Electrically Conductive Bacterial Cellulose by Incorporation of Carbon Nanotubes

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Electrically conducting polymeric membranes were prepared by incorporating multiwalled carbon nanotubes (MWCNTs) into bacterial cellulose pellicles produced by *Gluconacetobacter xylinum*. The MWCNTs were dispersed in a surfactant (cationic cetyl trimethylammonium bromide) solution, and cellulose pellicles were dipped into the solution for 6, 12, and 24 h. The surfactants were then extracted in pure water and dried. Electron microscopy showed that the individual MWCNTs were strongly adhered to the surface and the inside of the cellulose pellicle. The conductivity of the MWCNTs-incorporated cellulose pellicle, as measured by a four-probe at room temperature, was 1.4×10^{-1} S/cm, based on the total cross-sectional area (approximately 9.6 wt % of MWCNTs). This suggests that the MWCNTs were incorporated uniformly and densely into the pellicles.

1. Introduction

Since their discovery in 1991, carbon nanotubes (CNTs) have attracted a great deal of interest in both academia and industry for their applications in areas such as electronic devices, biosensors, field emission displays, hydrogen storage, and composites, on account of their extraordinary electrical, physical, chemical, and structural properties.[1−3] By introducing small amounts of CNTs in the form of small bundles or individual nanotubes, the mechanical strength, electrical conductivity, and thermal conductivity of polymer composites can be improved tremendously compared with those of the pristine polymer.[4−7] In particular, multiwalled carbon nanotubes (MWCNTs) have been used to reinforce a large variety of polymers.[8−10] The large aspect ratios of CNTs allow the electrical conductivity of polymer composites to be enhanced to a greater extent than with other spherical conducting particles.[11,12] Their effect on the electrical properties of polymers has been studied extensively because CNTs can be used as an alternative to currently used fillers (e.g., carbon black) to increase the conductivity of polymers.[9] Improving the electrical conductivity of bulk polymers is important for a number of applications. For example, static electrical dissipation is essential for applications such as computer housings and exterior automotive parts.[9,13−15] However, it is difficult to disperse CNTs using ordinary composite fabrication methods because they are extremely flexible and possess a high aspect ratio. CNTs generally form stabilized bundles through van der Waals forces, resulting in the formation of hollow ropes.[16] Therefore, obtaining a good dispersion of CNTs is one of the key issues in their application to composites.[17,18] To optimize this process, dispersion of CNTs in a polymer matrix has been studied from different points of view, including both the noncovalent and covalent functionalization of CNTs.[19−21]

In this study, MWCNTs were adsorbed and embedded uniformly in bacterial cellulose using an aqueous MWCNT dispersion containing a surfactant. *Gluconacetobacter xylinum* produces cellulose extracellularly. This bacterial cellulose is expected to become a new industrial material on account of its unique structure and properties in terms of its purity, high crystallinity, ultrafine network, high mechanical stability, and low density.[22−25] In comparison with synthetic membranes such as polypropylene or poly(ethylene terephthalate), a bacterial cellulose film shows remarkable mechanical strength.[25] A surfactant was used to disperse the MWCNTs in water in order to minimize damage to the inherent properties of the individual nanotubes induced by the chemical modification. The MWCNTs were sonicated in aqueous solutions of cationic cetyl trimethylammonium bromide (CTAB), to stabilize them against van der Waals attraction.[26−35] Unlike most studies on simple blends of CNTs with polymeric materials,[36−38] the MWCNTs were incorporated into cellulose pellicles in the aqueous state, which act as nanoscale fillers. In this way, the MWCNTs could be well-dispersed in the cellulose. The morphology and electrical conductivity of the cellulose containing well-dispersed MWCNTs was also investigated.

2. Experimental Section

2.1. Preparation of Bacterial Cellulose Pellicles. *Gluconacetobacter xylinum* pd-5 was obtained from Yonsei University and used to produce the bacterial cellulose pellicles. The bacterium was cultured on Hestrin and Schramm (HS) medium, which was composed of 2% (w/v) glucose, 0.5% (w/v) yeast extract, 0.5% (w/v) bacto-peptone, 0.27% (w/v) disodium phosphate, and 0.115% (w/v) citric acid. All the cells precultured in a test tube containing a small cellulose pellicle on the surface of the medium were inoculated into a 500 mL Erlenmeyer flask containing 100 mL of the HS medium. The flasks were incubated statically at 30 °C for 14 days. The cellulose pellicles were dipped into 0.25 M NaOH for 48 h at room temperature in order to eliminate the cells and components of the culture liquid. The pH was then lowered to 7.0 by repeated washing with distilled water. The purified cellulose pellicles were stored in distilled water at 4 °C to prevent drying.

2.2. Preparation of MWCNT Dispersion. The MWCNTs (Iljin Nanotech Co., Korea) were synthesized by thermal chemical vapor deposition (CVD). The purity of the as-received pristine MWCNTs was 97%. The impurities present within the MWCNTs (such as metallic

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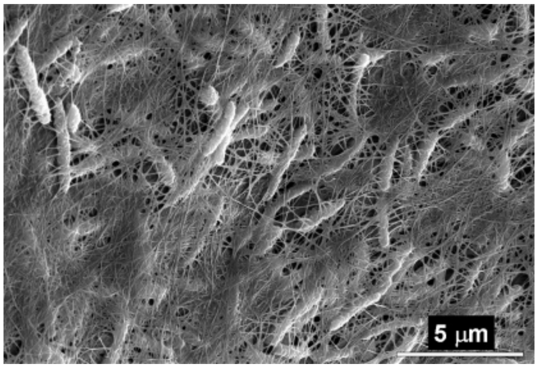

Figure 1. FESEM images of the freeze-dried surface of a bacterial cellulose pellicle cultured for 2 weeks.

catalysts) were eliminated by treating them with 3 M HNO_3 at 60 °C for 12 h, followed by refluxing in 5 M HCl at 120 °C for 6 h. The purity of the acid-treated MWCNTs was found to be 99% using thermogravimetric analysis (TGA, Polymer Lab., TGA1000, U.K.). The purified MWCNTs were then dispersed in pure water (0.5 mg/mL) with a cationic CTAB surfactant (0.3 wt % in water). Ultrasound was then applied to the MWCNT dispersion using an ultrasonic generator (Kodo Technical Research Co., Japan) with a nominal frequency of 28 kHz and a power of 600 W for 7 h at 25 °C.

2.3. Characterization. The surface morphology of all of the samples was observed using field emission scanning electron microscopy (FESEM, S-4300, Hitachi, Japan). The FESEM images were obtained by collecting the samples on an aluminum SEM disk, which was then coated with platinum. The acceleration voltages and working distances for each image were 15 kV and 6 mm, respectively. Transmission electron microscopy (TEM) was performed using a Philips CM 200 unit, operated at an acceleration voltage of 120 kV. The coagulants of bacterial cellulose particles and MWCNTs were observed by placing a drop of sample solution (concentration = 1 mg/mL) onto a 300 mesh copper grid coated with carbon. Approximately 2 min after deposition, the grid was tapped with filter paper to remove the surface water, which was followed by air-drying. The samples were vacuum-dried for 24 h at room temperature before the measurement. The electrical conductivity of the MWCNTs-adsorbed bacterial cellulose membrane was measured using a four-probe with a picoammeter containing an internal voltage source (487, Keithley, U.S.A.) and an impedance analyzer (4284A, HP, U.S.A.). Elemental analyses were performed with EA1112 (CE instrument, Italy) at the National Center for Inter-University Research Facilities of Seoul National University, Seoul, Korea.

3. Results and Discussion

The bacterial cellulose pellicles were cultivated in a flask for 2 weeks using glucose as the sole carbon source. FESEM of the freeze-dried gel surface showed the water-swollen cellulose gel to contain a random assembly of microfibrils with a diameter of approximately 30 nm (Figure 1). After extracting the cells with a 0.25 M NaOH solution for 48 h, the yellowish cellulose pellicle turned white, as shown in Figure 2a. The bacterial cellulose was characterized by its ultrafine network structure.

The purified MWCNTs were sonicated in aqueous solutions of the CTAB surfactants to stabilize them against van der Waals attraction. At the optimum surfactant concentration, the homogeneous dispersion of MWCNTs formed a single phase. Large and dense clusters of MWCNTs formed in the solution after sonication when the amount of surfactant was either too low or too high.[2,26−35] The optimum concentration of surfactant was approximately 0.3 weight % (wt %) in the case of the 0.05 wt % dispersion of MWCNTs. Once a homogeneous aqueous dispersion of MWCNTs had been obtained, the highly swollen gellike bacterial cellulose was immersed in a bath containing the MWCNTs dispersion with CTAB for 6, 12, and 24 h at room temperature, withdrawn, and rinsed several times in deionized water to remove the surfactants. The samples were then vacuum-dried at room temperature overnight (Figure 2). A 0.02 wt % dispersion of MWCNTs with 0.1 wt % of surfactant was also used to prepare the membrane with a different amount of MWCNTs for comparison. The morphology of the MWCNTs-adsorbed cellulose pellicle was observed using FESEM (Figure 3). The MWCNTs were densely adsorbed over the surface of the cellulose pellicle. The cross section and inner layer of the MWCNTs-adsorbed cellulose pellicles were also examined after fracturing them in liquid nitrogen (Figure 4). Two different domains could be distinguished, a continuous network of cellulose microfibrils and incorporated MWCNTs distributed among them. The bright regions in the images were attributed to the MWCNTs on account of their high conductivity, and the MWCNTs were distributed homogeneously in the cellulose pellicle without aggregation.[39] The homogeneous dispersion of CNTs in a polymer matrix is one of the most important requirements for achieving a uniform conductivity all over the composite. It was found that the individual MWCNTs adhered strongly to the cellulose pellicle surfaces even after sonication in deionized water. TEM and SEM provided evidence of an interaction between the cellulose and MWCNTs, even after sonication for 24 h in water (Figure 5). However, the precise mechanism of their interaction is unclear. The typical diameter of the MWCNTs observed by TEM is approximately 15−20 nm, as shown in Figure 5.

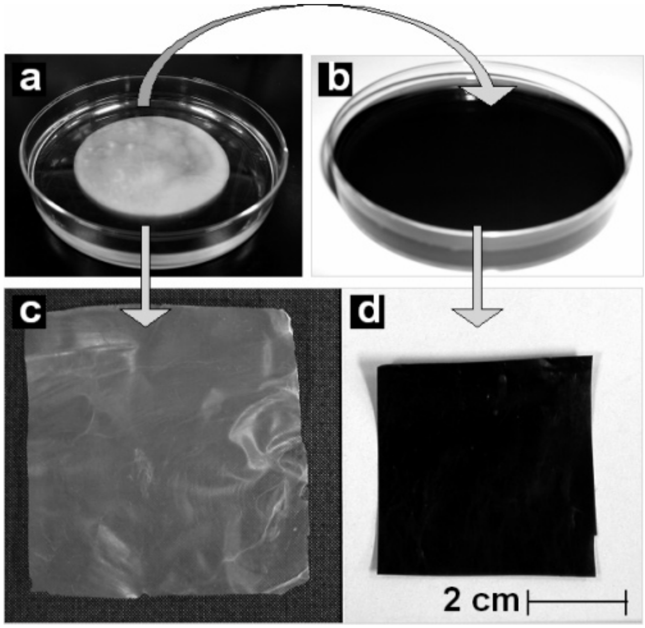

Figure 2. Preparation of the MWCNTs-incorporated bacterial cellulose membrane: (a) water-swollen gellike bacterial cellulose pellicle after cell extraction in a NaOH solution; (b) aqueous carbon nanotube dispersion (0.05 wt %) with a CTAB surfactant (0.3 wt %); (c) vacuum-dried cellulose pellicle; (d) MWCNTs-incorporated bacterial cellulose pellicle.

The adhesion of the nanotubes to the cellulose pellicles surface was assumed to be related to the interaction between the cellulose and the oxygen-containing species on the nanotubes, such as carboxylic acid groups introduced during purification.[26−35] Therefore, the same process was applied to Whatman cellulose filter paper (Grade 2). The SEM images showed that the nanotubes were adsorbed on the surfaces of

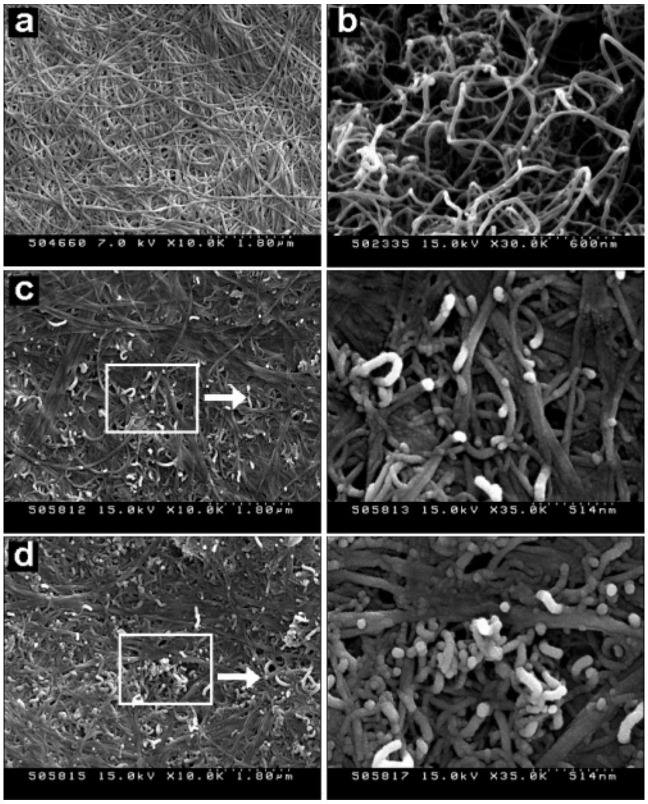

Figure 3. FESEM images of (a) purified bacterial cellulose pellicle; (b) purified MWCNTs; (c and d) surface of the MWCNTs-incorporated bacterial cellulose pellicle, (c) immersed in 0.02 wt % of MWCNTs dispersion for 24 h and (d) immersed in 0.05 wt % of MWCNTs dispersion for 24 h.

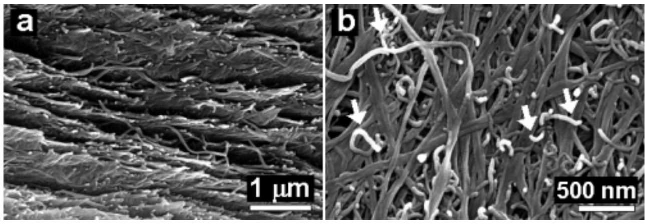

Figure 4. FESEM images of (a) the fractured surface and (b) the inner layer of the MWCNTs-incorporated bacterial cellulose pellicle; immersed in 0.05 wt % of MWCNTs dispersion for 24 h; arrows show MWCNTs.

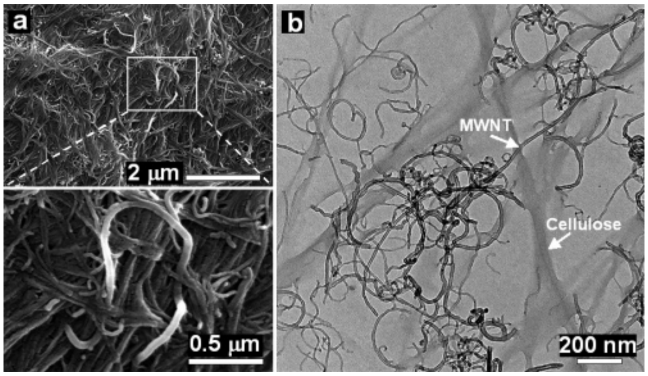

Figure 5. (a) FESEM and (b) TEM images of the MWCNTs-incorporated bacterial cellulose pellicles after sonication in water for 24 h.

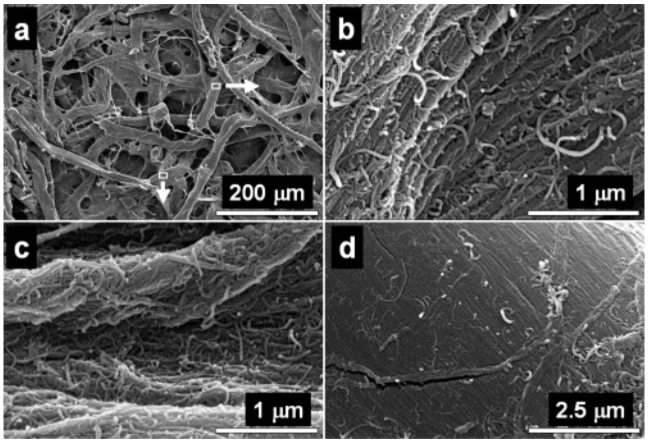

Figure 6. FESEM images of (a−c) the surface and (d) the inside of the MWCNT-adsorbed Whatman cellulose membrane filter.

this filter (Figure 6), confirming the likelihood of our hypothesis. Furthermore, the properties of bacterial cellulose are quite different from those of plant cellulose, which is related to the ultrafine network architecture, high hydrophilicity, and moldability during formation. During cultivation, *G. xylinum* produces a cellulose pellicle with a highly swollen fiber network, resulting in an extensive interior surface area. The cellulose pellicle is quite hydrophilic due to the presence of pore structures and tunnels within the wet pellicle.[25] The water retention value of the never-dried bacterial cellulose is approximately 1000%, which is superior to the 60% observed in typical plant cellulose like cotton linters.[25] Therefore, it is proposed that while dipping the cellulose pellicle in the nanotube dispersion, nanotubes with the CTAB surfactant migrate into the inside of the pellicle with a highly porous structure (Figure 7). After vacuum-drying at room temperature, the porous structure of the pellicle collapses into the dense structure with the MWCNTs, and this process is not reversible with water. To confirm this hypothesis, the process for incorporating nanotubes into a vacuum-dried cellulose pellicle was performed and observed by FESEM. The nanotubes were only adsorbed on the surface of the cellulose pellicle, as shown in Figure 8, because the water retention values of the vacuum-dried and reswollen bacterial cellulose with water were much lower and comparable with those of plant cellulose. This suggest that they do not maintain considerable porous structure after the nanotubes' migration to the interior.[25]

The electrical conductivity of the MWCNTs-incorporated cellulose pellicle was measured. The four-probe electrical measurements of the membrane gave a room-temperature dc conductivity (σ_{DC}) of approximately 2.0×10^{-2} to 1.4×10^{-1} S/cm, based on the total cross-sectional area. It should be noted that most of the MWCNTs were well-dispersed in the cellulose pellicles, even though the porosity of the cellulose pellicles might have contributed to lower the electrical conductivity. Moreover, the electrical conductivity of the pure MWCNTs used in this study was approximately 2.3×10^{1} S/cm.[40] An attempt was made to determine the amount of MWCNTs adsorbed in the cellulose membrane using thermogravimetric analysis (TGA) under a nitrogen atmosphere. However, this measurement was unsuccessful, because the cellulose membrane charred after burning at temperatures up to 600 °C and did not decompose completely.[41] Therefore, the contents of MWCNTs in cellulose were calculated using the results from elemental analysis, as shown in Table 1 according to the immersion time of the pellicles in two different MWCNTs concentrations (0.02 and 0.05 wt %). The contents of MWCNTs ranged from 3.2 to 9.6 wt % in cellulose, which was dependent on the immersion time and the initial concentration of MWCNTs in the dispersion. It should be noted that the nitrogen shown in Table 1 is from the bacteria remaining in the cellulose pellicles even after purifica-

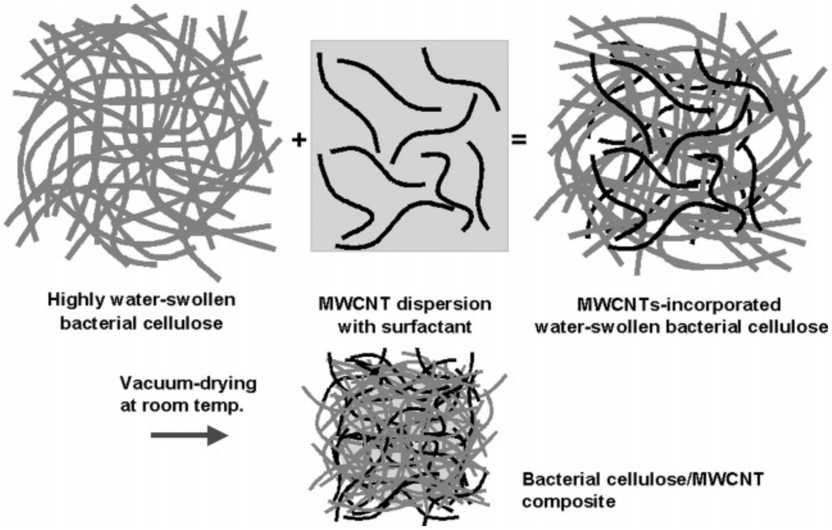

Figure 7. Schematic diagram of the process of incorporating the nanotubes into the water-swollen bacterial cellulose pellicle.

Table 1. Elementary Analysis of MWNT-Incorporated Bacterial Cellulose Pellicles and Their Electrical Conductivity

conc of MWCNT in water (wt %)	immersion time (h)	C (%)	H (%)	N (%)	content of MWCNTs in cellulose (wt %)	electrical conductivity (S/cm)
		43.57[a]	6.30[a]	0.8[a]		
0.02	6	45.44	6.42	0.57	3.2	2.3×10^{-2}
	12	46.04	6.75	0.66	4.2	2.0×10^{-2}
	24	46.83	6.88	0.79	5.7	2.6×10^{-2}
0.05	6	47.70	6.54	0.83	7.2	6.1×10^{-2}
	12	48.17	6.96	0.84	8.2	1.0×10^{-1}
	24	48.97	6.58	0.80	9.6	1.4×10^{-1}

[a] Pure bacterial cellulose after treatment with diluted NaOH solution.

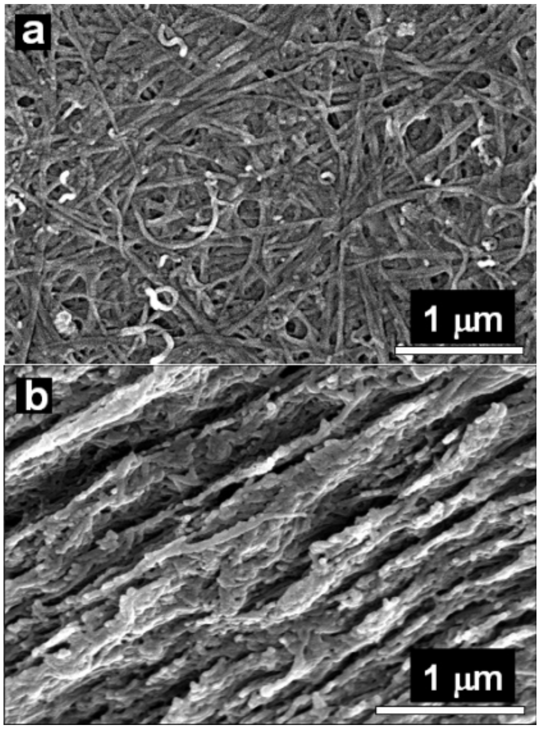

Figure 8. FESEM images of (a) the surface and (b) the fractured surface of the bacterial cellulose pellicles; the nanotubes with CTAB were incorporated into the vacuum-dried cellulose pellicle.

tion in dilute NaOH solution.[25] Their electrical conductivities were also dependent on the amount of MWCNTs in the cellulose membranes. Although MWCNTs were also incorporated into the Whatman cellulose filters, their conductivity could not be measured on account of their large pore size, as shown in Figure 6. The conductivity in a composite film made by melt compounding was reported to reach a plateau of approximately 3.5×10^{-2} S/cm at high MWCNT loadings (12 wt %).[42] Overall, in this study, a simple process was developed for producing an electrically conducting polymeric membrane containing MWCNTs uniformly incorporated in the cellulose pellicles.

4. Conclusions

MWCNTs-incorporated bacterial cellulose was prepared by effectively dispersing the MWCNTs by dipping a cellulose pellicle in an aqueous MWCNT dispersion containing a CTAB surfactant. This composite process produced electrically conducting cellulose pellicles containing well-dispersed and embedded MWCNTs, as observed by electron microscopy. The electrical conductivity of the cellulose/MWCNT composite was found to be approximately 1.4×10^{-1} S/cm. It was found that the incorporation process is a useful method not only for dispersing MWCNTs in an ultrafine fibrous network structure but also for enhancing the electrical conductivity of the polymeric membranes.

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