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Supplemental materials for:

Unlocking the Response of Lignin Structure to Improved Carbon Fiber Production and Mechanical Strength

Ran Zhang[1†], Qing Du[1‡], Lei Wang[†,§], Ze Zheng[†], Li Guo[▽], Xiaoyu Zhang[†], Xiangliang Yang*[,‡], Hongbo Yu*[,†]

[†]Key Laboratory of Molecular Biophysics of MOE, College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, China

[‡]National Engineering Research Center for Nanomedicine, College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, China

[§]Hubei Provincial Key Laboratory of Green Materials for Light Industry, School of Materials and Chemical Engineering, Hubei University of Technology, Wuhan 430068, China

[▽]Key Laboratory of Hubei Province for Coal Conversion and New Carbon Materials, School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, China

*Corresponding author: College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, China. Tel.: +86 27 87792108; E-mail: yuhongbo@hust.edu.cn, yangxl@hust.edu.cn

[1]These authors contributed equally to this work.

Materials and methods

Materials

N,N-dimethylformamide (DMF, 99.9%) was obtained from Aladdin. Graphite (99% carbon basis) and Polyacrylonitrile (PAN, average Mw=150000) were

purchased from Macklin.

Preparation of soda lignin and kraft lignin

Soda lignin (named as L-1) and kraft lignin (named as L-2) were prepared through mild soda pulping and kraft pulping combined with sequential membrane separation and purification processes as shown in Fig. S1. 100 g Black liquor (Soda pulping, S% (contents of total solids) = 50%, L% (lignin content among total solids) = 30%) and 100 g Black liquor (Kraft pulping, S% (contents of total solid) = 58%, L% (lignin content among total solids) = 26%) were supported by Research Institute of Pulp and Paper Engineering in Hubei University of Technology. Then the two types of black liquor were separately purified by sequential membrane processes using Pall Minim II Tangetial Flow Filtration System.[1]

In the first step, the two types of black liquor were separately with the highest membrane cut-off, 100 kDa, which will remove the macromolecular compounds such as tiny fiber and resins. In the second stage, the resulting permeate stream from the first step (P_{100KDa}) was further fractionated using the 3 KDa cut-off membrane, which will remove the salt, alkali, polysaccharide and other small molecular substances. In the third stage, the retentates from 3 kDa membrane (R_{3KDa}) from black liquor (Soda pulping) was furthermore processed using two tabular membranes with nominal cut-offs of 20 and 10 kDa, whilst R_{3KDa} from black liquor (Kraft pulping) was processed using two tabular membranes with nominal cut-offs of 50 and 30 kDa. Finally, the lignins in fractions R_{10KDa} from black liquor (Soda pulping) and R_{30KDa} from black liquor (Kraft pulping) were separately isolated by acid precipitation, washing, dried, weighed and conserved for use. The two types of lignin were separately named as L-1 and L-2. The yields of L-1 and L-2 were 85% and 88%, separately.

The yield of obtained lignin was calculated as follows：

$$Lignin\ yield\ (\%) = \frac{all\ collected\ acid - insoluble\ lignins\ (g)}{100\ (g, processed\ black\ liquor) \times S\% \times L\%} \times 100\%$$

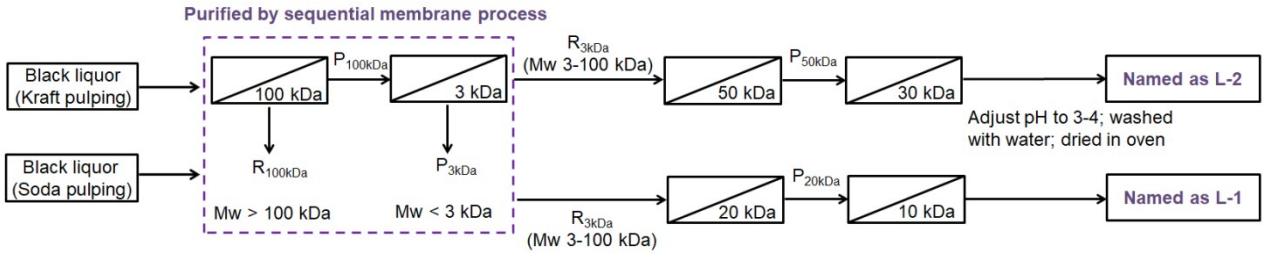


Fig. S1 The schematic representation of lignin preparation process.

Elecrospinning

Typically, PAN or PAN/lignin mixtures was dissolved in DMF overnight. The concentration of total polymer was maintained at 15% (wt%), and the weight ratio of PAN to L-1/L-2 was kept at 1/0.25 if it was not specified particularly. The resulting solution was mixed well and electrospun at an accelerating voltage of 15 kV. The membrane of as-spun fibers was collected on a grounded aluminum foil placed 15 cm below the spinneret. After the membrane with a certain thickness was obtained, it was peeled off from the foil using a tweezers and dried in a vacuum oven at 40ºC for 24 hr to remove residual DMF.

Thermostabilization and carbonization of as-spun fibers

Both thermostabilization and carbonization of as-spun lignin fibers were performed in a split tube furnace with a vacuum system (OTF-1200X, MTI Corporation, Richmond, CA). The conditions for thermostabilization were: heating at atmosphere from room temperature to 280℃ at a heating rate of 0.3℃/min. After holding for 1 h at 280℃, the furnace was automatically cooled down to room temperature. For carbonization, the thermostabilized fibers were put into the tube furnace, and the tube was then completely sealed. Before heating, the tube was purged with argon gas with vacuum pump purging until 1×10^{-2} torr for three times. The step was to ensure that no oxygen was left in the tube. The flow rate of argon was kept at 250 ccm (cm^3/min) during heating. The temperature was increased from room temperature to 1000℃ at a heating rate of 3℃/min.

Mechanical analysis of carbon fibers

The tensile stress and strain at break of the carbonized fiber mats were evaluated by uniaxial tensile testing using Lorentzen & Wettre testing machine. According to

ASTM C1557-03, a modified approach for test specimen preparation was adopted. Here, a fast-curing epoxy adhesive was used to adhere a fiber mat sample (40mm length×5mm width) to a paper mounting tab with gauge length of 20 mm. The tensile test started when the specimen was securely gripped and cut away both sides of the tab. The strain rate was 0.2 mm/min.

Young's modulus of all carbonized fibers was measured using Hysitron TI 950 Triboindenter. Before the measurement, carbon fibers were embedded in an epoxy resin (EpoFix embedding resin kit, Struers ApS, Denmark). The resin was polymerized in room temperature overnight. To get a smooth surface for nanoindentation, the resin was grinded and polished by a EcoMet 3 grinder/polisher (Buehler, Lake Bluff, IL) using 0.3 μm Alfa alumina powder spreading on sandpaper with different mesh in succession and until fibers can be clearly found on the epoxy resin surface under light microscope. Nanoindentation was carried out on transverse section of fiber and the indentation depth of the fibers was set at 40 nm. The Young' modulus was calculated by averaging ten repeated results.[2]

Lignin characterizations

The chemical composition analysis was according to methods established by the National Renewable Energy Laboratory (NREL).[3] The elemental analysis (CHNS-O) was conducted in an elemental analyzer (Vario Micro Cube, Elementar, Germany) using approximately 5 mg of lignin each time.

The molecular weight distributions of lignin was determined using a gel permeation chromatography (GPC) instrument (SHIMADZU, HPLC-20AT) equipped with differential refraction detector (SHIMADZU, RID-10A) and ultraviolet detector (SHIMADZU, SPD-20A) at 254 nm, calibrated with polystyrene (EasiVial PS-M, 4 ml) standards with molecular weight range of 162–400000 g/mol. Chromatographic column (Styragel HR4E, 7.8*300 mm, WATERS) and guard column (Styragel, 4.6*30 mm, WATERS) were connected in series and maintained at 50 °C. Dimethyformamide (DMF) with 0.1 mol/ L LiCl with a flow rate of 1.0 mL/min was used as the eluent.

Differential scanning calorimetry (DSC) was performed on soda lignin (L-1) and

kraft lignin (L-2) using Diamond DSC (PerkinElmer Instruments, Shanghai) with two heating cycles. Three milligram of lignin sample was placed in an aluminum pan. Under a nitrogen atmosphere, the sample was heated from room temperature to 250℃ at the heating rate of 20℃/min. After cooling down to 0℃ with a rate of 20℃/min, and the second cycle was repeated at the same heating/cooling condition. Tg was calculated from the second heating cycle of DSC analysis.

Two-Dimensional Heteronuclear Single-Quantum Correlation Nuclear Magnetic Resonance (2D HSQC NMR Analysis) was carried out referring to methods described by John Ralph.[4] In the case of the technical lignin, around 100 mg was dissolved in 0.75 mL of DMSO-d_6 by ultrasonic treatment for 30 min. NMR spectra were recorded at 25°C on a Agilent 600 MHz DD2 instrument equipped with a cryogenically cooled 3mm HCN auto triple resonance probe with inverse geometry with spectral widths of 5000 Hz (from 10 to 0 ppm) and 25,000 Hz (from 165 to 0 ppm) for the ^{1}H- and ^{13}C-dimensions. The number of collected complex points was 2048 for the ^{1}H dimension with a recycle delay of 1.75 s. The number of transients was 64, and 256 time increments were always recorded in the ^{13}C dimension. The $^{1}J_{CH}$ used was 140 Hz. The central solvent peak was used as an internal reference (δ_C 39.5; δ_H 2.50).

^{31}P NMR method has been applied in various substrates including coal, coal-derived products, and biomass lignins, involving phosphitylation of hydroxyl groups in a substrate using a ^{31}P reagent followed by quantitative ^{31}P NMR analysis.[5] In this study, the lignin samples were derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) and then analyzed by ^{31}P NMR following literature methods.[6] The phosphitylation reaction of lignin was as follows. A solvent mixture composed of pyridine and deuterated chloroform in a 1.6:1 v/v ratio was prepared. The solution was protected from moisture with molecular sieves (3A) and kept in a sealed container under nitrogen. The relaxation reagent solution and internal standard solution was then prepared by utilizing the above solvent mixture: chromium (III) acetylacetonate (Aldrich, Milwaukee, WI, 5.0 mg/mL) and cyclohexanol (Aldrich, 10.85 mg/mL) were served as relaxation reagent and internal standard, respectively. 30 mg of dry lignin was accurately weighed into a 1 mL volumetric flask. The sample

was then dissolved in 0.5 mL of the above solvent mixture. TMDP (0.1 mL) was then added, followed by the internal standard and the relaxation reagent solution (0.1 mL each). Finally, the solution was made up to the 1 mL mark with more solvent mixture. The volumetric flask was tightly closed and shaken to ensure thorough mixing. The reaction mixture is then transferred into a 5 mm NMR tube for ^{31}P NMR analysis. Quantitative ^{31}P NMR spectra were acquired for 150 scans with a 30^{o} pulse angle and a 25 s pulse delay based on the T1 experiments (for all internal standards used). The spectra were phased and calibrated using the signal of the reaction product of water with TMDP, which has been observed to give a sharp signal in pyridine/$CDCl_3$ at 132.2 ppm.

Morphology analysis of as-spun carbon fibers and carbonized fibers

The morphologies of as-spun fibers and carbon fibers were imaged using a FEI Helios Nanolab G3 FE-SEM (FEI Company, Hillsboro, OR). The samples were firstly coated with gold-palladium (10 nm thickness) using SCD2000 (KYKY, Beijing, China). The working distance was 10 mm, and the accelerating voltage applied was 5 kV. The average diameter of fibers was measured and calculated using Image J (National Institutes of Health (NIH), USA) based on more than 60 different fibers.

The elemental maps of the as-spun fibers were determined by an SEM system that was equipped with an energy-dispersive X-ray analysis spectroscopy detector (SEM-EDS, Nova NanoSEM 450).

The surface morphology of the as-spun fibers was studied by a transmission electron microscopy (TEM, Hitachi HT7700) at 100 kV.

Microstructure analysis of as-spun fibers and thermostabilized carbon fibers

An attenuated total reflectance (ATR) FTIR was employed to collect spectra data of as-spun fibers and thermostabilized fibers, and each spectrum is scanned 256 times with a resolution of 4 cm^{-1}.

Thermogravimetric analysis (TGA) of thermostabilized carbon fibers

TGA measurement was carried out using a Diamond TG/DTA instruments in a nitrogen gas environment (100 mL/min). Thermostabilized precursor fibers were placed in 90 μL alumina crucibles. Firstly, the crucible is heated from room

temperature to 110℃ and stay at 110℃ for 1 h to remove the water, and then go up to 1000℃ with the heating rate of 10 ℃/min.

Microstructure analysis of carbon fibers

The graphitic structure in carbon fibers was analyzed using x'pert3 powder instrument (PANalytical B.V., Netherlands). X-ray resource was generated at 40 mA current and 40 kV voltage with Cu Ka wavelength (λ) of 1.542 Å. The diffractograms of all samples were recorded in the 2θ range of 10^o-50^o. Scanning step size was set at 0.05^o, and the scanning rate was 10^o/min.

The distance between two crystalline lattices (d_{hkl}) was estimated using Bragg's law:

$$2d\sin\theta = n\lambda \qquad \text{Equation (1)}$$

Where d is the distance in nm; θ is the Bragg angle in degree; n is set as 1; λ is the X-ray wavelength (1.542 Å).

The crystalline size (L_{hkl}) was calculated using Scherrer equation:

$$L = \frac{K\lambda}{\beta\cos\theta} \qquad \text{Equation (2)}$$

Where L is the crystalline size, nm; K is shape factor, set as 0.89 in this calculation; λ is the X-ray wavelength (1.542 Å); β is the full width at half maximum (FWHM) in radian; θ is the Bragg angle in degree.

Carbon fiber mats were briefly put on a glass slide, and Raman spectra were taken using inVia reflex Confocal Microscope system with 532.16 nm laser, D 1 filter, 200 μm confocal pinhole, and 2 accumulations.

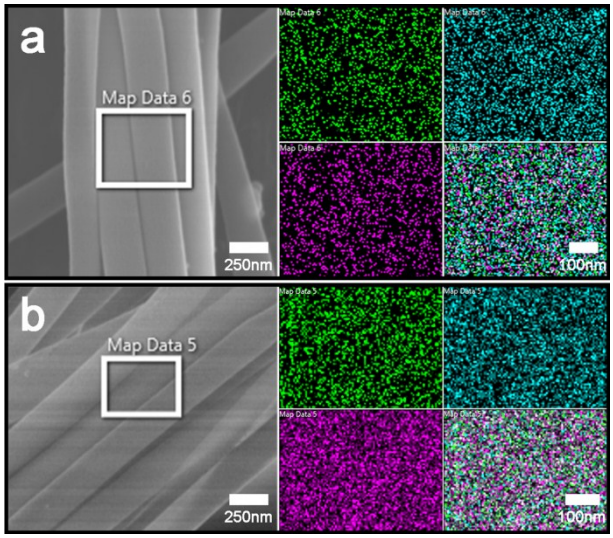


Fig. S2 SEM-EDS analysis of as-spun fibers PAN/L-1=1/0.25 and PAN/L-2=1/0.25: SEM image of PAN/L-1=1/0.25 (a) and PAN/L-2=1/0.25 (b), and corresponding EDX mapping images of N (green), O (blue), and S (purple) elements, and the overlaid images of the three elements.

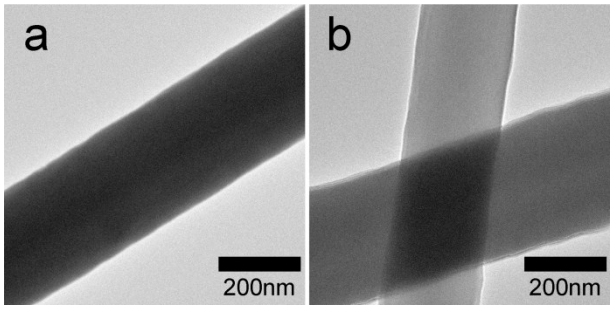
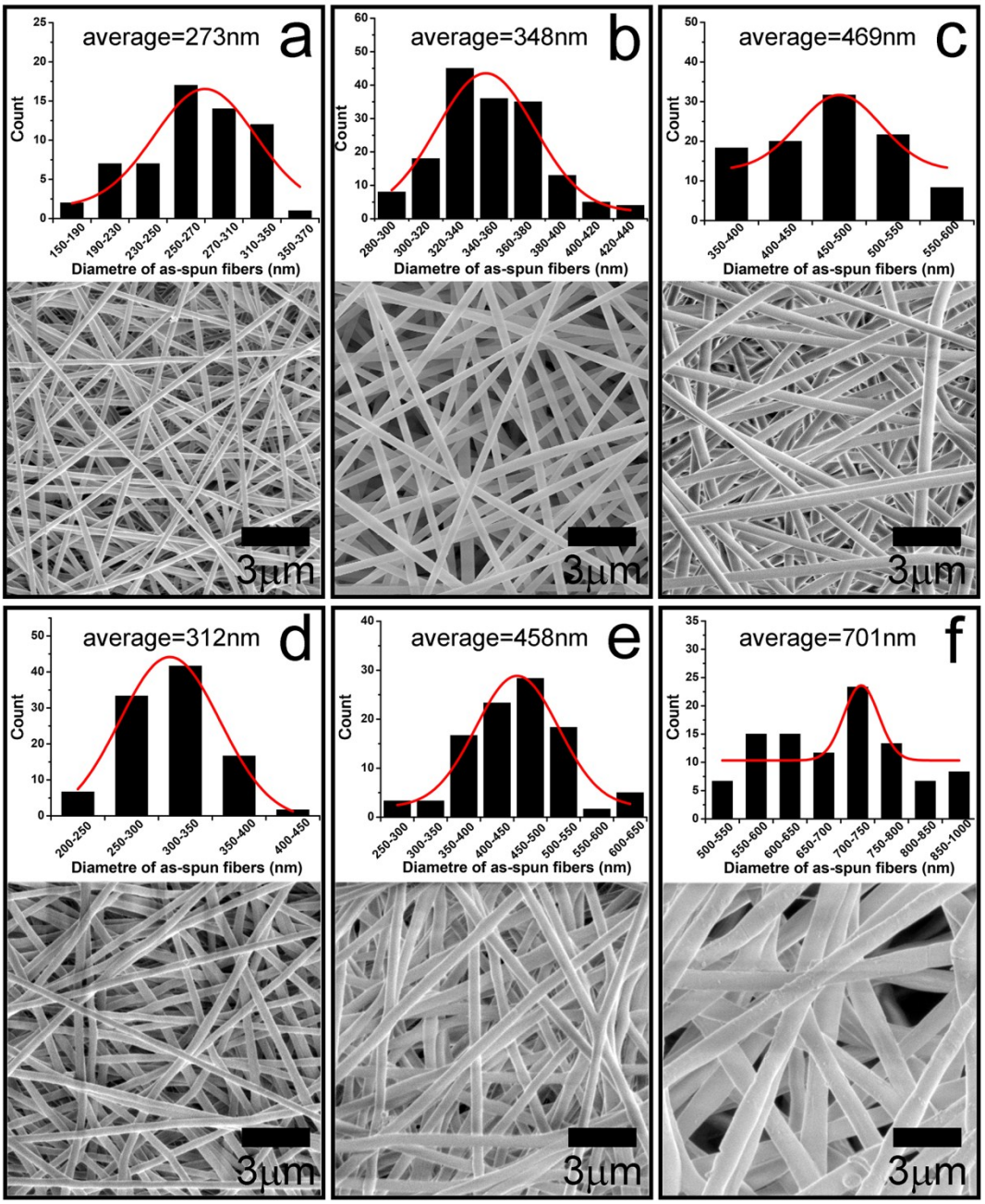


Fig. S3 TEM micrographs of as-spun fibers PAN/L-1=1/0.25 (a) and PAN/L-2=1/0.25 (b).



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218 **Fig. S4** SEM images of as-spun fibers from PAN/L-1 blend solutions (a-c) and PAN/L-2 blend

219 solutions (d-f) at weight ratio of 1/0.25, 1/0.5 and 1/0.75, separately.

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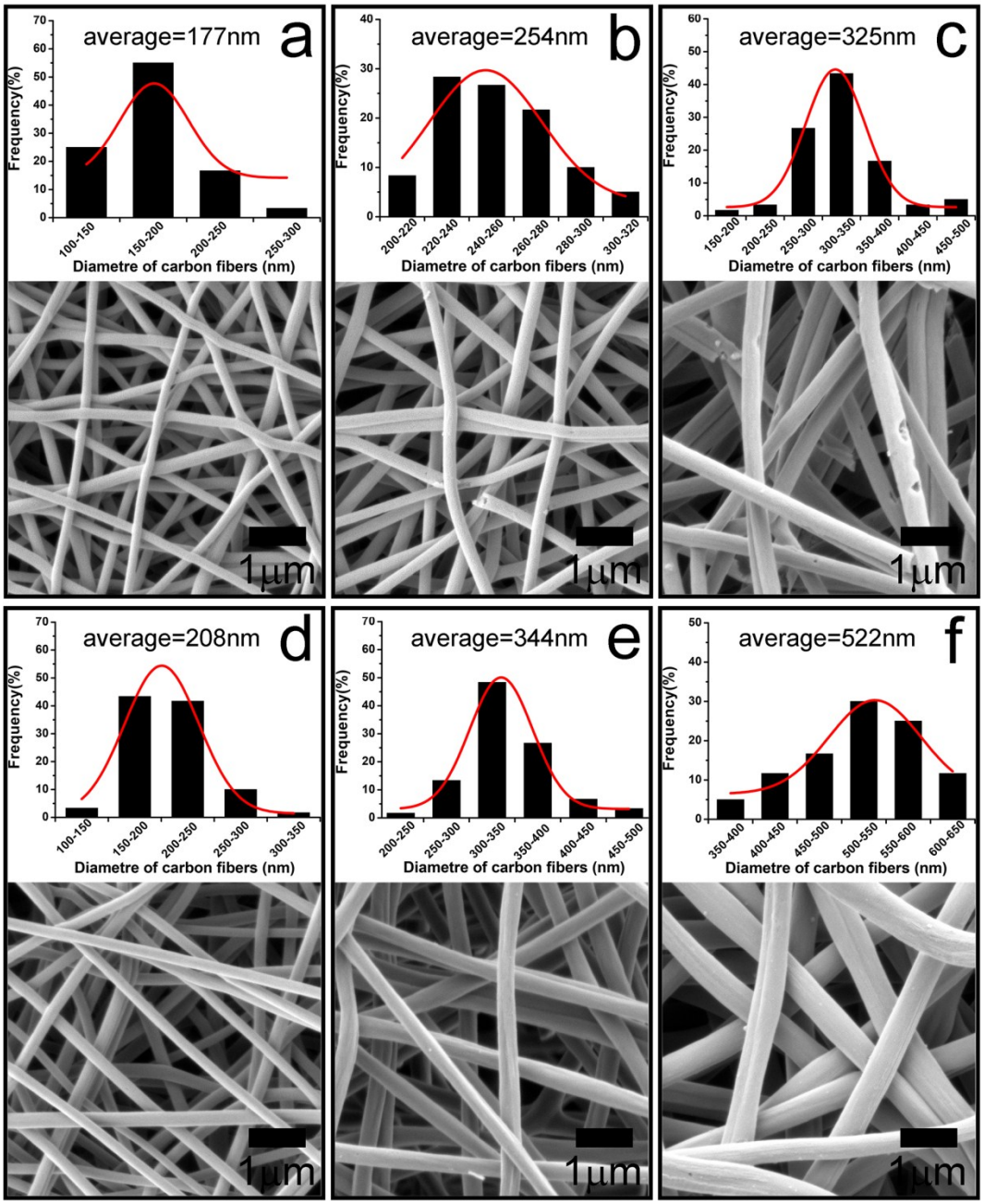
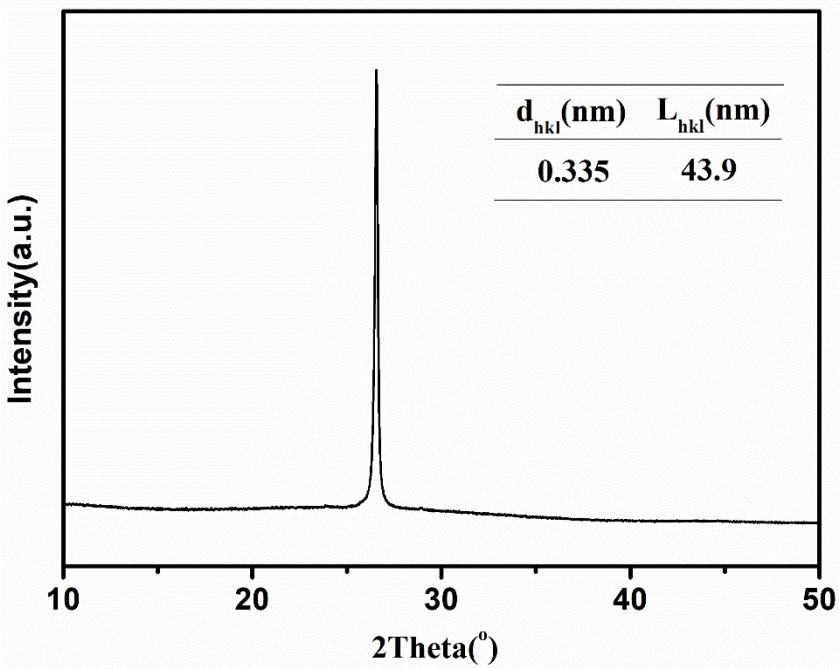


Fig. S5 SEM images of derived carbon fibers from PAN/L-1 blend solutions (a-c) and PAN/L-2 blend solutions (d-f) at weight ratio of 1/0.25, 1/0.5 and 1/0.75, separately.



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226 **Fig. S6** XRD spectrum of commercial graphite powder. The inserted table showed the distance

227 between crystallite interlayers (d_{hkl}) and the crystallite size (L_{hkl}).

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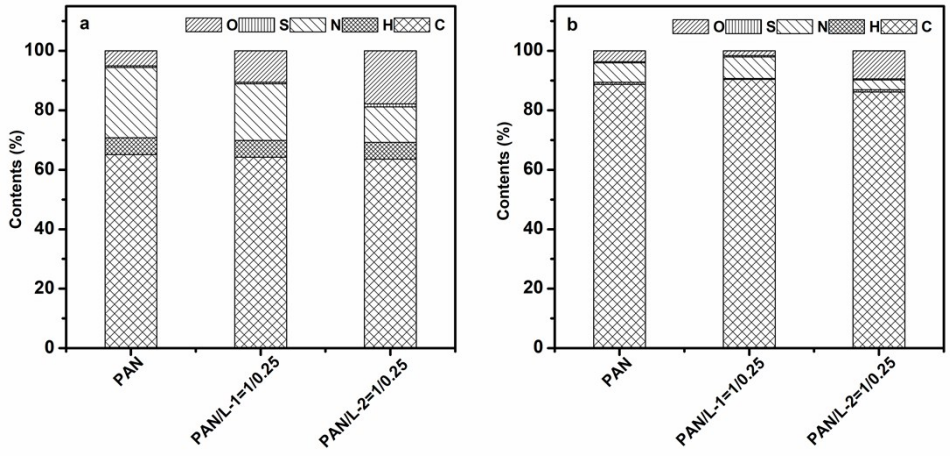

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230 **Fig. S7** Elemental analysis of as-spun precursor (a) and carbonized fibers (b).

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232 **Table S1**. Density of carbonized fibers based on PAN, PAN/L-1=1/0.25, and PAN/L-2=1/0.25

Fiber sample	**Density (g cm^{-3})**
PAN CF	1.7 ± 0.1
PAN/L-1=1/0.25 CF	1.6 ± 0.2
PAN/L-2=1/0.25 CF	1.7 ± 0.2

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