Supporting Information

Effects of NaOH Addition on Cellulose Nanocrystal Functionalization with 2,4-Dichlorophenoxyacetic Acid

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Methods for the Characterization of Feedstock CNC

Sulfate Half-Ester

CNC was diluted to 1 wt% with ultra-pure water then dialyzed (Spectra/Por 4, 12-14 kDa cutoff) for five days; the water being exchanged every 24 hours. An ion exchange column was set up using a strong acid cation exchange resin. Forty grams of resin were placed in an exchange column and washed with 1 L of ultra-pure water. 150 mg of protonated CNC was then further diluted in ultra-pure water until 200 mL was reached. To increase the initial conductivity of the diluted protonated CNC, 2 mL of 0.1 M NaCl solution was added. Then the obtained suspensions were titrated with 10 mM NaOH using titrator system sympHony B20PCI (VWR, Radnor, PA) to determine the equivalence point (**Table S1 and Figure S1**).

Charge Density

CNC was diluted to 0.5 wt% in ultra-pure water, and 25 mL p-DADMAC (0.001 N) was added to 15 mL of dispersion. The mixture was homogenized and centrifuged to separate any aggregates. 10 mL supernatant was collected and titrated against 0.001 N PVSK using a Chemtrac Laboratory Charge Analyzer (Chemtrac Inc., Norcross, GA).

Zeta Potential

Feedstock CNC was diluted to 0.25 wt% and bottle-rolled overnight prior to zeta potential analysis. CNC was then analyzed on a Zetasizer Nano ZS (Malvern Panalytical, Malvern, UK).

Thermogravimetric Analysis

TGA was conducted as described in the main text. Thermal degradation temperature was measured based on 5 % mass loss after an isothermal hold at 120 °C.

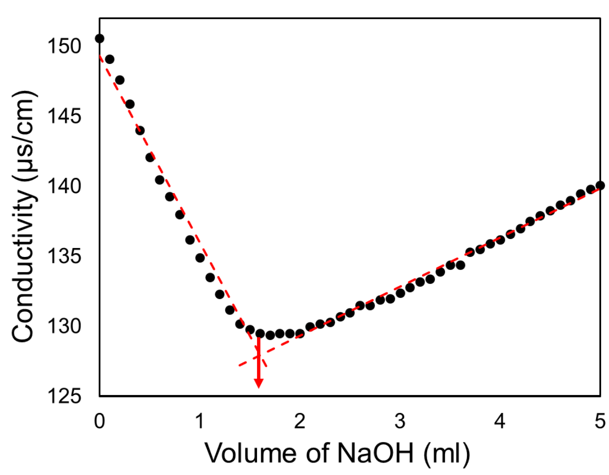
Atomic Force Microscopy

Tapping-mode atomic force microscopy (AFM) was performed on an Anton Paar Tosca 400 to acquire CNC size. Samples were prepared by first drop casting 20 µL of poly-L-lysine solution onto cleaved mica and allowing the solution to sit for two minutes before rinsing with ultra-pure water. Next, 20 µL of the solution of interest was drop cast onto the cationic mica wafer, allowed to sit for two minutes, and rinsed. Scans were performed with a resolution of 950-1000, scan rate of 0.2 lines/min, and processed with Gwyddion data analysis software (version 2.62) to level the obtained data and apply tip deconvolution. Dimensions were obtained for a minimum of 100 nanocrystals to get an average size of CNC.

Supplementary Table S1. Values from Characterization of Feedstock CNC.

Aspect Ratio	pH	Conductivity (µS/cm)	Charge Density (µeq/dry g)	Sulfur Percentage	Zeta Potential (mV)	Thermal Degradation Temperature (°C)
57 ± 20	6.7 ± 0.03	873 ± 1.8	424 ± 17	0.6%	-28.1 ± 0.71	239 ± 2.2

Uncertainty is the standard error for a minimum of three runs.



Supplementary Figure S1: Stock CNC sulfate half ester determination by conductometric titration via the standard testing method by the International Organization for Standardization. The equivalence point was found at 2.6 mL NaOH, and the sulfur content was calculated to be 0.6 %.

Model Fits for Rheological Data

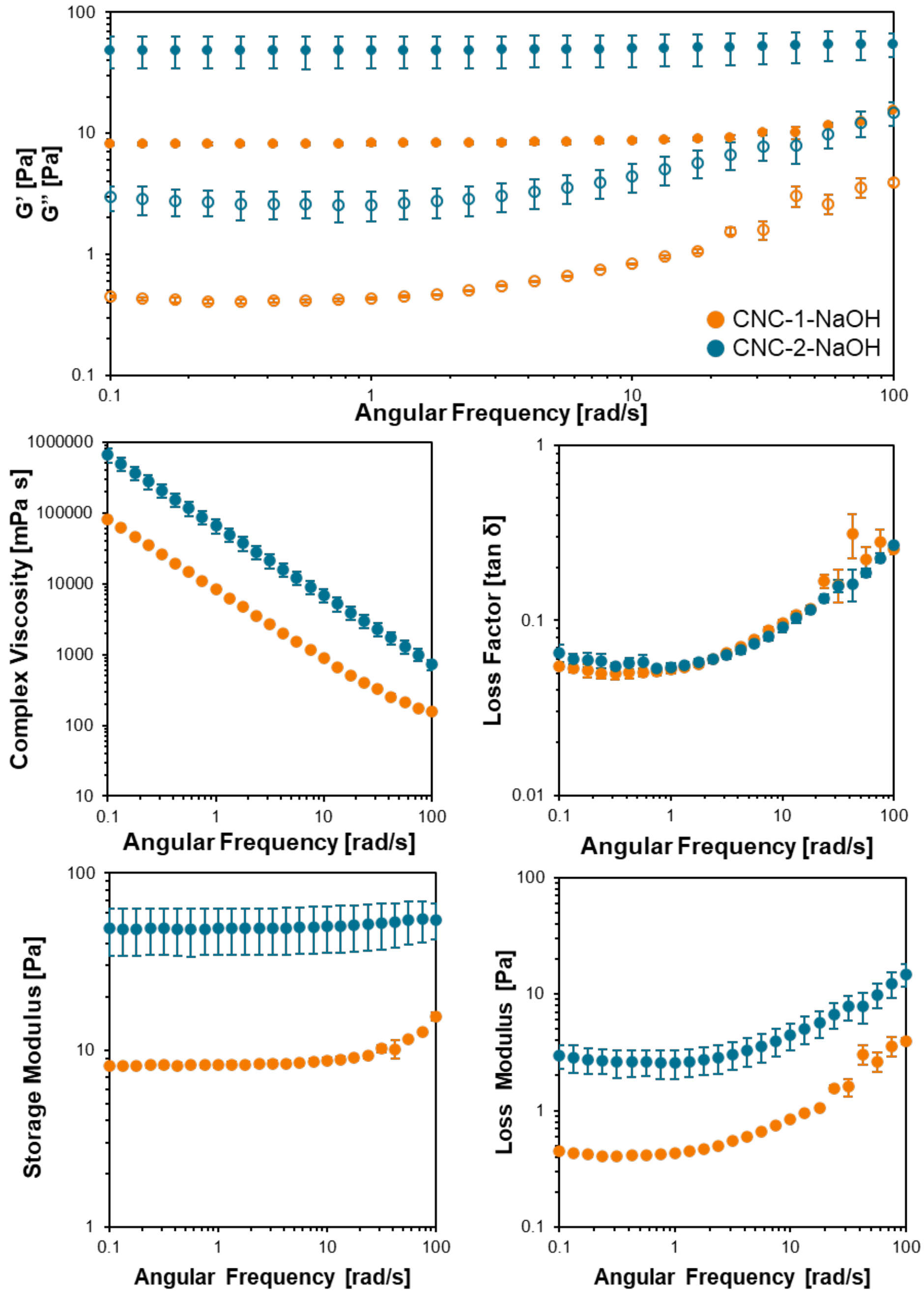
$$\eta = K(\dot{\gamma})^{n-1} \qquad \textbf{(Equation S1)}$$

K = Flow Consistency Index [mPa s], η = Viscosity [mPa s], n= Power Law Index, $\dot{\gamma}$= Shear Rate [1/s]

Supplementary Table S2. Power Law Model Parameters for Initial CNC Dispersions.

	K (mPa s)	**n**
CNC-1	8.36	0.92
CNC-1-NaOH Low Shear	58.05	0.29
CNC-2-NaOH High Shear	144.25	0.44
CNC-2	83.17	0.70
CNC-2-NaOH Low Shear	481.50	0.26
CNC-2-NaOH High Shear	3083	0.10

Viscoelastic Behavior of CNC-1-NaOH and CNC-2-NaOH



Supplementary Figure S2. (a) Repeated amplitude sweeps of three loads of CNC-1-NaOH (orange circle) and CNC-2-NaOH (blue circle). Solid symbols represent G' and hollow symbols represent G". (b) Complex viscosity of CNC-1-NaOH and CNC-2-NaOH, (c) loss factor of CNC-1-NaOH and CNC-2-NaOH, (d) storage moduli of CNC-1-NaOH and CNC-2-NaOH dispersions, and (e) loss moduli of CNC-1-NaOH and CNC-2-NaOH dispersions. Legend entire Figure is the same as Figure S2a. All error bars represent the standard error of three runs.