Indium Tin Oxide Nanoparticles as Anode for Light-Emitting Diodes

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ABSTRACT: Thin films of indium tin oxide (ITO) nanoparticles have been investigated as anode materials for polymer light-emitting diodes. A luminance efficiency (0.13 cd/A), higher than that (0.09 cd/A) obtained in a control devices fabricated on conventional commercial ITO anodes were found. The thin films were made by spin coating of a suspension followed by annealing. The ITO nanoparticle films have a stable sheet resistance of 200 Ω/sq, and an optical transmittance greater than 86% over the range of 400–1000 nm. Their textural property is also reported. These results demonstrate that ITO nanoparticle can form a high efficient reproducible anode material. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3125–3129, 2006

Key words: indium tin oxide; nanoparticles; light-emitting diode

INTRODUCTION

Scientific and technological progress has been achieved in the area of organic/polymeric light-emitting diodes (LEDs), driven by potential applications in a large variety of display technologies. The performance of an LED is affected not only by the properties of its constituent organic layers but also by the electrodes and their interfaces with the charge-transport layers. Several materials have been studied for suitability as an LED anode, including doped zinc oxide,[1,2] titanium nitride,[3] niobium diselenide,[4] Zr-doped ZnO,[5] and other transparent conducting oxides.[6,7] The most extensively used is indium tin oxide (ITO), which has high optical transparency, high conductivity, and provides high work function substrate for hole injection into a variety of organic materials. ITO has some disadvantages, including a considerable energy barrier for hole injection and the possibility of diffusion of indium into the organic layer during device operation.[8,9] ITO films also find wide applications in thin film solar cells, liquid crystal displays, and electrochromic display.[10–12] They can be prepared in a variety of ways, such as chemical vapor deposition,[13] pulsed laser deposition,[14] sputtering,[15,16] spray pyrolysis,[17] and sol–gel techniques.[18,19]

Recently, the formation of ITO nanoparticle thin films from different precursor materials has been reported.[20–23] Nanoparticles of ITO can provide transparent conducting films on plastic and glass substrate, using spray, dip, and spin coating processes[24,25] and have used as antiglare coatings.[19,20]

In this contribution, we report the first use of films produced from ITO nanoparticles as anode materials for PLED devices. The properties of these films in LED devices were compared with those of control LEDs fabricated using conventional ITO/glass substrates commercially available.

EXPERIMENTAL

Materials

ITO nanoparticle suspensions (powder 30% + resin 10%, particle size: 53.3 nm) and the emitting chromophore, poly[(9,9-dioctylfluorenyl-2,7-divinylenefluorenylene)-*alt-co*-(9,10-anthracene)] were obtained from American Dye Source, Inc. (Baie D'Urfe, Quebec). Acetone, ethanol, and chloroform (Aldrich) were used without further purification. An ancillary hole injection layer of poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS; Bayer Co.) was used.

Film fabrication

ITO nanoparticle suspensions in ethanol at a weight ratio of 1:1 were used. The glass substrates were ultrasonically cleaned in water for 10 min and boiled in acetone for 10 min. The ITO nanoparticle films were prepared by spin coating the suspension on the glass

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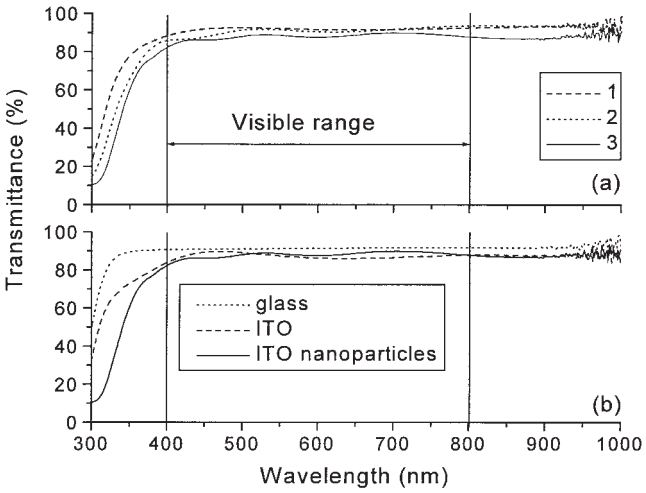

Figure 1 (a) Optical transmittance of annealed ITO nanoparticle films (1, 2, and 3 indicate number of coating). (b) Optical transmittance of glass, a commercial ITO/glass substrate, and a 560-nm-thick ITO nanoparticle film on glass.

with a final speed of 3000 rpm for 40 s. The coated substrate was then annealed at 600°C for 3 h in vacuum and slowly cooled to 30°C. Thicker coatings were prepared by repeating the procedure. Patterned electrodes were obtained by appropriate etching by immersion in $HCl:HNO_3:H_2O$ (20:5:75) solution at 50°C for 50 s. Upon completing the etching process, the substrates were immediately rinsed in a 10% aqueous solution of Na_2CO_3 and washed several times with water.

TABLE I
Thickness and Sheet Resistance Data for ITO Nanoparticle Films Annealed at 600°C for 3 h

No. of coating	Thickness (nm)	Sheet Resistance (Ω/sq)
1	200	2000
2	380	400
3	560	180

Film characterization

The film thickness was measured by a Dektak 3030 mechanical stylus profilometer. The optical spectrum was measured with a Hitachi U-3010 UV–vis spectrophotometer. The resistivities of the films were measured by the two-point probe method, using a True

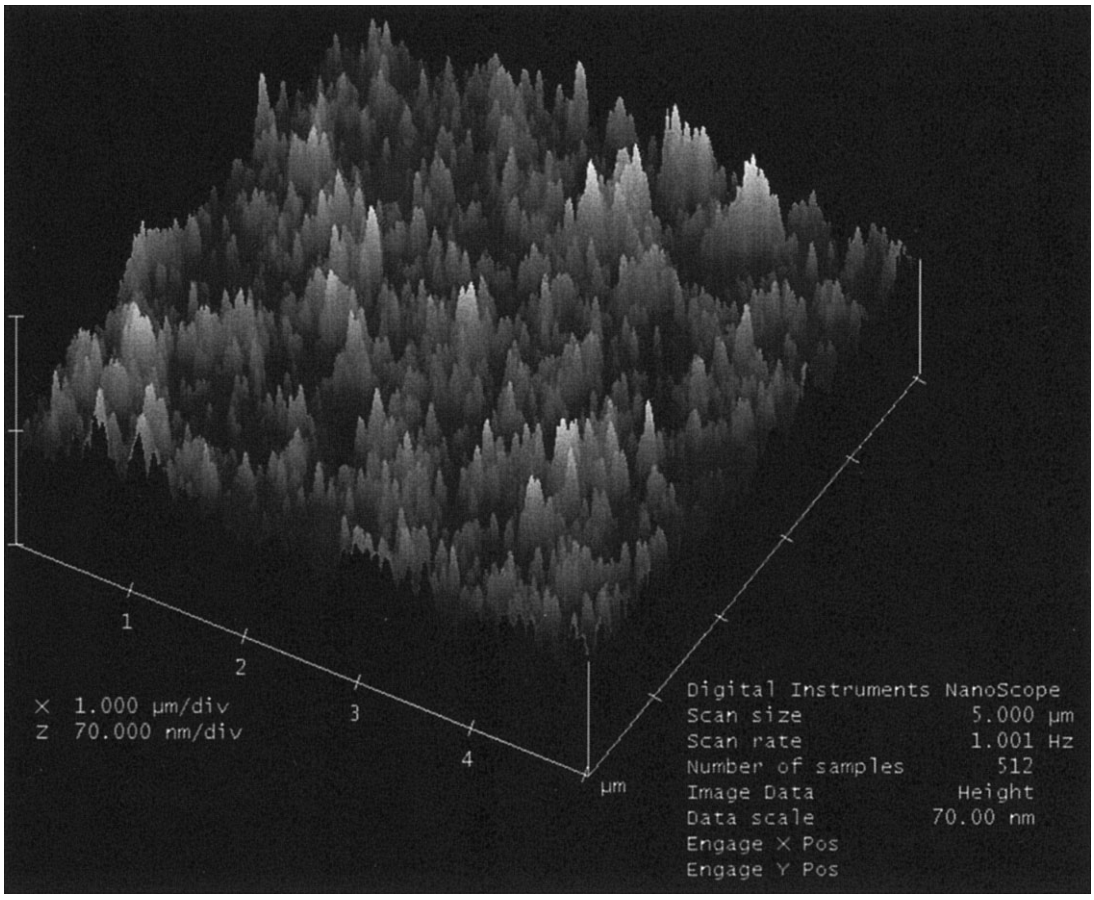

Figure 2 AFM image of a 560-nm-thick ITO nanoparticle film on glass substrate.

RMS Digital Multimeter. Morphological features were studied using an AFM in tapping mode (Dimension 3100, Digital Instruments Inc.). Root mean square (rms) roughness was calculated with AFM software (Nanoscope III 5.12r3, Digital Instruments Inc.).

LED fabrication

PLEDs with the configuration ITO/PEDOT/polymer/Ca/Al were fabricated on the ITO nanoparticle-coated glass slides and on control ITO films (Standish LCD, 160 Ω/sq). A hole injection layer of PEDOT:PSS was spin-coated on top of the conventional ITO or ITO nanoparticle films and dried at 100°C for 1 h under vacuum. A 100-nm layer of chromophore was spin-coated from chloroform solution onto the PEDOT:PSS layer under nitrogen. Finally, a 400-nm-thick calcium electron-injecting cathode was deposited on the polymer film by vacuum evaporation at a pressure $<2 \times 10^{-6}$ Torr, resulting in an active area of 6 mm^2, followed by a protective coating of aluminum. The devices were characterized using a system described previously.[26]

RESULTS AND DISCUSSION

Optical properties

For most applications (such as LED, electrochromic displays, etc.), high transmission in the visible range is important. The transmittance of ITO nanoparticle films on glass of different thicknesses is shown in Figure 1(a). The transmission at 600 nm measured in air is about 91.6% for single, 90.5% for double, and 87.6% for triple ITO nanoparticle layers. The glass itself has a transmittance of about 92%. Annealed ITO nanoparticle films and commercial ITO coatings show similar optical transmission [Fig. 1(b)]. A maximum transmission of ~86% was achieved in the visible spectral region for 600-nm-thick ITO nanoparticle films.

Electrical properties

The single layer ITO nanoparticle films had a sheet resistance around 2000 Ω/sq (Table I). In triple coated films, the sheet resistance was reduced to 180 Ω/sq. A study of the long-term stability of these films stored at room temperature in a desiccator showed that the sheet resistance of the annealed films slightly increases with time. After 30 days, the sheet resistance reached a plateau value of 200 Ω/sq.

Morphology of ITO nanoparticle film

The morphology of the coatings influences the porosity, electrical parameters, and LED device performance. Surface roughness is an important parameter. Prior to AFM measurements, the films were washed with acetone, chloroform, and cleaned with an O_2 plasma. Figure 2 shows AFM image of a 560-nm-thick film annealed as described. The measured rms roughness value was 10 nm; somewhat higher than that of the commercial ITO (4 nm).

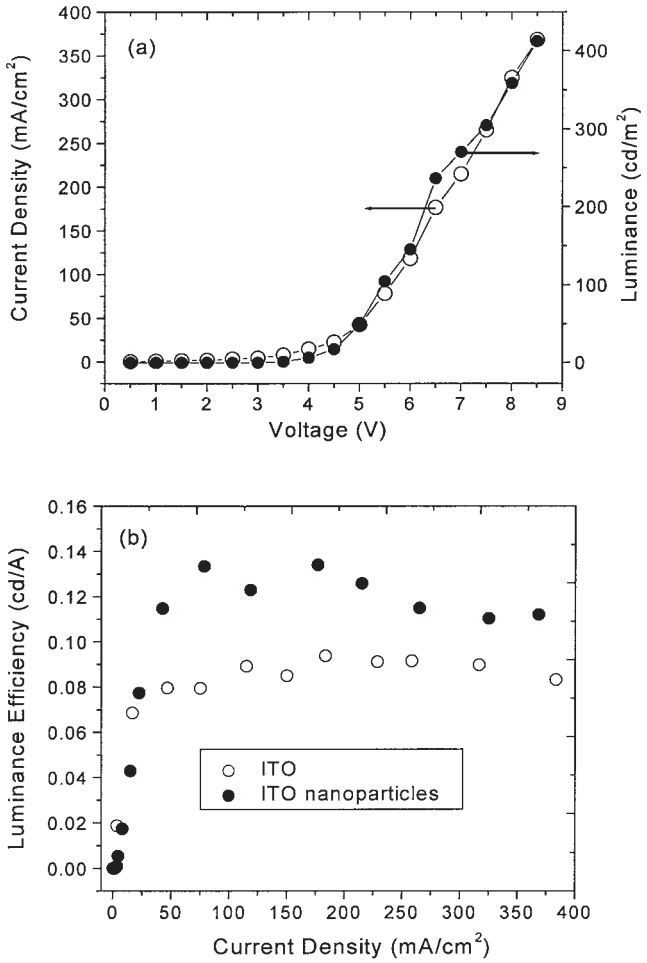

Figure 3 (a) Current density–voltage–luminance characteristics of ITO nanoparticle anode LEDs. (b) Luminance efficiency as a function of current density for commercial ITO and ITO nanoparticle anode LED devices.

LED device performance

The ITO nanoparticle films, as described, were used as anode materials in an LED device. Prior to fabrication, the films were cleaned with an O_2 plasma. Figure 3(a) shows the current density–voltage–luminance (JVL) characteristics of an LED fabricated on the ITO nanoparticle anode. The characteristics of these devices show typical diode behavior. At a current density of 100 mA/cm^2, the drive voltages for ITO nanoparticle and for commercial ITO de-

TABLE II
Experimental Characteristics of LED Devices using Commercial ITO and ITO Nanoparticles Anode Materials

Anode materials	Turn-on voltages (V)	Voltage at 100 mA/cm^2 (V)	Voltages at 400 cd/m^2 (V)	Luminance efficiency at 100 cd/m^2 (cd/A)
ITO	2.5	4.5	8.5	0.09
ITO nanoparticles	2.5	6	8.5	0.13

vices were 6 and 4.5 V, respectively. ITO nanoparticle-based and commercial ITO devices exhibit a turn-on voltage of 2.5 V with maximum luminance efficiency 0.135 and 0.09 cd/A, respectively (Table II). Figure 3(b) shows the luminance efficiency *versus* current density. At lower current densities, (<25 mA/cm^2) both devices show similar behavior and luminance efficiencies around 0.08 cd/A. However, as the current density increases from 25 to 175 mA/cm^2, the luminance efficiency of the ITO nanoparticle device reaches 0.13 cd/A; higher than that of the conventional ITO devices (0.09 cd/A).

The electroluminescence spectra of ITO nanoparticle and conventional ITO anode LEDs are shown in Figure 4(a). Both spectra are consistent with exclusive emission from the chromophore layer with minimal difference in λ_{max}. Voltage dependence of electroluminescence spectra for ITO nanoparticle device was also studied [Fig. 4(b)]. When different external voltages were applied to the device, the EL emission maxima are unchanged as was that observed for the control device.

CONCLUSIONS

Reproducible ITO nanoparticle films with optical and electrical properties suitable for LED application were prepared by spin coating and annealing processes. They show an optical transmission of over 86% in the visible region and also exhibit morphology and sheet resistance on a glass substrate comparable with commercial ITO films. The ITO nanoparticle films provided excellent performance as an anode contact for polymer LED devices. This work shows that ITO coatings substrate for LEDs can be readily fabricated from available nanoparticles. The luminance efficiencies for the ITO nanoparticle devices are comparable to or even higher than LEDs fabricated with commercial ITO anodes. Further investigations concerning the relationships between lifetime of the devices, surface roughness, and different device configurations are presently underway in our laboratories and will be described later in future.

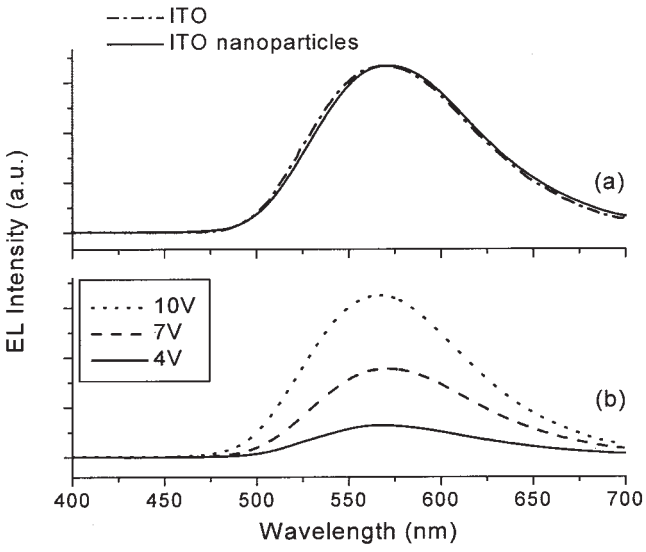

Figure 4 (a) EL spectra for commercial ITO and ITO nanoparticle anode LEDs. (b) Voltage dependence EL spectra for ITO nanoparticle anode LEDs.

References

1. Kim, H.; Horwitz, J. S.; Kim, W. H.; Mäkinen, A. J.; Kafafi, Z. H.; Chrisey, D. B. Thin Solid Films 2002, 420, 539.
2. Kim, H.; Gilmore, C. M.; Horwitz, J. S.; Piqué, A.; Murata, H.; Kushto, G. P.; Schlaf, R.; Kafafi, Z. H.; Chrisey, D. B. Appl Phys Lett 2000, 76, 259.
3. Adamovich, V.; Shoustikov, A.; Thompson, M. E. Adv Mater 1999, 11, 727.
4. Reynolds, K. J.; Frey, G. L.; Friend, R. H. Appl Phys Lett 2003, 82, 1123.
5. Kim, H.; Horwitz, J. S.; Kim, W. H.; Qadri, S. B.; Kafafi, Z. H. Appl Phys Lett 2003, 83, 3809.
6. Cui, J.; Wang, A.; Edleman, N. L.; Ni, J.; Lee, P.; Armstrong, N. R.; Marks, T. J. Adv Mater 2001, 13, 1476.
7. Qiu, C.; Xie, Z.; Chen, H.; Wong, M.; Kwok, H. S. J Appl Phys 2003, 93, 3253.
8. Kim, J. S.; Granström, M.; Friend, R. H.; Johansson, N.; Salaneck, W. R.; Daik, R.; Feast, W. J.; Cacialli, F. J Appl Phys 1998, 84, 6859.
9. Jong, M. P. D.; Simons, D. P. L.; Reijme, M. A.; Ijzendoorn, L. J. V.; Gon, A. W. D. V. D.; Voigt, M. J. A. D.; Brongersma, H. H.; Gymer, R. W. Synth Met 2000, 110, 1.
10. Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. Adv Funct Mater 2001, 11, 15.
11. Gordon, R. MRS Bull 2000, 25, 52.
12. Granqvist, C. G.; Hultåker, A. Thin Solid Films 2002, 411, 1.
13. Kim, Y. S.; Park, Y. C.; Ansari, S. G.; Lee, B. S.; Shin, H. S. Thin Solid Films 2003, 426, 124.
14. Craciun, V.; Craciun, D.; Wang, X.; Anderson, T. J.; Singh, R. K. Thin Solid Films 2004, 453, 256.
15. Shigesato, Y.; Takaki, S.; Haranoh, T. J Appl Phys 1992, 71, 3356.
16. Ray, S.; Banerjee, R.; Basu, N.; Batabyal, A. K.; Barua, A. K. J Appl Phys 1983, 54, 3497.

17. Ramaiah, K. S.; Raja, V. S.; Bhatnagar, A. K.; Tomlinson, R. D.; Pilkington, R. D.; Hill, A. E.; Chang, S. J.; Su, Y. K.; Juang, F. S. Semicond Sci Technol 2000, 15, 676.
18. Stoica, T. F.; Teodorescu, V. S.; Blanchin, M. G.; Stoica, T. A.; Gartner, M.; Losurdo, M.; Zaharescu, M. Mater Sci Eng B 2003, 101, 222.
19. Aegerter, M. A.; Al-Dahoudi, N. J Sol-Gel Sci Technol 2003, 27, 81.
20. Al-Dahoudi, N.; Bisht, H.; Göbbert, C.; Krajewski, T.; Aegerter, M. A. Thin Solid Films 2001, 392, 299.
21. Devi, P. S.; Chatterjee, M.; Ganguli, D. Mater Lett 2002, 55, 205.
22. Sun, J.; Velamakanni, B. V.; Gerberich, W. W.; Francis, L. F. J Colloid Interface Sci 2004, 280, 387.
23. Kim, K. Y.; Park, S. B. Mater Chem Phys 2004, 86, 210.
24. Goebbert, C.; Nonninger, R.; Aegerter, M. A.; Schmidt, H. Thin Solid Films 1999, 351, 79.
25. Ederth, J.; Johnsson, P.; Niklasson, G. A.; Hoel, A.; Hultåker, A.; Heszler, P.; Granqvist, C. G.; van Doorn, A. R.; Jongerius, M. J.; Burgard, D. Phys Rev B 2003, 68, 155410.
26. Ding, L.; Karasz, F. E. J Appl Phys 2004, 96, 2272.