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Organic photodiode for detection of herbicides in water using microalgal photosynthesis

V. Ventalon, F. Sekli, R. Izquierdo, P. Juneau, A. Tsopela, J. Launay, V. Bardinal, P. Temple-Boyer, L. Salvagnac, I. Séguy, E. Bedel-Pereira

Abstract—The growing interest for monitoring the quality of water has triggered the need of fast, portable and cheap detection systems. To answer this problematic, we developed a lab on a chip for herbicide detection based on micro algal photosynthesis. A blue organic light-emitting diode is used as the excitation source while the resulting algae luminescence is monitored using an organic photodiode (OPD). During the OPD optimization process, a correlation between fullerene acceptor concentration and dark current was supposed. Using a blend of DTS(PTTh₂)₂:PC₆₀BM without interfacial layers result in dark current lower than 10⁻⁶ mA/cm² at -2 V and EQE higher than 50% in the region of interest.

I. INTRODUCTION

Herbicides easily penetrate the soil, degrade slowly and accumulate in the environment particularly in river and groundwater [1]. Their detection and quantification are done in laboratory, using gas and liquid spectroscopy for product separation and mass spectroscopy is mostly used for quantification and identification of products. These techniques are very sensitive, selective and robust [2]. However, these protocols are costly in term of money and time. For a better monitoring of water quality, there is a need of rapid and low-cost on-site analysis systems.

Biosensors are analytical tools that used a biological element to interact with the analyte and a transducer to measure biological changes. By their nature, herbicides have a high impact on microorganism like algae making them ideal bioreceptors. Both luminescence and O₂ production are affected through photosynthesis perturbation [3]. Fast herbicides impact permits measurements to be done within a few minutes with great sensitivity and low limit of detection [4-5].

The lab on chip developed presents a microfluidic channel to inject mixture of the sample solution and algae *Chlamydomonas reinhardtii* in the analysis chamber. An organic light-emitting diode (OLED) and an organic photodiode (OPD) are disposed on each side of the fluidic chamber as excitation and detection systems respectively (Fig. 1). In accordance with algae absorbance (Fig. 2), a blue OLED (400 – 550 nm emission range) is used to stimulate algae photosynthesis process without interfering with algae luminescence signal. A 550 nm long pass excitation filter is associated to the optical detection in order to prevent excitation light to reach the OPD.

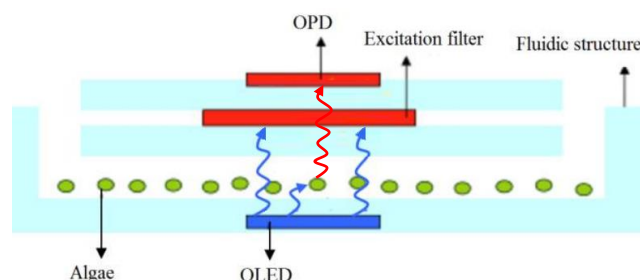


Figure 1: Schematic overview of the lab on chip.

II. ORGANIC PHOTODIODE

The prerequisite for photodiode integration in optical sensor systems is: (i) high external quantum efficiency (EQE) matching with biosensor emission spectra, and (ii) low dark current i.e. high “on/off” ratio in order to detect small luminescence intensities. OPD are a promising alternative to silicon-based photodetectors. They present high sensitivity in visible wavelength range, low dark current and are cheap to manufacture [6]. The basic structure of an OPD is an organic heterojunction constituted of an electron donor (D) and an electron acceptor (A) sandwiched between metallic and transparent electrodes.

In our system, the choice of D and A OPD materials is fixed by *Chlamydomonas reinhardtii* maximum luminescence emission at 700 nm (Fig.2). Hence, new low band gap donor molecules or polymers associated with fullerene derivatives are promising for our application [7]. They show power conversion efficiency (PCE) above 9% highly due to strong light harvesting and electronic conversion between 500 nm and 750 nm. In this work, small molecules are preferred because it means more batch-to-batch reproducibility, which is required to develop stable monitoring systems.

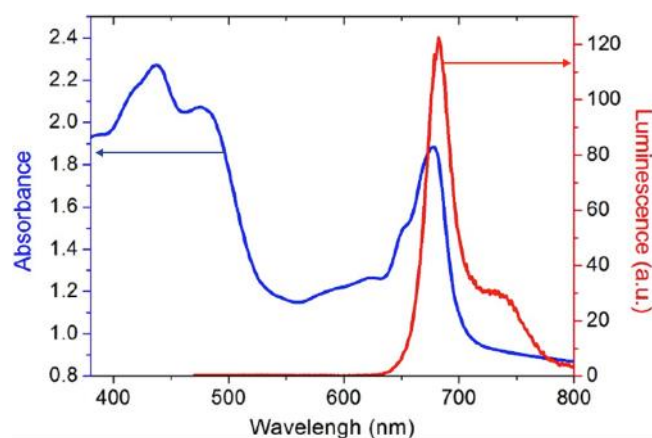


Figure 2: Absorbance (blue line) and luminescence (red line) of 6×10^6 cells of *Chlamydomonas reinhardtii* per milliliter of water.

V. Ventalon (corresponding author, phone: +33 6 42 06 31 05; e-mail: vventalo@laas.fr), F. Sekli, V. Bardinal, R. Izquierdo, P. Juneau, J. Launay, P. Temple-Boyer, L. Salvagnac, I. Séguy, A. Tsopela and E. Bedel-Pereira are with CNRS, LAAS, 7 avenue du colonel Roche, F-31400 Toulouse, France and Université de Toulouse, UPS, LAAS, F-31400 Toulouse, France. R. Izquierdo and P. Juneau are with Université du Québec à Montréal ; 201 Président Kennedy ; Montréal, Canada.

Thus, we choose to study OPD based on 5,5'-bis{(4-(7-hexylthiophen-2-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine}-3,3'-di-2-ethylhexylsilylene-2,2'-bithiophene DTS(PTTh₂)₂ as electron donor (D) associated with [6,6]-phenyl-fulleren (C₆₀ or C₇₀)-butanoate methyl (PCBM) which seems to fit with the LoC system [8].

III. PHOTODIODE OPTIMIZATION

The studied OPD structure is ITO/ DTS(PTTh₂)₂:A (100 nm) /Al with PC₆₀BM or PC₇₀BM as A materials. DTS(PTTh₂)₂ and fullerene derivatives are dissolved in warm chlorobenzene to obtain 40 mg.ml⁻¹ concentration solutions with D:A mass ratio of 70:30. Films are spin-casted at 1600 rpm for 60 s and annealed 10 min at 70 °C to remove residual solvent. Finally, 150 nm aluminum electrodes are evaporated on top of the bulk heterojunction (BHJ).

First tests performed with these two structures without any device optimization have shown encouragingly low dark current and reproducibility. Indeed, many ways are used to improve OPD performances like adding interfacial layers between electrodes and organic semiconductors to significantly reduce dark current. These layers act as blocking pathways for unwanted charges injection under reverse bias [9]. Active layer morphology can also have a significant impact on charges separation and leakage current [10].

PC₆₀BM and PC₇₀BM seem similar but generate very different BHJ thin films morphologies. Current-voltage characteristics performed in dark and under 680 nm illumination evidence that both of them provide similar charge photo-conversion in the desired wavelength area. However, PC₇₀BM displays slightly higher dark current (see bottom curve Fig. 3).

The speed of spin coating is also investigated for 1000, 1600 and 2000 rpm for PC₆₀BM to follow changes on film thickness or PC₆₀BM aggregation. Films spin coated at 1000 rpm were not uniform in contrast with films spin coated at 1600 and 2000 rpm that lead to similar device behavior.

Finally, the impact of D:A weight ratio on charges separation and dark current is studied for 60:40 to 80:20 BHJs. The dark current significantly decreases with smaller amount of PC₆₀BM. Many changes in EQE are also observed and will be discussed.

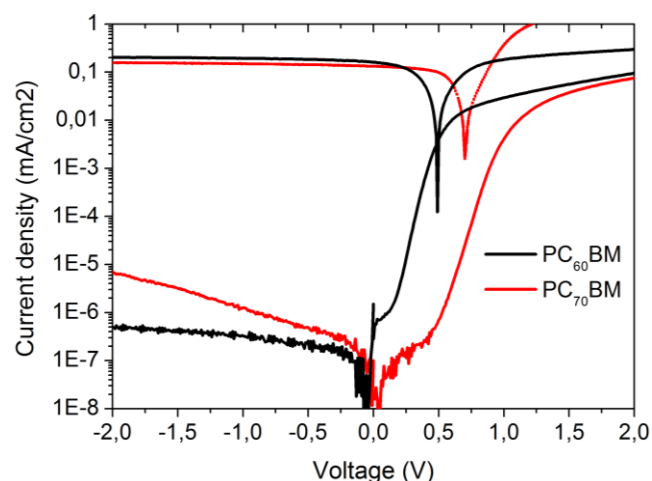


Figure 3: Dark current (bottom lines) and photogenerated current (upper lines) for 680 nm wavelength for PC₆₀BM (dark line) and PC₇₀BM (red line).

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