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Half-gate light-emitting electrochemical transistor to achieve centered emissive organic p–n junction

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ABSTRACT

Organic light-emitting electrochemical cells (LEC) are promising for lighting applications but in many cases these devices suffer from unbalanced electrochemical doping, which cause instability and degradation of the cells. A predominant p-doping over n-doping causes an off-centered emissive p–n junction, which leads to poor power-conversion efficiency. Here, we report a half-gate LEC transistor (HG-LECT), in which an ion-conductive gate made from poly(3,4-ethylenedioxythiophene)-poly-(styrenesulfonate) is employed to combat this instability problem. The gate material, covering half of the channel, is used to enhance the n-doping process in this part by employing an appropriate operation protocol. We demonstrate a centered light emission zone, closely following the geometry of the gate configuration. The HG-LECT with centered emission profile is shown to be more efficient than the corresponding LEC without the gate electrode, and its n-doping level is measured to be 15%.

1. Introduction

The electrical conductivity and electroluminescence of organic conjugated semiconductors, together with their processability, such as using inexpensive solution-based fabrication, are together attractive properties that may pave the way for radically novel light-sources. After the invention of organic light-emitting diodes in 1990 [1], other organic optoelectronic devices have been demonstrated, such as light-emitting electrochemical cells (LEC) [2–4] and light-emitting transistors (LET) [5–8].

Conventional LECs include a single electroluminescent layer sandwiched between two charge-injection electrodes. The electroluminescent material is usually a mixture of a light emitting polymer (LEP) and an electrolyte. Upon application of a voltage difference at the electrodes, ions redistribute within the LEP, leading to a p-doped region close to the anode and an n-doped region close to the cathode. The injected electrons and holes flow through the n- and p-doped LEP and recombine at the organic p–n junction to generate light emission.

Several groups have tried to apply the transistor structure in LECs, in order to simultaneously modulate the doping profile in the LEP material, the charge transport characteristics and photon generation. Adding a metal gate and a conventional gate insulator (such as inorganic SiO_2 or organic materials poly(vinyl alcohol)) to the LEC structure enables the control of electric current [9,10] as well as the intensity of the luminescence [11]. However, this approach requires a high operating voltage at the gate electrode as the electrostatic coupling between the gate and the LEP is weak. Bhat et al. employed a metal gate with an ion gel as gate insulator on the foundation of an LEP [12]. This transistor configuration leads to low gate-voltage operation due to the electrochemical doping between gate and LEP, but the device displays an emissive zone in proximity to the electron injection electrode (cathode), showing a lack of n-doping in the LEP. Indeed, a light-emitting junction adjunct to the cathode is one of the common

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drawbacks in LECs [13–16], as it leads to photon quenching at the electrode and decreases the power-conversion efficiency of luminescence in the device. The lack of n-doping is mainly due to that the reactants, which are involved in the n-doping process, are partially consumed in undesired electrochemical or chemical side-reactions [15,17] resulting in a dominant p-doping. To achieve balanced p- and n-doping for a centered emissive junction, n-doping needs to be favored. We have previously developed a class of light-emitting electrochemical transistors (LECT), with a polymer electrolyte as the gate insulator and a poly(3, 4-ethylenedioxythiophene)-poly-(styrenesulfonate) (PEDOT:PSS) as the gate electrode. The first generation of those LECTs includes a PEDOT:PSS gate that fully covers the channel. It was shown that both the p- and the n-doping region can be modified by the gate electrode, and an emissive p–n junction can be spatially controlled within the LEP channel [18]. The second generation of LECT features two gates, which controls n- and p-doping separately; it demonstrates a more static and centered p–n junction located between the two gates [19], thanks to a more balanced doping profile. The double-gate LECT provides a platform to study the physics of LECs when n-doping and p-doping are decoupled. However, if one only desires a centered emission zone aiming to maximize the efficiency in practical applications and to stabilize the emitting zone, we found that in the double gate configuration, the gate electrode responsible for controlling the p-doping can in fact be omitted. In this letter, we consequently demonstrate a half-gate LECT (HG-LECT), with a gate electrode partially covering the LEP channel that controls only the n-doping process. In this device, we demonstrate that a centered emission zone is achieved after a two-step operation protocol. We also compare the efficiency of devices with and without the gate electrode.

2. Structure, materials and operation modes

The HG-LECT, as shown in Fig. 1a, was fabricated on a SiO_2/Si substrate, where Au electrodes with a spacing of 500 μm were thermally evaporated through a shadow mask. Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV, Mn = 40,000–70,000, Sigma–Aldrich) dissolved in chloroform with a concentration of 10 mg/ml was spin-coated onto the substrate at 1000 rpm for 60 s, and then dried at 90 °C for 100 s, forming a dry film of 200 nm thickness. A drop of the electrolyte solution was then employed onto the MEH-PPV film, before a free-standing sheet of PEDOT:PSS (Orgacon EL-350, Agfa) was pressed onto the electrolyte drop with the PEDOT:PSS electrode facing down. The electrolyte solution was made by blending poly(ethylene oxide) (PEO, Mw = 600,000, Aldrich) and CF_3SO_3K (98%, Aldrich) with a mass ratio 5.4:1 into a 3:1 v/v mixture of 1-propanol (Sigma–Aldrich) and deionized water, followed by stirring on a hotplate at 90 °C for 24 h. Finally, the device was dried inside a cryostat, under a vacuum of 2×10^{-5} mbar at 70 °C, for 12 h. The bottom electrode directly beneath the gate electrode is here termed the cathode, and the other bottom electrode is termed the anode.

Two operation modes of the HG-LECT are introduced as follows: *n-doping mode* and *electroluminescence* (EL) *mode*. In n-doping mode, a voltage of 4 V is applied at the gate electrode in reference to the cathode, with the anode kept floating; see Fig. 1b. The further oxidation of PEDOT, in the PEDOT:PSS gate electrode, causes a cation migration within the electrolyte layer, which diffuses into the LEP layer causing reduction the conjugated polymer. By applying this process for sufficient amount of time, the part of the LEP below the gate terminal becomes n-doped, leaving the part of the LEP without gate coverage neutral. In EL mode (followed by n-doping mode), a potential of 4 V is applied between the anode and the cathode, with the gate voltage of 4 V still applied. This operation promotes p-doping of the previously neutral part of the LEP and also further enhances the n-doping level of LEP material located under the gate. Since the n-doping progresses relatively slower than p-doping, we expect that the p–n junction forms in close vicinity of the edge of the gate terminal, as shown in Fig. 1c. The application of the gate voltage continuously enhances the n-doping territory so that the p–n junction is stable after it is formed.

Electrical characterization of the HG-LECT was performed under vacuum in a cryostat using a Keithley 4200 Semiconductor Characterization System. An HG-LECT with the gate covering 50% of the channel (as shown in Fig. 2a) was operated following a two-step protocol: (1) 100 s of n-doping mode, by application of 4 V at the gate terminal and (2) 1000 s of EL mode by application of 4 V at the gate and

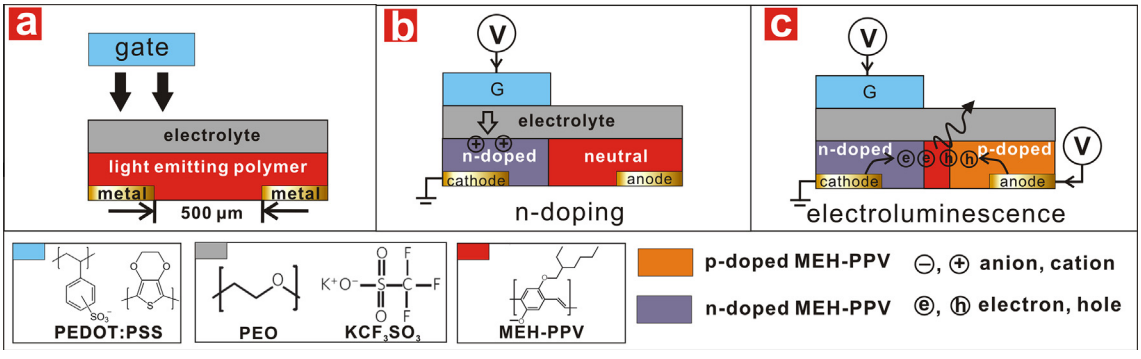

Fig. 1. The structure and operation modes of HG-LECT.