

Supporting Information

Helical fibers via evaporation-driven self-assembly of surface-acylated cellulose nanowhiskers

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1 General information

Microcrystalline cellulose (MCC) with an average particle size of 50 μm , 10-undecenoyl chloride, stearoyl chloride and hexanoyl chloride were purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). MCC was dried in vacuum oven for 24 hours at 80 $^{\circ}\text{C}$ before use. Dry pyridine and tetrahydrofuran (THF) were brought from Th. Geyer GmbH & Co. KG (Renningen, Germany). Other chemicals are all of analytical grade and used as received. Deionized water (DI water) was used in all experiments.

2 Experimental Part

2.1 Synthesis Description

Synthesis of cellulose nanowiskers with surface-attached 10-undecenoyl groups (CNWs-SU) and surface-attached hexanoyl cellulose nanowiskers (CNWs-SH)

CNWs were synthesized under heterogeneous conditions according to published procedures with a few modifications.^[1] Briefly, 1 g of MCC was fed into a three-necked flask. Then, 30 mL pyridine was added and MCC dispersed therein by stirring. After the mixture was heated up to 50 $^{\circ}\text{C}$, 2.73 mL or 2.05 mL 10-undecenoyl chloride (2 mol or 1.5 mol acid chloride per mol anhydroglucose units of cellulose) or 2.67 or 2.23 mL hexanoyl chloride (3 mol or 2.5 mol acid chloride per mol anhydroglucose units of cellulose) were added to the cellulose suspension under stirring. After 3, 7 or 20 h stirring at 50 $^{\circ}\text{C}$, the reaction mixture was poured into 200 mL methanol immediately. The precipitate was separated by centrifugation. Thereafter, the product was purified by a repeated dispersion and precipitation process using THF and methanol, respectively, before the product was dispersed in THF. Then, the suspension was centrifuged for 20 min at 14000 rpm at 4 $^{\circ}\text{C}$. After the centrifugation, the supernatant was removed and the solid was dispersed in THF again, which was centrifuged for 20 min at 3000 rpm at 20 $^{\circ}\text{C}$ to remove the micro-scaled segments. Finally, the purified product was separated on ultracentrifuge at 14000 rpm at 4 $^{\circ}\text{C}$ for 10 h, leading the corresponding CNWs with the yields of 11.6 \pm 2.4%. The DS of CNWs-SU under the conditions of 2 mol 10-undecenoyl chloride per mol anhydroglucose units of cellulose for 3, 7 and 20 h is 1.15, 1.32 and 1.66, namely CNWs-SU_{1.15}, CNWs-SU_{1.32} and CNWs-SU_{1.66}, respectively. With the condition of 1.5 mol 10-undecenoyl chloride per mol anhydroglucose units of cellulose for 7 h, CNWs-SU with the DS of 0.98 (named as CNWs-SU_{0.98}) was obtained. The degree of substitution of CNWs-SH synthesized with 3 and 2.5 mol hexanoyl chloride per mol anhydroglucose units of cellulose for 7 h was determined to be 1.57 and 1.37, respectively. The samples were referred to as CNWs-SH_{1.57} and CNWs-SH_{1.37}.

Synthesis of cellulose nanowiskers with surface-attached stearoyl groups (CNWs-SS) in a mixed solvent of N,N-dimethylacetamide (DMAc) and pyridine

1 g MCC was fed into a three-necked flask. Then, 30 mL DMAc and 2.5 mL pyridine was added and MCC dispersed therein by stirring. The mixture was heated up to 100 $^{\circ}\text{C}$ and 5.76 mL stearoyl chloride (2.5 mol stearoyl chloride per mol anhydroglucose units of cellulose) was added to the hot cellulose suspension under stirring. After 1 h stirring at 100 $^{\circ}\text{C}$, the hot reaction mixture was poured into 200 mL ethanol immediately. The precipitate was separated by centrifugation. Thereafter, the product was purified by a repeated dispersion and precipitation process using THF and ethanol, respectively, before the product was dispersed in THF. Then, the suspension was centrifuged for 20 min at 14000 rpm at 4 $^{\circ}\text{C}$. After the centrifugation, the supernatant was removed and the solid was dispersed in THF again, which was centrifuged for 20 min at 3000 rpm at 20 $^{\circ}\text{C}$ to remove the micro-scaled segments. Finally, the purified product was dispersed in THF for further use. The degree of substitution of CNWs-SS is 1.66 and the product is referred to as CNWs-SS_{1.66}.

Synthesis of polymeric cellulose 10-undecenoyl ester (PCUE) under homogeneous condition

Homogeneous synthesis was carried out according to reference with a few modifications.^[2] In brief, 1 g MCC and 40 mL DMAc was added into a three-necked flask and the mixture was heated up to 130 $^{\circ}\text{C}$ for 30 min under rigorous stirring before 3 g LiCl was added. The system was purged with nitrogen for at least 3 min. Then, the mixture was cooled down to room temperature under stirring for additional 3 hours, until a transparent cellulose solution was obtained. After that, the above cellulose solution was heated up to 50 $^{\circ}\text{C}$ and 2.73 mL of 10-undecenoyl chloride (2 mol 10-undecenoyl chloride per mol anhydroglucose units of cellulose) was added. Thereafter, 3.25 mL pyridine was added (3 mol pyridine per mol acid chloride) under stirring. The mixture was then stirred for additional 3 h at 50 $^{\circ}\text{C}$ and the reaction was stopped by adding the warm mixture into 5 volumes of methanol. Then, the product was purified by a repeated solubilization and precipitation process using THF and methanol, respectively, before the product was dispersed in THF for further use. The degree of substitution is 1.1 and the product is named as PCUE_{1.1}.

Synthesis of cellulose 10-undecenoyl ester with a degree of substitution of 3 (CUE₃)

CUE₃ was prepared according to our previous work with a few modifications.^[3] In a typical case, 1 g dried MCC was fed into a three-necked flask. Then, 30 mL pyridine was added and MCC was dispersed therein by stirring. The cellulose suspension was heated up to 100 $^{\circ}\text{C}$ and 8.4 mL 10-undecenoyl acid chloride (6 mol 10-undecenoyl chloride per mol anhydroglucose units of cellulose) was added into the hot cellulose suspension. After 1 h stirring at 100 $^{\circ}\text{C}$, the mixture was added into 200 mL methanol. The precipitate was separated by centrifugation. Thereafter, the product was purified by a repeated solubilization and precipitation process using THF and methanol, respectively. Finally, the product was dissolved in THF and stored in the dark for further use.

Synthesis of cellulose stearoyl ester with a degree of substitution of 3 (CSE₃)

CSE₃ was synthesized under heterogeneous conditions according to published procedures.^[2] Briefly, 1 g dried MCC was fed into a three-necked flask. Then, 30 mL pyridine was added and MCC dispersed therein by stirring. The cellulose suspension was heated up to 100 °C and 13.83 mL of stearoyl chloride (6 mol stearoyl chloride per mol anhydroglucose of cellulose) was added into the cellulose suspension. After 1 h stirring at 100 °C, the reaction mixture was poured into 200 mL ethanol. The precipitate was separated by centrifugation. Thereafter, the product was purified by repeated dissolution in THF and precipitation in ethanol. Finally, the product was dried in vacuum at 50 °C for 12 h.

2.2 Hydrophobization of Silicon Wafers

The hydrophobic silicon wafers were modified with chloro(dimethyl)octadecylsilane solution. Before the silanization, silicon wafers were treated with a plasma cleaner (Zepto Plasma cleaner, Diener Electronic, Germany). Then, the wafers were immersed in chloro(dimethyl)octadecylsilane solution of 15 mg/ml pyridine at 50 °C for 24 h. After that, the wafers were sonicated in THF for 10 min, in ethanol for 10 min and dried in the air, leading to silicon wafers with (dimethyl)octadecylsilyl groups at the surface.

2.3 Preparation of Polydimethylsiloxane (PDMS) Substrates

PDMS prepolymer and curing agent (Sylguard 184, Sigma-Aldrich) were mixed at a ratio of 10:1, stirred thoroughly, and then degassed in a vacuum desiccator. The prepolymer mixture was poured into a polystyrene Petri dish of 1 mm thick (VWR International GmbH, Darmstadt, Germany), degassed again in the vacuum desiccator, and cured in the oven at 80 °C for 1 h. Following the curing, flat PDMS slices were peeled from the dishes and cut into 1 cm × 1 cm slices.

2.4 Elemental Analysis

The contents of carbon and hydrogen were determined with an Elemental Analyser 4.1 vario EL III (Elementar, Germany). DS of corresponding groups was calculated according to the carbon contents, as the following formula.

$$DS = \frac{5.13766 - 11.5592 \times C\%}{0.996863 \times C\% - 0.856277 \times n + n \times C\%} \quad (1)$$

where C % is the content of element carbon and n is the number of carbon atoms in the acyl moieties, respectively.

2.5 Solid-State ¹³C CP-MAS NMR Spectroscopy

Solid-state ¹³C CP-MAS NMR measurements for all samples were acquired at ambient conditions using a Bruker AVANCE IIIHD 800WB spectrometer with a field strength of 18.8 T. Experiments were performed using a Bruker 1.3 mm MAS triple resonance probe with a MAS spinning frequency of 55.555 kHz. A ramped CP-MAS sequence was used with a ¹H excitation power of 138.8 kHz and a Hartman Hahn contact time of 2 ms with a ¹³C inherent radio frequency (rf) field strength of 62.5 kHz and ¹H rf field strength of 127.4 kHz. During acquisition of 27 ms a ¹H decoupling was performed with an inherent rf field of 14.7 kHz employing WALTZ-16 sequence.^[4] In a typical 8 h experiment, 15360 scans were accumulated with a recycle delay of 2 s.

The crystallinities of the samples were determined based on the solid-state ¹³C CP-MAS NMR spectra. The individual peaks ascribed to C4 in crystalline and amorphous regions were extracted by a peak deconvolution process in Origin 8.5 using Gaussian function (Supplementary Fig. 3). The crystallinity was calculated using the following equation:

$$\text{Crystallinity (\%)} = \frac{A_{cr}}{A_{cr} + A_{am}} \quad (2)$$

where A_{cr} and A_{am} represent the areas obtained by the integration of the fitting curves of the crystalline peak and amorphous peaks in C4 region, respectively.

2.6 Scanning Electron Microscopy (SEM)

SEM images were obtained on a LEO Supra-35 high-resolution field emission scanning electron microscope (Carl Zeiss AG, Germany) at an accelerating voltage of 5 kV. A layer of carbon or gold was coated on the surface of samples before SEM measurements.

2.7 Transmission Electron Microscope (TEM)

The TEM observation was performed on a CM 12 Transmission Electron Microscope (Philips, Netherland). The specimen was stained by phosphotungstic acid solution (0.2 wt % in THF) for about 2 min to enhance the contrast.

2.8 Atomic Force Microscopy (AFM)

AFM topographic measurements were performed using a Cypher S AFM (Asylum Research, Santa Barbara, CA) in tapping mode in air. Samples were prepared by transferring a drop of diluted solution (concentration of 0.0002 mg/mL) onto different substrates followed by drying in air. Silicon Nitride cantilevers with a tip radius of 7 nm, nominal spring constant of 2 N m⁻¹, and nominal

resonance frequency of 70 kHz (AC240TS-R3, Olympus) were used. Images processing and subsequent evaluation of sample geometrical parameters was performed with Gwyddion (Free Software Foundation, Inc., Boston, USA).

2.9 Static Water Contact Angles

The wetting properties of substrates were assessed on a Contact Angle System OCA 15EC (dataphysics, Filderstadt, Germany). Static water contact angles were measured using the sessile drop (4 μL) technique averaged over five repeats.

3 Results and Discussion

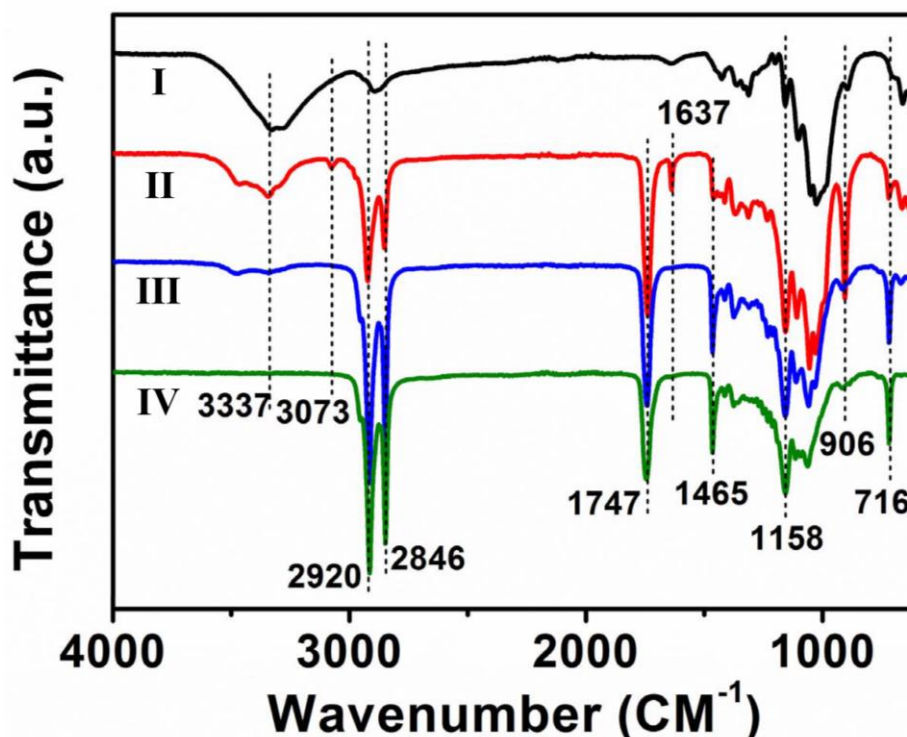


Figure S1. FTIR spectra of (I) microcrystalline cellulose (MCC), (II) CNWs-SU_{1.32}, (III) CNWs-SS_{1.59}, (IV) CSE₃.

Typical FTIR bands of cellulose are visible, such as the bands attributed to vibrations of O-H (3000-3600 and 1300-1450 cm^{-1}), C-H (2900 cm^{-1}), and C-O groups (950-1200 cm^{-1}).

Within the FTIR spectrum of CNWs-SU_{1.32}, new bands emerge at 3073, 1747, 1637 and 906 cm^{-1} , which are attributed to stretching vibrations of $\text{CH}_2=\text{CH}_2$, stretching vibrations of C=O, stretching vibrations of C=C, and deformation vibrations of alkene C-H groups, respectively.

Within the FTIR spectrum of CNWs-SS_{1.59} and CSE₃, new bands emerge at 1747, 1465, 1158 and 716 cm^{-1} , which are attributed to stretching vibrations of C=O, symmetric C-H deformation vibrations, C-O-C stretching vibrations and C-C rocking vibrations, respectively.

The intensities of signals at 2920 and 2846 cm^{-1} strongly increased, which are due to asymmetric and symmetric stretching vibrations of C-H groups of alkyl chains, respectively.

The peak at 3337 cm^{-1} attributed to stretching vibrations of hydroxyl groups at cellulose backbone strongly decreased due to the derivatisation by acyl groups.

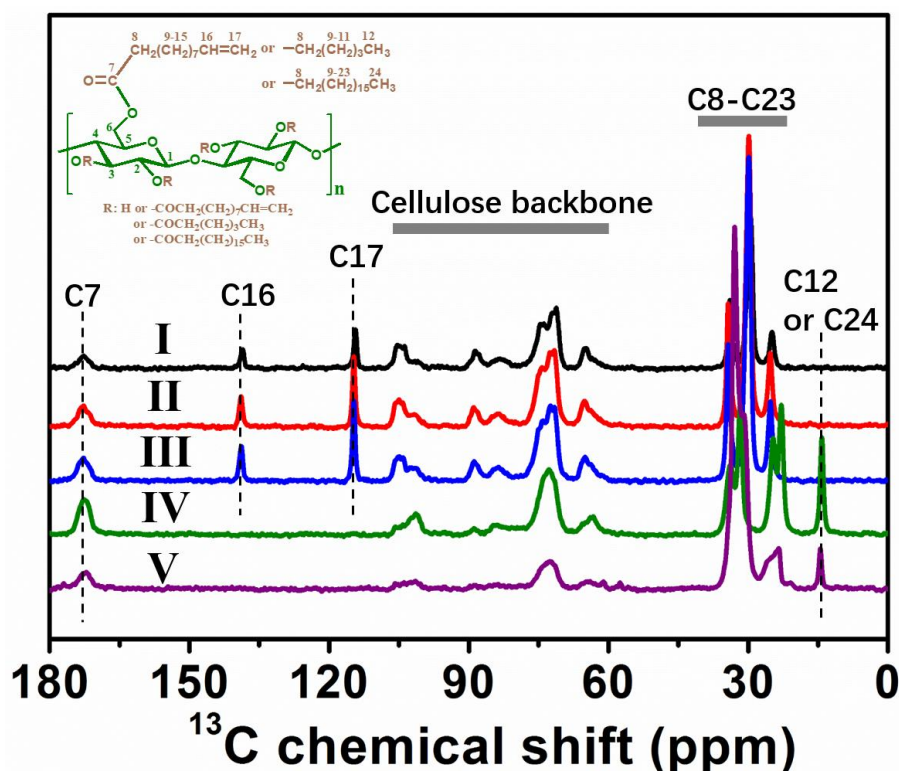


Figure S2. Solid-state CP-MAS ^{13}C NMR spectra of (I) CNWs-SU $_{0.98}$, (II) CNWs-SU $_{1.15}$, (III) CNWs-SU $_{1.66}$, (IV) CNWs-SH $_{1.57}$, (V) CNWs-SS $_{1.59}$.

The solid-state CP-MAS ^{13}C NMR spectrums show the signals assigned to the cellulose backbones, 10-undecenyl, hexanoyl and stearoyl groups. The signals between 55 and 110 ppm are ascribed to the carbons of anhydroglucose units of cellulose. The chemical shift at 172.6 ppm represents the carbon from the ester linkage. The signals at 114 and 139 ppm attribute to carbons in terminal olefin groups for (I) CNWs-SU $_{0.98}$, (II) CNWs-SU $_{1.15}$, and (III) CNWs-SU $_{1.66}$. The signals between 40 and 10 ppm represent the remaining carbon atoms of the 10-undecenyl, hexanoyl or stearoyl moieties.

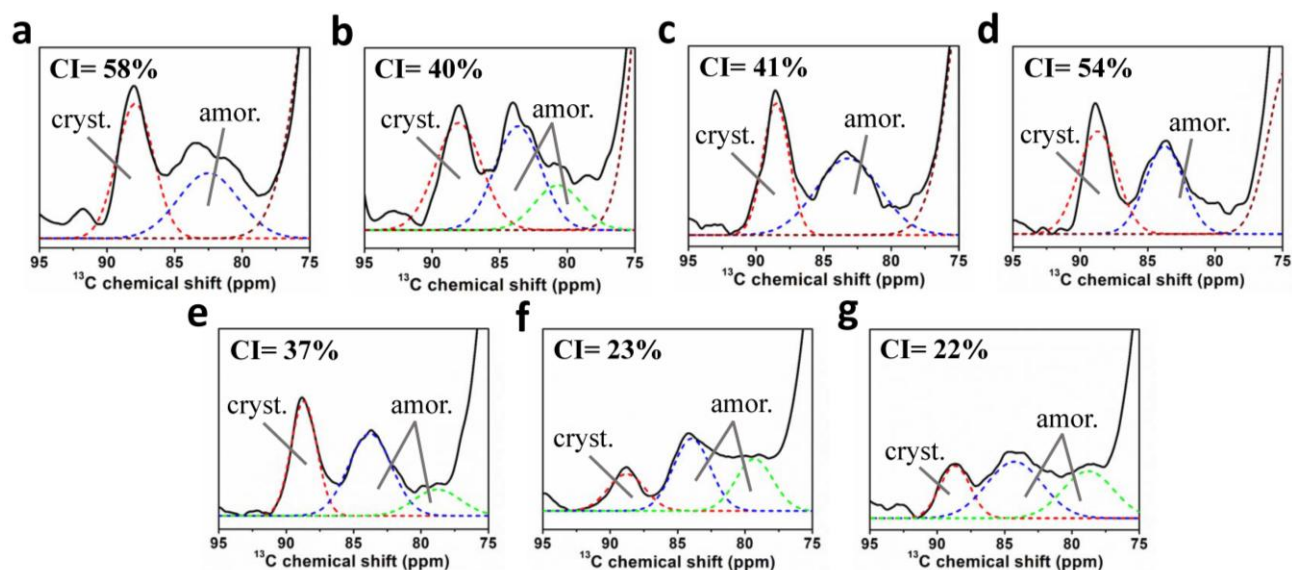


Figure S3. Peak deconvolution for the C4 region of solid-state CP-MAS ^{13}C NMR spectra of (a) microcrystalline cellulose, (b) CNWs-SU $_{1.32}$, (c) CNWs-SU $_{0.98}$, (d) CNWs-SU $_{1.15}$, (e) CNWs-SU $_{1.66}$, (f) CNWs-SH $_{1.57}$, (g) CNWs-SS $_{1.59}$.

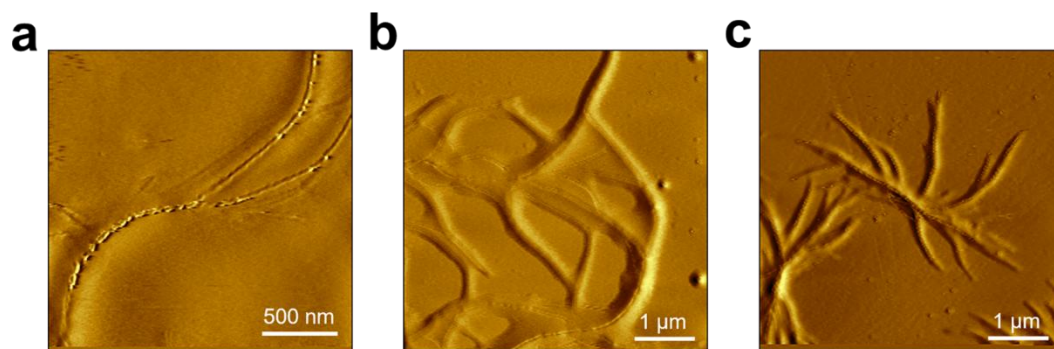


Figure S4. AFM images of (a) PCUE_{1.1}, (b) CUE₃, (c) CSE₃.

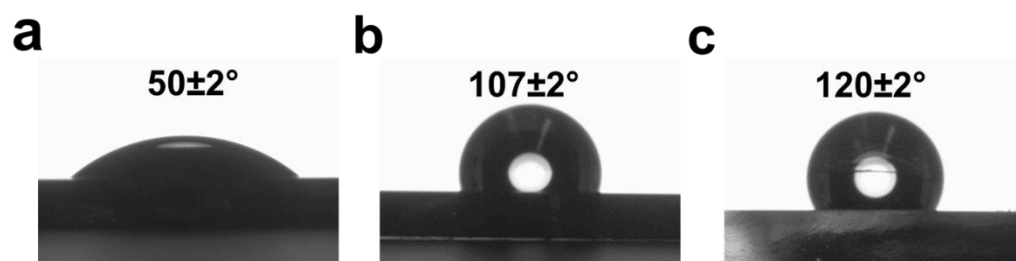


Figure S5. Static water contact angles on the corresponding surfaces. (a) Silicon wafer, (b) silanized silicon wafers with surface-attached (dimethyl)octadecylsilyl groups, (c) PDMS surface.

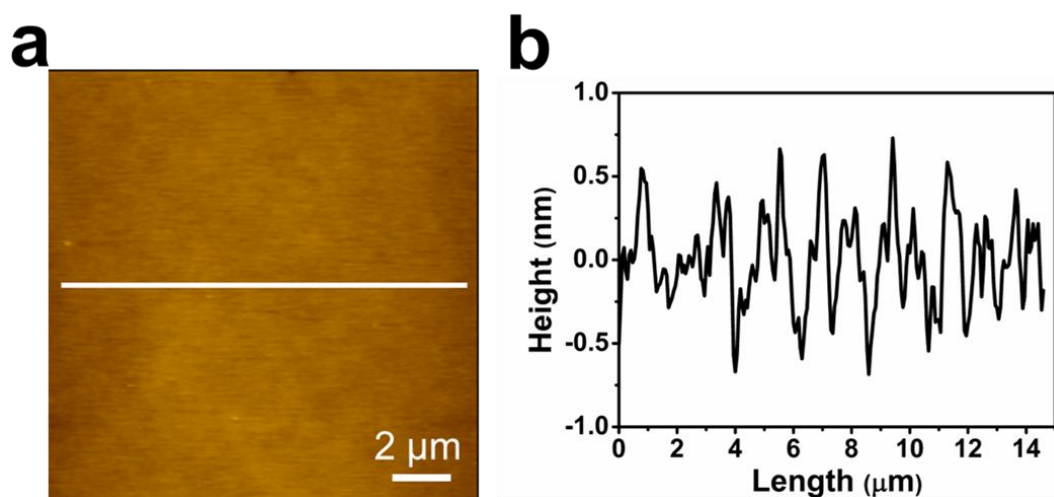


Figure S6. (a) AFM image and (b) corresponding height profile of PDMS surface as shown by the line in (a).

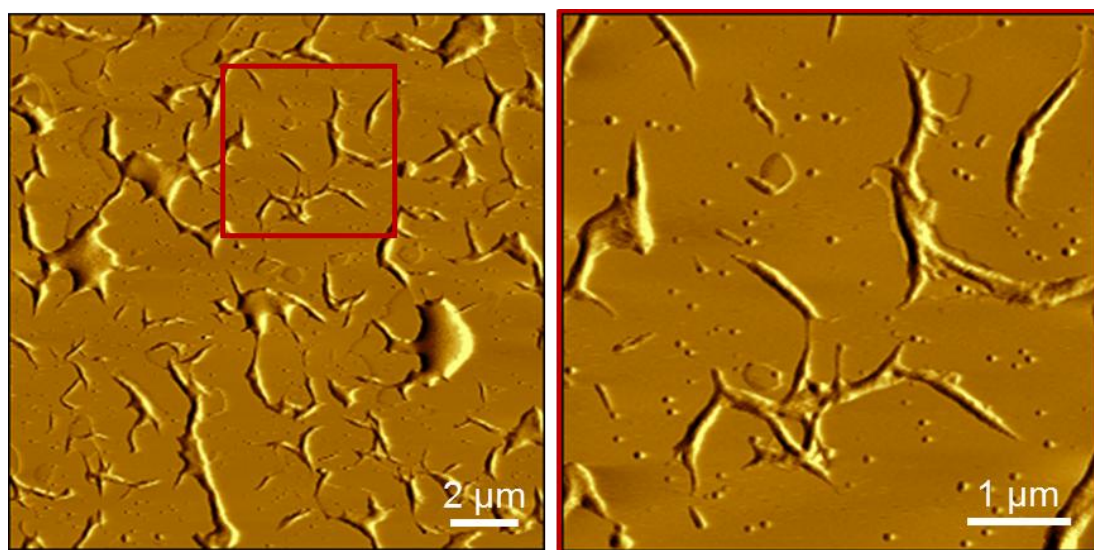


Figure S7. AFM images of dried CNWs-SU_{1.32} on the surface of hydrophobized silicon wafer using their THF suspensions at a concentration of 0.0002 mg/mL with two different magnifications.

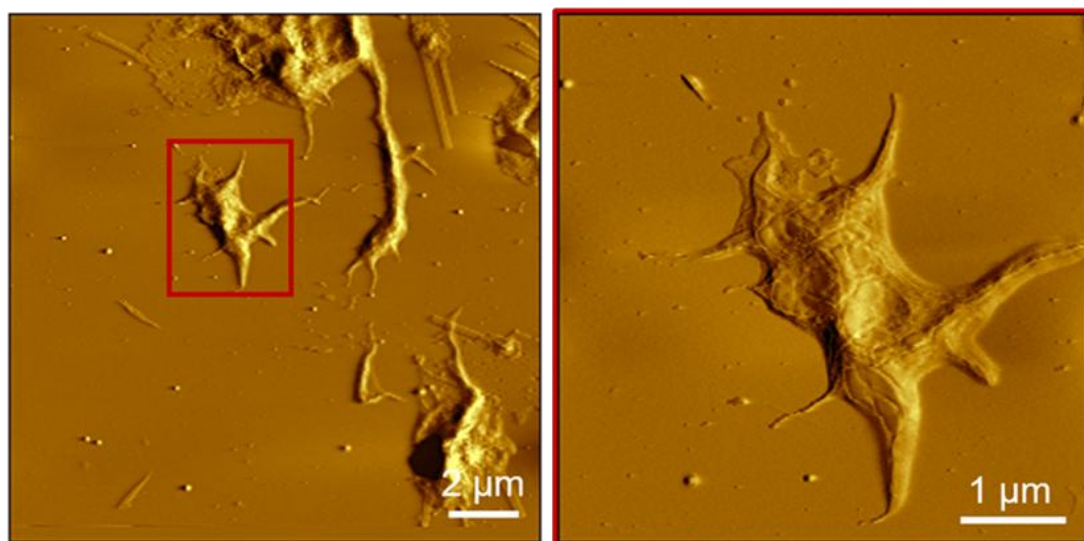


Figure S8. AFM images of dried CNWs-SU_{1.32} on silicon wafer using their toluene suspensions at a concentration of 0.0002 mg/mL with two different magnifications.

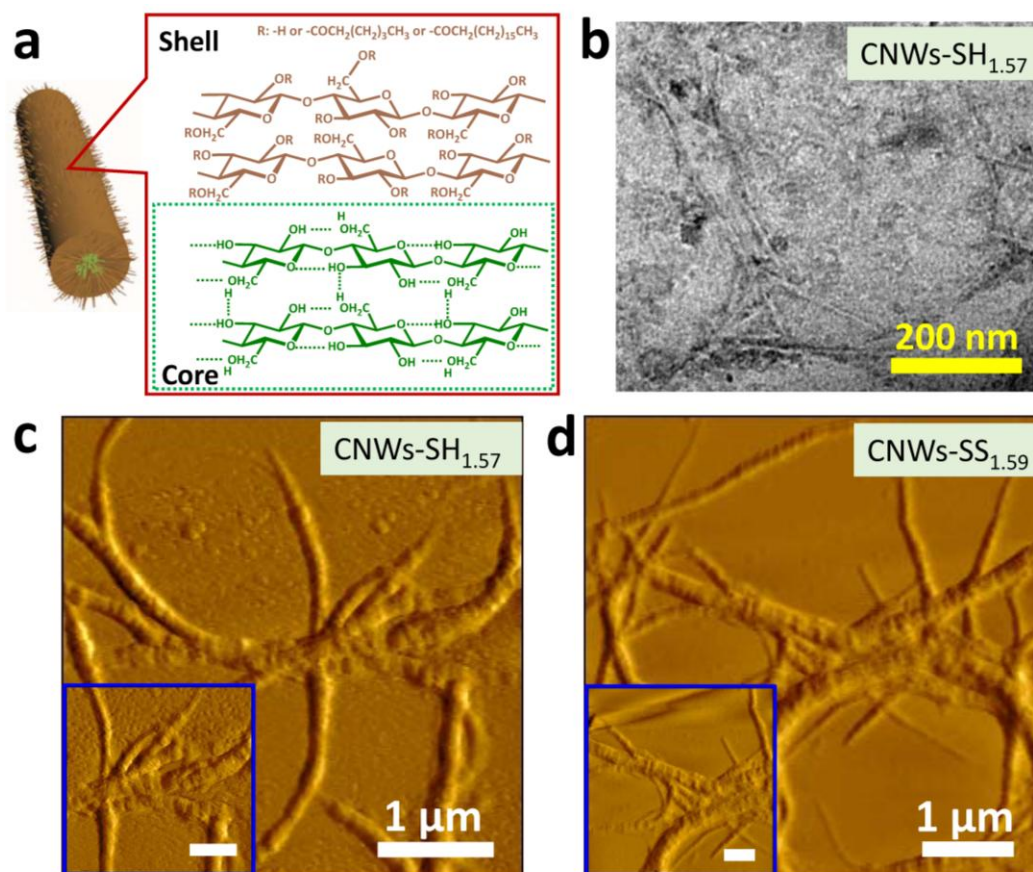


Figure S9. (a) Schematic representation of the surface-attached acyl groups in CNWs-SH_{1.57} and CNWs-SS_{1.59}. (b) A representative TEM image of CNWs-SH_{1.57}. (c) AFM amplitude image of CNWs-SH_{1.57} dried on silicon wafers using its THF suspension at a concentration of 0.0002 mg/mL. The scale bar in the inset is 500 nm. (d) AFM amplitude image of CNWs-SS_{1.59} dried on silicon wafers using its THF suspension at a concentration of 0.0002 mg/mL. The scale bars in the inset are 500 nm.

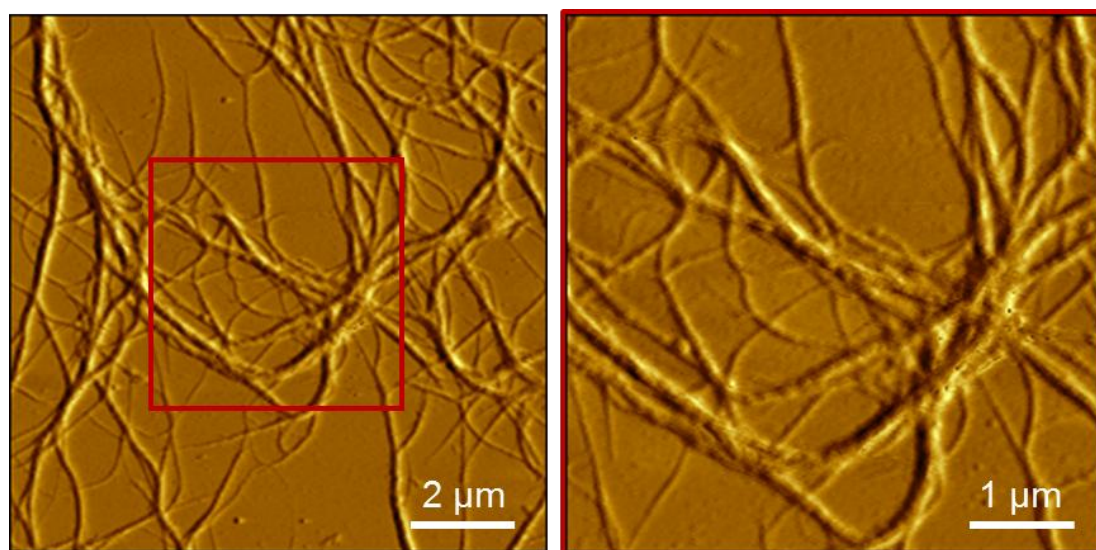


Figure S10. AFM images of dried CNWs-SH_{1.37} on silicon wafer using their THF suspensions at a concentration of 0.0002 mg/mL with two different magnifications.

4 References

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5 Author Contributions

K.Z. conceived the project. H.L. performed synthesis, characterization and self-assembly experiments. B.P. recorded the TEM images. H.L. and R.G. performed and analyzed the AFM measurements. L.A. and R.D. measured NMR spectra. H.L., L.C. and K.Z. discussed and proposed the mechanism. H.L. and K.Z. analyzed the results and all authors contributed to the discussion of the results. H.L. and K.Z. drafted the manuscript and all authors contributed to the writing of the manuscript.