Simple Freeze-Drying Procedure for Producing Nanocellulose Aerogel-Containing, High-Performance Air Filters

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S *Supporting Information*

ABSTRACT: Simple freeze-drying of 2,2,6,6-tetramethylpiper-idine-1-oxyl (TEMPO)-oxidized cellulose nanofibril (TOCN) dispersions in water/*tert*-butyl alcohol (TBA) mixtures was conducted to prepare TOCN aerogels as high-performance air filter components. The dispersibility of the TOCNs in the water/TBA mixtures, and the specific surface area (SSA) of the resulting TOCN aerogels, was investigated as a function of the TBA concentration in the mixtures. The TOCNs were homogeneously dispersed in the water/TBA mixtures at TBA concentrations up to 40% w/w. The SSAs of the TOCN aerogels exceeded 300 m^2/g when the TBA concentration in the aqueous mixtures was in the range from 20% to 50% w/w. When a commercially available, high-efficiency particulate air (HEPA) filter was combined with TOCN/water/TBA dispersions prepared using 30% TBA, and the product was freeze-dried, the resulting TOCN aerogel-containing filters showed superior filtration properties. This was because nanoscale, spider-web-like networks of the TOCNs with large SSAs were formed within the filter.

KEYWORDS: *nanocellulose, aerogel, freeze-drying, specific surface area, air filter*
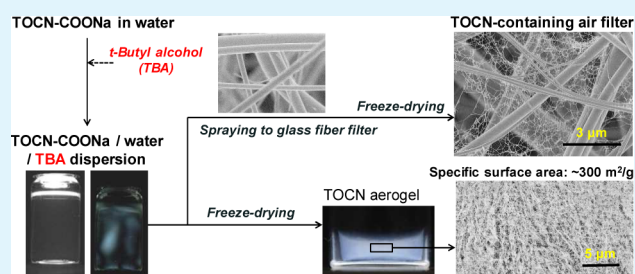
INTRODUCTION

Nanocelluloses can be used as components in porous materials with large specific surface areas (SSAs) to create high-performance products such as filters, adsorbents, catalyst supports, cell culture substrates, thermal insulators, and drug carriers.[1−7] Nanocelluloses show great promise for air filter applications. High-efficiency particulate air (HEPA) and ultralow penetration air (ULPA) filters are used as highly efficient air filters in cleanrooms for the electronics, food, and medical industries, and in related laboratories. HEPA and ULPA filters have filtering efficiencies of at least 99.97% against 0.3 μm particles, and at least 99.999% against 0.1−0.2 μm particles.[8] Excellent air filters have high air permeability (i.e., low pressure drop), and large surface areas that can capture more particles.[9,10] It is expected that nanocelluloses will be applied as highly efficient air filter materials, because nanosized fibers are able to reduce the air resistance in filters, and enhance the frequency of collision of particles with the fibers.[11−13]

A variety of nanocelluloses exist: these different materials differ in fiber width, length, and surface charge. The preparation procedures also vary depending on the end use. The mechanical disintegration of cellulose fibers is a basic method to downsize the fibers into fibrils; this method does, however, require large amounts of energy. Chemical or enzymatic pretreatments can lower the energy requirements for the disintegration.[14] One such pretreatments, 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO)-mediated oxidation of wood pulp

fibers, followed by mild homogenization, facilitates the complete individualization of cellulose nanofibrils in water, when carboxylate contents of oxidized wood celluloses are more than ~1 mmol/g.[15,16] The resulting TEMPO-oxidized cellulose nanofibrils (TOCNs) show extremely narrow (~3 nm) and uniform widths, and large SSAs, and they align in a nematic liquid-crystalline order when dispersed in water.[17] When aqueous TOCN dispersions are directly air-dried, transparent films with low oxygen permeability (i.e., high oxygen barrier properties) are obtained.[18,19] The air-drying of TOCN dispersions on porous supports was shown to result in the formation of nanoporous networks inside the pores of the supports.[20]

Freeze-drying and super critical drying have been proposed as techniques for the preparation of TOCNs with large SSAs.[5,17,21,22] Highly porous materials with large SSAs, called "aerogels", were produced using these procedures. To obtain aerogels with large SSAs using these processes, the medium in which the TOCNs are dispersed must be completely replaced with a low-polarity organic solvent before drying. However, TOCNs with sodium C6-carboxylate groups (TOCNs-COONa) and TOCNs with protonated C6-carboxyls (TOCNs-COOH) cannot be dispersed homogeneously in the

low-polarity organic solvents such as *tert*-butyl alcohol (TBA) and ethanol that are typically used in these drying processes. The addition of a small amount of TBA to an aqueous TOCN dispersion enables the TOCNs to be dispersed homogeneously in the mixtures, and increases the SSAs of the freeze-dried TOCNs.[23,24] However, the dispersibility and the SSAs have not been investigated systematically as a function of the TBA concentration in the water/TBA mixtures. Sehaqui et al. obtained a TOCN aerogel with a large SSA (254 m^2/g),[25] using a TOCN/water/TBA mixture with 67% v/v TBA. They centrifuged the TOCN dispersion after the addition of TBA; the results indicate that the TOCNs were not well dispersed in the mixture.

In this study, we investigated simple freeze-drying processes to obtain TOCN aerogels with large SSAs, using water/TBA mixtures as the dispersing medium for the TOCNs with the end goal of industrially applicable air filters in mind. The nanodispersibility of the TOCNs in the mixtures, and the SSAs of the resulting TOCN aerogels, were investigated as a function of the TBA concentration. Homogeneously nanodispersed TOCNs are advantageous for the preparation of TOCN aerogel-containing composites, because such TOCNs can penetrate deeper into the porous base materials. As a demonstration of such applications, we prepared TOCN aerogel-containing air filters, and their performances were compared with that of the base HEPA filter. High-quality HEPA filters containing nanocelluloses have not yet been reported as a result of the formation of numerous hydrogen bonds after the ordinary drying of aqueous nanocellulose dispersions.

■ MATERIALS AND METHODS

Materials. A never-dried softwood bleached kraft pulp (SBKP) containing approximately 90% cellulose and ~10% hemicelluloses was used as the cellulose sample.[17,20] Laboratory grade TEMPO, sodium bromide (NaBr), 12% sodium hypochlorite (NaClO) solution, and TBA were used as received from Wako Pure Chemicals Industries (Osaka, Japan).

Preparation of TOCN Dispersions. TOCNs were prepared from SBKP according to a previously reported method.[20] The fibrous TEMPO-oxidized cellulose had a carboxylate content of 1.3 mmol/g, which was measured using the conductivity titration method.[26] Some of the TEMPO-oxidized cellulose was mechanically disintegrated in water to prepare a 0.1% TOCN dispersion, and this TOCN dispersion was then concentrated to ~0.7% using a rotary evaporator. TOCN/water/TBA dispersions with various water/TBA weight ratios were prepared by adding designed amounts of water and TBA to the ~0.7% aqueous TOCN dispersion. The TOCN/water/TBA dispersions were then stirred vigorously for 5 min.

Preparation of Aerogels. Each TOCN/water/TBA dispersion (1 g) was poured into a 5 mL glass bottle with a screw cap, and was frozen by soaking the bottle in liquid nitrogen. The cap of the bottle was slightly loosened, and the bottle was set in a chamber at −20 °C for freeze-drying. The frozen sample was sublimated overnight in a freeze-dryer (VD-250F TAITEC, Tokyo, Japan) at −20 °C, under a pressure of 15 Pa, to prepare a TOCN aerogel. The vacuum chamber and samples were stored at approximately −20 °C, to avoid collapse of the dispersion solvents during freeze-drying.[27]

Preparation of TOCN Aerogel-Containing Air Filters. A nonwoven mat of borosilicate microglass fiber (Hokutsu-Kishu Paper, Tokyo, Japan) was used as a normal HEPA-grade filter; this filter had a pressure drop (ΔP) of ~300 Pa, a basis weight of 66 g/m^2, and a sheet size of 14 cm square. A 0.01% w/w TOCN dispersion in water or water/TBA (at 30% w/w TBA) was sprayed on the HEPA filter at a distance of ~15 cm between the spray nozzle and filter, and the dispersion-attached filters were freeze-dried using the same

procedure as that used to prepare the aforementioned TOCN aerogels. The amounts of the dispersion attached to the HEPA filter were measured from the weight increase after spraying, and the dry weights of TOCN attached to the filter were calculated from the TOCN content of the dispersion and the dispersion weights attached to the filter. The filter efficiency and pressure drop values were measured in a laboratory-made filter test apparatus that consisted of a particle generation unit, a filter holder, and a laser particle counter (LASAIR-1001: PMS Diecasting, Bramley, UK). Particles of poly α-olefin (Durasyn 164: BP Group, Tokyo, Japan), generated using a nebulizer, were used as a standard oil aerosol. The filter holder had an inner diameter of 113 mm, and the airflow was drawn through the filter using a vacuum pump. The flow rate through the filter was set to 32 L/min, or a face flow velocity of 5.3 cm/s. The particle penetration ratio (P, eq 1) was calculated from the upstream ($C_{upstream}$) and downstream ($C_{downstream}$) particle concentrations, which were detected using the laser particle counter; the upstream particles were diluted to 1/100 using an air dilution device (KD-06: RION, Tokyo, Japan). The particles were classified quantitatively into the three fractions 0.10−0.15 μm (average 0.125 μm), 0.15−0.20 μm (average 0.175 μm), and 0.20−0.30 μm (average 0.250 μm), depending on the particle size; this classification was achieved using software attached to the laser particle counter. The pressure drop (ΔP, eq 2) was determined from the upstream and downstream pressures, $P_{upstream}$ and $P_{downstream}$, using a manometer connected to the upstream and downstream ports. Quality factors (QFs; eq 3) are typically used to achieve a quantitative evaluation of fibrous filter performance. The QF values are independent of the thickness, porosity, and pressure drop of filters.[9]

$$P = C_{downstream}/C_{upstream} \tag{1}$$

$$\Delta P = P_{upstream} - P_{downstream} \tag{2}$$

$$QF = -\ln(P)/\Delta P \tag{3}$$

Analysis. The moisture content of TOCN aerogels was measured by heating the samples at 105 °C for 5 h, after conditioning at 23 °C and 50% relative humidity for 2 days. The light transmittance spectra of the TOCN/water/TBA dispersions were measured in the wavelength range from 300 to 800 nm, using a spectrophotometer (UV-1650PC Shimadzu, Tokyo, Japan). The TOCN aerogels subjected to SSA measurements were prepared in sample tubes, to avoid any contact with humid air. The 0.3−0.6% w/w TOCN dispersion (2.0−2.5 mL) was poured into the tube, and then frozen with liquid nitrogen. The frozen sample in the tube was sublimated using the same procedure as that used for the TOCN aerogel preparation described in the section just above. After sublimation, the aerogel samples (0.08−0.14 g) were degassed in an VacPrep 061 instrument (Micromeritics, GA, USA) at 105 °C for 5 h, and this was followed by N$_2$ adsorption performed at −196 °C. The SSA of the TOCN aerogels was measured using a nitrogen adsorption apparatus (Tristar 3020 II: Micromeritics, GA, USA). The Brunauer−Emmett−Teller SSA was determined from the N$_2$ adsorption isotherms, at relative vapor pressures of 0.03−0.3. Scanning electron microscopy (SEM) images were obtained using a field-emission-type microscope (SU8010: Hitachi High-Tech, Tokyo, Japan) operated at 1 kV. The SEM observation samples were coated with osmium before analysis, using an osmium coater (Neo: Meiwafosis, Tokyo, Japan) operated at 10 mA for 5 s. The thickness of the osmium layer was estimated to be ~2.5 nm under the conditions used.

■ RESULTS AND DISCUSSION

Preparation of TOCN/Water/TBA Dispersions. In general, nanocelluloses such as TOCNs or sulfonated cellulose nanocrystals (CNCs) form stable dispersions in water, because of the dissociation of the ionic groups. However, neither TOCNs nor CNCs are dispersible at the individual nanofibril or nanocrystal level in organic solvents with low polarities such as TBA, that can be used for freeze-drying.[24] In preliminary

experiments, however, we found that the direct freeze-drying of TOCN/water/TBA dispersions yielded TOCN aerogels with large SSAs of >310 m^2/g. No time-consuming steps such as centrifugation or solvent exchange were required in this case. Thus, TOCN dispersions in water/TBA mixtures were prepared via the direct addition of TBA to as-prepared aqueous TOCN dispersions. Figure 1 illustrates the process used to prepare the TOCN aerogels.
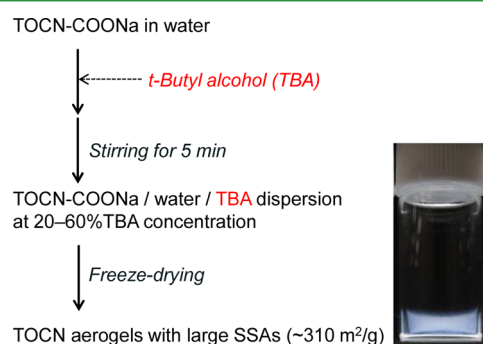

Figure 1. Scheme for the preparation of TOCN aerogels from TOCN/water/TBA dispersions.

Nanodispersibility of TOCNs in Water/TBA Mixtures. With the criterion of the individual dispersibility of nanomaterials in solvents in mind,[28] photographs of the TOCN/water/TBA dispersions were taken with and without cross-polarizers, to evaluate the upper limit of TBA concentration at which the nanodispersibility of the TOCNs in the mixtures could be maintained without agglomeration (Figure 2). The TOCN/
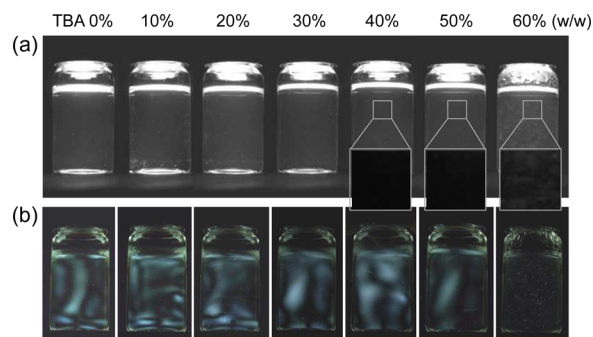

Figure 2. Photographs of 0.1% TOCN dispersions in water/TBA mixtures with 0−60% TBA (a), and corresponding photographs taken between cross polarizers (b).

water/TBA dispersions maintained high transparency and showed birefringence at TBA concentrations up to 40% w/w TBA, similar to the original TOCN/water dispersion. Small, gel-like, and agglomerated particles of TOCN were observed in the 50% TBA mixture. The 60% TBA mixture clearly showed gel-like particles formed from TOCN agglomerates. Birefringence was observed for the 0−50% TBA mixtures; however, no birefringence was observed for the 60% TBA mixture, showing that 50% TBA was the maximum TBA concentration at which the original nanodispersibility of TOCNs could be maintained at the individual nanofibril level in the water/TBA mixture. At TBA concentrations >50%, it is likely that the sodium carboxylates of the TOCNs were not able to dissociate in the water/TBA mixture, because of its low dielectric constant.

The light-transmittance spectra for the TOCN/water/TBA dispersions are shown in Figure 3. The 50% and 60% TBA
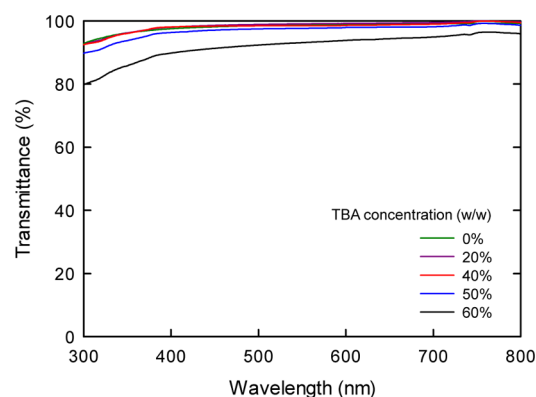

Figure 3. UV−vis transmittance spectra for 0.1% TOCN dispersions in water/TBA mixtures at various TBA concentrations.

mixtures showed transmittances of 98 and 94% at 600 nm, respectively, whereas the others showed values as high as 99%. The light transmittances of the dispersions shown in Figure 3 remained unchanged after being held at 50 °C for 2 days after preparation. The TOCN/water/TBA dispersions with 0−40% TBA maintained their high transparency and birefringence behavior at room temperature for more than 6 months. These results also supported the conclusion that the stable nanodispersibility of the TOCNs was achieved in the TBA concentration range of 40−50%.

SSA Values of TOCN Aerogels. The TOCN aerogels, which were prepared via the freeze-drying of TOCN/water/TBA dispersions with 0−60% TBA, had moisture contents of 14−16% after conditioning at 23 °C and 50% relative humidity. No clear relationship was observed between the moisture content of the TOCN aerogels and the TBA concentration in the dispersions. The SSA values of the TOCN aerogels were determined directly after freeze-drying, without conditioning.

As shown in Figure 4, the SSA of the TOCN aerogels prepared using freeze-drying significantly increased from 94 to 319 m^2/g when the TBA concentration was increased from 0 to 20%. Large SSA values of 301−319 m^2/g were obtained for the TOCN aerogels prepared from TOCN/water/TBA dispersions with 20−50% TBA. The SSA of the TOCN aerogel prepared
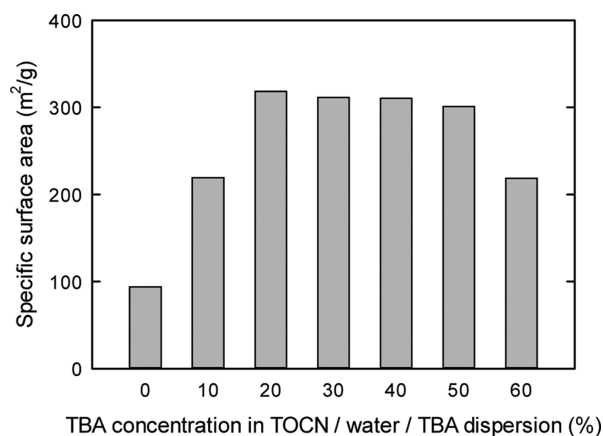

Figure 4. Specific surface area of the TOCN aerogels, estimated using the nitrogen adsorption method.

using the TOCN/water/TBA dispersion with 60% TBA was smaller (219 m²/g). The large SSA values for the TOCN aerogels prepared directly from the TOCN/water/TBA dispersions with 20−50% TBA were comparable with those (340−350 m²/g) determined for the aerogels prepared from the aqueous TOCN dispersion via complete solvent-exchange to TBA through ethanol.[17] When 100% aqueous TOCN dispersions were freeze-dried, micrometer-sized ice crystals formed during the freezing step, resulting in the condensation of TOCNs around each ice crystal.[29] Laminated TOCN layers formed around the voids, resulting in aerogels with small SSA values.

The large SSA values of the TOCN aerogels prepared via the freeze-drying of the TOCN/water/TBA dispersions with 20−50% TBA were thought to result from the efficient prevention of the growth of micron-sized ice crystals during the freezing process. Kasraian and DeLuca, as well as Daoussi et al., reported that aqueous mixtures with 15−20% TBA behaved as eutectic compounds, in which the crystal size of TBA/water in the frozen state is the smallest.[30,31] The freeze-drying was carried out for the sample bottles in a chamber at −20 °C to avoid collapse of TOCN aerogels, because the metastable eutectic point of water/TBA mixtures was approximately −10 °C.[30] Crystals of TBA hydrates were formed for the aqueous 30−60% TBA mixtures using freezing.[32] The gradual freezing of the TOCN/water/TBA dispersions did not provide the TOCN aerogels with SSA values as large as those shown in Figure 4, showing that the freezing temperature was a key factor; rapid freezing of the dispersions at temperatures below the TBA/water melting points was required, and liquid nitrogen was therefore used in this study.

The TOCN aerogels prepared from the TOCN/water/TBA dispersions with 20−50% TBA had large SSA values, probably because bulky pure water crystals were not formed. In these cases, it is likely that all water molecules in the mixtures were consumed to form crystals of TBA hydrates.[30] When the TBA concentration in the mixture was 60%, the formation of gel-like TOCN agglomerates likely caused the decrease in the SSA, because of a decrease in the space between the TOCNs. Sehaqui et al. prepared TOCN aerogels from TOCN/water/TBA dispersions with a water/TBA volume ratio of 1:2, which corresponded to ∼61% w/w TBA.[25] When this mixture (which probably contained gel-like TOCN agglomerates as shown in Figures 2 and 3) was freeze-dried directly, the aerogel had a SSA of 254 m²/g, a value similar to that (220 m²/g) obtained in this study using the TOCN/water/TBA dispersion with 60% TBA. When the gel-like TOCN agglomerates were solvent-exchanged with 100% TBA six times, the freeze-dried TOCN aerogel had a SSA of 284 m²/g.[25] Thus, the direct freeze-drying of the homogeneous TOCN/water/TBA dispersions with 20−50% TBA, in which the TOCNs maintained their nano-dispersed state, was the key factor for the preparation of TOCN aerogels with large SSA values of >300 m²/g.

Surface Morphology. SEM images of the surfaces of the TOCN aerogels prepared from 0.1% TOCN dispersions are shown in Figure 5. Micrometer-sized, large pores, and thin TOCN films were present in the TOCN aerogel prepared from the TOCN/water dispersion with 0% TBA; these morphologies were likely caused by the formation of large ice crystals of water. When the TBA concentration in the dispersions was in the range of 20−50%, the TOCN aerogels showed small pores and fine TOCN networks with similar morphologies. The network structures of the aerogels had uniaxially aligned
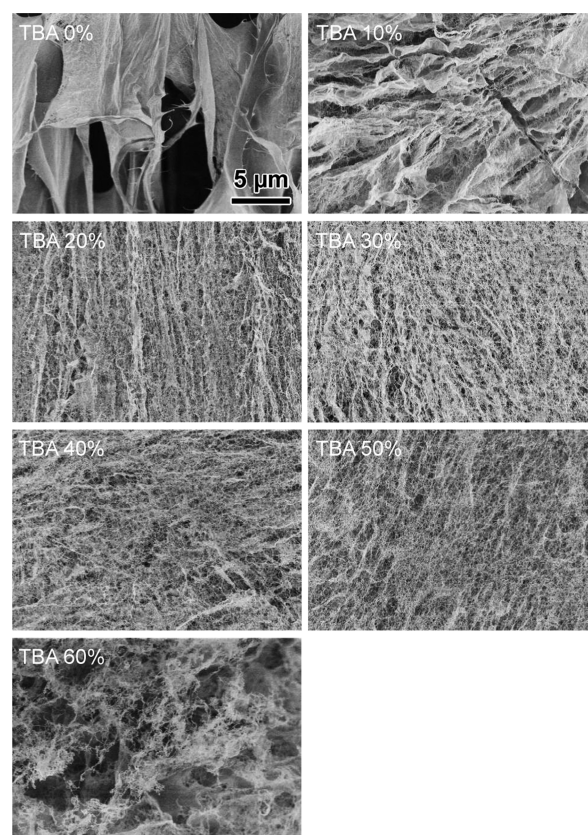

Figure 5. SEM images of the surface of the TOCN aerogels prepared from various TOCN/water/TBA dispersions with 0−60% TBA.

TOCNs, showing that the anisotropic alignment of the TOCNs that were present in the original dispersions (and which formed nematic-like ordered structures) was preserved in the TOCN aerogels.[5,17]

The large SSA values of the TOCN aerogels prepared from the TOCN/water/TBA dispersions with 20−50% TBA (Figure 4) could be explained in terms of the characteristic TOCN morphologies observed in Figure 5. The TOCN aerogel prepared from the TOCN/water/TBA dispersion with 10% TBA showed structures that were intermediate between those shown in the aerogels prepared from the dispersions with 0% TBA and 20% TBA. The aerogel prepared from the dispersion with 60% TBA showed large pores and film-like structures, together with fine TOCN networks. The SEM images in Figure 5 indicate that ice crystal sizes of several micrometers for the TOCN aerogels prepared with 0% TBA decreased several or several dozen nanometers for the TOCN aerogels prepared with 20−50% TBA.

Performance of TOCN Aerogel-Containing Air Filters. Nanosized fibers have the potential to enhance filtration efficiency, as a result of the lower pressure drops and higher ratios of particle capture produced by the diffusion mechanism.[9,10] Thus, TOCN aerogels with large surface areas and nanosized fibrous structures, obtained in the previous sections, are expected to be applied as novel air filters with high filter performance. Even though the TOCN dispersion was concentrated to ∼0.7% using a rotary evaporator for measurement of SSA values of TOCN aerogels in the previous sections, such evaporation is not required in preparation of the TOCN aerogel-containing air filters. We prepared TOCN aerogel-containing air filters by spraying the TOCN/water dispersions

Table 1. Air Filter Properties of HEPA-Grade Base Filter and TOCN Aerogel-Containing Filters

| TOCN dispersion before freeze-drying | TOCN content (g/m^2) | pressure drop (Pa) | | particle penetration ratio[a] | | |
		original base filter	TOCN-containing filter	[a] (10^{-3}%)	[b] (10^{-3}%)	[c] (10^{-3}%)
(reference)	0	305		40.1	21.8	6.7
water	0.005	298	298	43.1	19.7	5.0
water	0.015	299	303	36.9	15.4	4.1
water	0.030	299	305	39.6	15.9	4.1
water/TBA [d][b]	0.005	299	317	9.3	4.5	1.3
water/TBA [d]	0.015	299	329	3.2	1.2	0.3
water/TBA [d]	0.031	300	348	0.4	0.2	0.1

[a]Average particle sizes: [a] 0.125 μm, [b] 0.175 μm, and [c] 0.250 μm. [b][d]: The TBA concentration in the water/TBA mixture was 30% w/w.

or TOCN/water/TBA dispersions with 30% TBA and different TOCN contents on a base HEPA-grade filter consisting of glass fibers, and performing subsequent freeze-drying. Because commercial air-filters require not only filtration efficiency but also other properties such as dimensional stability, moisture-resistance, and high productivity,[8] the glass fibers containing small amounts of TOCN aerogels were prepared and their performances as ULPA- and HEPA-grade filters were evaluated in this study. Neither chemical nor ionic bonds are probably present between the TOCN aerogels and glass fibers in the composites.

Table 1 shows the filter properties of the base filter and the TOCN aerogel-containing filters. The amount of TOCNs added to the base filter was varied from 0.005 to 0.031 g/m^2. When the TOCN/water dispersions were used, the pressure drop and the particle penetration ratio were very similar for the TOCN aerogel-containing filters and the base filter. These results showed that the filters consisting of TOCN aerogels, which were prepared from TOCN/water dispersions and probably had low SSAs, did not improve the filtering efficiency. When the TOCN/water/TBA dispersions were used, the particle penetration ratios of the TOCN aerogel-containing filters prepared from the TOCN/water/TBA dispersions decreased significantly, despite the fact that the increases in the pressure drop were not as significant.

Figure 6 shows the QF values for the TOCN aerogel-containing filters for average particle sizes of 0.125 and 0.175 μm. The QF values show potential capacity as air filters, independent of pressure drop values.[9] The QF values of the TOCN aerogel-containing filters prepared using the TOCN/water/TBA dispersions increased from 0.0256 to 0.0357 and from 0.0276 to 0.0383 for the 0.125 and 0.175 μm particles, respectively. Despite the fact that only small amounts of the TOCN aerogels (from 0.005 to 0.031 g/m^2) were incorporated into the filter, the filter performance was significantly improved, probably because of their large SSA values and nanofibrous structures. These TOCN aerogel-containing filters could be applied as low-pressure-drop ULPAs, which should have 99.999% or higher filter efficiency against 0.1−0.2 μm particles (Supporting Information). This is the first demonstration that nanocelluloses can improve the quality factor of conventional HEPA or ULPA filters. Thus, TOCN aerogel-containing filters have the potential to capture efficiently fine particles.

The results in Figure 6 also illustrate another advantage of the TOCN aerogel-containing filters with a lower pressure drop, which is demonstrated from the QF data by calculation. For example, the pressure drop could be reduced from 300 to 219 Pa (reduction of 27%) via the addition of 0.031 g/m^2 of TOCN aerogel to the base filter, while maintaining the base filter's particle penetration ratio of 0.0401% against particles
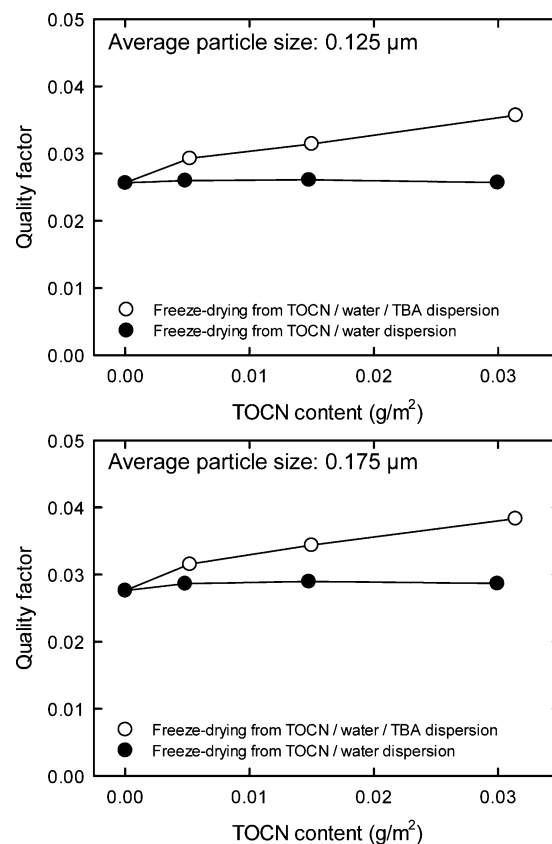

Figure 6. Quality factor of TOCN aerogel-containing filter as a function of the TOCN content, shown for different average particle sizes.

with an average size of 0.125 μm. This was demonstrated in the results shown in Figure 6, which also illustrate the superior filter performance of the TOCN aerogel-containing filters. Thus, the TOCN aerogel-containing filters have the potential to reduce energy consumption in air filtering systems, as a result of the lower pressure drop. TOCN aerogels are excellent materials for air filters, and can significantly improve the air filter performance.

Figure 7 shows SEM images of the base filter and the TOCN aerogel-containing filters prepared using a TOCN/water dispersion and a TOCN/water/TBA dispersion with 30% TBA. The TOCN content was ∼0.03 g/m^2 in both TOCN aerogel-containing filters. The TOCN/water dispersion caused the formation of film-like agglomerates of TOCNs between the glass fibers, resulting in no clear improvement in the QF values. In contrast, fine and spider-web-like network structures were preserved in the glass fibers when the TOCN/water/TBA was
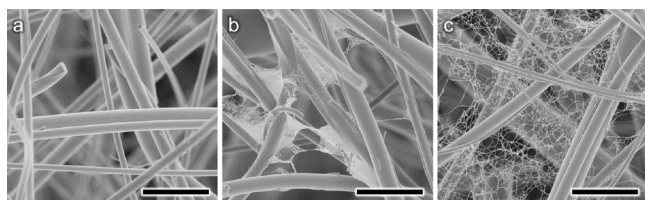
Figure 7. SEM images of the surfaces of the base filter (a), the TOCN aerogel-containing filters prepared with TOCN/water dispersions (b), and TOCN/water/TBA dispersions (c). The scale bar represents 3 μm.

used. However, relatively large pores with diameters >1 μm were also observed in Figure 7c, indicating that the coverage of the glass fibers with TOCN networks was not perfect. Thus, opportunities remain for the further improvement of the filtering efficiency of the TOCN aerogel-containing filters. Moreover, long-term stability of the filtration efficiency and moisture resistance of the TOCN/glass fiber composite air-filters prepared in this study should be studied in future.

CONCLUSION

TOCN aerogels with large SSAs (where the SSA values were similar to those of aerogels prepared via complete solvent-exchange from TOCN/water dispersions to TOCN/TBA dispersions) were prepared simply via the addition of TBA to aqueous TOCN dispersions, and subsequent freeze-drying. When the TBA concentration of the water/TBA mixtures was lower than 40% w/w, the TOCNs were homogeneously dispersed at the individual nanofibril level in the water/TBA mixtures. TOCN/water/TBA dispersions were impregnated into base filters to produce ULPA-like air filters with high filter performance, demonstrating TOCN aerogel-containing air filters as one of the promising applications for these TOCN aerogels. The TOCN aerogel-containing filters showed similar pressure drops, but significantly lower particle penetration ratios, in comparison with a base filter, and TOCN aerogel-containing filters prepared with TOCN/water dispersions. This was because fine and spider-web-like network structures of TOCNs with large SSAs were formed in the spaces between the glass fibers in the filter when the TOCN/water/TBA dispersions were applied to the base filter and subjected to freeze-drying. This is the first example of nanocelluloses significantly improving the air filter quality of conventional HEPA or ULPA filters.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b05841.

Detailed filtration efficiencies of the TOCN aerogel-containing filters (PDF).

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Notes

The authors declare no competing financial interest.

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