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Doctoral Dissertation

Functionalization of Cellulose Nanopaper
for Eco-friendly Sensor Devices

(環境調和型センサデバイスに向けた
セルロースナノペーパー機能発現)

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General Introduction

1. Background

In recent years, efforts have been made to use highly accurate and dense sensing of environmental information in various fields. Sensor devices having sensing and information transmission functions are indispensable for the monitoring of environmental information. A high-density sensor network comprising a large number of sensor devices installed in the environment would improve the efficiency of maintenance and management of various facilities, and social systems and contribute to the realization of a safe and sustainable society. For example, the following cases have been reported.

Agriculture: Environmental information such as temperature, humidity, and soil moisture content are very important in agricultural operations. By installing sensor devices throughout the field or directly on crops, various information can be collected to improve efficiency of crop production. For example, irrigation systems that utilize temperature, humidity, and soil-moisture-content information obtained from sensor devices installed in the soil have been reported.^{1,2} Monitoring of growth status using sensors directly attached to crops is also being attempted.^{3,4} Farming based on the information gathered by these sensors is expected to be more efficient than conventional farming based on senses and conventions of skilled farm workers.

City Management: Sensor devices are beginning to play an important role in city management. The collection of location information via sensor devices embedded in cars, buses, and other vehicles has facilitated the provision of accurate navigation to drivers and passengers.⁵ Efforts to automatically detect and collect information regarding exhaust gases emitted from automobiles and other vehicles using sensor devices are also underway.⁶ By attaching strain sensor devices to large structures such as bridges and buildings, it is possible to determine the degree of aging of the building and to streamline the maintenance period.⁷ Furthermore, sensor devices are also effective as disaster countermeasures. They contribute to safe and fast information gathering in various situations, such as the detection of landslides⁸ and earthquakes⁹ by installed sensor devices, detection of radiation levels by radiation detectors,¹⁰ and detection of wildfires.¹¹

Logistics: With the advent of lightweight and compact sensor devices, logistics has become increasingly efficient. Sensor devices attached to products or pallets for transportation transmit their location over time, thus contributing to the optimization of logistics and inventory management.¹² Sensors that can be attached to food to measure freshness would also improve quality control and help reduce food loss.¹³

These initiatives and trends, also known as the Internet of Things (IoT), are expected to continue in the future.¹⁴ As exemplified in the field of weather forecasting,¹⁵ environmental information obtained from installed sensor devices is also used for various simulations. The accuracy of the simulation depends on the number of observation points. The increasingly numerous sensor devices will synergize with the latest information processing technologies such as artificial intelligence and deep learning to contribute to the realization of a safe and prosperous society.

2. Electronic and Electrical Wastes (E-Wastes)

In the era of mass production and mass consumption of sensor devices, the increase of e-waste is an issue that cannot be ignored when attempting to realize a sustainable society. E-waste refers to discarded electronic devices, including sensor devices. E-waste is generated annually on an scale of approximately 50 million tons as of 2019, which is an increase of more than 20% compared to that in 2014. Of this, only 17.4% is recycled, and the rest is incinerated or landfilled.¹⁶ The main components of e-waste are plastics, metals, and semiconductors. Plastics do not decompose in the environment and remain semi-permanently after landfilling. In addition, e-waste generally contains heavy metals and gallium arsenide, which are harmful to the human body. E-waste that is disposed in landfills contains toxic substances that gradually contaminate the soil, water, and air, thus becoming a serious environmental problem, especially in developing countries.^{17,18} E-waste will continue to increase owing to the growing demand for electronic devices and is expected to double in the next 16 years.¹⁶ There is a need to reduce e-waste in order to realize a sustainable smart society.

3. Sustainable Materials for Electronic Device

Research on materials as alternatives to non-degradable petroleum-derived plastics, which account for a large portion of the ever-increasing volume of e-waste, is being actively conducted. Electronic circuit boards and dielectrics made of sustainable and biodegradable materials enable rapid decomposition of e-waste after landfill and contribute a reduced environmental impact. The following are examples of alternative materials.

Biodegradable Polymer: Biodegradable polymers, including polylactic acid (PLA), polyvinyl alcohol (PVA), and polyhydroxyalkanoic acid, are considered as electronic device substrates. The results of using these biodegradable polymers as wiring substrates,¹⁹ dielectric layers,^{20,21} and sensor substrates^{22,23,24} have already been reported. The advantages of biodegradable polymers are customizability and moldability. Their various properties, such as heat resistance and mechanical strength, can be controlled,²⁵ and their thermoplasticity makes it easy to mold them into desired shapes. However, its low heat resistance is a major problem in circuit fabrication. The glass transition point of PLA, a typical biodegradable polymer, is approximately 60 °C, but sintering of wires generally requires heat treatment at 120 °C to 150 °C.²⁶ To compensate for the low heat resistance of biodegradable polymers, research is being conducted on wire mounting methods using transfer-²⁴ and-heat-resistance-improvement technologies.²⁷

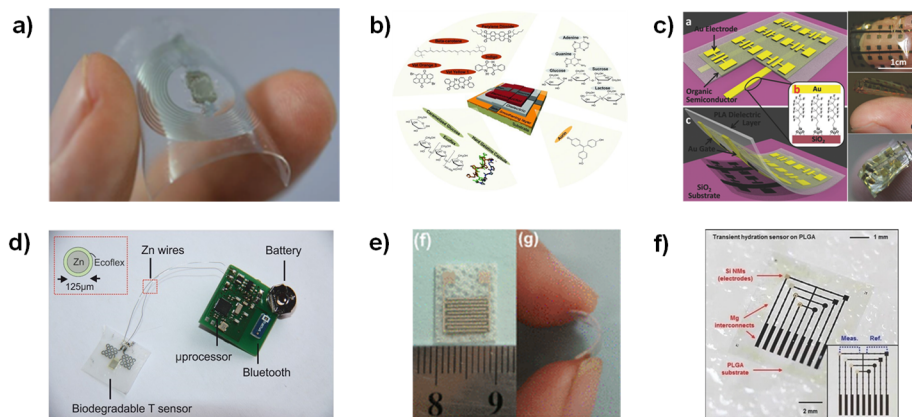


Fig. 1 a), b) Substrates c) dielectric layers, and d), e), f) sensors comprising biodegradable polymers. Reprinted and modified from references 19, 20, 21, 22, 23, 24.

Proteins: There have also been several reports regarding protein-based substrates, including silk fibroin^{28,29} and gelatin.^{30,31} Silk fibroin is a regenerated silk that can be prepared from silk yarn,³² and silk fibroin film has characteristics such as excellent mechanical strength, surface smoothness, and transparency.³³ Silk fibroin has excellent biocompatibility and is attracting attention as a material for in vivo devices. However, as silk fibroin is easily soluble in the majority of solvents, an aqueous circuit manufacturing process or chemical modification should be applied.³³

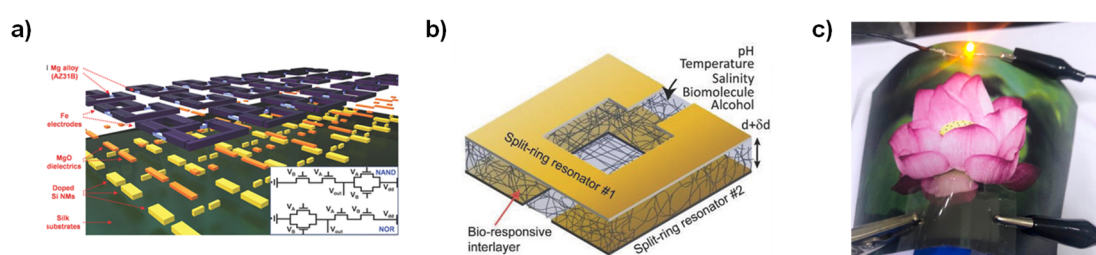


Fig. 2 a) Substrates, b) dielectric layers, and c) transparent conductive films fabricated using proteins such as silk fibroin and gelatin. Reprinted and modified from references 28, 29, 30.

Polysaccharides: Polysaccharides, including cellulose, chitin, chitosan, and alginate, are also promising alternative electronic materials. The advantage of cellulose and chitin is their abundant availability; cellulose and chitin are known to be the most and second most abundant biomass resources, respectively.³⁴ Furthermore, sensors based on cellulose layers^{35,36} and switching memories based on chitosan³⁷ have also been reported.

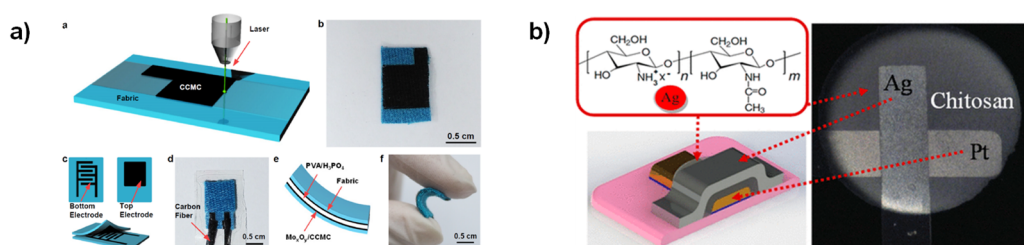


Fig. 3 a) Humidity sensors and b) switching memories fabricated using polysaccharides such as carboxymethyl cellulose and chitosan. Reprinted with permission from references 36, 37. Copyright 2022 American Chemical Society.

Pulp Papers: Pulp paper, manufactured by drying aqueous dispersions of wood-derived cellulose fibers (pulp), is used in a wide range of fields, including writing, printing, sanitary, and packaging paper, and is essential in our daily lives. Pulp paper has an advantage over other alternative materials in that it is cheaper and its mass production technology has been established. There are already many reports on the application of paper in electronic devices such as circuit boards,^{38,39} sensors,^{40,41} and supercapacitors.^{42,43} However, the application of pulp paper to electronic devices is hindered by its porosity and surface roughness. The width of the pulp fibers that make up pulp paper is approximately 10 μm , and there are countless pores in the pulp paper.⁴⁴ Therefore, when fabricating conductive lines and electronic components on pulp paper, a coating agent is often used to smooth the surface.⁴⁵ Multilayer circuit boards comprising multiple layers of pulp paper have also been reported,⁴⁶ but adhesives are required to bond the layers. These coatings and adhesives are mainly manufactured from non-degradable petroleum-derived products, which are undesirable from the standpoint of sustainability and biodegradability. Therefore, instead of using paper as a stand-alone material, attempts have been made to combine it with other alternative materials such as biodegradable polymers.⁴⁷

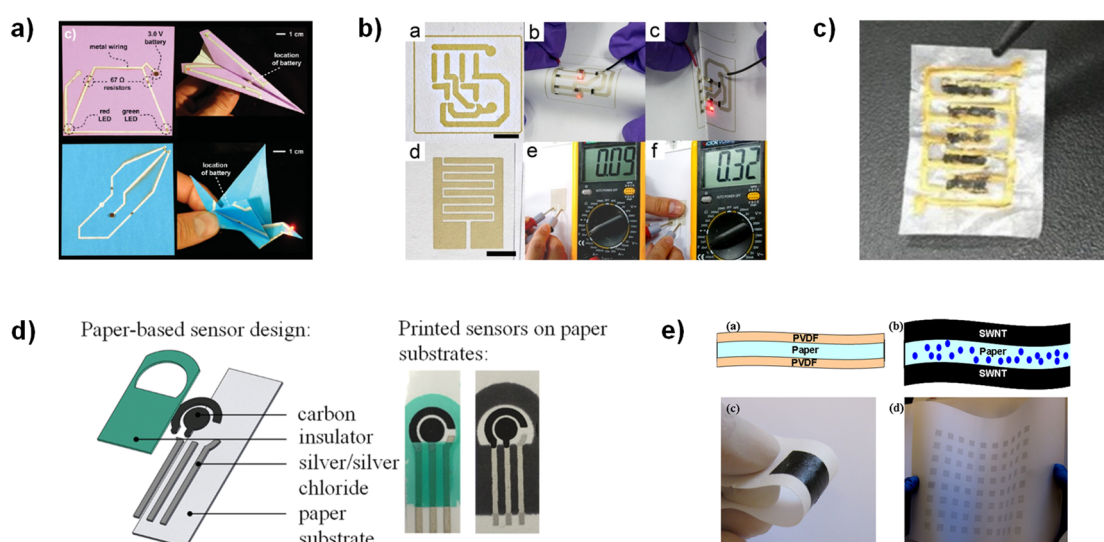


Fig. 4 a), b) Substrates, c), d) sensors, and e) supercapacitors fabricated using pulp papers. Reprinted and modified from references 38, 39, 40, 41, 42.

Cellulose Nanofibers and Nanopapers: Nanopaper^{48,49,50} is one of the most promising sustainable electronic materials. Nanopaper is a film prepared from cellulose nanofibers (CNFs) and was developed around 2008 to 2009. The structure and the preparation method are as same as common paper, therefore, Bergland et al.⁵⁰ and Nogi et al.⁴⁸ used the name "Nanopaper". CNFs can be prepared from wood and other plant tissues via a downsizing process.^{51,52} CNFs are the basic framework of the cell walls of plants as well as wood and are 3–15 nm wide. Trees have a hierarchical structure, and the CNFs synthesized in plant cell walls form cell walls and pulp fibers having a width of tens of micrometers inside the tree. CNFs have excellent properties such as light weight (1.6 g/cm³), high strength (tensile strength: 3 GPa), and low thermal expansion (0.1–0.2 ppm/K).^{53,54,55} Owing to these characteristics, CNFs are being used in various applications such as reinforced plastics.^{56,57,58}

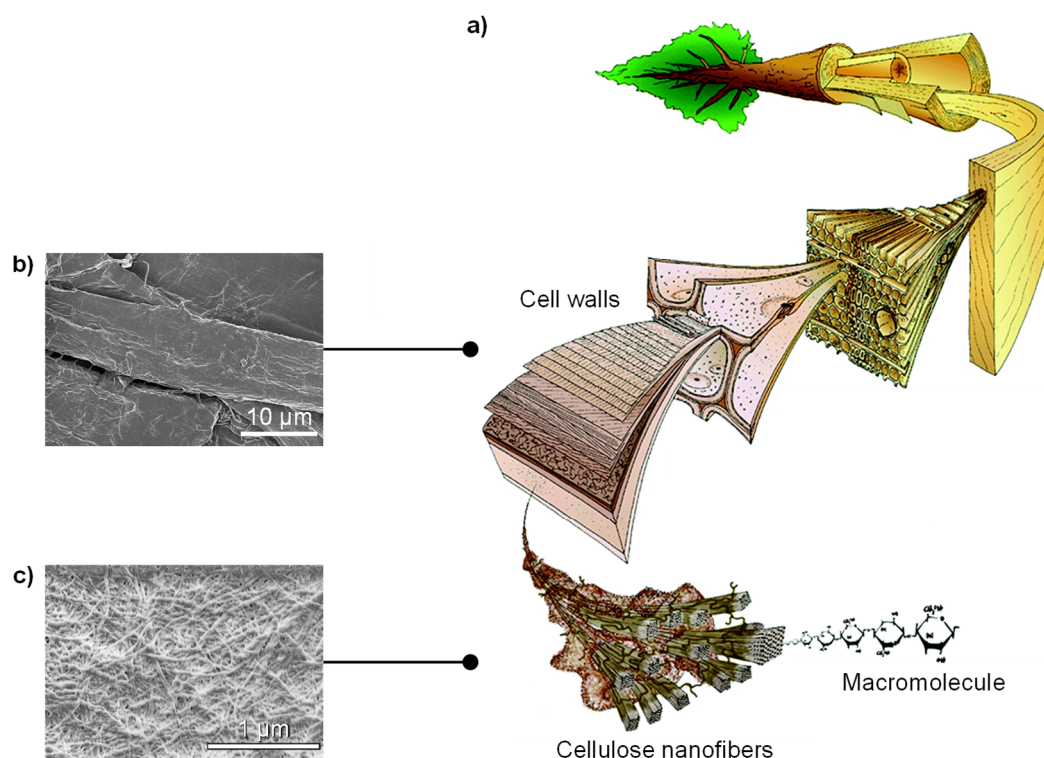


Fig. 5 a) Hierarchical structure from trees to cellulose molecular level (Copyright: University of Canterbury, 1996). b) Softwood-derived pulp fibers and c) CNFs prepared by down-sizing pulp fibers.

The technologies required to isolate CNFs from plant cell walls have been established in the last 15 years, and two such mainstream methods comprise mechanical fibrillation and chemical treatment for fibrillation.^{51,52}

Mechanical fibrillation is a method by which never-dried pulps are converted into CNFs by disintegrating them using powerful equipment such as grinders and water-jet systems.^{51,59} The width of the CNFs thus obtained is approximately 4.4 nm to 15 nm, but it is possible to isolate only CNFs having a width of 4.4 nm via centrifugation.⁶⁰ In the mechanical fibrillation, the condition of the pulp is important. For example, once the pulp has been completely dried, hornification occurs in the pulp, and the CNFs become tightly hydrogen-bonded to each other, resulting in a significant decrease in their disintegration efficiency.^{61,62} It has also been reported that a high hemicellulose content in pulp facilitates the disintegration into CNFs,^{60,61} and a particularly famous preparation technique is the hemicellulose-rich pulp preparation method using peracetic-acid (PAA) treatment.^{60,63} When wood chips are delignified using PAA, the lignin is selectively decomposed and removed, which yields a pulp containing hemicellulose.⁶³ The resulting hemicellulose-rich pulps are efficiently fibrillated into PAA-CNFs via mechanical fibrillation. PAA-CNFs prepared from hemicellulose-rich pulp form a core-shell structure in which hemicellulose covers the periphery of the CNFs; the hemicellulose covering the periphery of the CNFs not only facilitates disintegration but also contributes to improved dispersibility in aqueous dispersion.⁶⁴

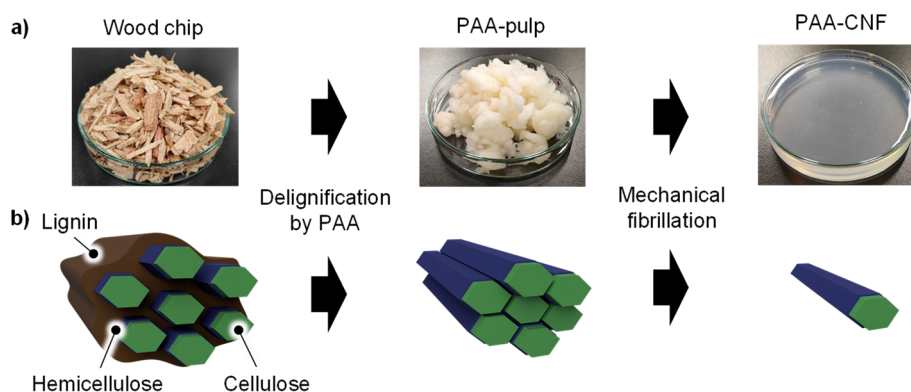


Fig. 6 a) Procedure for preparation of CNF from wood chips with PAA delignification and mechanical fibrillation. b) Schematic representation of PAA-CNFs.

Chemical treatments to obtain pulp, including 2,2,6,6-tetramethylpiperidine-1-oxyl-radical oxidation (TEMPO-oxidation),⁵² are used to improve the efficiency of the mechanical fibrillation process. Industrially mass-produced pulps, such as needle bleached kraft pulp (NBKP), have a low hemicellulose content and are therefore significantly low mechanical fibrillation efficiency.^{61,65,66} However, when NBKP is subjected to TEMPO-mediated oxidation, significant amounts of sodium carboxylate groups are formed by the oxidation of a part of the C6 primary hydroxyls exposed on the CNF surface.^{52,67} TEMPO-oxidized pulps can be fibrillated into TEMPO-oxidized CNFs (TO-CNFs) via mild mechanical fibrillation such as that with a blender and ultrasonic treatment. This is thought to be owing to the high density of sodium carboxylate groups formed on the CNF surface, which causes electrostatic repulsion and electric double-layer repulsion in water.⁶⁷ The carboxylate content introduced onto the CNF surface can be controlled by up to approximately 1.8 mmol/g, and the dispersibility in water depends on the carboxylate content.⁵² TO-CNFs are characterized by their uniform width, dispersibility, and the expression of various properties through ion exchange. In the case of wood pulp as a raw material, a high yield of TO-CNF having a width of approximately 3 nm can be obtained using mild mechanical fibrillation while introducing a large amount of carboxy groups (e.g., 1.5 mmol/g) through TEMPO-oxidation.⁵² Sodium carboxylate groups formed on the surface of CNFs can also adsorb various metal ions via ion-exchange behavior, and hydrogels^{68,69} and heavy-metal-ion extraction⁷⁰ have been proposed for utilizing the metal ion adsorption ability of TO-CNFs.

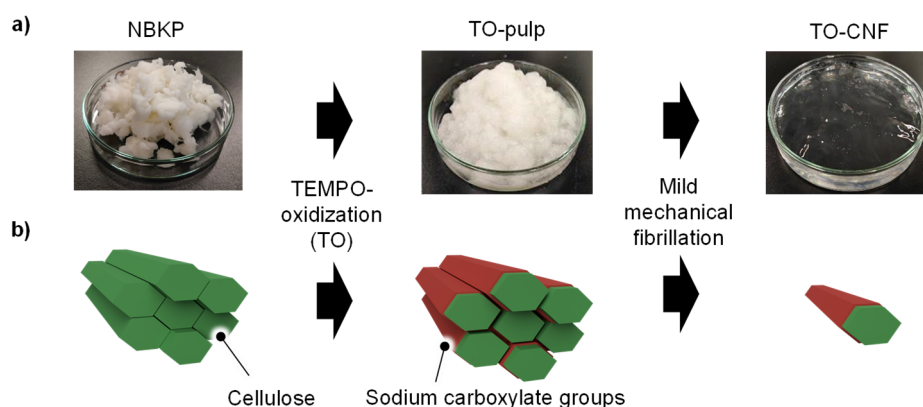


Fig. 7 a) Procedure for preparation of CNF from NBKP, comprising TEMPO-oxidization and mild mechanical fibrillation. b) Schematic representation of TO-CNFs.

Nanopapers can be prepared by drying a dilute CNF/water dispersion. The CNFs dispersed in water become densely packed during drying and eventually form a film having almost no voids. In the case of TEMPO-oxidized

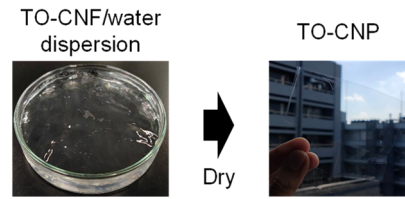


Fig. 8 Preparation of TO-CNP

cellulose nanopaper (TO-CNP) prepared from a TO-CNF/water dispersion and peracetic acid cellulose nanopaper (PAA-CNP) prepared from a PAA-CNF/water dispersion, the fibers are sufficiently fine such that light scattering does not occur, and the resulting nanopaper has a clearly transparent appearance (Fig. 8).^{48,49} In addition, in contrast to pulp paper, the nanopaper has a high surface smoothness.⁷¹ Nanopaper is highly heat resistant and can withstand continuous heating at 150 °C.⁷² In addition, its

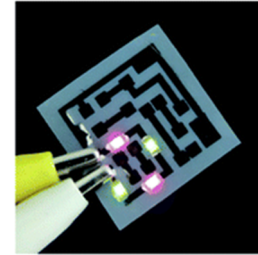


Fig. 9 Conductive lines fabricated on a nanopaper⁷²

coefficient of linear thermal expansion is as low as that of quartz glass (5–6 ppm/K).⁷³ The high heat resistance of nanopaper is important for circuit fabrication (Fig. 9). Nanopaper is also highly solvent-resistant and remains undissolved in common organic solvents.⁷³ Therefore, it is suitable for various circuit mounting technologies and various electronic device components such as substrates,⁷² solar cells,⁷⁴ transistors,^{71,73} memories,⁷⁵ and antennas⁷⁶ using nanopaper have been reported.



Fig. 10. a) Nanopaper-based transistors, b) solar cells, and c) memories. Reprinted and modified from references 73, 74, 75.

Nanopaper is a promising alternative eco-friendly material because it combines excellent suitability for electronic devices with sustainability and biodegradability. However, there have been no reports on nanopaper-based electronic devices that combine nanopaper-based components. This is thought to be owing to issues in nanopaper-based circuit manufacturing that are difficult to solve by only developing the components.

4. Sustainable Circuit Manufacturing Method

As in the case of electronic device materials, there is a need to consider sustainability in circuit manufacturing. Specifically, the key technologies comprise the use of non-toxic solvents, minimization of liquid waste, and low-energy-consumption manufacturing methods on a large scale. As a non-toxic solvent, the use of aqueous solvents has been promoted in recent years. By using aqueous solvents as solvents for battery electrolytes⁷⁷ and coating agents,^{78,79} it is possible to reduce the disposal costs and the environmental impact of solvent evaporation. The drop-on-demand method, used in printed electronics,^{80,81} is attracting attention in circuit manufacturing, which includes the manufacturing of wiring and intermediate layers. The most common methods used in circuit manufacturing are plating and etching (Fig. 11a), which produce large amounts of metal-containing waste liquid. In contrast, printed electronics technology has a minimal environmental impact because it facilitates the fabrication of conductive lines by simply printing conductive ink where necessary and sintering it (Fig. 11b).^{82,83} In printed electronics, various methods such as inkjet printing, screen printing, and laser printing are being considered, and nanopaper has a particularly high applicability in these methods.^{72,76}

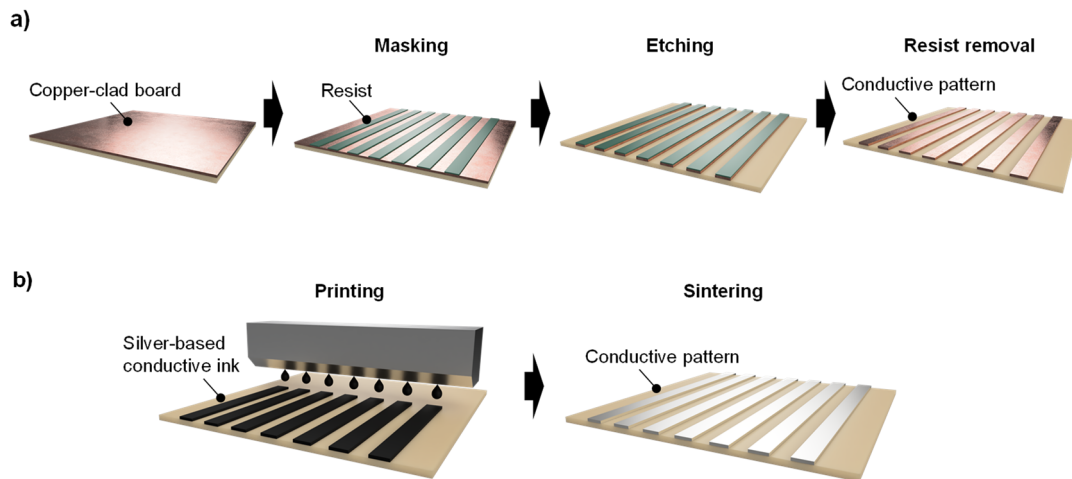


Fig. 11 a) Conventional circuit-pattern manufacturing by subtractive method and b) printed electronics technology (additive method).

5. Purpose and Outline of This Thesis

Nanopaper has many advantages; however, its manufacturing method is required to be optimized, and its application in sensor devices is also required to be addressed, especially in terms of circuit manufacturing and reliability. In this doctoral thesis, the author has focused on the control of the properties and structure of nanopaper and proposes efficient manufacturing methods for nanopaper and nanopaper-based, eco-friendly sensor-device manufacturing technology.

This doctoral thesis consists of an introduction, three parts, and a conclusion, as detailed below.

Chapter 1

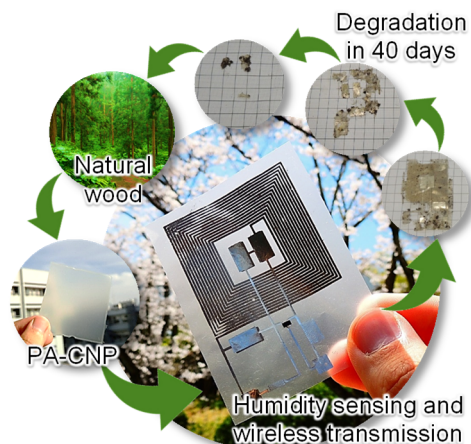
In this chapter, the effect of using a high-concentration CNF/water dispersion as a starting material on nanopaper was investigated. The effects of the starting-material concentration were evaluated for two different types of nanopapers (TO-CNP and PAA-CNP). When the dilute CNF/water dispersion (0.2 wt%) was dried,



transparent nanopapers with a haze of less than 10% were obtained for both the TO-CNP and PAA-CNP, as previously reported, but as the concentration of the starting material was increased, the haze of the PAA-CNP increased. The reason for the worsening of the haze was the inhomogeneous aggregations generated in the CNF/water dispersion, and it was confirmed that the aggregations could be disintegrated by dilution and sonication. It was possible to prepare transparent nanopapers using a highly concentrated CNF/water dispersion as the starting material with an appropriate pretreatment.

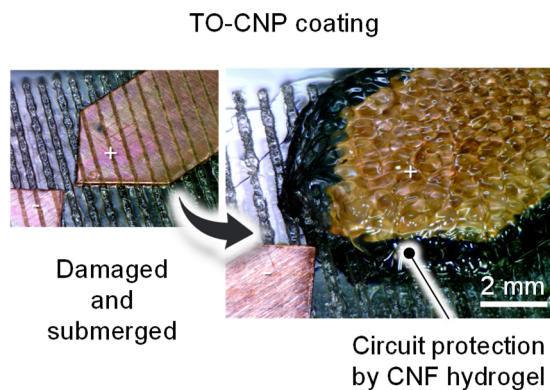
Chapter 2

In this chapter, a wireless humidity sensor device comprising the use of PAA-CNP as the substrate, capacitor dielectric layer, and insulating layer is reported. PAA-CNP has excellent properties not only as a substrate but also as a capacitor dielectric layer, and it could be used to fabricate multiple layers by casting and drying the PAA-CNF/water dispersions. The sensor device developed using the multi-layered PAA-CNP and printed electronics technology not only wirelessly transmitted the relative humidity (RH) information of the environment, but also showed excellent degradability, as more than 95% of its total volume was degraded in the soil.



Chapter 3

In this chapter, the use of a circuit-protection coating based on TO-CNP is proposed to improve the safety of nanopaper sensor devices. Electronic devices, including sensor devices, short-circuit within a few minutes owing to ion migration when wetted by water. However, the electrodes coated with TO-CNP did not short-circuit even after 24 h of water submersion. TO-CNFs, which constitute TO-CNP, redisperse upon wetting and migrate to the anode owing to the electric field between the electrodes and gels, effectively sequestering the copper ions eluted from the anode and inhibiting dendritic precipitation growth. The circuit protection provided by the TO-CNP was effective even when the coating was damaged and can reliably suppress short-circuit failures without compromising environmental compatibility.



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Chapter 1. Preparation of nanopapers using highly concentrated CNF dispersion

1.1 Introduction

Nanopaper has excellent characteristics such as high transparency,^{1,2} smooth surface,³ high heat resistance,^{4,5,6} low linear thermal expansion, solvent resistance,⁷ and biodegradability,^{8,9} which make it suitable as an alternative electronic material for realizing eco-friendly sensor devices. Using the current process, clear transparent nanopaper can be prepared by filtration^{1,2,10,11} or cast-drying^{4,11,12} of a low-concentration dispersion of less than 0.5 wt%,^{1,2,4} both of which are highly energy- and time-consuming, and this process also results in high transportation and storage costs for the dispersion because of the high water load (99.5 wt%). To reduce these costs and the amount of energy consumed, the fabrication of nanopaper should be started from a high-concentration dispersion.

In chapter 1, transparent nanopapers having a low haze and high thermal resistance were fabricated from a highly concentrated CNF/water dispersion. First, the dependence of the haze of the nanopapers on the concentration of the dispersion was evaluated using PAA-CNF and TO-CNF. Next, an appropriate pretreatment for producing transparent PAA-CNP with a low haze from highly concentrated PAA-CNF/water dispersions was clarified. Finally, the crystallinity and heat resistance of the PAA-CNP after the pretreatment were evaluated, and the PAA-CNP were then applied to flexible transparent conductive films.

1.2 Experimental section

Cellulose Pulp

TEMPO-oxidized cellulose pulp (TO-Pulp) was prepared using the steps described in a previous study.¹³ Never-dried softwood dissolving sulfite pulp (dry weight 20 g) was dispersed in distilled water (1500 mL) containing TEMPO (0.16 g) and NaBr (1.0 g). A NaClO solution (4 wt%) containing 0.4, 0.6, or 1.0 mmol/g cellulose (12.4, 18.48, or 30.8 mL) was then added to the cellulose slurry at room temperature under continuous stirring. Peracetic acid pulp (PAA-pulp) was also prepared using the steps described in a previous study.⁵ First, 60 g of Japanese cedar (*Cryptomeria japonica*) wood chips were dewaxed in a mixture of acetone/water (2700 mL/300 mL) at room temperature overnight with gentle stirring. The chips were then delignified in an acetic anhydride/hydrogen peroxide mixture (500 mL/500 mL) at 90 °C for 2 h. Next, the peracetic acid pulp was treated with 5 wt% potassium hydroxide at 20 °C for 2 h before being washed thoroughly with distilled water. The carboxylate content of the pulps was determined by the electric conductivity titration method.¹³

Nanofibrillation

The nanofibrillation of the pulps into nanofibers was performed using a water-jet nanofibrillation system.^{4,5} First, 2000 g of the pulp slurry (pulp content: 0.27 wt%) was homogenized using a high-pressure water jet system (Star Burst, HJP-25008, Sugino Machine Limited, Toyama, Japan) equipped with a ball-collision chamber. The injected slurry was repeatedly passed through a small nozzle with a 0.15-mm diameter under a high pressure of 245 MPa. After 50 passes through this nozzle, a 0.2 wt% CNF/water dispersion was obtained.

Conditioning of CNF/Water Dispersion

The concentration of the CNF/water dispersion was adjusted by condensation using a rotary evaporator (EYELA SB1200, TOKYO RIKAKIKAI CO., LTD., Tokyo, Japan) and/or by water dilution. The 20 mL dispersion was sonicated for 5–30 s using an ultrasonic homogenizer (US-300E, NISSEI CORPORATION, Tokyo, Japan) with a 26-mm probe tip diameter at 19.5 kHz and 300 W

output power. After the dispersion was conditioned by concentration adjustments and/or sonication, it was degassed using a centrifugal mixer (ARV-310, THINKY CORPORATION, Tokyo, Japan) at 1400 rpm for 3 min under vacuum and then at 1800 rpm for 7 min under ambient pressure.

Nanopaper

The dispersion was then cast evenly on an acrylic plate with an applicator. Cellulose nanopapers with thicknesses of $13 \pm 2 \mu\text{m}$ were obtained after subsequent oven-drying (DVS402, Yamato Scientific co., ltd, Tokyo, Japan) at 55°C under 25 %RH overnight. The thickness of nanopaper was measured by a micrometer.

Characterization

The haze of the cellulose nanopaper was measured using a haze meter (HZ-V3, Suga Test Instruments Co., Ltd., Tokyo, Japan). X-ray diffraction patterns were recorded using a MiniFlex600 (Rigaku Corporation, Tokyo, Japan) with $\text{Cu K}\alpha$ radiation and a scanning angle (2θ) range of $5\text{--}40^\circ$ at the 40 kV voltage and 15 mA current. The crystallinity index of cellulose I was calculated from the (200) reflection ($2\theta = \sim 22.6^\circ$), as previously described.⁶ The thermal durability of the nanopaper was evaluated using the 5% weight-loss point. Thermogravimetric analysis (TGA Q50N2, TA Instruments, New Castle, DE, USA) was performed under a nitrogen atmosphere (60 mL/min) at a heating rate of $10^\circ\text{C}/\text{min}$. The surface roughness of the nanopaper was determined using an atomic force microscope (AFM, Nanocute, SII Nano Technology Inc., Chiba, Japan) in the dynamic force microscope (DFM) mode (measurement range: $20 \mu\text{m} \times 20 \mu\text{m}$).

Silver Nanowire and Transparent Conductive Lines

Silver nanowires (50–100 nm in diameter and 5–10 μm in length) were synthesized via the reduction of silver nitrate in the presence of poly(vinylpyrrolidone) (PVP) in ethylene glycol.^{12,14} The silver nanowires were dispersed in ethanol to form printable inks. The silver nanowire/ethanol suspension was dropped onto the transparent nanopaper and then air-dried for 3–5 min. The air-dried silver nanowires on the nanopapers were heated at 150°C for 30 min in the air.^{12,14}

1.3 Results and Discussion

To investigate the dependence of the nanopaper haze on the concentration of the dispersion, TO-CNP having a thickness of 13 μm were prepared from 0.2–1.8 wt% TO-CNF/water dispersions (carboxyl contents of 0.4–1.0 mmol/g). For the TO-CNF containing 1.0 mmol/g carboxyl, all the dispersions (concentrations of 0.2–1.8 wt%) resulted in the production of transparent nanopaper having low haze values of less than 1.9% (Fig. 1-1▲).

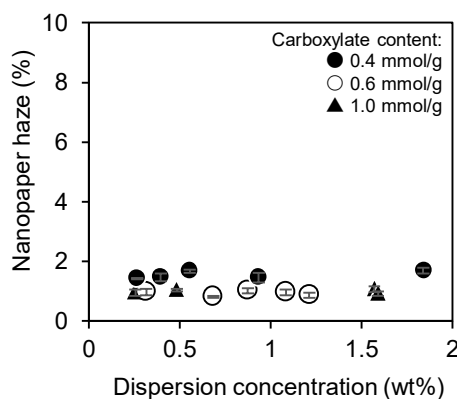


Fig. 1-1 Effect of concentration of starting CNF/water dispersion on haze of 13 μm -thick TO-CNP.

Because of the electric double-layer repulsion, the TO-CNF were homogeneously distributed in the water dispersions without the formation of inhomogeneous aggregations.¹⁵ The CNFs were so densely packed that there were no cavities, which generally causes light scattering either inside the film or at the surface.^{1,3} Even for the carboxyl contents of 0.6 and 0.4 mmol/g, the repulsion of the CNFs was retained. Therefore, the TO-CNP maintained their low haze values of less than 1.9% for all the concentrations (Fig. 1-1●, ○), which indicates that the use of these nanofibers would result in reduced drying, transportation, and storage costs of the dispersion as highly concentrated TO-CNF/water dispersions could be used to prepare low-haze transparent nanopaper.

To investigate the concentration dependence of the resulting haze value, PAA-CNP having a thicknesses of 13 μm were prepared from 0.2–2.2-wt% PAA-CNF/water dispersions (Fig. 1-2). Similar to the results reported in previous studies,^{4,5,6} low haze values of approximately 10% were achieved using the PAA-CNF/water dispersions with concentrations of less than 0.5 wt%. However, a drastic increase in the haze was observed when the

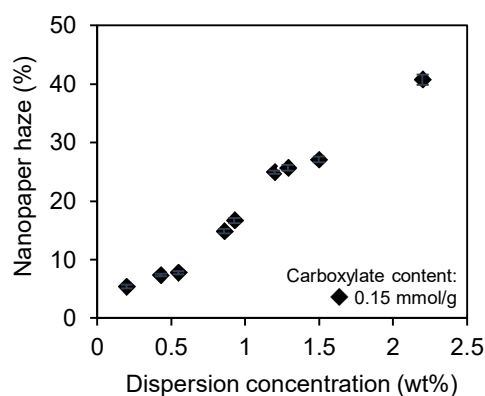


Fig. 1-2 Effect of concentration of starting CNF/water dispersion on haze of 13 μm -thick PAA-CNP.

0.9-wt% PAA-CNF/water dispersion was used, and finally, the use of the high-concentration 2.2 wt% dispersion yielded a high haze of 41%. The carboxyl content of all the PAA-pulps was 0.15 mmol/g. Therefore, the PAA-CNFs were homogeneously distributed in the low-concentration dispersions but tended to aggregate inhomogeneously in the high-concentration dispersions. As the CNFs were not densely packed, the presence of cavities between the nanofibers resulted in light scattering due to the difference in the refractive indexes of air and cellulose, resulting in the formation of hazy nanopaper.

Inhomogeneous aggregations in the CNF/water dispersions from the PAA-pulp without alkali-treatment are known to disintegrate with water dilution.¹⁵ When the concentrations of the PAA-CNF/water dispersions with initial concentrations of 2.0 wt% were diluted to 1.0–1.8 wt% and then subjected to oven drying, the PAA-CNP haze was reduced by 10–30% as compared with the values of PAA-CNP prepared without dilution (Fig. 1-4). However, as previously reported by Isobe et al., these PAA-CNPs were still hazy translucent even

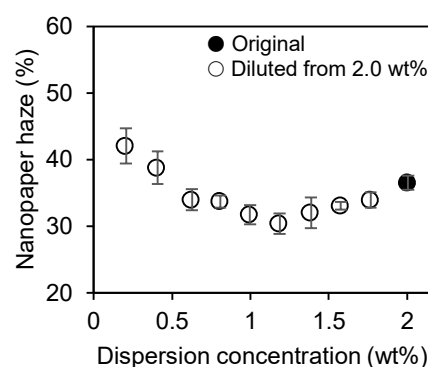


Fig. 1-3 Effect of dispersion concentration on the haze of PAA-CNP prepared using the original 2.0 wt% dispersion and diluted 0.2–1.8 wt% dispersions.

after the water dilution.¹⁵ Moreover, when the concentration of the PAA-CNP/water dispersion was diluted from 2.0 wt% to 0.2 wt%, the haze of the PAA-CNP slightly increased instead of decreasing (Fig. 1–3). These results suggest that the water dilution of high-concentration PAA-CNF/water dispersions does not cause the disintegration of the inhomogeneous aggregations and cannot produce clearly transparent PAA-CNP with haze values of less than 10%.

Sonication is also often applied to disintegrate pulp fibers into nanofibers in water dispersions.^{2,11,16} However, when the 2.0-wt% PAA-CNF/water dispersion was sonicated for 30 s, the obtained PAA-CNP maintained a high haze of approximately 35% because the high viscosity of the 2.0-wt% PAA-CNP/water dispersion resulted in the absorption of the vibrations (Fig. 1-4●). Therefore, the high viscosity of the dispersion was reduced using water to facilitate the efficient propagation of the vibration through the dispersion, and the dispersion was then subjected to

sonication. When the 1.1-wt% and 0.2-wt% PAA-CNP/water dispersions diluted from the 2.0-wt% PAA-CNP/water dispersion were sonicated for only 10 s, the inhomogeneous aggregations in the dispersions the disintegrated and the haze of the resulting transparent PAA-CNP reduced to less than 10% (Fig. 1-4○,△). In addition, the surface roughness (Rq) of the resulting

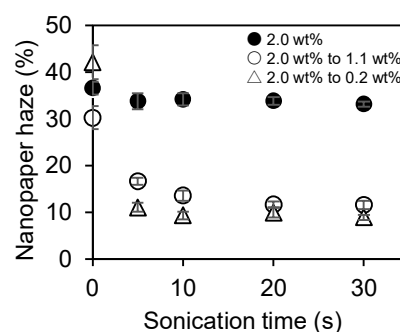


Fig. 1-4 Effect of sonication time on the haze of PAA-CNF prepared from dispersions with various concentrations.

to 0.2 wt%), and the diluted and sonicated dispersions were 43.5 and 30.2 nm, respectively. In a previous study, sonication was performed for 4–45 min because it was applied in a mechanical nanofibrillation process to produce CNFs from pulp fibers.^{2, 11, 16} In contrast, the purpose of the sonication process in this study was to disintegrate the inhomogeneous aggregation between the CNFs in the dispersion; therefore, the use of a short sonication period of 10–30 s was sufficient.

Such a short sonication time should only cause the dissolution of inhomogeneous aggregations without resulting in mechanical damage to the CNFs. To confirm this, the 2.0-wt% PAA-CNF/water dispersion was diluted to concentrations of 0.2–1.6 wt% and sonicated for 20 s, and PAA-CNP were then prepared by drying the dispersions. The resulting PAA-CNPs exhibited almost identical high crystallinity and high heat resistance irrespective of the conditions applied (Fig. 1-5a, b). Therefore, the dilution and sonication of the high-concentration PAA-CNF/water dispersion improved the haze of the PAA-CNP while retaining its high crystallinity and heat resistance.

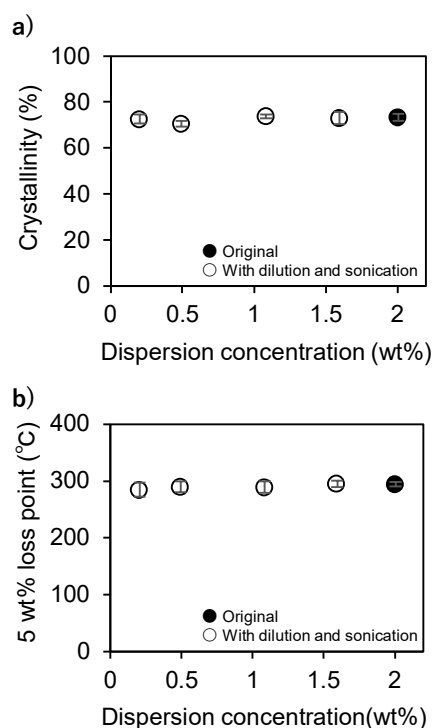


Fig. 1-5 (a) Crystallinity and (b) heat resistance under nitrogen of PAA-CNPs.

A summary of the results is presented below. The drying of the 2.0-wt% PAA-CNF/water dispersion

produced translucent nanopaper with a high haze of 36.6% (Fig. 1-6a, black bar). Because of the high viscosity of the 2.0-wt% dispersion, sonication for 10 s did not improve the nanopaper haze (34.2%, Fig. 1-7a, white bar). Dilution was also not very effective in improving the PAA-CNP haze (Fig. 1-6b–e, gray bars). For example,

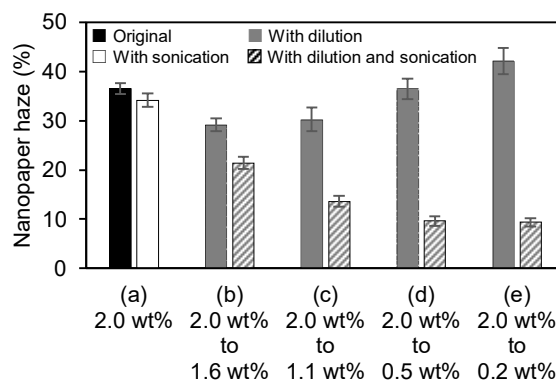


Fig. 1-6 Haze of PAA-CNP as a function of nanofiber dispersion conditions.

when the PAA-CNF/water dispersion was diluted from 2.0 wt% to 0.2 wt%, the haze of the PAA-CNP increased from 36.6% to 42.1%. However, the combination of dilution and sonication of the high-concentration PAA-CNF/water dispersion drastically improved the PAA-CNP haze (Fig. 1-6b–e, border bars). When the PAA-CNP/water dispersion was diluted from 2.0 wt% to 0.5 wt% (or 0.2 wt%) and then sonicated for 10 s, the haze of the PAA-CNP decreased from 36.6% to 9.6% (or 9.3%); these haze values are equivalent to those reported in previous studies for PAA-CNP prepared from low-concentration (less than 0.5 wt%) PAA-CNF/water dispersions.

The high thermal resistance of PAA-CNP has facilitated its use as a substrate in various electronic devices such as organic thin-film transistors, solar cells, and conductive lines.^{7,8,10,12} As a specific example of our achievement in electronic applications, transparent and conductive nanopaper was fabricated by depositing silver nanowires on PAA-CNPs. Transparent conductive films are generally produced by dropping silver nanowire suspensions onto transparent substrates, which is

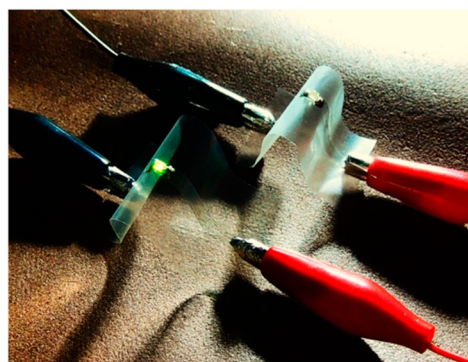


Fig. 1-7 PAA-CNPs prepared from high-concentration dispersions with (left) or without (right) dilution and sonication and their application to transparent conductive films.

followed by heating at 150–200 °C in air. Such high-temperature heating could not be applied for the TO-CNP, because it turned yellow or brown, but the PAA-CNP maintained its colorless transparency. The transparency of silver-nanowire transparent conductive films depends on the transparency of the

substrate and the silver nanowire content, and their electrical conductivity depends on the silver nanowire content.¹⁴ Therefore, when the high-haze PAA-CNP prepared by drying the high-concentration PAA-CNF/water dispersion without any conditioning was used as a transparent substrate, only a small amount of deposited silver nanowires were used to enhance the transparency of the transparent and conductive nanopaper. As a result, the electrical conductivity of the transparent and conductive nanopaper was insufficient to illuminate a light-emitting diode (LED) (Fig. 1-7, right). In contrast, when the low-haze PAA-CNP obtained by drying the diluted and sonicated dispersion was used as the transparent substrate, the high silver-nanowire content enhanced the electrical conductivity of the transparent and conductive nanopaper while retaining its high transparency. Thus, an LED mounted on the paper was successfully illuminated (Fig. 1-7, left). These preliminary achievements suggest that the dilution and sonication of high-concentration CNF/water dispersions would contribute not only to reducing transportation and storage costs but also to expanding device applications.

1.4 Conclusions

In conclusion, nanopapers equivalent to those obtained using low-concentration dispersions were prepared from high-concentration TO-CNF/water dispersions and PAA-CNF/ water dispersions. An increase in the concentration of PAA-CNF/water dispersions results in the generation of inhomogeneous aggregations of PAA-CNFs in the dispersion, thereby decreasing the clearness of the transparent nanopaper. The inhomogeneous aggregations were not disintegrated by dilution of the high-concentration PAA-CNF/water dispersions. In addition, although sonication often causes disintegration of the aggregations of CNFs, the inhomogeneous aggregations in the high-concentration dispersion in this study could not be disintegrated by sonication due to the high viscosity of the high-concentration PAA-CNF/water dispersion. However, after the dilution of the high-concentration PAA-CNF/water dispersion, the use of only 10–30 s of sonication resulted in the production of clearly transparent PAA-CNP with a haze of less than 10%. Because these procedures retained the high crystallinity of the PAA-CNP, the high heat resistance of the clearly transparent PAA-CNP was also retained. These achievements will reduce the manufacturing costs associated with nanopaper and encourage the widespread use of nanopaper-based sensor devices.

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Chapter 2 PAA-CNP based wireless humidity sensor device

2.1 Introduction

Several applications of sustainable and biodegradable materials in electronic components such as sensors,^{1,2,3,4} transistors,^{5,6,7} supercapacitors,^{8,9,10} memories,^{11,12} and substrates have been reported.^{13,14,15} As has been shown in many previous studies, the degradability is an indicator of its environmental compatibility. However, it is difficult to combine the functions required for sensor devices and degradability. Degradable sensor devices require three functions: wireless communication, sensing, and degradability. Although the sensor characteristics and biodegradability of eco-friendly components have been discussed in other studies,^{1,2,3} sensor-information collection currently requires wired communication with non-degradable external equipment. Sensors output environmental changes, such as temperature, humidity, and strain changes, as resistance and capacitance changes. These changes in the sensors are weak, and signal processing circuits consisting of numerous components, including resistors, coils, and capacitors, are essential to amplify and convert the signals for wired/wireless transmission. This is also the case in degradable sensor devices. Degradable sensor devices should include degradable sensors and degradable signal-processing circuits. Therefore, the substrate, sensor, and passive components constituting the device should exhibit degradability and an acceptable performance, and it is necessary to connect and mount them using an existing and eco-friendly method without impairing their degradability. To achieve this difficult challenge, a smart green material that combines heat resistance, degradability, and suitability for multiple purposes, such as substrates, dielectric layers, and sensors, is required.

Herein, a nanopaper sensor device for environmental monitoring that has the three functions of sensing, wireless communication, and degradability and uses PAA-CNP as the substrate, dielectric layer, and sensor has been reported. The suitability of the PAA-CNP for capacitor dielectric layers has been demonstrated, and the thermal resistance, low thermal expansion, and printability of the PAA-CNP have allowed all the necessary elements to be successfully integrated to realize a nanopaper wireless transmitter. The flexible and degradable sensor device is capable of humidity

sensing owing to the humidity sensitivity of the PAA-CNP, and it wirelessly transmits data and degrades in the soil after use.

2.2 Experimental Section

Cellulose Pulp and Nanofibrillation

PAA-pulp was prepared by the steps described in a previous study.¹⁶ First, 60 g of Japanese cedar (*Cryptomeria japonica*) wood chips were dewaxed in a mixture of acetone/water (2700 mL/300 mL) overnight at room temperature with gentle stirring. The chips were then delignified in an acetic anhydride/hydrogen peroxide mixture (500 mL/500 mL) at 90 °C for 2 h. Next, the PAA-pulp was treated with 5 wt % potassium hydroxide at 20 °C for 2 h before being thoroughly washed with distilled water. Disintegration of the PAA-pulp into PAA-CNFs was performed using a water-jet nanofibrillation system.^{17,18} The PAA-pulp slurry (2000 g, pulp content 0.5 wt %) was homogenized using a high-pressure water-jet system (Star Burst, HJP-25008, Sugino Machine Limited, Toyama, Japan) equipped with a ball-collision chamber. The injected slurry was repeatedly passed through a small nozzle with a 0.15 mm diameter under pressure of 245 MPa. After 50 passes through this nozzle, a 0.3 wt % PAA-CNF/water dispersion was obtained.

Conditioning of the Cellulose Nanofiber Dispersion

The concentration of the PAA-CNF/water dispersion was adjusted by condensation with a rotary evaporator (EYELA SB1200, TOKYO RIKAKIKAI CO., LTD., Tokyo, Japan) and/or water dilution. After the dispersion was conditioned by concentration adjustment, it was degassed using a centrifugal mixer (ARV-310, THINKY CORPORATION, Tokyo, Japan) at 1400 rpm for 3 min under vacuum and then at 1800 rpm for 7 min under ambient pressure.

PAA-CNP Substrate

The concentrated PAA-CNF/water dispersion (1.0 wt %) was then evenly cast on an acrylic plate with an applicator. PAA-CNP with thicknesses of $25 \pm 2 \mu\text{m}$ were obtained after subsequent

oven drying (DVS402, Yamato Scientific co., Ltd, Tokyo, Japan) at 55 °C under RH of 25%. For the thin layer and multilayered capacitors, a 0.4 wt % cellulose nanofiber dispersion was cast and dried on a glass plate, and PAA-CNPs with thicknesses of $8 \pm 1 \mu\text{m}$ were obtained. The thickness of the PAA-CNPs was measured by a micrometer and field emission scanning electron microscopy (SU8020, Hitachi High-Tech Corporation, Japan) at an accelerating voltage of 5.0 kV and a working distance of 16.9 mm.

Nanopaper Capacitor

The 5 mm $\times$ 5 mm electrodes were fabricated by inkjet printing silver nanoink (CCI-300, Cabot Printing Electronics and Displays, USA) on both sides of 25- μm -thick PAA-CNP, PET (Tetron HPE-25, Teijin Film Solutions Limited, Japan), and polyimide (Kapton(R) 100H, E. I. du Pont de Nemours and Company, USA) films using an inkjet printer (Dimatix DMP 2850, Dimatix-Fujifilm Inc., USA). Printed electrodes were sintered by heat treatment at 150 °C for 30 minutes. To confirm formation of the thin dielectric layer, 0.01–0.8 wt % cellulose nanofiber dispersions were cast and dried on 5.0 mm $\times$ 5.0 mm silver electrodes formed on PAA-CNP substrates. To prepare the multilayered nanopaper capacitor, a 0.1 wt % PAA-CNF/water dispersion was cast and dried on a 5.0 mm $\times$ 5.0 mm silver electrode prepared on a nanopaper substrate, another silver electrode was fabricated, and the procedure was repeated.

Nanopaper Wireless Transmitter

An oscillation circuit based on a Colpitts oscillation circuit was fabricated on a PAA-CNP substrate. First, conductive lines and electrodes for the top layer were fabricated on the top side of the PAA-CNP substrate. The conductive lines and electrodes for the coil and capacitors were fabricated with a screen printer (Air Suction Screen Printer, Taiyoseiki Co., Ltd., Japan) using binder-free silver paste (TEC-PAA-010, InkTec Co., Ltd., Korea). The resistors were fabricated with

an inkjet printer (Dimatix DMP 2850, Dimatix-Fujifilm Inc.) using silver nanoink (CCI-300, Cabot Printing Electronics and Displays). Printed lines and electrodes were sintered by heat treatment at 150 °C for 30 minutes. To focus on the effect of the humidity on the capacitors, chip resistors were used in some experiments instead of printed resistors. Second, conductive lines and electrodes for the bottom layer were fabricated on the bottom side of the PAA-CNP substrate, and a chip transistor for amplifying the signal was mounted and connected with silver paste.

Characterization of the Nanopaper Capacitors and Nanopaper Sensor Devices

The capacitance of the fabricated capacitors was measured with an LCR meter (LCR-6200, Texio Technology Corp., China) at 1 kHz and 1 V, and the humidity was adjusted using a constant temperature and humidity chamber (PR-2 KT, ESPEC Corp., Japan). The measurement was performed in a 0% RH environment by placing a desiccant (diphosphorus pentoxide) in a closed container. The wireless signal from the nanopaper sensor device was received by a rod antenna connected to a spectrum analyzer (GSP-9330, Texio Technology Corp., China).

Degradation Test

For the degradation experiment, natural soil was used. The soil (3 L) was collected at 34° 49' 31.4" N 135° 31' 22.6" E in February 2019 and kept in a plastic box. The temperature and humidity of the soil were well controlled at 27 ± 2 ° C and 99 %RH, respectively. As control experiments, wireless transmitters on polyimide and PET substrates were also investigated.

2.3 Result and Discussion

The nanopaper capacitors and sensor devices were fabricated while taking into consideration both the manufacturing process and materials for minimizing their environmental impact. Capacitors are essential elements in radio transmitters and other basic processing circuits. There are three important parameters for preparing capacitors of a sufficient capacitance (C [F]) for wireless transmission: the relative permittivity (ϵ_r) of the dielectric material (ϵ_0 [F/m]: dielectric constant of vacuum), thickness (d [m]) of the dielectric layer, and electrode area (A [m²]). The capacitance can be expressed as

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \quad (2.1)$$

There is a need for sustainable dielectric materials having a high relative dielectric constant, suitable insulating properties, and ability to withstand thinning and facilitate easy layering.

To evaluate the performance of the PAA-CNP as a capacitor dielectric layer, its performance was compared with that of other polymer materials.¹⁹ Capacitors comprising dielectric layers of identical thickness (25 μ m) were fabricated using the PAA-CNP, polyimide, polyethylene terephthalate (PET), and pulp paper, and their capacitances were measured with a LCR meter. The capacitance of the nanopaper capacitor was approximately 2.6 times higher than those of polyimide and PET (Fig. 2-1). Common polymer materials, such as engineering plastics (e.g., polyimide and PET) and biodegradable plastics (e.g., PLA) have a relative permittivity of approximately 3.^{19,20,21} In contrast, nanopaper has a dielectric constant of 5–6.²² The high capacitance of the nanopaper capacitor is considered to be owing to the high relative dielectric constant of nanopaper. Pulp paper derived from

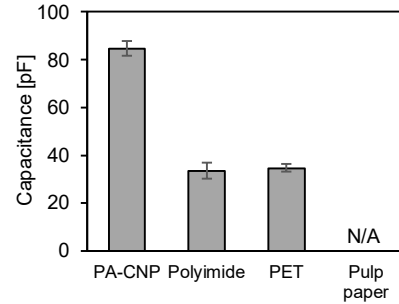


Fig. 2-1 Capacitance of PAA-CNP, polyimide, PET, and pulp paper dielectric layers at 25 °C and 0% RH.

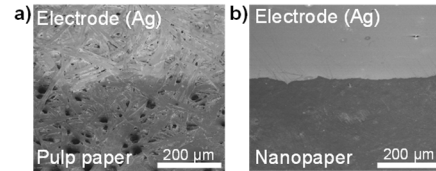


Fig. 2-2 (a) Pulp paper capacitor and (b) densely packed structure of the nanopaper capacitor.

wood is similar to nanopaper and has long been applied as capacitor dielectric layers.²³ However, pulp paper cannot be used as a thin capacitor dielectric layer because there are a large number of holes between the top and bottom electrodes, resulting in weak electrical insulation (Fig. 2-2a). Because the PAA-CNP is composed of CNFs of width 3–15 nm, it is possible to obtain a sufficiently smooth surface for realizing fabrication (Fig. 2-2b).

Next, the thin-film formation of the PAA-CNP was evaluated. The PAA-CNP was found to be sufficiently insulating for capacitance measurements of dielectric layers of 200 nm to 12 μm thickness, and the capacitance increased as the thickness of the dielectric layer was decreased (Fig. 2-3). The capacitance inversely increased with increasing thickness of the dielectric layer, as expected from Equation 2.1. The PAA-CNP could form a thin film of sufficient thickness for use as a capacitor dielectric layer.

Multilayer formation of the PAA-CNP was also investigated. A PAA-CNP substrate was first fabricated on a slide glass, and electrode and PAA-CNP dielectric layers were then repeatedly fabricated. The capacitance of the multi-layered nanopaper capacitor linearly increased as the number of layers was increased (Fig. 2-4 a). It is desirable to increase the electrode area to improve the capacitor performance (Equation 2.1). However, because the two-dimensional size is limited in mounting, the electrode area is generally increased three-dimensionally by laminating or winding it. In the case of the stacking of the nanopaper capacitors, the PAA-CNP dielectric layers could be stacked without any special pretreatment (Fig. 2-4 b). In other words, the multilayered nanopaper capacitor can be

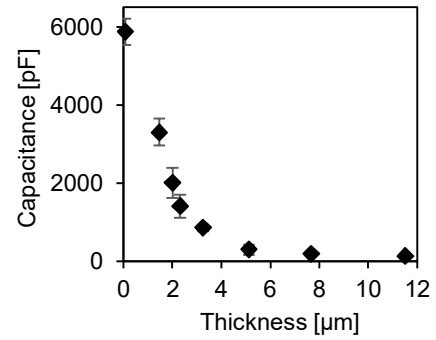


Fig. 2-3 Capacitance of nanopaper capacitors with 200 nm to 12 μm -thick dielectric layers.

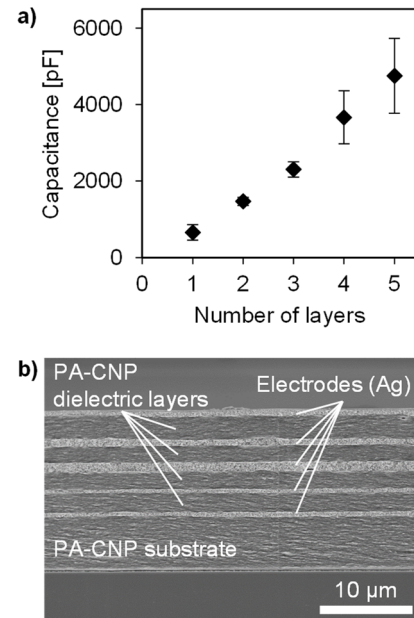


Fig. 2-4 a) Capacitance of multilayered nanopaper capacitors and b) the cross section of the multilayered nanopaper capacitor.

fabricated by a simple printing process having a low environmental impact, it does not require the use of a harmful solvent or high-energy deposition apparatus, and sufficient performance is expected when it is used for radio transmission.

Capacitors comprising nanopaper, polyimide, and PET dielectric layers were placed in an atmosphere of 25 °C and 20–80% RH, and the capacitance was measured (Fig. 2-5). The capacitance of nanopaper capacitor greatly increased as the humidity increased. The capacitance of the capacitors with polyimide and PET dielectric layers hardly changed. It is known that the physical properties of nanopaper, such as the size, strength, and gas barrier properties, are easily affected by humidity.^{24,25} The moisture content of the nanopaper varied from 2.5% to 14.3% under a 20–80% RH at 25 °C. The change in the capacitance is considered to be caused by the change in the moisture content in the nanopaper. The capacitance of the nanopaper capacitor increased by up to approximately 3.6 times according to the humidity.

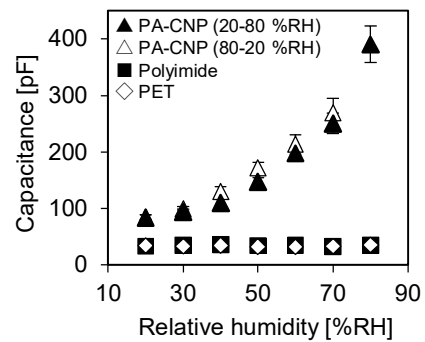


Fig. 2-5 Capacitance of the nanopaper capacitors at 25 °C and 20–80% RH

By successfully fabricating a nanopaper capacitor of sufficient performance, it was possible to fabricate a sensor device by printing and mounting the three main passive elements (capacitors (C), resistors (R), and coils (L)) on a PAA-CNP substrate (Fig. 2-6a, b). Wireless transmission in the megahertz band was confirmed by measuring the signal from the nanopaper sensor device with a spectrum analyzer (Fig. 2-7a). Typically, electronic devices are fabricated by integrating various elements, wires, and substrates prepared from different materials, such as silver, copper, solder, FR-4, polyimide, and PET. Because heat treatment, such as sintering of conductive lines, soldering, and preliminary heating, is frequently performed during

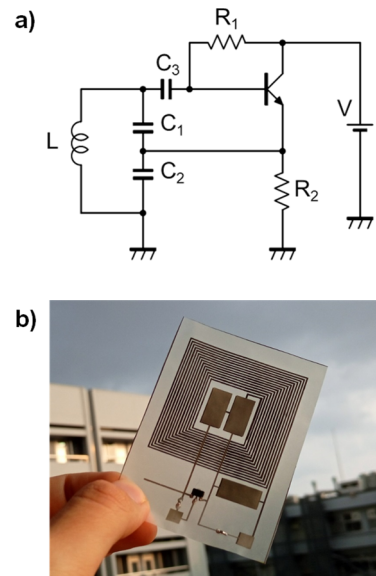


Fig. 2-6 a) Simplified circuit diagram and b) appearance of the nanopaper sensor device

device fabrication, it is necessary to understand and control the differences in the heat resistance and linear thermal expansion coefficient of each element of the device. In particular, heat treatment at 100 °C or higher is often required in the process of wiring fabrication or soldering.²⁶ To use a biodegradable plastic, such as PLA or PVA, as a substrate or a dielectric layer, a special method, such as transfer printing, is required.²⁷ In the fabrication of the nanopaper wireless transmitter, the substrate and dielectric layer were both prepared from high-heat-resistant nanopaper, and no effect was observed even after heat treatment at 150 °C for 30 min. Furthermore, because the same material is used for the substrate and dielectric layer, problems such as peeling owing to a difference in the coefficient of linear thermal expansion did not occur.

The environmental performance of the nanopaper sensor device was evaluated for environmental monitoring applications. The device was installed outdoors, and the change of the oscillation peak with time was observed. The results are presented in Fig. 2-6b. The oscillation frequency changed over time. The change in the signal was compared with meteorological information to clarify which parameters of the outdoor environment affected the oscillation frequency. The oscillation frequency followed the change in the RH (Fig. 2-6b). The theoretical oscillation frequency ($1/f$ [s]) can be expressed as

$$1/f = 2\pi \sqrt{L \frac{C_1 C_2}{C_1 + C_2}} \quad (2.2)$$

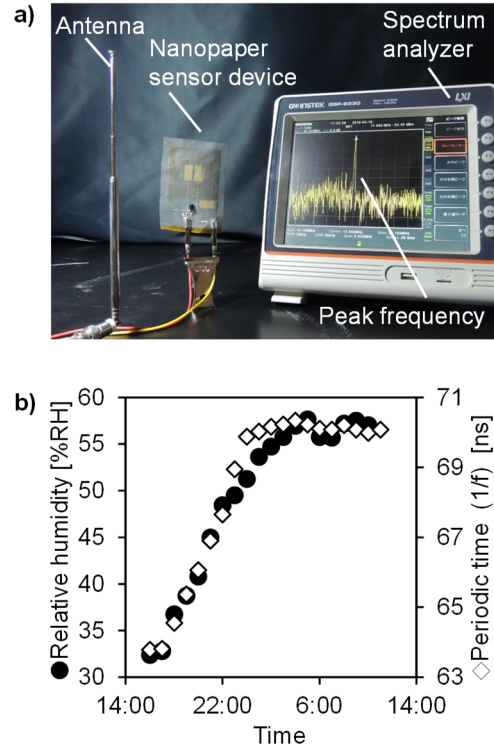


Fig. 2-6 a) MHz band radio emission from a nanopaper sensor device. b) Change of the peak frequency of the nanopaper sensor device with the RH.

In the measurement environment of the nanopaper sensor device, it is unlikely that the induction coefficient (L [H]) of the coil changed; however, the capacitance of the nanopaper capacitor (C [F]) changed owing to the influence of the humidity (Fig. 2-5). Owing to the large change in the capacitance, it is considered that a basic oscillation circuit could output the change in the humidity. These results show that the capacitor with nanopaper as the dielectric layer can be applied as a humidity sensor, and a wireless transmission circuit with the nanopaper capacitor can be used as a humidity sensor device.

To confirm the degradability of the nanopaper sensor device, a degradation test was performed in soil. More than 95% of the total volume of the nanopaper device degraded in 40 days (Fig. 2-6). In contrast, the polyimide and PET substrates were stable after 40 days without any degradation. On day 10, biodegradation of the substrate part of the nanopaper sensor device was visually confirmed. After day 10, primarily the degradation of the substrate occurred, and approximately 50% of the total volume was decomposed on day 20. By day 40, more than 95% of the total volume was degraded and lost. The substrate was biodegraded and the conductive lines were degraded such that they were indistinguishable from the soil particles. From the above results, it was confirmed that the fabricated sensor device has the three functions of sensing, information transmission, and degradability.

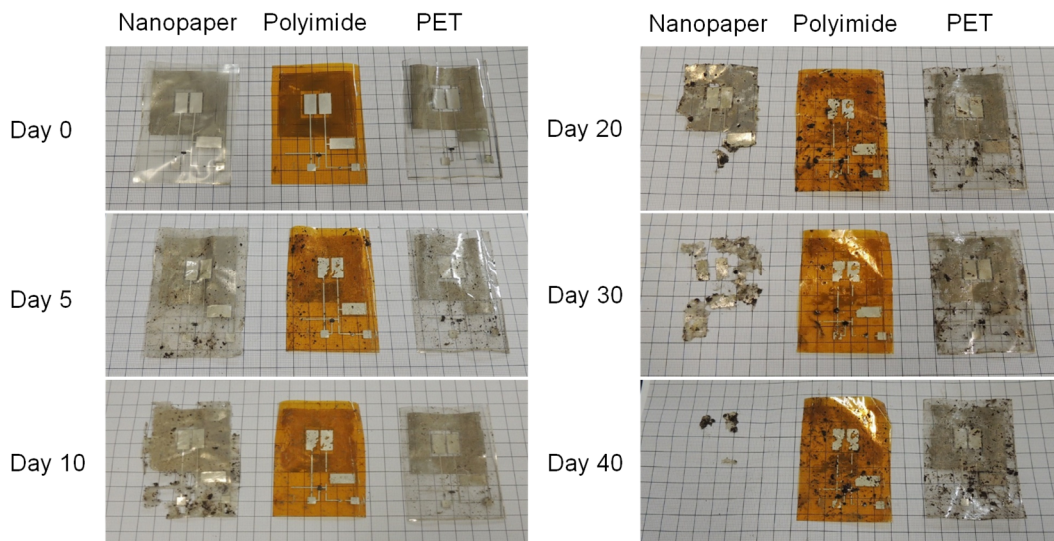


Fig. 2-7 Time series of photographs of the nanopaper, polyimide, and PET sensor devices after burying them in soil

The realization of degradable sensor devices makes it possible to realize a wide range of future sensor devices (Figs. 2-8a–c). The nanopaper sensor device can be mass-produced using only an eco-friendly process and resources. Because almost all the sensor device components decompose and do not need to be collected, the sensor devices can be used in large quantities. For example, it is possible to install a large number of weather observation devices in places such as streets and utility poles without worrying about their management and disposal, which provides a very powerful method of accurate weather prediction and capturing local weather changes, such as torrential rain and tornadoes. In addition, the spreading of humidity sensor devices on large farms and gathering information can improve the efficiency of water supply for crops. Information can be collected and managed for each crop, which makes it a powerful method of increasing food production and decreasing food loss. This method is more flexible than conventional methods for monitoring the natural environment, and it has great potential for applications such as automation of forestry by managing the growth of individual trees, environmental prediction, and maintenance and management of ecosystems. Other possible applications of nanopaper sensor devices include congestion prediction via highly accurate traffic-information collection, efficient operation of small-scale power-generation facilities, such as photovoltaic and wind power-generation facilities, energy management in factories and manufacturing plants, and prediction of disasters such as earthquakes and eruptions. The nanopaper sensor devices are expected to not only replace existing IoT devices, but also to significantly contribute to the development of new observation methods that take advantage of the disposability.



Fig. 2-8 Examples of the potential uses of nanopaper sensor devices such as a) a hyperdense meteorological observation network, b) real-time monitoring of the storage conditions of packages, such as agricultural products, and c) efficiency improvement of forestry by monitoring the growth of individual trees, environmental forecasting, and measurement.

2.4 Conclusion

In conclusion, a nanopaper sensor device having the three functions of sensing, information transmission, and degradability using PAA-CNP have successfully been fabricated. Because of its high dielectric constant, thin-film formability, and lamination properties, PAA-CNP exhibits high suitability for the dielectric layer of capacitors, which are essential for information transmission. A wireless transmission circuit was constructed using a PAA-CNP substrate and dielectric layer via an eco-friendly printing process, and it functions as a humidity sensing device owing to the moisture sensitivity of PAA-CNP. More than 95% of the total volume of the nanopaper sensor device decomposed in soil in 40 days. Nanopaper sensor devices can contribute to reducing environmental pollution and management and decrease the disposal costs of sensor devices, which are bottlenecks in the development of an IoT society. They also demonstrate the basic concept of next-generation sensor devices.

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Chapter 3. TO-CNP Coatings for Circuit Protection against Water-Induced Short-Circuit Failures

3.1 Introduction

It is well-known that water is detrimental to electronic devices such as sensor devices, which readily fail because of the adhesion of water droplets to them, condensation, and submersion. If the device is powered on when water is present inside the device, the difference in electrical potential between the wires causes metal ions from the metal wire anode to elute and migrate to the cathode. The metal ions that arrive at the cathode are reduced, and the metal is deposited at the cathode as dendrites. As the dendrite grows and reaches the anode, the electrodes short circuit and the electronic device malfunctions.¹⁻⁵ Once a short circuit occurs, even if the device is dried, the short circuits caused by dendritic precipitation continue. Therefore, electronic circuits inside electronic devices are tightly sealed using polymer coatings or rubber packing to prevent water ingress.

Coating and packaging with non-degradable petroleum-based polymers, such as epoxy and fluoropolymers, have been widely used as a circuit-protection technique. However, the partial use of non-degradable materials is undesirable as it significantly reduces the degradability of the electronic device.⁶

To date, a wide range of uses for nanocellulose (such as CNFs) has been proposed, as it is considered an eco-friendly and high-performance material for next-generation flexible devices such as solar cells,⁷ sensors,^{8,9} substrates,¹⁰ and insulating materials for capacitors¹¹ and memory devices.¹² In addition, as shown in Chapter 2, nanopaper is a promising material for realizing eco-friendly sensor devices. However, cellulose is a hydrophilic material that tends to attract water,^{13,14} which can damage the devices. This is a disadvantage of using CNFs in electronic devices, and their poor reliability is predicted because of electronic circuit malfunctions resulting from the presence of water.

In this study, a TO-CNP coating that can reliably prevent malfunctions caused by water in eco-friendly sensor devices has been reported. When uncoated Cu electrodes were wetted with distilled water and a voltage was applied, short circuits occurred after approximately 5 min because of the formation of dendrites between the electrodes. When the electrode surface was coated with

TO-CNP, short-circuit failure was inhibited for at least 24 h. The TO-CNFs were slightly dispersed by the water, aggregated at the anode, and reliably protected the electrode. Even if cracks were formed in the TO-CNP coating, the TO-CNFs migrated to the anode and repaired the cracks, thereby preventing the occurrence of short-circuit failure.

3.2 Experimental Section

Preparation of TO-CNF/water Dispersions

Never-dried bleached softwood kraft pulp was used as a starting material (carboxylate content of 0.1 mmol/g). A kraft pulp slurry (2000 g; pulp content, 0.50 wt %) was homogenized using a high-pressure water-jet system (Star Burst, HJP-25008, Sugino Machine Limited, Japan) equipped with a ball-collision chamber. The injected slurry was repeatedly passed through a small nozzle with a 0.17 mm diameter under a pressure of 245 MPa. After the slurry was passed 50 times through this nozzle, a 0.4 wt % CNF/water dispersion was obtained. TEMPO-oxidized pulp (carboxyl contents of 0.3, 0.6, or 1.3 mmol/g) was prepared by following a published procedure.¹⁵ Bleached softwood kraft pulp (dry weight, 20 g) was suspended in distilled water (1500 mL) containing TEMPO (0.16 g) and NaBr (1.0 g). An appropriate amount of NaClO solution was then added at room temperature under continuous stirring to achieve the final carboxylate content of TEMPO-oxidized cellulose pulp to the cellulose slurry. TEMPO-oxidized cellulose pulp (carboxyl content, 1.8 mmol/g) was supplied by DKS Co., Ltd. The TEMPO-oxidized cellulose pulp slurry was subjected to the same homogenization process to produce a 0.4 wt % TO-CNF/water dispersion. The carboxylate content of the pulp was determined by the electric conductivity titration method.¹⁵ All dispersions were diluted to 0.2 wt % by the addition of distilled water.

Preparation of Electrodes and Coatings

Two Cu plates were placed facing each other on a glass plate. The tip angle of the Cu electrodes was 90° and the gap between the Cu electrodes was set to 1 ± 0.1 mm. The Cu electrodes were ultrasonically cleaned in distilled water for 30 min. The Cu electrodes were masked, except for a 30-mm-diameter area centered on the gap between the Cu electrodes. A nanopaper coating with a thickness of 5 μ m was deposited on the Cu electrodes by dropwise addition of 2 mL of a CNF/water dispersion on the Cu electrodes, which was followed by drying at 6 h at 55 °C and 50% RH. For the scratch test, a part of the prepared TO-CNP was removed by a CO₂ laser system (Hajime CL1 PLUS, Oh-Laser Co. Ltd, Japan).

Water Submersion Test

The Cu electrode was covered with a glass tube (inner diameter, 25 mm) with a flange. Then the glass tube was subjected to dropwise addition of 5 mL of distilled water (resistivity, $<1 \mu\text{S/cm}$). A voltage was applied, and the electrical resistance was measured using a source measurement unit (B2902A, Keysight Technologies, USA). The applied voltage was set at 3 V and the upper current limit was set at 0.1 A. The measurement time was 24 h. The applied failure criterion was defined as the point at which the interelectrode resistance fell below 20% of the initial resistance.¹⁶ The formation of dendrites between the Cu electrodes was monitored visually and by an inverted microscope. The pH around the Cu electrodes was measured using a pH meter (LAQUA F-73 with a micro ToupH probe 9618S-10D, HORIBA, Ltd., Japan). The cross section of the cellulose nanofiber layer around the anode sliced by a microtome was observed with a scanning electron microscope (SEM, SU-8020; Hitachi High-Tech Corporation, Japan) after immersion in an ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate, Tokyo Chemical Industry Co., Ltd., Japan).¹⁷ The atomic distribution in the cellulose nanofiber layer was analyzed by energy-dispersive X-ray spectroscopy (EDS, Hitachi High-Tech Corporation, Japan).

3.3 Results and Discussion

For simulating the harsh conditions of a sensor device submerged in water, an uncoated Cu electrode with a gap of 1 mm between the anode and cathode was subjected to the dropwise addition of 5 mL of distilled water; subsequently, a voltage of 3 V was applied between the anode and cathode (Fig. 3-1a). A short circuit was defined as the point at which the interelectrode resistance fell below 20% of the initial resistance.¹⁶ The short circuit occurred within 5 min after the water and voltage were applied (Figs. 3-1b and c). In contrast, a short circuit in the Cu electrodes covered with a 5- μm -thick TO-CNP coating was prevented for at least 24 h (1440 min) in water (Figs. 3-1b and d). When water was dropped onto the TO-CNP coating, the coating did not repel the water; rather, it absorbed water and led to the dispersion of the TO-CNFs on the Cu electrodes. After a voltage was applied, the TO-CNFs were attracted to the anode by electrophoresis and formed a CNF hydrogel layer, which protected the electrodes for a long time.

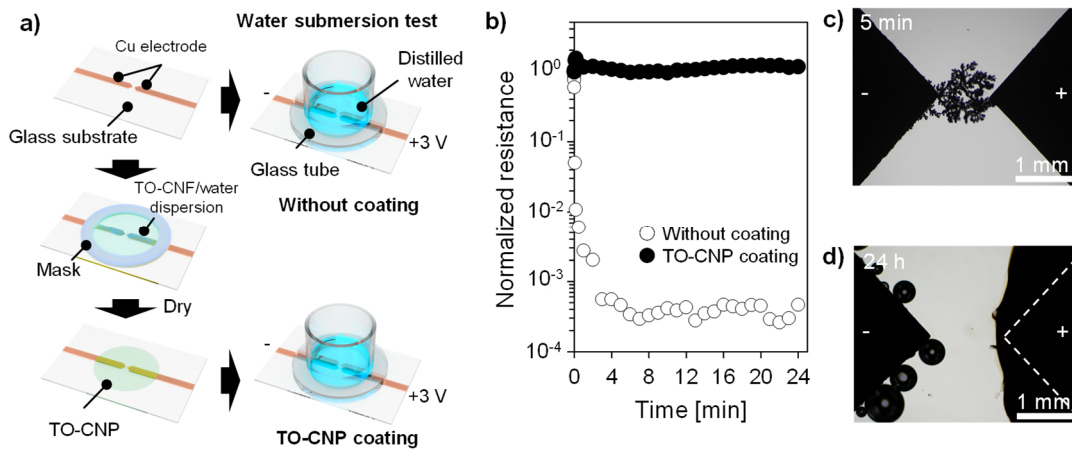


Fig. 3-1 a) Procedure for water submersion tests. b) Resistance change over time with reference to the initial resistance of the test. c) In the case of a Cu electrode without coating, Cu ions that eluted from the anode migrated to the cathode and were reduced to form dendrites that produced a short circuit after 5 min. d) The CNFs accumulate at the anode via electrophoresis and form a cohesive CNF layer, which provides long-term protection against the occurrence of a short circuit (at least 24 h).

The circuit protection behavior was observed in TO-CNFs with a carboxylate content of 1.8 mmol/g. The water submersion test was conducted with CNFs (carboxylate content in the range of 0.1–1.8 mmol/g) to better understand the effect of the carboxylate content. The time taken for a short-circuit failure to occur increased with the increase in the carboxylate content (from 0.1 mmol/g to a maximum of 1.8 mmol/g, Fig. 3-2a). However, the time required for a short-circuit failure to occur did not increase in proportion with the increasing carboxylate content (Fig. 3-2a). The time to short-circuit failure increased rapidly when the carboxylate content exceeded 0.6 mmol/g, and clear differences at the anode were confirmed (Figs. 3-2b–d). The trapping of metal ions using ion-exchange agents is one of the methods that can be used to suppress a short circuit.^{18–20} Carboxyl groups present on the surface of CNFs have also been used to trap metal ions.^{21,22,23} It was reported that the amount of Cu-ion adsorption increased up to four times on increasing the carboxylate content.²² However, in this study, the short-circuit suppression effect increased more than 80-fold as the carboxylate content was increased, and this cannot be explained by simple ion-exchange behavior.

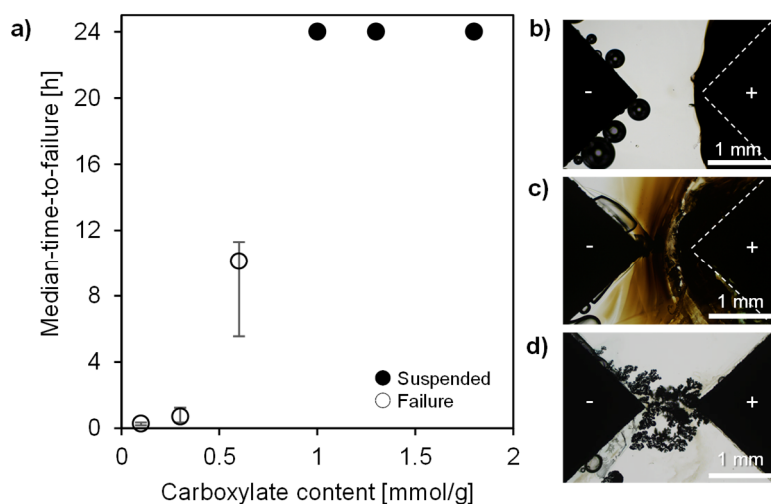


Fig. 3-2 a) Time to failure during water submersion tests of CNP coatings with a carboxylate content of 0.1–1.8 mmol/g. Condition around the electrode with b) TO-CNP coating (with carboxylate content of 1.8 mmol/g), c) TO-CNP coating (with carboxylate content of 0.6 mmol/g), and TO-CNP coating (with carboxylate content of 0.3 mmol/g).

The TO-CNP coating (with a carboxylate content of 1.8 mmol/g) was transparent and had a uniform thickness (5 μm) (Fig. 3-3a, b). One hour after the water and voltage were applied, the anode was covered with a 2-mm-thick gelatinous layer composed of CNFs (Figs. 3-3c, e). CNFs (width: 2–4 nm) are optically invisible.²⁴ However, sufficiently concentrated dispersions of CNFs appear as white areas (because of their optical birefringence and self-orientation properties) when viewed using cross polarizers.^{24,25,26,27,28} When cross polarizers are used, the white area was observed around the anode (Fig. 3-3d), indicating the birefringence due to the CNFs deposition and self-orientation. The slightly dispersed CNFs migrated toward the anode, where they formed a concentrated CNFs/water layer. The zeta potential of TO-CNFs with a carboxylate content of 1.8 mmol/g is between -70 mV and -80 mV.²⁴ As the TO-CNFs are negatively charged, they migrate from the cathode to the anode via electrophoresis. This is one of the factors that led to the formation of a thick layer of CNF hydrogel around the anode.

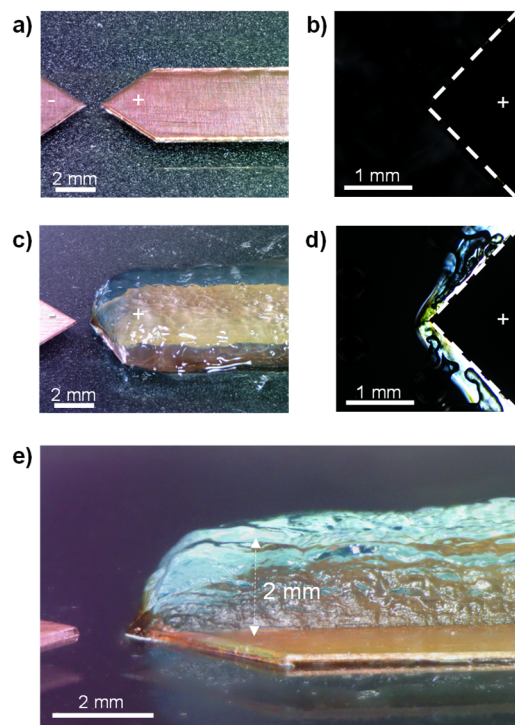


Fig. 3-3 a) Cu electrode with TO-CNP coating and b) observed with cross polarizers. c), d) 1 h after the start of the submersion tests. e) The cross section of the CNF hydrogel layer

Both the aggregation properties of CNFs and Cu ions in water are sensitive to pH changes.^{29,30,31} Therefore, the pH distribution around the electrodes was investigated. The water near the cathode was alkaline (pH 12–14) irrespective of the distance from the cathode (Fig. 3-4a) because of electrolysis of water. Furthermore, the outer part of the CNF hydrogel layer around the anode (a height of 4 mm from the anode) was also alkaline (pH 10–12). However, the boundary of the CNF hydrogel layer and water (a height of 2 mm from the anode) was neutral (pH 6–8), while the inner region (very close to the anode) was acidic (pH 1–2). The pH distribution is an important factor for understanding the formation of the CNF hydrogel layer. CNFs dispersed in water maintain their dispersed state under neutral and alkaline conditions. However, under acidic conditions, they

aggregate as the repulsive electric-double-layer force between the CNFs is lost, thus resulting in the formation of a stable hydrogel structure.²⁹ In addition, Cu ion trapping by CNFs is another factor contributing to the formation of the CNF hydrogel layer because TO-CNFs are cross-linked by Cu ions.²³ In summary, electrophoretic deposition, aggregation by an acidic environment, and cross-linking of TO-CNFs by adsorbed Cu ions occurred simultaneously. These processes contribute to the formation of a stable hydrogel structure; hence, the CNF hydrogel layer on the anode clearly separated the acidic and alkaline regions over a long term (Figs. 3-4b, c).

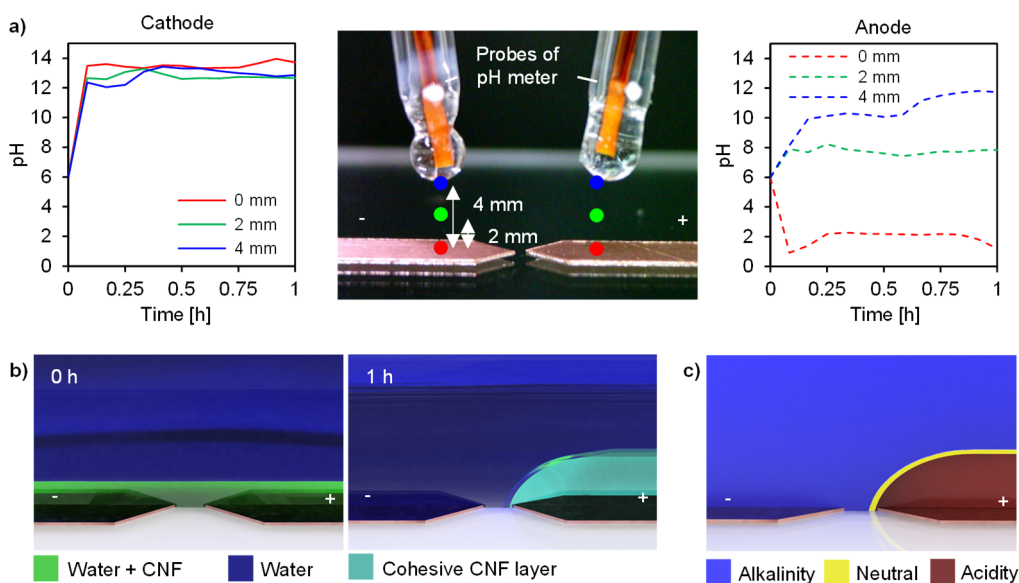


Fig. 3-4 a) pH was measured at 0, 2, and 4 mm from the top surfaces of the Cu electrodes during the water submersion test. b), c) Cross-sectional diagram of the formation of the CNF hydrogel layer around the anode and the resulting pH distribution.

Shortly after the start of the water submersion test, the CNF hydrogel layer around the anode changed its color, from transparent to light blue, indicating Cu ion absorption. After 10 min, the boundary of the CNF hydrogel layer and water changed to a darkish brown color. The darkish brown layer formed only at the boundary between the CNF hydrogel layer and the water (Fig. 3-5a) and was rich in Cu (Fig. 3-5b). The pH distribution presented in Fig. 3-4 and the nonuniformity of the Cu concentration presented in Fig. 3-5 suggest the following phenomena. There is a limit to the amount of Cu ions that can be adsorbed by ion exchange, even if the TO-CNF layer around the anode is

highly concentrated. The Cu ions that were not adsorbed by the TO-CNFs migrated because of the interelectrode electric field and gently passed through the CNF hydrogel layer toward the cathode. However, the border between the inside and outside of the CNF hydrogel layer became neutral and alkaline, and the concentration of hydroxide ions gradually increased (Fig. 3-4a). Therefore, the Cu ions that passed through the CNF hydrogel layer reacted with hydroxide ions at the border region; subsequently, they were converted to Cu hydroxide and/or Cu oxide and were anchored at the border (Fig. 3-5). Cu ions and Cu hydroxide and/or Cu oxide did not reach the cathode because of the CNF hydrogel layer; hence, the TO-CNP-coated Cu electrodes did not suffer short-circuit failures, even when exposed to water for 24 h, which is an exceedingly long time.

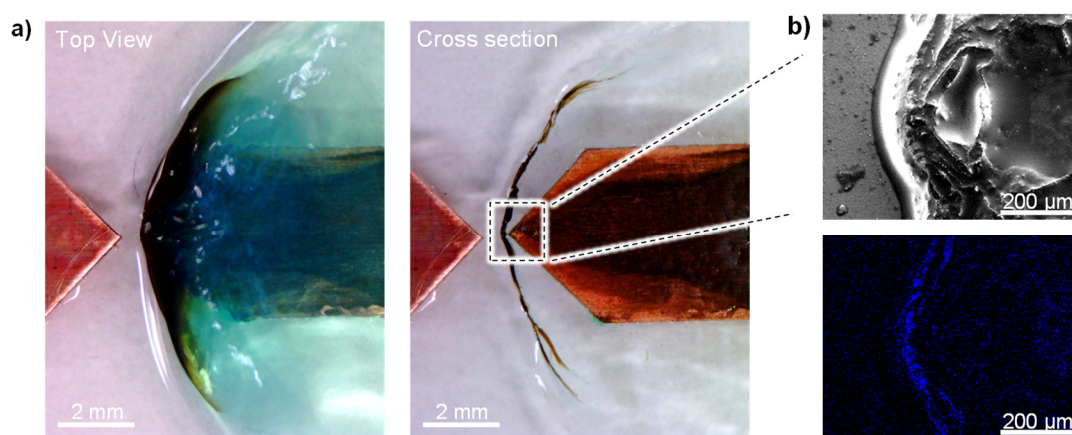


Fig. 3-5 a) CNF hydrogel layer on the anode 6 h after beginning the water submersion test. b) Cu (blue dots) was observed at the boundary between the CNF hydrogel layer and the water by scanning electron microscopy and energy dispersive X-ray spectroscopy, indicating copper-oxide and/or copper-hydroxide trapping.

The TO-CNP coating forms a CNF hydrogel layer on the anode by water absorption, redispersion, and electrophoresis and inhibits short-circuit failures. Therefore, when the TO-CNP coating was damaged, no short-circuit occurred, and the short-circuit protection provided was similar to that without scratches (Figs. 3-6a and b). In this manner, even if the TO-CNP coating was substantially damaged, the anode was covered with the CNF hydrogel layer, thus providing long-term short-circuit protection.

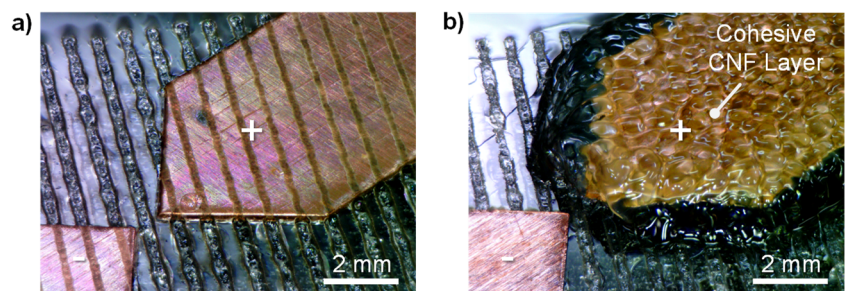


Fig. 3-6 a) Damaged TO-CNP coating. b) CNF hydrogel layer was formed on the anode after 1 h.

3.4 Conclusion

The use of hydrophilic materials in electronic devices has been avoided from the standpoint of reliability, as their susceptibility to water absorption can result in short-circuit failures. The hydrophilic TO-CNP coatings introduced in this study prevent interelectrode short-circuit failure of Cu electrodes submerged in water, thereby dramatically increasing the reliability of the circuits. The two main contributing factors that accelerate interelectrode short-circuit failure are the presence of water and electrical potential differences (electric fields). Redispersion of the TO-CNFs occurs in the presence of water. The applied electric field promotes the migration and dispersion of TO-CNFs toward the anode, thus contributing to the formation of a stable hydrogel layer. With the use of failure factors as a circuit-protection mechanism, interelectrode short circuits were prevented for at least 24 h after the submersion of the circuit in water. A short-circuit suppression technique comprising the use of TO-CNP can reliably suppress short-circuit failures without compromising the environmental compatibility of the entire sensor device and is expected to contribute to improving the safety of eco-friendly sensor devices.

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Conclusion

In this doctoral thesis, the author has summarized the results of the research conducted towards realizing an improved nanopaper fabrication method and realizing novel applications of nanopapers for eco-friendly sensor devices. A summary of the contents is presented below.

In Chapter 1, to reduce the cost of transportation and storage of CNF/water dispersion as the starting material, the effect of the concentration of CNF/water dispersion on the haze of the resulting nanopaper was investigated. In the case of TO-CNPs fabricated from a TO-CNF/water dispersion, it was confirmed that an increase in the dispersion concentration from 0.2 wt% to 1.8 wt% had almost no effect on the haze of the resulting nanopapers, thus reducing the transportation, storage, and drying costs. In contrast, in the case of PAA-CNP fabricated from a PAA-CNF/water dispersion, an increase in the haze caused by inhomogeneous aggregations was observed as the dispersion concentration increased from 0.2 wt% to 2.2 wt%. However, the inhomogeneous aggregations in the highly concentrated PAA-CNF/water dispersion were sufficiently disintegrated by dilution and short-time sonication. In combination with appropriate pretreatment, transparent nanopapers can be prepared from highly concentrated CNF/water dispersions, suggesting the possibility of reducing transportation and storage costs.

In Chapter 2, a PAA-CNP-based wireless humidity sensor device was developed. The PAA-CNP exhibited high relative permittivity and thin-film formation ability and was suitable as a capacitor dielectric layer. Owing to their low water absorption, the PAA-CNPs were laminated simply by repeatedly casting and drying the PAA-CNF/water dispersion, and multilayer capacitors and multilayer circuit boards were successfully fabricated. Owing to its low water absorption, PAA-CNPs were laminated simply by repeatedly casting and drying the PAA-CNF/water dispersion, and multilayer capacitors and multilayer circuit boards were successfully fabricated. The sensor device, in which the substrate, dielectric layer, insulating layer, and moisture-sensitive layer were fabricated using PAA-CNPs, was degraded by more than 95% within 40 days in the soil, thus exhibiting excellent characteristics as an environment-friendly sensor device.

In Chapter 3, a circuit-protection mechanism based on a TO-CNP coating that can reliably prevent water-induced short-circuit failure was demonstrated. TO-CNPs absorbed water upon being wetted, the TO-CNFs redispersed, and the TO-CNFs were electrophoretically deposited according to the electric field between the electrodes, thus forming CNF hydrogels at the anode. The CNF hydrogel separated the pH distribution into alkaline and acidic regions and inhibited the migration of eluted copper ions from the anode, thereby inhibiting the growth of dendritic precipitation from the cathode. Thus, the copper electrodes coated with TO-CNP did not short-circuit even after 24 h of submersion in water, which is in contrast to the uncoated copper electrodes that short-circuited within 5 min. As the short-circuit suppression effect of the TO-CNP coating is effective even when the coating is damaged, it is expected to be a novel safety-improvement technology for eco-friendly sensor devices.

List of Publications

1. Clearly Transparent Nanopaper from Highly Concentrated Cellulose Nanofiber Dispersion Using Dilution and Sonication

Takaaki Kasuga, Noriyuki Isobe, Hitomi Yagyu, Hirotaka Koga, and Masaya Nogi*

Nanomaterials, **2018**, 8 (2), 104.

DOI: 10.3390/nano8020104

2. “Return to the Soil” Nanopaper Sensor Device for Hyperdense Sensor Networks

Takaaki Kasuga*, Hitomi Yagyu, Kojiro Uetani, Hirotaka Koga, and Masaya Nogi*

ACS Applied Materials & Interfaces, **2019**, 11 (46), 43488–43493

DOI: 10.1021/acsami.9b13886

<https://pubs.acs.org/doi/10.1021/acsami.9b13886>

3. Cellulose Nanofiber Coatings on Cu Electrodes for Cohesive Protection against Water-Induced Short-Circuit Failures

Takaaki Kasuga*, Kojiro Uetani, Hirotaka Koga, and Masaya Nogi*

ACS Applied Nanomaterials, **2021**, 4 (4), 3861–3868

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Takaaki Kasuga