



## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

### ORGANIC ELECTROLUMINESCENT DEVICES WITH ELECTROCHEMICALLY DEPOSITED POLYANILINE AS HOLE INJECTION LAYER

Ju-Seung Kim<sup>a</sup>, Sang-Ki Kim<sup>b</sup> & Hal-Bon Gu<sup>b</sup>

<sup>a</sup> Research Institute of Energy Resources Technology,  
Chosun University, 375 Sesuk-dong, Dong-gu,  
Gwangju 501-759, Korea

<sup>b</sup> Dept. of Electrical Eng., Chonnam National  
University, 300 Yongbong-dong, Buk-gu, Gwangju  
500-757, Korea

Version of record first published: 15 Jul 2010

To cite this article: Ju-Seung Kim, Sang-Ki Kim & Hal-Bon Gu (2003): ORGANIC ELECTROLUMINESCENT DEVICES WITH ELECTROCHEMICALLY DEPOSITED POLYANILINE AS HOLE INJECTION LAYER, *Molecular Crystals and Liquid Crystals*, 405:1, 113-118

To link to this article: <http://dx.doi.org/10.1080/15421400390264216>

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## ORGANIC ELECTROLUMINESCENT DEVICES WITH ELECTROCHEMICALLY DEPOSITED POLYANILINE AS HOLE INJECTION LAYER

*Ju-Seung Kim*

*Research Institute of Energy Resources Technology,  
Chosun University, 375 Sesuk-dong, Dong-gu,  
Gwangju 501–759, Korea*

*Sang-Ki Kim and Hal-Bon Gu*

*Depat. of Electrical Eng., Chonnam National University,  
300 Yongbong-dong, Buk-gu, Gwangju 500–757, Korea*

*Conductive polyaniline (PANI)-camphosulfonic acid (CSA) film applied as a hole injection layer in ITO/PANI/P3HT/LiF/Al device. In the AFM images, electrochemically polymerized PANI-CSA films have the small particles and smooth sufficient for application as hole injection layer. By insertion of PANI-CSA buffer layer, the turn on voltage of ITO/PANI/P3HT/LiF/Al device lowered by 3 V, whereas that of ITO/P3HT/LiF/Al device shows 5 V.*

**Keywords:** AFM; buffer layer; electrochemically deposition; OLED; polyaniline

### INTRODUCTION

Many researchers have been effort to improve the efficiency and the life-time of the organic light-emitting diodes (OLED). A buffer layer, such as copper phthalocyanine (CuPc) and poly(ethylenedioxy thiophene)-PSS (PDOT-PSS), was usually interposed between the ITO electrode and the organic layer to improve the performance of devices [1,2].

Among the conducting polymers, polyaniline (PANI) is considered as one of the most attractive materials because it shows high environmental stability and is easily synthesized by chemical or electrochemical oxidation of aniline [3]. PANI films can be prepared using cyclic voltammetry through the electrochemical oxidation of the aniline monomer. It is known that PANI produced either by chemical or electrochemical method is completely insoluble when doped with common acids. However, electrochemically polymerized PANI with a functionalized acid was quite soluble in organic solvents, such as m-cresol.

Although, PANI-CSA can be solved in *m*-cresol, there are some problems to application of EL device because *m*-cresol has 203°C of boiling point. High boiling point of *m*-cresol make the difficult to producing sufficient uniform film of PANI due to heating of PANI film for removing the solvent.

In this work, we investigated the electrochemical synthesizing of polyaniline (PANI) with camphorsulphonic acid (CSA) and the possibility of application as hole injection layer in ITO/PANI/P3HT/LiF/Al device.

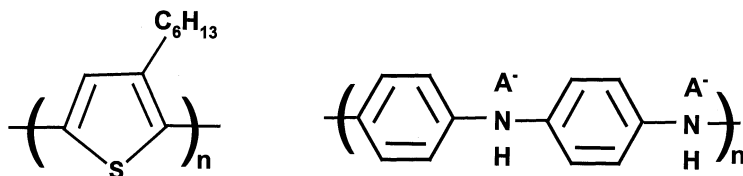
## EXPERIMENTAL

Figure 1 shows the chemical structures of poly(3-hexylthiophene) (P3HT) and PANI doped with CSA. The devices were fabricated onto a sufficiently cleaned indium-tin-oxide (ITO) glass substrate and have a structure of ITO/PANI-CSA/P3HT/LiF/Al. Electrochemical polymerization of PANI-CSA was performed by cyclic voltammetry in the range from  $-0.4$  V to  $0.9$  V vs. Ag/AgCl at 20 mV/s for several cycles. A three-electrode cell was used with platinum counter electrode and a Ag/AgCl electrode as a reference and the electrolyte contained 1 M aqueous camphosulfonic acid (CSA) and 0.5 M aniline. P3HT layer was spin-coated on the PANI-CSA layer, and LiF layer was heat evaporated subsequently in high vacuum chamber under the base pressure of  $10^{-6}$  Torr. 200 nm of Al electrode layer sequentially deposited after LiF layer in same condition.

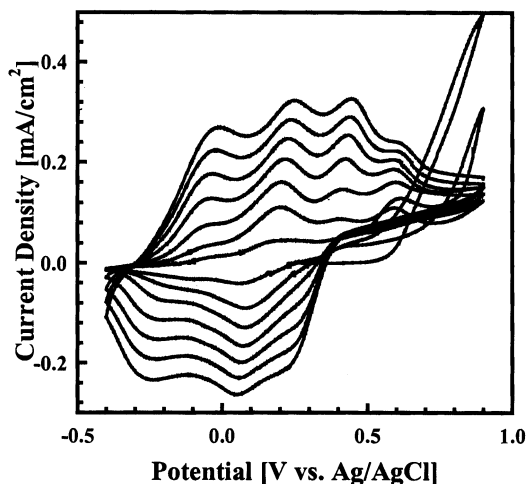
The transmittance for the PANI-CSA films was obtained using a Hitachi U3501 spectrometer and surface morphology of the PANI-CSA films was measured by atomic force microscopy (AFM). EL spectrum of the device measured by photodiode array, and the voltage-current-luminance were measured simultaneously combining the Newport 1830-c with Keithely 2400 sourcemeeter.

## RESULT AND DISCUSSION

Figure 2 shows the growth of PANI-CSA film on the ITO substrate by the cyclic voltammetry method at a sweep rate of 20 mV/s. As can be seen, in the first and second cycle a sudden increase in current was observed near 0.6 V vs. Ag/AgCl due to the generation of free radical. The electrochemical polymerization of PANI in CSA presented three major redox processes at 0,

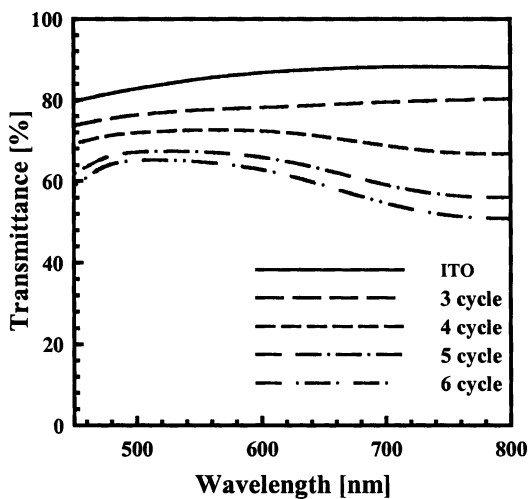


**FIGURE 1** Molecular structures of P3HT and PANI-CSA.



**FIGURE 2** Cyclic voltammetry of PANI-CSA film by sweeping the potential scan rate 20 mV/s.

0.2 and 0.4 V vs. Ag/AgCl, represented to polaron states of PANI. Smaller redox process at around 0.6 V vs. Ag/AgCl associated with monomer oxidation and degradation films were negligible.

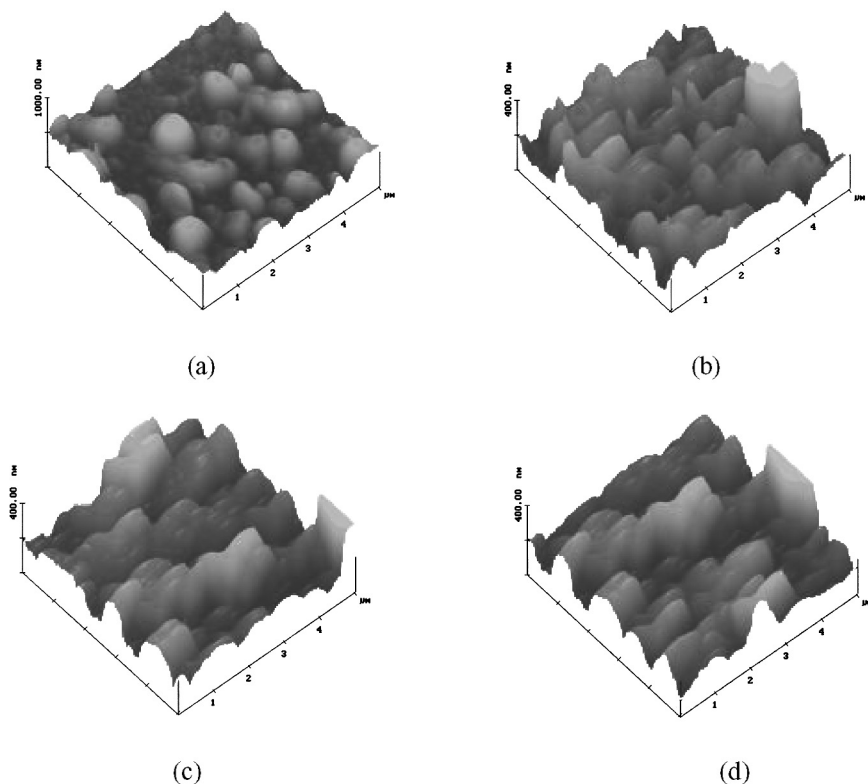


**FIGURE 3** Transmittance of the electrochemically deposited PANI films on ITO electrode.

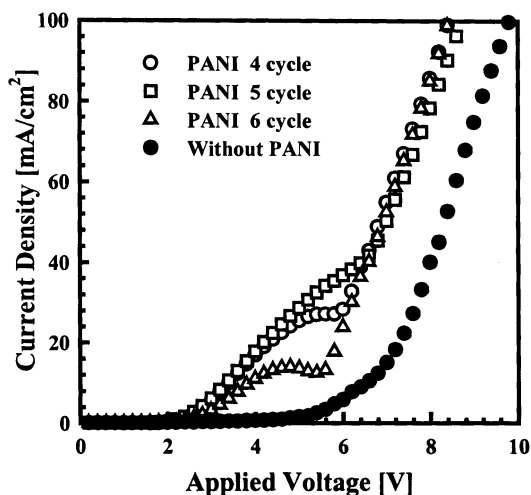
Figure 3 shows the visible spectrum of PANI-CSA films deposited on ITO electrode. The average transmittance of ITO electrode is 80%. Increasing with the deposition cycle number, transmittance of PANI-CSA films was gradually decreased. In the PANI-CSA film deposited during 6 cycle, the maximum transmittance is 65% at 500 nm and the average is over 60% in the range from 450 to 800 nm.

In order to analyze the morphology of the PANI-CSA films, AFM images were obtained in the tapping mode. Figure 4 presented AFM images of PANI-CSA deposited on ITO electrode. The surface consists of small particles, which have the dimension of 1  $\mu\text{m}$  in diameter. It is reported that the initial stage of PANI deposition on ITO electrode was strongly influenced by the state of substrate [4]. However, as it is seen, PANI-CSA films deposited on ITO electrode were showed relatively smooth and regular.

Figure 5 presented the voltage-current characteristics of ITO/PANI/P3HT/LiF/Al device. When the PANI-CSA film used as buffer layer, the turn

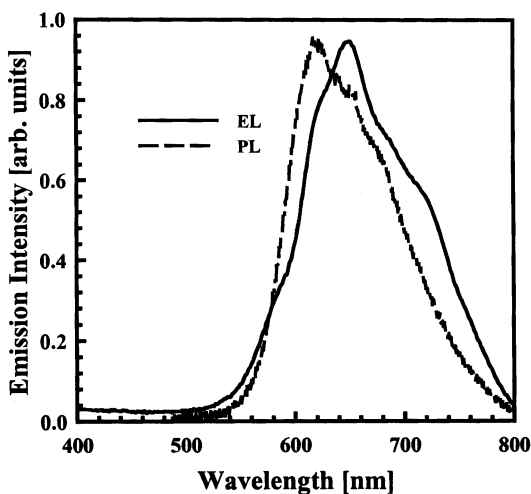


**FIGURE 4** AFM images of PANI-CSA films (a) 3 cycle, (b) 4 cycle, (c) 5 cycle and (d) 6 cycle.



**FIGURE 5** Voltage-current characteristics of ITO/PANI/P3HT/LiF/Al device.

on voltage of ITO/PANI/P3HT/LiF/Al device decreased than that of ITO/P3HT/LiF/Al device. The turn on voltage of ITO/PANI/P3HT/LiF/Al device measured at 3 V, whereas that of ITO/P3HT/LiF/Al device showed at 5 V. The current increased with increasing applied voltage, and showed a slope at 5 V unexpected in ITO/P3HT/LiF/Al device. This phenomenon indicates



**FIGURE 6** PL spectrum of P3HT film and EL spectrum of ITO/PANI/P3HT/LiF/Al device.

that the energy barrier exist in ITO/PANI/P3HT/LiF/Al device for electron and hole injection. The barrier height for hole injection from ITO electrode to P3HT is reduced by insertion of PANI-CSA film. Since the barrier height for hole injection is low, hole injection into P3HT is easier than electron injection. And the hole can easily be transported through P3HT. However, the electron injection from the Al electrode is difficult, because of energy barrier to electron. Therefore, electron shortage occurs during operating the device, resulting in unbalanced carrier injection.

The PL spectrum of P3HT layer and EL spectrum of ITO/PANI/P3HT/LiF/Al device showed in Figure 6. The PL and EL peak emission intensity of the spectrum are normalized. The emission peak of the PL and EL spectrum was observed around 650 nm.

## CONCLUSION

We investigated the electrochemical polymerization of PANI-CSA conducting film and the possibility of application as hole injection layer in ITO/PANI/P3HT/LiF/Al device. The electrochemically polymerized PANI-CSA films have the small particles of 1  $\mu\text{m}$  in diameter and relatively smooth and regular sufficient for application as hole injection layer. When the PANI-CSA film used as buffer layer, the turn on voltage of ITO/PANI/P3HT/LiF/Al device decreased than that of ITO/P3HT/LiF/Al device. If there are obtained the balance of carrier injection in EL device, PANI-CSA film role as effective buffer layer and enhance the efficiency of the device.

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