Electronic Supplementary Information

Cyclodextrin Nanofibers by Electrospinning

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1. Experimental

1.1. Materials

The *N,N*-dimethylformamide (DMF) (Riedel, %99), and urea (Merk, >%99.5) were purchased commercially. The water used was from Millipore Milli-Q Ultrapure Water System. The methyl-beta cyclodextrin (MβCD) (Cavasol® W7M: degree of substitution per anhydro glucose unit of 1.8) was obtained from Wacker Chemie AG (Germany). The materials were used without any purification.

1.2. Preparation of the solutions and electrospinning

Homogenous solutions were prepared by dissolving MβCD in two different solvent systems; water and DMF. Solutions were stirred for 2 hours at 50 ^{o}C thereafter they were cooled down to room temperature by stirring for additional 30 minutes. The MβCD concentration of 100%, 120%, 140% and 160% (w/v, with respect to solvent) were used for each solvent system. To investigate the hydrogen bonding effect on the electrospinning of MβCD, we have also added 17.5% urea ((w/w), with respect to MβCD) to the 140% (w/v) MβCD aqueous solution.

The MβCD solutions were placed in a 1 ml syringe fitted with a metallic needle of 0.45 mm of inner diameter. The syringe is fixed horizontally on the syringe pump (Model: SP 101IZ, WPI), one of the electrode of the high voltage power supply (Matsusada Precision, AU Series, Japan) was clamped to the metal needle tip and the other electrode was clamped to the cylindrical aluminum collector. The feed rate of solutions was 0.5 ml/h, the applied voltage was 15 kV and the tip-to-collector distance was kept at 10 cm. Electrospun nanofibers were deposited on a grounded stationary

cylindrical metal collector (height: 15 cm, diameter: 9 cm) covered by a piece of aluminum foil. The complete electrospinning apparatus was enclosed in Plexiglas box and the electrospinning was carried out at 22 ^{o}C at 30 % relative humidity.

1.3. Measurement and characterization

The viscosity of the MβCD solutions was measured at a constant shear rate of a 100 1/sec at 22 ^{o}C by using Anton Paar Physica MCR 301 rheometer equipped with a cone/plate accessory of spindle type CP40-2. The conductivity of the solutions was measured with Multiparameter meter InoLab® Multi 720 (WTW) at room temperature.

The morphology and the diameter of the MβCD nanofibers were investigated by using scanning electron microscope (SEM) (FEI – Quanta 200 FEG) and atomic force microscope (AFM) (PSIA – XE-100E). The average fiber diameter (AFD) was determined from the SEM images and around 100 fibers were analyzed. Samples that are put into SEM chamber were coated with 5 nm Au/Pd. The AFM imaging of fibers collected on a microscope slide was performed in intermittent contact mode in air with a scan rate of 0.1 Hz. TAP 300 (Budget Sensors) type of cantilever which has resonant frequency = 200-400 kHz and force constant = 20-75 N/m was used. The 3D representation and the roughness graph of the fibers were prepared from AFM images by using XEI software.

The x-ray diffraction (XRD) data of the MβCD nanowebs were obtained by using PANalytical X'Pert Powder diffractometer with Cu Kα radiation in a range $2\theta = 5^{o}$- 40^{o}. Thermal properties of the nanofibers were investigated by using differential scanning calorimetry (DSC) (TA Q2000) and thermogravimetric analyzer (TGA) (TA Q500). TGA

was performed with about 5 mg of fiber samples. The temperature of the samples was increased from 25 ^{o}C to 500 ^{o}C at 20 ^{o}C/min heating rate and nitrogen is used as a purge gas. DSC analysis was carried out in modulated mode. Nitrogen was used as a purges gas and also liquid nitrogen was used as cooling system. At the beginning, samples were equilibrated at 25 ^{o}C then they were heated to 300 ^{o}C at 10 ^{o}C/min.

Figures:

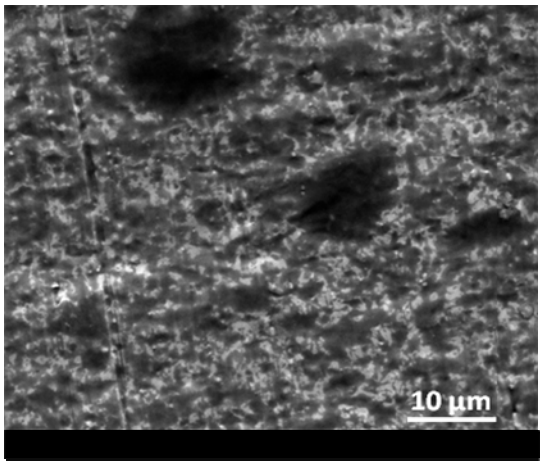

Figure S1. The electrospinning of 140% (w/v) MβCD aqueous solution containing urea (17.5% (w/w), with respect to MβCD) did not produce any fibers but only splashing occurred. Above is the SEM image of the area that MβCD splashes were collected.

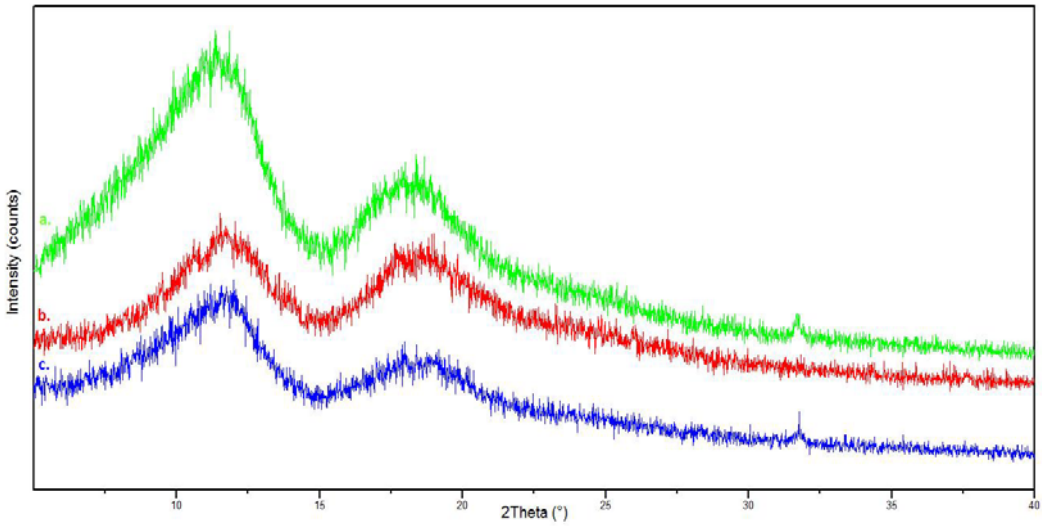

Figure S2. XRD patterns of (a) MβCD powder, (b) MβCD nanofibers electrospun from 160% (w/v) water solution, (c) MβCD nanofibers electrospun from 160% (w/v) DMF solution.

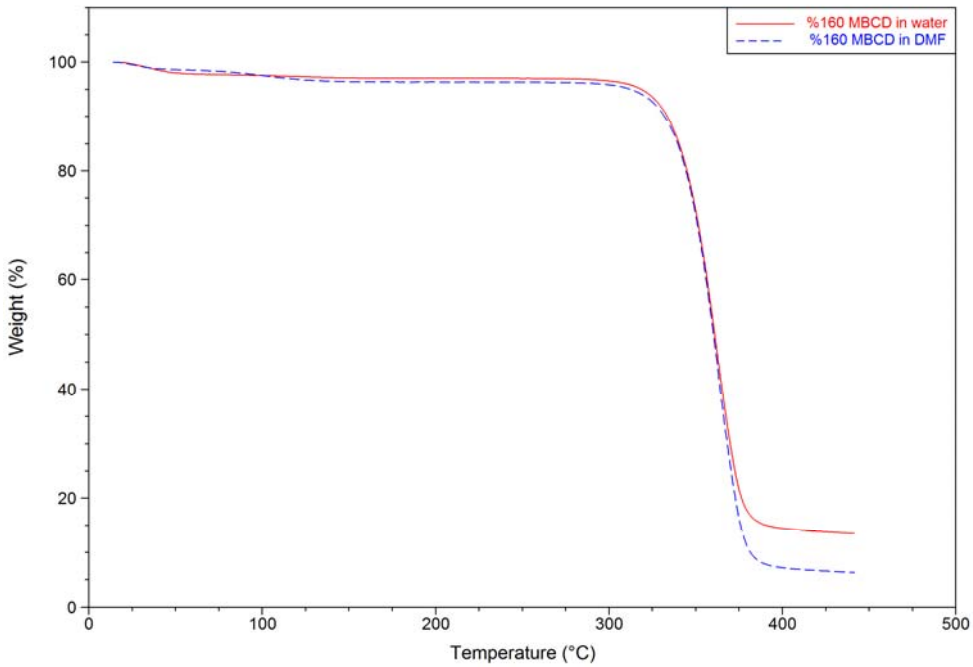

Figure S3. Thermogravimetric analysis (TGA) thermograms of MβCD nanofibers electrospun from 160% (w/v) water solution (red line) and MβCD nanofibers electrospun from 160% (w/v) DMF solution (blue line).

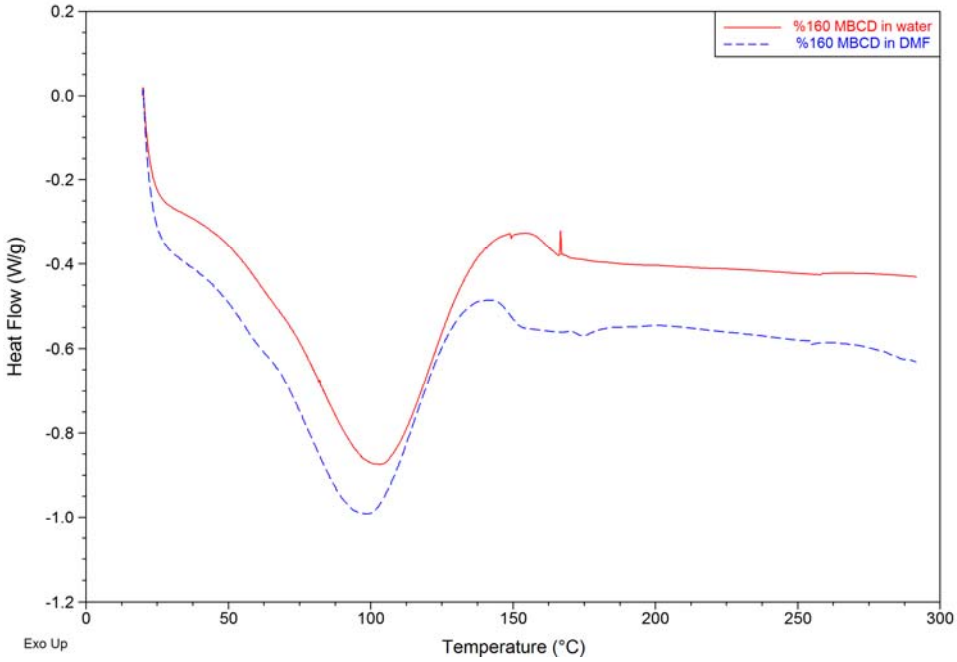

Figure S4. Differential scanning calorimetry (DSC) thermograms of MβCD nanofibers electrospun from 160% (w/v) water solution (red line) and MβCD nanofibers electrospun from 160% (w/v) DMF solution (blue line).

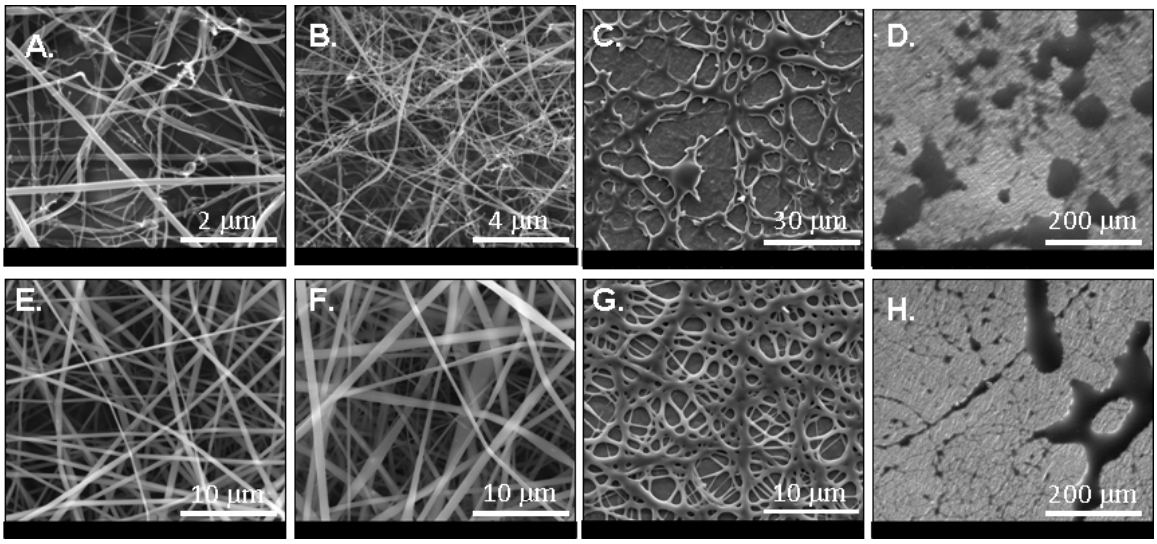

Figure S5. Scanning electron microscope (SEM) images of the electrospun MβCD nanofibers after thermal treatment at 100 ^{o}C, 150 ^{o}C, 175 ^{o}C and 200 ^{o}C for 2 hours in an oven. Thermal treated nanofibers obtained from 160% (w/v) MβCD in water at (A) 100 ^{o}C, (B) 150 ^{o}C, (C) 175 ^{o}C, (D) 200 ^{o}C. Thermal treated nanofibers obtained from 160% (w/v) MβCD in DMF at (E) 100 ^{o}C, (F) 150 ^{o}C, (G) 175 ^{o}C, (H) 200 ^{o}C. Note that the SEM images were not taken from the same exact locations.