Video Article

Highly Stable, Functional Hairy Nanoparticles and Biopolymers from Wood Fibers: Towards Sustainable Nanotechnology

Amir Sheikhi[1,2,3], Han Yang[1,2,3], Md. Nur Alam[1,2,3], Theo G. M. van de Ven[1,2,3]

[1]Department of Chemistry, McGill University

[2]Center for Self-Assembled Chemical Structures (CSACS), McGill University

[3]Pulp and Paper Research Center, McGill University

Correspondence to: Theo G. M. van de Ven at theo.vandeven@mcgill.ca

Abstract

Nanoparticles, as one of the key materials in nanotechnology and nanomedicine, have gained significant importance during the past decade. While metal-based nanoparticles are associated with synthetic and environmental hassles, cellulose introduces a green, sustainable alternative for nanoparticle synthesis. Here, we present the chemical synthesis and separation procedures to produce new classes of hairy nanoparticles (bearing both amorphous and crystalline regions) and biopolymers based on wood fibers. Through periodate oxidation of soft wood pulp, the glucose ring of cellulose is opened at the C2-C3 bond to form 2,3-dialdehyde groups. Further heating of the partially oxidized fibers (*e.g.*, T = 80 °C) results in three products, namely fibrous oxidized cellulose, sterically stabilized nanocrystalline cellulose (SNCC), and dissolved dialdehyde modified cellulose (DAMC), which are well separated by intermittent centrifugation and co-solvent addition. The partially oxidized fibers (without heating) were used as a highly reactive intermediate to react with chlorite for converting almost all aldehyde to carboxyl groups. Co-solvent precipitation and centrifugation resulted in electrosterically stabilized nanocrystalline cellulose (ENCC) and dicarboxylated cellulose (DCC). The aldehyde content of SNCC and consequently surface charge of ENCC (carboxyl content) were precisely controlled by controlling the periodate oxidation reaction time, resulting in highly stable nanoparticles bearing more than 7 mmol functional groups per gram of nanoparticles (*e.g.*, as compared to conventional NCC bearing << 1 mmol functional group/g). Atomic force microscopy (AFM), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) attested to the rod-like morphology. Conductometric titration, Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), dynamic light scattering (DLS), electrokinetic-sonic-amplitude (ESA) and acoustic attenuation spectroscopy shed light on the superior properties of these nanomaterials.

Video Link

The video component of this article can be found at https://www.jove.com/video/54133/

Introduction

Cellulose, as the most abundant biopolymer in the world, has been served recently as a key raw material to yield crystalline nanoparticles named nanocrystalline cellulose (NCC, also known as cellulose nanocrystals CNC)[1]. To understand the mechanism of NCC synthesis, the structure of cellulose fibers needs to be explored. Cellulose is a linear and polydispersed polymer comprising poly-beta(1,4)-D-glucose residues[2]. The sugar rings in each monomer are connected through glycosidic oxygen to form chains of (1-1.5) x 10^4 glucopyranose units[2,3], introducing alternating crystalline parts and disordered, amorphous regions, first reported by Nageli and Schwendener[2,4]. Depending on the source, crystalline parts of cellulose can adopt various polymorphs[5].

If a cellulose fiber is treated with a strong acid, such as sulfuric acid, the amorphous phase can be completely hydrolyzed away to disrupt the polymer and produce crystalline particles of various aspect ratio depending on the source (*e.g.*, wood and cotton yield more than 90% crystalline nanorods of width ~ 5-10 nm and length ~ 100-300 nm, whereas tunicin, bacteria, and algae produce 5-60 nm wide and 100 nm to several micrometer long NCCs)[6]. Readers are referred to the vast amount of literature available on the scientific and engineering aspects of these nanomaterials[2,5,7-16]. Despite numerous interesting properties of these nanoparticles, their colloidal stability has always been an issue at high salt concentrations and high/low pH due to their relatively low surface charge content (less than 1 mmol/g)[17].

Instead of strong acid hydrolysis, cellulose fibers can be treated with an oxidizing agent (periodate), cleaving C2-C3 linkage in the anhydro D-glucopyranose residues to form 2,3-dialdehyde units with no significant side reactions[18,19]. These partially oxidized fibers can be used as a valuable intermediate material to produce nanoparticles bearing both amorphous and crystalline regions (hairy nanocrystalline celluloses) using solely chemical reactions without any mechanical shear or ultrasonication[20]. When the partial oxidation degree DS < 2, heating oxidized fibers results in three batches of products, namely fibrous cellulose, water dispersible dialdehyde cellulose nanowhiskers called sterically stabilized

nanocrystalline cellulose (SNCC), and dissolved dialdehyde modified cellulose (DAMC), which can be isolated by precise control over the co-solvent addition and intermittent centrifugation[21].

Performing controlled chlorite oxidation on the partially oxidized fibers converts almost all the aldehyde groups to carboxyl units, which can introduce as high as 7 mmol COOH groups per gram of nanocrystalline cellulose depending on the aldehyde content[18], acting as stabilizers. These nanoparticles are called electrosterically stabilized nanocrystalline cellulose (ENCC). Furthermore, it has been confirmed that soft layers of charged hair-like protruding chains exist on ENCC[17]. This material has been used as a highly efficient adsorbent to scavenge heavy metal ions[22]. The charge of these nanoparticles can be precisely controlled by controlling the periodate reaction time[23].

Despite known oxidation reactions of cellulose, the production of SNCC and ENCC has never been reported by any other research groups most probably due to the separation challenges. We have been able to successfully synthesize and isolate various fractions of nanoproducts by precisely designing the reaction and separation steps. This visual article demonstrates with complete detail how to reproducibly prepare and characterize the aforementioned novel nanowhiskers bearing both amorphous and crystalline parts from wood fibers. This tutorial may be an asset for active researchers in the fields of soft material, biological, and medicinal sciences, nanotechnology and nanophotonics, environmental science and engineering, and physics.

Protocol

CAUTION: Read the material safety data sheets (MSDS) of all the chemicals before touching them. Many of the chemicals used in this work may cause severe health damages. Using personal protection such as lab coat, gloves, and goggles is a must. Do not forget that safety comes first. The water used throughout the synthesis is distilled water.

1. Preparation of Partially Oxidized Fibers as an Intermediate

1. Tear 4 g Q-90 softwood pulp sheets into small pieces of approximately 2 x 2 cm^2.
2. Soak the torn pulp sheets in water for at least one day.
3. Disintegrate the wet pulp using a mechanical disintegrator to achieve an almost-uniform dispersion.
4. To assemble the vacuum filter, secure a nylon filter in a Buchner funnel and place the funnel in a filter flask. Then, connect the filter flask to a vacuum pump using proper tubing. Turn on the pump and pour the disintegrated pulp solution in the funnel to separate the pulp from the liquid.
5. Measure the weight of wet pulp (m_1), and calculate the amount of absorbed water by pulp: $m_{w,1} = m_1 - 4$.
6. Preparation of periodate oxidizing solution
    1. For SNCC/DAMC synthesis: separately, dissolve 2.64 g sodium periodate ($NaIO_4$) and 15.48 g sodium chloride (NaCl) in 200-$m_{w,1}$ ml water.
    2. For ENCC/DCC synthesis: separately, dissolve 5.33 g sodium periodate ($NaIO_4$) and 15.6 g sodium chloride (NaCl) in 266-$m_{w,1}$ ml water.
7. Add the wet pulp separately to the solutions prepared in 1.6. Make sure that the total amount of water (absorbed by pulp plus added water) is equal to 200 ml for SNCC and 266 ml for ENCC syntheses.
8. Cover the beaker thoroughly with aluminum foil to prevent periodate deactivation while stirring at speed ~ 105 rpm in RT for a desired amount of time according to **Table 1** to achieve a favored aldehyde content. As an example, to obtain ~ 6.5 mmol/g aldehyde, react for 96 hr.
9. When the reaction time is elapsed, open the aluminum foil and add 1 ml (in case of SNCC/DAMC synthesis) or 3 ml (in case of ENCC/DCC synthesis) ethylene glycol to the mixture and stir for 10 min to stop the oxidation reaction by quenching periodate.
10. Collect the oxidized pulp by vacuum filtration (according to 1.4), redisperse it in 500 ml water, and stir it for 30 min. Repeat this step at least 5 times to clean the pulp from periodate thoroughly.
11. After the 5th water wash on the oxidized pulp, separate the pulp from solution by vacuum filtration and store it in a cold (4 °C) place.

2. Synthesis of SNCC and DAMC

1. Divide the partially oxidized wet pulp (m_1), obtained in 1.11, by four: $m_2 = m_1/4$, and measure the weight of absorbed water: $m_{w,2} = m_2 - 1$.
2. Disperse the pulp in (100 - $m_{w,2}$) g water in a round bottom flask (total water content = 100 g).
3. Place the round bottom flask in an oil bath and heat the partially oxidized pulp at 80 °C for 6 hr while gently stirring.
   Note: If pulp is completely oxidized with periodate (DS = 2), *e.g.*, by reacting 1 g pulp with 1.85 g $NaIO_4$ (8.65 mmol) in a solution comprising 3.87 g NaCl (8.64 mmol) and 65 ml water while stirring for 6 days, depending on the heating condition and residence time in water, the property of the dialdehyde cellulose (DAC) is changed (**Table 2**).
4. Cool down the solution to RT.
5. Centrifuge the solution at 18,500 x g for 10 min. The precipitate is unfibrillated cellulose (fraction 1).
6. Separate the supernatant carefully and weigh it (A).
7. Add 1.7(A) g propanol to the supernatant obtained in 2.6 while stirring to precipitate SNCC. Details about the separated SNCC and added propanol is available in **Figure 1**.
8. Centrifuge the biphasic solution at 3,000 x g for 10 min, and separate the resulted gel-like precipitate (second fraction, SNCC) by decantation, which is ready to be redispersed and dialyzed for further purification (section 4) and characterization (section 5).
9. To the supernatant obtained in 2.8, add 3.5(A) g propanol to yield a white precipitate (third fraction, DAMC).
10. Centrifuge the solution of 2.9 at 3,000 x g for 10 min, and collect the gel-like DAMC precipitate (by pouring the supernatant in a separate beaker) ready to be redispersed in water, purified by dialysis (details available in section 4), and characterized (section 5).

3. Synthesis of ENCC and DCC

1. Prepare a solution of 0.5 M sodium hydroxide (NaOH) by dissolving ~ 2 g NaOH in 100 ml water and keep it aside. This will be used in step 3.7.
2. Divide the wet oxidized pulp, obtained in 1.11, by four: $m_3 = m_1/4$, and measure the weight of absorbed water: $m_{w,3} = m_3 - 1$.
3. Separately, add 2.93 g sodium chloride (NaCl) and 1.41 sodium chlorite (NaClO$_2$) to (50 - $m_{w,3}$) ml water and stir to dissolve.
4. Suspend m_3 gram of wet oxidized pulp (containing ~ 1 g dry oxidized pulp) in the solution obtained in 3.3. Note that the final pulp concentration is 1 g in 50 ml total available water (free and absorbed water).
5. Place a pH meter in the solution of 3.4.
6. Add 1.41 g hydrogen peroxide (H$_2$O$_2$) to the mixture of step 3.4 dropwise.
7. Stir the suspension of 3.6 for 24 hr in RT at 105 rpm while maintaining the pH ~ 5 by gradually adding 0.5 M sodium hydroxide (NaOH) prepared in step 3.1.
    Note: The pH starts decreasing rapidly after ~ 15 min from the beginning of reaction, and it should be kept constant at 5 for at least the first 4 hr of the reaction. For convenience, it is suggested that the reaction is started at 1 PM and the pH is controlled until 5 PM, then the reaction is left O/N and early in the morning the pH is increased to 5 again. After such a long time, pH drop will not be significant, indicating that most of the conversion is achieved. Now, almost no solid can be observed in the solution (large fibers are broken down into nanoparticles). Note that if the reaction is left for a longer time, the crystalline part may be disrupted.
8. Divide the suspension obtained from 3.7 into equally weighted centrifuge tubes and centrifuge at 27,000 x g for 10 min, and separate the supernatant (ENCC + DCC) from the micro-fibrous precipitate.
9. Weigh the supernatant obtained from 3.8 and call the solution mass (B).
10. Slowly add 0.16(B) g ethanol to the solution of 3.9 while stirring to form a white precipitate (second fraction, ENCC).
11. Centrifuge the solution of 3.10 at 3,000 x g for 10 min, and separate the resulted gel-like ENCC precipitate by decantation. ENCC is ready to be redispersed in water, purified by dialysis (details available in section 4), and characterized (section 5).
12. To the supernatant obtained in 3.11, add equal mass of ethanol as the solution mass to yield a white precipitate (third fraction, DCC).
13. Centrifuge the solution of 3.12 at 3,000 x g for 10 min, and separate the gel-like DCC precipitate ready to be redispersed in water, purified by dialysis (details available in section 4), and characterized.

4. Dialysis Procedure to Purify SNCC, DAMC, ENCC or DCC

1. Redisperse the gel-like precipitate obtained in any steps of 2.8 (SNCC), 2.10 (DAMC), 3.11 (ENCC), or 3.13 (DCC) in 10 ml water by vigorous stirring for 1 hr.
2. Place the dispersion in a dialysis tubing (MW Cutoff = 12-14 kDa, Length ~ 30 cm, width ~ 4.5 cm) and secure the top and bottom by clipping.
3. Place the filled dialysis bag in ~ 4 L of distilled water and stir for 24 hr to eject the salts.
4. Collect the dialyzed solution in a container and store in a cold (4 °C) place.

5. Post-purification Characterization: Solid Phase and Charge Concentrations Measurement

1. **Concentration measurement**
    1. Weigh 3 ml of a desired dispersion in a weighting dish (Aluminum cup, 57 mm).
    2. Place the weighing dish containing the dispersion in an oven (50 °C) O/N.
    3. Weigh the dry film and calculate the concentration of nanoparticles or polymers in the dispersion:
        Concentration (w/v%) = 100 x mass of dry film / 3, or
        Concentration (w/w%) = 100 x mass of dry film / mass of dispersion

2. **Conductometric titration**
    1. **Conductometric titration of SNCC or DAMC to determine aldehyde content**
        1. Prepare 0.1 M hydrochloric acid (HCl) by adding 0.82 ml HCl to 25 ml water followed by adjusting the final volume to 100 ml.
        2. Separately, prepare NaOH 0.1 M by adding 0.4 g sodium hydroxide to distilled water to achieve 100 ml final solution.
        3. Following the hydroxylamine hydrochloride method[24], add a known amount of a desired dispersion to a desired amount of water (*e.g.*, 0.02 g in 50 ml H$_2$O).
        4. Adjust the pH to 3.5 using dilute HCl (0.1 M).
        5. Add 10 ml hydroxylamine hydrochloride solution (5% w/w) to the dispersion.
        6. Monitor the pH and keep it at 3.5 by adding 0.1 M NaOH until pH becomes stable at 3.5.
        7. Using the consumed volume of NaOH to neutralize the H$^+$ released from the reaction of aldehyde groups and NH$_2$OH·HCl, measure the aldehyde concentration (mole of consumed NaOH = mole of produced HCl during the reaction = mole of aldehyde groups on SNCC).

    2. **Conductometric titration of ENCC or DCC to determine carboxyl content**
        1. Following literature[25], add enough amount of a desired dispersion to have 0.02 g of solid in 140 ml distilled water.
        2. Separately, prepare 20 mM NaCl by dissolving 0.117 g NaCl in distilled water to achieve 100 ml final solution. Add 2 ml of 20 mM NaCl to 5.2.2.1.
        3. Reduce the pH to about 3 using dilute HCl (0.1 M).
        4. Perform the conductometric titration by adding standard sodium hydroxide (NaOH, 10 mM) in 0.1 ml/min increments up to pH ~ 11.

5. Using the consumed volume of NaOH to neutralize charged groups (details in **Figure 2**), measure the surface charge concentration (1 mole of consumed base equals to one mole COOH on the particle surface).

Representative Results

The mass portion and charge content of each fraction during the periodate and chlorite oxidation of pulp depends on the reaction time (**Table 1**). Moreover, DAC molecular weight depends on heating condition and residence time (**Table 2**). Once SNCC and DAMC are made, they precipitate out by adding propanol (**Figure 1**). To measure the charge content of ENCC, conductometric titration is performed (**Figure 2**). NCC and ENCC colloidal behavior is affected by the ionic strength and pH. The size and zeta-potential of NCC and ENCC versus KCl salt concentration and pH are presented in **Figure 3**. SNCC is a neutral particle and its size is affected by the added propanol (**Figure 3**). Transmission electron microscopy (TEM) and atomic force microscopy (AFM) images of NCC, ENCC, and SNCC (**Figure 4**) attest that these particles benefit from a similar crystalline body. Bearing a high carboxyl group content, ENCC is able to separate a high amount of copper ions from aqueous systems (**Figure 5**). FTIR spectra and ^{13}C NMR of ENCC/DCC and SNCC reveal the chemical structure differences with conventional NCC and cellulose pulp (**Figure 6**). Finally, X-ray diffraction (XRD) of various fractions of oxidized cellulose (**Figure 7**) shed light on the crystallinity of these materials.

Periodate oxidation time (hr)	Aldehyde content (mmol/g)	Fraction	Mass ratio (%)	Charge content (mmol/g)
10	1.5	1	90	1.2
		2	3.5	3.6
		3	7.5	3.95
16	2.5	1	82	2.15
		2	5	4.25
		3	12	4.6
24	3.5	1	69	2.9
		2	10	4.8
		3	21	5.25
96	6.5	1	9	4.05
		2	52	6.6
		3	40	6.95

Table 1. Mass portion and charge content of each fraction during periodate and chlorite oxidation of pulp[23].

Temperature (°C)	Heating time (hr)	Residence time in water at RT (days)	Average molar mass (kDa)	Degree of polymerization
80	6	1	85.1	532
80	6	15	41.3	258
80	6	61	4.1	26
80	10	61	3.4	21
90	6	61	3.3	21
90	17	61	1.6	10

Table 2. DAC molecular weight dependency on heating condition and residence time[21].
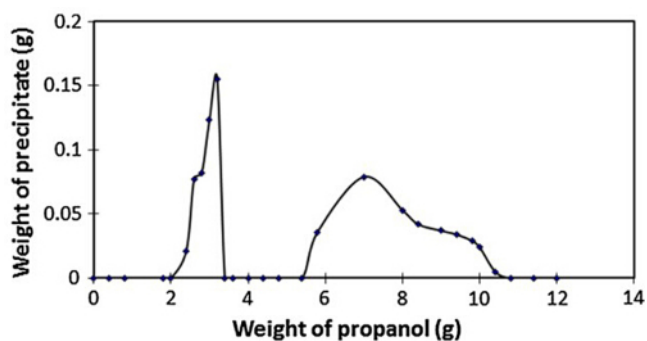
Figure 1. Precipitated SNCC and DAMC versus added propanol[21]. Please click here to view a larger version of this figure.
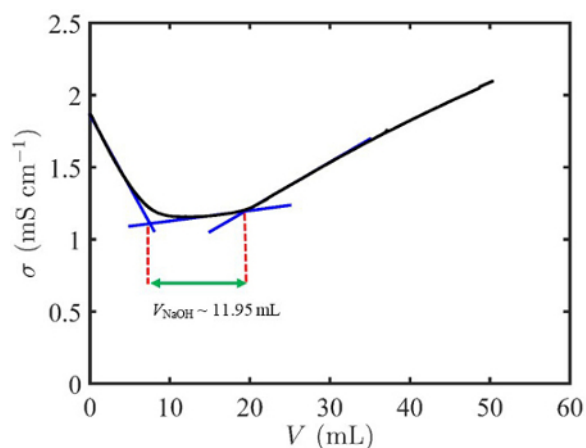

Figure 2. Conductometric titration graph for ENCC. COOH concentration = 0.01195 (V_{NaOH}) * 10 mM (NaOH concentration) / 0.02 g (initial ENCC) ~ 5.98 mmol/g. Please click here to view a larger version of this figure.
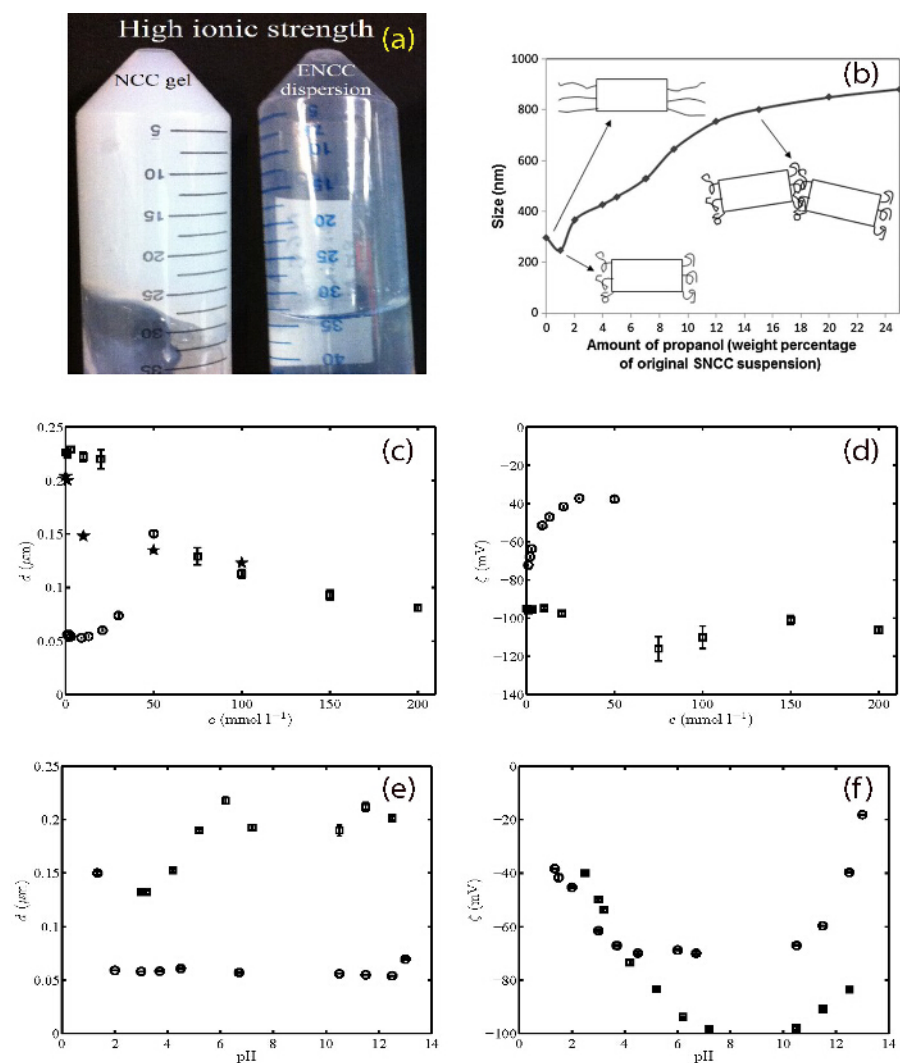
Figure 3. (**A**) NCC and ENCC behavior at high ionic strength[17]. (**B**) Size evolution of SNCC versus added propanol[21]. (**C-F**) NCC (circles) ENCC (squares) size and zeta potential versus KCl salt concentration and pH obtained from electrokinetic-sonic-amplitude (ESA) and acoustic attenuation spectroscopy[17]. Note that stars in panel (**C**) represent dynamic light scattering (DLS) size. Please click here to view a larger version of this figure.
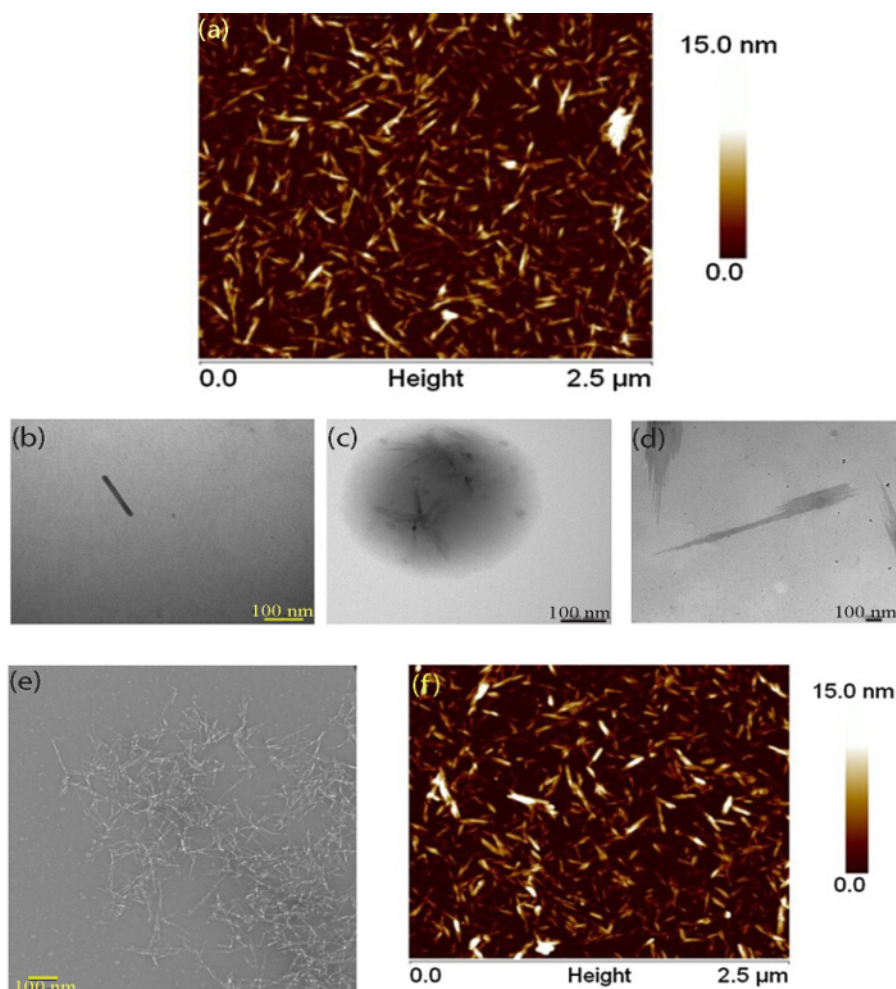
Figure 4. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) images of (**A**) NCC[21], ENCC at (**B**) 0 ppm, (**C**) 100 ppm, and (**D**) 300 ppm copper concentrations[22], and (**E&F**) SNCC[21]. Please click here to view a larger version of this figure.
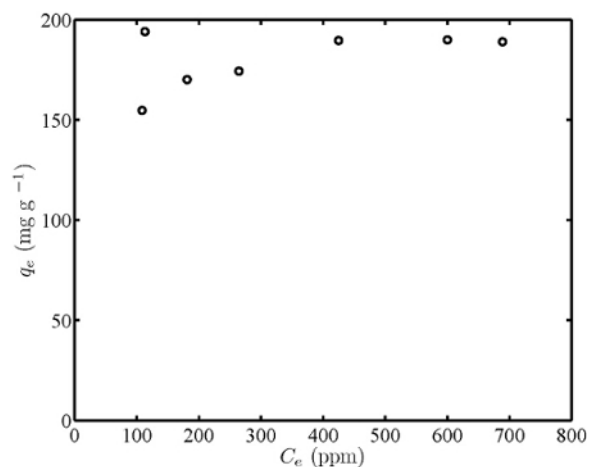

Figure 5. Copper removal capacity of ENCC q'_e versus equilibrium copper concentration C_e[22]. Please click here to view a larger version of this figure.
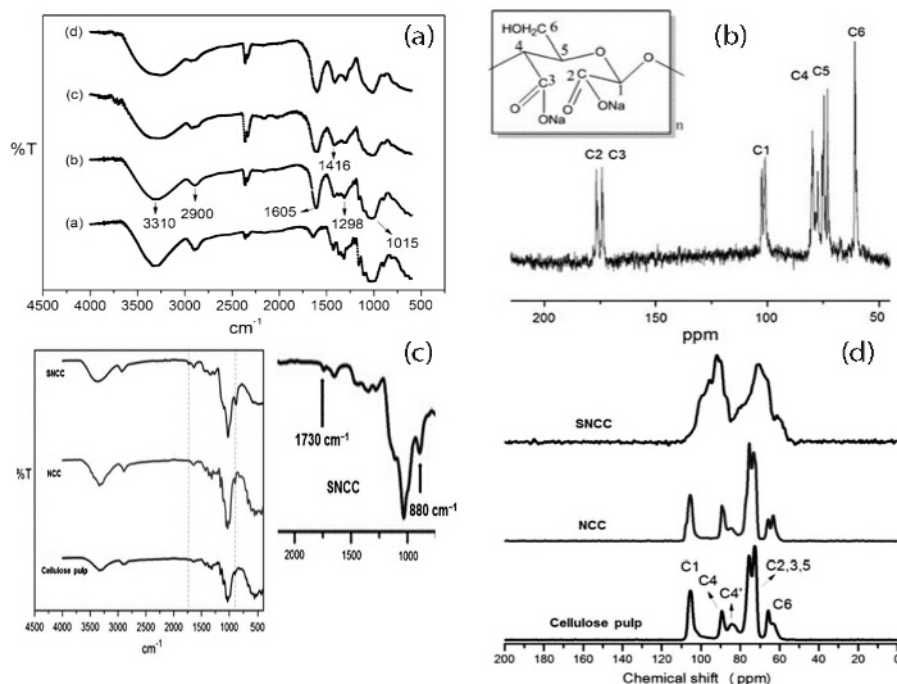
Figure 6. (**A**) FTIR spectra of cellulose pulp (a, with charge content 0.06 mmol/g), first fraction (b), second fraction (c, *i.e.*, ENCC), and third fraction (d, *i.e.*, DCC with charge content 3.5 mmol/g)[23]. (**B**) Liquid phase ^{13}C NMR of DCC (charge content 3.5 mmol/g)[23]. (**C**) FTIR spectra of cellulose pulp, NCC, and SNCC[21]. (**D**) Solid state ^{13}C NMR of cellulose pulp, NCC, and SNCC[21]. Please click here to view a larger version of this figure.
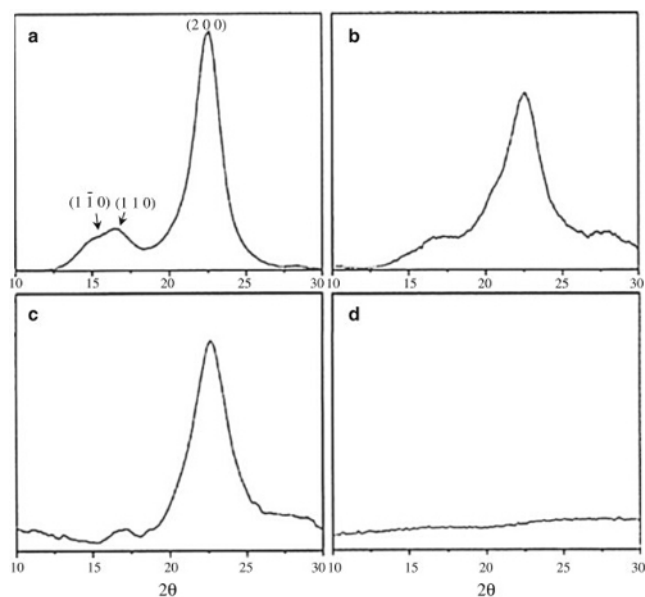

Figure 7. X-ray diffraction (XRD) of various fractions of oxidized cellulose. (**A**) Initial cellulose, (**B**) first fraction of oxidized cellulose, (**C**) second fraction from oxidized cellulose, and (**D**) third fraction from oxidized cellulose (charge content = 3.5 mmol/g)[23]. Please click here to view a larger version of this figure.

Discussion

Following the chemistry discussed in this visual paper, a spectrum of highly stable cellulose-based nanoparticles with tunable charge bearing both crystalline and amorphous phases (hairy nanocrystalline celluloses) are produced. Depending on the periodate oxidation time, as shown in **Table 1**, various products are yielded: oxidized fibers (fraction 1), SNCC (fraction 2), and DAMC (fraction 3) each of which providing unique properties, such as defined size, morphology, crystallinity, and aldehyde content. Further oxidation of these intermediate materials by chlorite results in various negatively charged species, namely fraction 1 (carboxylated pulp fibers), fraction 2 (ENCC), and fraction 3 (DCC) as stated in **Table 1**. If the periodate completely-oxidized pulp (DS = 2) is cooked, depending on the heating condition (temperature and incubation time), a series of dialdehyde cellulose (DAC) with various molecular weights and degrees of polymerization can be produced. **Table 2** presents the molecular weight of DAC versus heating condition. Heating provides a facile way of converting partially periodate oxidized pulp into neutral,

aldehyde functionalized nanoparticles (SNCC) and polymers (DAMC), which can be used as highly active intermediates. SNCC and DAMC are carefully isolated by adding a co-solvent such as propanol. In **Figure 1**, separated SNCC and DAMC versus added propanol is presented.

Once ENCC or DCC is made, simple conductometric titration is used to measure the surface charge (carboxyl) content as described in **Figure 2**. An equivalent amount of NaOH to neutralize the surface charge yields the charge density (*e.g.*, ~ 6 mmol/g in **Figure 2**). The high charge density of ENCC stabilizes them electrostatically, which along with the excluded volume of the protruding dicarboxylated cellulose (DCC) chains, provide an electrosterically stabilization. In **Figure 3A**, it is shown that at ionic strength ~ 50 mM, NCC forms a gel, whereas ENCC remains as a stable dispersion up to at least 500 mM KCl. Such behavior is confirmed by studying the size of NCC and ENCC using acoustic attenuation spectroscopy: NCC size increases from ~ 50 nm to ~ 150 nm by increasing the ionic strength from 0 to 50 mM, while ENCC size decreases from ~ 220 nm to ~ 80 nm by increasing KCl concentration from 0 to 200 mM due to the retraction of protruding DCC chains (**Figure 3C**). The stable zeta-potential of ENCC at ~ -100 mV as compared to the decreasing trend of NCC zeta-potential from ~ -75 mV to ~ -40 mV attests to a high, stable charge on ENCC (**Figure 3D**). Furthermore, ENCC surface acts as a weak acid as compared to the strong acid surface groups on NCC (**Figures 3E&F**), resulting in pH-dependent (pH-independent) zeta-potential (and size) for ENCC (NCC) at 3 < pH < 12. Interestingly, SNCC size is affected by the co-solvent concentration as depicted in **Figure 3B**.

TEM and AFM images (**Figure 4**) of NCC, ENCC, and SNCC attest to similar crystalline part. Also, in the presence of a divalent heavy metal ion, such as copper, ENCCs form highly stable star-like aggregates at low Cu(II) concentration (*e.g.*, 100 ppm, **Figure 4C**), whereas at high copper concentrations (*e.g.*, 300 ppm, **Figure 4D**), large raft-like, unstable aggregates are formed. This is attributed to the partial and complete charge neutralization of ENCC at low and high copper concentrations, respectively[22]. Such tendency to adsorb heavy metal ions encouraged us to use ENCC to separate copper ions from aqueous systems. **Figure 5** presents the copper removal capacity versus the equilibrium copper concentration[22]. Accordingly, 1 g ENCC is able to remove ~ 180 mg copper(II), which is equivalent to ENCC surface charge content. Such a high heavy metal ion removal capacity places this nanomaterial among highly efficient adsorbents[22].

Comparing the FTIR spectra of the different fractions of oxidized pulp (**Figure 6A**) suggests that by increasing the fraction number, the peak intensity at 1,605 cm^{-1} corresponding to COONa increases as compared to the peak at 1,015 cm^{-1} (CH_2-O-CH_2)[23]. This attests to the gradual increase in the carboxyl content of the fractions[23]. Interestingly, in **Figure 6C**, the characteristic peaks of SNCC at 1,730 and 880 cm^{-1}, as compared to cellulose pulp and NCC, reflect the stretching of carbonyl groups and the hemiacetal linkage, respectively[21]. The liquid phase ^{13}C NMR of DCC (**Figure 6B**) shows peaks at 59 ppm (C6), and multiple peaks at 75-80 ppm (C4 and C5), 102 ppm (C1), and 175 ppm (carboxyl groups on C2 and C3)[23]. **Figure 6D** presents the solid state ^{13}C NMR, which indicates the C4' shoulder peak corresponding to the amorphous phase of cellulose. The ratio of this peak to the sharp C4 peak (corresponding to crystalline cellulose) at 90 ppm is higher for NCC indicating higher crystallinity than cellulose pulp[21]. The broad peaks at 60-80 ppm and 85-105 ppm and the lack of carbonyl peaks at 175-180 ppm suggests hemiacetal linkage of aldehyde groups in SNCC[21]. X-ray diffraction (**Figure 7**) of cellulose and various oxidized fractions (1, 2, and 3) yields ~ 79%, 61%, 91%, and 23% crystallinity indices, respectively[23].

In this article, it has been demonstrated how to prepare new classes of neutral or highly charged biopolymers and hairy nanoparticles from wood fibers. These novel green materials have exceptional colloidal and surface properties as compared to conventional nanocrystalline cellulose (NCC). They can be facilitated in a wide spectrum of applications such as environmental remediation, nanomedicine, nanocomposites and materials science, and micro- and nanoelectromechanical systems (MEMS/NEMS). This research and discovery opens a new horizon in the cellulose-based nanotechnology.

Disclosures

The authors have nothing to disclose.

Acknowledgements

References

1. Habibi, Y., Lucia, L. A., & Rojas, O. J. Cellulose nanocrystals: Chemistry , self-Assembly , and applications. *Chem. Rev.* **110** (6), 3479-3500 (2010).
2. Samir, M. A. S. A., Alloin, F., & Dufresne, A. Review of recent research into cellulosic whisker, their Properties and their application in nanocomposites field. *Biomacromolecules.* **6** (2), 612-626 (2005).
3. Sjöström, E. *Wood chemistry: Fundamentals and applications.* Academic Press: New York, (1993).
4. Nageli, C., & Schwendener, S. *Das Mikroskop, Theorie und Anwendung desselben. 2. Verbesserte auflage.* Leipsig :W. Engelmann: Leipzig, (1877).
5. Moon, R. J., Martini, A., Nairn, J., Simonsen, J., & Youngblood, J. Cellulose nanomaterials review: structure, properties and nanocomposites. *Chem. Soc. Rev.* **40** (7), 3941-3994 (2011).
6. Klemm, D., Kramer, F., *et al.* Nanocelluloses: A new family of nature-based materials. *Angew. Chem. Int. Ed.* **50** (24), 5438-5466 (2011).
7. Wang, N., Ding, E., & Cheng, R. Surface modification of cellulose nanocrystals. *Front. Chem. Eng. China.* **1** (3), 228-232 (2007).
8. Siqueira, G., Bras, J., & Dufresne, A. Cellulosic bionanocomposites: A review of preparation, properties and applications. *Polymers.* **2** (4), 728-765 (2010).
9. Siaueira, G., Bras, J., & Dufresne, A. Cellulose whiskers versus microfibrils: Influence of the nature of the nanoparticle and its surface functionalization on the thermal and mechanical properties of nanocomposites. *Biomacromolecules.* **10** (2), 425-432 (2009).
10. Peng, B. L., Dhar, N., Liu, H. L., & Tam, K. C. Chemistry and applications of nanocrystalline cellulose and its derivatives: A nanotechnology perspective. *Can. J. Chem. Eng.* **89** (5), 1191-1206 (2011).

11. Lu, P., & Hsieh, Y. Lo Preparation and properties of cellulose nanocrystals: Rods, spheres, and network. *Carbohydr. Polym.* **82** (2), 329-336 (2010).
12. Liu, D., Chen, X., Yue, Y., Chen, M., & Wu, Q. Structure and rheology of nanocrystalline cellulose. *Carbohydr. Polym.* **84** (1), 316-322 (2011).
13. Lam, E., Male, K. B., Chong, J. H., Leung, A. C. W., & Luong, J. H. T. Applications of functionalized and nanoparticle-modified nanocrystalline cellulose. *Trends Biotechnol.* **30** (5), 283-290 (2012).
14. Kalia, S., Dufresne, A., *et al.* Cellulose-based bio- and nanocomposites: A review. *Int. J. Polym. Sci.* **2011**, 1-35 (2011).
15. Bai, W., Holbery, J., & Li, K. A technique for production of nanocrystalline cellulose with a narrow size distribution. *Cellulose.* **16** (3), 455-465 (2009).
16. Eichhorn, S. J., Dufresne, A., *et al.* Review: Current international research into cellulose nanofibres and nanocomposites. *J. Mater. Sci.* **45** (1), 1-33 (2010).
17. Safari, S., Sheikhi, A., & van de Ven, T. G. M. Electroacoustic characterization of conventional and electrosterically stabilized nanocrystalline celluloses. *J. Colloid Interface Sci.* **432**, 151-157 (2014).
18. Yang, H., Tejado, A., Alam, N., Antal, M., & Van De Ven, T. G. M. Films prepared from electrosterically stabilized nanocrystalline cellulose. *Langmuir.* **28** (20), 7834-7842 (2012).
19. Guthrie, R. D. The "dialdehydes" from the periodate oxidation of carbohydrates. *Adv Carbohydr Chem.* **16**, 105-158 (1961).
20. van de Ven, T. G. M.; Tejado, A.; Alam, M. N.; Antal, M. Novel highly charged non-water soluble cellulose products, includes all types of cellulose nanostructures especially cellulose nanofibers, and method of making them. *U.S. Provisional Patent Application 3776923-v3, WO 2012119229 A1.* (2011).
21. Yang, H., Chen, D., & van de Ven, T. G. M. Preparation and characterization of sterically stabilized nanocrystalline cellulose obtained by periodate oxidation of cellulose fibers. *Cellulose.* **22** (3), 1743-1752 (2015).
22. Sheikhi, A., Safari, S., Yang, H., & van de Ven, T. G. M. Copper removal using electrosterically stabilized nanocrystalline cellulose. *ACS Appl. Mater. Interfaces.* **7** (21), 11301-11308 (2015).
23. Yang, H., Alam, M. N., & van de Ven, T. G. M. Highly charged nanocrystalline cellulose and dicarboxylated cellulose from periodate and chlorite oxidized cellulose fibers. *Cellulose.* **20** (4), 1865-1875 (2013).
24. Kim, U. J., Kuga, S., Wada, M., Okano, T., & Kondo, T. Periodate oxidation of crystalline cellulose. *Biomacromolecules.* **1** (3), 488-492 (2000).
25. Araki, J., Wada, M., & Kuga, S. Steric stabilization of a cellulose microcrystal suspension by poly (ethylene glycol) grafting. *Cellulose.* **17** (1), 21-27 (2001).

July 2016 | 113 | e54133 | Page 10 of 10