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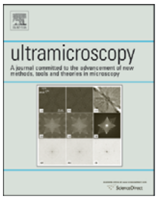

Effects of ITO surface modification using self-assembly molecules on the characteristics of OLEDs

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ABSTRACT

Indium tin oxide (ITO) has been commonly used as an anode of organic light emitting diode (OLED), because of relatively high work function, high transmittance, and low resistance. However, interface property between ITO and adjacent organic layer limits hole injection from the anode electrode. We have synthesized 4′-nitrobiphenyl-4-carboxylic acid (NBCA) and fabricated the hole-only device consisting of ITO/NBCA self-assembled monolayer (SAM)/TPD (1500 Å)/Al (500 Å) and the organic light emitting diode (OLED) consisting of ITO/NBCA SAM/TPD (600 Å)/Alq$_3$ (600 Å)/Al (600 Å). The prepared hole-only device with NBCA exhibited lower driving voltage than the device using 4-nitrobenzoic acid (NBA). OLED using NBCA also showed high external quantum efficiency.

1. Introduction

Indium tin oxide (ITO) has been commonly used as an anode of organic light emitting diode (OLED), because of the attractive combination of high optical transparency and good electrical conductivity. However, the ITO film has often a rough surface, relatively low work function compared with the adjacent organic layer, and its surface energy is not well matched to nonpolar organic film [1,2]. Many research groups have reported a variety of methods to facilitate hole injection into the organic layer and to improve interface property by special operations such as surface treatment using specific acid/base solution [3], plasma or ozone treatment [4] and introduction of specific self-assembled monolayers (SAMs) [5–7]. The ITO anode has been modified with both thin films and SAMs to reduce the barrier of hole injection and to improve adhesion characteristic at the anode–organic film interface and to inhibit the diffusion of material to anode.

The study on deposition of multilayers of a long-chain carboxylic acid onto a solid substrate was carried out by Blodgett [8]. Alkanethiols on gold surfaces and silanes on oxidized silicon are the most widely studied systems [9]. In most cases, the growth of self-assembled monolayers has advantages such as low cost and simple dipping process. Thus, the introduction of self-assembling technique on organic devices makes it possible to establish simple and better methodology.

Zuppiroli et al. [10] have demonstrated that it is possible to induce the work function shift of ITO electrode by interface treatment with grafting dipolar molecules. Furthermore, they have reported that 4-nitrobenzoci acid (NBA) is the most proper candidate material for hole injection among para-substituted benzoic acid derivatives grafted on ITO. It is wellknown that carboxylic acids are a promising attachment group on indium tin oxide [11]. In the present work, we have synthesized 4′-nitrobiphenyl-4-carboxylic acid (NBCA) and then fabricated OLEDs using NBCA as a hole injection self-assembled monolayer. The effects of interface modification treated with NBCA SAM onto the ITO on the performance of OLED were investigated.

2. Experiment

2.1. Chemical materials

1-Iodo-4-nitrobenzene, 4-methoxycarbonylphenylboronic acid, toluene, ethanol, lithium hydroxide, and palladium(0)tetrakis (triphenylphosphine) were purchased from Aldrich Chemical Co. (USA). Benzoic acid (BA), phenylbenzoic acid (PBA), 4-nitrobenzoic acid (NBA), *N*-*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (TPD), and tris-(8-hydroxyquinoline) aluminum

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(Alq$_3$) were purchased from TCI Co. (Japan). Potassium carbonate, ether, tetrahydrofuran (THF), and methanol were distilled from first-grade solvents purchased on the market. ITO glass fabricated by sputtering was purchased from Shinan SNP Co. (Korea).

2.2. *Synthesis of 4′-nitrobiphenyl-4-carboxylic acid (NBCA)*

Methyl 4′-nitro[1,1′-biphenyl]-4-carboxylate (**1**): A solution of 1-iodo-4-nitrobenzene (1.38 g, 5.6 mmol), 4-methoxycarbonylphenylboronic acid (1.0 g, 5.6 mmol), palladium(0)tetrakis(triphenylphosphine) (65 mg, 0.05 mmol), and K_2CO_3 (0.55 g, 5.6 mmol) in toluene/EtOH (9:1 v/v, 200 ml) was thoroughly degassed using a stream of dry N_2, and then stirred vigorously under reflux at 80 °C. After 24 h, the solution was concentrated by evaporation under vacuum and the residue was extracted with ether. The combined organic extracts were dried over $MgSO_4$ and evaporated. Recrystallization from ethylacetate solvent gave methyl 4′-nitro[1,1′-biphenyl]-4-carboxylate as a white solid (1.2 g, 84%). ^{1}H-NMR (400 MHz, D$_6$-DMSO); 8.34(d, $J = 8.0$, 2H); 8.09(d, $J = 8.0$, 2H); 8.04(d, $J = 8.0$, 2H); 7.95(d, $J = 8.0$, 2H). 4′-nitrobiphenyl-4-carboxylic acid (NBCA) (2): Carboxylate (1) (400 mg, 1.5 mmol) and lithium hydroxide (222 mg, 9.6 mmol) solution in THF (70 ml), methanol (20 ml), and water (20 ml) were stirred at room temperature for 15 h. The mixture was acidified with 1 M HCl solution. The NBCA compound was obtained by filtration and drying under vacuum (yield 86%, white solid) (Fig. 1). ^{1}H-NMR (400 MHz, D$_6$-DMSO); 13.10(s, 1H, COOH); 8.34(d, $J = 8.0$, 2H); 8.08(d, $J = 8.0$, 2H); 8.03(d, $J = 8.0$, 2H); 7.91(d, $J = 8.0$, 2H).

2.3. *Self-assembled monolayer on ITO*

ITO glass ($\leqslant 12\,\Omega/\square$, $20 \times 20\,\text{mm}^2$ slides) was purchased from Shinan SNP Co. Each slide was cleaned with deionized water, followed by a sequence of 60 min ultrasonic bath in acetone and methanol. The cleaned substrates were immersed into grafting solutions of BA, PBA, NBA and synthesized NBCA, respectively. Solute concentrations were 1 mM in THF. After a grafting time of 15 h, the samples were rinsed in pure THF to remove excess molecules from the grafted surface. These substrates were used for contact angle measurement and transferred to a thermal evaporator for device fabrication.

2.4. *Device fabrication and characterization*

The hole-only device and bilayer OLED were fabricated by high vacuum (10^{-6} Torr) thermal evaporation onto ITO substrates containing each grafting molecule. For the hole-only device, a 1500-Å-thick hole transport layer of TPD and a 500-Å-thick aluminum cathode were deposited sequentially. For the bilayer OLED, a 600-Å-thick TPD was deposited on ITO anode, followed by a 600-Å-thick light-emitting layer of Alq$_3$ and a 600-Å-thick aluminum cathode. Current density–voltage–radiance characteristics were measured using sourcemeter (KEITHLEY-2400, 237) and a Newport 1830-C photodiode under N_2 atmosphere at room temperature. Finally, ITO substrate with a 50-Å-thick TPD was fabricated and was investigated with atomic force microscopy (AFM, Autoprobe CP, PSI, USA) in non-contact mode at room temperature. AFM images were obtained at a scan rate of 1.0 Hz with a silicon cantilever (Ultralever 06B, PSI, USA). Then the surface energies of each sample were calculated using Owen–Wendt geometric method (Fig. 2).

3. Results and discussion

The head group, carboxylic acid, of the four self-assembly molecules such as BA, PBA, NBA, and NBCA has a high affinity for the surface OH group of ITO, which facilitates chemisorption of the self-assembly molecules onto the ITO substrate. The difference of surface properties that resulted from the body group and NO_2 terminal group showed the variation of wettability. The results of contact angle measurements of the four self-assembly molecules indicated that the introduction of phenyl ring in the body group reduces the wettability and surface energy, as shown in Table 1. The contact angle of bare ITO is 31°, which can be attributed to the OH group remaining on the surface [12]. It can be found that the difference in surface energy for the self-assembly molecules via Owen–Wendt geometric method [13] is mainly due to the polar components. Relatively low polar component of NBCA-assembled ITO improved the compatibility between ITO electrode and TPD layer. It was evident from the results of morphology analysis using AFM that the contact area of TPD layer onto the ITO surface modified with the self-assembly molecules was larger than that of

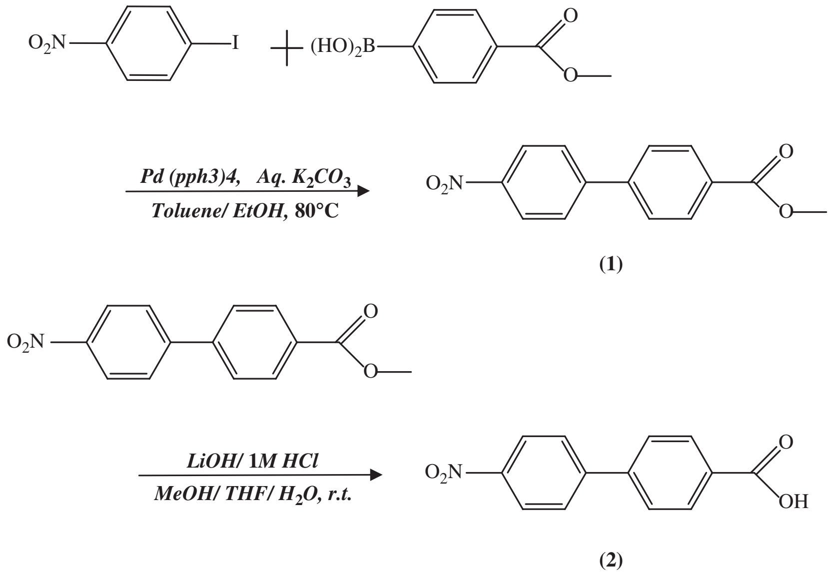

Fig. 1. Synthetic routes of NBCA.