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Commercial Polycarbonate Track-Etched Membranes as Optical Chemical Sensors †

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Abstract: Refractive index is the main parameter measured by current optical sensors. Among all the photonic structures available for their design, porous materials have become an excellent option, since they provide better sensitivities. In our work, commercially available polycarbonate track-etched membranes were used as porous photonic structures. By means of reflectivity measurements, we demonstrated their capability to detect the presence of ethanol in the medium and showed the possibility of reusing them in several sensing assays. This new material could become an easier-to-obtain and cheaper alternative to current porous materials commonly used in optical sensors for refractive index sensing.

Keywords: Optical sensor; polycarbonate track-etched membrane; refractive index sensing; silicon

1. Introduction

Sensors are devices widely spread in our daily life as they can be designed to detect physical, chemical or biological agents of interest in areas as diverse as industrial procedures, security, medical diagnosis or defense, among others. According to the transducer element, they can be classified as mechanical, optical, thermal, electromagnetic and electrochemical. Among all, in recent years, optical sensors have gained more interest due to their high sensitivity and specificity, real-time, direct and label-free detection and multiplexing capabilities, miniaturizing possibilities, cost-effectiveness and immunity to electromagnetic interferences [1].

There are different optical sensors, but those based on the measurement of changes of the refractive index (RI) are widely used as they allow the optical label-free detection of nonionic, transparent in the UV/vis range or non-fluorescent molecules [2]. For their design, different photonic structures have been developed. Most of them are based on the interaction of the evanescent optical field with the analyte [3]. However, the achievable sensitivity values of this sort of structures are low, as only a low-intensity region of the optical field interacts with the analyte in a small surface. This issue can be overcome by using porous structures, which allow the whole optical field to interact with the analyte, since the recognition occurs inside the light propagation medium. Moreover, the presence of pores on its surface increases the surface-to-volume ratio, which allows the adhesion of more receptors and hence, the detection of more analytes. Consequently, this favours the interaction of light with the analyte and leads to a sensitivity increase as well [4].

Porous silicon (PSi) is the most used porous photonic structure as it is easy, cheap and fast to fabricate. Furthermore, its surface chemistry has long been studied, thus its functionalization to create specific sensors for specific applications in different fields is relatively easy [5]. Besides PSi, several research groups are also working on other materials such as polymers [6] or metals [7] for the development of such structures.

The aim of this work is finding an alternative porous material to create porous photonic structures. For such purpose, we employed commercially available polycarbonate track-etched (PCTE) membranes. These membranes are porous layers that reminds the structure of a Fabry-Pérot (FP) interferometer typically made on PSi. These photonic structures consist of a monolayer of a porous material and have been long used for chemical and biochemical sensing [8], so we hypothesized the utility of PCTE membranes for such aim as well.

To assess it, we studied the optical behavior in the NIR region of PCTE membranes, optimized it by placing the membrane on a flat polished silicon surface and then performed reflectivity measurements in presence of two different concentrations of ethanol. What we observed was a spectral shift that confirms our hypothesis about the utility of commercial membranes for optical sensing. Furthermore, we could observe differences depending on the ethanol concentration they were exposed to. This could indicate the suitability of these kind of structures to perform quantitative assays, but further assays are needed to confirm it. Finally, we also saw that these sensors can be used more than once, allowing us to do continuous measurement cycles.

2. Materials and Methods

PCTE membranes (19 mm diameter and 30 nm pore diameter) were purchased from Whatman. Firstly, the surface of this commercial membranes where activated by oxygen plasma in a plasma asher (PVA TEPLA 200, PVA TePla AG, Germany) for 1 minute (50W, 1.5 mBar). Immediately, the samples where immerse in an aqueous solution of 5% 3-amino-propyltriethoxysilane (APTES, Sigma-Aldrich, St Louis, USA) at 80°C for 20 minutes. After that, the samples were removed from the solution and dried out in a cleanroom wipe. Once dried, they can be placed on a previously activated silicon wafer surface by piranha treatment (H_2SO_4:H_2O = 3:1) for 10 min.

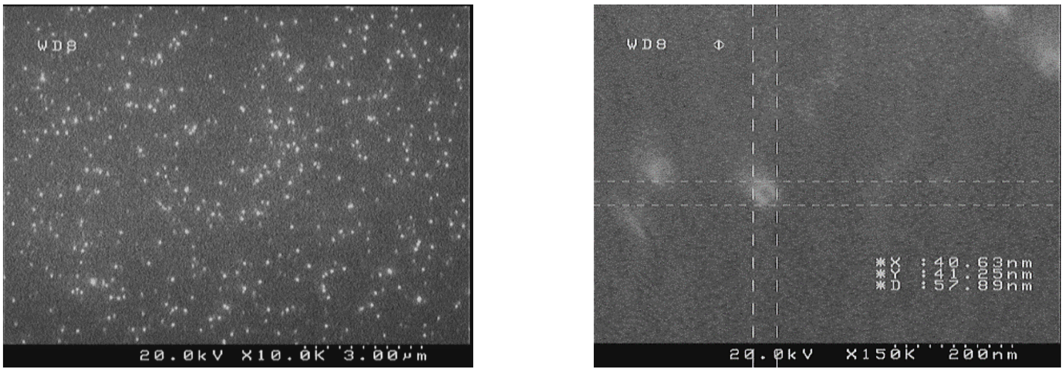
For measuring the refractive index changes caused by the presence of ethanol (Scharlab, Spain), a Bruker FTIR system was employed. The reflectivity measurements where performed in the NIR range (1110–2500 nm), with a resolution of 4 cm^{-1}. To enhance the S/N ratio, 30 scans were collected every minute to do a continuous monitoring of the spectrum shift evolution. For the graphical representation of the spectra, MATLAB R2016b (The MathWorks, Inc., USA) was used.

In order, to characterize the morphology of the surface of PCTE membranes, a Field-Emission Scanning Electron Microscope (FESEM) (Hitachi S-4500) was employed.

3. Results

3.1. Silicon substrate to enhance the optical response of PCTE membranes

The PCTE membranes are porous monolayers that reminds of the structure of FP interferometers (Fig. 1). For this reason, we hypothesize that PCTE membranes would have the same optical response as FP interferometers: an interference fringe pattern. It is the result of the interferences generated by the multiple reflections experimented by light while travelling through the different interfaces generated by the porous structure and its surroundings.



(**a**) (**b**)

Figure 1. Surface of a PCTE membrane employed in our assays. Images were taken with a FESEM microscope. (**a**) Randomly distributed pores cover the surface. (**b**) The diameter of the pores are around 30 nm as the manufacturer indicates.

Every porous monolayer, when illuminated, generates a reflectivity spectrum with maxima at particular wavelengths (λ_m) determined by the following formula:

$$\lambda_m = 2\, n_{eff}\, d/m, \tag{1}$$

where m is an integer, d is the layer thickness and n_{eff} is the effective refractive index of the porous layer [6]. When the medium surrounding the porous structure changes (e.g. when flowing a liquid on it), n_{eff} changes and hence, λ_m shifts. It is this shift what can be used to perform a sensing assay and detect the presence of the analyte.

To confirm that PCTE membranes could behave like FP interferometers, we characterized their optical response. For that aim, we used a FTIR microscope to perform reflectivity measurements of PCTE membranes surrounded by air in both faces in the NIR region. What we observed was a reflectivity spectrum with several lobes (Fig. 2), what is in agreement with the expected spectrum for a FP interferometer.

However, the reflectivity intensity was nearly zero, what could hinder the future sensing assays. Most solutions are prepared with water and it is well known that its absorption coefficient in the NIR region is high [9]. If part of light is absorbed by water and does not arrive to the PCTE membrane, the reflectivity signal will have an even lower intensity. To enhance it, we decided to place the PCTE membrane above a polished silicon wafer, which has a flat and higher-intensity reflectivity spectra in the NIR region studied as it can be seen in Fig. 2. This would also provide a mechanical stability to the membranes to be used in sensing assays. As we expected, by placing the PCTE membrane on a silicon substrate, the intensity of the reflectivity spectrum is 4-fold enhanced (Fig. 2).

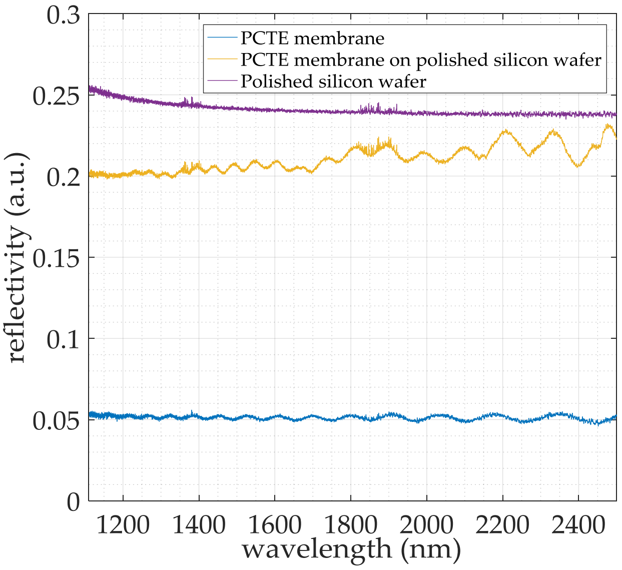


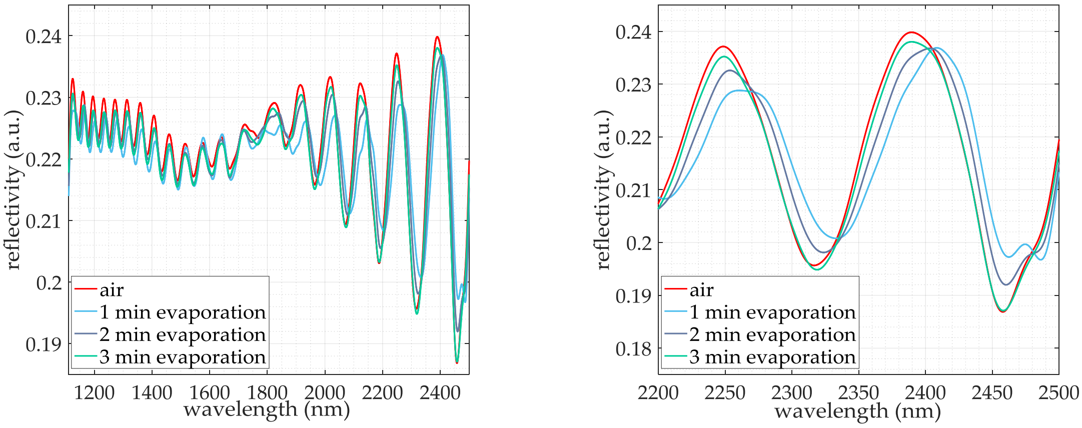
Figure 2. Reflectivity spectra of PCTE membranes with (yellow line) and without (blue line) a silicon substrate below them and a polish silicon wafer (violet).

In order to covalently bind the PCTE membranes to the silicon substrate we employed APTES as a crosslinking agent [10]. In this way, we ensure that membranes will not move while solutions are flowing in sensing assays.

3.2. Ethanol sensing assays

Once the optical response of PCTE membranes on a polished silicon wafer was characterized, pure ethanol-sensing assays were performed. For that end, a 10 µl drop of ethanol was placed on top of the sample in the area covered by the light beam that arrives from the FTIR. The measurements of the reflectivity spectrum of the sample where taken before the deposition of the drop and during the evaporation process of such drop to check if a spectral shift can be seen. What we would expect is that the spectrum shifted to longer wavelengths when the air inside the pores is replaced by ethanol, since the effective refractive index of the structure becomes higher (see Eq. 1). As ethanol evaporates, the spectrum should return progressively to its initial position, since the pores are being refilled by air and the effective refractive index of the structure decreases.

To check if shift has occurred, we will look at wavelengths between 2000 nm and 2500 nm, since here we have the highest-intensity lobes and this eases the tracking of the spectral shift. When pores are filled with pure ethanol we can observe a shift of the spectrum of around 20 nm (at around 2400 nm wavelength) towards longer wavelengths. When the ethanol is almost completely evaporated, after 3 minutes, the spectrum goes back to the same position it was initially, when the sample was dry (Fig. 3). Differences in reflectivity intensity during the measurement process are due to the layer of liquid created on top of the sample that increases the diffuse component of light reflected by the sample, thus reducing the number of beams arriving to the lenses of the FTIR microscope.

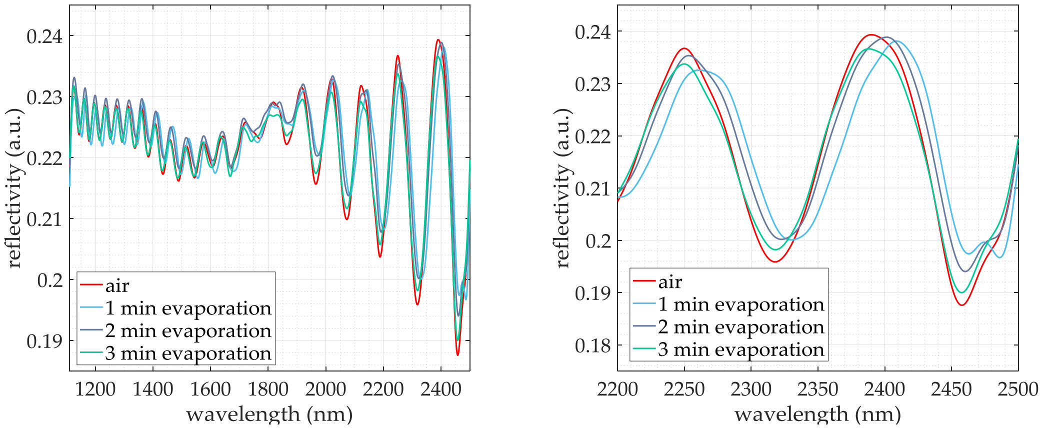


(**a**) (**b**)

Figure 3. Optical sensing measurements of pure ethanol employing PCTE membranes. (**a**) Reflectivity spectrum of the sample between 1110 and 2500 nm during the evaporation process of pure ethanol. (**b**) Reflectivity spectrum shifts around 20 nm at 2400 nm when pure ethanol fills the pores are observed. The spectrum returns to the same position it had when it was dry when ethanol evaporates.

Using the same sample, immediately after sensing pure ethanol, we placed another 10 µl drop of a 50% (v/v) aqueous solution of ethanol. What we can see is a shift of the spectrum of 16 nm (at around 2400 nm wavelength) towards longer wavelengths (Fig. 4). In comparison with previous measurement with pure ethanol, this difference in the shift magnitude could be explained by the fact that the refractive index of 50% solution is smaller than that of pure ethanol [11]. Hence, the effective refractive index of the medium is smaller when 50% solution is filling the pores and the spectral shift is smaller. However, we have to take into account that measurements are not been taken in real time but every minute and the evaporation rate of pure ethanol and its aqueous solutions are different. Therefore, differences in the spectral shift can be due to the refractive index differences of both solutions but also because the volume of air filling the pores at the same time after depositing the drop is different because the evaporation rate is different.

If we consider that the evaporation rate is not affecting our measurements and after a minute the pores are filled with pure or 50% ethanol, we can estimate that the sensitivity of our sensor is around 54 nm/RIU (50 nm/RIU when sensing 100% ethanol and 58 nm/RIU when sensing 50% ethanol).



(**a**) (**b**)

Figure 4. Optical sensing measurements of a 50% (v/v) aqueous solution of ethanol employing PCTE membranes. (**a**) Reflectivity spectrum of the sample between 1110 and 2500 nm during the evaporation process of 50% (v/v) ethanol. (**b**) Reflectivity spectrum shifts around 15 nm at 2400 nm when 50% (v/v) ethanol fills the pores are observed. The spectrum returns to the same position it had when it was dry when ethanol evaporates.

4. Discussion

These results suggest the utility of PCTE membranes as optical sensors for the detection of ethanol. We demonstrated that this kind of membranes behave like a FP interferometer when exposed to a light source in the NIR range, in our case. Furthermore, we were able to detect the presence of ethanol in the medium clearly and could demonstrate the possibility of reusing the same sensor twice, at least.

If we compare the sensitivity of our sensors with the sensitivity of PSi FP microcavities, we can see that our PCTE membrane sensors are less sensitive than those ones [5]. However, our sensors are easier to obtain since they are commercially available, which could reduce the cost of final devices. In order to explore ways of improving our sensitivity, a deeper research must be carried out.

On the other hand, it would be interesting to detect different ethanol concentrations. We could see in our results that the smaller the concentration of ethanol, the smaller the spectral shift. This might indicate that PCTE membranes could allow us to quantify and optically distinguish different concentrations of the analyte. However, it would be incautious to affirm that, since we did not perform real-time measurements and we just tested two different concentrations. Therefore, further assays must be done with different concentrations and trying to record measures in a shorter period. Moreover, we would like to explore the possibility of flowing the ethanol, instead of depositing the drop on the sample.

In conclusion, these results open a new path to explore in order to create chemical sensors easily. Furthermore, as polycarbonate can be chemically modified to bind biomolecules to its surface [12], also the development of an optical biosensor based on PCTE membranes could be explored.

5. Conclusion

For the first time, as far as we know, we present commercial PCTE membranes as new candidates to develop chemical optical sensors. Employing these membranes we were able to detect the presence of two different concentrations of ethanol in the medium. Furthermore, we could see differences in the spectral shift magnitude in presence of each concentration. This could indicate a possibility of being able to quantify with these new optical sensors. However, as these are early results, further work should be done to asses that these differences are due to concentration and not to the measurement setup.

This finding could mean a new way to develop easier and faster to obtain optical sensors. PCTE membranes are commercially available and the etching process required for the fabrication of current porous photonic structures will no longer be necessary. Furthermore, as polycarbonate surfaces can be chemically modified, specific sensors for specific applications could be developed.

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Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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