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Österberg, Monika; Peresin, Maria S.; Johansson, Leena-Sisko; Tammelin, Tekla
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Published in:
Cellulose

DOI:
[10.1007/s10570-013-9920-8](https://doi.org/10.1007/s10570-013-9920-8)

Published: 01/06/2013

Document Version
Peer reviewed version

Please cite the original version:
Österberg, M., Peresin, M. S., Johansson, L-S., & Tammelin, T. (2013). Clean and reactive nanostructured cellulose surface. Cellulose, 20(3), 983-990. <https://doi.org/10.1007/s10570-013-9920-8>

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1 **Clean and reactive nanostructured cellulose surface**

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13 **Abstract:**

14 A simple, solvent-free and low cost method to activate the surface of nanofibrillated cellulose
15 films for further functionalization is presented. The method is based on the oxidative properties of UV
16 radiation and ozone, to effectively remove contaminants from nanocellulosic surface, which remains
17 clean and reactive for at least a week. The efficiency of the method is demonstrated by X-ray
18 photoelectron spectroscopy and contact angle measurements. In clear contrast to previous results on
19 nanoscaled cellulose the relative atomic concentration of non-cellulosic carbon atoms was only 4%, and
20 water completely wetted the surface within seconds. After activation, neither chemical degradation nor
21 morphological changes on cellulose were observed. This surface activation is essential for further
22 functionalization of the film in dry state or nonpolar media. The surface activation was confirmed by
23 silylation and a four times higher degree of substitution was achieved on the activated sample compared
24 to non-activated reference film, as monitored with XPS.

25

26 **KEY WORDS:** microfibrillated cellulose, ozonation, film, cleaning, UV

27

28 **Introduction**

29 Cellulose is a natural polymer and an almost unlimited source for sustainable production of materials on
30 industrial scale. Recently the interest for nano-scaled cellulosic materials, like nanofibrillated cellulose
31 (cellulose nanofibrils, NFC) or cellulose whiskers (cellulose nanocrystals, CNC) has increased
32 exponentially (Habibi et al. 2010, Klemm et al. 2011, Nishiyama et al. 2008, Walther et al. 2010). The
33 main reasons for the growing interest in nanocellulose are the development of energy efficient and up-
34 scalable production methods (Pääkkö et al. 2007, Saito et al. 2007, Wågberg et al. 2008) and the

35 extraordinary properties of this renewable material (Eichhorn et al. 2010).

36 Due to the large surface area and enhanced hydrogen bonding ability of the fibrils, NFC forms
37 strong hydrogels at very low solids content. Furthermore, upon drying the nanofibrillar network in these
38 hydrogels has a high inherent tendency to form film-like structures which is especially interesting
39 feature when considering novel application areas. NFC films are strong, they exhibit low oxygen
40 permeability and they can appear as transparent or translucent plastic-like materials rendering them as
41 an attractive alternative to petroleum-based polymers for example in packaging applications (Lavoine et
42 al. 2012). Moreover, we have developed relatively fast and up-scalable methods to prepare NFC films
43 (Österberg et al. 2013, Peresin et al. 2012, Tammelin et al. 2011) which can be further surface modified
44 e.g. in aqueous media (Orelma et al. 2012).

45 Nevertheless, the unique properties of NFC hydrogels change dramatically and often
46 unpredictably upon drying or when exposed to nonpolar media. This is why most literature report on
47 application or modification of NFC in never-dried form (Klemm et al. 2011). In our recent paper we
48 proposed that this is due to the carbonaceous contamination layers that accumulates on the surface of
49 highly hydrophilic cellulosic nanofibrils and nanofibrillar films whenever exposed to nonpolar media,
50 e.g. upon drying (Johansson et al. 2011). The passivation layer impedes modification or application
51 based on interactions with the hydroxyl groups of cellulose, via occupying significant part of these
52 groups so that they are no longer available for further functionalization. However, we also found that
53 using appropriate solvent exchange procedure before drying of the NFC dispersion, the irreversible
54 passivation of the surface was avoided and the surface of the individual nanofibrils were highly
55 accessible for further functionalization (Johansson et al. 2011).

56 The remaining challenge is consequently how to re-activate dry nanocellulosic surfaces. In this
57 contribution we introduce a solvent-free method, to clean and re-activate the NFC film surface, based on
58 the combination of UV and ozone. Ozone is a powerful oxidation reagent used in many applications for

59 removal of organic contaminants from various surfaces like steel (Kumar and Biswas 2011), sensor
60 ceramics (Chen et al. 2007, Zhang et al. 2006), and atomic force microscopy (AFM) probes (French et
61 al. 2008). UV radiation in the presence of ozone (UV/O₃) was also found to be the most efficient
62 cleaning method in recycling gold nanoparticle junction arrays (French et al. 2008). Patterned
63 superhydrophilic arrays have also been obtained by UV/O₃ treatment (Luz et al. 2011).

64 The effect of UV/O₃ on the surface properties of dry films of nanofibrillated cellulose was
65 evaluated with atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), contact angle
66 (CA) and FT-IR experiments. The enhanced reactivity and accessibility of the hydroxyl groups on the
67 NFC film surface was verified with a simple and well-known silylation reaction. Significant
68 improvement in the surface reactivity of NFC films was observed upon UV/O₃ activation without any
69 severe changes in nanocellulose structure and chemistry.

70

71 **Experimental Section**

72 *Nanofibrillated cellulose* was prepared by disintegration of fully bleached never dried hard wood
73 kraft pulp using a high shear Fluidizer (Microfluidics Int. Co, USA). The pulp was washed into sodium
74 form prior to disintegration according to a method introduced by Swerin et al (1990) and passed six
75 times through the fluidizer. This treatment removes excess of salt from the pulp suspension and ensures
76 that only sodium ions are associated with anionic groups on the pulp. No chemical or enzymatic
77 pretreatment was applied and the charge density of the pulp was 0.0065 meq/g as determined by
78 conductometric titration according to Katz et al (1984). The 132 cm² large and around 100 μm thick
79 free-standing NFC films were prepared by over-pressure filtration of a 0.84% dispersion of fibrils
80 followed by hot pressing at 100°C and 1800 Pa (Österberg et al. 2013). Sefar Nitex polyamine fabric
81 was used for filtration and remained with the film during pressing. A commercial *UV ozonator* from
82 Bioforce Nanosciences was used to activate the NFC film surface. The nominal power of the UV source

83 was 80 W, the intensities of the most important wavelengths were 199 for 185 nm and 3975 for 254 nm
84 according to the manufacturer. The distance between sample and radiation source was 2.5 cm.
85 Treatment time for the films was 10 min. The sample size was about 2×4cm.

86 Efficiency of the activation of the film surface was demonstrated by a simple silylation reaction
87 performed on films obtained in pilot scale, according to Tammelin et al (2011) and Peresin et al (2012).
88 The modification protocol is a slight variation of the method used to modify nanofibrils in bulk
89 (Johansson et al. 2011). Films of about 100 mg were submerged in 150 ml Dimethylacetamide (DMA,
90 99 % - Sigma-Aldrich) in a reaction vessel under continuous Nitrogen flow to evacuate any remaining
91 oxygen. The film was kept in DMA under magnetic agitation until the temperature reached 80 °C.
92 Hexamethyldisilazan, (> 99 % purchased from Sigma-Aldrich) was added drop-wise while stirring (1 µl
93 reagent/mg of film). Reaction was continued over night at constant temperature. Films were thoroughly
94 washed with DMA and with methanol (HPLC grade; Rathburn) to remove any possible unreacted
95 chemicals. Finally, the films were allowed to dry in air.

96 *X-ray photoelectron spectroscopy, XPS* (Kratos Analytical AXIS 165 electron spectrometer with
97 monochromatic Al K α irradiation at 100 W), was used for surface chemical analysis of the free-
98 standing NFC films. More specifically the effect of UV/O₃ treatment and silylation on surface chemical
99 composition was monitored. The measurement procedures and acquisition parameters were optimized
100 for cellulosic samples as described by Johansson (Johansson 2002). Samples were analysed after one
101 week storage in desiccator. A minimum of three different areas were measured per sample.

102 *AFM* (Nanoscope IIIa scanning probe instrument from Digital Instruments, Santa Barbara, USA)
103 was used to probe the surface topography of the films before and after UV/O₃ treatment. Three different
104 areas on each sample were scanned in tapping mode in air using silicon cantilevers (SCD 15/AIBS,
105 MicroMasch, Talinn, Estonia). The nominal resonance frequency of the cantilevers was around 300
106 kHz.

107 *Contact angle measurements:* The sessile drop method was employed for determination of water
108 contact angle with a video camera based fully computer-controlled contact angle meter (CAM 200 from
109 KSV Instruments Ltd., Finland). The measurements were performed at room temperature using
110 deionized water further purified through a Milli-Q water purification unit. At least five separate
111 measurements were made for each sample either 15 min. or 1 week after UV/O₃ treatment. The samples
112 were stored in a desiccator prior to measurements.

113 *Fourier transform infrared spectroscopy (FTIR)* was applied to verify that no chemical
114 degradation of the cellulose occur during the UV/ozone treatment. With the BIO-RAD UMA 500
115 spectrometer (USA) equipped with a universal attenuated total reflection (ATR) germanium crystal the
116 films could be analyzed directly without further sample preparation, the analysis depth being about one
117 micrometer. The spectral data was processed with GRAMS AI software (Thermo Scientific, Galactic
118 Industries Corporation, New Hampshire, USA. All spectra were baseline-corrected and further
119 normalized to have the same value at 1200 cm⁻¹. An average spectrum of three measurements is
120 reported.

121

122 **Results and Discussion**

123 UV ozone treatment was evaluated as a method to clean the surface of NFC films. The method is
124 based on the power of ozone to decompose small molecular weight organic substances while not
125 affecting the cellulosic structure. UV light generates free radicals on the surface of low molecular
126 weight polymers leading to oxidative degradation. UV radiation (185 nm) reacts with atmospheric
127 oxygen and forms atomic oxygen and ozone, both strong oxidizers. Ozone absorbs the 254 nm UV
128 radiation and dissociates into molecular oxygen and atomic oxygen (Zhang et al. 2006). UV light
129 excites ambient oxygen molecules from their ground spin-triplet state into a spin-singlet state thus
130 creating a more reactive environment in which the immediate cleavage of organic bonds like C-C, C-H

131 and O-H into volatile organics takes place (Ye et al. 2005). This procedure has been found to be more
132 efficient than UV radiation or ozone treatment separately.

133 NFC films were prepared by overpressure filtration of native unmodified NFC (Österberg et al.
134 2013). After hot pressing, a strong, dense and translucent film was obtained within a couple of hours
135 (Fig. 1a). The density of the film is about 1250 kg/m³ (Österberg et al. 2013). XPS wide spectra were
136 recorded to confirm that the NFC film does not adsorb any foreign chemicals from the fabric during
137 pressing. Only carbon and oxygen signals were observed (Online resources 1). The film was then
138 treated with ozone created by UV light in a commercial UV ozonator, thus removing much of the
139 organic airborne contaminants from the surface.

140 **Fig. 1** a) Free-standing translucent NFC film with the diameter of 13 cm. In the inset an AFM
141 topography image of a 9 μm² area of the film surface is shown. b) XPS C 1s high resolution regions of
142 untreated film (blue lower spectrum) and UV/O₃ treated film (red upper spectrum). The measurements
143 were done one week after treatment. Observe the reduction in the C-C carbon. c) Corresponding water
144 contact angle values for untreated reference (blue squares), UV/O₃ treated after 15 min (unfilled red
145 triangles) and after one week (red filled triangles). Note that due to the rapid spreading of the water
146 droplet only a few measurement points close to 0s are visible 15 min after treatment.

147 The surface topography of the film was homogeneous and with only nanometer scaled
148 roughness, as seen in the AFM image in the inset of Fig. 1a). In our previous work, we demonstrated
149 that although pure and reactive when dispersed in aqueous media, NFC easily accumulates substantial
150 amount of non-cellulosic material upon drying which passivates the fibril surfaces (Johansson et al.
151 2011). Experimental evidence of such behavior was obtained by X-ray photoelectron spectroscopy
152 (XPS). A high amount of carbon atoms which are bonded only to other carbon or hydrogen atoms (C-C
153 carbon signal) was observed at the outmost surface of the nanofibrillated cellulose. Similar behaviour
154 was observed in the case of untreated film surface (Fig. 1b). The relative abundance of C-C carbon was

155 approximately 11 % for the untreated nanocellulose films which is comparable to the previously
156 reported results for nanocellulosic fibrils (Andresen et al. 2007, Littunen et al. 2011, Uschanov et al.
157 2011). Similar trend was perceived in the case of water contact angle values (Fig. 1c). The contact angle
158 for untreated film was around 30° in correlation with our previous findings, indicating the presence of a
159 passivation layer on the film surface. Nevertheless, after treating the sample with UV/O₃ for ten
160 minutes, the hydrophilicity of the sample increased and the water droplet completely wetted the surface
161 within a few seconds. Simultaneously the C-C carbon signal decreased to 4%, a very low value for
162 nano-scaled cellulose samples and a 36% decrease as compared to untreated sample.

163 It is worth noting that the surface remained very hydrophilic for at least one week after the
164 UV/O₃ treatment, as evidenced by contact angle values (Fig. 1c), suggesting that passivation of this
165 surface after UV/O₃ treatment is very slow. This behavior is the opposite to the one observed for most
166 mineral surfaces. After the same cleaning procedure, silica surfaces are extremely reactive. However,
167 they accumulate airborne contaminants within minutes when kept in ambient air. We suggest that the
168 unique behavior observed for cellulosic substrates is due to the amphiphilic character of the cellulose
169 molecule and its ability to rearrange the outermost surface molecules, hence minimizing its surface free
170 energy. This behavior may well be one reason for the overall stability of cellulose materials (Johansson
171 et al. 2011, Johansson et al. 2012). The rearrangement at the surface is reversible and thus, the cellulose
172 is fully reactive when immersed in aqueous media where the hydrophilic plane of the cellulose
173 molecules adapts to the hydrophilic media. It must be noted that although the NFC film was made from
174 nanofibrils, after the film formation and drying, it can be compared to macroscopic cellulose samples
175 like filter paper or wood fibres. During the drying process, hydrogen bonds are formed between fibrils
176 and although there is no evidence of increase in crystallinity, during the pressing the films become very
177 dense (Österberg et al. 2013). If, on the other hand, the same treatment is conducted on nano-scaled
178 ultrathin films of dispersed NFC fibrils, the same hydrophilicity and cleanliness is achieved but the film
179 is considerably more reactive and accumulates a passivation layer over time (results not shown). The

180 ultrathin film is more porous and thus has higher surface area, thus being less stable than macroscopic
181 cellulose films.

182 The effect of UV/O₃ treatment on activation of the surface was corroborated by means of a
183 simple surface reaction. Chemical modification through silylation chemistry was performed directly on
184 the surface of the dense NFC film before and after exposing the film surface to the UV/O₃ treatment.
185 The results of the reaction were evaluated by XPS analysis. XPS high resolution spectra for carbon
186 (C1s) and silicon (Si2p) are shown in Fig. 2.

187

188 **Fig. 2** XPS C 1s and Si 2p high resolution regions of untreated film (blue bottom spectrum), untreated
189 and silylated film (black middle spectrum) and UV/O₃ activated and silylated film (red upper spectrum).

190 In the high resolution carbon 1s spectra no clear differences between unmodified (blue) and
191 silylated unactivated film is observed. However an increase in the peak around 284 eV is observed for
192 the activated and silylated sample. In this region both C-C bonds and C-Si bonds appear. In the high
193 resolution Si 2p spectra the effect of surface activation is clearly seen. A small increase in the Si band is
194 observed for the silylated unmodified sample (black spectrum) but the increase is much higher for the
195 activated and silylated sample (red spectrum). The degree of substitution was calculated based on the
196 relative amount of silicon on the surface and was 0.07 for un-activated and 0.26 for UV/O₃-activated
197 sample, corresponding to a four-fold increase in surface activity due to the UV/O₃ treatment. From the
198 wide spectra and high resolution oxygen 1s spectra for the respective samples (Online resource 2 in
199 electronic online resources) we conclude that no significant chemical change except the silylation
200 reaction is occurring at the surface.

201 The oxidative reaction induced by ozone is very strong, introducing carboxylic acid or carbonyl
202 groups at the surface, and leading to severe degradation of low molecular weight polymeric substrates
203 like rubber or low density polyethylene (Hedenberg and Gatenholm 1996, Romero-Sánchez et al. 2005),

204 There is no available literature on the effect of ozone on NFC, although ozone is commonly used in
205 chlorine free delignification of pulp in the papermaking industry (Katz and Scallan 1983). Koljonen et
206 al. (Koljonen et al. 2003) demonstrated that the ozone oxidizes lignin on the pulp fibre surface, which is
207 seen as a decrease in C-C carbon (present in lignin) and increase in the O-C=O carbon in XPS data.
208 Yet, AFM imaging revealed that the cellulose microfibrils stayed intact during the ozone treatment.
209 Ozonation has moreover been used to increase the adhesion between low density polyethene and
210 cellulose fibres in composites (Hedenberg and Gatenholm 1996, Kurosu et al. 2009). As expected, while
211 ozone treatment of polyethene was proven to be efficient ozone treatment of cellulosic fibres decreased
212 the overall adhesion. In photochemical bleaching of pulp (Ohtsuki et al. 2011) or wood powder (Kurosu
213 et al. 2009) the power of UV/O₃ treatment is utilized to remove lignin without decreasing the strength of
214 the pulp (Kurosu et al. 2009). To ensure that there was no degradation occurring at the NFC film surface
215 due to the oxidation, the films were imaged with AFM before and after treatment and the chemical
216 composition of the film was evaluated using attenuated total reflection (ATR) IR (Fig. 3).

217 **Fig. 3** a) AFM topography images, and b) one representative line scan for untreated NFC free-standing
218 film (NFC reference, left) and NFC film that have been UV/O₃ treated (right). c) ATR IR spectra for the
219 two samples illustrate that the sample is not chemically modified due to the ozonation. The area of
220 dashed rectangle from 2000-1200 cm⁻¹ is shown magnified in the inset. Since the spectra overlap the
221 UV/O₃ spectrum was shifted up by 1 a.u. in the inset to facilitate comparison (the upper curve
222 corresponds to UV/O₃ treated sample).

223 From the AFM topography images (Fig. 3a) and the representative lines scans (Fig. 3b) it is
224 obvious that the fibrillar structure was maintained and there is no evidence of changes in the fibril width
225 that would indicate degradation although a decrease in molecular weight cannot be excluded based on
226 these results. The carbonyl groups are very IR active and are usually seen in ozone treated polymer
227 films in the 1700-1750 cm⁻¹ region although the reaction is taking place at the surface (Hedenberg and

228 Gatenholm 1996). However, as seen in the magnification of this region there are absolutely no changes
229 of the ATR IR spectra for the film before and after UV/O₃ treatment. As a matter of fact no chemical
230 changes are observed in the spectra. We further note that the carbon peak in XPS spectra (Fig. 1b) is
231 well resolved and there are no significant changes occurring in the C4 region suggesting that the surface
232 retains its chemical structure. This is in contrast to e.g. oxygen plasma treatment of cellulose fibres,
233 where quite short treatment times induces clear degradation, observed as increase in C–C carbon and
234 oxidation, observed as an increase in O–C=O carbon (Carlsson and Ström 1991).

235 The plastic-like nanocellulosic films can be seen as an emerging application area due to film's
236 peculiar features: the strong self-association tendency of nanofibrils during drying creates smooth,
237 strong, dense, flexible, transparent/translucent films with low transmission rates of gas molecules also at
238 humid conditions (Österberg et al. 2013, Sehaqui et al. 2011). Recently it has been shown that the film
239 manufacturing technology is up-scalable in order to produce films using industrially relevant roll-to-roll
240 technique (Tammelin et al. 2011). For optimum performance and in order to create functional materials
241 there is a need to modify the surface by chemical reactions. Therefore a simple, solvent-free cleaning
242 method, such as the one presented here, should be highly beneficial to boost the film surface reactivity
243 for further functionalizations, eliminating one of the obstacles hindering industrial applications of NFC.

244

245 **Conclusions**

246 A simple solvent-free method to clean and activate the NFC film surface was demonstrated. The method
247 based on UV/O₃ treatment enhanced significantly the reactivity and accessibility of the hydroxyl groups
248 on the cellulose surface thus increasing its hydrophilicity and simultaneously facilitating its more
249 efficient functionalization. Almost four times higher degree of silylation was achieved on activated NFC
250 films. Additionally, the effect was observed to be long-lasting and the treatment did not degrade the
251 cellulose. In this respect cellulose differs from both ceramics and metals that stay clean for only minutes
252 or other organic materials that are degraded by ozone. Due to the recent advances in up-scaling both

253 NFC production and NFC film manufacturing this simple method, based on a commercial technique, to
254 tailor the surface of the NFC film may have large practical implication.

255 **Electronic Supplementary Material**

256 XPS Wide spectra of untreated NFC film and UV/O₃ treated films before (Online Resource 1) and after
257 (Online Resource 2) silylation are shown in the Electronic Supplementary Material.

258

259 **Acknowledgements**

260 Finnish Funding Agency for Technology and Innovation, Tekes, and companies within the
261 Naseva II project are acknowledged for financial support. The NFC sample was received from UPM
262 Kymmene corporation. Dr Joseph Cambell is thanked for the XPS analysis and Ms Anu Anttila, Ritva
263 Kivelä, Rita Hatakka and Mirja Reinikainen are thanked for their excellent laboratory assistance. M.Sc.
264 Anni Lähdetie and Raili Pönni are thanked for advice regarding FTIR data analysis.

265

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