Environmentally benign all-wood biocomposites. (Final Report).

Abstract: Here we want to utilize commercial mechanical pulps to cost-efficiently produce new wood "fibres" suitable to use in composite applications without addition of petroleum based resins and matrix materials. This will allow for completely new product areas for composite materials from all renewable resources. The lessons learnt from our proposed project will also lead to more efficient use and production of conventional thermomechanical pulp (TMP) and chemi-thermomechanical pulp (CTMP). Noatbly and important, the removal of petroleum-based materials will gain significant energy savings and is environmentally friendly.
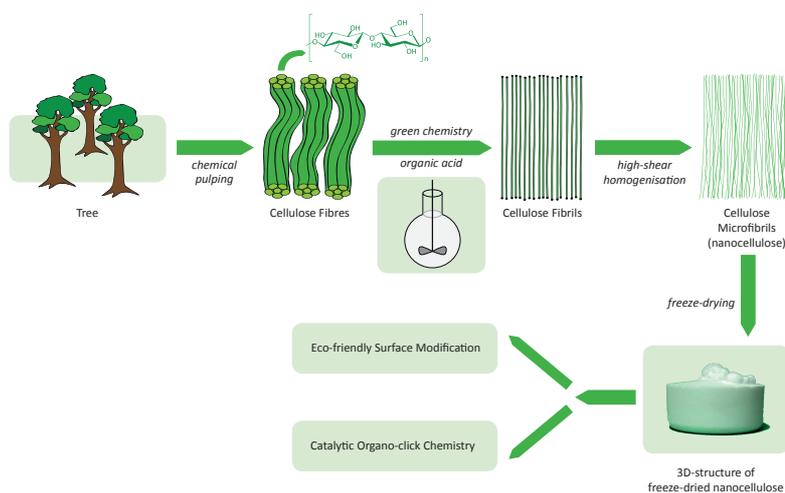

Figure 1. An example of a general novel eco-friendly design for scalable direct fabrication of nanocellulose developed by us.

A novel eco-friendly way of producing nanocellulose:
We began the project by selecting a set of commercial mechanical wood pulps as starting materials. The target is then to prepare mechanically modified wood fibers (pulps) by performing controlled disintegration/homogenization to obtain micro- and/or nano-sized fragments (nano-fibrils and fines). Here we discovered a new way of obtaining nanofibrillated cellulose (NFC, Figure 1). It is even more economical and environmentally benign than the chemical oxidation method (TEMPO/NaBr/NaClO) for the preparation of NFC since it avoids the use of radical initiators and chlorine based oxidants.[1] In fact, we found that when using lignin-containing pulps (e.g. TMP and CTMP) the chlorine is incorporated to the aromatic moieties of the lignin. This could in the long run lead to formation of toxic dioxins and dioxinlike compounds. The novel eco-friendly design for scalable direct fabrication of nanocellulose is based on the use of organocatalysis for converting the cellulose fibres to cellulose fibrilles (Figure 1). Thus, treating different pulps with an organic acid defibrillated the cellulose into cellulose fibrils. Next, homogenization and study of the resulting fibrils with transmission electron microscopy (TEM) determined that all the investigated
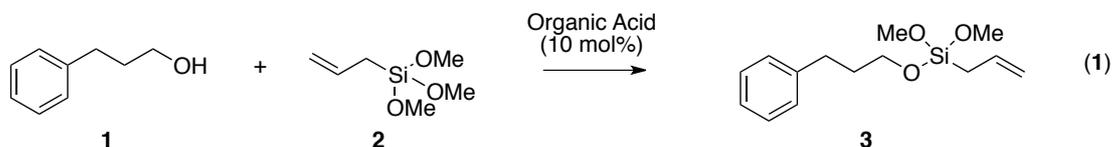
pulps (kraft pulps, TMP and CTMP) gave NFC in high yields. Hence, we could conclude that this is a new, simple and very energy saving way of preparing NFC (patent has been filed). We have performed several experiments and investigated different parameters and pulps that have been included in the patent application. We have also worked on the scaling-up of this technology and it has worked very well. The use of organic acid is both for softening the pulp and at the same time separate the fibrilles by autocatalytic esterification to produce NFC. It is new to use organic acid for direct production of NFC using this low temperature an avoiding the use of an additional catalyst. The method is very good since it can convert CTMP and TMP to NFC without incorporation of chlorine under energy-saving conditions.

Eco-friendly surface modification of lignocellulose: We wanted to investigate the possibility of catalytically modify the surface of lignocelluloses by the use of a metal-free catalyst and hydrophobic silanes. Here an important aspect to consider is the improved stability of the resulting silane-bonds as compared to ester-bonds on the cellulose. For example, the ester bond is not stable under basic conditions, which is a very important factor with respect to the washing of water-repellant textiles and packaging storage. This is also valid for previous organocatalytic direct esterifications of nanocellulosic materials.[2] In search of improving the stability of the covalent bonds, we began experiments investigating the same organic acids, which catalyze the direct esterification, ability to catalyze the covalent attachment of hydrophobic and functional organosilanes to heterogeneous cellulose (Figure 2).[3] It is noteworthy that water-repellant textiles prepared by this technology can be washed more than 10 times at p*H* 11 without decreasing its hydrophobicity.
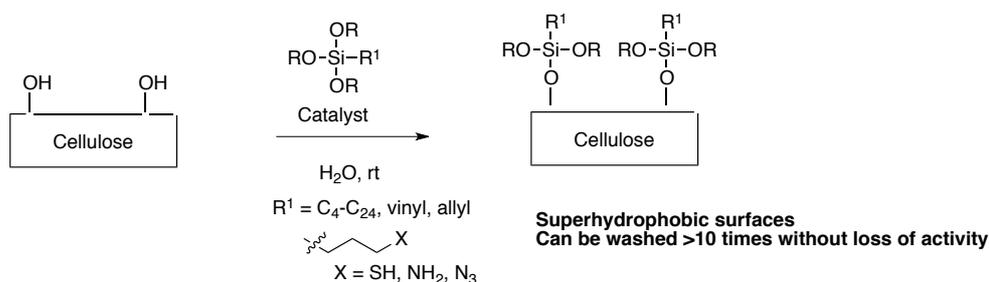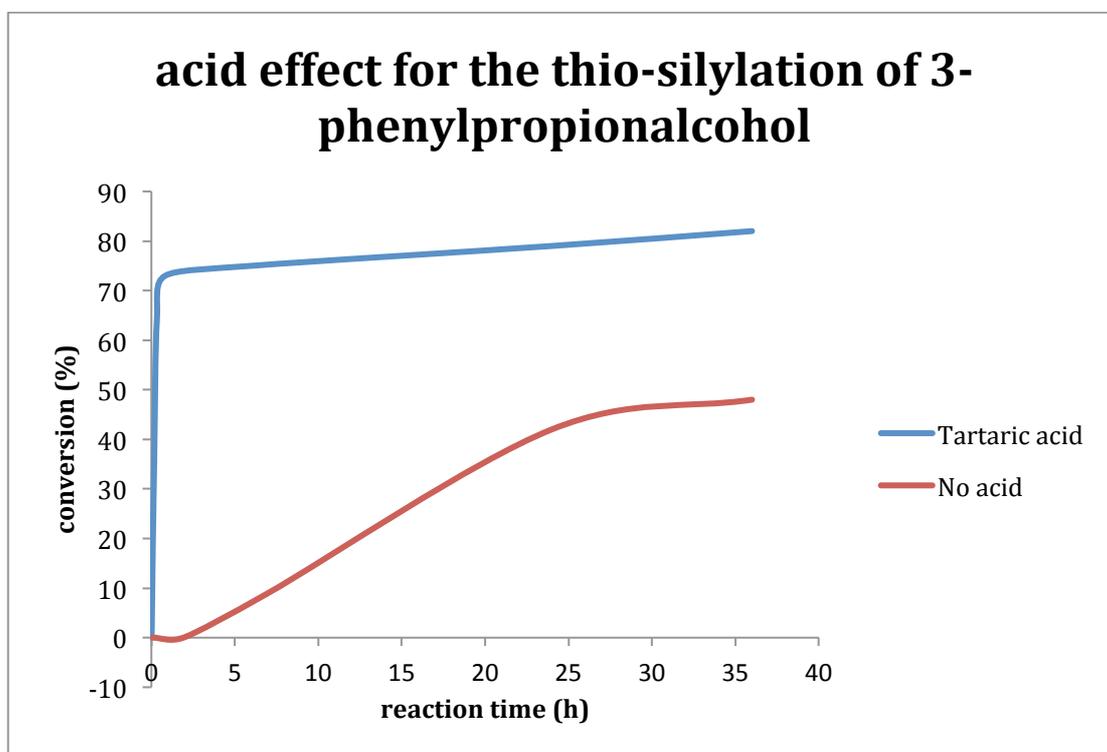

Figure 2. Organocatalytic surface modification of cellulose and lignocellulose.

We began our studies by investigating the effect of metal-free catalyst for the direct silylation between phenylpropion alcohol **1** and allylsilane **2** (equation 1, Figure 3).

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acid screening for the allyl silylation of 3-phenylpropionalcohol

Figure 3. Catalyst screening. The conversion is to the allyl silylated alcohol product **3**.

We found a significant accelerating effect by using non-toxic organic acids as catalyst for the silylation. We next investigated the organic acid-catalyzed direct silylation of phenylpropion alcohol **1** with 3-(trimethoxysilyl)propane-1-thiol **4** (equation 2, Figure 4). We found a significant rate enhancement when we employed the organic acid catalyst.
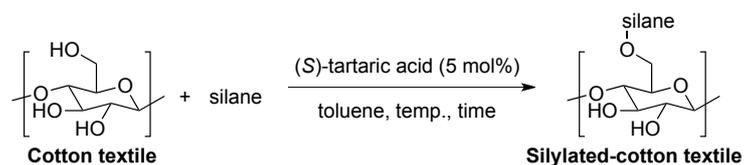
**Figure 4.** The tartaric acid catalyzed conversion of alcohol **1** to silylated alcohol product **4**.

With these results in hand, we began to investigate the hydrophobization of different cellulosic and lignocellulosic materials. For example, we found that various silanes could be attached to cotton (Table 1). The employment of organic acid catalyst accelerated the reaction but did not show big difference in contact angle. However, more silane was attached to the cellulose fibres when a catalyst was employed as determined by elemental analysis.
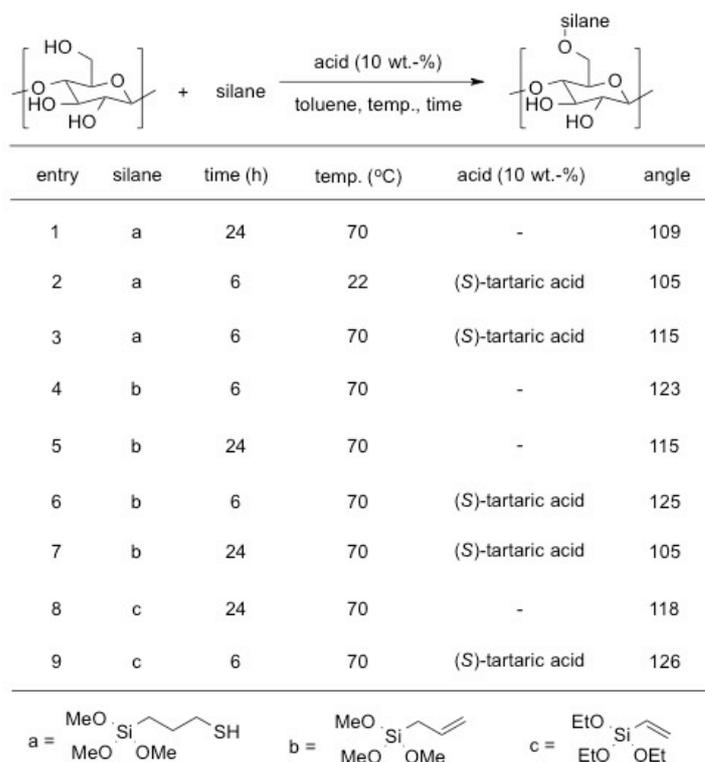
Table 1. Silylation of cotton.

Cotton textile + silane $\xrightarrow[\text{toluene, temp., time}]{(S)\text{-tartaric acid (5 mol\%)}}$ **Silylated-cotton textile**

Entry	silane	Time (h)	Temp. (°C)	Water repellency[a]	Angle
1	b	6	70	++++	110
2	b	14	70	++++	110
3	b	2	90	-	-
4[b]	b	6	70	n.d.	n.d.
5[c]	b	6	70	n.d.	n.d.
6[d]	b	6	70	-	-
7	d	6	70	++++	122
8[e]	d	6	70	++	n.d.
9	d	2	70	++++	115
10	d	1	70	++++	115
11[b]	d	3	70	++++	122
12	d	3	90	++++	115
13[f]	d	2	70	-	-
14	a	6	70	+	102
15	c	2	70	++++	106

[a] Water repellency: - = 5s <t <1 min, + = 1 <t <5 min, ++ = 5 min <t <10 min, +++ = 10 min <t <60 min, ++++ = >60 min. [b] neat reaction. [c] THF as the solvent. [d] EtOH/H_2O (25% v/v) as the solvent. [e] The reaction was performed without acid. [f] EtOH as the solvent n.d. = not determines
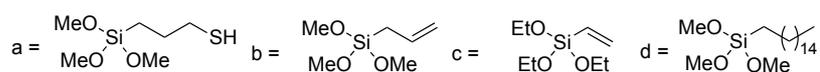
We also successfully hydrophobized lignocellulosic material (Table 2). The employment of tartaric acid as the catalyst increased the amount of silane, which was attached to the lignocellulosic material as determined by elemental analysis. For example, the silane content was 7 times higher when silane **4** was catalytically attached to the lignocellulose. CP/MAS ^{13}C NMR spectroscopy revealed that the cellulose had been covalently modified at the 6-position of the glucose unit.

Table 2. Silylation of lignocellulose

entry	silane	time (h)	temp. (°C)	acid (10 wt.-%)	angle
1	a	24	70	-	109
2	a	6	22	(S)-tartaric acid	105
3	a	6	70	(S)-tartaric acid	115
4	b	6	70	-	123
5	b	24	70	-	115
6	b	6	70	(S)-tartaric acid	125
7	b	24	70	(S)-tartaric acid	105
8	c	24	70	-	118
9	c	6	70	(S)-tartaric acid	126

Next, the catalytic silylation of the NFC was investigated. Here the NFC was first converted to a foam material by freeze drying and next catalytically modified. Here all types of NFC materials can be modified as exemplified by attachment of silanes **1**, **4** and a C-16 silane to the surface. The surface modified foams became highly hydrophobic (Figure 5).
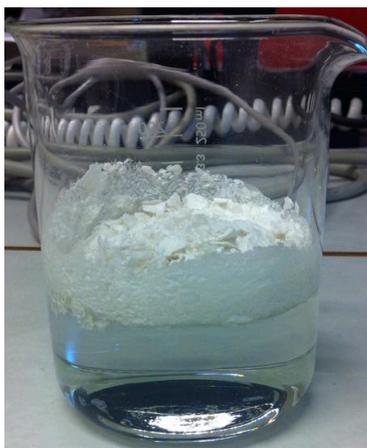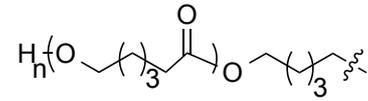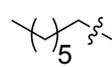

Figure 5. Nanocellulose foam after surface modification. Exhibiting hydrophobic property.

Click chemistry: After developing the organocatalytic surface modification we began to investigate the thiol-ene "click chemistry" reaction between thiols and alkenes for the highly modular functionalization of cellulose, TMP, CTMP and NFC. In Table 3, the results from the click reactions of allyl-functionalized lignocellulose are shown. We attached a biodegradable polyester, C-16 hydrocarbon chain and the bioactive molecule biotin. All reaction worked as established by IR and elemental analysis. The

contact angle was only improved when less hydrophobic allyl-functionalized cellulose was used as the starting material (entry 2 and 3).

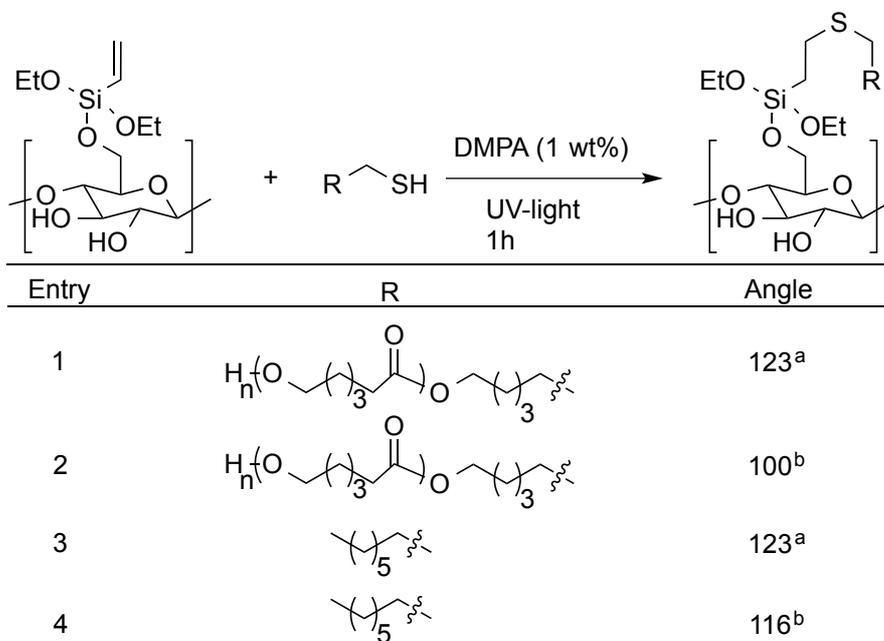**Table 3.** Click modification of allyl functionalized lignocellulose.
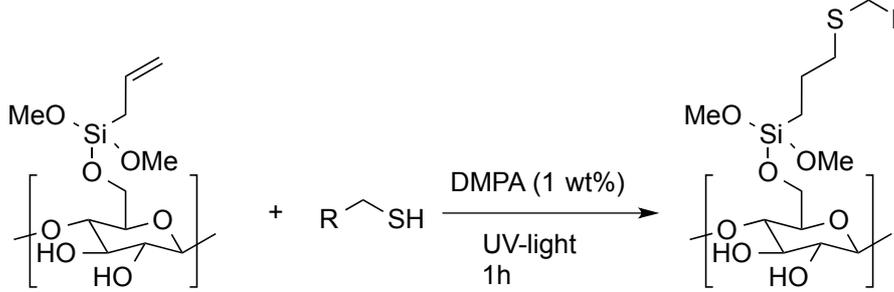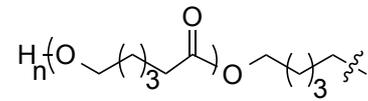
Entry	R	Angle
1		129[a]
2		124[b]
3		127[b]
4		n.d.
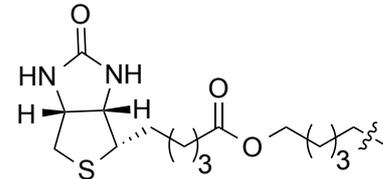
[a] Cellulose silylated with (*S*)-tartaric acid giving contact angle 125 prior to click reaction. [b] Cellulose silylated without acid giving contact angle 115 prior to click reaction.

After this, we investigated the click reaction on the vinyl-functionalized cellulose (Table 4). The reaction worked as determined by IR analysis of the polyester functionalized lignocellulose. However, we could not see an increase of the contact angle of the lignocellulose sheets in these cases.
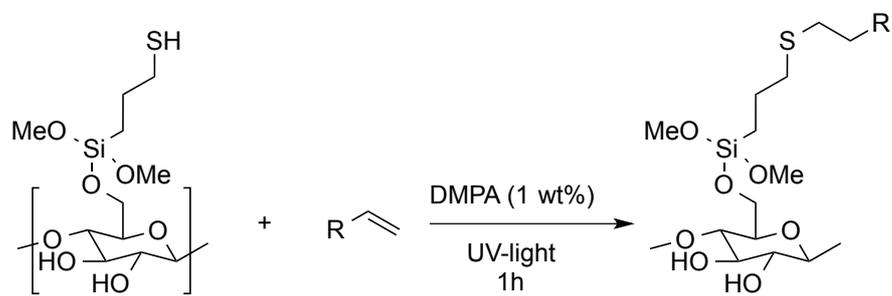
Table 4. Click modification of vinyl functionalized lignocellulose.

Entry	R	Angle
1	$H\!\left(O\!-\!CH_2CH_2\right)_n O\!-\!(CH_2)_3\!-\!C(=O)\!-\!O\!-\!(CH_2)_3\!-$	123[a]
2	$H\!\left(O\!-\!CH_2CH_2\right)_n O\!-\!(CH_2)_3\!-\!C(=O)\!-\!O\!-\!(CH_2)_3\!-$	100[b]
3	$(CH_2)_5\!-$ (branched)	123[a]
4	$(CH_2)_5\!-$ (branched)	116[b]

[a] Cellulose silylated with (S)-tartaric acid giving contact angle 126 prior to click reaction. [b] Cellulose silylated without acid giving contact angle 118 prior to click reaction.

The thiol-ene click reaction of thiol-functionalized cellulose using a large variety of alkenes was also investigated (Table 5). The reactions worked and an improved contact angle was obtained when a C-16 alkene was employed as a substrate (entry 1). Several biologically and UV active groups were also attached to the cellulose. The resulting cellulosic material exhibited UV activity. Thus, demonstrating that the molecules had been attached. It was also further confirmed by IR, NMR and elemental analysis.

Table 5. Click modification of thiol functionalized lignocellulose with alkenes.

Entry	R	Angle
1	(CH₂)$_{12}$ alkyl chain	129[a]
2	$H{-}(O{-}(CH_2)_3){-}C(=O){-}O{-}(CH_2)_2{-}$	117[a]
3	$H{-}(O{-}(CH_2)_3){-}C(=O){-}O{-}(CH_2)_2{-}$	101[b]
4	Ph	117[a]
5	pyridin-3-yl	n.d.
6	3,4-dihydroxyphenyl	n.d.
7	citronellal-type chain	111[a]
8	pinene-type	111[a]
9	quinine-type	n.d.
10	quinidine-type	n.d.
11	biotin ester	n.d.

[a] Cellulose silylated with (S)-tartaric acid giving contact angle 115 prior to click reaction.
[b] Cellulose silylated without acid giving contact angle 109 prior to click reaction.

The developed methodology is highly versatile and we also expanded it to cotton textiles and avicel (Figure 6). Here we attached UV active quinidine and hexadecane. We found that the contact angle significantly increased by attaching the hexadecene to the thiol-functionalized textile (108° to 134°).
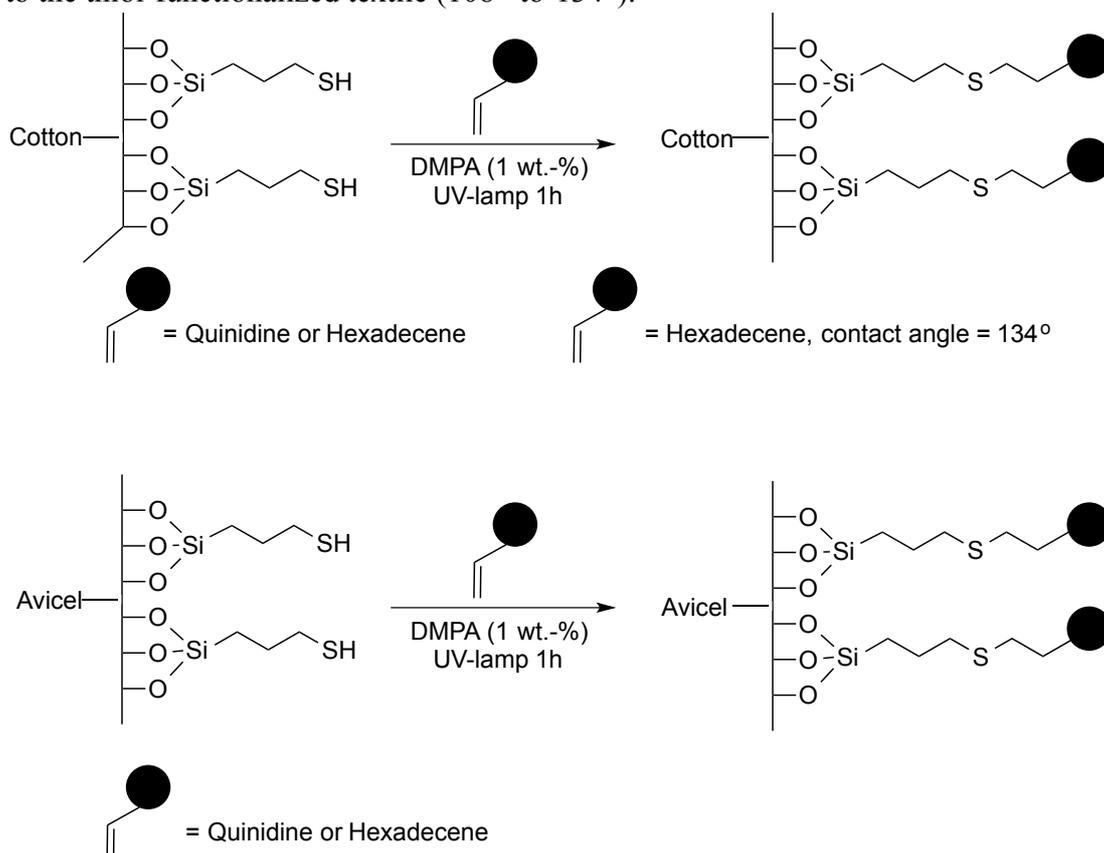
Figure 6. Click modification of thiol-functionalized avicel and cotton. Initial contact angle before click of the cotton textile was 102°.

The click reaction was also investigated on NFC and we found that it worked very well. For example, quinidine was employed since it is UV active and should be possible to detect by simple UV analysis (Figure 7). Indeed, in Figure 8, we see that the thiol-functionalized NFC (left) and Quinidine-functionalized NFC (right) on water and under a UV lamp. They are both hydrophobic and float on water but only the latter is UV active. The same UV activity of quinidine can be seen in Figure 9 were only the quinidine functionalized NFC (B) is UV active and not the thiol-functionalized NFC (A).
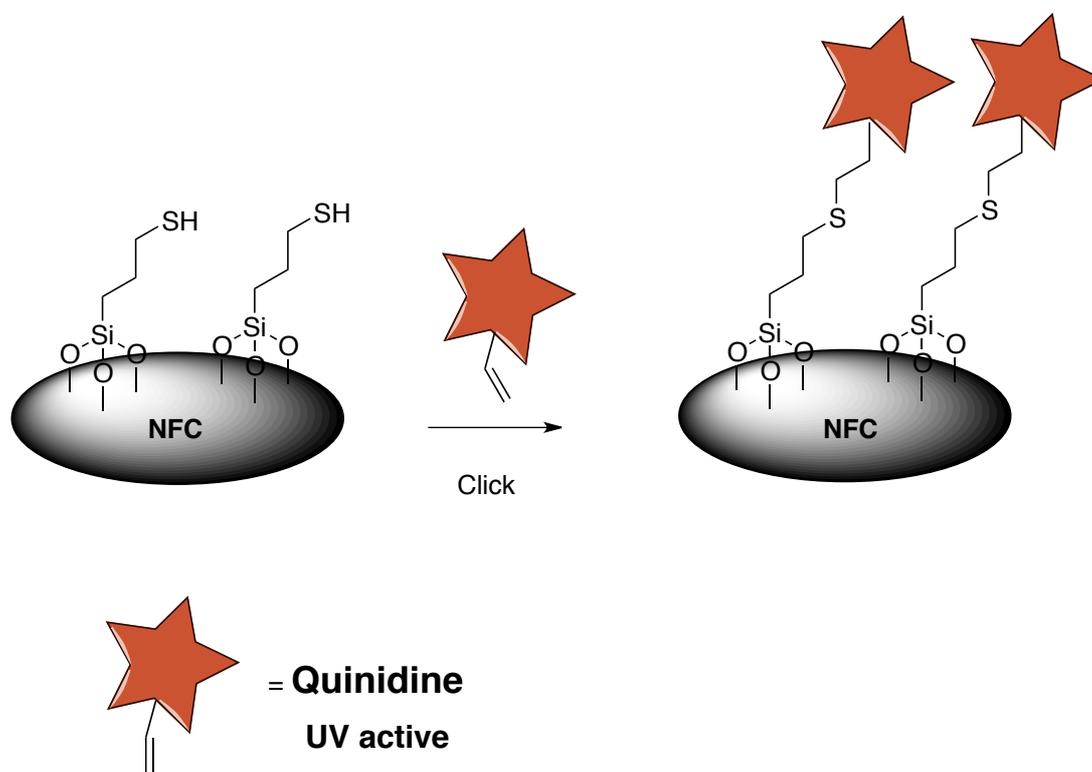
Figure 7. Click modification of thiol-functionalized NFC with a UV active group (quinidine, structure shown in Table 5 entry 10).

Figure 8. Thiol-functionalized NFC (left) and Quinidine-functionalized NFC (right) on water and under a UV lamp.
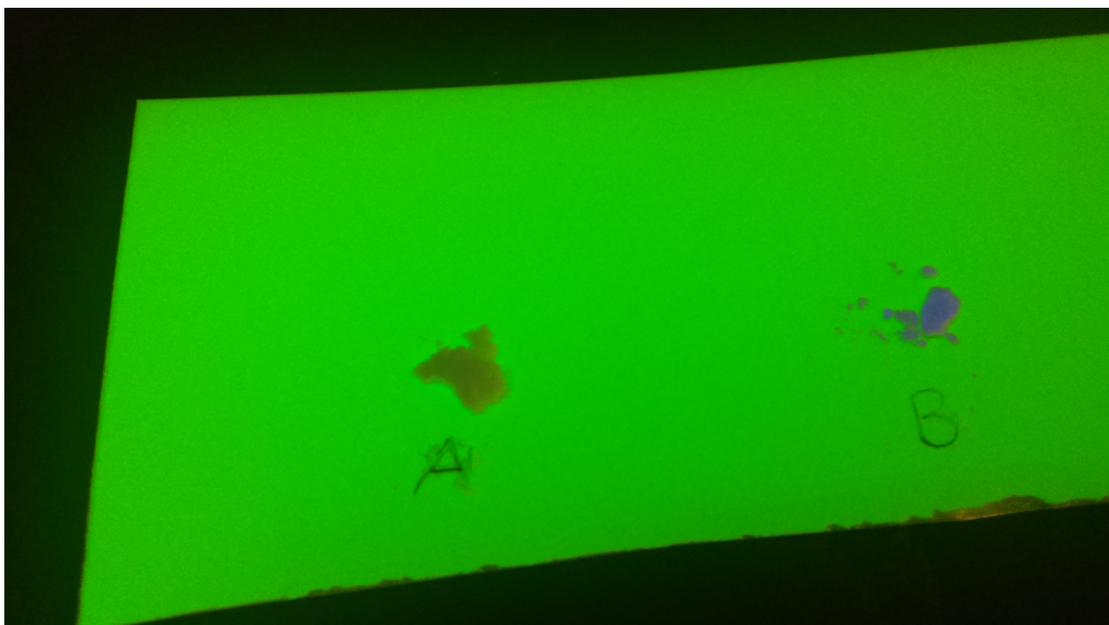
Figure 9. Thiol-functionalized NFC (A) and Quinidine-functionalized NFC (B) under a UV lamp.

Scale-up: All of the above described laboratory processes has now been further scaled-up and we have performed the reaction up to Kg scale. The fibrillated and modified softwood CTMP is now ready for investigation for applications in high-strength nanocomposite materials without use of any adhesive or resin (green chemistry). The processing method will be compression molding at high temperature (180°C) and thus thermally plasticize the lignin. Unmodified CTMP provides high-strength translucent wood nanocomposite with elastic modulus in the range 13.1-14.9 GPa and tensile strength in the range 215.1-242.8 MPa.[4] However, the main problem is a fairly strong discoloration of the material. These results makes us to expect that we can obtain more hydrophobic CTMP/TMP fibers (fragments) which can be stabilized with regard to thermal and light induced ageing and at the same time reach lower lignin softening temperature during compression molding. We can also attach colored groups to the CTMP.

Molding experiments: The fibrillated and modified softwood CTMP has been investigated in molding experiments. The results have shown very good results and the fibers have maintained their hydrophobicity without losing elastic modulus and strength. They also very good as materials in compressed bio-composites and are applied to several potential products (packaging and burial coffins). Here Organoclick AB has developed new technology for making strong eco-friendly burial coffins in on press. It is noteworthy that the developed technology and materials can be applied for creating the sustainable materials, which they are constructed from. Other applications are in packaging where the modified CTMP fibers are excellent additives.

Catalytic and metal binding properties: We also prepared amine-modified CTMP according to the above described organocatalytic technology. This material exhibits anti-bacterial activity and is also very good in binding noble metal salts. This was

demonstrated by binding Pd nanoparticles to the fibers and next use them as recyclable catalysts in different C-C bond forming reactions. Thus, the materials can be use as catalytically active sustainable materials. They have also anti-bacterial activities and can be used in filtration and purification of metals.

Conclusion:

We have created a novel green chemistry method for the preparation of nanofibrillated cellulose (NFC). We have also developed a unique "organoclick" chemistry platform for highly versatile surface modification of cellulose and lignocellulosic materials, which was inspired by the Cordova-Hafren strategy for surface modifications of cellulose (combination of organocatalysis and click-chemistry)[5]. We found that both TMP and CTMP can be efficiently modified and highly hydrophobic. The transformations can be scale-up and the resulting material can be used in compression molding. Hence, we have developed eco-friendly technology for cost-efficiently produce new wood "fibres" suitable to use in composite applications without addition of petroleum based resins and matrix materials. New products will be released to the market in 2016.

References

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