Supporting Information

Fabrication of the Uniaxial Cellulose Nanocrystal Thin Film for Coassembly of Single-Walled Carbon Nanotubes

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EXPERIMENTAL

Materials

Microcrystalline cellulose (MCC) powder and polyethylene glycol (the average M_w at 20000 g·mol^{-1}) were received from Sinopharm Chemical. The concentrated H_2SO_4 (96-98 wt%) was obtained from Xilong Chemical. Ethanol absolute (EtOH) was ordered from Huada Chemical. SWNT aqueous dispersion was bought from XFNANO. All chemical reagents in this study were of analytical grade and used without any further purification unless otherwise stated. Deionized water (18 mΩ·cm-1) was used throughout the work.

Sample Prepartion

Prepration of Cellulose Nanocrystal (CNC) Dispersion: MCC was hydrolyzed in the 64 wt% H_2SO_4 solution (1 g MCC in a volume of 8.75 mL H_2SO_4 solution) at 45°C for 30 min with vigorous mechanical stirring. Afterwards, the reacting mixture was then diluted with 10 volume cold H_2O to quench the hydrolysis and allowed to settle overnight. The supernatant was removed by centrifugation and the thick white suspension was placed inside a dialysis membrane (Spectra/Por 2, MWCO 12000-14000) and dialyzed against slow running DI H_2O for 2-4 d until the pH value remained constant for a period of 1 h. The mixture in the membrane was dispersed by subjecting it to the ultrasound treatment (Qsonica sonicator, Model Q55) for 7 min at 80 % power in an ice bath to avoid overheating. Finally, the aqueous dispersion obtained was filtered through a 0.45 μm Sartorius cellulose acetate membrane and then stored in refrigerator at 4°C. The final aqueous dispersion was approximately 2

wt% based on the gravimetric method (the dispersion was baked at 100°C for 10 h). The dispersion can be concentrated by an osmotic compression process in a dialysis tube (Spectra/Por CE Float-a-Laser, MWCO 1000) in the presence of a 20 wt% PEG 20000 aqueous solution.

Fabrication of the Nematic CNC Thin Films: Prior to use, coverslips various in size and shape were cleaned with acetone and Piranha solution. For fabricaton of the nematic thin films, a volume of 20 μL CNC dispersion various in concentrations was first dropped onto the coverslip 1.2 cm^2 in size. Afterwards, solvent evaporation occurred in the open air at ambient temperature.

Dip-Coating Process: The vertically-aligned coverslip was lifted at a constant rate from the CNC dispersion by using an electric motor. Both the lifting rate and CNC concentration are tunable to achieve CNC thin films bearing distinct forms under the polarizer. The temperature and humidity were 40-60 % and 25±1°C, respectively.

Fabrication of SWNTs thin films: A dispersion composed of 0.3 wt% SWNTs and 4 wt% CNC was used for the dip-coating process. The lifting rate was optimised at 0.5 mm/s to achieve the uniaxial SWNT-CNC hybrid thin film. Afterwards, the hybrids thin film was put into a tubular resistance furnace and gradually heated up to 400°C. The temperature was kept at 400°C for 1h to decompose organic ingredients to obtain the SWNT thin film.

Characterization

Polarized optical microscopy images were performed on an Olympus BX53 polarizing microscope equipped with a charge-coupled device (CCD) camera (Nikon

DXM1200). The atomic force microscope (AFM, DI Multimode, Veeco Inc., the tapping mode) was used to image topographic information of CNC thin films. The transmission electron microscopy (TEM, JEM-2100, 200 kV) was used to detect the morphology and size of CNCs. Polarized Raman spectra were measured using a LabRAM HR Evolution Raman microscope in the back-scattering mode, with an excitation wavelength of 532 nm and a spot size of ~1 μm^2. The polarization of the light was switched between parallel and perpendicular to the film by means of a $\lambda/2$ plate.

Caculation of the nematic order parameter

The nematic order parameter S is defined as

$$S = \frac{d \cdot \langle \cos^2 \theta \rangle - 1}{d - 1}, \quad (1)$$

where d is the dimensionality of the system, and θ is the angle between the director and the axis of particles.[1]

In 2D systems, d equals to 2, hence,

$$S = 2\langle \cos^2 \theta \rangle - 1, \quad (2)$$

the average orientation angle, $<cos^2\theta>$, is given by

$$\langle \cos^2 \theta \rangle = \frac{\sum_{i=1}^{N_{CNC}} \cos^2 \theta_i}{N_{CNC}}, \quad (3)$$

where N_{CNC} is the total number of counted CNCs, θ is the angle between the long axis of CNCs and the lifting direction.

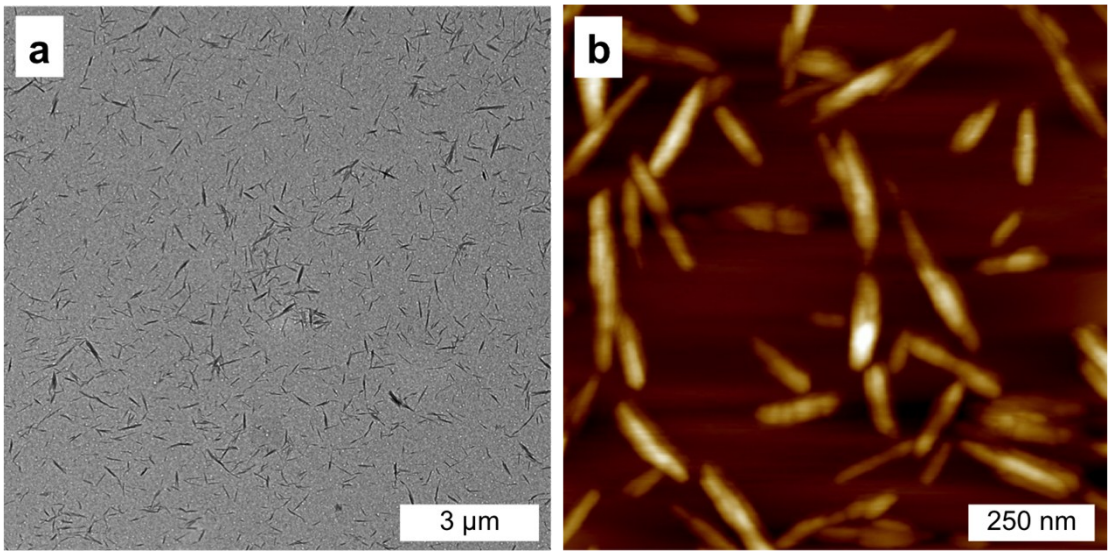

Figure s1. Transmission electron microscopy (a) and atomic force microscopy (b) images of CNCs used in the current study.

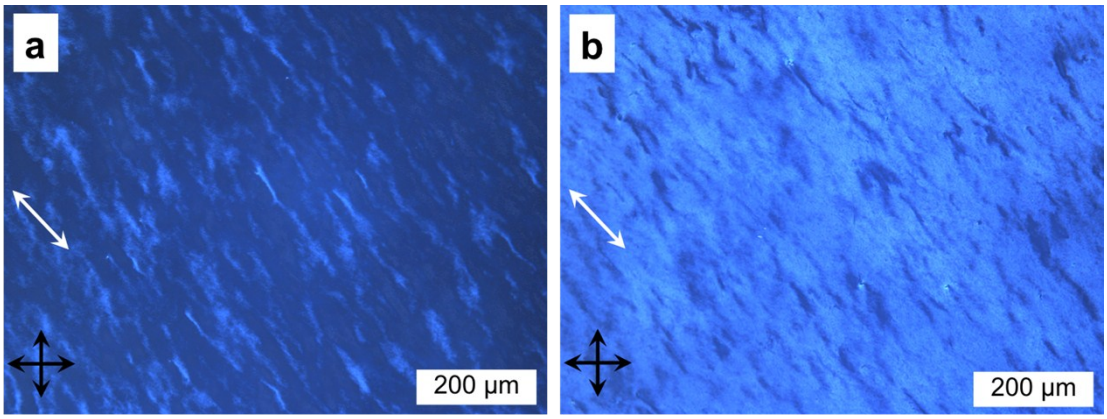

Figure s2. POM images of partially-aligned CNC thin films. The lifting rates were 10 (**a**) and 40 (**b**) mm/min. The white arrow in each image points to the lifting direction in a dip-coating process. The black crossed arrows show the polarization direction.

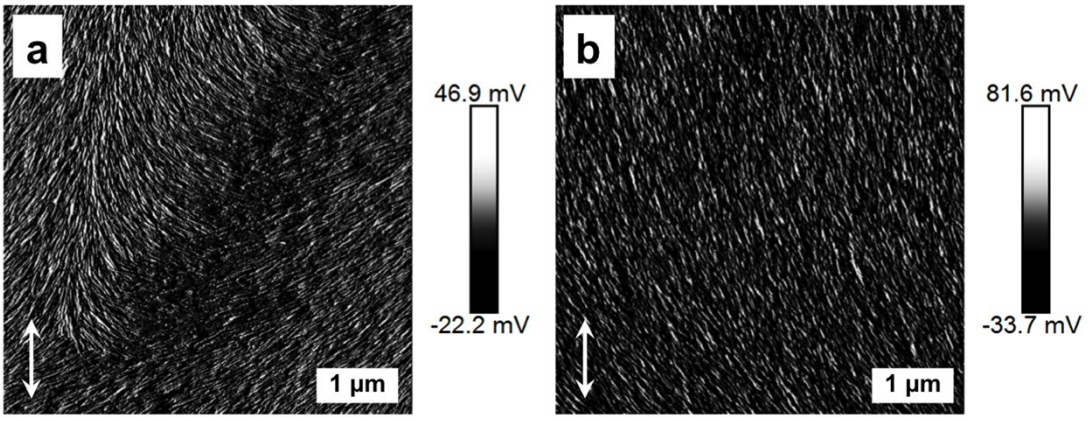

Figure s3. AFM images (the Amplitude mode) of partially-aligned CNC thin films. The lifting rates were 10 (**a**) and 40 (**b**) mm/min. The white arrow in each image points to the lifting direction in a dip-coating process.

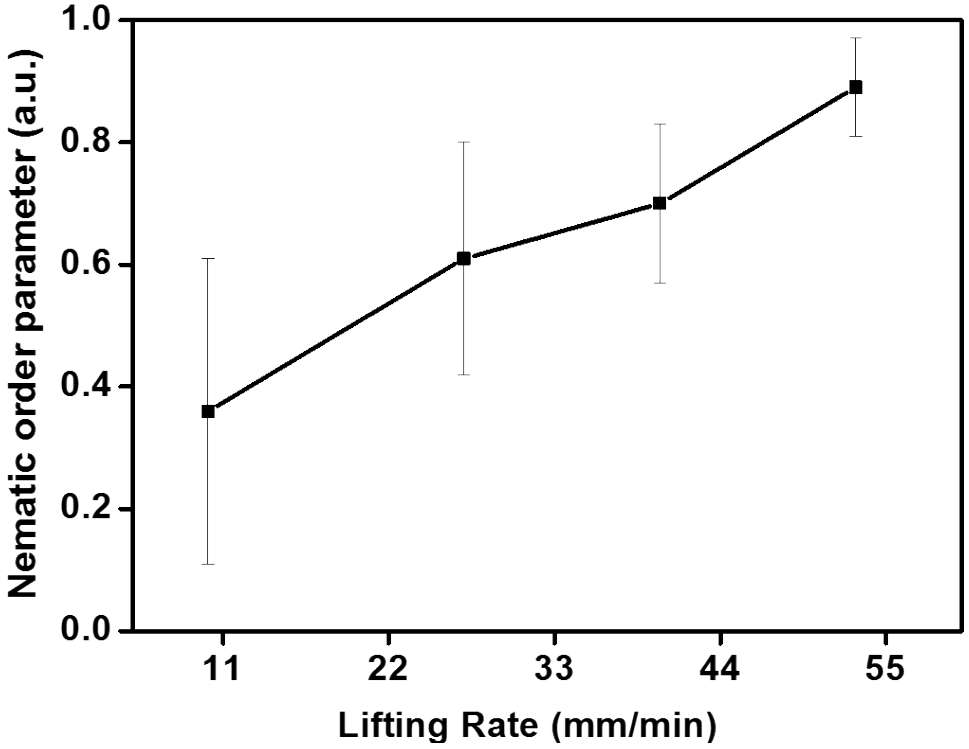

Figure s4. Curve showing lifting rate plotted against the 2D nematic order parameter.

At least three AFM images were analyzed to achieve the average values.

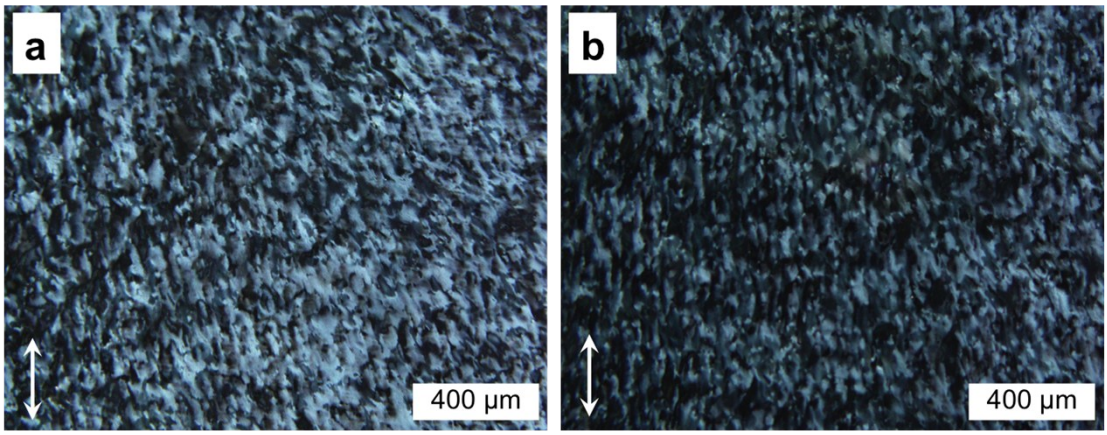

Figure s5. POM images of CNC thin films obtained with the high lifting rates at 70 (a) and 93 mm/min (b), respectively. The CNC concentration in the dispersion phase was 0.046 g/mL. The white arrows point to the lifting direction in a dip-coating process.

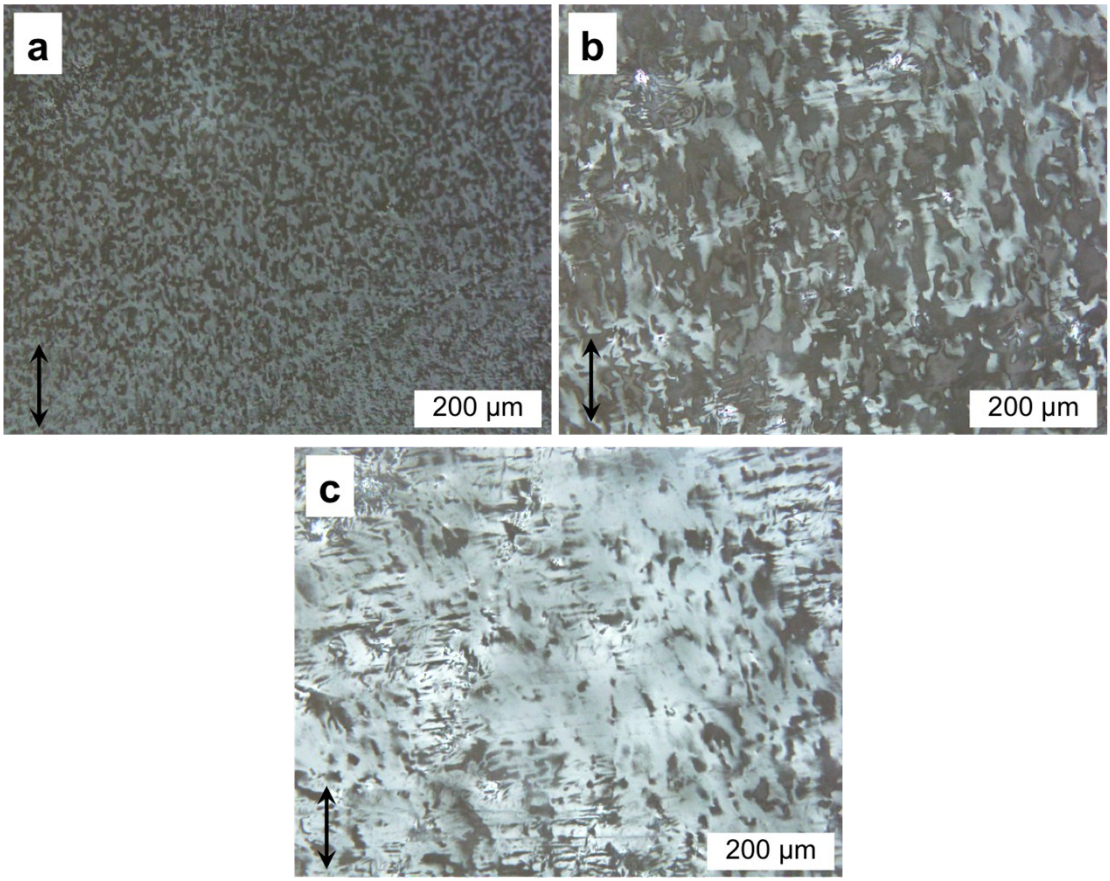

Figure s6. POM images of the CNC thin films obtained using different CNC concentrations at 0.015 (a), 0.035 (b), 0.040 (c) g/mL, respectively, in a dip-coating process. The lifting rate was 53 mm/min was used. The black arrows point to the lifting direction in a dip-coating process.

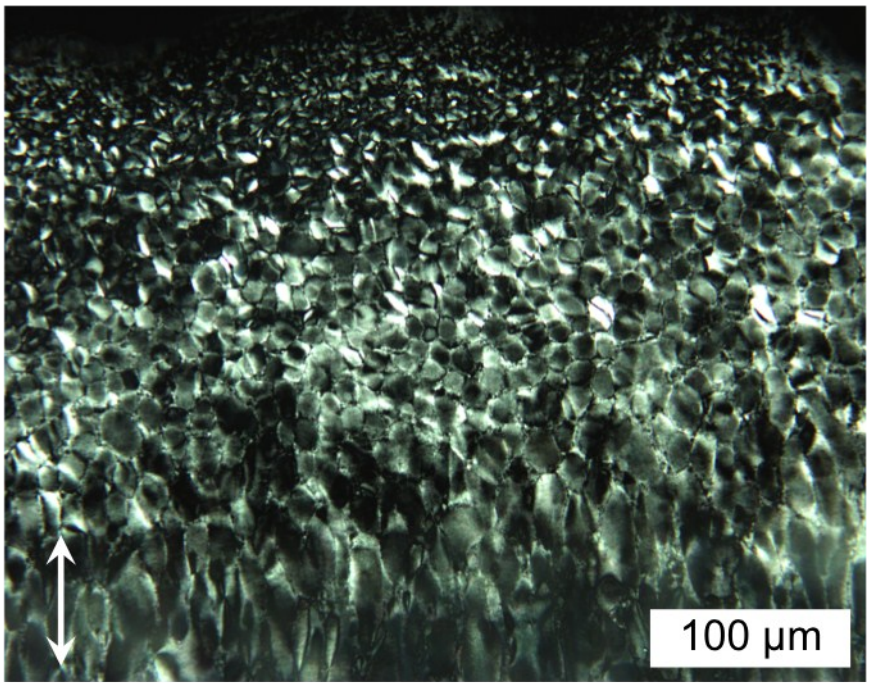

Figure s7. POM image of the initially formed area shows the structural transformation from being nematic to uniaxial. The lifting rate and [CNC] were at 53 mm/min and 0.046 g/mL, respectively. The white arrows point to the lifting direction in a dip-coating process.

Notes and references

1. A. A. Mercurieva and T. M. Birshtein, *Makromolekulare Chemie-Theory and Simulations*, 1992, **1**, 205-214.