ORIGINAL ARTICLE

Preparation of light-transmissive conductive film by free arc dispersed carbon nanotubes and thermos compression bonding

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Abstract

To investigate the effect of gas dispersing carbon nanotubes (CNTs) and hot pressing method on the transparency and the conductivity of thin films, the free arc was used to disperse the CNTs in a high dispersion rate, and the dispersed CNTs were rapidly pressed into the surface of the PET film by hot pressing to obtain electrical conductivity. The relationship between the light transmission and sheet resistance of the film was studied by changing the deposition time and the presence or absence of electrostatic adsorption. It was found that the CNTs modified film still retains good electrical conductivity (sheet resistance up to 6×10^4 Ω, light transmittance 69%) through the cleaning of surfactants and ultrasonic waves, which proves that hot pressing is a simple physical method to achieve effective combination of CNTs and films.

Keywords Thin film · Carbon nanotubes · Transparency · Conductivity · Free arc dispersion · Hot pressing method

1 Introduction

The light-transmitting conductive film is a kind of widely used film with good light transmittance and electrical conductivity. It is based on polymer and has effective conductive structure of thin film. Zhang et al. [1] prepared transparent conductive composite film with transparency up to 74% and resistance down to 9.40 x/sq at 550 nm. Edinger et al. [2] prepared highly transparent and conductive Zinc Oxide thin films by spray pyrolysis method with zinc acetate and indium acetone as precursors. Liu et al. [3] fabricated Ti-doped indium tin oxide thin films using a DC-magnetron sputtering deposition method. There are many preparation methods of transparent and conductive films. Aoki et al. [4] introduced the latest progress in the synthesis of polyacetylene films. An et al. [5] demonstrated the production of highly flexible, conductive and transparent nickel electrodes, which are widely used in engineering applications. Oytun et al. [6] prepared flexible transparent film heaters on a polysulfone film and showed the superior performance of the multilayer film. Walton et al. [7] prepared highly conductive carbon black-filled composite thin films using layer-by-layer assembly. These composite thin films were patterned using a traditional photolithographic lift-off process that could be used to process them for a variety of electronics applications. Kang et al. [8] proposed a method to modify both flexible PET substrates and CNT simultaneously with the same TES molecule. Zhang et al. [9] reported a spin spraying technique using flexible electronic devices to prepare highly conductive, corrosion-resistant and flexible hybrid films on multi-walled CNTs and nanomaterials. Oliveira et al. [10] prepared a light-transmitting conductive film with high conductivity and uniform composition based on synthetic cellulose and conductive polymer; Zhang et al. [11] proposed a new method for preparing Ag/CNTs composite films by rotary spraying, which supports the practicability of applications, Kim et al. [12] applied a PEDOT: PSS film on CNTs by spin coating or electrophoresis to prepare a hybrid transparent electrode, which improved its conductivity and flexibility, and obtained a certain degree of light transmission. Liu et al. [13] investigated the dispersion of CNT in water under thermal excitation by molecular dynamics simulation. The result shows that carbon nanotubes have a high separation tendency at high temperature with the aid of water. The reports on the dispersion of nanomaterials are abundant. Pierard et al. [14] reported a method for obtaining short MWCNTs by ball milling. Zapata-Massot et al. [15] studied the effects

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of ball milling on various properties of ground MWCNTs. Gao et al. characterized the effect of ultrasonication on the dispersion size of CNTs and graphene oxide. The findings of this study can promote the understanding of GO/CNT-OPC composites, helping to guide the implementation of ultrasonication in the future [16]. Zhang et al. [17] presented a new method to fabricate Ag/CNT composite films as conductive bonding units for flexible electronic device. Zhang et al. [18] described a new strategy for non-covalent functionalization of MWCNTs using supramolecular surfactants. Jiang et al. [19] mainly studied the effects of three aspects of surfactant, ultrasonic oscillation and centrifugation on the dispersion of CNTs. These treatments have both advantages and disadvantages in the preparation of the light-transmitting conductive film, because the dispersion treatment can significantly disperse the closely agglomerated nanomaterials. Therefore, while the nanomaterials themselves exhibit excellent physical and chemical properties, the modification of the nanomaterials themselves weakens the electrical conductivity of the materials to some extent. Li et al. [20] found for the first time that nanomaterials could disperse significantly under free arc excitation, and reported in detail the mesoscopic mechanism of the process, as well as the correlation between technical parameters and dispersion results. Free arcs have high-energy flux densities, and we use free arc excitation to treat the surface of CNTs. Thermal excitation is applied to the mixture of CNTs and the liquid working materials using a free arc. The liquid working materials undergoes a rapid phase change and a rapid volume expansion. CNTs aerogels with high dispersion and purity were prepared. In this work, CNTs are prepared by means of high dispersed vapor image dispersion (VDS). Combined with the hot pressing technology of the film, the preparation method of the transparent conductive film is innovated. The correlation between the accumulated amount of CNTs and the light-transmitting and conductive properties of thin films is studied.

2 Materials and methods

2.1 Materials

MWCNTs (Diameter = 5–15 nm, Length = 10–40 μm, purity: 99%, CP1002M;LG). Deionized water. PET film (Sheet resistance > 10^{13} Ω/square, transmittance: 88%, thickness: 80 μm). SDBS(purity: 1%, Shandong Linyi Yiqun chemical co. LTD).

2.2 Preparation of light-transmissive conductive film

In this work, the preparation of the light-transmissive conductive film was divided into two main stages. The first stage was to disperse and uniformly attach the CNTs to the surface of the film. The second stage was to bond the CNTs firmly to the surface of the film through a certain temperature and pressure. The specific steps are as follows: Firstly, referring to the meteorological dispersion method of CNTs reported by Li, the CNTs and deionized water were uniformly mixed at a mass ratio of 1:4 and pressed into strip electrode, using the self-made equipment to disperse the CNTs in the electrode. The PET film, cleaned with acetone, was spread 2 cm above the CNTs electrode and crossed over the linear CNTs dispersion area at a speed of $v = 0.01$ m/s. The first stage of the preparation was completed. Based on the roll coating machine, referring to the preparation of RPET/TPU Composites reported by Fang et al. [21]. The pet is in a viscous state at a temperature of 220–250 °C, allowing the CNTs to be well embedded, so the surface temperature of the steel roll is $T = 233$ °C, the surface pressure is $P = 2 \times 10^6$ Pa, and The line speed formula is:

$$\text{erfn} = \frac{t_w - t_{(x)}}{t_w - t_0} = \frac{2}{\sqrt{\pi}} \int_0^n \exp(-n^2)\mathrm{d}n$$

$$\frac{x}{2\sqrt{a\tau}} = \eta, \quad \tau = \frac{x^2}{\eta^2 a}$$

$$n = \frac{1}{T} = \frac{y}{2\pi r \tau} \times 60 = 307\, r/\text{min}$$

$$v = \pi d n = 0.8 \text{ m/s},$$

X—film thickness, a—film thermal diffusivity, τ—heat transfer time, y—heat transfer distance, erfn—error function, $x = 10^{-7}$ m, $a = 9.662 \times 10^{-8}$ m, $y = 10^{-4}$ m.

The film prepared in the first stage was hot pressed, where in one side of the carbon tube was opposite to the high temperature steel tube, and one side of the carbon free tube is opposite to the elastic silicone tube, the second stage of preparation is completed. To enhance the adsorption of CNTs in the atmosphere, to enhance the attraction of meteorological particles by means of electrostatic induction. Specifically, the electrode plate having a size of 20.0 cm × 10.0 cm was insulated with a thickness of 0.1 mm, and temporarily fixed to the film sample back, the electrode voltage is $U = 4.5$ kV, so that the front side of the film receives the CNTs. The details are shown in the figure.

To verify the bonding strength between the CNTs and the PET substrate, the prepared transparent conductive film samples were washed, details are as follows: the samples were immersed in an aqueous solution containing 5% by mass of SDBS, and ultrasonically shaken at room temperature for 30 min, rinse with deionized water, and bake at 50 °C for 60 min to remove surface moisture.

2.3 Characterization of light-transmitting conductive film

(a) Using SEM(SU-8010; Hitachi, Tokyo, Japan) to characterize the surface topography of the sample;

(b) Testing the conductivity of the surface of the sample using a dual-electron four-probe resistivity tester (Ningbo Rooko instrument Co., Ltd.); taking the midpoint of the diagonal line of the film as the center sampling point, and then select four on the diagonal line that are $d = 6$ cm away from the center sample point as the sample points, and taking the average value of the resistance values of the five sample points as the sample sheet resistance value;

(c) The light transmittance of the sample was tested using a UV-1600PC ultraviolet visible light photometer (AOE instrument Co., Ltd.).

The CNTs process and sample photos are shown in Fig. 1.

3 Results and discussion

3.1 Microscopic characterization of light-transmissive conductive films

All samples had significant CNT attachment. The CNTs in the sample with a deposition time of 30 s had a network island distribution. The CNTs were independently distributed in a region having a diameter of several tens of micrometers, and the CNTs in the region had a good dispersion morphology. Because of the pressure of the hot pressing stage, CNTs were embedded in the surface of the film with a flat structure. With the increase of deposition time, the size of the CNTs region did not change significantly, but the density of the CNTs was significantly increased. When the deposition time was 90 s, the islands of the CNTs were basically connected to each other, forming a conductive network region covering a larger area. There was no significant difference between the deposition time $T = 120$ s and the deposition time $T = 150$ s in the observation of SEM. The reason should be that the coverage area of CNTs has reached the limit and the accumulation of CNTs is verticalized. Theoretically, the surface-type conductive film relies on the continuity and homogenization of the conductive materials. Therefore, when the deposition time is shorter than 90 s, the conductive layer on the surface of the film is dominated by a small-area distribution, and the small conductive areas are limited in connection, so it is difficult to form a strong electrical conductive ability on the macroscopic scale; When the deposition time is longer than 90 s, the surface of the film has a relatively complete and continuous conductive structure. A stable conductive structure and properties should be formed based on the conductivity of CNTs. The SEM image of the film surface at different deposition time is shown in Fig. 2.

3.2 Electrical properties of light-transmissive conductive films

In this work, the CNT deposition time, the presence or absence of electrostatic adsorption, and the presence or absence of cleaning were taken as variables to characterize the electrical conductivity of the film under the cross of variables. Also, as a sample without cleaning, electrostatic adsorption can significantly reduce the resistance of the film. The reason is that the electric field generated by the electrode plate on the back side of the film significantly affects
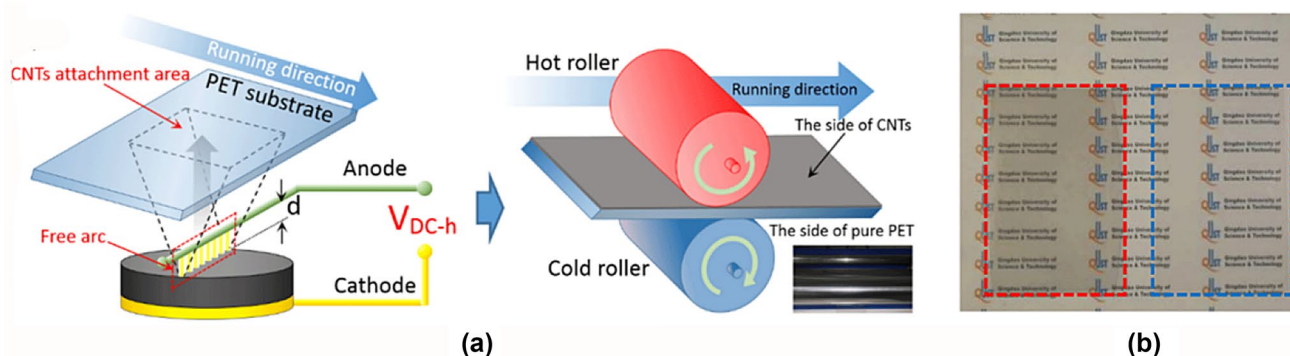

Fig. 1 Treatment and sample photos of CNTs. **a** Place the CNTs strip electrode on the cathode, keep the upper surface at a constant distance from the anode ($d = 1$ mm), turn on the Vdc $= 8$ kV power supply, and generate CNTs aerogel at the free arc. As shown in the figure, a certain amount of CNTs is attached to the lower surface, and the upper surface of the PET film is fixed on the insulating coating of the metal electrode plate. According to the experimental design, the metal electrode plate can be connected to the positive electrode of $V_h = 3$ kV to generate an induced electric field; the figure is a hot pressing diagram, and the bottom is a physical photo. **b** The red frame is a PET film (deposition time: 90 s) pressed into CNTs, and the blue frame is a PET film not treated with CNTs
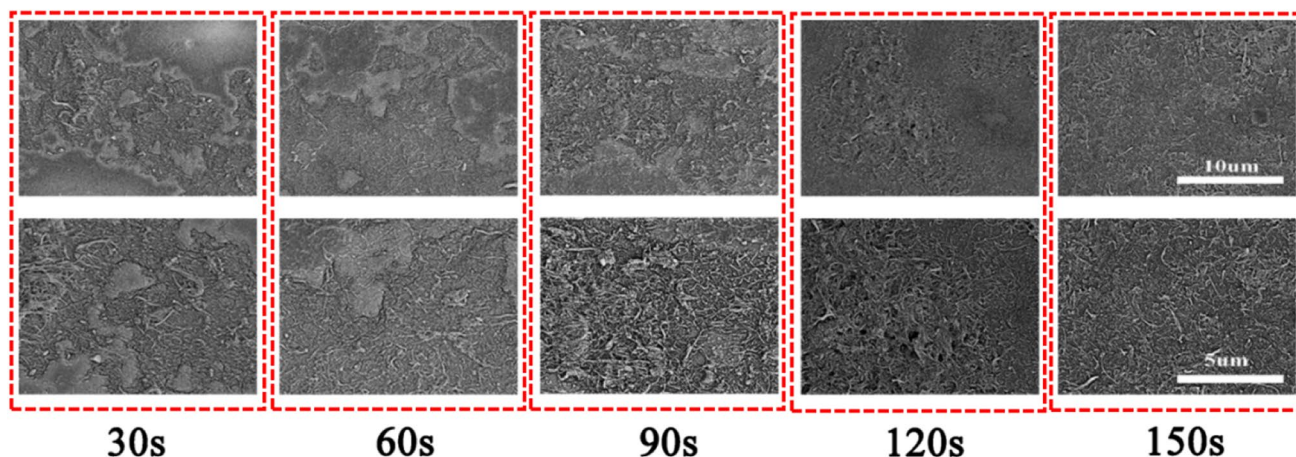
Fig. 2 SEM images of the film surface at 5 k times and 10 k times at different deposition times. It can be seen that at $t = 30$ s, 60 s, 90 s, the coverage area of CNTs increases with deposition time, while at $t = 90$ s, 120 s, 150 s, the increase of CNTs coverage area with deposition time is not significant

the movement trajectory of CNTs in the dispersed atmosphere. As a general physical phenomenon, the mechanism is not further discussed in this paper, but it is clear that the generation of electric field is conducive to the concentration and enrichment of CNTs on the surface of the film. As a result, in the same CNT deposition time, the surface of the sample with electrostatic adsorption has higher concentrations of CNTs, which significantly increases the conductivity of the sample under this parameter. Similarly, as a sample with electrostatic adsorption, cleaning can significantly reduce the conductivity of the sample, but the sample after cleaning still has high conductivity. Combined with the above microscopic characterization, it is shown that hot pressing can press a certain amount of CNTs on the surface of the film. The surface layer of the film forms a strong mosaic structure, and the CNTs effectively embedded in the matrix are difficult to be washed away, so the sample after washing still has high conductivity. At the same time, the cleaning can separate the CNTs that are not firmly embedded in the surface layer of the film, which will reduce the depth of the carbon tube region and reduce the thickness of the conductive structure. However, due to the influence of equipment precision, it is difficult to ensure the uniform force of the film on the micro scale, so the degree of CNTs on the surface of the film is different. And the cleaning will affect the continuity of the 2D planar CNT structure to some extent. All samples showed significant directivity from different CNT deposition time, that is, the conductivity of samples increased with the increase of deposition time. Combined with the above microscopic characterization, it can be further explained that the more complete macroscopic conductive region and the
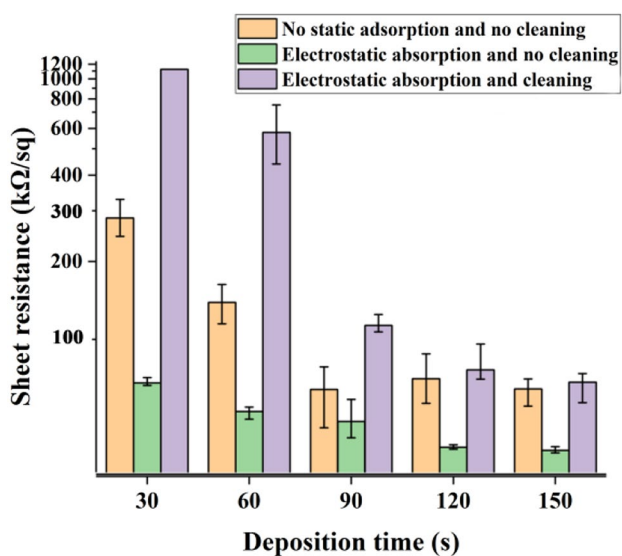

Fig. 3 Relationship between sheet resistance and deposition time of thin films. This is the results of research on the sheet resistance of the film electrostatically adsorbed but uncleaned, non-electrostatically adsorbed and unwashed, electrostatically adsorbed and cleaned at different deposition times. Since the deposition time is short and the amount of CNTs attached was small, only one set of data was measured for the films with deposition time of 30 s after cleaning with surfactant, so no error was indicated

Table 1 Relationship between deposition time and transmittance

Deposition time (s)	Transmittance before washing (550 nm)	Transmittance after washing (550 nm)	Increased (%)
30	59.3	76.9	29.68
60	56.8	71.9	26.58
90	46.6	70.3	50.86
120	44.8	69.3	54.69
150	41.2	68.1	65.29

depth of the conductive structure will be beneficial to the improvement of the conductivity of the film, but it should be pointed out that the CNT deposition time $T = 120$ s is not much different from the conductivity of $T = 150$ s. The reason is that the conductivity of the continuous macro-conducting region is limited. The conductivity of MWCNTs and the contact resistance between the tubes are one of the main reasons that restrict the conductive structure. Therefore, on the basis of the relatively complete macroscopic conductive region, further improving the depth of the conductive region has little contribution to the overall conductivity of the samples. The relationship between sheet resistance and deposition time of thin films is shown in Fig. 3.

3.3 Light transmission characterization of light-transmitting conductive film

Overall, the working samples have a low light transmission performance compared with the related reports. This study aims at large-scale preparation, so the conductive material selected is a cheaper MWCNTs. MWCNTs have higher resistance and stronger electromagnetic absorption than single-walled CNTs due to the structure of CNTs. From the material selection point of view, the two will make the light-transmitting conductive film have significant differences in conduction and light transmission. In connection with the above research results, the cleaning will reduce the amount of CNTs carried on the surface of the film to some extent, thereby improving the light transmittance of the film. Therefore, the light transmission performance of the sample after cleaning will be significantly improved The difference of light transmittance before and after cleaning is worth noting. As shown in Table 1.

The higher the deposition time of CNTs, the greater the change of light transmittance after sample cleaning, indicating that the CNTs firmly bound under hot pressing are limited. Although the longer the CNT deposition time, the more CNTs are carried on the surface of the film, the change in light transmittance after washing is more significant, Correspondingly, the light transmittance of samples with different deposition times of CNTs after cleaning is basically around 70%, which further indicates that the CNTs effectively embedded by hot pressing are relatively fixed. However, the conductivity of the samples with different CNT deposition time is significantly different. The reason is that as the deposition time increases, the CNTs attached to the PET film increase, forming a good conductive network structure. At the same time, it will negatively affect the light transmittance of the film, the transmittance of the film without CNTs is greatly reduced from 88 to 75% after hot pressing. However, the thickness or density of the conductive layer of the film samples with different deposition time of CNTs are slightly different after washing, which has a significant effect on the electrical conductivity, but not obvious on the light transmittance. The film transmittance at different deposition times is shown in Fig. 4.

4 Conclusions

In the process of CNTs dispersion, electrostatic induction can significantly increase the amount of CNTs on the surface of the thin film, thus significantly affecting on the conductivity of the film; the conductivity of the film increases with the deposition time of the CNTs; washing will remove a
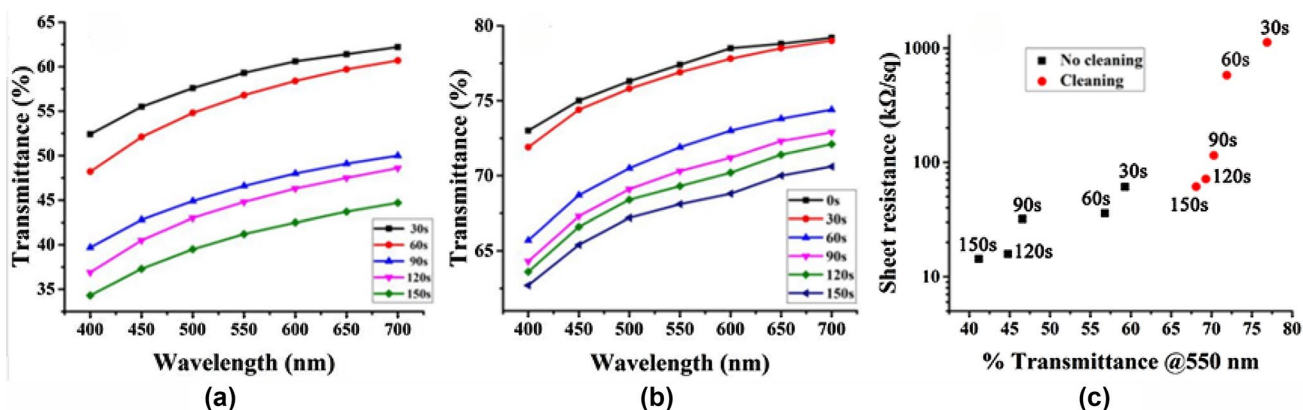

Fig. 4 Film transmittance at different deposition times. The relationship between light transmittance and sheet resistance: **a** the light transmittance of the uncleaned light-transmitting conductive film in the wavelength range of 400–700 nm; **b** the light-transmitting conductive film after cleaning with the surfactant in the wavelength range of 400–700 nm; **c** film resistance and light transmittance after cleaning are significantly higher than unwashed, and the film with deposition time longer than 90 s after cleaning has a light transmittance of 70%, sheet resistance still reach the electrostatic shielding level

large amount of CNTs, but hot pressing can firmly embed a certain amount of CNTs on the surface of the film so that the film retains a considerable conductivity; hot pressing causes the CNTs to be embedded in the surface of the film and greatly reducing the light transmittance of the film. In contrast, the content of CNTs has little effect on the light transmittance of the film. This work may provide a new technical approach for the preparation of large-scale light-transmissive conductive films.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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