

# Electrically conductive transparent films based on nylon 6 membranes and single-walled carbon nanotubes

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## ABSTRACT

Electrically conductive transparent films were fabricated from single-walled carbon nanotubes (SWCNTs) and electrospun nylon 6 membranes, and then the films were dipped in epoxy resins. The nylon 6 nanofibers aided the formation of two-dimensional networks within the SWCNTs and maintained a uniform dispersion of the nanotubes. The electrical conductivity of the membranes increased after they were dipped in a high concentration SWCNT dispersion. The electrically conductive films that were prepared using the 0.02 wt.% SWCNT dispersion exhibited an electrical percolation threshold. The transmittance increased after an epoxy resin was incorporated into the electrically conductive transparent film because the epoxy resin disturbed the optical scattering of the film. After the nylon 6 nanofibrous membrane that was obtained through electro-spinning with the 20 wt.% polymer solution was dipped in the 0.02 wt.% SWCNT dispersion, the membrane had a sheet resistance =  $9.5 \times 10^2 \Omega/\square$ . The transmittance of the epoxy resin-impregnated film was 77.4% (sheet resistance =  $2.1 \times 10^3 \Omega/\square$ ).

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## 1. Introduction

Thin, transparent, conducting films play critical roles as electrodes in modern electronic devices [1]. These thin films are also used as electrostatic discharge (ESD) and electromagnetic interference (EMI) shielding materials [2]. Currently, indium tin oxide (ITO) is the most commonly used material in the fabrication of these electrodes. However, ITO has some well-known disadvantages for use in low cost, flexible electronics. These disadvantages include its brittleness [3], the rapidly increasing costs of the scarce materials [4], and the high-temperature processing [5] steps that are incompatible with plastic substrates, such as polyethylene terephthalate (PET), which are often used in touch screen panels and flexible devices.

Therefore, new coating materials are being developed based on carbon nanotubes (CNTs) in order to replace ITO because CNTs possess outstanding electrical [6] and mechanical properties (flexibility) [7] as well as thermal stability [8]. Additionally, conducting nanotube coatings can be produced at room temperature, and therefore, CNTs-based films can be used in flexible electronic devices. Furthermore, CNTs have a high aspect ratio and form a two-dimensional nanowire network in the thin films, which is advantageous for the fabrication of transparent conducting materials. Composites that consist of a network of one-dimensional conducting wires or tubes have a much higher optical transparency

than composites that are covered with conducting spheres, even though these two types of materials possess the same number of conducting pathways and, therefore, have the same electrical conductivity [1a]. Single-walled carbon nanotubes (SWCNTs) are potentially the best CNTs for the production of optically transparent CNT films because the light absorption of multi-walled carbon nanotubes is higher than SWCNTs when the same number of CNTs cover the film [17].

However, the CNTs must be well separated from each other despite the van der Waals forces acting upon them, and the uniform dispersity of the CNTs must be maintained in the final products in order to obtain an ideal CNT network. In an attempt to satisfy these requirements, many researchers have tried to develop optically transparent CNT films with a high electrical conductivity using a variety of fabrication methods including vacuum filtration [10], Langmuir–Blodgett [11] deposition, spin coating [12], spray coating [1c], [9] and dip coating [13]. Among these methods, the spray coating and dip coating methods are the simplest fabrication techniques and are easy to scale up. The dip coating method is the most useful large scale production method for transparent CNT films in industrial applications because unwanted needle blockage is common during spray coating.

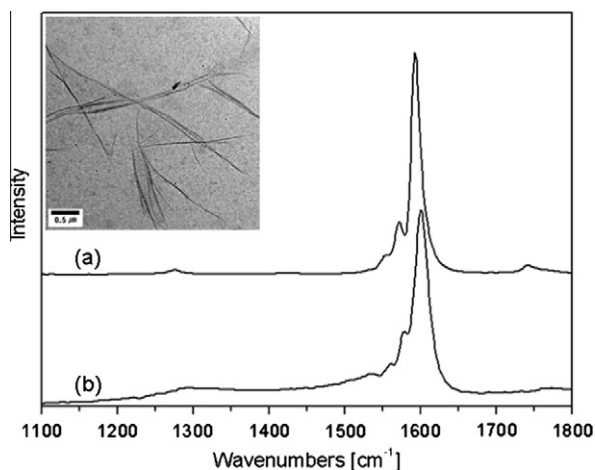
Nylon is one of the most versatile thermoplastic polymers and is used in a wide range of applications. Nylon more strongly interacts with CNTs than other polymers [14], and therefore, nylon is often together with CNTs. Polyamide can easily be formed into nanofibers through electro-spinning [15], and they can function as the template for the CNTs network.

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In this study, SWCNT-based electrically conductive transparent films were prepared using a nylon nanofibrous membrane and a commercial transparent polymer epoxy resin [16]. The transparent epoxy resin was incorporated into the nylon nanofibrous membrane and prevented optical scattering [17]. Electrospun nanofibers, with a diameter of  $\sim 100$  nm, were used to guide the SWCNT deposition and to create a two-dimensional network of nanotubes using a simple dip coating method.

## 2. Materials and methods

In this study, the SWCNTs were supplied by the Hwanwha Nanotech Co., Korea. These SWCNTs were synthesized using the arc discharge method, and their purity was 60–70 wt.%. The nylon 6 polymer (Aldrich) was used to fabricate the nanofibrous polymer membranes. The epoxy resin (ST-3000) was purchased from the Kukdo Chemical Co., Korea.



**Fig. 1.** Raman spectra of (a) the as-received SWCNTs and (b) the acid treated SWCNTs. After the acid treatment, the intensity ratio between G band ( $1599\text{ cm}^{-1}$ ) and D band ( $1280\text{ cm}^{-1}$ ) ( $I_G/I_D$ ) decreased from 52 to 23. Inset: TEM image of the acid treated SWCNTs.

### 2.1. Preparation of nylon nanofibrous membranes via electro-spinning

The nanofibers were produced by dissolving the nylon 6 pellets in formic acid (99%, Wako Pure Chemical Industries, Ltd.) at a concentration of 20 wt.%. The nanofibrous membrane was fabricated by electro-spinning the solution at 28 kV and a syringe pump speed of  $0.001\text{ mL min}^{-1}$  with a distance of 20 cm between the electrodes in a horizontal syringe configuration. Aluminum foil was used as the collecting electrode, and during the electro-spinning process, the foil was rotated in order to limit the effects of the local electric field inhomogeneities. The resulting nanofiber membranes were used as the substrate for the SWCNT deposition.

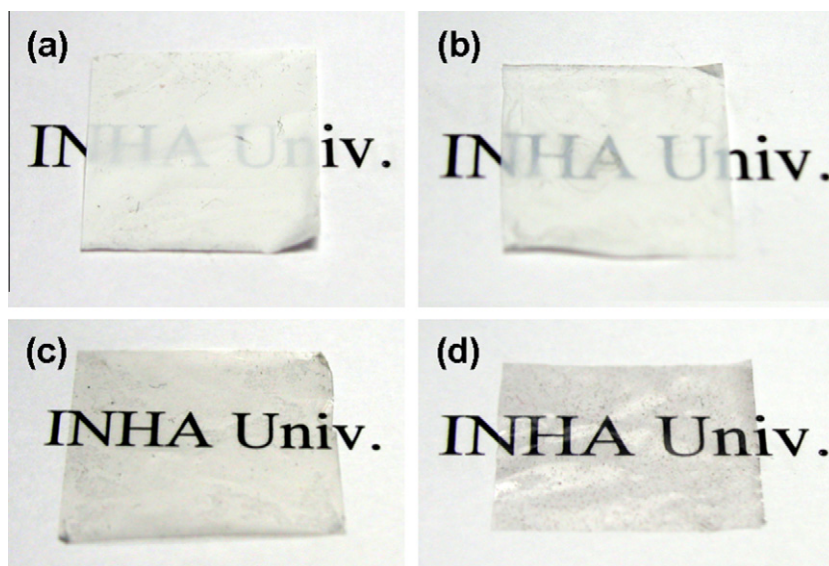
### 2.2. Preparation of SWCNTs solution

Carboxyl groups were grafted onto the SWCNTs, in order to promote hydrogen bonding between the SWCNTs and the polyamide fibers [18]. These carboxyl groups were created through an acid treatment that was described in a previous work. The SWCNTs were treated with a concentrated  $\text{H}_2\text{SO}_4/\text{HNO}_3$  (3/1 v/v, 95% and 60%, respectively) solution at  $60\text{ }^\circ\text{C}$  for 3 h. Fig. 1 shows the Raman spectra of both the as-received SWCNTs and the acid treated SWCNTs and a TEM image of the acid treated SWCNTs. After the acid treatment, intensity ratio between the G band ( $1599\text{ cm}^{-1}$ ) and D band ( $1280\text{ cm}^{-1}$ ) ( $I_G/I_D$ ) decreased from 52 to 23 in the Raman spectra because the carboxylic acid groups were added to the C–C  $\text{sp}^2$  bonds in the SWCNTs.

The acid functionalized SWCNTs were washed with di-water several times and dried in a vacuum oven at  $80\text{ }^\circ\text{C}$  overnight. Then the SWCNT solution was prepared through the dispersion of the acid treated SWCNTs in deionized water at a desired concentration. An ultrasound was applied to the solution to create a homogeneous dispersion using an ultrasonic generator (Kodo Technical Research, Korea) with a nominal frequency of 28 kHz and a power of 600 W for 1 h at  $25\text{ }^\circ\text{C}$ .

### 2.3. Preparation of electrically conductive and transparent films

The electrically conductive film was prepared by adsorbing the SWCNTs onto the surface of the nylon nanofibrous membranes. The membranes were dipped into the prepared SWCNT solutions,



**Fig. 2.** Optical photographs of the (a) nylon, (b) SWCNT-adsorbed nylon, (c) epoxy incorporated nylon (transparent film), and (d) epoxy incorporated SWCNT-adsorbed nylon (electrically conductive transparent film) membranes.

and then the SWCNT-adsorbed membrane was washed thoroughly with a large amount of deionized water in order to remove any residual SWCNTs that were not adsorbed. The final SWCNT-adsorbed membrane was dried at 50 °C overnight. The SWCNT-adsorbed membranes were impregnated with a neat epoxy resin in order to fabricate the electrically conductive, transparent films. Then the epoxy resin was cured through hot-pressing at 50 °C using a Carver laboratory press with an applied pressure of 300 kg for 2 h.

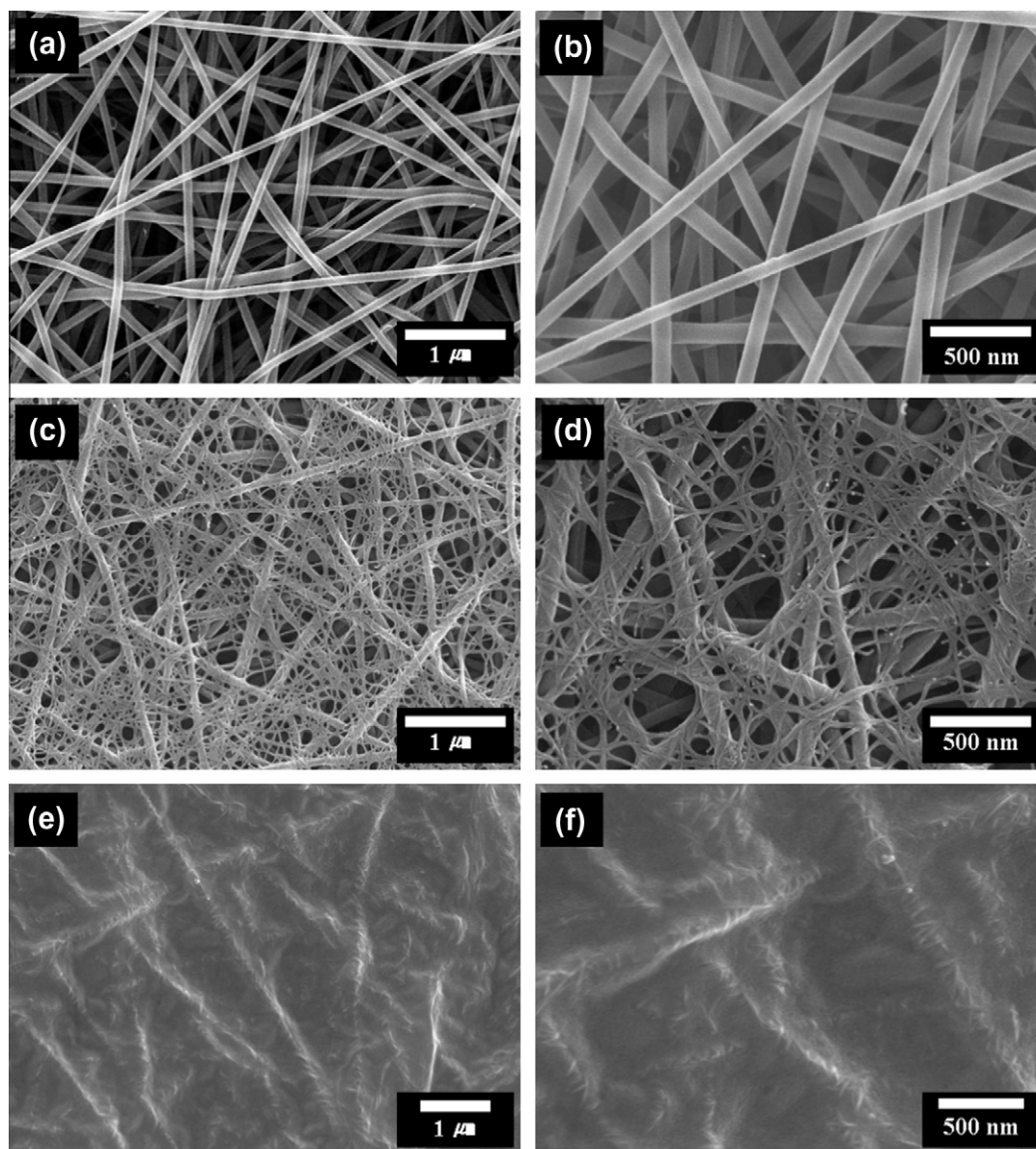
#### 2.4. Characterization

The morphologies of the nylon nanofibrous membrane and the electrically conductive transparent film were observed using field emission scanning electron microscopy (FESEM, S-4300SE, Hitachi, Japan) at an accelerating voltage of 15 kV. Before the analysis, all of the samples were pre-coated with a homogeneous Pt layer through ion sputtering (E-1030, Hitachi, Japan). The transmittances of the electrically conductive transparent films were measured using an

Agilent 8453 UV–visible spectrophotometer (Agilent Technologies, Germany) from 380 to 750 nm. The electrical conductivity of the SWCNTs-adsorbed nylon membrane was measured using a ring-probe method with an electrical conductivity meter (Hiresta-UP MCP-T450, Mitsubishi Chemical, Japan).

### 3. Results and discussion

In Fig. 2a, the nylon membrane was translucent and white, whereas the nanocomposite was not white but rather quite transparent. This transparent nanocomposite was produced by incorporating an epoxy resin into the nylon membrane (Fig. 2c). Interestingly, this optical tendency was also observed when the SWCNTs were compounded with the transparent nanocomposite (electrically conductive transparent film), in Fig. 2d. The electrically conductive film was quite transparent compared to the opaque, black SWCNT-adsorbed nylon membrane (Fig. 2b). The nylon membranes also exhibited good mechanical properties after



**Fig. 3.** FESEM images of (a and b) the nylon membrane, (c and d) the SWCNT-adsorbed nylon membrane, and (e and f) the electrically conductive transparent film at two different magnifications.



the addition of the epoxy resin, creating free standing, electrically conductive transparent films [16].

Fig. 3a and b shows the morphology of the as-deposited films that were obtained by electro-spinning the 20 wt.% nylon 6 solution. The nylon membrane consisted of a network of long fibrils (100 nm average diameter). Fig. 3c and d illustrate the morphology of the SWCNT-adsorbed nylon membrane. In these figures, a large number SWCNTs were well dispersed on the nylon membrane without aggregation. Although the SWCNTs were relatively thin compared to the nylon nanofibrils, the SWCNTs were tangled with the individual nylon nanofibrils because of the strong hydrogen bonding interactions between the two. The SWCNTs formed a percolated structure within the nylon nanofibrous films, even at very low concentrations [19]. The SWCNTs formed a network when they were coated on the membranes. The high dispersity of SWCNTs on the nylon membrane indicated that the electrically conductive transparent films had a high degree of transparency. Additionally, the epoxy resin was used as a coating material in order to improve the optical transparency of the nylon membrane and to avoid extricating the SWCNTs from the surface of the nylon membrane. Fig. 3e and f shows the surface of the electrically conductive transparent film. Only a small amount of the epoxy resin was used to prepare the electrically conductive transparent films, and most of it was used to fill the vacancies of the nylon membrane. Therefore, a large number of the SWCNTs were exposed on the surface of the electrically conductive transparent films even after the epoxy resin was incorporated into the SWCNT-adsorbed nylon membrane. Therefore, most of the SWCNTs that were present on the nylon membrane were uncovered or only slightly covered by the electrically nonconductive epoxy resin. The resulting morphology could have been responsible for the high electrical conductivity of the transparent films.

The electrical conductivities of the SWCNT-adsorbed nylon membranes were controlled by changing the concentration of the SWCNT dispersions. Fig. 4 shows the effect of the SWCNT dispersion concentration on the sheet resistance of the membranes, where the sheet resistances were  $4.1 \times 10^9$ ,  $9.5 \times 10^2$ ,  $9.4 \times 10^2$ , and  $9.4 \times 10^2 \Omega/\square$  for the 0.01, 0.02, 0.03, and 0.04 wt.% SWCNT dispersions, respectively. Therefore, the sheet resistance significantly decreased above a SWCNT dispersion concentration of 0.02 wt.%. Therefore, a concentration 0.02 wt.% was sufficient for the formation of a percolated network of SWCNTs with electrical pathways, and the presence of excess SWCNTs that enveloped

the network did not improve the electrical conductivity of the transparent film. The sheet resistances of the all of the films increased as the epoxy resin was added, exhibited similar tendencies to the SWCNT-adsorbed nylon membranes. The significantly large sheet resistance could not be measured (over  $1 \times 10^{10} \Omega/\square$ ), at a SWCNT dispersion concentration of 0.01 wt.%. The electrical conductivity decreased because the epoxy resin acted as an insulating material or an electrical barrier [1b]. In Fig. 5, the electrical conductivity of the transparent film was investigated for the 0.02 wt.% SWCNT dispersion at various bend angles by measuring the sheet resistance. The sheet resistances were  $2.1 \times 10^3$ ,  $2.0 \times 10^3$ , and  $2.0 \times 10^3 \Omega/\square$  at bend angles of 45, 90, and 135, respectively. The electrical conductivity slightly decreased with increasing bending angle. However, this change in the electrical conductivity was negligible for flexible display applications.

Fig. 6 shows the transparency of the electrically conductive transparent films in the presence of the SWCNTs. These electrically conductive transparent films were prepared using a dipping method with various concentrations of the aqueous SWCNT dispersions at the same adsorption time for each sample. As expected, the transmittance of the electrically conductive transparent films varied with respect to the aqueous SWCNT dispersion concentration. The transmittance spectra showed that the electrically conductive

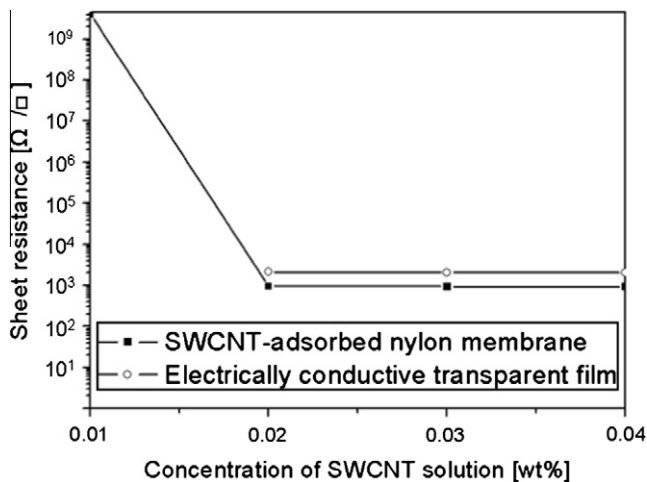


Fig. 4. Sheet resistances of the SWCNT-adsorbed nylon membranes and the electrically conductive transparent films with respect to the SWCNT dispersion concentration.

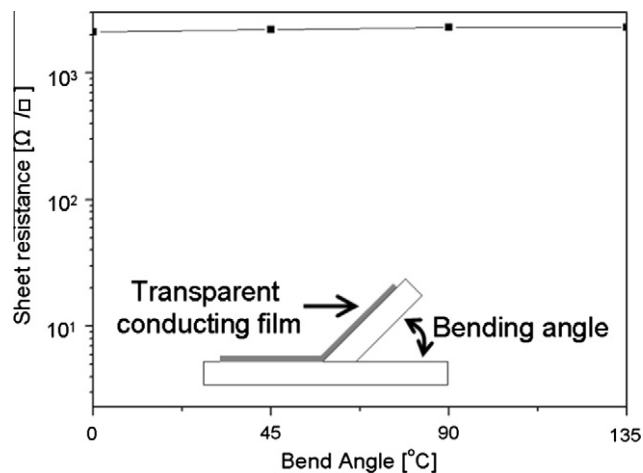


Fig. 5. Sheet resistances of the transparent film that was prepared with the 0.02 wt.% SWCNT dispersion as a function of the bend angle.

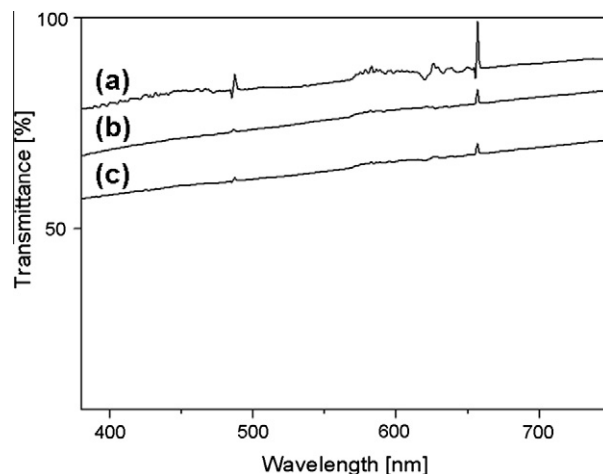


Fig. 6. Light transmittance of the electrically conductive transparent films that were fabricated using various SWCNT dispersion concentrations: (a) 0.01 wt.%, (b) 0.02 wt.%, and (c) 0.03 wt.%.

transparent films exhibited lower transparencies at higher SWCNT dispersion concentrations because more SWCNTs-adsorbed onto the nylon membrane after the same amount of dipping time. The electrically conductive transparent films transmitted 84.5%, 77.4%, and 63.5% of the light at 550 nm for the 0.01, 0.02, and 0.03 wt.% aqueous SWCNT dispersions, respectively. Interestingly, the transmittance decreased from 0.02 to 0.03 wt.% even though the sheet resistances of the two dispersions were the same. The excess SWCNTs possibly enveloped the network of SWCNTs on the nylon membrane above 0.02 wt.% SWCNTs. Therefore, a concentration of 0.02 wt.% was sufficient for the formation of a network with electrical pathways, and the presence of excess SWCNTs that enveloped the network did not improve the electrical conductivity of the transparent films. Consequently, the electrically conductive transparent film that was prepared using the 0.02 wt.% SWCNT dispersion exhibited the optimal transparency and electrical conductivity with a light transmittance of 77.4% at 550 nm and a sheet resistance of  $2.1 \times 10^3 \Omega/\square$ .

#### 4. Conclusions

Conducting 2-D networks were produced from electrospun nylon 6 nanofibers coated with SWCNTs. This technique improved the transparency of the films because the nanotubes did not form a uniform coating but rather a percolated network of SWCNTs, which was guided by the polymer nanofibers. Impregnating the films with an epoxy resin slightly increased the resistance but also improved the transmittance. The electrically conductive transparent films that were fabricated from the 0.02 wt.% aqueous SWCNT dispersion exhibited a light transmittance of 77.4% at 550 nm and a sheet resistance of  $2.1 \times 10^3 \Omega/\square$ . Therefore, these electrically conductive films can be applied as a transparent electrode in photo-electronics, such as flexible displays and touch screens, as well as in biological applications, such as actuators.

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