Supporting Information – The Effects of High Pressure and High Temperature in Semi-dilute Aqueous Cellulose Nanocrystal Suspensions

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CNC suspension before and after treatment

Fig. S1 shows the difference between 2.0 wt% CNC solution before and after PVT test. It was clear from the sample after PVT tests that there was aggregation of CNC particles and they formed a gel like phase at high temperature and pressure.

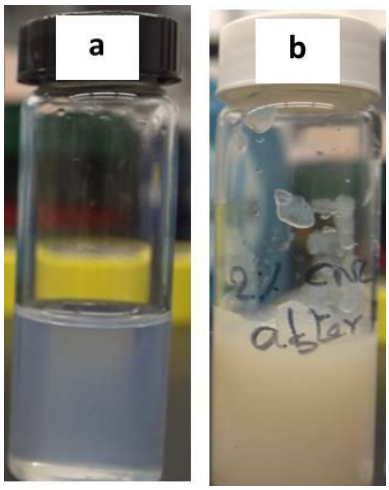

Fig. S1 2.0 wt.% CNC before (a) and after (b) high-P high-T test

The chemical modification of CNC particles after High-P high-T test was studied by FTIR, XPS and elemental analysis.

Fourier-Transform Infrared Spectroscopy (FTIR)

It was very difficult to predict any modifications based on FTIR analysis as CNC nano particles mostly composed of carbon, hydrogen and oxygen. There was no extra peak or lesser peak was observed for CNC nano particles as compared to that of the CNC nano particles after high-P high-T (Fig S2). We also tried to do some semiquantitative measurement depending on the peak at 1481 cm^{-1} which is C-H bending vibration, but did not provide any fruitful information.

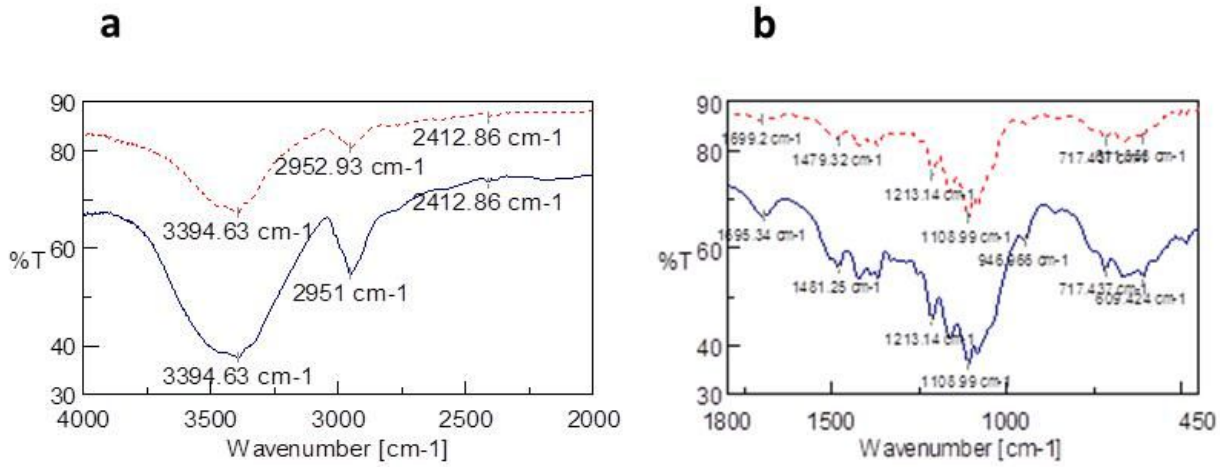

Fig. S2 FTIR of CNC particles: before (a) and after high-P high-T (b) test.

X-ray Photoelectron Spectroscopy (XPS)

The XPS measurements were performed on freeze dried samples of CNC before and after high-P high-T test on AXIS 165 spectrometer (Kratos Analytical) at the Alberta Centre for Surface Engineering and Science, University of Alberta. The base pressure in the analytical chamber was lower than 5 x 10^{-8} Pa. A monochromatic Al Kα source (hν = 1486.6 eV) was used at a power of 210 W. The analysis spot was 400 x 700 um and take-off angle was 90°. The resolution of the instrument is 0.55 eV for Ag 3d and 0.70 eV for Au 4f peaks. The survey scans were collected

for binding energy spanning from 1100 to 0 eV with analyzer pass energy of 160 eV and a step of 0.4 eV. The high-resolution spectra were run with pass energy of 20 eV. Electron flooding was used to compensate for sample charging. The binding energy of the C 1s of graphite was calibrated at 284.8 eV. Vision-2 instrument software was applied to process the data. Compositions were calculated from the major elemental peaks in survey spectra using symmetric Gaussian components with Shirley background and sensitivity factors provided by the database.

Desulfation of CNC nanoparticles during high-P high-T test was further confirmed by XPS analysis. The survey spectra of CNC particles before (Fig. S3a) and after (Fig S4a) showed that S2p peak which was present before High-P high-T test for CNC particles, was absent after high-P high-T test confirming desulfation of CNC particles.

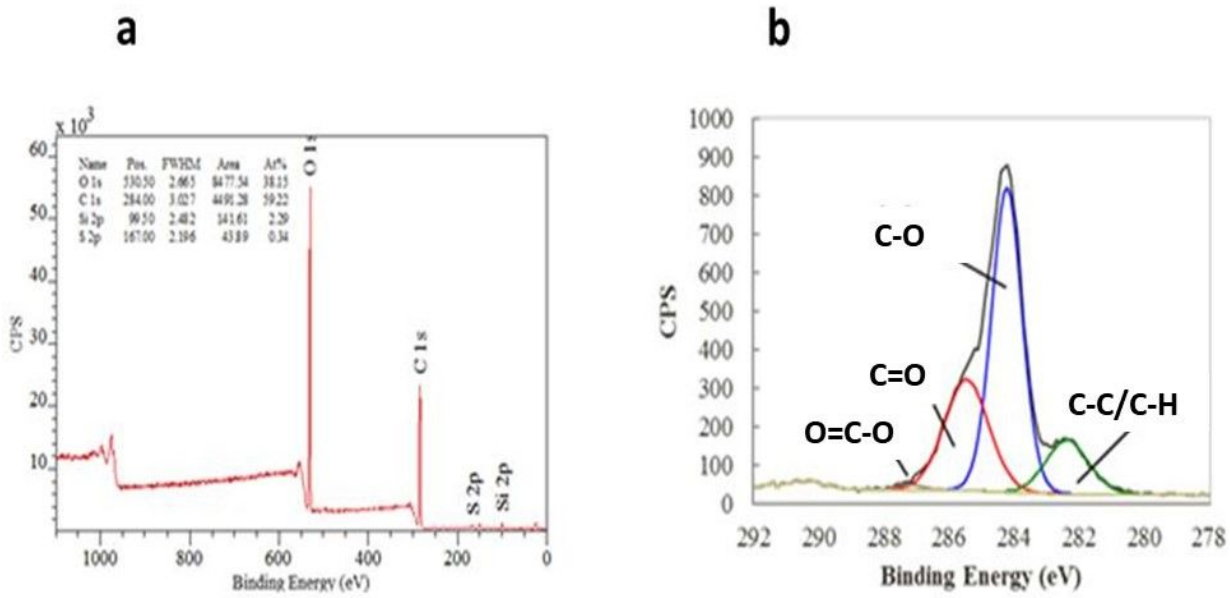

Fig. S3 The XPS survey spectra (a) and high resolution C1S deconvoluted peak of untreated CNC particles.

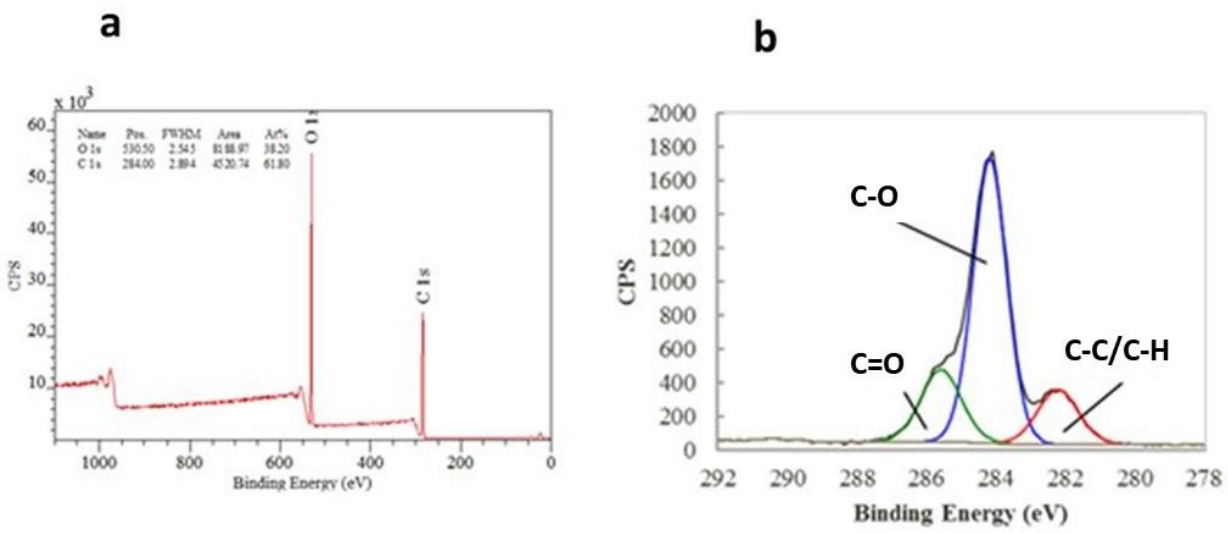

Fig. S4 The XPS survey spectra (a) and high resolution C1S deconvoluted peak of CNC particles after High-P high-T treatment

The high resolution deconvoluted spectra of C1s peak of CNC particles before and after high-P high-T test are presented in Fig. S3b and Fig. S4b respectively and the % conc of each group is listed in Table S1. The decrease in concentration of C-O bond after high-P high-T test was probably due to the truncation of surface sulfate ester groups. Consequently, the C-C/C-H and C=O groups concentration increased.

Table S1. Deconvoluted C1s peak and concentration of different bands

Binding Type[1]	**CNC untreated**	**CNC high-P high-T**
	%Conc	%Conc
C-C/C-H (C 1sa)	55.57	64.93
C-O (C 1sb)	29.65	15.23
C=O (C 1sc)	13.85	19.84
O-C=O (C 1sd)	0.92	0

References

1. Benkaddour, A.; Jradi, K.; Robert, S.; Daneault, C., Grafting of polycaprolactone on oxidized nanocelluloses by click chemistry. *Nanomaterials* **2013,** *3* (1), 141-157.