

Electronic Supplementary Information for “*Biomimetic scale-resistant polymer nanocomposites: Towards universal additive-free scale inhibition*”

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The supporting information includes Materials and methods and 3 figures.

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Materials and methods

Materials

Q-90 softwood kraft pulp sheets and freeze-dried conventional cellulose nanocrystal (CNC, from sulfuric acid treated cellulose fibrils, 0.96 wt% sulfur on dry CNC) were provided by FPIinnovations (Pointe-Claire, Canada). Black spruce Q-90 bleached softwood kraft pulp sheets were used as the source of cellulose to synthesize anionic hairy cellulose nanocrystals (also known as electrosterically stabilized nanocrystalline cellulose, ENCC) and dicarboxylated cellulose (DCC). Sodium hydroxide (NaOH, ACS reagent, $\geq 97\%$), sodium (meta)periodate (NaIO₄, $\geq 99.99\%$), sodium chloride (NaCl, ACS reagent, $\geq 99\%$), ethylene glycol (C₂H₆O₂, 99%), sodium chlorite (NaClO₂, 80%), and cellulose acetate (average Mn \sim 30,000 by GPC, acetyl \sim 39.3-40.3 wt %, water \leq 3 wt %) were purchased from Sigma-Aldrich, Canada and used as received. Hydrochloric acid (HCl, 36.5-38%) was provided by ACP Chemicals (Canada), and hydrogen peroxide (H₂O₂, 30%), 2-propanol (C₃H₇OH, 99.9%), and anhydrous ethanol (C₂H₅OH, 95.27%) were supplied by Fisher Scientific, Canada. To prepare suspensions of conventional cellulose nanocrystals (CNCs), freeze-dried CNC was dispersed in milli-Q water (electrical resistivity \sim 18.2 M Ω cm, Millipore Milli-Q purification system) at room temperature, followed by stirring vigorously overnight. Saturated calcium carbonate solutions were prepared using sodium bicarbonate (NaHCO₃, ACP Chemicals, Canada) and calcium chloride dihydrate (CaCl₂·2H₂O, certified ACS, Fisher scientific, Canada).

Methods

Bulk mineralization experiments: Calcium chloride (20 mM, 15 mL) was mixed with sodium bicarbonate (20 mM, 15 mL), including a desired amount of ENCC or CNC, and vortexed for 1 min, followed by incubation at rest on an acid-cleaned cover glass under ambient conditions. After

a desired time, the supernatant was decanted, and the precipitate was separated, thoroughly washed with milli-Q water three times, and dried at 50 °C for at least 1 day in an oven.

Scanning electron microscopy (SEM): SEM imaging was conducted on dried, Pt-coated specimens (4 nm-thick layer, using a vacuum sputtering instrument, Leica Microsystems EM ACE600 High Resolution Coater) using SEM (FEI Inspect F-50 FE-SEM).

Atomic force microscopy (AFM) imaging: An atomic force microscope (MFP-3D, Asylum Research, Santa Barbara, CA) was used to image ENCC in tapping mode with silicon cantilevers (Nanoworld, force constants $\sim 42 \text{ N m}^{-1}$, tip length $\sim 125 \text{ }\mu\text{m}$ and radius $\sim 8 \text{ nm}$ or less, and resonance frequency $\sim 320 \text{ kHz}$). A droplet of ENCC suspension was placed on a poly-L-Lysine coated, freshly cleaved mica, adhered to a glass slide. The droplet was washed off with milli-Q water after $\sim 5 \text{ min}$ incubation and air-dried before imaging.

ζ -potential and hydrodynamic size: Electrophoretic mobility was characterized based on the electrophoretic light scattering ELS in the universal dip cell kit using Zetasizer NanoZS, equipped with a 4mW-633 nm He-Ne solid-state laser, Malvern Instruments, UK, yielding the ζ -potential of nanoengineered celluloses, which confirmed their complexation with Ca^{2+} . Dynamic light scattering experiments were performed in disposable cuvettes using the same instrument to obtain the hydrodynamic size of colloidal particles.

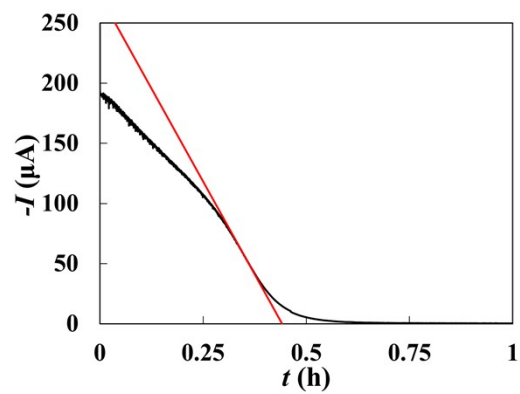


Figure S1. Typical chronoamperometry experiment with a bare rotating gold disk electrode, coated with an insulating, impenetrable layer of calcium carbonate. The scaling time ~ 26 min is obtained from the linear extrapolation of the Cottrell current I versus time t when $I \sim 0$ (red line).

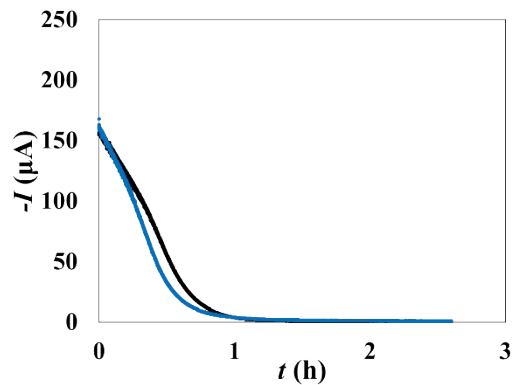


Figure S2. Dynamics of Cottrell current (I versus time t), obtained from chronoamperometry experiments using a cellulose acetate-coated 2D circular gold electrode, rotating at a constant speed (700 rpm) in the hard water (0.6 L, $\text{NaHCO}_3 \sim 270 \text{ mg L}^{-1}$ and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O} \sim 260 \text{ mg L}^{-1}$) at $T = 50^\circ\text{C}$. The membrane was coated on the electrode from 4 mg mL^{-1} cellulose acetate solutions, including 0 (black) and 0.2 wt% (blue) CNC. Incorporating CNC into the polymer matrix does not improve the antiscaling performance. Structural limitations of CNC prevent it from accommodating high densities of carboxylic acid groups, disqualifying this conventional nanocellulose for scale inhibition.

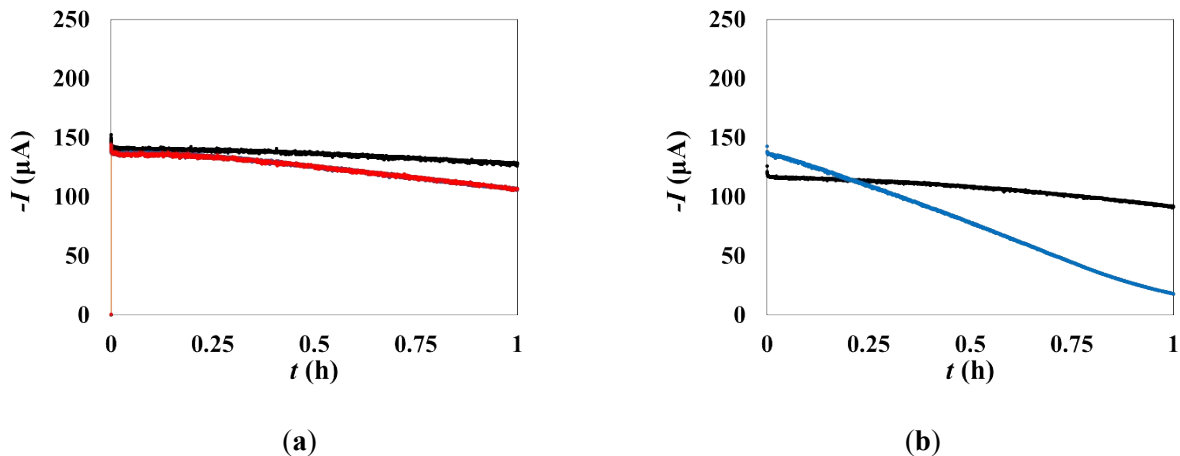


Figure S3. Effect of the acid-mediated regeneration of cellulose acetate membranes in terms of the evolution of Cottrell current (I) versus time (t), obtained from chronoamperometry experiments using a 2D circular gold electrode rotating at a constant speed (700 rpm) in the hard water (0.6 L , $\text{NaHCO}_3 \sim 270 \text{ mg L}^{-1}$ and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O} \sim 260 \text{ mg L}^{-1}$) at $T = 23^\circ\text{C}$. **(a)** The electrode was coated with cellulose acetate (stock solution of 2 mg mL^{-1}) containing 0.4 wt% ENCC and allowed to electrochemically scale (black color). The scaled electrode was cleaning with HCl solutions (blue: pH ~ 4.1 for 5.5 h while rotating at 700 rpm, and red: HCl, pH ~ 1 for 10 s) and the chronoamperometry experiments were repeated. Note that Blue is covered with red, showing a similar performance of the membrane after undergoing different regeneration procedures. Importantly, long-time exposure of cellulose to highly acidic media may result in hydrolysis and structural damages to the membranes. **(b)** The performance of the ENCC-free cellulose acetate membrane during the first cycle of scaling (black) and after cleaning in an HCl solution (blue, pH ~ 1 for 10 s), showing a significant efficiency loss. All the experiments were conducted in the absence of antiscalant additives.