Electronic supplementary information for *"Nanoengineering colloidal and polymeric celluloses for threshold scale inhibition: towards universal biomass-based crystal modification"*

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This Supporting Information includes Materials and methods and 3 figures.

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Materials and methods

Materials

Q-90 softwood kraft pulp sheets and conventional cellulose nanocrystal (CNC) powder (prepared by sulfuric acid treatment) were provided by FPInnovations (Pointe-Claire, Canada), and nanofibrillated cellulose (NFC, 1.2 mmol/g COONa, length ~ 500 nm, width ~ 5 nm, prepared from TEMPO-mediated oxidation) was provided by Forest Products Laboratory (Madison, WI, USA). Cellulose, sourced from black spruce Q-90 bleached softwood kraft pulp sheets was used to synthesize hairy nanocelluloses (HNC). Sodium hydroxide (NaOH, ACS reagent, ≥97%), sodium (meta)periodate ($NaIO_4$, ≥99.99%), sodium chloride (NaCl, ACS reagent, ≥99%), ethylene glycol ($C_2H_6O_2$, 99%), sodium chlorite ($NaClO_2$, 80%), 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO, 98%), and sodium carboxymethyl cellulose (NaCMC, M_w ~ 90 kDa with unit molecular mass ~ 146.16 + 97.03 DS, where the degree of substitution DS = 0.7) were purchased from Sigma-Aldrich, Canada, and used without purification. Hydrochloric acid (HCl, 36.5-38%) was supplied by ACP Chemicals (Canada), and hydrogen peroxide (H_2O_2, 30%), 2-propanol (C_3H_7OH, 99.9%), and anhydrous ethanol (C_2H_5OH, 95.27%) were provided by Fisher Scientific, Canada. Conventional cellulose nanocrystals (CNC) suspensions were prepared by dispersing freeze-dried CNC (0.96 wt% sulfur on dry CNC, FPInnovations, Pointe-Claire, Canada) in milli-Q water under ambient conditions (electrical resistivity $\rho = 18.2$ MΩ cm, Millipore Milli-Q purification system) followed by at least 24 h vigorous magnetic stirring (TEM length ~ 100 - 150 nm and width ~ 5 - 10 nm, ζ-potential ~ -30 mV at no added salt and neutral pH). Calcium chloride dihydrate ($CaCl_2.2H_2O$, certified ACS, Fisher scientific, Canada) and sodium bicarbonate ($NaHCO_3$, ACP Chemicals, Canada) were used for preparing the saturated calcium carbonate solutions. Industrial antiscalant KemGuard 269 was kindly provided by Kemira.

Methods

Dialdehyde modified cellulose (DAMC) synthesis

Dialdehyde modified cellulose (DAMC) is an intermediate in the preparation of DCC and ENCC.[1–5] Softwood pulp (4 g ~ 25 mmol glucose units) was torn into ~ 4 cm^2 pieces, soaked in water overnight, and disintegrated by vigorous shearing to achieve a near-uniform pulp slurry, followed by periodate oxidation (5.33 g) in DI water (total absorbed water by pulp plus free water was 266 g for ENCC). The reaction beaker was wrapped with aluminum foil to prevent periodate deactivation. To quench the reaction, ethylene glycol (3 mL for ENCC) was added to the mixture and stirred for 15 min followed by five times rinsing with water and vacuum filtration. After the final rinse, DAMC was stored at 4 °C. Note that the periodate-treated fibers remain intact, enabling them to be completely separated from the chemicals by facile rinsing and filtration. After the reaction, periodate may be recovered by reacting the produced iodate with hypochlorite under an alkaline condition.[6]

Dicarboxylated cellulose (DCC) and electrosterically-stabilized nanocrystalline cellulose (ENCC) synthesis[1–5]

DAMC (1 g) was stirred in a solution of sodium chlorite (1.41 g), hydrogen peroxide (1.41 g), and sodium chloride (2.93 g) in water (total of 266 mL) while the pH was maintained at 5 by intermittent NaOH (0.5 M) addition for 24 h. ENCC was isolated from the chlorite-oxidized pulp suspension by adding ethanol (0.16 g per 1 g of suspension), followed by centrifugation (3000 **g**, 10 min). ENCC with a crystalline body, similar to the conventional CNC, bearing flexible dicarboxylated cellulose (DCC) chains mostly located at the poles of the rod-shaped structure, resembles a hairy nanocrystal. Finally, more ethanol was added to the supernatant (1 g / 1 g) to precipitate the solubilized DCC, which was separated by centrifugation (3000 **g**, 10 min). ENCC and DCC were separately purified from the dissolved salts by dialysis (MWCO = 12-14 kDa, Spectra/Por dialysis tubing) against DI water. Conductometric titration of ENCC and DCC with sodium hydroxide solution yielded ~ 5.5 mmol and 5.7 mmol carboxylic acid groups per 1 g of ENCC and DCC, respectively (ζ-potential ~ -60 mV at no added salt, neutral pH). This charge content is more than one order of magnitude larger than that of conventional CNCs. The reaction yields were ~ 50% ENCC and ~ 50% DCC, with a total conversion of ~ 100%. ENCC was further modified by shortening the hairs through strong acid hydrolysis (3 N HCl at 45°C), yielding hydrolyzed ENCC (HENCC). This reduces the charge density of ENCC. Three forms of ENCC were prepared: ENCC1 (non-hydrolyzed), ENCC2 (hydrolyzed for 3 h) and ENCC3 (hydrolyzed for 16 h) for ENCC with long hairs (the original one), medium-sized hairs, and short hairs, with carboxyl contents of ~ 5.5, 3.4 and 2 mmol g^{-1}, respectively. The excess HCl was neutralized by adding sodium bicarbonate to stop the hydrolysis reaction, and the HENCCs were purified similar to ENCC.

CNC preparation and TEMPO-CNC synthesis

CNC dispersions were prepared by overnight stirring spray-dried CNC in DI water. TEMPO-oxidized CNC (TEMPO-CNC) was prepared by reacting 1 g of CNC with 0.8 mg of 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO), 0.56 g of $NaClO_2$, and 100 mL of phosphate buffer (pH 6.8) in a three-neck round-bottom flask, stirred at 500 rpm. Then, 0.125 mL of NaClO was added to the flask when the temperature reached 50 °C. The reaction was maintained at 60 °C for 24 hours, and the suspension was precipitated by adding ethanol, followed by rinsing with a water-ethanol solution and purifying through dialysis against DI water.

Powder X-ray diffraction (PXRD) analysis

The scale deposition process at limiting concentrations of antiscalants was monitored by the PXRD analysis of air-dried electrodes at intermittent scale deposition stages. The gold electrode was mounted in a custom-built poly(methyl methacrylate) holder and examined with a D2 Phaser equipped with an energy dispersive detector (Bruker) at room temperature to obtain the XRD spectrum.

Calcium carbonate precipitation

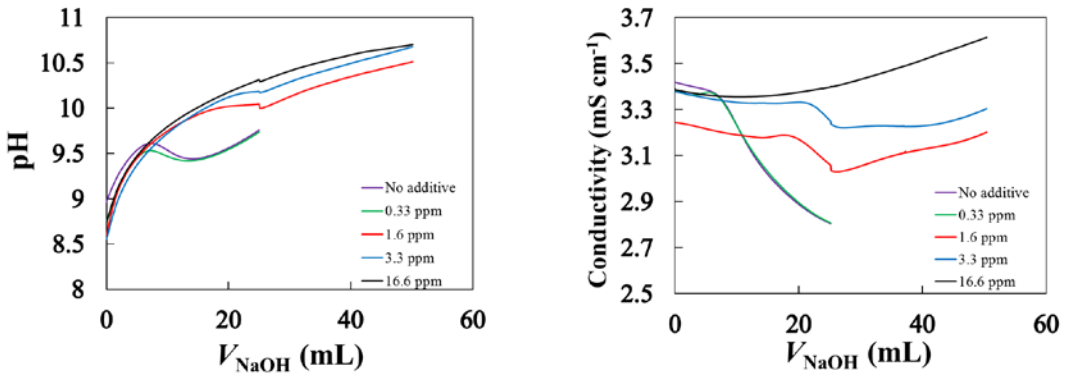
To study the mechanism of calcium carbonate mineralization, 15 mL of calcium chloride solution (20 mM) was mixed with 15 mL of sodium bicarbonate (20 mM) containing a desired concentration of a nanocellulose. The mixture was rigorously stirred for 1 min, incubated at room temperature with a cover glass, and allowed to rest without further agitation for a desired time. To stop the crystallization process, the supernatant was decanted, and the white precipitate-coated cover glass was thoroughly rinsed with milli-Q water three times and dried at 50 °C for 24 h in an oven. To induce secondary crystallization, supersaturation was increased by incubating the scaled cover glasses with ~ 50 μL of the supernatant in the oven and let dry at 50 °C for one day.

Scanning electron microscopy (SEM) and elemental analysis

The precipitated calcium carbonate on cover glasses were imaged using scanning electron microscopy. The imaging was performed on dried specimens, transferred from the mineralization media to adhesive carbon pads, mounted on a sample holder and coated with a 4 nm-thick layer of Pt using a vacuum sputtering instrument (Leica Microsystems EM ACE600 High Resolution Coater). SEM (FEI Inspect F-50 FE-SEM with energy dispersive spectroscopic equipment EDAX Octane Super 60 mm2 SDD and TEAM EDS Analysis System) was used for imaging and elemental analysis.

ζ-potential and hydrodynamic size

The ζ-potential of ENCC was measured through electrophoretic mobility (based on the electrophoretic light scattering ELS, conducted in the universal dip cell kit using Zetasizer NanoZS equipped with a 4 mW-633 nm He-Ne solid-state laser, Malvern Instruments, UK), which suggested the complexation with Ca^{2+}. Dynamic light scattering DLS in disposable cuvettes using the same instrument yielded the hydrodynamic size.



(a) **(b)**

Figure S1: Static jar test of a saturated solution (140 mL, [Ca^{2+}] = 71 ppm and [HCO_3^-] = 270 ppm, T = 23°C) including a desired amount of the anionic hairy nanocellulose, conducted by the gradual addition of sodium hydroxide while registering the solution pH (**a**) and conductivity (**b**). In an additive-free solution (purple) or when the ENCC1 concentration is noticeably low (green, 0.33 ppm), upon $CaCO_3$ formation at V_{NaOH} ~ 6 mL, pH and conductivity decrease, indicating the inorganic salt precipitation. While the conductivity keeps decreasing due to the reduction of free ions, pH increases again as a result of NaOH addition. By increasing the amount of ENCC1, the required NaOH to form precipitation increases (V_{NaOH} ~ 18 mL at ENCC1 ~ 1.6 ppm, and V_{NaOH} ~ 22 mL at ENCC1 ~ 3.3 ppm) until finally no precipitation is observed (ENCC1 ~ 16.6 ppm), which is reflected in a continuous increase in conductivity. This experiment proves that ENCC1 maintains the cations and anions soluble and prevents them from reacting with each other. This may be of utmost interest in pharmaceutical industries where the solubility of sparingly-soluble drugs needs to be enhanced.

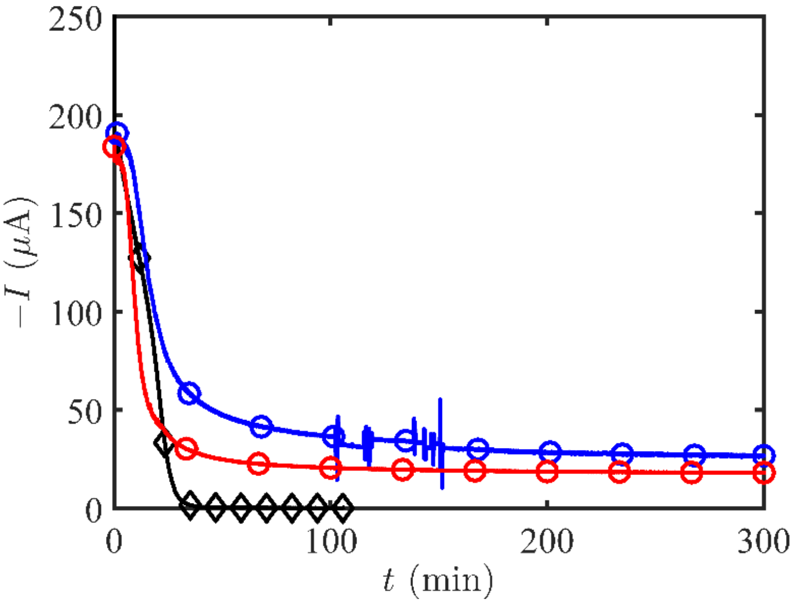


Figure S2: Antiscaling performance of one of the most efficient phosphorus-free scale inhibitors (polyacrylic acid sodium salt, PAA, M_w = 15 kDa) in a saturated system similar to **Figure 1**. At 16.6 ppm and 83.3 ppm, PAA is unable to control the scaling of $CaCO_3$ in our simulated scaling condition. Note that only 8.3 ppm DCC fully inhibited the scaling (**Figure 1a**).

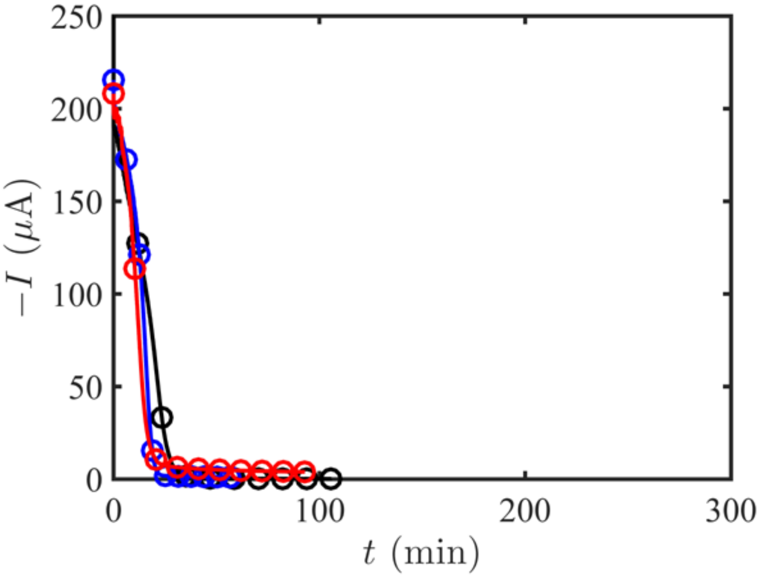


Figure S3: Antiscaling performance of carboxymethyl cellulose (NaCMC, Mw ~ 90 kDa, unit molecular mass ~ 146.16 + 97.03 DS, where the degree of substitution DS = 0.7) in a saturated system similar to **Figure 1**. NaCMC is unable to affect $CaCO_3$ scale formation even at high concentrations (blue: 16.6 ppm, red: 166.6 ppm).

References

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