Electronic Supplementary Information (ESI)

Tuning hierarchical aligned structure for high-strength PMIA/MWCNT hybrid nanofibers

Xiaoru Wang,[‡ab] Yang Si,[‡ac] Xianfeng Wang,[ac] Jianmao Yang,[d] Bin Ding,*[ac] Lei Chen,[a] Zuming Hu[a] and Jianyong Yu*[c]

[a] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China; E-mail: binding@dhu.edu.cn

[b] College of Textiles, Donghua University, Shanghai 201620, China

[c] Nanomaterials Research Center, Modern Textile Institute, Donghua University, Shanghai 200051, China; E-mail: yujy@dhu.edu.cn

[d] Research Center for Analysis and Measurement, Donghua University, Shanghai 201620, China

Supplementary Experimental Section

Materials

PMIA (Teijinconex®) was purchased from TEIJIN Co., Ltd., Japan. Carboxylic multi-walled carbon nanotube (MWCNT) (diameter of 10-20 nm and length of 10-30 μm) was purchased from Chengdu Organic Chemicals Co., Ltd. Lithium chloride (LiCl) and dimethylacetamide (DMAc) were were purchased from Shanghai Chemical Reagents Co., Ltd, China. All chemicals were of analytical grade and were used as received without further purification.

Preparation of precursor solutions

The LiCl/DMAc ionic liquid was used as the solvent for PMIA. The concentrations of PMIA and LiCl in the precursor solution were 14 and 2 wt%, respectively, and the concentrations of MWCNTs were 0, 0.5, 1, and 1.5 wt %, respectively. The detailed compositions are listed in Table S1. The setup for preparation of solution with MWCNT contents of 1.5 wt % is as follows. Firstly, 0.2 g of LiCl and 0.15 g of MWCNTs were added into 8.25 g of DMAc with ultrasonic treatment for 2 h to obtain homogeneous dispersion. Following, 1.4 g of PMIA was dried at 120 ^{o}C for 2 h in the vacuum oven, and added into the above solution with string at 80 ^{o}C for 12 h to be completely dissolved. After cooling to room temperature, the solution was treated using ultrasonic for another 3 h to obtain black electrospinning solution.

Fabrication of the CNTs reinforced PMIA aligned nanofibers

The electrospinning process was performed by using the DXES-1 spinning equipment (Shanghai Oriental Flying Nanotechnology Co., Ltd., China). Typically, the solution was loaded into a 10 mL syringe capped with a 6-G needle with a controllable feed rate of 0.2 mL/h. A high voltage of 25 kV was applied to the needle tip, resulting in the generation of a continuous jetting stream. The resultant CA nanofibrous membranes were deposited on the aluminum foil-covered grounded metallic rotating roller (rotating rate was 200 rpm) at a 15 cm tip-to-collector distance. The relevant temperature was 25±2 ^{o}C, and the humidity was adjusted to 25±2, 40±2, and 55±2% by using a CH948B humidity controller (WGI Inc, USA).

Raman spectra analysis

Raman spectrometer (inVia-Reflex, Renishaw, Co., UK, 785 nm diode laser) with a resolution of 2 cm^{-1} was used to determine the secondary structure of the electrospun fibers. Two-dimensional (2D) and three-dimensional (3D) Raman microscopic imaging (785 nm exciting laser) were used to characterize the dispersion of CNTs in the membranes. A 40 μm square mat was first scanned to obtain the one-dimensional (1D) spectra, which was then used to generate the 2D and 3D Raman microscopic imaging by choosing the characteristic peak of tangential mode (G band) of MWCNT ranging from 1500 to 1650 cm^{-1}.

Techniques of characterization

The viscosity of the precursor solutions were measured by a NDJ-79 rotary viscosimeter (Shanghai Changji Instrument co. Ltd., China) with rotary speed of 750 rpm at 25 ^{o}C. The conductivity was measured by a FE30 conductivity meter (Mettler-Toledo Instrument co. Ltd., Switzerland), 0.01 M KCl aqueous solution was used as calibration solution, and 20 g of samples was used for each test. The morphology of nanofibers was examined by field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi Ltd., Japan), all samples were coated with carbon for 5 min before analysis. Fifty fibers were randomly used to determine the average fiber diameters. Transmission electron microscopy (TEM) images were measured by a JEM-2100F, JEOL Ltd., Japan. The mechanical properties of the membranes were tested on a tensile tester (XQ-1C, Shanghai New Fiber Instrument Co., Ltd., China) with a constant stretching rate of 20 mm/min. The thickness and size of the membranes for test was 2±0.1 μm and 5×20 mm, respectively.

Supplementary Discussion

The formation mechanism of nanonets

The formation of 2D nanonets was attributed to the phase separation of charged droplets generated during electrospinning. In general, the instability of the Taylor cone induced by the high electric field results in the formation of the electrospray droplets. During the flight of charged droplets from the capillary tip to the collector, the microsized droplet was distorted and expanded into a thin film due to the comprehensive effects of the forces (columbic repulsion, electrostatic force, air resistance, gravity, surface tension and viscoelastic force) acting on it [1-2]. Following the thin film undergoes fast phase separation with the solvent rich domains to transform into pores, finally yielding the Steiner-tree nanonets structure according to the minimal energy principle (Fig. S2) [3].

Reference

[1] S. B. Yang, X. F. Wang, B. Ding, J. Y. Yu, J. F. Qian and G. Sun, *Nanoscale*, 2011, **3**, 564-568.
[2] A. Greiner and J. H. Wendorff, *Angew. Chem. Int. Ed.*, 2007, **46**, 5670-5703.
[3] J. Hu, X. Wang, B. Ding, J. Lin, J. Yu and G. Sun, *Macromol. Rapid Commun.*, 2011, **32**, 1729-1734.

Supplementary Table and Figures

Table S1 Composition and property of different electrospinning solutions.

Sample	PMIA (wt%)	LiCl (wt%)	CNTs (wt%)	Viscosity (cps)	Conductivity (μs cm^{-1})
1	14	2	-	4500	2.46
2	14	2	0.5	4900	2.24
3	14	2	1	5700	2.28
4	14	2	1.5	6300	2.35

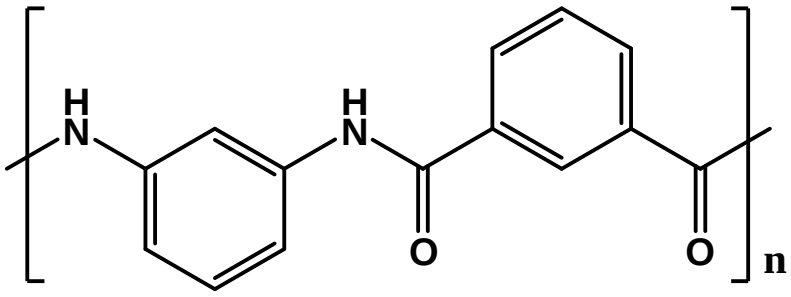

Fig. S1 Chemical structure of PMIA.

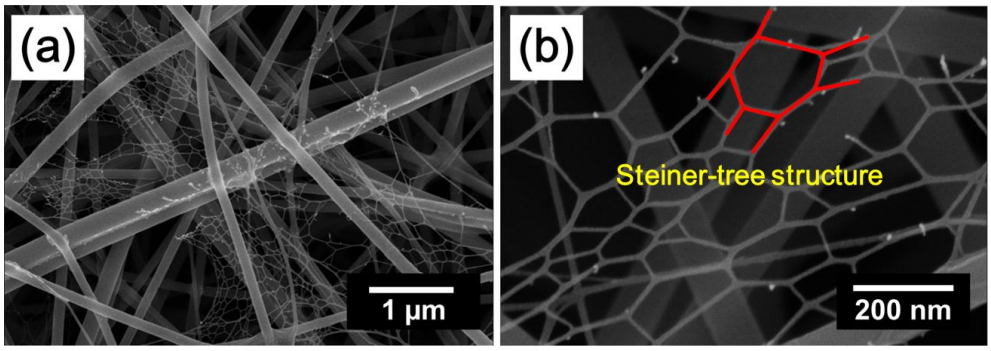

Fig. S2 (a) Low and (b) high magnification FE-SEM images of PMIA nanofibers showing the Steiner-tree structure.

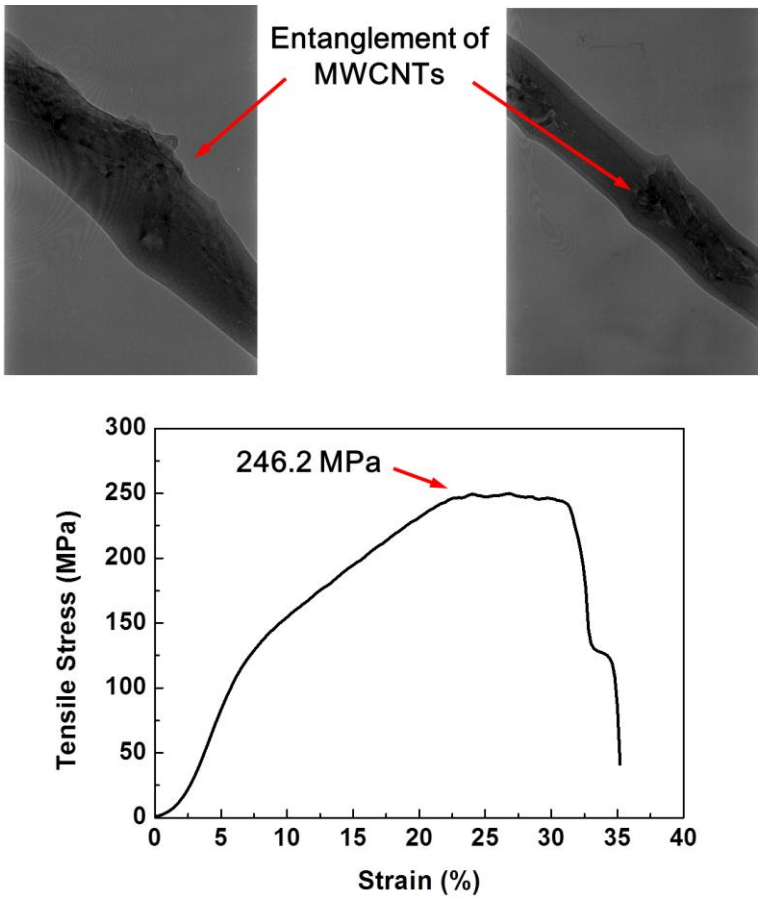

Fig. S3 TEM images and stress-strain curve of PMIA/MWCNT nanofibers with MWCNTs contents of 2 wt%.