# PANI-CSA: An Easy Method to Avoid ITO Photolithography in PLED Manufacturing

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**Summary:** In order to optimize polymer light emitting diode (PLED) performances, devices with holes injected through an Indium Tin Oxide (ITO) / Polyaniline (PANI) electrode into the polymer are much more efficient than devices fabricated with the anode made only by ITO. We demonstrated that by using doped PANI as hole injection layer in a polymer light emitting diode the manufacturing process can become simpler. Indeed, the pattern of conductive layer can be produced without ITO photolithography by UV exposition. As hole transporter layer, Poly(*N*-vinylcarbazole) (PVK) was spin coated over the doped PANI layer and a layer of tris (8-hydroxy) quinoline aluminum ($Alq_3$) was then thermally evaporated so as to form the electron transport layer. To complete the device structure, Aluminum contacts were deposited onto the organic layers by vacuum evaporation at low pressure. The layers were characterized by X-ray small-angle diffraction, IR Raman and UV-Vis spectroscopies. Devices without PANI and with PANI as HIL were studied.

**Keywords:** conducting polymers; doped polyaniline; light-emitting diodes (LED); spin coating; UV patterning

## Introduction

In the last decade, the interest in Organic Light Emitting Diodes (OLEDs) has largely grown, since these devices represent a very promising technology for full color displays realization. The research is mainly concerning many aspects related to the possible commercialization. In order to realize organic light emitting displays on polymeric substrates, which are flexible and economics, polymers are more advantageous than small molecule organic materials. Indeed, polymers allow flatter surfaces [1], better mechanical properties suitable for flexible substrates [2], and moreover they are deposited by spin coating process, not requiring high temperature deposition procedures which give problems in the case of polymeric substrates.

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Conductive polyaniline were often applied as a hole injection layer. High molecular weight polyaniline (PANI), for instance, is insoluble in most solvents and many authors developed PANI deposition in PLED manufacturing by electrochemical deposition [3] and anodic synthesis [4]. In 1993, Heeger et al. [5] reported the use of functionalized protonic acid solutes to dope polyanilines as well to render the resulting polyaniline complex soluble in common organic solvents in its conducting form. However, doped PANI deposition by spin coating is hindered by the high surface tension of PANI solutions. In 2001 Wu et al. showed as polyaniline film deposited on ITO substrate has better adhesion compared to those deposited on $SiO_2$ substrate. [6]. We show a simpler method where before the doped PANI deposition the substrates treatment in piranha solution creates a very hydrophilic substrates and improves its wettability [7] and we report on a study on doped PANI as hole injection layer.

## Experimental

All reagents and solvents were purchased from Aldrich. Commercial indium tin oxide (ITO) ($t_1$ = 200 nm) glass substrates (Delta Technologies) have been used as transparent conductive oxide (TCO). Substrates were treated with surfactant in boiling water; for 2 h in an ultrasonic bath. After that, substrates were rinsed with isopropyl alcohol for 5 min and dried under a nitrogen flow. The substrates were after treated with an oxiding piranha solution (30% vol. $H_2SO_4$/ 70% vol. $H_2O_2$ in water) and then rapidly withdrawn from the solution, rinsed with deionized water and blown dry with $N_2$ gas. This procedure creates a very hydrophilic substrate and improves its wettability [7]. The metallic emeraldine salt form of PANI is prepared by protonation with camphor-sulfonic acid (CSA), yielding a conducting PANI complex soluble in common organic solvents [8]. PANI-CSA solutions (3.5% by weight) were prepared using meta-cresol as the solvent. PANI in its emeraldine base form is mixed with CSA in molar proportions of 1:0.5 of CSA to the nitrogen unit in polyaniline. The resulting mixture is placed in m-cresol and treated in an ultrasonic bath for 48 h at 50°C. The polyaniline complexes dissolve to yield a viscous deep green solution and a small amount of insoluble gels, which can be removed by filtration. A photoinitiator, 1-hydroxycyclohexylphenylketon, is added to this solution. The thin PANI-CSA film was spin coated from solution in m-cresol (3.5% by weight) onto a commercial ITO ($t_1$ = 200 nm) glass

substrates without to carry out before the ITO patterning by standard photolithography and then evaporating the solvent on a hot plate at 50°C. The PANI-CSA film is exposed in nitrogen atmosphere to deep ultraviolet (UV 250nm) radiation through a mask [9]. Upon exposure the conducting polyaniline is reduced to the nonconducting leucoemeraldine form. The sheet resistance then increases from $10^4$ Ω/square to more $10^{10}$ Ω/square. The photoinitiator in the non-exposed parts is then removed by sublimation through heating the film at 110°C. To carry out a polymer light emitting diode structure, poly(*N*-vinylcarbazole) (PVK) thin films were spun over the substrates at 1500 rpm from a 1.36 * $10^{-5}$ M chlorobenzene solution for 30s. After deposition the films were bached at 90°C for 3h. The spin coating process was developed using a Brewer Science Limited Model 100 Spin Coater. Tris (8-hydroxy) quinoline aluminum ($Alq_3$) has been deposited by thermal evaporation. The process has been performed in a High Vacuum chamber. The base pressure was $10^{-8}$ mbar. The layer thickness was 750 Å. Al cathode, 1600 Å thick, has also been evaporated as a final layer. The film thickness and roughness were evaluated by a KLA Tecnor P-10 Surface Profiler. Raman spectra of the polymeric films were recorded on a Renishaw Model inVia Raman microscope and the spectra were excited with the 514nm line. All the electrical measures were performed by an Hp 4140B pA meter/ DC voltage source. For the optical measurements the samples were prepared in a form of thin films spin coated on quartz plates. UV-visible absorption measurements were performed with Perkin-Elmer lambda 900 spectrophotometer.

The PANI-CSA films were structurally characterized by X-ray diffraction (XRD) measurements carried out both in classical Θ-2Θ configuration and in thin film configuration with an MPD-X'PERT (Philips) diffractometer using a Cu $K_\alpha$ radiation source. The measurements were performed in the 2Θ range of 3 – 40 degree, with a step of 0.02 degree and a time for step of 60 seconds. For this characterization the samples were prepared in a form of thin films spin coated on glass plates.

## Results and Discussion

The typical thickness of the PANI-CSA films was 0.3 μm. The topography of the exposed film is less than 60nm and thus further planarization steps were not necessary. The PVK film thickness deposited on the PANI-CSA layer was 90nm and roughness was less than 1nm.

Fig.1 shows the resonance Raman spectra of PANI powders and PANI-CSA film. The band observed at 1333 $cm^{-1}$ ($CN^{\cdot+}$ stretching) is the most characteristic Raman band of the radical cationic, and the expected increase of this band explains the quinoid rings conversion to benzoid rings. The bands at 1488 and 1590 $cm^{-1}$, assigned to C=N stretching of the quinoid di-imine units and to the C=C stratching of the quinoid ring respectively, are not observed in PANI-CSA spectra. The most intensified bands shown in PANI-CSA film are related to vibrational modes of benzoid units: the 1620 and 1189 $cm^{-1}$ corresponding respectively to the C-C stretching and C-H bending [10-12]. All these changes are consistent with the transformation of quinoid units into benzoid ones.

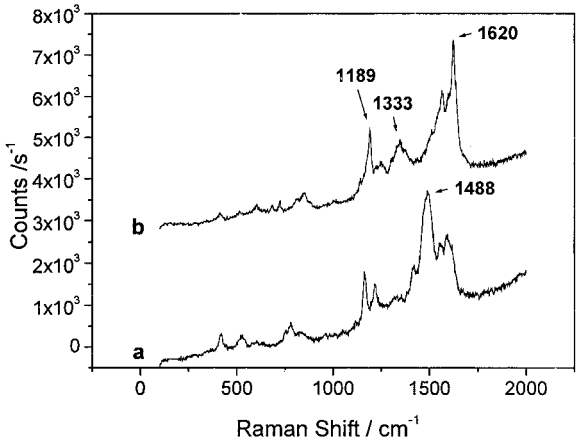


Figure 1. Resonance Raman spectra of PANI powders (a) and PANI-CSA film (b).

Fig. 2 shows the UV-Vis-NIR spectrum of PANI-CSA films in emeraldine salt and leucoemeraldine form. In the spectrum emeraldine salt form, a very broad band in the near IR region, assigned to free-carrier absorption [12-13], and a band located at about 430 nm, assigned to the radical cation segments [14], are observed. In the spectrum of leucoemeraldine form, the bands assigned to the protonated structure are not observed, because the conducting polyaniline was reduced upon exposure to deep ultraviolet radiation. The quinoid bands, 560/660 nm, are not observed in both spectra.

The basic correlations between the structure and electrical conductivity may be well studied for the PANI-CSA system [15]. The spectrum measured in classical Bragg-Brentano configuration shows sharp peaks indicating a crystalline material with oriented planes parallel

to the film surface. The presence of the same peaks, although with a changed intensity, in the spectrum measured in thin film configuration, confirms that the investigated film exhibits a highly oriented structure. The spectrum acquired in Bragg-Brentano configuration on the UV reduced film shows a complete amorphous structure (figure 3).

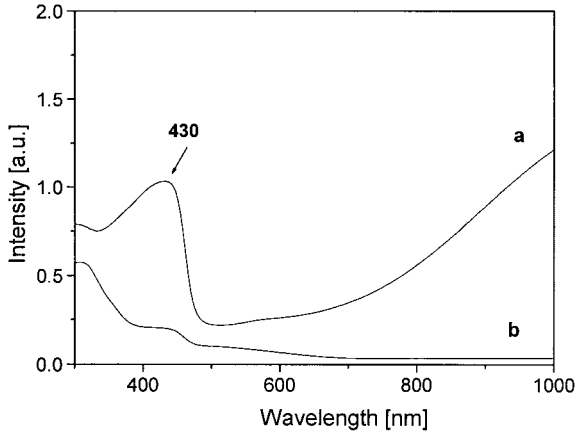


Figure 2. UV-Vis-NIR spectra of PANI-CSA films in emeraldine salt (a) and leucoemeraldine form (b).

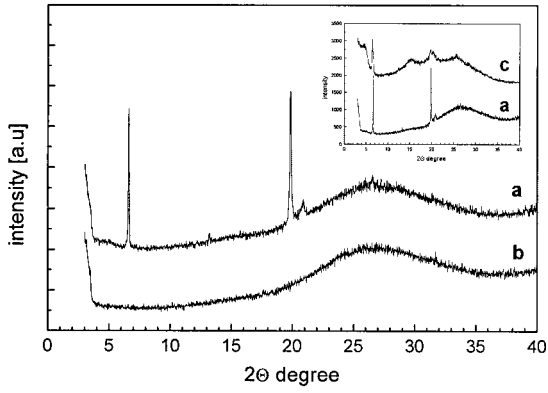


Figure 3. X-ray diffraction spectra of PANI-CSA films: spectrum in Bragg-Brentano configuration before (a) and after (b) reducing process; spectrum in thin film configuration before reducing process (c).

## Devices

We realized an array of luminescent devices. In order to fabricate physically separated pixels, a patterning of PANI-CSA and Al layers was realized. ITO, PVK and $Alq_3$ layers covered the whole device area. The single device had circular shape, 3mm diameter. The PANI-CSA patterning has been adopted instead of the traditional ITO patterning by photolithography. This procedure represents a simpler method than the ITO patterning and it is a modified version of the Heeger process [2]. Furthermore, it gives a flat surface, since no steps are created in the layer. This should lead to better properties of the interface with the organic transport layers. The tested base structure is the following device: glass as substrate; ITO as transparent anode; PVK as hole transport layer (HTL); $Alq_3$ as electron transport layer (ETL) and emitting layer (EL); Al as metallic cathode. This device (Fig. 4-1) has been compared with the one, obtained by placing a doped PANI layer between the anode and the HTL (Fig. 4-2), as hole injection layer (HIL). In the following, the device without PANI and with PANI as HIL will be referred as device 1 and device 2 respectively.

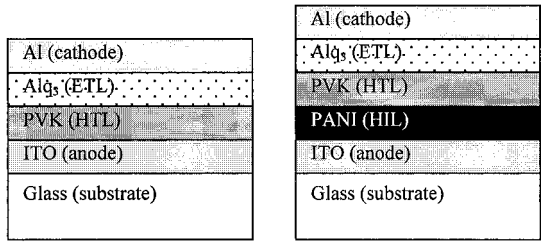


Figure 4. Devices structures 1) without and 2) with PANI layer.

The ITO work function is about 4.7 eV; PANI-CSA work function is about 0.1 eV higher [16]. This implies that a lower barrier is formed at the interface with PVK for the hole injection. Since the Highest Occupied Molecular Orbital (HOMO) of PVK is about 5.7 eV, the barrier reduction obtained by inserting the PANI layer is about 10% (Fig. 5).

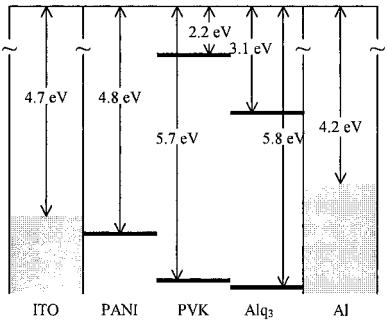


Figure 5. Device energy diagram.

In Fig. 6, a typical I-V characteristic of both devices is shown. The OLED turns out at about 17 V.

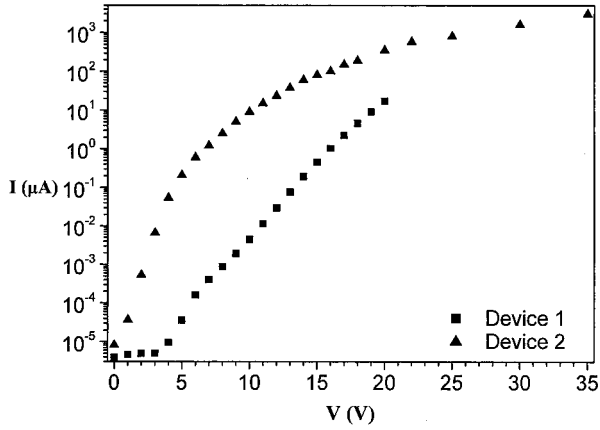


Figure 6. I-V characteristic of the device 1 (without PANI layer) and device 2 (with PANI layer).

In Fig. 7 and Fig. 8, a current density (J-V) characteristic of both devices and EL measurements for the device 2 are shown, respectively.

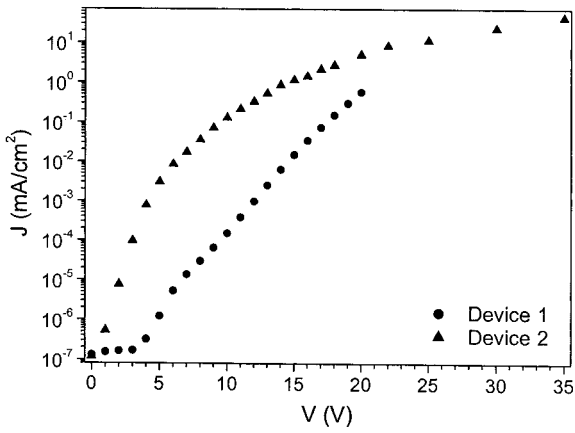


Figure 7. J-V characteristic of the device 1 (without PANI layer) and device 2 (with PANI layer).

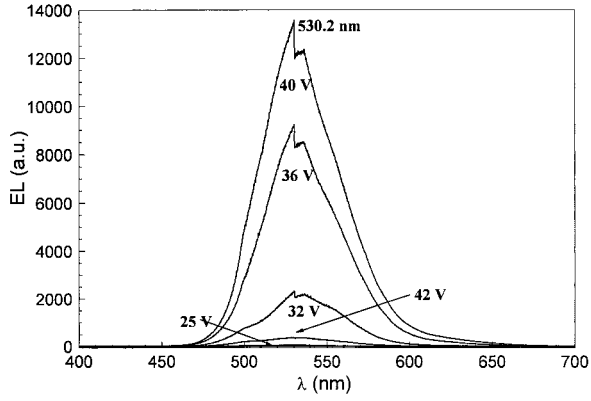


Figure 8. Electroluminescence spectra for the device 2 (device with PANI), acquired at several applied bias voltages.

The EL spectra reveal that the luminescence peak is located at lambda=530nm (green emission). It can also be noted that the device turn off at the voltage of 42 V, which is a quite high value. As a consequence of the PANI-CSA layer insertion, a lower turning on voltage has

been observed. Indeed, the device exhibited green light emission at about 11 V (no light was observed under reversed bias). Light emitting diodes fabricated by using semiconducting polymers are expected to exhibit carrier injection through tunneling mechanism [12]. In this regime, it has been predicted that the current voltage characteristic should satisfy the following relation:

$$I \propto V^2 \exp(-b/V) \qquad (1)$$

The parameter b takes into account the shape and the height of the tunneling barrier. The relation (1) can be linearized by plotting ln ($I/V^2$) as a function of 1/V. This is done in Fig. 9, where the linear shape is fairly evident. This plot confirms that the tunneling is the dominant channel for the carrier injection. The lower threshold voltage of the device 2 respect to the device 1, where the PANI layer is not present and the pixels are obtained by patterning the ITO anode, is probably due not only to the lower injection barrier. The flatter interface, as a consequence of the interposition of the PANI layer, probably also plays an important role in determining the better performances.

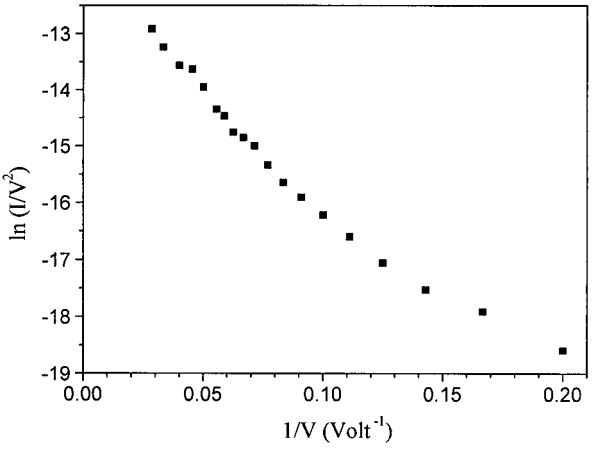


Figure 9. ln($1/V^2$) vs 1/V characteristic for the device 2 (device with PANI).

## Conclusions

In conclusion, we compared organic luminescent devices, realized with and without the presence of a PANI-CSA layer as hole injection layer.

The PANI-CSA layer is obtained by a simple chemical method, and deposited by spin coating. Furthermore, by placing and patterning this layer, the patterning of the ITO electrode by photolithography is not required. The structure was largely characterized both morphologically and structurally by a profilometer and X-Rays Diffraction; in the device with the PANI-CSA layer, better surface features and lower roughness.

From the comparison of the two different devices, we found that the turning voltage was lower in the one with PANI. This is probably due not only to the injection role of the PANI, but also to the flatter interface surface. The quantitative analysis of the I-V characteristics show that the tunneling is the dominant injection channel.

## Acknowledgement

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