Electronic Supplementary Information (ESI)

Construction of high strength hollow fibers by self-assembly of the stiff polysaccharide with short branches in water

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Experimental Methods

SMFS Experiment. For single molecule force spectroscopy (SMFS) experiments, about 10 μL AF1 solution with a concentration of 1.3×10^{-6} g/mL was deposited onto a clean silicon substrate and incubated for about 2 h at room temperature. Afterward, the substrate was rinsed with ultrapure water. The prepared samples were used for measurements immediately. The diluted samples were imaged to determine the surface density of AF1 chains. Force spectroscopy measurements were carried out with a Nanoscope IV AFM (Veeco). A drop of ultrapure water was put onto the substrate, and then the sample was brought into contact with the AFM tip. AF1 molecules might be adsorbed onto the tip, producing a connective bridge in between AFM tip and substrate. During the force-extension measurement, the adsorbed AF1 chain was stretched and the cantilever deflection was recorded.[1] The silicon nitride

cantilever (DNP probes Veeco) was used without further calibration. Different cantilevers were used to eliminate the error. To compare the force-extension relationship of the polymer chains with different stretching lengths, all the curves were normalized by dividing the corresponding lengths measured under the same force of 300 pN.[2] Despite different stretching lengths, the normalized curves can be well superimposed, indicating the single chain stretching in the experiment in SMFS experiments.[2] We fitted all the obtained force curves and calculated the elasticity of a single AF1 chain using the modified freely-jointed-chain (M-FJC) model.[2] The M-FJC model, which is based on the extended Langevin function shown in Eq. (S1),[3] treats a macromolecule as a chain of statistically independent segments. The segments, which are freely jointed together, can be deformed under stress.

$$x(F) = \{\coth[(FI_k)/(k_BT)] - (k_BT)/(FI_k)\}(L_c + nF/K_{segment}) \quad \text{(S1)}$$

Here, x and L_c are the extension and the contour length of the polymer chain, F is the applied force upon an individual polymer chain, I_k is the length of the statistically independent segment, n is the number of segments being stretched, and equals to L_c/I_k, k_B is the Boltzmann constant, and T is the temperature in Kelvin. The deformability of segments is characterized by the segment elasticity, $K_{segment}$. The product of the segment elasticity multiplied by the Kuhn length, K_0, represents the normalized segment elasticity of an individual polymer chain. $K_{segment}$ of different macromolecules is very difficult to be used for the comparison of elasticity, hence, K_0 was used for the comparison.[4]

Micorscopy. The SEM images of dry fibers in Fig. 8 and Fig. S6 were carried out

on a FE-SEM (SEM, Hitachi, S-4800, Japan) by using an accelerating voltage of 5 kV. In addition, the cross sections of the wet fibers in Fig. S6 were observed by using a SEM (SEM, Hitachi, S-570, Japan) with an accelerating voltage of 20 kV. The fibers were frozen in liquid nitrogen and snapped immediately, for the observation of the cross-section. The samples were coated with gold to facilitate SEM observation.

Experimental Results

Fig. S1 shows unstained TEM image of AF1 in water. The AF1 chains self-assembled into long tubular nanofibrils with a mean diameter of *ca.* 20 nm and lengths from about 500 nm to 1 μm. Additionally, there was an impurity (as the red circle shown in Fig. S1b) embedded in the AF1 nanofibril, which directly indicated the existence of the hollow nanofibers.

Fig. S2 shows the SEM image of AF1 nanofibers directly obtained from the aqueous solution with a concentration of 5×10^{-4} g/mL, and the diameter distribution of nanofibers gives an averages diameter of *ca*. 200 nm.

The fluorescent emission was increasing with the increasing acetonitrile (AN) fraction in the AN/H2O mixture as shown in Fig. S3. Since AN as nonsolvent for TPE salt, it aggregated in higher AN fraction resulting in the aggregation-induced emission.

Fig. S4 shows the fluorescence microscopy image of AF1/TPE-SO_3Na composites in aqueous solution with 1 μM TPE-SO_3Na. There are several blue dots in the image, which agrees with the FL spectra result, suggesting that TPE-SO_3Na entrapped into the cavity of nanofibers.

Fig. S5 shows the grain aggregations formed from the AIE in water, and the corresponding SAED pattern suggests a crystalline structure.

Fig. S6 shows SEM images of the surface (Fig. S6a, b) and cross-section (Fig. S6c~f) of the AF1 hollow fibers at dry and wet states. The hollow fibers obtained from the 0.02 g/mL AF1 solution by using syringe diameters of 0.5 mm (Fig. S6 left) and 0.1 mm (Fig. S6 right) exhibited tubular cross-section for both the oriented dry fibers (Fig. S6c, d) and the wet fibers (Fig. S6e, f). When the AF1 dope was extruded into the ethanol, it first formed gel lamella, and then the lamella could wind immediately. The lamella, a thick plate, at wet state resulted in uneven shrinkage to form lobulate cross-section, indicating that the wet fiber also had tubular cross-section. The modest drawing process with 7% elongation ratio lead to oriented slightly fibers. The oriented fiber at dry state showed a solid circular cross-section, and smooth surface.

References and Notes

1. H. Butt and M. Jaschke, *Nanotecnology*, 1995, **6**, 1.

2. Y. Yu, Y. H. Zhang, Z. H. Jiang and X. Zhang, *Langmuir*, 2009, **25**, 10002.

3. S. Zou, I. Korczagin, M. A. Hempenius, H. Schönher and G. J. Vancso, *Polymer*, 2006, **47**, 2483.

4. Q. Xu, S. Zou, W. Zhang and X. Zhang, *Macromol. Rapid Commun.*, 2001, **22**, 1163.

5. P. E. Marszalek, A. F. Oberhauser, Y. Pang and J. M. Fernandez, *Nature*, 1998, **396**, 661.

6. L. Zhang, C. Wang, S. Cui, Z. Wang and X. Zhang, *Nano Lett.*, 2003, **3**, 1119.

Table S1. The fit parameters for I_k, $K_{segment}$ and K_0 resulted from the simulation of M-FJC for AF1.

	Solvent condition	I_k (nm)	$K_{segment}$ (nN/nm)	K_0 (nN)	Model	Sources
AF1	water	0.51±0.04	33.9±4.9	17.3	M-FJC	This work
Amylose	water	0.45	5.6±0.8	2.5	M-FJC	Ref. 5
Curdlan	0.5 M NaOH	1.40±0.10	11±1	15.4	M-FJC	Ref. 6

Figure captions:

Fig. S1 Unstained TEM image of AF1 in water.

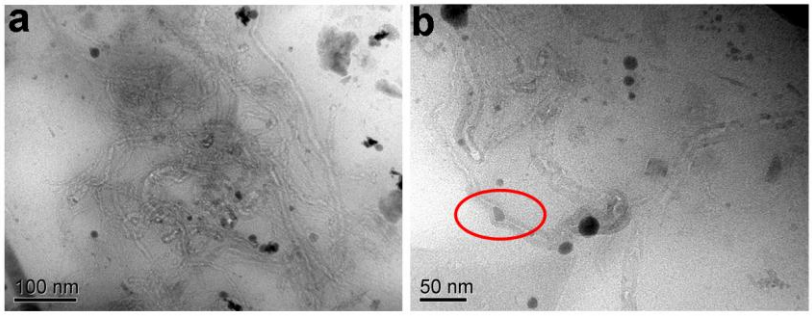
Fig. S2 SEM image and diameter distribution of AF1 nanofibers directly obtained from the aqueous solutions with a concentration of 5×10^{-4} g/mL. Scale bars = 2 μm.

Fig. S3 Fluorescence spectra of TPE-SO_3Na in AN/water mixtures. Concentration of TPE-SO_3Na = 1 μM; EX = 10.0 nm, EM = 5.0 nm, EX wavelength = 350 nm.

Fig. S4 Fluorescence microscopy image of AF1/TPE-SO_3Na composites in aqueous solution. Concentration of TPE-SO_3Na = 1 μM.

Fig. S5 TEM image (a) and SAED pattern (b) of corresponding TPE-SO_3Na in water.

Fig. S6 SEM images of the surface (top) and cross-section (middle) of the dry fibers and the cross-section (bottom) of the corresponding wet fibers with different syringe diameters and solution concentrations: 0.5 mm, 0.02 g/mL (a, c, e); 0.1 mm, 0.02 g/mL (b, d, f).



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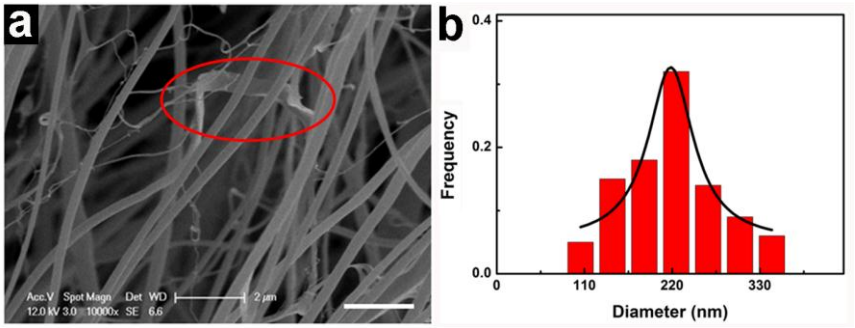

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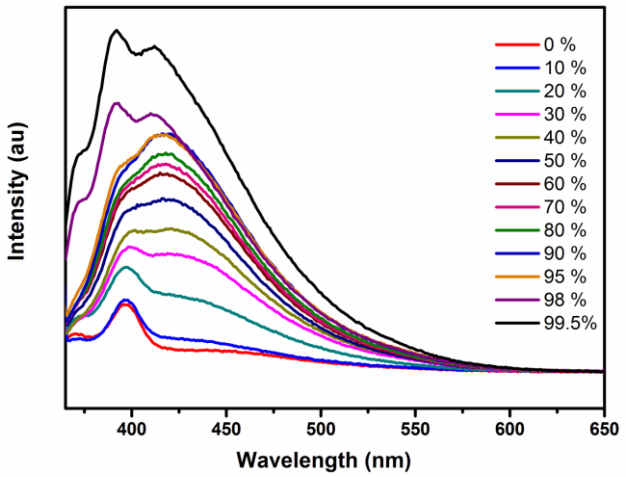

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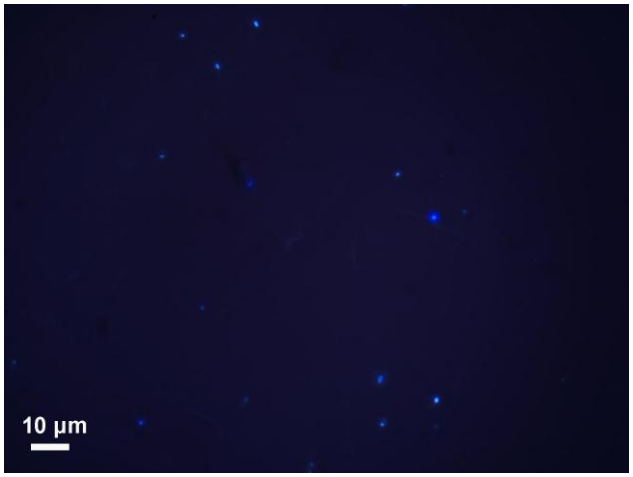

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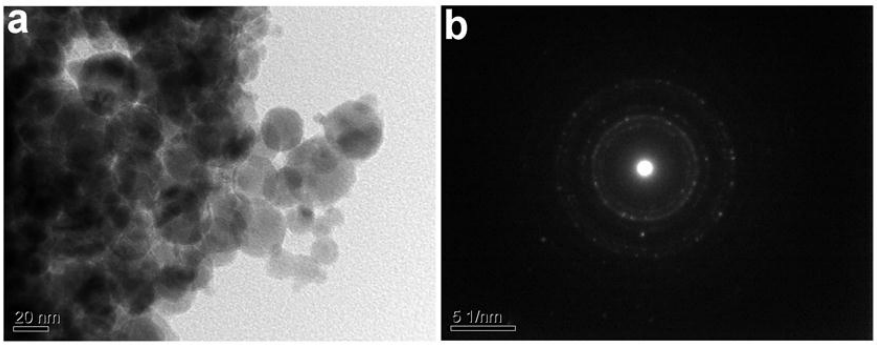

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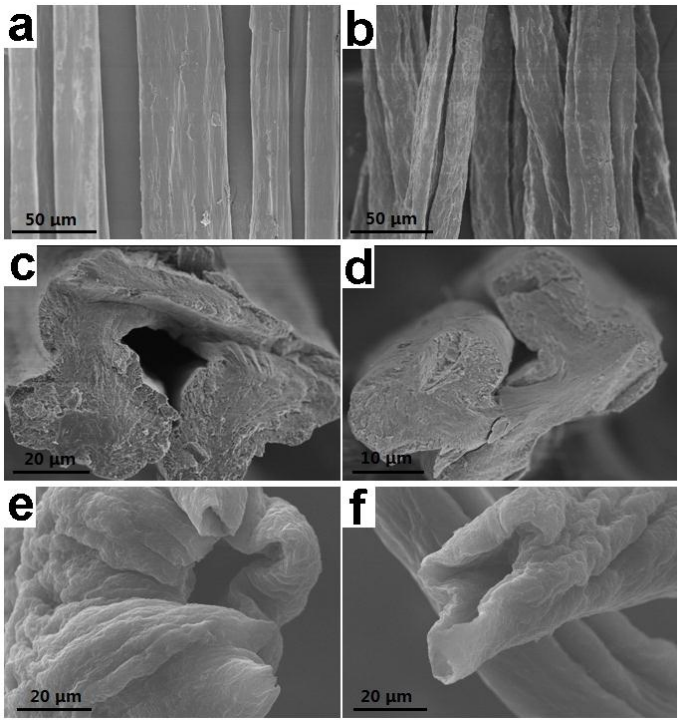

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