Supplementary file

Oxidative Enzyme Activation of Cellulose Substrates for Surface Modification

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Laleh Solhi[a,b], James Li[b,c], Joyce Li[a], Nathan M. I. Heyns[a,d], and Harry Brumer[*,a,b,c,d,e]

[a] *Michael Smith Laboratories, University of British Columbia, Vancouver, BC, V6T 1Z4, Canada.*
[b] *BioProducts Institute, University of British Columbia, 2385 East Mall, Vancouver, BC, V6T 1Z4, Canada*
[c] *Department of Biochemistry and Molecular Biology, University of British Columbia, 2350 Health Sciences Mall, Vancouver, BC, V6T 1Z3, Canada*
[d] *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada*
[e] *Department of Botany, University of British Columbia, 3200 University Blvd, Vancouver, BC, V6T 1Z4, Canada*
E-mail: brumer@msl.ubc.ca, phone: +1-604-827-3738

1. CNC preparation

Table SI.1. Optimized conditions for preparation of CNCs with different acids (2 g cellulose in 100 mL acid).

CNC	Acid concentration (wt.%)	Temperature (°C)	Time (min)	Homogenizer passes (0.01% suspension at 20000 psi)	Average length (nm) (TEM)
CNC-HCl	26.43	70	170	4	520±210
CNC-H_2SO_4	40.91	45	50	4	311±105
CNC-H_3PO_4	68.09	80	150	4	443±152

2. Cellulose oxidation

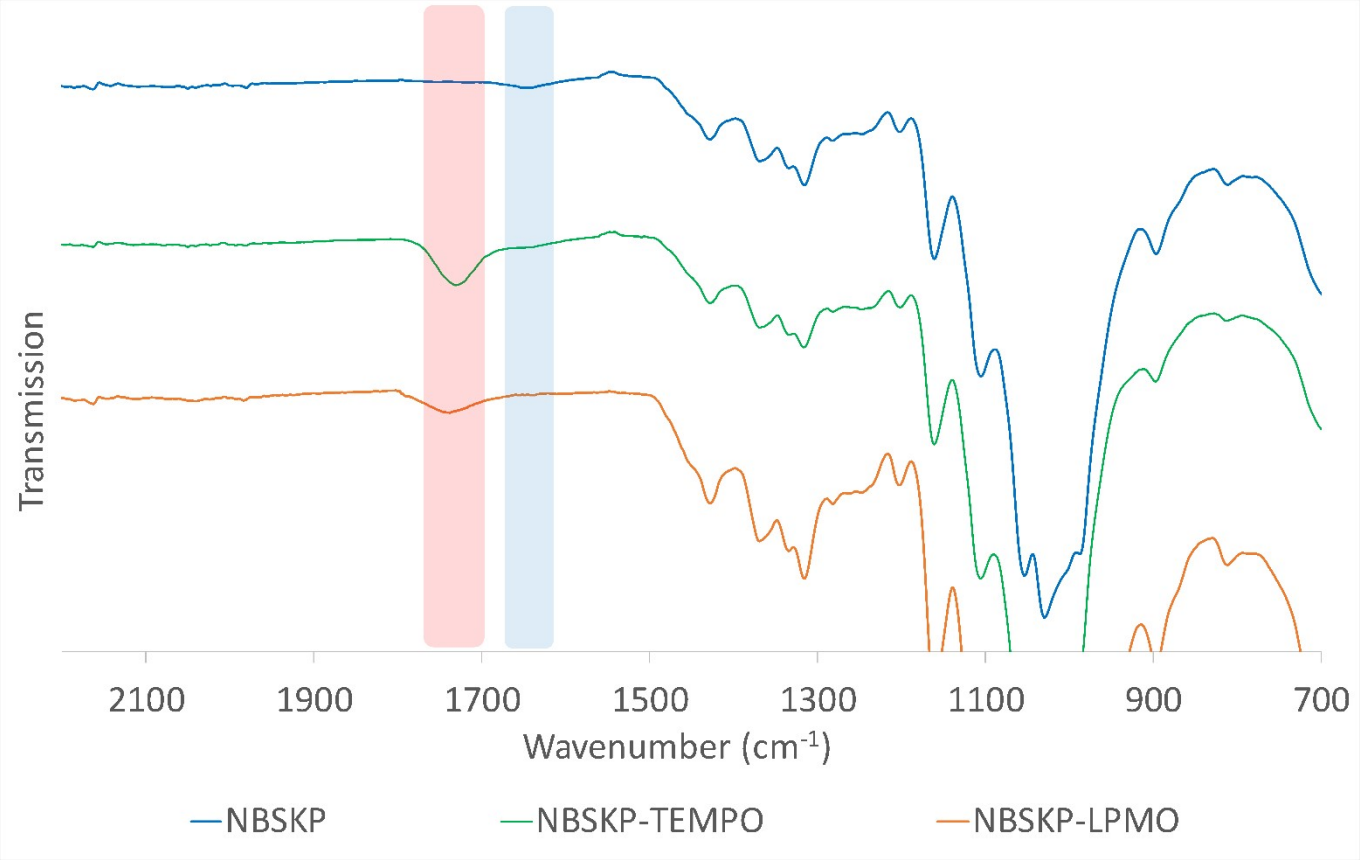

Figure SI.1. IR spectra of NBSKP, NBSKP-TEMPO, and NBSKP-LPMO (1µM). The area highlighted in blue shows the peaks at 1635 cm^{-1} related to the absorbed water in non-completely dried samples, while the emergence of the peak at 1730 cm^{-1}, highlighted in pink, in oxidized samples confirms the oxidation reaction.

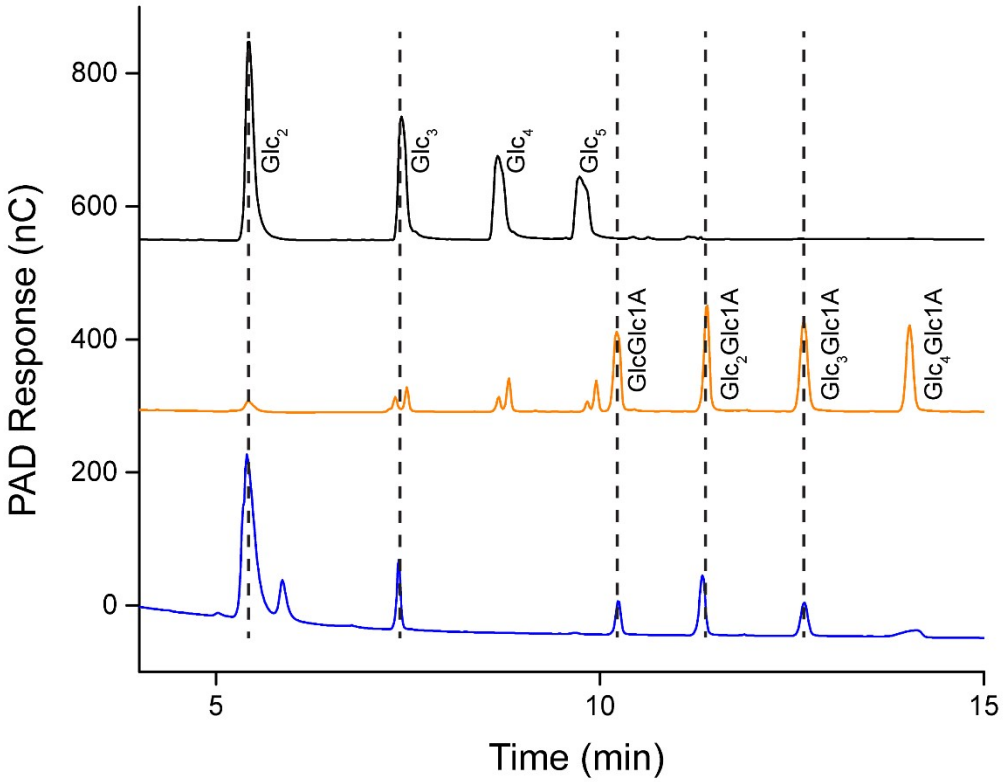

Figure SI.2. Representative HPLC analysis to quantify the LPMO oxidation of cellulose substrates. Black trace: mixed cello-oligosaccharide retention-time standards; orange trace: mixed C-1 oxidized cello-oligosaccharide retention-time standards; blue trace: products resulting from the oxidation of bacterial cellulose with *Cfla*LPMO10A (1 µM) followed by treatment of the released oligosaccharides with *Cellulomonas fimi* Cel5A (CenD). The area under the cellobionic acid (GlcGlc1A) peak was used for all samples to quantify oxidation versus a standard curve produced with pure cellobionic acid.

3. Conductometric titration

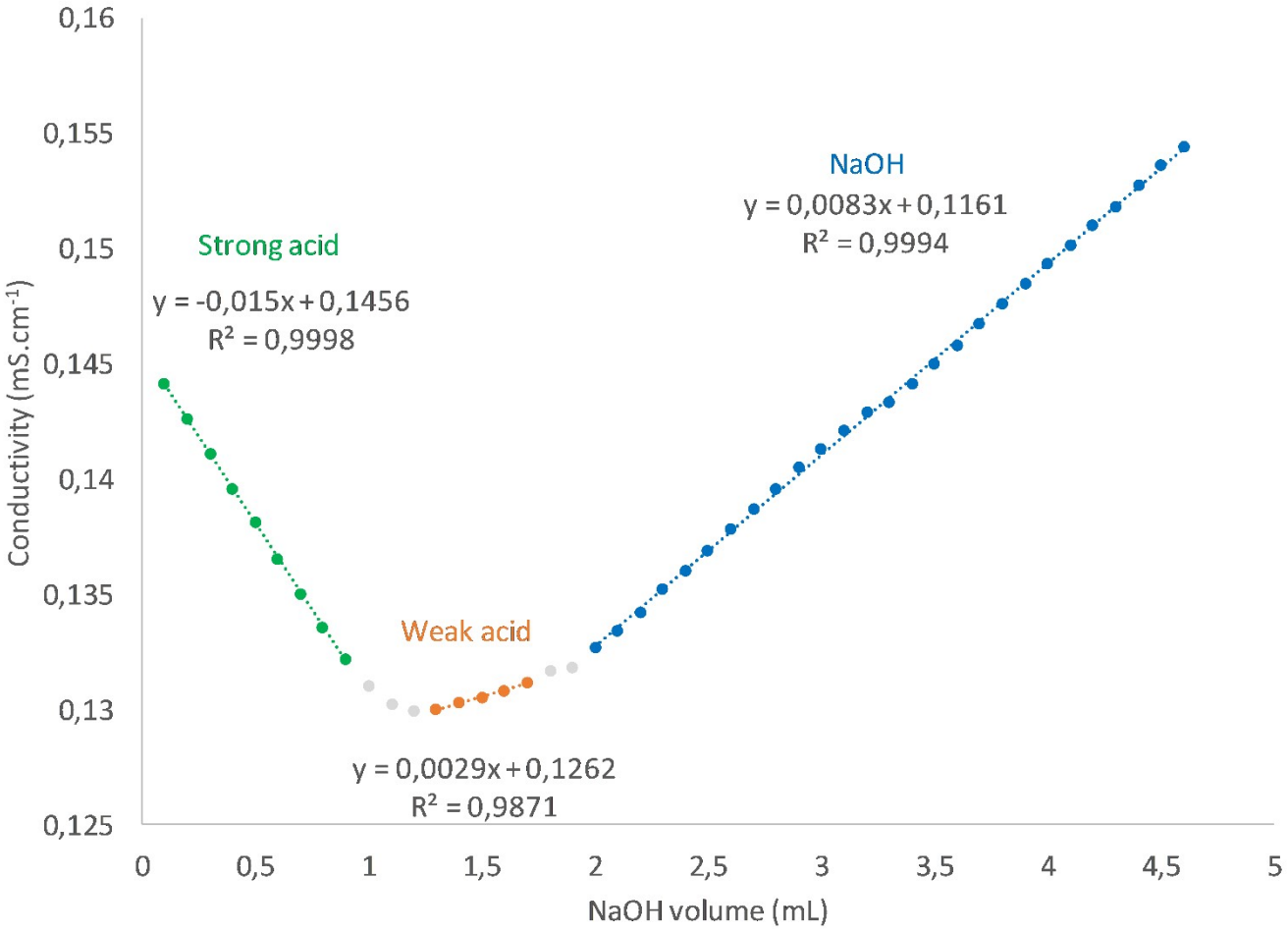

Figure SI.3. A representative conductometric titration curve. Carboxylic acid (weak acid) content is calculated based on the volume of titrant (NaOH) obtained by subtracting the volume values obtained at the intersection of the blue (NaOH regime) and green (strong acid regime) lines, respectively, with the orange (weak acid regime) line.

4. Substrate crystallinity

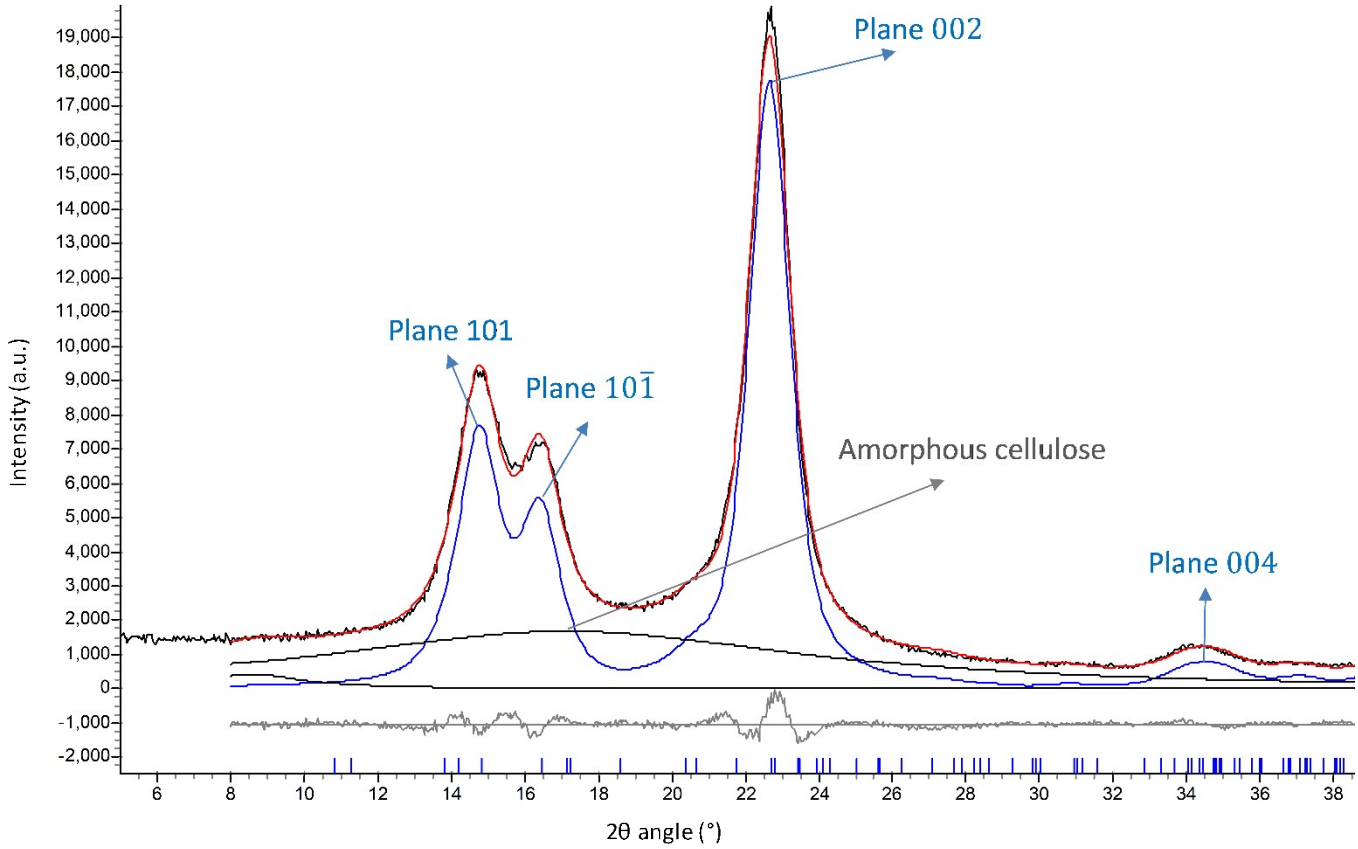

Figure SI.4. A representative XRD peak fitting curve for determination of crystallinity index (NBSKP). Black trace: experimental data; red trace: fitted curve by introducing an amorphous cellulose (broad grey trace) and a cellulose 1β crystalline component (blue trace). The grey trace at the bottom shows the difference between the fit and the experimental measurement. The crystallinity index (Table SI.2) was determined by dividing the area under the blue (crystalline portion) trace by the total area under the blue (crystalline portion) and grey (amorphous portion) traces.

Table SI.2. Crystallinity indices (CI) of cellulose substrates before and after TEMPO and LPMO (1μM) oxidation.

Material	NBSKP	NBSKP-TEMPO	NBSKP-LPMO	BC	BC-TEMPO	BC-LPMO	CNC-HCl	CNC-HCl-TEMPO	CNC-HCl-LPMO
CI (%)	65.43	64.73	64.11	70.58	70.39	69.61	76.21	75.92	75.78

5. CNC morphology

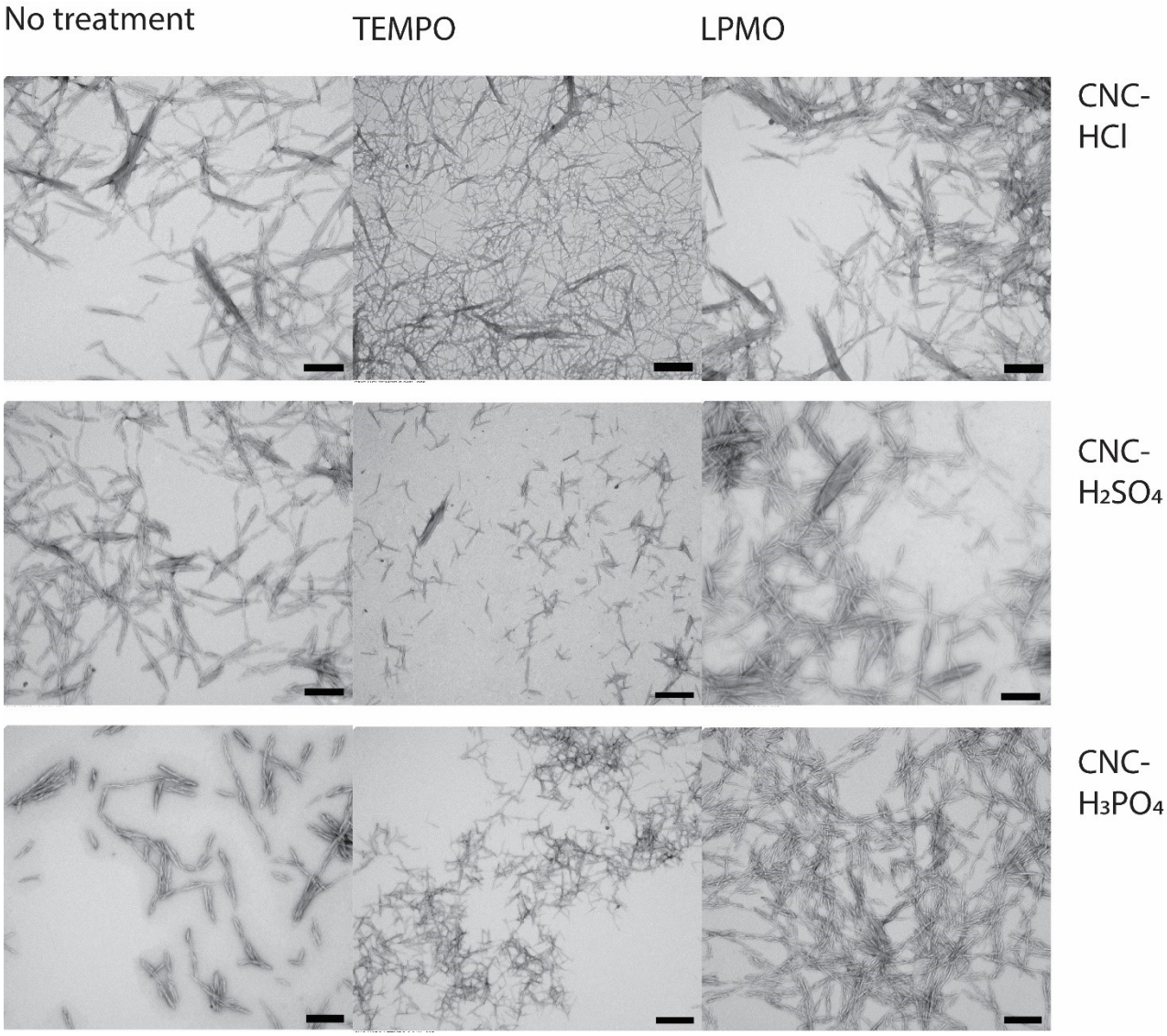

Figure SI.5. Morphology of TEMPO and LPMO oxidized CNCs produced by HCl, H_2SO_4, and H_3PO_4 treatment. Scale bars correspond to 500 nm.