Transparent Conducting Films Based on Nanofibrous Polymeric Membranes and Single-Walled Carbon Nanotubes

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ABSTRACT: Transparent and electrically conducting films were fabricated using a novel and simple method in which single-walled carbon nanotubes (SWCNTs) adsorbed onto bacterial cellulose membranes were embedded into a transparent polymer resin. The bacterial cellulose membranes consisting of numerous nanofibrils were found to play important roles in this process. The bacterial cellulose membranes impart optical transparency to the nanocomposites due to the size of the materials during the synthesis of the nanocomposite using a transparent polymer resin. The membranes play a secondary role as a template for depositing uniformly dispersed SWCNTs. This results in not only electrically conducting pathways but also prevents interference from the transmittance of optically transparent nanocomposites. Transparent conducting films with a wide range of transmittances and surface resistances could be obtained by controlling the immersion time and SWCNT concentration in the SWCNT dispersions. A transparent conducting film with a transmittance and surface resistance of 77.1% at 550 nm and 2.8 kΩ/sq, respectively, was fabricated from a 0.01 wt %. SWCNT dispersion for an immersion time of 3 h. In addition, the transparent conducting films were quite flexible and maintained their properties even after crumpling. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2864–2872, 2009

Key words: singlewalled carbon nanotubes; bacterial cellulose membrane; nanocomposites

INTRODUCTION

Carbon nanotubes (CNTs) are attractive candidates for polymer/CNT nanocomposites on account of their unique properties and structure.[1,2] Many studies have examined CNTs as an electronic material for applications to electronics.[3,4] In particular, transparent and electrically conducting films based on CNTs have been studied extensively owing to the outstanding electrical conductivity and mechanical properties of the CNTs and the relatively ambient processing conditions used for the manufacture of CNT films.[5,6] Electrically conducting composites using a one-dimensional wire type filler show better transparency than those using a spherical type filler when both have similar electrical conductivity. Therefore, CNTs with high aspect ratios are beneficial for forming conducting pathways in films to produce nanocomposites with high optical transparency.[7] Apart from being used with CNTs, conducting polymers are used mainly in transparent and electrically conducting films. However, films based on conducing polymers have relatively low conductivity and a bluish color due to the adsorption of light above 400 nm. This has prompted research into transparent and electrically conducting films based on CNTs.[7]

Transparent and electrically conducting films have attracted considerable attention for use in optoelectronic areas. Examples include organic light emitting devices, thin-film transistors, liquid crystal displays, and solar cells.[7–10] Currently, traditional transparent and electrically conducting films are available in the form of glasses coated with indium tin oxide (ITO).[11] However, these films have limitations in terms of how much they can improve the electric devices. ITO films show a considerable increase in surface resistance upon bending when coated on a flexible plastic substrate.[12,13] The other limitations are related to the requirements of complicated etching conditions, such as a vacuum state and high temperatures.[14] Therefore, highly flexible, transparent, and electrically conducting films are needed for state-of-the-art flexible products based on CNTs. Many studies have developed a variety of methods for fabricating transparent and electrically

conducting films based on CNTs. These include filtration, spraying, layer-by-layer, spin-coating, and an enhanced method that mixes dipping and spraying methods.[15–19]

In this study, flexible, transparent, and electrically conducting films were prepared using an adsorption method. The proposed method is quite convenient and uncomplicated, involving the simple adsorption of single-walled carbon nanotubes (SWCNTs) onto a bacterial cellulose hydrogel. This is followed by immersing the SWCNTs in the dried state into transparent polymer resin. The transparency of the nanocomposites originates from both the bacterial cellulose membrane and transparent polymer because the nanocomposites do not scatter light due to the nanofibrils in bacterial cellulose. In addition, electrical conductivity is possible with CNTs. In a previous study, transparent and electrically conducting films were formulated based on multiwalled carbon nanotubes (MWCNTs) using an identical method.[20] SWCNTs were selected to obtain films with advanced properties because their lower light adsorption than MWCNTs make them more suitable for transparent and electrically conducting films.[16] It is important to separate the SWCNT bundles individually to achieve suitable electrical properties. A SWCNT dispersion was previously achieved using the surfactant, sodium dodecylbenzene sulfonate (NaDDBS), which was also used in this study.[21] Furthermore, transparent and electrically conducting films based on CNTs require highly dispersed CNTs even after manufacturing the final product. Bacterial cellulose nanofibrils have the advantage of not only depositing but also maintaining a uniform SWCNT dispersion in the final product. Transparent and electrically conducting films fabricated by the proposed method represent novel means of processing these materials. The method is a candidate process for the production of optoelectronic devices.

EXPERIMENTAL

The SWCNTs were supplied by Hanwha Nanotech Co., Korea (ASP-100F). The SWCNTs were produced through purification with gas phase oxidation and an acid treatment. The SWCNTs were dispersed in deionized water with the anionic surfactant, NaDDBS (Aldrich), at a SWCNT to surfactant weight ratio of 10 : 1.[21] The SWCNT dispersions were fabricated at SWCNT concentrations of 0.005, 0.01, and 0.02 wt %. Ultrasound was applied using an ultrasonic generator (Kodo Technical Research Co., Korea) with a nominal frequency of 28 kHz and a power of 600 W for 4 h at 25°C to obtain a homogeneous dispersion.
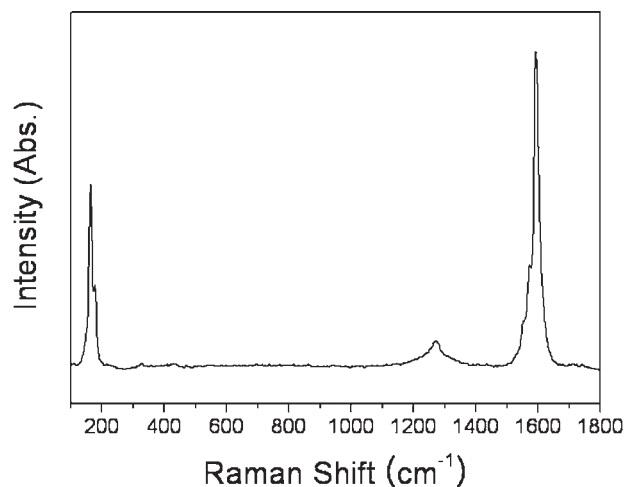
The bacterial cellulose membrane used in this study was synthesized from *Acetobacter xylinum* BRC

5. The bacteria was cultured in Hestrin and Schramm (HS) medium, which consisted of 2% (w/v) glucose, 0.5% (w/v) yeast extract, 0.5% (w/v) bactopeptone, 0.27% (w/v) disodium phosphate, and 0.115% (w/v) citric acid. All the cells used in the synthesis of the bacterial cellulose membrane were precultured in a test tube for 3 days until the activity of the bacteria reached a maximum. The active bacteria (50 μL) were then injected into a culture dish containing 5 mL of the HS medium. The medium was then incubated at 30°C for 3 days. The fabricated bacterial cellulose hydrogel was purified by immersing it into a 0.25 M aqueous sodium hydroxide (NaOH) solution for 48 h at room temperature. The NaOH-treated bacterial cellulose hydrogel was then neutralized by repeated washing with deionized water. The purified bacterial cellulose hydrogel was stored in deionized water at 4°C until needed. The bacterial cellulose membrane was obtained by drying the bacterial cellulose hydrogel under ambient conditions.

The cocoons used in this study (*B. mori*) were boiled for 30 min in an aqueous solution of 0.02 M Na_2CO_3, and rinsed thoroughly with deionized water to extract the glue-like sericin proteins. The extracted silk fibroin was dissolved in a 9.3 M LiBr solution at 60°C. The solution was then dialyzed in deionized water using Slide-a-Lyzer dialysis cassettes for 48 h.[22] The final concentration of the aqueous silk fibroin solution was ~2 wt %, which was determined by weighing the remaining solid after drying. The silk fibroin solution was cast on a polystyrene Petri dish surface for 24 h at room temperature. The completely dried silk fibroin film was then crystallized by annealing for 3 h using vapor in a vacuum.[23] In addition, the optical nanocomposite film was obtained by immersing the bacterial cellulose membranes in 1.5 g of a 2 wt % aqueous silk fibroin solution, which was followed by drying at room temperature. The optical nanocomposite film was crystallized using an identical method to that used for silk fibroin film.

The transparent conducting film was prepared by adsorbing the SWCNTs onto a bacterial cellulose hydrogel. The SWCNT-adsorbed bacterial cellulose hydrogel was washed with a large amount of deionized water to remove the residual surfactant and SWCNTs. The SWCNT-adsorbed bacterial cellulose membrane was prepared by drying the hydrogel at room temperature. The transparent conducting film was crystallized using the same method for crystallizing silk fibroin film and optical nanocomposite film.

Raman spectrum was obtained by neodymium (Nd) laser excitation at 1064 nm (Bruker RFS 100/s, Bruker Optics, Germany) using an InGaAs detector. The dispersity of the SWCNTs and the surface of the

Figure 1 Raman spectrum of SWCNT.

SWCNT-adsorbed bacterial cellulose membrane and transparent conducting film were observed by atomic force microscopy (AFM, SPA400, Seiko Ins., Japan) operated in tapping mode. The transmittance of the bacterial cellulose membranes, silk fibroin film, optical nanocomposite film, and transparent conducting films were measured over the wavelength range, 350–900 nm, using a UV-visible spectrophotometer (Model 8453, Agilent Technologies Inc., USA). The SWCNTs, bacterial cellulose and SWCNT-adsorbed bacterial cellulose membrane were observed by transmission electron microscopy (TEM, CM200, Philips, Netherlands) operating at an acceleration voltage of 100 kV. The morphology of the SWCNT-adsorbed bacterial cellulose membrane and transparent conducting film was observed by field emission scanning electron microscopy (FESEM) with energy dispersive spectroscopy (FESEM/EDS, S-4300SE, Hitachi, Japan). The FESEM images were obtained by collecting the samples on an aluminum a SEM disk, which was then precoated with platinum by ion sputtering (E-1030, Hitachi, Japan) before analysis. Dumb-bell specimens were made according to the ASTM D 638 standard for tensile testing. The tensile properties were tested on an Instron 4665 ultimate tensile testing machine at 20°C and 30% humidity. The cross-head speed was set to 5 mm/min. At least 10 specimens were averaged to collect the tensile properties of each sample. The electrical conductivity of the SWCNT-adsorbed bacterial cellulose membrane was measured using a four-probe with a picoammeter containing an internal voltage source (487, Keithley, Solon, OH) and an impedance analyzer (4284A, HP).

RESULTS AND DISCUSSION

SWCNTs tend to aggregate due to van der Waals attraction and exist in the form of bundles. A stable SWCNT dispersion consisting of individual SWCNTs is essential for employing the inherent properties of SWCNTs when making nanocomposites, e.g., transparent conducting films. Therefore, the preparation of an individual SWCNT dispersion is essential before adsorbing the SWCNTs onto the bacterial cellulose hydrogel. To create such a stable SWCNT aqueous dispersion, surfactant-stabilized SWCNTs in water were fabricated using NaDDBS, which is the optimal surfactant for individually stable SWCNTs.[21] Figure 1 shows a Raman spectrum of the SWCNT and Figure 2(a) shows the NaDDBS-assisted SWCNT dispersion at a concentration of 0.01 wt %. The photo image shows a homogeneous black solution. Information on the diameter and dispersity of the SWCNTs was obtained by AFM. For AFM analysis, the stabilized SWCNTs were deposited by uniformly coating a homogeneous SWCNT dispersion onto a silicon wafer. Figure 2(b) shows an AFM image of the dispersed SWCNTs. Suitably separated SWCNTs with diameters of ~2 nm were observed, indicating that the SWCNTs had been sufficiently debundled. The SWCNT dispersions at the other concentrations showed identical results. The individual state of the SWCNTs is an important
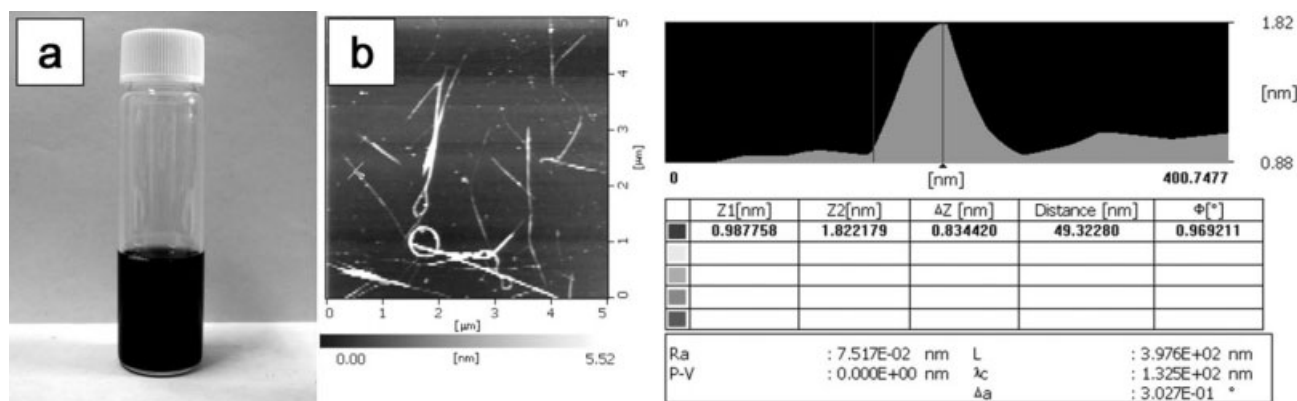
Figure 2 (a) SWCNT dispersion and (b) AFM image of SWCNTs on a silicon surface.
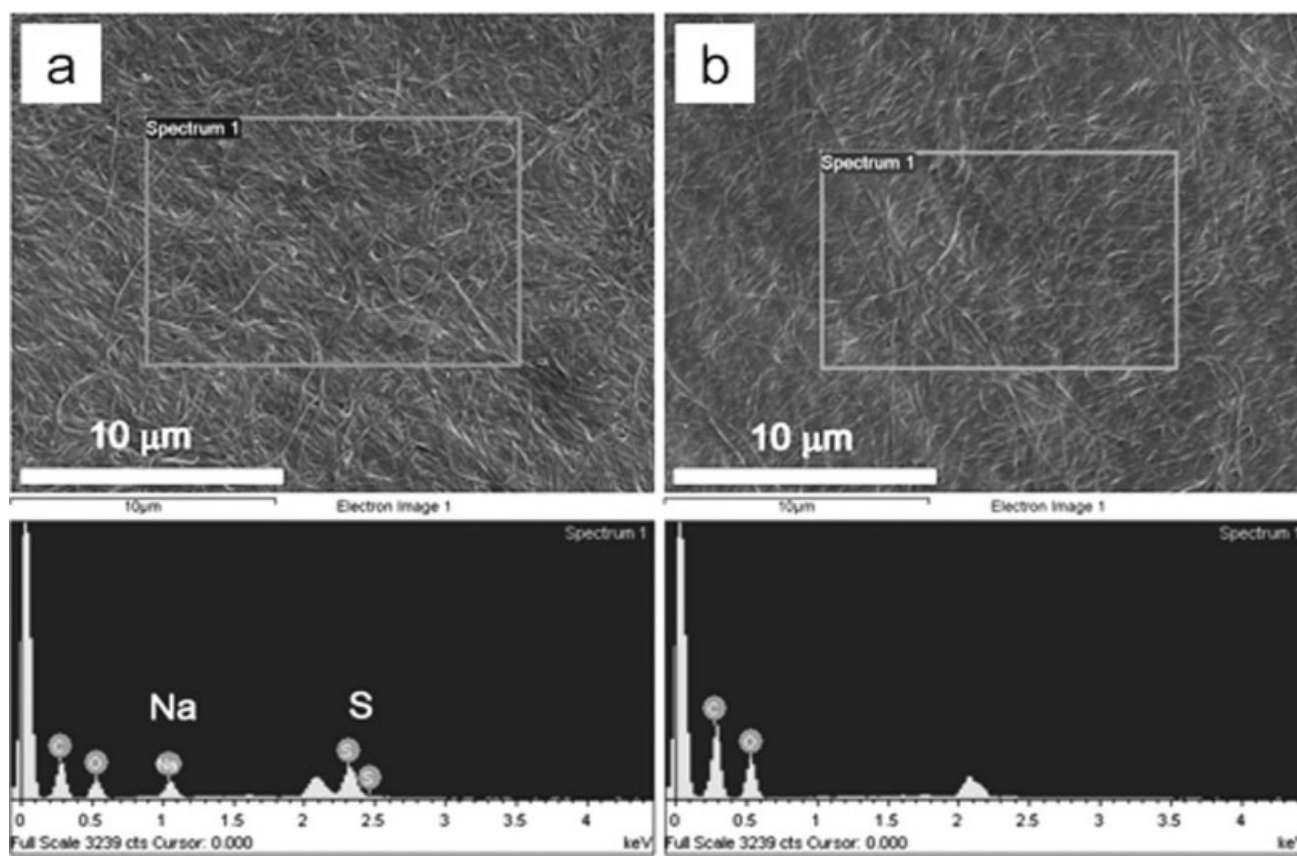
Figure 3 Elements analysis results by FESEM/EDS (a) SWCNTs onto a bacterial cellulose hydrogel with surfactant, and (b) after washing with a large amount of deionized water to remove the residual surfactant of the SWCNTs on the bacterial cellulose hydrogel.

factor when fabricating transparent conducting films with the appropriate electrical and optical properties. The transparent conducting films were prepared by adsorbing the SWCNTs onto a bacterial cellulose hydrogel. The SWCNT-adsorbed bacterial cellulose hydrogel was washed with a large amount of deionized water to remove the residual surfactant and SWCNTs (Fig. 3)

As shown in Figure 4, the transmittance of the bacterial cellulose membrane and silk fibroin film at 550 nm was 35.9 and 98.7%, respectively. This means that the bacterial cellulose membrane is quite opaque, whereas the silk fibroin film is transparent in the visible wavelength range. Indeed, a white bacterial cellulose membrane and a clear silk fibroin film were obtained. An optical nanocomposite film was prepared by immersing the bacterial cellulose membrane into a silk fibroin solution. The membrane was then dried. Although the optical nanocomposite film contained an opaque bacterial cellulose membrane, it was fairly transparent. The transmittance of the optical nanocomposite film was 93.7% at 550 nm. For these films to be suitable as an optically transparent composite material, they need to be free from optical scattering. One of the conditions related to

this is that the refractive index (RI) of the components in the composite materials be within 0.02 of each other.[24] For the optical nanocomposite film prepared with the bacterial cellulose membrane and silk fibroin, the RI of the cellulose fiber was 1.618 along
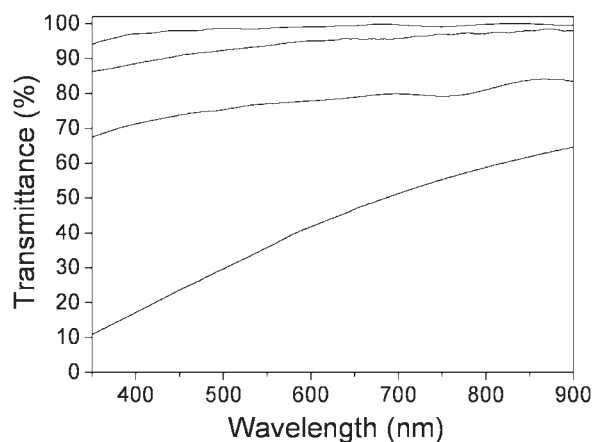

Figure 4 Light transmittance of silk fibroin film, optical nanocomposite film, transparent conducting film fabricated from a 0.01 wt % SWCNT dispersion for an immersion time of 3 h and a bacterial cellulose membrane (from high to low transmittance).
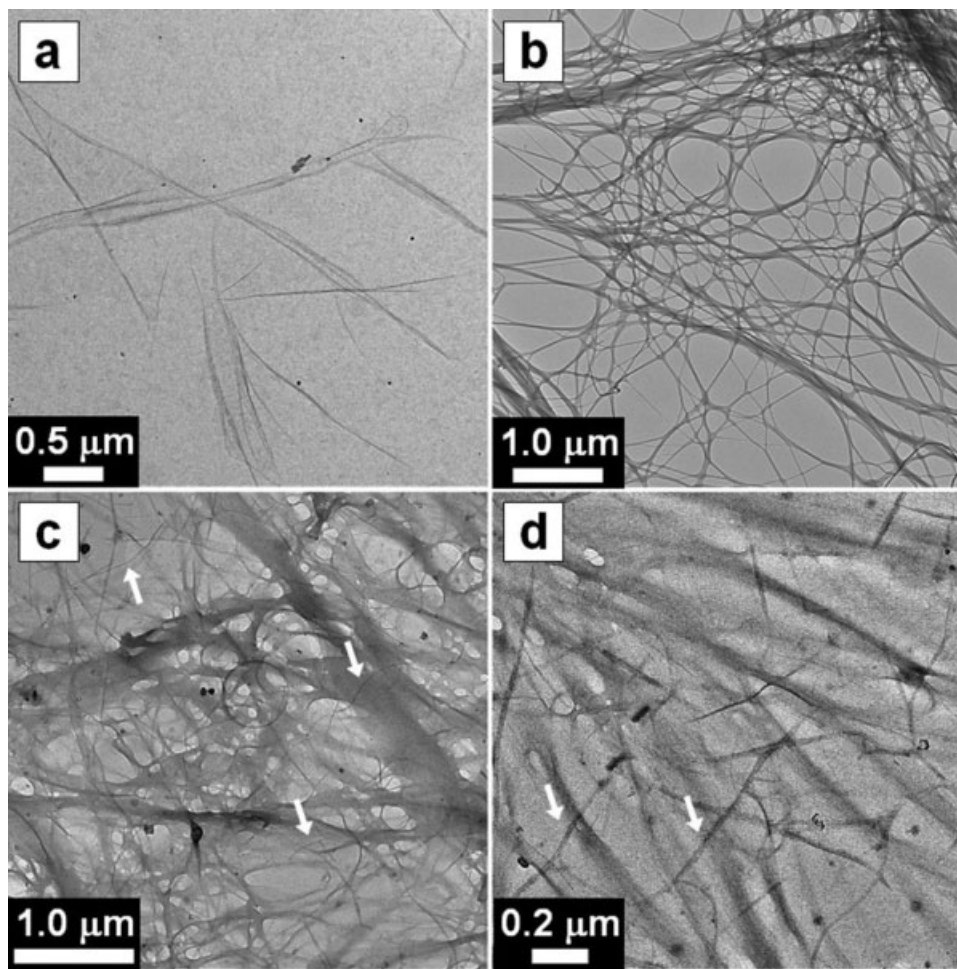
Figure 5 TEM images of (a) SWCNTs, (b) bacterial cellulose membrane, (c) SWCNT-adsorbed bacterial cellulose membrane and (d) magnified image.

the fiber and 1.544 in the transverse direction. On the other hand, the RI of the water-based crystallized silk fibroin film was 1.497 at 633 nm and 20°C.[20,25] Despite the large difference in RI between the bacterial cellulose membrane and silk fibroin film, the optical nanocomposite film maintained the transmittance of the silk fibroin film. The other requirement of optically transparent composite materials is that the additives incorporated into the transparent matrix, such as particles or fibers, have a diameter less than the wavelength of visible light. Additives with a diameter one-tenth of the wavelength of visible rays do not scatter light.[25] The optical nanocomposite film can be free from light scattering because the bacterial cellulose membrane has a network structure of numerous nanofibrils with diameters ranging from 10 to 50 nm, which fulfills the requirement of small additives.[26] The nanosize effect of bacterial cellulose nanofibrils can impart transparency to the optical nanocomposite film with only a slight decrease in light transmittance compared with a silk fibroin film. Several

studies of nanocomposites using nanofibrils have been carried out. Optically transparent nanocomposites based on epoxy resin have been prepared through reinforcement with an electrospun nylon-4,6 membrane as well as a bacterial cellulose membrane.[25,27] Studies using membranes with nanofibrils suggest that the high transparency is due to the nanosize effect of the nanocomposites. In addition to the transparency of nanocomposites, bacterial cellulose membranes have many advantages that make it an excellent nanocomposite material due to the unique properties of the material. The ribbon-shaped ultra-fine nanofibril network with extensive hydrogen bonds was reported to lead to an inherently high Young's modulus and tensile strength, which makes it suitable for use as a reinforcing material.[28] Moreover, high thermal conductivity and a low coefficient of thermal expansion make these materials potentially useful in optoelectronic fields, such as display technology.[29,30] One study reported that a bacterial cellulose membrane can be used as a substrate for flexible organic light emitting devices,
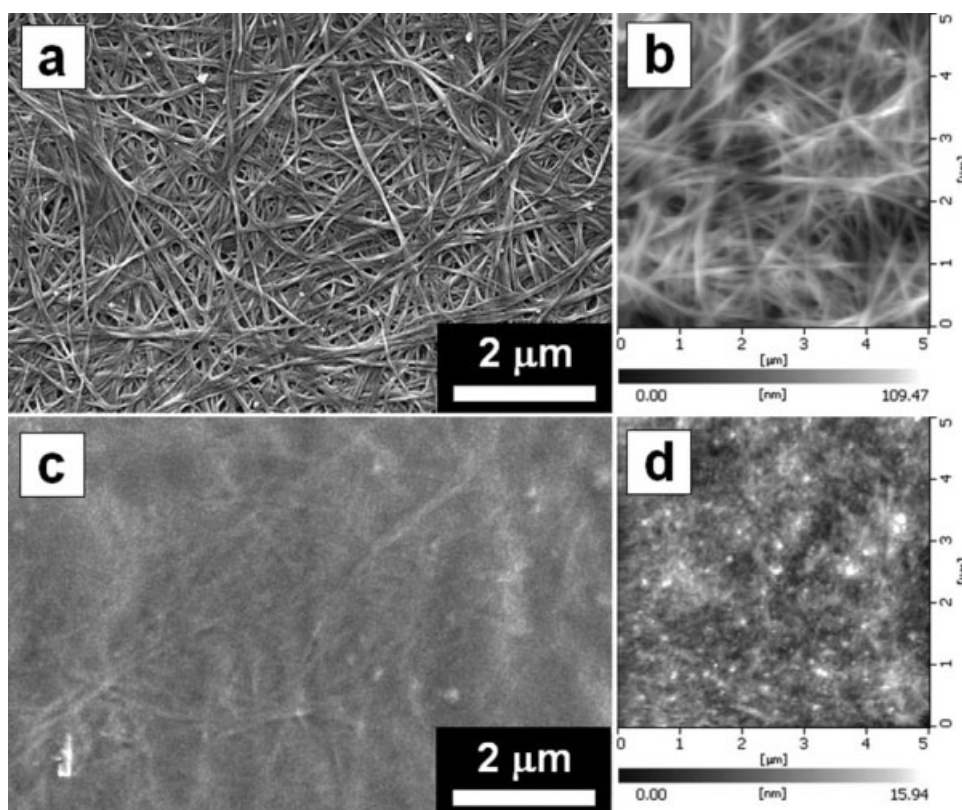
Figure 6 (a) FESEM image and (b) AFM image of the SWCNT-adsorbed bacterial cellulose membrane before the introduction of silk fibroin, (c) FESEM image and (d) AFM image of SWCNT-adsorbed bacterial cellulose membrane after the introduction of silk fibroin (transparent conducting film).

indicating potential applications in the flexible electronic device industry.[8] The many advantages of bacterial cellulose membranes make it a suitable material for use in transparent conducting films.

The SWCNT-adsorbed bacterial cellulose membrane was prepared by embedding a bacterial cellulose hydrogel into a homogeneous SWCNT dispersion that was previously fabricated. As shown in Figure 5(a,b), there was some structural similarity between the SWCNTs and bacterial cellulose nanofibrils. In addition, the bacterial cellulose hydrogel with a high water holding capacity is advantageous for adsorbing SWCNTs dispersed in an aqueous solution due to its affinity with water.[31] Therefore, individual SWCNTs will adhere uniformly to the bacterial cellulose nanofibrils while maintaining their dispersity. As a result, it is possible to obtain a SWCNT-adsorbed bacterial cellulose membrane. It was difficult to observe the SWCNTs adsorbed on the bacterial cellulose nanofibrils by FESEM due to the nanosize diameter of the SWCNTs and the similarity in morphology between these two materials [Fig. 6(a)]. Therefore, the SWCNT-adsorbed bacterial cellulose membranes were examined by TEM to confirm the addition of the SWCNTs to the bacterial cellulose nanofibrils. The images showed SWCNTs with the nanofibrils in the interior of the bacterial

cellulose membrane [Fig. 5(c,d)]. Although making a distinction between components is not straightforward by TEM, the straighter and shorter SWCNTs were introduced to the longer bacterial cellulose nanofibrils, as indicated by the arrows in the magnified TEM image of the SWCNT-adsorbed bacterial cellulose membrane. The electrical properties of the transparent conducting film depend on the adsorption of SWCNTs on the bacterial cellulose nanofibrils network to form an electrical pathway. Moreover, the SWCNTs dispersed uniformly on the bacterial cellulose nanofibrils can impart high transparency to the transparent conducting film.

Transparent conducting films were obtained by introducing silk fibroin into the SWCNT-adsorbed bacterial cellulose membrane. In addition to offering high transparency to the transparent conducting films, there are a number of benefits of using silk fibroin. Figure 6 shows the surface of the SWCNT-adsorbed bacterial cellulose membrane before [Fig. 6(a,b)] and after introducing silk fibroin, i.e., after creating a transparent conducting film [Fig. 6(c,d)]. Silk fibroin filled the spaces between the bacterial cellulose nanofibrils, and a small amount of it covered the surface of the bacterial cellulose membrane. As a result, the FESEM images show that the surface of the transparent conducting film is smoother than
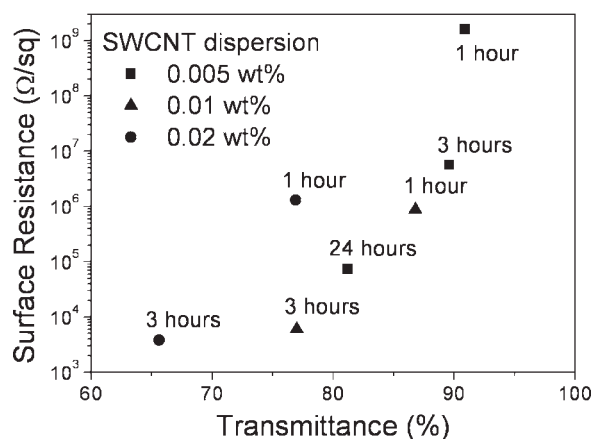
Figure 7 Surface resistance (Ω/sq) as a function of transmittance (%) at 550 nm of a transparent conducting film depending on the immersion time and SWCNT concentration of the SWCNT dispersion.

that of the SWCNT-adsorbed bacterial cellulose membrane. In practical applications, a rough surface might result in local heating that can ultimately lead to thermal damage, thereby reducing the lifetime of the devices.[32] The degree of roughness actually decreased from 109 to 15 nm after adding the nanofibrils silk fibroin, as observed by AFM. Silk fibroin has attracted considerable interest in many nanotechnology fields on account of its high mechanical and thermal properties.[33] Overall, the water-based crystallized silk fibroin film used in this study is suitable for use as a coating material for transparent conducting films because it is highly transparent and flexible.[23] Silk fibroin as a coating material can also prevent the loss of SWCNTs from the surface of the transparent conducting films.

Regarding the mechanical properties of transparent conducting films, the tensile strength and

Young's modulus of the optical nanocomposite film were 130.3 $\pm$ 3.2 MPa and 6.0 $\pm$ 0.8 GPa, respectively. The Young's modulus and tensile strength of the transparent conducting films were similar to optical nanocomposite films. These similar mechanical properties were attributed to the few SWCNT introduced in transparent conducting films.

Figure 7 shows the surface resistance-transmittance of the transparent conducting films. Two experimental conditions were varied when the transparent conducting films were prepared by embedding the bacterial cellulose hydrogel into the SWCNT dispersion: the immersion time of the bacterial cellulose hydrogel into the SWCNT dispersion and the concentration of SWCNT in the dispersion. As shown in Figure 7, at the same SWCNT dispersion, a longer immersion time led to a steady decrease in both the transmittance and surface resistance of the resulting transparent conducting films. With increasing immersion time, additional SWCNTs could be adsorbed on the bacterial cellulose nanofibrils, resulting in a decrease in transmittance and surface resistance. In contrast, different results were obtained when the electrical properties were examined as a function of the SWCNT concentration in the dispersions at identical immersion times. As expected, the transmittances of the transparent conducting films decreased with increasing SWCNT concentration. However, the surface resistance of the transparent conducting films produced from the 0.005, 0.01, and 0.02 wt % SWCNT dispersions were 1.6×10^9, 8.7×10^5, and 1.3×10^6 Ω/sq, respectively, at an immersion time of 1 h, and 5.6×10^6, 2.8×10^3, and 2.5×10^3 Ω/sq, respectively, at an immersion time of 3 h. This shows that the surface resistance does not decrease when a SWCNT dispersion with a concentration >0.01 wt % is used.
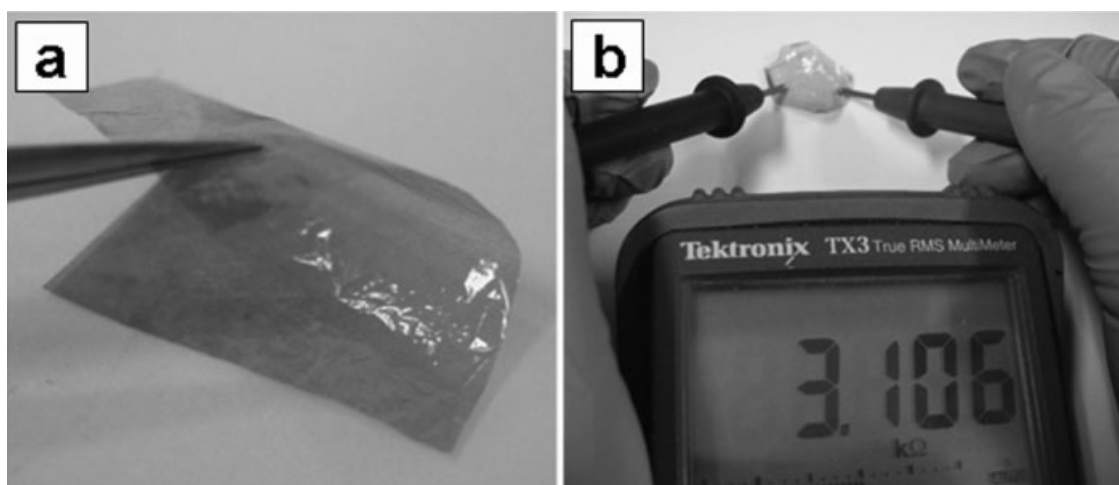

Figure 8 Optical photographs of (a) flexibility of the transparent conducting films, and (b) surface resistance measurement of a crumpled transparent conducting film fabricated from a 0.01 wt % SWCNT dispersion for an immersion time of 3 h.

It also suggests that 0.01 wt % is a critical concentration for the SWCNTs to create a sufficient conducting network to produce electrically conducting pathways. However, the transparent conducting films that used the 0.01 to 0.02 wt % SWCNT dispersions did not show any clear decrease in surface resistance. This suggests that a SWCNT concentration > 0.01 wt % does not decrease the surface resistance. It is possible to manufacture transparent conducting films with various transmittances and surface resistances by controlling the immersion time or SWCNT concentration of the SWCNT dispersions. The transparent conducting films prepared by immersing a bacterial cellulose hydrogel into a 0.01 wt % SWCNT dispersion for 3 h had a transmittance and surface resistance of 77.1% at 550 nm and 2.8 kΩ/sq, respectively. (Fig. 4 shows the transmittance of this film in the visible ray wavelength range.) The transmittance of the optical nanocomposite film without the SWCNTs was 93.7%. On the other hand, relative transmittance of the transparent conducting film to the optical nanocomposite film was enhanced from 77.1 to 83.4% at 550 nm. Therefore, this transparent conducting film is believed to be suitable for optoelectronic fields considering both the transmittance and surface resistance.

For flexible device applications, the surface resistance of transparent conducting films must be maintained after bending. [Fig. 8(a)] Table I shows the surface resistance of all transparent conducting films before and after random crumpling were similar.

In addition, Figure 8(b) shows the surface resistance of a transparent conducting film fabricated from a 0.01 wt % SWCNT dispersion for an immersion time of 3 h after random crumpling. The surface resistance of this film remained mostly unchanged during the crumpling test. As shown in Figure 9, the surface resistance was 2.8 × 10^3, 3.8 × 10^3, and 6.1 × 10^3 Ω/sq at bending angles of 45°, 90°, and 135°, respectively. The surface resistance increases slightly with increasing bending angle. However, this change in electrical conductivity is negligible from a flexible display point of view. Con-
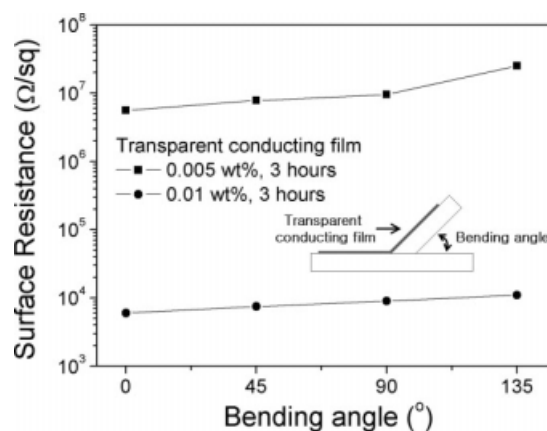
Figure 9 Change in the electrical conductivity of transparent conducting films according to the bending angles.

sequently, transparent conducting films showing optimal transparency and electrical conductivity might expand the applications of flexible, transparent, and electrically conducting films to flexible displays and devices.

CONCLUSIONS

Transparent and electrically conducting films based SWCNTs were synthesized using a combination of concepts regarding both the adsorption of SWCNTs and the nanosize effect of bacterial cellulose nanofibrils. Transparent conducting films were obtained when applying the same processing technique used with the optical nanocomposite films to the SWCNT-adsorbed bacterial cellulose membranes. The transparent conducting films fabricated from a 0.01 wt % SWCNT dispersion for an immersion time of 3 h showed acceptable transparency and electrical conductivity (transmittance and surface resistance of 77.1% at 550 nm and 2.8 kΩ/sq, respectively). Moreover, the transparent conducting films were quite flexible, and their inherent properties remained relatively constant even after random crumpling. In conclusion, these transparent conducting films can be applied to flexible electronic devices.

TABLE I
Sheet Resistance of Conducting Transparent Conducting Films Before and After Crumpling

Conc of SWCNT in water (wt %)	Immersion time (h)	Sheet resistance (Ω/sq)	
		Before crumpling	After crumpling
0.005	1	1.6 × 10^9	3.5 × 10^9
	3	5.6 × 10^6	7.5 × 10^6
	24	5.3 × 10^4	6.9 × 10^4
0.01	1	8.7 × 10^5	9.7 × 10^5
	3	2.8 × 10^3	3.1 × 10^3
0.02	1	1.3 × 10^6	3.6 × 10^6
	3	2.5 × 10^3	2.8 × 10^3

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