

INTEGRATED POLYMERIC LIGHT EMITTER FOR DISPOSABLE PHOTONIC LAB ON CHIP SYSTEMS

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ABSTRACT

This work presents the monolithic integration of a fluorophore-doped hybrid xerogel polymeric light emitter and a multiple internal reflection configuration (MIR) optofluidic system in a photonic lab on a chip (PhLoC). Two different air mirrors at both sides of the emitter were implemented that improves light coupling into the MIR system. The MIR inner walls were bio-functionalized with a peroxidase enzyme in order to develop a PhLoC analytical system for hydrogen peroxide model target analyte. Absorbance detection of the corresponding enzyme reaction was successfully carried out. The mean sensitivity and limit of detection were calculated to be 0.0119 A.U. μM^{-1} and 0.73 μM for H_2O_2 , respectively.

KEYWORDS

Integrated solid-state emitter, fluorophore-doped xerogel, biofunctionalization, absorbance detection.

INTRODUCTION

Heterogeneous integration of several optical/microfluidic components has already been demonstrated [1]. Nevertheless, despite their performance, they generally require accurate alignment between the different elements (filters, detectors and light emitters, mainly), which limit their portability, and increase their cost. Optimal configuration would be to have the light source integrated in the photonic system while holding the cost issues and alignment requirements at a minimum level. Previous works have shown the monolithic integration of liquid-state emitters [2], which, although effective, lack of mechanical robustness thus limiting its applicability.

When related to microfluidics, the most commonly used polymer is poly(dimethylsiloxane) (PDMS). Although optimal for prototyping, this material has high non-specific absorption, which is a severe drawback for biosensing applications. To this effect, a specific functionalization protocol has been applied so as to provide the PDMS with the require selectivity with the main premise of being completely compatible with the definition of both the emitter and the optofluidic system. This ambitious development has been addressed in the presented PhLoC with the integration of a fluorophore-based solid-state light emitter and the bio-functionalization of the PDMS for selective detection.

DESIGN

The disposable PhLoC that includes integrated polymeric emitter is illustrated in Fig. 1 (a). It integrates in the same structure the emitter structure and a multiple internal reflection (MIR) optofluidic system, which has already been reported by the group [3]. The integrated emitter architecture is composed of a pear-shaped reservoir (230 μm high) connected to fluidic inlet/outlet ports. Identical in behaviour than other fluorophore-based light sources, when externally excited, light from these structures is emitted in 4π Sr. Therefore, only a small fraction of the emission wavelength may be coupled to the MIR. To address this issue, two teeth-shaped air mirrors have been implemented at both sides of the emitter. Such air mirrors were described in [4] and are based on total internal reflection principles. Here, considering the refractive indices of PDMS ($n=1.41$) and air ($n=1.00$), if the light falls on this air mirror at an angle higher than 45° , it undergoes total internal reflection. Lower angles are able to transmit through

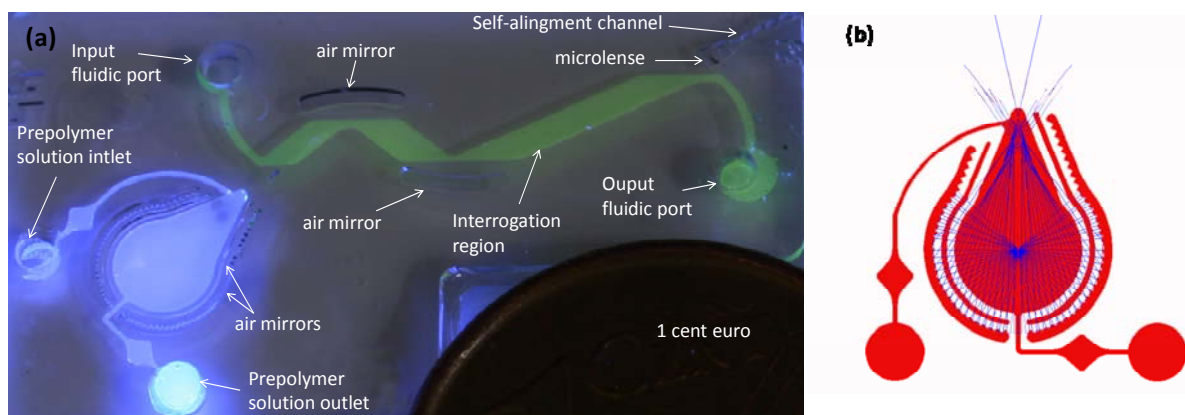


Figure 1: (a) Picture of the light emitter integrated on a PDMS-based multiple internal reflection device (see Ref. [3] for more details about this microoptic system). A 1 cent euro coin is shown as size reference (b) Design of the emitter; blue lines illustrate the working principle of the air mirrors.

this air mirror according to the Fresnel laws. At this point, light reaches the teeth-shaped mirror, which consists in two coupled air mirrors. Each part of the teeth works jointly, as they are able to reflect angles smaller than 45° . In this case, the first part of the teeth air mirror is tilted so as to ensure total internal reflection (TIR) at the light incidence point. The second part of the teeth has a double role. From one side, it also matches with the TIR conditions. From the other side, it is tilted in such a way that redirects the reflected light beam towards the MIR. Working jointly both the simple and the teeth-shaped air mirror assures an enhancement of the light coupled into the optofluidical system (Fig. 1(b)).

EXPERIMENT

The fabrication of the final device consisted in two different steps: fabrication of the PhLoC by microfabrication techniques and the synthesis of the light emitting polymer by the sol-gel method [5]. The PDMS/glass PhLoC was fabricated by soft lithography [6] following the protocol reported in ref 3. In general terms, the PDMS top part with the microfluidic channels and micro-optic elements defined was fabricated by standard master-replica molding [6], bonded to a glass substrate (by exposition to oxygen plasma, TePla plasma processor) and filled with the fluorophore-doped prepolymeric solution by an adaptation of the micromolding in capillaries soft-lithographic technique [6]. Here, the fluidic ports included in the emitter structure were opened and it was filled with the sol prepolymeric solution. Filling was achieved by capillary forces, thus avoiding the use of external pumps. The material had been previously synthesized by vigorously mixing 500 μl of phenyltrimethoxysilane (PhTMOs) (Sigma-Aldrich Co., St Louis, MO, USA) monomer with 300 μl of a pH 3 (adjusted with diluted HCl) Atto 390 (Atto-Tec GmbH, Siegen, Germany) 500 μM H_2O : DMSO 5:1 (v/v) solution. Once the emitter microstructure was filled, the device was shielded from light and left undisturbed to cure and dry at room temperature. Hydrolysis and polycondensation reactions crosslinked the sol into a polymeric matrix and Atto dye was trapped inside this network. At this point the PhLoC was ready to deal with the enzyme immobilization step.

A previously published protocol for protein immobilization in poly(dimethylsiloxane) (PDMS) microchannels was followed [7]. It consists in polyvinyl alcohol (PVA) adsorption and further silanization with 11-triethoxysilyl undecanal (TESU), which contains an aldehyde group that can be used as an anchoring point for proteins. Horseradish peroxidase enzyme was immobilized and used as recognition element for the development of a biosensor approach for hydrogen peroxide (H_2O_2) in a concentration range from 1.4 μM to 22 μM in presence of 5 mM 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS). For the biosensor approach reproducibility was tested by the calibration of three different biofunctionalized devices in consecutive days.

The setup for absorbance measurements is described below. A light emitted from a blue laser (405 nm, Laser module NANO 250-532-100, Linos Photonics, Germany) was coupled into a multimode 230 μm fiber optic (Thorlabs Inc., Dachau, Germany), which was positioned at the maximum emission region with the help of micropositioners in a 90° out-of-plane configuration at a working distance of approximately 3 mm. Fluorescence emitted from the Atto dye entrapped in the solid-state polymeric matrix entered in the interrogation region interacting with the solution containing the analyte. The readout comprised an identical fiber optic which was inserted into the output self-alignment channel at the end of the MIR system, and connected to a microspectrometer (QE 65000-FL, Ocean Optics, Dunedin, FL, USA).

RESULTS AND DISCUSSION

Atto 390 was selected because of its high molecular absorption ($24.000 \text{ cm}^{-1} \text{ M}^{-1}$) and quantum yield (0.90) as well as a large Stokes shift ($\lambda_{\text{abs}} = 390 \text{ nm}$, $\lambda_{\text{fl}} = 479 \text{ nm}$, in water). It is slightly hydrophilic, and solubility in polar solvents such as DMF or DMSO is high. High solubility was important to ensure compatibility with different chemical environments, crucial to obtain the homogeneous dispersion of the fluorophore molecules into the polymeric material shown in the solid-state emitter of the Fig. 1(a).

The absorbance value at 435 nm was chosen for the detection of H_2O_2 based on the colored conversion of ABTS mediator that takes place during the peroxidase enzymatic reaction (see Fig. 2).

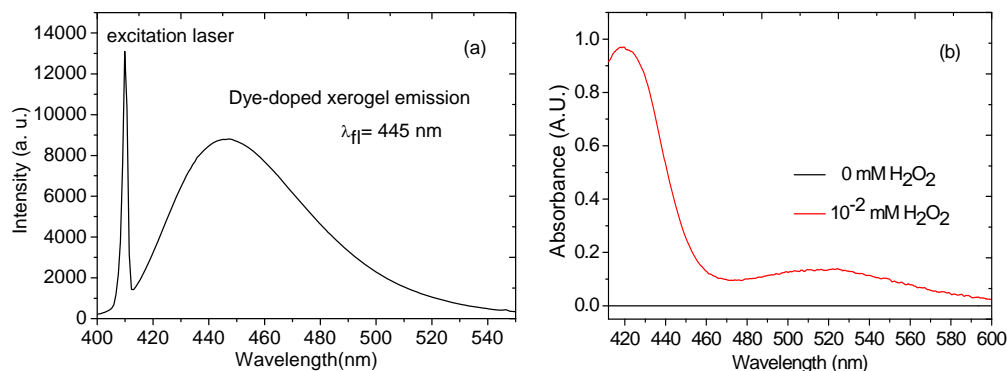


Figure 2: (a) Emission spectrum of the integrated emitter collected at the end of interrogation region channel (integration time 400 ms) (b) Absorption spectra of ABTS in absence of H_2O_2 and of the ABTS oxidized form in the presence of $10^{-2} \text{ mM H}_2\text{O}_2$.

The calibration curves presented in Fig. 3 showed a linear increase in the absorbance at 435 nm from 1.4 μM up to 8.2 μM , which is similar to the one observed using the same functionalization process for the same enzyme and analyte in a previous PhLoC [7]. A linear fitting was carried out in this range and the analytical parameters were calculated (Table 1). The limit of detection was around 20-fold lower than that of other previously reported optical biosensors for H_2O_2 [8-9].

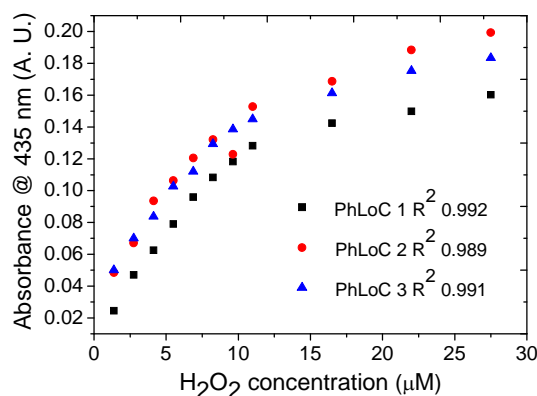


Figure 3: Absorbance as a function of H_2O_2 concentration measured at 435 nm.

Table 1: Analytical data extracted from the H_2O_2 calibration curves carried out with the presented PhLoC.

Device	Sensitivity/A.U. μM^{-1}	LOD*/ μM	R^2
1	0.0121 ± 0.0005	0.64 ± 0.02	0.992
2	0.0125 ± 0.0006	0.88 ± 0.09	0.989
3	0.0112 ± 0.0005	0.67 ± 0.02	0.991

* LOD calculated following the 3σ IUPAC criteria using the linear concentration range from 1.4 μM to 8.2 μM for H_2O_2 detection. Absorbance recorded at 435 nm.

CONCLUSIONS

We demonstrate the easy integration and successful performance of a xerogel polymeric light emitter in a PhLoC that also included auxiliary microoptical elements, such as air mirrors, and an optofluidic component, which was bio-functionalized for the selective detection of a model target analyte. Despite its high level of integration, the resulting photonic approach can be fabricated at low cost since the fabrication only requires one technological step. These results show the potential of the presented contribution for the development of disposable photonic μTAS .

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ACKNOWLEDGEMENTS

The research leading to these results has received funding from the European Research Council under the European Community's Seventh Framework Programme (FP7/2007-2013) / ERC grant agreement n° 209243 and Spanish MINECO, project ref. TEC2010-17274.

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