TEMPO-oxidized cellulose nanofibrils prepared from various plant holocelluloses

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ABSTRACT

Plant holocelluloses were prepared from softwood, gymnosperm, hardwood, and herbaceous species, and subjected to TEMPO-mediated oxidation using the TEMPO/NaBr/NaOCl and TEMPO/NaOCl/NaO₂Cl systems in water at pH 10 and 6.8, respectively. Weight recovery ratios of the water-insoluble TEMPO-oxidized holocellulose (TOH) fractions and their carboxylate contents, sugar compositions, and X-ray diffraction patterns were measured. When the oxidation at pH 10 was used, the carboxylate content of the TOHs increased up to 1.4–1.7 mmol g⁻¹. The oxidation at pH 6.8 resulted in higher weight recovery ratios of TOHs and their lower carboxylate contents (0.8–1.2 mmol g⁻¹) than those prepared by the oxidation at pH 10. Hemicelluloses in plant holocelluloses are preferentially degraded to water-soluble fractions and removed from TOHs in the oxidation at pH 10. In contrast, the TEMPO-mediated oxidation at pH 6.8 provides hemicellulose-rich TOHs in high weight recovery ratios, although their nanofibrillation yields were low. All TEMPO-oxidized holocellulose nanofibrils (TOHNs) obtained by mechanical disintegration treatment of TOHs in water had the same average widths of ~3 nm, when measured by atomic force microscopy in water, which were consistent with those of TOHs determined from X-ray diffraction patterns. The number-average lengths of TOHNs were 500–600 nm.

Keywords: cellulose microfibril, holocellulose, nanofibrillation, sugar composition, TEMPO-mediated oxidation

1. Introduction

Plant cellulose microfibrils have high crystallinities of 60–80%, high aspect ratios, and homogeneous widths of 3–6 nm [1]. They are unique crystalline and renewable bionanofibers abundantly present on earth. Nanofibrillated celluloses and nanocrystalline cellulose whiskers have recently attracted attention because of their promising properties as new bio-based nanomaterials [2–5]. Nanofibrillated celluloses are prepared by mechanical disintegration of native cellulose fibers with or without pretreatment. Mild cellulase treatment or partial carboxymethylation has been applied to wood celluloses to improve nanofibrillation efficiency [2]. When never-dried wood holocelluloses, which have significant amounts of hemicelluloses, are used as the starting materials, mechanical nanofibrillation in water proceeds more efficiently compared with once-dried wood chemical pulps [6,7]. Water-swallowable and non-crystalline hemicelluloses containing relatively large amounts of anionic carboxyl groups enhance nanofibrillation efficiency of plant celluloses.

We have developed catalytic oxidation systems of native wood celluloses with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in water to introduce anionic C6-carboxyl groups densely and regularly on the crystalline cellulose microfibril surfaces with position-selectivity [4,8–10]. The sodium C6-carboxylate groups were prepared from commercial bleached kraft pulps for papermaking. TEMPO-oxidized cellulose fibers have sufficient amounts of sodium C6-carboxyl groups (e.g., $>1.2 \text{ mmol g}^{-1}$) and can be converted to individual nanofibrils with high aspect ratios and homogeneous widths of $\sim 3 \text{ nm}$ by mechanical disintegration treatment in water [4,5]. The obtained TEMPO-oxidized wood cellulose nanofibrils (TOCNs) have high elastic moduli and tensile strengths of ~ 140 and $\sim 3 \text{ GPa}$, respectively [11,12]. Transparent and flexible TOCN films, prepared from the aqueous TOCN dispersions by casting and drying, have high mechanical strengths and oxygen-barrier properties under dry conditions [13].

A hemp bast (*Cannabis sativa* L. Subsp. *sativa*) holocellulose was oxidized using the TEMPO/NaBr/NaOCl system in water at pH 10 [14,15]. The obtained TEMPO-oxidized hemp bast holocelluloses were mechanically disintegrated in water to prepare nanofibrils. Almost completely individualized TOCNs were obtained, when carboxylate contents of the oxidized hemp bast holocelluloses were in the range of $1.5\text{--}1.7 \text{ mmol g}^{-1}$. When a softwood thermomechanical pulp (TMP), having almost the same cellulose, hemicelluloses, and lignin contents as those of the original softwood, was subjected to TEMPO/NaBr/NaOCl oxidation in water at pH 10 [16–18], almost pure TOCNs dispersed in water was obtained [18].

However, the addition of more NaOCl was needed to prepare oxidized TMPs with sufficient amounts of carboxylate contents for complete nanofibrillation. The additional NaOCl was needed since some of the NaOCl was consumed to degrade lignin in TMP.

In this study, five plant holocelluloses were oxidized using TEMPO-mediated oxidation systems in water at pH 10 and 6.8. The obtained TEMPO-oxidized holocelluloses (TOHs) were characterized in terms of their chemical and crystal structures. The effect of hemicelluloses present in holocelluloses on the efficiency of TEMPO-mediated oxidation was investigated. The TOHs were subjected to mechanical disintegration treatment in water, and the average width/width distribution and length/length distribution of the TEMPO-oxidized holocellulose nanofibrils (TOHNs) dispersed in water were characterized using atomic force microscopy (AFM) and transmission electron microscopy (TEM), respectively. The influence of hemicelluloses present in holocelluloses on nanofibrillation behavior of TOHs was studied.

2. Experimental

2.1. Materials

Japanese cedar (*Cryptomeria japonica*), ginkgo (*Ginkgo biloba*), birch (*Betula maximowicziana*), eucalyptus (*Eucalyptus globulus*), rice straw (*Oryza sativa L.*), and kenaf (*Hibiscus cannabinus*) were used as plant samples. Sieved plant powders (passed through an 80-mesh aperture screen) were prepared from the above milled or cut plant pieces, and de-waxed with an acetone/water mixture (9:1 by vol.) at room temperature for 1 day. Holocelluloses were prepared from the wax-free plant powders by repeated (4–5 times) treatment with NaO₂Cl in water at pH 4.5 and 75°C for 1 h (according to the Wise method [19]). A never-dried softwood bleached kraft pulp (Nippon Paper Industries, Tokyo, Japan), which had a ~90% α -cellulose content, was used as a reference. TEMPO, sodium bromide, 70% NaO₂Cl, a 13% NaOCl solution, sodium hydroxide, and other chemicals and solvents were of laboratory grade (Wako Pure Chemicals Co., Ltd., Japan) and used without further purification.

2.2. TEMPO-mediated oxidation of holocelluloses

Holocellulose sample (1 g) was suspended in water (100 mL), containing TEMPO (0.016

g) and NaBr (0.1g). TEMPO-mediated oxidation was started by adding a NaOCl solution, containing 2.5–15 mmol NaOCl, at pH 10 and room temperature using the TEMPO/NaBr/NaOCl system [8,9,20]. The mixture was maintained at pH 10 by continuous addition of 0.5 M NaOH using a pH stat until no NaOH consumption was observed (< 2 h). The water-insoluble TOH was washed thoroughly with water by filtration. Some of the oxidized holocelluloses were post-oxidized with 1% NaO₂Cl in water at pH 4.5 and room temperature for 2 days to convert C6-aldehydes to C6 carboxylate groups [20].

In the case of oxidation using the TEMPO/NaOCl/NaO₂Cl system, holocellulose sample (1 g) was suspended in 0.1 M sodium phosphate buffer (100 mL, pH 6.8) with TEMPO (0.16 mmol) and NaOCl (10 mmol) in an airtight flask. A 2 M NaO₂Cl solution (3.0 mmol) was added to the flask in a single step. The flask was immediately stoppered and the suspension stirred at 40 °C for 3 days [10,21]. After cooling the suspension to room temperature, the water-insoluble TOH was washed with water by filtration. The weight recovery ratios of the water-insoluble TOHs were calculated from dry weights before and after the TEMPO-mediated oxidation. The carboxylate content of each TOH sample was determined using the electrical conductometric titration method [22,23].

2.3. Mechanical disintegration treatment of TOHs in water

The TOH was suspended in water (25 mL) to provide a solid content of 0.1%. The suspension was homogenized for 2 min at 7500 rpm with a double-cylinder-type homogenizer (Physoctron NS-56, Microtec) and then sonicated for 4 min using an ultrasonic homogenizer equipped with a 7 mm probe tip (US-300T, Nihon Seiki) at 300 W of output power. The partly fibrillated or unfibrillated fraction was removed by centrifugation of the suspension at 12000g for 20 min, and the nanofibrillation yield was calculated from the dry weight of the unfibrillated fraction [20].

2.4. Analyses

α-Cellulose, lignin, and ash contents in holocelluloses were determined according to standard procedures [18,24–26]. After acid hydrolysis, the neutral sugar composition analysis was carried out using a high-performance liquid chromatograph (HPLC) according to a

previously reported method [15,27]. Freeze-dried TEMPO-oxidized and post-oxidized holocelluloses (0.04 g each) were dissolved in 0.5 M cupriethylene diamine, and their viscosity-average degrees of polymerization (DP_v) were calculated from their intrinsic viscosities [20]. X-ray diffraction patterns were recorded for pressed disk-pellet samples (0.1 g each) from 10 to 30° of 2θ diffraction angles using the reflection method by means of a Rigaku RINT 2000 with monochromator-filtered Cu K α radiation at 40 kV and 40 mA. The crystallinity index and (2 0 0) crystal width of cellulose I were calculated according to conventional methods from the X-ray diffraction patterns [15,18,28,29].

The mechanically disintegrated aqueous dispersion of TOH (without removing the unfibrillated fraction) was put into a disposable poly(methyl methacrylate) cuvette and the light transmittance spectrum of the dispersion was measured from 300 to 800 nm with a spectrophotometer (JASCO V-670). AFM images of nanofibrils (after removing the unfibrillated fraction) were obtained using a Nanoscope III Multimode (Digital Instruments, USA) by depositing aqueous 0.005% nanofibril dispersions on freshly exfoliated mica plates with $\sim 1 \times 1$ cm² in water without drying and in air after drying using tapping mode. Widths of ~ 60 and ~ 150 nanofibrils, observed in water and air, respectively, were measured from the AFM height profiles for each sample. A 10 μ L aliquot of 0.005% TOHNs dispersion (after removing the unfibrillated fraction) was mounted onto a glow-discharged carbon-coated Cu grid. The excess liquid was absorbed by filter paper. After drying, the sample grid was observed using a diffraction contrast method [10,30] with a JEOL JEM 2000-EXII microscope operated at an accelerating voltage of 200 kV. Lengths of approximately ~ 150 nanofibrils were measured from the TEM images for each sample.

3. Results and discussion

3.1. TEMPO-mediated oxidation of plant holocelluloses

Japanese cedar and ginkgo were used as softwood and gymnosperm, respectively, and birch and eucalyptus were used as hardwoods, while rice straw and kenaf were used as herbaceous species. Sieved powders of these plants were de-waxed and then delignified to prepare holocelluloses using the Wise method with NaO₂Cl. Japanese cedar and ginkgo were delignified five times with fresh chemicals, and the other samples were delignified four times. The experimental scheme to prepare and analyze plant holocelluloses, TOHs, and TOHNs are illustrated as Scheme S1 in the Supplementary content file.

α -Cellulose, hemicelluloses, and lignin contents of holocelluloses and their yields, based on the original de-waxed plant powders, are shown in Fig. 1. Lignin contents were estimated from their micro-Kappa numbers: lignin content $\approx 0.15 \times$ micro-Kappa number [18,24]. Lignin present in the original plant was removed by the repeated Wise method, and the lignin contents in the holocelluloses decreased to 0.8–2.8%. In contrast, significant amounts of hemicelluloses remained and were 26–41% of the holocellulose weights, except rice straw holocellulose (14%). This was because a significant amount (22%) of ash was present in the rice straw holocellulose [31]. Based on the lignin contents of these plant samples, ginkgo and birch holocelluloses had lower yields than those estimated from their lignin contents, probably because one additional delignification treatment was applied to these plant samples to remove lignin [32]. In general, the repetition numbers of the Wise delignification treatment were four and five for softwood and hardwood, respectively.

The plant holocelluloses were oxidized by the TEMPO/NaBr/NaOCl system in water at pH 10 with NaOCl of 2.5–15 mmol g⁻¹ and by the TEMPO/NaOCl/NaO₂Cl system in water at pH 6.8 and 40 °C. The oxidized holocelluloses were washed with water. Weight recovery ratios of the water-insoluble TOH fractions were obtained via freeze-drying. In all the plant samples, the TOHs prepared by oxidation at pH 6.8 had higher weight recovery ratios than those at pH 10. TEMPO-mediated oxidation at pH 10 with NaOCl of 5 mmol g⁻¹ gave higher TOH yields than those with NaOCl of 10 mmol g⁻¹. Thus, the TEMPO-mediated oxidation at pH 6.8 maintains significant amounts of hemicelluloses in the TOHs, whereas that at pH 10 degrades hemicelluloses. The higher the NaOCl addition level in the TEMPO-mediated oxidation at pH 10, the more the hemicelluloses in holocelluloses degraded to water-soluble compounds. Although quantitative analysis of ash in the TOHs prepared from rice straw was not carried out, a significant amount of Si K_{α1} due to silica was detected for these TOHs in the scanning electron microscopy images combined with energy-dispersive X-ray analysis (Fig. S1 in the Supplementary content file). Based on the mapping data shown in Fig. S1 and the high weight recovery ratios shown in Fig 2, the TOHs prepared from rice straw holocellulose still contained significant amounts of silica.

The carboxylate contents of TOHs prepared using the TEMPO/NaBr/NaOCl system in water at pH 10 are plotted to the NaOCl addition level in Fig. 3A/The carboxylate contents of the TOHs prepared by the two TEMPO-mediated oxidation systems at pH 10 and 6.8 are shown in Fig. 3B. The carboxylate contents of TEMPO-oxidized softwood bleached kraft pulp (SBKP) are included in Fig. 3 as references. All the plant holocelluloses, except kenaf holocellulose, increased in carboxylate content as the NaOCl addition level ranged from 2.5

to 10 mmol g⁻¹ then leveled off in the TEMPO/NaBr/NaOCl oxidation. Because all plant holocelluloses were prepared by the Wise method using NaO₂Cl as an oxidant, they had high carboxylate contents of 0.32–0.46 mmol g⁻¹ before the TEMPO-mediated oxidation: the NaO₂Cl oxidation can oxidize some of aldehyde groups of the reducing ends of cellulose and hemicellulose molecules to carboxyls.

In the TEMPO/NaBr/NaOCl oxidation with NaOCl of 2.5–5.0 mmol g⁻¹, SBKP containing ~10% hemicelluloses provided TEMPO-oxidized products with higher carboxylate contents than plant holocelluloses having higher hemicellulose contents. Thus, in this range of NaOCl addition, the hemicelluloses present in holocelluloses caused lower efficiency in the formation of carboxylate groups. When the NaOCl addition levels were in the range of 10–15 mmol g⁻¹, no significant differences in carboxylate content were observed between SBKP and holocelluloses, except kenaf. Since the kenaf holocellulose contained a relatively high cellulose content, it may have provided TOHs with a similar relationship between the NaOCl addition level and the corresponding carboxylate content to that of SBKP.

The TEMPO/NaOCl/NaO₂Cl oxidation system in water at pH 6.8 provided TOHs with carboxylate contents lower than those prepared using the TEMPO/NaBr/NaOCl system with NaOCl of 10 mmol g⁻¹ in water at pH 10 [21].

3.2. Characterization of TEMPO-oxidized plant holocelluloses

Changes in sugar compositions before and after TEMPO-mediated oxidation of plant holocelluloses are shown in Fig. 4. Japanese cedar and ginkgo had hemicelluloses of glucomannan and xylan, whereas the other plant holocelluloses primarily had xylan as the hemicellulose component. The neutral sugar composition of each TOH was determined through the acid hydrolysis-HPLC method using myo-inositol as an internal standard. The component “others including uronic acids” of each TOH in Fig. 4 was obtained by subtracting the total neutral sugar content from the TOH weight recovery ratio in Fig. 2. Because cellouronic acids or [1→4]-β-polyglucuronic acids have resistance to acid hydrolysis [33], glucuronic acid-containing surface molecules (including some glucosyl units linked to the glucuronosyl units) present on the surfaces of crystalline TEMPO-oxidized cellulose microfibrils in TOHs are likely to be included in this “others” component. In the case of the TOHs from rice straw, this “others” component contained silica particles, a part of which were not removed during the washing and filtration processes.

The TOHs, except rice straw TOH, prepared using the TEMPO/NaBr/NaOCl system at

pH 10 primarily constituted glucose and “others” components of 50–58% and 37–48%, respectively, based on the dry TOH weights. Although these TOHs contain slight amounts of xylosyl units, most hemicelluloses originally present in the holocelluloses were oxidized and removed from the TOHs as water-soluble fractions during the oxidation and washing processes. When the TOHs were prepared using the TEMPO/NaOCl/NaO₂Cl system at pH 6.8, significant amounts of xylosyl units remained in the TOHs for hardwood and herbaceous plant samples. Less than 20% of mannosyl units present in the Japanese cedar and ginkgo holocelluloses remained in TOHs after the TEMPO-mediated oxidation at pH 6.8, while 30–58% of xylosyl units originally present in the six plant holocelluloses remained in the corresponding TOHs. Thus, xylan in holocelluloses is more resistant to degradation than glucomannan during the TEMPO-mediated oxidation at pH 6.8, probably because the latter has C6-primary hydroxyl groups to be oxidized to C6-carboxyls by the TEMPO-mediated oxidation but the former does not. Consequently, in the case of TEMPO-mediated oxidation of holocelluloses at pH 6.8, oxidative degradation and the subsequent removal from TOHs as water-soluble fractions was more restricted than that at pH 10; hemicellulose-rich TOHs can be obtained from holocelluloses using the oxidation system at pH 6.8.

The DP_v values were measured for TOHs prepared from Japanese cedar and eucalyptus at pH 10, and for TEMPO-oxidized SBKP. All these oxidized samples decreased in DP_v with increasing NaOCl addition level (Fig. S2 in Supplementary content file). Thus, there was no significant difference in depolymerization behavior between TOHs and SBKP in terms of the NaOCl addition level, under the conditions at pH 10 [20]. The DP_v values of TOHs prepared at pH 6.8 may be higher than those prepared at pH 10. However, because these TOHs contained significant amounts of hemicelluloses, they did not completely dissolve in 0.5M copper ethylenediamine, so their accurate DP_v values could not be obtained.

The water-soluble fractions in TOHs present in filtrates during washing process were obtained as precipitates by ethanol addition to the filtrates. The dried materials were dissolved in D₂O for ¹³C-NMR analysis (Fig. S3 in the Supplementary content file). Glucuronosyl and mannuronosyl units were detected for the products from Japanese cedar holocellulose [18]. Thus, oxidative degradation and depolymerization of a part of glucomannan and cellulose molecules in Japanese cedar holocellulose during the TEMPO-mediated oxidation caused the formation of the water-soluble fractions. When the eucalyptus holocellulose was oxidized at pH 6.8, xylan (probably with some glucuronosyl branches) was the main component of the water-soluble product. The NMR spectrum of the water-soluble product prepared from eucalyptus holocellulose by the oxidation at pH 10 was clearly different from that obtained at

pH 6.8. According to the literature data, this product is likely to be C2/C3 dicarboxyl xylan [34–36]. The same signals were also detected in the NMR spectrum of the water-soluble product obtained from Japanese cedar holocellulose by the oxidation at pH 10. Thus, the C2-C3 bonds of xylan in holocelluloses are possibly cleaved to form C2/C3 dicarboxyls by the oxidation at pH 10, although further studies are needed.

X-ray diffraction patterns of Japanese cedar and eucalyptus powders and their holocelluloses before and after TEMPO-mediated oxidation are shown in Fig. 5. The holocelluloses had crystallinity index (C.I.) values higher than those of the original wood powders, because non-crystalline lignin was mostly removed from the holocelluloses. The C.I. values of TOHs were slightly lower than those of the original holocelluloses, indicating that decrystallization took place to some extent on crystalline cellulose microfibrils during the oxidation. The crystal widths of cellulose I calculated from the (2 0 0) diffraction peak were ~3 nm for all the samples and mostly unchanged before and after oxidation, showing that the oxidation occurred position-selectively on the C6-OH groups present on the crystalline cellulose microfibril surfaces. Other plant holocelluloses gave almost the same X-ray diffraction results as those of these two wood holocellulose samples.

3.3. Nanofibrillation of TEMPO-oxidized holocelluloses

The TOHs prepared at pH 10 and 6.8 were mechanically disintegrated in water under the same conditions, and their nanofibrillation behavior was evaluated. Fig. 6 shows UV-vis transmittance spectra of the dispersions. The TOHs prepared at pH 10 were mostly converted to highly transparent dispersions, except the rice straw TOH, and had transmittances of >90% at 600 nm wavelength, showing that almost complete nanofibrillation was achieved for these TOHs (Fig. 6 upper). The birch TOH gave slightly lower light transmittance, because it had a relatively high amount of xylan (Fig. 4). The rice straw TOH containing silica particles gave clearly lower light transmittance. The nanofibrillation yields of these dispersions were 91%, 97%, 93%, 92%, 61%, and 96% for Japanese cedar, ginkgo, birch, eucalyptus, rice straw, and kenaf TOHs, respectively. These TOHs, except rice straw, had high nanofibrillation yields of >90%.

The light transmittances of aqueous dispersions of TOHs prepared at pH 6.8 were lower than those of the corresponding dispersions of TOHs prepared at pH 10. Because the TOHs prepared at pH 6.8 had lower carboxylate contents and, in turn, higher hemicellulose contents than those prepared at pH 10, these factors may have caused lower nanofibrillation efficiency.

Photographs of aqueous dispersions prepared from TOHs of Japanese cedar and eucalyptus are shown in Fig. S4 in the Supplementary content file. The dispersions of TOHs prepared with NaOCl of 10 mmol g⁻¹ at pH 10 and those prepared at pH 6.8 indicated achievement of almost complete nanofibrillation, based on their high transparency and birefringence behavior when observed between cross-polarizers.

After removal of unfibrillated fractions, the aqueous nanofibrillated dispersions of TOHs prepared with NaOCl of 10 mmol g⁻¹ at pH 10 were subjected to AFM analysis in air and water to measure TOHN widths from their AFM height profiles. When the TOHN widths were measured from AFM height images taken in air, almost all the TOHN widths were ~2 nm, which are clearly smaller than those determined from the X-ray diffraction patterns of cellulose I (Fig. 5). We assumed that the high spring constant of the AFM cantilever, 40 N/m in air, caused such small TOHN widths. The spring constant of the cantilever decreased to 0.06 N/m in water according to catalog information provided by the manufacturer. The TOHN widths were measured from AFM height profiles captured in water. As shown in Fig. 7, the width distributions shifted to greater values when the AFM images obtained in water were used. The number-average and width-average TOHN widths measured from AFM images captured in air and water are summarized in Table 1. When the TOHN widths were measured in water, all the plant TOHN widths had similar value of 3.1–3.2 nm, which agreed with those determined from the X-ray diffraction patterns (Fig. 5). Probably, the large difference in cantilever spring constant between air and water in tapping mode may have resulted in the difference in TOHN width in Table 1. The large cantilever spring constant may have caused a deformation force for TOHN elements, although details are unknown at present. The results in Table 1 conclude that no significant difference in TOHN width existed between the plant holocelluloses.

Fig. 8 upper and lower show TEM images of TOHNs used in Fig. 7 and average TOHN lengths measured from TEM images, respectively. All the TOHNs had similar number-average lengths of 500–600 nm, which were greater than that of TEMPO-oxidized SBKP nanofibrils (~400 nm). Thus, when plant holocelluloses were used as starting materials in TEMPO-mediated oxidation in water at pH 10, the TOHNs with larger lengths could be obtained.

4. Conclusions

When the TEMPO/NaBr/NaOCl system at pH 10 was applied to plant holocelluloses, the

carboxylate content of the water-insoluble TOHs increased up to 1.4–1.7 mmol g⁻¹ at NaOCl addition levels of 2.5–10 mmol g⁻¹ and then leveled off in a similar manner between the used plant holocelluloses, except kenaf. When the TEMPO/NaOCl/NaO₂Cl system at pH 6.8 was used in the oxidation, weight recovery ratios of the TOHs were higher and their carboxylate contents were lower (0.8–1.2 mmol g⁻¹) than those prepared by the oxidation with NaOCl of 10 mmol g⁻¹ at pH 10. Hemicelluloses in plant holocelluloses were, therefore, mostly degraded to water-soluble fractions and removed from TOHs in the oxidation with NaOCl of 10 mmol g⁻¹ at pH 10. Some of the added NaOCl were consumed for degradation of hemicelluloses and cellulose depolymerization. The TEMPO-mediated oxidation of holocelluloses in water at pH 6.8 provided hemicellulose-rich TOHs in high weight recovery ratios, although their nanofibrillation yields were low. The TOHN widths, prepared from plant holocelluloses using the oxidation with NaOCl of 10 mmol g⁻¹ at pH 10 and measured using AFM tapping mode in water, were all ~3 nm, which were consistent with those determined from the X-ray diffraction method. The number-average lengths of TOHNs were 500–600 nm, which were larger than that prepared from SBKP. When rice straw holocellulose was used as the starting material, some silica particles were still present in both TOHs and TOHNs. Thus, TOHNs have some characteristic properties compared with those of TEMPO-oxidized SBKPs.

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Supplementary content

Supplementary content associated with this article can be found, in the online version, at <http://dx.doi.org/?????????>.

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Table 1

Widths (nm) of TEMPO-oxidized holocellulose nanofibrils obtained from AFM height profiles captured in air and water. All TEMPO-oxidized nanofibrils were prepared using the TEMPO/NaBr/NaOCl system with NaOCl of 10 mmol g⁻¹ at pH 10.

	Japanese cedar	Ginkgo	Birch	Eucalyptus	Rice straw	Kenaf
<i>in air</i>						
Number-average width	1.93±0.37	1.95±0.51	2.13±0.38	1.73±0.30	–	–
Width-average width	2.00	2.09	2.20	1.78	–	–
<i>in water</i>						
Number-average width	3.10±0.39	3.12±0.38	3.11±0.42	3.11±0.36	3.08±0.32	3.13±0.30
Width-average width	3.14	3.16	3.16	3.15	3.11	3.16

Figure Legends

Fig. 1. Yield of plant holocelluloses and weight ratios of four structural components in each holocellulose.

Fig. 2. Weight recovery ratios of water-insoluble TEMPO-oxidized holocelluloses prepared under various conditions, based on dry weight of holocelluloses.

Fig. 3. (A) Relationship between the amount of NaOCl added in TEMPO/NaBr/NaOCl oxidation at pH 10 and the carboxylate content of water-insoluble oxidized holocelluloses. (B) Carboxylate content of water-insoluble TEMPO-oxidized holocelluloses prepared using TEMPO/NaBr/NaOCl and TEMPO/NaOCl/NaO₂Cl systems.

Fig. 4. Sugar compositions of the original holocelluloses and water-insoluble TEMPO-oxidized holocelluloses prepared under various conditions.

Fig. 5. X-ray diffraction patterns of the original and water-insoluble TEMPO-oxidized holocelluloses prepared from Japanese cedar and eucalyptus under various conditions. (a,a') Original wood powder, (b,b') holocellulose, (c,c') TEMPO-oxidized holocellulose prepared using the TEMPO/NaBr/NaOCl system with NaOCl of 10 mmol g⁻¹ at pH 10, and (d,d') TEMPO-oxidized holocellulose prepared using the TEMPO/NaOCl/NaO₂Cl system at pH 6.8.

Fig. 6. Light transmittance spectra of TEMPO-oxidized holocellulose/water dispersions after mechanical disintegration treatment under the same conditions.

Fig. 7. AFM height images of TEMPO-oxidized holocellulose nanofibrils taken in water (upper). Width distributions of TEMPO-oxidized holocellulose nanofibrils obtained from AFM height profiles taken in air or water (lower). All TEMPO-oxidized holocellulose nanofibrils were prepared using the TEMPO/NaBr/NaOCl system with NaOCl of 10 mmol g⁻¹ at pH 10.

Fig. 8. TEM images of TEMPO-oxidized holocellulose nanofibrils (upper). Average lengths of TEMPO-oxidized holocellulose nanofibrils measured from TEM images. All TEMPO-oxidized nanofibrils were prepared using the TEMPO/NaBr/NaOCl system with NaOCl of 10 mmol g⁻¹ at pH 10.

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Graphic abstract

TEMPO-oxidized cellulose nanofibrils prepared from various plant holocelluloses

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