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Performance-determining factors in flexible transparent conducting single-wall carbon nanotube film

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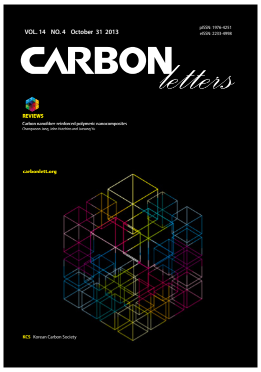

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Abstract

Flexible transparent conducting films (TCFs) were fabricated by dip-coating single-wall carbon nanotubes (SWCNTs) onto a flexible polyethylene terephthalate (PET) film. The amount of coated SWCNTs was controlled simply by dipping number. Because the performance of SWCNT-based TCFs is influenced by both electrical conductance and optical transmittance, we evaluated the film performance by introducing a film property factor using both the number of interconnected SWCNT bundles at intersection points, and the coverage of SWCNTs on the PET substrate, in field emission scanning electron microscopic images. The microscopic film property factor was in an excellent agreement with the macroscopic one determined from electrical conductance and optical transmittance measurements, especially for a small number of dippings. Therefore, the most crucial factor governing the performance of the SWCNT-based TCFs is a SWCNT-network structure with a large number of intersection points for a minimum amount of deposited SWCNTs.

Key words: single-wall carbon nanotube, transparent conducting film, dip coating method

1. Introduction

Flexible transparent conducting films (TCF) are technologically important for future wearable displays. Although present indium-tin-oxide thin films have excellent electrical properties and high optical transmittance, their flexibility upon bending is extremely poor. Therefore, development of an alternative material with high mechanical flexibility is highly desired. Carbon nanotubes (CNTs) have been recently proposed as a promising candidate to satisfy the desired flexibility, owing to their high aspect ratio and excellent elastic property, in addition to high electrical conductivity [1-3]. Consequently, the fabrication of flexible TCFs with CNTs has recently been carried out. These recent studies have shown that the electrical conductivity and optical transmittance of CNT films varies, depending on the coating methods and the intrinsic properties of the CNTs [4-14]. In general, the performance of CNT-based TCFs are typically governed by the inherent properties of the CNTs, such as purity, defect concentration, and electrical conductivity. Efforts have been made to associate material-induced factors with better TCF performance [1,15]. However, the characteristics of CNT-based TCFs are still not clear due to a lack of systematic studies on the relationship between preparation conditions and film properties. The performance of CNT-based TCFs depends strongly on the higher order structure of the CNTs, such as entangled and bundle structures. This feature could be evaluated while investigating the performance-determining factors for designing better TCFs.

We assume that the performance of CNT-based TCFs directly depends on the number of intersecting, interconnected CNT bundles, and the coverage of SWCNTs on the substrate.

In this study, we microscopically and macroscopically evaluated the performance of TCFs to elucidate performance-determining factors, by using experimental results of single-wall CNTs (SWCNTs)-coated TCFs on flexible polyethylene terephthalate (PET) film prepared by dip-coating process [14].

2. Experimental Details

Highly pure SWCNTs synthesized by arc discharge process were purchased from Iljin Nanotech. The SWCNT diameters were in the range of 1.4 to 1.5 nm with a length of 5 to 20 μm. Thermogravimetric analysis profile gave 1.3 wt% of metal catalyst.

The purified SWCNTs were well dispersed in 1,2-dichloroethane (DCE) solvent without additives [14,16,17]. The low vaporization temperature of DCE (83.5°C) allows more SWCNT to be deposited on the substrate. Ten milligram of SWCNTs were immersed in 100 mL of DCE solvent. These were then sonicated in a bath type sonicator for 500 min at room temperature, followed by centrifugation at a speed of 6800 rpm for 10 min. The supernatant was decanted and sonicated prior to film formation. The PET substrate was sonicated in acetone for 10 min and then washed with deionized water to clean the substrate surface. The PET substrate was vertically positioned above a container of the SWCNT-dispersed DCE solution and then immersed into the SWCNT solution for 2 s, and withdrawn upward, with a continuous speed of 50 mm/min. Then, the PET substrate was dried for 5 s. This procedure was repeated between 100 to 400 times. The dip-coating was conducted in a glove box in Ar atmosphere in order to avoid moisture adsorption into the DCE solvent.

Field emission scanning electron microscopic (FE-SEM) images of the SWCNT-based TCFs were obtained with a JSM-63301 (JEOL). Their electrical conductance was measured using a four-point probe method. Optical transmittance was measured using UV-visible spectrometry (Carry 5000) in the range of 400 to 800 nm.

3. Results and Discussion

Fig. 1 presents the FE-SEM images of SWCNT network films on the PET substrate as a function of the different number of dippings. With increasing number of dippings, the amount of coated SWCNTs increases considerably. However, the coating of the PET substrate is not enough after a dipping treatment of 100 times, although the DCE completely wets the PET substrate.

The DCE solvent is easily evaporated from the substrate, depositing the SWCNTs film on it. The SWCNT film consists of a network having many intersection points. The intersection points in the TCF film are a crucial factor for good electrical conductivity of the film. The FE-SEM images of SWCNT-coated TCFs according to dipping treatment number show that the number of intersection points increases significantly with the number of dippings. The percolation threshold should reach a minimum amount of SWCNT deposits to maximize optical transmittance [18-20].

Fig. 2 shows a schematic representation for estimating the performance-determining factors of the TCFs using the observed FE-SEM images. Figs. 2a and b show an optical image and an FE-SEM image after 100 dippings. We defined two factors that govern the SWCNT-TCF performance. First, the electrical conductance of the film is closely related to the intersection points in the SWCNT network; the electrical conductance of the SWCNT network film should be simply proportional to the number of intersection points of SWCNT bundles, and the number of SWCNT bundles that are interconnected at each intersection point. Therefore, we first define the conductance factor f_G as follows.

$$f_G = \sum_{i=1}^{n} B_i \qquad (1)$$

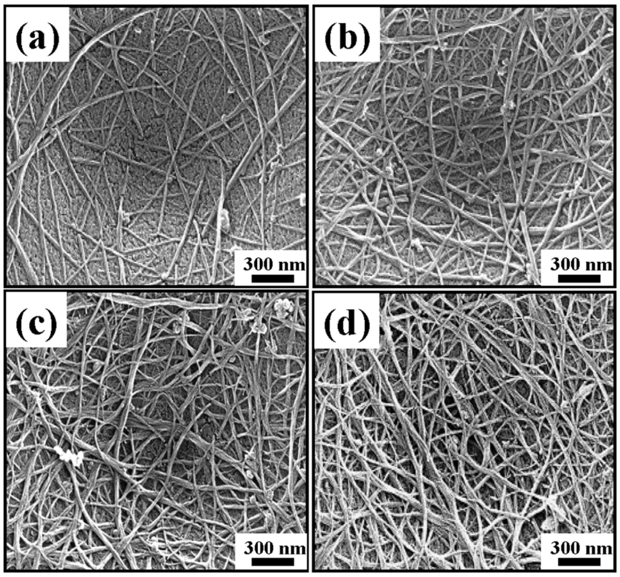

Fig. 1. Field emission scanning electron microscopic images of single-walled carbon nanotube network film coated with different dipping number; (a) 100, (b) 200, (c) 300, and (d) 400 times.

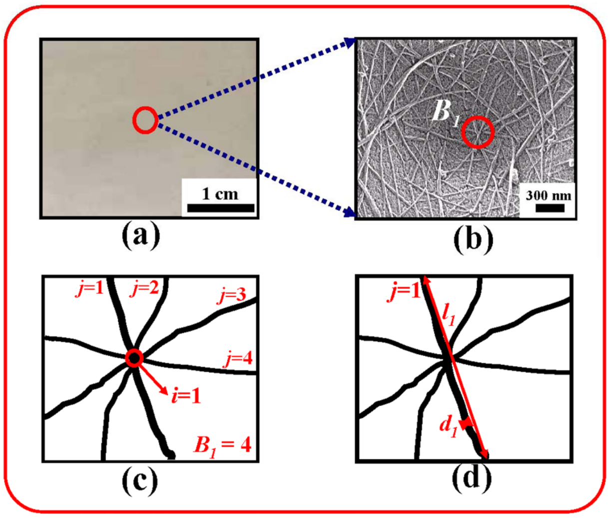

Fig. 2. (a) Optical image, (b) field emission scanning electron microscopic image after 100 dipping times, and schematic representations for determining (c) conductance factor (f_G) and (d) absorbance factor (f_A) in B_1 of (b).

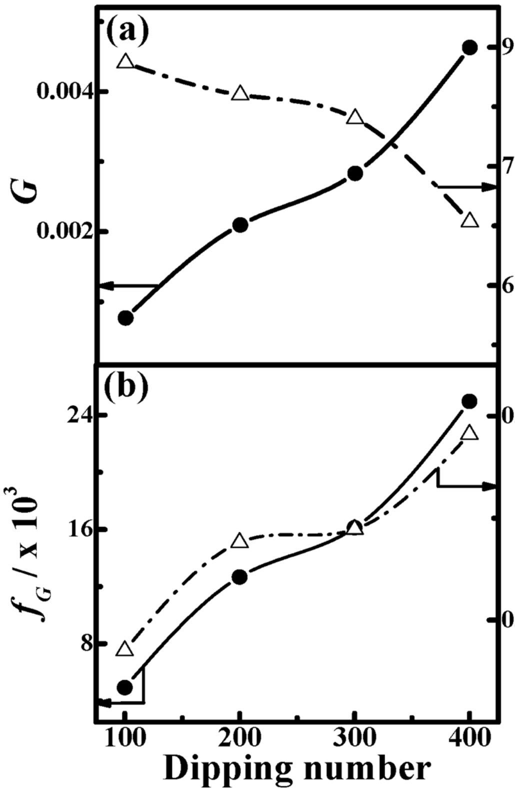

Fig. 3. (a) Electrical conductance (*G*) and optical transmittance (*T*) and (b) the conductance (f_G) and absorbance (f_A) factors of single-walled carbon nanotube-transparent conducting films as a function of the number of dipping.

where B_i is the number of interconnected SWCNT bundles (*j*) at each intersection point (*i*), as illustrated in Fig. 2c. Therefore, f_G is the sum of B_i at the intersection point (*i*). Second, the absorbance of the film is proportional to the coverage of SWCNTs on the substrate. Therefore, we also define the absorbance factor f_A, which is given by Eq. (2).

$$f_A = \left[\sum_{j=1}^{n}(l_j \times d_j)\right]/S \tag{2}$$

where l_j and d_j are the length and diameter of the *j*-th SWCNT bundle in the FE-SEM image, respectively, as illustrated in Fig. 2d, and *S* is the total area of the FE-SEM image.

Fig. 3a shows the changes of electrical conductance (*G*) and optical transmittance (*T*) of dip-coated SWCNT-TCFs with the number of dippings. With the increasing number of dippings, the electrical conductance of the SWCNT-TCFs increases, accompanied by a reduction of the optical transmittance; this is ascribed to the increase in the number of SWCNT intersection points and the coverage of SWCNTs on the substrate. The conductance (f_G) and absorbance (f_A factors determined by Eqs. (1) and (2) are shown in Fig. 3b. Since the optical transmittance is inversely proportional to the absorbance, the change of $f_A$value with the number of dippings has an opposite tendency to that of the *T* value. Both higher conductance and transmittance are simultaneously desired for better film performance. We need a film property factor including both properties. Thus, we define the microscopic film property factor (Q_{Mic}), as given by Eq. (3).

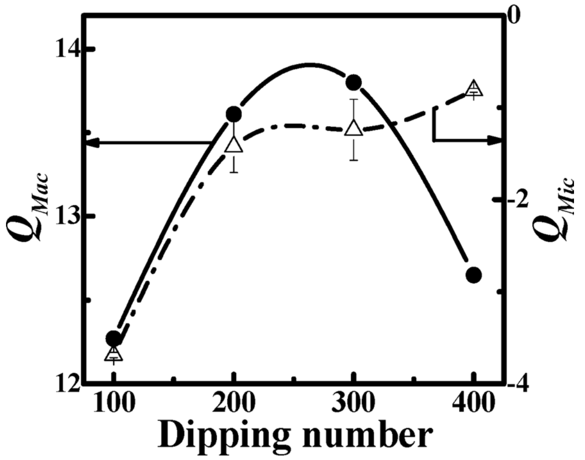

Fig. 4. Comparison of the microscopic film property factor (Q_{Mic}) with macroscopic film property factor (Q_{Mac}) as a function of the number of dipping.

$$Q_{Mic} = \left(-\frac{1}{\ln f_G}\right)\cdot\left(\frac{1}{f_A}\right) \tag{3}$$

Q_{Mic} can be compared with the macroscopic film property factor (Q_{Mac}) expressed with the measured electrical conductance (*G*) and optical transmittance (*T*), as given by Eq. (4).

$$Q_{Mac} = \left(\frac{1}{\ln G}\right)\cdot T \tag{4}$$

Fig. 4 presents the comparison of Q_{Mic} with Q_{Mac} as a function of the number of dippings. Q_{Mac} shows a sharp increase up to 200 dipping times and then decreases at 300 dipping times. Although the electrical conductance was increased, the optical transmittance decreased rapidly at a large number of dippings. As a consequence, the film performance is degraded. The Q_{Mic} resembled the Q_{Mac} in a similar way up to 300 dipping times. It should be noted, at a large number of dippings, counting the number of intersection points in the SWCNT network becomes ambiguous because these numbers increase very rapidly, as shown in Fig. 1. Thus the errors in counting these numbers dominate, making the data point uncertain.

4. Conclusions

In summary, SWCNT-TCFs were fabricated by dip-coating method. Our dip-coating approach provided reasonable quality SWCNT-TCF films. The film's microscopic property factor was defined by the number of interconnected SWCNT bundles at intersection points, and the coverage of SWCNTs on the substrate, in FE-SEM images. The microscopically extracted film property factors are in good agreement with macroscopically obtained values, especially for a small number of dippings. Our results clearly revealed that a sparsely entangled random network structure with a sufficient number of intersection points and a minimum SWCNT coverage is a key factor for improving SWCNT-TCF performance. However, the dispersion of SWCNTs is also an important factor influencing SWCNT-TCF performance. Therefore, dispersing SWCNT bundles into individual SWCNTs, or into a smaller bundle size, is desired to improve TCF electrical conductance and optical transmittance.

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