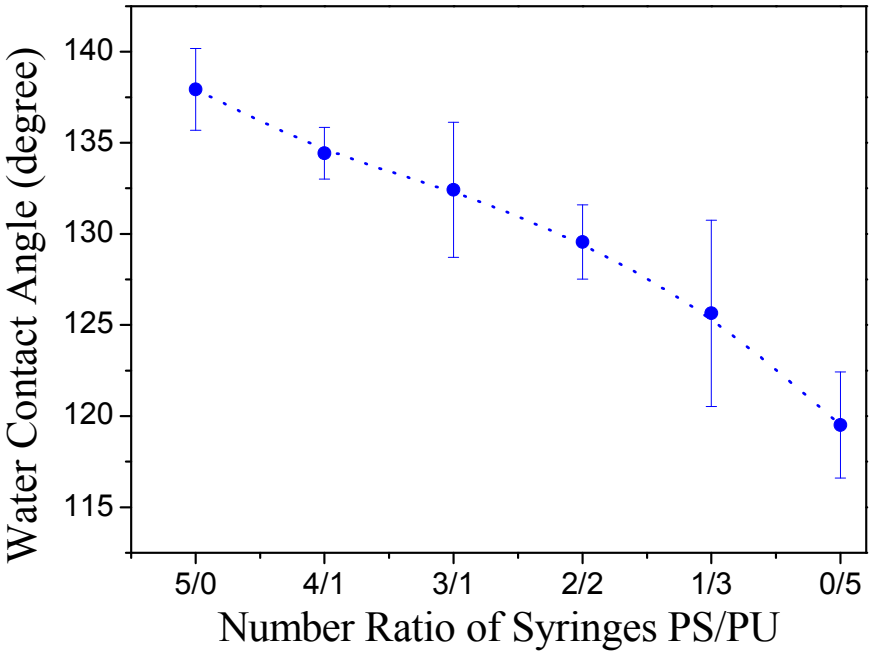


Figure S6. Water contact angles of as-prepared fibrous mats formed with various PS/PU nozzle ratios.

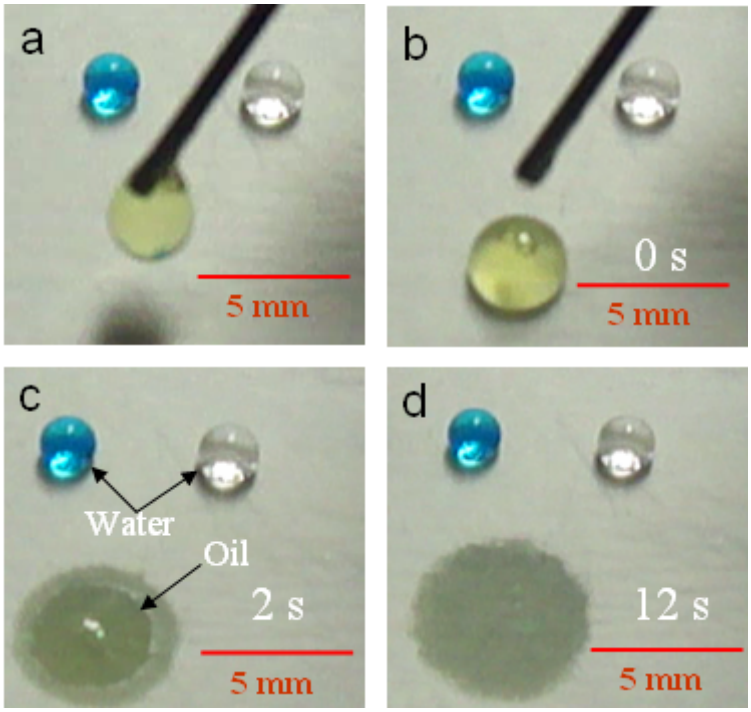


Figure S7. Hydrophobicity-oleophilicity of as-spun fibrous mat formed with a PS/PU nozzle ratio of 4/1.

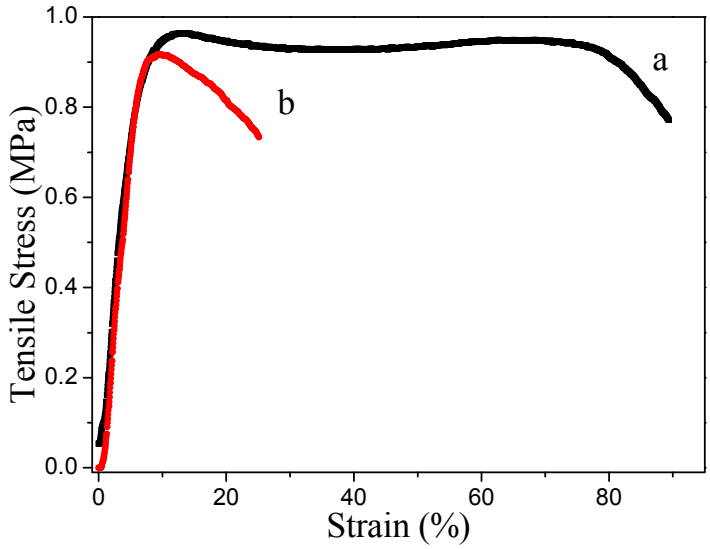


Figure S8. Typical tensile-strain curves of various PS fibrous mats with an addition of PU fibers formed from a 50 wt% PU resign.

Table S1. Surface characterization of as-prepared fibers.

Samples	SSA[a] (m^2/g)	TPV[b] (cm^3/g)	APW[c] (nm)
A	50.63	0.427	30.49
B	4.09	0.007	9.34
C	40.24	0.240	22.95
D	3.15	0.016	21.92
E	36.53	0.172	19.85
F	32.45	0.142	18.70

[a] Specific surface area (SSA) was calculated by the BET method. [b] TPV indicates total pore volume, which was calculated by the BJH method from the desorption branch of nitrogen physisorption isotherm. [c] APW indicates BJH desorption average pore width (4V/A). Samples A to F are the fibers shown in Fig. 1a, Fig. 1b, Fig. S1a, Fig. S1b, Fig. 4a and Fig. 4b, respectively.

Table S2. Tensile properties of fibrous mats with various PS/PU nozzle ratios. (PU was the initial solution.)

Samples	Tensile strength (MPa)	Elongation at break (%)	Yield stress (MPa)
Pure PS	0.26±0.02	4.99±1.40	0.23±0.02
4PS/1PU	0.84±0.09	223.37±7.52	0.63±0.07
3PS/1PU	1.21±0.09	277.13±14.38	0.44±0.03
2PS/2PU	1.32±0.04	89.82±34.56	0.88±0.15
1PS/3PU	1.74±0.05	195.27±124.21	1.16±0.05
Pure PU	1.76±0.07	108.65±6.20	1.17±0.07

Table S3. Tensile properties of various PS fibrous mats with an addition of PU fibers formed from a 50 wt% PU resign.

Samples	Tensile strength (MPa)	Elongation at break (%)	Yield stress (MPa)
A	0.91±0.04	43.79±45.39	0.78±0.09
B	0.89±0.10	11.31±1.20	0.77±0.08

References

1. J. Y. Lin, B. Ding, J. M. Yang, J. Y. Yu and G. Sun, *Nanoscale*, 2012, **4**, 176-182.

2. X. Zhang, Z. Xu, R. Tai, X. Zhen, Y. Wang, Z. Guo, R. Yan, R. Chang, B. Wang and M. Li, *J. Synchrot. Radiat.*, 2010, **17**, 804-809.

3. W. Morton and J. Hearle, *Physical properties of textile fibres*, Technomic Pub Co, Manchester, 1993.