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Single wall carbon nanotube/poly(3,4-ethylenedioxythiophene) nanocomposite film as a transparent electrode for flexible organic light-emitting diodes

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ABSTRACT

We prepared a flexible transparent electrode comprising a single wall carbon nanotube/poly(3,4-ethylenedioxythiophene) (SWNT/PEDOT) nanocomposite in which the PEDOT matrix was *in-situ* polymerized on the preformed SWNT conducting network. With the aid of the SWNT network, the SWNT/PEDOT nanocomposite film gave a much lower surface resistance (~160 Ω/□) with a high transmittance (86% at 550 nm), compared with the neat PEDOT film of the same thickness. Current mapping of the nanocomposite film surface by conductive-atomic force microscopy (C-AFM) exhibited that most of SWNTs participate in the conducting network while the PEDOT matrix provides electrical pathways across the separated SWNT chains and enables a smoother, pore-free film with a uniform current flow on the overall surface of the film. When the SWNT/PEDOT nanocomposite film was employed as an anode of Alq3-based flexible organic light-emitting diode (FOLED), the device demonstrated ~3 times enhanced brightness and ~1.9 times enhanced current efficiency than the device with the neat PEDOT anode.

1. Introduction

Indium-tin oxide (ITO) has been being widely used as a transparent electrode in various electro-optic and opto-electronic devices due to its excellent light transmittance and high electrical conductivity. However, the needs of flexible transparent electrode as well as the limited availability of indium and high production cost of ITO are causing many research groups to continue active researches to replace ITO [1–3]. Various conductive materials such as carbon nanotubes (CNTs) and conducting polymers have been proposed as alternatives to ITO [4,5].

CNTs have high enough electrical conductivity to be used for flexible electroluminescent devices [6]. But due to their intrinsic geometric structure with high aspect ratio, thin CNT films deposited on a flexible substrate have a highly porous surface morphology with protrusive tubes that may cause device failure [7]. Moreover, the rough surface of CNT films can affect the carrier mobility and shorten the lifetime of the device [8,9].

With conducting polymers, on the other hand, it is easy to form uniform thin films with varying optical and electrical properties onto various substrates using simple coating methods. However, the electrodes fabricated using conducting polymers alone are difficult to give high enough electrical conductivity and visible light transmittance to meet the requirements of a flexible and transparent electrode.

Many researchers have investigated conducting polymer-CNT composite films to improve the roughness of CNT films and increase the conductivity [10–13]. Also, they mentioned the electrical percolation threshold concentration of CNTs in the polymer matrix to improve the conductivity of the nanocomposites [14,15]. But the conductivity of the CNT-polymer composites is determined not only by the formation of CNT conducting network but also by the conductivity of polymer matrix.

In this paper, we report the single wall carbon nanotube/poly (3,4-ethylenedioxythiophene) (SWNT/PEDOT) nanocomposite film that is fabricated by the preformation of SWNT conducting network on a plastic substrate followed by the *in-situ* polymerization of 3,4-ethylenedioxythiophene (EDOT) monomers on the SWNT network. By employing this process instead of the conventional one that uses a polymer-dispersed SWNT coating solution, we could control the characteristics of the SWNT film and the PEDOT film separately to greatly enhance the conductivity of thin PEDOT film without much sacrifice of its transmittance. Then, we fabricated flexible organic light-emitting diodes (FOLEDs) with

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a neat PEDOT anode and also with a SWNT/PEDOT nanocomposite anode, and compared their performance to confirm the advantage of using the SWNT/PEDOT nanocomposite as a flexible transparent anode.

2. Experimental

2.1. Preparation and characterization of SWNT/PEDOT nanocomposite film

Flexible and transparent single wall carbon nanotube/poly(3, 4-ethylenedioxythiophene) (SWNT/PEDOT) nanocomposite films were deposited onto polyethylene naphthalate (PEN) substrates by the two-step procedure; preformation of SWNT network and *in-situ* polymerization of PEDOT onto the SWNT network. Fig. 1 illustrates the schematic procedure for preparing the SWNT/PEDOT nanocomposite film and the structure of the ITO-free flexible organic light-emitting diode (FOLED) fabricated using the nanocomposite film as an anode.

We used a commercial grade of SWNTs (AST-100F, Hanwha Nanotech, Republic of Korea) for the conducting network formation, which was produced by conventional arc-discharge method using Fe-based metal catalysts and purified by thermal treatment. The nanotubes dried in vacuum at 100 °C overnight were dispersed in dichloroethane (DCE) with a concentration of 1 g/L by ultrasonic agitation (100 W at 42 KHz for 6 h), followed by centrifugation at 10,000 rpm for 20 min. The centrifugation supernatant of the SWNT dispersion was deposited onto PEN substrates by multiple times of spin coating at 1,500 rpm and SWNT network films were obtained after the solvent evaporated during spin coating. And then the SWNT films were immersed in 60% nitric acid for 2 h in order to remove residual impurities and washed with deionized water. We observed the morphology of the SWNT film before and after the acid-treatment with a field emission scanning electron microscope (FE-SEM, LEO SUPRA 55 SEM, Carl Zeiss).

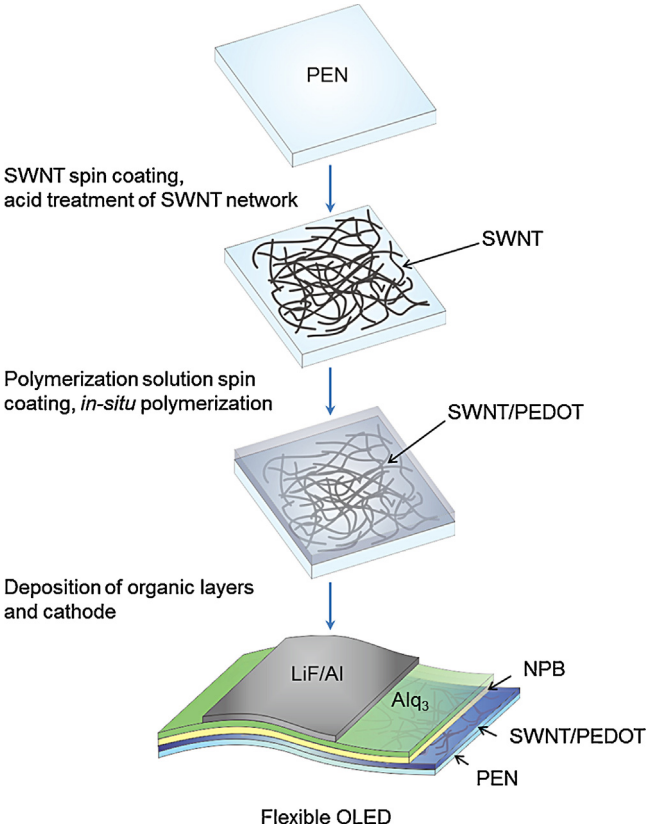

Fig. 1. Schematic procedure for preparing the SWNT/PEDOT nanocomposite film and the structure of the flexible OLED fabricated using the nanocomposite film as an anode.

The polymerization system for the *in-situ* polymerization of PEDOT on the preformed SWNT network film is basically composed of EDOT monomer (Baytron M, Bayer), ferric *p*-toluene sulfonate (FTS, Baytron C, Bayer) as an oxidizing agent and also a dopant, poly (vinylpyrrolidone) (PVP, Aldrich, Mw = 360,000 g/mol) as a binder, and pyridine as a base inhibitor, dissolved in *n*-butanol. EDOT and FTS were mixed with a weight ratio of 1:25 and the PVP and pyridine contents were fixed to be 30 and 70 wt% of the EDOT monomer, respectively, for a moderate polymerization rate. The mixed solution was spin coated on the preformed SWNT film at 1,500 rpm for 30 s, and then polymerized in a convection oven at 70 °C for 30 min. Finally, the nanocomposite film was washed with methanol to remove unreacted EDOT, FTS, or other residues on the film and dried at 70 °C for 5 min. For comparison, the neat PEDOT film without SWNTs was also prepared.

The thickness and surface resistance of the transparent conducting films were measured with a stylus profilometer (Detak 150, Veeco) and a low resistivity measurement system based on the four-pin probe method (MCP-T610, Mitsubishi), respectively. The optical transmittance was measured with a UV–vis spectrophotometer (Agilent 8453). Topographical characteristics of the SWNT/PEDOT nanocomposite as well as the preformed SWNT network films were examined by atomic force microscopy (AFM, Dimension 3100, Veeco Digital Instruments). Also, the current flowing on the film surfaces was visualized by the current mapping method using a conductive-AFM (C-AFM) to simultaneously investigate the surface morphology and the conduction routes.

2.2. Preparation and characterization of ITO-free flexible OLED devices

The ITO-free flexible organic light-emitting diodes (FOLEDs) were fabricated using both the SWNT/PEDOT nanocomposite and the neat PEDOT anode deposited on PEN substrates. The following organic and metal layers were successively deposited by thermal evaporation at a pressure of $<10^{-6}$ torr: *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB, 40 nm)/tris (8-hydroxyquinolinato)-aluminium (Alq3, 60 nm)/lithium fluoride (LiF, 1 nm)/aluminium (Al, 100 nm). Where, NPB was used as a hole transport layer (HTL), Alq3 as an emission layer (EML), and LiF/Al as a bilayer cathode.

The current density–voltage–luminance (J–V–L) characteristics and the electroluminescence (EL) efficiency of the fabricated FOLEDs were measured with a JBS I–V–L 300 EL characterization system equipped with a Keithley 2400 source/measure unit.

3. Results and discussion

3.1. Electrochemical and optical properties of SWNT network films

We fabricated SWNT conducting network films by repeated spin coating technique in order to reach the percolation threshold using a minimum amount of SWNT as well as to obtain a more uniform conducting network. Also, we could precisely control the thickness, transmittance, and surface resistance of the films depending on the spin coating number. With increasing number of spin coating, the thickness of the film increased while the transmittance decreased as shown in Fig. 2(a). Interestingly, the surface resistance dramatically decreased as the spin coating number exceeded one hundred as shown in Fig. 2(b). It is very likely that the percolation threshold was reached after spin coating the SWNT dispersion more than one hundred times. At this moment, a sufficient amount of SWNTs were deposited on