

Supporting Information

Preparation of Aqueous Dispersions of TEMPO-Oxidized Cellulose Nanofibrils with Various Metal Counterions, and Their Deodorant Efficiencies

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EXPERIMENTAL SECTION

Materials

Fibrous TEMPO-oxidized cellulose (TOC-Na) with a sodium carboxylate content of 1.4 mmol g^{-1} was produced from softwood bleached kraft pulp, and kindly provided in a never-dried state by the Nippon Paper Industries Co., Tokyo, Japan. This TOC-Na had almost no aldehyde groups. Distilled water, copper(II) acetate, cobalt(II) acetate, zinc acetate, calcium acetate monohydrate, aluminum(III) chloride hexahydrate, silver acetate, and other chemicals were laboratory grade (Wako Pure Chemicals Ltd., Tokyo, Japan) and used as received.

Methods

Preparation of fibrous TOC-M. The fibrous TOC-Na (1 g dry weight) was suspended in water (1 L), and aqueous 0.1 wt% copper(II) acetate (380 g) solution or aqueous 0.1 wt% silver acetate solution (350 g) was added to the TOC-Na slurry under gentle stirring. The molar amount of copper(II) acetate or silver acetate added was adjusted to 1.5 times that of sodium carboxylate groups in the TOC-Na. The mixture was stirred for 3 h to achieve ion exchange of TOC-Na to TOC-Cu or TOC-Ag. The fibrous TOC-M was repeatedly washed thoroughly with water by centrifugation. The prepared fibrous TOC-Cu and TOC-Ag were suspended in water at a 0.1% TOC-M concentration, and used for gas-adsorption tests.

Preparation of TOCN-Na and TOCN-M. Fibrous TOC-Na (1 g dry weight) was added to distilled water (1 L) and was converted to completely nanodispersed TOCN-Na (0.1 wt% TOCN-Na in water) by disintegration and subsequent centrifugation, according to a previously reported method.¹

Two methods were used to prepare TOCN-M/water dispersions from TOCN-Na (Figure 1 in the main text). In method A, a 0.1 wt% metal acetate or AlCl_3 solution was added to a 0.1% TOCN-Na/water dispersion, and the mixture was stirred for 3 h to exchange sodium carboxylate ions for metal carboxylate groups. The molar ratio of metal ions/sodium carboxylate groups in TOCN-Na was adjusted to 1.5–1.6. Agglomerated gel particles were formed in the mixture because of the salting-out effect. The

gel particles were washed five times with distilled water to remove excess metal salt by centrifugation. During washing, part of the TOCN-M fraction formed by nanodispersion in water was removed, which decreased the TOCN-M yield. The remaining gel particles were disintegrated in water using an ultrasonic homogenizer for 2 min. The mixture was centrifuged to remove the non-fibrillated fraction; the supernatant consisted of TOCN-M_A/water dispersion.

In method B, 1 N HCl solution was added to a 0.1 wt% TOCN-Na/water dispersion to adjust the pH to ~2, and the mixture was stirred for 1 h. Agglomerated gel particles with protonated carboxyl groups, i.e., TOCN-H, were formed in the mixture. These gel particles were washed five times with distilled water by centrifugation. A 0.1wt% metal acetate or AlCl₃ solution was added to the TOCN-H agglomerated gel particles/water mixture, and the mixture was stirred for 3 h for ion exchange of protonated carboxyl groups for metal carboxylate groups. The molar ratio of metal ions/protonated carboxyl groups in TOCN-H was adjusted to 1.5–1.6. The mixture was centrifuged five times with distilled water by centrifugation to remove excess metal salt. During washing, part of the TOCN-M fraction formed by nanodispersion in water was removed, which caused a decrease in the TOCN-M yield. The residual gel particles were sonicated in water for 2 min and centrifuged to remove the non-fibrillated fraction; the supernatant consisted of the TOCN-M dispersion.

Gas-adsorption tests using TOCN-M/filter paper or TOC-M/filter paper. A TOCN-M/water dispersion or fibrous TOC-M/water slurry was homogeneously spread and adsorbed on a filter paper of diameter 150 mm. The filter paper was dried at room temperature for 2 d or at 105 °C for 3 h in an oven. The metal contents of all the filter paper samples containing TOCN-M and TOC-M were adjusted to ~0.002 mmol. The filter paper was sealed in a plastic bag of air (5 L) containing 54 ppm H₂S or 58 ppm CH₃SH. The bag was kept at 23 °C and 50% relative humidity. Air samples were removed from the bag at designated and the H₂S or CH₃SH concentration in air was determined using a detector tube (Gas Detector Tubes IM004LLJ2 and IM0071J3, respectively, Gastec, Japan).²

Analyses. The solid TOCN concentrations in the dispersions were calculated from the dry weights of the dispersions after heating at 60 °C for 3 d in an oven. Carboxylate content of the fibrous TOC was determined by electric conductivity titration.³ The nanodispersibilities of the TOCN-M/water dispersions were confirmed from their light transmittances and birefringence behavior observed between cross-polarizers.⁴ The TOCN-M/water dispersions were diluted with distilled water, dropped on a freshly prepared mica plate, and dried at room temperature. The mica surface was examined using an atomic force microscope (Nanoscope III Multi-mode, Digital Instruments, USA) in tapping mode. TOCN-M/water dispersions were cast on petri dishes and dried at 40 °C for 2 d to prepare TOCN-M films. An FT-IR spectrometer (FT/IR-6100, JASCO, Japan) was used to record FT-IR spectra of the

dried TOCM-M films.¹ The metal contents of the TOC/water slurries and TOCN-M/water dispersions (~0.5 g each) were determined using inductively coupled plasma atomic emission spectroscopy (SPS 5100, SII NanoTechnology Inc., Japan), after wet degradation with concentrated H₂SO₄ and HNO₃ and dilution to 10 mL with water, using calibration lines of the metal ions used.⁵ The acetate and chloride ion contents of TOCM-Ag/water and TOC-Ag/water slurries were determined at 20 °C using an electrophoresis apparatus (G1602BA, Agilent Technology, Japan) at –25 kV with a capillary of effective length 72 cm and inner diameter 75 µm, and an Agilent buffer consisting of organic acids. The acetate and chloride contents of these samples were determined using an indirect light-absorption method.⁶ The concentrations of acetate and chloride ions in the TOCN-M/water dispersions (except TOCN-Ag or TOC-Ag) were determined, after dilution to 10 times with water, using ion chromatography (DX500, Dionex Corporation, USA, with AS12A and AG12A columns).⁷ A solution of 2.7 mM Na₂CO₃ and 0.3 mM NaHCO₃ was used the eluent at 1.5 mL min^{–1} at 35 °C. The zeta potentials of the TOCN/water dispersions were measured using a zeta potential measurement apparatus (Delsa Nano HC, Beckman Coulter, Japan).⁸ The metal and sulfur components in the filter papers used in the gas-adsorption tests were determined using an energy-dispersive X-ray fluorescence analyzer (EDX-8000, Shimadzu, Japan).¹

RESULTS AND DISCUSSION

Mechanism of nanodispersion in water of TOCN-M, prepared using ion exchange.

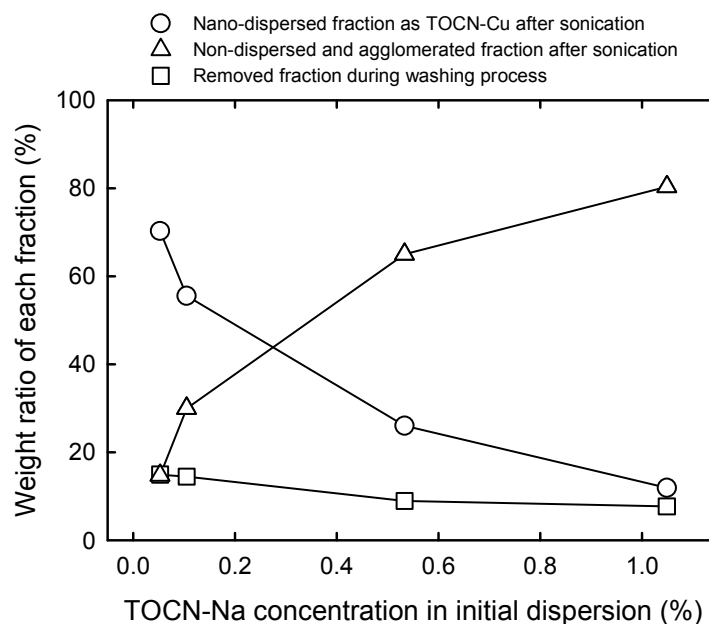


Figure S1. Weight ratios of three fractions, i.e., nanodispersed TOCN-Cu, agglomerated and non-dispersed TOCN-Cu, and TOCN-Cu removed during washing with water, prepared from TOCN-Na/water dispersions at various initial TOCN-Na concentrations using method A.

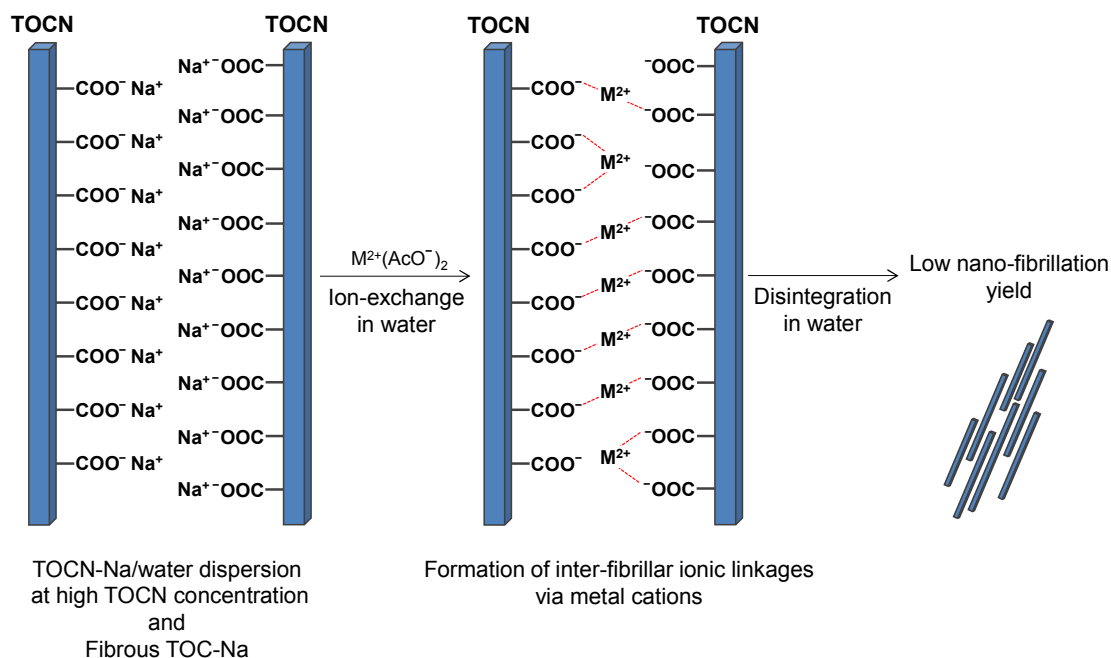


Figure S2. Schematic diagram of counterion exchange of Na^+ for M^{2+} (method A) for fibrous TOC-Na and TOCN-Na/water dispersions at high TOCN concentration.

Gas-adsorption behavior of TOCN-M containing filter paper prepared by drying at room temperature.

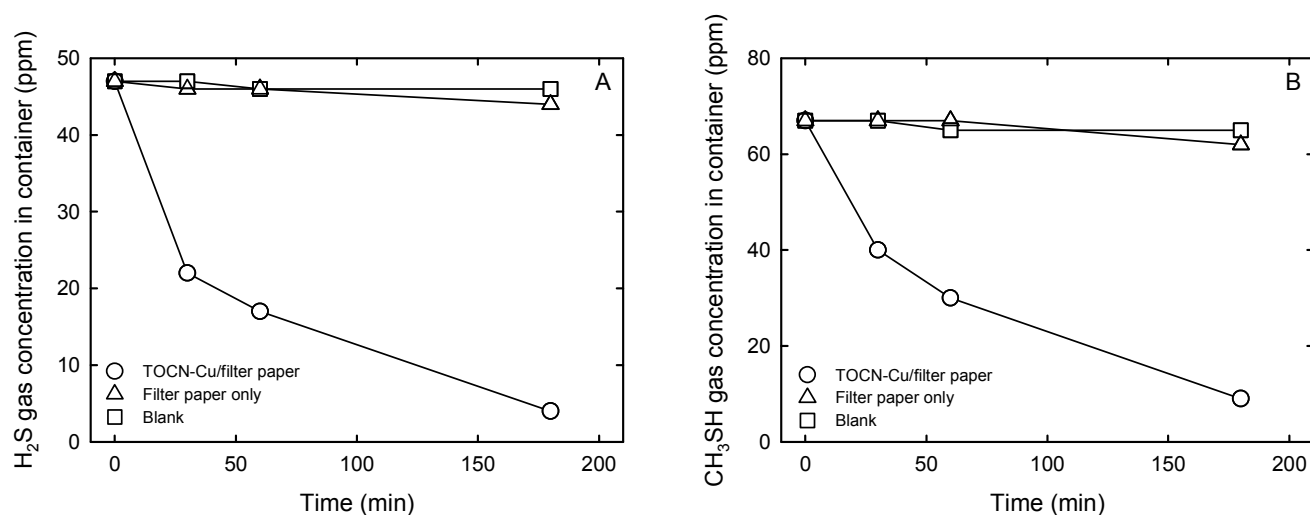


Figure S3. H_2S (A) or CH_3SH (B) gas-adsorption behavior of TOCN-Cu-containing filter paper prepared by drying wet TOCN-Cu-containing filter paper at room temperature.

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