Fabrication of transparent conducting films of carbon nanotubes using a spray method

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Abstract

Transparent conducting films were fabricated on polyethylene terephthalate substrate by a spray method using double-walled carbon nanotubes dispersed in organic solvent and water-based solution. We analyzed the films by absorption spectra, sheet resistance, and scanning electron microscopy. Transparent conducting films with high uniformity and high transparency were fabricated by the spray method. We found that the dispersion particularly nanodispersion of CNTs was of crucial importance to improve the film performance.

1. Introduction

Thin solid film that is semitransparent to visible light and electrically conducting was reported first by Badeker in 1907, who prepared CdO films by thermal oxidation of sputtered Cd films [1]. Because of the recent advances in flexible displays, the materials and techniques for producing transparent conducting films (TCFs) are of a great interest.

Based on the novel structure and remarkable properties, carbon nanotubes (CNTs) have attracted a tremendous attention since the discovery by Iijima in 1991 [2], and a great deal of efforts have been devoted to understanding and characterizing their properties and developing their applications [3]. It is generally known that carbon nanotubes show excellent mechanical and electrical properties. CNTs have an extremely high Young modulus, stiffness and flexibility, as well as high electrical conductivity.

Different methods have been introduced to fabricate TCFs by many scientists [4-8]. Our objective is to obtain TCFs with CNTs that can be deposited on a plastic substrate by a simple method. We chose the spray method to simply fabricate uniform thin films on the substrate. A schematic diagram of the spray coating system is shown in Fig.1. The size of a sprayed droplet of carbon nanotubes solution is influenced by the spray nozzle size, the viscosity and boiling point of solvent, and the concentration of the CNT solution. The CNT solution was supplied into the spray nozzle by Ar gas at a given constant pressure and flow rate. The substrate was maintained at room temperature (for dichloroethane (DCE) solution) or 100 ℃ (for water-based solution). Uniform distribution of CNTs in large-area substrate was affected by the scanning speed and step, which were controlled by the mechanical motor 2 and motor 1, respectively. The flow rate of the gas and the nozzle size strongly determine the spray pattern and the size distribution of droplets, and eventually the quality of the carbon nanotube films.

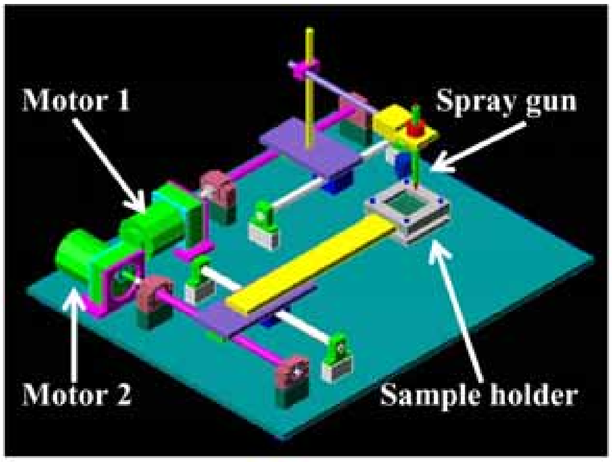

Figure 1. Schematic diagram of the spray coating system.

Double-walled carbon nanotubes (DWCNTs) synthesized by Hipco method were used to fabricate the TCFs. DCE was used as organic solvent and sodium dodecyl sulfate (SDS) was used as a surfactant to disperse DWCNTs in deionized water by ultrasonication and centrifuge methods comparatively. We analyzed the film by UV-VIS-NIR spectrometer at a visible range, sheet resistance, and field emission scanning electron microscopy (SEM). Several important parameters such as sonication time, centrifuge speed, and substrate temperature, were optimized to have high transmittance and low sheet resistance.

2. Results

We fabricated TCFs using spray method on polyethylene terephthalate (PET) film and analyzed the resulting samples by SEM, optical absorption, and DC electrical conductivity.

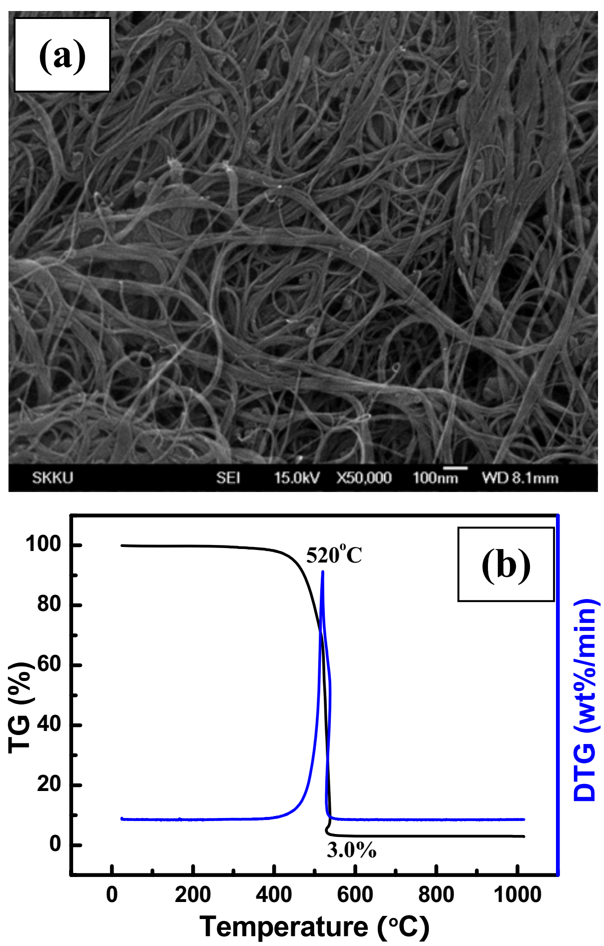

Figure 2. (a) SEM image(scale bar: 100nm) and (b) TGA of the DWCNTs

DWCNTs were characterized by SEM and thermo gravimetric analysis (TGA). Figure 2 shows the quality of the DWCNTs we used. The SEM image of Figure 2(a) shows that the DWCNTs are mostly bundled and have some carbonaceous particles. From the TGA of the DWCNTs, the burning temperature is 520℃ and the purity is about 97 wt%.

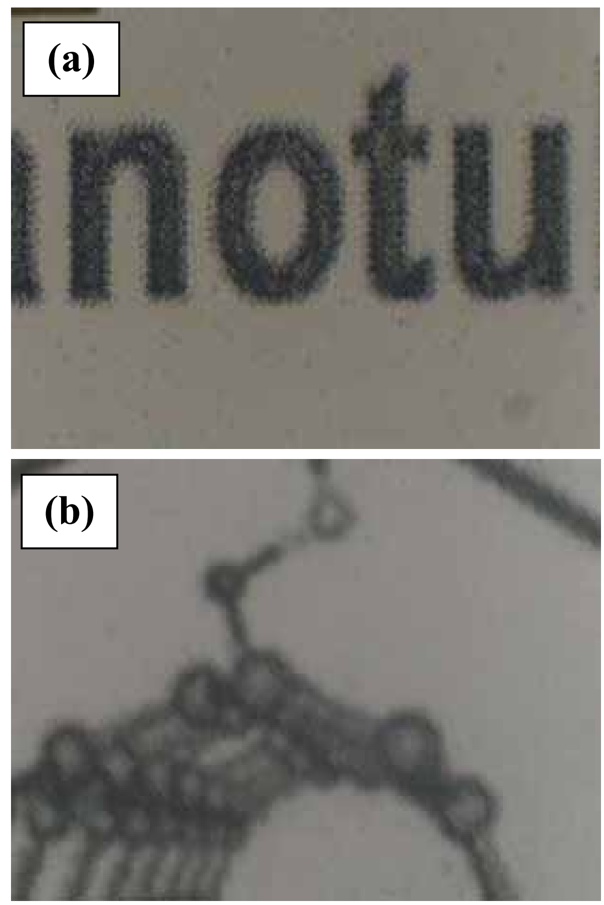

Figure 3. Photographs of DWCNT films sprayed on PET film using (a) DCE solvent and (b) SDS in deionized water.

Figure 3 illustrates the photograph of TCFs fabricated on the PET films using different kinds of solvents (a) DCE solvent and (b) SDS dispersed in deionized water. There are some letters or pattern behind the samples when the pictures were taken. Both pictures show the high uniformity and high transparency fabricated by the spray method. In addition, the surface morphology of the film with water-based solution has a high degree of uniformity and surface homogeneity. The roughness of the film is found to be better than that of the DCE solution.

The parameters, such as the CNT concentration, sonication time, sonication power, centrifuge speed, substrate temperature, and solution amount, were optimized to have high transmittance and low sheet resistance. The sheet resistance and the transmittance at 600 nm for two types of solvents are shown in Figure 4 for comparison. It is noted that the films prepared with DCE solvent have much higher sheet resistance than that with water-based solution at the same transmittance. The sheet resistance with DCE solvent is about 5 kΩ/sq and 10 kΩ/sq when the transmittance is 80% and 90% at 600 nm, respectively. For water solution, different wt% of SDS was used as a surfactant to disperse DWCNTs. The films have much lower sheet resistance than that of DCE solution, for example, about 220 Ω/sq, 370 Ω/sq, 500 Ω/sq, 1000 Ω/sq with transmittance of 50, 70, 80, and 90 %, respectively. These TCFs already fulfill the requirements for various applications, such as electrostatic dissipation and touch screen. The performance reaches close to the ITO resistance, which is the standard commercial film having about 100 Ω/sq at 80 % transmittance.

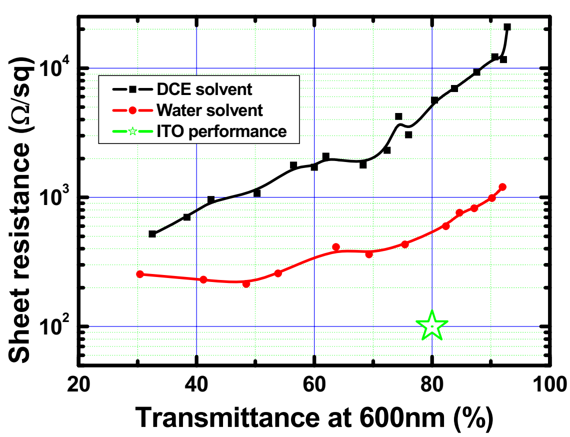

Figure 4. Sheet resistance as a function of transmittance at 600 nm. Comparisons between DWCNT films sprayed on PET film using DCE solvent and SDS in deionized water solution.

CNTs can tolerate mechanical treatment such as bending or even certain degree of defect creation without loss of conductivity [9]. For the CNT network on flexible plastic substrate, the electrical properties also maintain under bending since the conductivity persists at the contacts among the CNTs [10]. We measured the DC resistance of some films fabricated by spray method before and after bending 180 degrees. From table 1, we can see that the change of the DC resistance is negligible, no more than 4 %, after bending 180 degrees. The performance of the TCFs is combined with the CNTs and the flexible PET films. ITO does not reveal this property and fail during bending [11].

Table 1 Resistance after bending 180°

R_0 (Ω)	R_{180} (Ω)	changing ratio (%)
177.3	179.2	1.07
206.6	208.7	1.01
493.5	501.8	1.68
576.3	588.4	2.09
629.7	651.2	3.41

Figure 5 illustrates the SEM morphology of two TCFs. We observe some DWCNT bundles on the surface. It can be seen from (b) that the bundle sizes are much smaller than that of (a). This indicates that the dispersion of DWCNTs in water with SDS is much better than that of DCE solvent. The large bundle results in poor CNT network formation, yielding high resistance. Therefore the dispersion particularly nanodispersion of CNTs is of crucial importance to improve the film performance [12]. A further improvement in the performance of the transparent conductive film with lower electrical conductivity and higher optical transmission should be approached by enhancing the degree of dispersion of the CNTs in the water-based solution.

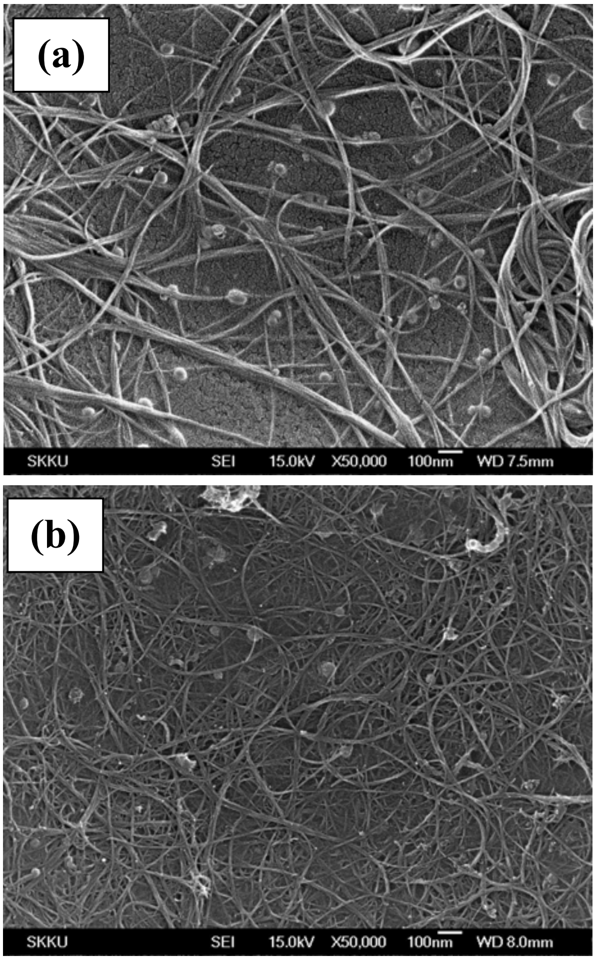

Figure 5. SEM image of DWCNTs films sprayed on PET film using (a) DCE solvent and (b) SDS in deionized water(scale bar:100 nm).

3. Conclusion

TCFs were fabricated using DWCNTs dispersed in DCE and water solution by the spray coating method. This method can be easily used to fabricate very large, high uniform TCFs. We investigated that the dispersion stability of DWCNTs is stable in DCE solution as well as in deionized water with the surfactant of SDS. The water-based solution films have better performance than the DCE solution films. The TCFs we obtained owning transmittance of 90 % and sheet resistance of 1000 ohms/sq can be applied for touch screen films. In addition, these films show robust flexibility and do not breakdown upon bending and folding in contrast with commercial films such as ITO. We believe that the spray method introduces the simple and rapid construction of flexible devices.

4. Acknowledgements

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5. References

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