

Conference paper

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A sustainable strategy for production and functionalization of nanocelluloses

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Abstract: A sustainable strategy for the neat production and surface functionalization of nanocellulose from wood pulp is disclosed. It is based on the combination of organocatalysis and click chemistry (“organoclick” chemistry) and starts with nanocellulose production by organic acid catalyzed hydrolysis and esterification of the pulp under neat conditions followed by homogenization. This nanocellulose fabrication route is scalable, reduces energy consumption and the organic acid can be efficiently recycled. Next, the surface is catalytically engineered by “organoclick” chemistry, which allows for selective and versatile attachment of different organic molecules (e.g. fluorescent probes, catalyst and pharmaceuticals). It also enables binding of metal ions and nanoparticles. This was exemplified by the fabrication of a heterogeneous nanocellulose-palladium nanoparticle catalyst, which is used for Suzuki cross-coupling transformations in water. The disclosed surface functionalization methodology is broad in scope and applicable to different nanocelluloses and cellulose based materials as well.

Keywords: click chemistry; cross-coupling reaction; heterogeneous catalysis; nanocellulose; NICE-2016; organocatalysis; surface engineering.

Introduction

Nanotechnology is the research on controlling, fabricating and understanding matter at dimensions of approximately 1–100 nm in order to design special properties and functionalities [1]. Nanomaterials from cellulose and lignocelluloses are renewable, hydrophilic, exhibit prominent environmental advantages over other nanomaterials in their production and play a major role in the nanotechnology field [2–9]. They have excellent material properties (e.g. high surface area-to-volume ratio, high tensile strength, high stiffness and high Young’s modulus) and have the potential to replace fossil-based materials as well as being biodegradable. Nanocelluloses have shown promise in several applications including strength additives, functional coatings, barrier coatings, films, emulsions, foams, optical devices, adhesives, composites, biomedical engineering materials, packaging, separation membranes, fillers and non-woven materials. Two types of nanocellulose can be derived from the cellulose in wood: nanofibrillated cellulose (NFC) and cellulose nanocrystals

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(CNC) [10]. NFC is long and flexible, composed of fibers less than 100 nm in diameter and several microns in length, containing both amorphous and crystalline regions. CNC consists mostly of rice-like crystals (no amorphous regions) with a diameter ranging from 10–20 nm and lengths of a few hundred nanometers. Therefore, different chemical methods have been developed for their construction. NFC fabrication from wood-derived pulp fibers was first achieved by mechanical agitation [4, 11, 12]. There are also chemical-mechanical methods such as the carboxymethylation route for NFC production [13]. These methods require high energy input as compared to other NFC production methods such as Isogai's manufacturing process [4, 14, 15]. The Isogai route starts with a regio-selective Anelli-Montanari oxidation ([2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), NaClO]-oxidation [16]) of the pulp and is followed by homogenization [4, 15]. NFC can also be prepared by enzymatic pretreatment methods [17]. Among the above manufacturing processes, the enzymatic pretreatment and mechanical agitation routes exhibit the lowest effect on the environment [18]. However, enzyme stability and use of biocides can be disadvantages for the former and high energy requirements for the latter method. When comparing the chemical treatment methods, the (TEMPO)-NaClO-oxidation-homogenization route has a lower environmental impact than the carboxymethylation route [19, 20]. However, in particular the use of a non-selective chlorine-based oxidant can be a disadvantage in large-scale production and can have a negative effect on the environment. CNC has no amorphous region and consist of small crystals with diameters in the range of 10–20 nm. The fabrication of CNC is generally performed by strong inorganic acid hydrolysis (e.g. H_2SO_4 , HCl, phosphoric acids) of the amorphous region resulting generally in lower yields as compared to the NFC production methods [11, 12, 21, 22].

The hydrophilicity and high moisture sensitivity of cellulose and nanocellulose materials is an important factor, which can be a major disadvantage. However, their surface is challenging to modify under environmentally friendly conditions. Therefore, the cellulosic materials are often dissolved in organic solvents, which can be harmful, and activated reagents are used for their modification. Hafren and Cordova disclosed the direct selective surface modification and hydrophobization of cellulose and lignocellulosic materials using organocatalysis [23, 24]. This strategy has also recently been applied to surface-functionalization of nanocellulose [25, 26]. Moreover, the selective installment of a specific functional group on the cellulose allows for additional derivatization of its surface using Sharpless and co-workers "click-chemistry" concept [27–32]. For example, Cordova and Hafren combined organic acid-promoted surface modification with click chemistry for modification of cellulose ("organoclick" chemistry) [28, 29]. Zimmerman and co-workers applied "organoclick" chemistry for selective functionalization of nanocellulosic materials [30]. Here we describe and discuss a strategy based on organocatalysis and "click" chemistry for fabrication and functionalization of nanocelluloses [14, 33].

Based on our research interest in catalytic surface engineering on cellulose and the challenges in nanocellulose production, we envisioned a mild route for production and selective surface functionalization of nanocelluloses by combining organic acid catalyzed hydrolysis and surface modification of wood pulp with "click" chemistry (Fig. 1).

Thus, mild organic acid mediated concurrent hydrolysis and regioselective esterification of wood pulp (Fig. 1, Scheme 1) in combination with mechanical treatment would lead to nanocellulose formation. Next, this would be combined with combinations of highly versatile organocatalytic direct silylations and chemoselective click chemistry for designing the surface properties of nanocelluloses (e.g. water-resistance, catalytic activity, fluorescence etc.).

Results and discussion

As compared to the enzyme pretreatment route, the organic acid fabrication approach would be mild but it would be more robust, no solvent would be required and the organic acid could be recycled. However, organic acids such as formic acids had previously only been used for the complete depolymerization of wood polymers to monomeric units (e.g. sugars and aryl units) [34, 35]. Thus, it may be difficult to control the organic acid catalyzed depolymerization of wood pulp for the production of NFC. Despite these challenges,

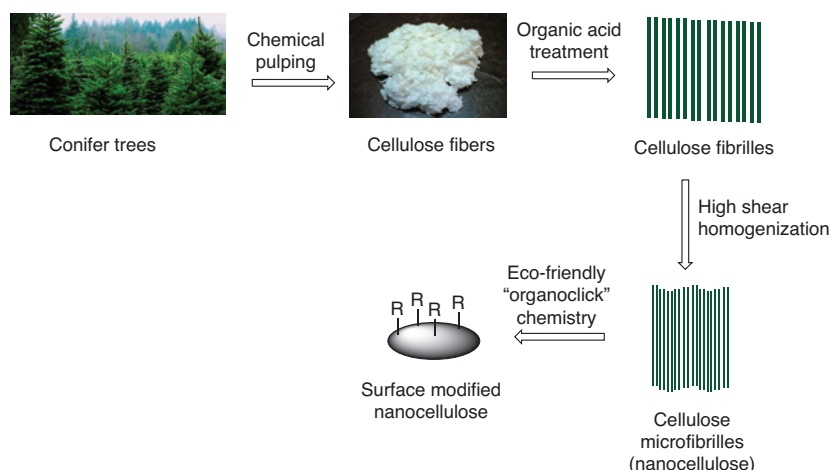
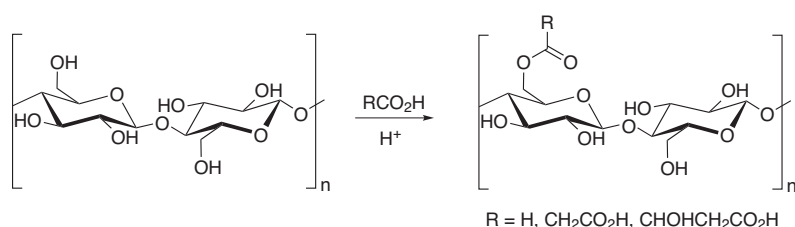


Fig. 1: The combined organic acid mediated neat production of NFC with “organoclick” surface modification of nanocellulose.



Scheme 1: Organic acid autocatalyzed esterification of the cellulose chain.

we began to investigate the nanocellulose fabrication using different organic acids (e.g. formic acid, malic acid and malonic acid) using neat (no solvent) conditions. Today, other reports have appeared on the possibility of producing CNC using formic acid, citric acid and malonic acid in combination with HCl or just oxalic acid pre-treatment [36–39]. For example, oxalic acid was used for simultaneous hydrolysis and esterification of bleached pulp to obtain oxalic acid esterified CNC [39]. Formic acid esterified CNC was also produced in neat formic acid using HCl as the catalyst [36]. This was also the case in the sustainable production of citric acid esterified CNC from Ramie cellulose [37]. Bleached sulfite softwood dissolving pulp [10 g dry mass of pulp (70 % Norway spruce (*Picea abies*) and 30 % Scots pine (*Pinus sylvestris*))] with an average molecular weight (M_w) of 392 KDa and a polydispersity index (PDI) of 11.1 was mixed with an organic acid (formic acid, malic acid or malonic acid) at various temperatures to give white milky dispersions in clear, colorless spent liquors. This step was followed by homogenization. We found that we were able to produce NFC in high yields (97–99 %, dry weight) at relatively low temperatures (70–90 °C) using formic acid. The other acid-catalyzed reactions were run at temperatures >130 °C. Transmission electron microscopy (TEM) studies of the white powder revealed separated fibers with nanoscale diameters (<20 nm, Fig. 2). The formic acid was also successfully recovered and reused for another cycle of NFC production. The IR-analysis of the NFC revealed that the organic acids simultaneously promoted hydrolysis and esterification of the cellulose chain. As compared to previous CNC production studies [40], the esterification step was autocatalytic and no HCl catalyst needs to be added (Scheme 1). Thus, the cellulose is esterified prior to the homogenization treatment. If wanted, the ester groups can be removed by basic work up (1 M NaOH) as determined by IR [14]. The NFC derived from formic acid has no charged groups as compared to NFC derived from the TEMPO–NaClO oxidation–homogenization of bleached sulfite softwood dissolving pulp or when the dicarboxylic acids (e.g. maleic acid, malonic acids) are used for the pretreatment process. The degree of substitution varied between <0.1–0.35 for formic acid, maleic acid and malonic acid, respectively. The average molecular weight (M_w) of the NFC was 112 KDa and the polydispersity index (PDI) was 6.8 as determined by size exclusion chromatography (SEC).

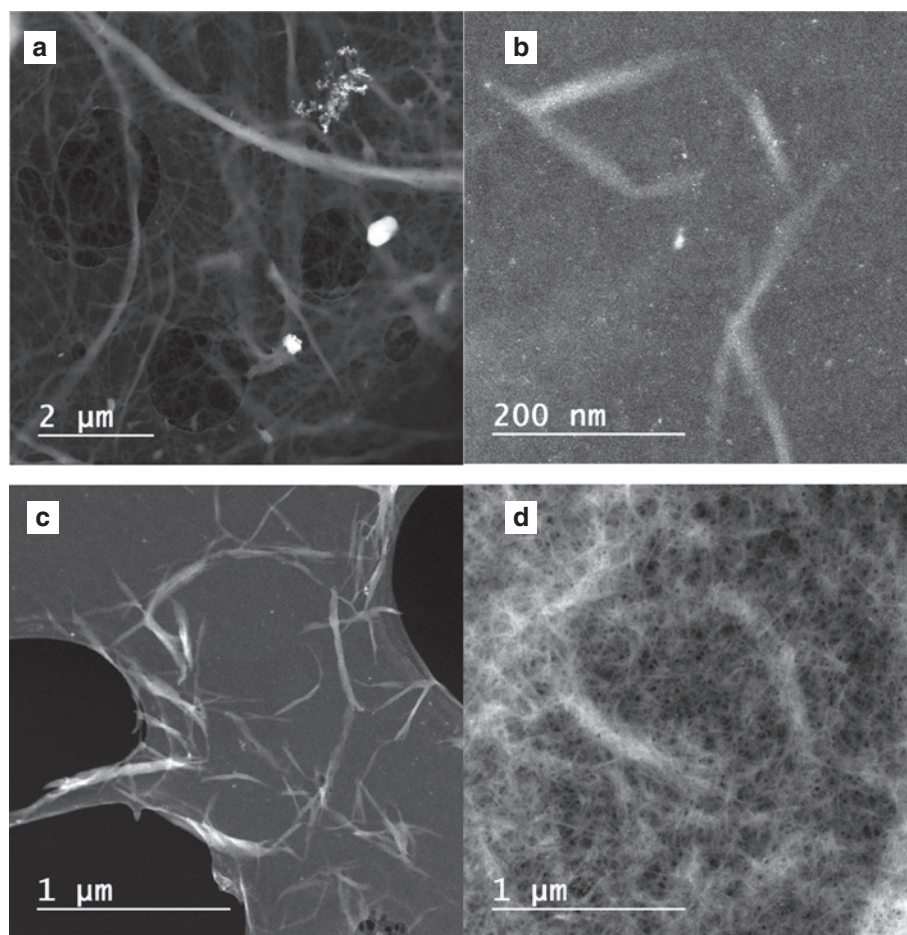


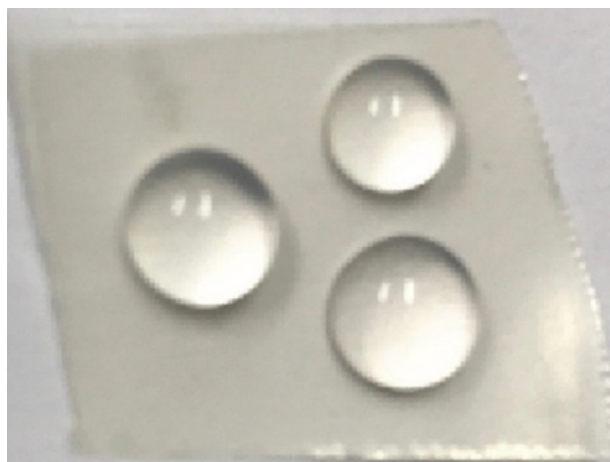
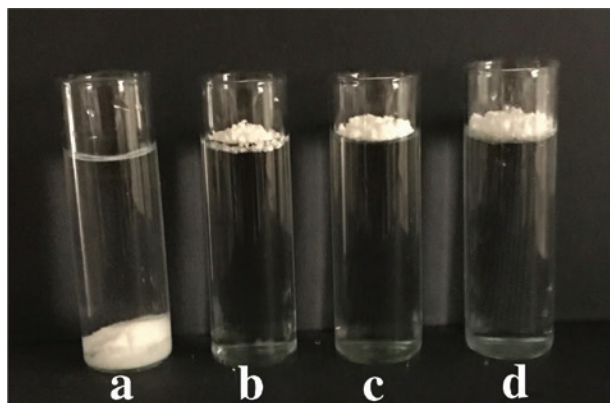
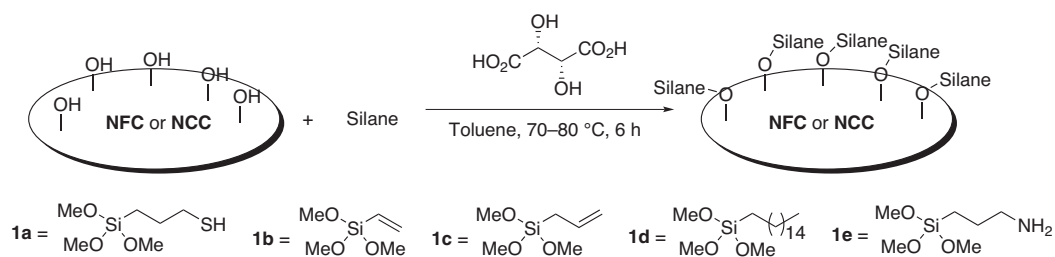
Fig. 2: TEM pictures: (a) Sulphite softwood dissolving pulp. (b) Formic acid fabricated NFC. (c) Formic acid fabricated NFC. (d) NFC derived from the TEMPO-NaClO oxidation-homogenization route. Reproduced with permission from *Global Challenges* (Wiley-VCH) [14].

NFC was also produced by initial catalytic aerobic oxidation (TEMPO/ O_2)-formic acid treatment. This simple metal-free aerobic oxidation/organic acid protocol use oxygen instead of NaClO as the terminal oxidant and can also introduce charges onto the NFC surface. We also successfully scaled up the formic acid method to 50 g of dry mass of pulp.

With these results in hand, the organoclick surface functionalization of nanocelluloses was investigated. We began converting different types of nanocelluloses, which we had produced or obtained from commercially sources (e.g. organic acid-derived NFC, TEMPO/NaClO-derived NFC, enzyme-homogenization NFC, CNC, mechanical treatment-derived NFC), to foams or films [41], respectively. Next, they were all used as substrates and treated with different types of functional silanes (e.g. alkyl, olefin, $-CH_2SH$, $-CH_2OH$, $-CH_2NH_2$). A catalyst screen of different organic acids for the silylation of 3-phenylpropionalcohol with thiapropylsilane (TPSi) **1a** or allylsilane **1c**, determined that (S)-tartaric acid and malic acid were excellent catalysts. Thus, functional silanes **1** were investigated as substrates for the (S)-tartaric acid-catalyzed silylation of the nanocellulosic materials (Scheme 2).

The surfaces of all investigated NFC samples had been modified as determined by elemental analysis (ds < 0.6). The (S)-tartaric acid-catalyzed attachment of hydrophobic silanes to the nanocellulose materials surface made them water repellent (Fig. 3). The contact angles for the different C-16-modified nanocellulose foams and films were up to $>120^\circ$. For example, a film made from CNC had a contact angle of 110° (Fig. 4) and a film made from enzyme-pretreatment had a contact angle of 116° .

The direct attachment of organic amines such as aminopropyl (AmP) silane **1e** to the nanocellulose materials is useful since it allows them to be used as binders of metals and sustainable supports for metals



(e.g. metals and enzymes) [7, 42]. For example, the AmP-NFC foam material efficiently bound Pd(II) salts to form AmP-NFC-Pd(II)-complexes. Reducing the surface bound Pd(II) with NaBH₄ gave the corresponding AmP-NFC-Pd(0) foam containing Pd nanoparticles with a narrow particle distribution (Fig. 5).

The AmP-NFC-Pd(0) is an efficient heterogeneous catalyst for Suzuki cross-couplings in water. We found that the catalyst provides the product in high yields after several recycling cycles (Table 1). However, the yield began to decrease after the third catalyst recycling cycle (Table 1).

With above results in hand, we next performed “organoclick” functionalizations on the NFC and CNC foams or films using a catalytic silylation/thiol-ene reaction sequence. Thus, (S)-tartaric acid surface

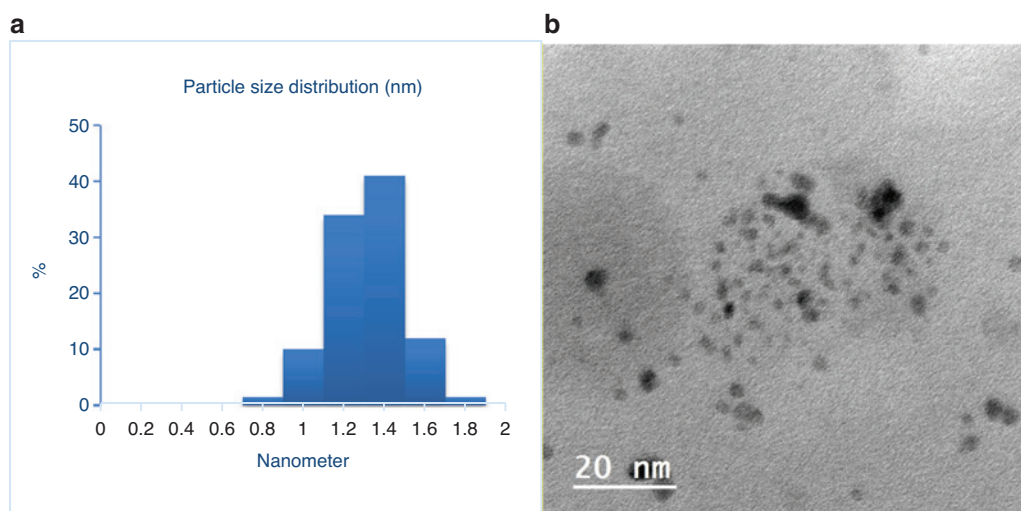
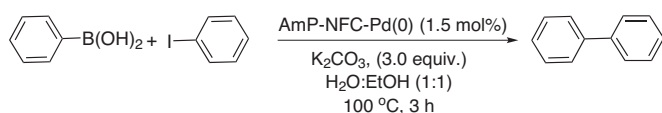


Fig. 5: (a) Pd nanoparticle size distribution of AmP-NFC-Pd(0). (b) Transmission electron micrograph bright field (STEM-BF) image of AmP-NFC-Pd(0). Reproduced with permission from *Global Challenges* (Wiley-VCH) [14].

Table 1: Recycling study of the AmP-NFC-Pd(0)-catalyzed Suzuki-Miyaura reaction between iodobenzene and phenylboronic acid.

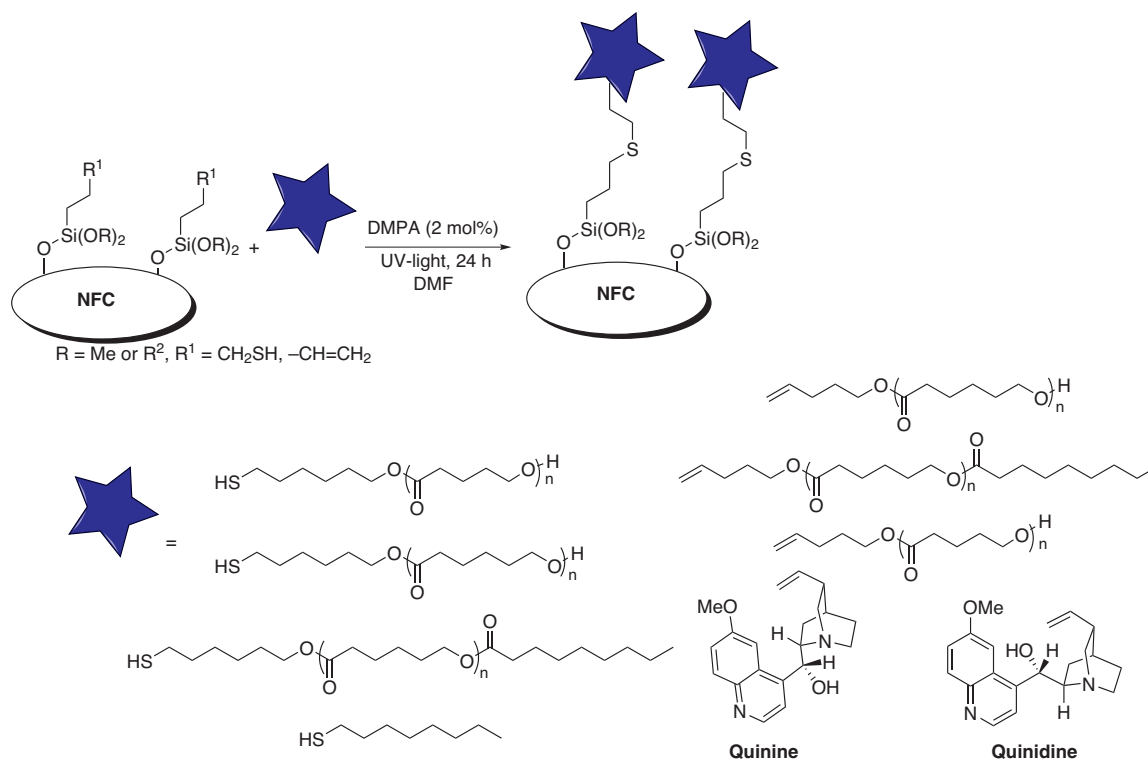


Cycle ^a	Yield (%) ^b
1	95
2	97
3	89
4	85

^aReaction conditions: AmP-NFC-Pd(0) (8.4 mg, 1.5 mol%), Iodobenzene (204.01 mg, 1.0 mmol, 1.0 equiv.), phenyl boronic acid (146.4 mg, 1.2 mmol, 1.2 equiv.), K₂CO₃ (414.6 mg, 3.0 mmol, 3.0 equiv.), solvent (3 mL), 100 °C, 3 h. ^bYield of purified product after silica-gel column chromatography.

functionalization of the NFC foams or films with TPSi **1a** or allylsilane **1c** was followed by thiol-ene click reactions on the corresponding TPSi-**1a**-NCF and **1c**-NCF, respectively, using a UV lamp and a metal-free initiator (Scheme 3). Thiol-end-group functionalized and 4-pentene-1-ol-initiated polyesters [poly(ϵ -caprolactone) (PCL) and poly(γ -valerolactone) (PVL)] were first investigated. The polyesters (PCL and PVL) were produced by chemoselective enzyme- or (*S*)-tartaric acid-catalyzed polymerizations [43, 44]. After Soxhlet extraction, FT-IR analysis determined that the polyesters poly(ϵ -caprolactone) (PCL) and poly(γ -valerolactone) (PVL) were successfully attached to the NFC. We also attached hydrophobic molecules such as *n*-octanethiol.

Delighted by these results, we continued with investigation of eco-friendly attachment of different molecules including fluorescent and UV-active compounds as well as organic molecules that serve as ligands or catalysts. These types of engineering of the cellulose surface is important since the resulting materials can have application in sensors and biology (e.g. cell uptake and viability) as well as in diagnostics and heterogeneous catalysis. It would also be an alternative to the current functionalization methods, which are not environmentally benign [e.g. use of acid chlorides, alkyl chlorides, LiCl/dimethyl acetamide (DMAC), pyridine and DMSO] [24]. Important proof of concept molecules would be the pharmaceutical agents such as quinine and quinidine (Scheme 3). These natural products display important biological activities (e.g. antimalaria,



Scheme 3: Examples of performed click reactions between TPSi-1a-NFC or allyl-1c-NFC with different thiols and olefins, respectively.

arthritis and antiarrhythmic heart). They are also fluorescent markers and employed as organic chiral ligands for metal catalysts and organocatalysts for asymmetric synthesis (e.g. conjugate additions, oxidations, kinetic resolutions, and Sharpless asymmetric dihydroxylation) [45, 46]. Thus, different types of NFCs and CNC were “organoclick” functionalized with cinchona alkaloids. The direct functionalization relay sequence began with (S)-tartaric acid catalyzed silylation of NFC with **1a** to give TPSi-1a-NFC, followed by the thiol-ene “click” reaction with quinine or quinidine, respectively. After basic washing and extensive Soxhlet extraction, both the quinidine-TPSi-1a-NFC and quinine-TPSi-1a-NFC were fluorescent, whereas the TPSi-1a-NFC and NFC were not (Fig. 6). It is noteworthy that the “organoclick” surface engineering strategy was successful on a broad range of cellulose substrates and not only limited to NFC and CNC (e.g. cellulose, filter paper, cotton textiles). Thus, this is a highly versatile strategy for direct surface engineering of a nanocelluloses and cellulosic materials and a plethora of different molecules can be attached in different combinations.

Experimental

For detail experimental procedures see reference [14].

Typical procedure for the formic acid mediated NFC production

To a round bottom flask (500 mL) was poured concentrated formic acid (200 mL). Next, sulfite softwood dissolving pulp (66.7 g, 15% consistency, 10 g dry mass of pulp) was added and the mixture was heated to 90 °C. After stirring the suspension with a mechanical IKA RW 20 digital stirrer (2400 rpm) for 24 h, the reaction temperature was decreased to room temperature and next ultra-sonicated in a bath for 1 h using a

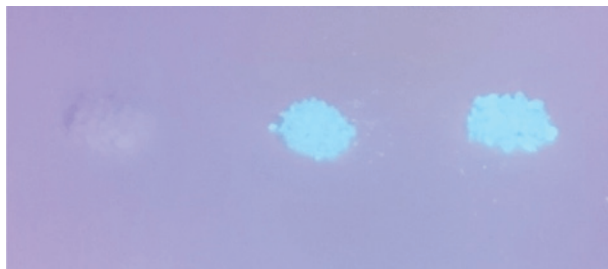


Fig. 6: UV-lamp (long wave length, 365 nm): Left: 3-thiopropylsilane-(TPSi)-**1a**-modified NFC (blank). Middle: Quinidine-TPSi-**1a**-NFC. Right: Quinine-TPSi-**1a**-NFC. Reproduced with permission from *Global Challenges* (Wiley-VCH) [14].

BANDELIN SONOREX DIGITEC. Next, the reaction mixture was diluted with water (800 mL) and neutralized to pH=7 by NaOH (aq. 1 M). Afterwards the suspension was centrifuged with EBA 21 Hettich ZENTRIFUGEN with 6000 rpm for 10 min and the supernatant was decanted away. The heterogeneous precipitate was further washed by water and subsequent centrifugation; this procedure was repeated three times. The material was further homogenized with IKA T 25 ULTRA TURRAX High Speed Homogenizer (15 000) rpm for 180 min.

Typical direct catalytic silylation procedure

To a flamed dried round-bottomed flask (250 mL) charged with a nanocellulose foam or film (200–600 mg, 1.0 equiv.) was added toluene (50–100 mL). Next, (S)-tartaric acid (10 mol%) and silane **1** (2.6 equiv.) were added and the reaction mixture was heated to 80 °C. After stirring for 6 h, the resulting **1**-modified nanocellulose foams or films were isolated, washed with CH₂Cl₂ (200 mL) and dried under reduced pressure. Before checking the contact angles the films and foams underwent soxhlet extraction using CH₂Cl₂.

Typical thiol-ene reaction procedure between allyl modified nanocellulosic materials and thiol-end group terminated polyesters

To a scintillation vial (20 mL) containing allyl-**1c**-nanocellulose foam or film (30 mg) and PCL or PVL with a free thiol-end-group (30 mg), was added THF (0.5 mL) and DMPA (3–6 mg). Next, the reaction was irradiated for 24 h using an UV-lamp (UV-B bulb, TL20W/12, 20 W). The UV-treated nanocellulose material was removed and next extracted using a Soxhlet extractor using acetone as the solvent for 17 h. The extracted nanocellulose material was subsequently dried overnight under reduced pressure.

TEM/STEM study

A droplet of solution containing the sample was transferred onto a Cu TEM grid with holey carbon supporting films. The grid was dried at room temperature. The TEM and high-angle annular dark-field STEM (HAADF-STEM) images were recorded using a JEOL JEM-2100F ($C_s = 0.5$ mm) operated at 200 kV with a Gatan Ultra-scan 1000 camera and annular dark-field (ADF) detector, respectively. For each specimen, more 10 different regions on the TEM grid were examined. The images shown are presentative. In the particle size analysis, more than 100 particles were measured.

Conclusion

In summary, we have disclosed a strategy based on combination of catalysis and “click” chemistry for the fabrication NFC and surface engineering of nanocelluloses. The nanocellulose is produced in high yields

under neat conditions with low energy input using a recyclable organic acid. It also avoids the use chlorine-based oxidants and radical initiators, which produce persistent pollutants (e.g. organochlorines, dioxins). The concept is significantly broadened by combining it with eco-friendly “organoclick” engineering using metal-free catalysis and UV light. This was demonstrated by the direct attachment of different functional silane groups (e.g. alkyl, thia, amino, allyl, vinyl) using an organic acid catalyst. In addition, the selective binding of metal ions was accomplished by the AmP-functionalized nanocellulose (AmP-NFC). This was exemplified by the binding of a Pd salt followed by its conversion to an AmP-NFC-Pd(0)-nanoparticle catalyst for an efficient C–C bond-forming Suzuki-Miyaura reaction. Sequential click chemistry reactions on the thiol and olefin-functionalized NFC under UV light allowed for additional versatile surface engineering with hydrophobic, biological active, fluorescent, metal ligands and catalysts. The “organoclick” chemistry strategy is broad in scope and can also be applied to other types of cellulosic materials. It has several advantages for future development of nanocelluloses such as sustainable production, versatile functionalization, improvement of water and moisture sensitivity. This will facilitate replacement of fossil-based materials and contribute to new uses of nanocelluloses in different areas (e.g. packaging, pharmaceuticals, heterogeneous catalysis, composite materials).

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