

Supporting Information

Regulating surface sulfonation on cellulose nanocrystals and self-assembly behaviors

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Experimental Section

Materials. Whatman filter paper (No. 1) was used as the source of native cellulose. Hydrochloric acid (HCl, 37%), isopropyl alcohol (C₃H₈O, 99.5%), sodium vinyl sulfonate solution (SVS, 25% in H₂O), sodium hydroxide (NaOH, 96%), acetic acid (CH₃COOH, 99.7%) and ethanol (C₂H₅OH, 99.7%) were supplied by Aladdin corporation and used without any purification. Pre-distilled water was used during the entire experiment.

Preparation of cellulose nanocrystals by hydrochloric acid hydrolysis. The hydrochloric acid hydrolysis was performed on native cellulose to obtain the crystalline nanoparticles.¹ Briefly, the diluted hydrochloric acid (245 mL, 4 N) was poured in a round bottom flask containing the shredded Whatman filter paper (7 g), and immersed in a preheated oil bath to 80 °C under mechanical stirring for 4 h. After hydrolysis, the suspension was transferred into a beaker containing sufficient ice water to quench the reaction, then purified by successive centrifugation (8000 rpm) and washed for three times. The product was filtered on a Nylon filtration fabric to remove the large particles and dialyzed against distilled water for 5 days to remove any residual acid. The powder from the aqueous suspension of cellulose nanocrystals was obtained after freeze-drying, denoted as pristine CNC and used for further characterizations.

Graded sulfonation of CNC by sodium vinyl sulfonate (SVS). The surface modification of CNC with various degrees of sulfonation was achieved based on the conjugate addition reaction with SVS.² The freeze-dried CNC (1 g) was redispersed in 2-propanol (100 mL), followed by sonication using a Branson Sonifier at 150 W for 3 min (3 cycles) in an ice bath. The desired amount of the SVS solution (25% w/w) was added into the CNC suspension under magnetic stirring for 20 min at room temperature. The NaOH powder (1: 10 v/w to the added SVS) was then introduced in the mixture with continuous stirring for 1 h, followed by a flow of the nitrogen gas into the system for 15 min. The system was sealed and the reaction continued at 80 °C

for 5 h. After the reaction, the suspension was centrifuged at 8000 rpm for 5 min to remove the solvent in order to collect the modified nanocrystals' suspension, which was redispersed in water and neutralized by the addition of acetic acid followed by precipitation in ethanol. The purification was performed by three series of centrifugation and washing with ethanol/water mixture (80/20, v/v). The product was redispersed again in water (100 mL) by sonication and dialyzed for 3 days against the water to further remove any residual reagents. The sulfonated CNC products were obtained in the aqueous suspensions, and freeze-dried to obtain the powder samples with the code of CNC-SVS.

Preparation of self-assembly films based on surface-sulfonated nanocrystals.

Solid films based on the self-assembly of CNC and CNC-SVS were prepared by the solvent-evaporation casting method.³ Typically, the aqueous suspension of CNC or CNC-SVS (1 wt%) was previously subjected to ultrasound treatment for 10 min at 150 W in an ice bath to avoid superfluous heating. The suspension (10 mL) was carefully poured in a glass Petri dish (53 mm in diameter) and transferred into an oven at 25 °C for 4 days to allow the slow evaporation for the self-assembly of nanocrystals. As a result, the solid cellulose nanocrystal-based films were obtained.

Characterizations.

Proofs of surface modification of cellulose nanocrystals. The freeze-dried CNC or CNC-SVS powder was mixed with anhydrous KBr, and then compressed as pellet sample for Fourier transform infrared spectroscopy (FTIR) analysis with a iS5 spectrometer (Nicolet, Madison, U.S.A) in the range of 4000-400 cm^{-1} with a 2 cm^{-1} resolution and an accumulation of 32 scans. Raman spectra were recorded on a Renishaw Invia Reflex Confocal Micro-Raman spectrometer with an excitation line of 785 nm as the Raman scattering excite. The Raman spectra were acquired in the range of 2000-250 cm^{-1} with a total scan number of 3 using the WIRE 3.4 software. The elemental change of the cellulose nanocrystals before and after modifications was investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi

spectrometer, Thermo Fisher Scientific, U.S.A) and elemental analysis (EA, Vario EL cube elemental analyzer, Elementar Analysensysteme GmbH). The XPS experiments were carried out with a monochromated Al K α X-ray source and operated at 15 kV under a current of 10 mA. Sensitive factors were provided by testing organization to calculate elemental concentration. Before the characterization, the samples were vacuum-dried treatment to remove the surface moisture and the percentage content of sulfur and carbon elements in both pristine and modified nanocrystals was determined. The degree of surface substitution ($DS_{surface}\%$) for the CNC-SVS samples was calculated according to the following equation:

$$DS_{surface}\% = \left(\frac{S\% \times 1000}{32}\right) / 1.554 \quad (1)$$

where, S% represents the sulfur content obtained from the EA results; 32 g/mol is the atomic mass of sulfur and 1.554 mmol/g is the amount of surface hydroxyl groups (-OH) per gram of cellulose nanocrystal according to our previous study.⁴

Investigation of cellulose nanocrystals before and after modification. The influence of gradiented modification on the crystalline structure of cellulose nanocrystals was analyzed by a D8 advanced X-ray diffractometer (XRD, Bruker, Germany) operated at 30 kV and 20 mA with Cu K α radiation ($\lambda = 0.154$ nm) in the 2θ range of 5-45 $^\circ$ using a fixed time mode with a step interval of 0.02 $^\circ$. The classical Segal equation was used to calculate the crystallinity index (χ_c) for all the samples.⁵ The morphology of cellulose nanocrystals was observed by transmission electron microscopy (TEM) on a Tecnai G2 F30 instrument (FEI, USA) at 300 kV. Before observation, one drop of the diluted suspension containing 0.1 wt% cellulose nanocrystals was placed on a carbon-coated grid, and negatively stained with uranyl acetate solution (0.1 wt%). The surface charge (ζ -potential) of cellulose nanocrystals was analyzed with a Malvern Zetasizer Nano ZS (Malvern Instrument Co., U.K.). The concentration of all the samples was diluted as 0.01 wt%, and the suspension was submitted to a sonication treatment for 5 min before the analysis. The surface hydrophilicity of cellulose nanocrystals was investigated by contact angle measurement. After vacuuming

treatment to remove the surface moisture of CNC and CNC-SVS samples, the powder was compressed to form thin pellet under 20 MPa. The images of water contact angles were captured by a contact angle goniometer (POWEREACH, China) with one drop of water on the sample at room temperature. All the measurements were performed three times.

Self-assembly behavior and solid films based on cellulose nanocrystals. The birefringence behavior is a typical phenomenon for the dispersion of rod-like cellulose nanocrystals, which was observed between two crossed polarizers under continuous magnetic stirring. All the suspensions contained 0.5 wt% cellulose nanocrystals in water, and were subjected to sonication for 5 min before the observation. The self-assembly behavior of cellulose nanocrystals in the suspension was further investigated by polarized optical microscopy (POM, XP-620, China). Briefly, the aqueous suspension (3 wt%) was ultra-sonicated for 5 min and then left for 7 days in the refrigerator at 4 °C to allow separation between the upper and lower phases. The lower anisotropic phase of the suspension was collected with a thin capillary tube, and placed on a glass slide for POM observation. The light transmittance ratio of cellulose nanocrystals-based solid films was measured by an ultraviolet spectrophotometer (UV-2600, Japan) in the wavelength range 200-800 nm. The self-assembly behavior and microstructure of cellulose nanocrystals in the solid films were observed by scanning electron microscopy (SEM, Hitachi S-4800 instrument, Japan) at an acceleration voltage of 10 kV. The films were cryo-fractured in liquid nitrogen and coated with gold using a sputter coater before observation. The half-pitch size ($P/2$) of the self-assembled structure in the film was defined as the distance between two adjacent planar patterns in the SEM images, which was measured by the Nanomeasure software.

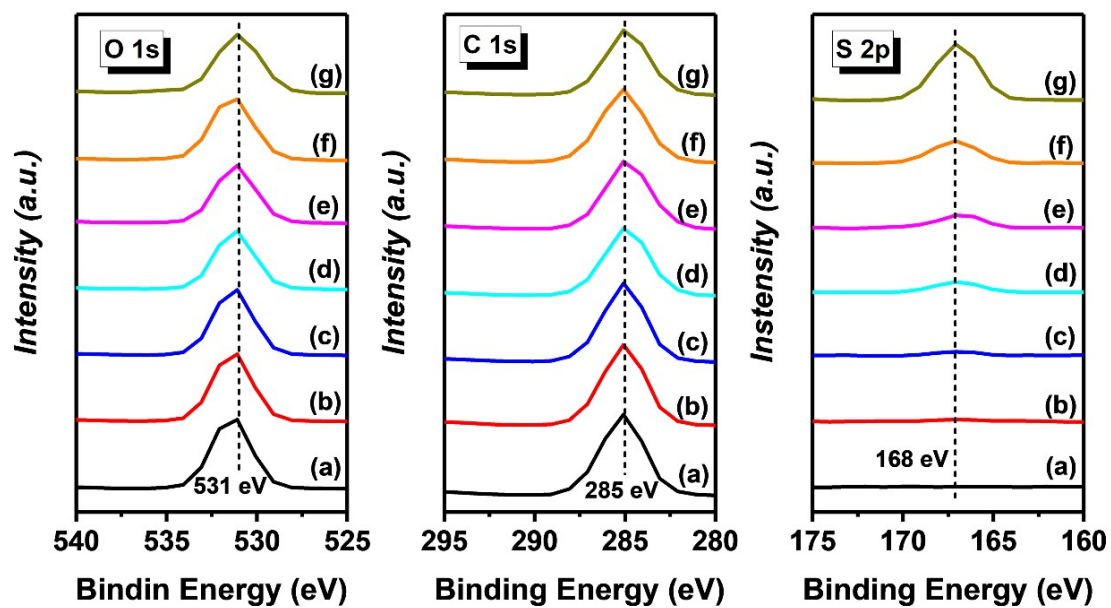


Figure S1. High resolution XPS of O 1s, C 1s and S 2p spectra for CNCs before and after modification: (a) CNC, (b) CNC-SVS1, (c) CNC-SVS2, (d) CNC-SVS3, (e) CNC-SVS4, (f) CNC-SVS5, (g) CNC-SVS6.

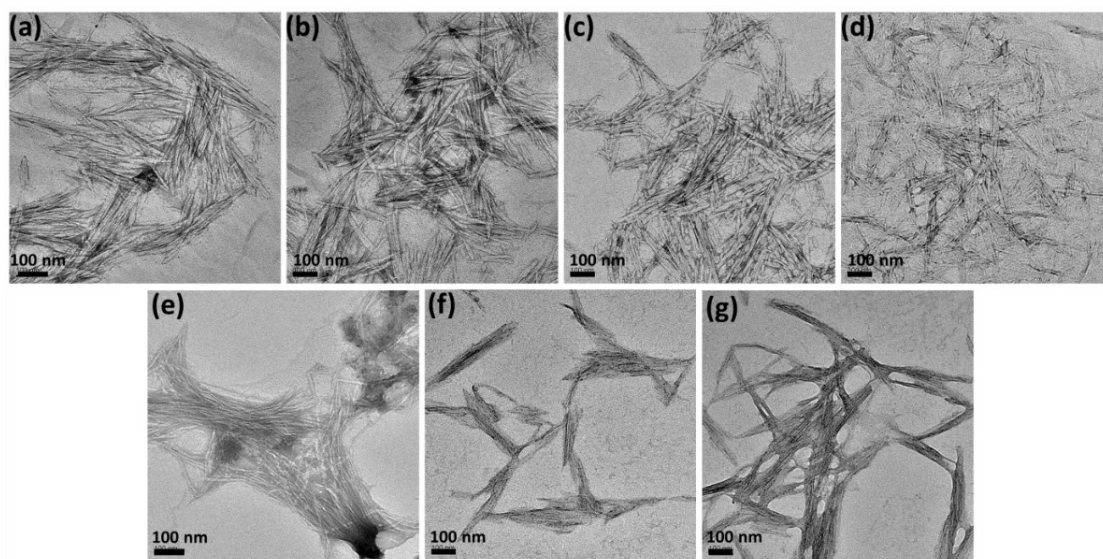


Figure S2. TEM images for cellulose nanocrystals before and after modification: (a) CNC, (b) CNC-SVS1, (c) CNC-SVS2, (d) CNC-SVS3, (e) CNC-SVS4, (f) CNC-SVS5 and (g) CNC-SVS6.

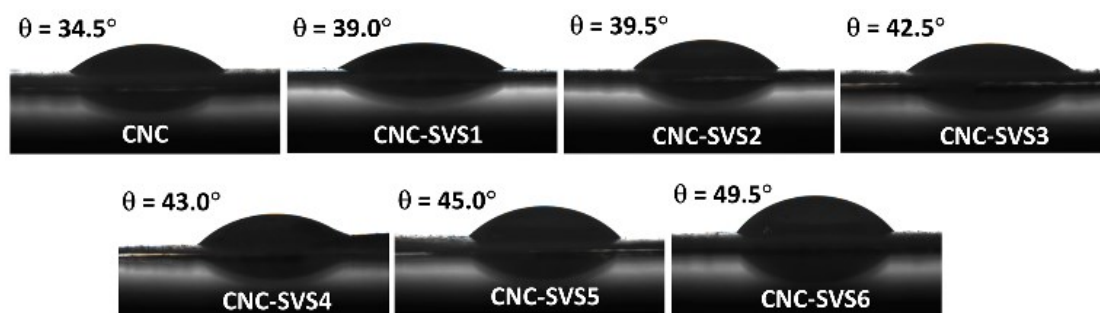


Figure S3. Water contact angle for CNC and CNC-SVS products.

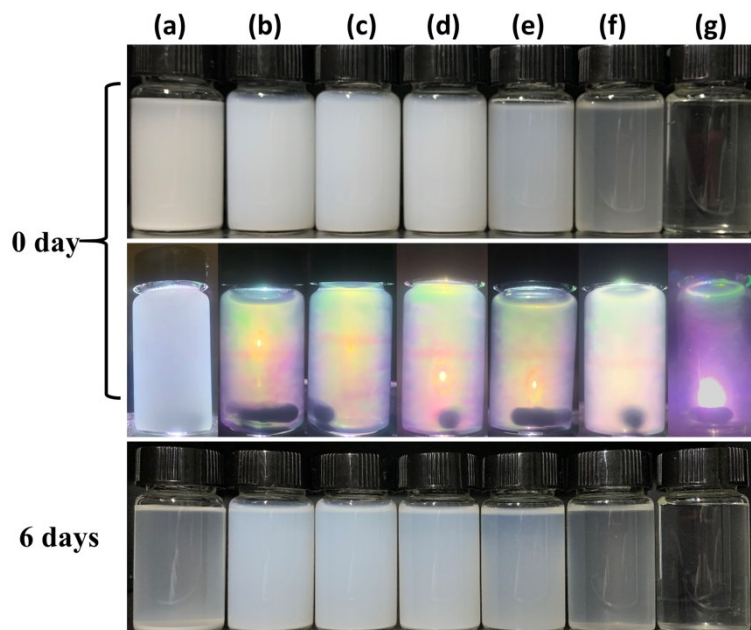


Figure S4. Birefringence observation (under two crossed polarizers) and dispersion stability (under natural light) over 6 days for cellulose nanocrystals before and after modification (0.5 wt% for all samples): (a) CNC, (b) CNC-SVS1, (c) CNC-SVS2, (d) CNC-SVS3, (e) CNC-SVS4, (f) CNC-SVS5, (g) CNC-SVS6.

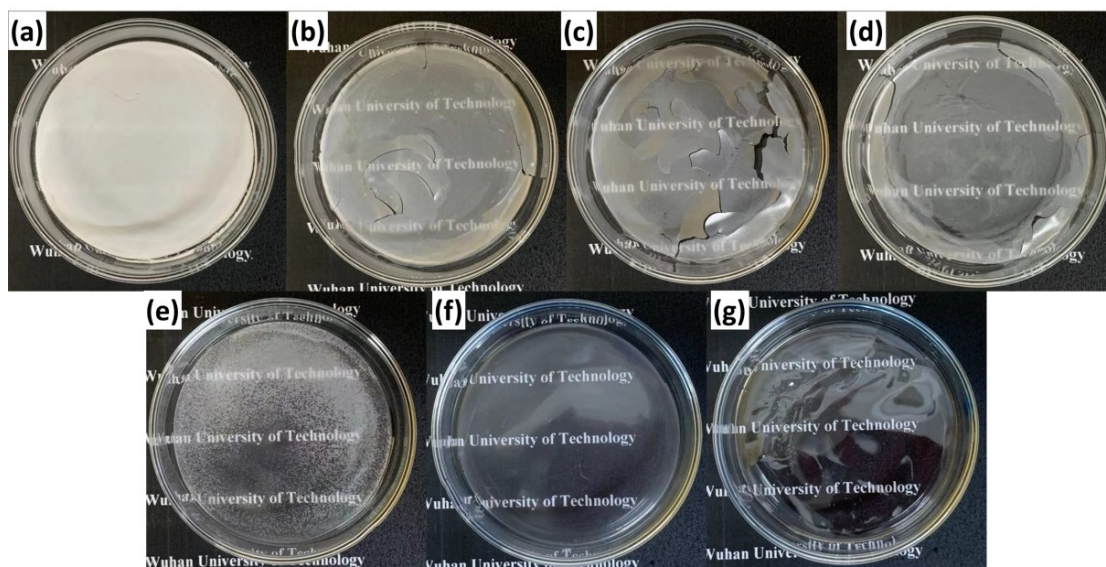


Figure S5. Digital photos showing the appearance of fabricated self-assembled films (the white words “Wuhan University of Technology” as the background under the glass): (a) CNC, (b) CNC-SVS1, (c) CNC-SVS2, (d) CNC-SVS3, (e) CNC-SVS4, (f) CNC-SVS5 and (g) CNC-SVS6.

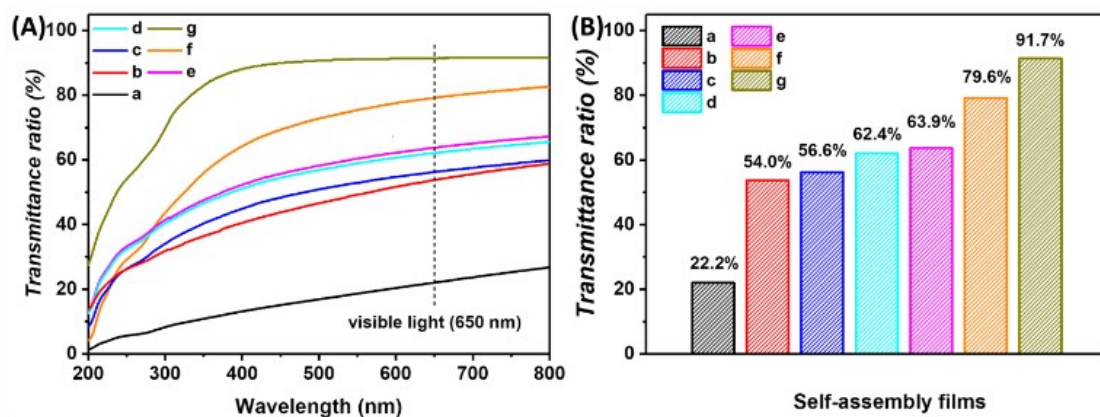


Figure S6 (A) UV broad spectra for the self-assembled films and (B) UV transmittance ratio of the self-assembled films at a wavelength of 650 nm: (a) CNC, (b) CNC-SVS1, (c) CNC-SVS2, (d) CNC-SVS3, (e) CNC-SVS4, (f) CNC-SVS5 and (g) CNC-SVS6.

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