Organic light emitting diodes based on multi-wall carbon nanotubes (MWNTs) modified electrode

MUJIE YANG*, QINGHUI ZHANG
Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China
E-mail: yangmj@cmsce.zju.edu.cn

Since their discovery in 1991, carbon nanotubes have attracted a lot of attention because of remarkable nanostructures combining high surface area, high electrical conductivity, good chemical stability and significant mechanical strength [1]. The multi-wall carbon nanotubes (MWNTs) and polymer composite of MWNTs/expoxy resin with mechanical method were first reported by Ajayan *et al.* [2]. Then, Romero *et al.* reported a rectifying heterojunction formed by MWNTs and a derivative of the poly(phenylene vinylene) (PPV) [3]. Ago *et al.* found that the MWNT layer acts as a hole-collecting electrode for the composite of MWNTs and PPV, and the light-emitting diodes based on MWNTs modified electrode have about twice the external quantum efficiency compared with the standard indiun-tin-oxide (ITO)-based electrode [4, 5], which was explained in terms of the high surface area of the MWNT film and the formation of a complex interpenetrating network (IPN).

In this work, we have fabricated light-emitting diodes with functional MWNTs modified electrode, where MWNTs were dispersed in a conducting polymer as a hole-conducting buffer.

An electroluminescent conjugated polymer, poly[(2-methoxy-5-(2′-ethyl-hexyloxy)phenylene vinylene)] (MEH-PPV), was synthesized as described elsewhere [6]. MWNTs with diameter 10–30 nm and length 0.5–500 nm were obtained from Shenzhen Nanotech Port Co. Ltd., China. MWNTs functioned with carboxylic acid groups were prepared by refluxing with HNO_3:H_2SO_4 (1:3 by volume) for 30 min [7, 8]. The MWNT suspension was prepared by dispersing 5 mg functional MWNTs in 10^{-6} m^3 deionized water with ultrasonic agitation. Then, it was allowed to stand for several days, and thereafter the majority of the unaggregated MWNTs suspension was piped off. The aqueous solutions polystyrenesulfonate (PSSNa)(2 wt%) and poly(vinyl alcohol) (PVA) (1 wt%) were prepared after sonication. Then, these two solutions were mixed 1:1 by volume. To this mixture was added the formerly prepared MWNTs aqueous solution through ultrasonic dispersion, which is 1 and 10 wt% relative to PSSNa content. Finally, the PSSNa:PVA mixture and MEH-PPV in chloroform (2 wt%) were spun at 2500 rpm in ambient conditions. This resulted in a film thickness of about 100 and 50 nm, respectively. A cathode metal, Al, was evaporated at pressure 2.0 × 10^{-3} Pa. The LEDs structures in this study are summarized as follows:

Device 1: ITO/MEH-PPV/Al
Device 2: ITO/PSSNa:PVA(pure)/MEH-PPV/Al
Device 3: ITO/PSSNa:PVA(MWNTs 1 wt%)/MEH-PPV/Al
Device 4: ITO/PSSNa:PVA(MWNTs 10 wt%)/MEH-PPV/Al

The light-emitting area is 5 mm × 5 mm. The current–voltage characteristics were measured with Keithley 4200 semiconductor characterization system.

The *I*–*V* characteristics of the devices are depicted in Fig. 1. They all show typical rectifying diode behavior. The devices 1, 2, 3 and 4 were light emitting at an operating voltages of 3.8, 5.5, 4.9 and 3.7 V, respectively. They were fully bright at voltages of 4.8 , 15.0, 10.0 and 4.0 V, respectively. This reveals that the threshold voltage reduces with the improvement of MWNTs concentration in PSSNa:PVA mixture, and the device turned bright more easily. In Fig. 1a–d, at the same voltage, devices 1 and 2 have much smaller current density

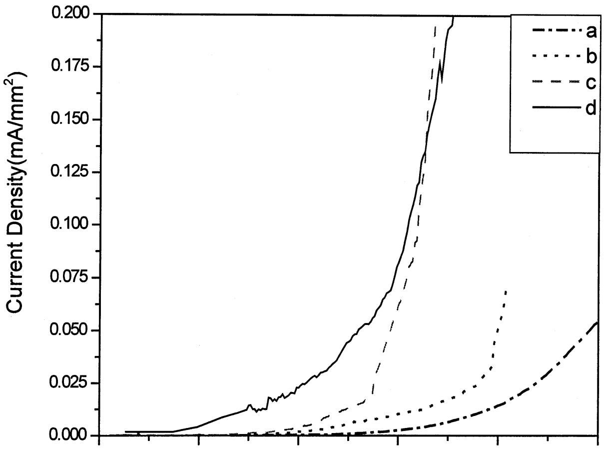

Figure 1 Current–voltage characteristics of the light-emitting diodes: (a) ITO/MEH-PPV/AL, (b) ITO/PSSNa:PVA(pure)/MEH-PPV/AL, (c) ITO/PSSNa:PVA(MWNTs 1 wt%)/MEH-PPV/AL, and (d) ITO/PSSNa:PVA (MWNTs 10 wt%)/MEH-PPV/AL.

---

*Author to whom all correspondence should be addressed.

0022–2461

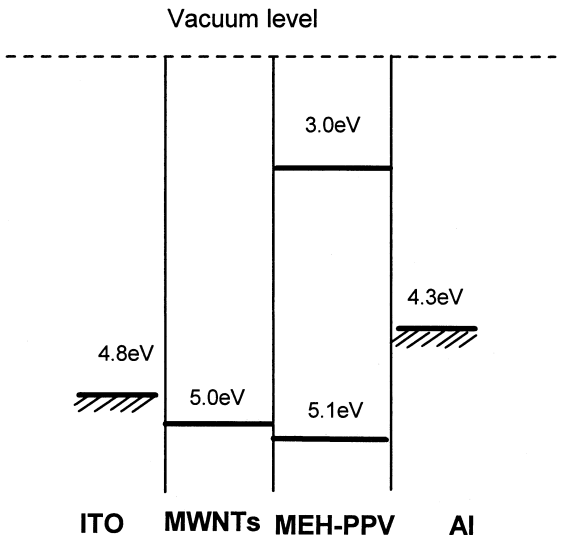

Figure 2 Schematic band diagrams of the ITO/MWNTs/MEH-PPV/Al device.

than devices 3 and 4, which reveals that there are high output powers for devices 3 and 4 at the same voltage.

Fig. 2 show band diagrams of the ITO/MWNTs/MEH-PPV/Al device. It reveals MWNTs have a higher workfunction (5.0 eV) than ITO (4.8 eV). This means that the hole could be transferred to from ITO to MWNTs easily, and there is a smaller band-offset between the MWNTs and MEH-PPV. However, one could argue the observed reduction in the applied electric field is due to the intrinsic interaction between the MEH-PPV and MWNTs. A better understanding of the interfacial interaction between π-conjugated polymer and carbon nanotubes is expected to follow from further investigations in progress.

Acknowledgment

This project was supported by Nation Natural Science Foundation of China (No. 29974025).

References

1. S. IIJIMA, *Nature* **354** (1991) 56.
2. P. M. AJAYAN, O. STEPHAN, C. COLLIEX and D. TRAUTH, *Science* **265** (1994) 1212.
3. D. B. ROMERO, M. CARRARD, W. DE HEER and L. ZUPPIROLI, *Adv. Mater.* **8** (1996) 899.
4. H. AGO, K. PETRITSCG, MILO S. P. SHAFFER, A. H. WINDLE and R. H. FRIEND, *ibid.* **11** (1999) 1281.
5. H. AGO, K. PETRITSCG, MILO S. P. SHAFFER, D. S. GINGER, A. H. WINDLE and R. H. FRIEND, *Phys. Rev.* **61** (2000) 2286.
6. M. K. RAM, N. SARKAR, P. BERTIBCELLO, A. SARKAR, R. NARIZZANO and C. NICOLINI, *Synth. Met.* **122** (2001) 369.
7. J. CHEN, M. A. HAMON, H. HU, Y. CHEN, A. M. RAO, P. C. EKLUND and R. C. HADDON, *Science* **282** (1998) 95.
8. MILO S. P. SHAFFER, X. FAN and A. H. WINDLE, *Carbon* **36** (1998) 1603.

Received 8 October 2003
and accepted 10 February 2004