Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis and Characterization of Multi-helical DNA-Silica Fibers

Yuanyuan Cao, Junjie Xie, Ben Liu, Lu Han* and Shunai Che*

School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composites, Key Laboratory for Thin Film and Microfabrication Technology of the Ministry of Education, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240 (P. R. China)
E-mail: luhan@sjtu.edu.cn; chesa@sjtu.edu.cn

Experimental section

Materials

DNA sodium salt from Herring testes is from Sigma, formly listed as Type XIV. The solution of sonicated DNA was prepared by dissolving DNA in deionized water and treating with an ultrasonic cell crusher in ice bath at 400W for 2.5 h (one ultrasonication process lasts for 10 s with 10 s intervals and repeated for 900 times). 3-aminopropyltrimethoxysilane (APTMS) and tetraethyl orthosilicate (TEOS) are from TCI, Japan. Hydrochloric acid, sodium hydroxide and zinc nitrate are from Sinopharm Chemical Reagent Co. Ltd. All the regents are used as received without further purification

Synthesis of MHDSFs and NHDSFs

In a typical experiment, DNA solution was prepared by dissolving the solid DNA into deionized water and stirring under room temperature for 12 h with the final concentration of 500 μg/g. 148.8 μL APTMS was dilute with 20 mL deionized water and the pH of APTMS solution was adjusted to 7 by 2 M HCl then the solution was stirred for 25 min for pre-hydrolysis. Then certain amount of the APTMS solution (2 mL for the molar ratio of APTMS/DNA of 6:1 and 1mL for the molar ratio of APTMS/DNA of 3:1) and 100 μL TEOS were successively added to the DNA solution under continuously stirring, the pH value of the mixture was adjusted to 8 by 0.1 M NaOH solution. After stirring for 15 min at 15 ^{o}C, the mixture was allowed to react under static conditions at 15 ^{o}C for 120 h. The products were collected by centrifugation and washed with deionized water for three times to remove the unreacted silica source and DNA. Then the products were freeze-dried and collected as white powder. To investigate the morphological and structural evolution of the MHDSFs, the SEM, TEM images and DRCD spectra of the products originating from the same initial mixture were prepared by freeze-dried from the same initial mixture at different reaction times.

Synthesis of DNA-silica rods

The DNA-silica rods were synthesised by sonicated DNA ranging from 100 to 300 bp in length. In a typical experiment, the stock solution of DNA with the concentration of 10 mg/g in H_2O was prepared by dissolving DNA in deionized water and stirring under room temperature for 12 h, then the solution was ultrasonic treated by an ultrasonic cell crusher at 400 W for 2.5 hours in ice bath to prevent the denaturation of DNA. The solution of sonicated DNA was diluted to a final concentration of 500 μg/g. After stirring the solution for 0.5 h with the addition of 4.22 mg $Zn(NO_3)_2 \cdot 6H_2O$ (for twisted DNA-silica rods) or without any addition (for un-twisted DNA-silica rods), certain amount of APTMS solution (2 mL for twisted rods and 1 mL for un-twisted rods) prepared as before and 100 μL TEOS were added to the sonicated DNA solution and the pH value of the mixture was adjusted to 8 by 0.1 M NaOH solution. The following process was the same as the synthesis of MHDFS, and the products were collected as white powder.

Characterization:

The macroscopic features of the samples were observed with SEM (JEOL JSM-7401F) with an accelerating voltage of 1.0 kV. TEM was performed with a JEOL JEM-2100 microscope operating at 200 kV (Cs = 1.0 mm, Point resolution 2.3 Å), the samples were dispersed in ethanol and dropped on a carbon thin film on a Cu grid. The CD spectra and DRCD spectra were taken on a JASCO J-815 spectropolarimeter fitted with DRCD apparatus.

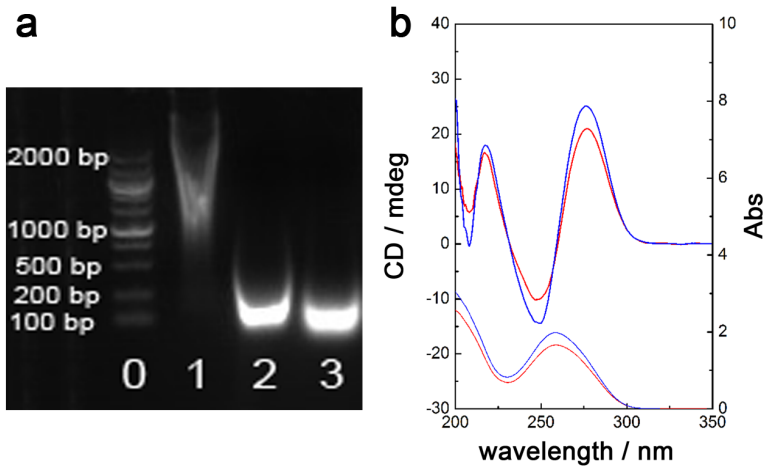

Fig. S1 2% agarose gel electrophoretic separation (a) and CD and UV/Vis spectra (b) of long DNA and short DNA. Lane 0, DL2000 Ladder; Lane 1 and red line, Type XIV DNA sodium salt from Herring tests from Sigma; Lane 2 and blue line, sonicated Type XIV DNA sodium salt; Lane 3, commercial DNA between 100 and 200 bp (DNA sodium salt from salmon milt, TCI). The lane of sonicated DNA is similar to the commercial DNA and the CD spectra of DNA solution before and after sonication treatment show the typical signals of B-DNA form, indicating the maintenance of B-form structure after sonication treatment.

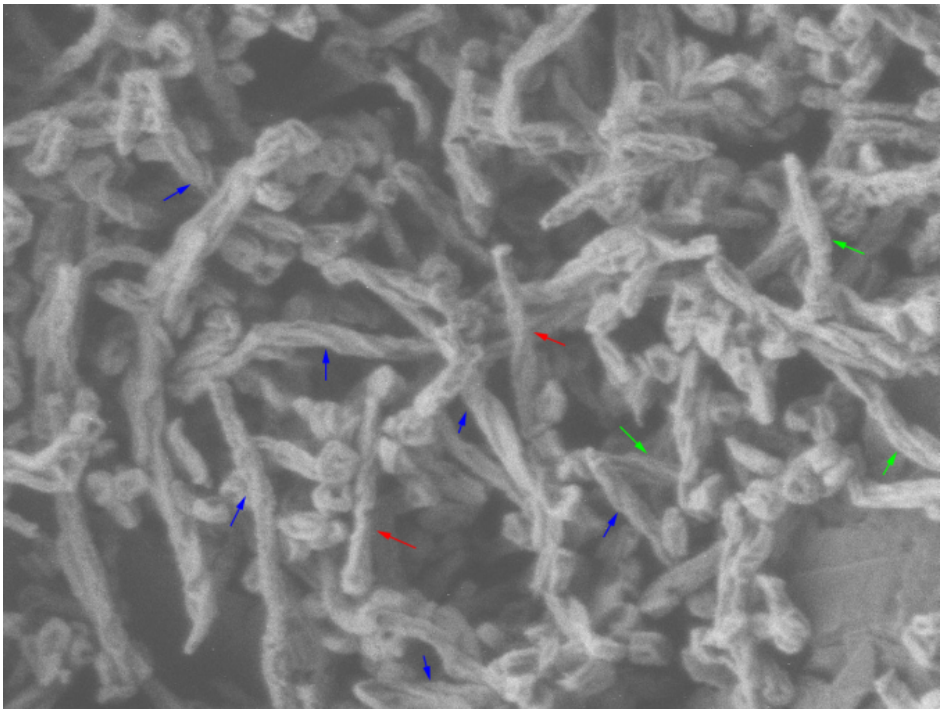

Fig. S2 Low magnification SEM images of MHDSFs including two-strand helical fibers (marked by red arrows), three-strand helical fibers (marked by blue arrows) and four-strand helical fibers (marked by green arrows).

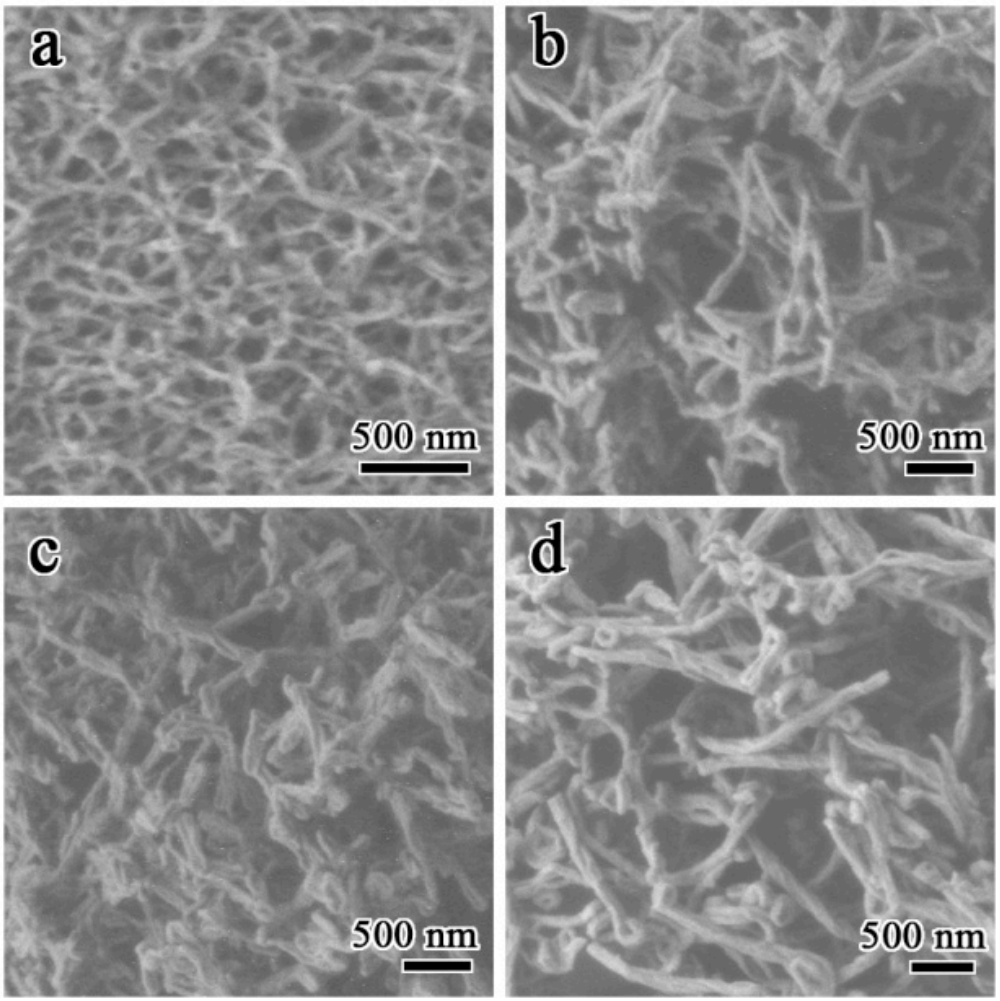

Fig. S3 SEM images of the fibers synthesised with APTMS/DNA molar ratios of 3 (a), 4 (b), 5 (c) and 6 (d).

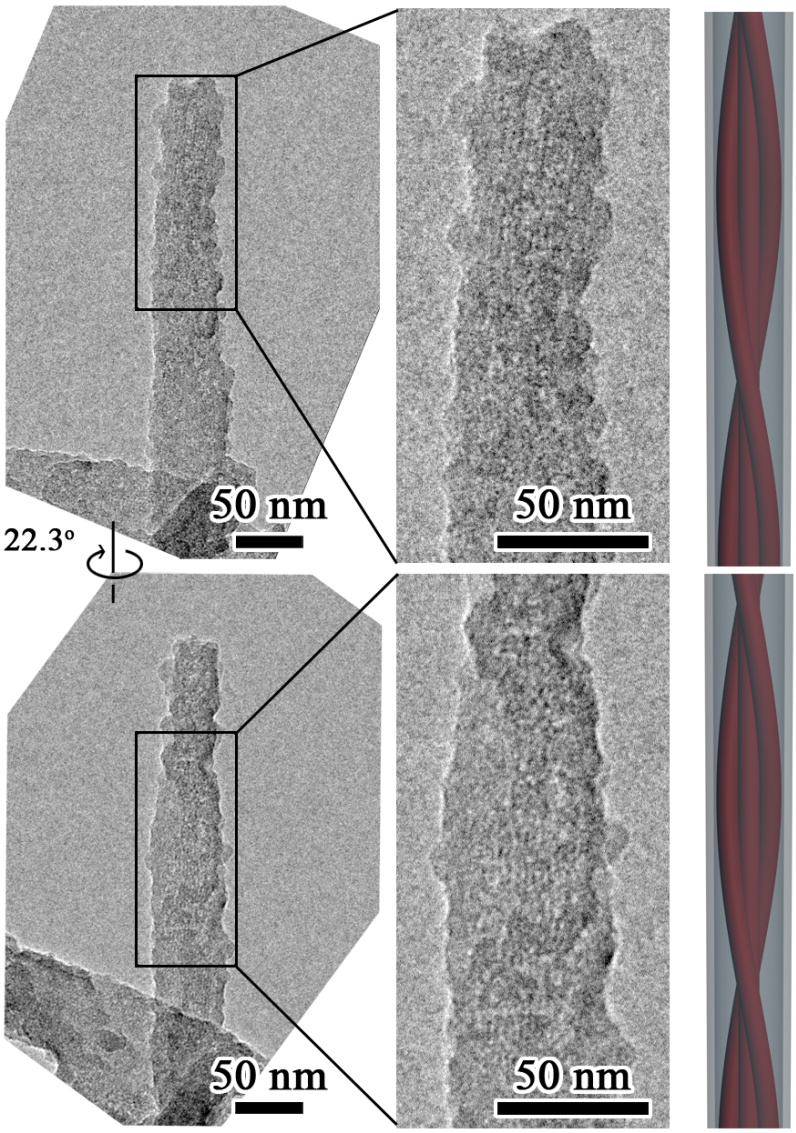

Fig. S4 HRTEM images of NHDSFs. The upper and bottom parts have been aligned by tilting the fiber counter-clockwise along its long axis by 22.3°, the channels at the top of the fiber gradually disappeared and moved downward, indicating the left-handed arrangement of the channels.

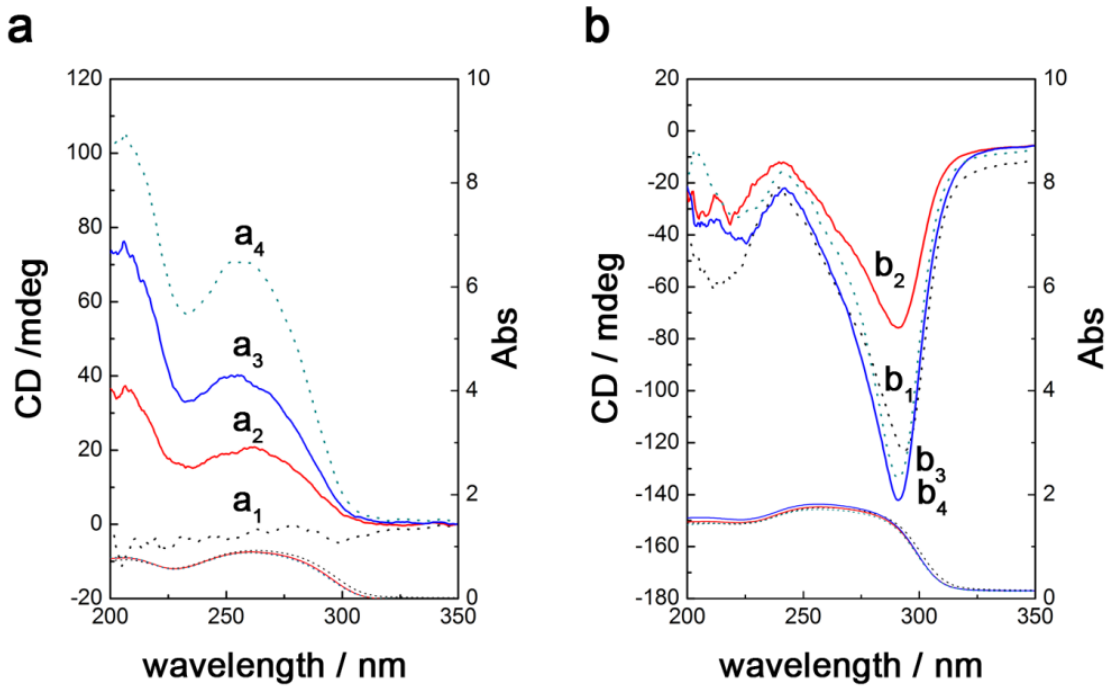

Fig. S5 DRCD and UV/Vis spectra of dry (a) and wet (b) DNA transcribed fibers synthesised with different APTMS/DNA molar ratios of 3 (a_1 and b_1, as shown in Fig. 2), 4 (a_2 and b_2), 5 (a_3 and b_3) and 6 (a_4 and b_4, as shown in Fig. 2), respectively.

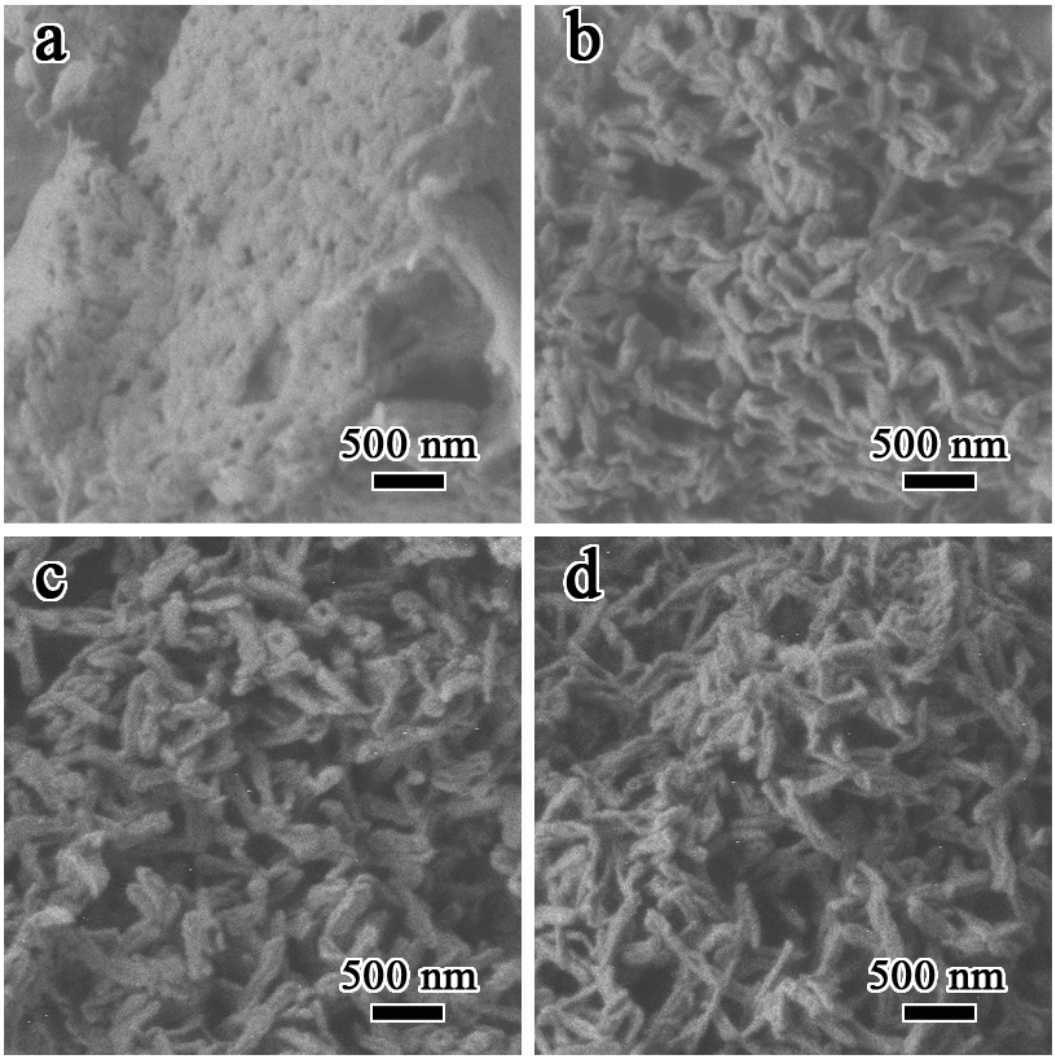

Fig. S6 low magnification SEM images of MHDSFs synthesised at different reaction periods of 5 h (a), 10 h (b), 30 h (c) and 60 h (d), respectively.

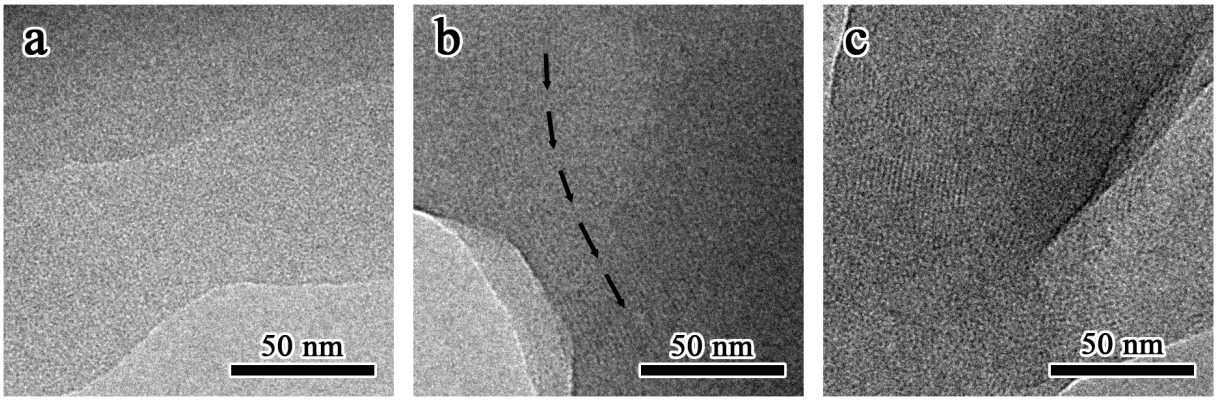

Fig. S7 HRTEM images of MHDSFs synthesised at different early reaction time of 5 h (a), 8.5 h (b) and 10 h (c), respectively.

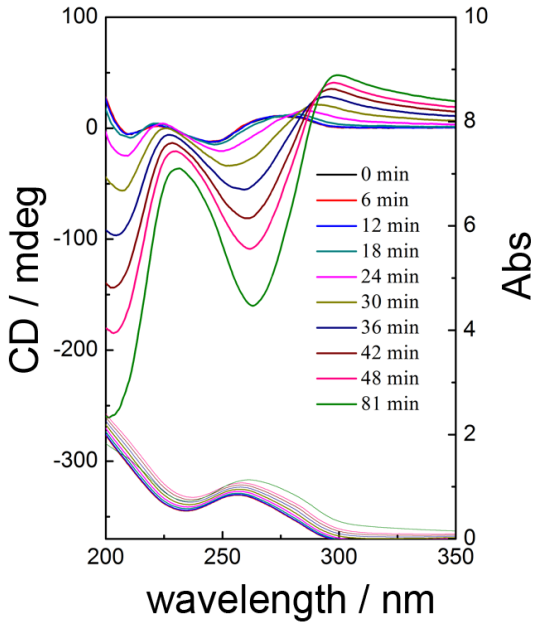

Fig. S8 CD and UV/Vis spectra of the reaction solution of MHDSFs synthesised at the early stage of reaction. The positive signals at around 300 nm resulted from the differential scattering effect of the DNA aggregation in solution.

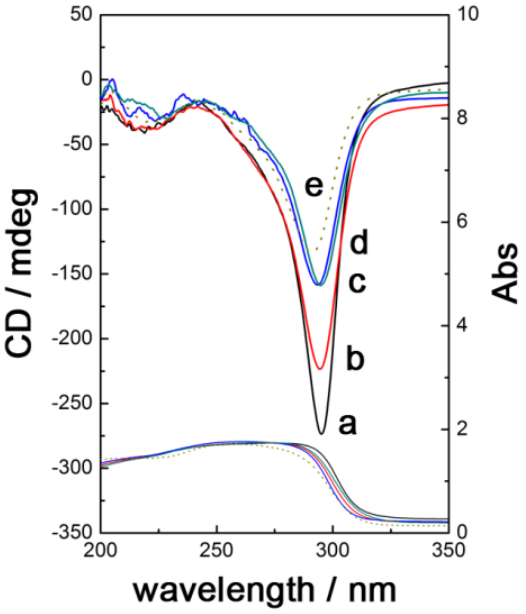

Fig. S9 DRCD and UV/Vis spectra of wet MHDSFs synthesised at different reaction periods of 5 h (a), 10 h (b), 30 h (c), 60 h (d) and 120 h (e), respectively.

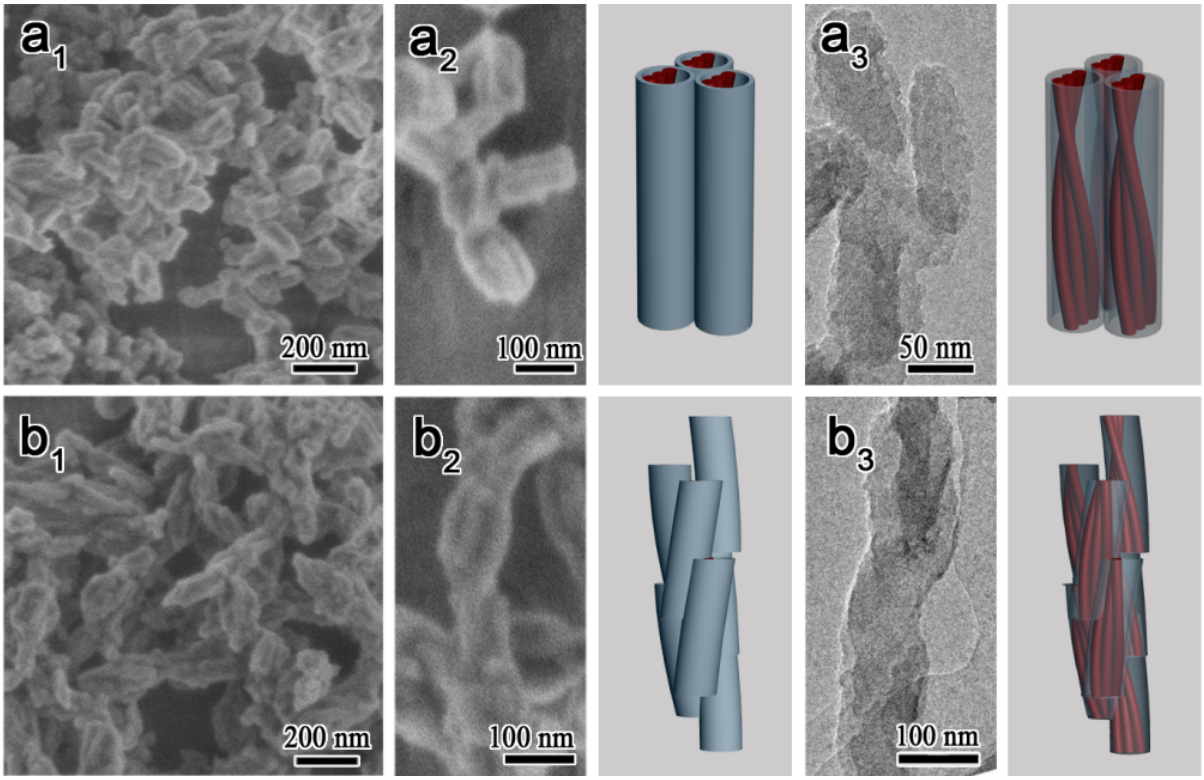

Fig. S10 SEM images (a_1, a_2, b_1 and b_2) and TEM images (a_3 and b_3) and the corresponding model of the non-helical rods and the helical rods synthesised from sonicated DNA molecules in the absence (a) and presence (b) of Zn^{2+} ions.

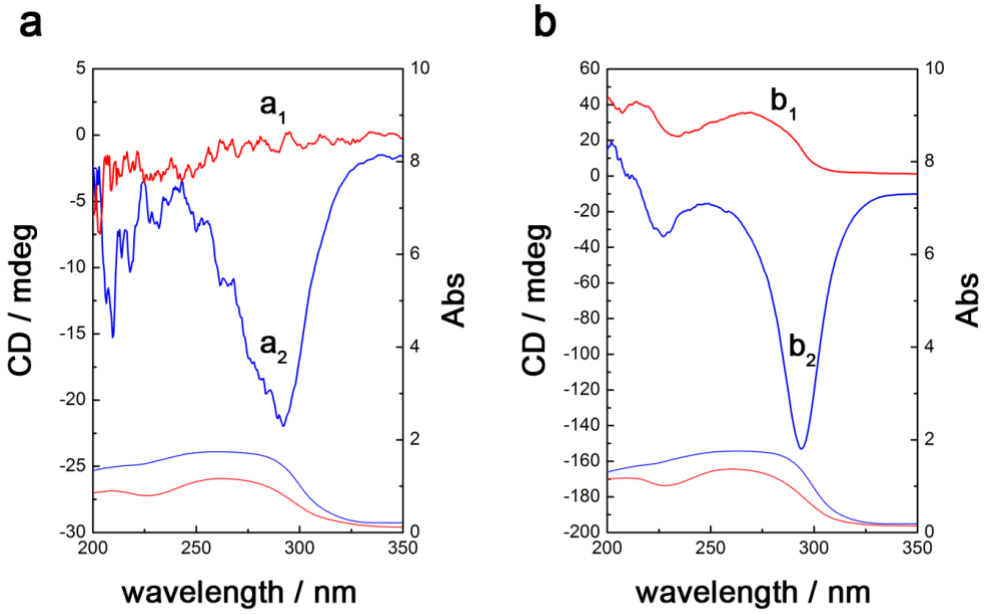

Fig. S11 DRCD and UV/Vis spectra of the sonicated DNA transcribed non-helical rods (a) and helical rods (b) under dry (red) and wet (blue) states, respectively.

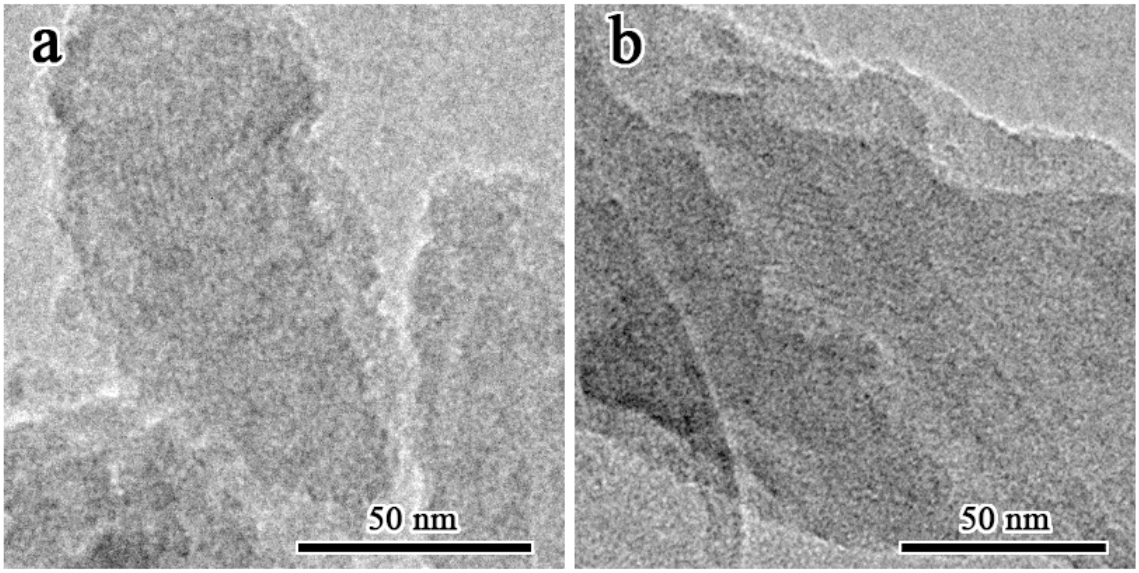

Fig. S12 HRTEM images of non-helical rods (a) and helical rods (b), respectively.