JOURNAL OF Materials CHEMISTRY

Electroless surface polymerization of polyaniline films on aniline primed ITO electrodes: a simple method to fabricate good modified anodes for polymeric light emitting diodes

Chun-Guey Wu,* Hsia-Tsai Hsiao and Yuh-Ruey Yeh

Department of Chemistry, National Central University, Chung-Li, Taiwan, 32054, Republic of China. E-mail: T610002@cc.ncu.edu.tw

Received 6th March 2001, Accepted 4th June 2001
First published as an Advance Article on the web 10th July 2001

Polyaniline (PANI) films were prepared by electroless surface polymerization of the aniline on an aniline–silane ($C_6H_5NHC_3H_6Si(OMe)_3$) modified (aniline primed) ITO electrode. Dense, smooth and strongly adhered films with thickness in the range of 100 nm to 1 μm were isolated. The polyaniline films deposited on aniline primed ITO electrodes (polyaniline/ITO) have a smoother surface, higher electrochemical activity and stability than those deposited on unmodified ITO electrodes or spin casting polyaniline films. The PANI films on ITO electrodes are very stable. The contamination on a used PANI/ITO modified electrode can be easily removed by washing the electrode with proper solvents and then drying under vacuum. Polyaniline film deposited on an aniline primed ITO electrode was used as a modified anode in a polymeric light emitting diode (PLED), which used poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) as an emitting layer and Al as a cathode. The PLED device, tested at an ambient atmosphere, has a turn on voltage 2.0 V lower than that of a device without a polyaniline interlayer. A PLED device using polyaniline/ITO as an anode can also sustain higher electric current, is more stable toward on/off switching, and has a better reproducibility compared to those without a polyaniline layer or using solution cast polyaniline film as an anode modification layer.

Introduction

Thin films of conducting polymers with their interesting optical and/or electronic properties have potential applications in optoelectronic and molecular electronic devices.[1] The techniques used for fabrication of conducting polymer thin films include the electrochemical growth of polymers on modified electrode surfaces,[2] Langmuir–Blodgett deposition,[3] self-assembly of polycation and polyanion of polymer derivatives,[4] and spin coating.[5] However, the polymer films prepared by these methods either involve complicated experimental procedures or need expensive materials. Thus, the preparation of good quality polymer films with commercially viable methods remains a challenge. We have succeeded in fabricating better ordered, optically flat conducting polymer films with good adhesion on monomer primed silicon oxide *via* molecular self-adsorption followed by electroless surface polymerization.[6] In this article, we use a similar synthetic strategy to prepare thin polyaniline films on ITO electrodes.

On the other hand, since the seminal work of the Cambridge group on the electroluminescence of poly(phenylenevinylene), PPV,[7] the polymeric light emitting diodes (PLED) are being examined as devices for technological applications. The external power efficiency, color versatility, brightness, processing and mechanical advantages, angular emission profile, and light weight of the PLED are all attractive for use in flat-panel, portable displays. The PLED typically consists of a transparent hole-injection anode, such as ITO, an electroluminescent conjugated polymer, and an electron injection cathode (Ca, Mg, or Al). The performance of the device depends on the charge injection properties at the interfaces between the electroluminescent polymer and electrode.[8] It was also known that the degradation and eventual failure of PLED using poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) as an emitting layer and ITO as an anode were due to the oxidation of MEH-PPV to form aromatic aldehyde.[9] Aromatic aldehydes were known as the fluorescence quenching species[10] and the ITO anode was proved to serve as the source of oxygen for carbonyl formation. Therefore, a layer of polyaniline was coated between ITO and MEH-PPV layers to prevent the oxidative degradation of the emitting layer.[11] Polyaniline in the PLED device acts as a barrier to oxygen migration and as a planarizing layer to inhibit electrical shorts, therefore improve device lifetime; and in addition, increase in device brightness and efficiencies.

In this article, we report the application of polyaniline film on the ITO electrode, prepared with our method, as a modified anode for polymeric light emitting diodes. The polyaniline films used in the present study differ from that reported by other groups in that it is *in situ* prepared by electroless surface polymerization of aniline in aniline primed ITO electrodes. In addition to the simple preparation procedure, the polymer film prepared by this method has the advantages of less impurity, well-controlled thickness, easy for large area fabrication, better adhesion on the electrode, and flatter and denser morphology. Furthermore, ITO is a common transparent conductor and is widely used as an electrode material in various electronic devices, such as solar cells, liquid crystal displays and PLEDs. Therefore, the studies of ITO surface modification will be interesting from the point of view of both fundamental and technological applications.[12]

Experimental

Reagents

$C_6H_5NHC_3H_6Si(OMe)_3$ was purchased from the United Chemical Technologies Inc., PA. Camphor-10-sulfonic acid, $(NH_4)_2S_2O_8$, HCl(aq), conc. H_2SO_4(aq), 30% H_2O_2(aq) and other chemicals were reagent grade and used as received unless specified. Ultra-pure water and HPLC grade solvents were used in the reactions. MEH-PPV was prepared following the

DOI: 10.1039/b102084f

literature procedure.[13] Aniline and toluene were dried over CaH_2 and freshly distilled prior to use. ITO glass was purchased from the Merck Display Technologies Ltd. with ITO thickness of 100 nm and surface resistance of ~20 Ω/□.

The clean procedure for ITO glass

The ITO glass was cut into a 2 × 2 cm slide, then cleaned first by ultrasonication in a solution of detergent for 30 min. They were rinsed copiously with deionized water, then rinsed again three times each in boiling trichloroethylene, acetone, and boiling methanol and dried at 250 °C to remove the organic solvents.[14] This procedure can clean the dust on the ITO surface and produce hydroxy groups at the same time. To produce more hydroxy groups, the cleaned ITO glass was dipped in (v/v = 3 : 7) conc. sulfuric acid–hydrogen peroxide (30%) solution at room temperature for 5 hours, then washed with copious amounts of water and dried with nitrogen gas. The acid treated, cleaned ITO slides were used right away or stored in methanol prior to use.

Surface modification of the ITO substrates

In a glove box, the cleaned ITO substrate was dipped in 11 mM $C_6H_5NHC_3H_6Si(OMe)_3$–MeOH solution for 20 hours. The aniline primed ITO glass was then washed with MeOH thoroughly, and dried with nitrogen gas at room temperature.

Electroless surface polymerization of the aniline on the aniline primed ITO glass

The aniline primed ITO was dipped into an 18 ml, 1.2 M HCl aqueous solution, which contained 1.8 mmole (0.17 g) aniline and then 18 ml of $(NH_4)_2S_2O_8$ (1.8 mmole) aqueous solution (1.2 M HCl) was added at 0 °C for polymer film deposition. The deposition time was used to control the thickness of polymer film. In a typical reaction, polyaniline film with thickness of 100 nm was obtained after reacting for 30 minutes. The polymer deposited ITO glass was then washed with H_2O and dried with nitrogen gas.

Protonation/deprotonation of polyaniline films

The emeraldine base form of polyaniline film was obtained by dipping the as-prepared polyaniline films on ITO in 0.01 M NH_4OH(aq) for 1 minute, then washing with distilled water, and blow-drying with nitrogen gas. The deprotonated polyaniline film (emeraldine base) can be reprotonated with various acids, such as camphor-10-sulfonic acid, hydrochloric acid, and sulfuric acid, by dipping it in the aqueous solution of the dopant. For very thin film, immersion-washing the protonated polyaniline film in water will cause the deprotonation of the polymer, therefore the protonated polyaniline film was rinsed three times with distilled water to remove the physically absorbed acid. The doping (protonation)/dedoping (deprotonation) process was achieved within a minute and its completeness was judged by the changes of the film colors and the UV/Vis/NIR absorption spectra.

PLED device fabrication and their performance test

MEH-PPV was dissolved in dry toluene (6 wt% solution) and spin-coated on top of polyaniline film at room temperature (500 Å for 2000 rpm), then dried at 70 °C to remove the solvent. To ensure that all MEH-PPV films used in the experiments have the similar thickness, the UV/Vis spectrum was taken for each sample. The *in situ* prepared polyaniline film does not dissolve in toluene, thus severe intermixing of layers will not occur. The cathode was made by evaporating a layer of Al (3000 Å, at a rate of 15–20 Å per second) at high vacuum (less than 10^{-6} mbar). To test the reproducibility, we fabricated 36 independent diodes, each 3.1 mm^2, on one substrate by depositing 36 separately accessible cathodes. In this geometry, the 36 devices share a common anode (ITO). Current voltage (*I–V*) characteristics were measured with a HP 4145B analyzer in voltage scan mode with steps of 0.1 V and a delay time of 200 ms before each measurement point. Synchronously the light output was monitored using an ORIEL 70680 photo multiplier calibrated with a commercial LED device. Photoluminescence and electroluminescence spectra were obtained with a HITACHI F-4500 Fluorescence Spectrometer. The wavelength of the excitation light for photoluminescence studies is 485 nm. For fair comparison, all devices to be tested are subject to nearly identical conditions.

Physicochemical studies

Fourier Transform Infrared (FTIR) spectra were recorded as pressed KBr pellets or films on Si substrate using a Bio-Rad 155 FTIR spectrometer. Static contact angles were measured with a home-made goniometer at room temperature and ambient humidity. Water was used as a probe liquid. A 2 μL water droplet was placed on the substrate with a syringe. The angle was obtained by estimating the tangent to the drop at its intersection with the surface, and three measurements were taken for the reported contact angle readings. The thickness of polymer films was measured with a Dektak ^{3}D surface profile measuring system. The scan length is 5 mm and the thickness is calculated from the average thickness of the length scanned. Cyclic voltammograms were collected at room temperature using an EG&G 263 potentiostat/galvanostat with a single compartment voltammetric cell equipped with three electrodes. The polyaniline film on ITO was the working electrode, platinum coil was the counter electrode, Ag/AgCl was the reference electrode, and 0.1 M H_2SO_4 aqueous solution was used as an electrolyte solution, UV/Vis/NIR spectra were obtained from a Varian Cary 5E spectrometer. Scanning electron microscopy (SEM) and energy disperse spectroscope (EDS) studies were performed with a Hitachi S-800 at 15 KV. The samples for SEM imaging were mounted on metal stubs with a conducting tape and gold coated. AFM micrographs were obtained with a Digit Instrument AFM system (Dolan-Jenner model 190). X-Ray photoelectron spectroscopy (Auger/ESCA) studies were carried out on a Perkin–Elmer 670PHI Xi spectrometer (with thermal field emitter and a Cylindrical Mirror Electron (CMA) energy analyzer) and a Perkin–Elmer PHI-590AM ESCA/XPS spectrometer system with a spherical capacitor analyzer. The X-ray sources were Al-Kα at 600 W and Mg-Kα at 400 W.

Results and discussion

The spontaneous absorption of monolayer aniline-containing silane on the surface of an ITO electrode

The formation and characterization of a self-assembled monolayer on the ITO surface is a challenging target from the point of view of both fundamental and technological applications.[12] There have been a few reports[15] on the adsorption of organic or organometallic compounds on ITO surfaces. Nevertheless, despite the large number of reports concerning devices using ITO as an electrode and the studies of the surface resistance, optical band gap, and structure of ITO, relatively few studies[16] have focused on a possible key issue of ITO surface chemistry. Therefore, the formation of an aniline–silane layer on the ITO surface was characterized in detail.

To adhering aniline molecules on an ITO electrode, we grafted the surface with a silane compound bearing an aniline molecule. This reaction was carried out by modifying the substrate's surface with $C_6H_5NHC_3H_6Si(OMe)_3$ *via* molecular spontaneous absorption. ITO glass was cleaned using the literature procedure[17] to remove the absorbed impurities, at the same time forming 0hydroxy groups on the surface. Aniline–silane molecules were formed on the ITO substrate when the OMe groups on Si reacted with the OH groups on the ITO surface. The presence of monolayer aniline–silane molecules on ITO glass was confirmed with the contact angle and XPS data. After treating with the silane compound, the surface contact angles of the ITO glass increased from 20 to 47 degrees. This result was consistent with the deposition of organic molecules on an inorganic surface.[18] XPS spectra, Fig. 1, of the aniline–silane modified ITO surface revealed Sn, In, Si, and N_{1s} peaks. The binding energy of N_{1s} peaks is 399.5 eV, which is similar to the binding energy of nitrogen in an amine site of the emeraldine base.[19] The Si and N_{1s} signals were not observed in the cleaned unmodified ITO electrode (Fig. 1a), therefore, the Si peak of aniline–silane modified ITO comes from the self-adsorption aniline–silane molecules. The distribution of the N and Si elements is very homogeneous in the whole substrate and the intensity ratio of N : Sn is quite reasonable for the formation of the monolayer of aniline–silane on the ITO electrode.

Electroless surface polymerization of polyaniline films on the aniline primed ITO electrode

The electroless surface polymerization of polyaniline, PANI, films on the aniline primed ITO was carried out by dipping the aniline primed ITO in an acidic solution containing aniline and oxidant. The pendant aniline functionality was to be used as the initiation site for polymerization and also served as a covalent anchor for polyaniline chain to grow on the ITO surface. The reaction conditions for deposition of polyaniline films on aniline primed ITO glass was similar to what we had reported previously.[6] The oxidant was $(NH_4)_2S_2O_8$ with the mole ratio of monomer to oxidant equal to 1 and the reaction was carried out in 1.2 M HCl aqueous solution at 0 °C. In order to prepare very thin polyaniline films with various thicknesses, the polymerization reactions were carried out in very low aniline concentration (0.05 M) and using the reaction time to control the film thickness. Polyaniline films with thicknesses of 500–1000 Å were obtained in a deposition time of 20–30 minutes. The formation of polyaniline films was characterized and confirmed with UV/Vis/NIR spectra. The characteristic polaronic absorption peak at *ca.* 800 nm confirms that polyaniline film was formed and is in its protonated state.[20] The deprotonation and reprotonation of polyaniline were carried out with the films on ITO glass. These processes finished within a minute and they can be repeated many times without damaging the adhesion and surface morphology of the polyaniline films.

The effects of the aniline–silane modification on the properties of polyaniline films on the aniline primed ITO glass

Surface morphology. Polyaniline film deposited on ITO substrate has better adhesion compared to those deposited on SiO_2 substrate. Thin polyaniline films on both unmodified and aniline–silane modified ITO glass passed our peeling test.[21] This is due to the amino group of aniline having a good affinity for the ITO material.[22] Under SEM (Fig. 2), polyaniline films deposited on both aniline–silane modified and unmodified ITO glass have a smooth surface, and there was no fibril morphology as observed in the electrochemically polymerized polymer.[23] Nevertheless, polyaniline films grown on aniline primed ITO glass have a denser and smoother surface as revealed by AFM studies, see Fig. 3. For polyaniline film with 1000 Å thickness, the surface roughness of polymer film deposited on aniline primed ITO glass is *ca.* 10 nm *vs. ca.* 17 nm for polymer film deposited on unmodified ITO. Furthermore, several scratched lines were observed on the polymer film deposited on unmodified ITO (Fig. 3b). This is due to the surface of the polyaniline being damaged by the tip of the cantilever when it was scanned through the polymer film. No damage was done on the polyaniline film deposited on aniline primed ITO glass when the cantilever scanned through it. This result suggested that polyaniline deposited on aniline primed ITO glass has a higher density compared to that deposited on unmodified substrate.

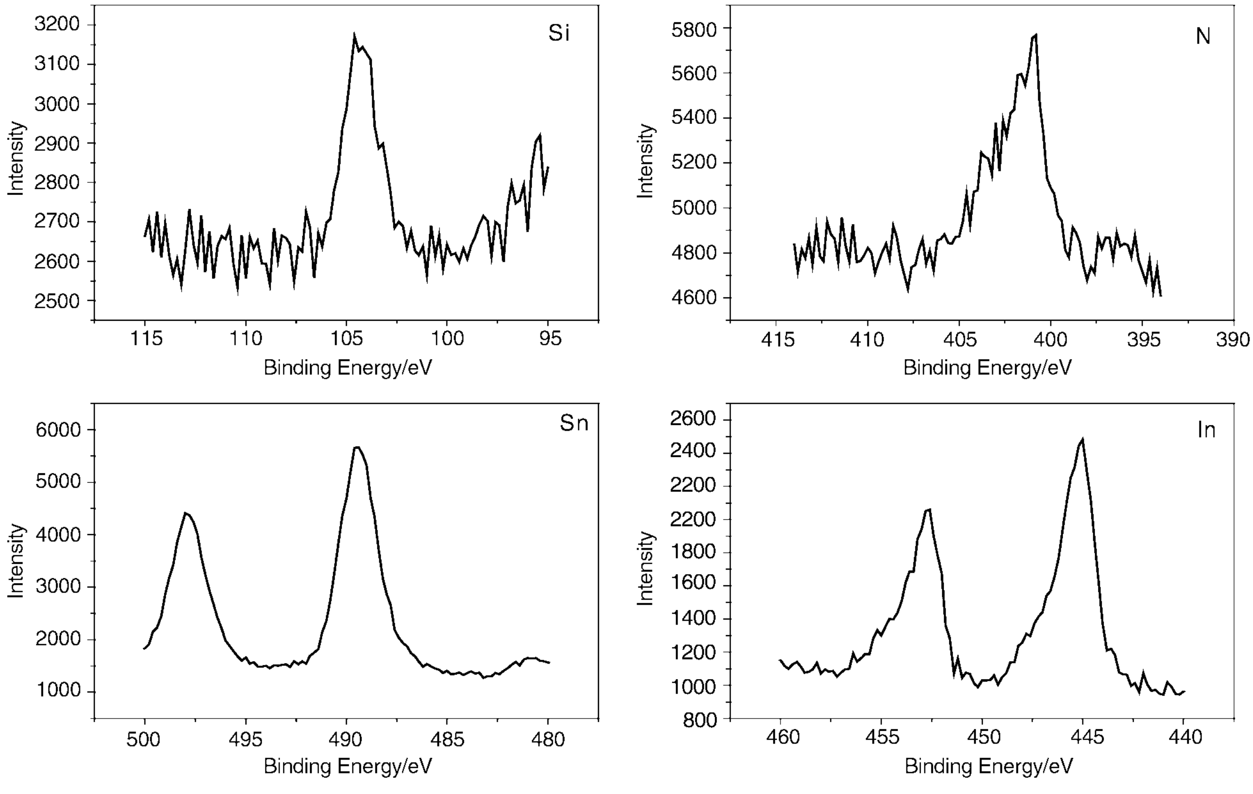

Fig. 1 XPS spectra of aniline–silane modified ITO glass.

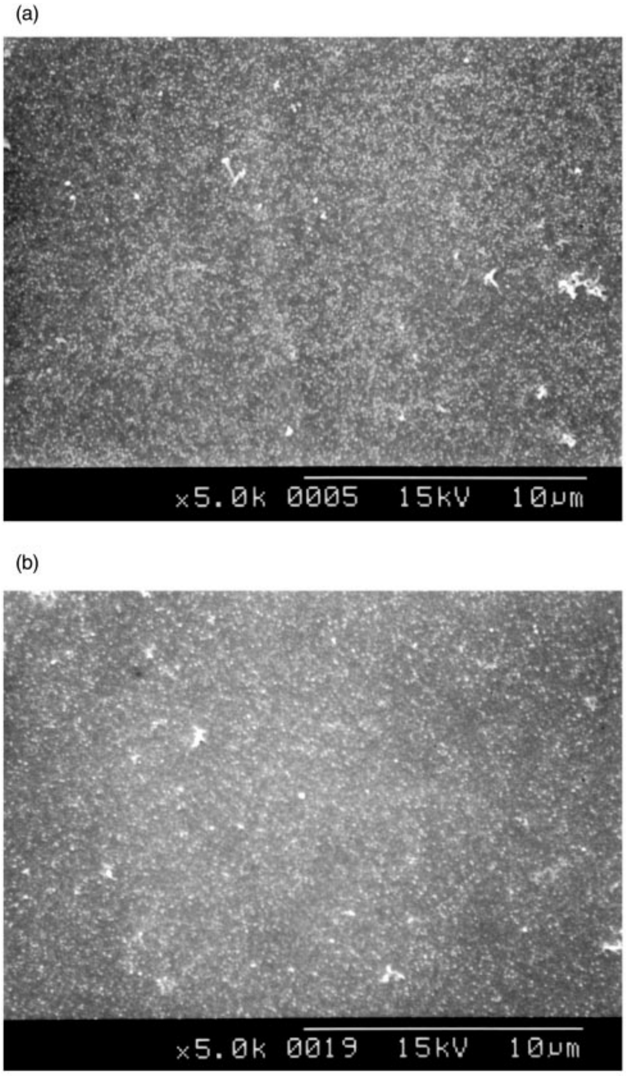

Fig. 2 SEM micrpgraphs of polyaniline films deposited on (a) aniline–silane modified ITO glass, (b) unmodified ITO glass.

The electrochemical properties. The cyclic voltammograms of polyaniline films deposited on aniline primed and unmodified ITO electrodes are shown in Fig. 4. It was found that for similar thickness films, polyaniline deposited on aniline primed ITO glass has a higher oxidation current than polyaniline deposited on unmodified substrate (120 μA *vs.* 90 μA for 850 Å films). Furthermore, the electrochemical stability of polyaniline deposited on aniline primed ITO glass is also better than polyaniline deposited on unmodified substrate. After 50 scan cycles (scans from −0.2 V to 0.8 V to −0.2 V *vs.* SCE), the oxidation current of polyaniline deposited on unmodified ITO decreased 12% compared to only a 7.5% decrease for polyaniline deposited on aniline primed ITO glass. Since polyaniline film deposited on aniline primed ITO has better electrochemical properties, it may also be a better anode modification layer for PLED.

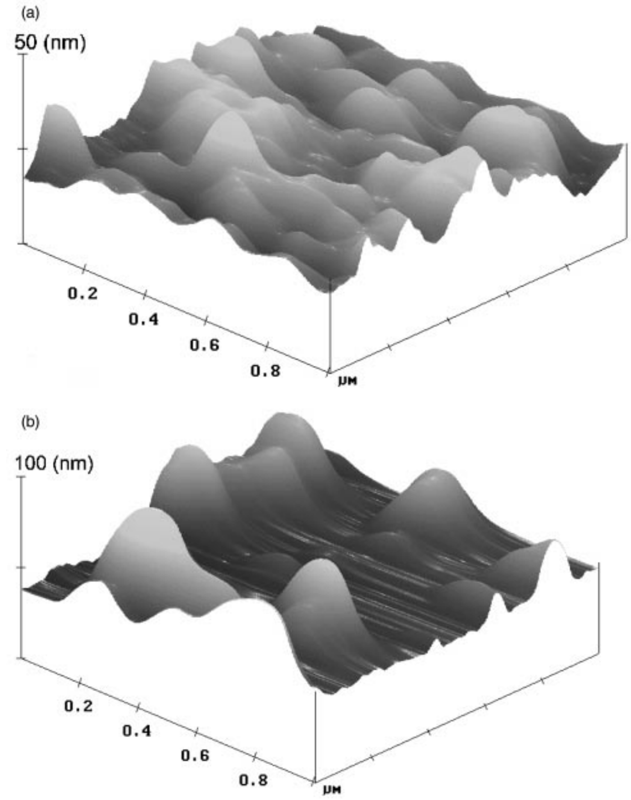

Fig. 3 AFM diagram of polyaniline films deposited on (a) aniline–silane modified ITO glass, (b) unmodified ITO glass.

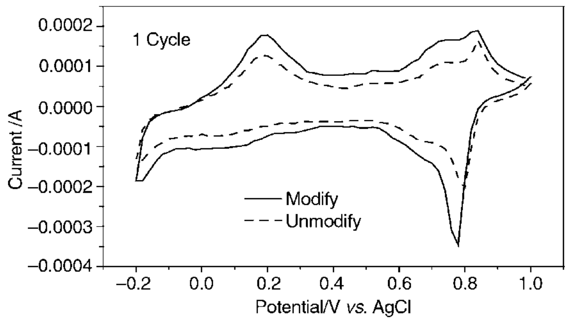

Fig. 4 Cyclic voltammograms of polyaniline films deposited on (a) aniline–silane modified ITO glass, (b) unmodified ITO glass.

The fabrication and properties of ITO/PANI/MEH-PPV/Al double layered PLED devices

The double layered PLED device was fabricated by spin coating the MEH-PPV on the polyaniline modified ITO electrode, then a layer of Al was deposited on top of the MEH-PPV film to be a cathode. The deposition of MEH-PPV does not affect the structure of polyaniline beneath when toluene is used as a solvent for MEH-PPV. Since polyaniline deposited on aniline primed ITO glass is a dense film, the intermixing of the two polymer layers is not serious. The depth profile ESCA analysis, Fig. 5, of the PANI/MEH-PPV double layered film revealed that the thickness of interlayer mixing is a couple of hundred angstroms. The polyaniline layer did not affect the λ_{max} of the absorption and photoluminescence of the

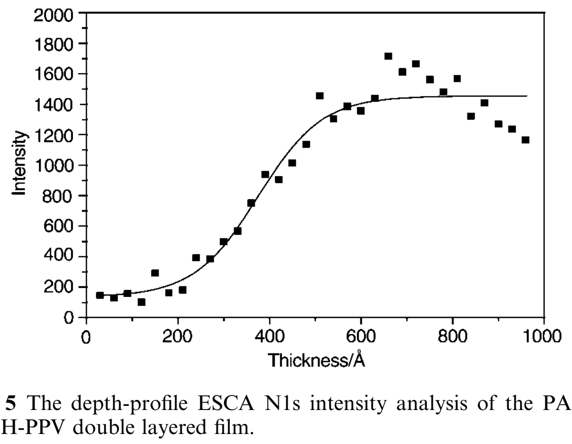

Fig. 5 The depth-profile ESCA N1s intensity analysis of the PANI/MEH-PPV double layered film.

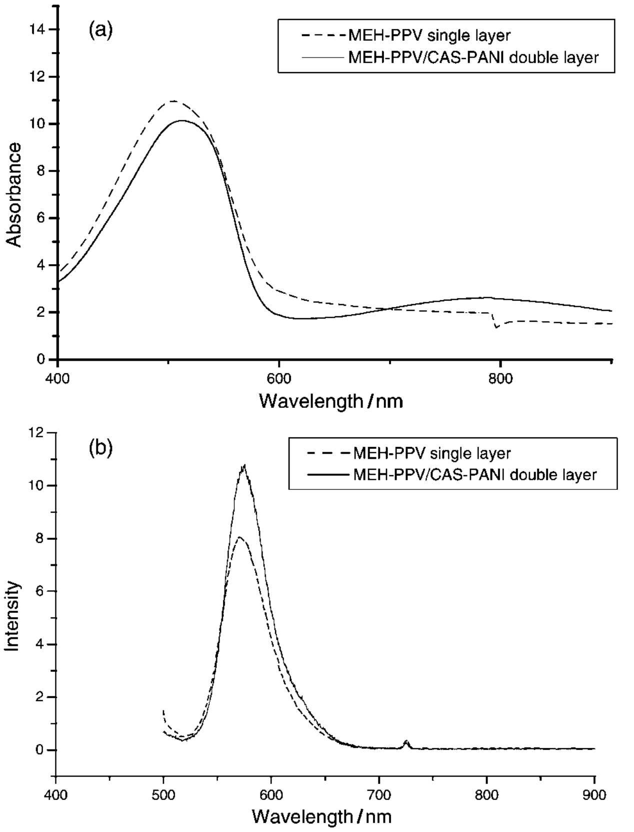

Fig. 6 The (a) UV/Vis absorption, (b) photoluminescence spectra of the CAS-PANI/MEH-PPV double layered film and the MEH-PPV single layered film.

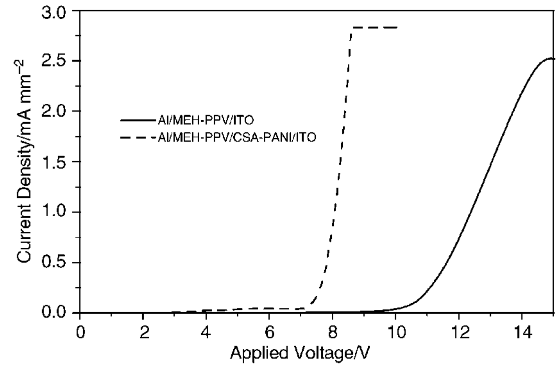

Fig. 7 The *I–V* curves of (a) the ITO/CAS-PANI/MEH-PPV/Al double layered device (ITO was modified with aniline–silane), and (b) the ITO/MEH-PPV/Al single layered device.

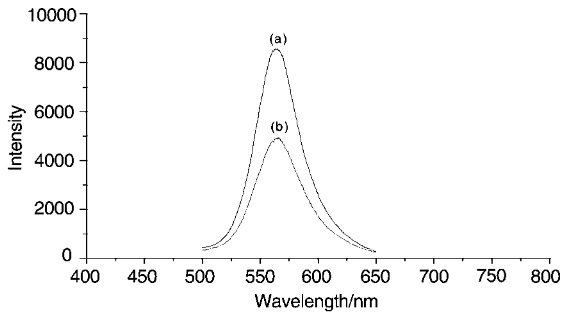

Fig. 8 Electroluminescence intensity of (a) the ITO/CAS-PANI/MEH-PPV/Al double layered device, and (b) the ITO/MEH-PPV/Al single layered device.

MEH-PPV film as evidenced by the UV/Vis and PL spectra shown in Fig. 6. This implied that the adding of the polyaniline layer did not change the electronic structure of MEH-PPV. Nevertheless, the turn-on voltage is lower (Fig. 7) and electroluminescence is higher (Fig. 8) for the PANI/MEH-PPV double layered PLED device compared to the MEH-PPV single layered device.

The effects of the polyaniline modification layer on the performance of polymeric light emitting diodes using ITO as an anode, MEH-PPV as an emitting layer, and Al as a cathode

To test the function of the polyaniline film in PLEDs, an ITO electrode was modified with different forms of polyaniline and the PLED devices were tested under similar conditions. It was found that the turn-on voltage is always lower for the double layered PLED device when polyaniline film was very thin, see Table 1. The double layered devices not only have a lower turn-on voltage and higher luminescence intensity, but also are more stable toward on/off switching. The turn-on voltage did not change after 100 times on/off switching in air. On the other hand, the turn-on voltage of the single layered device starts to shift to higher voltage when the on/off switching was repeated 30 times. Furthermore, all 36 double layered PLED devices fabricated on the same ITO anode were able to emit light at the turn-on voltage. Nevertheless, among the 36 single layered PLED devices fabricated on the same ITO anode, some devices always failed to emit light. It was found (see Table 1) that both the camphorsulfonic acid doped emeraldine salt and emeraldine base are good anode modification materials. This result suggested that electric and electronic properties of materials might not be the major concern for the anode modification layer. The function of the polyaniline layer may be just to level the anode, facilitating the hole injection and moving through the electrode and light emitting layer interface, and therefore, improving the performance of PLED. In fact, the important role of the organic–inorganic interface to the efficiency of the PLEDs is recognized. An appropriate surface modification of ITO may be able to enhance carrier injection from ITO to emitting layer and, consequently, better device performance. Detailed studies of the effects of ITO anode modification on the performance of polymeric light emitting diode will be reported elsewhere.[24]

Table 1 The turn-on voltages of double layered (ITO/PANI/MEH-PPV/Al) PLED devices using various forms of polyaniline as anode modification layers

Polyaniline form (PANI)	None	[b]Emeraldine base (*in situ*)	[c]CAS doped polyaniline	HCl doped polyaniline	H_2SO_4 doped polyaniline	[d]PAPSAH	[e]Emeraldine base (NMP)
[a]Turn-on voltage/V	8.5–10	7.3–8.5	7.5–8.0	7.5–8.5	6.0–8.5	7.0–8.0	7.0–9.0

[a]The turn on voltage was defined as the applied voltage, at which the photon current starts to increase nonlinearly. The values listed in the table are the range of the turn-on voltages measured from several tens of the devices. [b]Emeraldine base film prepared by electroless surface polymerization of aniline reported in this article. [c]CAS is camphor-10-sulfonic acid. [d]Film cast from the aqueous solution of poly(aniline-*co*-*N*-(3-sulfopropyl)aniline) [e]Emeraldine base film cast from *N*-methylpyrrolidinone solution.

The advantages of using electroless surface polymerization to fabricate polyaniline anode modification layer

In the literature, the polyaniline modification layer was prepared by spin casting from emeraldine base–NMP solution or an aqueous solution of water soluble polyaniline, such as poly(aniline-*co*-*N*-(3-sulfopropyl)aniline).[25] We have repeated similar experiments and found that the turn-on voltage and luminescence intensity of polyaniline modified double layered PLED devices are similar, independent of the preparation methods of polyaniline films. However, polyaniline film modified ITO anodes prepared with our method have the advantages of simpler preparation method, purer polymer, flatter film morphology, cheaper materials (only aniline was used), higher (*ca.* 100%) device yield,[26] and better luminescence stability,[27] compared to the literature procedure. Furthermore, the PANI films on ITO electrodes are very stable. The contamination on the old PANI/ITO modified electrode can be easily removed by washing the electrode with an appropriate solvent and then dried under vacuum. Therefore, no complicated electrode cleaning procedure was needed.

Conclusions

Optically flat, dense polyaniline films were deposited tightly on ITO substrates *via* molecular self-adsorption, followed by electroless surface polymerization. The as-prepared polyaniline film was used as a hole transport (or anode modification) layer in polymeric light-emitting diodes to reduce the turn-on voltage and increase the luminescence intensity and stability of PLED devices. Compared to other preparation methods, polyaniline films prepared with this reported method have the advantages of simple preparation procedure, and lower fabrication cost.

Acknowledgements

The financial support by the National Science Council of the Republic of China through project NSC-89-2113-M-008-007 is greatly acknowledged.

References

1. (*a*) *Application of Intrinsically Conducting Polymers*, NATO Advanced Research Workshop October 1992 Vermont USA; (*b*) *Synth. Met.*, 1995, **71**.
2. (*a*) E. Sabatani, A. Redondo, J. Rishpon, A. Rudge, I. Rubinstein and S. Gottesfeld, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 287–294; (*b*) I. Rubinstein, J. Rishpon, E. Sabatani and A. J. Gottesfeld, *J. Am. Chem. Soc.*, 1990, **112**, 6135; (*c*) R. V. Gregory, W. C. Kimbrell and H. H. Kuhn, *Synth. Met.*, 1989, **28**, C823–C835; (*d*) V. G. Kulkami, *Synth. Met.*, 1995, **71**, 2129–2131.
3. A. Riul, Jr., L. H. C. Mattoso, S. V. Mello, G. D. Telles and N. O. Oliveira, Jr., *Synth. Met.*, 1995, **71**, 2067–2068.
4. J. Paloheimo, K. Laakso, H. Isotalo and H. Stubb, *Synth. Met.*, 1995, **68**, 249–257.
5. V. G. Kulkami, *Synth. Met.*, 1995, **71**, 2129–2131.
6. (*a*) C.-G. Wu and J. Y. Chen, *Chem. Mater.*, 1997, **9**, 399–402; (*b*) C.-G. Wu and C. Y. Chen, *J. Mater. Chem.*, 1997, **7**(8), 1409–1413; (*c*) C.-G. Wu, J. Y. Chen, C. Y. Chen and Y. H. Chiou, *Polymer*, 2001, **42**, 2877–2885.
7. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackey, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature*, 1990, **347**, 29.
8. (*a*) R. N. Marks, D. D. C. Bradley, R. W. Jackson, P. L. Burn and A. R. Holmes, *Synth. Met.*, 1993, **55–57**, 4128; (*b*) D. Braun and A. J. Heeger, *Appl. Phys. Lett.*, 1991, **58**, 1982.
9. J. C. Scott, J. H. Kaufman, P. J. Brock, R. DiPietro, J. Salem and J. A. Goitia, *J. Appl. Phys.*, 1996, **79**, 1745.
10. M. Yan, L. J. Rothberg, F. Papadimitrikapoulos, M. E. Galvin and T. M. Miller, *Phys. Rev. Lett.*, 1994, **73**, 744.
11. (*a*) Y. Yang and A. J. Heeger, *J. Appl. Phys.*, 1994, **64**, 1245; (*b*) Y. Yang, E. Westerweele, C. Zhang, P. Smith and A. J. Heeger, *J. Appl. Phys.*, 1995, **77**, 694; (*c*) J. C. Scott, S. A. Carter, S. Karg and M. Angelopoulos, *Synth. Met.*, 1997, **87**, 1197–1200; (*d*) S. A. Carter, M. Angelopoulos, S. Karg, P. J. Brock and J. C. Scott, *Appl. Phys. Lett.*, 1997, **70**, 2066–2069.
12. (*a*) A. Ulman, *Chem. Rev.*, 1996, **96**, 1533–1554; (*b*) J. P. Folkers, C. B. Gorman, P. E. Laibinis, S. Buchholz, G. M. Whitesides and R. G. Nuzzo, *Langmuir*, 1995, **11**, 813–824.
13. C. F. Neef and J. P. Ferraris, *Macromolecules*, 2000, **33**, 2311–2314.
14. P. E. Burrows, Z. Shen, V. Bulovic and D. M. McCarthy, *J. Appl. Phys.*, 1996, **79**, 7991–8006.
15. (*a*) S.-Y. Oh, Y.-J. Yun, D.-Y. Kim and S.-H. Han, *Langmuir*, 1999, **15**, 4690–4692; (*b*) F. Mirkhalaf, D. Whittaker and D. J. Schiffrin, *J. Electroanal. Chem.*, 1998, **452**, 203–213; (*c*) G. Zotti, G. Schiavon, S. Zecchin, A. Berlin, G. Pagani and A. Canavesi, *Langmuir*, 1997, **13**, 2694–2698.
16. T. J. Gardner, C. D. Frisbie and M. S. Wrighton, *J. Am. Chem. Soc.*, 1995, **117**, 6927–6933.
17. P. E. Burrows, Z. Shen, V. Bulovic and D. M. McCarthy, *J. Appl. Phys.*, 1996, **79**, 7991–8006.
18. (*a*) N. Tillman, A. Ulman and T. L. Penner, *Langmuir*, 1989, **5**, 101–111; (*b*) Y. T. Tao, *J. Am. Chem. Soc.*, 1993, **115**, 4350–4358.
19. E. T. Kang, K. G. Neoh, S. H. Khor, K. L. Tan and B. T. G. Tan, *J. Chem. Soc. Chem. Commun.*, 1989, 695.
20. (*a*) I. Kulszewicz, *Macromolecules*, 1995, **28**, 610–613; (*b*) Y. Xia, J. M. Wiesinger, A. G. MacDiarmid and A. J. Epstein, *Chem. Mater.*, 1995, **7**, 443–445; (*c*) D. Chinn, J. DuBow, J. Tanata, J. Li and M. Josowicz, *Chem. Mater.*, 1995, **7**, 1510–1518.
21. The peeling test was performed with Scotch tape. The tape was first pressed on the polymer film then peeled off to see if the polymer film peels off with the tape, see reference 6.
22. S.-Y. Oh, Y.-J. Yun, D.-Y. Kim and S.-H. Han, *Langmuir*, 1999, **15**, 4690–4692.
23. (*a*) M. Wan, *Synth. Met.*, 1989, **31**, 51–59; (*b*) K. Kanamura, Y. Kawai, S. Yonezawa and Z.-I. Takeharhys, *J. Mater. Chem.*, 1994, **98**, 2174–2179.
24. C.-G. Wu and H. T. Hsiao, *Adv. Mater.*, submitted.
25. (*a*) Y. Yang and A. J. Heeger, *J. Appl. Phys.*, 1994, **64**, 1245; (*b*) Y. Yang, E. Westerweele, C. Zhang, P. Smith and A. J. Heeger, *J. Appl. Phys.*, 1995, **77**, 694; (*c*) S. A. Carter, M. Angelopoulos, S. Karg, P. J. Brock and J. C. Scott, *Appl. Phys. Lett.*, 1997, **70**, 2066–2069.
26. The device yield is defined as the device successes to emit light per devices fabricated.
27. The PLED device test was performed in air, therefore the stability may not be the same when the devices were tested in a controlled atmosphere.