

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

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Abstract

We have synthesized 4'-nitrobiphenyl-4-carboxylic acid (NBCA) and fabricated the hole-only device consisting of ITO/NBCA SAM/TPD (1500 Å)/Al (500 Å) and the organic light emitting diodes (OLEDs) consisting of ITO/NBCA SAM/TPD (600 Å)/Alq₃ (600 Å)/Al (600 Å). The prepared hole-only device with NBCA exhibited lower driving voltage than the device with 4-nitrobenzoic acid (NBA). OLEDs using NBCA also show high external quantum efficiency.

1. Introduction

Indium tin oxide (ITO) has been commonly used as the anode of organic light emitting diodes (OLEDs) because of the attractive combination of high optical transparency and good electrical conductivity. However, these ITO films often have a rough surface, relatively low work function compared to the adjacent organic layer and their surface energies are not well matched to nonpolar organic films [1-2]. Many research groups have reported a variety of method to facilitate hole injection into the organic layer and to improve interface property by special operation 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, improve adhesion characteristic at the anode-organic film interface and inhibit diffusion of material to anode. The study on the 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

combination of self assembling technique and organic devices makes it possible to establish the easy and better methodology. Zuppiroli et al. has 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-nitrobenzoic acid (NBA) is the most proper candidate material for hole injection among para-substituted benzoic acid derivatives grafted on ITO [10]. It is well known that carboxylic acids are promising attachment group onto 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 ITO on the performance of OLED were investigated.

2. Experimental

Synthesis of NBCA was carried out following the synthetic routes. 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 K₂CO₃ (0.55 g, 5.6 mmol) in toluene/EtOH (9:1 v/v, 200 ml) was thoroughly degassed using a stream of dry N₂, 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 MgSO₄ and evaporated. Recrystallization from ethylacetate solvent gave methyl 4'-nitro[1,1'-biphenyl]-4-carboxylate as a white solid (1.2 g, 84%). ¹H-NMR (400 MHz, D₆-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) Carboxylate (400 mg, 1.5 mmol) and lithium hydroxide (222 mg,

9.6 mmol) solution in tetrahydrofuran (70 ml), methanol (20 ml), and water (20 ml) was 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). $^1\text{H-NMR}$ (400 MHz, $\text{D}_6\text{-DMSO}$); 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)

ITO glass ($\leq 12 \Omega/\square$, 20×20 mm slides) was purchased from Shinan SNP Co. Each slide was cleaned a de-ionized water, followed by a sequence of 60 min ultrasonic baths 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 tetrahydrofuran (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 thermal evaporator for device fabrication. The hole-only devices and bilayer OLEDs were fabricated by high-vacuum (10^{-6} Torr) thermal evaporation onto ITO substrates containing each grafting molecules. For the hole-only devices, a 1500 Å thick hole transport layer of N-N'-diphenyl-N,N'-bis{3-methylphenyl}-{1,1'-biphenyl}-4,4'-diamine (TPD) and a 500 Å thick aluminum cathode were deposited sequentially. For the bilayer OLEDs, a 600 Å thick TPD was deposited on ITO anodes, followed by a 600 Å thick light-emitting layer of tris-(8-hydroxyquinoline) aluminum (Alq_3) and a 600 Å thick aluminum cathode. Fig 1. shows the molecular design of organic materials used in this work. Current density-voltage-radiance characteristics were measured using sourcemeters (KEITHLEY-2400, 237) and a Newport 1830-C photodiode under N_2 atmosphere at room temperature. Finally, for the surface topography, ITO substrates with a 50 Å thick TPD were fabricated and were investigated with atomic force microscopy (AFM, Autoprobe CP, PSI, USA) in non-contact mode at room temperature under air conditioning. AFM images were obtained at a scan rate of 1.0 Hz with a silicon cantilever (Ultralever 06B, PSI, USA). And the surface energies of each sample were calculated using Owen-Wendt geometric method.

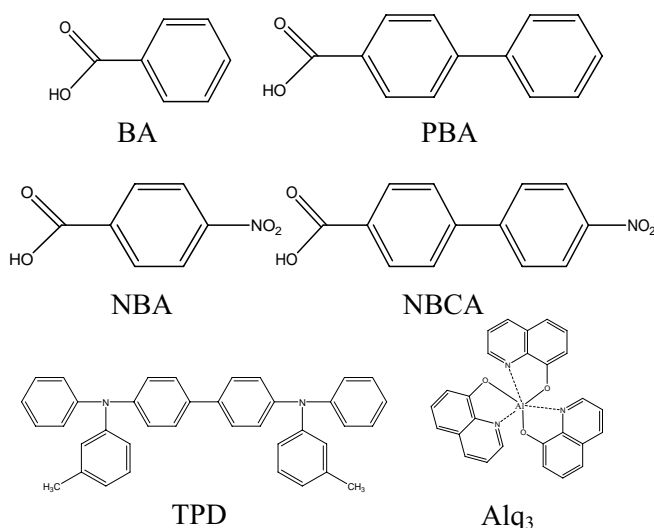


Fig. 1. Molecular design of self assembled molecules and organic materials used in this work

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 molecules onto the ITO substrate. The difference of surface properties resulted from body group and NO_2 terminal group shows the variation of wettability. The results of contact angle measurements of the four self-assembly molecules indicate that the introduction of phenyl ring in body group reduces the wettability and surface energy, see Table 1. The contact angle of bare ITO is 31° , which can be attributed to the OH group remaining on surface [12]. It can be argued that the analysis of surface energy via Owen-Wendt geometric method [13] shows the difference of polar components. Relatively low polar component of NBCA-assembled ITO increased the compatibility of TPD layer.

TABLE 1. Calculated surface energy of ITO modified with NBA and NBCA with Owens-Wendt geometric means

Anode	Water ($\pm 1^\circ$)	Formamide ($\pm 1^\circ$)	γ_s^d (mJ/m^2)	γ_s^p (mJ/m^2)	γ (mJ/m^2)
NBA	41	28	21.1	35.3	56.4
NBCA	45	30	22.7	32.3	53.9

The results of morphology analysis by AFM microscopy show that TPD layer growth on ITO surface modified with self-assembly molecules makes larger contact area than bare ITO. Fig. 1a shows the topographical images of a $1 \mu\text{m} \times 1 \mu\text{m}$ area of bare ITO. Fig. 2 b-d show AFM images of a $3 \mu\text{m} \times 3 \mu\text{m}$ area of a 50 \AA thick TPD films on bare ITO, NBA-assembled ITO, and NBCA-assembled ITO, respectively. TPD films were deposited with the same evaporation rate 1.5 \AA/s and directly transferred to AFM imaging systems. NBCA-assembled ITO has a well-dispersed TPD layer compared to the NBA-assembled ITO, which is caused to the high hydrophobic property and compatibility for TPD molecules.

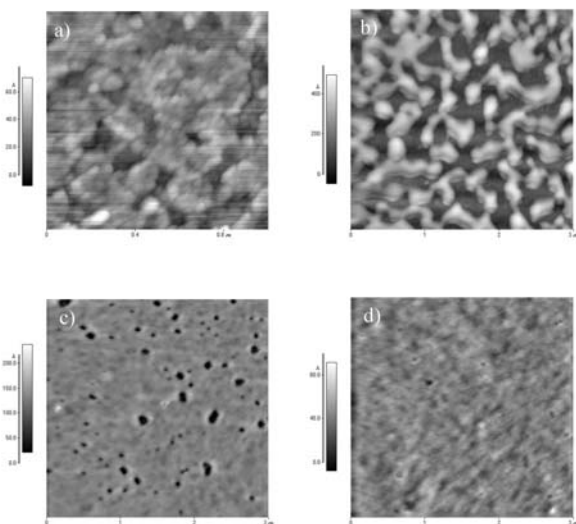


Fig. 2. AFM images for bare ITO (a) and a 50 \AA thick TPD films deposited on Bare ITO (b), NBA-assembled ITO (c) and NBCA-assembled ITO (d)

Prior to apply SAMs-modified ITO for electronic devices, it was investigated the transparency of each ITO in the range from 200 nm to 800 nm by UV/Vis spectrometer, see Fig. 3. In the visible region, ITO modified with various SAMs has the transparency of over 80% , and there is no variation compared to bare ITO. Thus, in the case of developing into electronic devices, SAMs on bare ITO do not affect the optical character of devices.

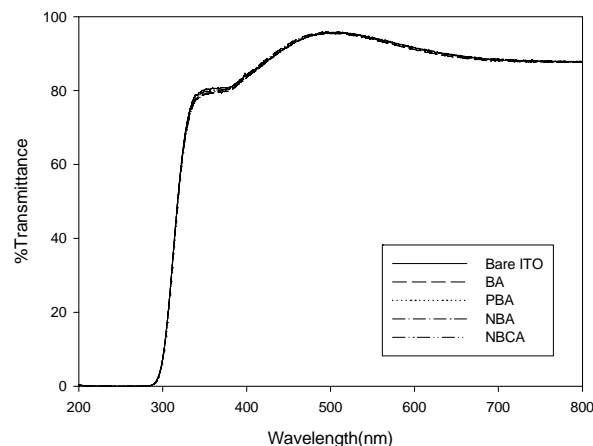


Fig. 3. UV/Vis spectra results of Bare ITO and ITO modified with various SAMs.

In order to explore the effects of SAMs modified ITO on the optoelectronic property of organic devices, the hole-only devices (ITO modified with SAMs/TPD (1500 \AA)/Al (500 \AA)) [14] and the typical OLEDs (ITO modified with SAMs/TPD (600 \AA)/Alq₃ (600 \AA)/Al (600 \AA)) were fabricated, where TPD is a hole-transporting organic material and Alq₃ is an emitting organic material. The effects of the SAMs modified ITO on the hole injection efficiency at the modified ITO anode/TPD interface were investigated. Due to the high work function of aluminum cathode, the electron injection is inhibited and the prepared device is considered to be a hole dominated device. Fig. 4 shows the current density-voltage characteristics of the hole-only devices. The driving voltages for the NBCA- and NBA-assembled devices are significantly improved compared to the PBA- and BA-assembled devices, which is mainly due to the decrease of energy barrier for hole injection by the high dipole moment of NO₂ group. Especially, NBCA-assembled device has lower turn-on voltage than NBA-assembled device, which may be caused to the good adhesion property for the interface between ITO anode and TPD layer owing to the high hydrophobic property. It can be concluded that the hole-only devices consisting of NBCA-assembled ITO/TPD/Al exhibited low driving voltage of 12 V , which implies that the prepared device has many active-sites for charge transfer owing to the well-dispersed TPD layer onto the NBCA-assembled ITO substrate.

Fig. 5 shows the external quantum efficiency-voltage characteristics of bilayer OLEDs. It can be noted that OLED using NBCA-assembled ITO shows maximum external quantum efficiency (0.28%) than

the other devices. This is attributed to the improvement of interface between ITO anode and TPD layer.

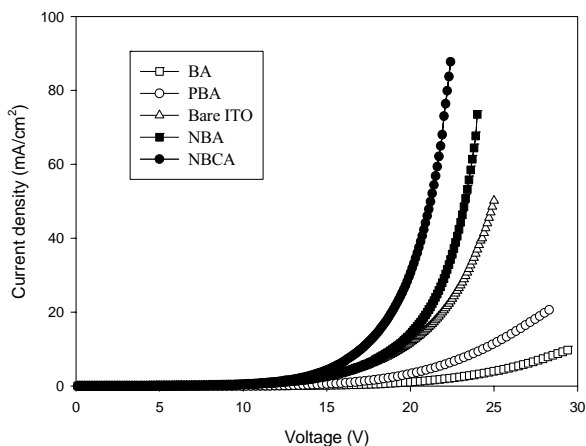


Fig. 4. Current density-voltage characteristics of the hole-only devices consisting of SAMs modified ITO/TPD (1500 Å)/Al (500 Å)

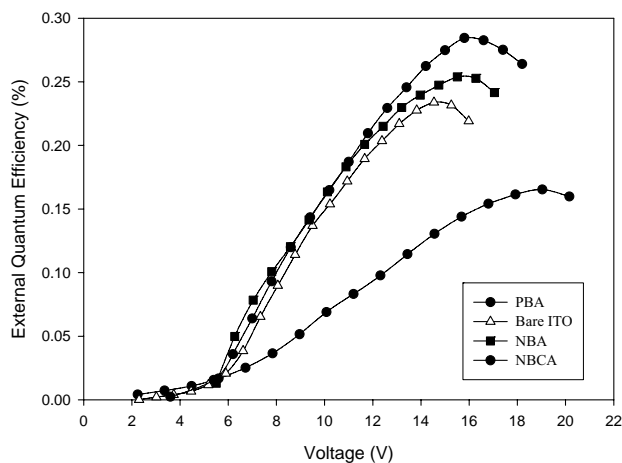


Fig. 5. External quantum efficiency-voltage characteristics of OLEDs consisting of SAMs modified ITO/TPD (600 Å)/Alq3 (600 Å)/Al (600 Å)

4. Conclusion

Surface modification of ITO with functional SAMs has already known as a good candidate to improve the performances of the organic devices. Various self-assembly molecules have been investigated and applied for the surface modification of ITO. Dipolar benzoic acid derivatives increase the work function of

ITO and facilitate hole injection into adjacent organic layer. In the present work, we have synthesized NBCA compound with nitrobiphenyl moiety where NO₂ functional group induces large dipole moment and highly-positive shift of ITO work function. Biphenyl moiety of NBCA results in the enhancement of hydrophobic characteristic and good adhesion with nonpolar organic material. Furthermore, OLEDs consisting of the NBCA-assembled ITO show relatively low driving voltage and high external quantum efficiency.

5. Acknowledgments

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6. References

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