Cellulose Nanofibrils Pulverized from Biomass Resources: Past, Present, and Future Perspectives[†]

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Abstract

Advances in nanotechnology have changed conventional concepts in materials science. This has also strongly influenced natural biomass products with hierarchically built-up structures. In general, hierarchical structures in biobased materials are built up by molecular self-assembly, followed by nanoassembly to form higher-level structures. Key to each step is the formation of interactions at each individual scale. Nature usually achieves such fabrication through a bottom-up process. However, fabrication can also be achieved through a top-down process, with various such downsizing methods now in development. This review article aims to describe trends in nanofiber technology among downsizing processes applied to cellulose as a representative biomass, ranging from fundamentals to recent techniques. The advantages of our recently developed technique, nanopulverization by aqueous counter collision, are also discussed. This method successfully decomposes interactions selectively without damaging the molecular structure, finally liberating components of various sizes into water to provide a transparent and homogeneous component–water system. As nanocellulose research is a broad area involving various fields, the cited references are limited to the scope of the author's knowledge.

Keywords: cellulose nanofibril, cellulose nanocrystal, nanocellulose, aqueous counter collision (ACC), TEMPOoxidized cellulose nanofibril, amphiphilicity, Janus-type nanofibril surface

1. Introduction

Nanotechnology, which is based on clarification of the surface structure of substances on the nanoscale and their interface interactions, has changed conventional concepts in materials science. Nanotechnology has also been extended to living organisms, known as nanobiotechnology. Furthermore, nanometer-scale interactions between macromolecules and organisms have the potential to create new structures (Drexler, 1992; Taton, 2003).

Regarding nanofiber technology in the field of textiles, the US government was quick to recognize the innovative effects of nanofibrils and consider them a strategically important technology. Japan has fallen behind in nanofibril development, information technology (IT), and human genome decoding owing to the absence of a national strategy. However, Japan shows great potential regarding fiber technology owing to its long history of cultivating fiber and textile industries. In the 21st century, evaluating the characteristics of practical fibers and controlling their structure at the nanoscale have become important. This can lead to light high-strength structural materials for optical and electronic devices, drug discovery, regenerative medicine, and environmental purification.

This review article focuses on cellulose as a representative natural fiber. A brief history of cellulose is provided, and then nanocellulose manufacturing methods are outlined, covering the nature of cellulose nanofibers and difficulties in their manufacture. Future perspectives on nanofibrils are also described.

Herein, the term "nanocellulose" represents nanosized cellulose materials with a fiber width of 100 nm or less, which are generally categorized as cellulose nanofibrils (CNFs) with high-aspect ratios (\geq 100) and cellulose nanocrystals (CNCs) with low-aspect ratios (<100).

2. History of cellulose and nanocellulose 2.1 Brief history of cellulose materials

Cellulose, the most abundant natural fiber, is a β -1,4glucan-linked carbohydrate polymer discovered in 1838 by French chemist Anselme Payen (1795–1871). After graduating from École Polytechnique, Payen became manager of a borax-refining factory in the suburbs of Paris and developed new methods for refining sugar and refining starch and alcohol from potatoes. In 1835, Payen became a professor of applied chemistry at École Centrale Paris, where he separated the components of wood by



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treating various woods with nitric acid. He discovered that a fibrous substance could be obtained, with elemental analysis revealing a chemical formula of $C_6H_{10}O_5$, that he named "cellulose" in an 1838 publication in Comptes Rendus (Payen, 1838). Today, the Anselme Payen Award is an annual prize awarded by the Cellulose and Renewable Materials Division of the American Chemical Society (ACS) to researchers that have made a major contribution to cellulose-related research.

Although cellulose has been known for around 180 years, its nanofibril has only recently become considered as a new biomaterial. As shown in **Fig. 1**, wood cell walls are composed of fiber bundles of cellulose at the microscale, which are constructed from a minimum aggregate (elementary fibril at the nanoscale) to form a higher order microfibril. Cellulose forms a complex hierarchical structure from the nanoscale to macroscale through lamination, resulting in the formation of a layered structure of lamellae as cell walls.

With advances in nanotechnology, cellulose nanofibrils or nanocrystals (known collectively as nanocellulose) with nanometer-scale widths have been developed. Furthermore, owing to its sustainability and wide-ranging applications, the use of nanocellulose will contribute to the conservation and maintenance of the global environment. In this context, technology for the preparation of nanocellulose has rapidly developed in the last 10–15 years, as described below.

2.2 Advantages of nanocellulose

Nanocellulose obtained by various preparation processes has exhibited specific gravity that is one-fifth that of steel and specific strength (1–3 GPa; Saito et al., 2013) more than five times that of steel. Nanocellulose also shows thermal expansion deformation that is only approximately one-fiftieth that of glass from -200 °C to 200 °C, and is a high-performance material with a specific surface area of $\geq 250 \text{ m}^2/\text{g}$ (Klemm et al., 2018). The advantages of nanocellulose are listed in Table 1.

2.3 Global research trends in nanocellulose

A proposal submitted by Canada for deliberation of the international standardization of nanocellulose has been accepted by the International Organization for Standardization (ISO/TS21346). In this proposal, the main target is cellulose nanocrystals, which are formed by treating cellulose microfibers with sulfuric acid.

Historically, Nickerson and Habrle (1947) first showed that crystalline cellulose of a certain size (degree of polymerization, approx. 200–250) can be obtained by refluxing with cellulose with 2.5 N sulfuric acid. Mukherjee and Woods (1953) confirmed that this material was nanosized crystalline cellulose (cellulose nanocrystals) by transmission electron microscopy. In Canada, Marchessault et al. (1959) reported that the dispersed water suspension became a gel-like substance at a concentration of \geq 13 wt%, indicating a nematic-order sequence, while Revol et al. (1992) confirmed the formation of a chiral nematic structure during evaporation of this dispersion. This historical research is closely related to the aforementioned Canadian ISO proposal.

Research on nanocellulose in the USA started late compared with Canada, Scandinavia, and Japan. However, in recent years, collaboration among industry, academia, and government has been promoted in the USA, with universities and research institutes providing samples without restrictions such as intellectual property rights. In addition to accelerated open innovation, the USA also plays a central role in the ISO.



Fig. 1 Hierarchical structure of natural cellulose containing nanocellulose.

Table 1	Common advantages i	n cellulose nanofibrils	(CNFs)) produced by	y various procedures
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[Nanocellulose having width less than 50 nm: sus	stainable, light weight, high strength]		
 -Plants are sustainable and abundant resources up to 1 trillion [t] = 6 x (oil deposits) -Plant cell walls comprise CNF as a basic skeletal component -CNF is a high-performance green nanofiber as the essential of a wood -CNFs, a microcrystal, are built up of cellulose molecules having extended polymer chain 			
Properties	Reference Value		
Fiber size	Length: $> 1 \ \mu m$ Width : $< 20 \ nm$		
Density	$\approx 1.6 \text{ g/cm}^3$		
Strength (7–8 × steel)	Elastic modulus: 140 Gpa Tensile strength: 3 Gpa		
Liner thermal expansion (≅ Quartz glass)	0.1 ppm/K (longitude)		
Thermal stability in elastic modulus	$-200 \ ^{\circ}C - +200 \ ^{\circ}C$		
Highly thermal conductivity (\cong Glass)	0.8 W/mK		

In Europe, the EU has conducted large-scale nanocellulose projects in recent years, centered in laboratories in Finland and Sweden (Finland National Technology Center (VTT) and Sweden Wallenberg Wood Science Center (WWSC)), which are now working toward practical use.

In Japan, companies such as Nisshinbo Holdings Inc., Daicel Co., and Asahi Kasei Co. have proposed patents on the miniaturization of natural cellulose fibers using a stone mill-type grinder. To our knowledge, Taniguchi was the first to prepare nanofibrils with a width of 20-90 nm, which is considered the beginning of nanocellulose research (Taniguchi and Okamura, 1998). When a suspension undergoes ultrafine defibrillation between two rotating desks with a shear force applied in a direction perpendicular to the long axis of the fiber, the fiber width ranges from a few nanometers to several tens of nanometers. Subsequently, various methods for nanocellulose production have been proposed, with Japan contributing to diverse methods worldwide. The Japan Revitalization Strategy, revised in June 2014, stated that the use of nanocellulose materials should be promoted. Subsequently, the Nanocellulose Forum centered on industry, government, and academia under an all-Japan system was founded. The Nanocellulose Forum was recently succeeded by Nanocellulose Japan (NCJ), a private-sector organization launched in 2020.

Accordingly, the production of cellulose nanofibrils and cellulose nanocrystals has been facilitated, and research and development sites are now considering how to use such nanosized natural materials in society. The practical application of nanocellulose is rapidly gaining momentum.

Nanocellulose production—Correlation between nanocellulose manufacturing method and chemical characteristics— 3.1 Ceneral aspects

3.1 General aspects

In the last two decades, various technologies have been developed for isolating cellulose nanofibrils derived from biomass raw materials (Kondo, 2008; Thomas et al., 2020; Isogai, 2021; Heise et al., 2021). Three typical methods proposed in Japan early on are compared in Fig. 2. The first is a chemical method, TEMPO (2,2,6,6-tetramethylpiperidine-1-oxy radical) catalytic oxidation, that has been applied to natural cellulose (Fig. 2, right) (Saito and Isogai, 2004). The second is nanofibril preparation by a stone milltype grinder, which is a chemical-free process that does not chemically modify the cellulose surface (Fig. 2, center) (Yano and Nakahara, 2004; Nakagaito and Yano, 2005a; Uetani and Yano, 2011). Furthermore, we have proposed an aqueous counter collision (ACC) method involving the collision of opposing high-pressure water jet streams of aqueous suspension samples. ACC can be applied not only to cellulose materials, but also to the nanominiaturization of biomass (Fig. 2, left) (Kondo et al., 2005; 2014a; Kose et al., 2011c).

Notably, nanocellulose exhibits different characteristics depending on the production method used. As shown in **Figs. 2** and **3**, the nanocellulose surface obtained by TEMPO oxidation and the grinder method exhibit high hydrophilicity similar to that of conventional natural cellulose fibers. In contrast, the nanocellulose surface obtained by the ACC method is more hydrophobic and amphiphilic (Kondo and Kasai, 2015; Tsuboi et al., 2014; Tsuji et al., 2021).





Fig. 2 Comparison of the three main cellulose nanofiber manufacturing methods proposed at an early stage in Japan.

3.2 Typical production methods for cellulose nanofibrils

3.2.1 Production of cellulose nanofibrils by chemical treatment

Chemical processes for the preparation of cellulose nanofibrils mostly involve initial loosening of the crystalline domains and interfibril interactions in cellulose raw materials before facile mechanical separation into nanofibrils.

3.2.1.1 Cellulose nanocrystals (CNCs) prepared by sulfuric acid treatment

Generally, CNCs are rod-like cellulose fibers that have been hydrolyzed to remove noncrystalline fibers by treatment with sulfuric acid (952 g/L) at 30 °C or 40 °C for 24 h, as described in Section 2.3. The degree of polymerization is almost constant, at approximately 200-250 (Nickerson and Habrle, 1947). CNCs are also known as cellulose nanowhiskers. In 1959, Marchessault et al. reported that acid-treated cellulose and chitin microcrystal (microfibril) gels at concentrations of >13 wt% exhibited birefringence, which was derived from the nematic order sequence, while Revol et al. (1992) reported that a chiral nematic structure was formed by a CNC dispersion through evaporation. CNCs are considered to be stably dispersed in water owing to electrostatic repulsion between the sulfuric acid groups partially introduced on the fiber surfaces. Based on this study, the self-assembly of cellulose (Araki et al., 1998; 1999) or grafted CNC (Araki et al., 2001; Heux et al., 2000; Gousse et al., 2002; Zhou et al., 2005; Lönnberg

et al., 2006) dispersions has been developed (Trache et al., 2017). Furthermore, the use of cellulose nanowhiskers or nanofibers with a high axial ratio (aspect ratio) as a reinforcing agent for composite materials has received attention (Oksman and Sain, 2006; also see the recent review by Shojaeiarani et al., 2021).

3.2.1.2 Cellulose nanofibrils prepared by TEMPO catalytic oxidation (TOCNFs)

Shibata and Isogai (2003) found that TEMPO (2,2,6,6tetramethylpiperidin-1-oxyradical) catalytic oxidation selectively oxidized the primary hydroxyl group at the C6 position of regenerated cellulose (viscose rayon) to an aldehyde under mild conditions, as shown in Fig. 3A. This reaction occurs in an aqueous medium at pH 10-11 and consumes sodium hypochlorite, but the catalytic amounts of TEMPO and sodium bromide can be recycled. Furthermore, Saito and Isogai (2004) showed that, when this TEMPO-catalyzed oxidation was applied to natural cellulose, specific surface modification occurred, introducing carboxyl groups and aldehyde groups at a high density only on the surface of crystalline cellulose microfibrils. When TEMPO-oxidized natural cellulose was subjected to simple mechanical treatment in water using a mixer or similar apparatus, a highly viscous transparent dispersion could be obtained by increasing the amount of carboxyl groups introduced. Transmission electron micrography showed that a transparent dispersion of isolated cellulose single microfibrils with a width of approx. 3 nm was obtained by mechanical treatment of TEMPO-oxidized



Fig. 3 Schematic diagrams of (A) chemical characteristics of nanocellulose obtained by TEMPO oxidation (Courtesy of Prof. Isogai at University of Tokyo) and (B) the ACC process, which is likely to expose hydrophobic van der Waals (200) faces normally hidden inside the native crystalline cellulose fibers to the surface.

wood cellulose (Saito et al., 2006). They also indicated that TEMPO-catalyzed oxidation does not oxidize the inside of crystalline microfibrils, meaning that C6 hydroxyl groups on the surface are selectively oxidized to the corresponding sodium carboxylate salt, which causes charge repulsion between the nanofibrils.

3.2.1.3 Nanoelements prepared by enzymatic hydrolysis

Using an enzyme derived from *Trichoderma*, Hayashi et al. attempted to hydrolyze microbial cellulose crystalline nanofibrils with a width of 40–60 nm secreted from *Gluconacetobacter* bacteria and natural cellulose fibers derived from seaweeds, which have both crystalline forms of cellulose (I α and I β). Crystalline phase I α has been reported to be more susceptible to enzymatic degradation (Hayashi et al., 1997a, b). Furthermore, the residue of a short elements (width, 10 nm; length, 350 nm) obtained by hydrolysis with an enzyme of the same *Trichoderma* origin was found to mainly comprise highly crystalline I β phase by wide-angle X-ray diffraction, electron diffraction, and FTIR measurements (Hayashi et al., 2005). This material has potential applications as an additive, especially in food and cosmetics.

3.2.1.4 CNFs prepared by mechanochemical treatment

Mechanochemistry using planetary ball milling (Endo et al., 1999; Takai-Yamashita et al., 2021) is a sustainable method for the synthesis of functionalized cellulose nanofibers (CNFs). In this process, changes in the microstructure of a CNF aqueous sol under planetary ball milling were investigated in terms of its rheological behavior, crystallinity, and diameter distribution. A decreased thixotropy hysteresis loop observed in the ball mill-treated CNFs indicated a weaker interaction among the fibers, but with a three-dimensional structure retained.

3.2.2 Production of cellulose nanofibrils (CNFs) by mechanical treatment

Mechanical processes for the preparation of cellulose nanofibrils mostly involve shear stress, where pulp is dispersed in water, pre-crushed using a Supermasscolloider[®] grinder (Masuko Sangyo Co. Ltd., Saitama, Japan), and further micro-/nano-fibrillated using a high-pressure homogenizer (M110P Microfluidizer, Microfluidics Corp., Newton, MA) (Yano and Nakahara, 2004; Nakagaito and Yano, 2005a; Uetani and Yano, 2011). Under typical treatment conditions, the pulp fibers are first processed under high shear in a Masuko Supermasscollider grinder for three passes, and then further fluidized using a microfluidizer equipped with 200- and 100-µm chambers at 2000 psi for 10–12 passes (Huan et al., 2017).

As a result, cellulose nanofibrils with a spider web-like network can be obtained. Additional compounding and dehydrating with a phenol resin, oxidized starch, and polylactic acid in a mold, followed by heat-pressing, allows a high-strength composite molded product to be obtained. Instead of the cellulose nanofiber network, when the bacterial nanocellulose pellicle (gel-like membrane produced





Fig. 4 Classification of energy loading effects vs strain rate onto materials (Yu and Qiu, 2018). Typically, ACC process provides both interfacial peeling and a thermodynamic effect onto samples. Adapted with permission from Ref. (Yu and Qiu, 2018). Copyright: 2018 Tsinghua University.

by *Gluconacetobacter* bacteria) composed of a threedimensional nanofibril network was subjected to heatpressing treatment, the resulting high-strength composite material had a Young's modulus of approx. 30 GPa, which was 1.5 times higher than that of the material obtained using wood cellulose nanofibrils (Nakagaito et al., 2005b).

This difference was attributed to the dense network in the bacterial cellulose pellicle, which was uniform at a scale of a few tens of nanometers (Yano et al., 2005). To our knowledge, this result was the starting point for subsequent research on resin nanocomposites with high tensile strength using nanocellulose. Nanocellulose being lightweight, more than five times stronger than steel, and having a low linear expansion (one-fiftieth that of glass) could lead to a reduction in weight of car bodies to encourage better gas mileage, especially through its use in automobile parts. This matches the current global direction of realizing a low-carbon society. Recently, Kitagawa and Yano proposed the "Kyoto Process" for integrated production of cellulose nanofiber materials (Kitagawa and Yano, 2012; Igarashi et al., 2018). Such research on developing resin materials with excellent strength per unit weight is being conducted extensively worldwide. Numerous studies on nanocomposites containing nanocellulose have been published to date. For coverage of literature in this area beyond the scope of this review, please see other recent reviews (Oksman et al., 2016; Klemm et al., 2018; Shojaeiarani et al., 2021).

3.2.3 Production of cellulose nanofibrils by physicochemical treatment

The key phenomenon in physicochemical processes for the preparation of CNFs is selective interfacial cleavage among weak intermolecular interactions by a propagating elastic–plastic wave (as shown in **Figs. 3B** and **4**), which is attributed to shockwaves generated by impact dynamics

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depending on the strain rate (s^{-1}) through impact energy transmission (Yu and Qiu, 2018). Namely, loading as total mechanical energy / areas induces impact energy transmission to cause an effect in materials that relates to strain rate. When heterogeneous interface of the material is suffered by such concentrated loading energy, interfacial peeling within it is likely to occur.

Our aqueous counter collision (ACC) method for the nanopulverization of bio-based materials is a typical physicochemical process without any chemical modification (Kondo et al., 2005; 2014a; Kose 2011c). The ACC method relies on the impingement of two high-speed jets of aqueous suspension of raw materials expelled through a pair of opposing nozzles. Typically, the ejection pressure of 200 MPa generates a supersonic flow of dual water jets at Mach 2. Schematic diagram is shown in Figs. 3B and 4.

The calculated kinetic energy generated by impingement of the water jets in the ACC method is up to 14.3 kJ/mol at an ejection pressure of 200 MPa (Kondo et al., 2014a). The relationship between water ejection pressure and calculated kinetic energy of water molecules in the ACC process is shown in Table 2, together with a summary of typical bonding energies. Regardless of dissipative energy loss during the ACC process, the kinetic energy, which can be converted into elastic-plastic waves, remains higher than the van der Waals forces and weak hydrogen bonds at an ejection pressure of 200 MPa (Kondo et al., 2014a). The width and size distribution of the nano-pulverized samples are dependent on the ACC ejection pressure and number of repeat cycles/passes, respectively. The propagation of shock waves resulting from ACC occurs through elastic crystalline domains to cleave the hydrophobic van der Waals (200) planes normally hidden inside native crystalline cellulose fibers (Cousins and Brown, 1995) with these hydrophobic planes eventually being exposed on the



 Table 2
 Energy barrier capable of being overcome by ACC.

(A) Calculated potential energy of a water molecule in ACC process

Ejecting pressure /MPa	Kinetic energy /kJ mol ⁻¹
50	3.6
100	7.2
150	10.8
200	14.3

(B) Hydrogen bonding energies

O−H…O Hydrogen-	$-\Delta E(kJ mol^{-1} Hydrogen bonds)$		
bonded compound	Dimer (gas)	Liquid	
CH ₃ COOH	29.3	24.3	
H ₂ O	21.0	14.2	
CH ₃ OH	16.8–18.9	19.7	
C ₂ H ₅ OH	16.8	17	
C ₂ H ₂ OH		25	

(C) Various bonding energies

Type of bond	Bonding energy /kJ mol ⁻¹
H-OH (covalent bond)	499
H-H (covalent bond)	436
Ion-ion	250
Medium hydrogen bond	21–62
Weak hydrogen bond	4.2×10^{-1} -4.2
London dispersion force	2
Dipole-dipole	0.6–2

surface (Li and Renneckar, 2011) (see **Fig. 3B**). The resulting ACC–CNFs have a Janus-type amphiphilic surface composed of both hydrophobic and hydrophilic planes in an aqueous system (Tsuji et al., 2021). Kose et al. (2011c) reported that ACC provides a single CNF from bacterial nanocellulose (BNC) pellicles, denoted ACC–BNC herein, which are nanofibers engaged in a 3D network secreted by *Gluconacetobacter* bacteria, that exhibited amphiphilic properties (Kose et al., 2011a). In BNC, which is already highly crystalline, shock waves are simply propagated through the elastic crystalline domains from the initial stage, resulting in the direct cleavage of certain interfaces.

Later, Kondo et al. (2014a) reported ACC pulverization steps for microcrystalline cellulose (MCC) containing 30 % noncrystalline domains derived from wood-based cellulose fiber (pulp). Regarding the nanopulverization behavior of MCC in the ACC method, initially, a shear stress is mainly generated through the ACC flow system to pulverize the MCC microfibers into fibers with widths of a few hundred nanometers. Highly crystalline domains remain in the cellulosic samples after the effects of shear stress. A drastic decrease in fiber width then occurs, presumably due to the cleavage of weak hydrogen bonds between crystalline domains of CNFs. Accordingly, ACC nanopulverization is considered to be an effective synergistic process that generates shear stress and propagating shock waves in various biomass resources (Kose and Kondo, 2011b; Kondo et al., 2014b; Jiang et al., 2016; Tsujita and Kondo, 2019; Ye et al., 2021).

Additionally, Kawano and Kondo (2014) reported that carbon materials without dissociative functional groups treated using the ACC method exhibited negative zeta potentials and dispersed in an aqueous system, which might be due to water molecules present on the surface. Therefore, the resulting ACC–CNFs might disperse in an aqueous system, even if hydrophobic planes are exposed on the CNF surfaces.

Recently, the ACC method afforded CNFs with different surface properties from various cellulosic raw materials comprising different hierarchical structures depending on the species present, as described later (Tsuji et al., 2021).

Nanocellulose is usually considered to comprise symmetrical nanofibrils, nanorods, or fibrillated nanofibrils, regardless of asymmetric effects caused by the presence of one reducing end. Asymmetrical nanocellulose would have considerably extended utility in new applications. We have produced an asymmetric cellulose nanofibril with a shape that changes from a thick nanobarrel at one end to a thinner cylinder with a few flourishes towards the reducing end. The "cellulose nanoanemone" fibrils, named after sea anemones, were fabricated by the ACC of bacterial cellulose pellicles cultured under dissolved oxygen conditions (see Fig. 5) (Utsunomiya et al. 2022; Nagashima et al., 2015). The cellulose Ia crystalline phase located on the fiber surface was transformed into cellulose IB crystalline phase owing to propagation of the collision energy of highspeed water jets in this treatment (Kose et al., 2011c).

4. Characteristic advantages of the ACC process

4.1 Amphiphilic Janus-type surface properties of ACC–CNFs

ACC–CNFs are likely to exhibit specific phenomena owing to their two anisotropic faces in aqueous media (Tsuji et al., 2021). Kose et al. (2011a) reported that the wettability of solid substrates, regardless of whether the surface was hydrophilic or hydrophobic, can be switched by spray-coating with ACC–CNFs. Tsuboi et al. (2014) reported that ACC–CNFs can be used as emulsifiers and/or emulsion stabilizers without a surfactant. The properties of the obtained emulsions differed depending on the starting raw materials used (Yokota et al., 2019). Recently, Kondo



et al. reported that the preferential adsorption of ACC– CNFs to hydrophobic polymer surfaces results in hydrophilic properties (Kondo et al., 2017; Ishikawa et al., 2021).

As mentioned above, ACC–CNFs are assumed to exhibit two distinct physicochemical properties (amphiphilicity) due to being composed of hydrophobic planes and the initial hydrophilic planes in aqueous systems. Therefore, a novel concept regarding the physicochemical surface properties of ACC–CNFs, namely, amphiphilic Janus-type fibers, is introduced, in which two anisotropic faces are present along the entire fiber axis that exhibit different physicochemical properties on the surface. An analogous concept, Janus particles, has been studied extensively. Janus particles, named after the two-faced ancient Roman god, have two anisotropic faces with different physicochemical properties owing to a half-and-half surface struc-



Fig. 5 Images of a typical asymmetric "cellulose nanoanemone". The TEM and schematic images (bottom of figure) define the "stem" and "branch" of the cellulose nanoanemone.

ture (Walther and Müller, 2008; Yabu et al., 2013; Jiang et al., 2010). However, such unique surface characteristics have yet to be reported in fibers. Therefore, the surface characteristics of ACC–CNFs are defined differently to typical Janus particles.

Amphiphilic Janus-type fibers are described as fibers with two types of surface bearing hydrophilic and hydrophobic faces that are individually present along the entire single fiber axis in aqueous systems (Kose et al., 2011a; Tsuboi et al., 2014; Yokota et al., 2019). Accordingly, amphiphilic Janus-type fibers can also be described as Janus-type faces along a single fiber axis, which is different to typical Janus particles with a half-and-half structure.

Recently, the surface characteristics of single ACC-CNFs have been visualized at the nanoscale using fluorescence microscopy (FM) observation with fluorescence probes (Tagawa et al., 2021). Fluorescent-probe carbohydratebinding modules (CBMs), Congo red (CR), and Calcofluor white (CFW) have been employed as reagents for the qualitative and quantitative evaluation of surface characteristics in ACC-CNFs, focusing on their hydrophobic and hydrophilic planes (Tsuji et al., 2021). CBMs are included in cellulase as a binding domain that anchors selectively to the hydrophobic phase of cellulose (Linder and Teeri, 1996), CR adsorbs onto cellulose crystalline surfaces as a monolayer (Hubbe et al., 2012; Nge et al., 2013; Mazeau and Wyszomirski, 2012), and CFW has been used to detect plant hydrophilic cellulose structures (Hughes and McCully, 1975) and CNFs (Peretz et al., 2019). The three-dimensional structure of CBM, and chemical structures of direct dyes CR and CFW, are shown in Fig. 6.

According to the fluorescence microscopy images, CNFs stained with CFW were approximately 10 times wider than those observed by field emission scanning electron microscopy (Tagawa et al., 2021). Therefore, the surface



(A) Carbohydrate-binding modules fused to green fluorescence protein (CBM-GFP)

Fig. 6 Site-specific fluorescence probes for CNF surfaces.



characteristics of CNFs can be visualized by confocal laser microscopy (CLMS) using site-specific fluorescence probes and a highly sensitive fluorescence detector.

The localization of hydrophobic and hydrophilic planes on the ACC-BNC surface was visualized by staining with typical site-selective fluorescent probes CFW, CBM fused with green fluorescent protein (CBM-GFP), and CR. ACC-BNC is a suitable model material for investigating ACC-CNFs because BNC is a pure cellulose sample. Nanofibrils cannot be observed by optical microscopy owing to resolution limitations. However, fluorescence-stained nanofibrils were visible by CLSM, as shown in Fig. 7, owing to the spread of fluorescence emissions with similar shapes. The width magnification achieved by fluorescence emission was approximately 13 times that achieved by transmission electron microscopy (TEM). The same fiber was observed separately by fluorescence staining, using CFW for hydrophilic surfaces or CBM-GFP for hydrophobic surfaces (Figs. 7a and 7b). Each fluorescent emission of CFW and CBM-GFP was distinguished in most fibers. When images (a) and (b) in Fig. 7 were merged, the hydrophobic areas (b) were fixed empty areas surrounded by hydrophilic areas (a) in the merged image (c) of Fig. 7. Therefore, ACC–BNCs can be concluded to have hydrophobic and hydrophilic faces on a single ACC-BNC surface. This result reflects the concept that, in ACC nanopulverization, shockwaves propagate through highly crystalline domains, samples are chopped into individual nanofibrils, and the resulting hydrophobic faces might be similar to exposed van der Waals (200) planes from the native cellulose crystals (Li and Renneckar, 2011).

In the visualization described above, the ACC–BNC surface had an amphiphilic Janus-type fiber structure with hydrophobic and hydrophilic faces in aqueous systems, and

CR was found to be a substitute for CBM in hydrophobic face evaluation. Therefore, CR can be used to quantitatively evaluate the hydrophobic face, partly because a CBM-GFP calibration curve by weight is difficult to prepare and some CNFs might aggregate in the acetate buffer. The hydrophobic and hydrophilic faces of ACC-BNC were determined by quantitative measurement of the amounts of CR and CFW adsorbed on a Langmuir monolayer. The maximum monolayer adsorption amounts of CR and CFW on ACC-CNFs were calculated from the Langmuir isotherms, as shown in Table 3. CR and CFW were adsorbed on all ACC-CNFs. Fig. 8 shows the relative occupied area (OA) ratio of CR to CFW on ACC-CNFs as a function of CR occupancy for the surface area of ACC-CNFs. The results indicated that the degree of hydrophobicity of the ACC-CNFs was in the order of BNC > BBKP > HBKP \approx MCC. Therefore, the surface hydrophobicity of ACC-CNFs depends on their origin (Tsuji et al., 2021). Considering the recent damage of bamboo as an unnecessary resource, despite this natural material containing various active ingredients, the above results are of interest and potential importance regarding the development of a functional biomass nanofibrous material.

4.2 Specific adsorption phenomena caused by two anisotropic faces in amphiphilic Janus-type ACC-CNFs

4.2.1 ACC-assisted oil-in-water Pickering emulsions

The characteristic surface of ACC–CNFs can be expected to expand common understanding of nanocelluloses. First, the amphiphilicity is promising for applications as emulsifiers and stabilizers. Oil-in-water Pickering emulsions with long-term stability are readily prepared by ultrasonic mixing of aqueous ACC–CNF dispersions with



Fig. 7 Hydrophilic and hydrophobic faces on the ACC-BNC surfaces stained separately with CFW and CBM-GFP.

Table 3 Characteristic values for individual ACC-CNFs from different origins.

(A) Maximum monolayer adsorption amounts of dyes onto CNFs based on the Langmuir adsorption isotherms and zeta potentials of individual CNFs.

Derivation	CR adsorption (mg/g CNF)	CFW adsorption (mg/g CNF)	Zeta potential (mV)
BNC	7.5 ± 0.9	87.0 ± 8.5	-18.8 ± 2.1
BBKP	7.1 ± 0.6	131.5 ± 10.2	-36.7 ± 2.1
НВКР	4.7 ± 0.6	103.7 ± 18.3	-44.7 ± 1.2
MCC	4.1 ± 0.8	119.1 ± 7.6	-29.3 ± 2.1

(B) Average height, width, and SSA values for ACC–CNFs based on AFM observation of the samples. Adapted with permission from Ref. (Tsuji et al., 2021) Copyright 2021 American Chemical Society.

Derivation	Height (nm)	Width (nm) (Data from TEM)	$SSA(m^2/g)$
BNC	12.1 ± 5.5	$50.5 \pm 15.9\;(34 \pm 13)$	127.9
BBKP	4.8 ± 2.8	$25.2\pm7.1\;(20.7\pm8.3)$	307.8
НВКР	4.2 ± 2.9	$31.8 \pm 11.8 \; (22.3 \pm 12.4)$	338.5
MCC	4.4 ± 1.9	22.4 ± 6.1 (15 ± 6)	337.4



Fig. 8 Relative occupied area (OA) ratio of CR to CFW on ACC–CNFs as a function of CR occupancy for the surface area of ACC–CNFs, indicating surface hydrophobicity depending on the origin.

Note: BNC: Bacterial nanocellulose pellicle; BBKP: Bamboo-derived bleached kraft pulp; HBKP: Hardwood-derived bleached kraft pulp; MCC: Microcrystalline cellulose (from wood kraft pulp). Longitudinal axis corresponds to relative ratio of OA of CR to CFW. Horizontal axis corresponds to OA of CR per surface area of CNFs based on AFM data.

nonpolar solvents. The emulsification abilities of ACC– CNFs for stable Pickering emulsions have been proven to be significantly greater than those of CNFs prepared by high-pressure homogenization or other chemical preparation methods. This is attributed to ACC exposing inherently hydrophobic surface planes of CNFs. Furthermore, the emulsification and stability of the Pickering emulsions were sensitive to solvent properties, such as permittivity, density and viscosity (Yokota et al., 2019).

In a stable emulsion prepared from a water dispersion of 0.1 wt% ACC–CNFs derived from bamboo pulp, hollow particles, similar to colloidosomes (Thompson et al., 2015),

were formed from the bamboo-based emulsion droplets by carefully washing the excess nanocellulose with water and then freeze-drying, as shown in Fig. 9 (left). The spherical particles were covered with a stable thin layer composed of ACC-CNFs and were completely hollow inside (Fig. 9b left), while fluffy fibrous objects (Yokota et al., 2019; Tsuboi et al., 2014) between spherical particles were negligible. By removing the unanchored CNF, the thin layer around droplets could be observed in higher magnification images. This thin layer contained pores approximately 10-500 nm in size, as shown in Figs. 9c and d (left). This suggested that the obtained emulsion droplets were fabricated and stabilized by adsorption of ACC-CNFs onto the oil surface to form an oil-in-water emulsion. Therefore, colloidosome microcapsules were formed in this Pickering emulsion without requiring further stabilization treatment.

To control the surface properties of ACC–CNFs, their surfaces at the oil–water interfaces of a Pickering emulsion can be selectively acetylated (Ishida et al., 2021). To achieve this, ACC–CNFs adsorbed on the surfaces of oil droplets containing the reaction reagents undergo localized interfacial reactions. Such acetylation reactions occur while maintaining the crystallinity and fibrous morphology of the original CNFs. The surfaces of films cast from these acetylated ACC–CNFs had unique self-aggregation properties (Ishida et al., 2021) that contrasted markedly with those of films cast from acetylated ACC–CNFs prepared in homogenous dispersions (Yokota et al., 2021).

4.2.2 Adsorption of Janus-type amphiphilic ACC– CNFs onto microparticles of semi-crystalline polymers

As a further development of the above research, ACC-





Fig. 9 Specific adsorption properties of ACC–CNFs: Pickering emulsion formation (left) and adsorption onto i-polypropylene (i-PP: right). Left: adapted with permission from Ref. (Yokota et al., 2019). Copyright 2019 Elsevier; adapted with permission from Ref. (Tsuboi et al., 014). Copyright 2014 De Gruyter. Right: adapted with permission from Ref. (Ishikawa et al., 2021) Copyright 2021 American Chemical Society.

CNFs tend to preferentially adsorb onto hydrophobic isotactic polypropylene (i-PP) microparticles (see Fig. 9, right) and linear low-density polyethylene (LLDPE), which demonstrates their characteristic amphiphilicity. This is achieved by simply mixing the components together in aqueous media (Ishikawa et al., 2021). The surfacecovered products were confirmed by visualization using CLMS. Furthermore, thermodynamics measurements obtained by differential scanning calorimetry (DSC) showed that the melting points of i-PP/ACC-CNFs and LLDPE/ACC-CNFs were lower than those of the untreated polymers, indicating interactions between the ACC-CNFs and polymer surfaces. Therefore, coating the polymer particles with the ACC-CNFs, as confirmed by CLMS, reduced their melting points. This demonstrated the possibility of a novel fusion between synthetic polymeric materials and biomass nano-objects (Kondo et al., 2021).

Prior to the CLSM observations, the i-PP particles were mixed with Janus-type amphiphilic ACC–CNFs in an aqueous medium, fully dried, and stained with CFW. As described earlier, nanoscale fibers can be observed by CLSM, even below the level of microscopic resolution, owing to scattering of the fluorescence emission.

Fig. 9 (right) shows a dark field fluorescent image of a particle coated with the ACC–CNFs. The bright spots indicate fluorescence due to stained ACC–CNFs on the surface of i-PP particles, showing that the i-PP spheres were completely covered by the ACC–CNFs. These images also indicated that, during the process of washing away excess CFW, the CNFs remained attached to the i-PP particle surface, demonstrating that interfacial interactions existed between the i-PP and ACC–CNF surfaces after adsorption had occurred by shaking in water.

Particles of other polymers, namely, high-density polyethylene (HDPE), linear low-density polyethylene

(LLDPE), and polyethylene terephthalate (PET), were also treated with an aqueous suspension of ACC–CNFs using the same method as for i-PP. The CLSM images indicated that more ACC–CNFs were present on the surface of LLDPE microparticles than on those of HDPE and PET particles (Ishikawa et al., 2021). Accounting for the self-fluorescence for PET showed that ACC–CNFs were not necessarily adsorbed on the PET surface. Furthermore, the high-magnification CLSM images suggested that i-PP and LLDPE particles were more efficiently coated with ACC–CNFs than HDPE and PET particles.

Among the materials tested, i-PP particles had the greatest affinity for ACC–CNFs. When the i-PP/ACC–CNFs were heated from 20 to 200 °C at 10 °C/min, they exhibited a small but typical endothermic shoulder peak at 142.6 °C after fusion commenced at approximately 113 °C and before the melting peak at approximately 162 °C. This indicated that coating with ACC–CNFs reduced the i-PP melting point in some areas (presumably surface areas coated with ACC–CNFs) and therefore the reduction probably occurred on the surface (skin side) of the microparticles. In agreement with the CLMS data, DSC analysis showed that ACC–CNFs coated the i-PP particles as a monolayer.

The effect of the origin of ACC–CNFs on their affinity for i-PP particles was also examined. ACC–CNFs from BBKPs and ACC–BNC derived from bacterial cellulose pellicles exhibited strong interfacial interactions with i-PP, while relatively hydrophilic ACC–MCC derived from microcrystalline wood cellulose had a lower affinity. A better understanding of the interfacial interactions between various polymer particles and ACC–CNFs will lead to the novel fusion of bio-based materials and synthetic polymer materials at the nanoscale (Kondo and Kasai, 2015; Kondo et al., 2017; Ishikawa et al., 2021).



5. Conclusions and future perspectives

Nanocellulose is a lightweight material, more than five times stronger than steel, and with a low linear expansion of one-fiftieth that of glass. Accordingly, Yano (2016) has proposed using this material to reduce car body weight, especially through its use in automobile parts. Therefore, a stream of resin materials with excellent strength per unit weight is undergoing vigorous development.

Our research group at Kyushu University, in collaboration with Chuetsu Pulp & Paper Co., Ltd., developed the Janus-type amphipathic ACC–CNFs described herein, which are more hydrophobic than other nanocellulose materials, and also proposed a novel fusion of bio-based materials and synthetic polymer materials at the nanoscale. Therefore, this section will discuss future perspectives and trends for the preparation of nanocomposites containing CNFs.

Various additives have been widely used to improve the production performance of tailor-made polymeric products. These include plasticizers, flame retardants, impact modifiers, antioxidants, antimicrobials, and UV stabilizers (Hahladakis et al., 2018). The global additives market expanded steadily to over 50.0 billion USD by the end of the last decade, with the total weight of additives anticipated to reach 17 megatons by 2020 (Marturano et al., 2017). As additives are often more expensive than resins, two different production designs are considered to counterbalance usage and cost, namely, "high-price and low-loading" or "low-price and high-loading". Inorganic materials, such as calcium carbonate, silica, glass fiber, and talc, which are relatively inexpensive, have usually been used in high volumes as fillers to improve the mechanical properties of polyolefins.

In recent years, nanoscale fillers, such as nanocarbon particles, various inorganic/organic nanoclays, and metal oxide nanoparticles, have been used at low loading levels (Winey and Vaia, 2007). Wood flour has been successfully mixed with various polyolefins to form wood-plastic composites for use as organic fillers (Clemons, 2002). Furthermore, in the last two decades, nanocelluloses (NCs) (Klemm et al., 2018; Nechyporchuk et al., 2016), including cellulose nanofibrils (CNFs), microfibrillated cellulose (MFC), and cellulose nanocrystals (CNCs), which are believed to be predominantly hydrophilic, have been extensively studied for use as fillers (Kargarzadeh et al., 2017). This results from their large surface areas of $>50 \text{ m}^2/\text{g}$ (Kose et al., 2011c; Klemm et al., 2018), high mechanical strength (Saito et al., 2013), and low thermal expansion in the direction of the fiber axis (Nishino et al., 2004).

As described herein, NCs can be manufactured using the following three methods, each of which has a different effect on the surface characteristics, dispersibility, and compatibility of the NCs regarding mixing with commodity polymers: (i) Mechanical processes, mostly involving shear stress; (ii) chemical processes that loosen crystalline domains and interfibril interactions; and (iii) physicochemical processes that selectively cleave weak intermolecular interactions by propagating generated shockwaves. Methods (i) and (ii) provide polar hydrophilic nanofibrils. Therefore, when such hydrophilic CNFs are added as fillers to polyolefins, their surfaces must either be chemically modified to render them hydrophobic, or they must be used in conjunction with a compatibilizer (Oksman et al., 2016; Nodera et al., 2016). Alternatively, chemically treated raw cellulose materials can be nano-pulverized and compounded with the polymer matrix in a parallel or sequential manner (Igarashi et al., 2018).

In contrast, aqueous counter collision (ACC) is a physicochemical process involving the impact-induced nanopulverization of bio-based materials using a pair of high-speed jets containing microsized target materials in aqueous media. The CNFs produced by ACC exhibit unique characteristics owing to the pulverization mechanism, as described herein.

Many plasticizers, which are used for solvation in matrix polymers, reduce intermolecular forces and decrease the relaxation temperature. Therefore, an evaluation of the affinity between matrix polymers and secondary ingredients is important for understanding their mutual contribution to the properties of the material, and the design of novel and sustainable multicomponent polymeric products. Regarding the use of nanocellulose in nanocomposites, such a study is still required.

Furthermore, applications to electronic devices (Kasuga et al., 2021) and other fields (Apelgren et al., 2019; Hai et al., 2020; Halim et al., 2019; Kim et al., 2021) appear feasible for practical use. From a future perspective, the expansion of nanocellulose research worldwide means that describing all potential application fields for nanocellulose is currently almost impossible.

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References

- Apelgren P., Karabulut E., Amoroso M., Mantas A., Martínez Ávila H., Kölby L., Kondo T., Toriz G., Gatenholm P., In vivo human cartilage formation in three-dimensional bioprinted constructs with a novel bacterial nanocellulose bioink, ACS Biomaterials Science & Engineering, 5 (2019) 2482–2490. DOI: 10.1021/acsbiomaterials.9b00157
- Araki J., Wada M., Kuga S., Okano T., Flow properties of microcrystalline cellulose suspension prepared by acid treatment of native cellulose, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 142 (1998) 75–82. DOI: 10.1016/ S0927-7757(98)00404-X
- Araki J., Wada M., Kuga S., Okano T., Influence of surface charge on viscosity behavior of cellulose microcrystal suspension, Journal of Wood Science, 45 (1999) 258–261. DOI: 10.1007/

KONA

BF01177736

- Araki J., Wada M., Kuga S., Steric stabilization of a cellulose microcrystal suspension by poly(ethylene glycol) grafting, Langmuir, 17 (2001) 21–27. DOI: 10.1021/la001070m
- Clemons C., Wood-plastic composites in the United States—the interfacing of two industries, Forest Products Journal, 52 (2002) 10–18. https://www.fs.usda.gov/treesearch/pubs/8778
- Cousins S.K., Brown R.M., Cellulose I microfibril assembly: computational molecular mechanics energy analysis favours bonding by van der Waals forces as the initial step in crystallization, Polymer, 36 (1995) 3885–3888. DOI: 10.1016/0032-3861(95)99782-P
- Drexler K.E., Nanosystems: Molecular Machinery, Manufacturing, and Computation, Wiley, 1992, ISBN: 978-0-471-57518-4.
- Endo T., Kitagawa R., Zhang F., Hirotsu T. Hisokawa J., Mechanochemical preparation of novel cellulose-poly(ethylene glycol) composite, Chemistry Letters, 28 (1999) 1155–1156. DOI: 10.1246/cl.1999.1155
- Goussé C., Chanzy H., Excoffier G., Soubeyrand L., Fleury E., Stable suspensions of partially silylated cellulose whiskers dispersed in organic solvents, Polymer, 43 (2002) 2645–2651. DOI: 10.1016/S0032-3861(02)00051-4
- Hahladakis J.N., Velis C.A., Weber R., Iacovidou E., Purnell P., An overview of chemical additives present in plastics: migration, release, fate and environmental impact during their use, disposal and recycling, Journal of Hazardous Materials, 344 (2018) 179–199. DOI: 10.1016/j.jhazmat.2017.10.014
- Hai L.V., Zhai L., Kim H.C., Panicker P.S., Pham D.H., Kim J., Chitosan nanofiber and cellulose nanofiber blended composite applicable for active food packaging, Nanomaterials, 10 (2020) 1752. DOI: 10.3390/nano10091752
- Halim A., Xu Y., Lin K.-H., Kobayashi M., Kajiyama M., Enomae T., Fabrication of cellulose nanofiber-deposited cellulose sponge as an oil-water separation membrane, Separation and Purification Technology, 224 (2019) 322–331. DOI: 10.1016/j.seppur.2019.05.005
- Hayashi N., Kondo T., Ishihara M., Enzymatically produced nano-ordered short elements containing cellulose I_β crystalline domains, Carbohydrate Polymers, 61 (2005) 191–197. DOI: 10.1016/j.carbpol.2005.04.018
- Hayashi N., Sugiyama J., Okano T., Ishihara M., Selective degradation of the cellulose Iα component in Cladophora cellulose with Trichoderma viride cellulase, Carbohydrate Research, 305 (1997a) 109–116. DOI: 10.1016/S0008-6215(97)00281-4
- Hayashi N., Sugiyama J., Okano T., Ishihara M., The enzymatic susceptibility of cellulose microfibrils of the algal-bacterial type and the cotton-ramie type, Carbohydrate Research, 305 (1997b) 261–269. DOI: 10.1016/S0008-6215(97)10032-5
- Heise K., Kontturi E., Allahverdiyeva Y., Tammelin T., Linder M.B., Nonappa, Ikkala O., Nanocellulose: recent fundamental advances and emerging biological and biomimicking applications, Advanced Materials, 33 (2021) 2004349. DOI: 10.1002/adma.202004349
- Heux L., Chauve G., Bonini C., Nonflocculating and chiralnematic self-ordering of cellulose microcrystals suspensions in nonpolar solvents, Langmuir, 16 (2000) 8210–8212. DOI: 10.1021/la9913957
- Huan S., Yokota S., Bai L., Ago M., Borghei M., Kondo T., Rojas O.J., Formulation and composition effects in phase transitions of emulsions costabilized by cellulose nanofibrils and an ionic surfactant, Biomacromolecules, 18 (2017) 4393–4404. DOI: 10.1021/acs.biomac.7b01452
- Hubbe M.A., Beck K.R., O'Neal W.G., Sharma Y.C., Cellulosic

substrates for removal of pollutants from aqueous systems: a review. 2. Dyes, BioResources, 7 (2012) 2592–2687. https://bioresources.cnr.ncsu.edu/wp-content/uploads/2016/06/BioRes 07 2 2592 Hubbe Cell Remov Pt2 Dyes.pdf

- Hughes J., McCully M.E., The use of an optical brightener in the study of plant structure, Stain Technology, 50 (1975) 319–329. DOI: 10.3109/10520297509117082
- Igarashi Y., Sato A., Okumura H., Nakatsubo F., Yano H., Manufacturing process centered on dry-pulp direct kneading method opens a door for commercialization of cellulose nanofiber reinforced composites, Chemical Engineering Journal, 354 (2018) 563–568. DOI: 10.1016/j.cej.2018.08.020
- Ishida K., Yokota S., Kondo T., Localized surface acetylation of aqueous counter collision cellulose nanofibrils using a Pickering emulsion as an interfacial reaction platform, Carbohydrate Polymers, 261 (2021) 117845. DOI: 10.1016/j. carbpol.2021.117845
- Ishikawa G., Tsuji T., Tagawa S., Kondo T., Adsorption of Janustype amphiphilic cellulose nanofibrils onto microspheres of semicrystalline polymers, Macromolecules, 54 (2021) 9393–9400. DOI: 10.1021/acs.macromol.1c01163
- Isogai A., Emerging nanocellulose technologies: recent developments, Advanced Materials, 33 (2021) 2000630. DOI: 10.1002/adma.202000630
- Jiang F., Kondo T., Hsieh Y.-L., Rice straw cellulose nanofibrils via aqueous counter collision and differential centrifugation and their self-assembled structures, ACS Sustainable Chemistry & Engineering, 4 (2016) 1697–1706. DOI: 10.1021/ acssuschemeng.5b01653
- Jiang S., Chen Q., Tripathy M., Luijten E., Schweizer K.S., Granick S., Janus particle synthesis and assembly, Advanced Materials, 22 (2010) 1060–1071. DOI: 10.1002/ adma.200904094
- Kargarzadeh H., Mariano M., Huang J., Lin N., Ahmad I., Dufresne A., Thomas S., Recent developments on nanocellulose reinforced polymer nanocomposites: a review, Polymer, 132 (2017) 368–393. DOI: 10.1016/j.polymer.2017.09.043
- Kasuga T., Yagyu H., Uetani K., Koga H., Nogi M., Cellulose nanofiber coatings on Cu electrodes for cohesive protection against water-induced short-circuit failures, ACS Applied Nano Materials, 4 (2021) 3861–3868. DOI: 10.1021/ acsanm.1c00267
- Kawano Y., Kondo T., Preparation of aqueous carbon material suspensions by aqueous counter collision, Chemistry Letters, 43 (2013) 483–485. DOI: 10.1246/cl.131046
- Kim J.-K., Choi B., Jin J., Transparent, water-stable, cellulose nanofiber-based packaging film with a low oxygen permeability, Carbohydrate Polymers, 249 (2020) 116823. DOI: 10.1016/j.carbpol.2020.116823
- Kitagawa K., Yano H., Microfibrillated cellulose composite resin and method for producing the same, JP Patent (2012) JP5030667B2. https://patents.google.com/patent/ JP5030667B2/en
- Klemm D., Cranston E.D., Fischer D., Gama M., Kedzior S.A., Kralisch D., Kramer F., Kondo T., Lindström T., Nietzsche S., Petzold-Welcke K., Rauchfuß F., Nanocellulose as a natural source for groundbreaking applications in materials science: today's state, Materials Today, 21 (2018) 720–748. DOI: 10.1016/j.mattod.2018.02.001
- Kondo T., New aspects of cellulose nanofibers, Mokuzai Gakkaishi, 54 (2008) 107–115. DOI: 10.2488/jwrs.54.107
- Kondo T., Kasai W., Method for imparting water repellency and oil resistance using cellulose nanofibers, JP Patent (2015) JP5690387B2. https://patents.google.com/patent/ JP5690387B2/en



- Kondo T., Kose R., Naito H., Kasai W., Aqueous counter collision using paired water jets as a novel means of preparing bio-nanofibers, Carbohydrate Polymers, 112 (2014a) 284–290. DOI: 10.1016/j.carbpol.2014.05.064
- Kondo T., Kumon D., Mieno A., Tsujita Y., Kose R., Preparation and characterization of two types of separate collagen nanofibers with different widths using aqueous counter collision as a gentle top-down process, Materials Research Express, 1 (2014b) 045016. DOI: 10.1088/2053-1591/1/4/045016
- Kondo T., Morita M., Hayakawa K., Onda, Y., Wet pulverizing of polysaccharides, US Patent (2005) US7357339B2. https:// patents.google.com/patent/US7357339B2
- Kondo T., Tanaka H., Yokota S., Nanocomposite and manufacturing method of nanocomposite, JP Patent (2021) JP6979083B2. https://patents.google.com/patent/JP6979083B2/en
- Kose R., Kasai W., Kondo T., Switching surface properties of substrates by coating with a cellulose nanofiber having a high adsorbability, Sen'i Gakkaishi, 67 (2011a) 163–167. DOI: 10.2115/fiber.67.163
- Kose R., Kondo T., Favorable 3D-network formation of chitin nanofibers dispersed in water prepared using aqueous counter collision, Sen'i Gakkaishi, 67 (2011b) 91–95. DOI: 10.2115/ fiber.67.91
- Kose R., Mitani I., Kasai W., Kondo T., "Nanocellulose" as a single nanofiber prepared from pellicle secreted by Gluconacetobacter xylinus using aqueous counter collision, Biomacromolecules, 12 (2011c) 716–720. DOI: 10.1021/ bm1013469
- Li Q., Renneckar S., Supramolecular structure characterization of molecularly thin cellulose I nanoparticles, Biomacromolecules, 12 (2011) 650–659. DOI: 10.1021/bm101315y
- Linder M., Teeri T.T., The cellulose-binding domain of the major cellobiohydrolase of Trichoderma reesei exhibits true reversibility and a high exchange rate on crystalline cellulose, Proceedings of the National Academy of Sciences, 93 (1996) 12251–12255. DOI: 10.1073/pnas.93.22.12251
- Lönnberg H., Zhou Q., Brumer H., Teeri T.T., Malmström E., Hult A., Grafting of cellulose fibers with poly(ε-caprolactone) and poly(l-lactic acid) via ring-opening polymerization, Biomacromolecules, 7 (2006) 2178–2185. DOI: 10.1021/ bm060178z
- Marchessault R.H., Morehead F.F., Walter N.M., Liquid crystal systems from fibrillar polysaccharides, Nature, 184 (1959) 632–633. DOI: 10.1038/184632a0
- Marturano V., Cerruti P., Ambrogi V., Polymer additives, Physical Sciences Reviews, 2 (2017) 20160130. DOI: 10.1515/ psr-2016-0130
- Mazeau K., Wyszomirski M., Modelling of Congo red adsorption on the hydrophobic surface of cellulose using molecular dynamics, Cellulose, 19 (2012) 1495–1506. DOI: 10.1007/ s10570-012-9757-6
- Mukherjee S.M., Woods H.J., X-ray and electron microscope studies of the degradation of cellulose by sulphuric acid, Biochimica et Biophysica Acta, 10 (1953) 499–511. DOI: 10.1016/0006-3002(53)90295-9
- Nagashima A., Tsuji T., Kondo T., A uniaxially oriented nanofibrous cellulose scaffold from pellicles produced by Gluconacetobacter xylinus in dissolved oxygen culture, Carbohydrate Polymers, 135 (2016) 215–224. DOI: 10.1016/j. carbpol.2015.08.077
- Nakagaito A.N., Iwamoto S., Yano H., Bacterial cellulose: the ultimate nano-scalar cellulose morphology for the production of high-strength composites, Applied Physics A, 80 (2005b) 93–97. DOI: 10.1007/s00339-004-2932-3

Nakagaito A.N., Yano H., Novel high-strength biocomposites

based on microfibrillated cellulose having nano-order-unit web-like network structure, Applied Physics A, 80 (2005a) 155–159. DOI: 10.1007/s00339-003-2225-2

- Nechyporchuk O., Belgacem M.N., Bras J., Production of cellulose nanofibrils: a review of recent advances, Industrial Crops and Products, 93 (2016) 2–25. DOI: 10.1016/j.indcrop. 2016.02.016
- Nge T.T., Lee S.-H., Endo T., Preparation of nanoscale cellulose materials with different morphologies by mechanical treatments and their characterization, Cellulose, 20 (2013) 1841–1852. DOI: 10.1007/s10570-013-9962-y
- Nickerson R.F., Habrle J.A., Cellulose intercrystalline structure, Industrial & Engineering Chemistry, 39 (1947) 1507–1512. DOI: 10.1021/ie50455a024
- Nishino T., Matsuda I., Hirao K., All-cellulose composite, Macromolecules, 37 (2004) 7683–7687. DOI: 10.1021/ma049300h
- Nodera A., Hashiba H., Tanaka H., Polyolefin resin composition, JP Patent, (2016) JP2016079311A. https://patents.google. com/patent/JP2016079311A/en
- Oksman K., Aitomäki Y., Mathew A.P., Siqueira G., Zhou Q., Butylina S., Tanpichai S., Zhou X., Hooshmand S., Review of the recent developments in cellulose nanocomposite processing, Composites Part A: Applied Science and Manufacturing, 83 (2016) 2–18. DOI: 10.1016/j.compositesa.2015.10.041
- Oksman K., Sain M., Cellulose Nanocomposites, Processing, Characterization and Properties, ACS Symposium Series, 938, American Chemical Society, Washington, DC, 2006, ISBN: 9780841239807. DOI: 10.1021/bk-2006-0938
- Payen A., Mémoire sur la composition du tissu propre des plantes et du ligneux, Comptes Rendus, 7 (1838) 1052–1056.
- Peretz R., Mamane H., Sterenzon E., Gerchman Y., Rapid quantification of cellulose nanocrystals by Calcofluor White fluorescence staining, Cellulose, 26 (2019) 971–977. DOI: 10.1007/s10570-018-2162-z
- Revol J.F., Bradford H., Giasson J., Marchessault R.H., Gray D.G., Helicoidal self-ordering of cellulose microfibrils in aqueous suspension, International Journal of Biological Macromolecules, 14 (1992) 170–172. DOI: 10.1016/S0141-8130(05)80008-X
- Saito T., Isogai A., TEMPO-mediated oxidation of native cellulose. The effect of oxidation conditions on chemical and crystal structures of the water-insoluble fractions, Biomacromolecules, 5 (2004) 1983–1989. DOI: 10.1021/bm0497769
- Saito T., Kuramae R., Wohlert J., Berglund L.A., Isogai A., An ultrastrong nanofibrillar biomaterial: the strength of single cellulose nanofibrils revealed via sonication-induced fragmentation, Biomacromolecules, 14 (2013) 248–253. DOI: 10.1021/bm301674e
- Saito T., Nishiyama Y., Putaux J.-L., Vignon M., Isogai A., Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose, Biomacromolecules, 7 (2006) 1687–1691. DOI: 10.1021/bm060154s
- Shibata I., Isogai A., Nitroxide-mediated oxidation of cellulose using TEMPO derivatives: HPSEC and NMR analyses of the oxidized products, Cellulose, 10 (2003) 335–341. DOI: 10.1023/A:1027330409470
- Shojaeiarani J., Bajwa D.S., Chanda S., Cellulose nanocrystal based composites: a review, Composites Part C: Open Access, 5 (2021) 100164. DOI: 10.1016/j.jcomc.2021.100164
- Tagawa S., Ishida K., Tsuji T., Kondo T., Facile size evaluation of cellulose nanofibrils adsorbed on polypropylene substrates using fluorescence microscopy, Cellulose, 28 (2021) 2917–2929. DOI: 10.1007/s10570-021-03759-0
- Takai-Yamashita C., Mabuchi Y., Ikeda J., Fuji M., Senna M., Ohya Y., Physicochemical effects and surface activity of

cellulose nanofiber sols induced by a planetary ball milling treatment, Journal of the Society of Powder Technology, Japan, 58 (2021) 164–169. DOI: 10.4164/sptj.58.164

- Taniguchi T., Okamura K., New films produced from microfibrillated natural fibres, Polymer International, 47 (1998) 291–294. DOI: 10.1002/(SICI)1097-0126(199811)47:3<291::AID-PI11 >3.0.CO;2-1
- Taton T.A., Two-way traffic, Nature Materials, 2 (2003) 73–74. DOI: 10.1038/nmat824
- Thomas P., Duolikun T., Rumjit N.P., Moosavi S., Lai C.W., Bin Johan M.R., Fen L.B., Comprehensive review on nanocellulose: recent developments, challenges and future prospects, Journal of the Mechanical Behavior of Biomedical Materials, 110 (2020) 103884. DOI: 10.1016/j.jmbbm.2020.103884
- Thompson K.L., Williams M., Armes S.P., Colloidosomes: synthesis, properties and applications, Journal of Colloid and Interface Science, 447 (2015) 217–228. DOI: 10.1016/j. jcis.2014.11.058
- Trache D., Hussin M.H., Haafiz M.K.M., Thakur V.K., Recent progress in cellulose nanocrystals: sources and production, Nanoscale, 9 (2017) 1763–1786. DOI: 10.1039/ C6NR09494E
- Tsuboi K., Yokota S., Kondo T., Difference between bamboo- and wood-derived cellulose nanofibers prepared by the aqueous counter collision method, Nordic Pulp & Paper Research Journal, 29 (2014) 69–76. DOI: 10.3183/npprj-2014-29-01-p069-076
- Tsuji T., Tsuboi K., Yokota S., Tagawa S., Kondo T., Characterization of an amphiphilic Janus-type surface in the cellulose nanofibril prepared by aqueous counter collision, Biomacromolecules, 22 (2021) 620–628. DOI: 10.1021/acs. biomac.0c01464
- Tsujita Y., Kondo T., A building block of collagen fibrils demonstrated by sequential aqueous counter collision process, Journal of Fiber Science and Technology, 75 (2019) 112–118. DOI: 10.2115/fiberst.2019-0014
- Uetani K., Yano H., Nanofibrillation of wood pulp using a highspeed blender, Biomacromolecules, 12 (2011) 348–353. DOI: 10.1021/bm101103p
- Utsunomiya H., Tsujita Y., Kondo T., Cellulose nanoanemone: an asymmetric form of nanocellulose, Cellulose, 29 (2022) 2899–2916. DOI: 10.1007/s10570-021-04231-9

Walther A., Müller A.H.E., Janus particles, Soft Matter, 4 (2008)

663–668. DOI: 10.1039/B718131K

- Winey K.I., Vaia R.A., Polymer nanocomposites, MRS Bulletin, 32 (2011) 314–322. DOI: 10.1557/mrs2007.229
- Yabu H., Kanahara M., Shimomura M., Arita T., Harano K., Nakamura E., Higuchi T., Jinnai H., Polymer Janus particles containing block-copolymer stabilized magnetic nanoparticles, ACS Applied Materials & Interfaces, 5 (2013) 3262–3266. DOI: 10.1021/am4003149
- Yano H., Nakahara S., Bio-composites produced from plant microfiber bundles with a nanometer unit web-like network, Journal of Materials Science, 39 (2004) 1635–1638. DOI: 10.1023/B:JMSC.0000016162.43897.0a
- Yano H., Nano Cellulose Vehicle Project, Ministry of the Environment of Japan (2016–2019). https://www.env.go.jp/ press/103177.html
- Yano H., Sugiyama J., Nakagaito A.N., Nogi M., Matsuura T., Hikita M., Handa K., Optically transparent composites reinforced with networks of bacterial nanofibers, Advanced Materials, 17 (2005) 153–155. DOI: 10.1002/ adma.200400597
- Ye W., Yokota S., Fan Y., Kondo T., A combination of aqueous counter collision and TEMPO-mediated oxidation for doubled carboxyl contents of α-chitin nanofibers, Cellulose, 28 (2021) 2167–2181. DOI: 10.1007/s10570-021-03676-2
- Yokota S., Kamada K., Sugiyama A., Kondo T., Pickering emulsion stabilization by using amphiphilic cellulose nanofibrils prepared by aqueous counter collision, Carbohydrate Polymers, 226 (2019) 115293. DOI: 10.1016/j. carbpol.2019.115293
- Yokota S., Tagawa S., Kondo T., Facile surface modification of amphiphilic cellulose nanofibrils prepared by aqueous counter collision, Carbohydrate Polymers, 255 (2021) 117342. DOI: 10.1016/j.carbpol.2020.117342
- Yu T., Qiu X., Chapter 2 Elastic-Plastic Waves, in: Yu T. and Qiu X. (eds), Introduction to Impact Dynamics, Tsinghua University Press, 2018, pp. 19–38, ISBN: 9781118929841. DOI: 10.1002/9781119113133.ch2
- Zhou Q., Greffe L., Baumann M.J., Malmström E., Teeri T.T., Brumer H., Use of xyloglucan as a molecular anchor for the elaboration of polymers from cellulose surfaces: a general route for the design of biocomposites, Macromolecules, 38 (2005) 3547–3549. DOI: 10.1021/ma047712k

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