Solution processed blue light emitting electrochemical cells fabricated and encapsulated fully in ambient environment

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***Abstract*—Light emitting devices such as OLECs are one form of electronic device that can be integrated into garments to realise light emitting textiles. In the development of wearable electrical devices, conductive organic materials such as conducting polymers, with the ability to emit light in almost all colours of the spectrum, could substitute expensive and complex in synthesis inorganic materials or metals. In this paper, we report the solution processed fabrication method of OLECs on ITO coated glass substrates using commercially available blue emitter (Merck NCMP) as the active layer. The fabrication and encapsulation process were done fully in the ambient environment for the first time. The optical and electrical performance of the blue emitting LECs have been demonstrated in operation in ambient environment. An encapsulation process was used to protect the glass based OLECs from oxygen and moisture, and to increase the stability and lifetime of the device performance as well as protecting against external physical damage. The devices show the brightness level of 472 cd/m^2 and the driven voltage of 6 V with bright light emission.**

Keywords — e-textiles, light emission, light emitting textiles, light emitting electrochemical cells, printing electronics.

I. INTRODUCTION

Solution processed electronics is a fast-growing research topic over the last two decades, particularly in light emitting devices. It is a field which brings together researchers from different disciplines including, novel chemical synthesis, material science, electronics, and deposition techniques, to investigate the feasibility and optimisation of solution processed light emitting devices to push the technology forward towards large scale commercialisation.

The use of organic light emitting diodes (OLEDs) is currently dominating the research activities. The organic light emitting electrochemical cell (OLEC) is another approach to realise light emission from a solution processed technique. Both OLEDs and OLECs thin film devices emit light, but their emitting colour is determined by the organic semiconductor energy gap. OLECs differ from OLEDs by the existence of mobile ions in the colour emitting active layer, which is not present or required in OLEDs [1, 2]. In addition, OLEDs require strict thickness control of each functional layer to achieve optimal levels of light emission, and the fabrication and measurement process must be undertaken under a high vacuum and/or in an inert atmosphere. In contrast, typical OLECs can be operated with a single colour emitting active layer sandwiched between two electrodes, thus removing many of the complex process steps involved in fabrication of an OLED device. The fabrication process for an OLEC device can typically use a set of cost effective and scalable solution processing techniques, for example, spray coating, and spin coating. In OLECs, the mobile ions blend internally [3] or externally [4] with the organic light emitting semiconductor in the active material master solution. Under biased condition, the mobile ions will re-distribute across the junction in the active layer. The electrons and holes formed within the active layer can be efficiently injected into a single layer of the OLEC active material from the top (cathode) and bottom (anode) electrodes, resulting a bright light emission [5-8]. However, during light emission, the devices must be encapsulated from the ambient environment, due to the organic light emitting semiconductor's un-stability when exposing to the oxygen and humidity.

Shi et al reported a solution-processed tri-layer light emitting p-n junction device architecture which is comprised of two hydrophobic conjugated layers with a hydrophilic intermediate layer in between. They demonstrated that the mobile ions residing in the conjugated polymer can redistribute and allow electrochemical doping when the voltage is applied. This p-n junction device emits blue light with wavelength at 450 nm and 484 nm, its high efficiency is achieved at 5.3 cd/A with a low drive voltage of 5 V [9]. J. Shu et al demonstrated a fully solution processed organic blue OLEC, using a combination of inkjet printing and spin-coating techniques, for on-chip fluorescent sensing. This prototype, achieved on an ITO glass substrate, with fabrication in a low temperature ambient environment, yielded a brightness of more than 2000 cd/m^2 and stability of more than 1000 cycles [10]. The same research group has reported the first fluorescence organic photodiode light detector on ITO glass slide, integrating a fully solution processed blue OLEC in a microfluidic chip. The blue OLEC was used as the excitation source, achieved brightness more than 2800 cd/m^2 at 50 V [11]. Recently the authors have demonstrated spray coated super yellow (SY) OLECs on flexible woven textile substrates [3, 4]. The encapsulated SY textile devices were scanned at different voltages to get the maximum brightness of 80 cd/m^2 at the voltage of 11 V. The reference OLECs

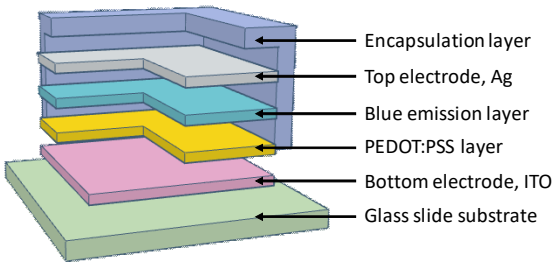

Figure 1 Schematic representation of the Merck blue (NCMP) OLECs on glass slide substrate using the standard OLEC device architecture of Glass/ITO/PEDOT:PSS/NCMP/Ag/Encapsulation.

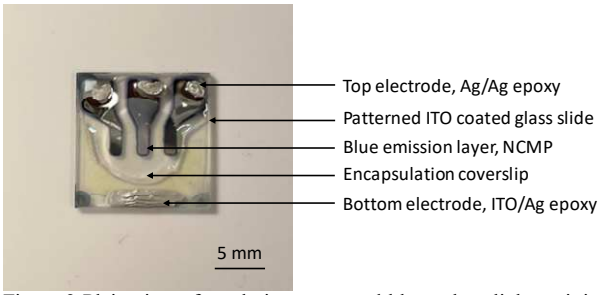

Figure 2 Plain view of a solution processed blue colour light emitting electrochemical cells on ITO glass slide, with the encapsulation of coverslip on top bonded by the UV curable epoxy.

fabricated on glass counterpart have achieved 200 cd/m^2 in brightness at 10 V. In both glass and textile substrates the turn on voltage were demonstrated at 5 V and 10 V, respectively [12]. In this paper, we fabricate OLECs using blue emitting polymer as a colour emitting active layer on ITO glass substrates. The thickness of PEDOT:PSS and active layer has been preliminarily optimised via spin coating technique and encapsulated via optical grade epoxy to achieve a set of prototypes with good optical performance via electrical biasing.

II. Fabrication of OLECs

In this section, the materials and fabrication detail are described in the sequence of the deposition, together with the blue light emitting active ink formulation. The blue colour OLECs are solution processed with a standard LEC device architecture, as shown in Figure 1. The fabricated blue emitting OLECs prototype is shown in Figure 2. The fabrication started with the indium tin oxide (ITO) pre-coated glass slide substrates (Guluo Glass, China), the slides were cleaned with IPA and acetone solvents prior to the fabrication of LEC devices, to achieve a homogeneous surface energy for the subsequent functional layer deposition. Then PEDOT:PSS (Clevios P VP 4083, Heraus) was spin coated on to the ITO glass substrates and annealed at 120 °C on a hot plate for 20 minutes. Subsequently, the blue colour emitting active layer was spin coated and annealed at 120 °C on a hot plate in ambient air condition for 30 minutes. The active material blend solution was prepared from separate master solutions of the light emitting polymer: (1) blue emitting polymer (NCMP, Livilux, Merck), (2) the ion-dissolving polymer, Trimethylolpropane ethoxylate (TMPE-OH, average Mn ~450 g/mol), Sigma-Aldrich), and (3) the salt, potassium trifluoromethanesulfonate (KTF, ~98%, Sigma-Aldrich). The TMPE-OH and KTF were separately dissolved in cyclohexanone (~99%, Sigma-Aldrich) to form master solutions, both solutions were at 10 mg/ml concentration. The NCMP master solution was prepared in a 10 mg/ml in cyclohexanone solvent. When making the blend solution, 1 ml of TMPE-OH solution and 0.2 ml of KTF solution were added into the NCMP master solution with the ratio of 1:1:0.2 to NCMP, TMPE-OH and KTF respectively. After mixing of the three solutions, the active material blend solution was stirred overnight at room temperature to achieve a homogenous solution before deposition. Finally, the sputter coating of silver (Ag) top electrode was deposited in the vacuum chamber at 2x10^{-2} mbar. Ag conductive paint is applied on top of the sputter coated Ag top electrode to form a robust contact point for testing purposes. To complete the device fabrication, all glass devices were encapsulated with cover slips and UV curable epoxy (Norland, NOA 61), which was then UV cured for 60 seconds to get a highly transparent and robust epoxy layer for encapsulation, to provide the protection for the cells operating in ambient environment.

III. Results and Discussion

Optical properties of blue emitter are pre-assessed prior to device fabrication, using the ultraviolet/visible (UV/Vis) spectrophotometer and photoluminescence (PL) by laser excitation. Figure 3 (a, b) exhibit the absorption spectra plots of both blue emitter in dilute cyclohexanone solution and thin film states at room temperature. The absorption spectra show the absorption peak around 404 nm on the solution state and the same wavelength for the thin film state which is π-π* transition of the blue polymer. The polymer is excited at the available laser diode of 340 nm wavelength and exhibited the deep emission peak for solution and a clear visible emission peak for solid thin film. As shown in figure 3 (c, d) the PL intensity spectrum plots were obtained from both the solution and the thin film state of blue emitter. The solution state PL plot shows a light sky-blue emission peak at 500 nm. Annealed blue emitter thin film's PL emission peak was observed at 495 nm with shoulder peaks of 422 nm and 447 nm. The blue emitter thin film PL spectra peak is slightly blue shifted around 5 nm compared to its solution PL emission which arises due to the close packing of the dense polymer in the thin film state.

The LEC devices were prepared on ITO coated glass substrate. The fabricated device consisting active materials with the structure of Glass/ITO/PEDOT:PSS/NCMP/Ag. To increase the cells reproducibility, we target the functional layers of the blue emitter and PEDOT:PSS to around 100 nm thick from spin coating technique. The cells have been tested against the IV sweep from 0 V to 8 V. Figure 3 (e) shows the IV plot of the blue colour OLEC, which demonstrates a very low turn on voltage of 2 V, then saturated from 3.5 V. EL spectra were measured by using constant voltage biasing across the cell. Figure 3 (f) shows electroluminescence (EL) spectra of blue region with the maximum peak at 512 nm. The EL spectra peak on the plot was shifted to longer wavelength as compared to their PL spectrum due to the intermolecular interaction in solid state of blue polymer. Lumen measurement depicts the maximum brightness of 472 cd/m^2 with low turn-on voltage of 2 V. This study reveals that the optimised devices can be utilised to fabricate fully solution processed

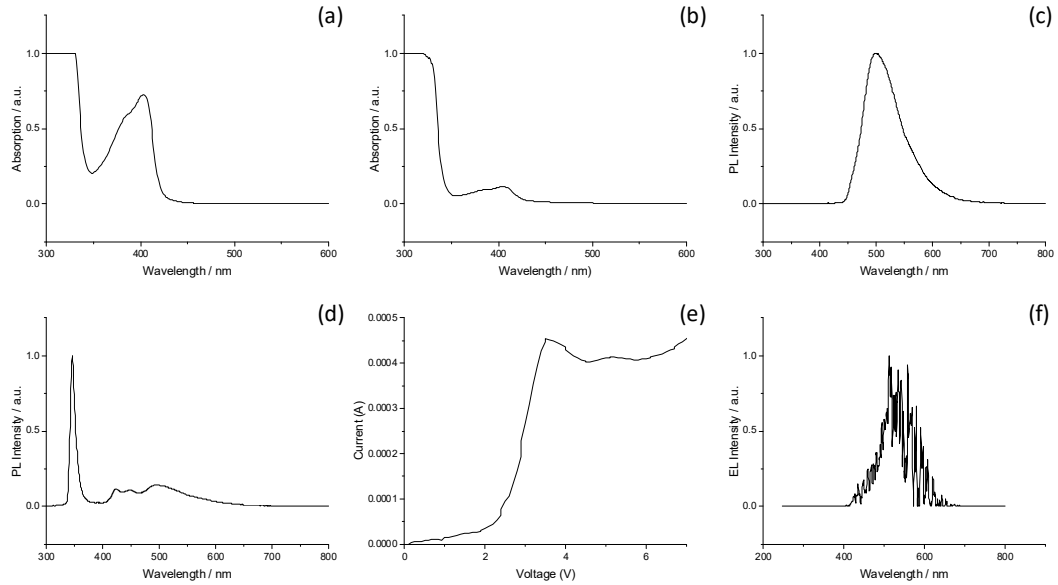

Figure 3 (a) UV/Vis absorption spectrum of Merck NCMP dissolved in cyclohexanone solution, (b) UV/Vis absorption spectrum of NCMP thin film, annealed in a box oven at temperature of 80ºC for 10 minutes, (c) Photoluminescent (PL) intensity spectrum obtained by laser excitation on the Merck NCMP in cyclohexanone solution, (d) PL intensity spectrum obtained by the laser excitation on the Merck NCMP thin film, (e) IV curve of the blue colour OLEC, and (f) Electroluminscent (EL) intensity spectrum obtained by electrical biased at 6 V on the NCMP OLEC.

OLEC devices. Eventually the device configuration will be used to fabricate OLECs on the textile substrates to realise light emitting e-textiles.

IV. Conclusions

Blue emitting OLEC devices have been successfully fabricated and encapsulated, in an ambient atmosphere, on ITO pre-coated glass substrates. Commercially available blue emitting polymer was utilised as the active layer. The PEDOT:PSS and blue emitter layers are around 100s nm each to get bright light emission devices and good junction resistance. All glass slide based devices were encapsulated in ambient environment to protect the devices from oxygen and moisture and also to increase durability of the devices. The device demonstrated low voltage of 6 V with the brightness level of 472 cd/m^2. These results indicate the importance of the development of the low voltage flexible colour displays, and its potential to realise the wearable light emitting textiles.

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