SHORT COMMUNICATION

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Organic electroluminescent device based on electropolymerized polybithiophene as the hole-transport layer

Abstract An ultrathin film of polybithiophene (PBTh), used in organic electroluminescent (EL) devices, was generated by an electrochemical method with a conducting indium tin oxide (ITO) glass as the working electrode. The light-emitting layer could be deposited directly onto the PBTh by using spin coating for fabrication of the organic EL devices. It was found that the film of PBTh as the hole-transport layer for the EL device could effectively raise the EL intensity and efficiency. The EL intensity of the ITO/PBTh/emitting layer/Al device is about 100 times as strong as that of the ITO/emitting layer/Al device at the same current density of 50 mA/cm^2.

Key words Electropolymerization · Polybithiophene · Hole-transport layer · Electroluminescence

Introduction

Since the two-layer organic electroluminescent (EL) device was developed using low-molecular-weight organic materials in the mid-1980s [1], it has been recognized as one of the most promising next-generation flat-panel display systems [2]. In order to enhance the recombination efficiency of holes and electrons injected from electrodes, different structures for the EL devices have been proposed [3, 4, 5, 6, 7, 8]. The film-forming

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technique is very important for fabricating the organic EL devices, and the vacuum evaporation method is widely used for film deposition, especially for the multilayer devices. However, evaporation requires costly ultra-high vacuum systems and more complex techniques to create uniform thin films [9]. On the other hand, spin-coating and self-assembly methods are also used for depositing the organic films [10, 11, 12]. So far, little has been reported on using electropolymerized films in the organic low-molecular-weight or polymeric EL devices as carrier-transport layers, although electrochemical methods have been commonly used to generate various electroactive polymer films. Compared with other methods, electrochemical deposition is a relatively simple direct film deposition process and requires no highly complex system, and the thickness of film can be controlled with relative ease. Another consideration is that, in fabrication of multilayer devices, the second organic layer, as the emitting layer or as the electron-transport layer on the first organic layer, usually has to be deposited by a vacuum evaporation method rather than via spin coating. This is because the evaporated or spin-coated first organic layer is easily damaged by the solvents during spin-coating of the second layer.

However, many electropolymerized films demonstrate their advantages such as thermal stability and chemical resistance in common solutions. Also, by controlling the experimental conditions, films can be deposited electrochemically according to specific requirements. The electrochemical polymerization of monomers such as thiophene, pyrrole, aniline and their derivatives leads to the direct deposition of redox-active conductive polymer films on the anode, and these conducting or semiconducting polymers [polythiophene (PTh), polypyrrole (PPy) and polyaniline (PAn)] can be easily doped electrochemically and have been studied widely owing to their many promising applications [13, 14, 15, 16]. An oligothiophene film deposited by the vacuum evaporation method, and enhancing hole injection to the emitting layer in the EL device, was reported as a p-type semiconductor with a band gap

of 2.3 eV and has a considerably large hole mobility (0.1 cm^2/V s) in a thin-film transistor [17]. Therefore it is interesting to investigate the possibility of using thiophene-based polymers as a hole-transport layer in EL devices. In previous work, bithiophene was electropolymerized to form thin films at very low potentials in aqueous solutions mixed with acetonitrile (0.6 V vs. Ag/AgCl) [18] compared with pure acetonitrile [16, 19]. Polybithiophene (PBTh) is also insoluble in common solvents, and highly uniform films with a band gap of 2.1 eV, calculated according to its absorption spectrum [18], can be deposited on indium tin oxide (ITO). In this work, we made use of the electropolymerized PBTh film as a hole-transport used in an organic EL device. The effects of the PBTh hole-transport layer on the light-emitting behavior of the device are discussed.

Experimental

Bithiophene as a monomer was used to electropolymerize the PBTh hole-transport layer in the EL device, and polyoctylthiophene (P3OT) and 1,1-bis(p-diethylaminophenyl)-4,4-diphenyl-1,3-butadiene (DEAB) were solution blended and spin coated to form the light-emitting layer. An EG & G PAR model 273 potentiostat/galvanostat was employed for electrochemical polymerization in a mixed solution system. Electrochemical deposition was carried out using a three-electrode system. Ag/AgCl and platinum (Pt) foil were used as the reference electrode and counter electrode, respectively, and an ITO-coated glass as the working electrode. Before the electrochemical deposition, the Pt electrode was cleaned in boiling 50% aqueous H$_2$SO$_4$ solution and rinsed in ultrapure water (Millipore SUPERQ). The ITO glass was cleaned using deionized water, ethanol, acetone, and a mixture of isopropyl alcohol and deionized water (volume ratio 1:1). The deposition of PBTh was carried out on the ITO electrode in a 0.02 M bithiophene and 1.0 M HClO$_4$ water/acetonitrile mixed solution of volume ratio 1:1. The solutions were purged prior to the experiments by argon bubbling.

The ultrathin film of PBTh was electropolymerized using the chronopotential method. The amount of the polymer deposited on the working electrode was controlled by the total amount of charge consumed by the reaction, h (μm) $= 3.33Q$ (Q in C/cm^2) [20]. After each polymerization, the polymer was thoroughly dedoped electrochemically at −0.1 V. The polymer films were then washed with acetonitrile and deionized water. Then they were dried under vacuum at 100 °C overnight. The mixed solution of P3OT and DEAB with a weight ratio of 1:2 was used for fabricating the light-emitting layer (LEL) using the spin-coating method. The top aluminum electrode was prepared using a vacuum vapor evaporator at a vacuum of 10^{-5} Torr. The emitting area was 3 × 4 mm^2. A single-layer light-emitting device without PBTh was also fabricated by the spin-coated method, and compared with the double-layer EL device. All measurements on the devices were carried out at room temperature in air.

Results and discussion

The PBTh film was deposited on the ITO as the working electrode using a chronopotentiometric experiment. Figure 1 shows a chronopotentiogram of bithiophene for film deposition in a solution of water/acetonitrile volume ratio of 1:1 at constant anodic current densities
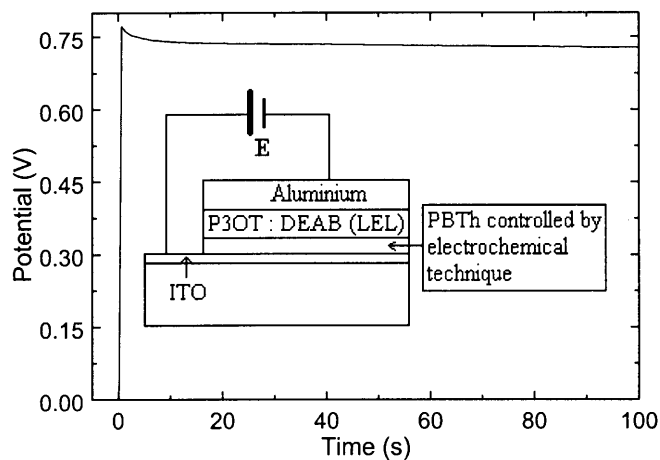

Fig. 1 Chronopotentiogram of bithiophene for film deposition in solution at a water/acetonitrile volume ratio of 1:1 at constant anodic current densities of 0.1 mA/cm^2. The *inset* shows the structure of the two-layer organic EL device

of 0.1 mA/cm^2. The inset displays the structure of the two-layer organic EL device. The thickness of the hole-transport layer is controlled with a deposition time of 20 s. Figure 2 depicts the atomic force microscope (AFM) image of PBTh film obtained at a scan rate of 0.5 Hz. It can be seen from the AFM image that the surface of the film is quite uniform.

Figure 3 shows the current density and EL intensity changing with the applied voltage for the devices. We can see that the current density through the device without the PBTh layer is much higher than that through the device with the PBTh layer, especially at the lower applied voltage range. This results from the hole-transport layer of PBTh, which also plays the role of blocking the electrons in the positive electrode. From Fig. 3, the EL intensity of the ITO/PBTh/P3OT:DEAB/
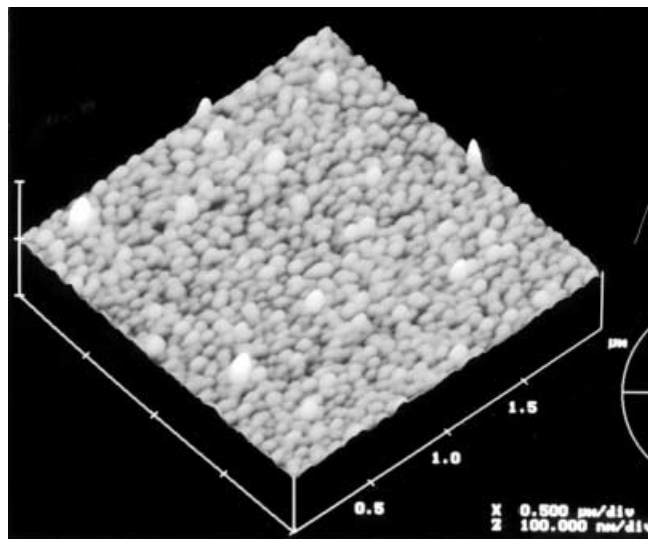

Fig. 2 Atomic force microscope (AFM) image (2 μm × 2 μm) of PBTh film obtained at a scan rate of 0.5 Hz
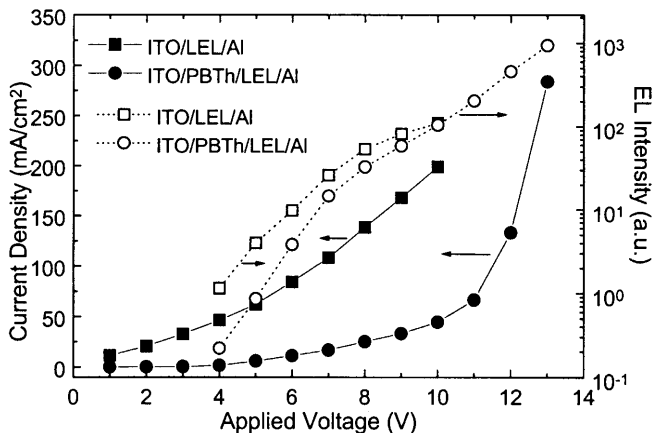
Fig. 3 Luminance-voltage (*solid line*) and current-voltage (*broken line*) characteristics of two typical devices: ITO/P3OT:DEAB as a light-emitting layer (LEL)/Al device and an ITO/PBTh/P3OT: DEAB(LEL)/Al device

Al device is lower than that of the ITO/P3OT:DEAB/Al device at the same lower voltage, and increases fast at the higher voltage. We can well understand this by using the relationship between EL intensity and carrier concentration. The radiative recombination luminance B can be given by:

$$B \propto \beta n_e n_h \tag{1}$$

where β represents the electron-hole radiative recombination probability, and n_e and n_h are the electron concentration and hole concentration, respectively. At low voltage, the EL intensity of the double-layer device is weaker owing to the lower current density, i.e., lower carrier concentration; at higher voltage, the EL intensity is enhanced because many carriers go through the device. According to Eq. 1, the current directly affects the EL intensity for the device. In terms of Fig. 3, we can easily obtain the relationship between the current density and the EL intensity, and normalized EL efficiencies of the two kinds of devices.

Figure 4 shows the EL intensity changing with the current density for these two kinds of devices. It can be seen that the EL intensity for the device with the PBTh layer is about 100 times as high as that without the PBTh at the same current denisty of 50 mA/cm². This means the former has higher EL efficiency, which is indicated more clearly from Fig. 5, where is displayed the relationship between EL efficiency and applied voltage. It can be seen that for the ITO/PBTh/P3OT:DEAB/Al device the efficiency is much higher than that for the ITO/P3OT:DEAB/Al device. From the EL spectrum of the double-layer device shown in the inset of Fig. 5, the EL spectrum for the device with PBTh changes little compared with that without PBTh (previous work [21]). This means that the hole-transport layer of PBTh can enhance the electron-hole recombination efficiency to generate more excitons in the light-emitting layer. This is the reason why the EL efficiency for the double-layer
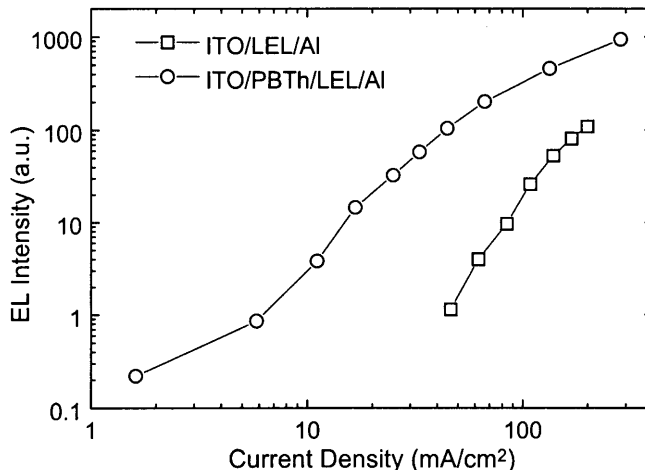

Fig. 4 Relationship between the current density and EL intensity for the two kinds of EL device
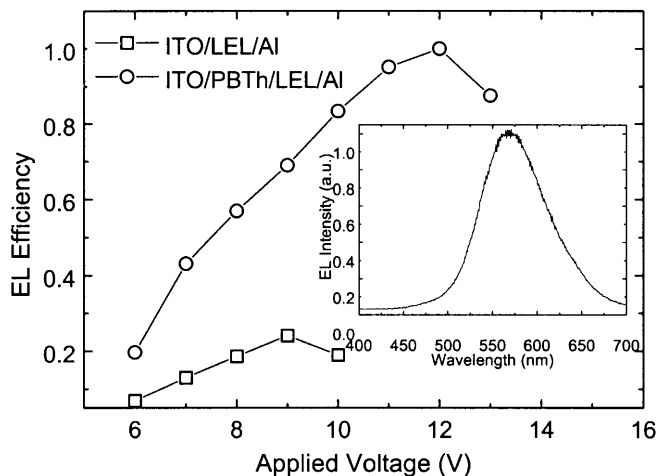

Fig. 5 EL efficiency changing with the applied voltage for the two kinds of EL device

device is much higher than that for the single-layer device.

Conclusion

Based on the above discussion, the following conclusions can be drawn. The uniform film of PBTh can be electropolymerized directly on the ITO conducting glass, and these electropolymerized PBTh films were successfully used as a carrier-transport layer in the fabrication of the organic EL device to enhance the EL intensity and EL efficiency. The EL intensity of the ITO/PBTh/light-emitting layer/Al device is about 100 times as high as that of the ITO/light-emitting layer/Al device at the same current density of 50 mA/cm².

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