A photo-iniferter polymerization for molecularly imprinted polymers (MIPs) synthesis on porous silicon (PSi) interferometers for chemical sensing

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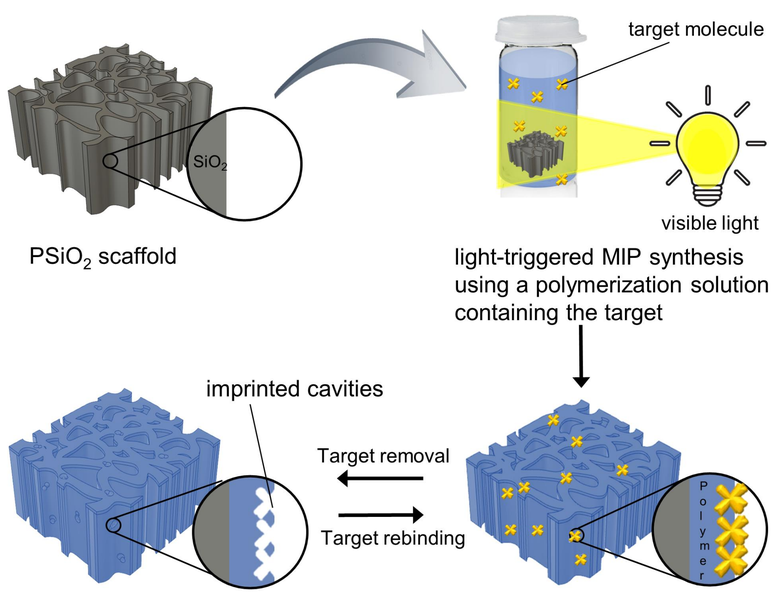
Abstract

Molecularly imprinted polymers (MIPs) are artificial biomimetic materials attracting increasing attention due to their easy synthesis combined with strength, robustness and molecular recognition capabilities on a pair with those of biological elements (e.g. antibodies and enzymes) [1]. As "antibody mimics", MIPs are used in a multitude of fields, and the number of applications is constantly increasing due to the improvement and development of new synthetic approaches. In this context, photostructuring of MIPs is particularly attractive because of the possibility of tightly controlling their features in terms of size, morphology and thickness. Herein, we propose to take advantage of photo-triggered, controlled radical polymerisation, for the deposition of MIPs on nanostructured porous silicon (nPSiO2), with high aspect ratio (100) and columnar pores with size around 50 nm, used as interferometer. nPSiO2 has been increasingly exploited in bio/chemosensing due to its huge specific surface, straightforward fabrication and low cost, which allows mass production of cheap biosensors for point-of-care application to be envisioned. In the present work, MIPs against propranolol (a β-blocker) as model target were synthesized within nanoporous silicon using low intensity visible light. Preliminary results show that the developed sensor exhibited excellent performance for label free detection of propranolol with high selectivity and sensitivity in organic and aqueous samples.

Methods

Nanostructured porous silicon (nPSiO2) scaffolds were prepared by anodic etching of p-type silicon square wafer samples using an already known procedure [2]. Later, nPSiO2 scaffolds were functionalized with MIP thin layers by light-triggered polymerization.



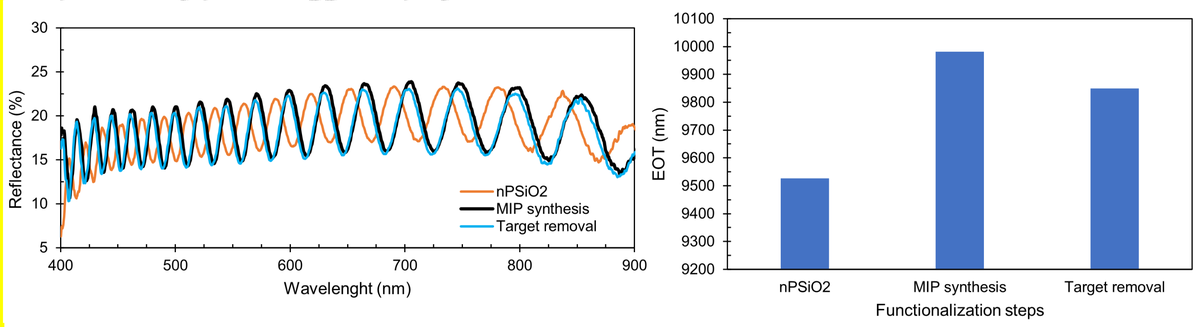
In brief, nPSiO2 was immersed in a solution containing iniferter, crosslinker, monomer and target molecule and then exposed to low- intensity visible light for a period sufficient to obtain a polymer thin film embedding the target within nPSiO2 membranes. The imprinted cavities (and then the MIP) were obtained by removal of the target molecules from the polymer matrix by a washing procedure.

Not-imprinted polymer (NIP) was synthesized by the same approach but using a polymerization solution without the template and used as control.

All the functionalization steps of nPSiO2 were monitored by UV-VIS spectroscopy, through the acquisition of reflectance spectra and calculation of EOT values. EOT (effective optical thickness) is an analytical parameter calculated by Fourier transform of the reflectance spectrum, described by the relationship: $EOT = 2nL$,
where "n" is the refractive index and "L" is the thickness of the porous layer.

Results and discussions

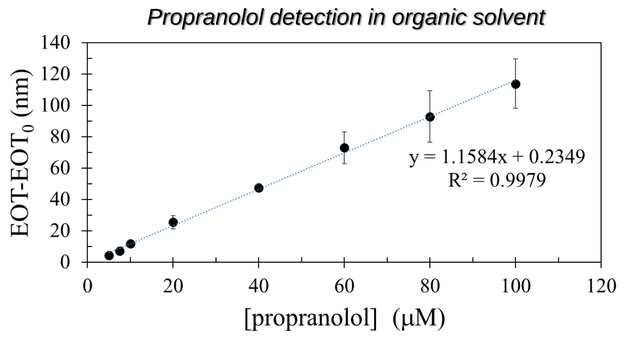
The following figure summarizes the changes in the EOT value measured after MIP deposition by photo-triggered polymerization.



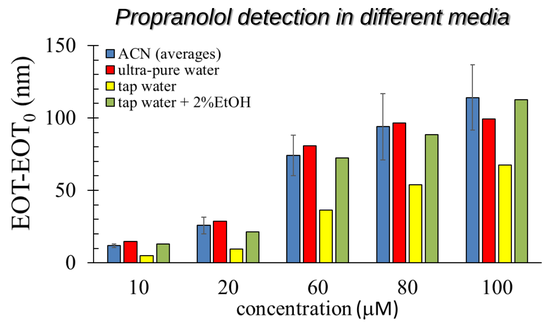
A clear red shift of the reflectance spectra can be observed after nPSiO2 scaffolds functionalization with the MIP polymer, with an increase in the EOT signal due to the increase of the effective refractive index of PSiO2 layer. On other hand, target removal from polymer matrix produces a blue-shift of the reflectivity spectra due to the decrease of the refractive index.

Propranolol detection tests were performed using MIP-based sensors with target solutions prepared in organic solvent (acetonitrile) and in aqueous media.

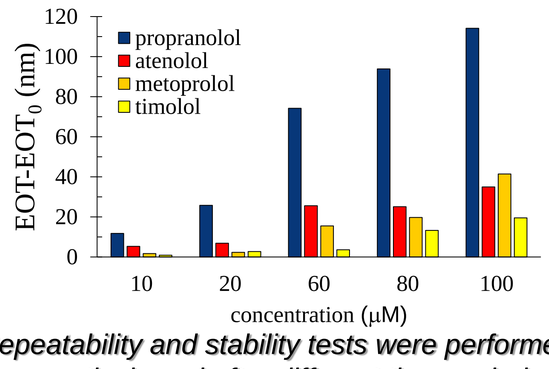
Propranolol detection in organic solvent



Propranolol detection in different media

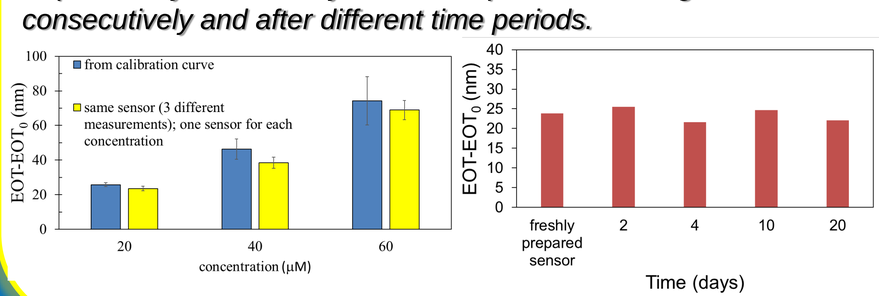


A good linearity (R^2: 0.9979) in the sensor response was recorded for the concentration range between 5 and 100 μM. Using the MIP-based sensor with propranolol solutions prepared in tap water the response is slightly lower compared with that recorded using solutions prepared in acetonitrile. However, adding ethanol (2%) to the tap solution to analyze the sensor response it seems to be not affected by the medium nature.
Selectivity tests were performed exposing the developed sensor to other b-blocker drugs (timolol, metoprolol and atenolol).



The sensor selectivity was tested with interfering molecules solutions at different concentrations. In all cases and for all the interfering molecules tested the sensor response is rather lower compared with that recorded for propranolol

Repeatability and stability tests were performed using the sensor for propranolol detection consecutively and after different time periods.



Measuring the signal different times consecutively (n=3), a very good RSD of 5.7% was recorded. Moreover, the sensor can be used without problems for at least 20 days (RSD: 7%)

Conclusions

The resulting sensor was challenged toward propranolol detection and preliminary results indicated good linearity in the concentration range from 5 to 100 μM with a LOD of 3 μM. Propranolol detection tests performed in tap water confirm the ability of the sensor to detect the target in real matrices. Moreover, detection tests using metoprolol, atenolol and timolol (other β-blockers) as interfering molecules demonstrate a good selectivity of the developed sensor.

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