Development of Electrically Conductive Cellulose Nanofiber Film Composited with Carbon Nanotubes Using a Spray Method

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Abstract. Nanocellulose is made from wood, cotton, cellulose-rich materials, and organisms by mechanical methods or chemical dissolution. Nanocellulose films are a flexible substrate with excellent thermal and chemical stability. These excellent properties are useful as electrodes for wearable type devices that replace plastic films. In addition, cellulose is both biodegradable and eco-friendly. Problem is that the cellulose film does not have electrical conductivity. In this study, a nanocellulose conductive film made of composite carbon nanotubes was produced by a simple spray method. It was investigated whether this conductive film is useful as an electrode for electrochemical measurement.

1. Introduction
Cellulose is the most abundant carbohydrate on earth. Nanocellulose is made from wood, cotton, cellulose-rich materials, and organisms by mechanical methods or chemical dissolution [1-6]. Nanocellulose can be roughly classified as cellulose nanofiber (CNF), cellulose nanocrystals, and bacterial nanocellulose. Nanocellulose films are a flexible substrate for preparation of electronic devices with excellent thermal and chemical stability.[1,5,6]. They are also biodegradable, eco-friendly, and readily disposable like paper [1,2]. These properties are important for substrate materials used in wearable disposable devices. Because many types of flexible, wearable, and disposable electronic devices have been developed for use as chemical and physical sensors, and many solar cells contain plastics that are difficult to biodegrade [7-9]. If the CNF-based thin film electrode can be made, a wearable, disposable, environment-friendly device electrode can be made. However, CNF does not have electrical conductivity. In this study, in order to fabricate an electrically conductive CNF, a composite electrode of CNF and carbon nanotubes (CNTs) was prepared by using simple spray method, and the electrochemical characteristics of the prepared electrode were examined.

2. Experimental
2.1 Materials
Nanoforest-S BB made from bamboo using the aqueous counter collision (ACC) method was used as the CNF, and was kindly supplied by Chuetsu Pulp and Paper Co., Ltd. (Tokyo, Japan). The ACC-
treated CNF has both surface properties of hydrophobic and hydrophilic [10,11].

Multi-walled carbon nanotubes (MWCNTs, outer diameter 10 (± 1) nm, inner diameter 4.5 (±0.5) nm, and length 3–6 mm) was obtained from Sigma-Aldrich. Potassium hexacyanoferrate(III) (K$_2$[Fe(CN)$_6$]) was obtained from FUJIFILM Wako Pure Chemical Industries. Water was purified with a Millipore Milli-Q water system. All other chemical reagents were of analytical grade and were used without further purification.

2.2 Preparation of electrically conductive MWCNT/CNF film
An electrically conductive MWCNT/CNF film was prepared as follows. First, 6-47 mg CNF and 4-20 mg MWCNTs were dispersed in 10 mL of water using an ultrasonic homogenizer (Sonifier 450AA, Branson Ultrasonics Division of Emerson Japan Ltd). Next, 2.5 mL of the MWCNT/CNF dispersion solution was sprayed several times to an Al plate of 15×15 mm under heating at approximately 200 °C on a hotplate. Then, the prepared thin film was peeled off from the Al plate. The thickness of the electrically conductive MWCNT/CNF film was approximately 200 μm.

2.3 Instrumentation
Scanning electron microscopy (SEM) imaging was performed using a JSM-7600F (JEOL, Japan). Each sample was coated with approximately 5 nm of osmium by sputtering before the SEM measurements. Field-emission transmission electron microscopy (FE-TEM) was performed using a Tecnai F-20 (Philips Electron Optics, Netherlands). Voltammetry measurements were performed with an electrochemical analyzer (ALS/CHI model 600A) with a conventional three-electrode cell. The reference electrode was Ag/AgCl/saturated KCl (+199 mV vs. the normal hydrogen electrode) and a platinum plate was used as the counter electrode. All potentials are reported with respect to Ag/AgCl/saturated KCl at 25 °C. Prior to the voltammetric measurement, UV–ozone treatment was performed to the prepared film surface using a UV–ozone system (OC-2503, Eye Graphics Co., Japan). Cyclic voltammograms were simulated with cyclic voltammetry simulation software (DigiSim 2.0, Bioanalytical Systems, Tokyo, Japan) [12].

3. Results and Discussion

3.1 Mixed dispersion solution of MWCNT and CNF
The mixed dispersion solution of MWCNTs and CNF did not show any separation or sedimentation after more than 2 weeks. Fig. 1 shows TEM images of the dispersed sample on a TEM grid. In these images, the CNF is dispersed in clusters measuring 10–50 nm in diameter, which is in good agreement with a previous report [11]. Interestingly, the dispersed MWCNTs are included into the CNF clusters as shown in Fig. 1b. The MWCNT surface was covered with the CNF. Formation of this supramolecular structure leads to good and stable dispersion of the MWCNTs in the aqueous solution.

The CNF used is prepared by using aqueous counter collision (ACC) method without any chemical modification [10,11]. The ACC-method treated CNF surface has both properties of hydrophobic and hydrophilic. For example, oil-in-water Pickering emulsions with long-term stabilities were easily prepared by just ultrasonically mixing aqueous ACC-prepared CNF with non-polar solvents [11]. This result is due to the CNF surfaces of hydrophobic and hydrophilic. In this study, the MWCNT also was rapped with the hydrophobic surface of the CNF.
3.2 Film structure and electrically conductivity

Fig. 2 shows the photographs of the MWCNT/CNF film, when the mixed solution of 10 mg MWCNT and 27 mg CNF (Fig. 2a), or the mixed solution of 10 mg MWCNT and 10 mg CNF (Fig. 2b) was used. The film of Fig. 2b was more black color than the film of Fig. 2a because of 2.7 times higher ration of MWCNT/CNF comparison to the film of Fig. 2a, which let us expected to be higher electrically conductivity of the film in Fig. 2b. The electrically conductivity was summarized in Table 1. Interestingly, the electrically conductivity was not strongly depended on the MWCNT/CNF ratio. The highest conductivity was observed the film prepared from 3 mg MWCNT and 7 mg CNF. This result let us suggest that the dispersed condition of the mixed solution is important. When the higher concentration solution of CNF and MWCNT, in other words, high ration of MWCNT/water and CNF/water, was used for the spraying solution, the CNF and MWCNT were not dispersed well each other in a micro revel, even if it appeared to be well mixed by eye. It is considered that the network of conductive MWCNTs is not well posted when the solution that is not dispersed well is used.

Fig. 3 shows the morphology of the surface and a cross section of the MWCNT/CNF film (200 cm$^{-1}$), when the mixed solution of 3 mg MWCNT and 7 mg CNF was used. The surface morphology was similar to carpet fiber. Random fibers with diameters of a few dozen nanometers were observed. The cross-section image (Fig. 3b) showed the structure was formed of many layers with nanometer-scale thickness. This laminated structure could have high conductivity in the horizontal dimension. This structure would be due to multi spraying and layering until the film was completed.
Table 1 Mixing ratio of MWCNT, CNF and water used in the spray method and electrical resistance of the produced film

| MWCNT (mg) | CNF (mg) | Water (ml) | Resistance (Ω/cm) |
|------------|----------|------------|-------------------|
| 4          | 6        | 10         | 1700              |
| 3          | 7        | 10         | 200               |
| 10         | 10       | 20         | 18000             |
| 10         | 20       | 10         | 1900              |
| 10         | 47       | 10         | 800               |

Figure 3. SEM images of the surface (a) and cross section (b) of the MWCNT/CNF film.

3.3. Electrochemical behaviors
To evaluate the performance of the MWCNT/CNF film (200 cm$^{-1}$) as an electrode, cyclic voltammetry of [Fe(CN)$_6$]$^{3-}$ in 1 mol dm$^{-3}$ KCl solution (pH 7) was conducted (Fig. 4). Separation between the anodic and cathodic peaks was approximately 300 mV. The redox reaction was a perfect diffusion-controlled process because the peak current was proportional to the square root of the potential sweep rate. To analyze the redox reaction, a voltammetric simulation was performed. This gave a simulated voltammogram that was a good fit for the background (electrical double layer capacitance) subtracted voltammogram (Fig. 4). The redox potential ($E^{\ddagger}$) and diffusion coefficient ($D$) were 0.27 (vs. Ag/AgCl/saturated KCl) and 1.4 × 10$^{-5}$ cm$^2$ s$^{-1}$, respectively, and were in good agreement with previously reported values [14]. The heterogeneous electron transfer rate ($k^{\ddagger}$) was estimated to be 6.5 × 10$^{-5}$ cm s$^{-1}$, which was almost 1/20th that of the previously reported value [13]. It was suggested that the electrode reaction of [Fe(CN)$_6$]$^{3-}$ was slightly inhibited by the CNF covered with the MWCNT. The estimated electrode surface area was 0.63 cm$^2$ even though the apparent electrode surface area was only 0.24 cm$^2$. The larger effective surface area could be attributed to the carpet fiber-like morphology of the surface. Even if the film was immersed in the solution for 1 week or more, it did not decompose and could be used sufficiently as an electrode.
4. Conclusion
A CNF-based film electrode was manufactured using MWCNTs as an electrically conductive material by using a simple spray method. CNF prepared by the aqueous counter collision method gave good dispersion of the MWCNTs, which gave us the useful condition for film production by the spray method. When prepared by the spray method of a solution in which the mixing ratio and concentration of CNF and CNT were optimized, a conductive MWCNT/CNF film could be prepared. It was also shown that the film does not decompose even when immersed in the solution for a long period of time and can be sufficiently used as an electrode in the solution.

Acknowledgment
We thank Chuetsu Pulp & Paper Co., Ltd. (Tokyo, Japan) for samples of Nanoforest-S BB.

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