Fabrication of flexible transparent conductive films from long double-walled carbon nanotubes

Naoki Imazu\textsuperscript{1,2}, Tsuyohiko Fujigaya\textsuperscript{2} and Naotoshi Nakashima\textsuperscript{2,3}

\textsuperscript{1}Film Products Development Center, Toray Industries, Inc., 1-1, Sonoyama 1-chome, Otsu, Shiga 520-8558, Japan
\textsuperscript{2}Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
\textsuperscript{3}International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

E-mail: nakashima-tcm@mail.cstm.kyushu-u.ac.jp

Received 27 January 2014
Accepted for publication 14 March 2014
Published 11 April 2014

Abstract
The fabrication of flexible transparent conducting films (TCFs) is important for the development of the next-generation flexible devices. In this study, we used double-walled carbon nanotubes (DWCNTs) as the starting material and described a fabrication method of flexible TCFs. We have determined in a quantitative way that the key factors are the length and the dispersion states of the DWCNTs as well as the weight-ratios of dispersant polymer/DWCNTs. By controlling such factors, we have readily fabricated a flexible highly transparent (94% transmittance) and conductive (surface resistivity = 320 \(\Omega\) sq\(^{-1}\)) DWCNT film without adding any chemical doping that is often used to reduce the surface resistivity. By applying a wet coating, we have succeeded in the fabrication of large-scale conducting transparent DWCNT films based on the role-to-role method.

Online supplementary data available from stacks.iop.org/STAM/15/025005/mmedia

Keywords: carbon nanotube, flexible transparent conducting film, flexible device material, supramolecular material

1. Introduction
Considerable attention has been focused on the design and fabrications of functional thin films for applications in flexible electronics \cite{1–3}. Especially, TCFs \cite{4, 5} have been widely used as electrodes for a variety of electronic devices, such as a resistive touch screen (for car navigation, handheld game console, electronic dictionary, etc), projected capacitive touch screen (for smart phone, tablet PC, etc), and electronic paper display (EPD, for electronic book, digital signage, electronic shelf label, etc). Especially, the markets for projected capacitive touch screens and EPDs are rapidly increasing. Moreover, for the next-generation flexible device development, flexible TCFs have attracted much attention as the materials for organic light-emitting diode (OLED) displays, and OLED lighting and organic photovoltaics.

The widely used TCF materials have been made using indium tin oxide (ITO), which is manufactured by sputtering ITO under vacuum on glass substrates and plastic films of
polyethylene terephthalate (PET) or other polymers. However, since indium is a rare metal, the development of alternate materials is a strong social demand. Moreover, ITO is a brittle inorganic metal oxide; thus, when ITO-based TCFs are bent or extended, many cracks are generated in the ITO layers, leading to very low electric conductivity. As candidates for ITO-alternate materials, silver nanowires, metallic grids, conjugated polymers and nanocarbons, such as carbon nanotubes (CNTs), graphene and combinations of these materials, have been extensively studied [6–12].

CNTs formed by rolling-up graphene sheets are classified to single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs) and multi-walled CNTs (MWCNTs) by the difference in the number of layers [13–15]. The number of CNT layers relates to the transparency of their films; namely, as the CNT’s layer number decreases, the transparency of their films increases. Compared to SWCNTs and MWCNTs, DWCNTs have advantages as a transparent electrode material because they can be easily purified by a simple chemical treatment, e.g., using a strong acid, without introducing many defects [16, 17].

In order to fabricate transparent highly conductive CNT films, we used long DWCNTs as the starting material because the use of long-length CNTs is important for the preparation of such films. To obtain long-length CNTs, their selective synthesis and length-sorted separation were studied in many different ways [18–22]. CNTs form a random network like a web structure, therefore, the conductivity of the films decreases as the contact resistance of the tubes increases; thus the use of long CNTs should result in a higher conductivity due to small number of contact points. Since CNTs are not soluble in water, many different kinds of dispersants, such as a surfactant, polymer and DNA are used to dissolve them in water [23–25]. After making films from such solubilized CNT solutions, removing the large excess amount of dispersants from the film is required to enhance its conductivity. Rinsing of the films with water, organic solvents and acid is the most commonly used technique [26–28]. However, this process (we call it the ‘rinsing process’), is not suitable for large-scale production, especially in the roll-to-roll coating process. In this paper, we describe the fabrication of highly conductive transparent films using long-length and pure DWCNTs without a rinsing process.

2. Experimental details

2.1. Materials

The DWCNTs synthesized by Toray Industries Inc., by a catalytic high-temperature chemical vapor deposition were used [29, 30]. The purity, diameter, G/D ratio determined by Raman spectroscopy, and volume resistivity were >90%, 1.5 ∼ 2 nm, > 80 and 4.4 × 10^{15} Ω cm, respectively. As a dispersant, we used carboxyl methyl cellulose sodium salt (CMC) purchased from Sigma-Aldrich Co.

![Figure 1. Average length of the DWCNTs as a function of the ratios of the CMC/DWCNTs (w/w%). Error bars are within 10%.](image)

2.2. Dispersion of DWCNTs

Dispersion of the DWCNTs was carried out using a tip-type sonicator (Ieda Trading Corporation, VCX-130) for 7.5, 20 or 45 min at 20 W at CMC/DWCNTs = 6 (w/w%), then ultracentrifugated (Hitachi Koki, himac, CP-WX) at 147 000 g for 8 h. The top-80% portion of the supernatant was collected, and the sediment was redispersed in water. The sediment/water = 0.04 (w/w%).

2.3. Measurements

For the atomic force microscopy (AFM, Shimadzu, SPM-9600) study, 0.003 wt% of the DWCNT dispersion was spin-coated on a mica substrate at 3000 rpm for 60 s. The DWCNT-length distribution was analyzed using selected 100 AFM images. Scanning electron micrograph measurements were carried out using an SEM (JEOL, JSM-6701F instrument).

To determine the amount of CMC in the collected supernatant, the anthrone method was used [31]. Anthrone is a tricyclic aromatic ketone, and is used for the assay of celulose, in which carbohydrates are hydrolyzed into simple sugars in the presence of hydraulic acid, and in a hot acidic medium, glucose is dehydrated to hydroxyethyl furfural, which reacts with anthrone to provide a blue-green colored product with an absorption maximum at 620 nm (for details, see the supplementary information, anthrone method procedure available at stacks.iop.org/STAM/15/025005/mmmedia).

2.4. Transparent DWCNT conductive film fabrication

The DWCNT dispersion was diluted in water to 0.04 wt%, which is the absolute content of DWCNTs in water. The obtained dispersion was solution cast using a #5 wire bar on a PET film, followed by heating at 125 °C for 1 min. The surface conductivity of the film was measured by the four-probe resistivity measurement method (MCP-T360, Mitsubishi Chemical Analytech). Transmittance was measured using a haze meter (NDH4000, Nippon Denshoku), and the data not including the reflectance of the used substrate are obtained.
2.5. Mechanical durability.

Bending durability test was carried out by measuring resistance between electrodes. The experimental conditions are: bending diameter = 10 mm, traverse distance = 120 mm, traverse speed = 60 mm s^{-1}. For comparison, a conventional ITO film (Toray Advanced Film Co., Ltd, NXC1, surface resistivity = 120 Ω sq^{-1}) was used.

3. Results and discussion

Longer-length CNTs are needed to obtain highly conductive CNT films [18]. We first examined the DWCNT average length dependence by changing the wt% ratios of the CMC/DWCNT in the case of sonication time of dispersion to 7.5, and the result based on the analysis of their AFM images is shown in figure 1, in which we recognized that the length increases with an increase in the ratios. At CMC/DWCNT = 6 (w/w%), the average length was 2.3 μm, and for the following experiment, we labeled this dispersion including the long DWCNTs as D1. Since the excess amounts of the CMC dispersant lower the conductivity of the DWCNTs, we need to remove the excess CMC from the dispersion. We thus carried out the ultracentrifugation of D1. Figure 2 shows the photos before (a) and after ultracentrifugation for 5 h (b) and 8 h (c). The top-80% portion of the supernatant (denoted D2) shown in figure 2(c) was collected, and the sediment was redispersed by adding only water to obtain a dispersion (denoted D3). The sediment/water = 0.04 (w/w%).

We determined the CMC/DWCNT (w/w%) ratios of D2 and D3 by the anthrone method (for details, see the supplementary information, anthrone method available at stacks.iop.org/STAM/15/025005/mmedia), and the obtained values were 65 and 1.6 for D2 and D3, respectively. It is evident that the amount of the dispersant (CMC) drastically decreased in D3 compared to those of D1 and D2.

Figure 3 shows the AFM images of D1, D2 and D3, from which we evaluated the distribution of their lengths and bundle heights. The distribution histogram is shown in figure 4. As shown in figure 4 and table 1, it was revealed that the length- and bundle-height distributions are significantly different among D1, D2 and D3. From table 1, the average length of D3 is the longest (average = 2.6 μm), and the average height was the smallest (average = 1.0 nm) in D2, which is close to the diameter of the DWCNTs used, indicating individual solubilization of the DWCNTs. The average heights of D1 and D3 were comparable. The average tube length of D3 (2.6 μm) that was obtained by the simple ultracentrifugation was slightly longer than that of the original dispersion, D1 (2.3 μm). The average tube length of D2 (2.0 μm) was smallest among the three samples. Conductivity of DWCNT films at 94% transmittance: we fabricated transparent DWCNT films on PET substrates using a wet coating (solution cast) method for D1, D2, and D3. As an example, a typical SEM image and a photo of D3 film are shown in figures 5(a) and (c), respectively.

The surface resistivities of the films from D1, D2 and D3 were measured, and the results are shown in table 1. These three films were found to show quite different surface resistivities; namely, the values at a 94% transmittance were 2100, 35 000 and 450 Ω sq^{-1} for the films from D1, D2 and D3, respectively. Interestingly, the surface resistivity of the film from D3 was dramatically reduced compared to those from D1 and D2. The observed high sheet resistance of the film from D2 would be due to its high CMC/DWCNT value, which the excess CMC molecules would disturb the high conductance of CNTs.

Next, we focused on the DWCNT length dependence on the resistivity. By changing the sonication time of dispersion to 7.5, 20 or 45 min, we prepared dispersions D4, D5, and D6 whose average lengths were 2.1, 1.1, and 0.8 μm at CMC/DWCNT = 3.0 (w/w%), respectively. We then fabricated DWCNT films from D4, D5, and D6, and rinsed them with water for 10 s to provide films of rinsed D4, D5 and D6 samples, respectively. The CMC/DWCNT (w/w%) values of all these films are 1.6 (w/w%). These results are shown in table 2. Interestingly, the film with the 2.6 μm length shows a surface resistance of 450 Ω sq^{-1} (D3), which is dramatically reduced from that of the 0.8 μm long tube (1510 Ω sq^{-1}, rinsed D6). Based on the results obtained for the films of rinsed and non-rinsed D4, D5, D6 samples, it was revealed that the surface resistance decreased by ∼40% after the water rinsing, indicating that the rinsing is important to reduce the surface resistivity. Thus, we applied this to the film from D3, obtained rinse D3, and found that by rinsing, the surface resistivity decreased from 450 Ω sq^{-1} (for D3) to 320 Ω sq^{-1} (for rinsed D3).

Figure 6 shows the mechanical stress durability of the CNT–TCF. Even after a 10 000-times bending test, the resistance of the CNT–TCF changed slightly compared to the
Figure 3. AFM images of original sample (D1) (a), supernatant (D2) (b) and dispersion from sediment (D3) (c) after ultracentrifugation 8 h (c) at 147 000 g.

Figure 4. Distribution histograms of length (a)–(c) and bundle height (d)–(f) obtained from the AFM images of D1 (a) and (d), D2 (b) and (e) and D3 samples (c) and (f).

Table 1. Properties of DWCNT dispersions and transparent conductive films.

| Sample         | Sample states   | Rinsing | CMC/DWCNTs (w/w%) | Average length (μm) | Surface resistivity at 94% (Ω sq⁻¹) |
|----------------|-----------------|---------|-------------------|---------------------|-------------------------------------|
| D1             | Original sample | No      | 6                 | 2.3                 | 2100                                |
| D2             | Supernatant     | No      | 65                | 2                   | 35 000                              |
| D3             | Dispersion from sediment | No | 1.6               | 2.6                 | 450                                 |
In sharp contrast, after 1000 cyclings, the resistance of a conventional ITO film increased by ∼10 000 times compared to the value before the bending test.

Figure 6. Bending durability test for the DWCNT film (blue) and for a conventional ITO film (red). Bending diameter = 10 mm, traverse distance = 120 mm, traverse speed = 60 mm s⁻¹, \( R_0 \) = initial resistivity, \( R \) = resistivity after given bending cycles.

Table 2. Properties of DWCNT dispersions and transparent conductive films.

| Sample | Sample states          | Rinsing | CMC/DWCNTs (w/w%) | Average length (μm) | Surface resistivity at 94% (Ω sq⁻¹) |
|--------|------------------------|---------|-------------------|---------------------|-------------------------------------|
| D3     | Dispersion from sediment | No      | 1.6               | 2.6                 | 450                                 |
| Rinsed |                        | Yes     | 1.0               | 2.6                 | 320                                 |
| D4     | Dispersion (sonication 3 min) | Yes     | 1.6               | 2.1                 | 700                                 |
| Rinsed |                        | Yes     | 1.6               | 1.1                 | 930                                 |
| D5     | Dispersion (sonication 7.5 min) | Yes     | 1.6               | 0.8                 | 1510                                |

4. Conclusions

In conclusion, we have described a method of how to prepare highly conductive transparent DWCNT films. We have revealed in a quantitative way that the key factors are the tube length, dispersion states and weight ratios of the dispersant CMC/DWCNT. By controlling such factors, we were able to fabricate a DWCNT film with a surface resistivity of

In figure 7, we compared our results to those of several other conventional electrode systems prepared without the postdoping processes [18, 32, 33]. As can be seen, the surface resistivity = 320 Ω sq⁻¹ at 94% of the rinsed D3 shows much higher conductivity than the electrodes prepared without the postdoping process. It is evident that our material has great advantage as a material for transparent flexible electrodes.
320.2 sq^{-1} at 94% transmittance without adding any chemical doping that is often used to reduce the surface resistivity. By applying wet coating, we have succeeded in the fabrication of large-scale conductive transparent DWCNT films based on the role-to-role method (see supplementary information, figure S1, available at stacks.iop.org/STAM/15/025005/mmmedia). Such materials are useful for both fundamental research and industrial applications.

Acknowledgements

This work was supported in part by the Low-Carbon Research Network (LCNet) and the Nanotechnology Platform Project (Molecules and Materials Synthesis) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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Figure 7. Surface resistivity as a function of transmittance at 550 nm (%) for films of D1, D3, rinsed D3 and for CNT films prepared without postdoping process that were reported in references [18, 32, 33].
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