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Fully Solution Processed Organic Light-emitting Electrochemical Cells (OLEC) with ZnO Interlayer for Lab-on-Chip Applications

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Abstract

Microfluidic lab-on-a-chip devices can be used for chemical and biological analyses such as DNA tests or environmental monitoring. In order to make a monolithic and cost-efficient/disposable sensing device, direct integration of excitation light source for fluorescent sensing is often required. A manufacturing process for fully solution-processed blue organic light-emitting electrochemical cells (OLECs) is presented, which consist of pre-patterned ITO, spin-coated ZnO buffer layer and blue light-emitting polymer plus dopants and an inkjet-printed PEDOT:PSS transparent top anode. Furthermore, the fully transparent blue OLEC is able to emit > 2000 cd/m^2 light under pulsed driving mode, which fulfils requirements for simple fluorescent on-chip sensing applications. Furthermore, ITO electrodes can be replace by PEDOT:PSS transparent electrodes when a ZnO interlayer is solution processed on top, which enable the mask-free and fully solution processing integration on chips.

Introduction

Thanks to significant demands for low-cost and disposable biological/medical sensing devices, tremendous efforts have been made to develop microfluidic lab-on-chip systems for point of care applications[1]. Microfluidic chips are miniaturized microanalysis labs fabricated on compact chip substrates, in which small fluid volumes can be controlled, mixed, and analyzed. In order to realize most of the basic functionalities required for the analysis on a microfluidic chip without external components, functional units such as valves, pumps, heaters, fluorescent light sources, and detectors are required[2]. Although fluorescent sensing is the most common analytical and diagnostic method in biological and medical applications, very few examples of fully integrated compact and low cost fluorescence sensing systems on microfluidic chips can be found[3]. This is mainly because widely used sensing units are based on lasers, LEDs, and silicon photodiodes that are normally integrated in a hybrid way by bonding. Organic light emitting diodes (OLEDs) have the advantages of self-emitting properties, high luminous efficiency, full-color capability, wide viewing angle, high contrast, low power consumption, low weight and flexibility. All these make OLEDs a suitable light source for microfluidic devices[4]. However, a low work function cathode and/or electron injection layers like Ba, LiF are indispensable for high brightness OLEDs, which require vacuum deposition and an inert fabrication atmosphere[5]. It is known that deep blue light (~ 480 nm) is widely used as the excitation light for medical fluorescent sensing applications. However, OLEDs in blue color normally show low efficiency due to high energy gap.

Hereby we introduce a fully solution processable deviation of OLEDs, organic light-emitting electrochemical cells (OLECs) as a low-cost excitation light source for a disposable microfluidic sensing platform. By mixing metal ions and a solid electrolyte with light-emitting polymers as active materials, an in-situ doping and in-situ PN-junction can be generated within a three layer sandwich device. Thanks to this doping effect, work function adaption is not necessary and air-stable electrode such as PEDOT:PSS and silver can be used[6]. Consequently, the in-situ generated PN-junction enable the relatively thick active layer (up to 1000 nm rather than ~ 80 nm for OLEDs), which is in favor of solution-processing such as spin-coating and inkjet printing. An ambient manufacturing process for fully solution-processed blue OLECs is presented.

Experimental

Material: Blue and yellow light-emitting polymer were purchase from Merck KGaA. Solid electrolyte dicyclohexano-18-crown-6 (DCH18C6), Poly(ethylene oxide) (PEO), salt Lithium trifluoromethanesulfonate ($LiCF_3SO_3$), Potassium trifluoromethanesulfonate (KCF_3SO_3) and ZnO precursor Zinc acetylacetonate hydrate ($Zn(acac)_2$) were purchased from Sigma-Aldrich. To prepare the blue OLEC ink, polymer was first dissolved into toluene, and followed by DCH18C6 and $LiCF_3SO_3$ to obtain polymer volume concentration 10 mg/mL and 1 : 0.1 : 0.02 mass ratio of polymer, DCH18C6 and $LiCF_3SO_3$[7]. The ink was stirring overnight and heated at 50 °C. The ink was filtered through 1 µm pore size PTFE filters before use. The SuperYellow OLEC ink follows the same procedure, but with different solid electrolyte PEO and metal salt KCF_3SO_3[8]. The solvent was cyclohexanone instead of toluene. The so-called high conductive PEDOT:PSS inks (PEDOT:PSS P Jet HC V2 and 700N) were purchased from Heraeus. The PEDOT:PSS ink was filtered through 0.2 µm pore size filters before injection into printer cartridge. Pre-patterned ITO glass substrates and encapsulation epoxy were purchased from Ossila Ltd.

Equipment: An Unijet Omni-100 inkjet printer (Unijet, South Korea) with a DMC printhead with 10 pL nozzles was used for inkjet printing experiments. A Zygo white light interferometer was used to measure the layer thickness and surface profile. A Plasma oven with 2.4 GHz generator with argon and oxygen flow was used for surface activation.

Solution processed blue OLEC on ITO fabrication: Pre-patterned ITO substrates were cleaned in a series of ultrasonic baths with various tenside. Afterwards, substrates were activated by oxygen ambient atmosphere plasma (200 W, 2 min). Then, 10 mg/mL OLEC ink was spin-coated with 1000 RPM, 60 s and wiped with Q-tips. Sample was then treated by an ambient atmosphere argon plasma treatment (50 W, 30 s) to achieve good wetting for PEDOT:PSS layer deposition. Transparent conductive PEDOT:PSS layer was inkjet printed with a dot-spacing 40 µm on top of the active layer. Finally, encapsulation epoxy was drop-cast and covered by a glass coverslip right after

15 min vacuum drying in order to remove oxygen content within devices. Encapsulation was completed by a short UV irradiation.

Fully solution processed yellow OLEC fabrication: Glass substrates were cleaned by acetone and dried by nitrogen flow. PEDOT:PSS layers were inkjet printed with a dot-spacing 40 µm, and annealed at 150 °C for 10 min. Then, 20 mg/mL $Zn(acac)_2$ in ethanol was spin-coated with 1500 RPM, 45 s. A ZnO layer was generated by annealing the sample at 120 °C for 45 s. Afterwards, 10 mg/mL SuperYellow OLEC ink was spin-coated with 1000 RPM, 60 s and wiped with Q-tips. The rest procedure is the same as samples fabricated on ITO substrates.

Results and discussion

As it can be seen from

Figure 1, thanks to the benefit of in-situ doping, the basic layer structure only consists of an ITO cathode, a spin-coated blue light-emitting polymer plus dopants on ITO and an inkjet-printed PEDOT:PSS transparent top anode, which is much simpler for solution processing, in particular inkjet printing. Lithium triflate is chosen as the dopant salt because of its good electrochemical behaviors in batteries. While DCH18C6 is selected for the solid electrolyte due to its good ionic solubility and compatibility with light-emitting polymers and non-polar solvents. Moreover, with this electrolyte, the fabricated OLECs can achieve much faster turn on time when the P-i-N junction is frozen at room temperature[9]. The mechanism is mainly because that crown ether has a melting point of ~50 °C, and it shows good ionic conductivity only when the temperature is higher than the melting point. Therefore the OLEC can show fast turn on if it is first doped at elevated temperature and "frozen" at room temperature.

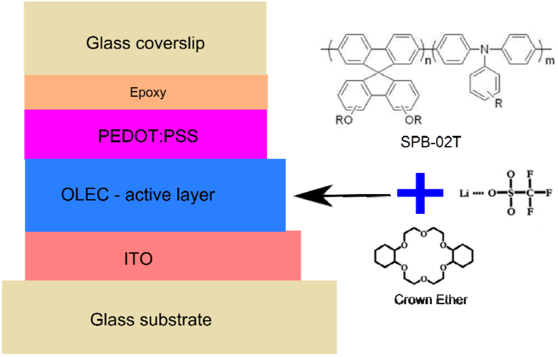

__Figure 1__, Layer architecture diagram of fully solution processed blue OLEC on ITO

The device did not emit more light at relatively low driving voltage (< 15 V), because the work-function of oxygen plasma activated ITO is higher than silver, which hinders the electron injection speed. However, when the blue OLEC on ITO sample was driven at pulse mode with much higher voltage (e.g. 45 V), a much higher brightness was achieved (see **Figure 3a**). The main reason could be the highly homogeneous surface of ITO electrode, which led to homogeneous pixel (see **Figure 2a&b**).

The device emits low light intensities at relatively low driving voltages (< 15 V). This is likely because the work-function of oxygen plasma activated ITO is relatively high (~ 4.8 eV), which hinders the electron injection capability. However, when the blue OLEC on ITO sample was driven at pulsed mode with much higher voltages (e.g. 45 V), a much higher brightness was achieved (see **Error! Reference source not found.**a).

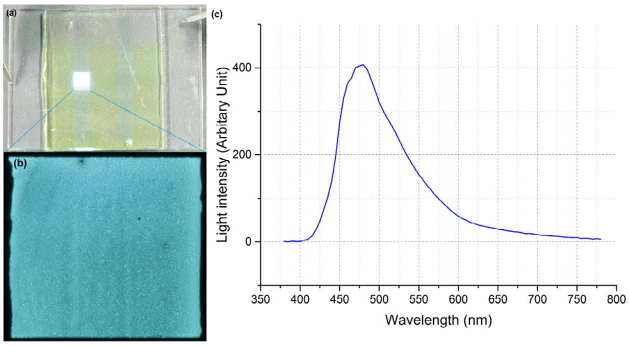

__Figure 2__, (a) Photograph of a blue OLEC on ITO sample with an illuminated pixel; (b) Photograph of a working pixel (1.5 mm × 1.5 mm); (c) electro-luminescence spectrum of fully solution processed OLECs on ITO

For disposable lab-on-a-chip fluorescent sensing applications, brightness higher than 2000 cd/m^2 and a moderate lifetime are required. The first lifetime measurement was test by pulse the OLEC on ITO sample with 100 ms on and 3 s intervals with > 2000 cd/m^2 brightness. The result was plot in **Figure 3b**. It can be seen that the sample is relatively stable form 1000 pulse operation, which is suitable for the basic disposable on-chip sensing applications[10]. .

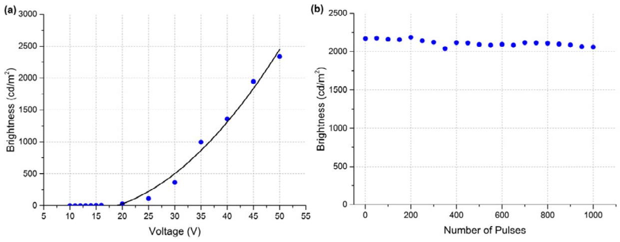

__Figure 3__, (a) Voltage – brightness curve of a blue OLEC sample driven at pulse voltage mode; (b) 1000 pulses lifetime measurement of a blue OLEC on ITO driven at pulse voltage mode with 100 ms on duty and 3 s interval.

In order to achieve fully integration organic light source directly on microfluidic chips, ITO electrodes need to be replaced because it is non-solution processable and high cost. The most straight-forward method is to simply replace ITO layer by a PEDOT:PSS layer, however it does not work well. It has also been found out that certain work function adaptation is still necessary to realize good performance[11]. Therefore, a solution processable buffer layer is necessary. ZnO is widely researched transparent electrodes for replacing ITO, and it can be solution processed through precursor and thermal decomposition under humid atmosphere[12]. Consequently, ITO electrodes can be replaced by an inkjet printed PEDOT:PSS layer and a spin-coated ZnO layer, so a really fully solution processed and mask-free organic light source can be directly integrated on chips. For the first test, more stable and efficient light emitting polymer SuperYellow was test in this ITO-free layer stacks. Figure 4 illustrates the working yellow OLECs without ITO. The ITO-free, fully solution processed blue OLECs is under investigation.

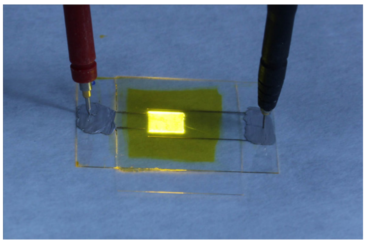

Figure 4, photograph of fully solution process yellow OLEC on glass substrates with a layer stack of PEDOT:PSS // ZnO // OLEC // PEDOT:PSS. The illuminated pixel has a dimension of 5 mm x 5 mm and it is driven at 15 V

1. Conclusion

In this paper, we demonstrated a fully solution fabrication process of blue organic light-emitting electrochemical cells (OLECs) combined by inkjet printing and spin-coating. As a low temperature, fully under ambient conditions and with only a short vacuum drying fabrication process, it is a promising light excitation source for portable and disposable lab-on-a-chip systems which require on-chip fluorescent sensing. By replace the silver cathode with ITO electrode, a brightness of > 2000 cd/m^2 and stable > 1000 cycles were achieved, which fulfils the basic requirement for on-chip fluorescent sensing. The on-chip fluorescence/absorption sensing test with inkjet printed organic photodiodes is under investigation and will be present in the near future. Moreover, the ITO electrode can be replaces by inkjet printed PEDOT:PSS layer and spin-coated ZnO layer, which provides mask-free and low cost integration on microfluidic chips.

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