Transparent conductive film based on carbon nanotubes and PEDOT composites

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Abstract
Single-walled nanotubes (SWNTs), thin multiwalled carbon nanotubes (t-MWNTs) and multiwalled carbon nanotubes (MWNTs) were treated with H2SO4 – HNO3 acid solution, under different chemical conditions. The acid-treated CNTs were dispersed in DI water and in poly(3,4-ethylenedioxythiophene) (PEDOT) solution. Furthermore, the finely dispersed CNTs/PEDOT solutions were employed to a simple method of bar coating to obtain the transparent conductive films on the glass and polyethylene terephthalate (PET) film. A sheet resistance of 247 \( \Omega \) and a transmission of 84.7% were obtained at a concentration of the acid-treated CNTs of 0.01 wt.%.

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1. Introduction

Extraordinary electrical, physical and thermal properties of carbon nanotubes (CNTs) make them good candidates for progressing polymer/CNTs composites [1–3]. The improvement of conductivity of transparent conducting film using conducting filler has received considerable amount of attention in the various fields, such as, display technologies, solar cells, flexible electronic devices and optical devices [4]. Furthermore, the traditional transparent conductive films of indium tin oxide (ITO), has a focus of various industries; however, it has several problems, such as flexibility and cost-effectiveness. Nowadays, CNTs have been recognized as one of the most reliable candidates for conductive materials due to its remarkable conductivities [5,6]. There are various methods used for fabricating thin nanotubes film such as filtration [7], airbrushing [8,9], drying from solvent [10], spin coating [11] and Langmuir–Blodgett [12] deposition. However, these methods have a number of limitations in preparing the films, such as film homogeneity and uniformity, efficiency of film production, film thickness controllability and flocculation due to van der Waals interactions between CNTs. In the present work, a novel method of bar coating is used for the fabrication of transparent conductive films of CNTs/PEDOT composites, which is found to be relatively simpler, cost-effective and quick to process over the conventional methods. To apply a wet coating thickness between 4 and 120 \( \mu \)m a wire-wound-bar is used. It is produced by winding precision-drawn steel wire onto a stainless steel rod resulting in a pattern of identical-shaped grooves. The grooves precisely control the film thickness. This method can coat the film homogeneously and the efficiently at large scales and easily control the thickness of film by changing the pitch of coil winding around the bar. The electrical and optical properties of acid-treated CNTs/PEDOT composites were investigated with emphasis on the dispersion of CNTs in the solutions and during forming the film. Raw CNTs have a substantial van der Waals attraction (950 meV/nm), nanotubes tend to aggregate easily and are difficult to suspend in DI water, various solvents and the host resin [13]. Moreover, it is
observed that, even if initially dispersed, they may re-agglomerate soon thereafter depending upon the viscosity of the matrix. Aggregation between CNTs hinders the use of the exceptional properties of CNTs and acts as an obstacle in most important parts of CNTs technology [14,15]. If CNTs do not disperse in the solution well, CNTs agglomerate each other in the transparent conductive film, resulting in bad effects on the electrical and optical properties. To make the good dispersion of CNTs, we use a covalent derivatization. This method has a beneficial effect on their solubility, and allows a stable dispersion of CNTs in various solvents. In this report, we develop a method to fabricate an electrically conductive and optically transparent nanocomposite thin film. Transparent conductive films were deposited on a glass or plastic substrate with using finely dispersed CNTs and PEDOT solution. Combination of optical transparency and good conductivity of CNTs composite film will open the way to new construction of optoelectronic devices.

2. Experiments

We used MWNTs, t-MWNTs and SWNTs from Iljin Nanotech Co., Ltd as a raw material. The diameter of MWNTs and t-MWNTs ranged from 10 to 20 nm and from 5 to 8 nm, respectively. The acid treatment of the as-deposited CNTs was carried out in a mixture of concentrated sulfuric and nitric acids (95% H2SO4/65% HNO3 = 3:1). Details of acid treatment were described in previous publication [16]. The acid treatment was carried out under mild ultrasonication conditions for a period of 4 to 7 h in order to minimize the damage of CNTs. After acid treatment, the CNTs were collected on a 0.2-m thick polytetrafluoroethylene (PTFE) membrane. The collected CNTs were ultrasonicated for 30 min. After samples were centrifuged for 1 h at 10 000 rpm, the supernatant was repetitively rinsed for 4 to 5 times with DI water completely to neutralize the acid-treated CNTs and dried at a temperature of 90 °C under the atmospheric conditions. The zeta potential, ζ, of the various CNTs, in order to evaluate the degree of dispersion, was measured in aqueous solution by electrophoretic light scattering spectrophotometry (ELS-8000, Otsuka). The dispersion stability of various CNTs as a function of time was measured by multiple light scattering (MA 2000, Turbiscan). The acid-treated various CNTs powders were dispersed in ranging from 0.01 wt.% to 0.03 wt.% without surfactants in DI water and the ultrasonication was carried out for 30 min. After samples were centrifuged for 1 h at 10 000 rpm, the supernatant was retained and ultrasonicated for 10 min. In the present work, we blended the finely dispersed CNTs solution and the PEDOT solution which contained 1 wt.% of PEDOT powder in DI water matrix and had a navy blue color and ultrasonicated the mixed solution for 30 min. These solutions were coated onto a glass and plastic substrates such as poly (ethylene terephthalate) (PET) film by bar coating method and immediately dried in air at 100 °C. The morphology of transparent conductive film was characterized by field emission scanning electron microscopy (FESEM, JEOL, JSM890). The sheet resistance and optical transmission properties of the transparent conductive film were measured by the four-point probe (CMT-SR100N) method and UV–visible spectrometry (UV S-2100, Scinco), respectively.

3. Results and discussions

3.1. Characterization of CNTs dispersion in aqueous and PEDOT solutions

The Table 1 summarized the absolute values of ζ of acid-treated CNTs and raw CNTs (0.01 wt.%) using various surfactants (0.03 wt.%). Traditionally, the ζ represent the degree of the dispersion of particles in the solution. If the absolute values of ζ is smaller than ~25 mV then the repulsive force is not strong enough to overcome the Van der Waals attraction between the particles, and hence each particles begins to agglomerate. By definition, the ζ of raw CNTs in DI water have a zero at the pH 7. Furthermore, the solution with the Gum–Arabic (GA) has slightly higher the absolute ζ than the sodium dodecyl sulfate (SDS) suspension. The ζ values of the acid-treated CNTs (0.01 wt.%) in the DI water were found to be changed as −36.73, −57.67 mV, for the MWNTs, t-MWNTs and SWNTs, respectively. This led to the optimization of the parameters of covalent derivatization for the dispersion method of CNTs in order to minimize the damage of CNTs. Furthermore, a considerable amount of change in optical transmission was found as a function of time, which is attributed to the dissolution, stability and clarification of the solution. Fig. 1 shows the dispersion stability of raw t-MWNTs and acid-treated t-MWNTs in DI water and PEDOT solution, respectively. The suspension was ultrasonicated for 30 min. These solutions were put in the measurement cell. Measurements were conducted the scanning for 12 h with scanning time of 10 min at the room temperature. It can be seen from Fig. 1(a) and (b) that, for the raw t-MWNTs dispersed in DI water, an abrupt increase in the optical transmission during the early stage of measurements is shown, whereas in the

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<th>Table 1</th>
<th>Summary of change in zeta-potential values with acid-treated various CNTs (MWNTs, thin MWNTs, SWNTs) and raw MWNTs using the surfactant (GA and SDS, CNTs/surfactant=1:3)</th>
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<tr>
<td>Raw MWNTs</td>
<td>MWNTs with Gum–Arabic</td>
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<td>Zeta-potential, ζ (mV)</td>
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case of acid-treated t-MWNTs in DI water, a relatively slow increase in the optical transmission is shown. An abrupt increase in the optical transmission at the early stage led to the sedimentation or a flocculation of the particles (CNTs).

Fig. 1(c) and (d) shows the dispersion stability in PEDOT solutions. Because light source in measurement system almost absorbed in the solution due to the navy blue color of PEDOT solution, dilution of PEDOT solution was necessary. In the case of dispersion stability of CNTs in PEDOT solutions, similar result to DI water was observed. From these results, we found that acid-treated t-MWNTs in DI water and PEDOT solutions maintain the very stable dispersion. Furthermore, it is important to prepare the transparent conductive film without deteriorating the electrical conductivity and optical transmission due to aggregation of CNTs. Fig. 1(e) shows the kinetic behavior of...
fluctuations of CNTs at the previous conditions. The transmission of raw t-MWNTs in DI water and PEDOT solutions steeply increase within 2 h and later on the rate of optical transmission lowers. The transmission of acid-treated t-MWNTs in DI water and PEDOT solution hardly changed in comparison with raw t-MWNTs in the same solutions.

3.2. Fabrication and properties of transparent conductive film with CNTs/PEDOT

Fig. 2 shows the morphology of transparent conductive film of various types of CNTs at 0.03 wt.%. Fig. 2(a) reports the raw PEDOT film without any acid-treated CNTs, which show that, the film is uniformly coated on the glass. It can be seen from Fig. 2(b) that the MWNTs are well dispersed without any insignificant aggregation across the surface of PEDOT and thickness of film was slightly found to be increased as compared with the raw PEDOT film due to the CNTs filler into the PEDOT matrices. In addition, the surface morphology of the film with t-MWNTs and SWNTs is shown in Fig. 2(c) and (d). In the case of t-MWNTs and SWNTs, the films have a high degree of uniformity, surface homogeneity and the roughness of film is found to be better than for the MWNTs. The comparison of sheet resistance and optical transmission for various types of CNTs as a function of acid-treated wt.% is shown in Fig. 3. It can be seen from Fig. 3 that, the raw PEDOT film without any CNTs showed a transmission of 87.8% at the wavelength of 600 nm and a sheet resistance of 1182 Ω/sq. The film showed a transmission of 87.6% and improved sheet resistance of 548.1 Ω/sq when the concentration of acid-treated MWNTs was 0.01 wt.%. The transmission of the film with the concentration of 0.03 wt.% of MWNTs was considerably deteriorated to 78.7%, whereas, the conductivity of the film showed an insignificant decrease 407.2 Ω/sq. In the case of acid-treated t-MWNTs and SWNTs, the transmission of the film was 82.7% and 81.4% and the sheet resistance of the film showed 249.2 and 310.5 Ω/sq when the concentration of CNTs was 0.01 wt.%, respectively. It was observed that the sheet resistance dramatically decreased when a small amount of acid-treated CNTs (0.01 wt.%) was added. When the concentration of acid-treated CNTs was larger than 0.03 wt.%, the transmission of the film with acid-treated t-MWNTs and SWNTs was severely deteriorated to 75.41% and 74.1%, respectively. But the conductivity of the film with acid-treated t-MWNTs and SWNTs was 189.6 and 390 Ω/sq that is almost same as the conductivity of film with acid-treated MWNTs. When the concentration of CNTs is over 0.03 wt.%, the transmission of film dramatically decreases due to the aggregation of CNTs. For macroscopic networks on flexible substrates, the electrical properties also maintain under bending since the conductivity sustain at the contacts between the CNTs [17,18]. Transparent conductive film with CNTs/PEDOT was demonstrated and shown in Fig. 4, which shows a homogeneous large area (10 cm × 5 cm) CNTs coating on the PET film as substrate, whereas the
flexibility of ITO film on flexible substrate is very limited compared to film of CNTs networks [19]. The CNT-coated PET film used in Fig. 4 shows a transmittance of about 81.6% and a sheet resistance of 390 \( \Omega \)/sq. The multimeter is used only to demonstrate the conductivity of the sample by means of bending of the film. Fig. 4(a) show surface resistance of 598 \( \Omega \) after slight bending and the film can be bent all the way without a significant change in resistance. Although we fold the film, it hardly changed the resistance (Fig. 4(b)). We believe that it leads to opportunities in the simple and rapid construction of flexible devices.

4. Conclusions

In the present study, a transparent conductive film was fabricated using a composite of PEDOT and the acid-treated various CNTs by the bar coating method. We investigated that the dispersion stability of acid-treated CNTs is very stable in PEDOT solution as well as DI water. To make a film shape, CNTs/PEDOT solutions must have a regular viscosity and wettability and preserve a state of dispersion in the PEDOT solution. The raw PEDOT film has a transmission of 87.8% and a sheet resistance of 1182 \( \Omega \)/sq. Electrical and optical properties of CNTs/PEDOT film was improved; a sheet resistance of 249.2 \( \Omega \)/sq and a transmission of 82.7% were obtained when the concentration of the t-MWNTs was 0.01 wt.%. In addition, these films show robust flexibility and do not breakdown upon bending and folding in contrast with commercial films such as ITO. A further improvement in the various properties of the transparent conductive film, such as its electrical conductivity and optical transmission, should be possible by enhancing the degree of dispersion of the CNTs in the PEDOT solution. These CNT/PEDOT thin films may be obtained, permitting one to fabricate transparent electronic devices such as a flexible display, solar cell and sensors, etc. It will be able to lead to important advances in developments of flexible optoelectronic devices and especially to alternatives to approach for transparent and conductive coatings such as commercial ITO films.

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