Native Cellulose Nanofibril-based Functional Materials

Miao Wang
Abstract

Cellulose is the most abundant polymeric source on earth, and it has been used for centuries in different applications ranging from paper making to technological materials. Recently, nanocellulose, cleaved from native cellulose fibers, has extensively been explored because of its excellent mechanical, optical and thermal properties, combined with renewability. It can be used to fabricate composites, transparent films, fibers, porous foams and aerogels for diverse applications. This thesis focuses on utilizing native cellulose nanofibrils as building blocks for selected novel functional materials.

Publication I addresses biomimetic nanocomposites, where the reinforcing hard cellulose nanofibrils form the majority of phases as separated by the soft rubbery block copolymeric domains. A facile ionic assembly is used to produce strong films with a promoted work-of-fracture showing a synergistic effect. This concept makes it possible to pursue biomimetic nanocomposites with further increased fracture toughness, while maintaining stiffness and strength.

Publication II studies the mechanical and electrical properties of cellulose nanofibril and few-walled carbon nanotube hybrid aerogels. Incorporating carbon nanotubes with cellulose nanofibrils allows us to combine the attractive features of both components: wide availability, easy processing, and the sustainability of nanocellulose and the advanced electrical properties of carbon nanotubes. The concept demonstrates that hybrid aerogels could potentially be used in pressure sensing applications.

Publication III further deals with the electrical behaviour of the above native cellulose nanofibril/carbon nanotube hybrid aerogels under repeated cyclic compression to explore “electrical fatigue”. The hybrid aerogels can be constructed to allow stable reversible resistance changes in cyclic compression.

Publication IV describes a nanocellulose film actuation with reversible bidirectional bending triggered by humidity. The films show a steady-state bending when exposed to humidity and then relaxed when removed from the imposed humidity continuously. The bending is highly sensitive to humidity, as demonstrated by its bending when exposed to a human hand at a distance of several millimeters. Such a film offers a facile route toward biomimetic actuation and novel types of active materials.

In conclusion, cellulose nanofibrils are versatile building blocks in hybrid materials with block copolymers to tune the self-assembly for mechanical properties, as templates for electroactive aerogels, and as films with new properties.

Keywords nanocellulose, native cellulose nanofibril, nanocomposite, biomimetic, carbon nanotube, aerogel, film, pressure sensing, actuation

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Preface

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This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their Roman numerals.

I. Wang, Miao; Olszewska, Anna; Walther, Andreas; Malho, Jani-Markus; Schacher, Felix H.; Ruokolainen, Janne; Ankerfors, Mikael; Berglund, Lars A.; Österberg, Monika; Ikkala, Olli. *Colloidal Ionic Assembly between Anionic Native Cellulose Nanofibrils and Cationic Block Copolymer Micelles into Biomimetic Nanocomposites*. Biomacromolecules 2011, 12, 2074-2081.


Author’s contribution

Publication 1: “Colloidal Ionic Assembly between Anionic Native Cellulose Nanofibrils and Cationic Block Copolymer Micelles into Biomimetic Nanocomposites”

The author designed and performed the experiments together with Anna Ol-szewska, analyzed all data, and wrote the first version of the manuscript and actively participated to complete the final form.

Publication 2: “Modifying Native Nanocellulose Aerogels with Carbon Nanotubes for Mechanoresponsive Conductivity and Pressure Sensing”

The author designed and executed most of the experiments and analyzed all data. The transmission electron microscopy was done by Jani Seitsonen. The carbon nanotubes were received from Ilya V. Anoshkin and he also helped for the pressure responsive test. The author wrote the first version of the manuscript and actively participated to complete the final form.

Publication 3: “Electrical behaviour of native cellulose nanofi-bril/carbon nanotube hybrid aerogels under cyclic compression”

The author designed and executed most of the experiments and analyzed all data. The transmission electron microscopy was done by Nonappa. The carbon nanotubes were received from Ilya V. Anoshkin. The author wrote the first version of the manuscript and actively participated to complete the final form.

Publication 4: “Driven Reversible and Bidirectional Bending of Nanocellulose Thin Films as Bio-Inspired Actuation”

The author designed and performed most of the experiments with the help of Tian Xuelin and analyzed all data. The author participated to write the first draft of manuscript with Tian Xuelin and actively contributed to complete the final form.
## List of abbreviations and symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>BC</td>
<td>Bacterial cellulose</td>
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<td>BCP</td>
<td>Block copolymer</td>
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<tr>
<td>CH$_4$</td>
<td>Methane</td>
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<tr>
<td>CNC</td>
<td>Cellulose nanocrystal</td>
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<td>CNF</td>
<td>Cellulose nanofibril</td>
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<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
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<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>Cryo-TEM</td>
<td>Cryogenic transmission electron microscopy</td>
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<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
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<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
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<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
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<tr>
<td>DP</td>
<td>Degree of polymerization</td>
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<tr>
<td>DS</td>
<td>Degree of substitution</td>
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<tr>
<td>FWCNT</td>
<td>Few-walled carbon nanotube</td>
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<tr>
<td>IPN</td>
<td>Interpenetrating polymer network</td>
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<tr>
<td>MFC</td>
<td>Microfibrillated cellulose</td>
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<tr>
<td>MgO</td>
<td>Magnesium oxide</td>
</tr>
<tr>
<td>Mo</td>
<td>Molybdenum</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotube</td>
</tr>
<tr>
<td>N</td>
<td>Total degree of polymerization</td>
</tr>
<tr>
<td>NaClO</td>
<td>Sodium hypochlorite</td>
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<td>NaBr</td>
<td>Sodium bromide</td>
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<tr>
<td>NaClO$_2$</td>
<td>Sodium chlorite</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>---------</td>
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<tr>
<td>NCC</td>
<td>Nanocrystalline cellulose</td>
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<tr>
<td>NFC</td>
<td>Nanofibrillated cellulose</td>
</tr>
<tr>
<td>OsO$_4$</td>
<td>Osmium tetroxide</td>
</tr>
<tr>
<td>PB</td>
<td>Poly (1, 2-butadiene)</td>
</tr>
<tr>
<td>PDMAEMA</td>
<td>Poly (dimethylaminoethyl methacrylate)</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyethylene imine</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly (methyl methacrylate)</td>
</tr>
<tr>
<td>QCM-D</td>
<td>Quartz crystal microbalance with dissipation monitoring</td>
</tr>
<tr>
<td>R</td>
<td>Resistance</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>SME</td>
<td>Shape memory effect</td>
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<tr>
<td>SMP</td>
<td>Shape memory polymer</td>
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<tr>
<td>SWCNT</td>
<td>Single-walled carbon nanotube</td>
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<tr>
<td>TEMPO</td>
<td>2, 2, 6, 6-tetramethylpiperidine-1-oxyl radical</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
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- $f_A$: Volume fraction of polymer block A
- $f_0$: Resonance frequency
- $\Delta f$: Change in frequency
- $\Delta m$: Adsorbed mass per unit surface
- $\Delta R$: Resistance change
- $\chi$: Flory-Huggins interaction parameter between the monomer units
1. Introduction

1.1 Cellulose as a sustainable material

The environmental awareness and the high demand for alternatives to non-renewable petroleum-based resources have forced and encouraged researchers to seek biomass-based renewable materials. Natural cellulosic polymers are excellent candidates for different applications due to their inherent advantages, for instance their wide availability, environmental-friendliness, biodegradability, cost-effectiveness, easy processability, and lower health risks. All these outstanding characteristics of cellulosic materials make them one of the most promising future materials for applications in multiple fields.

Cellulose is the main component of higher plant cell walls. It belongs to polysaccharide family and has a linear chain of glucose rings comprised of anhydroglucose rings \((\text{C}_6\text{H}_{10}\text{O}_5)\_n\), \(n = 10000\) to \(15000\), depending on the cellulose source materials, linked together through a so-called \(\beta (1 \rightarrow 4)\)-glucosidic bonds (Fig. 1.1). [1] The intrachain hydrogen bonding between hydroxyl groups and oxygens of the neighbouring molecules stabilizes the linkages and results in the ribbon-like configuration of the cellulose chain. The interchain hydrogen bonds between hydroxyl groups and oxygens of adjacent molecules promote packing of multiple cellulose chains and the formation of elementary fibrils that further aggregate into larger microfibrils (5-50 nm in diameter and several microns in length) (Figure 1.2). The intra- and inter- hydrogen bonding network promotes cellulose stability, and gives the cellulose fibrils high axial stiffness.
Introduction

Within the cellulose fibrils, there are highly ordered crystalline and less ordered amorphous domains, which make natural cellulose a semicrystalline polymer. [2, 3] Depending on the source, methods of extraction or treatment, cellulose exists in several polymorphs of crystalline cellulose (cellulose I, cellulose II, cellulose III and cellulose IV). [4] Natural cellulose is cellulose I, and it has two crystalline forms, Iα and Iβ, which can coexist in various proportions. [5] Its structure is thermodynamically metastable and it can be converted to cellulose II or cellulose III. Cellulose II is formed by regeneration (solubilisation and recrystallization) and mercerization with aqueous sodium hydroxide, and it contains antiparallel chains. [6] It has the most stable crystalline structure. Cellulose III is obtained by ammonia treatment of cellulose I or cellulose II in a reversible process and by subsequent thermal treatments, cellulose IV can be formed. [7]

1.2 Nanocellulose

Natural cellulose fibers have been the main materials used in paper and the paperboard industry for centuries. With increasing demands for better properties and novel applications to enhance industrial competitiveness, the nanoscale forms achieved from the natural cellulose fibers are attracting increasing scientific and industrial interest. Nanocellulose was first studied by Turbak et al. and Herrick et al. in the 1980’s. [8, 9] They produced nanocellulose using softwood pulp by passing it through a high-pressure homogenizer several times and finally resulting in strongly entangled networks of nanofibers. Thereafter, nanocellulose has been investigated extensively in a wide range of scientific and industrial fields. [10-12]

Depending on the preparation conditions, nanocellulose can, in fact, be divided into two categories: 1) cellulose nanofibrils (CNF), also known as nanofibrillated cellulose (NFC), or microfibrillated cellulose (MFC) [1, 4, 13]; 2) cellulose nanocrystals (CNC), also known as cellulose whiskers or nanocrystalline cellulose (NCC) [14-16]. Cellulose nanofibrils (CNF) contain both crystalline and amorphous domains of cellulose as a so-called fringed micellar structure. The nanofibers are typically long and entangled, are micrometers in length and have a lateral dimension in nanometers. However, CNCs exist only
in the crystalline phase, isolated from cellulose fibers normally using acid hydrolysis, leading to short and rigid rod-like fibers. In addition, nanocellulose can also be achieved from bacteria and tunicates. [17, 18] In this work, we only focus on native cellulose nanofibrils (CNF).

**Figure 1.2** Different kinds of nanocellulose. Reprinted with permission from ref. 11 © The Royal Society of Chemistry 2014.

Depending on the production conditions, CNFs have different morphologies and properties (Figure 1.2). [19] Mechanical disintegration of fibers into nanofibrils has reported to have energy consumption of 20,000-30,000 kWh/tonne, and even higher values reaching 70,000 kWh/tonne. [20-22] Due to the high energy consumption of the mechanical disintegration of CNF from cellulose fibers, pretreatments are typically required before the mechanical treatment. Native cellulose nanofibril cleaved from nature plant fibers can
be achieved by 2, 2, 6, 6-tetramethylpiperidine-1-oxyl radical (TEMPO) oxidation, enzymatic hydrolysis [23] or carboxymethylation (Figure 1.3).

1.2.1 TEMPO oxidized cellulose nanofibrils

Recently, researchers introduced the TEMPO oxidation as a pretreatment to produce nanocellulose. [24-27] In this procedure, cellulose fiber suspension is oxidized under aqueous mild conditions with sodium hypochlorite (NaClO) and a catalytic amount of sodium bromide (NaBr) and TEMPO at pH 10-11. Through this process, the C6 primary hydroxyl groups of cellulose are converted to carboxyl groups and a few aldehyde groups. The process mainly introduces the anionic carboxylate groups on the cellulose crystal surfaces with a high density up to 1.5 mmol/g (millimoles of COO per gram of dried fibers) leading to almost transparent and highly viscous hydrogels. [25, 26] Therefore, after TEMPO oxidization, the mechanical separation process is much easier because the charged cellulose surfaces loosen the adhesion between cellulose fibrils by preventing the formation of strong interfibril hydrogen bonds (Figure 1.1). The obtained nanofibrils are 3-5 nm wide and few micrometers long (Figure 1.3 b). [25, 27] Subsequently, a similar procedure has been developed at neutral or at slightly acidic conditions (pH 4-7) using a TEMPO/NaClO/NaClO₂ system. [28, 29] With this method, the oxidized cellulose has a carboxylate content of approximately 0.8 mmol/g with highly crystalline individualised fibrils 5 nm wide and at least 2 μm long. [28] Moreover, through this procedure, the degree of polymerization is high, which has an important influence on the strength, length, and flexibility of individual cellulose fibrils. Besides, no aldehyde group exists using this system, which is also beneficial for the thermal stability and dispersibility of the individual fibrils. [28, 29] Furthermore, TEMPO-electro-mediated oxidation was introduced without any chlorine-containing oxidant. [30] Interestingly, oxidation process of polysaccharides with periodate has also been reported to introduce aldehyde groups for further reactions. [31-33] After oxidation, mechanical treatment is needed to separate cellulose nanofibrils. The reported energy consumption for TEMPO mediated fibrillation process is around 2000 kWh/tonne. [34]

1.2.2 Enzymatically hydrolyzed cellulose nanofibrils

As ruminants are well-known to show, cellulose chains can be broken into glucose molecules by cellulase enzymes. Researchers also found that enzymatic hydrolysis can help to liberate microfibrillated fibers from natural cellulose fibers. [23, 35] Henriksson et al. and Pääkkö et al. have reported that endoglucanase pretreatment facilitates disintegration of MFC from wood fiber pulp. [23, 35] They demonstrated that the endoglucanases only attack the amorphous regions. A refining process was always applied before and after enzyme application to avoid clogging the equipment in the treatment process. At the end, the fiber slurry was passed through a homogenizer several times, resulting in a long and entangled fiber network. Different from the TEMPO oxidized process, there is no surface group introduced during enzymatic hydrolysis, and
therefore the liberated fibers have broad diameter range, 5-30 nm wide (Figure 1.3 a). [23, 36] Finally, a nanofibril bundle is obtained in comparison to the uniform diameter nanofibrils obtained from TEMPO oxidation process. The enzymatic hydrolysis has also been found to decrease the degree of polymerization (DP) and to increase the crystallinity index (the relative amount of crystalline material in cellulose). [35, 37-39] Ankerfors et al. have reported that the enzyme dosage should be low to avoid severe clogging and a dramatic DP drop. [40] The calculated energy consumption for enzymatic hydrolysis and homogenization of cellulose nanofibrils is around 1800-2300 kWh/tonne. [40] Compared to the process without pretreatments, where the energy consumption was 27,000 kWh/tonne, over 90% of energy is saved. [40, 41]

1.2.3 Carboxymethylated cellulose nanofibrils

Carboxymethylation is another chemical pretreatment process for producing cellulose nanofibrils. [42] Carboxymethyl cellulose has been a commercial industrial product since the 1920’s in Germany [43]; and reported by Wågberg et al. in 2008 [42] carboxymethylation efficiently promotes disintegration of CNF. The process uses high-pressure homogenization of carboxymethylated cellulose fibers followed by ultrasonication and centrifugation to remove the residual non-fibrillated fibers. It introduces anionic charges in the formation of carboxyl groups on the surface of nanofibrils, a similar procedure as in TEMPO oxidation to ease fiber liberation. The resulting nanofibrils have a cross-section of 5-15 nm and a length up to 1 μm (Figure 1.3 c). The surface charge density of carboxymethylated CNF is ca. 0.5 mmol/g at pH 7-8. [42] It has slightly lower and more uniform dimensions compared to nanofibrils received from enzymatically pretreated CNF. [44] Films, hydrogels and aerogels can be made using carboxymethylated CNF. [45-47] However, the main disadvantage of this process is the use of organic solvents. Therefore, it has higher negative environmental impacts comparing to the enzymatic pretreatment. [48] According to Taipale et al.’s calculation, the required energy of fluidization of such treatment after carboxymethylation is around 2200 kWh/tonne per pass through a microfluidizer, whereas this occurs at 5500 kWh/tonne per pass without carboxymethylation pretreatment. [49] More recently, there is also a routine reported by Chen et al. using recyclable solid organic acids at ambient pressure to introduce carboxyl group on CNF and CNC. [50] They have demonstrated that with this process, the thermal stability of CNF and CNC has been improved.
1.3 Potential applications of cellulose nanofibrils

It has been shown that cellulose I crystals within the native cellulose reach a Young’s modulus in the range of 140 GPa, and also a strength in the range of a few GPa might be achieved. [52, 53] According to the cellulose nanofibril density, the specific Young’s modulus of nanocellulose crystals, which is the ratio of Young’s modulus to density, is potentially higher than steel and similar to Kevlar. [13] Therefore, CNF is considered a fascinating reinforcement to be used with commercial soft plastics for making strong nanocomposite materials. [54-58]

Moreover, as a renewable, biodegradable, recyclable and thermal stable material with good mechanical and optical properties, CNF has great potential for making films, fibers, foams and aerogels. [59-65] CNF film is commonly made directly from nanocellulose suspension, either using vacuum filtration [59, 66, 67] or layer-by-layer deposition [42, 45]. Vacuum filtration is used more often since it is a facile and fast process to produce free standing CNF films. It removes most water quickly, and thereafter the wet cake is dried in a controlled or uncontrolled way to achieve desired properties. By incorporation with other polymers [68], conductive materials [67, 69, 70] or inorganic materials [71, 72], the resulting nanocomposite materials can incorporate good functionalities [60, 61, 73-78]. Directly air dried CNF film is translucent, but high trans-
Transparency nanopaper has been reported using cellulose nanofibrils by post-treatment or in-situ impregnation. [53, 79] Some examples of potential CNF products are illustrated in Figure 1.4. [12]

Figure 1.4 Examples of CNF products: (a) CNF films polished with acrylic resin (left) and unpolished (right) [75]; (b) light-emitting diode (LED) circuits on CNF film with: (1) gold sputtered lines, (2) inkjet-printed silver nanoparticle lines and (3) inkjet printed metallo-organic decomposition (MOD) silver lines [80]; (c) 3D printed human ear from hydrogel of CNF and alginate [81]; (d) tiny chair (dimension of ca. 25×10×15 mm) made of CNF aerogel produced using 3D bioprinting (Chalmers University of Technology). Reprinted with permission from © 2016 Elsevier B.V.

1.4 Outline of this thesis

This thesis focuses on utilizing cellulose nanofibrils for making functional nanocomposite materials. First, ionic complexes of anionic CNF with diblock copolymers (with cationic block and rubbery block) are discussed for biomimetic nanocomposites (Publication I). Since cellulose nanofibrils have good mechanical properties, the achieved composite material using cellulose nanofibrils also maintains its good mechanical state, that is, strength and ductility. Second, an approach is described incorporating conductive carbon nanotubes with cellulose nanofibril to produce conductive porous aerogel materials (Publication II). Different freeze-drying concepts are incorporated to give the skeleton structure and properties. The porous, non-brittle and conductive cellulose nanofibril carbon nanotube hybrid aerogels allow mechanoresponsive conductivity and have pressure sensing applications. Next, hybrid aerogels
consisting of cellulose nanofibers and carbon nanotubes are investigated under cyclic mechanical compression to explore “electrical fatigue”, specifically, how the electrical properties tolerate repeated mechanical compression cycling (Publication III). Finally, a simple cellulose nanofibril film is made for humidity-controlled reversible actuation owing to the hydrophilicity of cellulose materials and anisotropic humidity penetration into films (Publication IV). Related phenomena also exist in nature within the plant movements caused by anisotropic water swelling and deswelling within nano- and mesoscale cellulose fibrillar structures. The structure of this thesis is schematically presented in Figure 1.5.

Figure 1.5 Schematic layout of this thesis.
2. Native cellulose nanofibril hybrids with block copolymers for biomimetic nanocomposites

2.1 Block copolymer background

Self-assembly is ubiquitous in biology and modern material science. In static self-assembly the components spontaneously form organized structures or patterns due to competing interactions. [82, 83] It can take place at molecular level, nanometer size, or at larger length scale, depending on the constituent structural units. This makes it an important and interesting method to build novel ordered structures with functionalities in materials and biological sciences. Self-assembly is also applied in polymer chemistry to form different microphases in nanoscale using block copolymers. [84]

Block copolymers form a particular member of polymers consisting of two or more chemically different polymer chains (blocks) joined together by covalent bonds. Taking two distinct blocks, termed as A and B, linear diblock (AB), triblock (ABA), multiblock (ABABAB etc.) or star-block copolymers can be prepared. Pure diblock copolymer self-assemblies exist in four symmetries in bulk phase, depending on the volume fraction of each block: lamellar, gyroid, hexagonal cylindrical and body-centered cubic structures, as shown in Figure 2.1. [85] The morphology is driven primarily by composition, but temperature, and solvents also influence the equilibrium structure. When a diblock copolymer is dispersed in a solvent, and the solvent has preference to one of the blocks, micelles will form (Figure 2.1). The block soluble in solvent forms an exterior layer and the insoluble block forms interior layer, in which way the soluble layer prevents the contact of the insoluble block from solvent. If one block is hydrophobic and the other is hydrophilic, an amphiphilic block copolymer is obtained. Self-assemblies of amphiphilic block copolymers in selective solvents to form different nanostructures have been widely studied. [86-92] The diverse self-assemblies of amphiphilic block copolymers make them suitable for a wide range of applications from biology to biomedicine [93-98] and also in material science [99, 100].
Native cellulose nanofibril hybrids with block copolymers for biomimetic nanocomposites

Figure 2.1 Schematic representations of diblock copolymer morphologies based on the volume fraction of one block (termed as A, upper) and various amphiphilic block copolymers structures formed in a block-selective solvent (bottom). $\chi$: Flory-Huggins interaction parameter; $N$: degree of polymerization; $f$: volume fraction of one block. Reproduced with permission from ref [101, 102] © 2010 by the authors, licensee MDPI, Basel, Switzerland and © 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.2 Cellulose nanofibril-block copolymer biomimetic nanocomposites

Nature shows a wealth of composite materials with excellent mechanical properties, such as mollusk shells, bone, silk, antler, tooth enamel, or wood. In all those materials, a hierarchically ordered self-assemblies are observed with a delicate interplay between the hard and soft domains, [103-105] where typically a large fraction of hard and reinforcing aligned segments are surrounded by a soft biopolymer matrix, such as proteins or polysaccharides. It attracts scientists to make unremitting efforts to understand how biology creates synergistic material properties combing high stiffness, strength, and toughness from mostly relatively simple components. It has been found that all these soft phases, such as proteins and fibroins in pearl of nacre and lignin and hemicelluloses in wood, act as an advanced binder, allowing crack guidance and deflection and nanoscale lubrication between the reinforcing segments, thus promoting toughness.
The fascinating materials in Nature also inspire scientists to strive towards related materials aiming at combined stiffness, strength, and toughness with lightweight structure within the field of biomimetics. [106, 107] In order to achieve the targets, there exist several challenges. Firstly, construction of composites with high fraction of reinforcements that are hierarchically ordered into hard/soft mesostructured materials is the main challenge. Particularly, identifying routes for dissipative polymer layers between the reinforcements is not so easy. Additionally, we need to find pathways, components, and compositions that allow synergetic properties beyond the common rule of mixtures. Considering of synthesis efficiency, we also have to develop strategies with energy-efficient and fast processing. Herein, we aim to develop such a concept of hard/soft biomimetic ordered composites with stiff and strong native cellulose nanofibrils (CNF) and block polymer micelles (Publication I).

In this work, the hypothesis was to overcome the nanoscale dispersion problem and to generate hard/soft biomimetic composites by ionically complexing two oppositely charged colloidal level objects, that is, negatively charged CNF and positively charged block copolymer micelles with soft rubbery cores. We hypothesized that the latter could promote dissipation of fracture energy upon deformation, lubrication between the CNF domains, and potentially even allow sacrificial bond interactions. [108, 109] In our approach, we use an amphiphilic diblock copolymer that carries one cationic, water-soluble block and another hydrophobic block with softness and deformability as functionality. Herein, we chose a poly(1,2-butadiene)-block-poly(dimethylaminoethyl methacrylate) block copolymer (PB-b-PDMAEMA), whose amine group can be transformed into a strong polyelectrolyte via quaternization (methylation) of its nitrogen functions (PB-b-PDMAEMAq). Such amphiphilic block copolymers self-assemble in polar solvents, forming colloidal nanoparticles (micelles) [90] where the hydrophobic chains collapse into a core, [110] surrounded by a stabilizing corona of hydrophilic chains. We aimed at a beneficial lubricating effect of the hydrophobic rubbery polybutadiene phase because of its low glass transition temperature ($T_g \approx -30 ^\circ C$) and hence soft character at room temperature. Upon combination of the cationic PB-b-PDMAEMAq block copolymer micelles and carboxymethylated, anionically charged CNF, a colloidal ionic complex is expected where the cationic polyelectrolyte serves as an anchor for the hydrophobic polybutadiene phase inside the micelles. The concept is illustrated in Figure 2.2.
The cellulose nanofibrils were disintegrated from bleached sulfite pulp by using a high-pressure fluidizer and subsequently carboxymethylated in a chemical pretreatment step and then run once through the microfluidizer. The carboxymethylation of the pulp during the processing leads to a degree of substitution of $\text{DS} \approx 0.1$ in the nanofibrils and a charge density of ca. $0.5 \text{ mmol/g}$. [42] The final CNF has an average diameter at 7.5 nm (standard deviation = 2.3 nm) and a length distribution in the range of a few micrometers (Figure 2.3 a). The quaternized PB-\textit{b}-PDMAEMq diblock copolymers form the micelles by self-assembly during the dialysis from DMF into water (Figure 2.3 b-d). The size and shape of the micelles were assessed by combining scattering and imaging techniques. Dynamic light scattering (DLS) determines the $z$-average hydrodynamic diameter of the micelles around 65 nm with a low polydispersity index of 1.07. Additionally, the micelle morphology was further confirmed by liquid AFM imaging of never-dried micellar dispersion adsorbed onto freshly cleaved mica in water. A rather uniform size of spherical micelles can be observed (Figure 2.3 c). The measured height from AFM images was around 11-14 nm (Figure 2.3 d).
Native cellulose nanofibril hybrids with block copolymers for biomimetic nanocomposites

In order to understand the binding of two objects, fluorescence microscopy and quartz crystal microbalance with dissipation monitoring (QCM-D) was used to study the adsorption of ionically complexation of the two oppositely charged objects in the colloidal level. Fluorescence microscopy allows to visualize the binding of the PB-b-PDMAEMAq micelles to CNF upon incorporation of a hydrophobic fluorescent dye (Nile Red) into the non-polar PB core of the micelles (Figure 2.4 a). The fluorescence micrograph in aqueous medium depicts fibrils and fibrillar aggregates, indicating a strong coordination of the dye-stained micelles with the CNFs. The high contrast between dye-stained fibrils and non-fluorescing background demonstrates a strong affinity as free micelles would diminish the contrast.

QCM-D is another efficient tool to study the adsorption. The basic principles of the instrument have been described extensively. [111, 112] Without adsorbate, the crystal oscillates at its resonance frequency, $f_0$, and upon adsorption, the resonance frequency decreases to $f$. For rigidly and uniform adsorbed film, the change in frequency, $\Delta f$, is proportional to the adsorbed mass per unit surface, $\Delta m$ (mg/m²). To enable CNF model films, the slightly anionic QCM-D crystal resonator substrates were first spin-coated using a poly(ethylene imine) (PEI) primer layer. Next, aqueous CNF was added at $t=0$, and Figure 2.4 b shows a decrease in the QCM frequency (-50 Hz), which indicates that CNF quickly adsorbs on the PEI primer layer of the oscillator. The simultaneous increase in dissipation value ($17 \times 10^{-6}$) indicates that the CNF film is highly swollen and contains a substantial amount of water. Next, addition of aqueous PB-b-PDMAEMAq micelles causes a further decrease of frequency (-41 Hz),
explained by the absorption of the PB-b-PDMAEMAq onto the CNF layer on the oscillator. Interestingly, the dissipation value decreases upon addition of the block copolymer (7×10⁻⁶), suggesting that water is removed from the CNF network during the adsorption process. Therefore, the film becomes more rigid. The adsorption of PB-b-PDMAEMAq on the CNF surface is fast (see the inset of Figure 2.4 b) and the saturation value is reached in less than one minute. This rapid process underscores the high affinity of the cationic block copolymer micelles to the negatively charged CNF surface. After adsorption, the film was dried and imaged by AFM in air. Figure 2.4 c shows roughly globular structures on the CNF, where the diameter is in the range of 80 - 150 nm and height in the range of 8 - 14 nm. Such structures point towards adsorbed micelles on the CNF network layer. Although the glass transition temperature of PB is low (ca. -30 °C) and the micelles have soft cores, we do not observe evidence of opening and film formation of the micelles on the surface. This result has major implications for the composite structure and behaviour.

Scanning electron microscopy shows a layered internal structure on the mesoscale (Figure 2.4 e). The fracture surface displays some vertical holes and protrusion between the various nanocellulose layers, although the composites may have a certain limited void-content, previous work indicates that this is not critical to mechanical performance. [113] This is a consequence of the random-in-plane orientation distribution of CNF. In order to investigate the structural details down to the nanoscale, we used cross-sectional TEM, where the contrast of the PB domains of the block copolymer was increased via selective staining of the double bonds with OsO₄. The TEM micrograph for a CNF/PB-b-PDMAEMAq block copolymer nanocomposite is presented in Figure 2.4 f-g, showing approximately periodic structure with alternating CNF and PB-b-PDMAEMAq domains with a periodicity of around 160 - 200 nm. Interestingly, the micrographs also indicate rather equally-spaced darker spheres within the PB-b-PDMAEMAq domains. Since the darker parts in the micrograph originate from the stained PB double bonds, we conclude that the PB-b-PDMAEMAq micelles are observed also in the composites upon drying and are aligned in a pearl-necklace fashion on CNF strands (see Figure 2.4 f and schematically in Figure 2.2). This observation also coincides with the AFM imaging of the intact micelle layer in the QCM-D adsorption studies. The micellar shape is retained although the low glass transition temperature of the PB part could in principle allow for sufficient dynamics and a disintegration of the micelles. Since the periodicity perpendicular to the lamellae is closer to the diameter of a micelle than to individual CNF, it is likely that the micelles dominate the formation of the assembly at this length scale.
As we discussed before, we aim to achieve strong and tough composite material. Therefore we next investigate the mechanical properties. The stress-strain curves and work of fracture of the composites series are indicated in Figure 2.5. For pure CNF film, the Young’s modulus can reach 12.5 GPa, which is a typically found value for nanocellulose paper. [113] Upon small addition of PB-b-PDMAEMAq (compositions 10/1 and 5/1), the moduli become slightly decreased to values 10.4 GPa and 11.1 GPa (Publication I). Their stress-strain curves are very similar, indicating an only minor influence of the amount of PB-b-PDMAEMAq, see Figure 2.5 a. Still, both curves are remarkably different to the pure CNF, thus pointing to a different interaction between the nanofibrils. Further increase of PB-b-PDMAEMAq towards the composition 1/1 leads
to a decrease of the modulus to 6.2 GPa. The modulus decreases as expected as a function of added softer PB domains.

Typically, the rule of mixtures in mechanical properties behaves as in Figure 2.5 c, wherein with decreasing amount of reinforcement (here microfibrillated cellulose), the stiffness and strength decreased, but the strain-to-failure of the materials increased, thus leading to a higher work of fracture. [113] However, we find strong nonlinearities when looking at stress at break, maximum extension and in particular at toughness as a function of the composition (Figure 2.5 a-b). Toughness can be illustrated as the work of fracture as obtained from the area under the stress-strain curve. [59] We identify a synergetic behaviour of the mixture at a ratio of 2.5/1. The extension at break and also the toughness are reproducibly 2-3 times higher than those of the other compositions. Even compared to the pure CNF, we still find a more than 20% higher strain-to-failure. The suppressed brittleness of this synergetic mixture also allows reaching a high strength. We tentatively ascribe the synergy to the PB-b-PDMAEMAq micelles between the reinforcing CNF domains, where the catonic micellar shells serve as anchors to create assembled domains, while the soft PB part dissipates energy and allows friction reduction between the reinforcing CNF domains under stress. It has been demonstrated in literature that the crack propagation in the nanofibrillated TEMPO-oxidized celluloses with hydroxypropylcellulose matrix is similar to fracture-toughened intercalated clay-epoxy nanocomposites, [114] in which cracks follow a torturous path. Within the context of our work, we suggest that the soft PB phase serves two purposes. First, it enables a more effective crack deflection at the hard/soft (CNF/PB-b-PDMAEMAq) interface as compared to polymers with high $T_g$ and therewith it extends the crack path. [105] Additionally, the lubrication of the nanoscale fibers by synthetic block copolymer with low $T_g$ can favour a fiber pullout vs. a fiber fracture and henceforth contribute a second attractive benefit for toughening.
3. Modifying native cellulose nanofibrils with carbon nanotubes for functional aerogels

3.1 Carbon nanotubes

Carbon nanotubes are another most intensively investigated nanoscale materials. They were found in 1991 by Iijima. [115] He found this tubular material during the preparation of fullerenes using an arc-discharge evaporation method. He demonstrated the carbon structure consisting of needle-like tubes and each needle comprised coaxial tubes of graphitic sheets, ranging in numbers from 2 up to about 50. The diameter ranges from a few to a few tens of nanometers. The observed carbon tubes were so-called multi-walled carbon nanotubes (MWCNTs). Two years later, Iijima and Ichihashi at NEC, and Bethune and colleagues at IBM synthesized the so-called single-walled carbon nanotubes (SWCNTs) (Figure 3.1). [116] Since then carbon nanotubes have been exploited extensively in scientific and industrial fields.

Figure 3.1 TEM images of different CNTs (a: SWCNTs; b: MWCNTs with different layers of 5, 2 and 7). (c) TEM images of SWCNT bundle; (d) SEM image of entangled MWCNT agglomerates.[117] Adapted with permission © 2010 Elsevier Ltd.
Table 3.1 summarizes several carbon material properties. CNTs have advantages over other carbon materials, especially in electrical and thermal properties. These properties offer great potential for wide range of applications in numerous fields including composites [118], energy storage [119-121], biotechnology [122-124], coatings and films [125-128], fibers [129, 130], aerogels [131-134], and microelectronic [135-137].

<table>
<thead>
<tr>
<th>Property</th>
<th>Graphite</th>
<th>Diamond</th>
<th>Fullerene</th>
<th>SWCNT</th>
<th>MWCNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity (g/cm³)</td>
<td>1.9-2.3</td>
<td>3.5</td>
<td>1.7</td>
<td>0.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Electrical conductivity (S/cm)</td>
<td>4000 (p), 3.3 (c)</td>
<td>10⁻²⁻¹⁰⁻¹⁵</td>
<td>10⁻¹</td>
<td>10⁻¹⁻¹⁰⁻¹⁰</td>
<td>10⁻¹⁻¹⁰⁻¹⁰</td>
</tr>
<tr>
<td>Thermal conductivity (W/(mK))</td>
<td>298 (p), 2.2 (c)</td>
<td>900-2320</td>
<td>0.4</td>
<td>6000</td>
<td>2000</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (K⁻¹)</td>
<td>-1×10⁻⁶ (p), 2.9×10⁻³ (c)</td>
<td>(1⁻3)×10⁻⁶</td>
<td>6.2×10⁻⁶</td>
<td>Negligible</td>
<td>Negligible</td>
</tr>
<tr>
<td>Thermal stability in air (°C)</td>
<td>450-650</td>
<td>&lt;600</td>
<td>~600</td>
<td>&gt;600</td>
<td>&gt;600</td>
</tr>
</tbody>
</table>

p: in-plane; c: c-axis

CNTs also have very high mechanical properties. They could reach an elastic modulus approaching 1 TPa and a tensile strength of 100 GPa for individual MWCNTs. [138] This strength is higher than that of any industrial fiber. Individual CNT walls can be metallic or semiconducting depending on their chirality. MWCNTs are normally metallic and have current capacity up to 10⁹ A cm⁻². [139] Relying on the unorganized carbon nanotube architectures, most CNT production is used in bulk composite materials and thin films because of the limited properties. However, the CNT macrostructures such as yarns and films show significantly lower mechanical, thermal, and electrical properties than the individual CNTs because the probability of a critical flaw and weak CNT-CNT junctions increasing with volume, and therefore macroscale CNT yarns may never achieve the strength of the constituent CNTs. [140]

Chemical vapour deposition (CVD) is the main method for high volume CNT production. SWCNT synthesis by CVD requires much tighter process control than MWCNT synthesis. Therefore, bulk SWCNT prices are higher than MWCNTs. MWCNTs are widely used for reinforcement additives with polymers or used as electrically conductive fillers. The fabrication of CNT/polymer composites requires stable CNT dispersion. However, the very high aspect ratio of CNTs (>1000) and its extremely large surface area make them highly difficult to disperse in organic solvent or aqueous solution, and to have good interactions with polymer matrix. Additional surfactant or chemical surface modification of CNT is needed to improve CNT dispersibility in aqueous or solvent and also the interactions with polymer matrix. [117, 141]
3.2 Aerogels

Aerogels have been exploited extensively since introduced by Kistler in the 1930’s. [142] They are lightweight low density solid nanostructured materials with high porosity containing ~90-99% air by its volume. [143] They are typically produced from solvent-swollen wet gels by replacing the solvent in gels with gas while preventing the gel network from collapse and shrinkage. This requires specific preparation techniques, as collapse typically takes place during conventional solvent evaporation.

![Water phase diagram. Arrows point out the different drying processes.](image)

The first silica aerogels were made using supercritical drying. [143] Supercritical drying prevents the formation of liquid-vapour meniscus and the underlying liquid surface tension (Figure 3.2, red arrow). Suppression of surface tension thus avoids the pore collapse and keeps the interconnected porous nanostructures intact. The supercritical conditions vary depending on the supercritical fluids. Carbon dioxide is one common used supercritical fluid (72.7 atm, 31°C) as it allows low operating temperature and pressure (Table 3.2). [143] However, supercritical drying is laborious and an expensive technique.

![Table 3.2 Critical parameters of common fluids.](image)

<table>
<thead>
<tr>
<th>fluid</th>
<th>formula</th>
<th>$T_c$ (°C)</th>
<th>$P_c$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>H₂O</td>
<td>374</td>
<td>218</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>CO₂</td>
<td>31</td>
<td>72.7</td>
</tr>
<tr>
<td>acetone</td>
<td>(CH₃)₂O</td>
<td>235</td>
<td>46</td>
</tr>
<tr>
<td>methanol</td>
<td>CH₃OH</td>
<td>239.4</td>
<td>79.8</td>
</tr>
<tr>
<td>ethanol</td>
<td>C₂H₅OH</td>
<td>243</td>
<td>62.2</td>
</tr>
</tbody>
</table>

Alternatively, freeze-drying as another technique used to produce aerogels has been applied widely in applications. In this method, the solvent in the wet gel is first frozen and thereafter dried by sublimation (Figure 3.2, blue arrow).
Therefore, the formation of liquid-vapour meniscus is prevented. However, the achieved aerogel surface area and mesopore volume tend to be smaller in comparison with supercritically dried aerogel. Also, the gel network may eventually be affected by the nucleation and ice crystal growth, thus tending to produce large pores. [143, 144]

Owing to their attractive properties, highly porous aerogels have been used for lightweight construction, thermal and acoustic insulation, membranes, separation, chemical analysis, catalyst support, sensing, energy technologies, and energy absorption. [145-148] Classical aerogels based on silica or inorganic particles are relatively brittle, which can reduce their application potential. There has been extensive research for ductile and flexible aerogels using nanofibers. Therefore, polymers, carbon nanotubes, graphene, and native cellulose fibers have been studied to a great extent. In particular, reduced brittleness and even flexibility have been shown based on CNF or using bacterial cellulose (BC). [36, 149, 150]

CNF aerogels are typically produced from the hydrogels by removing water upon freeze-drying or supercritical drying, leading to interconnected sheet-like or fibrous skeleton respectively. [77] Ultralight and highly flexible aerogels with long cellulose I nanofibers have been produced via purification and defibrillation of wood fibers into cellulose nanofibers hydrogels, followed by freeze-drying, which allowed ultra-low density aerogels (0.2 ×10^{-3} g/cm³) and porosity as high as 98%. [151] The high porosity and mechanically strong CNF aerogel allows a variety of applications in filtration [152], insulation [148, 153], and as templates for functionalities [36, 62, 154-156]. Conducting CNF aerogels have been made by functionalizing with conjugated polymers [36, 157-159] or by mixing with single-walled carbon nanotubes [67, 160]. Recently a robust and rapid method has been shown for the layer-by-layer assembly of functional polymers and nanoparticles on cross-linked nanocellulose aerogels with a porosity close to 99%, high strength, and nanoscale shape integrity in water. [76] However, there still exist challenges to utilize CNF aerogels as the starting material since they are not tough comparing to the natural porous material, e.g. wood, bone and tendon. [161] Recently, tailored hierarchical structures nanocellulose composite biofoams have been made with high mechanical performance. [58, 162, 163] Biomimetic polysaccharide foams were prepared by the lyophilization technique with cellulose nanofibril content ranges from 10 to 70 wt% (dry weight basis). [58] Compared to the neat amylopectin foam, a significant improvement in modulus and yield strength was observed.

### 3.3 Cellulose nanofibril/carbon nanotube hybrid aerogels

As we discussed previously in this chapter, owing to their good mechanical and electrical properties of CNTs, there would be also interest to combine the mechanically strong CNF and CNT to produce a double network aerogel materials which can combine the bulk availability of CNF and advanced electrical properties of CNT. In a typical solvent-based process, CNTs are first chemically or
physically functionalized or mixed with binder polymers to increase the nanotube-nanotube interactions which, in turn, promote gelation and finally lead to aerogel formation upon freeze-drying or supercritical drying. [133, 164] It has also been reported that carboxymethylated CNF or hemicellulose can help the dispersion of CNT in water. [67, 165, 166] Interestingly, gas phase synthesis can lead to CNT elastic sponges even without binders and crosslinkers obviously due to entanglements. [167, 168] Such sponges allow pressure sensing in compression as the resistance depends on the stress level. Herein, we foresee that mixing CNF and CNT in a facile process could allow templates for functionalization using small weight fractions of CNT, thus combining their excellent properties. Figure 3.3 shows the schematic steps and the resulted morphology of CNF/CNT hybrid aerogels and their conductivity.

**Figure 3.3** a) Cellulose nanofibrils (CNF) form strong physical gels in aqueous medium due to the long and entangled hydrogen bonded native cellulose nanofibers of diameters in the nanometer range. b) Few-walled carbon nanotubes (FWCNTs) are modified to allow dispersion in the aqueous medium, mixed in the CNF hydrogel and homogenized by ultrasound treatment. c) The hybrid CNF/FWCNT hydrogel is inserted in a mold, and cooled by plunging into liquid propane or liquid nitrogen and freeze-dried to allow aerogels. d) Freeze-drying from liquid nitrogen leads to slow cooling and to sheet-like morphology due to aggregation of CNF and FWCNT, whereas freeze-drying from liquid propane leads to quicker cooling and to fibrillar morphology. e) Cryo-TEM images of CNF/FWCNT 75/25 wt/wt aerogel; at high magnification the FWCNT (black arrow) can be distinguished from CNF (red arrow). It is clear that CNF and FWCNT are in close contact. f) Conductivity of CNF/FWCNT aerogels. Reprinted with permission © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

CNF nanofibers were prepared from an aqueous native birch pulp by first grinding and then passing 16 times through a homogenizer, essentially as reported elsewhere. [36] After such a process, the entangled nanofibers have diameter of ca. 9 nm and they form a hydrogel at a concentration of 1.7 wt%
Regarding larger scale applications, few-walled carbon nanotubes (FWCNT) were selected instead of single-walled nanotubes, since they kept intact inner layers after chemical modifications. They were produced by catalytic pyrolysis of CH$_4$ in the presence of H$_2$ at 960 °C on the (Co-Mo)/MgO catalyst (Publication II), as described previously. [169] They have diameter of 3-7 nm, see Figure 3.3 e. In order to promote dispersibility in water, FWCNTs were surface functionalized by oxygen containing polar groups (mostly –COOH, >C=O, and -OH). Herein, the functionalized nanotubes are subsequently still denoted as FWCNTs. A FWCNTs dispersion at concentration 0.4 wt% was added into the CNF hydrogel, followed by mixing with a high-speed mixer and ultrasonic bath. The compositions of FWCNTs loading has minority phase, i.e. CNF/FWCNT 100/0, 95/5, 90/10, 85/15, 80/20, 75/25 wt/wt. The aerogels were next prepared by freeze-drying. We chose two cryogenic fluids for cooling and freezing, i.e. liquid nitrogen and liquid propane; their boiling points are at -196 °C and -42 °C respectively. Then the frozen hydrogels were inserted in a vacuum chamber on a pre-cooled metal support plate and pumped to remove the ice by sublimation. Liquid nitrogen was used for cooling relatively thick (3 mm) samples and liquid propane for thin (1 mm) samples.

The SEM micrograph for the CNF/FWCNT 95/5 wt/wt aerogel in Figure 3.3 d shows two different structures from different cryogenic liquids. The aerogels prepared from liquid nitrogen shows interconnected sheet-like structures of micrometer lateral dimensions. The connected nanofiber bundles have diameter up to ca. 100 nm. This structure can be qualitatively explained, as upon immersing the room-temperature aqueous gel sample in liquid nitrogen leads to a thin thermally insulating N$_2$-gas layer on the sample surface (the so-called Leidenfrost effect), thus slowing down the heat transfer between the sample and the cryogenic fluid. [77] This, in combination with the relatively large selected sample thickness causes slow cooling. Therefore, the ice crystals have time to grow during the cooling and they become large. This promotes the aggregation of nanofibrils into sheets, as known for CNF. [36] But also FWCNT has a tendency to form large sheets due to aggregation upon immersing in liquid nitrogen. A question arises whether CNFs and FWCNTs aggregate into separate nanosheets or form hybrid nanosheets. Due to their roughly similar diameter, it is difficult to recognize individual CNF and FWCNT nanofibers in the sheets by SEM observation. The TEM micrograph in Figure 3.3 e clearly points out the CNF and FWCNTs in the hybrid network, and may reveal there is no phase separation between them and suggest the co-aggregation structure after drying. This would not be surprising, as benzene rings and cellulose have direct affinity [170] and the present surface functionalization of FWCNT also promotes hydrogen bonding to CNF. It also shows the individual FWCNTs of diameter of ca. 3 nm and CNFs of lateral dimensions of ca. 9 nm. There exists intimate contacts between CNFs and FWCNTs. In another freeze-drying protocol, liquid propane cooled to liquid nitrogen temperature is used for cooling, leading to no thermally insulating boiling gas layer. Combining the thin sample this leads to drastically different
morphology, as no sheet-like fibrillar aggregates are formed (Figure 3.3d). The ice crystals are now smaller and the nanofibrillar network structure is mostly preserved upon freezing and sublimation of ice.

The electrical conductivities of CNF/ FWCNT aerogels are shown in Figure 3.3f for the two freeze-drying methods. Pure CNF aerogels are not conductive whereas the pure FWCNT aerogel has an electrical conductivity of 1.8 S·cm⁻¹ upon liquid nitrogen freeze-drying and an order of magnitude less for the liquid propane freeze-drying. In the hybrid aerogels the electrical conductivity increases upon increasing the FWCNT weight fraction, and liquid nitrogen freeze-dried CNF/ FWCNT 80/20 wt/wt aerogel shows a relatively high electrical conductivity of 1×10⁻² S·cm⁻¹. The sheet-like architectures, as observed for the liquid nitrogen freeze-dried samples of thickness 3 mm, show higher conductivities in all cases than the corresponding compositions following the liquid propane freeze-drying of 1 mm thick aerogels having the fibrillar structure. This observation was particularly clear for the composition CNF/ FWCNT 95/5 wt/wt, which did not conduct based on liquid propane freeze-drying. We tentatively assign the higher conductivity in case of the sheet architecture for a subtle hierarchical percolation: at the smaller length scale, the FWCNTs percolate within the essentially 2-dimensional aggregate sheets within the CNF matrix, and in the larger scale these essentially 2-dimensional conducting sheets percolate in the 3-dimension aerogel overall volume, also connected by fibrillar CNF and FWCNT. Therefore, we concentrate in the following solely on aerogels involving sheet-like architecture as achieved by the slow cooling in freeze-drying using the liquid nitrogen freeze-drying and thick samples.

![Figure 3.4](image)

Figure 3.4 Compression stress-strain curves of hybrid CNF/ FWCNT aerogels (The density is in the range of 0.02 g cm⁻³). For reference, the inset depicts the pure FWCNT aerogel (density = 0.054 g cm⁻³), which did not allow low-density aerogels without collapse. Reprinted with permission © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The stress-strain curves under compression are shown in Figure 3.4 for the liquid nitrogen freeze-dried aerogels involving sheet-like architecture up to FWCNT concentration of 25 wt/wt, having approximately a constant density ≈
0.02 g cm\(^{-3}\) (Publication II). The pure CNF aerogel has an essentially linear stress-strain curve at low strains without yield point and the maximum compression strain 70% is observed. This indicates a ductile behaviour of pure CNF aerogels with reduced brittleness, as expected from previous works for CNF. [36] Upon adding FWCNTs the shape of the stress-strain curve remains qualitatively similar, but the stress levels curiously become reduced and the maximum strain increases to 95% for the FWCNTs content approaching 20 wt/wt. In other words, replacing part of CNFs by FWCNTs in the compositions leads to plasticization, which is at first slightly surprising. But this might be explained by the smaller number of interaction sites in the functionalized FWCNT in comparison to the extensive amount of hydroxyl groups of CNFs, i.e. a FWCNT binds weaker with its local surrounding. The inset shows the stress-strain curve for pure FWCNT. But importantly, without added CNF, the pure FWCNT underwent some shrinkage after ice sublimation, which leads to higher density \(\approx 0.054\) g cm\(^{-3}\). This effect can be explained by the strong interaction which leads to the tendency to form FWCNT bundles. Therefore, CNF templating allowed reaching lower densities ca. 0.01 - 0.02 g cm\(^{-3}\) in the composite aerogels.

As discussed previously in this chapter, CNTs and their composites materials have been widely used for electrical applications, for example as sensing device. As potential application for our materials, the electrical properties upon compression were investigated by selecting the hybrid aerogels with sheet-like structure by liquid nitrogen freeze-drying. The aerogel was clamped between two conducting electrodes, and pressure was exerted by dry N\(_2\) gas. Figure 3.5 shows the relative resistance reduction vs. imposed pressure for the aerogel CNF/FWCNT 75/25 wt/wt having the density \(\approx 0.01\) g cm\(^{-3}\). A change of pressure of 0.1 bar induces a 10% relative change in the resistance. The stability is demonstrated by cycled 0.5 bar pressure. For comparison, for CNF/FWCNT 80/20 wt/wt having almost double density \(\approx 0.018\) g cm\(^{-3}\) but smaller weight
fraction of FWCNT, an almost similar compression stress strain curve was observed. Regarding the resistance change under pressure, in order to achieve 10% relative change in resistance, the imposed pressure has to be ca. 5 bar. This indicates the complex interplay within the overall percolation, as effected by the mechanical percolation by the aerogel structure and density, and the electrical percolation as controlled by the CNT concentration, and the hierarchical percolation due to the sheet formation.

We finally point out that addition of CNF was essential, as without CNF, the resistance did not behave reproducibly under compression using the present FWCNTs (Publication II, Figure S5). Previously, related mechanically elastic and electrically reversible compressional behaviour has been achieved using aerogel compositions where CNT or graphene form the majority phases, including minor fraction of binders or cross-linkers or also using subtle chemical vapour deposition concepts. By contrast, the present hybrid nanofiber/nanotube aerogel concept shows qualitatively similar behaviour using only a minor fraction of the more precious FWCNTs by combining with the nano-cellulose fibers. Taken the abundant availability of CNF, and the robustness, the concept is attractive. Also, CNF is herein the main source for good elastic mechanical properties whereas FWCNTs are responsible for the electrical properties, thus showing synergism between the nanofibers and nanotubes within the aerogels.

3.4 Electrical fatigue of native cellulose nanofibril/carbon nanotube hybrid aerogels

We have discussed the mechanoresponsive conductivity and pressure sensing materials by modifying CNF aerogels with few-walled carbon nanotubes (FWCNT) in chapter 3.3. The hybrid FWCNT/CNF aerogels were shown to be ductile in compression, and allowed systematic resistance change as a function of deformation. In this chapter, we explore the electrical stability of the system under repeated cycles, i.e. “electrical fatigue”. This is a nontrivial aspect, depending on the subtle details of percolations of FWCNT within the hybrid aerogel.

In this work, similar materials are selected, i.e. native CNF from birch pulp and chemically modified FWCNTs with oxygen containing groups. During freeze-drying, a mold was inserted to liquid nitrogen at a constant controlled rate of 6.6 mm/min and subsequently followed by ice sublimation. This method, in principle, could lead to anisotropic morphology in the aerogel porosity. Thus, the scanning and transmission electron microscopy images are shown in Figure 3.6.
From above, i.e. perpendicular to the ice-growth direction, SEM suggests honeycomb-like structures (Figure 3.6 a). The side-view, along the ice-growth front, indicates only slight anisotropy with tubular formation with skeleton-like tube walls (Figure 3.6 b). One can conclude that the aerogel structure is essentially isotropic as it involves in each direction a porous skeleton structure. This finding can be compared to previous studies, which showed macroporous honeycomb structures with continuous tubular walls based on multiwalled carbon nanotube aerogels taken into account that they involve an additional polymer phase as a crosslinking component. [133] In that case, it is much easier to form continuous honeycomb tube walls using the continuous polymer phase, in comparison to the present situation involving two 1-dimensional nano-objects. TEM is incorporated to investigate the structures in the nanoscale. Composite fibrillar network within the FWCNT/CNF is inferred in Figure 3.6 c-d where FWCNTs are incorporated within the CNF network forming the minority phase in FWCNT/CNF 20/80 wt/wt aerogels.
Modifying native cellulose nanofibrils with carbon nanotubes for functional aerogels

CNFs are hydrophilic because of the abundant hydroxyl groups leading to extensive water vapour absorption. The FWCNT used in this work also involves considerable amount of oxygen-containing groups, which will also make them hydrophilic. In order to gain some understanding how water vapour influences the resistance level of the present hybrid aerogels, the resistance of the aerogel is investigated between different humidity environments. Figure 3.7 illustrates the behaviour where FWCNT/CNF 20/80 wt/wt aerogel was first equilibrated overnight at a high humidity (55±5 % RH) in a humidity chamber and then taken out to lower humidity (25±5 % RH). Thereupon the resistance decreases ca. 30% and starts to approach an equilibrium in two hours. After five hours the resistance level maintains almost the same value as after the first two hours. The conclusion is that humidity has a large effect on the resistance. When practical applications are pursued, the aerogel has to be post-functionalized by hydrophobizations, as described in the literatures. [62, 154, 155]
Modifying native cellulose nanofibrils with carbon nanotubes for functional aerogels

We performed the cyclic compression and pressure sensing test to investigate the electrical fatigue under cyclic compression, where the setup was shown in Figure 3.8. The cyclic testing was set to 8% compression strain at 3 mm/min rate loading and unloading. Samples were connected with copper wires at the two ends using conductive silver glue. Resistance was detected simultaneously with a Keithley 2400 source meter. Both the compression clamps were insulated by Kapton tape.

Figure 3.9 a-b illustrates 100 cycled stress-strain curves up to strain 8% and the first and 100th cycles for the FWCNT/CNF 20/80 wt/wt aerogel. It shows reversible compression cycles for 100 cycles; as there is only a small change from the first cycle to the last cycle (Figure 3.9 b). In this test, we selected a strain level of 8% which is expected to be in the linear regime. Previous studies have demonstrated that the cellular nanofibrillar cellulose foam has an initial linear elastic regime up to a strain of about 12%. [161] In comparison with Figure 3.9 a, 8% strain is in the elastic region and the material recovers after unloading. The hysteresis between loading and unloading is relatively small. By contrast, in the first cycle of FWCNT/CNF 25/75 wt/wt aerogel, the hysteresis is bigger than the FWCNT/CNF 20/80 wt/wt aerogel (Publication III, Figure S3 b).
Modifying native cellulose nanofibrils with carbon nanotubes for functional aerogels

Figure 3.9 Cyclic mechanical and electrical compression studies for FWCNT/CNF 20/80 wt/wt hybrid aerogel. (a) 100 cycled stress-strain curves up to strain 8% and the first 16 compressive stress vs. time cycles illustrated (inset). (b) The first and the 100th cycle of compressive stress-strain curves. (c) 100 cycled resistance response vs. time under cyclic compression up to strain 8%. The insets show the first 16 cycles, and one characteristic cycle lasting 12 seconds. (d) Fractional resistance reduction during cyclic compression. Reprinted with permission © 2016 Royal Society of Chemistry.

The 100 cycled resistance and resistance reduction are illustrated as a function of time during cyclic compression stress (Figure 3.9 c-d). Resistance shows almost immediate response corresponding with compressive loading and unloading. Each cycle takes ca. 12 seconds. The fractional resistance ($\Delta R/R_0$) for FWCNT/CNF 20/80 wt/wt changes reversibly ca. 7%, and essentially is similar after 100 cycles. (Figure 3.9 c-d) For FWCNT/CNF 25/75 wt/wt aerogel the fractional resistance changes even larger 25% and also it stays after 100 cycles (Publication III, Figure S3 c-d). This indicates that the pressure sensing property of the aerogel materials shows good stability for these compositions. However, at small FWCNT loading 15 wt% the resistance is gradually decreasing upon compression, which can be explained that the conductivity is too low to render a reproducible behaviour (Publication III, SI 3 e-f). But high conductivity starts to show irreversibility in mechanical behaviour, i.e. with 25 wt% FWCNT loading (Publication III, SI 3 a-b). To conclude, FWCNT/CNF hybrid aerogels can be constructed to allow stable reversible resistance changes in cyclic compression. Composition involving FWCNT/CNF 20/80 wt/wt has been observed to be promising. In cyclic compressions this aerogel showed reversible resistance reduction, and only small changes were observed during 100 cycles. It gives the most reversible behaviour in both electrical and mechanical terms.
Modifying native cellulose nanofibrils with carbon nanotubes for functional aerogels
4. Cellulose nanofibril films for actuation

4.1 Actuators

Synthetic polymeric materials that change shape, size, or mechanical properties upon external stimuli have attracted considerable interest because of their potential as actuators in a broad range of applications. [171] Many approaches have been presented. They can be based on phase transitions at the molecular and/or atomic scale, and enable kinetic trapping of a temporary shape which is later recovered to the original phase under a selective thermal, chemical, magnetic or optical trigger. [172] Actuation can be based also on doping and dedoping of electroactive polymers leading local volume change [173], shape memory materials [172], light- or thermal-responsive elastomers [173, 174], and pH- or solvent-responsive gels [175-178].

Considering shape memory polymers (SMP) as they can be considered to be somewhat related to the present concept in this work, for a single transition temperature there exists only a temporary shape and then a recovery back to its permanent phase through one step. Recently, Li et al. have shown a multiple-shape memory effects (SME) in poly (methyl methacrylate)/poly (ethylene glycol) (PMMA/PEG) semi-interpenetrating polymer networks (IPN). [179] It provides multi-gradient glass transition temperatures and an additional melting temperature as transition temperatures for multi-step shape fixation and recovery in a single shape memory cycle (Figure 4.1 a). Fei et al. have investigated electrical resistance heating as a trigger to realize the spatial and temporal control of the shape memory process. [180] In this case, multiple shapes were obtained by selecting the place where the electrical voltage was applied or switching the power on/off (Figure 4.1 b). Unfocused light is also used to trigger shape recovery as demonstrated by Liu et al. [181] Therein they produced black ink pattern on both side of the polymer sheet by which provides localized absorption of light and heats the underlying polymer to temperatures above its glass transition (Figure 4.1 c). At these temperatures, the predefined inked regions relax and shrink, and thereby cause the planar sheet to fold into a three-dimensional object. Therefore, self-folding is achieved in a simple manner without the use of multiple fabrication steps.
Unlike synthetic polymeric materials, natural materials utilize remarkably different approaches. Biological machinery allows actuation movements in simpler systems, where the movements can be triggered by simple stimuli, such as temperature, light, humidity, or mechanical force. Instead of molecular phase transitions of combinations of different materials, biological materials program their internal microstructure by controlling the local positioning and orientation of stiff fibers. For example, sea cucumbers can alter the stiffness of their dermis within seconds to obtain survival advantages; the Venus flytrap can close their leaves in a second for efficient prey capture.

Figure 4.1 (a) The PMMA-PEG shape memory polymer changes to its different shapes according to different temperatures. Shape B: the first temporary shape, shape C: the second temporary shape, shape D: the third temporary shape, shape E: the fourth temporary shape, and shape A: the permanent shape. [179] Reprinted with permission © The Royal Society of Chemistry 2011. (b) Schematic illustration of the electro-triggered spatially and temporally controlled shape recovery and the realization of multi-shapes on demand of CNTs-filled SMP. [180] Reproduced with permission © The Royal Society of Chemistry 2012. (c) Self folding of shape memory polystyrene film patterned with ink to form rectangular, tetrahedral boxes using local light absorption. [181] Reproduced with permission © The Royal Society of Chemistry 2012.
and pine cones open and close in response to environmental humidity [187, 188] (Figure 4.2).

Figure 4.2 (a) A photo of sea cucumber in the relaxed (left) and stiffened (right) state. [185] Reproduced with permission © 2008, American Association for the Advancement of Science. (b) A Venus flytrap in its open and closed states. [186] Reproduced with permission © 2005, Right Managed by Nature Publishing Group. (c) A pine cone open and closed according to humidity. Reprinted with permission from [189].

Water or moisture is a common and simple trigger for biological materials to change their shapes. Beyond pine cones, in nature there are many plants responding to humidity by shrinking or swelling. Spruce branches typically curve upwards based on cell-wall swelling; [190] wild wheat awns bend with changing humidity to propelling the seeds lying on the ground; [191, 192] In this case, the wheat awn is also able to use solar energy. Surprisingly, there is no active metabolism involved in the movement since all the relevant cells in the awns are dead. The orientation of the cellulose fibrils in the cell walls is a crucial adjustment mechanism to bend the organs. [183, 193] The influx and efflux of water in the cell walls causes changes in cell and tissue geometry. It has been analyzed that water-caused swelling and shrinking are generally responsible for slow and small-scale movements, whereas elastic instabilities cause fast and large-scale movements. [184, 194]

The biological materials have inspired considerable research for biomimetic shape changes and actuation. Recently, a synthetic water transport system has developed based on the transpiration principle of trees. [195] Reversible switching hydrogels embedding with soft or stiff nanopillars have been made as actuation or gripping devices according to humidity changes. [196] Reyssat et al. fabricated plastic-paper bilayers to mimic hygromorphic plant behaviour. [188] They constructed a model device that opens and closes like flowers with changing humidity. A hierarchically arranged helical carbon nanotube fiber
actuator driven by solvents and vapours has been produced by Chen et al. [197] Rahman et al. made an asymmetric nanotube actuator using polyaniline nanotubes embedded in polycarbonate membrane through chemical route, i.e., chemically triggered actuation. [198] A water-responsive polymer film was described combining both a rigid matrix (polypyrrole) and a dynamic network (polyol-borate). [176] These actuation mechanisms are mainly based on bi-layer heterogeneic structures. Mu et al. have reported a multi-responsive water-driven actuator using graphene monolayer paper. [178] It contained a gradient reduced graphene oxide/graphene oxide structure. This graphene monolayer paper exhibited fast and powerful actuation performance which responded to moisture, heat, and light, making it potentially applicable in artificial muscles, robotic hands, and electromagnetic-free generators.

4.2 Humidity-driven reversible cellulose nanofibril films as bio-inspired actuation

The above-discussed plant-based actuation inspired us to investigate water swelling/deswelling-dependent bending in films consisting of CNF. We have discussed and demonstrated in this thesis that CNF has high tensile stiffness and strength, but due to their nanometer scale lateral dimensions they allow facile bending. On the other hand, previously it has been observed that upon placing a classic paper sheet on the surface of liquid water, it starts to bend, as water penetrates into the sheet from below and initiates asymmetric swelling. [199] Thus, a temporary “bilayer” is formed based on the bottom hydrated swollen layer and the upper more dry layer. However, when the water front reaches the sheet upper surface, the asymmetry is suppressed and the paper sheet recovers its original flat shape. It has to be noticed that classic papers are relatively thick due to their microscopic cellulose constituent fibers, thus providing relatively high flexural stiffness.

Our initial hypothesis was that if we use CNF instead of classic thick pulp fibers of high bending stiffness, we could achieve more sensitive actuation, even to allow triggering by water vapours, as the nanoscopic CNF allows facile bending and making thinner sheets than those of classic paper. Herein, we describe that sufficiently thin CNF-based films show highly sensitive and bidirectional water-vapour triggered bending (Figure 4.3) to allow even complex bent shapes. The mechanism has also shown recently by Bettotti et al., where the CNF films respond to water fluxes by a mechanical movement due to an interface-driven water sorption process. [200]
In our work, the CNF was prepared from an aqueous native birch pulp through a high-pressure homogenizer several times (detail described in Publication III). The films were prepared by filtration of aqueous dispersion of CNF, followed by drying under ambient conditions. Different thickness films were made to investigate the bending as a function of the films thickness.

Surprisingly, the CNF films start to bend in a few seconds while holding on a bare hand (Figure 4.4 a). The bending increases until it seems to acquire a steady-state value in tens of seconds. Importantly, it does not relax back even upon holding the film on the hand for prolonged times. However, the film recovers its original flat shape in tens of seconds when moving away from the hand, indicating that the bending is reversible. On the other hand, if the bent film on the hand was turned upside down, it becomes flat again and further continues to bend in the reverse direction (Figure 4.4 b). The reversible and bidirectional deflection processes take roughly tens of seconds.
This CNF film sensitively senses the presence of uncovered human skin, due to either the small temperature or the humidity gradient. We put a flat CNF film at the open door of a hot oven with its surface parallel to the door, but the film did not bend at all, suggesting that the actuation is not driven by a temperature gradient. To qualitatively verify the role of humidity, we put the flat CNF film on a latex glove-covered hand, whereupon no deflection was observed (Publication IV, Figure S3). Obviously, the glove acted as a humidity barrier between the skin and the film. Therefore, the higher humidity close to a bare hand should be responsible for the actuation. This is not surprising as the
physiochemical property of the CNF is important for the high moisture sensitivity of the film. As a hydrophilic polymeric material, CNF has numerous hydroxyl and oxygen-containing groups along the high surface area of the nanofibers, which makes it highly sensitive to humidity change and able to absorb moisture even from very dilute water vapour environment. In comparison, a CNF film was placed inside a humidity chamber (Figure 4.5). It did not bend at all, therefore, the CNF film bends only when there has humidity gradient, i.e., a bilayer is formed.

![CNF film](image)

**Figure 4.5** A CNF film was placed inside a closed chamber at controlled relative humidity of 45.4%, 22.2°C.
After these qualitative demonstrations, the bending was quantitatively studied by placing the films within an aperture of a humidity chamber thus rendering a controlled humidity gradient. Figure 4.6 a showed the bending curvature increased gradually from 0.3 to 0.75 cm⁻¹ as ΔRH was increased from 10 to 40%, as illustrated for the film of thickness 8 μm. When fixed the ΔRH at 40%, the steady-state bending curvatures of the CNF films with different thickness showed high bending curvature at less than 20 μm film, whereas the film with a thickness of ≈38 μm showed only moderately small bending of about 0.2 cm⁻¹.
and the one with thickness of \( \approx 48 \text{ \( \mu \text{m} \) } \) exhibited only a minimal curvature (Figure 4.6b). In addition, this reversible deflection-recovery process can be repeated for more than 20 cycles without observable fatigue (Figure 4.6c). In comparison with fast vapour absorption bending process, the recovery rate of desorption is slower. This is reasonable because of the fact that desorption of moisture is more difficult than its absorption in accordance with the highly hydrophilic and hygroscopic character of the CNF film.

![Remote shaping of a nanocellulose film](image)

**Figure 4.7** The sensitivity of the humidity-driven bending is demonstrated here where the bending is induced even by a finger at a distance of a few millimeters, i.e., without direct contact. Upward deflection from (a) left, (b) right parts, and downward deflection from (c) the central part by approaching a finger towards different parts of the film. The CNF film is placed on top of a plastic cap. Reprinted with permission © 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Finally, a demonstration of the high sensitivity for the humidity deflection was shown even induced at a distance by just approaching a finger towards it, i.e., remotely without direct touching (Figure 4.7). When a finger approached the CNF film from the bottom left or bottom right parts, local upward deflection at the corresponding parts readily took place. When the finger approached from the top middle part, the film deflected downward. Therefore, even a very slight and local humidity increase close to the CNF film can create local asymmetric swelling of the film and induce local bending.
5. Conclusions and outlook

This thesis has described several functional materials based on native cellulose nanofibrils (CNF). Approaches towards functional materials are shown based on the attractive properties of CNF, i.e. good mechanical properties, flexibility in bending, high surface area and water binding by hygroscopicity.

Publication I described a hard/soft biomimetic composites by ionically complexing two oppositely charged colloidal level objects, that is, negatively charged native cellulose nanofibrils and positively charged block copolymer micelles with soft cores. It mimics the natural composites materials where typically a large fraction of hard and reinforcing aligned segments are surrounded by a soft biopolymer matrix. The soft phase often acts as an advanced binder, allowing crack guidance and deflection and nanoscale lubrication, thus promoting toughness. In publication I, the assembled biomimetic nanocomposites that contain a large fraction of CNF reinforcements separated by rubbery domains. The complexation between the colloidal nanofibrils and colloidal micellar spheres prevents macroscopic phase separation and gives rise to composites with an alternating nanoscale hard/soft architecture. As a consequence of the improved mesoscale order, a synergetic performance of the components beyond the simple rule of mixture was identified. Since block copolymer structures can be widely tuned for different molecular weights, block constituents, and architectures, it offers great possibilities to pursue biomimetic nanocomposites with significantly increased fracture toughness, while maintain stiffness and strength.

Publication II and III introduced hybrid conductive aerogels consisting of native cellulose nanofibrils and carbon nanotubes (CNT). Aerogels using CNF or bacterial cellulose have shown reduced brittleness and even flexibility. CNF aerogels show high porosity, low density, and high surface area allowing to be a template for making functional materials. Incorporating both CNF and CNT within the aerogels allows combining the attractive features of both components: wide availability, easy processability, and the sustainability of the CNF majority component and the advanced electrical properties of the CNT minority component. The hybrid nanofiber/nanotube aerogels are ductile, with reduced brittleness. Notably, there is no binder between the nanofiber and nanotube network which is normally found in CNT aerogel materials. The aerogel morphology can be tuned by the freeze-drying process, i.e. different cryogenic liquids and slow and constant immersion speed to the cryogenic liquid. Publication II demonstrated the potential of CNF/CNT aerogels in pressure sensing
application, where a reproducible resistance change was shown under compression. Publication III described the electrical behaviour of the hybrid CNF/CNT aerogels under cyclic mechanical compressions to explore “electrical fatigue” of this material. The optimized composition illustrated only small changes in electrical and mechanical behaviour upon cycled compression showing good stability and reversibility. This combining of nanocellulose and carbon nanotubes allows responsive electroactivity, pressure sensing and functional materials.

Publication IV described the CNF film actuation triggered by humidity and showed highly sensitive and reversible bidirectional bending. Nature gives the lessons to inspire scientists to produce bio-inspired actuation materials, such as pine cone and wheat awn which can change their shape according to humidity change. The nanofibril arrangement has crucial role during this process. Such concepts encouraged us to explore bio-inspired actuation based on water swelling/deswelling in CNF films. Unlike the previously reported liquid water driven transient bending of paper sheets, the present CNF film showed a steady-state bending within a fraction of minute upon continued humidity exposure, and the film relaxed back upon removing the imposed humidity. The bending curvature becomes reduced when the film thickness increases, thus explaining that the effect is not observable in classic paper sheets. The bending is reversible, bidirectional, and allows cycling. It suggested that the formation of a dynamic bilayer-like structure in thin films dominant this phenomenon. The bending is highly sensitive to humidity, as demonstrated by the observation that the film bends even based on the small humidity of human hand from a distance of several millimeters. Such a bending of a cellulose nanofiber film offers a particularly simple route towards biomimetic actuation and novel types of active materials, for example, when combining with electroactive and other functional units, as well as devices allowing locomotions.

In general, the research using native cellulose nanofibrils as building block for functional materials is expanding, as there are lots of research groups and industrial companies springing up to exploit nanocellulose-based functional materials. There exists a growing effort producing nanocellulose towards classic paper sector, but importantly towards new emerging fields, for example, energy, electronics, composites, films, food, packaging, optics, and biomedicine. New enterprises are located all over the world, notably in Europe, Canada, U.S.A, South-America, and Japan. There is no doubt that potential of nanocellulose is great. But much work remains to be done to realize the potential. It has often been noticed that new development takes longer than expected and the slow pace of development should not discourage anyone. As Bill Gates famously said, “We always overestimate the change that will occur in the next two years and underestimate the change that will occur in the next ten years.”
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Native Cellulose Nanofibril-based Functional Materials

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